NMR IMAGING AND SPECTROSCOPIC INVESTIGATIONS OF BLOWING GASES IN POLYMER INSULATING FOAMS

by

ZHIMING MEI

M.S., The University of Science and Technology of China, 1989

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
September 1996
© Zhiming Mei, 1996
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chem. Dept

The University of British Columbia
Vancouver, Canada

Date Oct. 8, 1996
ABSTRACT

Rigid polystyrene and polyurethane plastic foams are extensively used as insulating materials in many important energy saving applications due to their extremely efficient thermal insulating and good mechanical properties. A critical foam component responsible for this superior performance is the chlorofluorocarbon (CFC) blowing agent, which has a much lower thermal conductivity than air and when trapped within the foam cells serves as the insulating gas. Over time, the CFC gas slowly diffuses out of the cells and causes a gradual decrease in the foam's thermal resistance. There has long been a need for a reliable and fast method for estimating the long-term thermal performance of foams, especially since recent environmental concerns require the fast development of new foam products with CFC replacements.

The $^{19}$F NMR microscopic imaging technique described in this thesis is demonstrated to be a non-destructive, efficient and reliable method for the investigation of fluorinated blowing agents in various foams. Detailed studies of polystyrene foams made with CFC, HCFC and HFC blowing agents show that $^{19}$F NMR microscopic imaging technique is ideally suited for monitoring the spatial distribution of gaseous blowing agents in foams and that it can yield a quantitative description of the distribution of cell gas in foams as a function of time and temperature as well as other factors. There is no other technique available which is able to directly measure and monitor the spatial distribution of the concentrations of blowing gases inside foams.
A detailed investigation on the measurement of the diffusion coefficients of the blowing gases in polystyrene foams shows that a one-dimensional imaging experiment can be used to obtain the quantitative spatial distribution of blowing gases in foams as functions of time and temperature. The diffusion coefficients for different sample geometries can be simply determined by fitting theoretical model calculations to the experimental data and results obtained from both ambient temperature and elevated temperatures. The technique makes it possible to predict long-term foam insulation performance and will provide valuable information for improving foam formulation and manufacturing methods.

Fast MAS high resolution $^{19}$F solid-state NMR spectroscopy has been used to investigate the effects of the dissolved blowing gas components in the polymer matrix. It is demonstrated that it is possible to detect and quantify the blowing gas dissolved in the solid-phase in polystyrene foam systems. The results are presented for different blowing gases in various PS foams and the effect of the dissolved gas on the diffusion process is also discussed.

Both the imaging and solid-state NMR experiments are extended to various polyurethane foam systems to investigate the diffusion process of blowing gases as well as the effect of the dissolved gas components. The results show a significant contribution from the dissolved component to the diffusion of the gaseous component in PU foams in the accelerated aging process. The theoretical models were therefore modified in order to address such an effect. Satisfactory results are obtained and the diffusion coefficients determined.
Foam systems which had been post-treated with a second blowing gas were also investigated to probe the outward and inward diffusion processes using the above techniques. The results are presented as functions of time and temperature. The diffusion coefficients determined for each gas in the opposing diffusion processes are presented.
# TABLE OF CONTENTS

ABSTRACT .......................................................................................................................... ii
TABLE OF CONTENTS ......................................................................................................... v
LIST OF TABLES .................................................................................................................. x
LIST OF FIGURES ............................................................................................................... xiii
LIST OF ABBREVIATIONS .................................................................................................. xx
ACKNOWLEDGMENTS ........................................................................................................ xxii

## CHAPTER 1. INTRODUCTION .......................................................................................... 1

1.1. RIGID PLASTIC CLOSED-CELL INSULATING FOAMS .................................................. 1
   1.1.1. Polyurethane and Polystyrene Foams ................................................................. 1
   1.1.2. Blowing Agents ............................................................................................... 5
   1.1.3. Aging Processes of Insulating Foams .............................................................. 8
   1.1.4. Potential Use of NMR Spectroscopy and NMR Imaging in the Investigation of
          Foams ..................................................................................................................... 11

1.2. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY ............................................ 12
   1.2.1. Multinuclear NMR Spectroscopy .................................................................. 12
   1.2.2. Nuclear Relaxation Processes ...................................................................... 14
   1.2.3. Quantitative NMR Measurements ............................................................... 20

1.3. NMR IMAGING ............................................................................................................ 21
   1.3.1. Back-Projection Imaging .............................................................................. 21
   1.3.2. Fourier Imaging ............................................................................................ 25

1.4. HIGH RESOLUTION SOLID STATE NMR SPECTROSCOPY .................................... 29
   1.4.1. Magnetic Interactions in Solids .................................................................... 29
   1.4.2. The Magic Angle Spinning Technique .......................................................... 32

1.5. PURPOSE OF THE THESIS RESEARCH ................................................................. 34

REFERENCES .................................................................................................................... 36
CHAPTER 2. PRELIMINARY NMR IMAGING INVESTIGATIONS OF
BLOWING AGENTS IN POLYSTYRENE FOAMS ........................................... 39

2.1. INTRODUCTION ................................................................................. 39

2.2. EXPERIMENTAL .............................................................................. 41
  2.2.1. Foam Samples ........................................................................... 41
  2.2.2. NMR Spectroscopy ................................................................... 47
    2.2.2.1. 1D $^{19}$F NMR Spectroscopy ................................................. 47
    2.2.2.2. Calibration ........................................................................... 49
  2.2.3. Measurement of $T_1$ and $T_2$ Relaxation Times ...................... 54
  2.2.4. Proton and Fluorine Imaging Experiments .............................. 55
    2.2.4.1. Pulse Sequences ................................................................ 55
    2.2.4.2. $^1$H and $^{19}$F Imaging .................................................. 61

2.3. RESULTS AND DISCUSSION .......................................................... 62
  2.3.1. Proton and Fluorine Relaxation Times of Fluorinated Gases in PS Foams .... 62
    2.3.1.1. Results .............................................................................. 62
    2.3.1.2. Relaxation Mechanism ...................................................... 66
    2.3.1.3. Investigation of Possible Concentration Dependence of $^{19}$F $T_2$ Values inside a Foam Matrix ...................................................... 68
  2.3.2. Quantitative Analysis of Gas-Phase Blowing Agents in PS Foams by 1D NMR ................................................................. 72
    2.3.2.1. Results .............................................................................. 72
    2.3.2.2. Effect of Temperature ...................................................... 76
  2.3.3. $^{19}$F Spin-Echo Imaging Studies on Foams ............................. 78
  2.3.4. Distributions of Single Blowing Agents in Foams ................... 90
    2.3.4.1. Typical Distribution of a Single Blowing Agent in Foams ........... 90
    2.3.4.2. Homogeneity of the Distribution of Blowing Agents ............... 93
    2.3.4.3. Effect of Diffusion on the Distribution of a Single Blowing Agent in Foams ........................................................................... 95
  2.3.5. Distributions of Mixed Blowing Agents within a Foam Matrix .... 98
    2.3.5.1. Case 1: Foam Board ......................................................... 98
### 2.4. CONCLUSIONS

- 2.3.5.2. Case 2: Post-Treated Foam Cylinder .......................... 100
- 2.3.6. Accelerated Aging at Elevated Temperatures .................. 105

### REFERENCES

- 2.4. CONCLUSIONS ......................................................... 107
- 2.3.6. Accelerated Aging at Elevated Temperatures .................. 105

### CHAPTER 3. INVESTIGATIONS OF DIFFUSION PROCESSES OF BLOWING GASES IN POLYSTYRENE FOAM ........................................ 109

#### 3.1. INTRODUCTION .......................................................... 109

#### 3.2. EXPERIMENTAL .......................................................... 111

- 3.2.1. Experimental Protocol A ............................................. 111
- 3.2.2. Experimental Protocol B ............................................. 113
- 3.2.3. Experimental Protocol C ............................................. 113

#### 3.3. MODELS FOR DIFFUSION IN FOAMS ................................. 115

- 3.3.1. Models for Diffusion in Foams ..................................... 115
- 3.3.2. Solution for Protocol A ............................................. 118
- 3.3.3. Solution for Protocol B ............................................. 120
- 3.3.4. Solution for Protocol C ............................................. 123
  - 3.3.4.1. Outward Diffusion ............................................. 123
  - 3.3.4.2. Inward Diffusion ............................................. 124

#### 3.4. MEASUREMENT OF GAS DIFFUSION IN FOAMS ...................... 125

- 3.4.1. NMR Imaging as a Technique for Monitoring Diffusion Processes .......... 125
- 3.4.2. Experimental Protocol A ............................................. 126
  - 3.4.2.1. Aging at Ambient Temperature .................................. 126
  - 3.4.2.2. Aging at Elevated Temperatures .............................. 131
- 3.4.3. Experimental Protocol B: Accelerated Aging Processes .............. 137
- 3.4.4. Experimental Protocol C: Diffusion Processes in Post-Treated Systems .... 138

#### 3.5. CONCLUSIONS .......................................................... 146

#### REFERENCES ............................................................. 148
CHAPTER 4. HIGH RESOLUTION $^{19}$F SOLID STATE NMR INVESTIGATIONS OF "DISSOLVED" BLOWING GASES IN POLYSTYRENE FOAM MATRICES

4.1. INTRODUCTION ........................................................................................................ 150
4.2. EXPERIMENTAL .................................................................................................... 153
   4.2.1. $^{19}$F MAS NMR Experiments ....................................................................... 153
4.3. RESULTS AND DISCUSSION ............................................................................... 158
   4.3.1. Qualitative Observations ............................................................................. 158
   4.3.2. Relaxation Time Measurements ................................................................... 162
   4.3.3. Quantitative Analysis of Blowing Gas Distributions in PS Foams by MAS NMR .................................................................................................................. 163
      4.3.3.1. Reference Sample Selection ................................................................... 163
      4.3.3.2. Quantitative Analysis ............................................................................. 167
   4.3.4. Distribution of HCFC-142b ($\text{CH}_3\text{CF}_2\text{Cl}$) between the Gas-Phase and Polymer Matrices in Aged PS Foams ....................................................................................... 168
      4.3.4.1. Aging at Ambient Temperature ................................................................ 168
      4.3.4.2. Aging at Elevated Temperatures .............................................................. 170
      4.3.4.3. Highly Accelerated Aging ...................................................................... 173
   4.3.5. MAS NMR Experiments on Post-Treated Foams ........................................... 178
4.4. CONCLUSIONS .................................................................................................... 182
REFERENCES ............................................................................................................... 184

CHAPTER 5. INVESTIGATIONS OF CFC AND HCFC GASES IN POLYURETHANE FOAMS

5.1. INTRODUCTION .................................................................................................... 185
5.2. EXPERIMENTAL .................................................................................................. 186
   5.2.1. Foam Samples .............................................................................................. 186
   5.2.2. ID $^{19}$F NMR Spectroscopy ....................................................................... 188
List of Tables

Table 1.1. Comparisons of thermal conductivities of air, CO₂ and CFC₁₃ in terms of their “k factors” (Btu-in./°F-ft²-hr).................................................................5
Table 1.2. Properties of CFC blowing agents and possible alternatives.............................8
Table 1.3. Summary of heat transfer routes through polyurethane foam together with the thermal conductivity of the solid polymer ........................................9
Table 2.1. Single blowing agent polystyrene foams (group #1)........................................42
Table 2.2. Polystyrene foams formed with two blowing agents (group #2)......................43
Table 2.3. Polystyrene foam samples (CH₃CF₂Cl) used in post-treated studies (group #3) ..............................................................................................................44
Table 2.4. Polystyrene foam samples blown with CH₃CF₂Cl and post-treated with CFC₁₃ at 69°C.................................................................45
Table 2.5. T₁ and T₂ relaxation times of the ¹H and ¹⁹F nuclei in gaseous blowing agents in PS foams.................................................................63
Table 2.6. Chemical shifts of the ¹⁹F nuclei in different blowing agents......................74
Table 2.7. The weight percent of cell gas in the different foam samples investigated together with the ages and densities of the foams........................75
Table 3.1. Diffusion characteristics of CH₃CF₂Cl in PS foam at room temperature........131
Table 3.2. Diffusion characteristics of CH₃CF₂Cl in PS at the different temperatures indicated ........................................................................................................133
Table 3.3. Calculated diffusion coefficients of CH₃CF₂Cl at 87°C after various diffusion times ........................................................................................................138
Table 3.4. Diffusion characteristics of CC₁₃F (CFC-11) into the foam cylinder at 69°C..141
Table 3.5. Diffusion characteristics of CH₃CF₂Cl (HCFC-142b) out of the foam cylinder at 69°C ................................................................. 145

Table 4.1. Summary of PS foam samples investigated in the fast MAS experiments ..... 157

Table 4.2. Relaxation times of Teflon tape and fluorine-containing blowing agents in gas-phase in the cells and also dissolved in the PS polymer matrix ................................. 162

Table 4.3. Amount of CH₃CF₂Cl dissolved in the solid polymer (sample #1) calculated from the Teflon reference ................................................................. 165

Table 4.4. Amount of CH₃CF₂Cl dissolved in the solid (sample #1) calculated using the known amount of its gas-phase component as reference ......................... 166

Table 4.5. Quantitative measurements of the percentage concentrations of gas-phase and dissolved blowing agents in PS foams ......................................................... 168

Table 4.6. Distribution of CH₃CF₂Cl in a PS foam at different locations ...................... 169

Table 4.7. Distribution of CH₃CF₂Cl between gas-phase and polymer matrix in a PS foam exposed for four months diffusion at the temperatures indicated ............ 172

Table 4.8. Distribution of CH₃CF₂Cl between the gas-phase and polymer matrix in a PS foam after highly accelerated aging (previous data on sample #1a is listed for reference) ........................................................................ 174

Table 4.9. Distribution of CH₃CF₂Cl and CFCI₃ between gas and polymer matrix in a post-treatment PS foam (previous data on sample #1a is listed for reference) 180

Table 5.1. Summary of the properties of the polyurethane foam samples studied ........ 187

Table 5.2. T₁ and T₂ relaxation times of the \(^1\)H and \(^{19}\)F nuclei in gaseous blowing agents in PU foams ......................................................................................................................... 191

Table 5.3. Chemical shifts of the \(^{19}\)F nuclei in different blowing agents ..................... 193

Table 5.4. The weight percent of cell gases in the different foam samples investigated together with the ages and densities of the foams ................................................................. 194
Table 5.5. Quantitative measurement of the concentrations of blowing agents in PU foams........................................................................................................................................200

Table 5.6. Distribution of CH$_3$CFCl$_2$ in PU foams aged at RT and at 87°C........................................202

Table 5.7. Distributions of blowing gases between gas-phase and polymer matrixes in PU foams before and after exposure for 8 days at 87°C.................................................................205

Table 5.8. Diffusion characteristics of CH$_3$CFCl$_2$ in PU at the different temperatures indicated........................................................................................................................................216

Table 5.9. Treatments of polyurethane foam samples blown with CH$_3$CFCl$_2$ and post-treated with CFCl$_3$........................................................................................................................................219
List of Figures

Figure 1.1. Schematic representation of the 180°-τ-90° inversion recovery sequence used to measure $T_1$ relaxation times .................................................................16

Figure 1.2. Schematic representation of the 90°-τ-180°-τ spin echo sequence used to measure $T_2$ relaxation times .................................................................18

Figure 1.3. Schematic representation of the effect of a linear field gradient ..................22

Figure 1.4. Schematic representation of a two-dimensional “back-projection” image obtained from the application of a number of field gradients in different directions .................................................................24

Figure 1.5. Basic sequence for the Fourier imaging method ........................................27

Figure 1.6. Schematic representation of the slice selection method. (a) Gradient $G_z$, (b) sample orientation, (c) distribution of Larmor frequencies in the sample with gradient $G_z$ on when the excitation is nonselective and (d) bandwidth of frequencies selected by the soft pulse .................................................................28

Figure 1.7. Geometric arrangement for a $I-S$ spin pair, illustrating the quantities of interest for the dipole-dipole interaction. $B_0$ is the magnetic field, and the $I-S$ vector of length $r$ makes an angle $\theta$ with the field direction .................................................................30

Figure 1.8. Macroscopic sample rotation at an angle $\beta$ to the applied magnetic field $B_0$, showing the geometric relationships involved .................................................................33

Figure 2.1. Schematic representation of the post-treatment experiment and the sample preparation ....................................................................................................46

Figure 2.2. Geometric arrangement of the horizontal solenoid r.f. coils .......................47

Figure 2.3. A cylindrical foam sample with a fractured depth $d$ below the surface due to the cutting .......................................................................................................50

Figure 2.4. Schematic representation of the sample preparation: The middle section of the foam cylinder, taken from the center area of the board, was used for the NMR measurements .......................................................................................................51

Figure 2.5. Plot of the intensity of the signal versus the radius $r$ of the PS foam cylinders, symbols indicate experimental data and the dashed line the curve from the least-squares fitting .......................................................................................................53
Figure 2.6. Plot of the relative loss of gas from the cutting, calculated from Equation (2.1), versus the radius r of the PS foam cylinders. C1, C2 are defined in text........53

Figure 2.7. (a). Spin-echo imaging pulse sequence with a Gaussian soft 90° pulse and a hard 180° pulse and slice selection. (b). Spin-echo imaging pulse sequence in which no slice is selected. (c). FLASH imaging pulse sequence in which no slice is selected.................................................................57

Figure 2.8. Chemical shift selective pulse sequence without slice selection with a Gaussian soft 90° pulse and a hard 180° pulse.................................................................60

Figure 2.9. Temperature dependence of the fluorine T1 and T2 relaxation times of CH3CF2Cl (HCFC-142b) in PS foam.................................................................64

Figure 2.10. Temperature dependence of the proton relaxation times in CH3CF2Cl (HCFC-142b). (a) T1 relaxation times versus 1/T. (b) T2 relaxation times versus 1/T. 65

Figure 2.11. The effect of the correlation time for molecular motion on T1 and T2 assuming a dipolar relaxation mechanism.................................................................67

Figure 2.12. (a). 1D projections of the 19F signal intensity of CH3CF2Cl in PS foam sample F1, center area as a function of the TE values. (i) TE = 1.6 ms, (ii) TE = 1.9 ms, (iii) TE = 3.5 ms, (iv) TE = 5.5 ms. (b). 1D projection of the 19F signal intensity of CH3CF2Cl in PS foam sample B1, edge area as a function of the TE values. (i) TE = 1.6 ms, (ii) TE = 2.5 ms, (iii) TE = 3.5 ms, (iv) TE = 5.5 ms. (c). 1D projection of the 19F signal intensity of CF2Cl2 in PS foam sample E1, center area as a function of the TE values: (i) TE = 1.6 ms, (ii) TE = 2.5 ms, (iii) TE = 3.5 ms, (iv) TE = 7.5 ms.................................................................70

Figure 2.13. Same projections as in Figure 2.11, scaled to the same maximum intensities.................................................................71

Figure 2.14. 19F NMR spectrum of CH3CF2Cl in PS foam sample K1 together with the reference sample (C6H5CF3) sealed in a capillary tube present in the coil........73

Figure 2.15. Normalized intensities of 19F signals of the blowing agents in the different foams indicated (see Table 2.7) as a function of time on exposure to an air atmosphere at 80°C.................................77

Figure 2.16. (a). 19F images of CF2Cl2 in PS foam (sample E1) obtained by different imaging sequences. (1) SE without slice. The echo time was 1.5 ms and the in-plane resolution was 260 μm. (2) SE with slice. The echo time was 1.9 ms, slice gradient strength 2.4 G/cm and the slice thickness was 0.9 mm. The in-plane resolution was 260 μm. (3) FLASH image. The echo time was 1.1 ms and the in-plane resolution 190 μm. 2.16(b). Same data presented in the form of histogram plots.................................................................82
Figure 2.17. $^{19}$F NMR imaging projections of CH$_3$CF$_2$Cl in a PS foam cylinder (sample H1) (a) with non-slice spin-echo sequence and (b) with slice-selecting spin-echo sequence. The slice thickness was 0.7 mm.

Figure 2.18. One-dimensional NMR projections along the axial direction (x) of CH$_3$CF$_2$Cl in PS foam (sample H1). (a) $^1$H. (b) $^{19}$F.

Figure 2.19. Two-dimensional $^1$H NMR image of a piece of PS foam sample containing CH$_3$CF$_2$Cl. The echo time was 7.3 ms, the read gradient strength 6.8 G/cm and the phase-encoding gradient strength 3.8 G/cm incremented through 128 experiments. The in-plane resolution was 220 µm and the experimental time 13 hours. (b). Same data presented in the form of histogram plot.

Figure 2.20. $^{19}$F images of CH$_3$CF$_2$Cl distribution in PS foam sample B1. The echo time was 1.5 ms, the frequency encoding gradient strength 6.8 G/cm and the phase-encoding gradient strength 11.7 G/cm incremented through 128 experiments. The in-plane resolution was 260 µm. (a). Grey scale image. (b). Stacked plot presentation. (c). 1D Projection along the axial direction.

Figure 2.21. $^{19}$F images of CH$_3$CF$_2$Cl in PS foam (sample B1). The echo time was 2.1 ms, the frequency encoding gradient strength 14 G/cm and the phase-encoding gradient strength 24.4 G/cm incremented through 256 experiments. The in-plane resolution was 60 µm.

Figure 2.22. Typical distribution of CH$_3$CF$_2$Cl in a 5 cm thick PS foam board (sample F1). The dashed line indicates where the sample was cut.

Figure 2.23. Distribution of CH$_3$CF$_2$Cl in a 10 cm thick PS foam board aged for 5 years (sample H1). The dashed line indicates where the sample was cut.

Figure 2.24. Three 1D projections of the distribution of blowing agent CF$_2$Cl$_2$ along the three orthogonal dimensions in a cubic sample of PS foam (sample E1).

Figure 2.25. CH$_3$CF$_2$Cl gas distribution in the center area of the PS foams (a) aged at room temperature for 2 months (sample F1) and (b) aged at room temperature for 5 years (sample H1).

Figure 2.26. CH$_3$CF$_2$Cl gas distribution in the edge area of a PS foam board (a) aged at room temperature for 2 months (sample F1) and (b) aged at room temperature for 5 years (sample H1).

Figure 2.27. Distributions of mixed blowing gases, CH$_3$CF$_2$Cl and CF$_2$Cl$_2$, in PS foam samples.(a) CF$_2$Cl$_2$ in the foams aged for (i) 2 months, (ii) 13 months.(b) CH$_3$CF$_2$Cl in the foams aged for (i) 2 months, (ii) 13 months.

Figure 2.28. (a). $^{19}$F 1D spectrum of the post-treatment sample of PS with the resonances assigned as indicated to the original foaming gas CH$_3$CF$_2$Cl and the post
treatment gas CF$_3$CH$_2$F. (b) Two-dimensional cross-section images of the distribution of CH$_3$CF$_2$Cl in the same sample. (c) Two-dimensional cross-section images of the distribution of CF$_3$CH$_2$F in the same sample. (d) One-dimensional projections. The intensities are normalized against the total number of fluorines found from the $^{19}$F 1D spectrum and thus represent the absolute gas concentrations. The selective pulse length was 300 µs and had a Gaussian shape. The echo time was 2.5 ms, read gradient strength 3.8 G/cm and the phase-encoding gradient strength 8.12 G/cm incremented through 128 experiments. The in-plane resolution was 220 µm. Grey scale and stacked plot presentations are shown here for the 2D images..........................101

Figure 2.29. Series of cross-section images of the two gases CH$_3$CF$_2$Cl and CFCl$_3$ in PS foam as a function of time exposed in CFCl$_3$ at 69 °C. (a) 5 days, (b) 9 days, (c) 15 days. The echo time was 2.2 ms, selective pulse length 300 µs with Gaussian shape and the read gradient strength 3.8 G/cm. The phase-encoding gradient strength was 8.12 G/cm incremented through 128 experiments and the in-plane resolution was 220 µm..........................104

Figure 2.30. (a). An image of CF$_2$Cl$_2$ in a fresh PS foam cube cut from the center of the board (sample E1). (b). After placing the sample in an oven at about 80 °C for 96 hours. The echo time was 1.5 ms, read gradient strength 6.8 G/cm and the phase-encoding gradient strength was 11.7 G/cm incremented through 128 experiments. The in-plane resolution was 260 µm. Grey scale and stacked plot presentations are shown here for the 2D images..........................106

Figure 3.1. Sketch of foam cylinder and schematic representation of the expected one dimensional projection of the $^{19}$F signal intensity along the x direction........112

Figure 3.2. Sketch of cross-section image of foam cylinder and the one dimensional profile from the center row of the image..........................................................114

Figure 3.3. Schematic representation of cylindrical coordinates.........................................116

Figure 3.4. Sketch of a cylinder-shaped porous body.........................................................118

Figure 3.5. Sketch of a foam cylinder taken from the center area of a foam block where the net diffusion of the fluorinated gas occurred only at the two end surfaces....127

Figure 3.6. Series of imaging projections of CH$_3$CF$_2$Cl measured at time intervals of (a)117, (b) 201 and (c) 234 days together with the corresponding theoretical curves calculated using Equation (3.6).................................................................130

Figure 3.7. Series of CH$_3$CF$_2$Cl imaging projections as a function of diffusion time at 87 °C after 145 days at ambient temperature together with the calculated curves (a) 21 days (b) 55 days and (c) 88 days.................................................................134
Figure 3.8. Temperature dependence of the diffusion coefficients of CH$_3$CF$_2$Cl in PS foams. The error bars (= 2 I A $D/D$ I) are calculated from Table 3.2. 

Figure 3.9. Diffusion of CCl$_3$F (CFC-11) into the PS foam cylinder at 69 °C at various time intervals. Experiments #1, #2 and #3 correspond to diffusion times of 120, 216 and 336 hours exposed to CCl$_3$F. Symbols indicate experimental data from the imaging profiles, lines indicate calculated data from the model for this case (see text).

Figure 3.10. Diffusion of CH$_3$CF$_2$Cl (HCFC-142b) out of the PS foam cylinder at 69 °C after 216 hours exposed to CCl$_3$F (CFC-11). Symbols indicate experimental data from the center rows of the images, lines indicate predicted data from the model for this case using the diffusion coefficient of CH$_3$CF$_2$Cl obtained in Section 3.4.2.2.

Figure 3.11. Diffusion of CH$_3$CF$_2$Cl (HCFC-142b) out of the PS foam cylinder at 69 °C at various time intervals. Experiments #1, #2 and #3 correspond to diffusion times of 120, 216 and 336 hours exposed to CCl$_3$F (CFC-11). Symbols indicate experimental data from the center rows of the images, lines indicate predicted data from the model for this case (see text).

Figure 4.1. Schematic representation of the sample preparations.

Figure 4.2. 1D $^{19}$F MAS NMR spectrum of CH$_3$CF$_2$Cl in a PS foam at a spinning rate of 9 kHz. The arrows indicate spinning sidebands. Chemical shifts are referenced relative to external CFCI$_3$ (0.0 ppm).

Figure 4.3. $^{19}$F MAS NMR spectra of CH$_3$CF$_2$Cl in a PS foam sample (same as in Figure 4.2.) at spinning rates of (a) 4.0 kHz, (b) 6.4 kHz and (c) 10 kHz. The arrows indicate spinning sidebands. Chemical shifts are referenced to external CFCI$_3$ (0.0 ppm).

Figure 4.4. 1D $^{19}$F MAS NMR spectrum of Teflon reference and CH$_3$CF$_2$Cl in a PS foam at the spinning rate 10 kHz. The arrows indicate spinning sidebands. Chemical shifts are referenced relative to external CFCI$_3$ (0.0 ppm).

Figure 4.5. Plots from Table 4.6 and Table 4.7, representing the distribution of CH$_3$CF$_2$Cl at different locations in a PS foam block exposed for diffusion at various temperatures for 4 months. (a) Aging at ambient temperature, (b) aging at 69 °C and (c) aging at 87 °C.

Figure 4.6. Distribution of CH$_3$CF$_2$Cl between gas and solid phases in a PS foam after highly accelerated aging. (a). Comparison between samples #6 and #7, showing the effect of temperature on diffusion. (b). Comparison between samples #1, #6 and #8, showing the effect of sample size on diffusion at ambient temperature.
Figure 4.7. $^{19}$F MAS NMR spectrum (spinning at 10 kHz) of a PS foam cylinder originally made with CH$_3$CF$_2$Cl and then exposed to CFCl$_3$ gas for 8 days at 69 °C. The arrows indicate spinning sidebands and chemical shifts are referenced to external CFCl$_3$ (0.0 ppm).

Figure 5.1. Plot of the intensity of the signal versus the radius $r$ of the PU foam cylinders, symbols indicate experimental data and the dashed line the curve from the least-squares fitting.

Figure 5.2. Plot of the relative loss of gas from the cutting versus the radius $r$ of the PU foam cylinders. C1, C2 are defined in text (see Chapter 2).

Figure 5.3. $^{19}$F NMR spectrum of blowing gases in PU foam sample PU-4 together with the reference sample (C$_6$H$_5$CF$_3$) sealed in a capillary tube within the coil. Chemical shifts are referenced relative to external CFCl$_3$ (0.0 ppm).

Figures 5.4. $^{19}$F NMR results obtained from PU sample PU-4 containing a blend of three gases: CFC-11 (CFCl$_3$), HCFC-141b (CH$_3$CFC$_2$) and HCFC-123 (CF$_3$CHCl$_2$) as indicated. (a). $^{19}$F NMR spectrum. (b). Cross-section images of CFCl$_3$, CH$_3$CFC$_2$ and CF$_3$CHCl$_2$. (c). 1D imaging projections of the three gases in the cross-section and axial directions.

Figure 5.5. Typical MAS spectrum spinning at 10 kHz of CH$_3$CFCl$_2$ in PU sample PU-1 with Teflon reference. The arrows indicate spinning sidebands. Chemical shifts are referenced relative to external CFCl$_3$ (0.0 ppm).

Figure 5.6. Plots from Table 5.6, representing the distribution of CH$_3$CFCl$_2$ at different locations in PU foam boards exposed for a diffusion at (a) ambient temperature and (b) at 87 °C.

Figure 5.7. Histogram plots from Table 5.7, representing the distribution of blowing gases in the PU cylindrical samples indicated. RT denotes fresh cut samples at RT, 87 °C denotes samples aged for 8 days at 87 °C.

Figure 5.8. 1D $^{19}$F imaging profiles of CH$_3$CFCl$_2$ obtained from PU foam sample PU-1 as functions of time and temperatures (a) after aging for 96 days at ambient temperature, 51 °, 69 ° and 87 °C and (b) after aging at 87 °C for i) 58, ii) 81 and iii) 96 days.

Figure 5.9. Diffusion of CH$_3$CFCl$_2$ (HCFC-141b) out of PU foam blocks (a) after aging at 87 °C for various time intervals. Experiments #1, #2, #3 and Calculations #1, #2, #3 correspond to diffusion times of 58, 81, and 96 days respectively (b) after aging for 96 days at the various temperatures indicated. Calculations #4, #5, #6 and #7 correspond to the curves for diffusion at ambient temperature, 51 °C, 69 ° and 87 °C respectively. Symbols indicate experimental data from the imaging profiles, lines indicate calculated data from the model for this case (see text). Normalized intensity ($I/I_0$) is defined in the text.
Figure 5.10. Temperature dependence of the diffusion coefficients of CH$_3$CFCl$_2$ in PU foams...

Figure 5.11. $^{19}$F NMR spectra of CH$_3$CFCl$_2$ and CFCl$_3$ in PU foam samples after exposure to CFCl$_3$ gas at 69°C for (a) PU-1f for 120 hours and (b) PU-1g for 360 hours...

Figure 5.12. Two-dimensional cross-section images of CFCl$_3$ in PU foam sample PU-1e after exposure to CFCl$_3$ at ambient temperature for 336 hours. The imaging parameters were the same as in Figure 2.28...

Figure 5.13. Typical MAS $^{19}$F NMR spectrum (spinning at 10 kHz) of CH$_3$CFCl$_2$, CFCl$_3$ and Teflon reference in sample PU-1g post-treated with CFCl$_3$ for 15 days at 69°C. The arrows indicate spinning sidebands. Chemical shifts are referenced relative to external CFCl$_3$ (0.0 ppm).

Figure 5.14. 1D $^{19}$F imaging profiles of (a) CH$_3$CFCl$_2$ and (b) CFCl$_3$ in the PU foam cylinder post-treated at 69°C for 120 hours and 360 hours as indicated...
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>o.d.</td>
<td>outer diameter</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>r.f.</td>
<td>radio frequency</td>
</tr>
<tr>
<td>CFCs</td>
<td>Chlorofluorocarbons</td>
</tr>
<tr>
<td>CPMG</td>
<td>Carr-Purcell-Meiboom-Gill NMR pulse sequence for measuring $T_2$ relaxation times</td>
</tr>
<tr>
<td>CRAMPS</td>
<td>Combined rotation and multiple-pulse spectroscopy</td>
</tr>
<tr>
<td>FID</td>
<td>Free induction decay</td>
</tr>
<tr>
<td>FLASH</td>
<td>Fast Low Angle Shot NMR imaging pulse sequence</td>
</tr>
<tr>
<td>GWP</td>
<td>Global warming potential</td>
</tr>
<tr>
<td>HCFCs</td>
<td>Hydrochlorofluorocarbons</td>
</tr>
<tr>
<td>HFCs</td>
<td>Hydrofluorocarbons</td>
</tr>
<tr>
<td>MAS</td>
<td>Magic-angle spinning</td>
</tr>
<tr>
<td>MDI</td>
<td>Methane diphenyl diisocyanate</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>ODP</td>
<td>Ozone depletion potentials</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PU</td>
<td>Polyurethane</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>TDI</td>
<td>Toluene diisocyanate</td>
</tr>
<tr>
<td>TE</td>
<td>Time to echo, the time between the middle of the 90° excitation pulse and the middle of the acquisition in a spin-echo type NMR imaging pulse sequence</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>TR</td>
<td>Repetition time, the time between each of a series of pulse train repetitions in an imaging sequence</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

First, I would like to take this opportunity to thank my supervisor Dr. Colin A. Fyfe for his insight, guidance and extreme patience throughout this research and the preparation of this thesis, and for giving me the opportunity to learn and work with NMR.

I would like to thank Dr. Hiltrud Grondey for her help, support and friendship. I am also very grateful to Drs. Nick Burlinson, Stephanie Isbell and Leslie Randall for their patience when I started to learn NMR. In addition, I would like to thank all the members in the Fyfe group for their support.

I am indebted to Mr. Tom Markus of the Electronic Engineering Services for his expertise and help concerning Bruker spectrometers. In addition, I am thankful to the people in the Mechanical Engineering Services for their assistance. I thank Du Pont (Canada) Inc. and DOW Chemical Co. for providing polystyrene and polyurethane foams for this research.

Finally, I wish to thank my family for their constant encouragement. To my husband Gang and my son Billy for giving me the strength to reach my dream through these years.
CHAPTER 1 INTRODUCTION

1.1. RIGID PLASTIC CLOSED-CELL INSULATING FOAMS

1.1.1. Polyurethane and Polystyrene Foams

Plastic foams made of polymers such as polystyrene (PS) and polyurethane (PU) are widely used due to their superior thermal insulating properties, high strength-to-weight ratios and moderate cost compared to their energy-saving potential. Thermal insulation is the second largest application of foamed plastics. At present, polyurethane foams are those most often used followed by polystyrene foams [1]. In 1994, more than 500 million pounds of rigid polyurethane foams were used in roofing and wall-insulation applications in the United States [2].

Both PS and PU foams may be flexible or rigid, depending on the chemical composition, the rigidity of the polymer backbone and the degree of cross-linking. Rigid foams can be defined as having a glass transition temperature above room temperature. Flexible foams have glass transition temperatures below room temperature.

The individual cells within the foam may be separated (closed-cell foams), where the cells are completely surrounded by a thin membrane of the solid polymer, or they may be interconnected (open cell foams). The closed-cell variety is obviously better suited for thermal insulation purposes. Whether a closed- or an open-cell structure is formed depends on a critical balance between the viscosity of the liquid polymer and the rate of
generation of the blowing gas. The PS and PU insulating foams investigated in this thesis were all rigid, closed-cell materials.

Foams can be made from polymeric materials by mechanical, physical or chemical means [3] and are available in many forms such as blocks, boards etc. The formation of PS and PU foams has been reported in detail by numerous authors [4-6]. Only a brief introduction will be given here.

The first commercial polystyrene foam was extruded board prepared by Munters and Tandberg [7] and developed by the Dow Chemical Co.. Molten polystyrene containing methyl chloride was extruded into large foam logs, which were then cut into the desired shapes. This product, Styrofoam, was introduced in the United States for military applications during World War II. Commercial acceptance continued after 1946, primarily for insulation and construction. For critical insulation purposes, the Styrofoam process has been developed by using blowing agents containing fluorocarbons to improve the insulation performance of the product [8]. The fluorocarbon blowing agent has a low thermal conductivity and other desirable properties and is mostly responsible for the superior insulation performance of the foams. Further discussion will be found in Section 1.1.2.

The widely used thermoplastic polystyrene is produced by free-radical polymerization of styrene monomers as illustrated by the equation below.

\[
n (\text{CH}_2 = \text{CH}) \rightarrow (\text{-CH}_2 - \text{CH})_n
\]
It is a linear polymer that has a low density and high molecular weight (between 100,000 and 400,000). Polystyrene can be easily formed into final products by a variety of methods because of its low $T_g$ value of about 373 K. It is lightweight and cost-effective.

The production of foamed plastic insulation involves three successive stages: liquid state polymer, introduction of bubbles of gas and solidification. The liquid state of polystyrene is produced by heating it until molten, then the blowing agent, mainly volatile liquid CFCI$_3$, CF$_3$CCI$_3$ dissolved in the liquid polymer under pressure, generates bubbles of gas under heating. Once the polymer has been expanded or "blown", the cellular structure must be stabilized rapidly, otherwise it would collapse. For PS foams, expansion is carried out above the softening or melting point, and the foam is then immediately cooled to below the melting temperature. Often expansion and simultaneous cooling occur as the polymer is extruded through a die and sizing units to produce continuous board or other shapes.

Since 1954, considerable progress has been made in product property improvements, molding process innovations and in applications. The combination of low density, rigidity, thermal insulation, non-toxicity, good color and chemical resistance of PS rigid foams has made it popular in mass markets.

The polyurethane foams were developed during 1941 - 1945 as rigid types by Bayer [9] and flexible types were first reported by Hochtlen [10].

Thermosetting plastic polyurethanes consist of urethane linkages formed by the reaction of isocyanates with molecules containing hydroxyl groups or other groups with active hydrogens. Most of the polyurethanes used worldwide are based on two aromatic isocyanates: toluene diisocyanate (TDI) and diphenyl methane diisocyanate (MDI). Compounds with active hydrogens, which make up the other half of the reaction system,
typically consist of polyoxypropylene glycols (polyether polyols). The polymerization process can be illustrated by the equation below:

$$\text{OCN-}R\text{-NCO} + \text{HO-}R'\text{-OH} \rightarrow (\text{O-}R'\text{-O-CO-NH-R-NHCO})_n$$

PU foams are manufactured by mixing liquid aliphatic polyols with liquid aromatic polyisocyanates, which react readily. For insulating foams, a blowing agent, mainly CFCs as in PS foams must be added, usually to the polyol. The blowing agents are boiled by the exotherm of the cure reaction, gas bubbles are produced and expanded when the reacting liquids have reached the optimum viscosity, then the cross-linking reaction is completed to stabilize the foam structure.

Most polyurethanes are manufactured using dispensing machines that combine the isocyanate and polyol streams at preset mixing ratios and outputs, and deliver the mixed components under controlled rates into various types of molds. Rigid foam can be made as a board or laminate, poured in place, frothed, or sprayed.

The rigid PU foams, primarily used as insulating materials, have many advantages including being the most efficient insulation, having the lowest weight for equivalent insulation and their excellent water, solvent and chemical resistances. In addition, they can be easily handled and attached in place because of their rigidity.

As discussed above, the unique properties of the rigid closed-cell PS and PU foams clearly distinguish them from the solid polymers and have made them particularly useful in practical applications. Basically, these properties result from their composite structure: a continuous phase of polymer and a gas phase dispersed in single closed cells giving them high rigidity/weight and strength/weight ratios. Their high thermal and electrical insulating abilities, the most important properties of foams are due to the very low conductivity of the gas phase. Thus the choice of the blowing gas becomes important, and fluorocarbons provide the highest thermal insulation as will be discussed in the next section.
1.1.2. Blowing Agents

As described in the previous section, plastic foams consist of two phases: a gaseous phase (blowing agent) and a solid phase (polymer). While the chemical nature of the solid polymer phase is the dominant factor in determining the mechanical properties of the foams, the composition of the gaseous phase has an important effect on some specific properties such as thermal insulation.

In mid 1958, chlorofluorocarbons (CFCs) were introduced as blowing agents for polyurethane foams, providing the first significant advance for the use of rigid PU foams as thermal and electrical insulators. There are significant advantages due to the particular properties of these blowing agents. For example, for the last two decades CFC-11 (CFCl₃) has been regarded by the rigid foam industry as the ideal blowing agent due to its low thermal conductivity, boiling point / vapor pressure properties, solubility and chemical compatibility in all typical formulations.

Table 1.1. Comparison of the thermal conductivities of air, CO₂ and CFCl₃ in terms of their “k factors” (Wm⁻¹ K⁻¹)(adapted from ref. [8] into SI units)*.

<table>
<thead>
<tr>
<th></th>
<th>32°F</th>
<th>68°F</th>
<th>86°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.0242</td>
<td>0.0260</td>
<td>...</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0146</td>
<td>0.0169</td>
<td>...</td>
</tr>
<tr>
<td>CFCl₃</td>
<td>0.00779</td>
<td>0.00822</td>
<td>0.0084</td>
</tr>
</tbody>
</table>

* k factor is defined as the rate of heat flow through a unit area of a unit thickness per unit temperature gradient in the direction perpendicular to the area.
Table 1.1 (from ref.[8]) shows the comparisons of thermal conductivities between air, CO₂ and CFC₃ (CFC-11) at various temperatures. It can be seen that CO₂, if used as a blowing agent has some advantages over air, but CFC-11 has only one-half as much conductivity as CO₂ and also the thermal conductivity of CFC-11 does not increase proportionately as air or CO₂ as the temperature rises. Another very important factor is that the CFCs will not diffuse quickly through cell walls of foams so that the insulating properties of these foams are lost, as is the case with CO₂.

In 1974 Rowland and Molina recognized the chlorine from CFCs can attack ozone and their work eventually led to an explosion of atmospheric chemistry research [11]. The studies showed that CFCs are so stable that they can reach the stratosphere, where the uniquely cold temperature and the intense UV radiation free active chlorine and chlorine monoxide (ClO) radicals from CFCs, which can then participate in several ozone-destroying catalytic chemical and photochemical cycles (shown below) allowing rapid ozone depletion [12]. Rowland and Molina together with Crutzen (who showed in 1970 that naturally occurring nitrogen oxides catalytically destroy ozone) received the 1995 Nobel Prize in Chemistry for their ozone depletion research.

\[ \text{Cl}^- + \text{O}_3 \rightarrow \text{ClO}^- + \text{O}_2 \]

\[ \text{ClO}^- + \text{ClO}^- + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \]

\[ \text{Cl}_2\text{O}_2 + \text{M} \rightarrow \text{Cl}_2 + \text{O}_2 + \text{M} \]

\[ \text{Cl}_2 + h\nu \rightarrow 2 \text{Cl}^- \]

net: \[ 2 \text{O}_3 + h\nu \rightarrow 3 \text{O}_2 \]

another possible cycle is:
On September 16, 1987, the United States and twenty-three other nations signed an international agreement, known as the “Montreal Protocol [13]”, to reduce production of CFCs (CFC-11 etc.) because of their adverse effects on the ozone layer. In this agreement, CFC production and use are to be banned by the year 2000.

Hydrochlorofluorocarbons (HCFCs) are viewed as acceptable interim alternatives to CFCs. Currently HCFC-141b and HCFC-22 are the preferred blowing agent replacements for CFC-11 in most rigid foam applications to achieve acceptable thermal insulation in closed-cell foams. The hydrogen atoms in HCFCs make them less chemically stable and susceptible to degradation in the low atmosphere (troposphere) resulting in much shorter atmospheric lifetimes than CFCs and consequently lower ozone depletion potentials (ODP) (about 5-11% of the ODP of CFCs), but small amounts of HCFCs can still reach the stratosphere and contribute to the ozone depletion. Their use will be eliminated in stages until a total phaseout is achieved by the year 2030. The selection of CFC and HCFC replacements is based on manufacturability, energy efficiency, toxicity/safety, reliability and impact on direct global warming. New blowing agents must have zero ozone depletion potential and global warming potential (GWP) and low thermal conductivity. Carbon dioxide, generated from the water-isocynate reaction, is being developed for non-insulation polyurethane applications. Development of zero-ODP blowing agents for insulation-critical foams is focusing on HFCs which are shown to be similar in performance to the current choice of blowing agents (HCFCs). The switch to new blowing agents should be completed within about five to 10 years. Thus it is very
important to have effective and reliable methods to evaluate the aging processes of insulating foams blown with new CFC alternatives.

Table 1.2. Properties of CFC blowing agents and possible alternatives (from ref.[14]).

<table>
<thead>
<tr>
<th></th>
<th>CFC-11 ((\text{CFCl}_{3}))</th>
<th>CFC-12 ((\text{CF}<em>{2}\text{Cl}</em>{2}))</th>
<th>HCFC-141b ((\text{CH}<em>{3}\text{CFCl}</em>{2}))</th>
<th>HCFC-22 ((\text{CHF}_{2}\text{Cl}))</th>
<th>HFC-134a ((\text{CH}<em>{2}\text{FCF}</em>{3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODP(^1)</td>
<td>1.0</td>
<td>1.0</td>
<td>0.15</td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td>GWP(^2)</td>
<td>1.0</td>
<td>3.0</td>
<td>0.15</td>
<td>0.34</td>
<td>0.26</td>
</tr>
<tr>
<td>thermal conductivity*</td>
<td>0.0093</td>
<td>0.011</td>
<td>0.014</td>
<td>0.013</td>
<td>0.017</td>
</tr>
</tbody>
</table>

* at 140 °F \((\text{Wm}^{-1}\text{K}^{-1})\)
1. determined by the chlorine content and the lifetime of the molecules with respect to CFC-11(set to 1.0).
2. determined by the relative infrared absorbance and the lifetime of the molecules with respect to CFC-11(set to 1.0).

1.1.3 Aging Processes of Insulating Foams

Rigid polyurethane and polystyrene foams are the most efficient insulating materials in commercial use. These foams are used in a variety of applications including building constructions and transportation. As discussed in previous sections, closed-cell foams containing CFC’s have the lowest thermal conductivities of any insulation materials currently available, other than a vacuum insulation system.

Heat is transferred through closed-cell foam insulation by

1. Conduction through the cell-gas.
2. Conduction through the solid polymer.
3. Radiation across the solid polymer.

Due to the small cells in the foam, large scale convective gas movements within the foam are prevented. It has been shown that at least 50 percent of the total heat is transferred by conduction through the blowing agents inside the cells, so it is advantageous to have a low conductivity gas inside of the foam, e.g. CFCs as discussed earlier. Table 1.3 clearly shows that the conductivity of the foam \((0.015 \text{ W m}^{-1} \text{ K}^{-1})\) is much lower than the solid polymer \((0.20 \text{ W m}^{-1} \text{ K}^{-1})\) due to the presence of low conductivity blowing gas.

Table 1.3. Summary of heat transfer routes through polyurethane foam together with the thermal conductivity of the solid polymer (from ref. 15).

<table>
<thead>
<tr>
<th>Heat transfer through polyurethane foams</th>
<th>Thermal conductivity (W m(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conduction through matrix (3 % vol/vol of total)</td>
<td>0.0055</td>
</tr>
<tr>
<td>Conduction through gas (97 % vol/vol of total)</td>
<td>0.0080</td>
</tr>
<tr>
<td>Radiation</td>
<td>0.0015</td>
</tr>
<tr>
<td>Convection in cells</td>
<td>0</td>
</tr>
<tr>
<td>Total heat transfer in foam</td>
<td>0.015</td>
</tr>
<tr>
<td>Heat transferred by conduction in solid polymer</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Initially, cells of fresh foams contain the highest fraction of blowing agent and the lowest fraction of air components. During the service life of the foam, the foam conductivity increases with age as air components diffuse into foam while CFCs (blowing agents) diffuse out to the environment. This effect is known as the aging effect. Ultimately
all of the blowing agent is replaced by air. Air components diffuse much faster than CFCs, and the out-diffusion of the CFCs usually lasts more than a decade. Therefore the diffusion of the blowing agents determines the long term thermal conductivity changes of foams. It is essential to quantify the aging rate of closed-cell foams to enable the industry to distinguish foams with good and bad aging properties and look more efficiently for the best alternative blowing agents. This is particularly important because of the impending elimination of CFCs as blowing agents for PU and PS foams because of their high ozone depletion potentials as discussed earlier.

For the purpose of evaluating long-term thermal insulation performance, the thermal conductivity of the foam was often used to monitor the diffusion process, but there is a possible non-linearity between the concentration of blowing gas and the thermal conductivity of the gas [16-17]. A more fundamentally reliable method of determining aging performance is by mass or concentration measurement. Gas chromatography, mass spectrometry, absorption-desorption (gravimetric) methods have been introduced to determine the amounts of blowing gas and other gaseous compounds present in polymer foam. These methods all require a destructive sampling method: the cell structure has to be destroyed to release the cell gas, generally by crushing the foam in a gasbag using a hydraulic press [18] or by first cooling the sample in liquid nitrogen and then crushing the brittle foam [19] as will be described in Chapters 3 and 4. The change of cell gas concentration with time can then be used to calculate the effective diffusion coefficients of the cell gases.
1.1.4. Potential Use of NMR Spectroscopy and NMR Imaging in the Investigation of Foams

Microscopic NMR imaging has emerged as a viable non-invasive and non-destructive technique by which the distribution of mobile fluids in polymeric materials can be monitored [20-21]. The principle advantage of NMR imaging is that it is possible to determine both the concentration and the location of a permeating liquid within a solid sample and provide a visual presentation of the distribution and diffusion in the form of an image. Such a presentation makes it possible to directly view the concentration and the location of the penetrant as functions of time and other factors. It also makes it possible to detect any imperfections (e.g. voids, non-uniform areas) in the sample studied which is important as it is generally difficult to interpret the result (e.g. diffusion behavior) if the sample is not homogeneous. In principle, it should be possible to perform similar experiments on samples which contain gaseous materials, the limiting factor being the achievable signal to noise (S/N). At the time the present work was initiated there were no literature reports of such experiments, but subsequently an $^{19}$F NMR imaging study of C$_2$F$_6$ and CF$_4$ gases in a ceramic was reported which showed delaminations and voids and revealed the layered nature of the material [22]. There is no published work on NMR imaging investigation of blowing gases in insulating foams to the best of our knowledge to date and only one preliminary study by solid state NMR spectroscopy of blowing gases dissolved in polymers which will be discussed in Chapter 4.
1.2. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

1.2.1. Multinuclear NMR Spectroscopy

Since its discovery in 1946, nuclear magnetic resonance (NMR) spectroscopy has become one of the most powerful techniques used in many different fields of chemistry, physics and medicine. The principles of NMR have been extensively described in both quantum-mechanical and classical physics formalisms in numerous textbooks and reviews [23-26]. Only a brief description of some basic concepts is given here.

About a hundred nuclear isotopes have an intrinsic angular momentum, or spin $I$, and a parallel (or anti-parallel) magnetic moment $\mu$, related to $I$ by

$$\mu = \gamma h I$$

(1.1)

where $\gamma$ is the gyromagnetic ratio, a characteristic of each nuclear species, and $h = h/2\pi$ ($h$ is Planck’s constant). When a magnetic field of strength $B_0$ is applied in a direction defined as $z$, a magnetic moment $\mu$ has an energy $E$ given by

$$E = - \mu \cdot B_0 = - \mu_z B_0$$

(1.2)

At thermal equilibrium at a temperature $T$, the macroscopic magnetization $M$ of a system of $N$ identical nuclear spins is parallel to the external field and of the form:

$$M = N \frac{\gamma h I}{T}$$

(1.3)

If by some means the magnetization is tilted so as to make an angle $\theta$ with the field $B_0$, its subsequent evolution is a precession around $B_0$ at constant angle $\theta$, at a frequency (in radians per second) equal to

$$\omega = |\gamma| B_0$$

(1.4)
This is the Larmor theorem. The frequency $\omega_o$ is called Larmor frequency, and falls in the radio-frequency domain.

The practical method for tilting the magnetization away from its equilibrium orientation is to apply a radio frequency pulse. If, besides the static field $B_0$, one applies a radio-frequency field $B_1 \ll B_0$, perpendicular to $B_0$ and rotating around it at a frequency $\omega_o$, the simplest way to analyze the evolution of the magnetization is through the use of a reference frame of axes rotating around $B_0$ at the same frequency $\omega_o$. It can be shown that under this condition in this rotating frame, the effective field is purely transverse and equals $B_1$. In this rotating frame of reference, the precession of the magnetization around $B_1$ at frequency $\omega_1 = |\gamma| B_1$ tilts this magnetization away from the direction of the static field $B_0$. If the field $B_1$ is applied during a time $\tau$, the angle between $M$ and $B_0$ is equal to $\theta = \omega_1 \tau = |\gamma| B_1 \tau$. This is called a pulse of angle $\theta$, after which the magnetization processes around $B_0$ at the Larmor frequency $\omega_o$. In practice the sample is surrounded with a coil which produces a linearly polarized radio-frequency (r.f.) field. The rotating transverse component of magnetization following the r.f. pulse induces an emf in the coil which is amplified and detected as the “free induction decay” (FID) of the NMR signal.

Hydrogen ($^1\text{H}$) and fluorine ($^{19}\text{F}$) have always been common NMR nuclei for reasons of sensitivity. They are both very sensitive because they have almost 100% natural abundance and large gyromagnetic ratios: $^1\text{H}$ has the second largest $\gamma$ value ($5.58 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$) and $^{19}\text{F}$ ($5.26 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$). They are both spin 1/2 nuclei with simple spectra except that $^{19}\text{F}$ NMR shows large values of $^{19}\text{F}$ chemical shifts and spin coupling constants. Thus it is often possible to obtain more information about molecular structures and dynamic molecular processes for fluorine-containing molecules than for the analogous hydrogen-containing systems. A particular advantage of $^{19}\text{F}$ NMR in investigating mixtures and heterogeneous materials is that $^{19}\text{F}$ NMR is often free of the interferences
from the background. Extensive studies carried out since the 1960's dealing with most aspects of $^{19}$F nuclear magnetic resonance can be found in refs. [27-28].

1.2.2. Nuclear Relaxation Processes

When a group of nuclear spins is placed in a static magnetic field $B_0$, a net magnetization $M_z$, develops along the direction of $B_0$ from the $z$ components of the aligned individual nuclear magnetic moments. At equilibrium, when the populations of the spin-energy levels are given by the Boltzmann distribution, the net magnetization in the $z$ direction, $M_o$, is given by the Curie law:

$$M_o = \frac{N\gamma^2 h^2 I(I+1)}{3kT} B_o$$  (1.5)

where $N$ is the number of spins, $\gamma$ is the gyromagnetic ratio, $h = h/2\pi$ ($h$ is Planck’s constant), $I$ the nuclear-spin quantum number, $k$ the Boltzmann constant and $T$ the absolute temperature. The rate at which $M_z$ approaches $M_o$ after a perturbation is generally given by a first-order differential equation:

$$\frac{dM_z}{dt} = -\frac{(M_z - M_o)}{T_1}$$  (1.6)

where $T_1$ is called the spin-lattice relaxation time. The term ‘spin-lattice’ relaxation derives from the fact that the relaxation process involves a transfer of Zeeman energy from an “excited” spin to the “lattice”, i.e. the environment. Note that this is an exponential process.
The most commonly used technique to measure $T_1$ is the inversion-recovery experiment, as illustrated in Figure 1.1. In this experiment, the sample is excited with a 180° r.f. pulse, then allowed to relax toward $B_0$ for a period of time $\tau$. Application of a 90° r.f. pulse then makes it possible to sample the progress of the magnetization towards its equilibrium value from the resulting FID. This experiment is repeated for various value of $\tau$ and the $T_1$ value can be obtained by fitting the intensities of the resulting signals to Equation (1.6). An accurate determination of $M_o$, the intensity value at $\tau \geq 5T_1$, is essential in order to obtain a $T_1$ value. Also, the repetition time of $5T_1$ is needed to ensure that $M_z$ has reached $M_o$ before each scan to obtain reliable data. Thus it is necessary to have some prior knowledge of the approximate $T_1$ value and the pulse repetition time can be very long.
Figure 1.1. Schematic representation of the 180°-τ-90° inversion recovery sequence used to measure $T_1$ relaxation times (from ref. [29]).
When an ensemble system of spins at equilibrium in a static magnetic field is subjected to a 90° r.f. pulse, the net z magnetization is rotated into the xy plane. In a perfectly homogeneous magnetic field, the decay of magnetization in the xy plane is governed by $T_2$, the spin-spin or transverse relaxation time,

$$\frac{d M_x}{d t} = -\frac{M_x}{T_2}, \quad \frac{d M_y}{d t} = -\frac{M_y}{T_2} \quad (1.7)$$

A spin-echo experiment is normally used to measure $T_2$ as illustrated in Figure 1.2. The sample is excited with a 90° pulse, then the magnetization in the transverse plane is allowed to decay for a time $\tau$ before being inverted by a 180° pulse. This pulse is to refocus the dephasing due to field inhomogeneities and chemical shifts but not that due to the true spin-spin $T_2$ relaxation. Thus at time $2\tau$, the magnetization will refocus and its intensity is determined by $T_2$ relaxation alone. This process is repeated for a series of different $\tau$ values and the $T_2$ value can be obtained by fitting the intensities of the signals to Equation (1.7).

Both $T_1$ and $T_2$ relaxation processes involve time-dependent magnetic or electric fields at the nucleus which are derived from the random thermal motions present in the sample. There are three principal types of magnetic interaction which contribute to relaxation of spin 1/2 nuclei. The most important is the dipole-dipole interaction, where the nucleus experiences a fluctuating field due to the motion of neighboring magnetic dipoles (unpaired electrons or other nuclei). This interaction will be discussed further in Section 1.4.1.
Figure 1.2. Schematic representation of the 90°-τ-180°-τ spin echo sequence used to measure $T_2$ relaxation times (from ref. [29]).
A second type of magnetic interaction arises because the chemical shielding of the nucleus depends on the orientation of the molecule with respect to the $B_0$ field direction. This is known as the chemical shift anisotropy. The shielding can be represented as a weak secondary magnetic field that is established when the electrons surrounding the nucleus also precess in the applied field $B_0$. This field is proportional to $B_0$ and fluctuates as the molecule tumbles. Since the relaxation rate depends on the square of the appropriate field at the nucleus, the rate of relaxation by chemical shift anisotropy increases as the square of the applied field strength $B_0$. Relaxation by chemical shift anisotropy becomes more important at higher fields. In some cases, it is possible that it may dominate all other mechanisms.

The third mechanism involves the spin-rotation interaction. As a molecule rotates, the moving charges of the electrons and nuclei create small electric currents which in turn induce a small magnetic field at the nucleus. The field at the nucleus fluctuates because the reorientational motion is not uniform but proceeds by a series of random jumps. This mechanism increases in effectiveness as the tumbling motion increases. Unlike the dipolar mechanism, spin-rotational relaxation is much more effective for small molecules in low-viscosity solutions at high temperatures or in the gas phase. Opposing temperature dependence can be used to distinguish the mechanisms as will be described further in Chapter 2.

A fourth, a rare relaxation mechanism known as spin-spin (scalar) relaxation relies on the weak magnetic field induced at the site of a spin $I$ by spin-spin coupling to a neighboring spin $S$. This is usually only an effective relaxation mechanism if $S$ is a quadrupolar nucleus or they are undergoing a fast chemical exchange.

In this thesis, the nuclei studied are $^1$H and $^{19}$F, both of which have $I = \frac{1}{2}$ and thus, the quadrupolar relaxation mechanism will not be discussed here.
1.2.3. *Quantitative NMR Measurements*

NMR spectroscopy possesses one very valuable property, i.e. the intensity of a given resonance peak is directly proportional to the number of nuclei contributing to that peak provided that certain experimental precautions are taken. This makes possible a quantitative determination of the relative amounts of two substances present in the sample, and the measurement can be made absolute by adding a carefully measured concentration of one of these substances as a reference. In this way, the absolute concentration of the second substance can be therefore obtained from the recorded spectrum.

Intensity is defined as the peak area. In situations where all the lines in the spectrum have the same width and shape, the peak height may be used as a simpler measure of intensity. In general, it is more accurate to measure the area by means of integration. In the case of only partially resolved resonance lines, curve-fitting is required to decompose them into their individual components.

Experimental precautions are necessary to ensure reliable intensity measurements in pulse-FT NMR experiments. For the purposes of this thesis, these include: selection of a repetition time 5 times the longest $T_1$ value in order to avoid saturation; use of a reference sample chosen so that its signal was within the uniform excitation range of the spectrum of interest as detailed in Chapter 2; and collection of sufficient data points and correct phasing of the entire spectrum before integration.
1.3. NMR IMAGING

NMR imaging extends NMR spectroscopy to the determination of three-dimensional spatial information about the distribution of nuclei within a sample. This section will describe some basic concepts and general techniques. Detailed descriptions of NMR imaging protocols can be found in ref. [30-31].

1.3.1. Back-Projection Imaging

The first demonstration that NMR could be used as an imaging technique was presented by Lauterbur in 1973 [32]. He recognized that the application of a "linear magnetic field gradient" over a sample provided spatial information on the location of the nuclei within the sample.

The basic experiment described by Lauterbur is illustrated in Figure 1.3. In the absence of the field gradient, a single sharp signal will be observed from the sample (two tubes of water) because the static magnetic field is homogeneous over the whole sample volume within the r.f. coil. In the presence of an additional linear field gradient as indicated, two separate signals will be observed which reflect the positions of the two water tubes. Quantitatively, the resonance frequency $\omega_o$ in a homogeneous field $B_o$ can be written

$$\omega_o = |\gamma| B_o$$  \hspace{1cm} (1.8)
Figure 1.3. Schematic representation of the effect of a linear field gradient.
If a field gradient $G_x = \frac{dB}{dx}$ is applied along the $x$-direction then the static magnetic field at some position $x$ becomes

$$B_z(x) = B_0 + G_x \cdot x \quad (1.9)$$

and the resonance frequencies of the nuclei now depend on their positions projected on the $x$-axis according to

$$\omega_x = \omega_0 + \gamma G_x \cdot x \quad (1.10)$$

This is the relationship between the resonance frequency and the position which is the basis for NMR imaging. The signal observed $S(t)$ in the presence of a single gradient $G_x$ will reflect the spin density $\rho(x)$ projected onto the $x$-axis as

$$S(t) = \int \rho(x) \exp \left[ i (\gamma G_x x) t \right] dx \quad (1.11)$$

if decay due to relaxation is neglected and $\omega_0 = 0$.

Thus the Fourier transform of $S(t)$ yields the spin density projection along the $x$-axis of the imaged object. Figure 1.4 illustrates how the successive application of a number of field gradients in different directions may be used to generate a data set from which the positions and dimensions of the two tubes of water may be reconstructed into the image space by “back-projection” techniques.
Figure 1.4. Schematic representation of a two-dimensional "back-projection" image obtained from the application of a number of field gradients in different directions (from ref. [32]).
1.3.2. Fourier Imaging

Back-projection was the first method used for NMR imaging. At present the method of "Fourier Imaging" is most commonly used. This protocol was first introduced by Kumar and Ernst in 1975 [33] and the principle is the following: After the initial r.f. pulse, one applies a gradient $G_y$ along $y$-axis during a time $\tau$, without observing the signal. This gradient is then suddenly switched off and replaced by a gradient $G_x$ along $x$-axis and the signal is observed as a function of the time $t$ following the gradient switching. The sequence is shown in Figure 1.5.

The observed signal is

$$S(t) = \iint \rho(x,y) \exp\left[i \left( \gamma G_x x t + \gamma G_y y \tau \right) \right] dx \ dy \quad (1.12)$$

The sequence is repeated incrementing the duration time $t_1$ of the $G_y$ gradient and acquiring the data for each experiment in $t_2$. The two-dimensional Fourier transform of the resulting 2D data set produces a two-dimensional image.

There are some practical problems with this protocol which are circumvented by the 'Spin-Warp' modifications by Edelstein et. al.[34]. One improvement is to use a series of regularly spaced values of the gradient $G_y$ while keeping the duration $t_1$ constant. Thus the relaxation effects during the times the gradients are applied are the same since $t_1$ is constant. Another improvement is to introduce an echo sequence which moves the data acquisition well away from r.f. pulse and the switching of the gradients. Also an increase in S/N can be achieved with an echo sequence instead of acquiring only half echo. The complete sequence will be discussed in Chapter 2.

The above methods can readily be extended to 3-dimensional objects. However, usually 2-dimensional images of a selection of slices are enough. This is done with the selective excitation of the nuclei in a slice through the object which is accomplished by a
combination of a frequency selective r.f. pulse and a magnetic field gradient perpendicular to the imaging plane. Selective pulses have different shapes (e.g. gaussian, sinc etc.) and are of much longer duration, so that they can be used to uniformly excite a small bandwidth of frequencies as shown in Figure 1.6. As in the figure, if a slice is to be taken in a plane perpendicular to the z-axis, then a z-gradient has to be applied. The signal from the sample will spread out over a frequency range shown in (c) during application of the gradient if the r.f. pulse is not selective and excites the whole frequency range. If, however, a selective pulse is used to excite only a small and well defined frequency range, then this corresponds to exciting the nuclei in only a small cross-section or “slice” through the sample as shown in (d). The shape and the bandwidth of the r.f. pulse and the amplitude of the slice-selection gradient determine the slice thickness and uniformity of the excitation.
Figure 1.5. Basic sequence for the Fourier imaging method.
Figure 1.6. Schematic representation of the slice selection method. (a) Gradient $G_z$, (b) sample orientation, (c) distribution of Larmor frequencies in the sample with gradient $G_z$ on when the excitation is nonselective, and (d) bandwidth of frequencies selected by the soft pulse.
As indicated above, the most common form of Fourier imaging is called spin-warp (spin-echo) imaging. This sequence uses $90^\circ \tau 180^\circ \tau$ acquire to form an echo in the presence of a field gradient as discussed in Chapter 2. A similar but not quite identical echo, the "gradient-echo", may be formed by omitting the $180^\circ$ r.f. pulse but reversing the sign of the gradient at this time while keeping its magnitude constant is used in another often used method called the FLASH (Fast Low Angle Shot) sequence as will be discussed in Chapter 2.

1.4. HIGH RESOLUTION SOLID STATE NMR SPECTROSCOPY

1.4.1. Magnetic Interactions in Solids

There are a number of contributions to the NMR spectra of solids, including the Zeeman, dipolar, electron shielding, scalar coupling and quadrupolar interactions, whose relative importance will depend on the nucleus being observed and the system under study. In this thesis, only spin 1/2 nuclei were observed. Thus, quadrupolar interactions will not be discussed further.

The Zeeman interaction of a nuclear spin in the solid state with a static magnetic field is exactly the same as in solution. The normally degenerate magnetic spin-energy levels become non-degenerate in the magnetic field, and the transitions between these levels produce the NMR resonance. The Hamiltonian for this interaction may be written

$$H_z = -\gamma h B_o I_z$$

where $\gamma$ is the gyromagnetic ratio, $h = h/2\pi$ (h is Planck's constant) and $I_z$ the spin operator. This interaction is linear with the applied magnetic field $B_o$. The higher the field
strength, the greater separation of the energy levels and thus the greater the sensitivity of
the experiment.

The dipolar interaction results from direct magnetic coupling of nuclear moments
through space, and can be either heteronuclear or homonuclear in nature. The dipolar
Hamiltonian for a isolated pair of spins $I$ and $S$, of gyromagnetic ratios $\gamma_I$, $\gamma_S$, is

$$
H_D = \frac{\gamma_I \gamma_S}{r^3} \hbar^2 \left( 1 - 3 \cos^2 \theta \right) I_z S_z
$$

As shown in Figure 1.7, $r$ is the internuclear distance, $\theta$ is the angle between the
internuclear vector and the external magnetic field.

Figure 1.7. Geometric arrangement for a $I$-$S$ spin pair, illustrating the quantities of interest
for the dipole-dipole interaction. $B_o$ is the magnetic field, and the $I$-$S$ vector of length $r$
makes an angle $\theta$ with the field direction.

This interaction depends on the magnitude of the magnetic moments, hence will
be most important for spin 1/2 nuclei with large $\gamma$ values (e.g. $^1H$, $^{19}F$).

The chemical shift interaction is due to the shielding effect of the fields produced
by the surrounding electrons on the nucleus and is described as

$$
H_{CS} = \gamma_I \hbar I \cdot \hat{\sigma} \cdot B_o
$$

(1.15)
where $\hat{\sigma}$ is the chemical shift tensor which describes the magnitude and direction of the three-dimensional shielding. This interaction is linear with the applied field and is proportionately larger and more important at larger magnetic field strengths. The chemical shielding constants depend on the orientation of the nuclear environment in the applied magnetic field. In a rigid solid, due to the lack of rapid molecular motions, the chemical shift depends on the orientation of each crystal with respect to the field. In the general case, $\sigma_{zz}$, the observed shielding constant in the direction of $B_o(z\text{-direction})$ is [24]

$$\sigma_{zz} = \frac{1}{3} Tr \hat{\sigma} + \frac{1}{3} \sum_{j=1}^{3} \left( 3 \cos^2 \theta_j - 1 \right) \sigma_{jj}$$  \hfill (1.16)

where $Tr$ stands for trace (i.e. $\sigma_{11} + \sigma_{22} + \sigma_{33}$), $\sigma_{jj}$ is the principal component, $\theta_j$ is the angle between the $j$th axis and $B_o$.

In solution, where the molecules are tumbling rapidly and isotropically, only the first term, i.e. $\frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33})$ is observed. But in a rigid solid, a broad resonance pattern is generally observed. $^{19}$F has quite a large chemical shift range (typically over 150 ppm) and its actual chemical shift "broadening" in the solid may be as large as several hundred ppm, therefore special methods are necessary in order to observe $^{19}$F in the solid state, as will be discussed in the next section. The spin-spin coupling interaction between a pair of spins is usually smaller than other interactions under consideration and will not be further discussed.

The difference between solution and solid-state NMR studies is that in solution, the fast and essentially isotropic motions of the molecules give an averaging of these interactions, whereas in the solid state these interactions are anisotropic due to the relatively fixed orientations of the molecules. For $^{19}$F solid-state NMR, which is used in this thesis, these anisotropic interactions, direct homo- and hetero- dipolar couplings and shielding anisotropy, can lead to very significant line broadening which has to be
eliminated in order to obtain useful information from solid state NMR experiments, as will be discussed in next section.

1.4.2 The Magic Angle Spinning Technique

As shown earlier, the equations defining the dipolar and chemical shift interactions which cause NMR line broadening for solids involve the geometric factor \(3\cos^2 \theta - 1\). When \(\theta\) is 54.7°, this term is zero as in solution. Consider the coherent rotation of a solid sample about an axis at angle \(\beta\) to \(B_0\) (Figure 1.8): It can be shown that the average of \(3\cos^2 \theta - 1\) about the conical path indicated is

\[
<3\cos^2 \theta - 1> = \frac{1}{2} (3\cos^2 \beta - 1)(3\cos^2 \chi - 1)
+ \frac{3}{2} \sin 2\beta \sin 2\chi \cos (\omega t) + \frac{3}{2} \sin^2 \beta \sin^2 \chi \cos (2\omega t) \quad (1.17)
\]

\(\omega\) is the spinning rate, a sufficiently high value of \(\omega\) averages the time-dependent terms of Eq.(1.17). \(\chi\) is fixed for a rigid solid, but \(\beta\) can be varied experimentally. If \(\beta = 54.7^\circ\), \((3\cos^2 \theta - 1) = 0\) for all orientations (i.e. all values of \(\chi\)). Thus just as for isotropic tumbling, dipolar broadening is eliminated and shift anisotropy averaged to its isotropic value, giving much higher resolution. This technique is referred to as magic-angle spinning (MAS) and was first used by Andrew [35] and independently by Lowe [36] in 1958-59. This technique applies to both homonuclear and heteronuclear dipolar interactions. However, the rate of rotation required to eliminate the dipolar interactions has to be greater than the static bandwidth expressed in Hz and sometimes this speed is difficult to achieve.
Figure 1.8. Macroscopic sample rotation at an angle $\beta$ to the applied magnetic field $B_0$, showing the geometric relationships involved.
Figure 1.8. Macroscopic sample rotation at an angle $\beta$ to the applied magnetic field $B_0$, showing the geometric relationships involved.

Because of limitations in achievable spinning rates, several multiple-pulse sequences have been proposed as alternative methods for achieving the suppression of the dipolar interactions. Also the combination of multiple-pulse sequences with MAS, called combined rotation and multiple-pulse spectroscopy (CRAMPS) method has been used to produce superior resolution in $^{19}$F and $^1$H solid-state NMR studies [37]. In this thesis, for the purpose of the investigation of blowing gases in polymer matrix of PS and PU foams the fast MAS technique alone is sufficient to obtain good resolution in the solid-state $^{19}$F NMR spectra from the dissolved gases.

1.5. PURPOSE OF THE THESIS RESEARCH

With the elimination of CFC blowing agents and their replacement with the environmentally more acceptable HCFCs or HFCs, evaluation of long term performance of foams manufactured with alternative blowing agents, becomes a high priority issue.

This thesis introduces the application of $^{19}$F NMR microimaging as a non-destructive, fast and reliable method for the investigation of the diffusion processes of CFCs, HCFCs and HFCs in various polystyrene and polyurethane insulating foams. It is concluded that this method has proven to be applicable to all foam and blowing agent combinations we have investigated to date, and can be used to investigate a wide range of polymer foam products containing fluorinated blowing agents.
Chapter 2 demonstrates that $^{19}$F NMR microscopy is ideally suited for measuring the changes that occur in the spatial distributions of gaseous blowing agents in foamed polystyrene samples as functions of time, temperature and other factors and that it yields quantitatively reliable information on the diffusion processes.

Chapter 3 describes in detail the measurement of the diffusion coefficients of the foaming gases in polystyrene foams. The one-dimensional $^{19}$F imaging experiment is shown to be a fast and simple way to obtain the spatial distributions of blowing agents as functions of both time and temperature. Theoretical model calculations are made for different sample geometries. The calculated curves are fitted to the experimental data and the diffusion coefficients determined at both ambient and elevated temperatures. From these experiments the activation barriers for diffusion are calculated.

In Chapter 4, fast MAS high resolution $^{19}$F solid-state NMR spectroscopy is used to detect and quantify the blowing gas dissolved in the solid-phase of polystyrene foams. Results are presented for various PS foam/blowing agent systems and the effect of the dissolved gas on the diffusion process is also discussed.

The above experiments and studies in Chapter 2, 3 and 4 are extended to various polyurethane foam/blowing agent systems in Chapter 5 and comparisons made with the PS systems. Also a modification is made to the theoretical calculation in order to address the different contribution of dissolved gas to the diffusion process which occurs in the PU systems.

A brief summary of the conclusions and suggestions for further work are presented in Chapter 6.
REFERENCES


CHAPTER 2  PRELIMINARY NMR IMAGING

INVESTIGATIONS OF BLOWING AGENTS IN

POLYSTYRENE FOAMS

2.1. INTRODUCTION

As discussed in Chapter 1, chlorofluorocarbons (CFC's) have been widely used as blowing agents for polymer foam insulation applications. In addition to acting as blowing agents, CFC's, by virtue of their low gas-phase thermal conductivities, contribute to the excellent thermal insulation of the overall product. In recent years, there has been considerable concern regarding the environmental impact of CFC's. The Montreal Protocol and subsequent international agreements have recommended a world wide phase-out of CFC's by the year 2000. In order to phase out of CFC's, non-ozone depleting blowing agents which have similar gas-phase thermal conductivities to the CFC's and which are also retained within the cellular structure during its useful lifetime have to be developed. Partially halogenated chlorofluorocarbons, hydrochlorofluorocarbons (HCFC's) have been identified as intermediate replacements for the CFC's, because they have lower ozone depletion potential (ODP) values. Hydrofluorocarbons (HFC's), which have ODP values of zero, are likely to ultimately become the blowing agents of choice in insulation based applications.
To evaluate the potential performance of CFC alternatives, the distribution of the blowing agent within the cellular plastic matrix has to be determined over a period of time. Analysis of the CFC gas content has typically been performed in a destructive fashion, in which the sample is immersed in liquid nitrogen and then pulverized and the gas content subsequently analyzed by gas chromatography [1]. Under these conditions, the spatial distribution of the gas within the sample can not be determined. Further, since the process is destructive, the sample cannot be further studied. Currently, there is no reliable and readily accessible technique by which the distribution of these gases can be detected or monitored.

Microscopic NMR imaging has recently emerged as an excellent non-invasive and non-destructive technique by which the distribution of mobile fluids in solid polymers can be monitored [2-6]. In principle, it should be possible to perform similar experiments on samples which contain gaseous materials, the limiting factor being the achievable signal to noise (S/N). This chapter will demonstrate that $^{19}$F NMR microscopic imaging is ideally suited for measuring the changes that occur in the concentrations and spatial distributions of gaseous blowing agents in foamed samples as a function of time and that it yields quantitatively reliable information on the diffusion process. These factors will be critical to the choice of blowing agents and in the fabrication of optimized insulating materials.
2.2. EXPERIMENTAL

2.2.1. Foam Samples

Three sets of aged polystyrene (PS) foam samples were provided by Du Pont (Canada) Inc. and DOW Chemical Co. Samples in the first group (A1-K1) contained only a single fluorinated gas as blowing agent, either HCFC-142b (CH₃CF₂Cl) or CFC-12 (CF₂Cl₂). Sample K1 was received as 3.8 cm thick, 61 cm by 30 cm foam boards and the others were core samples either 2.5 or 5 cm thick (except for sample H1, which is 10 cm thick), 10.2 cm by 10.2 cm square pieces cut from the original foam boards which had different densities. Before analysis, they had been aged at ambient temperature for various periods of time ranging from 7 days to 5 years as listed in Table 2.1.

Samples in group #2 (A2 and B2) had been manufactured with a mixture of two fluorinated gases, HCFC-142b (CH₃CF₂Cl) and CFC-12 (CF₂Cl₂). They also were 2.5 cm thick, 10.2 cm by 10.2 cm square core samples cut from the original boards which also had been aged for various times before analysis (see Table 2.2).
Table 2.1. Single blowing agent polystyrene foams (group #1).

<table>
<thead>
<tr>
<th>Sample (source*)</th>
<th>Color</th>
<th>Size (cm)</th>
<th>Density lb/ft³ (g/cm³)</th>
<th>Age</th>
<th>Blowing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1(DP)</td>
<td>blue</td>
<td>10.2 x 10.2 x 2.5</td>
<td>1.4 (0.022)</td>
<td>2 months</td>
<td>HCFC-142b (CH₃CF₂Cl)</td>
</tr>
<tr>
<td>B1(DP)</td>
<td>blue</td>
<td>10.2 x 10.2 x 2.5</td>
<td>1.4 (0.023)</td>
<td>14 months</td>
<td>HCFC-142b (CH₃CF₂Cl)</td>
</tr>
<tr>
<td>C1(DP)</td>
<td>pink</td>
<td>10.2 x 10.2 x 5</td>
<td>2.1 (0.034)</td>
<td>7 months</td>
<td>HCFC-142b (CH₃CF₂Cl)</td>
</tr>
<tr>
<td>D1(DP)</td>
<td>blue</td>
<td>10.2 x 10.2 x 5</td>
<td>1.7 (0.027)</td>
<td>7 months</td>
<td>HCFC-142b (CH₃CF₂Cl)</td>
</tr>
<tr>
<td>E1(DP)</td>
<td>white</td>
<td>10.2 x 10.2 x 2.5</td>
<td>4.0 (0.064)</td>
<td>7 days</td>
<td>CFC-12 (CF₂Cl₂)</td>
</tr>
<tr>
<td>F1(DP)</td>
<td>blue</td>
<td>10.2 x 10.2 x 5</td>
<td>1.71 (0.027)</td>
<td>10 days</td>
<td>HCFC-142b (CH₃CF₂Cl)</td>
</tr>
<tr>
<td>G1(D)</td>
<td>grey</td>
<td>10.2 x 10.2 x 5</td>
<td>1.86 (0.029)</td>
<td>5 years</td>
<td>CFC-12 (CF₂Cl₂)</td>
</tr>
<tr>
<td>H1(D)</td>
<td>blue</td>
<td>10.2 x 10.2 x 10</td>
<td>1.71 (0.027)</td>
<td>5 years</td>
<td>HCFC-142b (CH₃CF₂Cl)</td>
</tr>
<tr>
<td>K1(D)</td>
<td>blue</td>
<td>61 x 30 x 3.8</td>
<td>1.70 (0.027)</td>
<td>3.5 months</td>
<td>HCFC-142b (CH₃CF₂Cl)</td>
</tr>
</tbody>
</table>

* D = DOW Chemical Co., DP = Du Pont (Canada) Inc.
Table 2.2. Polystyrene foams formed with two blowing agents (group #2).

<table>
<thead>
<tr>
<th>Sample (source*)</th>
<th>Color</th>
<th>Size(cm)</th>
<th>Density (\text{lb/ft}^3 (\text{g/cm}^3))</th>
<th>Age</th>
<th>Blowing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2(DP)</td>
<td>pink</td>
<td>10.2 x 10.2 x 2.5</td>
<td>1.7 (0.028)</td>
<td>2 months</td>
<td>CFC-12 (CF₂Cl₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HCFC-142b (CH₃CF₂Cl)</td>
</tr>
<tr>
<td>B2(DP)</td>
<td>pink</td>
<td>10.2 x 10.2 x 2.5</td>
<td>1.4 (0.022)</td>
<td>13 months</td>
<td>CFC-12 (CF₂Cl₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HCFC-142b (CH₃CF₂Cl)</td>
</tr>
</tbody>
</table>

* D = DOW Chemical Co., DP = Du Pont (Canada) Inc.

Group #3 (A3-F3) included six cylindrical foam samples (10 mm o.d. x 40 mm) supplied by Du Pont which had been given a post-treatment. They were originally blown with HCFC-142b (CH₃CF₂Cl) and then were treated with a second gas, either HCFC-124a (CF₃CHFCl) or HFC-134a (CF₃CH₂F) at 79°C for 69 hours (Table 2.3) then kept at room temperature for two days before analysis.

In order to study diffusion processes during the post-treatment of foams, a series of cylindrical samples (A4-C4), about 10 mm in diameter and 38 mm long were cut with a cork borer out of the foam board (sample K1), which had been blown with a single blowing agent HCFC-142b(CH₃CF₂Cl). They were then placed inside a sealed pressurized device filled with a second blowing agent CFC-11(CFCl₃) for various periods of time at 69°C (Table 2.4). From the known device volume of 400 ml, for 2.2 g of added CFCl₃, the partial pressure of CFCl₃ inside the device was about 1 atm at 69°C. These foam plugs were removed from the device after different exposure times and studied with \(^{19}\text{F}\) NMR imaging.
Table 2.3. Polystyrene foam samples (CH$_3$CF$_2$Cl) used in post-treated studies (group #3).

<table>
<thead>
<tr>
<th>Sample (source*)</th>
<th>Color</th>
<th>Size</th>
<th>Density lb/ft$^3$(g/cm$^3$)</th>
<th>Age</th>
<th>The second blowing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3(DP)</td>
<td>pink</td>
<td>10 o.d. x 40 mm</td>
<td>1.7 (0.028)</td>
<td>2 days</td>
<td>HCFC-124a (CF$_3$CHFCl)</td>
</tr>
<tr>
<td>B3(DP)</td>
<td>pink</td>
<td>10 o.d. x 40 mm</td>
<td>1.7 (0.028)</td>
<td>2 days</td>
<td>HFC-134a (CF$_3$CH$_2$F)</td>
</tr>
<tr>
<td>C3(DP)</td>
<td>blue</td>
<td>10 o.d. x 40 mm</td>
<td>1.4 (0.022)</td>
<td>2 days</td>
<td>HCFC-124a (CF$_3$CHFCl)</td>
</tr>
<tr>
<td>D3(DP)</td>
<td>blue</td>
<td>10 o.d. x 40 mm</td>
<td>1.4 (0.022)</td>
<td>2 days</td>
<td>HFC-134a (CF$_3$CH$_2$F)</td>
</tr>
<tr>
<td>E3(DP)</td>
<td>blue</td>
<td>10 o.d. x 40 mm</td>
<td>1.7 (0.027)</td>
<td>2 days</td>
<td>HCFC-124a (CF$_3$CHFCl)</td>
</tr>
<tr>
<td>F3(DP)</td>
<td>blue</td>
<td>10 o.d. x 40 mm</td>
<td>1.7 (0.027)</td>
<td>2 days</td>
<td>HFC-134a (CF$_3$CH$_2$F)</td>
</tr>
</tbody>
</table>

* D = DOW Chemical Co., DP = Du Pont (Canada) Inc.
Table 2.4. Polystyrene foam samples blown with CH$_3$CF$_2$Cl and post-treated with CFCl$_3$ at 69°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exposure time with CFCl$_3$ at 69°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A4</td>
<td>120 hours</td>
</tr>
<tr>
<td>B4</td>
<td>216 hours</td>
</tr>
<tr>
<td>C4</td>
<td>336 hours</td>
</tr>
</tbody>
</table>

In order to eliminate the effects of diffusion through the ends of these foam cylinders, both ends of the cylinder were sealed with aluminum foil using epoxy during the post-treatment process, and only the middle section of the cylinder was used for the imaging measurements. Figure 2.1 is a schematic representation showing the post-treatment device and the sample preparation.
Figure 2.1. Schematic representation of the post-treatment experiment and the sample preparation.
2.2.2. NMR spectroscopy

2.2.2.1. 1D $^{19}$F NMR Spectroscopy

The NMR experiments were carried out on a Bruker MSL 400 MHz spectrometer (9.4 T), operating at a fluorine frequency of 376 MHz. This high magnetic field strength gives high signal-to-noise (S/N) required for the observation of trace quantities of materials and the high resolution required for mixtures. The spectrometer is equipped with a microimaging accessory with an imaging probe which will accommodate a maximum sample diameter of 25 mm. Probeheads with 10- and 15- mm horizontal solenoid coils (the coil axis along the x-axis and the static magnetic field along the z-axis) with superior r.f. homogeneity and sensitivity were constructed in house for the $^{19}$F NMR experiments (Figure 2.2). One dimensional $^{19}$F NMR spectra were obtained by the standard one pulse method and Cyclops phase cycling of the 90° r.f. pulse was used to correct for phase and amplitude errors in quadrature detection. The data were collected on an ASPECT 3000 computer and transferred to an Apple Centris 650 computer for further processing using NMRLink software and cables supplied by Bruker Spectrospin Canada Ltd.

![Figure 2.2. Geometric arrangement of the horizontal solenoid r.f. coils.](image-url)
In order to choose a reference material for the quantitative measurement of the concentrations of foam blowing agents, we investigated CeF$_6$ and CFCI$_3$ which are normally used as references in fluorine NMR measurements in solution. The spectrum of gaseous CFCI$_3$, a drop of liquid evaporated in a sealed capillary tube, has the same chemical shift value and peak shape as CFCI$_3$ in foams. Thus, this reference cannot be used for studies of foams which have been blown with CFCI$_3$. While liquid CeF$_6$ has a peak ($\delta = 165$ ppm) which is quite far away from the chemical shift region of the blowing agents ($\delta = -5$ to -250 ppm) and is suitable, other possibilities were investigated. Liquid C$_6$H$_5$CF$_3$ was also suitable; it has a sharp peak at $\delta = -62.4$ ppm, which is within the spectral region of interest and does not overlap with the signals of any of the blowing agents. We chose liquid C$_6$H$_5$CF$_3$, instead of CeF$_6$, as the reference for the quantitative determination of the concentrations of blowing agents by considering possible errors arising from the bandwidth of the r.f. pulse. The pulse bandwidth in our experiment is theoretically of order $t_p^{-1}$ ($t_p = 12.5 \mu s$), which is about 200 ppm, thus large enough to excite the $^{19}$F nuclei in both CeF$_6$ and in the blowing agents. However, it is probable that the tip angles for resonances far away from the center frequency might be less than 90°, which would affect the accuracy and reliability of the quantitative measurements.

10.0 (± 0.1) $\mu$l of C$_6$H$_5$CF$_3$ solution made with pure C$_6$H$_5$CF$_3$ liquid diluted six times with acetone was used as reference. The determination of the fluorine content in the reference sample was carried out as follows: the density of C$_6$H$_5$CF$_3$ is 1.199 g/ml, the molecular weight of C$_6$H$_5$CF$_3$ is 146.11 and the atomic weight of fluorine is 19.00; thus the fluorine content in this reference is found be

$$10.0 \times 10^{-3} \times 1.199 \times \frac{3 \times 19.00}{146.11} \times \frac{1}{6}$$

$= 0.78 \pm 0.02 \text{ mg}$.

This amount of liquid was injected into the capillary tube with a
syringe, frozen with liquid nitrogen, then sealed and used as the absolute reference for the $^{19}\text{F}$ studies.

The quantitative measurement of the foam cell gas was carried out by recording the $^{19}\text{F}$ spectrum of the foam sample and the reference, at the same time. Typical spectra were obtained using a spectral width of 38 kHz, 90° pulse of 12.5 $\mu$s and a 10 $\mu$s delay before acquisition. Although the fluorine spin-relaxation times of blowing agents are less than 10 ms, the reference liquid, $\text{C}_6\text{H}_5\text{CF}_3$, has a longer $T_1$ value of about 1 s. Thus, 7 s delays were used to make sure that the data were quantitatively reliable. The addition of sixteen transients generally provided spectra with good S/N. The chemical shift values for the blowing agents were referenced to external liquid CFCl$_3$ ($\delta$=0.0 ppm).

2.2.2.2 Calibration

For all of the measurements, the foam samples need to have appropriate dimensions for good filling of the r.f. coil. When possible, cylindrical samples were used for the measurements as this is the ideal geometry. They were obtained from the solid foam boards by using a sharpened cork borer. It is inevitable that the cutting process will damage some foam cells on the outside surface of the sample, and thus some blowing agent will escape from these fractured cells during the sample preparation. A simple method was developed as discussed below to calibrate the amount of blowing agent lost due to the cutting in order to obtain truly quantitative data.

Consider a cylindrical sample with radius $r$ and length $l$ (as shown in Figure 2.3), with a fractured depth $d$ due to the cutting which is assumed to contain no gas. The amount of gas inside the cylinder will be $C_1 = A \pi r^2 l$ and $C_2 = A \pi (r-d)^2 (l-2d)$.
before and after the cutting respectively where A is a constant. Thus, the relative loss of gas from the cutting,

\[
\frac{(C1-C2)}{C1} = 1 - (r-d)^2 \ast \frac{1-2d}{r^2} \ast l 
\]  

(1)

Figure 2.3. A cylindrical foam sample with a fractured depth \(d\) below the surface due to the cutting.

Standard \(^{19}\text{F}\) 1D NMR experiments were performed on a series of foams of various known radii from 1 to 10 mm together with the reference using a 25 mm vertical r.f. coil. These foam cylinders were taken from center areas of sample K1, and then both ends were cut off and only the middle section (25 mm long) used for the measurements (Figure 2.4). This eliminates effects from the prior loss of cell gases due to diffusion near the surface. Each sample has an uniform distribution of gas apart from the disruption of the cutting and the real gas concentration is at its maximum value.
Figure 2.4. Schematic representation of the sample preparation: The middle section of the foam cylinder, taken from the center area of the board, was used for the NMR measurements.
The intensity of the NMR signal from the gas in the foam is proportional to the amount of the gas inside the cells (C2) and a least-squares fitting to the plot of the intensity of the signal versus the radius \( r \) gives the characteristic damage depth \( d \) as 0.56 mm for the polystyrene foam samples (Figure 2.5). The uncertainty in the measurement of the \( d \) value is determined by the standard deviation of the fitting as 0.01. From scanning electron microscope (SEM) data (see Appendix 1), we know that the average cell diameter is about 120 \( \mu \)m in the PS foam matrix and thus the damage area is approximately 4 to 5 cell diameters.

The relative loss of gas from the cutting, \( \frac{(C1-C2)}{C1} \), was calculated and plotted against the radius \( r \) (Figure 2.6). Thus the actual amounts of blowing agents inside foam cylinders can be determined when we analyze samples of different sizes. In the 1D NMR experiments, the samples were 8.7 or 13.1 mm in diameter, and therefore the relative losses of the cell gas were 28.3% and 20% with uncertainties of \( \pm 2\% \) and \( \pm 1\% \) respectively. The quantitative results of the cell gas analyses from \( ^{19}\text{F} \) 1D NMR experiments will be corrected for the gas losses from cutting in all subsequent work.
Figure 2.5. Plot of signal intensity versus the radius $r$ of the PS foam cylinders. Symbols indicate experimental data and the dashed line the curve from least-squares fitting.

Figure 2.6. Plot of the relative loss of gas due to the cutting, as calculated from Equation (2.1), versus the radius $r$ of the PS foam cylinders. $C_1$, $C_2$ are defined in the text.
2.2.3. Measurement of $T_1$ and $T_2$ Relaxation Times

In order to devise the most appropriate imaging protocol, it is important to know the relaxation characteristics of the NMR active nuclei, $^1$H and $^{19}$F in the blowing agents. $T_1$ is the time constant for full recovery to thermodynamic equilibrium of the nuclear magnetization following an excitation pulse (r.f. pulse). It controls the maximum rate at which signals may be repetitively excited and, therefore, the total imaging time if quantitative reliability is desired. $T_2$ characterizes the loss of phase coherence of the transient magnetization. It controls the rate that the signal decays and determines the maximum time for echo formation. The CPMG (Carr-Purcell-Meiboom-Gill) pulse sequence [7-8] was used to determine the $T_2$ relaxation time constants and the inversion recovery pulse sequence was used to determine the $T_1$ spin-lattice relaxation times. These pulse sequences were previously described in Chapter 1.

To study the nuclear relaxation mechanisms, the relaxation times of the fluorine and proton nuclei in blowing agents were also measured as functions of temperature over the temperature range from 290 °K to 360 °K. The temperature of the sample in the probe was controlled by a thermostatically-controlled heater inserted in the probe and a variable temperature control unit was used to set the temperature values desired.
2.2.4. Proton and Fluorine Imaging Experiments

2.2.4.1. Pulse Sequences

Several pulse sequences for imaging were used to study the polystyrene foam sample (El) filled with CF₂Cl₂ in order to determine the best protocols to obtain optimum results. Figure 2.7(a) shows a typical spin-echo pulse sequence (discussed in Chapter 1) for generating a two-dimensional image based on the spin-echo sequences of Carr and Purcell and Meiboom and Gill [7,8]. The slice, phase and read gradients are arbitrarily assigned to z-, y- and x-axes, respectively. In any given experiment, these assignments may be changed as appropriate for the actual orientation of the sample in the r.f. coil. The r.f. timing shows a selective 90° pulse and non-selective 180° pulse. The selective pulse is applied in the presence of a z-gradient to select a slice plane perpendicular to the z-axis. The slice thickness is determined by the combined effect of the strength of the z gradient and the characteristics of the soft 90° r.f. pulse. Phase-encoding is in the y direction and frequency-encoding is in the x direction. Figure 2.7(b) also shows a spin-echo pulse sequence but in this case, no slice is selected. With hard-90° and hard-180° r.f. pulses both applied in the absence of a z gradient (slice selection gradient), a two-dimensional xy image is produced due to the magnetization from all the spins inside the whole sample. The advantage of non-slice imaging is that the signal-to-noise ratio is much better than for a slice-selected image, and thus, the imaging time can be much reduced. Also, the TE value is shorter (the length of a hard pulse is much shorter than that of a selective pulse). Figure 2.7(c) shows a modified pulse sequence based on the sequence known as FLASH (discussed in Chapter 1). In this sequence, one hard r.f. pulse (less than 90°) is applied in
the absence of a z gradient to excite the whole sample without selecting any slice. Instead of producing a spin-echo by the application of a 180° r.f. refocussing pulse as in a spin-echo sequence, FLASH uses a reversal of the frequency-encoding field gradient to form a gradient echo. The FLASH sequence allows for the use of r.f. pulses of less than 90°, and hence, it can significantly reduce the repetition time. However, it suffers from some disadvantages. A major limitation concerns the generation of the gradient echo. Since the echo is produced by switching the polarity of the frequency-encoding gradient, the experiments are more sensitive to the presence of magnetic field inhomogeneities, which are not refocussed at all.
Figure 2.7(a). Spin-echo imaging pulse sequence with slice selection using a Gaussian soft 90° pulse and a hard 180° pulse. (b). Spin-echo imaging pulse sequence in which no slice is selected. (c). FLASH imaging pulse sequence in which no slice is selected.
The spin-echo $^{19}$F images were acquired with the following parameters, except where noted in the text. The non-selective r.f. pulses were 12.5 μs for the 90° pulse and 25 μs for the 180° pulse. The selective r.f. pulse used for the slice selection was 1 ms long, had a Gaussian shape and the slice thicknesses were usually about 1 mm with the gradient strength of about 2.0 G/cm. The echo time was between 1.5 to 1.9 ms. The images were 128 x 128 pixels with an in-plane resolution of approximately 220 μm using a read gradient strength of about 6.8 G/cm. About 140 scans were accumulated for signal averaging in approximately 30 minutes with a 100 ms repetition time. The non-slice FLASH image used a 60° tip angle and the echo time was 1.1 ms. With a 100 ms repetition time, a 128 x 128 image also took about 30 minutes to complete and had an in-plane resolution of 190 μm.

For the samples containing mixtures of two different foaming gases, a chemical-shift selective pulse sequence (Figure 2.8) based on the non-slice spin-echo pulse sequence was used. A selective r.f. pulse with a Gaussian shape was used instead of the hard-90° pulse for the chemical-shift selective excitation in order to image each gas separately. Using high r.f. power, the selective r.f. pulse was reduced to 300 μs, which gave an echo time of about 2 ms while giving efficient selective excitation. An in-plane resolution of 220 μm was obtained using a read gradient strength of 6.8 G/cm.
Figure 2.8. Chemical shift selective pulse sequence without slice selection with a Gaussian soft 90° pulse and a hard 180° pulse.
2.2.4.2. $^1$H and $^{19}$F Imaging

Both $^{19}$F and $^1$H imaging experiments were performed on the foam filled with CH$_3$CF$_2$Cl blowing agent (sample H1) for purposes of comparison. The experiments were carried out on a Bruker MSL 400 spectrometer equipped with imaging accessories supplied by Bruker. Two 15-mm horizontal solenoid coils were constructed in house for the proton and fluorine experiments, and a non-slice, spin-echo pulse sequence was used (see Section 2.2.4.1, Figure 2.8). The proton images were obtained with the following parameters: The non-selective r.f. pulses were 10 $\mu$s for the 90° pulse and 20 $\mu$s for the 180° pulse, and the echo time was 7 ms. The 2D image was 128 x 128 pixels with an in-plane resolution of 220 $\mu$m with a read gradient strength of 7 G/cm. The parameters for the fluorine experiments were as described in Section 2.2.4.1. For both fluorine and proton experiments, Cyclops phase cycling was used to reduce the effects of variations in the 180° flip angle, as a result of r.f. field inhomogeneity or miscalibration of the flip angle. Pre-emphasis was applied to all gradients to reduce the effects of induced eddy currents.
2.3. RESULTS AND DISCUSSION

2.3.1. Proton and Fluorine Relaxation Times of Fluorinated Gases in PS Foams

2.3.1.1. Results

The longitudinal ($T_1$) and transverse ($T_2$) relaxation times of the fluorine nuclei for various CFC, HCFC and HFC gases were found to be in the range of 3-9 ms. Those of the proton nuclei were much longer: $T_1$ was about 200 times longer and $T_2$ was about 10 times longer as shown in Table 2.5. Thus, the fluorine nuclei in these fluorinated gases relax much faster than the proton nuclei in the same molecule. This means that the repetition times in fluorine experiments can be set much shorter than the corresponding times in proton experiments. Thus, quantitative studies on blowing agents in foams are more efficiently performed with fluorine detection. It also indicates that the relaxation mechanisms for the fluorine and proton nuclei may be different.
Table 2.5. $T_1$ and $T_2$ relaxation times of the $^1$H and $^{19}$F nuclei in gaseous blowing agents in PS foams.

<table>
<thead>
<tr>
<th>Blowing Agent</th>
<th>$T_1$ ($^1$H)</th>
<th>$T_1$ ($^{19}$F)</th>
<th>$T_2$ ($^1$H)</th>
<th>$T_2$ ($^{19}$F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CF$_2$Cl</td>
<td>1300 ms</td>
<td>5.6 ms</td>
<td>41.6 ms</td>
<td>4.7 ms</td>
</tr>
<tr>
<td>(HCFC-142b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF$_3$CHFCl</td>
<td>NA</td>
<td>8.2 ms</td>
<td>NA</td>
<td>5.8 ms</td>
</tr>
<tr>
<td>(HCFC-124a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF$_3$CH$_2$F</td>
<td>NA</td>
<td>7.4 ms</td>
<td>NA</td>
<td>3.0 ms</td>
</tr>
<tr>
<td>(HFC-134a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF$_2$Cl$_2$</td>
<td>NA</td>
<td>4.5 ms</td>
<td>NA</td>
<td>4.4 ms</td>
</tr>
<tr>
<td>(CFC-12)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFCl$_3$</td>
<td>NA</td>
<td>5.4 ms</td>
<td>NA</td>
<td>3.6 ms</td>
</tr>
<tr>
<td>(CFC-11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The temperature dependencies of the fluorine and proton relaxation times in the foaming gas CH$_3$CF$_2$Cl are shown in Figure 2.9 and Figure 2.10. For fluorine, both the spin-lattice relaxation time ($T_1$) and the spin-spin relaxation time ($T_2$) decrease as the temperature increases. However, the proton relaxation times ($T_1$ and $T_2$) in the same molecule show the opposite behavior: throughout the entire range of measurement, they increase as the temperature increases.

The relative uncertainty in the $T_1$ and $T_2$ measurements is typically about 3 % determined from the reproducibility of eight measurements.
Figure 2.9. Temperature dependence of the fluorine $T_1$ and $T_2$ relaxation times of CH$_3$CF$_2$Cl (HCFC-142b) in PS foam.
Figure 2.10. Temperature dependence of the proton relaxation times of CH₃CF₂Cl in PS foam. (a). $T_1$ relaxation times versus $1/T$. (b). $T_2$ relaxation times versus $1/T$. 
2.3.1.2. Relaxation Mechanisms

Two important relaxation processes (dipole-dipole interaction and spin-rotation) can occur from the interaction of the nuclear spin system with fluctuating local magnetic fields. The fluctuations in the fields are caused, in general, by molecular motions. The local fields themselves can have several origins. The principal source is usually the dipolar field of the nucleus. The modifications of the basic magnetic field by other factors, e.g. fields generated by molecular rotation etc., are usually secondary sources of local magnetic fields in a system of small and dilute mobile gas molecules containing spin-1/2 nuclei [9]. A correlation time, $\tau_c$, is defined as the length of the average time between molecular movements. Thus, molecules with short correlation times are in rapid molecular motion. Figure 2.11 shows the predicted $T_1$ and $T_2$ relaxation behaviors for a spin-1/2 system undergoing dipole-dipole induced relaxation, plotted as a function of $\tau_c$ [10]. It shows that, in the regime of short correlation times (higher temperatures) on the left of the plot, the relaxation times increase with temperature. Small mobile gas molecules have fast molecular motions, and thus short $\tau_c$ values. The relationship between relaxation times and temperature should be the same as shown on the left of the plot in Figure 2.11, if the dominant relaxation mechanism occurs via dipole-dipole interactions. The proton $T_1$ and $T_2$ relaxation times in the blowing agent of CH$_3$CF$_2$Cl show the expected temperature dependence for a dipolar relaxation mechanism (Figure 2.10). However, the fact that the proton $T_1$ and $T_2$ relaxation times are not the same may indicate some other relaxation mechanisms may be involved.

Apart from dipole-dipole interactions, the next most important relaxation mechanism for spin-1/2 nuclei, especially in small dilute molecules in the gas phase, is spin-rotation [9]. This mechanism arises from the interaction between the magnetic moment of the nucleus and the fluctuating magnetic fields around the nucleus, which are
generated by the motion of the molecular magnetic moment arising from the electronic distribution within the molecule. The electronic distribution also determines the chemical shift range of the nucleus. Electronic distributions which lead to a very large chemical shift range (e.g. $^{19}$F has a chemical shift range of about 800 ppm) will result also in large spin-rotation interactions [11]. If the relaxation mechanism were dominated by spin rotation, then $T_1$ is expected to decrease with increasing temperature. From Figure 2.9, it can be seen that there is a decrease in the fluorine spin-lattice relaxation time in gaseous CH$_3$CF$_2$Cl with increasing temperature. This shows that the fluorine relaxation mechanism is at least dominated by, if not completely determined by, the spin-rotation mechanism. Thus, in small gas molecules like CH$_3$CF$_2$Cl, the dipole-dipole interaction is the dominant relaxation mechanism for the protons, and the spin-rotation interaction is the dominant relaxation mechanism for the fluorine nuclei. Of all possible modulation mechanisms, only the spin-rotation interaction shows the opposite temperature dependence [12].

![Graph showing the effect of the correlation time for molecular motion on $T_1$ and $T_2$ assuming a dipolar relaxation mechanism.](image)

Figure 2.11. The effect of the correlation time for molecular motion on $T_1$ and $T_2$ assuming a dipolar relaxation mechanism.
2.3.1.3. Investigation of Possible Concentration Dependence of $^{19}$F $T_2$
Values inside a Foam Matrix

The spatial variation of $T_2$ relaxation times of fluorinated gases in a foam matrix
can be investigated by studying one-dimensional imaging projections obtained by
performing the imaging experiment with only one gradient in the frequency-encoding
direction as a function of TE. The image intensity depends on the concentration of the gas
as well as its $T_2$ relaxation time. Thus, as TE increases in the experiment, the signal
intensity will decrease due to $T_2$ relaxation. Figure 2.12(a) shows a series of projections
obtained from the center area of a low density foam (sample F1). These one dimensional
projections clearly show that the distribution of blowing agent (CH$_3$CF$_2$Cl) inside the foam
matrix along the frequency-encoding direction, in this sample, is basically uniform. The $T_2$
relaxation effect can be seen in the varying intensity of the signal as a function of the echo
time. Figures 2.12(b) and 2.12(c) show similar experiments on a low density foam (sample
B1) at the edge area and a high density foam (sample E1) in the center area, respectively.
In the first case, the intensity of the blowing agent, CH$_3$CF$_2$Cl decreases significantly
towards the foam edge. In the latter case, there is a drop in the intensity profile indicating
that a void existed inside and the blowing agent (CF$_2$Cl$_2$) was distributed unevenly across
this high density foam. Although these samples have different intensity distributions of
various blowing agents, the intensity changes within the series of projections as a function
of echo time are very similar, the signal-to-noise ratio decreasing by exactly the same
extent across the region as TE increases. This can be seen more clearly by scaling the
projections as presented in Figure 2.13. The large variation in 2.13(b) is due to the lower
S/N from the much lower gas concentration.
Figure 2.12
Figure 2.12(a). One-dimentional projections of the $^{19}$F signal intensity of CH$_3$CF$_2$Cl in PS foam sample F1, center area as a function of the TE values. (i) TE = 1.6 ms, (ii) TE = 1.9 ms, (iii) TE = 3.5 ms, (iv) TE = 5.5 ms.

2.12(b). One-dimentional projection of the $^{19}$F signal intensity of CH$_3$CF$_2$Cl in PS foam sample B1, edge area as a function of the TE values. (i) TE = 1.6 ms, (ii) TE = 2.5 ms, (iii) TE = 3.5 ms, (iv) TE = 5.5 ms.

2.12(c). One-dimentional projection of the $^{19}$F signal intensity of CF$_2$Cl$_2$ in PS foam sample E1, center area as a function of the TE values. (i) TE = 1.6 ms, (ii) TE = 2.5 ms, (iii) TE = 3.5 ms, (iv) TE = 7.5 ms.
Figure 2.13 Same projections as in Figure 2.11, scaled to the same maximum intensities.
The results clearly show that $T_2$ is uniform across the foam matrix although the concentration of gas varies considerably, i.e. $T_2$ is independent of concentration. This indicates that the mobility of the fluorinated gas is independent of the concentration of the gas, foam type and site in the matrix for the foam samples studied to date. Consequently, image intensities are proportional to the actual gas concentrations in the foam cells and are independent of TE, although TE should be kept as short as possible for a given sample/coil arrangement to maximize the signal intensity. Therefore, a 1D image projection can be used to determine the cell gas concentration as a function of location within a foam matrix for further quantitative study of diffusion process (Chapter 3).

2.3.2. Quantitative Analysis of Gas-Phase Blowing Agents in PS Foams by 1D NMR

2.3.2.1. Results

Figure 2.14 shows the $^{19}$F NMR spectrum of CH$_3$CF$_2$Cl in PS foam sample K1 with the reference sample (C$_6$H$_5$CF$_3$) sealed in a capillary tube also present in the coil. The signal at -53 ppm is due to the fluorine nuclei in the CH$_3$CF$_2$Cl gas while the other signal at -62 ppm is due to the reference, C$_6$H$_5$CF$_3$. The chemical shifts of other blowing agents are presented in Table 2.6.
Figure 2.14 $^{19}$F NMR spectrum of CH$_3$CF$_2$Cl in PS foam sample K1 together with the reference sample (C$_6$H$_5$CF$_3$) sealed in a capillary tube present in the coil.
Table 2.6. Chemical shifts of the $^{19}$F nuclei in different blowing agents.

<table>
<thead>
<tr>
<th>Blowing agent</th>
<th>CH$_3$CF$_2$Cl (HCFC-142b)</th>
<th>CF$_3$CHFCl (HCFC-124a)</th>
<th>CF$_3$CH$_2$F (HFC-134a)</th>
<th>CF$_2$Cl$_2$ (CFC-12)</th>
<th>CFCl$_3$ (CFC-11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical shift* (ppm)</td>
<td>-53</td>
<td>-89; -162</td>
<td>-85; -246.4</td>
<td>-12.6</td>
<td>-5</td>
</tr>
</tbody>
</table>

* Chemical shifts have been referenced relative to external CFCl$_3$ liquid ($\delta=0.0$ ppm).

With a known quantity of the reference sample (Section 2.2.2.1) sealed in the capillary tube together with the foam sample in the coil, and correcting for losses due to the sample preparation as described in Section 2.2.2.2, a quantitative measurement of the amounts of foaming gas in the samples can be obtained from their 1D $^{19}$F spectra. Table 2.7 shows the concentrations of cell gas found in the different PS foams investigated, using samples cut from the center of the boards where no loss of gas has occurred. The weight percent of cell gas ranges from about 3 to 10, depending on the foam type and age. The uncertainty of this measurement is about 10 % considering the errors accumulated from integrating peak areas of signals (2 %), measuring the quantity of reference sample (2 %) and correcting for the cutting loss (6 %). There are no published data on the amount of cell gas in PS foams currently available to the best of our knowledge. However, our measurements of the cell gas contents of various polyurethane foams (Chapter 5) are close to the published concentrations measured with other methods.
Table 2.7. The weight percent of cell gas in the different foam samples investigated together with the ages and densities of the foams.

<table>
<thead>
<tr>
<th>Foam Sample</th>
<th>Cell Gas Amount (%w/w)</th>
<th>Age</th>
<th>Density: lb/ft$^3$ or (g/cm$^3$)</th>
<th>Blowing Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>5.4</td>
<td>2 months</td>
<td>1.4 (0.022)</td>
<td>CH$_2$CF$_2$Cl</td>
</tr>
<tr>
<td>B1</td>
<td>4.8</td>
<td>14 months</td>
<td>1.4 (0.023)</td>
<td>CH$_3$CF$_2$Cl</td>
</tr>
<tr>
<td>C1</td>
<td>6.2</td>
<td>7 months</td>
<td>2.1 (0.034)</td>
<td>CH$_3$CF$_2$Cl</td>
</tr>
<tr>
<td>D1</td>
<td>5.6</td>
<td>7 months</td>
<td>1.7 (0.027)</td>
<td>CH$_3$CF$_2$Cl</td>
</tr>
<tr>
<td>E1</td>
<td>5.6</td>
<td>7 days</td>
<td>4.0 (0.064)</td>
<td>CF$_2$Cl$_2$</td>
</tr>
<tr>
<td>F1</td>
<td>10</td>
<td>10 days</td>
<td>1.9 (0.029)</td>
<td>CH$_3$CF$_2$Cl</td>
</tr>
<tr>
<td>G1</td>
<td>2.8</td>
<td>5 years</td>
<td>1.9 (0.029)</td>
<td>CF$_2$Cl$_2$</td>
</tr>
<tr>
<td>H1</td>
<td>6.3</td>
<td>5 years</td>
<td>1.7 (0.027)</td>
<td>CH$_3$CF$_2$Cl</td>
</tr>
<tr>
<td>K1</td>
<td>7.4</td>
<td>3.5 months</td>
<td>1.7 (0.027)</td>
<td>CH$_3$CF$_2$Cl</td>
</tr>
<tr>
<td>A2*</td>
<td>3.6</td>
<td>2 months</td>
<td>1.7 (0.028)</td>
<td>CH$_3$CF$_2$Cl CF$_2$Cl$_2$</td>
</tr>
<tr>
<td>B2*</td>
<td>4.5</td>
<td>13 months</td>
<td>1.4 (0.022)</td>
<td>CH$_3$CF$_2$Cl CF$_2$Cl$_2$</td>
</tr>
</tbody>
</table>

*Note: for samples A2 and B2, the table shows the total amount of the two blowing agents in the foam.*
2.3.2.2. Effect of Temperature

A most important property, the thermal conductivity of insulation foams, changes with the age of the foam due to diffusion of air into the foam and diffusion of the blowing agent out. Usually, the diffusion processes are very slow, but at elevated temperatures, insulation foams will lose blowing gases from inside the cells at a much faster rate. The effects of temperature on different foam samples were studied by monitoring the amount of blowing gas as a function of time at an elevated temperature. Six foam samples (A1, B1, C1, D1, A2, B2) with dimensions of 10 \times 10 \times 20 \text{ mm}^3, were cut from the center of foam boards, then placed in an oven at 80° C and taken out periodically for $^{19}$F 1D NMR measurements. The $^{19}$F intensities due to the total amount of blowing agent are shown as a function of time in Figure 2.15. The results show that the rates of loss of the blowing agents in various PS foams are similar, but the gas in the high density foam (sample C1) seems to diffuse out a little slower than that in the low density one (sample B1). Because the density reflects the relative amounts of the solid polymer and blowing gas in foams, the cell walls in the lower density foams may be thinner, which allows the cell gas to diffuse faster.
Figure 2.15. Normalized intensities of $^{19}$F signals of the blowing agents in the different foams indicated (see Table 2.7) as functions of time of exposure to an air atmosphere at 80°C.
Thus, $^{19}$F 1D NMR measurements allow quantitative determination of the total amounts of cell gases in foams, which will be useful in the study of the foam aging process. However, the spatial distribution of the cell gas inside the foam matrix and changes in this distribution as functions of time and temperature can only be obtained with NMR imaging techniques. The next section will show that $^{19}$F spin-echo imaging provides a direct measurement of the concentration profiles of the cell gas in foams, and makes possible a quantitative study of the diffusion process.

2.3.3. $^{19}$F Spin-Echo Imaging Studies on Foams

The images presented in this thesis follow the convention in which an inverse grey scale is used to indicate relative intensity. The darker the region on the image, the higher the concentration of the nuclei and thus the foaming gas. Figure 2.16(a) presents a series of greyscale images obtained by different image sequences: (1) is a non-slice spin-echo image, (2) is a slice-selected spin-echo image and (3) is a FLASH image. Figures 2.16(b) shows another presentation, a three-dimensional histogram plot of the same data. This latter kind of plot can give a more quantitative presentation of the data than the greyscale method. Individual components of the histogram are termed "rows", and are pixel intensities as functions of distance. These $^{19}$F NMR images of CF$_2$Cl$_2$ distributions were taken from the same PS foam sample (sample E1), a rectangular shaped piece cut from the edge area of the foam board. With the same number of scans and repetition time, each image was obtained in about 30 minutes. The images all show a decrease in intensity of the signal near the edge of the sample indicating a loss of gas in this region. Closer inspection reveals that the image (1) has the best quality and the image (2) has relatively poor S/N,
while the image (3) obtained with FLASH shows some intensity variation caused by artifacts.

The FLASH sequence is very sensitive to magnetic field inhomogeneity effects, as the dephasing due to magnetic field inhomogeneity is not refocused by the field gradient reversal. Thus, if the field is not perfectly homogeneous, the image suffers from loss of signal intensity and possibly some spatial distortion. The image may show some low intensity regions caused by magnetic field inhomogeneities [13]. Also, if tip angles less than 90° are used, the signal is significantly reduced. Thus, for the same number of scans, this image doesn’t have as good S/N as image (1). A major advantage of using the FLASH sequence is that tip angles less than 90° can be used, giving more efficient data accumulation for samples with long T₁ values. However in all of the foams studied, the spin-lattice relaxation times observed for the fluorine nuclei in gaseous CFC’s, HCFC’s and HFC’s were less than 10 ms (Section 2.3.1.1). Thus, the required TR for a spin-echo experiment is also very short (100 ms) and there is little advantage in using the FLASH sequence for the ¹⁹F imaging experiment in terms of the experimental time.

One can clearly see that the image obtained by the slice-selecting spin-echo sequence, Figure 2.16(2), has a relatively poor signal-to-noise ratio. Due to the minute amounts of foaming gas present in the foam cells, it takes much longer to generate an image with good S/N if a slice is taken. The data also need to be acquired with a short echo time (TE) between excitation and data acquisition due to the short T₂ values. Trying to reduce TE is one of the reasons that non-slice imaging pulse sequences were chosen, where a much shorter hard r.f. pulse is used (several μs) instead of a selective r.f. pulse (several ms). Thus, in order to save instrument time and reduce the echo time we chose the non-slice spin-echo imaging sequence for subsequent experiments. Because these are synthetic materials, it is possible select the geometry of the sample so that there is exactly the same information on the spatial distribution of the gas whether a slice is taken or not.
A cylinder was thus chosen as the sample geometry for imaging, Figure 2.17 illustrates two $^{19}$F NMR imaging projections of CH$_3$CF$_2$Cl in a foam cylinder cut from the board (sample H1). These one-dimensional projections are taken along the x-axis, which is the axis of the cylinder and the r.f. coil, and have been obtained by performing the imaging experiment with only one gradient in the frequency encode direction. Figures 2.17(a) is a non-slice spin-echo projection, and Figure 2.17(b) is a projection from the 0.7 mm thick slice from the same sample. Both show the same gas distribution. Therefore in all subsequent investigations of the diffusion of blowing agents in foams, we used non-slice spin-echo imaging sequences to obtain one-dimensional projections from cylindrical samples (Chapter 3).
Figure 2.16
Figure 2.16(a). $^{19}$F images of CF$_2$Cl$_2$ in PS foam (sample E1) obtained by different imaging sequences. (1) SE without slice. The echo time was 1.5 ms and the in-plane resolution was 260 $\mu$m. (2) SE with slice. The echo time was 1.9 ms, slice gradient strength 2.4 G/cm and the slice thickness was 0.9 mm. The in-plane resolution was 260 $\mu$m. (3) FLASH image. The echo time was 1.1 ms and the in-plane resolution 190 $\mu$m. 2.16(b). Same data presented in the form of histogram plots.
Figure 2.17 $^{19}$F NMR imaging projections of CH$_3$CF$_2$Cl in a PS foam cylinder (sample H1) (a) with non-slice spin-echo sequence and (b) with slice-selecting spin-echo sequence. The slice thickness was 0.7 mm.
The results of $^{19}$F and $^1$H imaging experiments, performed on a cylindrical sample taken from the edge portion of the foam board (sample H1) containing CH$_3$CF$_2$Cl, are illustrated in Figure 2.18. They clearly show the same gas distribution, a decrease in intensity towards the edge, but the experimental times for $^1$H and $^{19}$F are quite different. For a total of 128 scans, the $^{19}$F one-dimensional imaging projection takes 13s to complete while the corresponding $^1$H experiment needs about 13 minutes. Proton nuclei in gaseous CH$_3$CF$_2$Cl blowing agent have a $T_1$ value of 1300 ms while the fluorine nuclei have a $T_1$ value less than 10 ms. Because of this very significant difference in their relaxation times, the $^{19}$F experiment can be performed with a much shorter repetition time (100 ms) compared to the 6s needed for the corresponding proton experiment. Thus, a $^{19}$F image experiment takes a much shorter time to complete than the $^1$H experiment, which will be especially important for 2-dimensional imaging experiments. As an example, Figure 2.19 shows a proton image of CH$_3$CF$_2$Cl in a rectangular piece of foam. This 128 x 128 $^1$H image acquired with a total of 64 scans took about 13 hours to complete, while the same $^{19}$F image needed only 14 minutes. Thus, signal averaging and fast repetition times in $^{19}$F imaging experiments can be used to efficiently compensate for the low signal-to-noise ratio inherent in imaging the minute amounts of blowing gases in foams. This is the main reason that we chose $^{19}$F NMR experiments in the further investigation of the foams.
Figure 2.18. One-dimensional NMR projections along the axial direction (x) of CH$_3$CF$_2$Cl in PS foam (sample H1). (a). $^1$H (b). $^{19}$F.
Figure 2.19(a). Two-dimensional $^1$H NMR image of a piece of PS foam sample containing CH$_3$CF$_2$Cl. The echo time was 7.3 ms, the read gradient strength 6.8 G/cm and the phase-encoding gradient strength 3.8 G/cm incremented through 128 experiments. The in-plane resolution was 220 $\mu$m and the experimental time 13 hours.

(b). Same data presented in the form of histogram plot.
Figure 2.20(a) presents a typical grey scale $^{19}$F image of CH$_3$CF$_2$Cl in a rectangular piece of PS foam sample cut from the outside edge of a board (sample B1). Figure 2.20(b) is the stacked plot of the image and Figure 2.20(c) the corresponding one-dimensional projection along the axial direction. They clearly show that the concentration of cell gas (CH$_3$CF$_2$Cl) increases from the outside edge inwards. This 128 x 128 image has an in-plane resolution of 260 $\mu$m. The resolution can be improved as shown in Figure 2.21, where an in-plane resolution of 60 $\mu$m was achieved in this 256 x 256 image using a higher gradient strength of 14 G/cm. In this case, some individual cells can be clearly observed. However, such an image takes much longer to complete due to the increased number scans needed for the signal averaging and gives no substantial advantage in the quantitative investigation of the diffusion processes.
Figure 2.20. $^{19}$F images of CH$_3$CF$_2$Cl distribution in PS foam sample B1. The echo time was 1.5 ms, the frequency encoding gradient strength 6.8 G/cm and the phase-encoding gradient strength 11.7 G/cm incremented through 128 experiments. The in-plane resolution was 260 μm. (a). Grey scale image. (b). Stacked plot presentation. (c). 1D Projection along the axial direction.
Figure 2.21. $^{19}$F images of CH$_3$CF$_2$Cl in PS foam (sample B1). The echo time was 2.1 ms, the frequency encoding gradient strength 14 G/cm and the phase-encoding gradient strength 24.4 G/cm incremented through 256 experiments. The in-plane resolution was 60 μm.
2.3.4 Distributions of Single Blowing Agents in Foams

2.3.4.1 Typical Distribution of a Single Blowing Agent in Foams

The distribution of a single foaming gas in various foam boards was investigated. A cylindrical sample (50-mm long, 10-mm in diameter) was taken through a foam board which was 2 months old (sample F1). The sample was cut into three pieces to fit into the center part of the imaging coil (the coil is about 40-mm long) to ensure reliable measurements. A one-dimensional projection along the axial direction was obtained with a \(^{19}\text{F}\) non-slice spin-echo imaging experiment for each specimen, and then, they were plotted together as in Figure 2.22. The blowing gas, \(\text{CH}_3\text{CF}_2\text{Cl}\) shows an uniform distribution in the center part of the foam matrix, and a decrease in intensity near the edges due to the diffusion. Such a distribution of the blowing gas inside the foam matrix is typical for all the various blowing agent/foam systems studied so far. However, inside a very thick foam board (sample H1) or a foam with a very high density (e.g. sample E1), some areas in the center portion of the foam matrix show abnormally low signal intensities (see Figure 2.12(c)). The positions and the sizes of these "holes" vary inside the sample, and they seem to be randomly located in these foamed materials. Figure 2.23, as an example, shows the presence of a large "hole" in the gas concentration in the center of a 10-cm thick foam board (sample H1). This cylindrical sample piece was taken through the foam board from one edge to another with a cork borer. The sample length was 10 cm and was cut into six pieces to ensure reliable measurements. These projections are plotted together in Figure 2.23. Due to inadequate mixing during manufacture, voids or non-uniformity may be inevitable. It is important to avoid these "holes" inside foam matrices when sampling for quantitative diffusion measurements, and this can be easily achieved by looking at the one-dimensional imaging projections of the foam samples.
Figure 2.22. Typical distribution of CH$_3$CF$_2$Cl in a 5 cm thick PS foam board (sample F1).

The dashed line indicates where the sample was cut.
Figure 2.23. Distribution of CH$_3$CF$_2$Cl in a 10 cm thick PS foam board aged for 5 years (sample H1). The dashed line indicates where the sample was cut.
2.3.4.2 Homogeneity of the Distribution of Blowing Agents

Depending on the manufacturing process used for foam formation and expansion, it is possible that the foams could have different structures and properties in the direction of the foam rise and perpendicular to the direction of the foam rise. To study such possible anisotropic effects, the distributions of blowing agents along different directions in the samples were investigated by measuring the one-dimensional projections along the three orthogonal axis of x, y, and z of a cubic foam sample taken from the center of the board (sample E1). Figure 2.24 shows the resulting three projections of the blowing agent (CF$_2$Cl$_2$). All three projections clearly show that the signal intensity in each direction is exactly the same and is uniformly distributed as a function of distance. This indicates that the cell structure in this foam is isotropic, and properties such as diffusion should be the same in all directions.
Figure 2.24. Three 1D projections of the distribution of blowing agent CF$_2$Cl$_2$ along the three orthogonal dimensions in a cubic sample of PS foam (sample E1).
2.3.4.3. Effect of Diffusion on the Distribution of a Single Blowing Agent in Foams

In order to study the effect of diffusion on the distribution of blowing agents in foams, cylindrical samples (20-mm long, 10-mm in diameter) were cut from two foam boards with ages of about 5 years and 2 months (samples F1 and H1). Figures 2.25(a) and (b) illustrate the distributions of CH$_3$CF$_2$Cl through the center part of these two foam boards. The signal intensity is distributed uniformly throughout both samples, but the signal intensity in the older sample is lower, which means there is less cell gas inside the foam matrix due to diffusion. Figures 2.26(a) and (b) show the distributions of CH$_3$CF$_2$Cl at the edge of the two foam boards. Figure 2.26(a) shows a gradual decrease in intensity towards the edge of the 2-month-old foam board while 2.26(b) shows a much larger gradient, i.e. a faster drop in intensity at the edge of this 5-year-old foam board. These projections clearly show that diffusion of the blowing agents from the center area towards the edges is taking place as the foam board ages and suggest that it should be possible to study and model such diffusion processes quantitatively.
Figure 2.25. CH$_3$CF$_2$Cl gas distribution in the center area of the PS foams (a) aged at room temperature for 2 months (sample F1) and (b) aged at room temperature for 5 years (sample H1).
Figure 2.26. CH$_3$CF$_2$Cl gas distribution in the edge area of a PS foam board (a) aged at room temperature for 2 months (sample F1) and (b) aged at room temperature for 5 years (sample H1).
2.3.5. Distributions of Mixed Blowing Agents within a Foam Matrix

2.3.5.1. Case 1: Foam Board

Foams filled with two blowing agents (CH$_3$CF$_2$Cl and CF$_2$Cl$_2$) were investigated by the chemical shift-selective imaging sequence (see Figure 2.8). An image or projection for each blowing gas can be used to study and monitor the distribution of each independently. Samples A2 and B2 both contain a mixture of two blowing gases, and have been aged at ambient temperature for 2 months and 13 months, respectively. As before, cylindrical samples for imaging were cut from the edges of the boards. Figure 2.27(a) shows the signal intensity of CF$_2$Cl$_2$ as a function of distance in each sample and 2.27(b) that of CH$_3$CF$_2$Cl. It is clear that the shapes of the projections and the intensity levels for CF$_2$Cl$_2$ in the two foams are almost the same, and the fluorine concentrations of the two gases measured from the 1D $^{19}$F spectra are also the same. Thus, it appears that little of the CF$_2$Cl$_2$ inside the cells was lost during this period of time. Because 1D $^{19}$F NMR spectroscopy and imaging techniques used in this study detect only the blowing agents in the gas-phase and not any gas dissolved in solid, this implies that there has been replenishment from CF$_2$Cl$_2$ gas dissolved in the foam matrix of the cell gas CF$_2$Cl$_2$ lost due to diffusion. However, the projections are rather different for the case of CH$_3$CF$_2$Cl. Although there are similar distributions in both foams, the intensity in the 13-month-old sample has dropped by 46 % compared to that of the 2-month-old sample. Measurements of the corresponding $^{19}$F 1D NMR spectra are in agreement with the results from the image intensity comparisons. This means that little CH$_3$CF$_2$Cl gas was released from the solid to compensate the gas loss in cells. These results show that the diffusion and solubility behavior of CH$_3$CF$_2$Cl and CF$_2$Cl$_2$ in this PS foam are different. It
Figure 2.27. Distributions of mixed blowing gases, CH$_3$CF$_2$Cl and CF$_2$Cl$_2$, in PS foam samples.

(a). CF$_2$Cl$_2$ in the foams aged for (i) 2 months, (ii) 13 months.

(b). CH$_3$CF$_2$Cl in the foams aged for (i) 2 months, (ii) 13 months.
is important to investigate the dissolved blowing agents in the foam matrix while studying their diffusion behavior. Detailed studies on the dissolved blowing agents in the foam matrix were carried out and are described in Chapter 4.

2.3.5.2 Case 2: Post-treated Foam Cylinder

The distributions of blowing agents in a series of post-treated samples (A3-F3) were studied. To investigate the mechanism of the post-treatment process, cylindrical samples were taken from a board originally made with \( \text{CH}_3\text{CF}_2\text{Cl} \) and then post-treated with either \( \text{CF}_3\text{CH}_2\text{F} \) or \( \text{CF}_3\text{CHFCI} \) at 79° for 69 hours. The \( ^{19}\text{F} \) 1D spectra of these samples show that the post-treatment gas has penetrated the foam sample. For each sample, chemical shift-selective imaging experiments were performed for each gas. The results from the whole series of samples are very similar. Figures 2.28(a)-(d) show typical results from sample B3: (a) is the \( ^{19}\text{F} \) 1D spectrum showing the presence and relative concentrations of the two blowing agents inside the foam sample; (b) is the cross-section image of the initial blowing gas, \( \text{CH}_3\text{CF}_2\text{Cl} \), which has an almost uniform distribution in the center of the foam and a smooth decrease in intensity to the outside edge. This also can be clearly seen in the stacked plot display(c) of the image. At the same time, the post-treatment gas, \( \text{CF}_3\text{CH}_2\text{F} \), has diffused into the foam cylinder and is concentrated at the outside edge of the sample, forming a ring approximately 2-3 mm thick. In this case, the concentration of the gas decreases from the outside edge inwards. The quantitative distributions of cell gases can also obtained from the corresponding image projections as presented in (d). These show the actual intensity distributions of the blowing gases inside the foam cylinder as a function of distance from the center.
Figure 2.28
Figure 2.28(a). $^{19}\text{F}$ 1D spectrum of the post-treatment sample of PS with the resonances assigned as indicated to the original foaming gas $\text{CH}_3\text{CF}_2\text{Cl}$ and the post treatment gas $\text{CF}_3\text{CH}_2\text{F}$. (b) Two-dimensional cross-section images of the distribution of $\text{CH}_3\text{CF}_2\text{Cl}$ in the same sample. (c). Two-dimensional cross-section images of the distribution of $\text{CF}_3\text{CH}_2\text{F}$ in the same sample. (d) One-dimensional projections. The intensities are normalized against the total number of fluorines found from the $^{19}\text{F}$ 1D spectrum and thus represent the absolute gas concentrations.

The selective pulse length was 300 $\mu$s and had a Gaussian shape. The echo time was 2.5 ms, read gradient strength 3.8 G/cm and the phase-encoding gradient strength 8.12 G/cm incremented through 128 experiments. The in-plane resolution was 220 $\mu$m. Grey scale and stacked plot presentations are shown here for the 2D images.
Further experimental investigations of the diffusion processes during the imbibing of the post-treatment blowing agents into the foam, as well as the emission of the blowing gas initially inside the foams, were carried out and are described in Section 2.2.1. Figure 2.29 shows a series of cross-section images of the two gases inside the foam as a function of time. From the quantitative intensity distributions obtained from the profiles of these images, the diffusion behavior of the two blowing gases were modeled in detail, and the diffusion coefficient for each gas calculated (Chapter 3, Section 3.4.4).
Figure 2.29 Series of cross-section images of the two gases CH$_3$CF$_2$Cl and CFCl$_3$ in PS foam as a function of time exposed in CFCl$_3$ at 69°. (a) 5 days, (b) 9 days, (c) 15 days.
The echo time was 2.2 ms, selective pulse length 300 μs with Gaussian shape and the read gradient strength 3.8 G/cm. The phase-encoding gradient strength was 8.12 G/cm incremented through 128 experiments and the in-plane resolution was 220 μm.
2.3.6. Accelerated Aging at Elevated Temperatures

The diffusion of CFC-12 (CF$_2$Cl$_2$) out of a very high density polystyrene foam (sample E1) seemed to be very slow. An image of a fresh foam cube cut from the center of the foam board shows that the intensity of CF$_2$Cl$_2$ is quite uniform throughout the sample, as shown in Figure 2.30(a). After aging at room temperature for 2 days, its image shows no appreciable change. However, after aging in an oven at about 80° for 96 hours, the image changes significantly, as illustrated in 2.30(b). After aging, the signal-to-noise ratio has decreased and the maximum signal intensity in the center is reduced and smoothly decreases towards the edges of the foam. The profile from the image shows the quantitative distribution of the signal intensity through the cross-section. This result indicates that the elevated temperature has greatly accelerated the diffusion process of the gaseous blowing agent out of the foam. Further studies on accelerated diffusion of blowing agents at elevated temperatures is described in Chapter 3.
Figure 2.30(a). An image of CF$_2$Cl$_2$ in a fresh PS foam cube cut from the center of the board (sample E1). (b). After placing the sample in an oven at about 80° for 96 hours. The echo time was 1.5 ms, read gradient strength 6.8 G/cm and the phase-encoding gradient strength was 11.7 G/cm incremented through 128 experiments. The in-plane resolution was 260 μm. Grey scale and stacked plot presentations are shown here for the 2D images.
2.4 CONCLUSIONS

The results obtained on a variety of polystyrene insulation foams containing various fluorinated gas blowing agents clearly show that $^{19}$F NMR microscopy is ideally suited for the quantitative determination of amounts of cell gases present, for measuring distributions of foaming gases inside foams, monitoring changes in the amounts and distributions of all gases as functions of time and temperature and effects involved in the actual foam manufacturing. Also, the results indicate that quantitative investigation of the diffusion process of blowing agents in foam matrix will be possible with the $^{19}$F microscopic NMR imaging technique. The information obtained can be used to optimize the fabrication of these insulating materials in the future. It will also help to attain a better understanding of these materials and their effect on the environment. An additional advantage of NMR imaging is that it is a non-destructive, non-invasive technique with which to study polymer foam materials.
REFERENCES


3.1. INTRODUCTION

Closed-cell polystyrene foam filled with chlorofluorocarbon foaming gas has a very low thermal conductivity, which depends on the continued presence of the high molecular weight gas in the foam voids. As the foam ages in air, the foaming gas which is comparatively heavier than air, will slowly diffuse out and be replaced by air. Thus, the thermal conductivity will increase as foam products age with a corresponding degradation in their insulation properties. A thorough understanding of gas diffusion phenomena in foam systems is essential in many practical applications, from prediction of their insulation aging rates to the design and control of manufacturing processes.

Preliminary studies showed that the amount of blowing gases in foams was very small and the diffusion process at room temperature was very slow (see Chapter 2). In systems with low diffusion rates and low concentrations of diffusing material such as insulating foams, the measurement of the diffusion coefficients is extremely time-consuming and difficult. The traditional methods of measurement of the diffusion
coefficients of the blowing agents in closed cell foams include transmission methods and sorption-desorption methods. In the transmission method, one surface of the foam sample is exposed to a constant pressure of the diffusing gas, while the other surface is exposed to the same gas but at a lower pressure at the beginning of the experiment, thus, applying a partial pressure gradient across the sample. As the gas diffuses through the foam, it collects in this exit volume causing the pressure to increase until it reaches equilibrium. The permeation rate can be measured by a volumetric measurement, a pressure measurement, gas chromatography or mass spectroscopy. From the permeation rate, the diffusion coefficient can be computed. In the sorption-desorption methods, the change of weight of the sample is often measured as a function of time [1-3]. These methods all have disadvantages. They generally need very complex devices and the procedures are tedious and long. For example, the fastest-available transmission technique needs about 270 days to complete a measurement of the diffusion of blowing gas in a foam [2]. A newly developed constant-volume sorption technique [3] for measurement of gas diffusion in foams is based on the measurement of the transient pressure in an isolated-volume chamber containing the foam sample and the test gas, immediately after the test gas pressure surrounding the sample has been changed in a step fashion. In order to produce meaningful results, the apparatus must be very sensitive and stable over the long period of pressure measurements. The transient diffusion equation for the appropriate sample/chamber geometry has then to be solved to obtain the diffusion coefficient.
NMR imaging techniques have been used for the study of diffusion of a variety of chemicals in polymeric materials [4,5]. The principal advantages of NMR imaging are that it is possible to determine the concentration and location of a diffusing species in a solid sample, with a visual presentation of the data in the form of images. Moreover, this information is obtained in a non-invasive and non-destructive manner. In the previous chapter, it was shown that $^{19}$F NMR micro-imaging technique could be used to monitor the distributions of foaming gas in foam cells as functions of both time and temperature. In the present chapter, measurement of the diffusion coefficients of the foaming gas at room temperature and at higher temperatures by fitting the experimental imaging data to the appropriate solutions of Fick's equation [5] will be described. Compared to the conventional methods used in this area, NMR imaging will be demonstrated to be a very simple, fast and non-invasive way to study the diffusion process of blowing gases in foams for a better understanding of the dynamics of the diffusion process and the important contributing factors.

3.2. EXPERIMENTAL

3.2.1. Experimental Protocol A

Foam blocks with dimensions of $15 \times 15 \times 3.8$ cm$^3$ cut from PS foam sample K1 (Section 2.2.1) were placed in ovens at various temperatures, and samples taken periodically from these blocks for the imaging measurements. For each measurement, a
cylinder (1-cm in diameter) was cut out from the center of each block with a cork borer, and imaged in a 15 mm horizontal solenoid r.f. coil on a Bruker MSL 400 spectrometer using a non-slice spin-echo imaging sequence with a single gradient to give one-dimensional profiles of the distribution of the blowing agents in the foam cylinder along the axial direction (the experimental details were as described in Chapter 2). Such a projection shows the distribution of the total gas along the axial direction of the cylinder. A diagram of the foam cylinder and sketch of the NMR signal projection is shown in Figure 3.1.

The process was repeated with fresh cylinders, cut out of the blocks which were kept at the different temperatures over a range of exposure times (about 5 months) for diffusion. Thus a complete set of gas profiles as functions of time and temperature was obtained.

Figure 3.1. Sketch of foam cylinder and schematic representation of the expected one-dimensional projection of the $^{19}$F signal intensity along the x direction.
3.2.2. **Experimental Protocol B**

An accelerated diffusion experiment was carried out with a series of fresh foam cylinders taken from PS foam board sample K1 (Section 2.2.1) and then exposed to air inside an oven at an elevated temperature for various times. Periodically, one cylinder was taken out for the imaging measurement. Note that in this case, diffusion takes place from all surfaces of the foam cylinder. The gas concentration over the cross-section region of the cylinder is not constant and these experiments describe the diffusion characteristics of only the foam cylinder and not the original board.

One dimensional imaging projections along its axis were taken as a function of time. The imaging intensity at location x is proportional to the average concentration of blowing gas over the cross-section region at this position.

3.2.3 **Experimental Protocol C**

In the study of post-treatment of foams, a series of foam cylinders were prepared and exposed to a second gas as described in Section 2.2.1. In this case, we are interested in the two diffusion processes that are taking place simultaneously: One is the diffusion of the original blowing gas outward from the foam cylinder; the other is the diffusion of the second blowing gas inward into the foam cylinder. During the post-treatment with the
second gas, both end surfaces of the cylinders were sealed with aluminum foil, and just before the imaging measurement, both ends (each about one third of the total length) were cut off, only the middle section of the foam sample was used to obtain a cross-section image with a non-slice chemical shift selective pulse sequence (see Section 2.2.4.1). In this case, we do not consider diffusion processes along the axial direction of the cylinder. The intensity distribution obtained from the center row of the image reflects the diffusion processes through the convex surfaces of the cylinder (see Figure 3.2). Again these measurements are not directly related to the behavior of a whole board.

Figure 3.2. Sketch of cross-section image of foam cylinder and the one dimensional profile from the center row of the image.
3.3. MODELS FOR DIFFUSION IN FOAMS

3.3.1. Models for Diffusion in Foams

The diffusion behavior of gases in rigid, closed cell foams was shown to obey Fick’s law by Cuddihy and Moacanin [6]. The general diffusion equation, Fick’s differential equation, can be written for a constant diffusion coefficient as

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (3.1)
\]

Where \( C \) is the concentration in the center of a rectangular element of the region with infinitesimal sides \( dx, dy \) and \( dz \). It is assumed that \( D \), the diffusion coefficient, is a constant for all concentrations.

When diffusion is in one dimension only, this equation has a simpler form

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3.2)
\]

where \( x \) is the space coordinate measured along the direction of the diffusion.

For a cylindrical system, the equation has the form

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{1}{r^2} \frac{\partial^2 C}{\partial \phi^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (3.3)
\]

where \( r, \phi, z \) are the cylindrical coordinates as shown in Figure 3.3.
If the distribution of material about the z-axis is symmetrical at all times, then the equation has a simpler form

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2} \right)
\]  

(3.4)

In general, in order to obtain a solution of a diffusion problem, it is necessary to know the initial condition and the boundary conditions of the system. For a one-dimensional diffusion process as described in Equation (3.2), the initial condition, the description of the distribution of the diffusing material at the beginning of the diffusion, is usually represented by an equation of the type

\[ C = f(x) \text{ when } t = 0 \]

where \( x \) is the region of the diffusion.

In addition to the initial condition, it is necessary to know the properties of the boundaries of the system that cross the axis of diffusion. Since diffusion is assumed to
occur in only the $x$ direction, the absence of diffusion in other directions means either that
the system is closed or that it is infinite in these directions; in either case, there can be no
gain nor loss of material except in the direction of diffusion. One of the commonest
boundary conditions is a statement of the concentration of the diffusing substance that
exists at the boundary of the system throughout the time under consideration as in the
equation

$$C = f_1(t) \text{ when } x = 0$$

$$C = f_2(t) \text{ when } x = \ell$$

where $\ell$ is used to represent the length of the system in the direction of diffusion.

Blowing agents diffuse out from closed-cell foams and are replaced by air, this
process also being controlled by Fick's law. It is assumed that the foams are
homogeneous media because the cells are small. In the investigation of losses of foaming
gas from foam cells, it is useful to investigate the solutions of Fick's differential equations
under different conditions.
3.3.2 Solution for Protocol A

Consider a cylinder-shaped porous body as shown in Figure 3.4,

![Figure 3.4 Sketch of a cylinder-shaped porous body.](image)

The convex surface is considered to be sealed to prevent diffusion of gas. The diffusion process only takes place from both ends of the cylinder along the $x$ direction taken perpendicular to the diffusion faces, the central plane of symmetry being taken as $x = 0$, and the cylinder length $2h$. The boundary conditions of $C = 0$ at $x = h$ and $x = -h$, during the diffusion process

$$x = h \text{ and } x = -h,$$

during the diffusion process

and the initial condition

$$C = C_0 \text{ when } t = 0,$$

applies.

This case corresponds to the experimental protocol A where foam cylinders were cut from a board from side to side (Section 3.2.1).

Equation (3.2) can be used to describe the diffusion process in such a case. It is assumed that the diffusion constant is independent of concentration. Also, the concentration of the diffusing material is uniform throughout this cylinder-shaped body at
the beginning of the diffusion process, and that the concentration of the diffusing material on the surface of the body falls to zero. Thus, this differential equation can be solved [7] as a function of time $t$ and distance $x$, where $h$ is half the cylinder length as shown in Figure 3.4.

$$\frac{C}{C_0} = f(x,t)$$

$$= \frac{4}{\pi} \left[ \cos \frac{\pi x}{2h} \exp \left( -Dt \left( \frac{\pi}{2h} \right)^2 \right) \right]$$

$$- \frac{1}{3} \cos \frac{3\pi x}{2h} \exp \left( -9Dt \left( \frac{\pi}{2h} \right)^2 \right)$$

$$+ \frac{1}{5} \cos \frac{5\pi x}{2h} \exp \left( -25Dt \left( \frac{\pi}{2h} \right)^2 \right) - \cdots \right] \quad (3.5)$$

$D$ is the average diffusion coefficient in the time period $t$ during which the diffusion process takes place.

In the case of a diffusion process containing several time periods $t_i$ with different diffusion coefficients $D_i$, e.g. when the two periods have different temperatures, the above equation can be written as:
\[
\frac{C}{C_0} = f(x,t)
\]

\[
= \frac{4}{\pi} \cos \frac{\pi x}{2h} \exp \left(- \left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{\pi}{2h} \right)^2 \right)
\]

\[
- \frac{1}{3} \cos \frac{3\pi x}{2h} \exp \left(-9 \left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{\pi}{2h} \right)^2 \right)
\]

\[
+ \frac{1}{5} \cos \frac{5\pi x}{2h} \exp \left(-25 \left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{\pi}{2h} \right)^2 \right) \ldots \] (3.6)

where the summation is over the different diffusion conditions represented by \( D_i \) and \( t_i \).

### 3.3.3 Solution for Protocol B

In the case of a cylinder with the end surfaces sealed and diffusion occurring only from the convex surface, the differential Equation (3.4) can be written as

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) \quad (3.7)
\]

where \( r \) is distance from the axis of the cylinder.

For the boundary condition

\[
C = 0 \text{ at } r = a,
\]

and initial condition
\[ C = C_0 \text{ when } t = 0, \]

Note that this corresponds to the outward diffusion cases in foam cylinders described in Sections 3.2.2 and 3.2.3. The solution is also known [7-8] as a function of time and radial distance \( r \).

\[
\frac{C}{C_0} = f(r, t)
\]

\[
= 2 \sum_{n=1}^{\infty} \frac{J_0 \left( R_n \frac{r}{a} \right)}{R_n J_1 (R_n)} \exp \left[ - \left( \sum_{i=1}^{n} D_i t_i \right) \frac{R_n^2}{a^2} \right] \tag{3.8}
\]

Where \( J_0 \) and \( J_1 \) are Bessel functions of order zero and one, respectively. \( R_n \) is the \( n^{th} \) root of the equation \( J_0(x) = 0 \). For example, \( R_1 \) is the smallest value of \( x \) which gives \( J_0(x) = 0 \), \( R_2 \) is the next larger value of \( x \) which gives \( J_0(x) = 0 \) etc.

In the case of a cylinder with diffusion occurring from both end and convex surfaces, if one assumes that the two diffusion processes are independent, the solution can be written
\[
\frac{C}{C_0} = f(r,t)f(x,t)
\]

\[
= \frac{4}{\pi} \left[ \cos \frac{\pi x}{2h} \exp \left( -\left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{\pi}{2h} \right)^2 \right) \right] \\
- \frac{1}{3} \cos \frac{3\pi x}{2h} \exp \left( -9 \left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{\pi}{2h} \right)^2 \right) \\
+ \frac{1}{5} \cos \frac{5\pi x}{2h} \exp \left( -25 \left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{\pi}{2h} \right)^2 \right) \ldots \right]^{*} \\
\left\{ \sum_{n=1}^{\infty} \frac{J_n \left( R_n \frac{r}{a} \right)}{R_n J_1 (R_n)} \exp \left[ -\left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{R_n^2}{a^2} \right) \right] \right\} \\
(3.9)
\]

where \( r \) is distance from the center of the cylinder, \( x \) is distance along the axis of the cylinder.

Note that the concentration \( C \) is expressed as the amount of material per unit volume at any location inside the cylinder. To find the average concentration over the cross-section of the cylinder at location \( x \) along its axis at time \( t \), one can consider a cylindrical shell of any radius within the cylinder. The surface of the shell is \( 2\pi rh \) and its thickness \( dr \), making its volume \( 2\pi rhdr \). The content of the diffusing material of the shell will be

\[
C_{av} \pi a^2 h = \int_{0}^{a} C 2\pi hrdr
\]
Substituting for $C$ in Equation (3.9) and rearranging gives

\[
\frac{C_{av}}{C_o} = \frac{2}{a^2} f(x,t) \int_0^a f(r,t) r dr
\]  

(3.10)

Integrating this equation, gives the solution

\[
\frac{C_{av}(x,t)}{C_o} = f(x,t) \sum_{n=1}^{\infty} \frac{4}{R_n^2} \exp \left[ - \left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{R_n}{a} \right)^2 \right] \\
= \frac{4}{\pi} \cos \frac{\pi x}{2h} \exp \left[ - \left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{\pi}{2h} \right)^2 \right] \\
- \frac{1}{3} \cos \frac{3\pi x}{2h} \exp \left[ -9 \left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{\pi}{2h} \right)^2 \right] \\
+ \frac{1}{5} \cos \frac{5\pi x}{2h} \exp \left[ -25 \left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{\pi}{2h} \right)^2 \right] - \cdots \\
\times \sum_{n=1}^{\infty} \frac{4}{R_n^2} \exp \left[ - \left( \sum_{i=1}^{n} D_i t_i \right) \left( \frac{R_n}{a} \right)^2 \right] \\
i = 1, 2, 3 \ldots
\]  

(3.11)

3.3.4 Solution for Protocol C

3.3.4.1 Outward diffusion
In the case of a cylinder with the end surfaces sealed and diffusion occurring only from the convex surface outward, for an initial condition of $C = C_0$ when $t = 0$ and a boundary condition of $C = 0$ at $r = a$, the solution can be written as Equation (3.8) as given in Section 3.3.3 to describe the diffusion process outward from an internal concentration of $C_0$ inside a cylinder.

3.3.4.2 Inward diffusion

For the case where diffusion is inward from an external concentration of $C_0$ into an originally empty cylinder, the initial and boundary conditions for Equation (3.8) are slightly different:

The boundary condition is

$$C = C_0 \text{ at } r = a,$$

and initial condition is

$$C = 0 \text{ when } t = 0,$$

The solution may be written as

$$\frac{C}{C_0} = f(r, t)$$
FORTRAN programs were written to use the above Equations (3.6), (3.8), (3.11) and (3.12) to calculate diffusion curves in order to fit the experimental data. These programs are presented in Appendix 2.

### 3.4 MEASUREMENT OF GAS DIFFUSION IN FOAMS

#### 3.4.1 NMR Imaging as a Technique for Monitoring Diffusion Processes

Image intensity depends not only on the concentration of the fluorinated gas in the cells, but also on the nuclear relaxation times and experimental conditions. Because the $T_1$ values of foam samples are very small (in the millisecond range), it is easy to avoid $T_1$ effects by using a cycle time of 100 ms (Section 2.3.1.1). Although the parameter TE (time to echo) in the pulse sequence was made as short as possible (about 2 ms), some signal was still lost due to $T_2$ effects. However, since the $T_2$ values are uniform across the whole sample (Section 2.3.1.3), the image intensity distribution can be regarded as the distribution of blowing gas concentrations as function of distance. The initial concentration $C_0$ of the blowing gas is proportional to the maximum imaging intensity $I_0$ inside a freshly made foam board. As a reference, we take a cylindrical sample from a newly made foam board (sample K1); the one dimensional image projection along its axis
shows that a decrease in intensity only occurs near both end surfaces where they are exposed to air, the maximum intensity (i.e. $I_0$) in the center section is uniform and is the same independent of its location in the foam board as long as it is a few centimeters away from the edges. Thus we can normalize the imaging intensity against this maximum intensity obtained from the sample, and the above equations can be written as

$$\frac{C}{C_0} = \frac{I}{I_0} = f(x,t)$$

In this way, the values of the imaging intensity $I$ as functions of the distance ($x$) and the time ($t$) of the diffusion can be used to study the diffusion process of blowing agents in foams.

3.4.2. Experimental Protocol A

3.4.2.1. Aging at Ambient Temperature

In experimental protocol A, it is reasonable to assume that the net diffusion of the fluorinated gas occurred only at the two end surfaces because the cylinder sample was freshly cut before the imaging experiment from the center portion of the foam board, away from the side edges of the block (illustrated in Figure 3.5). The diffusion processes in and
out of the convex surfaces of the cylinder while it was an integral part of the center of the block were the same, and therefore there was no net gain or loss of the blowing agents through its convex surface. In this case, Equation (3.2) can be used to describe the diffusion of gas out of the foam cells along the axial direction of the foam cylinders. It is assumed that the diffusion constant is independent of the gas concentration. The gas concentration inside the foam is believed to be the same everywhere at the beginning of the diffusion when the foam was freshly made. Also, the gas concentration on the surface of the foam cylinder falls to zero. Under this condition, the solution to the Equation (3.2), i.e. Equation (3.6) can be fitted to the experimental data obtained from this experimental arrangement.

Figure 3.5. Sketch of a foam cylinder taken from the center area of a foam block where net diffusion of the fluorinated gas has occurred at only the two end surfaces.
In experimental protocol A, a set of one-dimensional imaging projections of \( \text{CH}_3\text{CF}_2\text{Cl} \) along the axis of the sample cylinder were obtained as a function of aging time \( t \) at room temperature. To increase the reliability of the projections, the cylinder was cut in the middle and the two halves positioned together so that the original end surfaces were in the center of the r.f. coil. Each projection presents the distribution of the total intensity \( I \) of the \( \text{CH}_3\text{CF}_2\text{Cl} \) as a function of the axial distance \( x \). The intensity \( I_0 \) was obtained as described earlier. After certain exposure time \( t_i \) for diffusion, \( D_i \), the average diffusion coefficient at room temperature during \( t_i \) can be determined by fitting the experimental data to calculated profiles using Equation (3.6). Figure 3.6 presents typical examples of experimental data from the image projections and the fitted curves as a function of time. \( D_i \) is determined from both the best visual fits and non-linear least squares fits \( (\chi^2) \) of the data using the Mathematica program [9]. Each experiment was repeated with foam cylinders (2 to 6) taken from different locations in the center area of the foam block (Table 3.1). The D values and errors are listed in Table 3.1. This diffusion process at room temperature was monitored by our imaging measurement over about 5 month period at time intervals of 117, 166, 174, 201 and 234 days. The diffusion coefficients were calculated for each diffusion time (shown in Table 3.1) and are very close except that the first one, \( D_1 \), \( (8.1 \pm 0.4) \times 10^{-9} \text{ cm}^2/\text{s} \) is significantly larger than the rest (1.8 to 2.3 \( \times 10^{-9} \)). This value was obtained from the fitting of the first imaging profile, obtained immediately after receipt of the foams. The diffusion period is measured from the time the foam was manufactured to the time of the imaging experiment. This result perhaps indicates that there was a loss of blowing agent right after the foam was made or that during the initial
period of aging the diffusion process was somewhat faster. The diffusion coefficient stayed very constant over the time span of all of our measurements. The literature data on the determination of diffusion coefficients of blowing gas in foams vary substantially depending on the methods used [10]. Our measurements of diffusion coefficients of CH₃CF₂Cl in PS foams are in agreement with the published data (ranged from 1.9 to 7.8 x 10⁹ cm²/s) [11] for similar PS foam samples. This result is used in the next section to calculate the initial diffusion process of CH₃CF₂Cl at room temperature before the accelerated diffusion process takes place at elevated temperatures. The results obtained here can now be used to predict the diffusion of CH₃CF₂Cl out of PS foam samples of any geometry at room temperature.
Figure 3.6. Series of imaging projections of CH$_3$CF$_2$Cl measured at time intervals of (a) 117, (b) 201 and (c) 234 days together with the corresponding theoretical curves calculated using Equation (3.6).
Table 3.1. Diffusion characteristics of CH$_3$CF$_2$Cl in PS foam at room temperature.

<table>
<thead>
<tr>
<th>Diffusion time (days)</th>
<th>Measurement</th>
<th>Diffusion Coefficient * (cm$^2$/s)</th>
<th>Reduced $\chi^2$ value</th>
<th>Average Diffusion Coefficient * (cm$^2$/s)</th>
<th>Average Diffusion Coefficient ** (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
<td>$7.6 \times 10^{-9}$</td>
<td>0.04</td>
<td>$(7.8 \pm 0.2) \times 10^{-9}$</td>
<td>$(8.1 \pm 0.4) \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>$7.8 \times 10^{-9}$</td>
<td>0.03</td>
<td>$8.0 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>#3</td>
<td>$8.0 \times 10^{-9}$</td>
<td>0.03</td>
<td>$7.9 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>#4</td>
<td>$8.2 \times 10^{-9}$</td>
<td>0.02</td>
<td>$8.7 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>#5</td>
<td>$8.0 \times 10^{-9}$</td>
<td>0.02</td>
<td>$8.6 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>117</td>
<td>#6</td>
<td>$7.5 \times 10^{-9}$</td>
<td>0.04</td>
<td>$7.8 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>#1</td>
<td>$1.9 \times 10^{-9}$</td>
<td>0.1</td>
<td>$(1.8 \pm 0.1) \times 10^{-9}$</td>
<td>$(1.8 \pm 0.2) \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>$1.7 \times 10^{-9}$</td>
<td>0.03</td>
<td>$1.6 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>#3</td>
<td>$1.8 \times 10^{-9}$</td>
<td>0.05</td>
<td>$1.7 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>#4</td>
<td>$1.9 \times 10^{-9}$</td>
<td>0.1</td>
<td>$1.9 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>166</td>
<td>#1</td>
<td>$1.8 \times 10^{-9}$</td>
<td>0.07</td>
<td>$(1.8 \pm 0.1) \times 10^{-9}$</td>
<td>$(2.0 \pm 0.3) \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>$1.8 \times 10^{-9}$</td>
<td>0.1</td>
<td>$2.2 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>#1</td>
<td>$2.0 \times 10^{-9}$</td>
<td>0.06</td>
<td>$2.4 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>$2.1 \times 10^{-9}$</td>
<td>0.05</td>
<td>$2.5 \times 10^{-9}$</td>
<td>$(2.3 \pm 0.3) \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>#3</td>
<td>$1.9 \times 10^{-9}$</td>
<td>0.03</td>
<td>$2.0 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>174</td>
<td>#1</td>
<td>$2.0 \times 10^{-9}$</td>
<td>0.2</td>
<td>$2.0 \times 10^{-9}$</td>
<td>$(2.05 \pm 0.1) \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>$2.0 \times 10^{-9}$</td>
<td>0.1</td>
<td>$2.1 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>201</td>
<td>#1</td>
<td>$2.0 \times 10^{-9}$</td>
<td>0.1</td>
<td>$2.0 \times 10^{-9}$</td>
<td>$(2.05 \pm 0.1) \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>$2.0 \times 10^{-9}$</td>
<td>0.1</td>
<td>$2.1 \times 10^{-9}$</td>
<td>$(2.05 \pm 0.1) \times 10^{-9}$</td>
</tr>
<tr>
<td>234</td>
<td>#1</td>
<td>$2.0 \times 10^{-9}$</td>
<td>0.1</td>
<td>$2.0 \times 10^{-9}$</td>
<td>$(2.05 \pm 0.1) \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>$2.0 \times 10^{-9}$</td>
<td>0.1</td>
<td>$2.1 \times 10^{-9}$</td>
<td>$(2.05 \pm 0.1) \times 10^{-9}$</td>
</tr>
</tbody>
</table>

* obtained from best visual fits.
** obtained from the non-linear least squares fits.
The error limit is based on the 90% confidence level of "Student t probability distribution" [12].

3.4.2.2 Aging at Elevated Temperatures

The above results indicate that the diffusion of CH$_3$CF$_2$Cl blowing agent out of PS foam at room temperature is very slow. Observation of a full sized sample under operating conditions is impractical as the time for substantial blowing agent loss may be decades.
There are two methods commonly used to accelerate foam aging processes. One is to cut the diffusion path, i.e. to use a sample with small dimensions. The other method is to use an elevated temperature, e.g. in industry, a test called the accelerated aging test [13] is often used to evaluate foam products.

In experimental protocol A, elevated temperatures were used to accelerate the diffusion process of the blowing agent inside the foam board. With cylindrical samples taken from different whole PS foam boards exposed to different temperatures $T$, several sets of imaging projection data of CH$_3$CF$_2$Cl along the axis of the sample cylinder were obtained as a function of the aging time $t$ at temperature $T$. Each aging time $t$ includes $t_i$, a variable diffusion time at $T$ and an initial diffusion period $t_0$, measured from the time the foam was manufactured to the time when the foam board was exposed to temperature $T$. During this $t_0$, the foam board had aged at ambient temperature. $D_0$, the diffusion coefficient of CH$_3$CF$_2$Cl at room temperature, was available from previous experiments (Section 3.4.2.1). Thus $D_i$, the diffusion coefficient of CH$_3$CF$_2$Cl at each temperature $T$, was calculated using Equation (3.6) corresponding to each $t_i$. These $D_i$ values were then averaged as the diffusion coefficient of the CH$_3$CF$_2$Cl in foams at this temperature $T$. The temperature range was from 319 °K to 360 °K and the diffusion times ranged up to 5 months. Measurements of the accelerated diffusion process were made at six temperatures and at each temperature, 2 to 5 measurements were carried out. Table 3.2 shows the calculated diffusion coefficient values for each temperature. The uncertainty in the measurements is less than 10%. Figure 3.7 shows a representative series of fitting results for various diffusion times at 87° C.
Table 3.2. Diffusion characteristics of CH₃CF₂Cl in PS at the different temperatures indicated.

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Diffusion Time at T (days)</th>
<th>Diffusion Coefficient (cm²/s)*</th>
<th>Diffusion Coefficient (cm²/s)**</th>
<th>Reduced $\chi^2$ value</th>
<th>Average Diffusion Coefficient at T* (cm²/s)</th>
<th>Average Diffusion Coefficient at T** (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>***</td>
<td>1.9 x 10⁻⁹</td>
<td>2.0 x 10⁻⁹</td>
<td>***</td>
<td>(1.9 ± 0.1) x 10⁻⁹</td>
<td>(2.0 ± 0.1) x 10⁻⁹</td>
</tr>
<tr>
<td>319</td>
<td>46</td>
<td>3.2 x 10⁻⁹</td>
<td>2.9 x 10⁻⁹</td>
<td>0.2</td>
<td>(3.3 ± 0.1) x 10⁻⁹</td>
<td>(3.5 ± 0.1) x 10⁻⁹</td>
</tr>
<tr>
<td>328</td>
<td>28</td>
<td>5.6 x 10⁻⁹</td>
<td>6.8 x 10⁻⁹</td>
<td>0.2</td>
<td>(5.6 ± 0.1) x 10⁻⁹</td>
<td>(5.6 ± 0.1) x 10⁻⁹</td>
</tr>
<tr>
<td>342</td>
<td>24</td>
<td>8.2 x 10⁻⁹</td>
<td>8.3 x 10⁻⁹</td>
<td>0.05</td>
<td>(8.8 ± 0.5) x 10⁻⁹</td>
<td>(9.0 ± 0.6) x 10⁻⁹</td>
</tr>
<tr>
<td>346</td>
<td>34</td>
<td>11.0 x 10⁻⁹</td>
<td>10.7 x 10⁻⁹</td>
<td>0.1</td>
<td>(10.5 ± 0.5) x 10⁻⁹</td>
<td>(10.6 ± 0.5) x 10⁻⁹</td>
</tr>
<tr>
<td>352</td>
<td>18</td>
<td>11.0 x 10⁻⁹</td>
<td>11.0 x 10⁻⁹</td>
<td>0.06</td>
<td>(11.9 ± 0.6) x 10⁻⁹</td>
<td>(11.2 ± 1.0) x 10⁻⁹</td>
</tr>
<tr>
<td>360</td>
<td>21</td>
<td>18.4 x 10⁻⁹</td>
<td>18.6 x 10⁻⁹</td>
<td>0.05</td>
<td>(17.1 ± 1.0) x 10⁻⁹</td>
<td>(18.8 ± 0.8) x 10⁻⁹</td>
</tr>
</tbody>
</table>

* obtained from best visual fits.  
** obtained from the non-linear leastsquares fits.  
*** the various diffusion times are listed in Table 3.1.
Figure 3.7. Series of CH$_3$CF$_2$Cl imaging projections as a function of diffusion time at 87°C after 145 days at ambient temperature together with the calculated curves. (a) 21 days (b) 55 days (c) 88 days.
The ln $D$ values from Table 3.2 are plotted against $T^{-1}$ shown in Figure 3.8.

Assuming a simple Arrhenius equation for the temperature dependence of the diffusion coefficient, the slope from a least-squares fitting of the diffusion coefficients of CH$_3$CF$_2$Cl, seen in Figure 3.8, yields an activation energy of 32.73 ± 0.02 kJ/mol. This information is useful to estimate the degree of acceleration of the diffusion process of blowing agents in similar PS foam systems at elevated temperatures.
Figure 3.8. Temperature dependence of the diffusion coefficients of CH$_3$CF$_2$Cl in PS foams. The error bars ($= 2 | \Delta D/D |$) are calculated using the data in Table 3.2.
3.4.3 Experimental Protocol B: Accelerated Aging Processes

In experimental protocol A, the diffusion behavior of CH$_3$CF$_2$Cl in PS foams was investigated using foam blocks (15 x 15 x 3.8 cm$^3$). The net diffusion of CH$_3$CF$_2$Cl occurred only at the two end surfaces of the cylindrical sample (Section 3.4.2.1). In order to accelerate the diffusion process, in experimental protocol B, a set of foam cylinders (10 mm in diameter and 38 mm in length) were studied at an elevated temperature of 87°C as a function of diffusion time. The sample was the center portion (about 25 mm in length) of the cylinder, ends cut off to ensure the uniform initial distribution of the gas concentration within the sample. In this case, the aging is accelerated by both the larger surface area to volume ratio of the sample and also the elevated temperature. In this case, gas diffusion occurs through all the surfaces of the foam cylinders. The one-dimensional imaging projection provides a total signal intensity over the cross-section region as a function of the distance along the axial direction of the cylinder. Thus the signal intensity ratio ($I/I_0$) at the location x is proportional to the average concentration ratio ($C_{av}/C_0$) at the same location x, as described by Equation (3.11). The diffusion coefficient was obtained from fitting the imaging data to the calculated curves calculated from Equation (3.11). Table 3.3 shows the calculated diffusion coefficient corresponding to each diffusion time. The average diffusion coefficient of CH$_3$CF$_2$Cl at 87°C is calculated as $(2.0 \pm 0.3) \times 10^{-8}$ cm$^2$/s. This result is close to the value, $(1.88 \pm 0.08) \times 10^{-8}$ cm$^2$/s, obtained from experimental protocol A from heating the large intact foam blocks as described in Section 3.2.1, but is obtained in a much shorter period of time (86 hours versus 88 days). Although the sample length was corrected for the cutting damage due to cutting off the cylinder ends, the error
in this measurement still somewhat larger (15 %). In principle, it may not be appropriate to assume the axial diffusion is independent. However, the close agreement with the unambiguous data obtained previously from the treatment of the large block suggests that it is a viable approach for the sample.

Table 3.3. Calculated diffusion coefficients of CH$_3$CF$_2$Cl at 87°C after various diffusion times.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Diffusion Time at 87°C (hours)</th>
<th>Diffusion Coefficient* (cm$^2$/s)</th>
<th>Diffusion Coefficient** (cm$^2$/s)</th>
<th>Reduced $\chi^2$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>38</td>
<td>1.9 x 10^{-8}</td>
<td>2.1 x 10^{-8}</td>
<td>0.03</td>
</tr>
<tr>
<td>#2</td>
<td>62</td>
<td>1.7 x 10^{-8}</td>
<td>1.6 x 10^{-8}</td>
<td>0.10</td>
</tr>
<tr>
<td>#3</td>
<td>86</td>
<td>2.2 x 10^{-8}</td>
<td>2.3 x 10^{-8}</td>
<td>0.06</td>
</tr>
</tbody>
</table>

* obtained from best visual fits.
** obtained from the non-linear least-squares fits.

3.4.4. Experimental Protocol C: Diffusion Processes in Post-Treated Systems

Previous studies of the diffusion processes of blowing agents in foams have always been on only the outward diffusion of the blowing gas from the foam matrix. As discussed in Chapter 2, the microscopic NMR imaging technique makes it possible to independently monitor the concentrations of two blowing agents based on their chemical shift values. In
this thesis, I have also investigated the imbibing of a second blowing agent as well as the emission of the blowing gas originally inside the foam. A mathematical model was used to analyze the experimental data and independently obtain the diffusion coefficients of the two blowing gases, which are diffusing in opposite directions.

Experimental protocol C was used to study diffusion processes during posttreatment. The 1D and imaging experiments (Chapter 2) showed that when a foam was exposed to a second blowing gas in a pressurized device, the initial blowing gas diffused out of, while the second blowing gas diffused into the foam matrix. The diffusion models discussed in Section 3.3.4 can be used here to study both the outward and the inward diffusion processes of the blowing gases.

To study the inward diffusion of gas CCl₃F into a PS foam, three chemical-shift selective images were taken after various exposure times to the presence of CCl₃F. Thus three one-dimensional profiles of the pixel intensity were obtained from the center row of each image as functions of the distance from the axis of the foam cylinder, corresponding to each exposure time for diffusion. These profiles represent the cross-sectional distribution of CCl₃F concentration inside the foam at different stages of inward diffusion. Equation (3.12) was used to calculate the curves for the inward diffusion process of CCl₃F. Figure 3.9 shows the experimental data, together with the calculated curves at time intervals of 120, 216 and 336 hours of exposure time to CCl₃F. The diffusion coefficient was determined to be (2.8 ± 0.3) x 10⁻⁸ cm²/s for CCl₃F at 69°C. The complete results are listed in Table 3.4.
Figure 3.9. Diffusion of CCl$_3$F (CFC-11) into the PS foam cylinder at 69°C at various time intervals. Experiments #1, #2 and #3 correspond to 120, 216 and 336 hours of exposure to CCl$_3$F. Symbols indicate experimental data from the imaging profiles; lines indicate calculated data from the model for this case (see text).
Table 3.4. Diffusion characteristics of CCl$_3$F (CFC-11) into the foam cylinder at 69°C.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Diffusion Time (hours)</th>
<th>$D$ (cm$^2$/s)*</th>
<th>$D$ (cm$^2$/s)**</th>
<th>Reduced $\chi^2$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>120</td>
<td>$2.8 \times 10^{-8}$</td>
<td>$3.0 \times 10^{-8}$</td>
<td>0.03</td>
</tr>
<tr>
<td>#2</td>
<td>216</td>
<td>$2.2 \times 10^{-8}$</td>
<td>$2.5 \times 10^{-8}$</td>
<td>0.02</td>
</tr>
<tr>
<td>#3</td>
<td>336</td>
<td>$2.8 \times 10^{-8}$</td>
<td>$3.0 \times 10^{-8}$</td>
<td>0.03</td>
</tr>
</tbody>
</table>

* obtained from best visual fits.
** obtained from the non-linear leastsquares fits.

The diffusion coefficient of CH$_3$CF$_2$Cl measured from heating the foam block at 69°C, as described in Section 3.4.2.2. Equation (3.8) was used to predict the diffusion process of CH$_3$CF$_2$Cl out of the PS foam cylinder exposed to CCl$_3$F at 69°C. Three chemical-shift selective images were taken at 120, 216 and 336 hours of exposure to CCl$_3$F. Figure 3.10 shows an example of the predicted diffusion curve calculated for a diffusion time of 216 hours and the corresponding experimental data from the imaging profiles (the rows through the center of the image). The experimental and calculated data are in reasonably good agreement.
Figure 3.10. Diffusion of CH$_3$CF$_2$Cl (HCFC-142b) out of the PS foam cylinder at 69°C after 216 hours of exposure to CCl$_3$F (CFC-11). Symbols indicate experimental data from the rows through the center of the image; line indicates the predicted data from the model for this case using the diffusion coefficient of CH$_3$CF$_2$Cl obtained in Section 3.4.2.2.

In order to illustrate the difference between the predicted values and the actual experimental data, the best visual fit was made to obtain the diffusion coefficient for this case. Each of the calculated diffusion curves and the corresponding experimental data are plotted together for various diffusion times in Figure 3.11. The diffusion coefficient was determined to be $(1.6 \pm 0.4) \times 10^{-8}$ cm$^2$/s for CH$_3$CF$_2$Cl at 69°C. The complete set of results is listed in Table 3.5. This value, is close to that $(9.0 \pm 0.1) \times 10^{-8}$ cm$^2$/s obtained previously. Note that the diffusion coefficient used to predict the outward diffusion of
CH$_3$CF$_2$Cl was obtained from a different experimental arrangement (Section 3.4.2.2), and some discrepancy is expected (Figure 3.10).
Figure 3.11. Diffusion of CH$_3$CF$_2$Cl (HCFC-142b) out of the PS foam cylinder at 69°C at various time intervals. Experiments #1, #2 and #3 correspond to 120, 216 and 336 hours of exposure to CCl$_3$F (CFC-11). Symbols indicate experimental data from the center rows of the images, lines indicate calculated data from the model for this case (see text).
Table 3.5. Diffusion characteristics of CH$_3$CF$_2$Cl (HCFC-142b) out of the foam cylinder at 69°C.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Diffusion Time (hours)</th>
<th>$D$ (cm$^2$/s)*</th>
<th>$D$ (cm$^2$/s)**</th>
<th>Reduced $\chi^2$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>120</td>
<td>$1.3 \times 10^{-8}$</td>
<td>$1.8 \times 10^{-8}$</td>
<td>0.01</td>
</tr>
<tr>
<td>#2</td>
<td>216</td>
<td>$1.0 \times 10^{-8}$</td>
<td>$1.4 \times 10^{-8}$</td>
<td>0.06</td>
</tr>
<tr>
<td>#3</td>
<td>336</td>
<td>$1.1 \times 10^{-8}$</td>
<td>$1.6 \times 10^{-8}$</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* obtained from best visual fits.
** obtained from the non-linear leastsquares fits.

The diffusion coefficient of CCl$_3$F gas at 69°C measured from the study of the inward diffusion under the post-treatment condition is about twice as fast as the emission of the initial blowing gas of CH$_3$CF$_2$Cl. This could be caused by the different diffusion behaviors of CH$_3$CF$_2$Cl and CCl$_3$F in PS foams and needs to be further investigated. The effect of the blowing agents dissolved in the foam matrix on the diffusion process of the cell gases will be studied in Chapter 4.
3.5 CONCLUSIONS

NMR microscopy has been demonstrated to be an excellent method to monitor and study diffusion phenomena of the gaseous blowing agents in insulating polymer foams. One-dimensional profiles provide a fast and simple way to obtain the distributions of the concentration of blowing agents as functions of both time and temperature. These can be easily simulated with theoretical model calculations and diffusion coefficients obtained directly from the fitting results.

The results of experiments at room temperature show that the diffusion of blowing agents in foams is very slow, and the diffusion coefficients stay the same when monitored over a 5-month time period. The results of experiments at elevated temperatures show that the magnitudes of the diffusion coefficients increase with temperature as expected, and that the temperature dependence of the diffusion coefficient can be well characterized by an Arrhenius equation and the activation energy determined. These data will be invaluable for the prediction of the gas loss from these systems at any given temperature and for any sample geometry. The results of investigations of the post-treated system show that the diffusion rates of the blowing agents are different for the inward and outward processes. The inward diffusion of the blowing gas CCl₃F is about twice as fast as the outward diffusion of the initial blowing CH₃CF₂Cl gas.

In this study, we did not measure or monitor the diffusion behavior of the air components (nitrogen and oxygen) in PS foams. Previous studies [1, 13] show that the diffusion rates of nitrogen and oxygen are significantly larger than CFC's, over one to two
orders of magnitude. Thus long-term performance of foams as thermal insulation will
mainly depend on the out-diffusion process of the blowing agents. However, if the
diffusion rates of blowing agents and air components can all be determined and monitored
as functions of time, temperature, and other factors, such knowledge would give
additional insight into foam aging behavior. It should be possible to investigate the
diffusion process of air components (containing $^{15}$N labeled nitrogen and $^{17}$O labeled
oxygen) using $^{15}$N and $^{17}$O imaging techniques. This could be an area of further study.
REFERENCES


4.1. INTRODUCTION

Gas transport phenomena in polymer foam systems are very important in many practical applications, from the prediction of the aging rates of foam insulation to the design and control of manufacturing processes. The two central parameters controlling these processes are the diffusion coefficient, which quantifies transient transport processes, and the solubility, which characterizes steady-state storage capacity. They can be used to understand the behavior of the blowing agent in the foam system, to predict the aging rate of a foam insulation board, and to provide information in the screening of alternative non-CFC blowing agents. The diffusion of blowing agents was studied in Chapter 3 and the present chapter will investigate the distribution of the blowing gas dissolved in the polymer matrix in PS foams (polyurethane foams will be discussed in Chapter 5).

As discussed in Chapter 1, the closed cell foam insulation is a three-dimensional matrix composed of blowing agent-filled voids defined by cell walls supported by a grid of solid polymer struts. The blowing agents are distributed not only inside the closed cells but
also in the solid polymer making up the cell structure. However, it is difficult to determine how much of the fluorocarbon gas is dissolved in the solid-phase using conventional techniques [1-3] and how this relates to the concentration in the gas-phase. Experimental techniques which have been developed for the measurement of diffusion and solubility in other applications are generally not sensitive or stable enough to yield useful or reliable information in the area of closed-cell foam insulation. By volume, the solid occupies only about 2 percent of the foam; because of this, as well as the limitations of the measurement techniques used in previous studies of blowing gas distributions, the storage of the blowing agents in the solid has been always assumed to be very small [1-5]. Only the concentrations of the gases of blowing agents inside the cells were taken into consideration. Consequently, the capacity of the foam to store gases has been determined by using the ‘ideal gas’ law [5].

Recently, a few attempts have been made to measure the amounts of dissolved blowing agents in foams. The results have shown that the above assumption is not always true and up to 50 to 60% of the total blowing gas in the sample was found in the polymer phase in some polyurethane foams [6-7]. The method developed to determine the dissolved blowing agents in foams is basically fluorine or chlorine analysis. The foam samples were shredded and ground in a liquid nitrogen cooled mill to release the gaseous component. The amount of chlorine was then determined by using an oxygen flask combustion and ion chromatography [6]. For fluorine analysis, the powdered foam is burned in a Wickbold oxyhydrogen torch, the resulting HF collected in water, buffered and determined potentiometrically [7]. Due to the long, complex procedure involved in
this destructive method of sample preparation, significant errors may be introduced during the determination. Also, fluorine analysis is often not sensitive enough to detect small amounts of dissolved blowing agents in foams; while for foams which have chlorine-containing fire retardants, the chlorine analysis can not be used. It will be demonstrated in this chapter that MAS solid-state $^{19}\text{F}$ NMR is a fast, simple and powerful tool for the quantitative investigation of the concentrations of blowing agents dissolved in the foam matrix and that these data can be used together with the previous gas-phase measurements to provide a more complete picture of the diffusion process.

Because of the large dipole-dipole interactions and shielding anisotropies in the solid-state, NMR spectra of abundant spin systems often show very broad, featureless absorptions. Solution-state $^{19}\text{F}$ NMR is characterized by a large chemical-shift range (over 1000 ppm) and complex scalar coupling patterns. In solids, shielding anisotropies can be correspondingly large. However, they are inhomogeneous in character and can therefore be averaged by the magic angle spinning (MAS) method (discussed in Chapter 1), yielding resonances at their isotropic average chemical-shift values with associated sidebands at integral multiples of the spinning frequency. Homonuclear $^{19}\text{F}/^{19}\text{F}$ dipolar broadening can be averaged by MAS but because the spinning frequency required to average the dipolar interactions has to be greater than the static bandwidth expressed in Hz, the homonuclear dipolar broadening can be eliminated only when very fast spinning speed can be achieved in MAS experiments.

For the analysis of polymer foam blowing agents described in Chapter 2, static $^{19}\text{F}$ NMR provides spectra of only the gas-phase fluorinated blowing agents trapped inside
polystyrene foams. To observe spectra of blowing agents that are dissolved in the polymer matrix (because the fluorines in these immobilized molecules are strongly dipolar coupled, both to the fluorines, protons and chlorines in other fluorine containing molecules, and also to protons in the polymer matrix). Fast MAS spinning must be used to obtain narrowed spectra. The only previous work in this area is a preliminary study by Harris et al [8]. In that work, it was shown that, polyurethane foams agents, the dissolved CFC components can be observed with MAS $^{19}$F NMR at spinning rates greater than 11 kHz.

This chapter will describe how the blowing agents dissolved in the polymer matrix were identified and the amount of each component determined quantitatively using fast spinning MAS $^{19}$F NMR. The information obtained may be used to accurately predict the long term aging characteristics of foams. A knowledge of how much blowing gas is in the gaseous phase, and how much is dissolved in the polymer matrix in a production sample will give a better understanding of the dynamics of the diffusion processes in foams.

4.2. EXPERIMENTAL

4.2.1. $^{19}$F MAS NMR Experiments

Solid state $^{19}$F NMR experiments were performed on a Bruker MSL-400 spectrometer, where the resonance frequency for $^{19}$F was 376 MHz. The probehead was
home-built and incorporated a Doty Scientific 'Supersonic' 5 mm spinner system with a solenoid r.f. coil. The spinner is a fluorine transparent, cylindrical shaped ceramic sample container which is spun about its long axis. The 'Magic Angle' of 54°44' was set by observing the rotational echo pattern due to the spinning sidebands of a reference sample of Na₂SiF₆ and maximizing its relative intensity. Spinning speeds in different experiments ranged up to 13 kHz, as measured from the sidebands present in the ¹⁹F spectra of Na₂SiF₆, Teflon tape or foam samples. A typical 90° pulse length was 2.2 μsec, as measured from the value obtained for the 180° null pulse. The spectra were acquired using a 120 kHz spectral width and several hundred scans were signal averaged to obtain good signal-to-noise ratios.

The PS foams studied in this work are listed in Table 4.1. Sample #1 was a square piece (10 x 10 x 3.8 cm) of block cut from the center of a PS foam board (sample K1, see Section 2.2.1) containing CH₃CF₂Cl which had been aged at ambient temperature for 17 months before analysis. Samples #2 and #3 were also square pieces cut from PS foam boards (samples E1 and G1, see Section 2.2.1) containing CF₂Cl₂. Samples #4 and #5 were cut from the foam board sample #1, then heated at temperatures of 69°C and 87°C, respectively, for about 4 months. Samples #6 and #7 were cylinders taken from foam board sample #1. They had diameters of 8.7 mm and had been exposed to air for 21 days at ambient temperature (sample #6) and at 87°C (samples #7). Sample #8 was a cylinder with a smaller diameter of 3.4 mm, also taken from foam board #1, and exposed to allow for diffusion for 21 days at ambient temperature. Sample #9, taken from foam board #1, was exposed to a second foaming gas, CFCl₃, in a post-treatment experiment. For studies
of the block samples #1 to #5, fresh foam cylinders (3.4 o.d. x 38 mm) were prepared just before the MAS experiment from one surface of the board to the other; then the edge and middle sections were studied. For cylindrical samples (#6 to #9), the middle sections were taken for the measurements (Figure 4.1). All final samples for MAS NMR studies were in the form of cylinders 3.4-mm in diameter and 10-mm in length, so they could be fitted into the spinner to obtain fast spinning rates. For quantitative measurements of CFC's, HCFC's and HFC's present in the foams, the $^{19}$F resonance of a known quantity of Teflon tape was used as an external reference.
Figure 4.1. Schematic representation of the sample preparations.
Table 4.1. Summary of PS foam samples investigated in the fast MAS experiments.

<table>
<thead>
<tr>
<th>Foam Sample</th>
<th>Blowing agent</th>
<th>Size (mm)</th>
<th>Shape</th>
<th>Aging History</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1(K1*)</td>
<td>CH₃CF₂Cl</td>
<td>100 x 100 x 38</td>
<td>block</td>
<td>17 months at RT</td>
</tr>
<tr>
<td>#2(E1*)</td>
<td>CF₂Cl₂</td>
<td>100 x 100 x 25</td>
<td>block</td>
<td>14 months at RT</td>
</tr>
<tr>
<td>#3(G1*)</td>
<td>CF₂Cl₂</td>
<td>100 x 100 x 50</td>
<td>block</td>
<td>6 years at RT</td>
</tr>
<tr>
<td>#4(K1*)</td>
<td>CH₃CF₂Cl</td>
<td>100 x 100 x 38</td>
<td>block</td>
<td>13 months at RT, then 4 months at 69°C</td>
</tr>
<tr>
<td>#5(K1*)</td>
<td>CH₃CF₂Cl</td>
<td>100 x 100 x 38</td>
<td>block</td>
<td>13 months at RT, then 4 months at 87°C</td>
</tr>
<tr>
<td>#6</td>
<td>CH₃CF₂Cl</td>
<td>8.7 o.d x 38</td>
<td>cylinder</td>
<td>taken from #1, then aged at RT for 21 days</td>
</tr>
<tr>
<td>#7</td>
<td>CH₃CF₂Cl</td>
<td>8.7 o.d x 38</td>
<td>cylinder</td>
<td>taken from #1, then aged at 87°C for 21 days</td>
</tr>
<tr>
<td>#8</td>
<td>CH₃CF₂Cl</td>
<td>3.4 o.d. x 38</td>
<td>cylinder</td>
<td>taken from #1, then aged at RT for 21 days</td>
</tr>
<tr>
<td>#9</td>
<td>CH₃CF₂Cl</td>
<td>8.7 o.d. x 38</td>
<td>cylinder</td>
<td>taken from #1, then exposed to CFCI₃ at 69°C for 8 days</td>
</tr>
</tbody>
</table>

*see Section 2.2.1.
4.3. RESULTS AND DISCUSSION

4.3.1. Qualitative Observations

One-pulse $^{19}$F MAS experiments with signal averaging over a number of scans were carried out and the $^{19}$F MAS spectra obtained. Figure 4.2 shows the MAS spectrum of CH$_3$CF$_2$Cl in a PS foam sample taken from the center area of board (sample #1) where no diffusion has occurred. At a spinning rate of 9 kHz, the $^{19}$F spectrum exhibits a sharp peak from the gas-phase CH$_3$CF$_2$Cl trapped in the cells and a broader peak from the dissolved component in the polymer matrix. The additional broadening of the latter signal probably results from a distribution of isotropic chemical shifts due to the amorphous nature of the PS matrix. Because MAS averages the chemical shift anisotropy to zero, the -CF$_2$- resonance appears at its isotropic chemical shift value for the dissolved state. Since the spinning frequency is smaller than the chemical-shift anisotropy of the dissolved -CF$_2$- resonance, a set of sidebands is observed at multiples of the spinning rate away from the isotropic signal (center band). The spectrum shows sufficient resolution to clearly integrate each peak. The sidebands of the dissolved CH$_3$CF$_2$Cl peak are very small, with a total area of about 7% of the total dissolved gas signal. Because it takes a long time to accumulate sufficient scans to accurately measure the contribution from the small sidebands of the dissolved components, in subsequent work only the center band of the dissolved gas was measured and a correction made for the contribution from the sidebands.
Figure 4.2. 1D $^{19}$F MAS NMR spectrum of CH$_3$CF$_2$Cl in a PS foam at a spinning rate of 9 kHz. The arrows indicate spinning sidebands. Chemical shifts are referenced relative to external CFCl$_3$ (0.0 ppm).
Figure 4.3 demonstrates the effect of the spinning rate on the $^{19}$F MAS spectrum of CH$_3$CF$_2$Cl in a PS foam sample (same as in Figure 4.2.). Figure 4.3(a) shows that at a spinning rate of 4.0 kHz, only one resonance is observed and is assigned to the blowing agent CH$_3$CF$_2$Cl in the gas-phase; (b) and (c) show the corresponding spectra at spinning rates of 6.4 kHz and 10 kHz respectively. These latter spectra contain two resonances; meaning that these spinning rates are sufficient to observe the dissolved component of the blowing gas. Note that the dissolved peak is narrower when the spinning rate is higher because the higher spinning rate gives some further spectral narrowing. For the study of dissolved blowing gases, the dissolved components can be clearly observed and measured at spinning rates above 7 kHz.
Figure 4.3. $^{19}$F MAS NMR spectra of CH$_3$CF$_2$Cl in a PS foam sample (same as in Figure 4.2.) at spinning rates of (a) 4.0 kHz, (b) 6.4 kHz and (c) 10 kHz. The arrows indicate spinning sidebands. Chemical shifts are referenced to external CFCl$_3$ (0.0 ppm).
4.3.2 Relaxation Time Measurements

The spin-lattice (T$_1$) relaxation times for the dissolved gas components and the Teflon tape reference were measured using the inversion-recovery pulse sequence as previously (see Section 2.2.3) in order to determine the appropriate acquisition parameters for quantitative MAS $^{19}$F NMR experiments. The relative uncertainty in the T$_1$ values of the dissolved components is estimated at about 5%, from the reproducibility of five measurements. The results together with the relaxation times for the gas-phase components are shown in Table 4.2.

Table 4.2. Relaxation times of Teflon tape and fluorine-containing blowing agents in the gas-phase in the cells and dissolved in the PS polymer matrix.

<table>
<thead>
<tr>
<th>Component</th>
<th>$T_1$ (gas-phase) (ms)</th>
<th>$T_2$ (gas-phase) (ms)</th>
<th>$T_1$ (solid-phase) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-11 (CCl$_3$F)</td>
<td>5.4</td>
<td>4.4</td>
<td>1500</td>
</tr>
<tr>
<td>HCFC-123 (CHCl$_2$CF$_3$)</td>
<td>13.8</td>
<td>8.0</td>
<td>1150</td>
</tr>
<tr>
<td>HCFC-141b (CH$_3$CCl$_2$F)</td>
<td>7.1</td>
<td>5.4</td>
<td>1000</td>
</tr>
<tr>
<td>Teflon tape</td>
<td>N/A</td>
<td>N/A</td>
<td>3000</td>
</tr>
</tbody>
</table>
In general, the components of the blowing agents dissolved in the solid-phase have \( T_1 \) relaxation times in the range of 1 to 1.5 seconds. The Teflon tape has a longer \( T_1 \) of 3 seconds. Thus for measurements of absolute values of the amount of dissolved gas in foams, with Teflon tape as the reference, the repetition time was chosen as 20 seconds, ensuring that quantitatively reliable spectra of both the blowing agents and the Teflon reference as well as the gas-phase components are obtained.

4.3.3. Quantitative Analysis of Blowing Gas Distributions in PS Foams by MAS NMR

4.3.3.1. Reference Sample Selection

A reference sample is needed in order to quantitatively determine the quantities of the blowing agents dissolved in the polymer matrix. A small piece of Teflon tape was chosen as an external reference for MAS \(^{19}\)F NMR experiments. It was carefully weighed with an analytical balance and then put into the spinner together with the foam sample. Figure 4.4 presents MAS spectra (spinning at 10 kHz) of the Teflon reference and \( CH_3CF_2Cl \) in a PS foam sample taken from the center area of board (sample #1), where no diffusion has occurred. Signals were observed from the blowing agents in both the gas-phase and the solid-phase, as well as the Teflon. A set of sidebands of the Teflon is also observed at multiples of the spinning rate away from its isotropic signal (center band) and
Figure 4.4. 1D $^{19}$F MAS NMR spectrum of Teflon reference and CH$_3$CF$_2$Cl in a PS foam at a spinning rate 10 kHz. The arrows indicate spinning sidebands. Chemical shifts are referenced to external CFCl$_3$ (0.0 ppm).
contribute to the total signal intensity. The spectrum shows sufficient resolution to accurately integrate each resonance lines and estimate the total signal intensity.

The Teflon \((\text{CF}_2\text{-CF}_2)_n\) tape used as reference in the MAS \(^{19}\text{F}\) NMR experiment weighed \(0.277 \pm 0.005\) mg, and had a fluorine content of \(0.277\) mg \(\times 4\text{F}/(\text{C}_2\text{F}_4) = 0.210 \pm 0.004\) mg (F). The total signal intensity of the Teflon center peak and the side bands is \(60.1 \pm 1.2\). The signal intensity for the component of \(\text{CH}_3\text{CF}_2\text{Cl}\) dissolved in polymer is \(7.37 \pm 0.15\). Therefore, the amount of \(\text{CH}_3\text{CF}_2\text{Cl}\) dissolved in the solid phase can be calculated to be \(0.069 \pm 0.004\) mg (Table 4.3).

Table 4.3. Amount of \(\text{CH}_3\text{CF}_2\text{Cl}\) dissolved in the solid polymer (sample #1) calculated from the Teflon reference.

<table>
<thead>
<tr>
<th></th>
<th>Peak area (arbitrary units)</th>
<th>Amount of fluorine (mg)</th>
<th>Amount of (\text{CH}_3\text{CF}_2\text{Cl}) (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon ((\text{CF}_2\text{-CF}_2)_n)</td>
<td>(60.1 \pm 1.2)</td>
<td>(0.210 \pm 0.004)</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3\text{CF}_2\text{Cl}) dissolved in solid</td>
<td>(7.37 \pm 0.15)</td>
<td>(0.0258 \pm 0.0015)</td>
<td>(0.069 \pm 0.004)</td>
</tr>
</tbody>
</table>
The gas-phase component of CH$_3$CF$_2$Cl also appears in the MAS spectrum, and an accurate measure of the concentration of CH$_3$CF$_2$Cl in the gas-phase is independently available from the previous static 1D $^{19}$F NMR experiments using liquid C$_6$H$_5$CF$_3$ as the reference, as described in Chapter 2. For this specific foam sample, the amount of CH$_3$CF$_2$Cl in the gas-phase that is trapped in the cells is 0.188 ± 0.016 mg. Thus, the signal of the gas-phase component can also be used as an independent reference to determine the amount of dissolved component: With its relative peak area measured as 20.60 ± 0.41 in the MAS spectrum, the amount of CH$_3$CF$_2$Cl in the polymer matrix is then calculated to be 0.067 ± 0.008 mg (Table 4.4), in excellent agreement with the result obtained using the Teflon reference, 0.069 ± 0.004 mg. Therefore, either an external reference of Teflon or the internal reference of the gas component of the blowing agent can be used to quantify the amount of blowing agent dissolved in polymer matrix. For foam systems with a single blowing agent, Teflon was used as the reference, and for foam systems with multiple blowing agents, the signals from the gas-phase components were used in order to minimize spectral overlap.

Table 4.4. Amount of CH$_3$CF$_2$Cl dissolved in the solid (sample #1) calculated using the known amount of its gas-phase component as reference.

<table>
<thead>
<tr>
<th></th>
<th>Peak area (arbitrary units)</th>
<th>Amount of CH$_3$CF$_2$Cl (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CF$_2$Cl in cells*</td>
<td>20.60 ± 0.41</td>
<td>0.188 ± 0.016</td>
</tr>
<tr>
<td>CH$_3$CF$_2$Cl dissolved in solid</td>
<td>7.37 ± 0.15</td>
<td>0.067 ± 0.008</td>
</tr>
</tbody>
</table>

* the value does not include the correction for the cutting loss.
4.3.3.2. Quantitative Analysis

With Teflon tape as reference, quantitative measurements of the quantities of dissolved blowing gases were made for various PS foam samples from $^{19}$F MAS NMR experiments. Table 4.5 presents the absolute amounts of blowing agents within the gas phase and solid phase found for samples #1 to #3. The concentrations of the gases are represented as weight of blowing gas per gram of foam. Due to the small sample size used in MAS experiments (3.4 mm in diameter), the loss of cell gas from the damaged surfaces by cutting is about 57% (see Figure 2.6), giving increased errors. The amounts of cell gases given in the tables below have been corrected for this loss. The results show that about 13% of CH$_3$CF$_2$Cl in PS foam sample #1 is dissolved in the polymer matrix. About 20% of the CF$_2$Cl$_2$ in PS foam samples #2 (high density foam) or #3 (over 5 years old) is dissolved in the solid matrix. It seems that CF$_2$Cl$_2$ is more soluble than CH$_3$CF$_2$Cl in PS foams.
Table 4.5. Quantitative measurements of the percentage concentrations of gas-phase and dissolved blowing agents in PS foams.

<table>
<thead>
<tr>
<th>Foam Sample</th>
<th>Blowing Agent</th>
<th>Component in Gas-phase* (%w/w)</th>
<th>Component in Polymer matrix (%w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>HCFC-142b (CH₃CF₂Cl)</td>
<td>6.3</td>
<td>0.95</td>
</tr>
<tr>
<td>#2</td>
<td>CFC-12 (CF₂Cl₂)</td>
<td>4.8</td>
<td>1.2</td>
</tr>
<tr>
<td>#3</td>
<td>CFC-12 (CF₂Cl₂)</td>
<td>2.6</td>
<td>0.8</td>
</tr>
</tbody>
</table>

* the value was corrected for the cutting loss using the data in Figure 2.6.

4.3.4 Distribution of HCFC-142b (CH₃CF₂Cl) between the Gas-Phase and the Polymer Matrices in Aged PS Foams

4.3.4.1. Aging at Ambient Temperature.

The distributions of HCFC-142b (CH₃CF₂Cl) blowing agent in the gas-phase and the solid-phase at the edge and middle portions of a PS foam block (sample #1) were investigated by MAS ¹⁹F NMR experiments. Intensity ratios determined with respect to a neighboring spinning side band of the Teflon signal (100 arbitrary units) are shown in
Table 4.6. This reference peak was chosen to have a comparable intensity level to the dissolved gas peak, in order to minimize the absolute error in the measurement of the dissolved gas component. The cell gas intensities were corrected for the cutting loss as described in Section 2.2.2.2.

Table 4.6. Distribution of CH$_3$CF$_2$Cl in a PS foam at different locations.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Ratios of the intensities: dissolved CH$_3$CF$_2$Cl /gaseous * CH$_3$CF$_2$Cl /Teflon ref.</th>
<th>Sample location</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1a</td>
<td>32.8 / 219 / 100</td>
<td>middle section</td>
</tr>
<tr>
<td>#1b</td>
<td>32 / 183 / 100</td>
<td>edge section</td>
</tr>
</tbody>
</table>

* cell gas intensity was corrected for the cutting loss using the data in Figure 2.6.

The results show that about 87 % of CH$_3$CF$_2$Cl is distributed in the gas phase of this PS sample, which has been exposed for diffusion at ambient temperature for 17 months. There is a decrease in the amount of the gaseous component at the edge section of the foam block compared with the middle section as described in previous chapters, indicating that diffusion occurs from the center area of the foam board outwards to the edges as the foam ages. No appreciable loss of the dissolved component at the edges was observed, indicating that the effect of the dissolved CH$_3$CF$_2$Cl on the diffusion behavior of
gaseous CH$_3$CF$_2$Cl is not significant under these particular conditions, and to a first approximation may be ignored.

4.3.4.2. Aging at Elevated Temperatures

Both Figure 4.5 and Table 4.7 show the distributions of CH$_3$CF$_2$Cl within the gas-phase and polymer matrices in a PS foam board, as functions of temperature and sampling location, together with the previous data on sample #1 for reference.

The results show that the intensity of gaseous CH$_3$CF$_2$Cl from the middle section is higher than at the edge, reflecting the diffusion of gas out of the foam as a function of time and temperature, as previously discussed. The amounts of dissolved CH$_3$CF$_2$Cl at the edge and middle sections of the foam board differ only slightly. However, they are both lower than the original concentration of dissolved gas, indicating that some dissolved gas has been released into cells from the solid phase after heating at elevated temperatures.
Figure 4.5. Plots from Table 4.6 and Table 4.7, representing the distribution of CH$_3$CF$_2$Cl at different locations in a PS foam block exposed to various temperatures for 4 months:

(a). Aging at ambient temperature; (b). Aging at 69°C; (c). Aging at 87°C.
Table 4.7. Distribution of CH$_3$CF$_2$Cl between gas-phase and polymer matrix in a PS foam exposed for four months diffusion at the temperatures indicated.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Temp.</th>
<th>Ratios of the intensities: dissolved CH$_3$CF$_2$Cl /gaseous * CH$_3$CF$_2$Cl /Teflon ref.</th>
<th>Sample location</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1a</td>
<td>RT</td>
<td>33 / 219 / 100</td>
<td>middle section</td>
</tr>
<tr>
<td>#1b</td>
<td>RT</td>
<td>32 / 183 / 100</td>
<td>edge section</td>
</tr>
<tr>
<td>#4a</td>
<td>69°C</td>
<td>21 / 214 / 100</td>
<td>middle section</td>
</tr>
<tr>
<td>#4b</td>
<td>69°C</td>
<td>17 / 167 / 100</td>
<td>edge section</td>
</tr>
<tr>
<td>#5a</td>
<td>87°C</td>
<td>13 / 190 / 100</td>
<td>middle section</td>
</tr>
<tr>
<td>#5b</td>
<td>87°C</td>
<td>12 / 114 / 100</td>
<td>edge section</td>
</tr>
</tbody>
</table>

* cell gas intensity was corrected for the cutting loss using the data in Figure 2.6.

Sample #4 has been allowed to diffuse at a temperature of 69°C for 4 months; about one third of dissolved CH$_3$CF$_2$Cl has been released into cells. As the temperature is increased to 87°C, in sample #5, more than half of the dissolved CH$_3$CF$_2$Cl has been released into the cells and contributes to the effective diffusion of the gaseous blowing gas. However, because the amount of dissolved gas is at most about 13% of the total, the amount of gas which has been released from the solid is still negligible. However, some error may be introduced under extreme accelerated aging conditions, if the effect of
dissolved gas is not considered when investigating the effective diffusion process of the
gaseous blowing agents in foams and results obtained under such conditions should be
interpreted with some caution.

4.3.4.3. Highly Accelerated Aging

The foam aging process is usually considered to last for years. There are two
principal means to accelerate the diffusion process: Shortening the path length for
diffusion and increasing the temperature: e.g. industry often evaluates foam products at
elevated temperatures [9]. Alternatively, some studies have used thin-slices of foams to
accelerate the measurements of the foam aging process [10]. In the present work, as
discussed in Chapter 4, instead of using large foam blocks, a series of PS foam cylinders
(samples #6, #7 and #8) with diameters of 8.7 mm or 3.4 mm were exposed at room
temperature or at an elevated temperature of 87°C for 21 days. 19F MAS experiments
were carried out using the center sections of these cylinders. The results of these studies
are presented in Figure 4.6, plotted from the data in Table 4.8.
Table 4.8. Distribution of CH$_3$CF$_2$Cl between the gas-phase and polymer matrix in a PS foam after highly accelerated aging (previous data on sample #1a is listed for reference).

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Temp.</th>
<th>Time** (days)</th>
<th>Sample Size (mm)</th>
<th>Ratios of the intensities: dissolved CH$_3$CF$_2$Cl / gaseous* CH$_3$CF$_2$Cl / Teflon ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1a</td>
<td>RT</td>
<td>510</td>
<td>100 x 100 x 38 block</td>
<td>33 / 219 / 100</td>
</tr>
<tr>
<td>#6</td>
<td>RT</td>
<td>21</td>
<td>8.7 o.d x 38 cylinder</td>
<td>32 / 190 / 100</td>
</tr>
<tr>
<td>#7</td>
<td>87°</td>
<td>21</td>
<td>8.7 o.d x 38 cylinder</td>
<td>3.6 / 28 / 100</td>
</tr>
<tr>
<td>#8</td>
<td>RT</td>
<td>21</td>
<td>3.4 o.d. x 38 cylinder</td>
<td>9.3 / 35 / 100</td>
</tr>
</tbody>
</table>

* cell gas intensity was corrected for the cutting loss using the data in Figure 2.6.

**for samples #6 to #8, this represents the additional treatment time after cutting the cylinder from sample #1a.
Figure 4.6. Distribution of CH$_3$CF$_2$Cl between gas and solid phases in a PS foam after highly accelerated aging: (a). comparison between samples #6 and #7, showing the effect of temperature on diffusion; (b). comparison between samples #1, #6 and #8, showing the effect of sample size on diffusion at ambient temperature.
After exposure to ambient air for only 21 days, cylinder #6 (with a diameter of 8.7 mm) already shows an appreciable amount of gas loss from the cells; the signal intensity from the gaseous component has dropped 13% compared to sample #1a taken from the center portion of a PS foam board where little diffusion has occurred. The intensity from the dissolved component remains about the same, indicating that little CH$_3$CF$_2$Cl was released from the polymer matrix during this period of diffusion at room temperature, as to be expected from Section 4.3.4.1. However, cylinder #7 with the same diameter of 8.7 mm, exposed in air for 21 days at the elevated temperature of 87°C, showed a very significant decrease in the intensity of the CH$_3$CF$_2$Cl signals in both the gas-phase and polymer matrix. The results show that about 87% of the gaseous CH$_3$CF$_2$Cl has now diffused out of the cells, and about 89% of dissolved CH$_3$CF$_2$Cl has been released from the polymer matrix. Thus, it seems that this elevated temperature not only accelerates the diffusion rate of the gaseous CH$_3$CF$_2$Cl but also the release rate of the dissolved CH$_3$CF$_2$Cl.

Sample #8 had a much smaller diameter of 3.4 mm and was exposed to air for 21 days. About 84% of the cell gas has been lost due to the diffusion, and the intensity from the dissolved component has dropped about 72% compared to sample #1a. Thus, even at room temperature, the dissolved CH$_3$CF$_2$Cl gas can eventually be released into the cells when most of the cell gas has been lost due to diffusion. This indicates that the rate of desorption of the CH$_3$CF$_2$Cl dissolved in the polymer matrix into the gas-phase CH$_3$CF$_2$Cl in cells can be influenced by elevated temperatures or by significant concentration changes.
in the gas-phase component to reach equilibrium. At room temperature, because the diffusion of the cell gas is very slow, the release of the dissolved gas is also slow unless extreme conditions are used (e.g. very small sample). At elevated temperatures, the out-diffusion of the cell gas has been accelerated, causing a significant loss of cell gas, perhaps also causing a change in the solubility of the gas in the polymer-phase, resulting in a faster release of the dissolved component. However, due to the fact that the dissolved gas in this PS foam is only 13% of the total gas in the foam, the contribution to the cell gas from the dissolved component is still small. For foams containing high concentrations of blowing agents in the polymer matrix, the effect of dissolved gas on the diffusion behavior of cell gas may have to be considered as will be discussed in the next chapter.
4.3.5. **MAS NMR Experiments on Post-treated Foams**

In Chapter 2, $^{19}$F 1D spectroscopy and imaging experiments were used to demonstrate that when a PS foam has been exposed to a second foaming gas for a period of time, this second gas can diffuse into the matrix. $^{19}$F MAS experiments have now been used to study the distribution of the two foaming gases between the gas and polymer phases during the post-treatment process. Figure 4.6 shows a MAS $^{19}$F NMR spectrum of the edge portion of sample #9, a PS foam cylinder (with a diameter of 8.7 mm) which originally contained CH$_3$CF$_2$Cl and was then exposed to CFCl$_3$ vapor in a closed environment for 8 days at 69°C. The spectrum clearly shows that the CFCl$_3$ has diffused into the foam matrix and is present in both the gas-phase and the solid phase.
Figure 4.7. $^{19}$F MAS NMR spectrum (spinning at 10 kHz) of a PS foam cylinder originally made with CH$_3$CF$_2$Cl and then exposed to CFCI$_3$ gas for 8 days at 69°C. The arrows indicate spinning sidebands and chemical shifts are referenced to external CFCI$_3$ (0.0 ppm).
The results in Table 4.9 show that the intensity of the original gaseous CH$_3$CF$_2$Cl in this cylinder has decreased about 18% over 8 days due to diffusion at 69°C, consistent with the results from the previous imaging study. About 45% of the dissolved CH$_3$CF$_2$Cl has been released from the polymer matrix due to the accelerated aging conditions. It is also clear that CFCl$_3$ has diffused into the cells of this PS foam and has also dissolved in the polymer matrix. The ratio of the dissolved component to gaseous CFCl$_3$ is about 1:2 which is much higher than the ratio of CH$_3$CF$_2$Cl distributed between the two phases.
indicating that CFCI$_3$ is more soluble than CH$_3$CF$_2$Cl in PS foams. A series of post-treatment experiments as functions of time and temperature were also carried out on polyurethane foams, and are discussed in Chapter 5.
4.4. CONCLUSIONS

The results presented in the present chapter show that the blowing gas components in the gas-phase and the solid-phase of polystyrene foams can be measured quantitatively and simultaneously with high resolution $^{19}$F solid-state NMR spectroscopy with fast MAS spinning at rates above 7 kHz. In the various PS foams investigated, about 13% CH$_3$CF$_2$Cl, 20% CF$_2$Cl$_2$ and up to 33% CFCl$_3$ were found to be dissolved in the solid matrix. The amount of dissolved CH$_3$CF$_2$Cl in the foam matrix was approximately the same at different locations in a large foam board after exposure at ambient temperature for 17 months. However, the signal intensity from dissolved CH$_3$CF$_2$Cl decreased at elevated temperatures, indicating that it was being released into the cells. Also, a decrease in intensity of CH$_3$CF$_2$Cl in the polymer matrix was observed for a PS sample under highly accelerated aging conditions when most of the gaseous CH$_3$CF$_2$Cl had been lost due to diffusion at ambient temperature. These results suggest that the small amount of dissolved CH$_3$CF$_2$Cl in PS foam is fairly strongly held in the polymer matrix, and significant loss can only be found under extreme conditions (e.g. high temperature or small size). Because the amount of dissolved gas CH$_3$CF$_2$Cl in PS foam is quite low (13%), the influence of the dissolved CH$_3$CF$_2$Cl on the diffusion behavior of gaseous CH$_3$CF$_2$Cl in PS foams is negligible under moderate conditions as assumed in Chapter 4. Post-treatment results show that CFCl$_3$ easily diffuses at 69°C into the cells of PS foams originally containing...
CH₃CF₂Cl and also dissolves in the polymer matrix after a short exposure. Further post-treatment experiments on other foams will be discussed in Chapter 5.

In order to evaluate the performance of insulation foams, and to accurately predict aging rates, it is essential to know the quantities of the blowing agents in both phases and their variation as functions of time and temperature. The use of fast MAS high resolution ¹⁹F solid-state NMR spectroscopy provides such information in an efficient and simple manner, and future studies should no doubt increase our understanding the interaction between polymer and CFC's (or their alternatives).
REFERENCES


CHAPTER 5 INVESTIGATIONS OF CFC AND HCFC GASES IN POLYURETHANE FOAMS

5.1. INTRODUCTION

In previous chapters, the investigations of blowing agents in polymer foam insulation focused on thermoplastic polystyrene foams. Another popular polymer foam insulation is made with a thermosetting polymer material called polyurethane (PU). PS and PU foams have many different properties: e.g. when exposed to a sufficient high temperature, PS foams will soften or melt before undergoing pyrolysis; while PU foams will just form a char as they pyrolyze depending on the conditions. As described in Chapter 1, they are also manufactured in a different fashion. However, both PS and PU insulating foams contain CFC's as their main blowing agents in order to achieve superior insulating performance due to the low gas thermal conductivities, low diffusion rates and other excellent properties of CFC's (see Chapter 1). As discussed previously, in order to phase out CFC's because of environmental concerns, it is very important to develop a reliable and fast method to effectively evaluate the performance of a foam product made with CFC's or their alternatives. As demonstrated in previous chapters, NMR imaging and spectroscopy have proved to be excellent, non-destructive and non-invasive tools to study blowing agents in foams. The results obtained from the study on PS foams showed that the amounts of blowing agent in the cells and dissolved in the polymer matrix could be quantitatively analyzed and the distribution of the blowing
agent within the cellular plastic matrix monitored as a function of time and temperature. Thus, the diffusion behavior of blowing agents in PS foams could be measured and predicted. In the present chapter, $^{19}$F NMR imaging and spectroscopy will be used to investigate fluorine containing blowing agents in polyurethane foams. The results show that there are similarities but also differences in the properties and behavior of the blowing agents in PU and PS foams. The distributions of blowing gases in the cells as well as in the polymer matrix will be described as functions of time and temperature, and the diffusion behavior of blowing gases in PU systems will be studied and modeled theoretically.

5.2. EXPERIMENTAL

5.2.1. Foam Samples

Two sets of aged polyurethane (PU) foam samples were provided by DOW Chemical Co. Sample PU-1 contained only a single fluorinated gas HCFC-141b ($\text{CH}_3\text{CFCI}_2$) as blowing agent and was received as 5.1-cm thick, 68.6 cm by 30.5 cm foam boards. Before analysis, they had been aged at ambient temperature for about 3 months. Samples PU-2 to PU-6 were 10 cm x 10 cm x 3 cm yellow foam blocks received as core parts of 30.5 cm x 30.5 cm x 5.1 cm laminate boards which had been aged at ambient temperature for 7 years. These samples had been manufactured with a mixture of two or three fluorinated gases, HCFC-141b ($\text{CH}_3\text{CFCI}_2$), CFC-11 ($\text{CFCI}_3$) and HCFC-123 ($\text{CF}_3\text{CHCl}_2$) as listed in Table 5.1.
Table 5.1. Summary of the properties of the polyurethane foam samples studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size (cm)</th>
<th>Age</th>
<th>Density (g/cm³)</th>
<th>Blowing Agent</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-1</td>
<td>68.6 x 30.5 x 5.1</td>
<td>3 months</td>
<td>0.0264</td>
<td>HCFC-141b (CH₃CFCI₂)</td>
<td></td>
</tr>
<tr>
<td>PU-2</td>
<td>10 x 10 x 3</td>
<td>7 years</td>
<td>0.0297</td>
<td>CFC-11 (CFCl₃)</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HCFC-123 (CF₃CHCl₂)</td>
<td>89</td>
</tr>
<tr>
<td>PU-3</td>
<td>10 x 10 x 3</td>
<td>7 years</td>
<td>0.0289</td>
<td>CFC-11 (CFCl₃)</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HCFC-123 (CF₃CHCl₂)</td>
<td>89</td>
</tr>
<tr>
<td>PU-4</td>
<td>10 x 10 x 3</td>
<td>7 years</td>
<td>0.0328</td>
<td>CFC-11 (CFCl₃)</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HCFC-123 (CF₃CHCl₂)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HCFC-141b (CH₃CFCI₂)</td>
<td>32</td>
</tr>
<tr>
<td>PU-5</td>
<td>10 x 10 x 3</td>
<td>7 years</td>
<td>0.0267</td>
<td>CFC-11 (CFCl₃)</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HCFC-123 (CF₃CHCl₂)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HCFC-141b (CH₃CFCI₂)</td>
<td>81</td>
</tr>
<tr>
<td>PU-6</td>
<td>10 x 10 x 3</td>
<td>7 years</td>
<td>0.0271</td>
<td>CFC-11 (CFCl₃)</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HCFC-141b (CH₃CFCI₂)</td>
<td>14</td>
</tr>
</tbody>
</table>

* sample code set by the manufacturer (Dow Chemical Co.).
In order to study accelerated aging behavior, a series of foam blocks (150 x 150 x 51 mm) was taken from sample PU-1, then exposed to different temperatures for various times. In addition, a series of cylindrical samples (8.7 o.d. x 30 mm) was cut with a cork borer out of each block sample PU-2 through PU-6 and then exposed at an elevated temperature for periods of time. Details of these samples will be given later in Sections 5.6 and 5.7.

In order to study diffusion processes during the post-treatment of foams, a series of cylindrical samples about 8.7-mm in diameter and 51-mm long was cut with a cork borer out of the foam board (sample PU-1) containing the single blowing agent HCFC-141b (CH₃CFCI₂). They were treated with a second blowing agent CFC-11(CFCI₃) for various periods of time at various elevated temperatures using the method described in Chapter 2, Section 2.2.1. These samples are listed in Section 5.8.

5.2.2. 1D \( ^{19}F \) NMR spectroscopy

The NMR experiments were carried out on a Bruker MSL 400 MHz spectrometer (9.4 T), operating at a fluorine frequency of 376 MHz as previously described. The quantitative measurement of the foam cell gas was carried out by simultaneously recording the \( ^{19}F \) spectrum of the foam sample and the reference, \( C_6H_5CF_3 \). In order to correct for the gas loss from the damaged polyurethane foam surfaces, standard \( ^{19}F \) 1D NMR experiments were also performed on a series of PU foams of various known radii from about 1 to 10 mm together with the reference using a 25 mm vertical r.f. coil. The intensity of the NMR signal from the gas in the foam is proportional to the amount of the gas inside the cells and a least-squares fitting of the plot of the intensity of the signal.
Figure 5.1 Plot of the intensity of the signal versus the radius $r$ of the PU foam cylinders. Symbols indicate experimental data and the solid line the curve from the least-squares fitting.

Figure 5.2. Plot of the relative loss of gas from the cutting versus the radius $r$ of the PU foam cylinders. $C_1, C_2$ are defined in text (see Chapter 2).
versus the radius $r$ (Figure 5.1) gives the characteristic damage depth $d$ as 0.40 mm for the polyurethane foam samples, similar to the value of 0.56 mm obtained from PS foams. The uncertainty in the measurement of the $d$ value is determined by the standard deviation of the fitting as 0.01. From scanning electron microscope (SEM) data (see Appendix 1), we find that the cell diameter in the PU foam matrix ranges from 100 up to 300 $\mu$m and thus the damage area is approximately 2 to 4 cell diameters for the PU foam samples.

The relative loss of gas from the cutting, $(C_1-C_2)/C_1$, was calculated and plotted against the radius $r$ (Figure 5.2). Thus the actual amounts of blowing agents inside foam cylinders can be determined when we analyze samples of different sizes. In the 1D NMR experiments, the sample size is 8.70 mm in diameter; while in the MAS experiments, the sample size is 3.40 mm in diameter: The relative losses of the cell gas are 20.8% and 43.9% with uncertainties of ±1.4% and ±3.0% respectively. The quantitative results of the cell gas analyses were corrected for the losses from cutting damage in all experiments.

5.3. MEASUREMENT OF $T_1$ AND $T_2$ RELAXATION TIMES

In order to devise the most appropriate imaging protocol, it is important to know the relaxation characteristics of the NMR active nuclei, $^1$H and $^{19}$F in the blowing agents. The CPMG (Carr-Purcell-Meiboom-Gill) pulse sequence was used to determine the $T_2$ relaxation time constants and the inversion recovery pulse sequence to determine the $T_1$ spin-lattice relaxation times (see Chapter 2). The longitudinal ($T_1$) and transverse ($T_2$) relaxation times of the fluorine nuclei for various CFC and HCFC gases in PU foams were found to be in the range of 4-15 ms. Those of the proton nuclei were in the range of about
20 to 1100 ms, as shown in Table 5.2. The relative uncertainty in the $T_1$ and $T_2$ measurements is about 3% determined from the reproducibility of eight measurements.

Table 5.2. $T_1$ and $T_2$ relaxation times of the $^1$H and $^{19}$F nuclei in gaseous blowing agents in PU foams.

<table>
<thead>
<tr>
<th>Blowing Agent</th>
<th>$T_1$ ($^1$H)</th>
<th>$T_1$ ($^{19}$F)</th>
<th>$T_2$ ($^1$H)</th>
<th>$T_2$ ($^{19}$F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CFC$_2$</td>
<td>1113 ms</td>
<td>6.9 ms</td>
<td>27.3 ms</td>
<td>5.2 ms</td>
</tr>
<tr>
<td>(HCFC-141b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF$_3$CHCl$_2$</td>
<td>1090 ms</td>
<td>14.5 ms</td>
<td>24.4 ms</td>
<td>7.8 ms</td>
</tr>
<tr>
<td>(HCFC-123)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFCl$_3$</td>
<td>NA</td>
<td>5.4 ms</td>
<td>NA</td>
<td>4.0 ms</td>
</tr>
<tr>
<td>(CFC-11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Considering the results obtained from PS foams in Chapter 2, the $T_1$ and $T_2$ relaxation times of fluorine and proton nuclei for various blowing agents in both PU and PS foams are very similar. This means that in the cells of PS and PU foams, the mobilities and the environments of the blowing gases are very alike. As discussed previously, the relaxations of proton and fluorine nuclei are dominated by different relaxation mechanisms and it is most efficient to perform fluorine NMR experiments to investigate blowing gases in PU foams as was previously the case for PS foams.
Figure 5.3. $^{19}$F NMR spectrum of blowing gases in PU foam sample PU-4 together with the reference sample $(C_6H_5CF_3)$ sealed in a capillary tube within the coil. Chemical shifts are referenced relative to external CFCl$_3$ (0.0 ppm).
5.4. 1D $^{19}$F NMR SPECTROSCOPY

Figure 5.3 shows the 1D $^{19}$F NMR spectrum of a mixture of blowing gases in PU foam sample PU-4 with the reference sample (C$_6$H$_5$CF$_3$). This foam was made with a mixture of three blowing gases: CFCI$_3$, CF$_3$CHCl$_2$ and CH$_3$CFCI$_2$. The signal at -62 ppm is due to the reference, C$_6$H$_5$CF$_3$ and the chemical shifts of the blowing agents are presented in Table 5.3.

Table 5.3. Chemical shifts of the $^{19}$F nuclei in different blowing agents.

<table>
<thead>
<tr>
<th>Blowing agent</th>
<th>CH$_3$CFCI$_2$ (HCFC-141b)</th>
<th>CF$_3$CHCl$_2$ (HCFC-123)</th>
<th>CFCI$_3$ (CFC-11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical shift* (ppm)</td>
<td>-51.4</td>
<td>-84.2</td>
<td>-5</td>
</tr>
</tbody>
</table>

* Chemical shifts are referenced relative to external CFCI$_3$ (0.0 ppm).

By using a known quantity of the reference sample (Section 2.2.2.1) sealed in a capillary tube and correcting for losses due to the sample preparation as described in Section 2.2.2.2, a quantitative measurement of the amounts of the different foaming gases in the PU samples can be obtained from their 1D $^{19}$F spectra. Table 5.4 shows the concentrations of the different cell gases found in the different PU foams investigated, using samples cut from the center of the boards. The gas concentrations are represented as weight of blowing gas per gram of foam. The weight percent of cell gas in sample PU-1, a commercial foam board, is about 7.9 % ± 0.9 %, in agreement with the published value of
9.39% obtained with other methods for similar foams [1]. In samples PU-2 to PU-6, which were specially made with mixtures of two or three blowing gases, the gas concentrations are much higher, up to 35% ± 4% (w/w). The errors in these measurements were obtained the same way as described in Chapter 2, i.e. considering the errors accumulated from integrating peak areas of signals (2%), measuring the quantity of reference sample (2%) and correcting for the cutting loss (6.7%).

Table 5.4. The weight percent of cell gases in the different foam samples investigated together with the ages and densities of the foams.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age</th>
<th>Density (g/cm³)</th>
<th>Blowing Agent</th>
<th>Cell Gas Amount (%w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-1</td>
<td>3 months</td>
<td>0.0264</td>
<td>HCFC-141b (CH₃CFCl₂)</td>
<td>7.9</td>
</tr>
<tr>
<td>PU-2 (75-16)*</td>
<td>7 years</td>
<td>0.0297</td>
<td>CFC-11 (CFCl₃) HCFC-123 (CF₃CHCl₂)</td>
<td>3.6 25</td>
</tr>
<tr>
<td>PU-3 (75-16-11)*</td>
<td>7 years</td>
<td>0.0289</td>
<td>CFC-11 (CFCl₃) HCFC-123 (CF₃CHCl₂)</td>
<td>4.8 24.3</td>
</tr>
<tr>
<td>PU-4 (75-18)*</td>
<td>7 years</td>
<td>0.0328</td>
<td>CFC-11 (CFCl₃) HCFC-123 (CF₃CHCl₂) HCFC-141b (CH₃CFCl₂)</td>
<td>19 1.2 7</td>
</tr>
<tr>
<td>PU-5 (75-23)*</td>
<td>7 years</td>
<td>0.0267</td>
<td>CFC-11 (CFCl₃) HCFC-123 (CF₃CHCl₂) HCFC-141b (CH₃CFCl₂)</td>
<td>4.4 0.3 23</td>
</tr>
<tr>
<td>PU-6 (40784-27-19)*</td>
<td>7 years</td>
<td>0.0271</td>
<td>CFC-11 (CFCl₃) HCFC-141b (CH₃CFCl₂)</td>
<td>35 0</td>
</tr>
</tbody>
</table>

* sample code set by the manufacturer (Dow Chemical Co.).
5.5. IMAGING EXPERIMENTS

As discussed before in Chapter 2, $^{19}$F NMR imaging experiments were carried out using the non-slice selected spin-echo imaging sequence to investigate the blowing agents in PU foams. For the samples containing mixtures of two or three different foaming gases, a chemical-shift selective pulse sequence was used to independently study and monitor the distribution of each gas. Because the relaxation times of blowing gases in PU foams are very similar to those in PS foams, the typical parameters used in the imaging protocol were the same as those presented in Chapter 2.

As before, cylindrical samples were cut from the foam board. The signal intensities of the blowing gases as a function of the distance from the center of the board were obtained from the $^{19}$F NMR imaging experiments. As expected from the results of Chapter 2, the distributions of the blowing gases are quite uniform in these PU foam samples as demonstrated in Figure 5.4. Data were obtained from sample PU-4 containing a blend of three gases: CFC-11 (CFC$_3$), HCFC-123 (CF$_3$CHCl$_2$) and HCFC-141b (CH$_3$CFCl$_2$); (a) is the $^{19}$F NMR spectrum showing the presence and relative concentrations of the three blowing agents inside the foam sample; (b) represents cross-section image of each blowing gas showing that the distribution is uniform for each gas, and that the relative intensity of each gas corresponds to the signal intensity in the 1D spectrum. This can be seen more clearly from the 1D imaging projections of each gas along the axial direction and the cross-section shown in (c). These results are very similar to those obtained for the PS foams.
Figure 5.4
Figures 5.4. $^{19}$F NMR results obtained from PU sample PU-4 containing a blend of three gases: CFC-11 (CFCl$_3$), HCFC-141b (CH$_3$CFCl$_2$) and HCFC-123 (CF$_3$CHCl$_2$) as indicated.

(a). $^{19}$F NMR spectrum. (b). Cross-section images of CFCl$_3$, CH$_3$CFCl$_2$ and CF$_3$CHCl$_2$.

(c). 1D imaging projections of the three gases along the axial and the cross-section directions.
5.6. \(^{19}\text{F SOLID STATE NMR EXPERIMENTS}\)

The results presented in Chapter 4 showed that in order to accurately predict the long term aging characteristics of foams, it is important to know how much dissolved blowing gas is present in the polymer matrix. By using fast spinning MAS \(^{19}\text{F NMR}, the dissolved blowing agents in the polymer matrix can be identified and the amount of each component can be determined quantitatively. Therefore, MAS experiments were carried out to investigate the PU foams. The experimental protocol was the same as that described in the previous chapter.

With Teflon tape as the reference, quantitative \(^{19}\text{F MAS NMR measurements of the dissolved blowing gas have been made for various PU foam samples. Figure 5.5 shows a typical MAS spectrum (spinning at 10 kHz) of CH\(_3\)CFCI\(_2\) in sample PU-1 with Teflon reference. Table 5.5 presents the amounts of gas-phase and solid-phase blowing agents in samples PU-1 to PU-6. The amount of dissolved gas component was obtained by measuring the peak area with respect to a neighboring spinning side band of the Teflon signal. This reference peak was chosen to have a comparable intensity level as the dissolved gas peak, thus the absolute error in the measurement of the dissolved gas component can be reduced. The fluorine content in this reference side band of the Teflon signal can be accurately obtained by recording Teflon spectrum (which has excellent signal to noise ratio) at the same spinning rate. As discussed earlier, the loss of cell gas from the damaged surfaces by cutting is about 44 % (see Figure 5.2) and the amount of cell gas presented in the tables below has been therefore corrected. The concentrations of the gases are represented as weight of blowing gas per gram of foam. The results show that about 27 % of the CH\(_3\)CFCI\(_2\) in PU foam sample PU-1 is dissolved in the polymer matrix. For samples PU-2 to PU-6 (core parts from aged foam boards filled with a mixture of two or three foaming gases), the previous NMR imaging data show that all the foaming agents
Figure 5.5. Typical MAS spectrum spinning at 10 kHz of CH₃CFCl₂ in PU sample PU-1 with Teflon reference. The arrows indicate spinning sidebands. Chemical shifts are referenced relative to external CFCl₃ (0.0 ppm).
are still distributed in the foam matrix homogeneously although they may well not be present at their original concentrations. In these samples, the results show that the amount of dissolved gas was much higher. About 27 to 47 % of CFC\textsubscript{13}, 33 to 37 % of CH\textsubscript{3}CFC\textsubscript{12} and 36 to 44 % of CF\textsubscript{3}CHCl\textsubscript{2} in these old PU samples are dissolved in the solid matrix.

These results are in agreement with published data which show that the amount dissolved blowing gases in various PU foams ranges from 33 % to 50 % depending on foam type, age and manufacturing conditions [1-2]. Compared to the amount of blowing gas

<table>
<thead>
<tr>
<th>Sample</th>
<th>Blowing Agent</th>
<th>Age</th>
<th>Component in Gas-phase (% w/w)</th>
<th>Component in Polymer matrix (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-1</td>
<td>HCFC-141b (CH\textsubscript{3}CFC\textsubscript{12})</td>
<td>3 months</td>
<td>7.9</td>
<td>2.9</td>
</tr>
<tr>
<td>PU-2</td>
<td>CFC-11 (CFC\textsubscript{13}) HCFC-123 (CF\textsubscript{3}CHCl\textsubscript{2})</td>
<td>7 years</td>
<td>3.6 12.3</td>
<td>3.2 7.9</td>
</tr>
<tr>
<td>PU-3</td>
<td>CFC-11 (CFC\textsubscript{13}) HCFC-123 (CF\textsubscript{3}CHCl\textsubscript{2})</td>
<td>7 years</td>
<td>4.6 25.2</td>
<td>1.5 14.3</td>
</tr>
<tr>
<td>PU-4</td>
<td>CFC-11 (CFC\textsubscript{13}) HCFC-123 (CF\textsubscript{3}CHCl\textsubscript{2}) HCFC-141b (CH\textsubscript{3}CFC\textsubscript{12})</td>
<td>7 years</td>
<td>14.3 1.0 6.9</td>
<td>5.4 0.8 4.1</td>
</tr>
<tr>
<td>PU-5</td>
<td>CFC-11 (CFC\textsubscript{13}) HCFC-123 (CF\textsubscript{3}CHCl\textsubscript{2}) HCFC-141b (CH\textsubscript{3}CFC\textsubscript{12})</td>
<td>7 years</td>
<td>4.8 0.3 21</td>
<td>2.1 0.15 10.5</td>
</tr>
<tr>
<td>PU-6</td>
<td>CFC-11 (CFC\textsubscript{13}) HCFC-141b (CH\textsubscript{3}CFC\textsubscript{12})</td>
<td>7 years</td>
<td>32 0</td>
<td>17.2 0</td>
</tr>
</tbody>
</table>

Table 5.5. Quantitative measurement of the concentrations of blowing agents in PU foams.
dissolved in PS foams, the contents of the dissolved blowing gases in PU polymer matrices are about 2 to 3 times higher. This may have an important influence on the diffusion process of the cell gas in PU foams.

To study the effects of diffusion on the distributions of blowing gas in the gas-phase and the polymer matrix, two square pieces (15 x 15 x 5.1 cm) of block were cut from the center of foam boards containing CH₃CFCl₂ (sample PU-1): one block was exposed at ambient temperature and another at 87° for about two and a half months before analysis as listed in Table 5.6. As before, the middle and edge portions of these PU foam blocks (samples PU-1a to PU-1d) were investigated. Table 5.6 shows the results presented as intensity ratios between CH₃CFCl₂ dissolved in polymer and gaseous CH₃CFCl₂ in the cells with respect to the center band of the Teflon reference (100 arbitrary units). The cell gas intensities were corrected for the cutting loss by the method described in Section 2.2.2.2.

The results from Table 5.6 are plotted in Figure 5.6: (a) shows that after aging at ambient temperature for 6 months, there is a decrease in the amount of the gaseous component in the edge section of the foam block compared to the middle section, indicating that a diffusion process from the center area of the foam board towards the edges is taking place as the foam ages, as described in previous chapters. The intensity of the dissolved component in the edge area has also decreased about 16% compared with the middle indicating some dissolved CH₃CFCl₂ has been released into cells. However, this change is not very significant and thus it is still possible to ignore this contribution to the diffusion behavior of gaseous CH₃CFCl₂ at ambient temperature.
Table 5.6. Distribution of CH$_3$CFCl$_2$ in PU foams aged at RT and at 87°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size and location</th>
<th>Aging History</th>
<th>Ratios of the intensities: dissolved CH$_3$CFCl$_2$ /gaseous * CH$_3$CFCl$_2$ /Teflon ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-1a</td>
<td>middle section of block(15 x15 x 5.1)</td>
<td>6 months at RT</td>
<td>37 / 103 / 100</td>
</tr>
<tr>
<td>PU-1b</td>
<td>edge section of block(15 x15 x 5.1)</td>
<td>6 months at RT</td>
<td>31 / 90.4 / 100</td>
</tr>
<tr>
<td>PU-1c</td>
<td>middle section of block(15 x15 x 5.1)</td>
<td>3.5 months at RT, then 2.5 months at 87°C</td>
<td>14 / 114 / 100</td>
</tr>
<tr>
<td>PU-1d</td>
<td>edge section of block(15 x15 x 5.1)</td>
<td>3.5 months at RT, then 2.5 months at 87°C</td>
<td>12.4 / 94 / 100</td>
</tr>
</tbody>
</table>

* cell gas intensity was corrected for the cutting loss using the data in Figure 5.2.
Figure 5.6. Plots from Table 5.6, representing the distribution of CH$_2$CFCl$_2$ at different locations in PU foam boards exposed for a diffusion at (a) ambient temperature and (b) at 87°C.
However, for sample aged at 87°C for 2.5 months, the cell gas intensity in the middle section has increased about 11% while the dissolved gas has dropped over 50% compared to the sample aged at ambient temperature. A similar situation exists for the edge section. Note that although the NMR experiments were carried out at ambient temperature, they still represent the gas distribution between the gas-phase and the solid at 87°C. Because the measurement time was very short compared to the much slower processes of the diffusion of cell gas and the desorption of the dissolved gas in foams (in this case, the foam was heated for 2.5 months while the NMR measurement took about a hour). It is clear that under these conditions, the contribution from the dissolved gas to the diffusion processes can no longer be ignored. The diffusion models in Chapter 3 will not be valid to describe this kind of behavior and the contribution from the dissolved gas has to be taken into consideration in order to modify the theoretical diffusion model. This will be further discussed in the next section.

For samples PU-2 to PU-6 containing two or three blowing gases, two sets of cylindrical samples (8.7 mm in diameter) were cut with a cork borer. One set of foam cylinders was heated at 87°C for 8 days in an oven. Another set of samples was taken from the boards just before analysis as listed in Table 5.7 together with the results obtained.
Table 5.7. Distributions of blowing gases between gas-phase and polymer matrixes in PU foams before and after exposure for 8 days at 87°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aging history</th>
<th>Ratio of the intensity: solid-phase component/gas-phase component/Teflon ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-2a (8.7 o.d.)</td>
<td>fresh cut from PU-2</td>
<td>13.8 / 15.7 / 100 CFC-11&lt;br&gt;105 / 164 / 100 HCFC-123</td>
</tr>
<tr>
<td>PU-2b (8.7 o.d.)</td>
<td>taken from PU-2, then 8 days at 87°C</td>
<td>2.7 / 21.2 / 100 CFC-11&lt;br&gt;41 / 209.8 / 100 HCFC-123</td>
</tr>
<tr>
<td>PU-3a (8.7 o.d.)</td>
<td>fresh cut from PU-3</td>
<td>4.8 / 14.9 / 100 CFC-11&lt;br&gt;129.7 / 228 / 100 HCFC-123</td>
</tr>
<tr>
<td>PU-3b (8.7 o.d.)</td>
<td>taken from PU-3, then 8 days at 87°C</td>
<td>0.8 / 12.6 / 100 CFC-11&lt;br&gt;48.4 / 282 / 100 HCFC-123</td>
</tr>
<tr>
<td>PU-4a (8.7 o.d.)</td>
<td>fresh cut from PU-4</td>
<td>19 / 50.3 / 100 CFC-11&lt;br&gt;14 / 23.4 / 100 HCFC-141b&lt;br&gt;10 / 12.5 / 100 HCFC-123</td>
</tr>
<tr>
<td>PU-4b (8.7 o.d.)</td>
<td>taken from PU-4, then 8 days at 87°C</td>
<td>7.2 / 55 / 100 CFC-11&lt;br&gt;4.7 / 27.3 / 100 HCFC-141b&lt;br&gt;5.4 / 16 / 100 HCFC-123</td>
</tr>
<tr>
<td>PU-5a (8.7 o.d.)</td>
<td>fresh cut from PU-5</td>
<td>5.4 / 12.5 / 100 CFC-11&lt;br&gt;32.2 / 64.1 / 100 HCFC-141b</td>
</tr>
<tr>
<td>PU-5b (8.7 o.d.)</td>
<td>taken from PU-5, then 8 days at 87°C</td>
<td>0.1 / 14.3 / 100 CFC-11&lt;br&gt;12 / 63.5 / 100 HCFC-141b</td>
</tr>
<tr>
<td>PU-6a (8.7 o.d.)</td>
<td>fresh cut from PU-6</td>
<td>28 / 53 / 100 CFC-11&lt;br&gt;0 / 0 / 100 HCFC-141b</td>
</tr>
<tr>
<td>PU-6b (8.7 o.d.)</td>
<td>taken from PU-6, then 8 days at 87°C</td>
<td>11 / 47 / 100 CFC-11&lt;br&gt;0 / 0 / 100 HCFC-141b</td>
</tr>
</tbody>
</table>
Samples PU-2a, PU-2b

Samples PU-3a, PU-3b

Figure 5.7  Samples PU-4a, PU-4b
Figure 5.7. Histogram plots from Table 5.7, representing the distribution of blowing gases in the PU cylindrical samples indicated. RT denotes freshly cut samples at RT, 87 °C denotes samples aged for 8 days at 87 °C.
Figures 5.7 presents histogram plots from Table 5.7 above where each plot shows a comparison of the gas intensities in each sample before and after the heating. We can see that in these samples, the amounts of the blowing agents distributed in the solid-phase are very high before the heating. After accelerated aging at 87 °C for 8 days in an oven, the intensity from the dissolved components decreases significantly (over 50% in different samples), while the concentrations of the cell gases have either increased or stayed about the same. The results clearly show that the dissolved components have been released into the cells during the heating to augment the amount of gas inside the cells which was diffusing out of foam. It seems that the amounts of the blowing agents which diffuse out of the cells are less than or equal to the amounts coming into the cells from the solid phase. CFCI₃, CF₃CHCI₂ and CH₃CFCI₂ blowing gases behaved similarly in these old PU samples. Note that this again represents the gas distribution situation at 87 °C.

5.7. INVESTIGATION OF DIFFUSION PROCESSES

As the previous results show, in PU foams the amount of dissolved gas is much higher than PS foams. For sample PU-1, at room temperature, the release of the dissolved CH₃CFCI₂ from PU foam is very slow. The distribution of cell gas in center portion of the foam board is quite uniform and shows a decrease in the intensity at the edge portion of the foam board due to the diffusion. But after accelerated aging, the loss of cell gas due to the diffusion has been compensated by the release of the dissolved gas components as will be shown below. The diffusion behavior of cell gas in PU foams was studied as described in Section 3.2.1 for the PS foams. Foam blocks with dimensions of 15 x 15 x 5.1 cm³ cut from PU foam sample PU-1 were placed in ovens at various temperatures (ambient
Figure 5.8. 1D $^{19}$F imaging profiles of CH$_3$CFCl$_2$ obtained from PU foam sample PU-1 as functions of time and temperatures (a) after aging for 96 days at ambient temperature, 51 °C, 69 °C and 87 °C and (b) after aging at 87 °C for i) 58, ii) 81 and iii) 96 days.
temperature, 51 °C, 69 °C and 87 °C), and cylindrical samples were taken periodically from these blocks for the imaging measurements. One-dimensional profiles of the distribution of CH$_3$CFCl$_2$ in the foam cylinder along the axial direction were obtained using a non-slice spin-echo imaging sequence as before. The process was repeated with fresh cylinders cut from the blocks kept at the different temperatures over a range of exposure times (about 3 months) for diffusion. Thus, complete sets of intensity profiles of the gas concentrations across the foam board from one side to the other as functions of time and temperature were obtained and are presented in Figure 5.8. (a) shows a series of profiles as a function of temperature obtained after aging for 96 days at ambient temperature, 51 °C, 69 °C and 87 °C; (b) shows a series of profiles as a function of diffusion time at 87 °C. As expected from the previous MAS results, the overall intensity of gaseous CH$_3$CFCl$_2$ has increased after the accelerated aging due to the release of the dissolved CH$_3$CFCl$_2$ from the polymer matrix. For foam aged at ambient temperature, the overall intensity does not show any appreciable increase over a 3-month period because the rate of desorption from the solid is very slow. However, note that the dissolved gas is still slowly released and if this effect is not taken into account, the diffusion coefficient calculated may be different when measured for foams of different ages where the dissolved gas contents are different. The published diffusion coefficients of blowing gases in PU foams show a large scatter, ranging from 2.25 x 10$^{-9}$ to 6.3 x 10$^{-11}$ cm$^2$/s [3]. In addition to other factors, the fact that these values were obtained with foams of very different ages may contribute to the errors.

In order to modify the theoretical model, we have to analyze the diffusion process in this kind of system. There are two possible processes, the diffusion of cell gas and the desorption (or absorption) of the dissolved gas, which in general are coupled together and we have to consider two processes simultaneously.

210
Previous results have clearly shown that in PU foams aged at elevated temperature the dissolved gas is being released into cells to contribute to the cell gas which simultaneously is diffusing out of the foam. Consider diffusion in one dimension where the diffusing material is created at a rate $A$. This latter effect must be added to the right side of Equation (3.2) in Chapter 3, which can now be written

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + A$$

where $x$ is the space coordinate measured along the direction of the diffusion. $A$ is the rate of creation per unit of volume. While the solution of the general form of the above equation presents formidable mathematical difficulties [4], certain special cases still can be dealt with. Assuming the desorption of dissolved gas in polymer-phase is a first-order process, it will have a rate $A$ proportional to the concentration of the dissolved gas. According to Henry's law, in solutions at low concentrations the vapour pressure of the solute is proportional to its mole fraction in the solution. In general, with the gas at pressure of 1 to 2 atmospheres, Henry's law is found to be obeyed for gases dissolved in the solid polymer[5]. In foam systems the partial pressure of the blowing gas in cells is less than 1 atmosphere and therefore the concentration of gas dissolved in the polymer can be related directly to the partial pressure of the gas above the surface, which in our case is the concentration of the cell gas. Therefore the release rate $A$ of the dissolved gas from the polymer matrix can be treated as being directly proportional to the cell gas concentration $C$ and may be written as $kC$, where $k$ is a constant. Equation (5.1) then becomes

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + kC$$

Let $C_1$ be the solution of Equation (3.2) for diffusion in one dimension in the absence of the release of dissolved gas from the polymer as discussed in Chapter 3, i.e.
\[
\frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2} \quad (5.3)
\]

If the same initial and boundary conditions are used as were imposed on \( C_1 \) in Equation (3.2), the solution of Equation (5.2) can be written, using Danckwert's method [5]

\[
C = -k \int_0^t C_1 e^{kt} dt + C_1 e^{kt} \quad (5.4)
\]

From Section 3.3.2, \( C_1 \) is

\[
\frac{C_1}{C_0} = f(x,t)
\]

\[
= \frac{4}{\pi} \cos \frac{\pi x}{2h} \exp \left( -Dt \left( \frac{\pi}{2h} \right)^2 \right)
\]

\[
- \frac{1}{3} \cos \frac{3\pi x}{2h} \exp \left( -9Dt \left( \frac{\pi}{2h} \right)^2 \right)
\]

\[
+ \frac{1}{5} \cos \frac{5\pi x}{2h} \exp \left( -25Dt \left( \frac{\pi}{2h} \right)^2 \right) - \ldots
\]

\[
= \frac{4}{\pi} \sum_{2n-1} \frac{(-1)^{n+1}}{2n-1} \cos \frac{(2n-1)\pi x}{2h} \exp \left[ -(2n-1)^2 Dt \left( \frac{\pi}{2h} \right)^2 \right] \quad (5.5)
\]

Substituting for \( C_1 \) in Equation (5.4) and integrating this equation, gives the solution

\[
\frac{C}{C_0} = f(x,t)
\]

\[
= \frac{4}{\pi} \sum_{2n-1} \frac{(-1)^{n+1}}{2n-1} \cos \frac{(2n-1)\pi x}{2h} \cdot \left\{ \begin{array}{l}
\frac{k}{(2n-1)^2 D \left( \frac{\pi}{2h} \right)^2 - k} \left[ \exp \left( -\frac{(2n-1)^2 \pi^2}{(2h)^2} Dt + kt \right) - 1 \right] + \exp \left( -\frac{(2n-1)^2 \pi^2}{(2h)^2} Dt + kt \right) \end{array} \right\} \quad (5.6)
\]

212
As discussed before in Chapter 3, the imaging intensity ratio $I/I_0$ is proportional to $C/C_0$ in the above equation, and $I_c$ is the maximum imaging intensity obtained from the 1D imaging profile from the center portion of a freshly made foam sample.

A FORTRAN program (listed in Appendix 2) was written to use the above equation to calculate diffusion curves in order to fit the experimental diffusion data of Figure 5.8. The resulting curves together with the experimental data are shown in Figure 5.9.
Figure 5.9. Diffusion of CH$_3$CFC$_1$$_2$ (HCFC-141b) out of PU foam blocks (a) after aging at 87° for various time intervals. Experiments #1, #2, #3 and Calculations #1, #2, #3 correspond to diffusion times of 58, 81, and 96 days respectively (b) after aging for 96 days at the various temperatures indicated. Calculations #4, #5, #6 and #7 correspond to the curves for diffusion at ambient temperature, 51°, 69° and 87° respectively. Symbols indicate experimental data from the imaging profiles, lines indicate calculated data from the model for this case (see text). Normalized intensity (I/I$_0$) is defined in the text.
Figure 5.9 presents typical examples of experimental data from the image projections in previous figure and the fitted curves as functions of temperature and time. D and k values were determined from the fitting results obtained from the best visual fit and are presented in Table 5.8. Each measurement was repeated two to four times with different samples and the uncertainty in the measurements is about 6%. It is clear that the k values increase as a function of temperature, meaning that there is an increase in the desorption of gas from the polymer matrix as also shown from the MAS experiments. At ambient temperature, the k value is too small to be estimated accurately by observing its effect on the diffusion projection. It is, however, found to be significantly smaller than those at elevated temperatures, indicating that some structural change may occur between ambient temperature and 51°C (e.g. some sort of localized reorientation of polymer chains due to the heating).

Table 5.8. Diffusion characteristics of CH₃CFCl₂ in PU at the different temperatures indicated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aging History</th>
<th>k value * (l/s)</th>
<th>k value ** (l/s)</th>
<th>Reduced ( \chi^2 ) value</th>
<th>Diffusion Coefficient * (cm²/s)</th>
<th>Diffusion Coefficient ** (cm²/s)</th>
<th>Reduced ( \chi^2 ) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>edge section of block PU-1 (10x10x5)</td>
<td>96 days at RT</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1.2 x 10⁻⁹</td>
<td>1.0 x 10⁻⁹</td>
<td>0.08</td>
</tr>
<tr>
<td>edge section of block PU-1 (10x10x5)</td>
<td>96 days at 51°C</td>
<td>1.1 x 10⁻⁸</td>
<td>1.1 x 10⁻⁸</td>
<td>0.08</td>
<td>2.1 x 10⁻⁹</td>
<td>2.0 x 10⁻⁹</td>
<td>0.1</td>
</tr>
<tr>
<td>edge section of block PU-1 (10x10x5)</td>
<td>96 days at 69°C</td>
<td>2.0 x 10⁻⁸</td>
<td>2.0 x 10⁻⁸</td>
<td>0.06</td>
<td>3.3 x 10⁻⁹</td>
<td>3.0 x 10⁻⁹</td>
<td>0.06</td>
</tr>
<tr>
<td>edge section of block PU-1 (10x10x5)</td>
<td>96 days at 87°C</td>
<td>2.6 x 10⁻⁸</td>
<td>2.3 x 10⁻⁸</td>
<td>0.07</td>
<td>4.5 x 10⁻⁹</td>
<td>4.7 x 10⁻⁹</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* obtained from best visual fits.
** obtained from the non-linear least squares fits.
The In D values from Table 5.8 are plotted against $T^{-1}$ in Figure 5.10. As discussed before, by assuming a simple Arrhenius equation for the temperature dependence of the diffusion coefficient, the slope from a least-squares fitting of the diffusion coefficients of $\text{CH}_3\text{CFCI}_2$ yields an activation energy of $20.30 \pm 0.02$ kJ/mol which can be compared to the value of $32.73$ kJ/mol obtained for $\text{CH}_3\text{CFCI}_2$ in PS foams.

Figure 5.10. Temperature dependence of the diffusion coefficients of $\text{CH}_3\text{CFCI}_2$ in PU foam.
The diffusion behavior of cell gas in PU foams at elevated temperatures shown above is quite different from that in the PS foams described in Chapter 3. For PS foams, the amount of dissolved gas is much lower and its effect on the diffusion of cell gas is negligible. However for PU foams, the amount of dissolved gas is much higher and the overall intensity of the cell gas in the imaging projection had increased due to the replenishment of the dissolved gas after aging at elevated temperatures. This effect from the gas dissolved in the polymer matrix on the out-diffusion of the cell gas can no longer be ignored and the mathematical model used to describe PS foam system needs to be modified for PU foams. The modified equation used here well describes the diffusion process in PU foams aged at elevated temperatures and the diffusion coefficients of PU foams obtained are quite close to those of PS foams.

5.8. POST-TREATMENT EXPERIMENTS

Further experimental investigations of the diffusion processes occurring during the imbibing of post-treatment blowing agents into the foam as well as the emission of the initial blowing gas inside the foams were carried out on PU foam (sample PU-1). A series of cylindrical samples (listed in Table 5.9) were produced and treated with CFCl₃ in a sealed container as described previously.
Table 5.9. Treatments of polyurethane foam samples blown with CH₃CFCI₂ and post-treated with CFCl₃.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exposure with CFCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-1e: Cylinder(8.7 mm x 5.1) freshly cut from center of foam block PU-1</td>
<td>336 hours at RT</td>
</tr>
<tr>
<td>PU-1f: Cylinder(8.7 mm x 5.1) freshly cut from center of foam block PU-1</td>
<td>120 hours at 69°C</td>
</tr>
<tr>
<td>PU-1g: Cylinder(8.7 mm x 5.1) freshly cut from center of foam block PU-1</td>
<td>360 hours at 69°C</td>
</tr>
<tr>
<td>PU-1h: Cylinder(8.7 mm x 5.1) freshly cut from center of foam block PU-1</td>
<td>2 months at 69°C</td>
</tr>
</tbody>
</table>

As expected from the previous post-treatment experiments on PS foams, the second blowing gas CFCl₃ diffuses into the foam while the original CH₃CFCI₂ gas diffuses out of the foam matrix after exposure to CFCl₃ at 69°C for some time. This is evident in the 1D ¹⁹F NMR spectra of foam samples PU-1f and PU-1g shown in Figure 5.11. The ¹⁹F NMR cross-section image of sample PU-1e shows that even at ambient temperature, after 14 days of exposure, CFCl₃ had been taken in and distributed within the outside edge of the sample forming a ring approximately 1-mm thick (Figure 5.12). Imaging results obtained from sample PU-1h show that after 2 months of post-treatment, the CFCl₃ had saturated the foam cylinder while a small amount of CH₃CFCI₂ still remained in the center of the foam indicating that the diffusion rates of the two gases were different.
Figure 5.11. $^{19}$F NMR spectra of CH$_3$CFCl$_2$ and CFCl$_3$ in PU foam samples after exposure to CFCl$_3$ gas at 69°C for (a) sample PU-1f for 120 hours and (b) sample PU-1g for 360 hours.
Figure 5.12. Two-dimensional cross-section images of CFCl$_3$ in PU foam sample PU-le after exposure to CFCl$_3$ at ambient temperature for 336 hours. The imaging parameters were the same as in Figure 2.28.
Figure 5.13. Typical MAS $^{19}$F NMR spectrum (spinning at 10 kHz) of CH$_3$CFCl$_2$, CFCl$_3$ and Teflon reference in sample PU-1g post-treated with CFCl$_3$ for 15 days at 69°C. The arrows indicate spinning sidebands. Chemical shifts are referenced relative to external CFCl$_3$ (0.0 ppm).
A typical MAS $^{19}$F NMR spectrum (spinning at 10 kHz) of sample PU-1g (Table 5.9) post-treated for 15 days at 69°C is shown in Figure 5.13. It is clear that both the post-treatment gas (CFCl$_3$) and the original gas (CH$_3$CFCI$_2$) are distributed in both the gas-phase and the polymer matrix. The ratios of the dissolved CFCl$_3$ to gaseous CFCl$_3$ in the three foam samples PU-1e, PU-1f and PU-1g are about the same indicating that the equilibrium between the dissolved component and the gaseous CFCl$_3$ can be established in the time frame of weeks at various temperatures.

As before, from the quantitative intensity distributions (Figure 5.14) obtained from the rows of the cross-section images of blowing agents, the diffusion coefficients of the two blowing gases can be calculated using the same method described in Section 5.7, assuming that the behavior of each gas (i.e. diffusion and the effect of the dissolved component) is independent of another. In this case, because the diffusion path is different from the previous case, modifications should be made to Equations 3.7 in Chapter 3 as will be described below. For the outward diffusion case a plus sign is used for the additional term $kC$ as before to describe the rate of release of the dissolved gas from the solid and for inward diffusion case a minus sign is used to describe the opposing process. Thus Equations 3.7 can be written

for the outward process:

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) + kC \quad (5.7)$$

for the inward process:

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) - k'C \quad (5.8)$$

As described before, the solution of Equation (5.7) can be obtained by...
\[ C = -k \int_0^t C_1 e^{kt} \, dt + C_1 e^{kt} \quad (5.9) \]

where \( C_1 \) is the solution in the absence of the \( kC \) term in Equation (5.7) which is available from Section 3.3.4.

\[ \frac{C_1}{C_o} = f(r,t) \]

\[ = 2 \sum_{n=1}^{n=\infty} \frac{J_0 \left( \frac{R_n}{a} \right)}{R_n J_1 \left( R_n \right)} \exp \left( -D t \frac{R_n^2}{a^2} \right) \quad (5.10) \]

Substituting for \( C_1 \) in Equation (5.9) and integrating the equation, gives the solution for the outward process

\[ \frac{C}{C_o} = f(r,t) \]

\[ = 2 \sum_{n=1}^{n=\infty} \frac{J_0 \left( \frac{R_n}{a} \right)}{R_n J_1 \left( R_n \right)} \cdot \left\{ \frac{k}{D \frac{R_n^2}{a^2} - k} \left[ \exp \left( -D t \frac{R_n^2}{a^2} + kt \right) - 1 \right] + \exp \left( -D t \frac{R_n^2}{a^2} + kt \right) \right\} \quad (5.11) \]

For the inward process, the solution is a little different

\[ C = k' \int_0^t C_1 e^{-kt} \, dt + C_1 e^{-kt} \quad (5.12) \]
Also from Section 3.3.4, \( C_1 \) is

\[
\frac{C_1}{C_0} = f(r,t) = 1 - 2 \sum_{n=1}^{n=\infty} \frac{J_o \left( R_n \frac{r}{a} \right)}{R_n J_1(R_n)} \exp \left(-Dt \frac{R_n^2}{a^2} \right)
\]

Thus the solution for the inward process is

\[
\frac{C}{C_0} = f(r,t) = 1 - 2 \sum_{n=1}^{n=\infty} \frac{J_o \left( R_n \frac{r}{a} \right)}{R_n J_1(R_n)} \left[ \exp \left(-D t \frac{R_n^2}{a^2} - k^* t \right) - 1 \right] + \exp \left(-D t \frac{R_n^2}{a^2} - k^* t \right)
\]

FORTRAN programs (given in Appendix 2) were written for Equations (5.11) and (5.14) to calculate the diffusion processes for outward and inward diffusion cases. Figure 5.15 shows the calculated curves and the results of the fitting. The outward diffusion coefficient of \( \text{CH}_3\text{CFCI}_2 \) is determined as \( 5.0 \times 10^{-9} \) \((k = 1.9 \times 10^{-8})\), close to the value of \( 3.0 \times 10^{-9} \) \((k = 2.0 \times 10^{-8})\), obtained from the block foam samples shown earlier.

The inward diffusion coefficient of \( \text{CFCl}_3 \) is determined to be \( 9.9 \times 10^{-9} \) cm\(^2\)/s \((k^* = 2.0 \times 10^{-7})\). In this case, the \( k \) value is about 10 times larger than the one for the outward diffusion coefficient of \( \text{CH}_3\text{CFCI}_2 \), meaning that the dissolved \( \text{CFCl}_3 \) component has a larger effect on the diffusion process of the cell gas. The inward diffusion process of \( \text{CFCl}_3 \)
is about twice as fast as the outward diffusion of CH$_3$CFCl$_2$ and a similar observation was also found in the PS foam system described in Chapter 3.
Figure 5.14. 1D $^{19}$F imaging profiles of (a) CH$_3$CFC$_2$ and (b) CFC$_3$ in PU foam cylinders post-treated at 69°C for 120 and 360 hours as indicated.
Figure 5.15. (a). Diffusion of CH$_3$CF$_2$Cl (HCFC-142b) out of the PU foam cylinder (samples PU-1f and PU-1g) (b) CCl$_3$F (CFC-11) into the PU foam cylinder after post-treatment at 69° for various time intervals. Circles and squares correspond to diffusion times of 120 and 360 hours exposed to CCl$_3$F. Symbols indicate experimental data from the imaging profiles, lines indicate calculated data from the model for this case (see text).
5.9. CONCLUSIONS

In the present chapter, polyurethane foams containing CFC or HCFC blowing gases were investigated with $^{19}$F NMR spectroscopy and NMR imaging techniques as a comparison study to the work on polystyrene foams presented in previous chapters. It is clear that CFC, HCFC and HFC blowing gases in PS or PU foams distribute quite uniformly in foam boards and slowly diffuse out as the foam ages, and the aging processes are accelerated by elevated temperatures or smaller sample sizes. MAS experiments show that these blowing gases not only distribute in cells but also dissolve in the polymer matrix in both PS and PU foams. However, the content of the dissolved gas in PU foams is much higher than PS foams. Also, the dissolved components are relatively easily released into the cells of PU foams to contribute to the diffusion process and the effect of the dissolved gas in PU foams has to be taken into consideration when modeling the diffusion processes, while this effect can be ignored in PS foams under most conditions. Satisfactory results were obtained when a modified theoretical model was used to determine the diffusion coefficients of blowing gases in PU foams. Again, $^{19}$F NMR microscopic imaging and $^{19}$F fast MAS high resolution $^{19}$F solid-state NMR spectroscopy are demonstrated to be powerful techniques for the investigation of fluorinated blowing gases in polymer foams.
REFERENCES


CHAPTER 6 CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

6.1. CONCLUSIONS

The work presented in this thesis has demonstrated that $^{19}$F NMR microscopic imaging and fast MAS high resolution $^{19}$F solid-state NMR spectroscopy are powerful techniques for the investigation of fluorinated blowing gases in polymer foams.

It was demonstrated in Chapter 2 that $^{19}$F microscopic NMR imaging technique was able to quantitatively determine the amounts of blowing gases in foam cells, measure the distributions of the gases inside foams and monitor changes in the amounts and distributions of the gases as functions of time and temperature and other effects involved in the actual foam manufacturing. Investigations carried out on various polystyrene insulation foam/blowing agent systems show that the quantitative determination of the diffusion process of blowing agents in foam matrix is possible with the non-destructive, non-invasive $^{19}$F microscopic NMR imaging technique.

In Chapter 3, the $^{19}$F microscopic NMR imaging technique was used to produce one-dimensional distributions of the cell gas concentrations inside polystyrene insulation foams as functions of both time and temperature in order to monitor and study their diffusion phenomena. The results were simulated with theoretical model calculations and diffusion coefficients were obtained directly from fitting the experimental data.

The diffusion of blowing gases in PS foams was found to be very slow at ambient temperature. At elevated temperatures, the magnitudes of the diffusion coefficients...
increase with temperature as expected, and that the temperature dependence of the diffusion coefficient can be well characterized by an Arrhenius equation and the activation energy was determined. The results can be used to predict the diffusion behavior of blowing gases in similar PS foam systems at any given temperature and for any sample geometry. Also a PS foam system was post-treated with a second gas and investigated to determine the inward and outward diffusion processes of gases. The inward diffusion of the CCl₃F was found to be faster than the outward diffusion of the initial blowing gas (CH₃CF₂Cl).

In order to accurately predict the diffusion behavior of blowing gases in foam cells, it is essential to know the quantities and the changes of the blowing agents dissolved in polymer matrix as functions of time and temperature. In Chapter 4, fast MAS high resolution ¹⁹F solid-state NMR spectroscopy was used to provide such information in PS foam systems. It was shown that the blowing gas components in the gas-phase and the solid-phase can be measured quantitatively and simultaneously with fast MAS experiments. The amount of dissolved CH₃CF₂Cl gas in PS foams was found to be quite low (< 13 %) and its influence on the diffusion behavior of gaseous CH₃CF₂Cl in PS foams negligible under moderate conditions. The results from the post-treated PS foam system showed that the second gas, to which the foam was exposed for several weeks at various elevated temperatures, not only diffused into the foam cells but also dissolved in the solid matrix.

Various polyurethane foam systems containing CFC or HCFC blowing gases were investigated with ¹⁹F NMR spectroscopy and NMR imaging techniques in Chapter 5 in a comparison study to the previous work on polystyrene foams. It was found that blowing gases distribute quite uniformly in PU foams and slowly diffuse out as the foam ages as expected. MAS experiments reveal that the content of the dissolved gas in PU foams is much higher than PS foams and they are easily released into the cells to contribute to the
diffusion process of the cell gas at elevated temperatures. Thus the effect of the dissolved
gas in PU foams must be taken into consideration when modeling the diffusion processes,
while this effect can be safely ignored in PS foams under most conditions. Satisfactory
results were obtained when a modified theoretical model was used to determine the
diffusion coefficients of blowing gases in PU foams.

It is concluded from the work in this thesis that $^{19}$F NMR microscopic imaging and
fast MAS high resolution $^{19}$F solid-state NMR spectroscopy should be applied to
investigate a wide range of polymer foam products containing fluorinated blowing agents
and to effectively evaluate the performance of foam products blown with CFC
alternatives.
6.2. SUGGESTIONS FOR FUTURE WORK

The work in this thesis focused on blowing agents containing fluorinated gases which determine the long-term performance of foams as thermal insulation. It would be interesting to also investigate the diffusion behavior of air components (nitrogen and oxygen) in PS and PU foams. $^{15}$N labeled nitrogen gas and $^{17}$O labeled oxygen gas could be used with the NMR microscopic imaging technique. If the diffusion rates of air components could be determined and monitored as functions of time, temperature, and other factors, then the results could be compared to the data from the blowing gases and such knowledge would give more insight into the foam aging behavior.

Preliminary imaging results in Chapter 2 suggest that in a PS foam blown with a mixture of CF$_2$Cl$_2$ and CH$_3$CF$_2$Cl blowing gases, the diffusion behavior of each gas seems different. Fast MAS $^{19}$F solid-state NMR spectroscopy and microscopic imaging could be both used in such systems to simultaneously monitor the changes of the contents of each gas in both gas-phase and solid-phase as a function of time and temperature. The results could be compared to the corresponding single gas foam systems and the effects of the dissolved gas components on the diffusion process of each gas could be determined.

MAS solid-state NMR experiments could be performed on a PU foam sample sealed in a tube to avoid any out diffusion effects, to measure and to monitor variations in the equilibrium concentrations of the dissolved and gas components inside the foam as a function of temperature. The results would show the distribution of the blowing agents between the gas and solid phases with temperature as a function of time, and provide further insight into the interaction between the blowing agents and the polymer and the effect of temperature.
In the post-treated foam systems investigated in this thesis, CFCI\textsubscript{3} was used as the second gas to study the process of its inward diffusion into foams. However, similar foam samples blown with CFCI\textsubscript{3} were not available in order to study and monitor the outward diffusion process of CFCI\textsubscript{3}. Further experiments could be performed in order to compare the two opposing diffusion processes of the same gas in similar foam systems, and investigated any effects from the adsorption and desorption processes of the gas in the polymer matrix. Similar studies could be carried out with other gases.

The work in this thesis has shown that the dissolved blowing agent can be a very important factor in the diffusion process of the cell gas. It could be useful to examine how this equilibrium is affected by factors such as the environmental and service conditions in which the foamed insulation performs, formulation variables (polyol, isocyanate, blowing agent, catalysts), manufacturing conditions and various aging stages. The information obtained from these studies may lead to significant improvements in long-term performance of foams produced with alternative blowing agents.
APPENDIX 1. SCANNING ELECTRON MICROSCOPE PHOTOGRAPHS OF POLYSTYRENE AND POLYURETHANE FOAMS

The following photographs of typical PS and PU foams were taken using the scanning electron microscopy (SEM) technique. The cell structure and sizes are shown in the pictures. (a) PS foam with a magnification of x 50, (b) PS foam with a magnification of x 200 and (c) PU foam with a magnification of x 150.
APPENDIX 2. FORTRAN PROGRAMS WRITTEN FOR NUMERICAL SIMULATIONS BASED ON THE DIFFUSION EQUATIONS IN CHAPTERS 3 AND 5

The following FORTRAN programs were written for numerical simulations based on the diffusion equations (3.6), (3.8), (3.11) and (3.12) in Chapter 3 and diffusion equations (5.6), (5.11) and (5.14) in Chapter 5. They can be run either with MacFortran on a Macintosh computer or with the f77 (the sun FORTRAN compiler) software package on a UNIX system.
C
C THIS PROGRAM WAS WRITTEN FOR THE EQUATION 3.6, THE
C SOLUTION FOR THE DIFFUSION PROTOCOL A IN
C CHAPTER 3
C D AND D1 DENOTE DIFFUSION COEFFICIENTS DURING T AND
C T1 RESPECTIVELY
C THIS PROGRAM RUNS WITH MACFORTRAN ON MACINTOSH

PROGRAM DIFF1.F

INTEGER P
REAL*8 H,D,D1,T,T1,EP,EN
REAL*8 X,C,SUMP,SUMN
DIMENSION X(101), C(101)

C DEFINE SOME PARAMETERS
PARAMETER(PI=3.14159265,H=1.9,C1=0.0,C0=1.0)
PARAMETER(P=101,S=101)

C READ THE INPUT DATA: DIFFUSION TIMES AND
C THE ESTIMATED D VALUES
WRITE(*,*)'READ D,D1,T AND T1'
READ(*,*) D,D1,T,T1

C OPEN THE OUTPUT FILE
OPEN (UNIT=4,FILE='CALC1', STATUS='UNKNOWN')
DO 10 I=1,P
X(I)=2.0*H*(I-1)/(P-1)-H
SUMP=0.0
SUMN=0.0
DO 5 J=1,S,2
EP=DEXP(-(D*T+D1*T1)*(2.0*J-1)**2)*(PI/2.0/H)**2)
EN=DEXP(-(D*T+D1*T1)*(2.0*J+1)**2)*(PI/2.0/H)**2)
SUMP=SUMP+1.0/(2.0*J-1)*DCOS(PI*X(I)*(2.0*J-1)/(2.0*H))*EP
SUMN=SUMN-1.0/(2.0*J+1)*DCOS(PI*X(I)*(2.0*J+1)/(2.0*H))*EN
5 CONTINUE
C
C(I)=C1+4.0*(C0-C1)*(SUMP+SUMN)/PI
WRITE(4,11) X(I),C(I)
10 CONTINUE
11 FORMAT(2F7.3)

CLOSE(4)
STOP
END

239
Program #2: Diff2.f

THIS PROGRAM WAS WRITTEN FOR THE EQUATION 3.11, THE SOLUTION FOR THE DIFFUSION PROTOCOL B IN CHAPTER 3.
D DENOTE DIFFUSION COEFFICIENT DURING THE TIME T.
THIS PROGRAM RUNS WITH MACFORTRAN ON MACINTOSH.

PROGRAM DIFF2.F

INTEGER P
REAL*8 H,A,S,D,T,EP,EN,SEN
REAL*8 X,C,SUMP,SUMN
DIMENSION X(101), C(101), R1(50)

DEFINE SOME PARAMETERS
PARAMETER(PI=3.14159265, H=1.9,A=0.44,C1=0.0,C0=1.0)
PARAMETER(P=101, S=101)

READ THE INPUT DATA: DIFFUSION TIMES AND THE ESTIMATED D VALUES
WRITE(*,*)'READ D,T'
READ(*,*)D,T

OPEN THE INPUT AND OUTPUT FILE
OPEN (UNIT=4,FILE='CALC2', STATUS='UNKNOWN')
OPEN (UNIT=5,FILE='R1VALUES',STATUS='OLD')
S=0.0
DO 20 N=1,50
READ(5,12) R1(N)
SEN=DEXP(-D*T*(R1(N)/A)**2)
S=S+(4.0/R1(N)**2)*SEN
20 CONTINUE

DO 10 1=1,P
X(I)=2.0*H*(1-1)/(P-1)-H
SUMP=0.0
SUMN=0.0
DO 5 J=1,S,2
EP=DEXP(-(D*T+D1*T1)*(2.0*J-1)**2)*(PI/2.0/H)**2)
EN=DEXP(-(D*T+D1*T1)*(2.0*J+1)**2)*(PI/2.0/H)**2)
SUMP=SUMP+1.0/(2.0*J-1)*DCOS(PI*X(I)*(2.0*J-1)/(2.0*H))*EP
SUMN=SUMN-1.0/(2.0*J+1)*DCOS(PI*X(I)*(2.0*J+1)/(2.0*H))*EN
5 CONTINUE
C(I)=C1+4.0*(C0-C1)*(SUMP+SUMN)/PI
C(I)=S*C(I)
WRITE(4,11) X(I),C(I)
10 CONTINUE
11 FORMAT(2F7.3)
12 FORMAT(F7.3)

CLOSE(4)
CLOSE(5)
STOP
END
Program #3: Diff3.f

This program was written for the equation 3.8, the solution for the outward diffusion protocol C (Chapter 3). The program runs in UNIX using F77 software package including the Math Library (CMILIB) containing sub-program which can calculate Bessel functions.

D denotes diffusion coefficient during the time T.

Program Diff3.f

REAL S,U,X1,C1,K,T
DOUBLE PRECISION DE,A
DIMENSION X1(100),C1(100),R(50),AJ1(50)

DEFINE SOME PARAMETERS
PARAMETER (A=0.44)
READ THE INPUT DATA: DIFFUSION TIMES AND THE ESTIMATED D VALUES
WRITE(*,*) 'READ D,T'
READ(*,*) D,T
OPEN THE INPUT AND OUTPUT FILE
OPEN (UNIT=10,FILE='CALC3', STATUS='UNKNOWN')
OPEN (UNIT=11,FILE='R1VALUES',STATUS='OLD')
DO 30 J = 1,50
READ(11,12) R(J)
Q=R(J)
AJ1(J)=BESJ1(Q)
CONTINUE
DO 6 N=1,100
S=N*A/100
SUM=0.
DO 3 J=1,50
U=S*R(J)/A
AJ0=BESJ0(U)
DE = DEXP(-D*T*(R(J)/A)**2)
SUM=SUM+AJ0/(R(J)*AJ1(J))*DE
CONTINUE
C1(N)=2.*SUM
X1(N)=N*0.01*A
WRITE(10,11) X1(N),C1(N)
CONTINUE
11 FORMAT(1X,E14.5, 5X,E14.5)
12 FORMAT(E14.5)
CLOSE(10)
CLOSE(11)
STOP
END
Program #4: Diff4.f

THIS PROGRAM WAS WRITTEN FOR THE EQUATION 3.12, THE
SOLUTION FOR THE INWARD DIFFUSION PROTOCOL C (CHAPTER 3)

THE PROGRAM RUNS IN UNIX USING F77 SOFTWARE PACKAGE INCLUDING
THE MATH LIBRARY (CMLIB) CONTAINING SUB-PROGRAM WHICH CAN
CALCULATE BESSEL FUNCTIONS

D DENOTE DIFFUSION COEFFICIENT DURING T

PROGRAM DIFF4.F

REAL S,U,X1,C1,K,T
DOUBLE PRECISION DE, A
DIMENSION XI(100),C1(100),R(50),AJ1(50)

DEFINE SOME PARAMETERS

PARAMETER(A=0.44)

READ THE INPUT DATA: DIFFUSION TIMES AND
THE ESTIMATED D VALUES

WRITE(*,*)'READ D,T'
READ(*,*)D,T

OPEN 'THE' INPUT AND 'OUTPUT FILE

OPEN (UNIT=10,FILE='CALC4', STATUS='UNKNOWN')
OPEN (UNIT=11,FILE='R1VALUES',STATUS='OLD')

DO 30 J = 1,50
READ(11,12) R(J)
Q=R(J)
AJ1(J)=BESJ1(Q)
30 CONTINUE

DO 6 N=l,100
S=N*A/100
SUM=0.
DO 3 J=l,50
U=S*R(J)/A
AJ0=BESJ0(U)
DE = DEXP(-D*T*(R(J)/A)**2)
SUM=SUM+AJ0/(R(J)*AJ1(J))*DE
3 CONTINUE

C1(N)=2.*SUM
C1(N)=1.-C1(N)
X1(N)=N*0.01*A
WRITE(10,11) XI(N),C1(N)
6 CONTINUE

11 FORMAT(1X,E14.5, 5X,E14.5)
12 FORMAT(E14.5)
CLOSE(10).
CLOSE(11)
STOP
END
Program #5: Diff5.f

This program was written for the equation 5.6 (Chapter 5)
the solution for the modified diffusion protocol A
D denote diffusion coefficient during the time T
the program runs in UNIX using F77 software package

Program DIFF5.F

REAL*8 H,D,K,T,U
DIMENSION X1(100), C1(100)

DEFINE SOME PARAMETERS

PARAMETER (PI=3.14159265, H=1.5)

U=PI/2./H

X=0.0

READ THE INPUT DATA: DIFFUSION TIMES AND
THE ESTIMATED D AND K VALUES

WRITE(*,*) 'READ D, T, K'
READ(*,*) D, T, K

OPEN THE OUTPUT FILE

OPEN (UNIT=5, FILE='CALC5', STATUS='UNKNOWN')

DO 10 N=1,100

DX=H/100.

X1(N)=X

X=X+DX

CD=0.

DO 9 I=1,200

XX=COS((2*I-1)*U*X)

TT=D*U*U*(2*I-1)*(2*I-1)*(-1)*XX

TT=-K/(TT-K)*(EXP(-TT*T)*EXP(-K*T)-1.)+EXP(-TT*T-K*T)

CD=CD+4./PI*(-1)**(I+1)/(2*I-1)*XX*TT

9 CONTINUE

CI(N)=CD

10 WRITE(5,*) X1(N), CI(N)

CLOSE(5)

STOP

END
THIS PROGRAM WAS WRITTEN FOR THE EQUATION 5.11 (CHAPTER 5)
THE SOLUTION FOR THE MODIFIED OUTWARD DIFFUSION IN PROTOCOL C
D DENOTE DIFFUSION COEFFICIENT DURING THE TIME T
THE PROGRAM RUNS IN UNIX USING F77 SOFTWARE PACKAGE INCLUDING
THE MATH LIBRARY (CMLIB) CONTAINING SUB-PROGRAM WHICH CAN
CALCULATE BESSEL FUNCTIONS

PROGRAM DIFF6.F

REAL*8 A,D,DE,T,EP,EN
DIMENSION X(100),C1(100),R(50),AJ1(50),C(100)

DEFINE SOME PARAMETERS
PARAMETER (PI=3.14159265)

READ THE INPUT DATA: DIFFUSION TIMES AND
THE ESTIMATED D AND K VALUES

WRITE(*,*) 'READ D,T,K'
READ(*,*) D,T,K

OPEN THE OUTPUT FILE

OPEN (UNIT=10,FILE='CALC6', STATUS='UNKNOWN')
OPEN (UNIT=11,FILE='R1VALUES', STATUS='OLD')

A=0.40
DO 30 J = 1,50
READ (11,12) R(J)
Q=R(J)
AJ1(J)=BESJ1(Q)
30 CONTINUE
DO 6 N=1,100
S=N*A/100
SUM=0.
SUM1=0.
DO 3 J=1,50
U=S*R(J)/A
AJ0=BESJ0(U)
RR=AJ0/(R(J)*AJ1(J))
DE=EXP (-D*T*(R(J)/A)**2)
SUM1=SUM1+RR*DE
SUM=-K*RR/(K-D*(R(J)/A)**2)
SUM=SUM*(EXP(K*T-D*(R(J)/A)**2*T)-1.)
3 CONTINUE
C1(N)=2.*SUM1
C(N)=2.*SUM+C1(N)*EXP(K*T)
X(N)=N*0.01*A
WRITE (10,11) X(N),C(N)
11 FORMAT (1X,E14.5,5X,E14.5)
12 FORMAT (E14.5)
3 CONTINUE
CLOSE (10)
CLOSE (11)
STOP
END
Program #7: Diff7.f

THIS PROGRAM WAS WRITTEN FOR THE EQUATION 5.14 (CHAPTER 5)
THE SOLUTION FOR THE MODIFIED INWARD DIFFUSION IN PROTOCOL C,
D DENOTE DIFFUSION COEFFICIENT DURING THE TIME T
THE PROGRAM RUNS IN UNIX USING F77 SOFTWARE PACKAGE INCLUDING
THE MATH LIBRARY (CMLIB) CONTAINING SUB-PROGRAM WHICH CAN
CALCULATE BESSEL FUNCTIONS

PROGRAM DIFF7.F

REAL*8 A, D, DE, T, EP, EN
DIMENSION X(100), C1(100), R(50), AJ1(50), C(100)

DEFINE SOME PARAMETERS
PARAMETER (PI=3.14159265)

READ THE INPUT DATA: DIFFUSION TIMES AND
THE ESTIMATED D AND K VALUES

WRITE(*,*) 'READ D,T,K'
READ(*,*) D, T, K

OPEN THE OUTPUT FILE

OPEN (UNIT=10, FILE='CALC7', STATUS='UNKNOWN')
OPEN (UNIT=11, FILE='R1VALUES', STATUS='OLD')

A = 0.40
DO 30 J = 1, 50
READ (11, 12) R(J)
Q = R(J)
AJ1(J) = BESJ1(Q)
CONTINUE

DO 6 N = 1, 100
S = N*A/100
SUM1 = 0.
SUM = 0.
DO 3 J = 1, 50
U = S*R(J)/A
AJ0 = BESJ0(U)
RR = AJ0/(R(J)*AJ1(J))
DE = EXP(-D*T*(R(J)/A)**2)
SUM1 = SUM1 + RR*DE
SUM = SUM + K*RR/(K - D*(R(J)/A)**2)
SUM = SUM*(EXP(K*T - D*(R(J)/A)**2*T) - 1.)
CONTINUE

C1(N) = 2.*SUM1
C(N) = 2.*SUM + C1(N)*EXP(K*T)
C(N) = 1.0 - C(N)
X(N) = N*0.01*A
WRITE (10, 11) X(N), C(N)
CONTINUE

11 FORMAT (1X, E14.5, 5X, E14.5)
12 FORMAT (E14.5)
CLOSE (10)
CLOSE (11)
STOP
END