RHEOLOGY OF ASSOCIATING POLYMERS: EFFECTS OF IONIC AND

HYDROGEN BONDING INTERACTIONS

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Abstract

Associating polymers, consisting of relatively small functional groups capable of forming reversible physical associations, represent an important class of materials since they can be used in stimuli-responsive systems. They have found numerous applications in self-healing systems, and they can be used as shape memory polymers and biomaterials. Their complex behavior depends on the delicate interplay between the chemistry of functional groups and polymer dynamics. Therefore, it is essential to understand the physics of these complicated networks to exploit their full potential for important/innovative applications.

Two classes of associating polymers, namely ion-containing polymers (ionomers), and hydrogen bonding polymers, were studied. Using a rotational rheometer and the Sentmanat extensional fixture, a full rheological characterization of several commercial ionomers and a series of novel amine-containing polynorbornenes and polycyclooctenes was conducted. Emphasis has been placed on the distribution of the relaxation times to identify the characteristics times such as reptation, Rouse times and the characteristic lifetime of the ionic and hydrogen bonding associations. These characteristic relaxation times were related to the structure of these polymers using developed scaling theories.

Complete removal of ions was performed to produce copolymers in order to study the relative effects of ionic associations. It was demonstrated that ionic interactions increase the linear viscoelastic moduli and the viscosity by up to an order of magnitude and cause significant strain hardening effects in uniaxial extension. Similarly, for the novel hydrogen bonding polymers, the reversible associations significantly increase the rheological properties and thus delay their relaxation, causing chains to strain-harden before failure. Additionally, it was discovered that the

amine-containing polymers exhibit outstanding self-healing properties. Optimal, fast self-healing response was achieved by varying the molecular weight and structure of these materials.

Finally, the capillary flow of several commercial ionomers was studied both experimentally and numerically. The excess pressure drop due to entry, the effect of pressure on viscosity, and the possible slip effects on the capillary data analysis were examined. Rheological data were successfully fitted to a viscoelastic model developed by Kaye, Bernstein, Kearsley, and Zapas, (known as the K-BKZ model) to perform relevant capillary flow simulations.

Lay Summary

Two classes of associating polymers were studied in this thesis. One group possesses strong ionic associations (ionomers) and the second group has hydrogen bonds (polynorbornenes and polycyclooctenes). The goal was to study the flow properties (rheology and dynamics) of these materials and relate them to their molecular characteristics. Additionally, important applications emerged for the polymers used in this work. First, for the ionomers, this study has shown a way to process them and investigate their flow behavior numerically by using an integral model. This model was capable of capturing both the rheological and flow behavior accurately. Based on this work, the model can further be used to simulate the behavior of ionomers in other processing operations, such as injection molding and film blowing. In addition, the polycyclooctenes developed in this work were found to exhibit a remarkably fast self-healing behavior and equally fast recovery of their mechanical properties after fracture/failure.

Preface

Some parts of this thesis are reproduced with permission from the published research articles. Chapter 2. Sample preparation and experimental procedures are partially taken from the following publications: T. Tomkovic and S.G. Hatzikiriakos, *J. Rheol.*, (2018), **62**, 1319; T. Tomkovic et al., *J. Non-Newtonian Fluid Mech.*, (2018), **262**, 131; T. Tomkovic et al., *Phys. Fluids*, (2019) **31**, 1; Provisional patent app. UBC-18-076 "Amine-functionalized polyolefins and methods of preparation and use thereof".

Chapter 3. Most of this chapter has been previously published as T. Tomkovic and S.G. Hatzikiriakos, *J. Rheol.*, (2018), **62**, 1319. Both authors participated and designed the research. I did all the experimental work and the analysis of the data in terms of a scaling theory to extract the characteristics times of the relaxation with some guidance from professor S.G. Hatzikiriakos.

Chapter 4. Most of this chapter has been previously published in two research articles. T. Tomkovic et al., *J. Non-Newtonian Fluid Mech.*, (2018), **262**, 131; T. Tomkovic et al., *Phys. Fluids*, (2019) **31**, 1. I performed all experimental work, analysis of the data, and the fitting using the K-BKZ model with some guidance from professor S.G. Hatzikiriakos. Professor E. Mitsoulis run all numerical simulations.

Chapter 5. Some parts are used for the papers to be submitted for publication with guidance from both professor S.G. Hatzikiriakos and professor L.Schafer. Synthesis of functionalized polynorbornenes had been performed by N. Kuanr as well as the molecular characterization of these polymers. Some experimental results of functionalized polycyclooctenes have been published in the Provisional patent app. UBC-18-076 "Amine-functionalized polyolefins and methods of preparation and use thereof". D. Gilmour synthesized these polymers and carried out

the molecular characterization. For both polymers, I did all thermal and rheological characterization as well as the self-healing experiments.

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List of Symbols

a_p	pressure shift factor
a_T	horizontal shift factor
b_T	vertical shift factor
C_1	parameter in the Williams-Landel-Ferry equation
C_2	parameter in the Williams-Landel-Ferry equation
C_p	heat capacity
C_t	Cauchy-Green tensor
C_t^{-1}	Finger strain tensor
D	capillary diameter
Ð	polydispersity
Dres	reservoir diameter
E_a	energy of associations
Eact	activation energy for flow
Eact,c	flow activation energy for copolymer
Eact,i	flow activation energy for ionomer
<i>f</i> маа	mol fraction of methacrylic acid
G	relaxation modulus
Gʻ	storage modulus
<i>G</i> ''	loss modulus
$ G^* $	absolute magnitude of the complex modulus
G_g	glassy modulus

G_i	relaxation strength
$G^0_{\scriptscriptstyle N}$	plateau modulus due to the entanglements
G_{rep}	modulus corresponding to reptation
G _{Rouse}	modulus corresponding to Rouse relaxation
G _{SR}	modulus corresponding to sticky Rouse relaxation
h	damping function
ΔH_i	heat of fusion of imperfect crystallites
ΔH_m	heat of fusion of primary crystallites
$I_{C_t^{-1}}$	first invariant of Finger strain tensor
I_{C_t}	first invariant of Cauchy-Green tensor
k	thermal conductivity
L(t)	length of sample at time t
L	capillary length
L/D	length-to-diameter ratio
Δl_i	particle's time corresponding to the residence time Δt '
L_0	initial length of sample
L_{v}	length of the vortex in the reservoir
m	power-law parameter
M_E	molecular weight of a segment between entanglements
M _{MAA}	molecular weight of methacrylic acid
M_n	number average molecular weight
M_S	molecular weight of a segment between stickers

M_w	weight average molecular weight
n	viscosity shear thinning exponent
n	Wagner parameter
Ν	number of segments of the chain
N_{I}	first normal stress difference
N_2	second normal stress difference
Na	Nahme-Griffith number
n_c	power-law index
Ne	number of segments per entanglement
n_p	power-law parameter
Ns	number of segments per ionic group
р	pressure
ΔP	pressure drop
ΔP_{end}	end pressure drop
Pe	Peclet number
Q	volumetric flow rate
R	ideal gas constant
R	die radius
t	time
Τ	temperature
T_c	crystallization temperature

T_g	glass transition temperature
T_i	melting temperature of imperfect crystallites
T_m	melting temperature of primary crystallites
U	average velocity in the capillary die
ū	velocity vector
V_i	particle velocity
Z_E	average number of entanglements per chain
Z_S	average number of associations per chain

List of Greek symbols

α	degree of crystallinity
2α	contraction angle
β	material constant in the damping function h
β_p	pressure coefficient of viscosity
${oldsymbol{eta}}_p^{ ext{sup} er}$	shear rate dependent pressure coefficient
γ	shear strain
γ́	shear strain rate
γο	shear strain amplitude
$\dot{\gamma}_0$	shear rate amplitude
$\dot{\gamma}_A$	apparent shear rate
$\dot{\gamma}_{ij}$	strain rate tensor

$\dot{\gamma}_w$	true wall shear rate
δ	phase shift (loss angle)
Е	Hencky strain
Ė	Hencky strain rate
η	shear viscosity
$ar\eta$	nominal viscosity
η'	real part of the complex viscosity (dynamic viscosity)
η"	imaginary part of the complex viscosity
η^+	shear stress growth coefficient
$ \eta^* $	absolute magnitude of the complex viscosity
η_0	zero shear viscosity
$\eta^{\scriptscriptstyle +}_{\scriptscriptstyle E}$	tensile stress growth coefficient
$\eta_{_{P_0}}$	viscosity at ambient pressure
heta	material constant in the K-BKZ model
λ_i	relaxation time
ξ	particle's time
ρ	density
σ	shear stress
σ^+	transient shear stress
σ_0	shear stress amplitude
σ_A	apparent shear stress
σ_w	true wall shear stress

= $ au$	extra stress tensor
το	attempt time for thermal motion
$ au_e$	Rouse time
$ au_{e,c}$	Rouse time for copolymer
$ au_{ij}$	stress tensor
$ au_{rep}$	reptation time
$\tau_{rep,c}$	reptation time for copolymer
$ au_S$	associations lifetime
$ au_{S,c}$	associations lifetime for copolymer
ϕ	degree of neutralization
ψ_{cl}	stream function at the centerline
$\psi^*_{v,\max}$	relative vortex intensity
ψ_w	stream function at the wall
ω	angular frequency
ω_e	angular frequency corresponding to Rouse relaxation
Wrep	angular frequency corresponding to reptation time

List of Abbreviations

СРР	cone-partitioned plate
DCM	dichloromethane
DSC	differential scanning calorimetry
DTG	derivative thermogravimetry
ЕНМ	Eisenberg Hird Moore model
E-MAA	ethylene-co-methacrylic acid
FTIR	Fourier transform infrared spectroscopy
GPC	gel permeation chromatography
HCl	hydrochloric acid
HDPE	high density polyethylene
K-BKZ	Kaye Bernstein Kearsley Zapas model
LAOS	large amplitude oscillatory shear
LDPE	low density polyethylene
LVE	linear viscoelastic envelope
MAA	methacrylic acid
MCR	modular compact rheometer
NMR	nuclear magnetic resonance spectroscopy
PE	polyethylene
PTFE	poly(tetrafluoroethylene)
ROMP	ring opening metathesis polymerization
SAOS	small amplitude oscillatory shear

SEPDM	sulfonated ethylene-propylene-diene terpolymer
SER	Sentmanat extensional rheometer
TG	thermogravimetry
TGA	thermogravimetric analysis
THF	tetrahydrofuran
ТМА	time marching algorithm
tTS	time-temperature superposition principle
UPy	ureidopyrimidinone
WLF	Williams Landel Ferry

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To my family

Chapter 1: Introduction

In the early 20th century, when polymer chemistry was born, the majority of scientists believed that materials like rubber, silk, and cotton consisted of small molecules grouped into large aggregates which formed superstructures that possessed specific properties.^{1,2} However, Staudinger and Carothers were the first supporters of a new theory that coined the term macromolecules. They described them as small molecules connected with covalent bonds into much larger structures, with much higher molecular weight which was responsible for all material properties.³ Both of them were publicly criticized for their ideas which were not believed to be possible in nature or laboratories at that time. Ultimately, they managed to convert skeptics and prove their theories through "proof by synthesis" when one of the most important polymeric material, nylon, was formed.⁴

In the late 80s, an revolutionary idea was born with the introduction of supramolecular polymer chemistry when small molecules were connected into long telechelic polymers through reversible intermolecular forces.^{5,6} These forces can actively assemble small molecules into networks by forming crosslinked structures with enhanced mechanical and physical properties. This class of polymers consists of associating groups that are capable of forming reversible interactions and therefore tuning the polymer properties. Associating polymers include two groups of polymers. One group are charged polymers such as ionomers and polyelectrolytes, and the second group are metal-ligand complexes^{7–11} and hydrogen bonding polymers^{12–14}.

This thesis examines the rheological properties of two different classes of associating polymers in order to determine their relaxation processes and dynamics. The first class is ion-containing polymers, which are thermoplastic carboxylic ionomers, i.e. sodium salt of ethylene–methacrylic acid copolymers. These polymers have various degrees of neutralization and content

of carboxylic groups, where significant ionic interactions exist between individual molecules which form clusters and multiplets.⁷ The second class is hydrogen bonded polymers, aminecontaining polynorbornenes and amine-containing polycyclooctenes, where the hydrogen bond interactions are present between molecules (intermolecular associations) and elements of the same molecule (intramolecular associations).

1.1 Definition, Characteristics, and Application of Associating Polymers

Conventional polymers widely used in everyday life, such as polyethylenes and polypropylenes, contain macromolecules in which the repetition of small structural units are mainly connected by covalent bonding. On the other hand, associating polymers consist of pendant side- or end-groups on a polymer backbone which can undergo reversible breaking and reformation. These reversible bonds are based on various non-covalent, transient interactions such as hydrogen bonding^{14–19}, ionic interactions^{20–22} metal-ligand coordinations^{4,23–27}, π - π interactions^{28,29}, host-guest complexes^{30,31}, and mixed interactions^{32–34}.

Physical crosslinks are formed through interactions of the associating groups, which are in the literature referred to as "stickers"³⁵, and this terminology is used throughout the thesis. One important feature of polymer networks consisting of associating groups is the reversibility of the transient bonds compared to networks built of covalent bonds. The presence of associating groups can drastically change the viscoelastic characteristics of polymer networks.^{8,36,37} Another significant property of these complex networks is the chain mobility due to the capability of dynamic bonds to dissociate and reassociate multiple times. The dynamic nature of these bonds might affect the relaxation times, not only of the whole molecules, but also of the chain segments
and individual supramolecules^{11,35,38–45}. These characteristics are crucial for associating networks to respond to external stimuli.

Associating polymers are employed in many disciplines where the formation of dynamic reversible bonds plays a significant role. Dynamic rearrangement of complex networks represents the basis of the stimuli-responsive nature of these materials^{46–48}. They can have intrinsic self-healing abilities^{16,27,49–55}, where formed damage can be autonomously repaired with or without external stimuli. They can also be used in tissue engineering applications^{56–60}, due to the similarities in stress relaxation with soft tissues. Another interesting property is their ability to return to their original shape that was changed after applying certain force.^{61–63} Their value lies in their numerous applications such as adhesives^{64,65}, coatings^{56,66}, biomedical implants^{67,68}, controlled drug delivery and release systems^{69–71}, and flocculants for treating waste-water⁷². To fully utilize the potential of associating polymers for important applications, a complete understanding of their rheological behavior is needed in both shear and extensional flows. Additionally, a thorough study of their flow behavior in simple flows such as capillary rheometry (simple contraction flows) would help to understand their processing capabilities.

1.2 Ionomers

An important class of associating polymers is the ion-containing polymers, because of their wide range of applications. In this section, the general characteristics of ionomers are described. It includes their definition, the different ways of their synthesis, their structure and composition of certain commercially available ionomers, and finally their distinct properties important in processing.

1.2.1 Definition of Ionomers

Ionomers belong to a special polymer class that is built of hydrocarbon backbone (polyethylene, polystyrene) with pendant groups (acrylic, methacrylic, or sulfonic acid) that are partially or fully neutralized with different metal ions (alkali, alkaline earth metals, or transition metals). Since their discovery, the ionomer definition has changed several times. Rees and Vaughan⁷³ developed the first class of these materials and named them 'ionomers' to describe the pendant ionic group on the olefin-based polymer backbone. As the development of ion-containing polymers was ascending, Tant and Wilkes⁷⁴ defined ionomers as thermoplastic copolymers comprising of a small percentage of ionic groups, typically about 15 *mol*%. This ionomer definition is widely used till today. Due to the lack of distinction between ionomers and polyelectrolytes, Eisenberg and Rinaudo⁷⁵ refined the definition of ionomers. They described them as materials whose bulk properties are influenced by the interaction between ions within ionic aggregates.⁷⁵ Ionic aggregates are explained in further detail in the following section.

1.2.2 Preparation and Composition of Ionomers

Overall, ionomers consist of non-ionic repeating units that form polymer backbone and ionic groups that can be placed at various positions along the polymer chains. The properties of ionomers greatly depend on the distribution of ionic groups within the polymer matrix. Ionic groups can be placed at one end (monochelic) or both ends (telechelic) of the polymer chain.^{76,77} They can be distributed within the polymer backbone in random or systematic fashion (ionenes).⁷ A common design is in the form of copolymers (block or random), where one polymer consists of pendant ionic groups.⁷⁸ However, in all these cases ionomers tend to form ionic aggregates despite the position of ionic groups. The rheological and mechanical properties of ionomers strongly

depend on the structure of the polymer backbone, concentration, type and distribution of ions.⁷ Whereas the architecture of the polymer backbone, i.e., linear, branched, star, grafted (comb-like) can have a significant impact on polymer characteristics, varying the amounts of ionic species, as well as the type and concentration of ions, can alter the polymer properties to a large extent.

In general, ionomers can be synthesized using two different routes: i) functionalization of previously prepared polymer, and ii) block or random copolymerization of nonionic monomer and a small amount of functionalized monomer. ^{78–80} Commercial ionomers mostly consist of carboxyl or sulfonic groups prepared either by copolymerization or post polymerization functionalization which is more common for sulfonate ionomers.^{81,82} The acid groups can be further neutralized with different metal ions when the strong ionic bond is formed between ionic species and metal cations.⁷⁸

The industrial synthesis route to prepare carboxylated ionomers is through free radical copolymerization of acrylic or methacrylic acid with olefin type monomer (ethylene). This method is mostly used to synthesize thermoplastic and elastomeric ionomers. The most famous thermoplastic ionomers are Surlyn[®] ionomers, produced by DuPont, which consist of two comonomers ethylene and methacrylic acid partially neutralized with various metal hydroxides. Additionally, carboxylated rubbers are a copolymer of butadiene and acrylic acid, and terpolymers of styrene-butadiene-acrylic acid and butadiene-acrylonitrile-acrylic acid.⁷⁹ The functionalization of pre-formed polymer is widely used for the preparation of sulfonated ionomers. During this preparation the ionic groups are incorporated onto the polystyrene backbone by electrophilic substitution of unsaturated aromatic rings, and then neutralized by using metal hydroxides.⁸³ In all these cases the ionic groups are randomly distributed along the polymer chain.

Thermoplastic ionomers like Surlyn[®] (DuPont), IotekTM (ExxonMobil), AmplifyTM (Dow Chemicals) are very popular commercial ion-containing materials. Despite their higher viscosity and slower relaxation compared to nonionic counterparts they can be easily processed by film blowing, injection molding, or extruded into pellets. Moreover, their popularity is based on advantageous characteristics such as transparency, tear and abrasion resistance, low temperature impact toughness, tensile strength, and resistance to many solvents.^{74,84,85} Therefore, they have found a wide range of applications in food packaging, cosmetics, and medical devices, covers for golf balls and ski boots, membrane formations, automobile parts, coatings, and more advanced systems such as self-healing materials that are used by the military and space industry.^{86,87}

1.2.3 Morphology of Ionomers

In connection with the great interest in this type of materials, due to their excellent mechanical and rheological properties, as well as their wide range of applications, many researchers have explored the connection of ionomers properties to morphology in detail.^{7,78,85} Despite years of research, many questions about the ionomer structure remain unanswered. This is because the ionic structure depends on not only on the number of ionic groups, but also on their distribution and topology of the polymeric backbone.

Ionic groups promote unique attractions that give ionomers a distinctive microstructural character. It is well known that ion-counter ion through electrostatic (Coulombic) interactions and dipole-dipole associations strongly interact, which result in the formation of multiplets. They present the smallest possible form of ionic aggregates that are in a most likely spherically shaped.⁷ Several factors play a crucial role in formation of multiplets, such as electrostatic interactions between the ion pairs, the ion content, and the properties of the host polymer.⁸⁸ According to

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Eisenberg et al.^{7,88} the presence of multiplets reduces the chain mobility, which affects the glass transition temperature (T_g) of the polymer in bulk. Therefore, an increase of ion content would reduce the distance between the multiplets, which will eventually overlap, and a large region of ionomer with restrained mobility will be formed. This continuous region is referred to as a cluster, that has the characteristics of the second phase within the polymer, and even possesses an independent T_g . This behavior is related to microphase separation, where the aggregates of ionic groups are dispersed into a nonpolar polymer matrix.⁸⁸ The properties of ionomers are greatly affected by the presence of these aggregates that act as reversible crosslinks.

Numerous molecular theories were formulated to describe the morphology of ionomers and connect it to their mechanical characteristics. Detailed description of these theories can be found elsewhere.^{89,90} These models could explain some of the ionomer properties, but they were not completely consistent with all experimental findings since they were developed for specific systems. Eisenberg, Hird, and Moore⁸⁸ formulated the model named EHM that was the most successful in linking properties of ionomers with their morphology. This model represents multiplets as discrete regions that restrict the mobility of chain segments surrounding them. They can be observed as physical crosslinks formed within the polymer, which limit the mobility of chains considerably.^{91–93} An increase of ionic content leads to the growth of these regions which eventually overlap and form clusters. Although this model was the most effective in explaining almost all properties of ionomers, there are still some that cannot be interpreted.

The morphology of ionomers was examined by a variety of experimental techniques, such as small-angle X-ray scattering and scanning transmission electron microscopy. The latter has revealed the structure of ionomers in bulk consisting of roughly spherical aggregates of ionic groups about 2 *nm* in diameter.⁹⁴ The authors showed an increase in the density of ionic aggregates as the neutralization level increased.

1.2.4 Thermal, Physical, and Mechanical Characteristics of Ionomers

The characteristics of ionomers are mainly influenced by the presence of ionic groups that form complex and unique microstructures. The impact of ionic content on physical and mechanical properties of ionomers were extensively studied by many researchers that identified significant effects of multiplets and clusters.^{95–97} The powerful effect of ionic groups is evident in various properties, such as glass transition and melt temperature, rheological behavior, stiffness, and tensile strength.^{7,85,98} For instance, testing the mechanical properties of sulfonated polystyrene ionomers with different content of ionic groups has shown a remarkable increase in toughness and tensile strength, compared to parent polymer without ions.⁹⁶ Similarly, carboxylated polyethylene ionomers exhibit a significant rise in modulus when starting from the parent copolymer and increasing the number of ions to 80 %.^{73,97} In comparison to conventional polymers, elastomeric ionomers possess improved toughness, abrasion resistance, adhesion, and strength.^{7,85}

Due to the commercial importance of ionomers, which are processed in the melt state, the effect of ionic groups on melt flow behavior is of particular interest. As previously explained, the ionic aggregates could form reversible crosslinks that significantly affect the flow of polymer. Consequently, the viscosity and relaxation times of ionomers rise by about an order of magnitude compared to their nonionic counterpart.⁷⁸ Despite their high viscosity, ionomer melts can be processed using conventional processing equipment. The mechanism that explains the flow of ionomers was first described by Cooper⁹⁹ and Hara¹⁰⁰ as 'ion-hopping'. The ionic interactions are described by the associations lifetime representing the time necessary for the ionic group to find a

new partner after dissociation.^{35,42} This associations lifetime is the average time that the ionic group spends in an aggregate before it 'hops' to another one. Within that time, the polymer chain that holds the ionic group relaxes allowing ionomer to flow. Consequently, the reptation time or terminal relaxation time required for the whole polymer chain to disentangle is higher due to the presence of temporary crosslinks that reduces the chain mobility. To completely understand the flow behavior of ionomers, and the associated processing capabilities, it is essential to determine these characteristic relaxation times. Existing molecular theories can be applied to analyze ionomer dynamics, as discussed in later sections.

1.3 Amine-Containing Polymers

One of the major benefits of associating polymers is the reversibility of temporary crosslinks that allows material to respond to external stimuli like temperature, pH, or solvents.¹² One of the most popular reversible interactions in associating polymers is hydrogen bonding. Two distinct groups of hydrogen-bonded polymers are discussed in this section, which belongs to a class of amine-containing polymers. The main difference is in their polymer backbone where in one case we have polynorbornene and the other polycyclooctene. This change in the backbone structure significantly alters the material characteristics. A short introduction of hydrogen bonds will be presented, followed by an introduction of functionalized polynorbornenes and polycyclooctenes that have two distinct backbone structures.

1.3.1 Hydrogen Bonding

As mentioned previously, molecules that contain groups capable of forming hydrogen bonds (dipole-dipole interactions) are frequently used to synthesize crosslinked polymer networks. The structure and properties of many biological systems depend on the presence of hydrogen bonds. Broadly speaking hydrogen bonding systems can be divided into strong, medium or weak strength bonds.¹⁰¹ The difference between strong and medium or weak hydrogen bonds is significant. On the one hand, strong H-bonds are present in systems like $F-H\cdots F^-$, or $O-H\cdots O^-$ where the H atom is somewhere between two other atoms (fluorine or oxygen), therefore, the distance is short, and the association energy is high, about 40 *kJ/mol.*¹⁵ Medium and weak hydrogen bonds are associated with systems with donor and acceptor as an electronegative atom (D-H…A⁻) in which the directionality is partially lost, and the association energy is lower, ranging from 15 to 20 *kJ/mol.*¹⁰² The strength of hydrogen bonds greatly depends on the type of solvent. It is very well known that in polar solvents hydrogen bonds become much weaker. Therefore, the synthesis of supramolecular polymers is usually done in aprotic or nonpolar solvents.¹⁰³ Overall, the strength of hydrogen bonds is determined by the count of individual bonds and if more of them are involved the binding strength will become greater.¹⁰⁴

These non-covalent interactions are very popular in the formation of polymer blends where they play the role of a compatibilizer between two immiscible polymers.¹⁰⁵ Hydrogen bonds are easily adjustable, and depending on the system or material property their strength can be altered by increasing or decreasing their number, changing solvent, or its pH, or varying the temperature.^{105–108} Using the functional groups with hydrogen bonding, tunable and reversible crosslinked polymer networks can be created that have the ability to respond to temperature. The lifetime of these interactions decreases at higher temperatures. Thus molecular chains can relax faster and consequently the viscosity drops which allows their easy processability.¹⁰⁹ However, at lower temperatures polymers with a large number of hydrogen bonds, can have long relaxation times and form transient networks.^{16,52} Due to their remarkable properties such as self-healing and 10 adhesion, there are many applications for these materials, as coatings, adhesives, or elastomeric materials.^{16,110}

1.3.2 Functionalized Polynorbornenes

Polynorbornene is a very popular material because of its many applications, and it is favorable for functionalizations or creation of various copolymers and blends. Norbornadiene monomers can be functionalized using different reactions, such as Diels-Alder reaction¹¹¹ or hydroaminoalkylation reaction¹¹². Polymerization of functionalized norbornene can be performed by various routes, like ring opening metathesis polymerization (ROMP), vinyl-type, and radical or cationic polymerization.^{111,113–115} ROMP polymerization is one of the most popular reactions for the synthesis of polynorbornenes used by both researchers and industry. It is extensively employed in the preparation of Norsorex[®] (polynorbornene rubber) which has double bonds along the backbone suitable for vulcanization.^{113,116,117} Polynorbornene rubber has distinct elastomeric properties after crosslinking and can be employed as a sealant. Moreover, it can be used as a sound barrier, in shock-proof bumpers, and as a material in vibration dampening in engines.^{113,118} Due to its porous structure and water insolubility, powdered polynorbornene can be used to clean ocean oil spills.¹¹⁸

ROMP polymerization is very useful for synthesizing the functionalized polynorbornenes that can possess a wide range of characteristics from elastomeric to rigid plastic.^{119–123} Research is mostly focused on polynorbornene rubber.¹¹⁶ Although polynorbornene has a rigid backbone its unique property, porosity of powdered polymer, allows adsorption of processing oil or ester plasticizer which lowers the T_g . After crosslinking, the material behaves as elastomer with excellent mechanical properties.¹¹⁶ Incorporation of functional groups considerably influence the properties of the final material. For instance, bulky side groups can significantly alter the glass transition temperature and form thermoplastic or elastomeric materials.¹²⁴ Some studies revealed that functionalized polynorbornenes could be used as shape memory polymers that belong to the class of stimuli-responsive materials.¹²⁵ Varying the pendant side groups considerably tune the rheological and mechanical behavior by increasing the tensile strength and extensibility for rubberlike samples or creep and abrasion resistance for thermoplastic polynorbornenes.^{112,126,127} Additionally, many copolymers were synthesized using ROMP polymerization where various comonomers were used such as polystyrene, poly(ε-caprolactone), poly(ethylene glycol), polyimide, polyethylene, polycyclooctene, to name just a few.^{128–134} Thus, different copolymers were formed, namely graft, block, diblock, and triblock which can be used as a compatibilizer between polynorbornene and poly(vinyl chloride) or nitrocellulose, or as substrates for flexible displays.^{130,135}

Considering that polynorbornene has amorphous but highly rigid structure its properties can be improved by making blends with polymers which have distinct but complementary characteristics. The essential feature of any blend is miscibility since phase separation influences its physical properties. Therefore, incorporating molecules that can interact with blend components allows better miscibility of polymers. One of the powerful tools is having components with pendant side or end groups that contain available hydrogen bonds. Some of reported polynorbornene based blends are with poly(styrene-*co*-hydroxystyrene), poly(vinyl chloride), and ethylene-propylene terpolymer.^{136–138} Functionalized polynorbornenes that have attractive interactions facilitate the formation of miscible blends with different polymers. Additionally, it is known that the presence of double bonds in the polymer backbone causes oxidation and one way to avoid that is by hydrogenation of polynorbornene backbone. Hydrogenated functionalized

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polynorbornenes were blended with polycarbonate and poly(2-vinylpyridine).¹²³ Overall these blends show enhanced mechanical properties and potential to form materials that vary from rubberlike polymers to thermoplastics with distinct thermal properties.

1.3.3 Functionalized Polycyclooctenes

Polynorbornene was the first commercial metathesis polymer placed on the market in 1976 (Norsorex[®]) and not long after, in 1980, polycyclooctene under the trade name Vestenamer[®] was made.¹³⁹ It is a polyolefinic material that contains hydrocarbon backbone which can have a linear and cyclic structure. In contrast to norbornene that has high strain energy, the polymerization of cyclooctene requires a more active catalyst, and thus the development of functionalized polycyclooctenes is much more complex.¹⁴⁰ Therefore, there are limited reports of functionalized polycyclooctenes in the literature.^{140–142} As the importance of ROMP polymerization was growing many active catalysts were discovered, and nowadays many researchers are focusing on the synthesis of functionalized polycyclooctene backbone such as silyl groups, poly(ethylene glycol) chains, fluorescent metal complexes to produce many different materials for sealings, adhesives, coatings, and various applications in biotechnology.^{143,145,146}

Besides the introduction of functional groups, another important use of polycyclooctene is the formation of various copolymers that can be utilized in a wide range of applications.^{147–150} According to the literature, several polymers were used to prepare copolymers with polycyclooctene, such as polystyrene to form ABA type triblock copolymer¹⁵¹, various norbornene and cyclooctene derivatives¹⁵², and poly(ethylene glycol) graft copolymer¹⁵³. The physical properties can be changed by altering the glass transition temperature, and one way to achieve that is by the addition of comonomer with a rigid structure. Hino et al.¹⁴⁷ synthesized copolymers of polycyclooctene and functionalized polynorbornenes that have a wide range of T_g between -60 and 130 °*C*. Additionally, the polycyclooctene backbone can be easily hydrogenated which can be useful for synthesizing functionalized polyethylenes.^{146,151,154–156}

Polycyclooctene is a semi-crystalline polymer with negative glass transition temperature and low melting point, thus crosslinking is necessary to enhance the mechanical properties.¹⁵⁷ Chemical crosslinking is the most common process that improves the stability of polymer at increased temperatures.^{158,159} Due to unusual behavior of this polymer, which is a thermoplastic material that behaves as a non-crystalline elastomer at temperatures higher than the melting point, it can be used in the rubber industry, such as in manufacturing tires, in the recycling of rubber, and as a component of rubberized asphalt for sound adsorption.¹⁶⁰ Additional application of polycyclooctene and its derivatives is a shape memory polymer that has been a popular subject in the literature nowadays.^{125,157,161–163} These stimuli-responsive materials have the ability to return from temporary to their predefined shape when exposed to external stimuli, such as heat, magnetic and electrical fields, light, and moisture.^{164–168}

1.4 Rheological Properties of Associating Polymers

Before presenting a literature review of the rheological studies of associating polymers, certain principles of rheology useful in understanding the behavior of these complex structures are described in the following section. In addition, the various rheological techniques used to study the associating polymers are discussed, and characteristics examples are presented.

1.4.1 Rheology

Rheology is defined as the science of flow and deformation of matter. Associating polymers are viscoelastic materials that exhibit both viscous and elastic responses depending on the type of deformation. Due to this complex nature, more than one rheological property is needed to describe their rheological behavior. These properties which are known as material functions include shear viscosity, viscoelastic moduli, relaxation modulus, and several others.^{169–171} Another aspect of rheology is the development of equations that relate deformation (strain) and rate of deformation (shear rate) to forces (stress), which are known as constitutive equations or rheological equations of state.¹⁷² Such constitutive equations play a multiple role in rheology (i) they are used to model the rheological data of polymers (ii) the physical parameters in these models can be related to polymer structure and therefore can be used for property optimization and (iii) they can be used in flow simulations for process optimization.

To this end appropriate rheological experiments are performed in which simple flow histories are imposed to the material (such as simple shear or extension), and its response is recorded and used to relate the physical parameters of the model to polymer structure and molecular characteristics. In this section, some of the rheometers used in this work, their principles of operation and rheological results obtained from the use of these rheometers are presented.

1.4.1.1 Rheometers

A rheometer is the apparatus for measuring rheological properties. There are two different types, namely strain-controlled and stress-controlled rheometers. In the first one, the rotational speed is fixed, and the torque is measured, while in the second the reverse, i.e., the rotational speed is measured, and torque is fixed. More details are discussed in the book by Macosko.¹⁷¹ In the

following subsections the main rheometers and fixtures which have been used in this study are described.

1.4.1.1.1 Rotational Rheometer

Parallel plate and cone and plate geometries are the most extensively used rheological fixtures to produce simple shear flow. The parallel plate geometry has two parallel concentric disks with specific diameter and distance (gap) between them while the cone and plate geometry consists of a cone of certain angle (typically 4-7°) and a disk. The disk or cone can rotate with respect to the other plate, shown in Figure 1.1, where the angular rotation is imposed, and the torque is measured, or the reverse, depending on the type of the rheometer. The advantages from the use of cone and plate is that it can be used to measure the first normal stress difference, and it produces homogenous deformation. On the contrary, the flow field in the parallel plate geometry is not homogenous and the applied shear rate increases linearly from the center to the edge of the plate.¹⁷¹



Figure 1.1 Schematic illustration of parallel plate and cone and plate fixtures used to generate shear flow

Whereas the benefit of these geometries is that only a small amount of material is needed for testing, it is not able to reach high shear rates and strains due to edge fracture of the sample and presence of secondary flows.^{169–171} Edge fracture has a destructive effect on rheological measurements because it significantly affects the torque (in strain-controlled rheometer) or rotational speed (in stress-controlled rheometer).¹⁷³ Apart from this, strong secondary flows are building inside the sample which expands the edge fracture and additionally affects the measurements.¹⁷³ However, this problem has been resolved with the use of the cone-partitioned-plate that consists of a standard cone at the bottom and the upper geometry that has small standard plate integrated into a stationary coaxial ring and directly connected to the torque transducer (Figure 1.2).



Figure 1.2 Schematic of the cone and partitioned plate (CPP) geometry

The benefit of this setup is that the flow is generated by the rotation of the lower cone and the torque is measured by the upper plate. The sample is placed between plates and must cover the outer ring to obtain valid measurements. Thus, the well-known effect of edge fracture will not affect the measurements immediately, and the higher strains or shear rates can be imposed compared to standard cone and plate geometry.¹⁷³ This type of geometry has been evaluated by many researchers.^{173–178}

1.4.1.1.2 Sentmanat Extensional Rheometer

The Sentmanat extensional rheometer (SER) is a suitable and easy-to-use fixture that can be used together with a rotational rheometer to generate uniaxial extensional data.^{179–181} This rheometer fixture consists of two drums (Figure 1.3) where the main drum rotates by the host rheometer shaft and the slave drum counter-rotates due to the existence of intermeshing gears that connects the two drums. The sample could be either as a strip or cylindrical shape clamped firmly in the center by means of two clips. While drums rotate the sample undergoes a uniform uniaxial stretching (extension) which is used to measure the viscosity and stress relaxation of thermoplastic polymers and elastomers.^{179,180}



Figure 1.3 Schematic of the Sentmanat extensional rheometer (SER)

1.4.1.1.3 Capillary Rheometer

Capillary is one of the most industrially used instruments for measuring the viscosity of polymer melts. It is a pressure driven rheometer; thus, the flow is nonhomogeneous, and it can be used to measure viscosity in steady shear flow only. As shown in Figure 1.4, it consists of a heated reservoir (barrel) that contains the polymer melt and a piston which drives the material through the capillary die, located at the bottom of the barrel. Each capillary die is characterized with the length, *L*, diameter, *D*, and entrance (contraction) angle, 2α .



Figure 1.4 Schematic representation of a capillary rheometer

The load cell measures the force needed to move the piston with the applied velocity. The force is used to calculate the pressure which together with the velocity is employed in obtaining the apparent shear stress, σ_A , and the apparent shear rate, $\dot{\gamma}_A$, from the following equations, where

Q, ΔP , D, and L are volumetric flow rate, applied pressure, capillary diameter and capillary length, respectively.

$$\dot{\gamma}_A = \frac{32Q}{\pi D^3} \tag{1.1}$$

$$\sigma_A = \frac{D\Delta P}{4L} \tag{1.2}$$

The calculated apparent shear rate and apparent shear stress are subject to two corrections.^{169,171} First, the total pressure that drives the polymer flow should be corrected for the extra pressure needed by the melt to flow from the reservoir into the capillary die. This correction is known as the end pressure or Bagley correction.^{169,171} It can be calculated by plotting the pressure versus die length-to-diameter ratios, L/D, at fixed apparent shear rate values and then extrapolating the straight lines to zero L/D (see Figure 1.5). The true shear stress at the capillary wall, σ_W , can be calculated from Eq. 1.3.^{169,171}

$$\sigma_{w} = \frac{\Delta P - \Delta P_{end}}{4(L/D)}$$
(1.3)



Figure 1.5 Typical Bagley correction for capillary data (ionomer example at 140 °C)

The second correction is the so-called Rabinowitsch correction that corrects the apparent shear rate to the true wall shear rate, $\dot{\gamma_w}$, shown by the Eq. 1.4, where *n* is the viscosity shear thinning exponent defined as $n = dlog(\sigma_w)/dlog(\dot{\gamma_A})$.¹⁷¹

$$\dot{\gamma}_{w} = \frac{3n+1}{4n} \dot{\gamma}_{A} \tag{1.4}$$

Having the wall shear stress for several values of the wall shear rate, the viscosity material function can be calculated using Eq. 1.5.

$$\eta(\dot{\gamma}) = \frac{\sigma_w}{\dot{\gamma}_w} \tag{1.5}$$

1.4.1.2 Rheological Experiments

Theoretical background with examples of several rheological experiments, namely small amplitude oscillatory shear, stress relaxation, steady shear, and uniaxial extension, is presented in this section. As examples typical experimental results of one of ionomer are chosen.

1.4.1.2.1 Small Amplitude Oscillatory Shear

In this type of experiment, the strain (stress) could be either within the linear viscoelastic regime, which is called small amplitude oscillatory shear (SAOS) or within the nonlinear, that is referred to as large amplitude oscillatory shear (LAOS). Frequency sweep can be used to determine the dynamic response of associating polymers where the upper plate is set to an oscillatory motion at a constant strain over a wide range of frequencies, while the stress is recorded.^{169,171} The oscillatory strain is defined by Eq. 1.6, where γ_0 is the strain amplitude, and ω is the oscillation frequency. The measured stress is shifted by a phase shift (loss angle), δ , with respect to strain (Eq. 1.7).

$$\gamma = \gamma_0 \sin(\omega t) \tag{1.6}$$

$$\sigma = \sigma_0 \sin(\omega t + \delta) \tag{1.7}$$

Shear stress consists of two components, in-phase σ ' and out-of-phase σ '' that are used to obtain the storage (defining the elastic nature of polymer) and the loss (defining the viscous nature of polymer) moduli, *G*' and *G*'', respectively, which are defined as the ratio of stress components and strain. The shear strain rate is given as:

$$\dot{\gamma} = \frac{d\gamma}{dt} = \dot{\gamma}_0 \cos\left(\omega t\right) \tag{1.8}$$

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The ratio of the shear stress (in-phase and out-of-phase) and shear rate gives the dynamic and imaginary viscosity, η' and η'' , respectively which can then be combined to result the complex viscosity, $|\eta^*|$, (see Eq. 1.9).

$$\left|\eta^{*}\right| = \sqrt{\eta^{'2} + \eta^{''2}} = \frac{\sqrt{G^{'2} + G^{''2}}}{\omega}$$
(1.9)

Frequency sweep can be performed over a wide range of temperatures depending on the material thermal characteristic. The obtained data can be further superimposed on the reference curve by shifting it along the frequency axis using the horizontal shift factor, a_T , in order to obtain the master curve. This procedure is called the time-temperature superposition principle (tTS) that is beneficial to identify the rheological response of material over a wide range of frequencies which cannot be determined with a single experiment. Commonly, polymers that obey the tTS by using only horizontal shift factor are referred to as 'thermorheologically simple' and those that need an additional vertical shift, b_T , are called 'thermorheologically complex' materials. In most cases, the associating polymers belong to a group of thermorheologically complex polymers.^{10,182,183} Figure 1.6 shows typical master curves of G', G'' and $|\eta^*|$ for an ionomer studied in this work.



Figure 1.6 Typical master curve of dynamic moduli and complex viscosity (ionomer example at 140 °C)

The continuous lines in Figure 1.6 represent the fit of the Maxwell model given by the Eq. 1.10, where the relaxation spectrum, { G_i , λ_i }, represents the minimum number of pairs of relaxation strength and relaxation time, respectively needed to accurately describe the experimental dataessentially the relaxation modulus given by Eq. 10.^{169,171}

$$G(t) = \sum_{i=1}^{N} G_i \left[\exp\left(-t/\lambda_i\right) \right]$$
(1.10)

The functions for G' and G'' are given below.

$$G'(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega\lambda_i)^2}{1+(\omega\lambda_i)^2}$$

$$G''(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega\lambda_i)}{1+(\omega\lambda_i)^2}$$
(1.11)

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The Maxwell model and the relaxation spectra are useful to indicate the distribution of the characteristic relaxation times of polymers and are also used in constitutive equations for flow simulations as essential ingredients of nonlinear constitutive rheological models.

1.4.1.2.2 Stress Relaxation

In this experiment, the relaxation shear stress (modulus) is recorded after imposing sudden step strains of certain size. These data are plotted first as relaxation modulus, G(t), versus t in a log-log plot. As an example, Figure 1.7 (left) shows such a set of data for an ionomer at 140 °C for several imposed step strains. For small strains usually much less than 1, the curves coincide indicating that the response is independent of the strain (linear viscoelasticity). However, the dependence on strain becomes evident for larger strains when the limit of linear viscoelasticity is crossed. These data are superposed in Figure 1.7 (right) to determine the damping function.



Figure 1.7 Relaxation moduli after imposition of various sudden step shear strains (left) and vertically shifted relaxation moduli on the linear relaxation modulus to determine the damping function (right) (ionomer example at 140 $^{\circ}$ C)

The damping function represents the shift factors, $h(\gamma)$, used to superpose the stress relaxation data for several step strain of various magnitude. These values can be plotted versus strains, γ , in order to fit various models that are used in formulating nonlinear constitutive rheological models.^{169–171} An example of the damping function obtained from the superposition of stress relaxation data for ionomer is plotted in Figure 1.8.



Figure 1.8 The damping function obtained from stress relaxation experiments (ionomer example at 140 °C)

1.4.1.2.3 Steady Shear

In this experiment, a constant shear rate is applied to the material, and the steady state shear stress (response) is recorded. Repeating this experiment for several shear rates and plotting the shear stress as a function of shear rate, defines the flow curve of the polymer. Viscosity is the main material function determined from this type of experiment (ratio of shear stress and shear rate). Typical results for this experiment are plotted in Figure 1.9 for an ionomer in terms of the shear stress growth coefficient which is defined as $\eta^+ = \sigma^+/\dot{\gamma}$, where σ^+ denotes the transient shear stress and $\dot{\gamma}$ the imposed shear rate. The steady-state values from each curve are clearly seen and they can be used to determine the viscosity as discussed above.



Figure 1.9 The shear stress growth coefficient at various values of constant shear rates (ionomer example at 140 °C)

1.4.1.2.4 Uniaxial Extension

In polymer processing, polymer melts experience both shear and elongation deformations. The above described rheological tests include only shear components, and they are insufficient to characterize the rheological behavior of a material completely. Therefore, uniaxial testing is usually performed to complete the rheological testing of a polymer melt.

In a steady uniaxial elongation experiment, a sample of initial length, L_0 , is stretched at a constant Hencky strain rate, $\dot{\varepsilon} = d\varepsilon/dt$, where ε is the Hencky strain defined by the following equation.

$$\varepsilon(t) = \ln \frac{L(t)}{L_0} \tag{1.12}$$

Moreover, considering the Boltzmann's superposition principle of linear viscoelasticity, it can be shown that in the case of transient elongation viscosity, at short times the following relationship is valid which is known as the Trouton's rule.^{169–171}

$$\eta_E^+(t) = 3\eta^+(t) \tag{1.13}$$

Figure 1.10 plots the tensile stress growth coefficient, η_E^+ , versus time for an ionomer as an example. The solid line represents the linear viscoelastic envelop determined by fitting the dynamic moduli data using the multimode Maxwell model.



Figure 1.10 A typical tensile stress growth coefficient as a function of time for associating polymers at several Hencky strain rates

1.4.2 Review of Rheological Studies of Associating Polymers

For this study, two groups of associating polymers were used, namely ionomers and hydrogen bonding polymers. Thus, in this section, the rheological properties of only these two groups of associating polymers are reviewed. Moreover, there are numerous types of ionomers, but the focus will be placed on ionomer melts, more specifically sulfonated and carboxylated ionomers. They can have different structures, such as telechelic that have ionic groups at both ends of chains, block copolymers where one comonomer consists of ionic groups and random ionomers with ionic groups randomly distributed along the polymer chains.^{77,90,100,184–187} Since the ionomers used in this study are random copolymers primary these types of ionomers are discussed.

1.4.2.1 Review of Rheological Studies of Ionomers

Many researchers have explored the rheological properties of ionomers with different types of ions, level of neutralization, and concentration of comonomers that contain ionic groups. Two interesting classes of comonomers that contribute to the formation of ionomers are carboxylate and sulfonate types of acids. Numerous comonomers have been used to prepare copolymers in the literature, such as ethylene, styrene, butadiene, and isobutylene, to name a few.

As previously mentioned, the focus is on the melt rheological properties of ion-containing polymers. There are many studies on the effect of different cations and ion content on flow, for example, Na⁺, Li⁺, Ca²⁺, and Mg²⁺ in the case of ethylene-acrylic/methacrylic acid ionomers.^{94,188–190} In early stage of study the authors concluded that the type of cation did not affect the viscosity much, whereas the neutralization level had a more significant influence. These conclusions were later proved wrong by performing dynamic and steady shear experiments.^{189,191} Considering that they conducted capillary experiments they could not test these polymers at low shear rates where the effect of divalent ions is evident compared to monovalent.

Additionally, changing the counterion significant changes in the ionomer behavior has been reported, although they cannot be easily explained. By introducing sulfonate acid into polyethylene or polystyrene, the rheological properties were greatly changed.^{90,192–195} Whereas the carboxylated ionomers can be partially neutralized with various metal ions, the sulfonated ionomers are not thermally stable unless they are completely neutralized. Thus, by changing the number of sulfonate groups, the ion content could be changed. In order to compare the ionomers with different counterions, it is necessary to synthesize polymers with identical molecular weight and molecular weight distribution which in general is a difficult task. Therefore, there are not many studies that show the influence of different ionic groups on the rheological properties.^{192,196}

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Industrially important sulfonated ethylene-propylene-diene terpolymers (SEPDM) that is synthetic rubber were investigated. As for the carboxylated ionomers, the viscosity of SEPDM ionomers was increasing when the content of sulfonate groups was increased.¹⁹² The authors experienced problems with accurate measurements of viscosities when common alkali and alkaline earth metals were incorporated, and only Zn and Pb containing ionomers were found to have lower viscosities.^{192,193} Other systems showed considerable dependence of viscosities on the counterion concentration, level of neutralization, and cation type.^{92,197–201}

Vanhoorne and Register performed significant work on carboxylated thermoplastic ionomers at the low shear rate to examine their behavior in the terminal zone.²⁰² A comprehensive study of dynamic and steady shear experiments that accurately identified values of zero shear viscosities was conducted. They explained the applicability of the time-temperature superposition as the consequence of two characteristic relaxation mechanisms (ion-hopping and terminal relaxation) being independent of each other, and/or they are experiencing the same temperature dependence.²⁰² Furthermore, they confirmed previous findings that the viscosity is significantly increasing with an increase of the level of neutralization. Compared to their parent copolymers the ionomers also showed elevated activation energy, that implied requirements of higher energy to flow which is a direct consequence of the presence of ionic associations.²⁰²

First and foremost, free radical copolymerization of ethylene and ionic comonomer, methacrylic acid, generate copolymer with broad molecular weight distribution and long chain branching that has a significant impact on their rheology and processing.^{202–205} At the same time, neutralization of copolymer introduces the formation of ionic multiplets and clusters, which affect the relaxation processes of ionomers and their thermophysical properties. Most of the carboxylated ionomers are partially neutralized that means some of the carboxylic acid groups are capable of

forming hydrogen bonds. Moreover, they allow the exchange of H^+ with the metal cation that permits diffusion of polymer chains without the necessity of ionic groups to interchange between aggregates.^{202,205} Another important effect of free carboxylic groups is their ability to plasticize the ionic aggregates.^{202,205–207} It has been shown that ionomers are very sensitive to the presence of moisture and proper drying is essential to obtain accurate measurements.²⁰⁸

1.4.2.2 Review of Rheological Studies of Hydrogen Bonding Polymers

Associating polymers have a very complex structure and rich dynamics and thus vast application opportunities. The linear rheology is a great tool to i) understand their complex dynamics and ii) verify existing theories in the literature. Associating polymers are capable of forming strong networks without having entanglements and these temporary interactions are described as an additional frictional source that affects the relaxation of the whole molecule and drives it to the longer times.^{11,35} The introduction of entanglements makes it much more complicated since now, besides the reversible associations, topological constraints posed by the entanglements play a significant role in their total relaxation that is now influenced by two major time scales. Therefore, associations, in general, have the tendency to aggregate that can cause phase separation and additionally affect the relaxation processes.^{11,211,212} The architecture of associating polymer network is important because it considerably influences the rheological behavior of these materials.

Considering hydrogen bonding polymers, two different cases were reported. One when hydrogen bonding groups are located at both ends of polymer chains (telechelic polymers) and the other when these associations are distributed along the polymer backbone. Since hydrogen bonds are highly directional interactions in telechelic polymers they tend to group and create clusters and as result thermoplastic elastomers are formed.^{213–215} However, some telechelic polymers have end groups that form only dimers, without aggregates and physical crosslinking, and can create long sequences of molecules.^{216,217} The rheological properties of both systems are considerably enhanced compared to one without the presence of hydrogen bonding interactions. The formation of aggregates significantly increase the modulus even for low molecular weight polymers and influence the activation energy of flow.²¹⁵

The second class includes polymers where functional groups can be grafted on the backbone, and randomly, or systematically distributed along the chains. Various systems have been synthesized and their rheological properties investigated. The rheological properties of these systems greatly depend on the strength of hydrogen bond interactions and their number density of pendant groups. Lewis et al.¹⁴ synthesized a series of poly(butyl acrylate) copolymers and elastomers with various pendant groups that are capable of forming hydrogen bonding. They observed significant increase and extension in rubbery plateau when functional groups that form strong hydrogen bonds were used, which led to the formation of soft solids. On the contrary, weak hydrogen bonding moieties created copolymers that showed no significant change in their rheological behavior due to their fast relaxation compared to the relaxation of the whole polymer chain. Seiffert²¹⁸ demonstrated the major influence of the so-called 'interchain sticking' on the rheology of associating networks at low frequency, which is the regime of full polymer relaxation and flow. Cate et al.²¹⁹ synthesized ureidopyrimidinone (UPy) based polymers that contain hydrogen bonded associations whose strength strongly depends on the number of functionalities. Although their reference material behaved as Newtonian fluid, incorporation of functional groups increased the viscosity and created reversible viscoelastic networks. Nair et al.²²⁰ presented the

potential to alternate the mechanical properties of polynorbornenes by introducing various pendant groups. They indicated that the transition from highly viscous liquids to highly elastic solids greatly depend on the hydrogen bonding motifs which can induce reversible crosslinking with the polymer backbone. Perry et al.¹¹² synthesized several amine-containing polynorbornenes and clearly showed the effects of hydrogen bonding on their rheological properties by comparing it directly with neat polynorbornene.

Studying nonlinear rheological behavior is important to understand the conditions under which material failure is happening. Associated polymer networks that exhibit solid-like behavior can be classified either as a brittle or ductile determined by viscous dissipation.^{221–223} The nonlinear behavior of systems comprising hydrogen bonding groups is not well understood due to challenges in preparing well-defined samples on a larger scale in order to allow consistent rheological analysis. Whereas some available data in the literature on hydrogen bonding polymers have reported on their nonlinear behavior in shear, the extensional rheology has not been widely explored. Several researchers suggested that these polymers exhibit strain hardening behavior and have the ability to resist large deformations.^{209,224–227} It was demonstrated that transient networks with a large number of associations mostly reveal brittle behavior in the linear viscoelastic regime, but the presence of weak interactions display strain hardening behavior.²²⁴ Two important factors determine the mechanism of sample breakage, i.e., the strength of junctions and their dynamics. Simultaneously, associating groups have to hold strong enough and to allow dissociation and association of present bonds to prevent brittle fracture.

1.5 Dynamics of Associating Polymer Network

The rapid growth of synthetic polymer materials required investigation of their dynamics that will answer important questions on how big these giant molecules are and how do they move. Pioneers of this fundamental research were Flory¹, Stockmayer and Zimm^{228,229}, Edwards²³⁰, Kuhn²³¹, Graessley²³², and Rouse²³³. The initial theories that described polymer chain dynamics were developed by Rouse²³³ and Zimm²²⁹. Whereas they showed how the polymer chain is behaving in dilute solutions, these theories were the foundation of chain dynamics in concentrated polymer solutions. As the concentration of polymer solution is increasing the polymer chains, start to overlap and form entanglements. Therefore, the motion of the chain is restricted by the presence of the neighboring chains. If we observe the motion of only one chain, the path which this chain will follow is called the 'primitive path'^{234,235}.

Edwards²³⁶ and de Gennes²³⁴ simplified the complex topological problems of polymer networks by suggesting the tube-like regions around macromolecules and the primitive path can be seen as a center line of the tube. Based on the tube theory, the polymer chain is placed in a tube with the radius *a*, that limits any motion perpendicular to the tube's axis above the defined radius. The motion of the macromolecule in the tube was coined by de Gennes²³⁴ as 'reptation' due to the snake-like wriggling. Doi and Edwards^{235,237–240} developed the tube concept and explained the stress relaxation process through three stages. Starting with the relaxation of the segment between entanglements, contraction of the contour length, and finishing with chain diffusion out of the tube²⁴¹. Their major contribution is the development of constitutive equations for calculating the stress after the imposition of deformation within the linear and nonlinear viscoelastic regime^{235,238,239,241}.

Tube theory with predominant reptation relaxation mechanism could successfully explain the origin of shear thinning and plateau region and give an approximate scaling of the longest relaxation time (reptation time) with polymer chain length. However, the tube model failed in capturing the experimental results of the entire relaxation. Therefore, to address the shortcomings it was necessary to improve the model by incorporating additional relaxation mechanisms, such as contour length fluctuations^{242–245} and constraint release^{246–248}. Modified models were verified with experimental results of linear monodisperse polymers. Nevertheless, more complex architectures, such as polydisperse polymers, binary blends, liquid crystal polymers, and associating polymers, require the formation of new, improved theories that can capture these specific rheological properties.

Considering associating polymers, a key issue is to understand the relation between their structure and dynamics. To describe the stress relaxation in these systems, two basic molecular theories were formulated. One was developed by Cates and Candau^{38,249} and another one by Leibler, Rubinstein, Colby, and Semenov^{35,40,41,43,250}. Using the previously described theories for the dynamics of linear polymers both models are developed by incorporating characteristic parameters that can describe the effect of stickers. Leibler, Rubinstein, Colby, and Semenov^{35,40,41} modified the existing Rouse and reptation theories for polymers without stickers and formulated the so-called sticky Rouse and sticky reptation models by including the effect of reversible associations on polymer dynamics. Which of these two will be used depends on the level of entanglements in the polymer network.

Cates and Candau^{38,249} focused on associating polymers with end groups and tubular micellar systems that are acting as living polymers, undergoing reversible sticker dissociation and association. The proposed theory showed the impact of stickers on stress relaxation due to their

breakage and recombination. When the lifetime of associations is shorter than the reptation time, the relaxation process will slow down, and it will take more time for the polymer chain to 'reptate' out of the tube. On the other hand, Leibler, Rubinstein, Semenov, and Colby were investigating system with many pendant side groups that are separated by the same number of carbons along the polymer chain^{35,40,41}. Based on their theory the relaxation process strongly depends on the polymer concentration, molecular weight, and sticker density.

Since in this thesis only polymer melts are studied, the dynamics of this type of networks will be reviewed. In the case of highly concentrated polymer solutions or polymer melts more intramolecular associations between pendant groups are formed which affect the relaxation process. Since the dynamics of associating polymer network is controlled only by intermolecular interactions, the transition from intramolecular to intermolecular associations will have a significant impact on stress relaxation^{41,250}. The additional influence of the high number of stickers is prolonged associations lifetime because of the reduced possibility of one sticker to find a new partner and the chance to reassociate with the same one is much higher^{41,250}. Consequently, multiple reassociations of a sticker with the same partner lead to increased associations lifetime^{41,250}. Numerous experiments were performed to verify this theory both qualitatively and quantitatively^{13,37,251,252}. Whereas there are some shortcomings mostly due to reduced sticker mobility and uneven spacing between them, this theory was successful in explaining the dynamics of some associating polymer networks. It is well known that the elastic modulus is the crucial property of associating polymer networks and strongly influence their applications. Despite many existing theories, predicting the elastic modulus cannot be accurately accomplished. Thus, the models have to be modified for specific transient network.^{253,254}

1.6 Research Objectives and Thesis Organization

In this section the main objective is presented first separated into two parts followed with the organization of this thesis.

1.6.1 Thesis Aims

The main focus of this work is to investigate the influence of ionic and hydrogen bonding groups on the rheological and mechanical properties of ionomers and functionalized polynorbornenes and polycyclooctenes. In particularly this thesis comprises of two parts.

1. A comprehensive thermal and rheological investigation of thermoplastic carboxylic ionomers was performed. In specific, sodium salt of poly (ethylene-co-methacrylic acid) and their corresponding copolymers, were studied to understand the influence of metal ions on their thermorheological properties. Various ionomers are used with different methacrylic acid content and a similar level of neutralization. A comparative study between the ionomers and their corresponding copolymers was achieved by removing ions to reveal the effects of ionic interactions. The theories described in section 1.5 were used to determine the characteristic relaxation times (Rouse time, reptation, and associations lifetime) whose interplay has a significant effect on the relaxation of ionomers. The comprehensive set of generated rheological data would be extremely useful for testing rheological constitutive models for associating polymers. These carboxylated thermoplastic ionomers were chosen for several reasons. They are commercially available, well-known, and commonly studied systems that can be melt processed. Therefore, they are suitable for all experiments in melt state, such as capillary measurements that can be used to understand the effects of ionic interactions on their flow behavior. The capillary flow was employed to identify the relative effects of ionic and hydrogen bonding associations on the entry
pressure, vortex size, and strength in the contraction flow. In the simulations, an integral viscoelastic model was used^{255,256} for which parameters were determined from the generated rheological data.

2. A complete thermal and rheological characterization of novel functionalized polynorbornenes and polycyclooctenes capable of forming reversible hydrogen bonds was performed. These polymers were synthesized by our collaborators in the chemistry department at the University of British Columbia. Monomers that contain aryl amine functional groups were synthesized using a novel catalyst and subsequently polymerized.²⁵⁷ As in the case of ionomers, both the linear and nonlinear rheological properties were studied and explained based on existing molecular theories for associating polymers. The various characteristic times underlining the relaxation behavior of individual chains were found to be central in this study. Additionally, investigation of potential self-healing properties of the functionalized polycyclooctene was performed. The main target was to identify the optimum structure and molecular characteristics that exhibit the best/fastest self-healing behavior.

1.6.2 Thesis Overview

Chapter 1 presents a literature review of the properties of the studied polymers (ionomers and hydrogen bonding polymers). Moreover, rheological methods and testing, as well as instruments used for such material characterization, are presented. Typical experimental results obtained from these methods are also provided as examples. In Chapter 2, the polymers and experimental methods for their characterization are discussed in detail. Specifically, the various analytical techniques used to investigate the thermal properties and molecular characteristics of the studied polymers are presented, together with their structures and routes of synthesis. Chapter

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3 presents the complete rheological characterization of several commercial ionomers and their corresponding parent copolymers. Emphasis is placed on the distribution of the relaxation times to identify the characteristic times such as reptation, Rouse, and associations lifetime. Existing scaling laws are used to calculate the order of magnitude of the associations lifetime and the association energy that are important parameters to gain a better understanding of their rheological behavior. Chapter 4 describes the capillary flow study of several commercial ionomer melts both experimentally and numerically. The excess pressure drop, due to entry, the effects of pressure on viscosity, and the possible slip effects on the capillary data analysis are examined. The experimental rheological data is fitted to a viscoelastic (K-BKZ) model to perform the flow simulations. The rheological study of the novel functionalized polymers, that are capable of forming hydrogen bonds of various strengths, is demonstrated in Chapter 5. Two types of aminefunctionalized polymers with considerably different backbone structures, namely polynorbornene and polycyclooctene are examined. Their rheological behavior is compared to reference materials that have no hydrogen bonding interactions. Moreover, the self-healing capabilities of some of these polymers are examined and quantified in terms of tensile testing. Finally, the overall conclusions, contributions, and recommendations for future work are presented in Chapter 6.

Chapter 2: Materials and Experimental Methodology

In this Chapter two distinct groups of materials, namely ethylene methacrylic acid ionomers, functionalized polynorbornene, and functionalized polycyclooctene, along with their route of synthesis are presented. Since these materials have distinct structural properties details of their thermal and rheological investigations are explained for each of them.

Some parts of the following sections are reproduced with permission from the following publications: T. Tomkovic and S.G. Hatzikiriakos, *J. Rheol.*, (2018), **62**, 1319; T. Tomkovic et al., *J. Non-Newtonian Fluid Mech.*, (2018), **262**, 131; T. Tomkovic et al., *Phys. Fluids*, (2019) **31**, 033102; Provisional patent app. UBC-18-076 "Amine-functionalized polyolefins and methods of preparation and use thereof".

2.1 Materials

As mentioned in the previous chapter, two different classes of associating polymers are used in this work, (i) polymers that contain ionic interactions, namely ionomers and (ii) polymers with hydrogen links, which can have either flexible or stiff backbones. Structural formulas of ioncontaining polymers, namely sodium salt of ethylene-methacrylic acid and corresponding copolymer are presented in Figure 2.2. Hydrogen bonding polymers with a rigid backbone are functionalized polynorbornenes (see the structure in Figure 2.4) and those with a flexible backbone are functionalized polycyclooctenes (see the structure in Figure 2.6).

2.1.1 Ethylene-Methacrylic Acid Ionomers

Copolymers of ethylene and methacrylic acid (E-MAA) were synthesized by DuPont via high-pressure free-radical copolymerization that results in the random distribution of methacrylic acid (MAA) groups along the polymer chain (see Figure 2.1).



Figure 2.1 Synthesis route of ethylene methacrylic acid copolymer followed by neutralization with sodium hydroxide

This type of polymerization produces copolymers comprising of low-density polyethylene, that has long-chain branching, and a small amount of methacrylic acid. The molecular weight and molecular weight distribution can be measured by using high-temperature gel permeation chromatography (GPC). The approximate values of weight-average molecular weight, polydispersity index, and the degree of long-chain branching were performed by DuPont and results reported by Vanhoorne and Register.²⁰² It was reported that these polymers have high polydispersity and long-chain branching. The same resin was used in this work; thus, the reported results were adopted. The partial neutralization of copolymers with sodium hydroxide results in

the formation of ionomers where more than half of protons on the carboxylic group were exchanged with sodium. There are two different ways to prepare the ionomers, melt neutralization and neutralization in solution. Ionomers used for this study were prepared by DuPont using the melt neutralization process in a twin-screw extruder with sodium hydroxide (see Figure 2.1).



Figure 2.2 Structural formulas of a) ethylene methacrylic acid copolymer and b) ethylene methacrylic acid ionomer

To examine the influence of ions, present in partially neutralized E-MAA ionomers, sodium was removed, and ionomers were converted into corresponding copolymers. The method used to prepare this set of copolymers was as follows. Typically, 2 g of finely ground ionomer sample was refluxed in 100 ml tetrahydrofuran (THF), and 10 ml diluted hydrochloric acid (HCl, 1M) at the temperature of 60 °C for 24 hours. The acid solution was then precipitated with a mixture of cold methanol and deionized water (1:1), filtered and washed at least 4 to 6 times with a mixed solvent of methanol and water before drying for about 24 hours. Fourier transform infrared spectroscopy (FTIR) was used to determine if the complete removal of ions was performed.

Ionomers used in this work contain various amounts of methacrylic acid (MAA), which were determined by titration of carboxylic groups using the well-known analytical method.²⁵⁸ The obtained copolymer of ethylene and methacrylic acid (0.02 g) was refluxed in 30 ml of a mixed toluene-isobutyl alcohol (75 ml:25 ml) solvent under nitrogen flow at the temperature of 70 °C.

Once the polymer completely dissolved, titration of the acid groups was conducted with a 0.0225*M* sodium methoxide solution using phenolphthalein as an indicator. Due to the buildup of methanol vapor, a gap in the flask must be left. A blank titration is necessary.

Sample preparation. The presence of moisture has a significant impact on the mechanical properties of the ionomers and their corresponding copolymers.²⁰⁸ Therefore, proper drying of the samples is essential. A series of annealing processes were performed to determine the optimal drying conditions, and it was found that seven days of vacuum drying at 75 °*C* was necessary to have consistent results (see Figure 3.1 in the section 3.3.2). After drying, the pellets were molded into films by using poly(tetrafluoroethylene) (PTFE) sheets at the temperature of 130 °*C* and applied pressure of about 10 *MPa*. The prepared samples are stored in a desiccator over anhydrous CaSO₄ at room temperature before testing.

2.1.2 Functionalized Polynorbornenes

Functionalized polynorbornenes were synthesized in the chemistry department at UBC by Nirmalendu Kuanr and Mitchell Perry (members of the Prof. Schafer's group) (see Figure 2.3 for synthesis reaction). Starting from norbornadiene by utilizing new catalytic protocol for monomer synthesis novel molecules bearing the pendant side aryl amine groups were prepared.¹¹² For this purpose, hydroaminoalkylation reaction was employed with novel mono-pyridonate tantalum amido catalyst, which was developed by Prof. Schafer's group.



Figure 2.3 Synthesis reaction of functionalized polynorbornenes. The first step is hydroaminoalkylation reaction and the second ring opening metathesis polymerization, where R can be various groups

Subsequently, the ring opening metathesis polymerization (ROMP) of prepared monomers was performed and, as a result, polymers with controlled incorporation of a variety of hydrogenbonding amine groups designed. Various possible side groups can be incorporated, and several structures of polymers used in this work are presented in Figure 2.4. Each of these pendant side groups along the polymer chain retains the ability to form reversible hydrogen bonds. Commonly used techniques for characterization of polymer structure, such as FTIR, GPC, and nuclear magnetic resonance spectroscopy (NMR) were carried out by Nirmalendu Kuanr.

Sample preparation. All synthesized amine-functionalized polynorbornenes were first dissolved in THF or dichloromethane (DCM) at room temperature following the solution casting into molds of various sizes made of PTFE. After evaporation of the solvent, films were formed and dried in a vacuum oven over 24 hours at the temperature of 40 °*C*. After drying, the samples were stored in a desiccator at room temperature.





ACN-ref

ACN-H

'n

ACN-OMe

'n







ACN-CAT

ACN-F

ACN-Cl



ACN-Br

Figure 2.4 Various structures of functionalized polynorbornenes

2.1.3 Functionalized Polycyclooctenes

As with functionalized polynorbornenes, functionalized polycyclooctenes were synthesized in the chemistry department at UBC by Damon Gilmour (a member of the Prof. Schafer's group) (see Figure 2.5 for synthesis reaction).²⁵⁷ In this case, a functionalized polymer was produced from a previously prepared monomer, amine-functionalized cyclooctene. Using similar catalyst reaction, pendant side aryl amine groups were integrated into cyclooctadiene by performing hydroaminoalkylation reaction.



Figure 2.5 Synthesis route of functionalized polycyclooctenes. The first step is hydroaminoalkylation reaction and the second ring opening metathesis polymerization, where R can be a various group

The obtained monomers were polymerized afterwards by using the ROMP polymerization, and polymers with various structures were produced (see Figure 2.6). Furthermore, these polymers were hydrogenated by adding p-toluenesulfonyl hydrazide to the reaction to form pendant aminecontaining polyethylenes. As mentioned earlier, these pendant side groups are capable of forming transient hydrogen linkages. Damon Gilmour conducted regular techniques (NMR, FTIR, GPC) to investigate the polymers structures. **Sample preparation.** The preparation of amine-functionalized polycyclooctenes is very similar to that of functionalized polynorbornenes. Dissolved polymers were molded using the same procedure and the formed films were dried for one day at the temperature of 40 $^{\circ}C$. After drying, they were stored in a desiccator at room temperature. Due to the adhesion to the PTFE before testing, the films had to be cooled down to the temperatures below their glass transition temperatures, which was achieved by using dry ice.





АСС-Н

ACC-ref













Figure 2.6 Various structures of functionalized polycyclooctenes

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2.2 Experimental Methods

Several experimental techniques were used in this work. Although the emphasis was placed on rheological experiments, other analytical methods were used as well. To examine the level of neutralization of ionomers and determine if the elimination of sodium ions was complete, FTIR was employed. In general, before performing any rheological tests, it is essential to know the thermal properties of polymeric materials, such as transition temperatures, which were determined by differential scanning calorimetry (DSC) and degradation temperatures identified by thermogravimetric analysis (TGA).

2.2.1 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was used to analyze the chemical structures of ethylene methacrylic acid copolymers after ion removal, and the amount of sodium ions present in ionomers. For this purpose, thin films were formed by applying pressure of about 10 *MPa* at the temperature of 130 $^{\circ}C$. Then they were analyzed using a PerkinElmer Frontier FTIR spectrometer (PerkinElmer, Waltham, MA, USA) by collecting the spectra between 650 and 4000 cm^{-1} at 4 cm^{-1} resolution. The obtained results are included in Appendix A. The number of sodium ions was determined by identifying the absorbance ratio, which was calculated through the integration of the two characteristic peak areas of the carboxylic acid dimer (1700 cm^{-1}), and polyethylene band (1465 cm^{-1}).²⁵⁹ Moreover, the complete removal of sodium ions was followed by checking if the peak exists at 1560 cm^{-1} , whose intensity depends on the content of sodium ions.

2.2.2 Thermogravimetric Analysis

The thermal stability of the polymers was performed by using a Shimadzu TA-50 thermogravimetric analyzer. Experiments were carried out on a small amount of dried samples (2-5 mg) by continuously passing a high purity nitrogen stream (99.5 % N₂) into the furnace at a flow rate of 50 *mL/min* and atmospheric pressure. Weight loss as a function of time was continuously monitored in the range of temperatures from 25 °*C* to 600 °*C* at a heating rate of 10 °*C/min*. In order to remove moisture, the sample was isothermally heated at 105 °*C* for at least 10 minutes. The results are presented in Appendix B.

2.2.3 Differential Scanning Calorimetry

DSC was used to determine transition temperatures of all polymers used in this study (see Appendix B). The procedures for ionomers were different than those for functionalized polynorbornenes and polycyclooctenes due to variations in their structures. Calibration of DSC instruments was performed using indium standard.

Ionomers. Three characteristic thermal transitions in ionomers, i.e., the melting of imperfect crystallites, T_i , the melting temperature, T_m , and the crystallization temperature, T_c , important in this work, were obtained by using a TA Instruments Q1000 differential scanning calorimeter. Additionally, the heat of fusions and the crystallinity were calculated. Experiments were performed in three cycles as follows. About 5-7 *mg* of the sample was packed and sealed into an aluminum pan and heated under nitrogen atmosphere. The first cycle was performed by heating the sample from room temperature to 150 °C at a heating rate of 10 °C/min and isothermally held at 150 °C for 5 min in order to eliminate thermal history. Then the sample was cooled down to room temperature at a cooling rate of 5 °C/min, followed by the second heating cycle to 150 °C at

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the same heating rate of 5 °*C/min*. The melting temperature used was determined from the second heating cycle.

Functionalized polynorbornenes. These polymers are amorphous materials; thus, the T_g is essential to be known for their rheological testing. It was measured on a Netzsch DSC 214 Polyma differential scanning calorimeter under an inert atmosphere. Approximately 5-10 mg of the sample was placed in a ceramic pan and heated from room temperature to 150 °C and then held isothermally at 150 °C for 5 *min* to eliminate any thermal history. In the next cycle, the sample was gradually cooled to 0 °C followed by a second heating cycle to 150 °C. The same heating/cooling rate of 5 °C/min was used for all cycles. The glass transition temperatures were determined from the second heating ramp.

Functionalized polycyclooctenes. As functionalized polynorbornenes, polycyclooctenes are amorphous polymers with negative T_g values. DSC experiments were performed on a TA Instruments DSC Q2000 calorimeter equipped with a TA Instruments Refrigerated Cooling System 90. In the first heating cycle, the thermal history was removed, while holding the sample at an elevated temperature (120 °*C*). For functionalized polycyclooctenes, the temperature range used was from -90 °*C* to 120 °*C*. The same heating/cooling rate of 5 °*C/min* was used for all three cycles, and finally, the T_g was obtained from the second heating cycle.

2.2.4 Rheological Measurements

The rheological properties of all polymers used in this thesis were measured by using shear rheometry, uniaxial extension, and capillary flow. The linear and nonlinear viscoelastic behavior of polymers were studied by using the Anton Paar MCR 501 and MCR 702 rotational rheometers equipped with various geometries, depending on the tests performed. Simple extensional

experiments were performed using the second generation Sentmanat extensional rheometer (SER2). Finally, capillary experiments were performed by using the Instron 5967 Dual Column Tabletop Testing System, equipped with a load cell (30 kN capacity; ± 0.5 % accuracy) and barrel (diameter 0.952 cm). The experimental procedures for all these different tests are summarized below.

2.2.4.1 Ionomers

Ionomers and their corresponding copolymers are semi-crystalline materials with a melting point of around 90 °*C* (see Appendix B). The temperatures chosen for performing a comprehensive rheological study were well above the melting temperature to ensure that all crystals were melted.

Dynamic oscillatory shear experiments. Several dynamic oscillatory tests were performed within the limits of linear viscoelasticity as follows. Firstly, the time sweep test to determine the thermal stability of polymers by isothermal heating of the sample under applied continuous oscillations (frequency of 0.1 Hz and strain amplitude of 0.05) for more than three hours at different temperatures (120 - 180 °C). Second, the strain sweep was performed to identify the threshold of linear viscoelasticity at a constant temperature of 140 °C and a frequency of 0.1 Hz. Finally, the frequency sweep at a constant strain of 0.05 was done to determine viscoelastic moduli at several temperatures from 120 - 180 °C. Using the time-temperature superposition principle, the obtained curves were shifted horizontally to construct the master curves of storage, loss moduli, and complex viscosity at the reference temperature of 140 °C. These experiments were performed by using the MCR 501 rheometer equipped with the cone-and-plate geometry (diameter of 25 *mm* and 4° angle).

Transient shear experiments. Two experiments, namely stress relaxation and start-up of steady shear, were performed at a given temperature. First, the stress relaxation tests were performed at different strains (0.05 to 10) in order to obtain the damping function, $h(\gamma)$ (discussed in Chapter 1) at the reference temperature of 140 °*C*. Second test is the start-up of steady shear which is used to obtain the viscosity and define the flow curve of the polymer. At the reference temperature, a constant shear rate was applied starting from a small shear rate of 0.1 s^{-1} and increasing it to as high as 20 s^{-1} . The Anton Paar MCR 702 rheometer equipped with a cone-partitioned-plate geometry is used for these experiments. The top part consists of a stationary ring whose has a diameter of 25 *mm* and a plate of 8 *mm*. The latter is placed in the central part of the ring and connected to the transducer. The bottom plate is in the shape of a cone with an angle of 4° and diameter of 25 *mm*.

Uniaxial extensional experiments. The second generation SER2 was used for simple extensional experiments. The uniaxial extension was conducted at the reference temperature of 140 °*C* and at several Hencky strain rates (0.5 to 5 s^{-1}) on the samples prepared as films with a width of 9.2 *mm* and thickness of 1 *mm* to obtain the extensional properties of polymers. Simple extensional experiments are significant for ionomers, as the level of strain hardening can be related to the level and strength of ionic associations.

Capillary experiments. To understand the flow properties of associating polymers in pressure driven flows, capillary experiments were performed. A series of capillary dies having the same diameter, D, and different length-to-diameter L/D ratios were used in order to apply the end pressure correction to the experimental data and to determine the effect of pressure on viscosity. Additionally, capillary dies with the same length-to-diameter ratio, and various diameters were

employed to identify the presence of slip. Different shear rates in the range of 5 to 1000 s^{-1} were applied to the sample at the reference temperature.

2.2.4.2 Functionalized Polynorbornenes

Amine derivatives of polynorbornene polymers have T_g around 45 – 80 °C due to their rigid polymer backbone and depending on the type of functional group. Additionally, the presence of side functional groups that can form strong hydrogen bonds lead to the formation of a threedimensional network, and as a result, a soft solid is formed. Therefore, all rheological measurements should be performed at elevated temperatures. Two distinct groups of experiments were used to characterize the rheological response of these polymers.

Dynamic oscillatory shear measurements. As previously noted for ionomers, three oscillatory shear tests were performed, namely time, strain, and frequency sweep experiments. The time sweep test was done to ensure the thermal stability of the sample for at least one hour at a high temperature, that is enough to complete testing. It was carried out at several temperatures (100 - 200 °*C*) with an applied frequency of 0.1 *Hz* and strain amplitude of 0.01. For the strain sweep test, the used frequency was 0.1 *Hz* at the reference temperature of 120 °*C*. Finally, the frequency sweep was conducted in the range of temperatures from 100 to 200 °*C* and strain of 0.01. The construction of master curves was achieved by applying horizontal and vertical shift factors. All these tests were performed by using the MCR 702 equipped with cone-partitioned plate that was described in the previous section.

Uniaxial extensional experiments. Simple extension experiments were performed by using SER2 at a reference temperature of 120 °*C* and several Hencky strain rates (0.01 to 5 s^{-1}). Samples were cut as a strip with a specific width of 6 *mm* and thickness of 0.2 *mm*. The level of

strain hardening can be related to the degree and strength of hydrogen bonding in aminefunctionalized polynorbornene polymers.

2.2.4.3 Functionalized Polycyclooctenes

Amine-containing polycyclooctenes are amorphous polymers that have low T_g values of around -10 °*C* which is influenced by the nature of attached pendant side groups. Thus, all rheological measurements were performed at room temperature. As discussed for the functionalized polynorbornenes, these elastomeric materials were examined by using dynamic oscillatory shear measurements. Since this material clearly shows self-healing characteristics, additional tests were conducted to demonstrate this unique property.

Dynamic oscillatory shear measurements. Once again, time, strain, and frequency sweep tests were used to characterize these materials within the linear viscoelastic region. The time sweep was done at several temperatures ($30 - 90 \ ^{\circ}C$), frequency of 0.1 *Hz* and strain 0.01. The linear viscoelastic region was obtained from the strain sweep by applying a constant frequency of 0.1 *Hz* at the reference temperature of $30 \ ^{\circ}C$. Lastly, the frequency sweep test was conducted at several temperatures ($30 - 90 \ ^{\circ}C$) and strain of 0.01. In contrast to the case of functionalized polynorbornenes, these materials are thermorheologically simple. Therefore, master curves were obtained by applying only horizontal shift factors. Since these materials can be produced on the gram-scale, tests were carried out by using the cone partitioned plate geometry installed on the MCR 702 rheometer.

Self-healing experiments. The ability of self-healing of functionalized polycyclooctenes was demonstrated by performing tensile tests at room temperature without employing any external stimuli, such as pressure, heat, or solvent. This procedure consists of the following steps as follows.

Firstly, the stress-strain curve of the virgin sample was recorded at room temperature by applying a small Hencky strain rate of $0.005 \ s^{-1}$. Then the sample was cut into two pieces, and its parts were gently brought into contact without using any external stimuli. These were allowed to spontaneously heal as a single component for different times at ambient conditions. Finally, the stress-strain curve was recorded under the same conditions as in the case of the virgin sample. The cycle of stretching, breaking and healing was repeated numerous times.

Chapter 3: Dynamics of Ethylene Methacrylic Acid Ionomers

3.1 Introduction

In this chapter, a comprehensive study of polymer dynamics of a series of ethylene methacrylic acid ionomers melts alongside the nonlinear rheology (shear and extensional) is discussed. The rheological behavior of these ionomers is compared to their corresponding parent copolymers, and the effects of ionic associations are examined. The interplay of the characteristic relaxation times (Rouse time, reptation, and a lifetime of associations) is assessed by using existing theories of associating polymers dynamics^{11,35,260} in an attempt to understand the contribution of the ion presence on the dynamics of these molecules. A version of this chapter was previously published in T. Tomkovic and S.G. Hatzikiriakos, *J. Rheol.*, (2018), **62**, 1319.

3.2 Experimental

The structure of the studied ethylene methacrylic acid ionomers and their corresponding copolymers has been presented in section 2.1. Additionally, the experimental methods used to investigate their dynamics and nonlinear rheological behavior have been described (see section 2.2).

3.2.1 Materials

As discussed above and presented in Chapter 2, the thermoplastic ionomers used for this study are ethylene methacrylic acid copolymers partially neutralized with sodium hydroxide, kindly supplied by DuPont Co., (Experimental Station, Wilmington, DE, USA). One way to look at an ionomer is as a terpolymer that consists of ethylene, methacrylic acid, and partially 58

neutralized methacrylic acid with sodium ions. Therefore, besides ionic interactions, ionomers can form hydrogen bonds. The content of MAA groups is in the range of 1.5 to 7.2 mol% (obtained by titration; explained in section 2.1.1) that can participate in both types of interaction (ionic and hydrogen bonding). Considering that ionomers are partially neutralized materials and due to the high degree of neutralization, their bulk properties are controlled by strong ionic interactions that form ionic clusters. However, hydrogen bonding is insignificant at elevated temperatures. In other words, the relatively small amount of unneutralized MAA groups that can potentially form hydrogen bonds have a negligible effect on their bulk properties at the applied temperatures.⁷ It has been reported that this type of functional groups forms relatively weak to medium strength hydrogen bonds. If the amount of MAA is up to 6 mol% hydrogen bonding associations have little to no effect on material properties.^{14,209} The complete list of studied materials is presented in Table 3.1 along with various thermophysical and rheological properties described below. The samples used in this work are labeled hereafter as X - Na Y, where X indicates the weight percent content of MAA, and Y is the degree of neutralization by sodium. Unneutralized polymeric samples are labeled as X - Na 0. Additionally, the grades of the original ionomers as received and labeled by DuPont Co., are also provided in Table 3.1.

Sample	MAA content, mol%	^а ф, %	^b M _w , g/mol	°η₀, kPa·s	^d E _{act} , kJ/mol
4.3 – Na 0		-	72,380	7	75.5
4.3 – Na 69 (Surlyn [®] 1601)	1.5	69	72,570	86.4	87.3
4.9 – Na 0		-	114,180	33	69.0
4.9 – Na 63 (Surlyn [®] 1605)	1.6	63	114,490	55.4	81.9
11.5 – Na 0			70,490	6.4	76.0
11.5 – Na 65 (Surlyn [®] 1707)	4.1	65	71,000	176	90.3
19.2 – Na 0		-	64,380	4.7	64.1
19.2 – Na 65 (Surlyn [®] 1802)	7.2	65	65,190	33.9	79.3

Table 3.1 List of ionomers and corresponding copolymers studied in this work together with their thermophysical and rheological characteristics

^aDegree of neutralization with sodium hydroxide; ^bThe estimated molecular weight; ^cZero shear viscosity at 140 °C; ^dActivation energies correspond to Arrhenius fit of time-temperature superposition horizontal shift factors.

3.2.2 Experimental Methods

The following experimental methods were used for this study which was already discussed in Chapter 2. They are listed here again, and some additional information is added. **FTIR spectroscopy**. This method is used to determine the degree of neutralization in the ionomers and validate the complete removal of sodium ions. (see section 2.2.1 for more details). The obtained results are presented in Appendix A.

TGA analysis. The degradation temperatures and the dependence of mass loss on temperature were determined by performing thermogravimetric analysis on ionomers and their corresponding copolymers. More details of the experimental procedure are given in section 2.2.1 and results presented in Appendix B.

DSC calorimetry. The transition temperatures of various ionomers and copolymers were obtained by using DSC (for more details see section 2.2.1). DSC thermograms are given in Appendix B.

Rheological measurements. After preparing the samples, the rheological characterization in the linear viscoelastic regime was conducted as explained previously in Chapter 2. Time sweep tests have shown that the ionomers and copolymers are thermally stable at the tested temperatures. Four temperatures, namely 120, 140, 160, and 180 °C for ionomers and 110, 120, 130, and 140 °C for copolymers were applied to determine the dynamic moduli and complex viscosity. Lower temperatures were used for the copolymers since at temperatures higher than 160 °C carboxylic acid dimers form linear and cyclic anhydrides.²⁶¹ The reference temperature of 140 °C for both ionomers and their parent copolymers was used to perform the time-temperature superposition principle and generate master curves of dynamic moduli and complex viscosity. To study the nonlinear viscoelastic properties experiments were carried out as described in section 2.2.4.1. Three different types of experiments were performed, i.e., stress relaxation, start-up of steady shear, and uniaxial extension.

3.3 Results and Discussion

3.3.1 Structural and Thermal Characteristics

These organic polymers consist of a small content of comonomer bearing pendant ionic groups which, due to the electrostatic forces, associate into aggregates. Salts of ethylene methacrylic acid copolymers have a very complex morphology including the crystalline structure of polyethylene, amorphous chain segments, and aggregates of ionic groups. Further complexity comes from the fact that these ionomers are partially neutralized, meaning that besides the ionic interactions hydrogen bonding associations are possible. Therefore, it is of utmost importance to identify the content of methacrylic acid comonomer and the level of neutralization. As described in Chapter 2, these two ionomer characteristics were determined by using the FTIR spectroscopy and titration analysis and results summarized in Table 3.1. All ionomer samples have different content of MAA but a similar degree of neutralization. These values are useful to calculate the number of ionic associations, which are needed for analyzing/calculating the lifetime of ionic associations and thus other characteristic relaxation times.

The thermal properties of ionomers were obtained by using the DSC technique. DSC thermograms can be found in Appendix B. All transition temperatures are listed in Table 3.2.

	I Heating							Cooling		II Heating		
Sample	Secondary PE crystallites		Primary PE crystallites			Primary PE cryst.		Primary PE crystallites				
	^a T _i ,	^b ΔH _i ,		^c T _m ,	$^{d}\Delta H_{m},$	еα,		$^{f}T_{c}, ^{\bullet}C$		<i>T</i> _{<i>m</i>} ,	ΔH_m ,	α,
	•C	J/g		•C	J/g	%				•C	J/g	%
4.3 – Na 0	44	2		98	51	18		80		98	64	23
4.3 – Na 69	80	32		100	37	13		63		99	48	17
4.9 – Na 0	43	3		94	50	18		75		94	63	23
4.9 – Na 63	55	11		94	38	14		64		96	42	15
11.5 – Na 0	49	2		93	43	15		72		94	45	16
11.5 – Na 65	57	13		94	33	12		53		94	27	10
19.2 – Na 0	43	2		97	78	28		82		97	79	28
19.2 – Na 65	56	7		99	43	15		69		99	57	21

Table 3.2 Differential scanning calorimetry (DSC) results for ionomers and corresponding copolymers

^aMelting peak temperature of imperfect polyethylene crystallites during the first heating cycle. ^bHeat of fusion of imperfect polyethylene crystallites during the first heating cycle. ^cMelting peak temperature of primary polyethylene crystallites. ^dHeat of fusion of primary polyethylene crystallites. ^eDegree of crystallinity of primary polyethylene crystallites. ^fCrystallinity peak temperature of primary polyethylene crystallites.

The DSC thermograms revealed typical two endothermic peaks during the first heating that are denoted by T_i and T_m .^{262–265} The lower temperature peak, T_i , represents the melting of imperfect polyethylene crystallites firstly explained by Marx and Cooper²⁶⁵ and later verified by Loo et al.²⁶⁴. The higher temperature peak, T_m , belongs to the melting of the polyethylene crystallites. During cooling, polyethylene chains are crystallizing, which is observed by the formation of a single exothermic peak, denoted by T_c . The second heating reveals only one endothermic peak at the temperature that is almost the same as T_m , with practically similar values of heat of fusion. During this cycle of heating the lower temperature peak, T_i has vanished. This endothermic peak, coming from small 'secondary' crystallites of PE which cannot be reformed during fast cooling, was observed after annealing at room temperature or temperatures well below the melting point of primary PE crystallites, T_m . The degree of crystallinity, α , was calculated from the heat of fusion by taking the heat of fusion for 100% crystalline polyethylene to be 278 J/g.²⁶⁶

Whereas the neutralization of copolymers with sodium ions does not have a significant effect on the melting temperature of polyethylene crystals, the degree of crystallinity is reduced by approximately 30%. The Young's modulus is significantly increased, shown by Wakabayashi and Register²⁶⁷, which they explained by the growth of the amorphous-phase modulus in spite of the crystallinity reduction. The development of spherulite crystals in ionomers is affected by the content of MAA and ions, since the acidic and salt groups are located in an amorphous phase and on the surface of crystals.²⁶⁵

3.3.2 Linear Viscoelasticity

As mentioned above, the rheological properties of the ionomer were determined using the cone and plate geometry. First strain sweep experiments were performed to determine the limits of linear viscoelasticity at the angular frequency of 6.28 rad/s and the temperature of 140 °C. Linear viscoelasticity has been observed within strain amplitudes of about 0.2 or less practically for all samples studied.

The effect of drying (moisture content) on the rheological measurements is shown in Figure 3.1. A minimum of 7 day-drying at 75 °*C* should be performed to obtain consistent results as the results for seven day- and 14 day-drying were found to be nearly identical. None or less than seven

days of drying leads to a decrease of rheological properties, i.e. complex viscosity. This decrease is due to the sorption of water molecules to multiplets and clusters leading to weakening of the ionic interactions.²⁰²



Figure 3.1 The effect of drying (moisture content) on the rheological measurements for sample 4.9–Na 63 at 140 $^{\circ}C$

Dynamic shear measurements were carried out at 20 °C intervals, ranging from 120–180 °C. The resulting storage, G', and loss moduli, G'', were shifted to the reference temperature of 140 °C using the time-temperature superposition principle. The master curves of dynamic moduli and complex viscosity of all samples are depicted in Figures 3.2 a)-d). In each Figure, the linear viscoelastic properties of ionomers are compared with those of the corresponding copolymers,

where the effect of ionic associations is evident. In most cases, an increase of these properties (G', G") by one order of magnitude is observed (particularly at the terminal zone). Horizontal shifting of the ionomer data superposes well with that of its copolymer, indicating a similar thermal dependence of relaxation with simply longer relaxation times for the ionomers (see Appendix C). To this end, the negligible effect of the present hydrogen bonds in both ionomers, and their corresponding copolymers simplifies the picture. It is expected that ionomers with a lower degree of neutralization and higher MAA content would exhibit more complex dynamics. The differences in G' and G'' between ionomers and corresponding copolymers seem to decrease at higher frequencies as the inverse of these frequencies (time scales) are closer to the lifetime of ionic associations. In other words, if the lifetime of ionic associations defined here as τ_s , is less than the inverse of a particular frequency, $1/\omega_s$, its effect on the linear viscoelastic measurements is negligible or slowly diminishes at frequencies $\omega < \omega_s$. The experimental data of Figure 3.2 shows that the lifetime of ionic associations are small, practically of the order of $10^{-4} - 10^{-3}$ s. As will be shown later the lifetime of hydrogen bond associations are even lower, well separated from those of ionic associations. A detailed discussion of the various relevant relaxation times is postponed until a subsequent section. In spite of the good applicability of tTS to produce the master curves, it should be made clear that this is not expected to be the case at lower temperatures (closer to T_m) where hydrogen bonding is stronger.^{14,209}



Figure 3.2 The master curves of the storage and loss moduli (symbols) along with the Maxwell model fit (lines) for all ionomer samples (filled symbols) and corresponding copolymers (unfilled symbols) studied in this work at the reference temperature of 140 $^{\circ}C$

The continuous lines in Figure 3.2 represent fits of the Maxwell model (Equation 3.1).

$$\tau_{ij}(t) = \int_{-\infty}^{t} \sum_{i=1}^{N} G_i \exp\left(-\frac{t-t'}{\lambda_i}\right) \dot{\gamma}_{ij}(t') dt' \qquad (3.1)$$

Where G_i is the relaxation strengths and λ_i are the relaxations times. These values are summarized in Table 3.3 for all ionomers and their corresponding copolymers and plotted in Figure

3.3. Six relaxation times are enough for both ionomers and their corresponding copolymers to provide optimum representation. The relaxation time distribution is shifted to higher values of the relaxation modulus and higher times obviously due to the effect of ionic interactions. The relaxation time distributions of ionomers and copolymers converge at small relaxation times, and extrapolation of these distributions indicate that at time scales in the range of $10^{-4} - 10^{-3} s$, the effects of ionic interactions are negligible.

Table 3.3 Maxwell relaxation spectrum of all ionomers and corresponding copolymers at the reference temperature of 140 $^{\circ}C$

Relaxation time	Relaxation modulus G: Pa	Relaxation time	Relaxation modulus G: Pa		
Ai, S	01, I W	Ai, S	0,, 1 0		
Sample 4	4.3 – Na 69	Sample 4.3 – Na 0			
5.43×10^{-4}	5.32×10^{5}	2.73×10^{-4}	3.49×10^{5}		
7.15×10^{-3}	2.16×10^{5}	2.66×10^{-3}	9.44×10^4		
7.11×10^{-2}	8.37×10^4	2.17×10^{-2}	3.18×10^4		
0.692	2.35×10^4	1.66×10^{-1}	9.09×10^{3}		
6.77	4.76×10^{3}	1.22	1.89×10^{3}		
69.2	5.11×10^{2}	9.36	2.28×10^2		
Sample	4.9 Na 63	Sample 4.9 Na 0			
6.12×10^{-4}	5.42×10^5	3.88×10^{-4}	3.92×10^{5}		
8.77×10^{-3}	1.85×10^{5}	5.58×10^{-3}	1.25×10^{5}		
8.42×10^{-2}	6.20×10^4	6.31 × 10 ⁻²	4.39×10^4		
0.798	$1.59 imes 10^4$	7.05×10^{-1}	$1.17 imes 10^4$		

Relaxation time	Relaxation modulus	Relaxation time	Relaxation modulus G _i , Pa		
λ_i, s	G _i , Pa	λ_i, s			
Sample	4.9 Na 63	Sample 4.9 Na 0			
7.48	3.02×10^{3}	8.33	2.35×10^{3}		
75.5	2.72×10^2	-	-		
Sample 2	11.5 Na 65	Sample 11.5 Na 65			
4.95×10^{-4}	6.90×10^{5}	2.01×10^{-4}	2.49×10^{5}		
7.62×10^{-3}	3.12×10^{5}	2.29×10^{-3}	7.85×10^{4}		
7.83 × 10 ⁻²	1.37×10^{5}	2.02×10^{-2}	2.81×10^4		
0.761	4.15×10^4	1.70×10^{-1}	8.09×10^{3}		
7.85	8.57×10^3	1.39	1.60×10^{3}		
86.9	9.34×10^2	16.8	1.22×10^2		
Sample 2	19.2 Na 65	Sample 19.2 Na 0			
5.29×10^{-4}	4.92×10^5	4.05×10^{-4}	2.90×10^{5}		
6.66×10^{-3}	1.64×10^{5}	4.03×10^{-3}	5.90×10^4		
6.22 ×10 ⁻²	5.41×10^4	3.07×10^{-2}	1.95×10^4		
0.565	1.40×10^4	2.30×10^{-1}	5.06×10^{3}		
4.96	2.60×10^{3}	1.67	9.24×10^2		
44.6	2.32×10^2	14	7.77×10^1		

Figure 3.3 The distribution of the Maxwell relaxation strengths and times for all ionomers and their corresponding copolymers

The time-temperature superposition (tTS) worked well over the entire frequency range as the temperature range used (120 – 180 °C) does not seem to affect the Rouse relaxation and the ionic dissociation significantly.¹⁹⁴ The Van Gurp-Palmen method has been used to conclude the applicability of tTS (see Appendix C).²⁶⁸ Good superposition of the linear viscoelastic data of ionomers similar to those of the present work was reported by others^{187,191,202,203,205,269,270} except in work by Earnest and MacKnight²⁷¹, who have reported the failure of tTS to their loss modulus data, although they have questioned the precision of their measurements. Failure of tTS is typically observed for storage modulus at small frequencies in the terminal zone ($\omega \ll 1/\tau_{rep}$) since $G' \sim \lambda_i^2$ and $G'' \sim \lambda_i$, making G' more sensitive to subtle changes in the microstructure. The horizontal shift factors, α_T , determined from the superposition of *G*' and *G*'', were found to follow the Arrhenius equation given below (Eq. 3.2), where E_{act} is the flow activation energy (see Appendix C). The calculated activation energies for all ionomers and their corresponding copolymers are listed in Table 3.1. The E_{act} values for the ionomers are much greater than that of their corresponding copolymers, an effect also reported by Tierney and Register.²⁰⁵ These differences will be used later to calculate the characteristic lifetimes of ionic associations.

$$a_{T} = \exp\left[\frac{E_{act}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$
(3.2)

It should be noted however that the energy of activation, E_{act} , is a function of molecular weight, its polydispersity, and branching²⁷², i.e., E_{act} increases with the increase of these three parameters. It is also a function of the degree of neutralization, and content of methacrylic acid comonomer.^{191,202,204,205,269–271} Table 3.4 summarizes values of the energy of activation reported in the literature for sodium ionomers.^{202,204,205,269–271} The values listed in Table 3.4 indicate that the energy of activation increases with the increase of the degree of neutralization (significantly) as well as with the increase of the MAA content (moderately). While trends can be observed from the reported values, the available data is limited to be used in order to derive quantitative correlations due to the dependence of the energy of activation on several parameters (MAA content, degree of neutralization, molecular weight, branching).

Reference	E _{act} , kJ/mol	MAA mol%	Degree of Neutralization, %	M _n , g/mol	Mw, g/mol	₫Ð
191	84	4.1	59	-	-	-
271	70	3.5	70	-	-	-
204	98	5.4	54	19,200	94,500	4.9
202	80	4.1	65	17,750	71,000	4
269	75	5.4	20	19,200	94,500	4.9
205	70-80	4.1	0-80	17,750	71,000	4
270	103	6.4	58	21,200	215,500	10.2
270	96	6.4	54	21,200	215,500	10.2
Present work	90	4.1	65	17,750	71,000	4

Table 3.4 List of reported energy of activation, E_{act} , values for sodium containing ionomers and their corresponding molecular characteristics

^{*a*}Polydispersity, M_w/M_n

Figure 3.4 compares the complex viscosity curves of the various polymers in order to obtain an idea of molecular weight differences between samples. The zero-shear viscosity is an indication of the molecular weight, and it is used here to estimate the molecular weights of the various polymers used. The molecular weight of sample $11.5 - Na \ 65$ is 71,000 g/mol as its viscosity material function matches the one studied by Register et al.^{202,205}. Its corresponding copolymer $11.5 - Na \ 0$ should have slightly smaller molecular weight due to the small amount of metals ions that it contains. The zero-shear viscosities of the other copolymers can be used together with the scaling law $\eta_0 \propto M_w^{3.4}$ to provide an estimate of their molecular weights and

corresponding ionomers once the number of ionic groups are estimated (discussed below). It should be mentioned that although the scaling $\eta_0 \propto M_w^{3.4}$ is applicable mostly for linear polymers, Janzen and Colby²⁷³ found that this works for branched polymers of similar simple structure. In fact, the parent copolymers have a simple, similar branched structure ("quasilinear")²⁷³ since the terminal zone (zero-shear viscosity) is reached at frequencies of about 0.1 *rad/s*. The values of the estimated molecular weights, M_w , of all polymers used are listed in Table 3.1.

Figure 3.4 The master curves of the complex viscosities of ionomers and corresponding copolymers at the temperature of 140 °C. Solid lines represent the Maxwell model

3.3.3 Characteristic Relaxation and Associations Lifetime

Following the scaling analysis of Leibler et al.³⁵ of entangled ionomers and further summarized by Chen et al.⁴⁴, an attempt was made here to provide an approximation based on scaling arguments. Starting first with the reptation time that can be written as $\tau_{rep} = \tau_e (N/N_e)^3 =$ $\tau_s N^3 N_e^{-1} N_s^{-2}$, where τ_e is the Rouse time of an entanglement strand, $\tau_e = \tau_s N_e^2 N_s^{-2}$, τ_s is the associations lifetime, N_e is the number of segments per entanglement, N_s is the number of segments per ionic group, and N is the number of segments of the full chain.^{35,44} These scaling laws can be expressed in terms of the average number of ionic associations per chain, Z_s , and the average number of entanglements per chain, Z_E , as $\tau_s = \tau_{rep}/(Z_E Z_s^2)$ and $\tau_e = \tau_s Z_s^2/Z_E^2$, respectively. It is noted that the last three parameters specify the structure of the polymer.⁴⁴ Knowing these characteristic relaxation times, the isothermal modulus can be calculated as contributions from glassy, Rouse, sticky Rouse and sticky-double reptation (excluding the contribution of the glassy part which is important at extremely high frequencies) shown below.⁴⁴

$$G(t) = G_g(t) + G_{Rouse}(t) + G_{SR}(t) + G_{rep}(t)$$
(3.3)

The glassy modulus, G_g , is related to low temperature (high frequencies) and in the case of ionomers consists of two elements; one corresponds to lower T_g (fast relaxation) and the second is affected by higher T_g of the polymer segments that are constrained by stickers (ionic interactions).⁴⁴ The relaxation of the part of the chain between entanglements that contain stickers consists of two Rouse relaxation mechanisms. The first one, G_{Rouse} , corresponds to Rouse motion between stickers shorter than the associations lifetime and the second one, G_{SR} , is delayed by associations of ions with lifetime, τ_s .^{11,44,274} Finally, the sticky-double reptation modulus, G_{rep} , represents the terminal relaxation of sticky chains and is driven by a disentanglement when either
of two chains diffuses away from its tube.^{44,274} The detailed expressions for each contribution can be found elsewhere.^{11,44}

The reptation time can be calculated from linear viscoelasticity by finding the interception of the two limiting behaviors, $G' \sim \omega^2$ and $G'' \sim \omega$, at ω_{rep} and inverting this to obtain $\tau_{rep} =$ $1/\omega_{rep}$. For the sake of simplicity, the longest relaxation time was determined from the Maxwell fit of the linear viscoelastic moduli and the longest relaxation time was taken as the reptation time, τ_{rep} (Table 3.3). The determined values of the lifetime of ionic associations are listed in Table 3.5. The calculations for the associations lifetime proceed as follows. Considering a molecular weight of 71,000 g/mol and the entanglement molecular weight of polyethylene 1,200 g/mol²⁷⁵ the number of entanglements per chain is $Z_E = 71,000/1,200 \approx 59$. The value of the number of ionic associations per chain, Z_S , can be estimated by using the determined content of MAA and degree of neutralization as follows, $Z_S = f_{MAA}\phi_{Na} \frac{M_w}{M_{MAA}}$, where f_{MAA} is the mol fraction of MAA, ϕ_{Na} is the degree of neutralization, and M_{MAA} is the molecular weight of the MAA comonomer. For instance, the number of ionic associations for sample 4.3 – Na 69 was calculated as $Z_S =$ $0.015 \times 0.69 \times (72,570/86) \approx 8$.

Sample	MAA, mol%	Mw, g/mol	φ, %	Z_E	Zs	$ au_{rep}$, s	τ _s , s	$ au_s/ au_{s,\mathcal{C}}$
4.3 – Na 69	1.5	72,570	69	60	8	69.2	1.6×10^{-2}	3.5
4.9 – Na 63	1.6	114,490	63	95	14	75.5	4.3×10^{-3}	3.3
11.5 – Na 65	4.1	71,000	65	59	22	86.9	3.0×10^{-3}	2.2
19.2 – Na 65	7.2	65,190	65	54	35	44.6	$6.5 imes 10^{-4}$	1.3

Table 3.5 Estimation of characteristic times of the various ionomers

The following discussion arises from the calculated associations lifetime. The values of the lifetime of associations practically are of the order of $10^{-4} - 10^{-2} s$, with most to be of the order of $10^{-3} s$ or lower which was also concluded from Figure 3.3, where the viscoelastic moduli of ionomers and those of their corresponding copolymers seem to converge. A value of $1.3 \times 10^{-3} s$ was reported for the lifetime of associations (referred to as 'ion hoping') by Tierney and Register²⁰⁵ for an ionomer similar to 11.5 - Na 65, a value to be compared with the value of $3.0 \times 10^{-3} s$, reported in Table 3.5. An estimation of $10^{-4} s$ has been reported by Chen et al.¹¹ In addition, τ_s is decreasing with increase of Z_s , and scales as $\tau_s \propto Z_s^{-2}$ i.e., increase of the number of association defines smaller chain segments that relax faster. Although the values listed in Table 3.5 are estimates, they are certainly of the correct magnitude. Note also that for all the ionomers studied here $Z_E > Z_s$ (number of entanglements per chain exceed the number of ionic interactions per chain) and the Rouse time of segment between stickers is smaller than the Rouse time of segment between entanglements and as such its effect is not evident in Figure 3.2.²⁷⁰

An alternative method to calculate associations lifetime is by using the energy of association, E_a , an important parameter for associative polymers which can be related to the

lifetime of associations by $\tau_s = \tau_0 exp(E_a/RT)$, where τ_0 is an attempt time for thermal motion, taken as the motion time scale without stickers.⁴⁵ The association energy, E_a can be hypothesized to be equal to the difference of the activation flow energy of the ionomer, $E_{act,i}$, and the activation flow energy of the corresponding copolymer, $E_{act,C}$ (see Table 3.6) (*R. H. Colby, private communication*). The attempt time τ_0 can be approximated with the Rouse time of the copolymer⁴⁵, a good assumption as these copolymers contain a low degree of MAA that form hydrogen bonds of negligible effect.¹⁴ In turn, this can be calculated from the reptation time of the copolymer (longest relaxation time listed in Table 3.3), $\tau_{rep,C}$ and the scaling law, $\tau_{rep,C}/\tau_{e,C} = (N/N_e)^3$. The values of associations lifetimes are listed in Table 3.6 and they can be compared with those in Table 3.5, which seem to be of the correct magnitude.

Sample	M _w , g/mol	$E_a = E_{act,i} - E_{act,C},$ kJ/mol	Z_S	$ au_{rep,C}$, s	$ au_{e,C} = au_0, s$	$ au_s, s$
4.3 – Na 69	72,570	11.8	8	9.36	4.3×10 ⁻⁵	1.3×10 ⁻³
4.9 – Na 63	114,490	13.0	14	8.33	1.0×10 ⁻⁵	4.1×10 ⁻⁴
11.5 – Na 65	71,000	14.3	22	16.8	8.3×10 ⁻⁵	5.3×10 ⁻³
19.2 – Na 65	65,190	15.2	35	14.0	9.1×10 ⁻⁵	7.6×10 ⁻³

Table 3.6 Estimation of the energy of ionic interactions

It should be realized that a small experimental error in the calculation of the activation energy is augmented due to the exponential function used for its calculation. Despite that, the energy of associations, E_a , weakly correlates with the number of associations per chain Z_s (see Tables 3.1 and 3.5). Finally, the various methods discussed, give an estimate of the times τ_s to be in the range of 10⁻⁴ to 10⁻³ s.

An estimate of the lifetime of hydrogen bond associations can also be performed. Using the scaling $\tau_{rep} = \tau_e (N/N_e)^3 = \tau_s N^3 N_e^{-1} N_s^{-2}$ for both ionomer and corresponding copolymer, the following expression can be produced for the ratio of both lifetimes of ionic and hydrogen bonding associations, $\tau_s/\tau_{s,C} = (\tau_{rep}/\tau_{rep,C})\phi^2$, where ϕ is the degree of neutralization and $\tau_{s,C}$ is the lifetime of hydrogen bonding in the copolymers (see Table 3.5). As seen the lifetime of hydrogen bonds are much smaller than those of ionic associations with the exception of the last polymer. This ionomer contains the higher amount of MAA groups (7.2 mol%), where the effects of hydrogen bonds start becoming more significant.¹⁴ The fact that the two associations lifetimes are sufficiently separated (not both probed in a single isothermal experiment) might be the reason for the applicability of tTS discussed above.

3.3.4 Nonlinear Rheology of Ionomers and Parent Copolymers

3.3.4.1 The Damping Function

Stress relaxation experiments after the imposition of step strains were performed using the cone-partitioned plate geometry. The relaxation modulus was measured at various strains from 0.05 to 10 at the reference temperature of 140 $^{\circ}C$. The threshold between the linear and nonlinear region was found to be at the shear strain of 0.2 with the relaxation curves obtained at lower values to be independent of strain.

Figure 3.5 a) depicts the relaxation modulus of ionomer 4.3 - Na 69 (taken as an example) and corresponding copolymer, 4.3 - Na 0, at different shear strains. Figure 3.5 b) plots the reduced relaxation modulus of these two samples obtained by shifting the data of nonlinear to the linear viscoelastic regime.¹⁶⁹ Excellent superposition is obtained for both ionomer and parent copolymer. Similar results were obtained for all other samples. The shift factors essentially define the damping function, $h(\gamma)$, that is defined by following equation, where G(t) and $G(\gamma,t)$ is the linear and nonlinear relaxation modulus, respectively.¹⁶⁹

$$h(\gamma) = \frac{G(\gamma, t)}{G(\gamma)}$$
(3.4)



Figure 3.5 a) Relaxation moduli after imposition of various sudden step shear strains for the 4.3 - Na 69 melt at the reference temperature of 140 °C; b) Vertically shifted relaxation moduli at various strains on the linear relaxation modulus to determine the shift factors for the damping function

The obtained values of the shift factors that make up the damping function were plotted against shear strain (Figure 3.6) and fitted using the Wagner damping function which for simple shear is reduced to equation 3.5, where *n* is the Wagner parameter.²⁷⁶

$$h(\gamma) = \exp(-n\gamma) \tag{3.5}$$

A good fit of the experimental results was obtained with the Wagner parameter with values n = 0.11 to 0.17, depicted in Figure 3.6 with values of n listed in the legend. Overall the corresponding damping function values of ionomers are higher than those of their parent copolymers. In other words, the ionic interactions slow down the relaxation of the polymers, the more so for the lower molecular weight polymers.



Figure 3.6 The damping function of ionomers and corresponding copolymers obtained from step strain relaxation experiments and its fit using the Wagner model

3.3.4.2 Start-up of Steady Shear

Using the Anton Paar rotational rheometer (MCR 702) equipped with cone-partitioned plate geometry, start-up of steady shear was performed for ionomers and their corresponding copolymers. Figure 3.7 shows the experimental shear stress growth coefficient of the ionomer 4.9 - *Na* 63 (taken as an example) and its parent copolymer 4.9 - *Na* 0 at five shear rates from 0.1 s^{-1} to 20 s^{-1} . The corresponding LVE envelopes are also plotted showing excellent agreement with the steady shear data. The viscosity values from the steady shear tests have been found to agree with those of dynamic viscosity implying that the Cox-Merz rule applies for these polymers.



Figure 3.7 Shear stress growth coefficient at various values of constant shear rates for sample 4.9 - Na 63 and its corresponding copolymer 4.9 - Na 0, at the reference temperature of 140 °C. Continuous lines represent the linear viscoelastic envelope (LVE)

3.3.4.3 Uniaxial Extension

As discussed above, using the SER2 fixture, uniaxial extension experiments were conducted at the reference temperature of 140 °*C* at several Hencky strain rates, namely 0.5, 2, and 5 s^{-1} . The results for all four ionomers and their corresponding parent copolymers are presented in Figure 3.8 where the presence of strain hardening is evident. The strain hardening for the copolymers is due to a combination of the effects of branching and hydrogen bonding. It is clear from Figure 3.8 that strain hardening effects are stronger in the case of ionomers and these differences scale with the number of associations per chain, Z_5 . For example, compare the differences for samples with the lowest amount of MAA, 4.3 - Na 69, and 4.3 – Na 0 in Figure 3.8

a) ($Z_S = 8$) and those of samples with the highest content of MAA, 19.2 - Na 65, and 19 - Na 0 in Figure 3.8 b) ($Z_S = 35$). In addition, the growth of η_E^+ is more abrupt in the case of ionomers which is due to the extra relaxation mode of the lifetime of associations at short time scales.



Figure 3.8 Comparison of uniaxial stress growth coefficient for ionomers and corresponding copolymers at different Hencky strain rates and temperature of 140 $^{\circ}C$

3.4 Summary

The rheology of entangled polydisperse ethylene methacrylic acid ionomers was studied using a cone and plate rheometer equipped with a partitioned plate, and the SER. The ionomers were unneutralized by removing the ions to produce their parent copolymers in order to examine the effects of ionic interactions. Emphasis had been placed on the distribution of the relaxation times to identify the characteristics times such as reptation, Rouse, and the associations lifetime. As such scaling laws have been used to calculate the order of magnitude of the lifetime of associations and the association energy that are important parameters for their rheological modeling. The lifetime of associations, τ_s , was found to scale with the number of associations per chain, Z_s ($\tau_s \propto Z_s^{-2}$), and to be of the order of 10⁻⁴ to 10⁻² s using three different methods showing that their effects at time scales greater than 10⁻² s are significant. For comparison, these time scales are smaller than the Rouse times for the cases where the number of associations is smaller than the number of entanglements per chain. The energy of association was found to be of the order of 10-15 *kJ/mol* and it was found to scale weakly with the number of associations per chain.

Additionally, the rheological comparison of ionomers and corresponding copolymers included the linear viscoelastic moduli, the damping function, steady shear and extensional rheology showing the significant effects of ionic interactions. Overall due to the presence of ionic associations the relaxation processes slow down, and the modulus shifts to significantly higher values, the more so as the number of associations increases.

Chapter 4: Contraction Flow of Ionomers and Corresponding Copolymers

4.1 Introduction

Capillary rheometry is extensively used in both industry and academia to assess the rheological behavior of polymer melts at high shear rates. It can also be used to bridge the gap between fundamental rheology and processability of polymers in processes such as film blowing, blow molding and lately 3-D printing.^{169,171} When such a flow is used, and the raw data are collected, a number of important corrections should be applied before the rheological data can be compared with corresponding data from a rotational rheometer discussed in Chapter 1.^{277,278}

First, capillary involves flow through a contraction of a certain angle, where there is a large pressure drop known as entrance pressure (equivalent to Bagley correction if the exit pressure is considered negligible).^{277–279} This pressure is required to calculate the true shear stress and also frequently the apparent extensional rheology of molten polymers, a method well practiced in industry.^{280–282} Therefore, it is important to understand the origin of this excess pressure and consequently to be able to predict it. While many studies have previously attempted to examine the origin of entrance pressure and its prediction for high-density polyethylenes^{283,284}, low-density polyethylenes^{283,285–291}, linear low-density polyethylenes²⁸³, polylactides²⁹², and various pasty materials^{293–295}, the case of ionomers has not received any attention.

In this chapter, a comprehensive study of the capillary flow of several ionomers and their corresponding copolymers both experimentally and numerically is conducted by considering all possible capillary effects, combined and separately. Namely, the effects of entry pressure, pressure dependence on viscosity, and viscous heating will be considered in order to assess their significance. The flow behavior of the ionomers is compared to that of their corresponding 85

copolymers in order to signify the effects of ionic interactions on the flow patterns, corner vortex formation, strength, and size. Some parts of the following sections are reproduced with permission from the following publications: T. Tomkovic et al., *J. Non-Newtonian Fluid Mech.*, (2018), **262**, 131; T. Tomkovic et al., *Phys. Fluids*, (2019) **31**, 033102.

4.2 Experimental

4.2.1 Materials

Polymers used in this study were previously presented in Chapter 2, and their thermal and rheological properties were listed in Chapter 3 (Table 3.1). Pellets were annealed for one week at 75 °*C* prior measurements to obtain consistent results.

4.2.2 Capillary Measurements

The rheological characterization of all ionomers presented in Chapter 3 is used here to calculate the parameters of the constitutive integral model, namely the K-BKZ (Kaye, Bernstein, Kearsley, and Zapas) equation which is used for the flow simulations presented below.

Capillary flow tests were performed by using a constant piston speed capillary rheometer (Instron 5967 Dual Column Tabletop Testing System) with a reservoir of diameter 0.952 cm. The end pressure (Bagley correction) and the viscosity as a function of the wall shear stress, σ_w , and the apparent shear rate, $\dot{\gamma}_A = 32Q/\pi D^3$, were determined at the reference temperature of 140 °C, where Q is the volumetric flow rate and D is the capillary diameter.^{169,171,279} For the evaluation of the end-pressure effects, and the effect of pressure on the viscosity of the ionomer, several dies of the same diameter (D = 0.762 mm) and various length-to-diameter (L/D = 4, 14, 33), all having a

contraction angle of $2\alpha = 180^{\circ}$ were used. Also, an orifice die with the same diameter was used to determine the entrance pressure directly as a function of the apparent shear rate. To study possible slip effects, three capillary dies with the same *L/D* ratio, and various diameters (0.432, 0.889, and 1.22 *mm*), having a contraction angle of $2\alpha = 180^{\circ}$ were employed.

4.3 Governing Equations and Rheological Modelling

Conservation of mass, momentum and energy for incompressible fluids under nonisothermal, creeping, steady-flow conditions are given below.^{296,297}

$$\nabla \cdot \overline{u} = 0 \tag{4.1}$$

$$0 = -\nabla p + \nabla \cdot \bar{\tau} \tag{4.2}$$

$$\rho C_p \bar{u} \cdot \nabla T = k \nabla^2 T + \bar{\tau} : \nabla \bar{u}$$
(4.3)

Where ρ is the density, \bar{u} the velocity vector, p the pressure, $\bar{\tau}$ the extra stress tensor, T the temperature, C_p the heat capacity, and k is the thermal conductivity.

The K-BKZ constitutive model proposed by Wagner²⁷⁶ and modified by Luo and Tanner^{298,299} was used as a viscoelastic model:

$$\overline{\overline{\tau}} = \frac{1}{1-\theta} \int_{-\infty}^{t} \sum_{i=1}^{N} \frac{G_i}{\lambda_i} \exp\left(-\frac{t-t'}{\lambda_i}\right) \exp\left[-n\left(\beta I_{C_i^{-1}} + (1-\beta)I_{C_i} - 3\right)^{1/2}\right] \left[C_t^{-1}\left(t'\right) + \theta C_t\left(t'\right)\right] dt'$$
(4.4)

where λ_i and G_i are the relaxation times and relaxation modulus coefficients, N is the number of relaxation modes, n and β are material constants, and I_{C_t} , $I_{C_t^{-1}}$ are the first invariants of the Cauchy-Green tensor C_t and its inverse C_t^{-1} , the Finger strain tensor. The material constant θ is given by

$$\frac{N_2}{N_1} = \frac{\theta}{1 - \theta} \tag{4.5}$$

where N_1 and N_2 are the first and second normal stress differences, respectively. It is noted that θ is not zero for polymer melts, which possess a non-zero second normal stress difference. Its usual range is between -0.1 and -0.2 in accordance with experimental findings.²⁹⁶

The influence of the pressure on the viscosity of 19.2 - Na 65 and therefore for all others was found to be significant (results presented below). The viscosity dependence on pressure is defined by an exponential function, known as the Barus equation, which is:

$$a_p = \frac{\eta}{\eta_{p_0}} = \exp(\beta_p p) \tag{4.6}$$

where β_p is the pressure coefficient of viscosity, η_{p_0} is the viscosity at ambient pressure, and p the absolute pressure. The value of the absolute pressure was assumed to be $\Delta p/2$ based on the assumption that the pressure is dropping linearly along with the die, where Δp is the pressure drop along the whole length of the die including the entrance.

4.3.1 Non-isothermal Modelling

Luo and Tanner²⁹⁹ applied the time-temperature shifting concept in order to obtain the nonisothermal form of the K-BKZ model (Eq. 4.4). This was done by replacing the observer's time *t* in Eq. (4.4) with the particle's time ξ . They used the Morland-Lee hypothesis in a differential form to obtain the integral relation between the particle's elapsed time and the observing period:

$$d\xi = \frac{dt}{a_T(T)} \tag{4.7}$$

where ξ is the time measured by the material's internal clock, *t* is the observer's time, and the denominator is the time-shift factor.

$$\xi = \int_{0}^{t} a_{T}^{-1}[T(t')]dt'$$
(4.8)

Thus, as a fluid particle is tracked along a streamline segment, Δl_i , the particle's time corresponding to the residence time $\Delta t'$ is given by the following equation.

$$\Delta \xi = \frac{\Delta l_i}{V_i a_T(T_i)} \tag{4.9}$$

where V_i is the particle velocity. The resulting version of the constitutive equation becomes:

$$\overline{\overline{\tau}} = \frac{1}{1-\theta} \int_{-\infty}^{\xi(t)} \sum_{i=1}^{N} \frac{G_i}{\lambda_i} \exp\left(-\frac{\xi-\xi'}{\lambda_i}\right) \exp\left[-n\left(\beta_i I_{C_i^{-1}} + (1-\beta_i) I_{C_i} - 3\right)^{1/2}\right] \left[C_{t(\xi)}^{-1}(t'(\xi')) + \theta C_{t(\xi)}(t'(\xi'))\right] d\xi'$$

$$(4.10)$$

The shifting function for $a_T(T)$ is given by:

$$a_T(T) = \frac{\eta}{\eta_0} = \exp\left[\frac{E_{act}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$
(4.11)

where η_0 is a reference viscosity at T_0 , E_{act} is the activation energy constant already determined from rheological measurements, R is the ideal gas constant, and T_0 is a reference temperature (in *K*).

An additional method for the development of the non-isothermal constitutive equation using the isothermal one consists of shifting the relaxation times, λ_i , from the temperature history within the material's time scale.^{296,300} The equation used to shift the relaxation times in the material's history is given by the following equation.^{296,300,301}

$$\lambda_i \left(T'(t') \right) = \lambda_i \left(T_0 \right) a_T \left(T'(t') \right) \tag{4.12}$$

Both methods have been applied before for the process of film $blowing^{301}$ with virtually similar results. Test runs here confirmed this finding, and the current results were derived with the ξ -approach.

The thermal properties of the ionomer melt needed for the non-isothermal flow simulation have been gathered from various sources. The density was taken for LDPE at 140 $^{\circ}C$ given by Fetters et al.³⁰². The heat capacity and the thermal conductivity were taken from DuPont handbook.³⁰³ The time-temperature superposition was used to get the activation energy. All these properties are listed in Table 4.1.

$ ho, kg/m^3$	784		
k, J/mKs	0.255		
C _p , J/kgK	1,970		
Eact, J/mol	91,671		
m, MPa^{n_p-1}	0.37		
n _p	0.89		

Table 4.1 Various parameters of 19.2 - Na~65 at the reference temperature of 140 $^{\circ}C$

The various thermal and flow parameters are combined to give appropriate dimensionless numbers, namely the Peclet number, *Pe*, and the Nahme-Griffith number, *Na*:

$$Pe = \frac{\rho C_p UR}{k} \tag{4.13}$$

$$Na = \frac{\overline{\eta} E_{act} U^2}{k R T_a^2} \tag{4.14}$$

90

Where $\bar{\eta} = f(U/R)$ is a nominal viscosity at a nominal shear rate of U/R, and $U = \dot{\gamma}_A R/4$ is the average velocity in the capillary die. The *Pe* number represents the ratio of heat convection to conduction, and the *Na* number indicates the extent of coupling between the momentum and the energy equations.³⁰⁴ The values of the Peclet and the Nahme-Griffith dimensionless numbers are given in Table 4.2.

Apparent shear rate, $\dot{\gamma}_A$, s ⁻¹	Peclet number, P _e	Nahme-Griffith number, N_a
5	1.1	0.001
11	2.4	0.002
26	5.7	0.007
64	14.1	0.023
170	37.4	0.087
400	87.9	0.264
1000	219.8	0.835

Table 4.2 Dimensionless parameters of 19.2 – Na 65 melt at the reference temperature of 140 °C

Using the properties listed above and a die radius of $R = 0.0762 \ cm$, the dimensionless thermal numbers are in the ranges: $1.1 < P_e < 219$; $0.001 < N_a < 0.835$, showing a relatively strong convection ($P_e >> 1$), and a moderate coupling between momentum and energy equations ($N_a \sim 1$), which is in agreement with the findings for LDPE for similar die diameter.²⁹⁶

4.3.2 Method of Solution

Using the time-pressure superposition principle where the stresses were calculated at different pressures the pressure shift factor, a_p , was obtained.²⁹⁶ This factor alters the relaxation moduli, G_i , for viscoelastic models (K-BKZ model (Eq. 4.4)). The relaxation moduli were modified using the following equation:

$$G_i(p(t')) = G_i(p_0)a_p(p(t'))$$

$$(4.15)$$

The value of a_p is obtained from the Barus equation (Eq. 4.6) and since it is an exponential function of β_p indirectly may depend on pressure.

The solution to the above conservation and constitutive equations is carried out for the viscoelastic flows.³⁰⁵ The mesh-independence of the results has been addressed in the present work in a similar way as previously by considering grids of different density.^{286,287,289–291} The boundary conditions can be found elsewhere.^{296,305} Briefly, no-slip at the walls is assumed; a fully-developed velocity profile is imposed at the entry; at the outlet, the free boundary condition is used; symmetry is assumed at the centerline. To get decent results from the viscoelastic simulation at high apparent shear rates such as 1000 *s*⁻¹ it is necessary to define good initial flow fields. Such viscoelastic computations at elevated shear rates under isothermal conditions using relaxation moduli that depend on pressure were applied for the first time by Ansari et al.²⁹⁶. The same full viscoelastic simulations were employed in our case. Briefly, the starting point is a viscous non-isothermal solution with pressure dependence which is then used as an initial solution to continue iterations for the viscoelastic non-isothermal solution. As in the previous paper²⁹⁶, it is more challenging to handle the pressure-dependence of viscosity that does not have a constant value of β_p .

4.4 Results and Discussion

4.4.1 Rheological Modeling

As explained in chapter 2 various rheological tests were performed to determine the parameters of the K-BKZ model for all ionomers and corresponding copolymers, listed in Table 3.1. Figures 4.1-4.8 present the rheological results for all polymers in the same order as listed in Table 3.1. The continuous lines in these Figures represent the fits of the K-BKZ model. The fitted parameters in the K-BKZ model, n, β , and θ , for all polymers simulated, are listed in Table 4.3. Multi-mode Maxwell parameters, λ_i and G_i , are provided in Table 3.3. Details of the rheological behavior of these materials have been discussed in the previous chapter. The main conclusions are summarized below to provide explanations for their capillary flow behavior with respect to entry pressure (an indication of extensional viscosity), vortex formation, strength, and size.

The rheological properties of ionomers are much higher than those of their corresponding copolymers obviously due to the profound effects of ionic associations. These differences can reach up to one order of magnitude for the ionomers having smaller molecular weight and a high number of associations, Z_s , in other words, smaller molecular weights between associations. For example, the ratio of the zero shear viscosities for samples 11.5 - Na 0 and 11.5 - Na 65 (copolymer and its ionomer) is $27.5 (Z_s = 22, M_w = 71,000 \text{ g/mol})$, while for samples 4.9 - Na 63 and 4.9 - Na 0 this ratio is only $1.6 (Z_s = 14, M_w = 114,490 \text{ g/mol})$. However, Z_s is not the only factor affecting the rheological properties as the number of MAA groups affects the chain configurations and thus the number of ionic associations formed particularly at high MAA content, i.e. in other words not all functional groups shown by the number Z_s participate in reversible interactions.

The zero-shear viscosity of ionomers, (Table 3.1) is not controlled by the molecular weight i.e. $\eta_0 = 176 \ kPas$ for the sample 11.5 - Na 65 with $M_w = 71,000 \ g/mol$, that is much higher than $\eta_0 = 55.4 \text{ kPas}$ for sample 4.9 - Na 63 with $M_w = 114,490 \text{ g/mol}$. Instead of M_w , the number of ionic associations, Z_S (Table 3.5) play a dominant role, i.e., $Z_S = 22$ for sample 11.5 - Na 65 with the smaller M_w , compared to $Z_S = 14$ of sample 4.9 - Na 63 of higher M_w . However, for the case of copolymers, η_0 correlates with M_w . Copolymers form only hydrogen bonds which are much weaker than the ionic associations at the tested temperature and their contributions to rheological data are insignificant.^{14,209} It has been reported that MAA groups form relatively weak hydrogen bonds and that these interactions in polymers containing MAA content up to 5 mol%, have little to no effect on material properties.^{14,209} Thus only in sample 19.2 - Na 65 the effects of hydrogen bonding seems to start becoming noticeable. However, at higher MAA contents, larger ionic nanodomains form, which might possibly lead to microphase separation of the ionic domains dispersed in a continuous polyethylene-like matrix. This might be the reason for the relatively smaller rheological properties (including η_0 listed in Table 3.1) of sample 19.2 – Na 65 although it has the highest value of $Z_S = 35.^9$

The stress growth coefficients in the start-up of steady shear exhibit overshoots which are more pronounced in the case of ionomers, once again due to strong ionic associations. All ionomers and their copolymers show strain hardening effects in uniaxial extension, with these effects to be more pronounced in the case of ionomers due to the strong ionic associations. In some cases (for example, a high number of associations per chain, Z_S , see sample 19.2 - Na 65 in Figure 4.8) the increase of the stress growth coefficient is so abrupt that cannot be captured by the K-BKZ model.

Strong strain hardening effects are due to ionic interactions. Relatively rapid increases of the elongational viscosity are observed which the model misses in some cases. However, it is noted

that the total Hencky strain experienced by a fluid element flowing from the reservoir to die along the centerline is approximately³⁰⁶

$$\varepsilon \equiv \int_{0}^{t_0} \dot{\varepsilon} dt = \int_{v_z(-\infty)}^{v_z(z=L)} \frac{dv_z}{v_z} = \ln\left[\left(\frac{D_{res}}{D}\right)^2\right] = 5.05$$
(4.16)

Where t_0 is the time spent in the centerline and D_{res}/D is the contraction ratio and the reservoir diameter $D_{res} = 9.525 \ cm$ and die diameter $D = 0.762 \ mm$. Eq. 4.16 has been confirmed numerically previously.²⁹¹ For this level of Hencky strain ($\varepsilon = 5.05$), η_E^+ attains its steady-state value. For example, from Figure 4.8, the maximum value of η_E^+ at Hencky strain rate of 5 s⁻¹ is attained at the time of about 0.4 s, which corresponds to a strain of 2, that is much less than 5.05. Therefore, the delay in rising η_E^+ to its steady state value does not affect the final predictions as long as the steady state level of η_E^+ is predicted correctly.



Figure 4.1 (a) The linear viscoelastic moduli and complex viscosity, (b) the damping function, (c) the shear stress growth coefficient in the start-up of steady shear, and (d) the uniaxial tensile stress growth coefficient in the start-up of uniaxial extension for sample 4.3 - *Na* 0 at 140 °*C*. Continuous lines are fits of the K-BKZ/Wagner model to the experimental data with the values of the parameters listed in Table 4.3



Figure 4.2 (a) The linear viscoelastic moduli and complex viscosity, (b) the damping function, (c) the shear stress growth coefficient in the start-up of steady shear, and (d) the uniaxial tensile stress growth coefficient in the start-up of uniaxial extension for sample 4.3 - *Na 69* at 140 °*C*. Continuous lines are fits of the K-BKZ/Wagner model to the experimental data with the values of the parameters listed in Table 4.3



Figure 4.3 (a) The linear viscoelastic moduli and complex viscosity, (b) the damping function, (c) the shear stress growth coefficient in the start-up of steady shear, and (d) the uniaxial tensile stress growth coefficient in the start-up of uniaxial extension for sample 4.9 - Na 0 at 140 °C. Continuous lines are fits of the K-BKZ/Wagner model to the experimental data with the values of the parameters listed in Table 4.3



Figure 4.4 (a) The linear viscoelastic moduli and complex viscosity, (b) the damping function, (c) the shear stress growth coefficient in the start-up of steady shear, and (d) the uniaxial tensile stress growth coefficient in the start-up of uniaxial extension for sample 4.9 - Na 63 at 140 •C. Continuous lines are fits of the K-BKZ/Wagner model to the experimental data with the values of the parameters listed in Table 4.3



Figure 4.5 (a) The linear viscoelastic moduli and complex viscosity, (b) the damping function, (c) the shear stress growth coefficient in the start-up of steady shear, and (d) the uniaxial tensile stress growth coefficient in the start-up of uniaxial extension for sample $11.5 - Na \ 0$ at 140 °C. Continuous lines are fits of the K-BKZ/Wagner model to the experimental data with the values of the parameters listed in Table 4.3



Figure 4.6 (a) The linear viscoelastic moduli and complex viscosity, (b) the damping function, (c) the shear stress growth coefficient in the start-up of steady shear, and (d) the uniaxial tensile stress growth coefficient in the start-up of uniaxial extension for sample *11.5* - *Na* 65 at 140 °*C*. Continuous lines are fits of the K-BKZ/Wagner model to the experimental data with the values of the parameters listed in Table 4.3



Figure 4.7 (a) The linear viscoelastic moduli and complex viscosity, (b) the damping function, (c) the shear stress growth coefficient in the start-up of steady shear, and (d) the uniaxial tensile stress growth coefficient in the start-up of uniaxial extension for sample $19.2 - Na \ 0$ at 140 °C. Continuous lines are fits of the K-BKZ/Wagner model to the experimental data with the values of the parameters listed in Table 4.3



Figure 4.8 (a) The linear viscoelastic moduli and complex viscosity, (b) the damping function, (c) the shear stress growth coefficient in the start-up of steady shear, and (d) the uniaxial tensile stress growth coefficient in the start-up of uniaxial extension for sample *19.2* - *Na* 65 at 140 °*C*. Continuous lines are fits of the K-BKZ/Wagner model to the experimental data with the values of the parameters listed in Table 4.3

Sample	n	β	θ
4.3 – Na 0	0.15	0	-0.15
4.3 – Na 69	0.11	0.05	-0.15
4.9 – Na 0	0.15	0.05	-0.15
4.9 – Na 63	0.17	0.01	-0.15
11.5 – Na 0	0.15	0	-0.15
11.5 – Na 65	0.14	0.001	-0.15
19.2 – Na 0	0.15	0.05	-0.15
19.2 – Na 65	0.14	0	-0.15

Table 4.3 K-BKZ/Wagner parameters of ionomers and corresponding copolymers studied at the reference temperature of 140 $^{\circ}$ C

4.4.2 Experimental Results on Capillary Flow

4.4.2.1 End Pressure and its Effect on Viscosity

The pressure drop of the sodium salt of $11.5 - Na\ 65$ at the reference temperature of 140 °*C* as a function of the length-to-diameter ratio of dies is presented in Figure 4.9, also known as the Bagley plot. Several different apparent shear rates in the range from $5\ s^{-1}$ to $1000\ s^{-1}$ were used. However, only a few are plotted here for the sake of clarity. The results show a slight upward curvature at higher shear rates, which is consistent with the assumption of pressure-dependent viscosity given by Eq. 4.6. Using a linear function (second order polynomial for higher shear rates) to fit the experimental data at each apparent shear rate and extrapolating to zero die length, the end pressure values were obtained (explained in section 1.4.1.1.3).

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The end-pressure results which are essentially the entry pressure ones assuming that the exit pressure is negligible, are presented in Figure 4.10 and are compared with the values of entry pressure obtained directly from the orifice die. The small differences between the pressures obtained using the orifice die and those determined by the Bagley method are due to the experimental error. These entry pressures are much higher than those determined before for other polymers. For example, although the viscosity of the ionomer is lower than those obtained for the LDPE²⁹⁶ and the HDPE²⁸⁴, the values of the end pressure of the ionomer at the highest shear rate are about two times higher. This will also be reflected upon the size of the corresponding vortices that are presented below.



Figure 4.9 The Bagley plot for sample 19.2 - Na 65 melt at the temperature of 140 °C



Figure 4.10 The effect of apparent shear rates on the end pressure for 19.2 - Na 65 melt at the reference temperature of 140 °C as determined by the Bagley method (filled symbols), an orifice die (empty symbols), and K-BKZ model (solid line)

4.4.2.2 Flow Curves

The Bagley method was used to correct the pressure drop for the entry effects to calculate the true wall shear stress using Eq. 1.3. Figure 4.11 plots the flow curves of the ionomer at the reference temperature of 140 °C obtained with capillary dies of the same diameter and three different L/D ratios, namely 4, 14 and 33 with a contraction angle of $2\alpha = 180^{\circ}$. The linear viscoelastic data at the reference temperature is also plotted and indicated a fairly good agreement with the data at L/D = 4, where the effect of pressure is expected to be minimal. Results at higher L/D ratio show the relatively significant effect of pressure on viscosity. These flow curves can be used in conjunction with the Barus equation (Eq. 4.6) to determine the coefficient β_p that reveal the effect of pressure on viscosity.



Figure 4.11 The Bagley corrected flow curves for *19.2 - Na 65* melt at 140 °*C* for three dies with various *L/D* ratios. The solid line represents the LVE results at the same temperature

The experimental data obtained with capillary dies with higher values of L/D were shifted horizontally to superpose with the LVE data and as a result the shear-rate-dependent pressure coefficient β_p^{super} was obtained. As in the case of LDPE²⁸⁴, this parameter could be related to the Barus pressure coefficient β_p , given in a following equation.

$$\beta_p = n_C \beta_p^{\text{super}} \tag{4.17}$$

where n_c is the power-law index. As previously reported^{284,307}, β_p depends on pressure following a power-law equation:

$$\beta_p = m p^{-n_p} \tag{4.18}$$

The power-law parameters of Eq. 4.18 are listed in Table 4.1, and it was plotted in Figure 4.12. As the apparent shear rate increases, β_p decreases at a constant temperature. Eq. 4.18 accurately captures the coefficient β_p .



Figure 4.12 The pressure dependency coefficient of viscosity on pressure along with power-law equation

Fig. 4.13 depicts the flow curves at various levels of L/D after applying the end pressure correction. The data superposes well, and the capillary data agrees well with the LVE data showing the consistency of the experimental results. Moreover, the agreement shows that the Cox-Merz rule also applies.



Figure 4.13 The end-pressure corrected flow curves of $19.2 - Na \ 65$ at the reference temperature of 140 °*C* for three dies with various L/D ratios

4.4.2.3 Slip Effect

The die diameter dependence has been studied in order to assess the slip behavior of ionomer. Fig. 4.14 plots the flow curves of 19.2 - Na 65 at the reference temperature acquired by using three capillary dies with significantly different diameter and the same L/D ratio. The experimental results show that the flow curves practically superpose indicating that this polymer does not slip due to strong interactions between the chains and the ionic groups at the interface with the wall.



Figure 4.14 The effect of the die diameter to check the possibility of slip at the wall for *19.2 - Na 65* at the reference temperature 140 °*C*. The solid lines represent the LVE results at the same temperature

4.4.3 Comparison of Capillary Flow Results with Simulations

As shown above, the K-KBZ captures quite accurately the end pressure (Figure 4.10). In this section, the experimental flow curves with results from flow simulations at various die lengths were compared. As seen in Figure 4.15 the K-BKZ flow simulations can describe the capillary flow quite well. Comparisons are shown for both the end-pressure corrected flow curves (Figure 4.15b) as well as the uncorrected flow curves (Figure 4.15a). In both cases the agreement is remarkable.


Figure 4.15 Flow curves for *19.2 - Na 65* melt at 140 °*C* for three dies with various *L/D* ratios compared to simulations (a) before and (b) after Bagley correction. The solid lines represent the K-BKZ simulation results

4.4.4 Flow Simulations for Ionomers and Corresponding Copolymers

4.4.4.1 Entry Pressure

Using the K-BKZ model and the parameters calculated from fitting the rheological data (Table 4.1), capillary flow simulations were performed for all ionomers and their copolymers. Figure 4.16 a) plots the simulated end pressure of ionomers and that of their corresponding copolymers Figure 4.16 b) at 140 °C in a capillary having an entrance angle $2\alpha = 180^{\circ}$. The same scale has been used in both graphs for direct comparison. Symbols indicate the increasing steps for the continuation procedure to go from 5 s^{-1} to 1000 s^{-1} . The end pressures of ionomers are much higher than those of their corresponding copolymers due to the strong effects of ionic interactions, resulting in the strong strain-hardening effects discussed above.



Figure 4.16 (a) The simulated end pressure of ionomers and (b) that of their corresponding copolymers at temperature of 140 °*C* in a capillary having an entrance angle $2\alpha = 180^{\circ}$

The end pressure of ionomer sample 11.5 - Na~65 is the highest due to the combined effect of its molecular configuration and number of associations resulting in strong strain hardening (Figure 4.16a). This can be seen from the highest value of sticky-reptation time, τ_{rep} , of 86.9 *s*, listed in Table 3.3 and the highest zero-shear viscosity of 176 *kPas* amongst all ionomers. The end pressures of the other ionomers scale with the sticky-reptation times and zero-shear viscosities. The smallest end pressure is exhibited by ionomer 4.3 - Na 69 that possesses the least ionic associations. Therefore, it is not the molecular weight and the number of entanglements that contribute to the end pressure but the strong ionic interactions that give rise to strong extensional strain-hardening effects important in entry flows.³⁰⁸ On the other hand, in the case of copolymers, sample 4.9 - Na 0 exhibits the highest end pressure which possesses the highest molecular weight. As discussed above, the degree of hydrogen bonding is not significant for these samples and therefore the M_w and the number of entanglements play the dominant role. All other end pressures scale with the M_w of the copolymers, which are similar due to similar molecular weights of these copolymers (64,380 to 72,380 g/mol).

4.4.4.2 Vortex Size and Strength

The vortex corner size can be defined in Figure 4.17 by the length of the vortex in the reservoir, L_{v} (length along the reservoir wall in the direction of flow) normalized by the diameter of the reservoir, D_{res} (9.525 mm). It has been reported that the vortex size scales with the extensional viscosity of the polymers (polymers with strong strain-hardening exhibit large vortices).^{308,309} Figure 4.18 a) plots the simulated normalized vortex length of ionomers, and that of their corresponding copolymers is plotted in Figure 4.18 b) at the reference temperature 140 $^{\circ}C$ in a capillary with the same entrance angle as mentioned in the previous section. To compare the relative effect between ionomers and copolymers the same scale was used in both graphs. Equivalent to previous Figure 4.16 symbols indicate the increasing steps for the continuation procedure to go from 5 s^{-1} to 1000 s^{-1} . The normalized vortex length of ionomers is much higher than those of their corresponding copolymers due to the strong effects of ionic interactions, resulting in stronger strain-hardening effects for ionomers compared to that of their corresponding copolymers (Figures 4.1 - 4.8). The vortex size in all cases initially increases with apparent shear rate and subsequently levels off due to the suppression resulting from the higher pressure at higher apparent shear rates.^{308,309}



Figure 4.17 Schematic representation for an abrupt circular contraction (capillary flow)

As in the case of end pressure, ionomer $11.5 - Na\ 65$ exhibits the highest vortex length due to its strong strain-hardening effects (Figure 4.18a). In contrast, ionomer $4.3 - Na\ 69$ has the lowest vortex length due to the lowest number of ionic associations (Figure 4.18a). Similarly, copolymer $4.9 - Na\ 0$ exhibits the highest vortex length due to its highest M_w in the absence of ionic interactions (Figure 4.18b). The rest of the vortex lengths scale with M_w and their associated strain-hardening effects.



Figure 4.18 (a) The simulated vortex length of ionomers and (b) that of their corresponding copolymers at temperature of 140 °*C* in a capillary having an entrance angle $2\alpha = 180^{\circ}$

In order to quantify the vortex intensity, we can compute the maximum difference between the stream function value in the vortex region and the value on the wall. The relative vortex intensity is then calculated as the ratio of this maximum difference to the flow rate in the mainstream according to the following equation, where Ψ_w and Ψ_{cl} are the stream function values at the wall and centerline, respectively.

$$-\psi_{\nu,\max}^{*} = \frac{\psi_{\nu,\max} - \psi_{w}}{\psi_{cl} - \psi_{w}}$$
(4.19)

Figure 4.19 plots the relative vortex intensity versus apparent shear rate for the ionomers and the copolymers. As in the case of vortex length, ionomer 11.5 - Na 65 exhibits the highest vortex intensity due to its strong strain-hardening effects. However, ionomer 4.3 - Na 69 has the lowest vortex intensity due to the lowest number of ionic associations. Similarly, the highest M_w for the copolymer 4.9 - Na 0 contributes to the highest vortex length in the absence of ionic interactions at least in the low to middle range of apparent shear rates. Its length and intensity are suppressed

at high apparent shear rates due to the high pressure. The rest of the copolymers scale with M_w and their associated strain-hardening effects.



Figure 4.19 (a) The simulated relative vortex intensity of ionomers and (b) that of their corresponding copolymers at temperature 140 °*C* in a capillary having an entrance angle $2\alpha = 180^{\circ}$

4.4.4.3 Flow Patterns

Flow patterns are shown for the streamlines in the reservoir of the entry flow to the capillary. Firstly, streamlines are presented in Figure 4.20 for the ionomer 19.2 - Na 65 at three different apparent shear rates a) $\dot{\gamma}_A = 5 s^{-1}$, b) $\dot{\gamma}_A = 100 s^{-1}$, c) $\dot{\gamma}_A = 400 s^{-1}$. The vortex size and intensity are increasing substantially as evidenced by the separating streamline that strikes the reservoir wall. Similarly, but at much lower reduced vortex size and intensity are shown the streamline patterns for the copolymer 19.2 - Na 0, in Figure 4.21. The differences signify the strong effects of ionic interactions that give rise to strong strain hardening effects. In general, the flow patterns (vortex size and intensity) scale with M_w in the case of copolymers and with a number

of ionic interaction (strong strain hardening effects) in the case of ionomers. Similar flow patterns and differences have been obtained with the other ionomers and their corresponding copolymer.



Figure 4.20 Flow patterns (streamlines) for the ionomer 19.2 - Na 65 at 140 °C for a die with L/D = 33 at different apparent shear rates obtained with the K-BKZ/Wagner model. a) apparent shear rate is 5 s⁻¹, b) apparent shear rate is 100 s⁻¹, c) apparent shear rate is 400 s⁻¹



Figure 4.21 Flow patterns for the copolymer $19.2 - Na \ 0$ at 140 °C for a die with L/D=33 at different apparent shear rates obtained with the K-BKZ/Wagner model. a) apparent shear rate is 5 s⁻¹, b) apparent shear rate is 100 s⁻¹, c) apparent shear rate is 400 s⁻¹

4.5 Summary

Several commercial ionomers and their corresponding copolymers have been studied rheologically, and the experimental results were used to fit the parameters of a K-BKZ model in order to perform flow simulations in abrupt contraction (capillary) flows. It was found that the K-BKZ model can predict well the capillary flow of ionomers and it can safely be recommended to be used in more complex flows in polymer processing. The pressure has a mild effect on the viscosity of these polymers with the parameters of the Barus equation calculated from experimental results. The effects of ionic and hydrogen bonding associations on the entry pressure drop have been studied in detail. In addition, their effects on the length (size) of the corner vortex as well as on the vortex strength have also been studied. In all cases, the ionomers exhibit much more significant effects (higher entry pressure, larger and stronger corner vortices) compared to their copolymers, the more so as the number of ionic associations present in their backbone increases. This is due to strong ionic associations present in the ionomers that give rise to strong strain hardening effects important in entry flows. Compared to ionic associations, the effects of hydrogen bonds are insignificant particularly at levels less than 5 mol%. Therefore, in the case of copolymers, their molecular weight and number of entanglements play the dominant role in the entry pressure, size and strength of corner vortices.

Chapter 5: Dynamics of Associating Networks with Hydrogen Bonding Interactions

5.1 Introduction

Reversible associations can be implemented by introducing functional groups, capable of forming hydrogen bonds, on the polymer backbone. Those associations can dissociate and reform due to thermal changes or external stimuli. The main difference of associating networks compared to chemically crosslinked ones is the presence of transient associations, which enable specific rheological and mechanical behavior suitable for many interesting applications. Understanding network dynamics is important to control and optimize the properties of these materials. For instance, changing the sticker number density or the associations strength, it is possible to influence the self-healing time scales.¹⁶ The interplay of polymer architecture and number of stickers per chain control the dynamics of the entire associative network. In this chapter, an extensive analysis of novel functionalized polynorbornenes and polycyclooctenes in shear and extensional flow is studied. The main objective is to understand the influence of hydrogen bonding on the rheological properties of associating polymer networks. Changes in molecular weight, chain length, and the number density of stickers significantly influence the rheological behavior of associative polymer networks.^{43,250}

Depending on polymer topology various theories were employed in describing the behavior of polymers that have associative side groups, (e.g., sticky Rouse or sticky reptation theories). Theories for associating polymers developed by Leibler et al.³⁵, Rubinstein et al.^{41,250}, Semenov et al.^{40,43,310}, Chen et al.^{11,44}, Zhang et al.³¹¹ and Ruymbeke et al.^{182,312–314} were used to estimate the characteristic relaxation times in functionalized polynorbornenes and polycyclooctenes that mainly control their dynamics and therefore their rheological behavior. Some parts of the following sections are reproduced with permission from the Provisional patent app. UBC-18-076 "Amine-functionalized polyolefins and methods of preparation and use thereof".

5.2 Experimental

The synthetic route of functionalized polynorbornenes was discussed in section 2.1.2 and functionalized polycyclooctenes in section 2.1.3 along with a list of several different polymer structures of both polymers synthesized and analyzed in this study. All these novel polymers were investigated by using NMR, FTIR spectroscopies, GPC, thermal and rheological methods which were discussed in Chapter 2.

5.2.1 Materials

As indicated in Chapter 2, amine-functionalized monomers were prepared by hydroaminoalkylation reaction, which is an efficient catalytic reaction for amination of both terminal and internal alkenes.^{112,257,315} These amine-containing monomers can undergo ROMP reaction at room temperature to produce linear polymers. Polymer structure was characterized using NMR and FTIR spectroscopies. The number average- and weight average-molecular weight, as well as polydispersity, were obtained by using gel permeation chromatography. These materials are comprised of hydrogen donor and acceptor as pendant side groups that allow the formation of the reversible network through hydrogen bonding. Every monomeric unit has one functional group, although not all of them can participate in the formation of the polymer network. There can be many dangling and looped groups which are free or isolated from interactions. Therefore, a

distinct and rich behavior of these polymers is anticipated to depend not only on the number of stickers, but also on the interplay between chain mobility, polymer topology, stereochemistry, reversible network associations, and effects induced by shear or extensional flows.

5.2.1.1 Functionalized Polynorbornenes

As previously described, amine-containing polynorbornenes were prepared in a combination of two subsequent steps: i) hydroaminoalkylation reaction, and ii) ROMP polymerization starting from simple and inexpensive materials. ¹H NMR spectroscopy was used to monitor complete polymerization by observing the removal of olefinic resonances from monomers and the appearance of broad olefinic resonances coming from polymers.¹¹² GPC was used to determine the molecular weight of polymers and their polydispersity. The obtained results show higher values of M_n than the theoretically predicted one and slightly increased polydispersity (D = 1.1 - 1.6).

Tertiary amine-containing polynorbornene (marked as a reference sample, ACN-ref) does not contain an available hydrogen atom that can participate in the formation of hydrogen linkage as it was substituted with methyl benzene. After its much faster polymerization compared to secondary amine-containing polynorbornenes, the isolated polymer appeared to be distinct from secondary amine since it did not conglomerate. This might be explained by the absence of hydrogen. Several other polymers with various structures were prepared, and all of them are listed in Table 5.1 along with their molecular characteristics. The samples used in this study are labeled hereafter as ACN-X where ACN represents the polymer backbone with aniline side group, and X is a group present in *para* position (methoxy, tethered catechol, fluorine, chlorine, or bromine).

Sample	^a M _n , g/mol	^b DP	${oldsymbol{G}}^2$
ACN-ref	138,000	495	1.18
ACN-H	92,000	470	1.26
ACN-OMe	83,000	387	1.18
ACN-CAT	81,000	330	1.24
ACN-F	28,000	131	1.10
ACN-Cl	36,000	151	1.15
ACN-Br	99,000	373	1.16

Table 5.1 List of functionalized polynorbornenes and their molecular characteristics

^aNumber averaged molecular weight obtained by using GPC; ^bDegree of polymerization; ^cIndex polydispersity M_w/M_n .

The dynamics of several polymers, namely ACN-H, ACN-OMe, ACN-CAT, were investigated by estimating the characteristic relaxation times. Two different molecular weights of each of these polymers were synthesized. They are given in Table 5.2 along with their polydispersity. Although polynorbornene is a semi-crystalline polymer with low crystallinity, the synthesized amine-containing polynorbornenes are amorphous polymers with a rigid backbone, and the glass transition temperature above room temperature. These materials are stable at high temperatures up to 300 $^{\circ}C$, which was determined by using thermogravimetric analysis.

Sample	^a M _w , g/mol	$^{b}\!D$	
	25,000	1.59	
АСМ-П	119,000	1.25	
	45,000	1.58	
ACIV-OIMe	113,000	1.28	
	112,000	1.42	
ACN-CAI	186,000	1.24	

Table 5.2 Selected amine-containing polynorbornenes used to investigate characteristic relaxation times

^aWeight averaged molecular weight determined from GPC; ^bDispersity M_w/M_n .

5.2.1.2 Functionalized Polycyclooctenes

Amine-containing polycyclooctenes were prepared similarly to that of functionalized polynorbornenes by employing the hydroaminoalkylation reaction and ROMP polymerization. High conversion of monomer and high yields were achieved at room temperature. As in the case of functionalized polynorbornenes, ¹H NMR was used to follow the polymerization of amine-containing polycyclooctenes. The molecular weight of these materials was obtained from GPC. Moreover, the polydispersity indicates that all prepared polymers are slightly polydisperse ($\Phi = 1.2 - 1.9$). Dried functionalized polycyclooctenes with methoxy and fluorine groups were not possible to dissolve in THF, and thus their molecular weights and polydispersity could not be determined. Insolubility was attributed to the creation of strong hydrogen bonding associations. Additionally, tosyl hydrazine was used as a hydrogen source to reduce double C=C bonds and form amine-containing polyethylene (ACP-H). This reaction was followed by ¹H NMR and FTIR spectroscopies.²⁵⁷

Six functionalized polycyclooctenes were prepared with different pendant side groups, including tertiary amine-containing polymer, which was used as a reference sample, are presented in Table 5.3. The labeling is similar to that used for the functionalized polynorbornenes (ACC-X). The polymer backbone with aniline side group was marked as ACC and X is a group present in the *para* position (methoxy, fluorine, or bromine). The hydrogenated sample that represents amine-containing polyethylene was labeled as ACP-H. As previously mentioned, the reference sample (ACC-ref) does not have any available hydrogen atom for interactions through hydrogen bonding. Several unsubstituted aryl amine polycyclooctenes (ACC-H) were prepared to determine the molecular weight effect (see Table 5.3). For ACC-OMe and ACC-F the molecular weight and polydispersity could not be measured since they could not be dissolved.

Sample	^a M _n , g/mol	b D	
ACC-ref	30,000	1.80	
	5,000	1.85	
	15,000	1.70	
АСС-Н	18,000	1.40	
	37,000	1.75	
	82,000	1.32	
АСР-Н	71,000	1.22	
ACC-Br	35,000	1.65	

Table 5.3 List of amine-containing polycyclooctenes along with molecular characteristics

^{*a*}Number averaged molecular weight obtained by using GPC; ^{*b*}Index polydispersity M_w/M_n .

5.2.2 Experimental Methods

In this section experimental methods used to study hydrogen bonded polymers, functionalized polynorbornenes, and functionalized polycyclooctenes are presented. They have been previously discussed in Chapter 2 in detail and are briefly mentioned again here. Several methods used to follow the polymerization process and to analyze the molecular structure of polymers, such as ¹H NMR and FTIR spectroscopies and GPC, were performed in the chemistry department by Damon Gilmour and Nirmalendu Kuanr (both PhD students at the time).

TGA analysis. Thermal stability and degradation temperatures of all synthesized polymers were determined using the thermogravimetric analyzer. This procedure was described in section 2.2.2.

DSC calorimetry. DSC calorimetry was used to obtain the transition temperatures of all prepared polymers. Due to differences in the structures of functionalized polynorbornenes and polycyclooctenes, it was necessary to apply different experimental procedures to obtain their glass transition temperatures (see section 2.2.1).

Rheological measurements. For rheological characterization, it was necessary to prepare the samples by solution casting as described in Chapter 2. Two distinct experiments were performed for both functionalized polynorbornenes and polycyclooctenes, namely small amplitude oscillatory shear and uniaxial extension (see sections 2.2.4.2 and 2.2.4.3). Amine-containing polynorbornenes are amorphous polymers with T_g from 45 – 80 °C. Thus, the rheological properties can be determined over a wide range of temperatures. The functionalized polycyclooctenes are also amorphous polymers but have much higher T_g values about -10 °C. Before the frequency sweep test, it was necessary to perform time sweep tests at several temperatures to study the thermal stability of polymers. Additionally, strain sweep tests were

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performed to determine the threshold strain of linear viscoelastic regime. Furthermore, the frequency sweep experiments were carried out at several temperatures (100 - 200 °C) in order to determine the dynamic moduli and complex viscosities over a wide range of frequencies. The master curves of storage and loss moduli and complex viscosity were obtained by performing the time-temperature superposition principle at the reference temperatures. These temperatures were chosen based on glass transition temperature for both types of polymers.

The nonlinear viscoelastic characteristics were determined as described in section 2.2.4.2 for the functionalized polynorbornenes and section 2.2.4.3 for the functionalized polycyclooctenes. The uniaxial extension was performed at various Hencky strain rates and reference temperature depending on the structure of functionalized polynorbornenes. Additionally, since the functionalized polycyclooctenes has shown self-healing capabilities, they were tested using the uniaxial extension at low Hencky strain rate and at room temperature.

5.3 **Results and Discussion**

In this section, thermorheological results are presented first for functionalized polynorbornenes. Discussion starts with thermal properties of several polymers that have different functional groups, followed by dynamic oscillatory shear results. The differences in the properties of tertiary and secondary amine-containing polynorbornenes are emphasized. A modified tube model known as the time marching algorithm (TMA) developed by Ruymbeke et al.^{312–314} was used as a fitting model to determine several characteristic relaxation times for this type of associating polymers. Uniaxial extensional rheological results are also presented. In the second part of this section, the thermorheological results of functionalized polycyclooctene are described. First, results of TGA and DSC measurements followed by linear viscoelastic properties were

performed. Recovery tests to demonstrate the self-healing of functionalized polycyclooctenes are also discussed.

5.3.1 Functionalized Polynorbornenes

5.3.1.1 Thermal Properties

In this section, results of thermogravimetry and differential scanning calorimetry are presented. Before performing any rheological characterization, it is essential to determine the range of temperatures at which tests can be performed. Besides degradation temperatures that are obtained by the TGA instrument, it is necessary to know the type of polymer (amorphous or semicrystalline) and its transition temperatures determined by the DSC method.

5.3.1.1.1 Thermogravimetric Analysis

As described in section 2.2.2, the synthesized materials were tested using the TGA analysis that provides an immediate indication of polymer thermal decomposition and its degradation temperatures. The degradation curves (TG (thermogravimetry) and corresponding DTG (derivative thermogravimetry)) for all isolated polymers prepared using a ratio of monomer/initiator 100:1 are shown in Figure 5.1. The characteristic degradation temperatures are presented in Table 5.4. Results were collected and presented from room temperature up to 600 °C under nitrogen atmosphere indicating several stages of their degradation behavior.



Figure 5.1 The TG (solid lines)/DTG (dashed lines) curves recorded in nitrogen atmosphere for the synthesized functionalized polynorbornenes, namely a) ACN-ref, b) ACN-H, c) ACN-OMe, d) ACN-CAT, e) ACN-F, f) ACN-Cl, and g) ACN-Br (inset represents whole DTG curve for ACN-Br)

The first thermogravimetric step recorded for all functionalized polynorbornenes (except ACN-H) is in a similar temperature range from ~30 °*C* to ~228 °*C* (see Table 5.4). The DTG peak temperatures are between 120 °*C* and 150 °*C* depending on polymer structure. Considering that all samples were dried before executing these tests, the moisture was reduced to the level where water was inter- and intra-molecularly bonded to functional groups, shown by initial mass loss. The first DTG peak refers to water removal/evaporation¹⁵² except in the case of ACN-H which does not

have available functional groups that can bond to water molecules or bonded at miniscule amounts which are difficult to detect.

Sample	Mass, mg	Step I		Step II		Step III		Step IV	
		∆ <i>T</i> , •C	<i>Т</i> _{<i>d</i>1} , •С	⊿ <i>T</i> , °C	Т _{d2} , •С	<i>∆T</i> , °C	Т _{d3} , •С	∆ <i>T</i> , °C	Т _{d4} , •С
ACN-ref	4.195	98- 198	141.2	198- 284	398.9	284- 502	398.9	-	-
ACN-H	4.802	-	-	155- 277	232.0	350- 490	441.9	-	-
ACN-OMe	4.691	30- 194	140.0	194- 307	252.8	307- 507	421.9	-	-
ACN-CAT	4.599	45- 228	150.2	228- 357	317.4	357- 566	428.9	-	-
ACN-F	4.718	50- 204	121.7	204- 330	274.9	330- 505	429.6	-	-
ACN-Cl	4.879	45- 211	123.5	211- 318	279.9	318- 515	425.3	-	-
ACN-Br	4.874	75- 217	146.1	217- 249	231.3	249- 357	278.9	357- 503	423.5

Table 5.4 The characteristic temperatures for the decomposition of amine-functionalized polynorbornenes

Significant decomposition of polymer chains occurs in the third step (~250 - 560 °*C*) due to the degradation of polymer matrix, where T_{d3} represents the temperature when the highest degree of degradation occurs, while the second DTG peak is related to side groups scission. In the

case of ACN-Br, the degradation process develops differently (i.e., where the main chain scission starts at a lower temperature). A char residue represents about 8 % for ACN-ref, ACN-H, ACN-OMe, and ACN-F, about 14 % for ACN-CAT and ACN-Cl, and lastly 28 % for ACN-Br of the total mass. It is well known that polymers with aromatic rings yield char residue under nitrogen atmosphere since pyrolysis reaction takes place and residual carbon cannot be decomposed.

5.3.1.1.2 Differential Scanning Calorimetry

One of the most effective thermal analysis methods for polymers is DSC. It is used to determine the energy which is released/absorbed by a sample during heating or cooling. Transition temperatures (T_g , T_m , and T_c) can be obtained using this technique. It is noted that the test procedure for the functionalized polynorbornenes was explained in section 2.2.3. Experiments were performed at temperatures up to 150 °*C*, and all samples were thermally stable up to this temperature. DSC thermograms revealed the amorphous behavior of these amine-containing polynorbornenes (Figure 5.2) with glass transition values listed on the graphs for each polymer.



Figure 5.2 DSC traces of functionalized polynorbornenes with indicated glass transition temperatures

Previous work by Esteruelas et al.³¹⁶ indicated that the values of T_g of polynorbornene to be around 40 °*C*, which is similar to the ACN-ref sample as expected. The T_g values of all other samples are significantly higher due to the presence of functional groups that can form hydrogen bonds, which make the polymer backbone more rigid.

5.3.1.2 Rheological Characterization

5.3.1.2.1 Linear Viscoelasticity

The rheological measurements were conducted on a stress-controlled Anton Paar MCR 702 device equipped with cone partitioned plate geometry, and an air/nitrogen convection oven for accurate temperature control ($\pm 0.1 \ ^{\circ}C$) (details can be found in Chapter 2). Before obtaining the dynamic moduli, two different tests were conducted (time sweep and strain sweep tests). Dynamic time sweep tests were carried out at constant frequency and strain, 0.1 *Hz* and 0.01 respectively, to ensure the thermal stability of the samples. The limits of the linear viscoelasticity were determined using strain sweep experiments. Dynamic frequency sweeps were performed from 100 to 200 $^{\circ}C$ by applying a strain amplitude of 0.05.

The time-temperature superposition principle was used to generate the master curves of dynamic moduli by applying both horizontal and vertical shift. First, in order to accurately determine the horizontal shift factors, a_T , the $tan\delta$ curves were shifted along the frequency axis for every temperature to superimpose them onto the reference one. Then, the complex modulus $/G^*/$ curves were shifted vertically to superimpose the reference curve in order to obtain the vertical shift factors, b_T . Figure 5.3 plots the obtained master curves of storage and loss moduli at the reference temperature. Since the glass transition temperature varies depending on the molecular structure, the reference temperature was chosen to be 60 °*C* higher than the corresponding T_g value. As previously mentioned, all polymers were prepared using the theoretical ratio of monomer-to-initiator 100:1. For several polymers, namely ACN-H, ACN-OMe, and ACN-CAT, additional polymers were synthesized with reduced molecular weight to demonstrate how rheological properties depend on molecular weight.



Figure 5.3 Evolution of dynamic moduli versus the angular frequency at the reference temperature (T_g + 60 °*C*) for all synthesized functional polynorbornenes. For three selected polymers (ACN-H, ACN-OMe, and ACN-CAT) two different molecular weights are presented

The horizontal shift factors were found to be nearly identical for all samples regardless of polymer structure, which indicated that all polymers possess a similar structure. This allowed fitting of the data with the Williams-Landel-Ferry (WLF) equation (Eq. 1) using a single set of parameters, $C_1 = 10.42$, $C_2 = 190.3$, and $T_0 = T_g + 60$ °C. The temperature dependence of the horizontal shift factors for all samples are presented in Figure 5.4.



Figure 5.4 The temperature dependence of the horizontal shift factors used to construct the master curve for all synthesized samples. The solid line represents the fit of the WLF equation

The reference sample (tertiary amine-containing polynorbornene (ACN-ref)) exhibits classical behavior of polydisperse polymer melts with delayed terminal relaxation due to the presence of π - π interactions.¹⁷⁰ The terminal relaxation was obtained at frequencies around 0.8 *rad/s*, corresponding to a reptation time of the order of 1.3 *s* (inverse of the frequency). The presence of functional groups capable of forming reversible associations (hydrogen bonding) delays the relaxation significantly at time scales greater than 10⁸ *s* (Figure 5.3 b-g), which is

impossible to observe experimentally. Whereas ACN-F did not show the formation of any plateau, the storage modulus of the other secondary amine-containing polynorbornenes is independent of frequency. As explained by Zhang et al.⁴⁵ associating polymers that possess the molecular weight of the segment between stickers to be smaller than the molecular weight of the segment between entanglements exhibit two characteristic plateau regions. The classical Rouse time of the strand between associations is much smaller than that of associations lifetime. The first plateau is due to the presence of both associations and entanglements, where its end marks the associations lifetime (determined as the inverse of frequency). The second plateau is due to the presence of entanglements only. The data of functionalized polynorbornenes show only the first plateau region that is the result of present both associations and entanglements.

As in the case of ionomers the number of associations per chain, Z_S , was calculated for all polymer samples. It was found that is much higher than that for ionomers since every monomeric unit contains a functional group. Therefore, a network of polymer strands interconnected with reversible hydrogen bonding associations is formed. The linear viscoelasticity of these polymers is solely controlled by the lifetime of these reversible associations, and is characterized by the molecular weight of a strand between associations M_S . Obviously, not all functional groups present in a single molecule can form associations due to restrictions in their configurational entropy (i.e., the bulky and numerous functional groups stiffen the molecules and the number of entanglements per chain, Z_E , that may form is indeed very small compared to the number of associations). Using the ACN-ref reference sample data, the molecular weight between entanglements was calculated to be 9,230 g/mol. All obtained results are listed in Table 5.5.

Sample	M _w , g/mol	$G_N^0(1+Z_S/Z_E),$ kPa	Z_S	ZE	$\tau_{e,0}(Z_S/Z_E)^2,$	τς, ς	Trep, S
ACN-ref	175,000	85	-	19	2.0×10 ⁻²	-	1.3
ACN-H	25,000	14	130	3	5.4×10 ⁻²	2.4×10^{4}	1.1×10 ⁹
	119,000	53	602	13	1.8×10 ⁻³	8.5×10 ⁴	4.0×10 ¹¹
ACN-OMe	45,000	55	197	5	6.7×10 ⁻²	1.3×10^{4}	2.4×10^{9}
	113,000	63	496	12	8.0×10 ⁻³	5.0×10 ⁶	1.5×10^{13}
ACN-CAT	112,000	25	408	12	6.2×10 ⁻²	7.9×10^4	1.6×10 ¹¹
	186,000	40	679	20	3.3×10 ⁻³	3.2×10 ⁶	2.9×10 ¹³
ACN-F	31,000	-	146	3	-	-	-
ACN-Cl	41,000	-	179	5	-	-	-
ACN-Br	115,000	23	414	12	3.0×10 ⁻³	2.6×10 ³	5.5×10 ⁹

Table 5.5 Molecular properties and characteristic relaxation times of synthesized functional polynorbornenes

Although these polymers are slightly polydisperse, the plateau modulus (predominately due to reversible associations) is clearly obtained experimentally over a wide range of frequencies (several decades). Due to the numerous associations, the polymer strands of molecular weight M_S form a network whose dynamic behavior is controlled by the associations lifetime at frequencies larger than 10^{-6} rad/s. Therefore, the effect of polydispersity on the chain dynamics is masked by the numerous individual segments between associations. This plateau modulus is given by $G_N^0(1 + Z_S/Z_E)$, where G_N^0 is the plateau modulus of entanglements.^{44,45,317} The entanglement plateau modulus, G_N^0 , in the present case can be obtained at very smaller frequencies, and is

inaccessible experimentally. Its value is expected to be small due to the small number of entanglements that these stiff polymers may create.

The first plateau modulus show dependence on the molecular weight (i.e., increases with increasing the molecular weight). The modulus becomes independent of the molar mass of the network strands in the limit of very long strands.³⁶ It seems that the impact of molecular weight on the molar mass of the strands is small in all cases. The longer chains form intramolecular associations in addition to the intermolecular due to the presence of entanglements.⁴² Smaller molecules with practically no entanglements are topologically impossible to form such intramolecular associations. This also influences the Rouse relaxation which is not independent of the molecular weight although in all cases the Rouse scaling $G' \approx G'' \sim \omega^{0.5}$ is clearly obtained as indicated in Figure 5.5.

The plateau modulus $G_N^0(1 + Z_S/Z_E)$ is dependent on the structure as seen from Figure 5.5, where three polymers, namely ACN-H, ACN-OMe, and ACN-CAT of similar molecular weight are compared. Based on these structure, ACN-CAT is the stiffest molecule amongst the three presented due to the presence of tethered catechol group that significantly reduces the flexibility of chains. Although this polymer may potentially create more and stronger associations, topological restrictions cause the formation of fewer associations which is reflected in the magnitude of the plateau modulus. On the other hand, ACN-OMe has both amine and methoxy groups capable of creating stronger hydrogen associations, while retaining its relatively higher flexibility. As a result, it possesses the highest modulus compared to the ACN-H and ACN-CAT. Moreover, its transition from Rouse relaxation to a plateau regime occurs at smaller frequencies (longer times) due to these stronger reversible interactions.



Figure 5.5 Master curves of storage and loss moduli of samples ACN-H, ACN-OMe, and ACN-CAT that have similar molecular weights (ACN-H $M_w = 119,000 \text{ g/mol}$ red symbols; ACN-OMe $M_w = 113,000 \text{ g/mol}$ blue symbols, and ACN-CAT $M_w = 112,000 \text{ g/mol}$ green symbols). The reference temperature is 60 °C higher than the T_g

In order to determine the associations lifetime, the time-marching algorithm (TMA) was used to fit the obtained data with a few fitting parameters. This algorithm has been developed for predicting the LVE behavior of polymers with various architectures such as linear, star, tree-like, H, and pom-pom polymers.^{312–314} The parameters needed for these calculations include the molecular weight between associations, M_S , and the molecular weight between entanglements, M_E , although the number of entanglements plays a minor role. Since it is not possible that all functional groups participate in the formation of hydrogen bonding, due to present loops and dangling chain segments, we assumed that only half of these functional groups could form associations. This assumption resulted in the best fit to the experimental data. Another important parameter for the model is the plateau modulus which was obtained from the experimental results and corresponded

to $G_N^0(1 + Z_S/Z_E)$. Lastly, the equilibration time is a fitting parameter that corresponds approximately to frequencies in the transition from the Rouse relaxation to plateau modulus of the associations.

The associations lifetime can be determined from the TMA model, which corresponds to the lower limit of the first plateau. As seen from Figure 5.6, these are quite long times (i.e., several hours) due to the numerous reversible associations. The sticky-reptation times that corresponds to the terminal relaxation can be calculated by the following scaling, $\tau_{rep} = \tau_S Z_E Z_S^2$ (see Table 5.5). The reptation time can be as low as $1.1 \times 10^9 s$ for the low M_w of ACN-H and as high as 2.9×10^{13} s for the high M_w of ACN-CAT. The predictions of the TMA model for several polymers are plotted and compared with the experimental data in Figure 5.6. They are reasonably well matched with the experimental data in all cases.



Figure 5.6 Master curves of storage and loss moduli for a) reference sample, b) ACN-H, c) ACN-OMe, and d) ACN-CAT along with TMA fit

5.3.1.2.2 Extensional Rheology

Results of extensional rheology for all functional polynorbornene samples are shown in Figure 5.7. The solid lines represent the linear viscoelastic envelop determined by fitting the dynamic moduli data using the multimode Maxwell model (the best-fit parameters, λ_i and G_i , are given in Appendix D).



Figure 5.7 Uniaxial stress growth coefficient obtained at different Hencky strain rates at the reference temperature for samples prepared using a ratio of monomer/initiator 100:1. a) ACN-ref, b) ACN-H, c) ACN-OMe, d) ACN-CAT, e) ACN-F, f) ACN-Cl, g) ACN-Br. The linear viscoelastic results were fitted using multimode Maxwell model, and corresponding LVE envelope is represented with the solid lines. For the comparison purpose, y-axis on all graphs has the same scale

In comparison to the reference polymer, all other samples contain polar groups capable of forming hydrogen bonding associations. Therefore, the ACN-ref does not have reversible associations, and thus no strain hardening effect can be seen. The terminal zone for the ACN-ref was not completely achieved, which is due to the presence of very weak electrostatic interactions between polarized aromatic ring referred to as π - π interactions.³¹⁸ However, the corresponding LVE envelope shows flattening, essentially asymptotically approaching the zero shear viscosity.

As noted above, the stress growth coefficient at different Hencky strain rates follow the LVE envelope, which is typical behavior of polymers with a small number of entanglements (no strain hardening effects). Other samples exhibit strong strain hardening with tensile stress growth coefficients several orders of magnitude higher than the reference sample. At short times, the tensile stress growth coefficient curves follow the linear viscoelastic envelope, whereas at long times there is a distinct increase, a phenomenon known as strain hardening. Compared to the ACN-ref sample, these results clearly show the strong effect of hydrogen bonding associations. Even though hydrogen bonding represents one of the weakest non-covalent associations, several studies have demonstrated that systems with a high number density of stickers induce strong strain hardening effects.^{209,224,319}

Images of samples shown in Figure 5.8 were recorded during the extensional experiment. It represents the case of ACN-OMe, which was tested at a low Hencky strain rate of 0.01 s^{-1} and at the reference temperature of 120 °C. During the uniaxial extension of all samples, a single crack was formed that propagated gradually across the sample in a direction perpendicular to the extension, until the final rupture. Several other studies have shown similar findings with parabolic and wedge crack opening profiles that are typical for polymers with permanent crosslinks, such as elastomers and permanent gels.^{222,224,320–323} Regardless of the fact that functionalized polynorbornenes possess only temporary crosslinks through the formation of hydrogen bonds, their behavior resembles to that of materials with permanent crosslinks due to the numerous associations. Therefore, these findings show the similarities of these polymers with those of solid-like materials where the sample breaks without necking.



Figure 5.8 Pictures of the crack propagation across ACN-OMe at 120 °C and Hencky strain rate of 0.01 s⁻¹

5.3.2 Functionalized Polycyclooctenes

5.3.2.1 Thermal Characteristics

As in the case of functionalized polynorbornenes, the results of the thermogravimetric analysis are given in addition to differential scanning calorimetry in this section. Specific degradation temperatures and mass loss were determined by TGA analysis, whereas DSC was used to obtain transition temperatures.

5.3.2.1.1 Thermogravimetric Analysis

The thermogravimetric methodology was explained in section 2.2.2 for the functionalized polycyclooctenes that are similar to those of functionalized polynorbornenes. TG and DTG curves for all polymers synthesized by the monomer-to-initiator ratio of 100:1 are displayed in Figure 5.9, and the degradation temperatures are listed in Table 5.6. As in the case of functionalized

polynorbornenes, several characteristic regimes of degradation can be distinguished on the degradation curves.



Figure 5.9 The TG (solid lines) and DTG (dashed lines) curves recorded in a nitrogen atmosphere for synthesized functionalized polycyclooctenes, namely a) ACC-ref, b) ACC-H, c) ACP-H, d) ACC-OMe, e) ACN-F, and f) ACN-Br

The DTG curves of functionalized polycyclooctenes do not indicate the presence of any peaks at the temperatures up to about 300 °*C*, except in the case of ACC-Br where the main chain degradation started at a lower temperature. As shown in Table 5.6, two distinct regimes can be seen for most of the secondary amine-containing polycyclooctenes. Only the reference sample and ACP-H degraded in a single step when the main chain scission started to occur. The degradation of pendant side groups was not detected. The first thermogravimetric step recorded is in the temperature range from 200 to 340 °*C* with the DTG peak at around 300 °*C* for ACC-H, ACC-OMe, and ACC-F and 227 °*C* for ACC-Br. This represents the degradation of the pendant side groups that is similar to the findings for functionalized polynorbornenes. Decomposition of
polymer matrix occurred at about the same temperature of 440 $^{\circ}C$ regardless of polymer structure (see Table 5.6). A char residue for the reference and ACP-H samples was very low (~2% of the total mass), whereas for the other samples this quantity was much higher. ACC-H and ACC-F had char residue of 7% and ACC-OMe and ACC-Br of 15% of the total mass.

Sample	Mass, mg	Step I		Step II		Step III	
		⊿ <i>T</i> , °C	T_{d1} , •C	⊿ <i>T</i> , °C	<i>T</i> _{<i>d</i>2} , • <i>C</i>	∆ <i>T</i> , °C	<i>T</i> _{<i>d</i>3} , • <i>C</i>
ACC-ref	5.129	-	-	-	-	370-490	462
АСС-Н	5.628	250-340	291.1	-	-	340-480	444.2
ACP-H	5.759	-	-	-	-	370-488	457.9
ACC-OMe	5.122	223-342	305	-	-	342-495	425.6
ACC-F	6.016	245-325	298.2	-	-	325-490	443.6
ACN-Br	5.492	200-245	227	245-384	318	384-495	444.6

Table 5.6 The characteristic decomposition temperatures of functionalized polycyclooctenes

5.3.2.1.2 Differential Scanning Calorimetry

The highest temperature used for DSC was 120 °C, and at this temperature there was no observable degradation. All samples are amorphous with negative glass transition temperatures, which make them flexible at ambient temperature. This indicates that all samples possess high segmental mobility at ambient conditions, allowing polymer chains to flow. DSC traces are depicted in Figure 5.10 with indicated T_g values. These temperatures do not have a strong

dependence on the polymer structure like in the case of functionalized polynorbornenes where the difference was much larger.



Figure 5.10 DSC thermograms of functionalized polycyclooctenes with the glass transition temperatures indicated on the graphs

5.3.2.2 Linear Viscoelasticity

Linear rheological measurements were conducted using the Anton Paar MCR 702 rotational rheometer, equipped with a cone-partitioned plate geometry. First, the time sweep experiment was performed to determine the thermal stability of the sample over a certain period which is needed to perform all other experiments. All samples were stable at all tested temperatures (30-90 °*C*) for about 2 hours, which was more than enough to complete the tests to determine the linear viscoelastic dynamic moduli. The threshold of linear viscoelasticity was obtained by

conducting a strain sweep test at a constant frequency of 0.1 Hz and temperature of 30 °C. The strain of 0.01 was used to perform frequency sweep tests to determine the dynamic moduli, and the complex viscosity at several temperatures, namely 30, 50, 70, and 90 °C. The time-temperature superposition principle was used to construct the master curves for all samples by applying a horizontal shift at the reference temperature of 30 °C. The difference in the glass transition temperatures for all samples is very small, and as such the same reference temperature was taken. The same procedure to create the master curve as in the case of functionalized polynorbornenes was used. The obtained master curves for the functionalized polycyclooctenes are presented in Figure 5.11.



Figure 5.11 Evolution of dynamic moduli against angular frequency at the reference temperature of 30 °*C* for all synthesized functional polycyclooctenes prepared by using the monomer-to-initiator ratio of 100:1. a) ACC-ref, b) ACC-H, c) ACP-H, d) ACC-OMe, e) ACC-F, and f) ACC-Br

The reference polymer shows a liquid-like behavior over the whole frequency range with a terminal zone typical for linear polymers. A slight deviation in storage modulus from the classical dependence, $G' \propto \omega^2$, is an indication of the presence of π - π interactions (professor Evelyne van Ruymbeke, private communication). Due to slightly high polydispersity, these polymers do not show the presence of any plateau region. The behavior of all secondary amine-containing polycyclooctenes is about the same regardless of polymer structure. In comparison to ACC-H hydrogenated ACP-H does not have any double bonds present in the polymer backbone. Thus, the polymer chains are more flexible which can also be seen from the value of T_g . Despite the lower T_g and the higher flexibility of polymer chains, ACP-H exhibit gel-like behavior, $G' \approx G'' \propto \omega^{0.5}$, since more entanglements and associations can be formed and therefore assume a gel structure.

Compared to functionalized polynorbornenes where the strong effect of hydrogen bonding was observed even at lower molecular weights, in the case of functionalized polycyclooctenes, this effect is much smaller due to easier dissociation of hydrogen bonds. Translation of intramolecular associations to intermolecular one requires less energy since the polymer chains are much more flexible. The rheological behavior of these polymers is therefore strongly dependent upon the molecular weight, the type of hydrogen bonding groups, and the details of the molecular interactions (i.e., intra- vs. inter-molecular associations). This dependence can be observed in the comparison of linear viscoelastic behavior of the same polymer structure, but various molecular weights as illustrated in Figure 5.12.



Figure 5.12 Master curves of storage and loss moduli versus angular frequency of several molecular weights of ACC-H at the reference temperature of 30 °*C*

Figure 5.12 shows that the viscoelastic moduli are independent of molecular weight at high frequencies, where short segments are relaxing. The shape and magnitude of the master curves strongly depend on molecular weight. Whereas for the case of low molecular weight where the terminal relaxation was achieved, the high molecular weight samples reveal the strong hydrogen bonding effects where the emergence of a plateau region is clearly appearing similar to the case of functionalized polynorbornenes. ACC-H with a molecular weight higher than 60k possesses stronger associations and a higher number of entanglements. As a result, the plateau region which is due to the presence of both associations and entanglements, is well established.

Using the experimental data for ACC-H ($M_w = 64,000 \text{ g/mol}$), it was possible to extract the value of associations lifetime to be $\tau_s = 1.3 \times 10^4 \text{ s}$. This time corresponds to the inverse of the frequency at the end of the first plateau. Associations lifetime can be compared with the

appropriate value for functionalized polynorbornenes (see Table 5.5). Comparison of both functionalized polynorbornenes and functionalized polycyclooctenes, with higher molecular weight and the same pendant side group, revealed similar results of the associations lifetime in the order of 10⁴. Additionally, the reptation time, τ_{rep} , which for ACC-H was estimated to be 3.6×10¹⁰ s was found to be almost equal. On the other hand, it can be noted that functionalized polycyclooctenes with lower molecular weight are relaxing much faster than the functionalized polynorbornenes, due to their more flexible polymer chains, and easier dissociations from intramolecular to intermolecular interactions. Only samples with moderately high molecular weight exhibit plateau. The wide span of the plateau region of functionalized polynorbornenes is due to the presence of many more associations compared to those of entanglements. This ratio is less in the case of functionalized polycyclooctenes. Although the functionalized polycyclooctenes still have a molecular weight between stickers much smaller than the molecular weight between entanglements, the number of entanglements is higher due to their greater flexibility. Therefore, the relaxation process of these polymers with smaller molecular weight is occurring at shorter time scales.

5.3.2.3 Self-mending Properties

During material characterization, a remarkable self-healing property was discovered for the functionalized polycyclooctene polymers. This property was demonstrated by performing recovery extensional experiments at ambient temperature and a small Hencky strain rate of 0.005 s^{-1} . Initially, the virgin sample was tested, and the control stress-stain curve was established. Then the sample was cut with a razor blade into two pieces, and consequently, the two parts were gently placed into contact (see Figure 5.13). They were left at ambient conditions without applying any 152

external stimuli (pressure, heat, solvent) for various amounts of time in order to determine the amount of time needed to achieve complete healing. Ultimately, measurements were performed by extending the sample until breakage at the healing scar, although after long healing times, the cut was not clearly visible. It was possible to break and reversely reform the same sample numerous times.



Figure 5.13 Illustration of the self-mending experiment. a) virgin sample, b) sample was cut by a razor blade into two pieces, and c) parts of the sample were brought into contact without applying any external stimuli sample and was left to self-heal for various times

Figure 5.14 displays an example of stress-strain curves for two samples (a, b) that have the same structure, but different molecular weight, ACC-H, and the third sample (c) is the hydrogenated polymer, ACP-H. Both ACC-H samples have low molecular weight compared to ACP-H.



Figure 5.14 Self-mending of a) ACC-H M_n = 37,000 g/mol, b) ACC-H M_n = 15,000 g/mol, and c) ACP-H M_n = 71,000 g/mol

As the healing time was increased the mended polymers were able to sustain deformations up to linear elongation of about 330 %. In the case of ACC-H with a molecular weight of 37k (Figure 5.14a), one hour of self-healing resulted in complete recovery. In addition, the recovered sample at short healing time of 5 *min*, when a small number of available functional groups could link, it was extended up to ~ 220 % before failure. This is about half of the ultimate elongation of the virgin sample. After 30 minutes of healing, the sample could be deformed up to about 300 % before failure. By reducing the molecular weight of ACC-H, the mending time can be significantly decreased (faster self-mending). Although the elongation to break is reduced since samples with low molecular weight contain a low number of entanglements, a healing time as short as 20 *min* resulted in full recovery. To the best of our knowledge this is the fastest self-healing elastomeric material. The results show that after only 5 *min* of mending, the sample can recover up to about 80 % of total deformation.

Even samples with high molecular weight were able to self-heal, which can be observed almost instantaneously to a certain degree. However, to achieve complete recovery, a longer time was needed compared to that needed for a low molecular weight polymer. To demonstrate this, the ACP-H sample with a moderately high molecular weight of 71,000 *g/mol* was used (Figure 5.14c). Using the same procedure, it was found that about two hours of mending time, at ambient conditions without any external stimuli, was needed to obtain complete healing. ACP-H possesses a hydrogenated backbone that is more flexible, and T_g value is slightly lower than the corresponding polymer with double bonds (ACC-H). However, complete self-mending takes a longer time, and this is associated with the higher molecular weight of ACP-H.

It was shown that the presence of reversible associations is necessary in the polymer matrix in order to achieve self-mending at short time scales. To fabricate a successful self-healing material, it is essential to have numerous free functional groups at the cut surface. Therefore, the associations strength must be lower than the strength of covalent bonds. Having many available functional groups ready to interact/associate and connect allows samples to mend and maintain large deformations. Besides the required numerous functional groups, chain flexibility is another important factor that contributes to fast self-mending process. One can argue that by allowing enough time any material with low T_g is capable to self-heal. However, we did not observe such behavior. The reference sample, ACC-ref, has a low T_g and exhibited liquid-like behavior over the entire frequency range (see Figure 5.11a) at ambient conditions. It did not show any tendency to self-heal after cutting, not even after being in contact for a long period of several months.

Besides self-mending property, functionalized polycyclooctenes have ability to adhere to various surfaces, such as metal, rubber, glass, and various polymers including PTFE. These polymers behave as typical pressure-sensitive adhesives, which can be safely applied because they are solid-like materials, no solvent is needed, and they can be precisely placed between two surfaces. Their self-adhesive properties were demonstrated qualitatively by placing ACC-H sample between two untreated PTFE sheets and applying a low pressure manually. By pulling the

two PTFE sheets apart in a T-peel fashion debonding involves the formation of fibrils. Figure 5.15 demonstrates the debonding of the two PTFE sheets and the formation of fibrils through cohesive failure. It is well-known that the presence of hydrogen bonding associations improves interfacial adhesion and inhibit creep and cohesive failure.^{324,325} Only functionalized polycyclooctenes with low molecular weight show self-adhesive performance due to low level of chain entanglement. However, the presence of hydrogen bonding, that acts as physical crosslinking, increases the chain cohesion which significantly affects the mechanical and physical properties of adhesives.



Figure 5.15 Images of fibrillation formation occurring during debonding of the pressure-sensitive functionalized polycyclooctenes

5.4 Summary

Two different types of associating polymers capable of forming strong hydrogen bonds, namely functionalized polynorbornenes and functionalized polycyclooctenes, were studied thermally and rheologically. Several different functional groups were introduced. Thus, various structures were obtained for both types of polymers. The main difference between these two materials is in their backbone. In the case of ACN type polymers, the backbone is rigid with glass transition temperatures between 40 and 80 °*C* depending on the structure. On the other hand, the ACC type has a more flexible backbone, and its T_g is about -10 °*C*. Therefore, a higher activity/flexibility of polymer chain segments is present. Rheological properties in both cases can

be significantly modified by altering the functional groups and the molecular weight of the materials.

The dynamics of polymer chains was investigated by estimating their characteristic relaxation times such as Rouse, sticky-reptation times, and associations lifetime using the scaling laws developed by Leibler et al.³⁵. This could be achieved by employing the modified tube model in combination with the time marching algorithm.³¹² It was found that for the functionalized polynorbornenes, the relaxation processes are considerably slow ($\tau_S \approx 10^4 s$ and $\tau_{rep} \approx 10^{10} s$) due to strong hydrogen bonding associations. Moreover, it was not possible to synthesize smaller molecular weight samples that could potentially relax faster. In the case of functionalized polycyclooctenes, various molecular weights were prepared, and the rheological properties were tuned from liquid- to solid-like behavior. By comparing ACN-H and ACC-H samples with similar structure and high molecular weight, the relaxation times, such as sticky-reptation and associations lifetime, were found to be equivalent.

In a comparison of extensional rheology of ACN-ref and other functionalized polynorbornenes, it was evident that the presence of hydrogen bonds induce significant strain hardening. Functionalized polycyclooctenes behaved similarly. Additionally, due to the numerous associations and low T_g value that allows increased flexibility of polymer chains at ambient conditions, ACC types of material possess a remarkable self-mending property. By tuning the molecular weight, it was possible to significantly reduce the mending time, and thus the self-healing capabilities. Moreover, it was shown the functionalized polycyclooctenes can adhere to various surfaces including PTFE which is known for its anti-stick properties.

Chapter 6: Conclusions and Recommendations

6.1 Conclusions

Associating polymers is a fast-growing class of materials that have been successfully used in various applications such as self-healing, self-assembly materials, shape memory polymers, conductive electrolytes, and devices for cell/protein delivery. However, the physics of these complex associating networks is still not fully understood. The main reason for this is the interplay of their chemistry and polymer topology which gives rise to very complex behavior that depends on several time scales. In this thesis, one of the goals was to investigate the dynamics of polymer chains of associating polymers with different structures. Three different classes of materials were used in this study: i) ionomers, ii) functionalized polynorbornenes, and iii) functionalized polycyclooctenes.

First, the entangled polydisperse copolymers of ethylene and methacrylic acid ionomers neutralized with sodium hydroxide were studied using a cone and plate, cone-partitioned plate rotational rheometers, the SER fixture with rotational rheometer, and finally the capillary rheometer. The commercially available ionomers were chemically treated to remove the ions and produce their parent copolymers in order to examine the effects of ionic interactions. A scaling theory was used to calculate the distribution of the relaxation times and identify the characteristics times such as Rouse and reptation times and associations lifetimes. These calculated characteristic times turned out to be useful in understanding their dynamics and correlate them with their performance in processing to identify possible applications. The lifetime of associations, τ_s , was found to scale with the number of associations per chain, Z_s , and to be of the order of 10⁻⁴ to 10⁻² *s* using three different methods showing that their effects at time scales greater than 10⁻² *s* are 158 significant. For comparison, these time scales are smaller than the Rouse times for the cases where the number of associations is smaller than the number of entanglements per chain. The energy of association was found to be of the order of $10-15 \ kJ/mol$, and it was found to scale weakly with the number of associations per chain.

To perform a comparative study of the effects of ionic associations, sodium ions were eliminated from the ionomers, and their rheological behavior was compared directly with their associative counterparts. Overall, due to the presence of associations the relaxation processes slow down, and the modulus shifts to significantly higher values. These modulus increases is more pronounced as the number of associations increased. At least one order of magnitude difference was identified in some cases where the number of reversible ionic associations was high.

One of these ionomers has been experimentally studied in capillary flow, and the results were used to compare with numerical simulations performed by using the integral K-BKZ constitutive equation. The parameters of the K-BKZ model were calculated by using rheological data obtained as described in Chapter 4. In particular, the behavior of this polymer was studied in entry flows through tapered dies with different length-to-diameter ratios to predict the Bagley correction and describe the rheological behavior of such materials in capillary flow. The experiments have shown a distinct pressure-dependence of viscosity with a pressure coefficient to be a power-law function of pressure. This effect was found to be significant in long capillary dies, and a pressure dependency coefficient should be used in flow simulations for reliable predictions. Finally, the influence of strong ionic interactions has been demonstrated with increased and strong vortices at the entry compared to relatively weak ones observed for its parent copolymer. To further confirm these findings, all ionomers and their corresponding copolymers have been studied rheologically, and the experimental results were used to fit the parameters of a K-BKZ model in

order to perform flow simulations in abrupt contraction (capillary) flows. It was found that the K-BKZ model can represent their rheological behavior well, and moreover it is capable of predicting the capillary flow of ionomers. Therefore, such a model can safely be recommended to be used in more complex flows in polymer processing. The effects of ionic and hydrogen bonding associations on the entry pressure drop and capillary flow have been assessed in detail. Specifically, it was found that the length (size) of the corner vortex as well as on the vortex strength depends strongly on the number of reversible ionic associations. In all cases, the ionomers exhibit much more significant effects (higher entry pressure, larger and stronger corner vortices) compared to their copolymers, the more so as the number of ionic associations present in their backbone increases. This is due to strong ionic associations present in the ionomers that give rise to strong strain hardening effects important in entry flows. Compared to ionic associations, the effects of hydrogen bonds are insignificant, particularly at levels less than 5 *mol%*. Therefore, in the case of copolymers, their molecular weight and number of entanglements play the dominant role in the entry pressure, size and strength of corner vortices.

Besides ion-containing polymers, other types of materials with strong hydrogen bonding was examined. Specifically, linear viscoelastic experiments were carried on several functionalized polynorbornenes (ACN-X) and functionalized polycyclooctenes (ACC-X) that possess a variety of functional groups capable of creating strong associations to understand their dynamics. Starting with thermal studies, both ACN-X and ACC-X polymers were found to be an amorphous material. The flexibility of polymer backbone dictated the glass transition temperature, where ACN-X have T_g in the range of 40 to 80 °C varying with the polymer structure and for ACC-X polymers this value is much lower around -10 °C.

The extensive thermorheological studies of ACN-ref revealed typical liquid-like behavior similar to that of linear polymers with delayed terminal relaxation due to the existence of π - π interactions. On the contrary, linear viscoelasticity results of the secondary amine-containing polynorbornenes showed solid-like behavior with terminal relaxation time scales of about 10⁸ *s* and higher due to the extended H-bonding network among the polymer chains. Apart from the relaxation times, such as the lifetime of reversible associations (between 10³ and 10⁶ *s*) the plateau modulus was found to depend on the type of *p*-substituted aniline group within the polymer chain. This plateau was also found to depend on the molecular weight to a certain degree, showing that the dynamics of these polymers depend on the molecular conformations and intramolecular associations. These are difficult to control due to the presence of numerous reversible associations.

As a result of these reversible associations, extensional experiments have shown that the tensile stress growth coefficients are several orders of magnitude higher than the reference sample, which does not exhibit any strain hardening. At short times, extensional results follow the linear viscoelastic envelope, whereas at long times there is a distinct increase in extensional viscosity (i.e., strain hardening), which clearly originate from the strong effect of hydrogen bonding interactions. It was shown that in uniaxial extension, the extended samples were forming parabolic crack openings that are the property of polymers with permanent crosslinks. Although functionalized polynorbornenes contain only reversible hydrogen interactions, their behavior corresponds to materials with permanent crosslinks due to the numerous associations.

Several functionalized polycyclooctenes were rheologically examined by directly comparing the findings of reference material to secondary amine-containing polycyclooctenes. As in the previous case of functionalized polynorbornenes, ACC-ref shows a liquid-like behavior over the whole frequency range with a slight deviation in storage modulus that is an indication of the

presence of π - π interactions. Compared to ACN-X polymers which exhibit plateau that spans over several decades of frequencies, ACC-X samples show plateau over a shorter frequency range due to more flexible polymer backbone. Therefore, the molecular weight of the sample, type of hydrogen bonding groups, and overall polymer architecture has a significant impact on the rheological behavior. This was shown by linear viscoelastic properties of ACC-H with several different molecular weights. Samples with low molecular weight have short relaxation times compared to high molecular weight polymers, which possess numerous hydrogen bonding groups along the polymer chains besides the higher number of entanglements. The associations lifetime of functionalized polycyclooctene samples with moderately high molecular weight was found to be similar to that of functionalized polynorbornenes and exhibits a clear plateau region.

The hydrogen bonding ability of the polymers can be tuned by exploiting different hydrogen bond accepting groups on the aryl ring and this, in turn, can tune the rheological properties of these polymers. This strategy has opened a new avenue to make amine-functionalized materials with varying interesting bulk thermorheological and mechanical properties. One remarkable property is the ability of functionalized polycyclooctenes to self-mend spontaneously with no use of any external stimuli. It was shown that in the case of ACC-H with low molecular weight, self-mending is occurring much faster although exhibiting relatively low ultimate elongation due to the insufficient number of entanglements. On the other hand, hydrogenated polymer, ACP-H that represents functionalized polyethylene, demonstrated complete fast healing in about two hours. On-going work explores the effect of controlled addition of various functionalities on self-mending and adhesion, and how these properties can be modulated in blends and copolymers with other polymers. Additionally, low molecular weight functionalized

polycyclooctenes behaves as pressure-sensitive adhesives that can adhere to various surfaces including PTFE.

6.2 Contributions to Knowledge

The overall objective of this work was to understand the characteristic relaxation processes present in associating polymers. This study resulted in several unique contributions to knowledge.

1) Based on a scaling theory, a method was developed to calculate the various relaxation times that play a significant role in the dynamics of reversible associating polymers. The scaling laws have been combined with experimental finding to calculate important time scales such as the associations lifetime that mostly control their dynamics.

2) The significant effects of ionic associations in polyethylene-based ionomers have been studied in detail by comparing their dynamics with that of their corresponding copolymers after removing the sodium ions. These effects have been quantified in terms of differences in their rheological properties and flow behavior in capillary flow, i.e., entry pressure related to extensional viscosity, vortex strength, and size.

3) It was found for the first time that a K-BKZ integral model can represent well the rheological properties of associating polymers in spite of their strong strain hardening effects. This model was also capable of calculating the entry pressure in capillary flow and predicting it accurately. Therefore, such a model can be used to study the processing of these polymers in more complex flows.

4) The dynamics of associating polymers capable of forming strong hydrogen bonding namely functionalized polynorbornenes and functionalized polycyclooctenes was studied in detail as functions of the types of functional group present and molecular weight. It was found that the properties of such systems can be tuned and tailored depending on the desired applications, such as self-healing materials, adhesives, and additives to improve the mechanical properties of other polymeric materials.

6.3 Recommendations for Future Work

There are a number of opportunities and challenges in which this work could be continued by exploring the dynamics of associating polymer networks. First, the dynamics of the sodium salt of ethylene-methacrylic acid copolymers was performed in this study. However, the MAA groups of these polymers can be associated with other ions, such as Zn²⁺, Ca²⁺, Mg²⁺ which are bivalent as opposed to monovalent Na⁺. Therefore, it is expected that their dynamics could be much more enhanced.

Second, in capillary rheometry polymer melts flow through converging zones where the melts experience considerably high tensile stresses which may possibly lead to flow-induced crystallization (FIC). Moreover, due to excessive stresses, these polymers might experience instabilities such as melt fracture phenomena. Therefore, a study of flow-induced crystallization and melt fracture of these polymers is proposed. In addition, the adhesion properties of these ionomers should be studied to identify which reversible associations (ionic or hydrogen bonding) play a more significant role.

Third, the study of dynamics of functionalized polynorbornenes and functionalized polycyclooctenes should be extended by performing additional experiments on samples with several different molecular weights. The changes in the plateau modulus with chain lengths or functional groups can be further investigated. Additionally, controlling the number of reversible

associations can give a better insight into the relaxation processes. This could be achieved by synthesizing copolymers or making blends with other polymeric materials.

Finally, the investigation of the possible application of functionalized polynorbornenes as a shape memory material could be carried out, since there is an indication in the literature that similar types of polymers possess this property. Moreover, exploring the potential adhesion properties of functionalized polycyclooctenes could be the focus of future work.

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Appendices





Figure A.1 FTIR spectra of ionomer 4.3 - Na 69 and corresponding copolymer 4.3 - Na 0 with characteristic peaks indicated on the graph



Figure A.2 FTIR spectra of ionomer 4.9 - Na 63 and corresponding copolymer 4.9 - Na 0 with characteristic peaks indicated on the graph



Figure A.3 FTIR spectra of ionomer 11.5 - Na 65 and corresponding copolymer 11.5 - Na 0 with characteristic peaks indicated on the graph



Figure A.4 FTIR spectra of ionomer 19.2 - Na 69 and corresponding copolymer 19.2 - Na 0 with characteristic peaks indicated on the graph

Appendix B Thermal Properties



B.1 Thermogravimetric Analysis

Figure B.1 TG curves for studied ionomers namely 4.3 – Na 69, 4.9 – Na 63, 11.5 – Na 65, and 19.2 – Na 65

B.2 Differential Scanning Calorimetry



Figure B.2 DSC thermogram for studied ionomers namely 4.3 – Na 69, 4.9 – Na 63, 11.5 – Na 65, and 19.2 – Na 65



Appendix C Supporting Information for Chapter 3

Figure C.1 Superposition of the master curves of storage and loss moduli for ionomer $(4.3 - Na \ 69)$ and corresponding copolymer $(4.3 - Na \ 0)$



Figure C.2 The horizontal shift factors estimated from the tTS principle obtained by constructing the master curves of storage and loss moduli for 11.5 - Na 65 and 11.5 - Na 0. Solid lines represent Arrhenius fit



Figure C.3 Van Gurp-Palmen plot for ionomer 4.3 – Na 69 (filled symbols) and corresponding copolymer 4.3 – Na θ (unfilled symbols)

Appendix D Supporting Information for Chapter 5

Sample	λ_i, s	G _i , Pa
ACN-ref	2.15×10 ⁻⁴	3.15×10 ⁵
	3.86×10 ⁻³	6.20×10 ⁴
	3.63×10 ⁻²	3.35×10 ⁴
	2.80×10 ⁻¹	1.02×10^4
	2.22	1.12×10 ³
	31.0	26.4
ACN-H	5.26×10 ⁻⁴	4.92×10 ⁵
	6.58×10 ⁻³	1.64×10^{5}
	6.05×10 ⁻²	5.42×10^4
	5.80×10 ⁻¹	1.46×10^4
	5.28	2.55×10^{3}
	43.3	2.29×10^{2}
ACN-OMe	2.85×10 ⁻²	3.04×10 ⁴
	2.95×10 ⁻²	2.98×10^4
	1.01×10 ⁻¹	2.94×10^4
	2.12×10 ⁻¹	3.32×10 ⁴
	1.32	2.27×10^{4}
	77.9	4.66×10^4
ACN-CAT	9.05×10 ⁻⁴	3.85×10 ⁴
	1.35×10 ⁻²	6.48×10 ³
	1.19×10 ⁻¹	3.66×10 ³
	9.84×10 ⁻¹	1.65×10^{3}

 Table D.1 Maxwell model parameters for the functionalized polynorbornenes

Sample	λ_i, s	G _i , Pa
ACN-CAT	8.28	8.91×10 ²
	1.02×10^{3}	73.6
ACN-F	1.10×10 ⁻³	2.00×10^{5}
	1.95×10 ⁻²	6.46×10^4
	2.31	8.36×10 ³
	2.04×10^2	2.08×10^{3}
	1.99×10 ³	8.02×10^2
	4.29×10 ⁴	3.97×10^{2}
ACN-Cl	9.48×10 ⁻⁵	5.03×10 ⁵
	6.44×10 ⁻⁴	2.72×10^4
	2.91×10 ⁻²	1.41×10^4
	5.69×10 ⁻¹	5.93×10 ³
	11.0	2.74×10^{3}
	2.02×10^2	3.77×10^{3}
ACN-Br	1.84×10 ⁻⁴	5.85×10 ⁵
	3.97×10 ⁻³	4.89×10^{4}
	4.45×10 ⁻²	1.85×10^{4}
	4.47×10 ⁻¹	8.55×10 ³
	5.05	3.81×10 ³
	8.72×10 ²	2.49×10 ²