LIQUID CRYSTALLINE TACTOIDS IN MICROSCOPIC ORDERED-DISORDERED INTERFACES: EMERGENCE OF SELF-ASSEMBLY AND TOPOLOGICAL DEFECTS

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Abstract

Liquid crystalline tactoids are discrete anisotropic microdroplets coexisting with continuous disordered phases. In this thesis, an in-situ photopolymerization method was designed to rapidly capture and solidify liquid crystalline tactoids in a crosslinked polymer matrix, which facilitated the direct observation of these fluid ordered microdroplets by scanning electron microscopy with the resolution of individual liquid crystal mesogens. Different stages of the evolution of tactoids were captured and examined, where the emergence of small-sized tactoids in initially disordered phases, the coalescence of multiple tactoids, the generation of topological defects in coalescence, and the sedimentation of tactoids were directly observed by electron microscopy.

The in-situ photopolymerization method was then extended to inverse emulsions, where the structure and evolution of chiral nematic liquid crystalline tactoids in geometrical confinement of microspheres were investigated by both optical and electron microscopy. This study revealed the microstructures of topological defects of frustrated chiral nematic order in spherical confinement. Moreover, polymer and mesoporous silica microspheres with helical structures were obtained.

The behavior of tactoids in the presence of colloidal doping nanoparticles was examined by electron microscopy at the resolution of individual particles, which showed that liquid crystalline tactoids have size-selective exclusion effects on foreign nanoparticles. This principle was applied to the separation of polymer nanospheres, gold nanoparticles, and paramagnetic nanoparticles by size. These results suggest an approach to size-selectively separate nanoparticles using lyotropic liquid crystals, where nanoparticles smaller than a threshold size will be selectively collected into the liquid crystalline tactoids and thus transferred from the disordered phase to the ordered phase during phase separation.
The phase separation of liquid crystals in the presence of paramagnetic doping nanoparticles and gradient magnetic fields was studied. In this case, the disordered phases have higher volume magnetic susceptibility than liquid crystalline tactoids due to the exclusion effects of tactoids on paramagnetic nanoparticles. Thus, the movement and orientation of tactoids could be controlled by gradient magnetic fields as weak as several hundred Gauss/cm. This approach enables control of the phase separation rate and configuration, as well as the orientation of director fields in both discrete tactoids and continuous macroscopic ordered phases.
Lay Summary

When rod-shaped particles form a stable dispersion, due to their anisotropic geometry, they may adopt a similar orientation above a critical concentration, which is termed a lyotropic liquid crystal. When a lyotropic liquid crystal initially forms in a disordered system, microdroplets with widths of several tens to hundreds of micrometers, in which the rod-shaped particles are orderly arranged, may appear, and these microdroplets are called "tactoids". It was difficult to study the microscopic structures of tactoids as they are soft and fluid. To address this issue, a method was developed in this thesis, by which tactoids can be rapidly captured in a jelly-like polymer matrix and further solidified. This approach enabled observation of the internal structures of tactoids at the resolution of individual particles, and provided insights into the emergence of lyotropic liquid crystals.
Preface

All the work presented in this thesis was carried out under the supervision of Prof. Dr. Mark J. MacLachlan. All the cellulose nanocrystals were kindly provided by Dr. Wadood Y. Hamad at FPInnovations. I am the principal author of this thesis and I performed all of the experiments.

Chapter 2: A version of this chapter, "Structure and transformation of tactoids in cellulose nanocrystal suspensions",\textsuperscript{53} has been published: Wang, P.-X.; Hamad, W. Y.; MacLachlan, M. J. Nat. Commun. \textbf{2016}, 7, 11515. I performed all of the experiments and wrote the first draft of the manuscript, and contributed to the final version of the manuscript.

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In addition, a review article of the research work presented in Chapter 2 and Chapter 3 has already been published: "Liquid crystalline tactoids: ordered structure, defective coalescence and evolution in confined geometries", Wang, P.-X.; MacLachlan, M. J. Phil. Trans. R. Soc. A 2018, 376, 20170042. I wrote the first draft of the manuscript of this review article, and contributed to the final version of the manuscript.
# Table of Contents

Abstract........................................................................................................................................... iii

Lay Summary................................................................................................................................... v

Preface........................................................................................................................................... vi

Table of Contents.......................................................................................................................... viii

List of Tables................................................................................................................................ xiii

List of Figures............................................................................................................................... xiv

List of Symbols........................................................................................................................... xxxi

List of Abbreviations................................................................................................................... xxxii

Glossary.................................................................................................................................... xxxiii

Acknowledgements................................................................................................................... xxxiv

Dedication................................................................................................................................. xxxvi

Chapter 1: Introduction.................................................................................................................... 1

  1.1 Liquid Crystals................................................................................................................... 1
      1.1.1 History and Definition of Liquid Crystals.............................................................. 1
      1.1.2 Classification of Liquid Crystalline Phases......................................................... 1
      1.1.3 Applications of Liquid Crystals............................................................................ 2

  1.2 Liquid Crystalline Tactoids.................................................................................................. 6
      1.2.1 Tactoids in Lyotropic Liquid Crystals................................................................. 6
      1.2.2 Emergence of Tactoids in Disordered Phases...................................................... 6
      1.2.3 Geometries and Director Fields of Tactoids....................................................... 8

  1.3 Cellulose Nanocrystals...................................................................................................... 10
1.3.1 Chiral Nematic Phases Formed by Cellulose Nanocrystals

1.3.2 Liquid Crystalline Tactoids of Cellulose Nanocrystals

1.4 Aims and Scope

Chapter 2: Structure and Transformation of Liquid Crystalline Tactoids

2.1 Introduction

2.2 Solidification of Liquid Crystalline Tactoids by In-Situ Photopolymerization

2.3 Electron Microscopy Observations of Liquid Crystalline Tactoids

  2.3.1 Microstructures of Chiral Nematic Liquid Crystalline Tactoids

  2.3.2 Coalescence of Tactoids and Formation of Topological Defects

  2.3.3 Gravitational Sedimentation of Liquid Crystalline Tactoids

2.4 Conclusions

2.5 Experimental Methods

  2.5.1 Capture of Tactoids by In-Situ Photopolymerization

  2.5.2 Concentration and Density of Ordered and Disordered Phases

  2.5.3 Materials

  2.5.4 Characterization

Chapter 3: Liquid Crystalline Tactoids in Geometrical Confinement

3.1 Introduction

3.2 Microspheres with Chiral Nematic Order from Liquid Crystalline Tactoids

  3.2.1 Evolution of Liquid Crystalline Tactoids in Spherical Confinement

  3.2.2 Solidification of Microdroplets by In-Situ Photopolymerization

  3.2.3 Structure of Liquid Crystalline Tactoids in Spherical Confinement

  3.2.4 Spherical Chiral Nematic Tactoids under Electron Microscopy
3.2.5 Tactoids in Geometrical Confinement with Different Dimensions...................... 67

3.3 Mesoporous Silica Microspheres with Chiral Nematic Order................................. 73

3.4 Conclusions.................................................................................................................. 78

3.5 Experimental Methods................................................................................................ 79

3.5.1 Fabrication of Polymer Microspheres with Chiral Nematic Order....................... 79

3.5.2 Preparation of Chiral Nematic Mesoporous Silica Microspheres......................... 80

3.5.3 Materials............................................................................................................... 81

3.5.4 Characterization.................................................................................................... 81

Chapter 4: Size-Selective Exclusion Effects of Liquid Crystalline Tactoids on Nanoparticles:
Separation by Microscopic Ordered-Disordered Interfaces........................................... 83

4.1 Introduction.................................................................................................................. 83

4.2 Size-Selective Exclusion of Nanoparticles by Liquid Crystalline Tactoids................. 84

4.2.1 Liquid Crystalline Tactoids in Mixtures of Nanorods and Nanospheres.............. 84

4.2.2 Exclusion of Large-Sized Nanoparticles by Liquid Crystalline Tactoids............ 89

4.2.3 Coalescence of Tactoids Traps Nanoparticles in Topological Defects................. 96

4.2.4 Existence of Small-Sized Nanoparticles in Liquid Crystalline Tactoids............. 100

4.2.5 Size-Selective Particle Permeability of Ordered-Disordered Interfaces.............. 104

4.3 Size-Selective Separation of Nanoparticles with Lyotropic Liquid Crystals......... 108

4.3.1 Separation of Plasmonic Gold Nanoparticles by Size........................................ 108

4.3.2 Multiple-Cycle Size-Selective Separation of Magnetic Nanoparticles............. 114

4.4 Conclusions................................................................................................................ 119

4.5 Experimental Methods............................................................................................ 120

4.5.1 Photopolymerization of Liquid Crystals with Doping Nanoparticles................. 120
4.5.2 Diffusion of Nanoparticles through Ordered-Disordered Interfaces.............. 120
4.5.3 Size-Selective Separation of Gold Nanoparticles by Liquid Crystals.......... 121
4.5.4 Recycling of Liquid Crystalline Phases for Multicycle Separations.......... 121
4.5.5 Materials............................................................................................................. 122
4.5.6 Characterization.................................................................................................. 123

Chapter 5: Movement and Orientation Control of Liquid Crystalline Tactoids in Competitive Acceleration Fields: Phase Separations Beyond Gravity.................................................. 124

5.1 Introduction................................................................................................................... 124
5.2 Magnetic Buoyancy Forces on Tactoids with Lower Magnetic Susceptibility .. 127
5.3 Unidirectional Phase Separations: Acceleration by Gradient Magnetic Fields..... 130
    5.3.1 Lyotropic Liquid Crystals Doped with Paramagnetic Nanoparticles........ 130
    5.3.2 Orientation of Liquid Crystalline Tactoids in Gradient Magnetic Fields..... 136
    5.3.3 Vertically Aligned Chiral Nematic Layers: Reversed Phase Separation..... 144
5.4 Competitions between Gravitational and Magnetic Acceleration Forces........... 153
5.5 Conclusions................................................................................................................... 158
5.6 Experimental Methods............................................................................................... 159
    5.6.1 Synthesis of Superparamagnetic Magnetite (Fe₃O₄) Nanoparticles...... 159
    5.6.2 Solidification of CNC-Fe₃O₄ Mixtures by In-Situ Photopolymerization.... 159
    5.6.3 Materials............................................................................................................. 160
    5.6.4 Characterization.................................................................................................. 160

Chapter 6: Conclusions and Future Perspectives............................................................ 161

6.1 Conclusions............................................................................................................... 161
6.2 Future Perspectives................................................................................................... 164
6.2.1 Liquid Crystalline Tactoids in Other Soft Matter Systems.................................164

6.2.2 Size-Selective Separation of Molecules by Liquid Crystalline Tactoids............164

Bibliography......................................................................................................................166
List of Tables

Table 3.1. Preparation parameters for CNC-PAAm chiral nematic microspheres....................... 52
Table 5.1. Phase separation times of CNC-Fe₃O₄ binary mixtures.............................................154
Table 5.2. Distribution ratio of Fe₃O₄ NPs in isotropic and liquid crystalline phases............... 156
List of Figures

**Figure 1.1.** Phase transitions of thermotropic liquid crystals as the temperature increases........3

**Figure 1.2.** Phase transitions of lyotropic liquid crystals as the concentration decreases........ 3

**Figure 1.3.** Arrangement of rod-shaped mesogens in nematic liquid crystals. The mesogens have a long-range collective orientational order.............................................................4

**Figure 1.4.** Arrangement of rod-shaped mesogens in smectic liquid crystals, where in addition to the long-range collective orientational order, the mesogens also have long-range positional order in one dimension...........................................................................................................4

**Figure 1.5.** Arrangement of mesogens in chiral nematic (cholesteric) liquid crystals, which adopt a helical superstructure......................................................................................................................5

**Figure 1.6.** Nematic liquid crystalline tactoids formed in a dispersion of tobacco mosaic viruses, which are spindle-shaped birefringent microdroplets.\(^{12}\).................................................................9

**Figure 1.7.** Chiral nematic liquid crystalline tactoids formed in a polypeptide solution, which are spherical microdroplets with periodically spaced birefringent layers.\(^{14}\)..................................................9

**Figure 1.8.** TEM micrographs of cellulose nanocrystals used in this research. Scale bars, (A) 200 nm, (B) 100 nm, (C,D) 50 nm............................................................................................................12

**Figure 1.9.** POM micrograph showing discrete chiral nematic liquid crystalline tactoids formed in an aqueous dispersion of cellulose nanocrystals. Scale bar, 50 μm.........................................................13

**Figure 2.1.** By adding the nonionic precursors of polyacrylamide into an aqueous suspension of cellulose nanocrystals, this system could be captured in a cross-linked polymer matrix by in-situ photopolymerization, forming a CNC-PAAm composite hydrogel. The diameter of the Petri dish in this photograph is about 50 mm.................................................................17
**Figure 2.2.** Photograph showing a completely dried CNC-PAAm composite polymer matrix, in which the microstructures of tactoids have been solidified..........................17

**Figure 2.3.** SEM micrographs of a newly emergent liquid crystalline tactoid formed by cellulose nanocrystals. Scale bars, (A) 2 μm, (B) 1 μm, (C) 300 nm, (D) 200 nm, (E,F) 100 nm..............19

**Figure 2.4.** Cross-sectional SEM micrographs showing the boundary of a newly emergent liquid crystalline tactoid near its (A,B) left and (C,D) bottom regions. The boundary of this tactoid is a microscopic ordered-disordered interface, which sharply separates the liquid crystalline domain from the isotropic phase surrounding it. Scale bars, (A,C) 200 nm, (B,D) 100 nm..................20

**Figure 2.5.** High-resolution SEM micrographs showing the ordered arrangements of rod-shaped cellulose nanocrystal mesogens in a newly emergent liquid crystalline tactoid. The mesogens are unidirectionally aligned into a nematic phase since this tactoid is smaller than a half helical pitch, however, the director field is still slightly twisted in long ranges due to the chirality of this phase. Scale bars, (A-D) 100 nm..............................................................................................................21

**Figure 2.6.** Cross-sectional SEM micrographs showing a liquid crystalline tactoid with only one chiral nematic layer. Scale bars, (A) 1 μm, (B,C) 300 nm, (D-F) 200 nm..............................22

**Figure 2.7.** 3D model showing the left-handed chiral nematic order of CNC mesogens (depicted as rods in a golden brown color) in a newly formed liquid crystalline tactoid with only one chiral nematic band. The rod-shaped mesogens in the pseudo nematic layers rotate by 180 degrees from one end to the other.................................................................23

**Figure 2.8.** Additional SEM micrographs showing liquid crystalline tactoids with (A,B) one, (C) zero, or (D-F) three chiral nematic layers. Scale bars, (A) 2 μm, (B) 400 nm, (C) 1 μm, (D) 3 μm, (E) 500 nm, (F) 200 nm.................................................................................................................24
Figure 2.9. Cross-section SEM micrographs showing a liquid crystalline tactoid with four chiral nematic layers. Scale bars, (A) 5 μm, (B,D) 2 μm, (C,E) 1 μm, (F) 300 nm................................. 25

Figure 2.10. Cross-sectional SEM micrographs of a large-size liquid crystalline tactoid with nine chiral nematic layers. Scale bars, (A) 10 μm, (B,C) 2 μm, (D-F) 1 μm................................. 26

Figure 2.11. SEM micrographs showing several chiral nematic liquid crystalline tactoids sitting at a right-angled edge. Scale bars, (A) 200 μm, (B) 50 μm, (C,D) 10 μm, (E,F) 3 μm.............. 27

Figure 2.12. SEM micrographs showing the (A-C) top and (D-F) front views of a tactoid sitting at a right-angled edge. Scale bars, (A) 10 μm, (B,D) 2 μm, (C,E) 1 μm, (F) 500 nm............. 28

Figure 2.13. SEM micrographs showing the (A-C) left and (D-F) right views of a chiral nematic liquid crystalline tactoid. Scale bars, (A,D) 500 nm, (B,E,F) 300 nm, (C) 200 nm.............. 29

Figure 2.14. Three-dimensional model showing the contact between two discrete chiral nematic liquid crystalline tactoids in an aqueous dispersion of cellulose nanocrystals...................... 32

Figure 2.15. POM micrographs showing the coalescence of two chiral nematic liquid crystalline tactoids in a CNC dispersion................................................................. 33

Figure 2.16. SEM micrograph showing the initiation of coalescence between two chiral nematic tactoids. Scale bar, 10 μm................................................................. 33

Figure 2.17. SEM images showing the microstructures of the contact point between two tactoids. Scale bars, (A) 2 μm, (B) 1 μm, (C) 500 nm, (D) 300 nm........................................... 34

Figure 2.18. SEM images showing the aggregation and contact between multiple chiral nematic liquid crystalline tactoids. Scale bars, (A) 20 μm, (B,C) 10 μm, (D-F) 5 μm....................... 35

Figure 2.19. SEM images of liquid crystalline tactoids with topological defects of dislocated or folded chiral nematic layers. Scale bars, (A) 5 μm, (B-F) 10 μm................................. 36
Figure 2.20. Cross-sectional SEM micrograph showing the gravitational sedimentation of chiral nematic liquid crystalline tactoids to the bottom of a CNC dispersion, where the tactoids coalesce together to form a macroscopic continuous ordered phase. Scale bar, 20 μm... 38

Figure 2.21. SEM micrographs showing topological defects as an array of folded chiral nematic layers. Scale bars, (A) 20 μm, (B,C) 2 μm, (D) 1 μm, (E,F) 500 nm... 39

Figure 2.22. SEM micrographs showing topological defects as an array of folded chiral nematic layers. Scale bars, (A) 10 μm, (B) 3 μm, (C) 1 μm, (D) 500 nm... 40

Figure 2.23. POM micrograph showing the fingerprint-like texture in a solid-state chiral nematic film formed by CNCs. Scale bar, 50 μm... 41

Figure 2.24. 3D model showing the left-handed chiral nematic arrangement of rod-shaped CNC mesogens in a liquid crystalline tactoid... 43

Figure 2.25. 3D models showing the coalescence of liquid crystalline tactoids and the formation of topological defects as folded chiral nematic layers... 44

Figure 2.26. 3D model showing topological defects as an array of folded chiral nematic layers in the continuous liquid crystalline phase at the bottom of a CNC dispersion... 45

Figure 3.1. POM micrographs showing the evolution of chiral nematic liquid crystalline tactoids in spherical confinement. The evolution time and diameter of these microdroplets are as follows: (A) 0.5 h, 118 μm; (B) 1 h, 58 μm; (C) 3 h, 64 μm; (D) 6 h, 78 μm; (E) 9 h, 57 μm; and (F) 12 h, 114 μm... 51

Figure 3.2. Sketch showing the in-situ photopolymerization of aqueous CNC microdroplets in an inverse emulsion. Using this approach, CNC-PAAm composite microspheres with chiral nematic structures could be obtained... 53
Figure 3.3. Optical micrographs of dried CNC-PAAm microbeads (A) observed under reflected white light or (B) with transmitted light between crossed polarizers. Scale bars, 50 μm. 56

Figure 3.4. POM micrograph of a CNC-PAAm chiral nematic microgel that has swelled in water. Scale bar, 20 μm. 56

Figure 3.5. Optical micrographs of CAMB-M microgels (after swelling in water) observed (A,C) between crossed polarizers or (B,D) under reflected white light. Scale bars, 50 μm. 57

Figure 3.6. Orthogonal views of a chiral nematic microsphere obtained by confocal fluorescence microscopy. Here the imaging region is 178 μm in width and 130 μm in height. The sample was stained by immersing the microspheres in an aqueous solution of rhodamine B (about 0.1 wt.%), then redispersed in pure water before imaging. This microsphere was flattened by gravity. 58

Figure 3.7. A three-dimensional reconstructed confocal fluorescence microscopy image showing the chiral nematic layers in a microsphere as a series of concentric spherical shells. A topological defect can be observed at the center of this microsphere, which was formed due to the frustration of the chiral nematic liquid crystalline order in the spherical confinement. 59

Figure 3.8. POM images of CNC-PAAm microspheres showing chiral nematic tactoids captured at different evolution stages. Diameter of microspheres, (A) 85 μm, (B) 136 μm, (C) 142 μm and (D) 141 μm. 60

Figure 3.9. Three-dimensional models showing the evolution of chiral nematic liquid crystalline tactoids in spherical confinement. 61

Figure 3.10. A three-dimensional model showing the chiral nematic layers of a liquid crystalline tactoid in spherical confinement, which are organized into a series of concentric shells. 61

Figure 3.11. SEM micrographs showing the surface morphology of the solid-state CNC-PAAm (CAMB-M) composite microspheres. Scale bars, 20 μm. 63
**Figure 3.12.** SEM micrographs showing the onion-like structure of chiral nematic layers inside a CNC-PAAm microsphere, which was cracked in liquid nitrogen. As frost immediately formed on the cold fracture surface, softened and smoothed it after melting (due to the hydrophilicity of the polyacrylamide matrix), the arrangement of individual CNCs cannot be distinguished. Scale bars, (A) 10 μm, (B) 5 μm..........................................................63

**Figure 3.13.** SEM images showing a fracture surface of an epoxy resin containing CNC-PAAm microspheres. Scale bars, (A) 200 μm, (B) 50 μm........................................................................64

**Figure 3.14.** SEM image showing the cross-section of a microsphere that has been split into two parts by using an epoxy resin. Scale bar, 10 μm...........................................................................64

**Figure 3.15.** Cross-sectional SEM micrograph showing the spiral structure of the chiral nematic liquid crystalline tactoid inside a CNC-PAAm microsphere. This tactoid consists of two different chiral nematic layers. The chiral nematic ordering of the liquid crystalline phase is frustrated due to the spherical confinement, which results in the formation of a topological defect in the center of this tactoid. Scale bar, 5 μm..............................................................................65

**Figure 3.16.** Cross-sectional SEM images showing the left-handed chiral nematic order of CNCs in a microsphere. Scale bars, (A) 2 μm, (B,C) 500 nm, (D) 200 nm.............................................66

**Figure 3.17.** SEM micrographs showing the size distributions of completely dried CNC-PAAm microspheres. (A,B) CAMB-M, (C) CAMB-L, and (D) CAMB-S. These micrographs were taken at the same magnification. Scale bars, 200 μm..........................................................69

**Figure 3.18.** POM micrographs of CAMB-M microspheres. Typically, the chiral nematic liquid crystalline tactoids inside a microsphere have been well integrated into a single liquid crystalline core with a spherical geometry, which is located at the center of the microsphere and surrounded by an isotropic shell. Most of these integrated tactoids have highly-ordered onion-like structures
of multiple concentric spherical shells. These micrographs were taken at the same magnification. Scale bars, 50 μm .......................................................... 70

**Figure 3.19.** POM micrographs showing CAMB-S microspheres in water, the diameters of these small-size microspheres are about 2 to 3 times the helical pitch of the CNC chiral nematic phase. Typically, the liquid crystalline tactoids in a microsphere have also been well integrated, forming a series of concentric spherical chiral nematic shells near the boundary of the microsphere, which leaves an isotropic core in the central region. Interestingly, in some cases there may be a discrete tactoid left inside the isotropic core. All these micrographs were taken at the same magnification. Scale bars, 50 μm .......................................................... 71

**Figure 3.20.** POM images showing CAMB-L microspheres. The chiral nematic liquid crystalline tactoids in these large-sized microspheres were not well integrated during the period of standing, which might be caused by the relatively long distances between them. These POM micrographs were taken at the same magnification. Scale bars, 50 μm .......................................................... 72

**Figure 3.21.** POM images of mesoporous silica microspheres. Scale bars, 10 μm .................. 75

**Figure 3.22.** IR spectra of CNC-PAAm-SiO$_2$ (blue) and SiO$_2$ microspheres (red curve) ........ 75

**Figure 3.23.** SEM images showing the chiral nematic order of a mesoporous silica microsphere. Scale bars, (A) 10 μm, (B) 2 μm, (C,E) 500 nm, (D) 1 μm, (F) 200 nm ......................... 76

**Figure 3.24.** Nitrogen adsorption-desorption isotherm (77 K) of mesoporous silica microspheres. The sample mass was 117.3 mg in this measurement. The desorption data are presented as empty circles .................................................................................................................. 77

**Figure 4.1.** SEM images for large polystyrene nanoparticles (denoted as L-PSNPs, diameters of 265-280 nm) used in this work. Scale bars, (A) 200 nm, (B) 100 nm .............................. 85
Figure 4.2. Optical microscopy images showing chiral nematic liquid crystalline tactoids formed in the presence of L-PSNPs (265 to 280 nm in diameter), which were observed between crossed polarizers (A) or under reflected white light (B). Scale bars, 50 μm................................................................. 85

Figure 4.3. SEM images of small-size polystyrene nanoparticles (denoted as S-PSNPs, diameters of 30-57 nm) used in this work. Scale bars, 50 nm........................................................................... 86

Figure 4.4. Optical microscopy images showing chiral nematic liquid crystalline tactoids formed in a binary mixture of CNCs and S-PSNPs (30-57 nm in diameter), which was observed between crossed polarizers (A) or under reflected white light (B). Scale bars, 50 μm............................... 86

Figure 4.5. 3D model showing the exclusion effect of a liquid crystalline tactoid (mesogens are depicted as golden brown rods) on large-sized doping nanoparticles (purple spheres).................. 87

Figure 4.6. 3D model showing that small-sized nanoparticles (depicted as red spheres) can enter a liquid crystalline tactoid.............................................................................................................. 88

Figure 4.7. SEM image of a tactoid formed in a CNC/L-PSNP mixture. Scale bar, 2 μm......... 91

Figure 4.8. SEM images showing the inside area of a newly formed liquid crystalline tactoid in a CNC/L-PSNP binary mixture. Scale bars, (A) 1 μm, (B) 500 nm................................................................. 91

Figure 4.9. SEM images of (A) the upper left, (B,C) the left, and (D-F) the upper boundaries of a newly emergent chiral nematic liquid crystalline tactoid in a CNC/L-PSNP mixture. Scale bars, (A,C,E) 500 nm, (B,D) 1 μm, (F) 200 nm................................................................................................................. 92

Figure 4.10. SEM images showing L-PSNPs in disordered phases. Scale bars, 200 nm........... 93

Figure 4.11. 3D model for the emergence of a small tactoid in a CNC/L-PSNP mixture........... 93

Figure 4.12. SEM micrographs of a liquid crystalline tactoid with about 10 chiral nematic layers formed in a CNC/L-PSNP mixture (A), as well as the boundary (B-D) and chiral nematic layers of this tactoid (E,F). Scale bars, (A) 5 μm, (B,C) 1 μm, (D,E) 500 nm, (F) 200 nm................. 94
Figure 4.13. 3D model showing the coalescence of two liquid crystalline tactoids in the presence of large-sized foreign nanoparticles.................................................................95

Figure 4.14. (A) A few large-sized doping nanoparticles (depicted in purple) could be trapped at the contact point between two coalescing tactoids. (B) A lot of large doping nanoparticles can be sealed within the broad isotropic region surrounded by several merging tactoids. (C) Topological defects generated during the coalescence of tactoids would eventually remain in the macroscopic liquid crystalline phases with a large number of doping nanoparticles sealed inside.......................96

Figure 4.15. (A) Cross-sectional SEM micrograph showing the initiation of coalescence between two liquid crystalline tactoids formed in a CNC/L-PSNP binary mixture. The boundaries of these two tactoids can exclude the large-sized doping nanoparticles (B), but several nanoparticles were trapped at the contact point between them (C,D), which would be sealed in the liquid crystalline phase. Scale bars, (A) 5 μm, (B,C) 1 μm, (D) 200 nm...............................................................97

Figure 4.16. SEM images showing the contact between two tactoids in a CNC/L-PSNP mixture (A), the exclusion of L-PSNPs by tactoid boundaries (B,C), and L-PSNPs trapped in the contact region (D-F). Scale bars, (A) 3 μm, (B,E) 500 nm, (C,D) 1 μm, (F) 200 nm..........................98

Figure 4.17. Cross-sectional SEM images of a CNC/L-PSNP mixture showing large-size doping nanoparticles trapped in the topological defects of the macroscopic liquid crystalline phase (A-B and C-F). Scale bars, (A,D) 1 μm, (B,E) 500 nm, (C) 2 μm, (F) 200 nm..............................99

Figure 4.18. SEM images showing the existence of small-sized doping nanoparticles (diameters of 30-57 nm) as about 50 nm hemispherical cavities in tactoids formed in a CNC/S-PSNP binary mixture (A-C and D-F). Scale bars, (A) 3 μm, (B,C,F) 100 nm, (D) 2 μm, (E) 200 nm..........101
Figure 4.19. (A-E) SEM images showing hemispherical cavities created by S-PSNPs in a "baby" tactoid in a CNC/S-PSNP mixture. (F) Image showing the coexistence of S-PSNPs and CNCs in the disordered phase. Scale bars, (A) 2 μm, (B) 200 nm, (C,D,F) 100 nm, (E) 50 nm.

Figure 4.20. 3D models illustrating (A) the size-selective permeability of an ordered-disordered interface to foreign nanoparticles, and (B) the exclusive force from this interface on an invading nanoparticle with a width larger than the gaps in the liquid crystalline lattice.

Figure 4.21. Photographs showing that the downward diffusion of L-PSNPs was stopped by the ordered-disordered interface of a phase-separated CNC dispersion.

Figure 4.22. (A) Cross-sectional SEM micrograph showing the ordered-disordered interface of a phase-separated CNC dispersion, which is the upper boundary of the macroscopically continuous chiral nematic liquid crystalline phase. (B-D) Expanded views near the interface showing that the downward diffusion of the large-sized polystyrene nanoparticles (diameters of 265-280 nm) was dramatically stopped by the upper boundary of the liquid crystalline phase. Scale bars, (A) 2 μm, (B) 1 μm, (C,D) 500 nm.

Figure 4.23. High-resolution cross-sectional SEM image showing the microscopic structures of the interface between the disordered phase (upper) and the chiral nematic liquid crystalline phase (lower) in a completely phase-separated cellulose nanocrystal dispersion, where the organization of individual liquid crystal mesogens can be directly observed. This ordered-disordered interface dramatically blocked the downward diffusion of the large-sized doping nanoparticles (L-PSNPs), which could be observed in the upper disordered phase as either hemispherical cavities or partly stretched nanospheres. Scale bar, 200 nm.

Figure 4.24. SEM images showing that when small-size polystyrene nanoparticles (diameters of 30 to 57 nm) were added on the top of a phase-separated cellulose nanocrystal suspension, these
nanoparticles were able to pass through the isotropic-anisotropic interface by diffusion, resulting in hemispherical cavities (about 50 nm in diameter) in the chiral nematic liquid crystalline phase. Scale bars, (A) 500 nm, (B-D) 100 nm.

**Figure 4.25.** Photographs (with transmitted white light) for phase-separated CNC-AuNP binary mixtures.

**Figure 4.26.** UV-Vis absorption of a phase-separated CNC/S-AuNP binary mixture.

**Figure 4.27.** UV-Vis absorption of a phase-separated CNC/L-AuNP binary mixture.

**Figure 4.28.** UV-Vis absorption spectra of the isotropic (Iso) and liquid crystalline (LC) phases of a phase-separated CNC/L&S-AuNP ternary mixture.

**Figure 4.29.** (A) UV-Vis absorption spectra of a phase-separated CNC dispersion, which exhibit no absorption peaks between 400 nm and 800 nm. (B) Additional UV-Vis absorption spectra of the small and large sized gold nanoparticles used in this study.

**Figure 4.30.** (A,B) TEM micrographs showing the coexistence of the large and small sized gold nanoparticles in the disordered phase of a completely phase-separated CNC/L&S-AuNP ternary mixture. (C,D) Inside the liquid crystalline phase, only the small-sized gold nanoparticles could be observed. Scale bars, (A,B) 100 nm, (C,D) 200 nm.

**Figure 4.31.** Particle size distributions of AuNPs in the isotropic (Iso) and liquid crystalline (LC) phases of a phase-separated CNC/L&S-AuNP ternary mixture, measured by TEM.

**Figure 4.32.** A depiction showing the size-selective collection of the small foreign nanoparticles (small nanoparticles in red, large particles in purple) by chiral nematic liquid crystalline tactoids of CNCs. Due to the higher density, tactoids will gradually settle to the bottom part of the dispersion and coalesce into a macroscopic ordered phase with a significantly higher ratio of small nanoparticles.
**Figure 4.33.** Photographs showing phase-separated dispersions of cellulose nanocrystals mixed with 8.7 nm (left), 8.7 nm & 107 nm (middle), and 107 nm (right) superparamagnetic magnetite nanoparticles, taken with transmitted white light.............................................. 115

**Figure 4.34.** Photographs showing phase-separated dispersions of cellulose nanocrystals mixed with 8.7 nm (left), 8.7 nm & 107 nm (middle), and 107 nm (right) superparamagnetic magnetite nanoparticles. The photos were taken with reflected white light................................. 116

**Figure 4.35.** UV-Vis absorption spectra for phase-separated CNC/S-MNP (A) and CNC/L-MNP (B) binary mixtures......................................................................................................................116

**Figure 4.36.** TEM images showing the changes in the size distribution of magnetic nanoparticles during the multiple-cycle size-selective separation process, which was conducted with a ternary mixture of S-MNPs, L-MNPs, and CNCs. (A) The initial mixture of S-MNPs and L-MNPs used in the multicycle separation. (B) MNPs in the liquid crystalline phase of the 1st separation cycle. (C) MNPs isolated from the liquid crystalline phase of the 9th separation cycle. (D) MNPs in the isotropic phase of the 9th separation cycle. All the images were taken at the same magnification. Scale bars, (A-D) 100 nm............................................................................................................ 117

**Figure 4.37.** Photographs showing the phase separations of a CNC/L&S-MNP ternary mixture in the 1st, 3rd, 5th, 7th, and 9th separation cycles. The photographs were taken with reflected white light..............................................................................................................................................118

**Figure 4.38.** The size distributions of MNPs in the initial mixture of L-MNPs and S-MNPs (red color), in the liquid crystalline phase of the 1st (green) and the 9th (cyan) separation cycles, and in the isotropic phase of the 9th separation cycle (blue).............................................................118

**Figure 5.1.** 3D Model showing the exclusion effects of liquid crystalline tactoids (mesogens are depicted as golden-brown rods) on superparamagnetic magnetite doping nanoparticles (depicted
as black spheres), thus the disordered phase has significantly higher magnetic susceptibility than liquid crystalline tactoids. However, the tactoids have a higher density than isotropic phases due to the ordered arrangements of mesogens. 

**Figure 5.2.** When a paramagnetic-nanoparticle-doped lyotropic system is subjected to a gradient magnetic field (H), the movement direction and velocity of a discrete liquid crystalline tactoid is determined by the vector sum of four external forces: the weight ($F_g$) in the vertically downward direction, the magnetic body force ($F_m$) along the gradient magnetic field to the high field region, the magnetic buoyancy force ($F_{bm}$) along the gradient magnetic field to the low field region (this force is exerted by the continuous isotropic phase surrounding the tactoid), and the gravitational buoyancy force ($F_{bg}$) in the vertically upward direction exerted by the continuous isotropic phase as well. The unidirectional movement of tactoids (which is mainly driven by $F_{bm}$) results in shear forces, by which the chiral nematic layers are oriented parallel to the magnetic field.

**Figure 5.3.** TEM micrographs of the superparamagnetic magnetite (Fe$_3$O$_4$) nanoparticles used in this study. Scale bars, (A,B) 30 nm, (C,D) 20 nm.

**Figure 5.4.** When only affected by the gravity, a CNC-MNP binary mixture phase-separates into a liquid crystalline phase (exhibiting higher brightness between two crossed polarizers) below a disordered phase over several hours. The CNC-MNP binary mixture has a volume of 1.0 mL and the phase separation process was observed between two crossed polarizers (in the horizontal and vertical directions) with transmitted white light.

**Figure 5.5.** Photographs of phase-separated CNC dispersions (colorless) and CNC-MNP binary mixtures (yellow colored). A grid background was used to distinguish the isotropic phase (which is clear) from the liquid crystalline phase (which is birefringent) in (B).
Figure 5.6. In a horizontally oriented gradient magnetic field (1050 Gauss/cm) from a permanent magnet placed beside the vial, the CNC-MNP binary mixture phase-separated into a macroscopic liquid crystalline phase (with a lighter yellow color) in the low-magnetic-field region as well as a disordered phase in the high-magnetic-field region (A), while the pure CNC suspension was not significantly affected (B)........................................................................................................................................133

Figure 5.7. In a vertical gradient magnetic field (intensity about 1050 Gauss/cm) from a magnet under the vial, phase separation of the CNC-MNP binary mixture results in a macroscopic liquid crystalline phase (with a higher brightness between crossed polarizers) above a disordered phase. This process is much faster than in the absence of the gradient magnetic field..........................134

Figure 5.8. In a vertical gradient magnetic field from a permanent magnet placed under the vial, the CNC-MNP binary mixture phase-separated into a macroscopic liquid crystalline phase (with a lighter yellow color) above a disordered phase (A). However, the pure CNC dispersion was not significantly influenced by the magnetic field (B)........................................................................................................................................135

Figure 5.9. Photographs of phase-separated CNC-MNP binary mixtures captured in cross-linked polyacrylamide networks by in-situ photopolymerization. The phase separation of these systems occurred in (A) horizontally or (B) vertically oriented gradient magnetic fields.........................137

Figure 5.10. POM images of a CNC-MNP dispersion (no magnets). Scale bars, 50 μm...........138

Figure 5.11. Cross-sectional SEM micrographs for a phase-separated CNC-MNP dispersion (no magnetic fields). Chiral nematic layers in the macroscopically continuous ordered phase adopt a horizontal orientation, while discrete liquid crystalline tactoids in the continuous isotropic phase are nearly randomly oriented. Scale bars, (A) 10 μm, (B) 1 μm, (C) 200 nm, (D) 100 nm....... 139

Figure 5.12. 3D model of a CNC-MNP binary mixture (no magnetic fields)..............................140

Figure 5.13. SEM images of a pure CNC dispersion. Scale bars, (A) 40 μm, (B) 20 μm...........140 xxvii
**Figure 5.14.** SEM images showing the ordered-disordered interfaces of CNC-MNP suspensions that phase-separated in a horizontal gradient magnetic field. The interfaces are tilted. Scale bars, (A) 10 μm, (B) 2 μm, (C,F) 1 μm, (D) 500 nm, (E) 3 μm..........................141

**Figure 5.15.** 3D model showing the unidirectional orientation of chiral nematic layers in both the continuous ordered phase and discrete liquid crystalline tactoids of a phase-separated CNC-MNP binary mixture. The phase separation of this system occurred in a horizontally oriented gradient magnetic field, which resulted in a nearly vertical ordered-disordered interface...................142

**Figure 5.16.** POM micrographs showing the unidirectional orientation of chiral nematic layers of liquid crystalline tactoids in a CNC-MNP suspension subjected to an external gradient magnetic field (in the direction from left to right with respect to these images). The system was captured in a crosslinked polyacrylamide matrix by photopolymerization during the phase separation process (after a standing time of 60 minutes). The orientation of chiral nematic layers in these tactoids is parallel to the external gradient magnetic field. From (A,B) to (C) and (D), the imaging area was increasingly further from the high-magnetic-field region at the magnetic pole. These micrographs indicate that tactoids were driven by magnetic buoyancy forces (from the continuous disordered phase that has a higher magnetic susceptibility) and move to lower magnetic field regions, where they aggregate and coalesce into continuous liquid crystalline phases. Scale bars, 50 μm.........143

**Figure 5.17.** POM micrograph of a CNC-MNP binary mixture that phase-separated in a vertical gradient magnetic field, where the chiral nematic layers in both the continuous ordered phase and discrete liquid crystalline tactoids are vertically oriented. Scale bar, 50 μm.........................145

**Figure 5.18.** SEM images showing the vertical orientation of chiral nematic layers in continuous ordered phases and discrete liquid crystalline tactoids. Scale bars, (A) 15 μm, (B) 10 μm........ 145
Figure 5.19. High-resolution SEM micrographs revealing the ordered arrangements of cellulose nanocrystal mesogens in the continuous liquid crystalline phase of a CNC-MNP suspension that phase-separated in a vertical gradient magnetic field. The pseudo nematic layers formed by these CNC mesogens are in the vertical direction, which are parallel to the external gradient magnetic field. Scale bars, (A) 300 nm, (B,C) 200 nm, (D) 100 nm..........................................................146

Figure 5.20. Cross-sectional POM micrographs showing the continuous liquid crystalline phase of a CNC-MNP binary mixture, which phase-separated in a vertical gradient magnetic field. The chiral nematic layers are aligned in a vertical orientation throughout this liquid crystalline phase, from the liquid-air interface at the top of the dispersion (A) to the ordered-disordered interface at the bottom of the anisotropic phase (B-D). Scale bars, 50 μm....................................................147

Figure 5.21. SEM images showing the horizontal ordered-disordered interface and vertical chiral nematic layers in a CNC-MNP binary system that phase-separated in a vertical gradient magnetic field. Scale bars, (A) 5 μm, (B) 3 μm, (C) 2 μm, (D) 1 μm, (E) 500 nm, (F) 200 nm.................148

Figure 5.22. SEM images showing the horizontal ordered-disordered interface and vertical chiral nematic layers in a CNC-MNP binary system that phase-separated in a vertical gradient magnetic field. Scale bars, (A) 30 μm, (B) 10 μm, (C) 3 μm, (D) 1 μm, (E) 300 nm, (F) 150 nm.............149

Figure 5.23. Additional SEM images showing the vertical orientation of chiral nematic layers in a phase-separated CNC-MNP binary mixture. These chiral nematic layers are aligned parallel to the external gradient magnetic field, perpendicular to the horizontal ordered-disordered interface. In this case, the cross-sectional appearance of chiral nematic structures is also determined by the fracture angle when the cross-section surface was created from the CNC-MNP-PAAm composite polymer matrix. Scale bars, (A) 5 μm, (B) 2 μm, (C) 1 μm, (D) 400 nm.................................150
Figure 5.24. 3D model showing the cross-sectional structure of a CNC-MNP binary mixture that phase-separated in a vertical gradient magnetic field from a magnet placed under the suspension. In this system, chiral nematic layers in both the continuous ordered phase (the upper region) and discrete liquid crystalline tactoids (in the lower region) are vertically oriented, while the interface between the ordered and disordered phases is in the horizontal direction. 

Figure 5.25. SEM images showing the liquid-air interface at the top of a CNC-MNP suspension that phase-separated in a vertical gradient magnetic field. The chiral nematic layers are vertically oriented near this interface. Scale bars, (A) 100 μm, (B) 30 μm.

Figure 5.26. SEM micrographs showing the biphasic region in a CNC-MNP binary mixture. The system was captured by photopolymerization while the phase separation process was ongoing in a vertical gradient magnetic field from a magnet placed under the dispersion. The chiral nematic layers in both the continuous ordered phase and discrete liquid crystalline tactoids are vertically oriented. Scale bars, (A) 20 μm, (B) 10 μm.

Figure 5.27. Phase separation times of CNC-MNP dispersions (volume of 1.0 mL) with different doping concentrations of Fe₃O₄ nanoparticles (0 to 140.5 ppm by weight) and in vertical gradient magnetic fields with different strengths (0, 600, 1050, and 3050 Gauss/cm). The striped columns represent reversed phase separations, where the liquid crystalline phase forms above the isotropic phase. (Errors in the determination of phase separation times are +/− 10 minutes).

Figure 5.28. UV-Vis absorption spectra of the isotropic phase (red curve) and liquid crystalline phase (blue curve) of a phase-separated pure CNC dispersion. The two phases were isolated and diluted by water to 10 times their original volumes.

Figure 5.29. Absorbance of MNPs in isotropic (red) and liquid crystalline phases (blue).
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nabla )</td>
<td>the Nabla operator</td>
</tr>
<tr>
<td>°</td>
<td>degrees</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>( \mu_0 )</td>
<td>vacuum permeability, or magnetic constant</td>
</tr>
<tr>
<td>( \mu_L )</td>
<td>microliters</td>
</tr>
<tr>
<td>( \mu_m )</td>
<td>micrometers, or microns</td>
</tr>
<tr>
<td>( \rho )</td>
<td>density</td>
</tr>
<tr>
<td>( \chi_m )</td>
<td>volume magnetic susceptibility</td>
</tr>
<tr>
<td>A</td>
<td>Amperes</td>
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<tr>
<td>d</td>
<td>differential of a function</td>
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<tr>
<td>F</td>
<td>force vector</td>
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<tr>
<td>g</td>
<td>grams</td>
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<tr>
<td>( \mathbf{g} )</td>
<td>gravitational acceleration vector</td>
</tr>
<tr>
<td>H</td>
<td>magnetic field vector</td>
</tr>
<tr>
<td>M</td>
<td>magnetization vector, or magnetic moment per unit volume</td>
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<tr>
<td>N</td>
<td>Newtons</td>
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<tr>
<td>pH</td>
<td>power of hydrogen</td>
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<tr>
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<td>parts per million</td>
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## List of Abbreviations

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<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D</td>
<td>three dimensional</td>
</tr>
<tr>
<td>CAMB</td>
<td>cellulose nanocrystal and polyacrylamide composite microbead</td>
</tr>
<tr>
<td>CNC</td>
<td>cellulose nanocrystal</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier transform</td>
</tr>
<tr>
<td>HPLC</td>
<td>high-performance liquid chromatography</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>Iso</td>
<td>isotropic</td>
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<tr>
<td>LC</td>
<td>liquid crystalline</td>
</tr>
<tr>
<td>MNP</td>
<td>magnetite nanoparticle</td>
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<tr>
<td>NP</td>
<td>nanoparticle</td>
</tr>
<tr>
<td>PAAm</td>
<td>polyacrylamide</td>
</tr>
<tr>
<td>POM</td>
<td>polarized optical microscopy</td>
</tr>
<tr>
<td>RPM</td>
<td>revolutions per minute</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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<tr>
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<tr>
<td>$F_g$</td>
<td>weight</td>
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<tr>
<td>$F_{bg}$</td>
<td>gravitational buoyancy force</td>
</tr>
<tr>
<td>$F_m$</td>
<td>magnetic body force</td>
</tr>
<tr>
<td>$F_{bm}$</td>
<td>magnetic buoyancy force</td>
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to my parents

“为学日益 为道日损”

道德经 第四十八章
Chapter 1: Introduction

1.1 Liquid Crystals

1.1.1 History and Definition of Liquid Crystals

Liquid crystals are a phase of matter in the form of a liquid while exhibiting anisotropy due to the ordered arrangement of molecules or particles (termed mesogens) resembling crystals. The first observation of liquid crystalline phases dates back to 1888, when Friedrich Reinitzer tried to determine the melting point of cholesteryl benzoate.\(^1\)\(^2\) The crystalline solid initially melted into a cloudy liquid, which then became clear and transparent at a higher temperature. Compounds like cholesteryl benzoate are thermotropic liquid crystals, which undergo phase transitions in specific temperature ranges (Figure 1.1).\(^3\) Liquid crystalline phases can also form in specific dispersions of molecules or nanoparticles exceeding a critical concentration, and this type is called lyotropic liquid crystals (Figure 1.2).\(^4\)

1.1.2 Classification of Liquid Crystalline Phases

Liquid crystals are generally divided into three classes: nematic, cholesteric (chiral nematic), and smectic. The nematic phases are characterized by long-range collective orientational order of the mesogens (Figure 1.3), while smectic phases additionally have long-range positional order in one dimension (Figure 1.4). The cholesteric phases, which are also known as the chiral nematic phases, have twisted structures (Figure 1.5), and this type of liquid crystals was first observed in cholesterol derivatives.
1.1.3 Applications of Liquid Crystals

Liquid crystals have many applications due to their unique optical, electrical, and magnetic properties. The most important industrial application is liquid crystal displays, which is based on the twisted nematic effect first discovered by Schadt and Helfrich in 1971. Some types of chiral nematic liquid crystals could be used in temperature sensing devices since the helical pitch (and therefore the color) of these materials changes with temperature. Lyotropic liquid crystals, such as those formed by the self-assemble of surfactants or amphiphilic block-copolymers, have been widely used in the template-synthesis of mesoporous materials.
Figure 1.1. Phase transitions of thermotropic liquid crystals as the temperature increases.

Figure 1.2. Phase transitions of lyotropic liquid crystals as the concentration decreases.
**Figure 1.3.** Arrangement of rod-shaped mesogens in nematic liquid crystals. The mesogens have a long-range collective orientational order.

**Figure 1.4.** Arrangement of rod-shaped mesogens in smectic liquid crystals, where in addition to the long-range collective orientational order, the mesogens also have long-range positional order in one dimension.
Figure 1.5. Arrangement of mesogens in chiral nematic (cholesteric) liquid crystals, which adopt a helical superstructure.
1.2 Liquid Crystalline Tactoids

1.2.1 Tactoids in Lyotropic Liquid Crystals

Liquid crystalline tactoids are discrete ordered microdroplets (sizes from tens to hundreds of micrometers) coexisting with continuous disordered phases. Since the pioneering work of Zocher on vanadium pentoxide sols in 1925, tacticoids have been observed in various types of lyotropic liquid crystals such as tobacco mosaic virus, iron oxyhydroxide nanorods, polypeptides, and cellulose nanocrystals. Small tacticoids (several micrometers in size) spontaneously emerge from disordered phases; these liquid crystalline microdroplets gradually grow larger by coalescence as the system relaxes, and eventually merge into macroscopically continuous ordered phases. Thus, tacticoids mediate the transitions between isotropic and liquid crystalline phases in these lyotropic systems.

1.2.2 Emergence of Tactoids in Disordered Phases

When an originally isotropic dispersion (below the critical concentration) is concentrated by evaporation, the formation of tacticoids as birefringent microdroplets can be observed by polarized optical microscopy (POM). While the direct and real-time monitoring of liquid crystal mesogens during the emergence of a tacticoid is still difficult, this process has been theoretically investigated since the 1930s. The formation of a liquid crystalline tacticoid requires both an attractive force to gather together the mesogens into a microdroplet and a repulsive force to arrange these mesogens into liquid crystalline order. The interactions between mesogens are typically simulated using the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory, where the electrostatic repulsion between the charged mesogens is balanced by the van der Waals attractive forces. However, Langmuir
demonstrated that the electrostatic attractive forces between the liquid crystalline mesogens and oppositely charged intervening counterions are enough to balance the repulsive interactions, such as the osmotic pressures and hydration.\textsuperscript{17,20}

Although the above thermodynamic simulations can partly explain how tactoids are created by competitive repulsive and attractive forces, it remains unclear whether these liquid crystalline microdroplets have any unique intrinsic characteristics that distinguish them from the disordered environment. Are the mesogens in a tactoid somehow different from those in the nearby isotropic phase? This is a difficult issue to address due to the lack of direct microscopic observations, but studies on phase-separated lyotropic liquid crystals might give some hints since phase separation in these systems is usually mediated by the coalescence and sedimentation of tactoids.

In a recent study based on phase-separated cellulose nanocrystal dispersions, the rod-shaped mesogens in liquid crystalline phases were found to have significantly longer lengths and higher aspect ratios than those in the isotropic phases.\textsuperscript{21} This discovery is consistent with the theoretical simulations based on the Onsager theory,\textsuperscript{22} which reveals that when phase separation occurs in a dispersion of rod-shaped nanoparticles with different aspect ratios, there will be a higher fraction of the longer nanorods in the liquid crystalline phase than in the disordered phase. As it has been confirmed that the phase transitions in cellulose nanocrystal dispersions are mediated by tactoids, which kinetically transfer liquid crystal mesogens from one phase to the other, the enrichment of high-aspect-ratio mesogens in the macroscopic liquid crystalline phases may have occurred since the nucleation of tactoids.

According to the Onsager theory,\textsuperscript{23} the critical concentration for phase separation in a rod dispersion decreases as the aspect ratio of the rods increases. Because the emergence of a liquid crystalline tactoid is intrinsically a process of microscopic phase separation that occurs when the
local critical concentration is reached, if an initially isotropic dispersion of rod-shaped mesogens is slowly and homogeneously concentrated, liquid crystalline tactoids will first emerge from the microdomains that are rich in high-aspect-ratio rod-shaped mesogens because of the lower local critical concentrations, and thus selectively collect these mesogens into the macroscopic ordered phase by coalescence and sedimentation.

### 1.2.3 Geometries and Director Fields of Tactoids

As demonstrated by a series of studies on vanadium pentoxide tactoids,\textsuperscript{24–26} the geometry of a large-sized nematic tactoid is determined by the competition between the surface energy from the ordered-disordered interfacial tension,\textsuperscript{27} which favors a spherical shape, and the orientational elastic energy of the nematic liquid crystalline phase, which tends to elongate the tactoid. On the other hand, a small-sized tactoid is shaped by the competition between the surface energy and the anchoring energy at the boundary of the tactoid, where the latter is caused by the deviation of the director field from the tangential orientation at the ordered-disordered interface.

Experimentally, the geometry and director field configurations of a tactoid can be examined by polarized optical microscopy as the alignment of mesogens results in birefringence. Nematic tactoids formed in lyotropic liquid crystals of rod-shaped particles, such as vanadium pentoxide nanoribbons,\textsuperscript{28} aluminum oxyhydroxide nanorods,\textsuperscript{29} or tobacco mosaic viruses (Figure 1.6),\textsuperscript{30} are elongated spindle-shaped microdroplets with circular arc boundaries. Tactoids in smectic liquid crystals, such as fd virus dispersions, are spindle-shaped microdroplets with a number of smectic rings periodically spaced along the long axes.\textsuperscript{31} Chiral nematic liquid crystalline tactoids, such as those formed in polypeptide solutions and cellulose nanocrystal suspensions (Figure 1.7),\textsuperscript{14,15} are spherical or ellipsoidal-shaped microdroplets with periodic birefringent chiral nematic layers.
Figure 1.6. Nematic liquid crystalline tactoids formed in a dispersion of tobacco mosaic viruses, which are spindle-shaped birefringent microdroplets.\textsuperscript{12}

Figure 1.7. Chiral nematic liquid crystalline tactoids formed in a polypeptide solution, which are spherical microdroplets with periodically spaced birefringent layers.\textsuperscript{14}
1.3 Cellulose Nanocrystals

1.3.1 Chiral Nematic Phases Formed by Cellulose Nanocrystals

Cellulose nanocrystals (CNCs) are rod-shaped nanoparticles obtained by partial hydrolysis of natural cellulose in sulfuric acid. They have lengths of 100 to 400 nm, and widths of 10 to 30 nm (Figure 1.8). Due to the negatively charged sulfate ester groups on the surface, CNCs could form a stable colloidal suspension in water. In 1959, Marchessault and coworkers first observed the formation of permanently birefringent gels from colloidal dispersions of cellulose crystallites after acid hydrolysis. In 1992, Gray and Marchessault demonstrated that cellulose nanocrystals could self-assemble into chiral nematic liquid crystalline phases in aqueous suspensions above a critical concentration.

As a sustainable nanomaterial that can be easily extracted from forests and fields, cellulose nanocrystals have attracted widespread interest in recent years for their optical, mechanical, and electromagnetic properties that are being developed for a variety of applications. The lyotropic liquid crystalline behavior of CNCs is especially valuable since it could be used for the template synthesis of many organic and inorganic materials. In 2010, MacLachlan and coworkers reported the fabrication of mesoporous silica films with chiral nematic structures. Afterwards, a series of other materials with chiral nematic ordering and photonic properties were synthesized.

Despite the growing interest in the solution and solid-state properties of CNCs, there is still a large gap in our understanding of the liquid crystallinity and microstructures of these materials. One hypothesis is that the chirality originates from a helical twist of the crystals, and several researchers have observed twisting of cellulose microfibrils or CNCs by electron microscopy and atomic force microscopy, but the twisting is quite subtle. Bergström and coworkers reported
that the chiral nematic phase has already been established when the CNCs are about 50 nm apart in water.\footnote{51} It is not clear how chirality is mediated between the CNCs over these distances. Some researchers postulated that there would be a chiral charge distribution of the sulfate ester groups on the surface resulting from the sulfuric acid hydrolysis process.\footnote{15} The transition from isotropic to lyotropic liquid crystalline phases in the case of CNCs have been difficult to study, but critical understanding might come from the microstructures of tactoids, which are key components in the evolution of liquid crystallinity in CNC suspensions.

1.3.2 Liquid Crystalline Tactoids of Cellulose Nanocrystals

Above a critical concentration, tactoids will spontaneously emerge in the isotropic phases of CNC dispersions, which can be observed by polarized optical microscopy (POM) as birefringent ellipsoidal microdroplets with periodically spaced chiral nematic layers (Figure 1.9). As tactoids coalesce and settle, the system phase-separates into a liquid crystalline phase below an isotropic phase. When dried, a solid chiral nematic film will be formed.

The significance of tactoids in improving the properties of CNC-derived materials has been noticed. Lagerwall and coworkers reported that applying shear forces to CNC dispersions as they dried can improve the alignment of the tactoids and, consequently, improve the optical properties of the chiral nematic films.\footnote{52} While hypothetical models of tactoids have been built, the structure of tactoids and the arrangement of liquid crystalline mesogens within them had not been directly observed with electron microscopy due to the difficulty of capturing these soft microdroplets in a solid-state matrix while maintaining their ordered structures, yet this information can be valuable because tactoids are the earliest evolution stages and smallest units of liquid crystalline phases.
Figure 1.8. TEM micrographs of cellulose nanocrystals used in this research. Scale bars, (A) 200 nm, (B) 100 nm, (C,D) 50 nm.
Figure 1.9. POM micrograph showing discrete chiral nematic liquid crystalline tactoids formed in an aqueous dispersion of cellulose nanocrystals. Scale bar, 50 μm.
1.4 Aims and Scope

The research presented in this thesis focuses on the microscopic structures and fundamental physical properties of liquid crystalline tactoids. While most experiments herein were conducted with cellulose nanocrystals, these results might help to understand the evolution and dynamics of other lyotropic liquid crystals and soft matter systems.

In Chapter 2, a generalized method was developed to enable direct observations of tactoids by electron microscopy. Using an in-situ photopolymerization approach, a cross-linked polymer matrix could be rapidly formed to capture and solidify liquid crystalline tactoids in a fluid system without significant distortions. This approach allowed to directly visualize, for the first time, the arrangement of liquid crystal mesogens within individual tactoids by electron microscopy.53

In Chapter 3, the structure and evolution of chiral nematic liquid crystalline tactoids in the geometrical confinement of spherical microdroplets were examined by both optical and electron microscopy. Polymer microspheres with left-handed chiral nematic order were obtained through in-situ photopolymerization in inverse emulsions. By using a double-matrix templating method, mesoporous silica microspheres with chiral nematic structures were fabricated, which may have potential applications in optical devices and chiral separations.54

In Chapter 4, the structure and evolution of tactoids in the presence of doping nanoparticles were directly investigated by scanning electron microscopy at the resolution of individual liquid crystal mesogens, which revealed the size-selective exclusion effects of liquid crystalline tactoids on foreign nanoparticles. This phenomenon indicates a new approach to size-selectively separate nanoparticles using lyotropic liquid crystals, where the nanoparticles with widths smaller than a threshold size will be selectively transferred from the disordered phase into the ordered phase by
liquid crystalline tactoids during the phase separation process. This principle was applied to the separation of polymer nanospheres, gold nanoparticles, and magnetic nanoparticles by size.\(^5^5\)

In Chapter 5, the phase separations of lyotropic liquid crystals in competitive gravitational and magnetic acceleration fields were investigated. A significant difference in volume magnetic susceptibility was created between liquid crystalline tactoids and disordered phases based on the exclusion effects of tactoids on superparamagnetic doping nanoparticles, which enabled position and orientation control of liquid crystalline tactoids by static gradient magnetic fields as weak as several hundred Gauss/cm. The movement of tactoids is determined by the competition between the magnetic and gravitational acceleration fields. This approach allowed control of the rate and configuration of phase separation, as well as the orientation of the director fields in both discrete tactoids and continuous macroscopic ordered phases.
Chapter 2: Structure and Transformation of Liquid Crystalline Tactoids

2.1 Introduction

Until a few years ago, structural studies of liquid crystalline tactoids were mainly based on optical microscopy or other non-destructive testing methods due to the highly deformable nature of these fluid microscopic structures. Unfortunately, optical techniques are usually not capable of revealing the arrangement of mesogens due to their limited resolution. A possible solution is to capture and solidify these liquid crystalline microdroplets by introducing a cross-linked polymer matrix into the fluid system, during which the ordered microstructures of tactoids should be well maintained without distortions.

2.2 Solidification of Liquid Crystalline Tactoids by In-Situ Photopolymerization

Aqueous dispersions of cellulose nanocrystals were combined with the non-ionic precursors of polyacrylamide (PAAm), which are acrylamide (monomer), a crosslinker, and a photoinitiator. After homogenization, the dispersion was allowed to stand in the dark for a prescribed period of time (1 to 12 hours). Afterwards, ultraviolet radiation (wavelength of 300 nm) was applied to the system, and a crosslinked polymer matrix rapidly formed to capture the liquid crystalline tactoids in the fluid system (Figure 2.1). After removal of solvent, the polyacrylamide matrix turned into a solid-state plastic with the microstructures of tactoids stabilized inside the matrix (Figure 2.2). This results in a "fossil record" that represents a transition stage of the evolution of this lyotropic liquid crystalline phase. The solid polymer matrix can be cracked to give fresh fracture surfaces, where the microscopic structures of tactoids and other liquid crystalline entities could be directly observed by electron microscopy at the resolution of individual mesogens.
Figure 2.1. By adding the nonionic precursors of polyacrylamide into an aqueous suspension of cellulose nanocrystals, this system could be captured in a cross-linked polymer matrix by in-situ photopolymerization, forming a CNC-PAAm composite hydrogel. The diameter of the Petri dish in this photograph is about 50 mm.

Figure 2.2. Photograph showing a completely dried CNC-PAAm composite polymer matrix, in which the microstructures of tactoids have been solidified.
2.3  Electron Microscopy Observations of Liquid Crystalline Tactoids

2.3.1  Microstructures of Chiral Nematic Liquid Crystalline Tactoids

As revealed by the cross-sectional scanning electron microscopy (SEM) observations of the solid-state samples captured by in-situ photopolymerization, liquid crystalline tactoids formed in CNC dispersions are discrete ordered microdroplets with spherical or ellipsoidal boundaries that are clearly distinguishable from the isotropic phase. Small tactoids seem to be unwound nematic due to the boundary conditions since cellulose nanocrystal mesogens in them are unidirectionally aligned (Figure 2.3). As a discrete liquid crystalline microdomain, this tactoid is separated from the surrounding disordered phase by an arc-shaped sharp boundary (Figure 2.4). CNC mesogens inside this liquid crystalline tactoid are arranged into nematic layers (Figure 2.5), while outside this domain they are substantially disordered, consistent with an isotropic phase. Larger tactoids adopt left-handed chiral nematic order appearing as a series of periodically spaced parallel layers (Figure 2.6 to Figure 2.10), where each of these periodic layers represents a half-helical pitch of the chiral nematic phase, i.e., the mesogens twist by 180 degrees from one end to the other.

To obtain three-dimensional microstructures of liquid crystalline tactoids, an intersection of two fracture surfaces that are perpendicular to each other was created from a dried CNC-PAAm composite matrix (Figure 2.11 and Figure 2.12), where the left-handed chiral nematic order in a tactoid was clearly confirmed by direct electron microscopy observations from multiple angles at the resolution of individual CNC mesogens (Figure 2.13).
Figure 2.3. SEM micrographs of a newly emergent liquid crystalline tactoid formed by cellulose nanocrystals. Scale bars, (A) 2 μm, (B) 1 μm, (C) 300 nm, (D) 200 nm, (E,F) 100 nm.
Figure 2.4. Cross-sectional SEM micrographs showing the boundary of a newly emergent liquid crystalline tactoid near its (A, B) left and (C, D) bottom regions. The boundary of this tactoid is a microscopic ordered-disordered interface, which sharply separates the liquid crystalline domain from the isotropic phase surrounding it. Scale bars, (A, C) 200 nm, (B, D) 100 nm.
Figure 2.5. High-resolution SEM micrographs showing the ordered arrangements of rod-shaped cellulose nanocrystal mesogens in a newly emergent liquid crystalline tactoid. The mesogens are unidirectionally aligned into a nematic phase since this tactoid is smaller than a half helical pitch, however, the director field is still slightly twisted in long ranges due to the chirality of this phase. Scale bars, (A-D) 100 nm.
Figure 2.6. Cross-sectional SEM micrographs showing a liquid crystalline tactoid with only one chiral nematic layer. Scale bars, (A) 1 μm, (B,C) 300 nm, (D-F) 200 nm.
Figure 2.7. 3D model showing the left-handed chiral nematic order of CNC mesogens (depicted as rods in a golden brown color) in a newly formed liquid crystalline tactoid with only one chiral nematic band. The rod-shaped mesogens in the pseudo nematic layers rotate by 180 degrees from one end to the other. This is an idealized model, while in reality the CNCs might not be perfectly layered and aligned.
Figure 2.8. Additional cross-sectional SEM micrographs showing liquid crystalline tactoids with (A,B) one, (C) zero, or (D-F) three chiral nematic layers. Scale bars, (A) 2 µm, (B) 400 nm, (C) 1 µm, (D) 3 µm, (E) 500 nm, (F) 200 nm.
Figure 2.9. Cross-section SEM micrographs showing a liquid crystalline tactoid with four chiral nematic layers. Scale bars, (A) 5 μm, (B,D) 2 μm, (C,E) 1 μm, (F) 300 nm.
Figure 2.10. Cross-sectional SEM micrographs of a large-size liquid crystalline tactoid with nine chiral nematic layers. Scale bars, (A) 10 μm, (B) 2 μm, (C-F) 1 μm.
Figure 2.11. SEM micrographs showing several chiral nematic liquid crystalline tactoids sitting at a right-angled edge. Scale bars, (A) 200 μm, (B) 50 μm, (C,D) 10 μm, (E,F) 3 μm.
Figure 2.12. SEM micrographs showing the (A-C) top and (D-F) front views of a tactoid sitting at a right-angled edge. Scale bars, (A) 10 μm, (B,D) 2 μm, (E) 1 μm, (C,F) 500 nm.
Figure 2.13. SEM micrographs showing the (A-C) left and (D-F) right views of a chiral nematic liquid crystalline tactoid. Scale bars, (A,D) 500 nm, (B,E,F) 300 nm, (C) 200 nm.
2.3.2 Coalescence of Tactoids and Formation of Topological Defects

As the total concentration of a CNC suspension increases or as the lyotropic system relaxes, bigger tactoids with more chiral nematic layers appear. By tracking the evolution of tactoids in a drying dispersion by POM for hours, the coalescence of liquid crystalline tactoids was observed, during which time several smaller tactoids merged together to form a larger tactoid (Figure 2.14 and Figure 2.15). Because the resulting tactoid favors a spherical geometry, the driving force for this coalescence mechanism is the ordered-disordered interfacial tension on the boundaries of the fusing tactoids. The interfacial tension is of the order of magnitude of $10^{-4}$ mN/m as measured by Gray and coworkers; for comparison, the interfacial tension between hexane and water is about 50 mN/m. These data could help explain the relatively slow phase separation rates of cellulose nanocrystal dispersions. It should be noted that other growth mechanisms, for example, Ostwald ripening, might be simultaneously active.

In some situations, especially when two tactoids come together with the helical axes of their chiral nematic structures perpendicular to each other, the coalescence between tactoids will result in the formation of topological defects in the director field of the resulting tactoid, as this process is the combination of multiple liquid crystalline microdomains with initially random orientations. The chiral nematic layers would bend, fold, elongate or dislocate during the coalescence process. Interestingly, the layers seem to be soft and flexible enough to deform while accommodating the union. The topological defects could be healed by the reorientation of the director fields because they are thermodynamically unstable, as planar chiral nematic layers are favored structures under weak confinement and surface anchoring conditions, which are respectively caused by the weak ordered-disordered interfacial tension at the boundary of a tactoid and the relatively large sizes of
CNC mesogens. In some cases, however, the defective structures remain in the fused tactoid for a long time due to the slow relaxation rates of the liquid crystalline mesogens.

By capturing the CNC suspensions in crosslinked polyacrylamide matrices, the coalescence of liquid crystalline tactoids was further investigated by scanning electron microscopy, where the encounter and direct contact between multiple tactoids that have random helical axis orientations (Figure 2.16 to Figure 2.18) as well as tactoids with fusion defects of dislocated or folded chiral nematic layers (Figure 2.19) were observed. These results indicate a new method to examine the microstructures of topological defects in lyotropic liquid crystals, where the in-situ formation of a crosslinked polymer matrix not only provides high structural stability for electron microscopy analysis, but also permanently captures a thermodynamically metastable transition state from an always-changing liquid crystalline system.
Figure 2.14. Three-dimensional model showing the contact between two discrete chiral nematic liquid crystalline tactoids in an aqueous dispersion of cellulose nanocrystals.
Figure 2.15. POM micrographs showing the coalescence of two chiral nematic liquid crystalline tactoids in a CNC dispersion.

Figure 2.16. SEM micrograph showing the initiation of coalescence between two chiral nematic tactoids. Scale bar, 10 μm.
Figure 2.17. SEM images showing the microstructures of the contact point between two tactoids. Scale bars, (A) 2 μm, (B) 1 μm, (C) 500 nm, (D) 300 nm.
Figure 2.18. SEM images showing the aggregation and contact between multiple chiral nematic liquid crystalline tactoids. Scale bars, (A) 20 μm, (B,C) 10 μm, (D-F) 5 μm.
Figure 2.19. SEM images of liquid crystalline tactoids with topological defects of dislocated or folded chiral nematic layers. Scale bars, (A) 5 μm, (B-F) 10 μm.
2.3.3 Gravitational Sedimentation of Liquid Crystalline Tactoids

The CNC mesogens would be more closely packed inside liquid crystalline tactoids as they adopt a similar orientation in each pseudo nematic layer, which enables them to occupy the space more efficiently. This may lead to a higher density of CNCs inside tactoids than in the isotropic phases. Quantifying the density of the discrete tactoids would be difficult due to their small sizes and unstable structures, but this value could be estimated from the density of macroscopic liquid crystalline phases as they are formed by the same mesogens adopting the same ordered structures.

In this study, an aqueous dispersion of CNCs (4.08 wt.%) was allowed to stand in a sealed separatory funnel for one week to reach phase equilibrium, afterwards, the concentration of the CNCs in the ordered phase was measured to be 4.46 wt.%, while the CNC concentration in the disordered phase was 3.75 wt.%. The densities of the liquid crystalline and isotropic phases are 1.0165 g/cm$^3$ and 1.0150 g/cm$^3$, respectively.

As tactoids have a higher density than the isotropic phase due to a more efficient packing of the liquid crystalline mesogens, they gradually settle to the bottom of the dispersion as driven by gravity, and eventually coalesce together to form a macroscopically continuous liquid crystalline phase, in which the chiral nematic layers are horizontally stacked (Figure 2.20).

Fusions could also occur between discrete liquid crystalline tactoids and continuous ordered phases when tactoids encounter the horizontal ordered-disordered interface at the bottom of the dispersion, and join the macroscopic chiral nematic phase by coalescence. This process may also result in the formation of topological defects due to the random orientation of the helical axis of discrete tactoids.

As a result of the coalescence between tactoids with different director fields, a large number of kinetically arrested topological defects could be observed in the macroscopic liquid crystalline
phase (Figure 2.21 and Figure 2.22), which have significantly longer periodicity (about 5 to 10 micrometers) than the half helical pitch of the chiral nematic structure of CNCs (shorter than one micrometer). These topological defects may be one of the possible origins of the fingerprint-like textures observed in solid-state chiral nematic films formed by CNCs (Figure 2.23).

**Figure 2.20.** Cross-sectional SEM micrograph showing the gravitational sedimentation of chiral nematic liquid crystalline tactoids to the bottom of a CNC dispersion, where the tactoids coalesce together to form a macroscopic continuous ordered phase. Scale bar, 20 μm.
Figure 2.21. SEM micrographs showing topological defects as an array of folded chiral nematic layers. Scale bars, (A) 5 μm, (B,C) 2 μm, (D) 1 μm, (E,F) 500 nm.
**Figure 2.22.** SEM micrographs showing topological defects as an array of folded chiral nematic layers. Scale bars, (A) 10 μm, (B) 3 μm, (C) 1 μm, (D) 500 nm.
Figure 2.23. POM micrograph showing the fingerprint-like texture in a solid-state chiral nematic film formed by CNCs. Scale bar, 50 μm.
2.4 Conclusions

With the aid of an in-situ photopolymerization method, liquid crystalline tactoids formed in CNC dispersions were rapidly captured and solidified in crosslinked polymer matrices, enabling direct electron microscopy observations of these metastable soft matter entities at the resolution of individual liquid crystal mesogens. The results reveal that the tactoids themselves have chiral nematic liquid crystalline structures and they are already highly ordered (Figure 2.24).

According to optical and electron microscopy observations, tactoids grow by a coalescence mechanism, where several smaller tactoids merge together to form a larger one. This coalescence process is driven by the ordered-disordered interfacial tension, and usually generates topological defects in the director field of the resulting tactoid since this is the combination of multiple liquid crystalline microdomains with initially random orientations. The defects could be healed by the reorientation of the director field as they are thermodynamically unstable, but, in some cases, the defective structures remain in the fused tactoid for a long time because of the slow relaxation rate of the mesogens.

As tactoids have a higher density than the isotropic phase due to a more efficient packing of the mesogens, they will gradually settle to the bottom of the suspension and eventually coalesce into a macroscopic continuous liquid crystalline phase containing kinetically arrested topological defects (Figure 2.25 and Figure 2.26).
Figure 2.24. 3D model showing the left-handed chiral nematic arrangement of rod-shaped CNC mesogens in a liquid crystalline tactoid.
Figure 2.25. 3D models showing the coalescence of liquid crystalline tactoids and the formation of topological defects as folded chiral nematic layers.
Figure 2.26. 3D model showing topological defects as an array of folded chiral nematic layers in the continuous liquid crystalline phase at the bottom of a CNC dispersion.
2.5 Experimental Methods

2.5.1 Capture of Tactoids by In-Situ Photopolymerization

The in-situ photopolymerization capture of tactoids was conducted with nonionic precursors of polyacrylamide, which are compatible with the self-assembly of CNCs in aqueous dispersions. In a typical experiment, acrylamide (1.0 mg, monomer), N,N'-methylenebisacrylamide (100 mg, cross-linker) and 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiofenone (5 mg, photoinitiator; can be replaced by 50 mg of 2,2-diethoxyacetophenone) were mixed with an aqueous dispersion of CNCs (10 mL, 4 wt.%, conductivity = 2.19 mS/cm, pH = 2.44). After sonication for about 10 minutes in cold water, the homogeneous mixture (total volume of about 11.2 mL) was placed in a polystyrene Petri dish (diameter of about 50 mm) to evaporate under ambient conditions in the dark for a prescribed period of time (1, 3, 6, 9, 12 or 24 hours). Afterwards, an ultraviolet-B light source (wavelength of 300 nm, 8 W) was used to initiate the in-situ photopolymerization process. Ultraviolet irradiation was applied to the system for about 30 minutes, a cross-linked hydrogel of polyacrylamide was rapidly generated to capture the liquid crystalline tactoids and other ordered microscopic structures formed by the self-assembly of CNCs (in general, robust hydrogels could be obtained in 20 minutes).

Samples for SEM observations were obtained by heating the hydrogels in air at 60 °C for 12 hours, then breaking the resulting hard and brittle plastic blocks into small pieces with a hammer.

2.5.2 Concentration and Density of Ordered and Disordered Phases

To determine the concentration and density of the isotropic and liquid crystalline phases, an aqueous dispersion of CNCs (volume of about 200 mL) was placed in a sealed separatory funnel
to stand at 8 °C for 7 days. The two phases were then separated and the concentrations of CNCs were determined as follows: the mass of a CNC suspension (10.0 mL) in a pre-weighed vial was measured with an analytical balance, which was then completely dried by heating at 75 °C for 24 hours, cooled and weighed again. Densities of the two phases were determined by measuring the mass of a suspension in a volumetric flask (volume of 10.0 mL) and comparing with the mass of deionized water of the same volume.

2.5.3 Materials

CNC suspensions (4 wt.% in water, conductivity = 2.19 mS/cm, pH = 2.44) were provided by FPInnovations. The CNCs were obtained from hydrolysis of wood pulp in sulfuric acid using a literature procedure. TEM micrographs of these crystals gave dimensions of 19 ± 9 nm by 245 ± 135 nm (based on the measurements of 98 cellulose nanocrystals). Acrylamide (Aldrich, 98%), N,N’-methylenbisacrylamide (Aldrich, 99%), 2,2-diethoxyacetophenone (Acros, 98%), as well as 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Aldrich, 98%) were used without further purification.

2.5.4 Characterization

Optical microscopy was performed with an Olympus BX41 microscope. Scanning electron microscopy (SEM) experiments were conducted on a Hitachi S4700 electron microscope at an acceleration voltage of 10 kV. Samples were sputter-coated with 8.0 nm of platinum-palladium (80 to 20) alloy before imaging. Transmission electron microscopy (TEM) images were obtained with a Hitachi H7600 electron microscope at an acceleration voltage of 62 kV. Samples for TEM measurements were prepared by diluting an aqueous suspension of CNCs to about 0.002 wt.%,
sonicating the diluted suspension for 3 hours in cold water, then drop-casting the suspension onto carbon-coated copper grids.

A Durasonix 3 Litre Ultrasonic Cleaner (frequency of 40 kHz, power of 120 W) was used in this study for sonication treatments of CNC dispersions.
Chapter 3: Liquid Crystalline Tactoids in Geometrical Confinement

3.1 Introduction

The behavior of liquid crystals in confined geometries is significant both for understanding the topological properties of these ordered soft matters and for the development of novel optical devices.\textsuperscript{57,58} However, since most previous studies were based on molecular thermotropic liquid crystals with fast phase transition rates, the intermediate states in these systems were difficult to distinguish and elucidate. New insights would be provided by lyotropic liquid crystals because they generally have much slower kinetics that would enable tracking of the phase transitions in geometrical confinement during a relatively long period of time.

Herein, using an inverse-emulsion photopolymerization method, the structure and evolution of chiral nematic liquid crystalline tactoids confined in spherical microdroplets were investigated by both optical and electron microscopy. Subsequently, solid-state microspheres with left-handed chiral nematic structures were fabricated, the diameters of which could be tuned between tens to hundreds of micrometers. Mesoporous silica microspheres with chiral nematic order were further synthesized through a double-matrix method. These novel polymer and silica microspheres with chiral nematic structures may offer new opportunities for HPLC and other applications. As well, the observations in this study might provide a new approach to understand the evolution of chiral nematic liquid crystals in geometrical confinement, especially spherical confinement, which has attracted considerable attention due to its potential applications in optics and sensing.\textsuperscript{59–61}
3.2 Microspheres with Chiral Nematic Order from Liquid Crystalline Tactoids

3.2.1 Evolution of Liquid Crystalline Tactoids in Spherical Confinement

In this research, the microdroplets of lyotropic liquid crystals were prepared by emulsifying a homogenized aqueous dispersion of cellulose nanocrystals in a non-polar organic solvent such as cyclohexane. The evolution of chiral nematic tactoids in these microdroplets was tracked as a function of time, where the samples were taken from the emulsion system at 30-minute intervals and immediately examined by POM.

Initially, newly emergent tactoids are small enough to avoid the confinement effect from the microdroplet boundary, therefore they have planar parallel chiral nematic layers similar to those formed in bulk dispersions (Figure 3.1 A). As time passes, more tactoids emerge in the isotropic phase, they coexist in the same microdroplet and grow by coalescence (Figure 3.1 B, C). When a tactoid is large enough to be affected by the spherical confinement of the microdroplet boundary, its chiral nematic layers would be curved to accommodate the water-oil interface (Figure 3.1 D), which leads to the formation of a concentric spherical multi-shell structure with radially oriented helical axes (Figure 3.1 E). The chiral nematic cores may keep growing and finally occupy most of the space in the aqueous microdroplets (Figure 3.1 F).

Although the confinement of chiral nematic liquid crystals in spherical geometries has been extensively investigated, in most cases only thermotropic liquid crystals were studied, which are molecular substances that can self-assemble very quickly. As large rod-shaped nanoparticles, CNCs have much slower dynamics. Therefore, the evolution of liquid crystalline phases in CNC dispersions can take many hours, providing a good opportunity to study the formation of a chiral nematic phase in a confined geometry starting from an isotropic dispersion.
Figure 3.1. POM micrographs showing the evolution of chiral nematic liquid crystalline tactoids in spherical confinement. The evolution time and diameter of these microdroplets are as follows: (A) 0.5 h, 118 μm; (B) 1 h, 58 μm; (C) 3 h, 64 μm; (D) 6 h, 78 μm; (E) 9 h, 57 μm; and (F) 12 h, 114 μm.
3.2.2 Solidification of Microdroplets by In-Situ Photopolymerization

In a standard experiment, a CNC dispersion (4.0 wt.%) was homogeneously mixed with the nonionic precursors of polyacrylamide (i.e., acrylamide, a crosslinker, and a photoinitiator), then emulsified under nitrogen or argon protection in cyclohexane (1:10 v/v) facilitated by surfactant Span-80 (0.8% w/v) and moderate stirring (400 rpm) to give liquid microspheres. Chiral nematic tactoids of CNCs were allowed to grow in the microdroplets for a prescribed period of time (6 to 9 hours) with the system sealed, then photopolymerization was initiated by ultraviolet irradiation (wavelength of 300 nm, 8W) to capture the tactoids in crosslinked polyacrylamide microspheres (Figure 3.2). After the removal of solvents, solid-state CNC-PAAm composite microbeads with chiral nematic structures were obtained. The microspheres prepared in this way have an average diameter of 125 μm (denoted as CAMB-M, Table 3.1).

Table 3.1. Preparation parameters for CNC-PAAm chiral nematic microspheres.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Cyclohexane (mL)</th>
<th>Span-80 (g)</th>
<th>CNC Dispersion (mL)</th>
<th>Stirring Speed (RPM)</th>
<th>Average Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAMB-M</td>
<td>80</td>
<td>0.6</td>
<td>6.0</td>
<td>400</td>
<td>125</td>
</tr>
<tr>
<td>CAMB-S</td>
<td>80</td>
<td>1.2</td>
<td>6.0</td>
<td>600</td>
<td>30</td>
</tr>
<tr>
<td>CAMB-L</td>
<td>80</td>
<td>0.4</td>
<td>6.0</td>
<td>300</td>
<td>220</td>
</tr>
</tbody>
</table>
Figure 3.2. Sketch showing the in-situ photopolymerization of aqueous CNC microdroplets in an inverse emulsion. Using this approach, CNC-PAAm composite microspheres with chiral nematic structures could be obtained.
3.2.3 Structure of Liquid Crystalline Tactoids in Spherical Confinement

The as-prepared CNC-PAAm composite microspheres initially dried from ethanol are white and opaque, but transparent and colorless microbeads could be obtained by redispersing them in water then drying again under ambient conditions (Figure 3.3 A). The chiral nematic tactoids of CNCs can be observed in the microspheres by POM between crossed polarizers (Figure 3.3 B). They showed concentric retardation lines with a periodic spacing of about 5 μm, which indicates radially oriented helical axes. Many of the microspheres showed a distinct Maltese cross pattern when observed by POM, indicative of their spherical symmetry.

These microspheres can swell into transparent microgels in water due to the hydrophilicity of polyacrylamide, in which the chiral nematic layers of the captured CNC tactoids can be more clearly observed by POM both between crossed polarizers (Figure 3.4) and under reflected white light (Figure 3.5). The structures of chiral nematic layers in these microspheres could be further revealed by confocal laser scanning microscopy after staining the samples with a fluorescent dye (e.g., rhodamine B) aqueous solution (Figure 3.6 and Figure 3.7). Here the contrast might arise from the uneven scattering of the emitted fluorescence due to the optical anisotropy of the chiral nematic layers, rather than an uneven distribution of the dye. It is obvious that the chiral nematic layers are organized into a series of concentric spherical shells (an onion-like structure), which is consistent with the concentric circle patterns observed by POM. However, the overall geometry of the layers is a spiral shape, leaving a topological defect at the center.

Interestingly, in some CNC-PAAm microspheres, the liquid crystalline tactoids have planar parallel chiral nematic layers (Figure 3.8 A), which are similar to those formed in the bulk CNC dispersions. Tactoids with curved (arc-shaped) chiral nematic layers were also observed in some microspheres (Figure 3.8 B,C). Nevertheless, in most cases, the chiral nematic layers of tactoids
are well organized as concentric spherical shells (Figure 3.8 D). These structures may represent different stages of the evolution of liquid crystalline tactoids in spherical microdroplets. Initially, a newly formed tactoid in the center of an aqueous microdroplet has planar chiral nematic layers due to the long distance between its edge and the water-oil interface (Figure 3.9 A). The size of this tactoid gradually increases over time, accompanied by the generation of new chiral nematic layers, and eventually the growth of this tactoid will be constrained by the boundary of the water microsphere. The chiral nematic layers would bend to fit the spherical geometry of the water-oil interface (during this process an $S = +1/2$ disclination is formed), they keep extending along the interface (Figure 3.9 B,C), which finally results in a concentric spherical multi-shell structure (in an ideal situation) or a spiraling structure (Figure 3.9 D and Figure 3.10).
Figure 3.3. Optical micrographs of dried CNC-PAAm microbeads (A) observed under reflected white light or (B) with transmitted light between crossed polarizers. Scale bars, 50 μm.

Figure 3.4. POM micrograph of a CNC-PAAm chiral nematic microgel that has swelled in water. Scale bar, 20 μm.
Figure 3.5. Optical micrographs of CAMB-M microgels (after swelling in water) observed (A,C) between crossed polarizers or (B,D) under reflected white light. Scale bars, 50 μm.
Figure 3.6. Orthogonal views of a chiral nematic microsphere obtained by confocal fluorescence microscopy. Here the imaging region is 178 μm in width and 130 μm in height. The sample was stained by immersing the microspheres in an aqueous solution of rhodamine B (about 0.1 wt.%), then redispersed in pure water before imaging. This microsphere was flattened by gravity.
Figure 3.7. A three-dimensional reconstructed confocal fluorescence microscopy image showing the chiral nematic layers in a microsphere as a series of concentric spherical shells. A topological defect can be observed at the center of this microsphere, which was formed due to the frustration of the chiral nematic liquid crystalline order in the spherical confinement.
Figure 3.8. POM images of CNC-PAAm microspheres showing chiral nematic tactoids captured at different evolution stages. Diameter of microspheres, (A) 85 μm, (B) 136 μm, (C) 142 μm and (D) 141 μm.
Figure 3.9. Three-dimensional models showing the evolution of chiral nematic liquid crystalline tactoids in spherical confinement.

Figure 3.10. A three-dimensional model showing the chiral nematic layers of a liquid crystalline tactoid in spherical confinement, which are organized into a series of concentric shells.
3.2.4 Spherical Chiral Nematic Tactoids under Electron Microscopy

As revealed by SEM observations (Figure 3.11), most of the CNC-PAAm microbeads have a spherical geometry, where the surface patterns may represent the turbulent flow of the liquid in these aqueous microdroplets during the polymerization process. After smashing (with a hammer) some microbeads flash frozen in liquid nitrogen, tactoids in the center of the cracked microbeads could be examined by SEM, which have onion-like microstructures of concentric spherical shells (Figure 3.12). These preliminary results are consistent with the polarized optical microscopy and confocal microscopy observations.

Because the helical pitch of the chiral nematic ordering in these microspheres is much larger than the wavelength of visible light, the chirality of these structures cannot be characterized with circular dichroism (CD) spectroscopy. Fortunately, the large sizes of CNC mesogens allow their orientations in the microspheres to be directly observed by electron microscopy. Although these CNC-PAAm spheres could be briefly cracked in liquid nitrogen, frost immediately forms on the cold fracture surface, softens and smooths it after melting. However, high-quality cross-sections with intact morphology could be obtained by cracking these microspheres after embedding them in epoxy resins (Figure 3.13 and Figure 3.14), thereafter the organization of CNC mesogens can be directly examined by SEM.

The chiral nematic layers of the tactoids generally form a spiral structure with a topological defect at the center rather than perfect concentric spherical shells (Figure 3.15). The left-handed chiral nematic ordering of mesogens is apparent at high magnifications (Figure 3.16). As shown by POM observations, outside the liquid crystalline tactoid is the disordered phase, where CNCs are randomly arranged. This is the result of the phase separation of CNC lyotropic liquid crystals in geometrical confinement.
**Figure 3.11.** SEM micrographs showing the surface morphology of the solid-state CNC-PAAm (CAMB-M) composite microspheres. Scale bars, 20 μm.

**Figure 3.12.** SEM micrographs showing the onion-like structure of chiral nematic layers inside a CNC-PAAm microsphere, which was cracked in liquid nitrogen. As frost immediately formed on the cold fracture surface, softened and smoothed it after melting (due to the hydrophilicity of the polyacrylamide matrix), the arrangement of individual CNCs cannot be distinguished. Scale bars, (A) 10 μm, (B) 5 μm.
Figure 3.13. SEM images showing a fracture surface of an epoxy resin containing CNC-PAAm microspheres. Scale bars, (A) 200 μm, (B) 50 μm.

Figure 3.14. SEM image showing the cross-section of a microsphere that has been split into two parts by using an epoxy resin. Scale bar, 10 μm.
Figure 3.15. Cross-sectional SEM micrograph showing the spiral structure of the chiral nematic liquid crystalline tactoid inside a CNC-PAAm microsphere. This tactoid consists of two different chiral nematic layers. The chiral nematic ordering of the liquid crystalline phase is frustrated due to the spherical confinement, which results in the formation of a topological defect in the center of this tactoid. Scale bar, 5 μm.
Figure 3.16. Cross-sectional SEM images showing the left-handed chiral nematic order of CNCs in a microsphere. Scale bars, (A) 2 μm, (B,C) 500 nm, (D) 200 nm.
3.2.5 Tactoids in Geometrical Confinement with Different Dimensions

The average diameter of the microspheres could be easily controlled from 30 μm to 220 μm by changing the amount of surfactant and stirring speed used. A larger amount of surfactant and a higher stirring speed resulted in smaller microspheres, as confirmed by SEM measurements of the dried samples (Table 3.1 and Figure 3.17). After swelling into highly transparent microgels in water, the existence of chiral nematic tactoids in these microspheres could be clearly observed under POM (Figure 3.18, Figure 3.19, and Figure 3.20 for CAMB-M, CAMB-S, and CAMB-L, respectively).

Not surprisingly, although most of the tiny microspheres (about 30 μm in diameter, denoted as CAMB-S) show liquid crystalline tactoids with chiral nematic layers organized into concentric spherical shells, generally they have only one or two half-helical-pitches near the boundary, with an isotropic core in the center (Figure 3.18). On the other side, liquid crystalline tactoids in large microspheres (about 220 μm in diameter, named as CAMB-L) were not efficiently integrated due to the rather long distances between them (Figure 3.19); thus, the multiple discrete tactoids were not forced to merge into a single one. To obtain single and integrated chiral nematic tactoids, the size of the microdroplets should be comparable to that of individual tactoids, which corresponds to the situation of CAMB-M (about 125 μm in diameter) (Figure 3.20).

According to the literature, the geometrical confinement of a liquid in a limited space may result in enhanced viscosity and slow relaxation; when the space is sufficiently narrow, the liquid would be solidified, where shear flows will not be allowed until a critical shear stress is exceeded. This solidification phenomenon occurs especially when the spatial confinement is narrower than four particle dimensions thick. Nevertheless, in the present experiments, the sizes of the aqueous microdroplets are always significantly larger than the lengths of cellulose nanocrystal mesogens,
therefore the influence of confinements on the viscosity of CNC dispersions should be negligible in these studies.

In the present studies, the liquid crystalline tactoids of CNCs seemed not to be significantly influenced by the confinement of large-size microdroplets, which have diameters about 15 times larger than the helical pitch (about 14 micrometers) of the chiral nematic phase formed by CNCs. However, it has been reported that chiral nematic liquid crystals are able to form highly ordered concentric-spherical-shell structures in droplets with diameters of more than 30 times the helical pitch. Therefore the influence of the geometrical confinement on the structure of chiral nematic liquid crystals may vary depending on their physical properties, such as the relaxation rate of the liquid crystalline mesogens.
Figure 3.17. SEM micrographs showing the size distributions of completely dried CNC-PAAm microspheres. (A, B) CAMB-M, (C) CAMB-L, and (D) CAMB-S. These micrographs were taken at the same magnification. Scale bars, 200 μm.
Figure 3.18. POM micrographs of CAMB-M microspheres. Typically, the chiral nematic liquid crystalline tactoids inside a microsphere have been well integrated into a single liquid crystalline core with a spherical geometry, which is located at the center of the microsphere and surrounded by an isotropic shell. Most of these integrated tactoids have highly-ordered onion-like structures of multiple concentric spherical shells. These micrographs were taken at the same magnification. Scale bars, 50 μm.
Figure 3.19. POM micrographs showing CAMB-S microspheres in water, the diameters of these small-size microspheres are about 2 to 3 times the helical pitch of the CNC chiral nematic phase. Typically, the liquid crystalline tactoids in a microsphere have also been well integrated, forming a series of concentric spherical chiral nematic shells near the boundary of the microsphere, which leaves an isotropic core in the central region. Interestingly, in some cases there may be a discrete tactoid left inside the isotropic core. All these micrographs were taken at the same magnification. Scale bars, 50 μm.
Figure 3.20. POM images showing CAMB-L microspheres. The chiral nematic liquid crystalline tactoids in these large-sized microspheres were not well integrated during the period of standing, which might be caused by the relatively long distances between them. These POM micrographs were taken at the same magnification. Scale bars, 50 μm.
3.3 Mesoporous Silica Microspheres with Chiral Nematic Order

Based on these results, this inverse emulsion method was further extended to the fabrication of mesoporous silica microspheres with chiral nematic ordering. In a typical procedure, an acidic dispersion of CNCs was mixed with the nonionic precursors of polyacrylamide (i.e., acrylamide, a crosslinker, and a photoinitiator) and tetramethyl orthosilicate (TMOS), then homogenized by sonication, and used as the aqueous phase. Other experimental conditions were kept the same as those used for the preparation of CAMB-M samples. TMOS underwent a sol-gel transition in the acidic environment during the growth of liquid crystalline tactoids in the aqueous microdroplets. After a period of time (9-12 hours), photopolymerization was initiated by UVB irradiation, and a crosslinked polyacrylamide matrix rapidly formed to capture the chiral nematic order of tactoids in solid microspheres. An ethanolic solution of ammonium hydroxide was then quickly added to accelerate the condensation of silanol groups of the silica gels inside the microspheres, therefore forming an additional matrix of silica to support the chiral nematic structures of CNCs, which is a double-matrix method. After complete drying, the microspheres were calcined at 540 °C in air to remove all the organics including CNCs and PAAm, yielding mesoporous silica microspheres with chiral nematic order.

After calcination, the chiral nematic ordering of liquid crystalline tactoids remained intact in many of the silica microspheres, which could be observed by POM (Figure 3.21). The complete removal of cellulose nanocrystals, polyacrylamide and other organic compounds was confirmed by IR spectroscopy and elemental analysis. The IR spectrum (Figure 3.22) of CNC-PAAm-silica composite microspheres showed characteristic peaks of cellulose (1161 cm\(^{-1}\) for pyranose rings and 3339 cm\(^{-1}\) for hydroxy groups) and polyacrylamide (1450 cm\(^{-1}\) for methylene bridges, 1617 cm\(^{-1}\) for amino groups, and 1656 cm\(^{-1}\) for carbonyl groups);\(^{67,68}\) however, after calcination, only
the Si-O-Si bending and stretching vibration bands (806 cm\(^{-1}\) and 1056 cm\(^{-1}\) peaks) of the silica matrix remained.\(^6\)\(^9\) Elemental analysis of the CNC-PAAm-silica composite microspheres showed 8.27 wt.% nitrogen, 31.02 wt.% carbon, and 5.26 wt.% hydrogen, but these three elements were all lower than the detection limit in the silica microspheres after calcination.

For electron microscopy examination, cross-sections of the mesoporous silica microspheres were obtained by cracking an epoxy resin with the samples embedded inside, and then the chiral nematic structures in these silica microspheres could be directly observed by SEM (Figure 3.23). As revealed by high magnification images, the silica microspheres are composed of grain-shaped nanoparticles which adopt a left-handed helical superstructure (Figure 3.23 D).

The mesoporous properties of the silica microspheres were evaluated by nitrogen adsorption and desorption measurements (Figure 3.24). The samples showed a BET specific surface area of 257 m\(^2\)/g, a BJH adsorption cumulative pore volume of 0.993 cm\(^3\)/g, as well as a BJH adsorption average pore width of 14.6 nm. With high surface area, mesoporosity, good thermal stability, and chiral nematic ordering, these silica microspheres may have potential applications in asymmetric catalysis or chiral separations.
Figure 3.21. POM images of mesoporous silica microspheres. Scale bars, 10 μm.

Figure 3.22. IR spectra of CNC-PAAm-SiO₂ (blue) and SiO₂ microspheres (red curve).
Figure 3.23. SEM images showing the chiral nematic order of a mesoporous silica microsphere. Scale bars, (A) 10 μm, (B) 2 μm, (C,E) 500 nm, (D) 1 μm, (F) 200 nm.
Figure 3.24. Nitrogen adsorption-desorption isotherm (77 K) of mesoporous silica microspheres. The sample mass was 117.3 mg in this measurement. The desorption data are presented as empty circles.
3.4 Conclusions

In this study, cellulose nanocrystals were allowed to self-assemble in aqueous microdroplets of an inverse emulsion system. Liquid crystalline tactoids with chiral nematic order were formed and further captured in crosslinked polyacrylamide microspheres by in-situ photopolymerization. The chiral nematic structures of CNCs are preserved within the polymer matrix, as characterized by both optical and electron microscopy. The size of the microspheres can be easily adjusted by changing the stirring speed and the amount of surfactant used. Furthermore, it was found that, to obtain single, integrated chiral nematic cores with concentric spherical multi-shell structures, the size of the water microdroplets in the inverse emulsion should be similar to that of discrete CNC tactoids.

This method was then extended to the fabrication of silica microspheres with chiral nematic order, which exhibit high surface area, mesoporosity, and high thermal stability. These materials may have potential applications in sensing, optics and chiral separation.

In this work, microdroplets of cellulose nanocrystals were generated by an inverse emulsion method, which is low-cost and scalable. However, the microspheres obtained in this approach are usually polydispersed. Monodispersed microspheres of cellulose nanocrystals can be synthesized by using microfluidics devices, and the chiral nematic order in those microspheres could be well controlled by adjusting the concentration of CNCs, the diameters of the microdroplets, and other experimental parameters.70–72
3.5 Experimental Methods

3.5.1 Fabrication of Polymer Microspheres with Chiral Nematic Order

In a standard experiment, sorbitane monooleate (0.60 g, also known as Span-80, surfactant) and cyclohexane (80 mL, non-polar phase) were placed in a 250 mL single-necked round-bottom flask, which was equipped with a magnetic stir bar and a rubber stopper. The stirring speed was set at 400 revolutions per minute (rpm), and the system was deoxygenated by bubbling argon or nitrogen through the solution for 15 minutes (via a long stainless-steel needle).

Afterward, a homogeneous mixture of a cellulose nanocrystal dispersion (4.0 wt.% in water, 6.0 mL), acrylamide (1.2 g, monomer), N,N'-methylenebisacrylamide (120 mg, crosslinker), and 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (6 mg, photoinitiator) which had been sonicated for about 5 minutes was slowly injected into the cyclohexane solution. The system was deoxygenated for another 15 minutes, then kept stirring under an argon (or nitrogen) atmosphere for about 9 hours to achieve a stable water-in-oil emulsion, during which time the chiral nematic liquid crystalline tactoids of CNCs were allowed to evolve in the aqueous microspheres, and the system was sealed to prevent the evaporation of cyclohexane or water. Then, a UVB light source (wavelength of 300 nm, power of 8 W) was used in the photopolymerization process, and the UV irradiation was applied to the system for about 2 hours.

After adding ethanol (150 mL), the CNC-PAAm composite microspheres could be collected as white powders by filtration. To remove insoluble oligomers from the products, the as-prepared microspheres were redispersed in fresh ethanol (50 mL) and sonicated for about 5 minutes. After sedimentation of the microspheres (which are heavier than the oligomers), the turbid supernatant suspension was removed. This washing process was repeated for several cycles until the freshly
added ethanol remained clear after sonication and sedimentation. The cleaned microspheres were collected by filtration and finally dried in air at 60 °C for 12 hours. In a typical experiment, about 1.1 g of microspheres could be obtained.

The above experimental conditions give CAMB-M microspheres with an average diameter of 125 μm. For preparation of CAMB-S samples, 1.2 g Span-80 and a stirring speed of 600 rpm were used to give an average diameter of about 30 μm; the CAMB-L microspheres, which have an average diameter of about 220 μm, were fabricated with 0.4 g Span-80 and a stirring speed of 300 rpm (Table 3.1).

### 3.5.2 Preparation of Chiral Nematic Mesoporous Silica Microspheres

The concentration of an acidic CNC suspension (initial pH = 2.8) was raised from 4.0 wt.% to 6.1 wt.% by heating at about 60 °C in air. Such a concentrated CNC suspension (5.0 mL) was mixed with acrylamide (600 mg, monomer), N,N’-methylenebisacrylamide (60 mg, crosslinker), 2-hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiofenone (3 mg, photoinitiator), and tetramethyl orthosilicate (2.0 mL, TMOS, silica precursor), then the mixture was homogenized by sonication for 5 minutes, and used as the aqueous phase to form the water-in-oil emulsion system. All other experimental conditions were kept exactly the same as those used for the synthesis of CAMB-M microspheres. After UVB irradiation, a mixture of 30.0 mL ammonium hydroxide (28.0 wt.% in water) and 120.0 mL ethanol was added, and the products were allowed to stand for 2 hours, then washed and further dried as previously described. In a typical synthesis, about 1.60 g composite microspheres could be obtained after drying. The mesoporous silica microspheres were prepared by calcination in air. An appropriate amount of completely dried CNC-PAAm-Silica composite microspheres were first heated to 90 °C for 8 hours, then the oven temperature was increased to
540 °C during a period of 4 hours, and kept at 540 °C for another 4 hours to burn off all organic components. In a representative experiment, 495 mg of the dried CNC-PAAm-Silica composite microspheres were calcined to give 211 mg of mesoporous silica microspheres.

### 3.5.3 Materials

Cellulose nanocrystal suspensions (4.0 wt.% in water, pH = 2.8, conductivity = 2.16 mS/cm) were provided by CelluForce, which were obtained from hydrolysis of wood pulp in sulfuric acid using the literature method. TEM measurements of the cellulose nanocrystals gave dimensions of about 20 nm in width and 245 nm in length. Cyclohexane (Anachemia, 99%), Span-80 (sorbitane monooleate, Croda), acrylamide (Aldrich, 98%), N,N’-methylenebisacrylamide (Aldrich, 99%), 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Aldrich, 98%), ammonium hydroxide (28.0-30.0 wt.% ammonia in water, Fisher), tetramethyl orthosilicate (TMOS, Aldrich, 98%) and Rhodamine B (Aldrich, 95%) were used without further purification.

### 3.5.4 Characterization

Confocal laser scanning microscopy (CLSM) was performed on a Zeiss LSM 510 confocal microscope. Dried CNC-PAAm microspheres were allowed to swell in a 0.1 wt.% Rhodamine B aqueous solution for 1 hour, then collected by filtration and briefly washed with water to remove residual dye. The stained microspheres (i.e., microgels) were dispersed in pure water again, and placed onto a glass slide for CLSM characterizations. The samples were excited at 543 nm with a Helium-Neon green laser beam, then a BP 560-615 IR LSM emission filter was used in front of the detector. Confocal Z-stack micrographs of the chiral nematic microspheres were acquired at 1.0 micron intervals.
Other characterization methods, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and polarized optical microscopy (POM), are the same as those used in the previous chapters.
Chapter 4: Size-Selective Exclusion Effects of Liquid Crystalline Tactoids on Nanoparticles: Separation by Microscopic Ordered-Disordered Interfaces

4.1 Introduction

Nanomaterials have great potential for applications in catalysis, pharmaceuticals, energy harvesting, and sensing. Many of these applications require the separation of nanoparticles by size and/or shape. Reported techniques include centrifugation, diafiltration, electrophoresis, size exclusion chromatography, and field flow fractionation, each is applicable to a different range of particles, and some depend on the charge of the nanoparticles. Thus, the development of new methods for separating nanoparticles is an important challenge for this field.

Here, the interactions between tactoids and doping nanoparticles were studied. By scanning electron microscopy (SEM), it was observed that liquid crystalline tactoids have a size-selective exclusion effect on foreign nanoparticles, where tactoids exclude particles larger than a threshold size. This principle was then successfully applied to the separation of gold nanoparticles by size. Afterwards, the recycling of liquid crystalline phases for multiple-cycle size-selective separation was investigated with superparamagnetic magnetite (Fe₃O₄) nanoparticles, where the isolation of the small nanoparticles from the cellulose nanocrystal mesogens makes it possible to completely separate small particles from large ones.
4.2 Size-Selective Exclusion of Nanoparticles by Liquid Crystalline Tactoids

4.2.1 Liquid Crystalline Tactoids in Mixtures of Nanorods and Nanospheres

These studies are concerned with the structure and evolution of liquid crystalline tactoids in the presence of doping nanoparticles, where the nanoparticles have widths larger or smaller than the average separation distance between adjacent liquid crystal mesogens in the ordered phases. For cellulose nanocrystals used in the following experiments, this distance was reported to range from 25 to 51 nm, depending on the total concentration of the system.83

Aqueous dispersions of CNCs (4.0 wt.%) and carboxyl-functionalized (negatively charged) polystyrene nanoparticles (PSNPs, about 10 wt.%, white in color) were homogeneously mixed in a 9:1 volume ratio. The binary mixture of CNCs and large-sized PSNPs (L-PSNPs, diameters of 265-280 nm, Figure 4.1) was initially isotropic and white, then chiral nematic tactoids gradually appeared as birefringent microdroplets with periodic layers that can be observed between crossed polarizers (Figure 4.2 A). Under reflected white light, the tactoids showed up as dark regions on a bright white background (Figure 4.2 B), which indicates a significantly lower concentration of L-PSNPs in tactoids than in isotropic phases. Tactoids were also observed in the binary mixtures of CNCs and small-sized PSNPs (S-PSNPs, diameters of 30-57 nm, Figure 4.3) between crossed polarizers (Figure 4.4 A) and under reflected white light (Figure 4.4 B), where they exhibited a white color comparable to that of the surrounding isotropic phase, which indicates the existence of S-PSNPs in tactoids. These results suggest that liquid crystalline tactoids can exclude foreign nanoparticles that are larger than a threshold size (Figure 4.5), while smaller particles can enter these ordered microdroplets (Figure 4.6).
Figure 4.1. SEM images for large polystyrene nanoparticles (denoted as L-PSNPs, diameters of 265-280 nm) used in this work. Scale bars, (A) 200 nm, (B) 100 nm.

Figure 4.2. Optical microscopy images showing chiral nematic liquid crystalline tactoids formed in the presence of L-PSNPs (265 to 280 nm in diameter), which were observed between crossed polarizers (A) or under reflected white light (B). Scale bars, 50 μm.
Figure 4.3. SEM images of small-size polystyrene nanoparticles (denoted as S-PSNPs, diameters of 30-57 nm) used in this work. Scale bars, 50 nm.

Figure 4.4. Optical microscopy images showing chiral nematic liquid crystalline tactoids formed in a binary mixture of CNCs and S-PSNPs (30-57 nm in diameter), which was observed between crossed polarizers (A) or under reflected white light (B). Scale bars, 50 μm.
Figure 4.5. 3D model showing the exclusion effect of a liquid crystalline tactoid (mesogens are depicted as golden brown rods) on large-sized doping nanoparticles (purple spheres).
Figure 4.6. 3D model showing that small-sized nanoparticles (depicted as red spheres) can enter a liquid crystalline tactoid.
4.2.2 Exclusion of Large-Sized Nanoparticles by Liquid Crystalline Tactoids

For SEM observations, nonionic precursors (compatible with the lyotropic liquid crystalline phase of CNCs) of polyacrylamide (acrylamide, crosslinker, photoinitiator) to the binary systems of CNCs and PSNPs. After standing for a period of time (3 to 15 h), in-situ photopolymerization was initiated by ultraviolet-B light. A cross-linked polymer matrix rapidly formed to capture and preserve the fluid microscopic structures. After solidification, tactoids and doping nanoparticles could be observed at the resolution of individual mesogens by scanning electron microscopy.

In a CNC/L-PSNP system, a newly formed tactoid (captured after 3 h growth) was observed as an ordered microdomain with one chiral nematic layer and an elliptical boundary (Figure 4.7). Inside this tactoid is the liquid crystalline phase, in which CNCs adopt left-handed chiral nematic order, but no doping nanoparticles were observed (Figure 4.8). In the isotropic phase outside the boundary of this tactoid (Figure 4.9), in which the CNC mesogens are disordered, the L-PSNPs could be distinguished as either hemispherical cavities or partly stretched spheres with long tails outside the cross-section surface (Figure 4.10).

Here the hemispherical cavities and long-tail-shaped protrusions are left by the polystyrene nanoparticles when the polyacrylamide matrix is cracked. In a typical situation, when a piece of polyacrylamide plastic block containing cellulose nanocrystals and polystyrene spheres is being cracked, the polystyrene nanospheres located along the fracture become stretched (they initially adhere to both sides) until they break free from one of the two side. This process leaves an empty hemispherical cavity on one surface and a protruding tail (i.e., a stretched polystyrene sphere) on the other.

The phase behavior of rod/sphere binary mixtures has been modeled by the Onsager theory in previous literature, in which the phase transitions are driven by the tendency to minimize the
excluded volume of the dispersed particles. This principle explains why newly formed tactoids in CNC/L-PSNP mixtures are free from L-PSNPs (Figure 4.11), since the presence of large doping nanoparticles in the tactoid will increase the excluded volume of the mesogens by disrupting the liquid crystalline order.

Furthermore, the L-PSNPs were scarcely observed in large tactoids with five or more chiral nematic layers (Figure 4.12). These results indicate that tactoids can exclude large-sized foreign nanoparticles. This can be explained by the coalescence mechanism for the evolution of tactoids, in which multiple small tactoids that are free from foreign nanoparticles merge together to form a larger tactoid (Figure 4.13).
Figure 4.7. SEM image of a tactoid formed in a CNC/L-PSNP mixture. Scale bar, 2 μm.

Figure 4.8. SEM images showing the inside area of a newly formed liquid crystalline tactoid in a CNC/L-PSNP binary mixture. Scale bars, (A) 1 μm, (B) 500 nm.
Figure 4.9. SEM images of (A) the upper left, (B,C) the left, and (D-F) the upper boundaries of a newly emergent chiral nematic liquid crystalline tactoid in a CNC/L-PSNP mixture. Scale bars, (A,C,E) 500 nm, (B,D) 1 μm, (F) 200 nm.
Figure 4.10. SEM images showing L-PSNPs in disordered phases. Scale bars, 200 nm.

Figure 4.11. 3D model for the emergence of a small tactoid in a CNC/L-PSNP mixture.
Figure 4.12. SEM micrographs of a liquid crystalline tactoid with about 10 chiral nematic layers formed in a CNC/L-PSNP mixture (A), as well as the boundary (B-D) and chiral nematic layers of this tactoid (E,F). Scale bars, (A) 5 μm, (B,C) 1 μm, (D,E) 500 nm, (F) 200 nm.
Figure 4.13. 3D model showing the coalescence of two liquid crystalline tactoids in the presence of large-sized foreign nanoparticles.
4.2.3 **Coalescence of Tactoids Traps Nanoparticles in Topological Defects**

As revealed by SEM, large-sized doping nanoparticles could be trapped at the contact point between two coalescing liquid crystalline tactoids (**Figure 4.14 A** and **Figure 4.15**), or inside the isotropic region surrounded by several merging tactoids (**Figure 4.14 B** and **Figure 4.16**). Due to the higher density of tactoids than the isotropic phase, eventually numerous tactoids coalesce into a macroscopically continuous liquid crystalline phase at the bottom of the suspension, while the isotropic regions enclosed between tactoids are transformed into topological defects (e.g., folded or dislocated CNC chiral nematic layers) with the large-sized doping nanoparticles sealed inside (**Figure 4.14 C** and **Figure 4.17**).

**Figure 4.14.** (A) A few large-sized doping nanoparticles (depicted in purple) could be trapped at the contact point between two coalescing tactoids. (B) A lot of large doping nanoparticles can be sealed within the broad isotropic region surrounded by several merging tactoids. (C) Topological defects generated during the coalescence of tactoids would eventually remain in the macroscopic liquid crystalline phases with a large number of doping nanoparticles sealed inside.
Figure 4.15. (A) Cross-sectional SEM micrograph showing the initiation of coalescence between two liquid crystalline tactoids formed in a CNC/L-PSNP binary mixture. The boundaries of these two tactoids can exclude the large-sized doping nanoparticles (B), but several nanoparticles were trapped at the contact point between them (C,D), which would be sealed in the liquid crystalline phase. Scale bars, (A) 5 μm, (B,C) 1 μm, (D) 200 nm.
Figure 4.16. SEM images showing the contact between two tactoids in a CNC/L-PSNP mixture (A), the exclusion of L-PSNPs by tactoid boundaries (B,C), and L-PSNPs trapped in the contact region (D-F). Scale bars, (A) 3 μm, (B,E) 500 nm, (C,D) 1 μm, (F) 200 nm.
Figure 4.17. Cross-sectional SEM images of a CNC/L-PSNP mixture showing large-size doping nanoparticles trapped in the topological defects of the macroscopic liquid crystalline phase (A-B and C-F). Scale bars, (A,D) 1 μm, (B,E) 500 nm, (C) 2 μm, (F) 200 nm.
4.2.4 Existence of Small-Sized Nanoparticles in Liquid Crystalline Tactoids

In CNC/S-PSNP binary mixtures, the small-sized doping nanoparticles could be observed as hemispherical cavities and partly stretched spheres both in the isotropic phases and inside liquid crystalline tactoids (Figure 4.18). These small doping nanoparticles already exist in the initially formed "baby" tactoids (Figure 4.19), which could be explained by the excluded volume theory, as small doping nanoparticles can exist in the gaps in the liquid crystal lattice of a tactoid without disrupting its overall liquid crystalline order.

In addition to the thermodynamic model based on the excluded volume theory, it would also be possible to explain the size-selective exclusion effect of tactoids using a kinetic approach. The uniformly aligned nanorod mesogens at the boundary of a liquid crystalline tactoid may work as a microscopic filter which can size-selectively block foreign nanoparticles larger than the gaps in the liquid crystal lattice, while particles smaller than these gaps can pass through the boundary of this tactoid and therefore enter the ordered phase (Figure 4.20 A).

As demonstrated by Bergström and Lagerwall, the interaction between CNCs in the chiral nematic phase is repulsive for separation distances up to 30 nm and attractive at longer distances. According to this data, when a large foreign nanoparticle hits the boundary of a liquid crystalline tactoid from the outside (i.e., from the side of the disordered phase), the ordered lattice of liquid crystal mesogens in front of the invading nanoparticle will be compressed in the normal direction of the contact surface (the interface between the nanoparticle and the tactoid) and stretched in the tangential directions, which results in normal repulsive forces and tangential attractive forces in the liquid crystalline lattice (Figure 4.20 B). Therefore, the tactoid boundary repels the large-size invading nanoparticles.
Figure 4.18. SEM images showing the existence of small-sized doping nanoparticles (diameters of 30-57 nm) as about 50 nm hemispherical cavities in tactoids formed in a CNC/S-PSNP binary mixture (A-C and D-F). Scale bars, (A) 3 μm, (B,C,F) 100 nm, (D) 2 μm, (E) 200 nm.
Figure 4.19. (A-E) SEM images showing hemispherical cavities created by S-PSNPs in a "baby" tactoid in a CNC/S-PSNP mixture. (F) Image showing the coexistence of S-PSNPs and CNCs in the disordered phase. Scale bars, (A) 2 μm, (B) 200 nm, (C,D,F) 100 nm, (E) 50 nm.
Figure 4.20. 3D models illustrating (A) the size-selective permeability of an ordered-disordered interface to foreign nanoparticles, and (B) the exclusive force from this interface on an invading nanoparticle with a width larger than the gaps in the liquid crystalline lattice.
4.2.5 Size-Selective Particle Permeability of Ordered-Disordered Interfaces

Although it was difficult to directly measure the interaction forces between the boundary of a liquid crystalline tactoid and invading nanoparticles, similar results might be obtained from the studies of macroscopic ordered-disordered interfaces since they have the same microstructures as tactoid boundaries.

In a preliminary experiment, an aqueous PSNP dispersion was added on top of the isotropic phase of a phase-separated CNC suspension. The PSNPs (with a white color) gradually diffused downwards through the isotropic layer to the ordered-disordered interface. This interface blocked the diffusion of L-PSNPs toward the liquid crystalline phase (Figure 4.21), as further confirmed by cross-sectional SEM observations after capturing the system in a cross-linked polymer matrix (Figure 4.22 and Figure 4.23). However, the small-size foreign nanoparticles passed through the ordered-disordered interface, and thus entered the liquid crystalline phase (Figure 4.24).

![Figure 4.21](image)

Figure 4.21. Photographs showing that the downward diffusion of L-PSNPs was stopped by the ordered-disordered interface of a phase-separated CNC dispersion.
Figure 4.22. (A) Cross-sectional SEM micrograph showing the ordered-disordered interface of a phase-separated CNC dispersion, which is the upper boundary of the macroscopically continuous chiral nematic liquid crystalline phase. (B-D) Expanded views near the interface showing that the downward diffusion of the large-sized polystyrene nanoparticles (diameters of 265-280 nm) was dramatically stopped by the upper boundary of the liquid crystalline phase. Scale bars, (A) 2 µm, (B) 1 µm, (C,D) 500 nm.
Figure 4.23. High-resolution cross-sectional SEM image showing the microscopic structures of the interface between the disordered phase (upper) and the chiral nematic liquid crystalline phase (lower) in a completely phase-separated cellulose nanocrystal dispersion, where the organization of individual liquid crystal mesogens can be directly observed. This ordered-disordered interface dramatically blocked the downward diffusion of the large-sized doping nanoparticles (L-PSNPs), which could be observed in the upper disordered phase as either hemispherical cavities or partly stretched nanospheres. Scale bar, 200 nm.
Figure 4.24. SEM images showing that when small-size polystyrene nanoparticles (diameters of 30 to 57 nm) were added on the top of a phase-separated cellulose nanocrystal suspension, these nanoparticles were able to pass through the isotropic-anisotropic interface by diffusion, resulting in hemispherical cavities (about 50 nm in diameter) in the chiral nematic liquid crystalline phase. Scale bars, (A) 500 nm, (B-D) 100 nm.
4.3 Size-Selective Separation of Nanoparticles with Lyotropic Liquid Crystals

4.3.1 Separation of Plasmonic Gold Nanoparticles by Size

To generalize the size-selective separation ability of tactoids, the lyotropic liquid crystals of CNCs were homogeneously mixed with gold nanoparticles of different sizes (average diameters of 20 and 70 nm). After complete phase separation, size distributions of gold nanoparticles in the isotropic and liquid crystalline phases were measured by ultraviolet-visible (UV-Vis) absorption spectroscopy and TEM. When using small-sized gold nanoparticles (denoted as S-AuNPs, about 20 nm in diameter, absorption peak at 523 nm in water, red colored), the liquid crystalline phase showed a pink-red color and a plasmon resonance peak at 521 nm, which is slightly blue-shifted as compared to the 526 nm absorption peak of the isotropic phase (Figure 4.25 and Figure 4.26).

When using large-sized gold nanoparticles (denoted as L-AuNPs, average diameter of about 70 nm, absorption peak at 557 nm in water, blue-purple colored), the liquid crystalline phase was colorless, and its UV-Vis absorption spectrum showed no plasmon resonance peaks (Figure 4.25 and Figure 4.27).

Finally, when the mixture of large and small sized gold nanoparticles (L&S-AuNPs, with an absorption peak at 543 nm in water, purple-red colored) was mixed with the aqueous suspension of CNCs, after complete phase separation, the liquid crystalline phase exhibited a pink-red color and a plasmon resonance peak at 524 nm (Figure 4.25 and Figure 4.28), indicating a significant enrichment of the small-sized gold nanoparticles in this ordered phase as the plasmon resonance peak is very close to that of pure S-AuNPs (at 523 nm). On the other side, the absorption peak of the isotropic phase at 547 nm is red-shifted by 4 nm as compared to the UV-Vis spectrum of the original L&S-AuNP mixture, probably due to a higher proportion of L-AuNPs. The presence of
CNCs would not change the UV-Vis absorption peak position of the gold nanoparticles as CNCs have almost no absorption in the range from 500 nm to 600 nm (Figure 4.29). The difference in the size distribution of the doping nanoparticles in the ordered and disordered phases was further directly confirmed by transmission electron microscopy (Figure 4.30 and Figure 4.31).

As demonstrated in the present experiments, liquid crystalline tactoids work as microscopic separators that can size-selectively collect small foreign nanoparticles from the disordered phase based on the widths of the gaps in the liquid crystal lattice. Eventually, all the tactoids will settle to the bottom of the dispersion and coalesce into a macroscopically continuous liquid crystalline phase with a significantly higher ratio of the small nanoparticles (Figure 4.32).

![Figure 4.25. Photographs (with transmitted white light) for phase-separated CNC-AuNP binary mixtures.](image)
Figure 4.26. UV-Vis absorption of a phase-separated CNC/S-AuNP binary mixture.

Figure 4.27. UV-Vis absorption of a phase-separated CNC/L-AuNP binary mixture.
Figure 4.28. UV-Vis absorption spectra of the isotropic (Iso) and liquid crystalline (LC) phases of a phase-separated CNC/L&S-AuNP ternary mixture.

Figure 4.29. (A) UV-Vis absorption spectra of a phase-separated CNC dispersion, which exhibit no absorption peaks between 400 nm and 800 nm. (B) Additional UV-Vis absorption spectra of the small and large sized gold nanoparticles used in this study.
Figure 4.30. (A,B) TEM micrographs showing the coexistence of the large and small sized gold nanoparticles in the disordered phase of a completely phase-separated CNC/L&S-AuNP ternary mixture. (C,D) Inside the liquid crystalline phase, only the small-sized gold nanoparticles could be observed. Scale bars, (A,B) 100 nm, (C,D) 200 nm.
**Figure 4.31.** Particle size distributions of AuNPs in the isotropic (Iso) and liquid crystalline (LC) phases of a phase-separated CNC/L&S-AuNP ternary mixture, measured by TEM.

**Figure 4.32.** A depiction showing the size-selective collection of the small foreign nanoparticles (small nanoparticles in red, large particles in purple) by chiral nematic liquid crystalline tactoids of CNCs. Due to the higher density, tactoids will gradually settle to the bottom part of the dispersion and coalesce into a macroscopic ordered phase with a significantly higher ratio of small nanoparticles.
4.3.2 Multiple-Cycle Size-Selective Separation of Magnetic Nanoparticles

The separation medium of liquid crystals could be recycled for multiple-cycle separation by isolating the small nanoparticles from the ordered phase after equilibration; in the next separation cycle, the regenerated liquid crystalline phase is homogeneously mixed with the isotropic phase, then the dispersion phase-separates again. It was found that when small-sized superparamagnetic magnetite nanoparticles (denoted as S-MNPs, about 8.7 nm in diameter) were mixed with CNCs, they could exist in the liquid crystalline phase after phase separation, as indicated by the yellow color observed with both transmitted (Figure 4.33) and reflected white light (Figure 4.34). The concentration of S-MNPs in the liquid crystalline phase was about 30% to 33% of that inside the disordered phase as determined by UV-Vis absorption spectroscopy (Figure 4.35 A), where the S-MNPs had been magnetically isolated from the dispersions and then redispersed in pure water to eliminate the influence of liquid crystal mesogens.

On the other hand, when large-sized superparamagnetic magnetite nanoparticles (denoted as L-MNPs, about 107 nm in diameter) were used to dope CNCs, after phase separation, the liquid crystalline phase was colorless (Figure 4.33), with negligible absorption in the ultraviolet-visible region (Figure 4.35 B), indicating the absence of L-MNPs in this phase. In the case of a mixture of large and small sized magnetite nanoparticles (denoted as L&S-MNPs), the liquid crystalline phase exhibited a yellow color, similar to when S-MNPs were used (Figure 4.33).

Furthermore, recycling of the separation medium (the lyotropic liquid crystalline mesogens) was investigated using a CNC/L&S-MNP ternary mixture (Figure 4.36). After phase separation, the liquid crystalline phase was extracted into a separate vial, then the MNPs were magnetically isolated from the liquid; the regenerated cellulose nanocrystals were reused in the next separation cycle to keep separating small-sized MNPs from large ones. The concentration of S-MNPs in the
liquid crystalline phase (also in the whole system) decreases after each separation cycle, resulting in a lighter brown color (**Figure 4.37**). As revealed by TEM observations, the initial L&S-MNP mixture contains about 98.5% S-MNPs and 1.5% L-MNPs by number (**Figure 4.36 A**). Either in the 1st or in the 9th separation cycles, the liquid crystalline phase contains almost only S-MNPs (**Figure 4.36 B, C**), confirming the size-selectivity. Moreover, after the 9th separation cycle, the disordered phase contains about 38% L-MNPs and 62% S-MNPs by number (**Figure 4.36 D** and **Figure 4.38**), which indicates L-MNPs are dominant in mass as they are about 1000 times larger than S-MNPs by volume. These results suggest that it should be possible to completely separate small-sized nanoparticles from large ones by multiple-cycle separations.

**Figure 4.33.** Photographs showing phase-separated dispersions of cellulose nanocrystals mixed with 8.7 nm (left), 8.7 nm & 107 nm (middle), and 107 nm (right) superparamagnetic magnetite nanoparticles, taken with transmitted white light.
Figure 4.34. Photographs showing phase-separated dispersions of cellulose nanocrystals mixed with 8.7 nm (left), 8.7 nm & 107 nm (middle), and 107 nm (right) superparamagnetic magnetite nanoparticles. The photos were taken with reflected white light.

Figure 4.35. UV-Vis absorption spectra for phase-separated CNC/S-MNP (A) and CNC/L-MNP (B) binary mixtures.
Figure 4.36. TEM images showing the changes in the size distribution of magnetic nanoparticles during the multiple-cycle size-selective separation process, which was conducted with a ternary mixture of S-MNPs, L-MNPs, and CNCs. (A) The initial mixture of S-MNPs and L-MNPs used in the multicycle separation. (B) MNPs in the liquid crystalline phase of the 1st separation cycle. (C) MNPs isolated from the liquid crystalline phase of the 9th separation cycle. (D) MNPs in the isotropic phase of the 9th separation cycle. All the images were taken at the same magnification. Scale bars, (A-D) 100 nm.
Figure 4.37. Photographs showing the phase separations of a CNC/L&S-MNP ternary mixture in the 1st, 3rd, 5th, 7th, and 9th separation cycles. The photographs were taken with reflected white light.

Figure 4.38. The size distributions of MNPs in the initial mixture of L-MNPs and S-MNPs (red color), in the liquid crystalline phase of the 1st (green) and the 9th (cyan) separation cycles, and in the isotropic phase of the 9th separation cycle (blue).
4.4 Conclusions

In this study, the structures and evolution of tactoids in the presence of doping nanoparticles were investigated by optical and electron microscopy, where the size-selective exclusion effects of liquid crystalline tactoids on foreign nanoparticles were observed. Nanoparticles smaller than the gaps in the liquid crystal lattice are able to enter tactoids, while larger particles are excluded from these ordered microdroplets. Using tactoid-mediated phase separation process of lyotropic liquid crystals, polydisperse gold nanoparticles were separated by size. Afterwards, the recycling of liquid crystals for multicycle separation was demonstrated with superparamagnetic magnetite nanoparticles. Interestingly, in each case, the smaller nanoparticles are partitioned into the lower phase, while the larger, heavier particles remain in the top, isotropic phase. Thus, this separation process proceeds counter to gravity. These new insights into the structures and behavior of CNC tactoids may provide an explanation for the enrichment of nanoparticles in the isotropic phase as well as the aggregation of nanoparticles in the topological defects of liquid crystals. Moreover, the size-selective uptake of nanoparticles by liquid crystalline tactoids may be the basis of a new separation method for nanomaterials.
4.5 Experimental Methods

4.5.1 Photopolymerization of Liquid Crystals with Doping Nanoparticles

In a representative experiment, acrylamide (1.0 g), N,N'-methylenebisacrylamide (100 mg), and 2-hydroxy-4’-(2-hydroxyethoxy)-2-methylpropioophenone (5 mg) were added to an aqueous dispersion of cellulose nanocrystals (volume of 9.0 mL, 4 wt.%), then an aqueous suspension of either L-PSNPs or S-PSNPs (1.0 mL, 10 wt.%) was added, and the mixture was homogenized by sonication in cold water for 10 minutes. After standing in the dark for a prescribed period of time (3 to 15 hours), the system was irradiated with ultraviolet light (wavelength of 300 nm, power of 8 W) for 10 to 20 minutes to form a crosslinked polyacrylamide matrix, which was further dried by heating in air at 60 °C for 12 hours. Samples for cross-sectional scanning electron microscopy observations can be obtained by cracking the completely dried polymer matrix into small pieces with a hammer. Samples for optical microscopy were prepared by homogeneously mixing CNC and PSNP dispersions in a 9:1 volume ratio, then the binary mixture was observed between two parallel glass slides that are separated by 0.087 mm thick spacers.

4.5.2 Diffusion of Nanoparticles through Ordered-Disordered Interfaces

An aqueous dispersion of cellulose nanocrystals (2.0 mL, 4 wt.%) was allowed to stand in a sealed vial (inner diameter of 12.60 mm) until complete phase separation, afterwards, an aqueous suspension of either L-PSNPs or S-PSNPs (volume of 1.0 mL) was added on top of the isotropic phase to form a metastable system consisting of three different liquid layers (from top to bottom: a white opalescent PSNP layer, a clear isotropic layer, and a birefringent liquid crystalline layer). Then PSNPs in the top layer gradually diffused downwards during the following 12 hours, where
the process was photographed at different time intervals. For SEM observations, polyacrylamide precursors (ratio as described above) were added to the CNC and PSNP mixtures before starting the experiments, after the diffusion of the PSNPs had reached equilibrium (here the existence of non-ionic polymer precursors does not change the diffusion of either L-PSNPs or S-PSNPs), the system was irradiated with ultraviolet light to rapidly form a crosslinked polymer matrix, which was then taken out from the vial and dried for scanning electron microscopy analysis.

4.5.3 Size-Selective Separation of Gold Nanoparticles by Liquid Crystals

An aqueous dispersion containing CNCs (4.0 wt.%) and gold nanoparticles (0.05 wt.%) was homogenized by sonication, then allowed to stand in a separatory funnel until macroscopic phase separation, where the isotropic and liquid crystalline phases were separately collected in different containers. A separated phase could be diluted to 5 times its volume with pure water for UV-Vis absorption spectroscopy, or to 50 times for TEM observations.

4.5.4 Recycling of Liquid Crystalline Phases for Multicycle Separations

An aqueous dispersion of CNCs (9.0 mL, 4 wt.%, pH = 6.4) was combined with dispersions of citrate-stabilized L-MNPs (0.2 mL, 2 wt.%) and S-MNPs (0.1 mL, 5 wt.%), this mixture was sealed in a vial (inner diameter of 16.50 mm) and thoroughly homogenized by sonication. After complete phase separation, the liquid crystalline phase was extracted from the bottom of the vial using a syringe equipped with a long needle, and transferred into a clean vial. The paramagnetic magnetite nanoparticles in this phase (mainly S-MNPs) were magnetically isolated, and then the regenerated cellulose nanocrystals were recombined with the isotropic phase in the initial vial to start the next separation cycle. The isolated MNPs could be redispersed in pure water to 5 times
the original volume for UV-Vis absorption spectroscopy measurements, or to 50 times for TEM observations.

4.5.5 Materials

Cellulose nanocrystal suspensions (4.2 wt.% in water, pH = 2.1, conductivity = 2.1 mS/cm) were provided by CelluForce, which were obtained by hydrolysis of wood pulp in sulfuric acid.

The large and small sized polystyrene nanoparticles were synthesized according to literature methods using a mixture of methacrylic acid and styrene (1:9 v/v) as monomers. The PSNPs were purified by dialysis in pure water to remove electrolytes, and prepared as 10 wt.% aqueous dispersions. The gold nanoparticles were synthesized by reducing HAuCl$_4$ with sodium citrate at high temperature following a literature method. Citrate-stabilized magnetite nanoparticles were synthesized using literature methods. Both the small and large sized magnetite nanoparticles are superparamagnetic. The large-sized magnetite nanoparticles are composed of numerous small magnetite nanocrystals with widths of about 5 to 10 nm, which endowed the large nanoparticles with superparamagnetism.

Polyacrylamide precursors are the same as those used in the previous experiments. Styrene (Aldrich, 99%), methacrylic acid (Aldrich, 99%), potassium persulfate (Fisher, 99.9%), sodium dodecyl sulfate (Aldrich, 99%), iron (II) chloride tetrahydrate (Aldrich, 98%), iron (III) chloride hexahydrate (Aldrich, 99%), tetrachloroauric (III) acid (Aldrich, 99.9%), sodium citrate tribasic dihydrate (Aldrich, 99%), and citric acid anhydrous (Fisher, 99.8%) were used as received.
4.5.6 Characterization

The UV-Vis spectra were recorded on a Varian Cary 5000 UV-Vis-NIR Spectrophotometer.

Other characterization methods are the same as those used in the previous chapters.
Chapter 5: Movement and Orientation Control of Liquid Crystalline Tactoids in Competitive Acceleration Fields: Phase Separations Beyond Gravity

5.1 Introduction

In many lyotropic systems, the phase transitions are mediated by liquid crystalline tactoids, where they spontaneously emerge from disordered phases, grow larger by coalescence (or other mechanisms), and eventually merge into macroscopically continuous ordered phases. From the perspective of tactoids, there are two primary driving forces for phase separation processes: the ordered-disordered interfacial tension and gravity. The interfacial tension tends to minimize the overall interfacial energy of the boundary between ordered and disordered phases, promoting the coalescence of discrete tactoids into continuous macroscopic liquid crystalline regions. Gravity, the other driving force, leads to the unidirectional movement of all tactoids to the bottom of the dispersion as tactoids have a higher density than isotropic phases due to the ordered arrangement of mesogens. Therefore, phase separation generally results in the formation of a disordered phase above a macroscopic liquid crystalline phase.

Although controlling the orientation of tactoids and macroscopic liquid crystalline phases in lyotropic systems could be important for the development of new materials and devices, tactoids are difficult to manipulate as they are similar in chemical composition and physical properties to disordered phases. In this study, a new approach is demonstrated, which allows control over the movement and orientation of discrete tactoids and the resulting macroscopic ordered phases. The key to this approach is the discovery that disordered phases could be endowed with significantly higher volume magnetic susceptibility ($\chi_v$) than liquid crystalline tactoids based on the exclusion
effects of tactoids on paramagnetic magnetite doping nanoparticles (Figure 5.1). When applying an external gradient magnetic field, the disordered phases experience unidirectional acceleration (driven by magnetic body forces) parallel to the magnetic field and move to high magnetic field regions; meanwhile, since liquid crystalline tactoids are discrete microdroplets with much lower volume magnetic susceptibility (due to the exclusion effects of tactoids on doping nanoparticles), they will be accelerated by magnetic buoyancy forces from the surrounding continuous isotropic phases and move in the opposite direction to low magnetic field regions. Moreover, the tactoids are simultaneously oriented with the nematic layers parallel to the gradient magnetic field, which is driven by the shear forces from the isotropic phase. As tactoids are only slightly denser than isotropic phases, even weak gradient magnetic fields of several hundred Gauss/cm can override the gravitational effects, enabling control of the phase separation configuration (i.e., the relative positions of the ordered and disordered phases) and rate, as well as the orientation of the director fields in both discrete tactoids and continuous liquid crystalline phases, by changing the direction and strength of the gradient magnetic field.

As shown in the following experiments, the phase separation of a lyotropic system generally results in the formation of a disordered phase above a liquid crystalline phase when gravity is the only macroscopic driving force for the movement of tactoids. However, in the presence of other acceleration fields, the effects of gravity to control the direction and rate of phase separation may be overridden. In the case of superparamagnetic nanoparticles that are excluded from the tactoids and thus preferentially concentrated in the isotropic region, the isotropic phase could be attracted to the bottom by a gradient magnetic field despite its lower density, therefore reversing the phase separation observed under normal conditions.
Figure 5.1. 3D Model showing the exclusion effects of liquid crystalline tactoids (mesogens are depicted as golden-brown rods) on superparamagnetic magnetite doping nanoparticles (depicted as black spheres), thus the disordered phase has significantly higher magnetic susceptibility than liquid crystalline tactoids. However, the tactoids have a higher density than isotropic phases due to the ordered arrangements of mesogens.
5.2 Magnetic Buoyancy Forces on Tactoids with Lower Magnetic Susceptibility

Regarding lyotropic liquid crystals that have been doped with paramagnetic nanoparticles as ferrofluids, the magnetic body force per unit volume can be calculated based on the Kelvin law:

\[ dF_m = \mu_0 (M \cdot \nabla)H \ dV = \mu_0 \chi_m (H \cdot \nabla)H \ dV \]

Here \( F_m \) is the Kelvin magnetic body force, \( \mu_0 \) is the vacuum permeability (N/A²), \( M \) is the magnetization, \( \nabla \) is the Nabla operator, \( \chi_m \) is the volume magnetic susceptibility of the material, \( H \) is the magnetic field (A/m), and \( dV \) is the volume element.

A discrete liquid crystalline tactoid in a continuous isotropic phase mainly experiences four kinds of external driving forces that can affect its movement direction and velocity (here despite the viscous resistance from the isotropic phase since it is not a primary driving force), which are the weight \( (F_g) \) of the tactoid, the gravitational buoyancy force \( (F_{bg}) \) and the magnetic buoyancy force \( (F_{bm}) \) both exerted by the continuous disordered phase surrounding this tactoid (for an ideal case where there is only one liquid crystalline tactoid in an infinite continuous disordered phase, the continuous phase could be considered as a quasi-static phase that does not move), as well as the magnetic force \( (F_m) \) from the external gradient magnetic field (Figure 5.2):

\[ dF_g = \rho_{(LC)} \ g \ dV_{LC} \]
\[ dF_{bg} = - \rho_{(Iso)} \ g \ dV_{LC} \]
\[ dF_m = \mu_0 \chi_{m(LC)} (H \cdot \nabla)H \ dV_{LC} \]
\[ dF_{bm} = - \mu_0 \chi_{m(Iso)} (H \cdot \nabla)H \ dV_{LC} \]

Where \( \rho_{(LC)} \) and \( \rho_{(Iso)} \) are the densities of the liquid crystalline (LC) tactoid and isotropic (Iso) phases; \( g \) is the standard gravitational acceleration; \( \chi_{m(LC)} \) is the volume magnetic susceptibility of the liquid crystalline tactoid; \( \chi_{m(Iso)} \) represents the volume magnetic susceptibility of the isotropic...
phase; and $dV_{LC}$ is the volume element of the tactoid. Generally, there are $\rho_{(LC)} > \rho_{(Iso)}$ due to the ordered arrangements of mesogens in tactoids and $\chi_{m(Iso)} \gg \chi_{m(LC)}$ caused by the exclusion effects of tactoids on paramagnetic doping nanoparticles (i.e., the nanoparticle concentration in tactoids is lower than that in the isotropic phases).

The total force on a liquid crystalline tactoid $\mathbf{F}_{LC} = \mathbf{F}_g + \mathbf{F}_{bg} + \mathbf{F}_m + \mathbf{F}_{hm}$ is the vector sum of the four external forces affecting its movement direction:

$$d\mathbf{F}_{LC} = [\rho_{(LC)} - \rho_{(Iso)}] \mathbf{g} \, dV_{LC} - \mu_0 \left[ \chi_{m(Iso)} - \chi_{m(LC)} \right] (\mathbf{H} \cdot \nabla) \mathbf{H} \, dV_{LC}$$

or, in another form:

$$d\mathbf{F}_{LC} = [\rho_{(LC)} - \rho_{(Iso)}] \mathbf{g} \, dV_{LC} + \mu_0 \left[ \chi_{m(Iso)} - \chi_{m(LC)} \right] \left[ - (\mathbf{H} \cdot \nabla) \mathbf{H} \right] dV_{LC}$$

Herein, the vector $[- (\mathbf{H} \cdot \nabla) \mathbf{H}]$ is in the opposite direction of the magnetic body force, away from the magnetic pole to low magnetic field regions. This equation reveals that in the presence of superparamagnetic doping nanoparticles, the movement direction of liquid crystalline tactoids is determined by the competition between the acceleration forces resulting from gravitational and magnetic fields:

$$\mathbf{F}_{grav} = [\rho_{(LC)} - \rho_{(Iso)}] \mathbf{g} \, V_{tactoid}$$

$$\mathbf{F}_{mag} = \mu_0 \left[ \chi_{m(Iso)} - \chi_{m(LC)} \right] \left[ - (\mathbf{H} \cdot \nabla) \mathbf{H} \right] V_{tactoid}$$

Note that the direction and magnitude of $\mathbf{F}_{mag}$ could be controlled by changing the gradient magnetic field and the doping concentration of paramagnetic nanoparticles, but $\mathbf{F}_{grav}$ is a nearly constant vector always in the vertical direction as $[\rho_{(LC)} - \rho_{(Iso)}]$ will not be significantly affected by trace amounts of doping nanoparticles.
Figure 5.2. When a paramagnetic-nanoparticle-doped lyotropic system is subjected to a gradient magnetic field ($H$), the movement direction and velocity of a discrete liquid crystalline tactoid is determined by the vector sum of four external forces: the weight ($F_g$) in the vertically downward direction, the magnetic body force ($F_m$) along the gradient magnetic field to the high field region, the magnetic buoyancy force ($F_{bm}$) along the gradient magnetic field to the low field region (this force is exerted by the continuous isotropic phase surrounding the tactoid), and the gravitational buoyancy force ($F_{bg}$) in the vertically upward direction exerted by the continuous isotropic phase as well. The unidirectional movement of tactoids (which is mainly driven by $F_{bm}$) results in shear forces, by which the chiral nematic layers are oriented parallel to the magnetic field.
5.3 Unidirectional Phase Separations: Acceleration by Gradient Magnetic Fields

5.3.1 Lyotropic Liquid Crystals Doped with Paramagnetic Nanoparticles

Experiments in this study were conducted with the chiral nematic liquid crystals formed by cellulose nanocrystals in aqueous dispersions, where tactoids appear as ellipsoidal microdroplets with periodically spaced birefringent layers. Citrate-coated superparamagnetic magnetite (Fe$_3$O$_4$) nanoparticles (MNPs) with diameters of 15-20 nm were used to dope the lyotropic liquid crystals of CNCs (Figure 5.3), forming homogeneous aqueous dispersions of CNCs (4.0 wt.%, pH = 6.4) and MNPs (typically 140.5 ppm by weight).

Without external magnetic fields, the CNC-MNP mixture phase separates into a birefringent liquid crystalline phase below a clear disordered phase with the relative positions determined by gravity (Figure 5.4), which is identical to pure CNCs (Figure 5.5).

When a static gradient magnetic field (about 1050 Gauss/cm) is applied to the binary system of CNCs and MNPs, phase separation occurs along the direction of the magnetic field, where the macroscopic isotropic phase forms in the high-magnetic-field region with the ordered-disordered interface nearly perpendicular to the magnetic field (Figure 5.6); in a vertically oriented gradient magnetic field, the isotropic phase could even form below the liquid crystalline phase which has a higher density, indicating that $\Sigma F_{\text{mag}} > \Sigma F_{\text{grav}}$ and therefore $\Sigma F_{\text{mag}}$ is the main driving force that determines the configuration of phase separation (Figure 5.7 and Figure 5.8).
Figure 5.3. TEM micrographs of the superparamagnetic magnetite (Fe$_3$O$_4$) nanoparticles used in this study. Scale bars, (A,B) 30 nm, (C,D) 20 nm.
Figure 5.4. When only affected by the gravity, a CNC-MNP binary mixture phase-separates into a liquid crystalline phase (exhibiting higher brightness between two crossed polarizers) below a disordered phase over several hours. The CNC-MNP binary mixture has a volume of 1.0 mL and the phase separation process was observed between two crossed polarizers (in the horizontal and vertical directions) with transmitted white light.
Figure 5.5. Photographs of phase-separated CNC dispersions (colorless) and CNC-MNP binary mixtures (yellow colored). A grid background was used to distinguish the isotropic phase (which is clear) from the liquid crystalline phase (which is birefringent) in (B).

Figure 5.6. In a horizontally oriented gradient magnetic field (1050 Gauss/cm) from a permanent magnet placed beside the vial, the CNC-MNP binary mixture phase-separated into a macroscopic liquid crystalline phase (with a lighter yellow color) in the low-magnetic-field region as well as a disordered phase in the high-magnetic-field region (A), while the pure CNC suspension was not significantly affected (B).
Figure 5.7. In a vertical gradient magnetic field (intensity about 1050 Gauss/cm) from a magnet under the vial, phase separation of the CNC-MNP binary mixture results in a macroscopic liquid crystalline phase (with a higher brightness between crossed polarizers) above a disordered phase. This process is much faster than in the absence of the gradient magnetic field.
Figure 5.8. In a vertical gradient magnetic field from a permanent magnet placed under the vial, the CNC-MNP binary mixture phase-separated into a macroscopic liquid crystalline phase (with a lighter yellow color) above a disordered phase (A). However, the pure CNC dispersion was not significantly influenced by the magnetic field (B).
5.3.2 Orientation of Liquid Crystalline Tactoids in Gradient Magnetic Fields

To directly observe the microstructures of liquid crystalline tactoids and ordered-disordered interfaces by scanning electron microscopy, nonionic precursors of polyacrylamide (acrylamide, crosslinker, and photoinitiator) were added into the dispersions, after the magnetic-field-induced phase separation, photopolymerization was initiated by ultraviolet light (wavelength of 300 nm), rapidly forming crosslinked polymer networks to solidify these fluid systems (Figure 5.9).

If the phase separation of a CNC-MNP binary mixture is only driven by gravity, most chiral nematic layers in the continuous ordered phase will be horizontally oriented, whereas the discrete tactoids in the isotropic phase have random orientations, as revealed by both POM (Figure 5.10) and SEM micrographs (Figure 5.11). These structures are similar to those observed in pure CNC dispersions (Figure 5.12 and Figure 5.13).

As previously demonstrated, if the paramagnetic-nanoparticle-doped lyotropic liquid crystal phase-separates in a gradient magnetic field (about 1050 Gauss/cm), the macroscopic continuous ordered phase will form in the lower magnetic field region with the ordered-disordered interface perpendicular to this gradient magnetic field, or, more precisely, perpendicular to the vector sum of \((\Sigma F_{\text{mag}} + \Sigma F_{\text{grav}})\) (Figure 5.14 and Figure 5.15). Besides, during the phase separation process, discrete liquid crystalline tactoids will be unidirectionally oriented with the chiral nematic layers parallel to the gradient magnetic field, as revealed by cross-sectional POM (Figure 5.16).

Here the alignment may be caused by the shear forces exerted on tactoids by the continuous disordered phase during the unidirectional movement of tactoids driven by magnetic acceleration forces.\textsuperscript{52} In our work, the chiral nematic layers of tactoids are oriented parallel to a weak gradient magnetic field (maximum 1600 Gauss, i.e., 0.16 Tesla) during the phase separation process, but changing the direction of the magnetic field (by moving the magnet to a different side of the vial)
after completion of the phase separation will not lead to reorientation of the chiral nematic layers parallel to the new magnetic field direction, although the positions of the disordered and ordered phases will follow the magnetic field. This mechanism is different from the magnetic alignment of liquid crystals reported by Gray and others, where the chiral nematic layers of tactoids can be directly aligned perpendicular to a strong magnetic field (about 7 Tesla) due to the paramagnetic or diamagnetic anisotropy of the mesogen nanocrystals themselves.92–96

Figure 5.9. Photographs of phase-separated CNC-MNP binary mixtures captured in cross-linked polyacrylamide networks by in-situ photopolymerization. The phase separation of these systems occurred in (A) horizontally or (B) vertically oriented gradient magnetic fields.
Figure 5.10. POM images of a CNC-MNP dispersion (no magnets). Scale bars, 50 μm.
Figure 5.11. Cross-sectional SEM micrographs for a phase-separated CNC-MNP dispersion (no magnetic fields). Chiral nematic layers in the macroscopically continuous ordered phase adopt a horizontal orientation, while discrete liquid crystalline tactoids in the continuous isotropic phase are nearly randomly oriented. Scale bars, (A) 10 μm, (B) 1 μm, (C) 200 nm, (D) 100 nm.
Figure 5.12. 3D model of a CNC-MNP binary mixture (no magnetic fields).

Figure 5.13. SEM images of a pure CNC dispersion. Scale bars, (A) 40 μm, (B) 20 μm.
**Figure 5.14.** SEM images showing the ordered-disordered interfaces of CNC-MNP suspensions that phase-separated in a horizontal gradient magnetic field. The interfaces are tilted. Scale bars, (A) 10 μm, (B) 2 μm, (C,F) 1 μm, (D) 500 nm, (E) 3 μm.
**Figure 5.15.** 3D model showing the unidirectional orientation of chiral nematic layers in both the continuous ordered phase and discrete liquid crystalline tactoids of a phase-separated CNC-MNP binary mixture. The phase separation of this system occurred in a horizontally oriented gradient magnetic field, which resulted in a nearly vertical ordered-disordered interface.
Figure 5.16. POM micrographs showing the unidirectional orientation of chiral nematic layers of liquid crystalline tactoids in a CNC-MNP suspension subjected to an external gradient magnetic field (in the direction from left to right with respect to these images). The system was captured in a crosslinked polyacrylamide matrix by photopolymerization during the phase separation process (after a standing time of 60 minutes). The orientation of chiral nematic layers in these tactoids is parallel to the external gradient magnetic field. From (A,B) to (C) and (D), the imaging area was increasingly further from the high-magnetic-field region at the magnetic pole. These micrographs indicate that tactoids were driven by magnetic buoyancy forces (from the continuous disordered phase that has a higher magnetic susceptibility) and move to lower magnetic field regions, where they aggregate and coalesce into continuous liquid crystalline phases. Scale bars, 50 μm.
5.3.3 Vertically Aligned Chiral Nematic Layers: Reversed Phase Separation

Phase separation of a CNC-MNP binary mixture in a vertical gradient magnetic field (from a magnet placed under the dispersion) leads to the vertical orientation of all chiral nematic layers in both the discrete liquid crystalline tactoids and macroscopically continuous ordered phases, as revealed by POM (Figure 5.17) and SEM micrographs (Figure 5.18). Moreover, high-resolution SEM images confirm that all the pseudo nematic layers in the chiral nematic phase are aligned in the vertical direction (Figure 5.19). This alignment is strong enough to overcome the anchoring energy near the boundary of the liquid crystalline phase, as the vertical chiral nematic layers are perpendicular to both the horizontal ordered-disordered interface at the bottom and the horizontal liquid-air interface at the top (Figure 5.20 to Figure 5.25).

Based on SEM observations of the biphasic regions (Figure 5.26), discrete liquid crystalline tactoids in the isotropic phase are also vertically oriented with their chiral nematic layers aligned parallel to the gradient magnetic field. As previously discussed, this alignment might result from the shear forces exerted on tactoids by the continuous disordered phase during the unidirectional movement of tactoids, which is mainly driven by the magnetic acceleration forces ($\Sigma F_{\text{mag}}$).

These results reveal that in the presence of a gradient magnetic field, the phase separation of a paramagnetic-nanoparticle-doped liquid crystal may result in the reversed phase configuration, where the macroscopic ordered phase forms above the disordered phase, despite the fact that the ordered phase has a higher density due to the more efficient packing of the mesogens. This study also suggests a new approach to control the orientation of ordered microstructures in soft matter systems, which may help develop new optical devices.
Figure 5.17. POM micrograph of a CNC-MNP binary mixture that phase-separated in a vertical gradient magnetic field, where the chiral nematic layers in both the continuous ordered phase and discrete liquid crystalline tactoids are vertically oriented. Scale bar, 50 μm.

Figure 5.18. SEM images showing the vertical orientation of chiral nematic layers in continuous ordered phases and discrete liquid crystalline tactoids. Scale bars, (A) 15 μm, (B) 10 μm.
**Figure 5.19.** High-resolution SEM micrographs revealing the ordered arrangements of cellulose nanocrystal mesogens in the continuous liquid crystalline phase of a CNC-MNP suspension that phase-separated in a vertical gradient magnetic field. The pseudo nematic layers formed by these CNC mesogens are in the vertical direction, which are parallel to the external gradient magnetic field. Scale bars, (A) 300 nm, (B,C) 200 nm, (D) 100 nm.
Figure 5.20. Cross-sectional POM micrographs showing the continuous liquid crystalline phase of a CNC-MNP binary mixture, which phase-separated in a vertical gradient magnetic field. The chiral nematic layers are aligned in a vertical orientation throughout this liquid crystalline phase, from the liquid-air interface at the top of the dispersion (A) to the ordered-disordered interface at the bottom of the anisotropic phase (B-D). Scale bars, 50 μm.
Figure 5.21. SEM images showing the horizontal ordered-disordered interface and vertical chiral nematic layers in a CNC-MNP binary system that phase-separated in a vertical gradient magnetic field. Scale bars, (A) 5 μm, (B) 3 μm, (C) 2 μm, (D) 1 μm, (E) 500 nm, (F) 200 nm.
Figure 5.22. SEM images showing the horizontal ordered-disordered interface and vertical chiral nematic layers in a CNC-MNP binary system that phase-separated in a vertical gradient magnetic field. Scale bars, (A) 30 μm, (B) 10 μm, (C) 3 μm, (D) 1 μm, (E) 300 nm, (F) 150 nm.
Figure 5.23. Additional SEM images showing the vertical orientation of chiral nematic layers in a phase-separated CNC-MNP binary mixture. These chiral nematic layers are aligned parallel to the external gradient magnetic field, perpendicular to the horizontal ordered-disordered interface. In this case, the cross-sectional appearance of chiral nematic structures is also determined by the fracture angle when the cross-section surface was created from the CNC-MNP-PAAm composite polymer matrix. Scale bars, (A) 5 μm, (B) 2 μm, (C) 1 μm, (D) 400 nm.
Figure 5.24. 3D model showing the cross-sectional structure of a CNC-MNP binary mixture that phase-separated in a vertical gradient magnetic field from a magnet placed under the suspension. In this system, chiral nematic layers in both the continuous ordered phase (the upper region) and discrete liquid crystalline tactoids (in the lower region) are vertically oriented, while the interface between the ordered and disordered phases is in the horizontal direction.
Figure 5.25. SEM images showing the liquid-air interface at the top of a CNC-MNP suspension that phase-separated in a vertical gradient magnetic field. The chiral nematic layers are vertically oriented near this interface. Scale bars, (A) 100 μm, (B) 30 μm.

Figure 5.26. SEM micrographs showing the biphasic region in a CNC-MNP binary mixture. The system was captured by photopolymerization while the phase separation process was ongoing in a vertical gradient magnetic field from a magnet placed under the dispersion. The chiral nematic layers in both the continuous ordered phase and discrete liquid crystalline tactoids are vertically oriented. Scale bars, (A) 20 μm, (B) 10 μm.
5.4 Competitions between Gravitational and Magnetic Acceleration Forces

When a magnet is placed under a CNC-MNP dispersion, the phase separation configuration and rate will be determined by the competition between $\Sigma F_{\text{mag}}$ and $\Sigma F_{\text{grav}}$ since these two vectors are in opposite directions (i.e., $\Sigma F_{\text{mag}}$ vertically upwards, $\Sigma F_{\text{grav}}$ vertically downwards):

1. $|\Sigma F_{\text{mag}}| < |\Sigma F_{\text{grav}}|$ leads to "Normal" phase separations, where the liquid crystalline phase forms below the isotropic phase;

2. $|\Sigma F_{\text{mag}}| > |\Sigma F_{\text{grav}}|$ leads to "Reverse" phase separations, where the liquid crystalline phase forms above the isotropic phase;

3. $|\Sigma F_{\text{mag}} + \Sigma F_{\text{grav}}|$ determines the phase separation rate, i.e., for either the "Normal" or the "Reverse" phase separation, a higher absolute value of the vector sum of $\Sigma F_{\text{mag}}$ and $\Sigma F_{\text{grav}}$ means a faster phase separation rate, or a shorter phase separation time.

For experimental verification, influences of the doping concentration of superparamagnetic Fe$_3$O$_4$ nanoparticles (maximum 140.5 ppm by weight) and strength of the gradient magnetic field (0, 600, 1050, and 3050 Gauss/cm) on the phase separation rates of CNC-MNP binary mixtures (volume of 1.0 mL) were investigated, where the experimental results agree with the theoretical predictions above: increasing either the gradient magnetic field (raising the $|H|$) or the total Fe$_3$O$_4$ concentration (raising $[\chi_m(\text{iso}) - \chi_m(\text{LC})]$) will increase $\Sigma F_{\text{mag}}$ and therefore slow down a "Normal" or accelerate a "Reverse" phase separation process (Table 5.1 and Figure 5.27). And moreover, the phase separation time reaches the maximum value when the inversion between the "Normal" and "Reverse" configurations occurs, where the magnitude of the vector sum of $(\Sigma F_{\text{mag}} + \Sigma F_{\text{grav}})$ approaches zero.

As verified by ultraviolet-visible absorption spectroscopy (at 300 nm wavelength), there is a positive correlation between $[\chi_m(\text{iso}) - \chi_m(\text{LC})]$ (the magnetic susceptibility difference) and the total
concentration of paramagnetic Fe₃O₄ nanoparticles, where the distribution ratio of Fe₃O₄ doping nanoparticles in the isotropic and liquid crystalline phases ([Fe₃O₄]Iso/[Fe₃O₄]L.C) increased from around 2.40 to 4.41 as the total Fe₃O₄ concentration increased from 11.7 to 140.5 ppm by weight (Table 5.2; Figure 5.28 and Figure 5.29). These results should be applicable to liquid crystalline tactoids as the coalescence of discrete tactoids leads to the formation of macroscopic continuous ordered phases.

**Table 5.1.** Phase separation times of CNC-Fe₃O₄ binary mixtures.

<table>
<thead>
<tr>
<th>Conc. of Fe₃O₄ NPs (wt. ppm)</th>
<th>Zero Gauss/cm</th>
<th>600 Gauss/cm</th>
<th>1050 Gauss/cm</th>
<th>3050 Gauss/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6 h 06 min N</td>
<td>6 h 09 min N</td>
<td>5 h 57 min N</td>
<td>6 h 08 min N</td>
</tr>
<tr>
<td>11.7</td>
<td>5 h 54 min N</td>
<td>6 h 20 min N</td>
<td>7 h 53 min N</td>
<td>9 h 46 min R</td>
</tr>
<tr>
<td>23.4</td>
<td>5 h 59 min N</td>
<td>6 h 32 min N</td>
<td>24 h 08 min N</td>
<td>7 h 57 min R</td>
</tr>
<tr>
<td>35.1</td>
<td>5 h 52 min N</td>
<td>6 h 47 min N</td>
<td>13 h 47 min R</td>
<td>3 h 03 min R</td>
</tr>
<tr>
<td>46.8</td>
<td>5 h 49 min N</td>
<td>7 h 04 min N</td>
<td>7 h 57 min R</td>
<td>1 h 52 min R</td>
</tr>
<tr>
<td>93.7</td>
<td>5 h 27 min N</td>
<td>14 h 03 min R</td>
<td>2 h 54 min R</td>
<td>55 min R</td>
</tr>
<tr>
<td>140.5</td>
<td>5 h 48 min N</td>
<td>4 h 13 min R</td>
<td>2 h 21 min R</td>
<td>49 min R</td>
</tr>
</tbody>
</table>

Notes: The CNC-MNP dispersions were placed in glass vials (inner diameter of 12.60 mm, outer diameter of 15.00 mm); the completion of phase separation was determined by the formation of a clear and smooth boundary between two phases (the errors are about +/- 10 minutes); "N" means normal phase separation, where the isotropic phase forms above the liquid crystalline phase; "R" represents reverse phase separation, where the isotropic phase forms below the liquid crystalline phase.
Figure 5.27. Phase separation times of CNC-MNP dispersions (volume of 1.0 mL) with different doping concentrations of Fe$_3$O$_4$ nanoparticles (0 to 140.5 ppm by weight) and in vertical gradient magnetic fields with different strengths (0, 600, 1050, and 3050 Gauss/cm). The striped columns represent reversed phase separations, where the liquid crystalline phase forms above the isotropic phase. (Errors in the determination of phase separation times are $+/-$ 10 minutes).
Table 5.2. Distribution ratio of Fe₃O₄ NPs in isotropic and liquid crystalline phases.

<table>
<thead>
<tr>
<th>Conc. of Fe₃O₄ NPs (ppm by weight)</th>
<th>Abs. of Fe₃O₄ NPs (Isotropic Phase)</th>
<th>Abs. of Fe₃O₄ NPs (Ordered Phase)</th>
<th>[Fe₃O₄]<em>{iso}/[Fe₃O₄]</em>{LC}</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.7</td>
<td>0.120</td>
<td>0.050</td>
<td>2.40</td>
</tr>
<tr>
<td>23.4</td>
<td>0.200</td>
<td>0.073</td>
<td>2.74</td>
</tr>
<tr>
<td>35.1</td>
<td>0.260</td>
<td>0.085</td>
<td>3.06</td>
</tr>
<tr>
<td>46.8</td>
<td>0.325</td>
<td>0.094</td>
<td>3.46</td>
</tr>
<tr>
<td>93.7</td>
<td>0.622</td>
<td>0.153</td>
<td>4.07</td>
</tr>
<tr>
<td>140.5</td>
<td>0.854</td>
<td>0.193</td>
<td>4.41</td>
</tr>
</tbody>
</table>

Notes: The distribution ratios of Fe₃O₄ nanoparticles were determined by UV-Vis absorbance at the wavelength of 300 nm, where the absorbance of cellulose nanocrystals has been subtracted.

Figure 5.28. UV-Vis absorption spectra of the isotropic phase (red curve) and liquid crystalline phase (blue curve) of a phase-separated pure CNC dispersion. The two phases were isolated and diluted by water to 10 times their original volumes.
Figure 5.29. Absorbance of MNPs in isotropic (red) and liquid crystalline phases (blue).
5.5 Conclusions

In this study, by doping lyotropic liquid crystals with paramagnetic magnetite nanoparticles, the disordered phases were endowed with significantly higher magnetic susceptibility than liquid crystalline tactoids since tactoids have an exclusion effect on paramagnetic doping nanoparticles. Due to the lower magnetic susceptibility, the movement direction and orientation of tactoids are determined by the competition between gravitational and magnetic acceleration fields, where the tactoids are mainly driven by magnetic buoyancy forces. This method enables control of the rate and configuration of phase separation, as well as the orientation of the director fields in both the discrete tactoids and macroscopic continuous ordered phases. These results may help understand the physical properties of liquid crystalline tactoids and other soft matter systems, and might also provide new methods to precisely control self-assembly processes for developing new functional materials.
5.6 Experimental Methods

5.6.1 Synthesis of Superparamagnetic Magnetite (Fe₃O₄) Nanoparticles

Citrate-stabilized superparamagnetic magnetite (Fe₃O₄) nanoparticles were synthesized by a coprecipitation method. In a typical synthesis, iron (II) chloride tetrahydrate (0.994 g, 5 mmol) and iron (III) chloride hexahydrate (2.703 g, 10 mmol) were thoroughly dissolved in pure water (50.0 mL). The system was stirred (at 1150 RPM) and deoxygenated by bubbling argon through the solution. An ammonium hydroxide solution (28-30 wt.% in water, 6.0 mL) was added to the system using a syringe. After 30 minutes, an aqueous solution of citric acid (1.50 g of citric acid anhydrous dissolved in 2.0 mL of pure water) was introduced into the reaction mixture, then the system was stirred at room temperature for another 120 minutes. The Fe₃O₄ nanoparticles could be magnetically isolated then redispersed in pure water for several cycles to remove electrolytes, and eventually a stable homogeneous dispersion of Fe₃O₄ nanoparticles (about 1.41% by weight) was obtained.

5.6.2 Solidification of CNC-Fe₃O₄ Mixtures by In-Situ Photopolymerization

In a standard experiment, an aqueous dispersion of superparamagnetic Fe₃O₄ nanoparticles (1.41 wt.%, 50 µL) was added to a cellulose nanocrystal suspension (4.0 wt.%, pH 6.4, 5.0 mL), then the system was mixed with acrylamide (500 mg, monomer), N,N'-methylenebisacrylamide (50 mg, crosslinker), and 2-hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone (2.5 mg, the photoinitiator). The CNC-Fe₃O₄ dispersion was allowed to stand in the dark (with or without an external gradient magnetic field) for about 12 hours, during which the phase separation occurred. Afterwards, UV-B irradiation (wavelength of 300 nm, 8 W) was applied to the system to initiate
the photopolymerization process, rapidly forming a crosslinked polyacrylamide (PAAm) matrix to capture liquid crystalline tactoids and other microstructures. After complete removal of water (by heating at 65 °C in air), the solid-state polyacrylamide matrix could be cracked to give fresh cross-sections for SEM observations.

5.6.3 Materials

The cellulose nanocrystal dispersions (4.0 wt.%, pH = 6.4, conductivity = 395 μS/cm) were provided by FPInnovations. Other chemicals are the same as those used in previous chapters.

5.6.4 Characterization

Three different permanent magnets were used in the performance of magnetic-field-induced phase-separation experiments. The strengths of the gradient magnetic fields were measured with a Bell Model 620 Hall Effect Gaussmeter. For each of these permanent magnets, the strengths of its magnetic field at the surface of the magnetic pole and at 1.0 centimeter away from the surface (on the central axis) were measured, which are 1600 Gauss / 550 Gauss, 1000 Gauss / 400 Gauss, and 3600 Gauss / 550 Gauss for the three magnets, respectively. Other characterization methods are the same as those used in previous chapters.
Chapter 6: Conclusions and Future Perspectives

6.1 Conclusions

The improvements in observational techniques or methods, which can provide higher spatial and temporal resolutions, are the material basis of a better understanding of physical phenomena and therefore new theoretical models. For condensed matter physics, electron microscopy is one of the most important characterization methods, as it can directly reveal the microstructures of a system at the resolution of individual particles.

An attractive topic in condensed matter physics is the spontaneous emergence and evolution of ordered structures in an initially disordered system, for example, the formation of anisotropic phases in isotropic dispersions. In lyotropic liquid crystals, this process is generally mediated by tactoids, which are discrete ordered microdroplets in continuous disordered phases. However, the structural studies of tactoids were difficult as these soft fluid droplets cannot be directly observed by electron microscopy.

In Chapter 2 of this thesis, a new method was developed to enable the direct observation of liquid crystalline tactoids by electron microscopy, where these metastable ordered microdroplets could be rapidly captured in a crosslinked polyacrylamide matrix by in-situ photopolymerization. This method provides an approach to the solidification of soft matter systems and preservation of lyotropic liquid crystalline structures while removing the solvents, enabling electron microscopy observations of tactoids with the resolution of individual liquid crystal mesogens. The emergence of tactoids in initially disordered phases, the coalescence of multiple tactoids and the generation of topological defects, as well as the sedimentation of tactoids and the formation of macroscopic continuous liquid crystalline phases were systemically investigated, which provides new insights...
into the structure and evolution of tactoids, topological defects and other microscopic metastable transition states in lyotropic liquid crystals.

In Chapter 3 of this thesis, the in-situ photopolymerization of lyotropic liquid crystals was extended to an inverse emulsion system. The structural transformation of chiral nematic tactoids in spherical confinement was captured at different evolution stages and examined by both optical and cross-sectional electron microscopy. Furthermore, solid-state polymer and mesoporous silica microspheres with chiral nematic ordering were obtained, which may have potential applications in optics, sensing and chiral separation.

Chapter 4 of this dissertation focuses on the behavior of tactoids in the presence of foreign nanoparticles. Based on the in-situ photopolymerization method, liquid crystalline tactoids were observed to have size-selective exclusion effects on doping nanoparticles. This research directly revealed the initial emergence of self-assembly in binary mixtures of nanorods and nanospheres by electron microscopy, and investigated the interactions between ordered-disordered interfaces and foreign nanoparticles. The observations in these experiments provide new information about the metastable transition states in multicomponent colloidal systems, and could help explain the aggregation of doping nanoparticles in topological defects of lyotropic liquid crystals. Moreover, a size-selective separation method for nanoparticles was successfully developed according to the exclusion effects of tactoids, which may have applications in the purification of nanomaterials.

In Chapter 5 of this thesis, the influence of gradient magnetic fields on the phase separation of paramagnetic-nanoparticle-doped lyotropic liquid crystals was investigated. This research was based on the exclusion effects of tactoids on doping nanoparticles, by which the liquid crystalline tactoids could be endowed with significantly lower volume magnetic susceptibility than isotropic phases. This difference in magnetic properties facilitates the manipulation of tactoids by gradient
magnetic fields, where the movement and orientation of liquid crystalline tactoids are determined by the competition between gravitational and magnetic acceleration forces, which allows control over the phase separation rate and configuration, as well as the orientation of the director field in both discrete tactoids and continuous ordered phases. These studies provide new insights into the evolution of tactoids and phase separation processes of lyotropic liquid crystals, and may help to develop new functional materials with ordered microstructures.

In summary, this thesis investigates the microscopic structures of liquid crystalline tactoids, which are representative of the metastable transition states of lyotropic systems. Microstructures of transition states are difficult to observe since they are always moving and changing, especially when these structures are in the nanoscale or atomic scale, where electron microscopy or atomic force microscopy is required to achieve sufficiently high resolution. This thesis partly addresses the above issue by an in-situ photopolymerization method, where the metastable transition states of lyotropic liquid crystals can be rapidly captured and solidified in a crosslinked polymer matrix for electron microscopy observations. Moreover, these studies also provide new insights into the early stages of self-assembly processes, e.g., the emergence of tactoids from an initially isotropic phase. This phenomenon may be of significance since it might share some common features with the origin of highly ordered hierarchical structures in plants and animals, such as those observed in Pollia fruits, butterflies, and beetles.
6.2  Future Perspectives

6.2.1  Liquid Crystalline Tactoids in Other Soft Matter Systems

In this dissertation, the direct electron microscopy observation of liquid crystalline tactoids was successfully achieved; however, the lyotropic liquid crystal formed by cellulose nanocrystals is not a perfect model for the study of self-assembly structures or processes. Although individual cellulose nanocrystals could be directly observed by scanning electron microscopy, these organic nanoparticles are not very stable under an electron beam. Furthermore, the chirality of this liquid crystal makes the structures more complicated, especially near the ordered-disordered interfaces and topological defects. To avoid these problems, nematic or columnar liquid crystals formed by inorganic (e.g., metal hydroxides or metal phosphates) nanoparticles would be better candidates for the structural studies of tactoids and topological defects.

6.2.2  Size-Selective Separation of Molecules by Liquid Crystalline Tactoids

Another hypothesis worth further investigation is the size-selective separation of proteins or other organic macromolecules during the tactoid-mediated phase separation process of molecular lyotropic liquid crystals, for example, the nematic phase formed by Sunset Yellow FCF. These studies would provide valuable information about the interactions between mesogens in tactoids and macroscopic ordered phases, and may help to develop new separation techniques for organic compounds, atom clusters or biomacromolecules.

As the smallest units of ordered phases and early stages of self-assembly, liquid crystalline tactoids play an important role in the phase transitions of lyotropic systems. The investigation of tactoids can provide a better understanding of the formation and properties of liquid crystals, and
promote the development of functional materials with ordered microstructures. Furthermore, the in-situ photopolymerization method may be used to capture and solidify the metastable transition states in other soft matter systems, such as foams, colloids, and some biological materials, which would enable the direct observation of these fluid microstructures by electron microscopy.
Bibliography


710-712.

(9) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature* 1998, 396, 152-
155.

(10) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D.


(29) Zocher, H.; Török, C. Kolloid Z. 1960, 170, 140-144.


