RICE UNIVERSITY

Phase Behavior and Rheology of Single-Walled Carbon Nanotubes (SWNTs) in Superacids with Application to Fiber Spinning

by

Virginia Angelica Davis

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

Matteo Pasquali
Associate Professor, Co-Chair
Chemical and Biomolecular Engineering

Richard E. Smalley
University Professor, Co-Chair
Carbon Nanotechnology Laboratory

Robert H. Hauge
Distinguished Faculty Fellow
Chemistry

George J. Hirasaki
A. J. Hartsook Professor
Chemical and Biomolecular Engineering

Michael S. Wong
Assistant Professor
Chemical & Biomolecular Engineering

HOUSTON, TEXAS
JANUARY 2006
Copyright
Virginia Angelica Davis
2006
ABSTRACT

Phase Behavior and Rheology of Single-Walled Carbon Nanotubes (SWNTs) in Superacids with Application to Fiber Spinning

by

Virginia Angelica Davis

This dissertation describes the first discovery and characterization of a SWNT liquid crystalline phase. The protonation of SWNTs in superacids enables their dispersion at concentrations up to 12 % vol. (10 % wt.); this concentration is an order of magnitude higher than has been achieved for pristine SWNTs in any other solvent. The dispersed SWNTs behave as rigid rods; with increasing concentration the dispersions transition from a dilute phase of Brownian non-interacting rods, to a semidilute phase in which rod rotation is inhibited, to a biphasic regime where an isotropic phase coexists with a liquid crystalline phase, and finally to a single phase liquid crystal. This phase behavior was determined using a combination of rheology, optical microscopy, and differential scanning calorimetry.

For monodisperse rods interacting only through hard rod repulsion, the phase boundaries are only a function of the rods' aspect ratio. For SWNTs in superacids, the phase transitions are also affected by the extent of SWNT protonation as well as aspect ratio polydispersity. SWNT protonation has significant effects on the concentration at which the system becomes biphasic, the liquid crystalline morphology, and the response of the system to non-solvents. In contrast, SWNT protonation has little effect on the concentration at which the system becomes a single liquid crystalline phase; this transition appears to be primarily controlled by SWNT polydispersity.

The ability to form a lyotropic nematic SWNT liquid crystal directly impacts the development of applications requiring macroscopic assemblies of highly aligned SWNTs. Highly aligned macroscopic SWNT fibers ranging from 30 to 100 μm in diameter and up to 100 m in length have been produced by solution spinning liquid crystalline SWNT-102% H₂SO₄ dispersions. The direct impact of liquid crystalline phase behavior and liquid crystal morphology on fiber microstructure was demonstrated by producing fibers from SWNTs dispersed in 102% H₂SO₄ and CISO₃H. The results of this research provide a key example of how liquid crystalline phase behavior can be used to facilitate the development of macroscopic structures comprised of anisotropic nanomaterials.
Acknowledgements

There are numerous people who have my gratitude for enabling me to pursue my Ph.D. and for their direct and indirect contributions to this research. A few of them are listed below.

My advisors and dissertation committee:
- Richard E. Smalley for the vision that made this research possible and his constant search for scientific truths.
- Matteo Pasquali for teaching me that understanding rheology is about more than knowing how to characterize a polymer melt.
- Robert H. Hauge for innumerable valuable discussions and insights related not only to this work but research in general.
- Michael S. Wong and George Hirasaki for their classroom instruction and interest in my research.

The other researchers at Rice, the University of Pennsylvania, and Georgia Institute of Technology involved in SWNT fiber spinning research especially:
- Lars Ericson, Ramesh Sivarajan, and Rajesh Saini who were there from the beginning of this project. Many experiments, discussions, and debates went into the development of our motto for SWNTs in superacids “they dissolve, they align, they spin fibers.”
- Alario Nicholas Gerrado Parra-Vasquez and Valentin Prieto for their insights in numerous brainstorming sessions and for all the experiments they conducted in support of this research.
- Pradeep Rai and Wei Zhou for developing methods that made it possible to more accurately quantify the boundaries of the biphasic region.

My friends and family, especially
- My husband Ed for his constant support and encouragement.
- My son Benjamin for his laughter and for reminding me that world is a pretty funny place.
- My mother for teaching me the value of researching the literature and always having an application for your research.
Contents

1 Introduction ........................................................................................................................................... 1

2 Background .......................................................................................................................................... 8
  2.1 Single-Walled Carbon Nanotubes (SWNTs) .............................................................................. 8
  2.2 Defining SWNT length distributions ......................................................................................... 13
  2.3 Supercrystals .............................................................................................................................. 18
  2.4 Liquid Crystals .......................................................................................................................... 20
  2.5 General Phase Behavior of Rods in Solution ........................................................................... 23
  2.6 Rheology of Solutions of Rods ................................................................................................. 29
  2.7 Rheological Characteristics of Rod-like Polymer Solutions ....................................................... 34
  2.8 Comparison of Criteria for Assessing Liquid Crystallinity ..................................................... 49
  2.9 Fiber Spinning ........................................................................................................................... 50

3 Experimental Details ......................................................................................................................... 56
  3.1 Single-Walled Carbon Nanotube (SWNT) Preparation ............................................................ 57
  3.2 Acid Preparation and Titration .................................................................................................. 59
  3.3 Dispersion Preparation .............................................................................................................. 59
  3.4 Fiber Spinning ........................................................................................................................... 67
  3.5 Characterization Methods ........................................................................................................... 69

4 Phase Behavior and Rheology of SWNTs in Supercrystals .............................................................. 76
  4.1 Dispersion of SWNTs in Supercrystals ..................................................................................... 77
  4.2 Dilute Regime ............................................................................................................................. 79
  4.3 Applications of Dilute Phase Behavior .................................................................................... 83
4.4 Semidilute Regime ................................................................. 88
4.5 Biphasic Regime ................................................................. 90
4.6 Single-Phase Nematic Liquid Crystal ..................................... 92
4.7 Effect of Temperature on Rheology and Phase Behavior ............. 114
4.8 Viscoelasticity of SWNTs in 102% H₂SO₄ ................................ 121
4.9 Summary of Phase Boundaries ............................................... 132
4.10 Conclusions ..................................................................... 133

5 Controlling SWNT - Supercritical Phase Behavior ....................... 134
  5.1 Role of polydispersity ......................................................... 135
  5.2 Effect of salt addition ........................................................ 141
  5.3 Effect of SWNT Protonation on φl ....................................... 146
  5.4 Effect of SWNT Protonation on φN ....................................... 151
  5.5 Effect of SWNT Protonation on Liquid Crystal Morphology ....... 157
  5.6 Impact of SWNT Protonation on Fiber Morphology ................. 161
  5.7 Conclusion ..................................................................... 166

6 Conclusions ........................................................................ 170

References ........................................................................... 173
List of Figures

Figure 2.1  Honeycomb lattice of a 2D graphite sheet ................................................. 10
Figure 2.2  Armchair, chiral and zig-zag SWNTs ......................................................... 11
Figure 2.3  Characteristic lengths of a log normal distribution ..................................... 15
Figure 2.4  A typical bundle of SWNTs ........................................................................ 17
Figure 2.5  Pictorial representation of the primary classes of liquid crystals .................. 23
Figure 2.6  Rheological regimes for rigid rod polymer solutions .................................... 24
Figure 2.7  Hypothetical phase diagram of a rod-like polymer system ......................... 25
Figure 2.8  Schematic of lyotropic phase diagram ....................................................... 26
Figure 2.9  The effect of aspect ratio on the phase transitions ....................................... 28
Figure 2.10 Tumbling of elongated molecules in a shear field ........................................ 30
Figure 2.11 Viscosity of PBG (M_w = 335000) in m cresol ........................................ 36
Figure 2.12 Viscosity versus concentration of PPTA in sulfuric acid ............................ 38
Figure 2.13 Relative viscosity of PPTA solutions ....................................................... 28
Figure 2.14 Three region flow curve for liquid crystalline polymers ............................ 39
Figure 2.15 Example of the negative first normal stress difference ............................. 43
Figure 2.16 Start-up of shear flow of 40 % wt. HPC in acetic acid ................................. 45
Figure 2.17 Complex viscosity and steady shear viscosity ........................................... 46
Figure 2.18 Characteristic nematic Schlieren texture .................................................... 48
Figure 2.19 Banded structure in dried films of 15 % wt. PBLG. .................................... 48
Figure 2.20 Examples of rod-like polymers .................................................................. 51
Figure 2.21 Schematic of the wet jet wet spinning process .......................................... 53
Figure 2.22. Effect of temperature on PBA/DMAC viscosity ........................................... 55
Figure 3.1. The Trubore mixer ......................................................................................... 62
Figure 3.2. The Daca mixer ......................................................................................... 63
Figure 3.3. The Haake MiniLab Mixer ........................................................................... 64
Figure 3.4. The Spinning Bob Mixer (SBM) ................................................................. 65
Figure 3.5. The mini-mixer ............................................................................................ 66
Figure 3.6. Ares 100 FRT rheometer ......................................................................... 70
Figure 3.7. RDA III rheometer .................................................................................... 70
Figure 3.8. Key features of the Raman spectra of a carbon nanotube ......................... 73
Figure 4.1 Reduced viscosity versus shear rate in the dilute regime ......................... 80
Figure 4.2. AFM height image of individual SWNT ..................................................... 83
Figure 4.3. Reduced viscosity versus shear rate in the semidilute regime ................. 89
Figure 4.4. SWNT spaghetti ......................................................................................... 91
Figure 4.5. 5.1 % vol. (4 % wt.) SWNT under cross-polarized light ......................... 93
Figure 4.6. Response to start up of shear flow ............................................................ 95
Figure 4.7. Comparison of steady shear and transient data ........................................ 96
Figure 4.8. Relationship between viscosity and concentration .................................. 97
Figure 4.9. Dispersions greater than 1.9% vol. display a significant yield stress ......... 98
Figure 4.10. Viscosity versus shear rate. ...................................................................... 99
Figure 4.11. A sample from the top of the Daca screw ................................................. 100
Figure 4.12. Comparison of steady and dynamic shear viscosity ............................... 101
Figure 4.13. Rearrangement of SWNTs into aligned species ...................................... 103
Figure 4.14. a) Bucky-paper from 6 % wt. SWNT in 102% H₂SO₄ ............................... 104
Figure 4.15. Alewives from 4 % wt SWNT in 102% H₂SO₄ ................................................. 106
Figure 4.16. Alewives surrounded by ropes ......................................................................... 107
Figure 4.17. Ether quenched 4wt% SWNT/oleum samples ..................................................... 108
Figure 4.18. Raman spectroscopy of alewives ........................................................................ 108
Figure 4.19. Vanadium pentoxide tactoids ............................................................................. 109
Figure 4.20. SEM image of a 75 µm diameter SWNT fiber ....................................................... 110
Figure 4.21. Cross sections of fiber from 4 wt% SWNT ............................................................ 111
Figure 4.22. Macrostructure of fiber extruded from 5.3 % vol. SWNT. ................................. 112
Figure 4.23. Dogbone structure of early SWNT fibers ............................................................ 113
Figure 4.24. Microscopic SWNT alignment follows curvature ............................................... 113
Figure 4.25. Breaks between SWNT bundles created defects in the fiber ................................. 114
Figure 4.26. The viscosity of 104 ppm vol. SWNT-102% H₂SO₄ : 25-70 °C ......................... 117
Figure 4.27. The viscosity of 390 ppm vol. SWNT-102% H₂SO₄ : 25-70 °C ......................... 118
Figure 4.28. The viscosity of 0.19 % vol. SWNT-102% H₂SO₄ : 25-70 °C ......................... 119
Figure 4.29. The viscosity of 2.6 % vol. SWNT-102% H₂SO₄ : 25-70 °C ................................. 120
Figure 4.30. tan(δ) versus % strain for 0.005 % vol. <φ< 12 % vol ........................................... 122
Figure 4.31. tan(δ) versus frequency for SWNTs for 0.004 < φ < 12 % vol .............................. 125
Figure 4.32. Elastic (storage) modulus G’ as a function of frequency ................................. 127
Figure 4.33. Viscous (loss) modulus G” as a function of frequency ............................... 127
Figure 4.34. The elastic modulus versus the reduced volume fraction ................................. 129
Figure 4.35. G’, G”, and η* as function of concentration ......................................................... 131
Figure 5.1. General phase diagram for a lognormal distribution of rods ............................... 137
Figure 5.2. Increase in SWNT-102% H₂SO₄ strand diameter with K₂SO₄ .......................... 142
Figure 5.3. SWNTs dispersion in 96% H₂SO₄ with and without K₂S₂O₈ .................. 144
Figure 5.4. Raman spectra of SWNT-96% H₂SO₄ with and without K₂S₂O₈ .......... 145
Figure 5.5. Raman spectra of SWNT-102% H₂SO₄ with and without K₂S₂O₈ .......... 146
Figure 5.6. Structureless isotropic fluids ............................................................... 148
Figure 5.7. Optical microscopy after exposure to moisture ................................. 148
Figure 5.8. Optical microscopy 0.15 % wt. SWNTs in 10/90 vol. ClSO₃H .......... 150
Figure 5.9. Maximum concentration in the isotropic phase .............................. 151
Figure 5.10. DSC comparison of transitions in 102% H₂SO₄ and 120% H₂SO₄ ....... 153
Figure 5.11. Microscopy images of SWNT - 120% H₂SO₄ solutions .................... 155
Figure 5.12. Comparison of the shear thinning 102% H₂SO₄ and 120% H₂SO₄ ...... 156
Figure 5.13. Optical microscopy 4.2 % ol. SWNT in ClSO₃H .............................. 157
Figure 5.14. Morphology near the onset of the biphasic region ....................... 158
Figure 5.15. Comparison of liquid crystalline morphology .............................. 159
Figure 5.16. Rearrangement of 0.19 vol % 70/30 ClSO₃H/H₂SO₄ ....................... 160
Figure 5.17. Coalescence of SWNTs in 70/30 ClSO₃H/H₂SO₄ .............................. 160
Figure 5.18. Micro- and macrostructure of fibers spun from ClSO₃H ............... 162
Figure 5.19. Additional SEM of microstructure of fibers spun from ClSO₃H ........ 163
Figure 5.20. Macroscopic pleating of fibers spun from ClSO₃H ....................... 164
Figure 5.21. SWNT-ClSO₃H dispersion coagulated in water ............................ 165
Figure 5.22. SEM of control fibers .............................................................. 166
Figure 5.23. Phase diagram for SWNTs in superacids .................................... 168
Figure 5.24. Phase diagram for SWNTs in superacids with model predictions .... 168
List of Tables

Table 2.1. Indications of the transition to a single liquid crystalline phase .................. 49
Table 4.1. Rheology and AFM comparison of unpurified SWNT length ....................... 87
Table 4.2. Summary of SWNT-102% H₂SO₄ phase transitions ................................. 132
Table 5.1. Predicted values for φl ........................................................................ 139
Table 5.2. Predicted values for φN ........................................................................ 140
Table 5.3. Impact of acid composition on δ⁺ and φl ................................................ 149
Chapter 1

Introduction

This dissertation delineates research into the rheology and phase behavior of single walled carbon nanotubes (SWNTs) in superacids. Several key results are highlighted: 1) the long anticipated (Davidson, Gabriel et al. 1993; Gabriel and Davidson 2003) discovery of a lyotropic nematic SWNT liquid crystalline phase, 2) the characterization of rheology and phase behavior over three decades of concentration – less than 0.01 % vol. to 10 %, vol. and 3) the production of the first highly aligned pure macroscopic SWNT fibers. These first steps in the nascent fields of SWNT liquid crystals, rheology and fiber spinning will facilitate the development of SWNT applications thereby enabling their promising nano- to micro- scale properties to be manifested in macroscopic materials.

The protonation of single-walled carbon nanotubes (SWNTs) in superacids enables their dispersal at sufficiently high concentrations for the formation of nematic liquid crystalline phases which facilitate the production of highly aligned macroscopic pure SWNT fibers. SWNT liquid crystals and fibers are of interest because of the outstanding combination of properties observed for individual and small bundles of SWNTs; electrical conductivity and current carrying capacity similar to copper (Tans, Devoret et al. 1997; Hone, Llaguno et al. 2000), thermal conductivity higher than diamond (Hone, Whitney et al. 1999; Berber, Kwon et al. 2000), and mechanical strength
higher than any naturally occurring or man-made material (Buongiorno-Nardelli, Yakobson et al. 1998; Krishnan, Dujardin et al. 1998). If these properties could be manifested on the macroscopic scale, SWNTS could revolutionize 21st century materials engineering just as polymers revolutionized 20th century materials engineering. For example, macroscopic SWNT fibers could be utilized in a broad range of applications including thermal management systems, clothing for space and other hazardous environments, highly efficient electrical conduits, structural reinforcements for military and aerospace vehicles, jet engine rotors, and artificial muscles (Davis and Pasquali 2005). They could, perhaps, even form the cables for the space elevator envisioned in the science fiction novel, The Fountains of Paradise (Clarke 1978; Yakobson and Smalley 1997).

Realization of potential SWNT applications requires the development of both scalable SWNT production techniques and processing techniques. At least one solution to the economic mass-production of SWNTs now exists through the development of the high pressure carbon monoxide (HiPco) process (Bahr, Mickelson et al. 2001) and potentially by other scalable routes (Kitiyanan, Alvarez et al. 2000; Dai 2001). However, the fundamental research required to develop processing techniques is at a very early stage. For example, research into spinning SWNT fibers is at a very early stage; the first pure macroscopic SWNT fibers were produced as part of this research. Most common macroscopic fibers such as carpet fibers are produced via melt processing techniques. However, melt phase processing is not an option for pure SWNT materials; SWNTs decompose before melting at 2000 °C in argon and at 750 °C in air. Solid phase assembly of SWNTs, particularly as part of the production process, may be useful in
some cases, but the majority of macroscopic articles consisting solely of SWNTs will need to be produced through liquid phase processing techniques. Therefore, understanding the dispersal and behavior of SWNTs in liquids is critical to applications development.

Until now, research into dispersing SWNTs in liquids has met with limited success. Due to high van der Waals interactions between SWNTs, approximately 500 eV/μm (Thess, Lee et al. 1996), SWNT solubility is limited to less than 0.5 % wt. in most solvents; this includes small molecule organic solvents such as dichlorobenzene and aqueous solutions of surfactants such as sodium dodecyl sulfate (SDS). Ongoing research into SWNT functionalization and wrapping may provide new means for solvating higher concentrations of SWNTs in these solvents (Bahr, Mickelson et al. 2001; Georgakilas, Voulgaris et al. 2002; Liang, Sadana et al. 2004); but, thus far even functionalized nanotubes have limited solubility. Furthermore, functionalization disrupts SWNTs’ electronic structure markedly deteriorating their outstanding electrical properties. In contrast, protonation of SWNT sidewalls in superacids allows their dispersion at concentrations as high as 10 % wt., over an order of magnitude higher than can be achieved in other solvents. The protonation mechanism is fully reversible and occurs without deteriorating the SWNTs’ structure or performance properties. The ability to disperse SWNTs at such high concentrations enabled this research into the rheology and phase behavior of purified (Chiang, Brinson et al. 2001; Xu, Peng et al. 2005) HiPco (Bronikowski, Willis et al. 2001) SWNTs in superacids.

In the first part of this investigation, the phase behavior and rheology of SWNTs in 102% H₂SO₄ (2 % wt. excess SO₃) was found to generally follow that expected for
rods in solution (Doi and Edwards 1986). At low concentrations, the SWNTs individually disperse and their rheological behavior is that of dilute Brownian rods; this behavior enabled the development of a new method for the rheological determination of the average length to diameter (aspect) ratio of a bulk sample of SWNTs (Davis, Ericson et al. 2004; Pasquali, Davis et al. 2005). As concentration is increased, rod (or SWNT) motion becomes increasingly confined and the system transitions from the dilute phase in which rods are free to rotate and translate, to the semidilute phase in which rotation starts to become inhibited, and then to the isotropic concentrated phase in which rod movement is highly confined (Doi and Edwards 1986). With further increases in concentration, the system reaches a critical concentration $\phi_1$ above which the system is no longer completely isotropic; portions of the rods start to spontaneously align creating a liquid crystalline phase in equilibrium with the isotropic phase. The alignment results from hard rod repulsion; the increase in translational entropy resulting from alignment more than compensates for the corresponding loss of orientational entropy (Onsager 1949). In this biphasic region, the relative proportion of the liquid crystalline phase increases with increasing concentration until a second critical concentration $\phi_N$ is reached and the system becomes completely liquid crystalline. The existence of the liquid crystalline SWNT phase was established using known criteria for evaluating liquid crystallinity in rod-like polymer solutions. These criteria included key rheological characteristics such as a maximum in the viscosity versus concentration curve and the ability of the SWNTs to form a variety of aligned species.

In the second part of this research, the critical concentrations for the SWNT-102% $\text{H}_2\text{SO}_4$ system were compared to the critical concentrations predicted by Onsager (1949)
for monodisperse rods interacting solely through hard rod repulsion. Based on a number average SWNT aspect ratio of 350, the experimentally measured transition to the biphasic region $\phi_l$ was an order of magnitude lower than the theoretical value; the experimentally measured transition to the single phase liquid crystal $\phi_N$ was more than five times greater than the Onsager prediction. Broad biphasic regions are usually the result of a combination of rod flexibility, polydispersity, or solvent quality. The potential impact of rod flexibility was not considered due to the high persistence length and rod-like behavior of SWNTs (Yakobson and Couchman 2004; Duggal 2005; Duggal and Pasquali in preparation). However, based on the Gaussian ODF Model for the phase behavior of polydisperse rods (Speranza and Sollich 2003; Wensink and Vroege 2003), the high value of $\phi_N$ can be explained solely by the polydispersity; experimental data shows that $\phi_N$ is also somewhat influenced by solvent quality. In contrast, based both the Gaussian ODF and Onsager $P_2$ Models (Speranza and Sollich 2003); polydispersity is not the primary cause of the low value of $\phi_l$. Therefore, the role of solvent quality in determining $\phi_l$ was investigated.

For lyotropic polymeric liquid crystals, solvent quality, and therefore the breadth of the biphasic region, can be controlled by altering the temperature of the system. However, while SWNT-superacid dispersions share many characteristics with lyotropic polymeric liquid crystals, they also exhibit characteristics of inorganic (mineral) liquid crystals, including their phase behavior being insensitive to temperature fluctuations (Davidson, Gabriel et al. 1993). Since temperature could not be used to control phase behavior, the impact of chemical additives was explored; additives studied included potassium sulfate, potassium persulfate, sulfur trioxide ($SO_3$) and chlorosulfonic acid
(ClSO$_3$H). Qualitative data that $\phi_1$ increased with increasing SWNT protonation was obtained by optical microscopy in conjunction with Raman spectroscopy; this provided further support to the proposed mechanism of SWNT dispersal by sidewall protonation. In these studies, the minimum concentration at which the liquid crystalline phase could be visualized was determined; this provided an upper bound for the value of $\phi_1$. A subsequent, more detailed study using mixtures of 102% H$_2$SO$_4$ and SO$_3$ or ClSO$_3$H focused on the effect of SWNT protonation on phase behavior. Biphasic dispersions were centrifuged and SWNT concentration in the top phase was measured by UV-vis-nIR spectroscopy. These measurements provided the lower bound for $\phi_1$ in each system (the maximum concentrations at which the dispersions were isotropic); these values were in close agreement with the results obtained by optical microscopy. For SWNTs in pure ClSO$_3$H, $\phi_1$ was approximately 5000 ppm vol., more than an order of magnitude higher than the approximately 200 ppm vol. obtained for SWNTs in 102% H$_2$SO$_4$.

The fundamental rheological and phase behavior knowledge garnered by this research directly impacts the development of macroscopic solution spun SWNT fibers. Solution spinning, a commercial process used to produce high performance fibers such as DuPont Kevlar™, consists of five steps: dispersal in a solvent, mixing, extrusion out an orifice, coagulation and post processing. Rheology and phase behavior have a significant influence on these interrelated steps; therefore, understanding rheology and phase behavior can be key to optimizing fiber processing and properties. For example, knowing the onset of the liquid crystalline phase is important for producing highly aligned fibers. Also, knowing that temperature does not significantly affect phase behavior or rheology is key to avoiding unnecessarily high processing temperatures
(which may result in degradation reactions) in the hopes of reducing viscosity and improving processability. Furthermore, the morphology of the liquid crystalline phase and the response of the dispersion to coagulants directly relates to fiber microstructure.

This dissertation summarizes research on the phase behavior, rheology and fiber spinning of SWNTs in superacids. Chapter 2 provides background information on single-walled carbon nanotubes, acid chemistry, liquid crystals, rheology and phase behavior of rods dispersed in liquids, and fiber spinning. Chapter 3 provides information on instrumentation and experimental techniques. Results and discussion are divided into two chapters: Chapter 4 provides information on the phase behavior, rheology, and fiber spinning of SWNTs in 102 – 123 % H₂SO₄, Chapter 5 describes the effects of polydispersity, additives to the sulfuric acid system, and SWNT protonation on phase behavior and liquid crystalline morphology. In addition, Chapter 5 describes the impact of phase behavior and liquid crystalline morphology on fiber microstructure. Finally, Chapter 6 summarizes the conclusions of this research and provides possible directions for future work in the field of SWNT liquid crystals.
Chapter 2

Background

This chapter provides general background information relevant to this research. Topics covered include single-walled carbon nanotubes, superacids, liquid crystals, phase behavior and rheology of solutions of rods, and fiber spinning.

2.1 Single-Walled Carbon Nanotubes (SWNTs)

The significant interest in SWNTs and macroscopic SWNT materials is due to their outstanding combination of properties. Theoretical modeling and experiments have shown that individual and small groups of SWNTs exhibit remarkable properties including

- Tensile strength at least 37 GPa and strain to failure at least 6% (Walters, Ericson et al. 1999; Yu, Files et al. 2000)
- Young's modulus ~ 0.62 to 1.25 TPa (Gao, Cagin et al. 1998; Krishnan, Dujardin et al. 1998; Yu, Files et al. 2000)
- Electrical resistivity ~ 100 $\mu\Omega$ cm (Hone, Llaguno et al. 2000)
- Thermal conductivity equal or better than diamond ~ 3000 W / m K (Hone, Whitney et al. 1999)
A key question is whether macroscopic SWNT materials will retain these amazing properties. The answer to this question will have a significant impact on which of the numerous potential SWNT applications achieve fruition.

2.1.1 Structure

Carbon nanotubes, discovered by Iijima in 1991, are an allotrope of carbon. Other allotropes include diamond, graphite and $C_{60}$ or Buckminsterfullerene ("buckyballs"). Carbon nanotubes can most easily be considered as a sheet of graphite rolled into a cylindrical structure (Figure 2.1). If only one graphite cylinder exists, the nanotubes are termed single-walled carbon nanotubes (SWNTs); if there are several concentric cylinders the nanotubes are termed multi-walled carbon nanotubes (MWNTs). This section focuses on single-walled carbon nanotubes as they were the only type used in this research.

A sheet of graphite can be rolled and closed in a number of ways; the nomenclature of carbon nanotubes is given by an integer pair $(n,m)$ which refers to the tube’s chiral vector, $C_h$, where,

$$
\overline{C}_h = n \overline{a}_1 + m \overline{a}_2
$$

(2.1)

The cylinder connecting the hemispherical caps of the nanotube is formed by superimposing the two ends of the vector $C_h$ and the joint is made by the two lines $OB$ and $AB$ in Figure 2.1. Both these lines are perpendicular to the vector $C_h$ at each end of $C_h$. The chiral vector also defines the diameter $d$ according to

$$
d = \frac{\sqrt{3}a\sqrt{m^2 + mn + n^2}}{\pi} = \frac{C_h}{\pi}
$$

(2.2)
Figure 2.1 (a) The chiral vector $\mathbf{OA}$, or Ch is defined on the honeycomb lattice of a 2D graphite sheet, by the unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ and the chiral angle, $\theta$. Along the zigzag axis, $\theta = 0$. The lattice vector of the 1D nanotube unit cell, $\mathbf{QR} = \mathbf{T}$ is also shown. The rotation angle, $\varphi$, and the translation, $\tau$, constitute the basic symmetry of the nanotube. The construction shown is for $(n,m) = (4,2)$. (b) Possible vectors for general carbon nanotubes including zigzag, armchair, and chiral nanotubes. Below each value of $(n,m)$ is the number of caps that be joined to the nanotube defined by $(n,m)$. The encircled dots are for metallic nanotubes and the single dots are for semi-conducting nanotubes (Dresselhaus and Avouris 2001).
where $a_1$ equals the carbon bond length, approximately 1.42 nm for graphite. For example, a (10,10) tube denotes a graphite sheet that is rolled by going ten cells in the $a_1$ direction and ten cells in the $a_2$ direction. Based on the chiral vector, this corresponds to a one nanometer diameter SWNT. The chiral vector also defines SWNT chirality and electronic properties (Figure 2.1). The vectors $(n,0)$ and $(0,m)$ denote zigzag nanotubes and the vectors $(n,n)$ denote armchair nanotubes (Figure 2.2). Both the armchair and zigzag nanotubes have a mirror plane and are therefore achiral; all other vectors $(n,m)$ correspond to chiral nanotubes. Differences in the chiral angle and nanotube diameter result in differences in nanotube properties; if $n - m$ is divisible by three the nanotube is metallic, if $n - m$ is not divisible by three the tube is semiconducting. In Figure 2.1b values of $(n,m)$ that result in metallic SWNTs are marked with a double circle and values of $(n,m)$ that result in a semiconducting SWNT are shown with a single circle.

Drawings of each type of tube are shown in Figure 2.2.

Figure 2.2 (a) An armchair $(n,n) = (5,5)$ nanotube, $\theta=30^\circ$. (b) a zigzag $(n,0) = (9,0)$ nanotube $\theta=0^\circ$. (c) a chiral $(n,m) = (10,5)$ nanotube in a general $\theta$ direction such as $OB$ shown in Figure 2.1 (Dresselhaus and Avouris 2001).
2.1.2 Production

There are several carbon nanotube production routes: arc discharge, laser ablation, chemical vapor deposition, and gas phase catalytic growth (Dai 2001). In both the arc discharge and laser ablation methods, bundles of MWNTs and SWNTs held together by van der Waals forces are generated by the condensation of carbon atoms generated from the evaporation of solid carbon sources. In arc discharge, the carbon is evaporated by helium plasma ignited by high currents passed through an opposing carbon anode and cathode; this method requires the use of a metal catalyst such as cobalt. The second method, laser ablation method uses intense laser pulses to ablate a carbon target containing \( \sim 0.5 \% \) at. of nickel and cobalt in a 1200 °C tube furnace. The relative amount of SWNTs, MWNTs, and impurities produced by these methods is dependent on the exact reactor conditions. Impurities include fullerenes, metal catalyst particles encapsulated by graphitic polyhedrons, and amorphous carbon. The majority of impurities can be removed by purification processes such as refluxing the reactor output in nitric acid (Dresselhaus and Avouris 2001).

The third method, chemical vapor deposition (CVD), involves flowing a hydrocarbon gas over a catalyst in a tube furnace. The catalyst is typically transition metal nanoparticles on a support such as alumina. Materials grown on the catalyst are collected after cooling the furnace to room temperature. Key process parameters are the hydrocarbon and catalyst types as well as the operating temperature. Production of MWNTs typically involves ethylene or acetylene feedstock with an iron, nickel or cobalt catalyst and operating temperatures of 550 - 750°C. Production of SWNTs uses methane or ethane feedstock, similar catalysts, and operating temperatures of 850 - 1000 °C.
The fourth method, gas phase catalytic growth of SWNTs, involves reacting hydrocarbons or carbon monoxide with catalyst particles generated in-situ. In one variation of this method, Cheng and coworkers developed a method using benzene as a feedstock, hydrogen as the carrier gas and ferrocene as the catalyst precursor (Cheng, Li et al. 1998). Another variation, the HiPco process, was developed by Smalley and coworkers (Bronikowski, Bradley et al. 2000). The HiPco process is considered one of the most commercially viable processes and was used to produce the SWNTs used in this dissertation. The HiPco process feedstock is high pressure (up to 10 atm) carbon monoxide feedstock and catalyst particles generated from the decomposition of iron pentacarbonyl; the reactor temperatures range from 800 - 1200 °C. Under typical operating conditions the catalyst partial pressure is 52 mtorr and the total reactor pressure is 30 atm. SWNTs have a log normal distribution of lengths and diameters with an average diameter of 1.09 nm and a number average length of approximately one micron (Carver, Robert L. Carver et al. 2005). Post-processing of SWNTs such as oxidative purification methods, exposure to hot piranha (70 °C, 30% H₂O₂, 70% 96% H₂SO₄ by volume) or ozone, or prolonged sonication may alter the length and diameter distribution (Ziegler, Gu et al. 2005).

2.2 Defining SWNT length distributions

There is currently significant research on controlling the length distribution of HiPco SWNTs (Carver, Robert L. Carver et al. 2005; Ziegler, Gu et al. 2005). Understanding the effectiveness of these routes requires the ability to compare distributions. This problem is similar to one previously addressed by the polymer industry; their methods for
Comparing molecular weight distributions can be readily applied to SWNT length distributions. Where $M$ is the mass of a polymer chain and $N(M)$ is the number of chains of mass $M$, the molecular weight distribution can be characterized by several parameters which are functions of the moments of the distribution: the number average molecular weight, the weight average molecular weight, the $z$-average molecular weight, the viscosity average molecular weight and the polydispersity. By substituting SWNT length $L$ for $M$ similar parameters can be used to define the SWNT length distribution:

1. The number average length $L_n$

$$L_n = \frac{\sum_{i} N_i L_i}{\sum_{i} N_i} = \langle L \rangle = 1^{st} \text{ Moment of the distribution} \quad (2.3)$$

2. The weight average molecular weight $L_w$

$$L_w = \frac{\int \frac{dL}{L N(L)}}{\int \frac{dL}{LN(L)}} = \frac{\sum_{i} N_i L_i^2}{\sum_{i} N_i L_i} = \frac{\langle L^2 \rangle}{\langle L \rangle} = 2^{nd} \text{ Moment of the distribution} \quad (2.4)$$

3. The $z$-average length $L_z$

$$L_z = \frac{\int \frac{dL}{L N(L)}}{\int \frac{dL}{L N(L)}} = \frac{\sum_{i} N_i L_i^3}{\sum_{i} N_i L_i^2} = \frac{\langle L^3 \rangle}{\langle L^2 \rangle} = 3^{rd} \text{ Moment of the distribution} \quad (2.5)$$

4. The viscosity average molecular weight $L_v$

$$L_v = \left( \frac{\sum_{i} N_i L_i^a}{\sum_{i} N_i} \right) = \frac{\langle L^a \rangle}{\langle L^0 \rangle} \quad \text{where } a \text{ is a constant for the system} \quad (2.6)$$

For dilute Brownian rods, the Batchelor Modification to the Kirkwood-Auer Equation (Chapter 2.6.1) gives the viscosity average length $L_{KA}$.
\[ L_{KAB} = \frac{\langle L^2 \rangle}{\langle L \rangle} \]  

(2.7)

The number average length, \( L_n \), is useful for detecting significant shifts in the mean of the distribution, but not very sensitive to other changes. The z-average length, \( L_z \), is the most sensitive to long tubes. \( L_w \) and \( L_{KAB} \) have an intermediate level of sensitivity to long tubes. For a typical lognormal distribution of SWNT lengths, \( L_z > L_{KAB} > L_w > L_n \) as shown in Figure 2.3.

![Figure 2.3. Characteristic lengths of a log normal distribution. Data shown is for HiPco SWNTs produced with a catalyst partial pressure of 15 mtorr and total pressure of 30 atm (Carver, Robert L. Carver et al. 2005).](image)

Another way to characterize the distribution is by determining the full width at half-maximum. For a log normal distribution

\[ y = A \exp \left( \frac{-\ln^2(L/L_c)}{2\sigma^2} \right) \]  

(2.8)

where \( L_c \) is the maximum of the distribution., the full width at half maximum (FWHM) is
\[ FWHM = I_c \left( \exp\left(\sqrt{-2\sigma^2 \ln(1/2)}\right) - \exp\left(-\sqrt{-2\sigma^2 \ln(1/2)}\right) \right) \]  \hspace{1cm} (2.9)

FWHM is related to the polydispersity and the moments of the distribution through the variance, \( \sigma^2 \)

\[ \sigma^2 = L_n^2 \left( \frac{L_n}{L_o} - 1 \right) = \left( \frac{\langle L^2 \rangle}{\langle L \rangle} - 1 \right) \]  \hspace{1cm} (2.10)

2.2.1 Persistence length

The persistence length \( (L_p) \) of SWNTs can be estimated from the bending stiffness \( \kappa \) of a hollow cylinder (Kudin, Scuseria et al. 2001)

\[ \kappa = \frac{\pi CD^3}{8} \]  \hspace{1cm} (2.11)

and the by the relationship between persistence length and bending rigidity

\[ L_p = \frac{\kappa}{(k_B T)} \]  \hspace{1cm} (2.12)

Taking \( C = 345 \text{ N/m} \) as characteristic in-plane rigidity of SWNTs (Kudin, Scuseria et al. 2001) and \( 0.8 < D < 1.5 \text{ nm} \) as the range of HiPco diameter (Bachilo, Strano et al. 2002) yields \( 25 < L_p < 90 \text{ \mu m} \) at room temperature (Yakobson and Couchman 2004)

In contrast, the persistence length of the stiffest rod-like polymers (e.g., PBO, PBZT, PBA, PBLG) is usually reported to range between 50 and 200 nm (Donald and Windle 1992; Mark 1999), approximately two orders of magnitude lower than the estimated persistence length of individual SWNTs. Calculations of SWNT persistence length based on the Young’s Modulus of ropes (Baughman, Zakhidov et al. 2002) yield a value which is approximately one order of magnitude lower (a few micrometers); thus, the persistence length of SWNTs is one to two orders of magnitude higher than that of
rigid rod polymers. Therefore, SWNTs less than 2.5 to 9.0 μm in length behave as rigid rods in solution since their contour length is much smaller than their persistence length.

2.2.2 Dispersal

Obtaining a uniform dispersion of SWNTs, the first step in liquid phase manufacturing process, is not a trivial task. During the production process, SWNTs aggregate into bundles 10 – 20 nm in diameter which are very difficult to disperse due to the 500 eV/nm van der Waals attraction between SWNTs (Thess 1996).

![Figure 2.4. A typical bundle of SWNTs showing that SWNTs aggregate into a hexagonal lattice that is visible as the bundle bends through the image plane of the transmission electron microscope. This “classic” picture is for laser ablation produced SWNTs, but similar bundles are also seen for SWNTs produced by the HiPco process. (Thess, Lee et al. 1996).](image)

Prior this research methods for stabilizing SWNT dispersions were limited to steric stabilization by polymer wrapping (O'Connell, Boul et al. 2001), stabilization in surfactants (Moore, Strano et al. 2003) or nanotube functionalization.
2.3 Superacids

Acids stronger than 100% H$_2$SO$_4$ are generally referred to as superacids. The superacids in this study are part of the general class of proton or Bronsted acids – species which can act as a source of protons and protonate a base according to

$$\text{HA} + \text{B} \rightleftharpoons \text{BH}^- + \text{A}^- \quad (2.13)$$

where HA is the Bronsted acid and B is the base. The relative strengths of Bronsted acids are generally quantified in terms of pH. The pH scale is based on the ability of the acid to protonate water

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \quad (2.14)$$

$$\text{pH} = -\log_{10} \left[ \text{H}_3\text{O}^+ \right] \quad (2.15)$$

The pH scale is inappropriate for measuring the strength of strong and superacids because they are all fully ionized in dilute aqueous solution and therefore appear to have the same strength leveled to that of the hydronium ion. Also, most superacids are destroyed by reaction with water. For strong and superacids, the Hammett Acidity function is a common method of comparing acid strength (Gillespie 2001). The Hammett Acidity function H$_0$ was developed by L.P. Hammett in the 1930s to quantify the acidity of sulfuric acid-water mixtures ranging from 0 to 100% sulfuric acid using primary aromatic amines as indicators (Hammett and Deyrup 1932). While other approaches to measuring acidity have been developed, Hammett Acidity continues to be deemed one of the most practical and widely used method for comparing the acidities of strong and superacids (Olah, Prakash et al. 1985). The indicators used are weak bases and their
ionization ratios are determined from a change in the absorption or NMR spectra that results from protonation or weak bases. $H_0$ is defined from

$$B + AH_2^+ \rightleftharpoons BH^+ + AH$$ \hspace{1cm} (2.16)

Since the proton is solvated ($AH_2^+$) and AH is the solvent,

$$B + H^+ \rightleftharpoons BH^+$$ \hspace{1cm} (2.17)

Therefore the thermodynamic equilibrium constant $K_{BH^+}$ is

$$K_{BH^+} = \frac{a_{H^+} \cdot a_B}{a_{BH^+} \cdot C_{BH^+}} = \frac{C_B}{f_{BH^+}} \cdot f_B \cdot f_{BH^+}$$ \hspace{1cm} (2.18)

Where a is the activity, C is the concentration f is the activity coefficient. Therefore,

$$\frac{C_{BH^+}}{C_B} = \frac{1}{K_{BH^+}} \cdot a_{H^+} \cdot \frac{f_B}{f_{BH^+}}$$ \hspace{1cm} (2.19)

The ratio of $C_{BH^+}$ to $C_B$ is the degree of protonation. Assuming that the ratio $f_B/f_{BH^+}$ is the same for all bases used in a given solution to determine the acidity across the full range of concentration, $H_0$ is

$$H_0 = -\log a_{H^+} \cdot \frac{f_B}{f_{BH^+}} = -\log K_{BH^+} + \log \frac{C_B}{C_{BH^+}} = pK_{BH^+} - \log \frac{[BH^+]}{[B]}$$ \hspace{1cm} (2.20)

where,

$K_{BH^+}$ is the dissociation constant of the acid form of the indicator

$$\frac{[BH^+]}{[B]}$$ = the ionization ratio of the indicator

As the activity coefficients approach unity, $H_0$ becomes identical with pH.

Unfortunately, acidity is not solely a function of the acid it is also a function of the solute (McNaught and Wilkinson 1997); therefore true quantitative characterization of
SWNT superacid solvents would require measuring the Hammett Acidity of a series of superacids using SWNTs as the indicator. Furthermore, even literature data using the same indicators disagrees for fuming sulfuric acid (Brand 1950; Gillespie, Peel et al. 1971). Therefore, Hammett Acidity was not used to characterize the SWNT-supercacid dispersions.

2.4 Liquid Crystals

Liquid crystalline phases possess both the alignment of a crystal and the fluidity of a liquid. Such phases have been produced from a vast array of anisotropic building blocks including tobacco mosaic virus, M13 virus, rod-like polymers, small organic molecules, and self-assembling amphilic soap molecules. In fact there are more than 80,000 known examples or organic and organometallic liquid crystalline compounds (Gabriel and Davidson 2003). Noteworthy applications include DuPont Kevlar which is produced by solution spinning liquid crystalline poly (p-phenylene terephthalate) in sulfuric acid and liquid crystalline display devices produced from polymer dispersed small molecule liquid crystals such as fluorinated tolans. Liquid crystals comprised of completely inorganic species, known as mineral liquid crystals, have historically not been as well studied as their organic counterparts.

The advent of nanotechnology has rejuvenated liquid crystalline science by facilitating the production new anisotropic materials such single-walled carbon nanotubes (SWNTs) and inorganic nanorods in sufficient quantities for the identification of new liquid crystalline phases (Davidson, Batal et al. 1997). In fact, two other groups
reported liquid crystalline dispersions of carbon nanotubes during the course of this research (Song, Kinloch et al. 2003; Islam, Alsayed et al. 2004).

2.4.1 Nomenclature

Systems which are capable of forming liquid crystals are called mesogenic; they are generally semi-rigid or contain rigid units called mesogens. Such systems can be thermotropic or lyotropic. Thermotropic liquid crystals are formed from a single species; the liquid crystalline state exists in a temperature range bounded on the low side by the transition to a solid and on the high side by the transition to a liquid. The tendency to form a liquid crystal is controlled by the ratio between the Kuhn segment length (twice the persistence length) and the molecule's diameter (Larson 1999). In general stiffer molecules, those with higher persistence lengths, are more likely to form liquid crystalline phases. However, stiffness can also induce crystallinity, so molecules which form thermotropic liquid crystals usually contain flexible spacers along the polymer backbone which retard the onset of crystallinity. In other words, most thermotropic liquid crystals are semi-flexible molecules whose persistence length $L_p$ is much shorter than the molecular length $L$ (Larson 1999). In contrast, lyotropic liquid crystals consist of more rigid species in a solvent; the solvent retards the onset of crystallinity.

The molecules in lyotropic liquid crystals do not need to be dissolved as individuals. For example, depending on solution preparation, cellulose in DMAC + LiCl can be either a molecular level solution or stable aggregates consisting of seven fully extended molecules organized side-by-side. The possibility of mesophases stabilized by aggregates rather than individual molecules has also been used to explain the formation
of liquid crystalline phases by cylindrical micelles and inorganic liquid crystals (Donald and Windle 1992).

There are three primary types of liquid crystals named Friedelan classes after Friedel who first identified them in 1922 (Figure 2.5). Nematics possess long range orientational order and short range positional order. Within each domain in a nematic liquid crystal, the molecules are preferentially aligned parallel to a director $n$. The degree of this alignment is characterized by an order parameter $S$ where $S = 0$ corresponds to a completely isotropic distribution of molecular orientations and $S = 1$ corresponds to a perfectly parallel orientation of all rod like species.

$$ S = \frac{3}{2}(\cos^2 \theta)^{-1/2} $$ (2.21)

Cholesterics are similar to nematics, but are twisted around an axis perpendicular to the director $n$. Cholesterics are generally formed by chiral mesogenic molecules. Smectic liquid crystals have a layered structure and have both long range positional and orientational order; within each layer alignment is parallel to the director. Their name is derived from the Latin *smecticus* meaning having the properties of soap – the amphilic nature of many detergents enables them to form smectic phases. Smectic phases can be formed by other polymeric and inorganic molecules with fairly uniform diameters; the formation of smectic phases is suppressed by diameter polydispersity. The two most common types of smectic liquid crystals are the smectic A phase in which there is no correlation between the molecules in successive layers and the smectic C phase in which each layer is inclined at the same angle from the layer normal.
Figure 2.5. Pictorial representation of the primary classes of liquid crystals (Donald and Windle 1992).

2.5 General Phase Behavior of Rods in Solution

Figure 2.6 shows that as the concentration of the dissolved rods is increased, the solution goes through several distinct phases. The dilute regime exists at very low concentrations where the rods can move freely without interacting with one another. As concentration is increased, the solution becomes semidilute and the rods inhibit one another’s rotations. Further increases in concentration result in an isotropic concentrated phase where both rotation and translation are hindered. Eventually, the concentration is increased to the point where steric effects force the rods to align (Doi and Edwards 1986).
Figure 2.7 depicts the general phase behavior of rods in solution as a function of temperature and polymer concentration. This behavior is based on theoretical results by Onsager and Flory and experimental work on systems such as PPTA, PBO, and PBZT. Onsager (1949) considered rigid anisotropic solutes separated by repulsive forces where the equilibrium orientation of the particles is determined by competition between thermal agitation (entropy) and their orientation dependent repulsive energy (enthalpy). The solvent was assumed to be athermal, thus having no effect on the behavior of the rods. This competition was evaluated by finding the maximum in the free energy as expressed by a virial expansion in distribution of anisotropic particle orientations. This resulted in the finding that at volume fraction of rods \( \phi \) where \( \phi < \phi_I \) the solution is isotropic. At \( \phi_I < \phi < \phi_N \) the solution becomes biphasic where one phase is isotropic and has a low concentration \( \phi_I \) of solute, and the other phase is anisotropic (liquid crystalline) and has a higher concentration of solute \( \phi_N \). This two phase region is often referred to as the "biphasic chimney." Within the biphasic chimney the concentration of each phase remains constant, but the relative amounts of each phase change. The chimney is
bounded on the left hand (lower concentration) side by a single phase isotropic concentrated solution. On the right hand (higher concentration) side of the chimney it is a single liquid crystalline phase.

![Phase Diagram](image)

Figure 2.7. Generic phase diagram of a solution of monodisperse rods interacting only through hard-rod repulsion (Pasquali, Davis et al. 2001).

In addition to showing higher transition concentrations, experimentally determined phase diagrams are typically more complicated than the cartoon in Figure 2.7 due to the formation of crystal solvate phases or multiple nematic or isotropic phases. Crystal solvates are polymer crystals with a fixed proportion of solvent incorporated into the lattice. This can result in more complicated phase behavior such as that shown in Figure 2.8. Although they can also occur in uncharged systems, crystal solvates can often be considered as salts of the protonated polymer polycation and anions of the solvent acid. For example, PPTA solutions form a crystal solvate with sulfuric acid upon cooling. Crystal solvates can also be formed by exposure to a third component such as
water. In the case of PBZT / PPA and PBO / PPA two distinct forms of crystal solvates are formed based on the amount of water exposure (Cohen, Buchner et al. 1992).

![Schematic of lyotropic phase diagram](image)

Figure 2.8. Schematic of lyotropic phase diagram including the isotropic (I), liquid crystal (LC), crystal solvate (CS), polymer crystal (C) and combination phases (Papkov 1984).

### 2.5.1 Onsager versus Flory

The theoretical phase boundaries for lyotropic nematic systems are predicted using models derived either from Onsager theory (1949) or Flory theory (1956). Fifty years after these seminal works, debate continues as to which theory best explains the phase behavior of anisotropic species. In general, the phase behavior of mineral liquid crystals and rod-like viruses are compared to Onsager theory, while the phase behavior of polymeric systems are compared to Flory theory.

Onsager theory is based on hard rod repulsion of spherocylinders where the equilibrium orientation of the particles is determined by the competition between
orientational entropy and translational entropy. The free energy is truncated at the second virial coefficient, as a result critics of Onsager theory cite that it is less accurate for high concentration solutions and should only be used for systems where \( L >> D \). The critical concentrations and order parameters resulting from Onsager’s variational method are (Khokhlov 1991):

\[
\phi_i = 3.34 \left( \frac{D}{L} \right) \quad \text{(2.22)}
\]

\[
\phi_N = 4.49 \left( \frac{D}{L} \right) \quad \text{(2.23)}
\]

\[
w = \frac{\phi_N}{\phi_i} - 1 = 0.34 \quad \text{(2.24)}
\]

\[
S = \frac{\langle 3 \cos^2 \Theta - 1 \rangle}{2} = 0.84 \quad \text{when } \phi_i = \phi_N \quad \text{(2.25)}
\]

In contrast to Onsager, Flory (1956) did not treat the system as a continuum but confined the molecules to a fixed lattice and used a combinatorial approach by constructing a partition function from the number of ways rigid rods can be packed into a lattice and calculating the free energy as a function orientation. Critics of Flory theory say that this treatment is artificial and provides less accurate results than Onsager theory. The critical transitions based on Flory theory in the absence of attractive interactions are

\[
\phi_i \approx \frac{8}{\frac{L}{D}} \left( 1 - \frac{2}{\frac{L}{D}} \right) \quad \text{(2.26)}
\]

\[
\phi_N \approx \frac{12}{\frac{L}{D}} \quad \text{(2.27)}
\]

Numerical calculations showed that the approximations above are accurate within 2% for \( L/D > 10 \) (Flory 1956). Adaptations of the initial theory accounted for the effect of the Flory-Huggins interaction parameter, \( \chi \), and molecular flexibility. The biphasic region widens with decreasing \( \chi \) (for less favorable solvents) and for increasing
flexibility or polydispersity (Flory 1956; Kiss 1979; Abe and Balluff 1991). The biphasic chimney is also wider at lower temperatures where $\chi$ is smaller and the entropy of mixing ($T\Delta S_{mix}$) is insufficient to overcome chemically driven segregation. For these reasons, the predicted phase transitions shown in Equations 7 and 8 tend to be lower than experimental values (Kiss 1979; Larson 1999). Furthermore, it has been found that beyond a certain molecular weight (aspect ratio) for a given polymer, the critical concentrations remains constant as the molecules no longer behave as rigid rods (Robinson, Ward et al. 1958). This was found to be the case for PBLG in dioxane as shown in Figure 2.9.

![Graph showing the effect of aspect ratio on phase transitions for PBLG in Dioxan](image)

Figure 2.9. The effect of aspect ratio (or chain length) on the phase transitions where the system is fully isotropic (less than $\phi_i$) and fully liquid crystalline (greater than $\phi_N$) (Robinson, Ward et al. 1958).
2.6 Rheology of Solutions of Rods

Elongated molecules, such as ellipsoids or rods, in a shear field will tumble end over end, they rotate about an axis perpendicular to both the direction of flow and the velocity gradient (Figure 2.10). The rotation is called a Jefferey orbit (Jefferey 1928). The period, $P$, of a rotation of $\pi$, is

$$P = \frac{\pi}{\dot{\gamma}} \left( \frac{L}{D} + \frac{1}{L/D} \right)$$  (2.28)

The period goes to infinity for an infinitely thin prolate ellipsoid, $L/D \to \infty$ or an infinitely flat oblate one, $L/D \to 0$. In these limits, and in the absence of Brownian motion, the particle only rotates until it is parallel to the direction of flow and then rotation ceases. For a finite aspect ratio, the particle continues to rotate, but rotates more slowly when its long axis is roughly parallel to the flow direction. Neglecting inertial effects and Brownian forces, the frequency of rotation is one half of the shear rate and the viscosity is Newtonian (Kiss 1979)

$$\eta = \eta_s (1 + \nu \phi)$$  (2.29)

where,

$\eta_s = $ solvent viscosity

$\phi = $ volume fraction of the anisotropic molecules

$\nu = $ a constant dependent on molecule geometry
Figure 2.10. Tumbling of elongated molecules in a shear field.

Whether or not the behavior is Brownian depends on the rotational Peclet number,

\[ Pe = \frac{\dot{\gamma}}{D_r} \]

(2.30)

where \( \dot{\gamma} \) is the shear rate and \( D_r \) is the rotational diffusion coefficient. Peclet number is commonly used in suspension literature, and the corresponding quantity is referred to as the Deborah or Weissenberg number in polymer literature. In general, particles whose longest dimension exceeds \( \sim 10 \) \( \mu \)m can be considered non-Brownian. Particles with an aspect ratio \( > 10 \) for which the smallest dimension is greater than \( \sim 1 \) \( \mu \)m are also usually non-Brownian (Larson 1999, p. 281).

If the dissolved, or suspended, rods are small enough that Brownian forces are significant, the rod orientations will be randomized, reducing the relative amount of time they are parallel to the shear direction and having the least influence on viscosity. Thus, the viscosity is determined by the balance of the orienting effects resulting from shear and the randomizing effect of Brownian motion. As shear rate is increased, the tendency for the particles to orient in the shear field will become increasingly more significant, resulting in a decrease in viscosity with increasing shear rate; this is known as shear-thinning.
2.6.1 Dilute solutions

The rate at which a particle reorients by Brownian motion in dilute solution is based on the rotary diffusivity of the particle, $D_{ro}$. Based on the expressions of Kirkwood and Auer (1951) and Doi and Edwards (1986), the rotary diffusivity of a rod of length $L$ and diameter $D$ is given by

$$D_{ro} = \frac{3k_B T \ln(L/D) - 0.8}{\pi \eta_s L^3}$$  \hspace{1cm} (2.31)

where, $k_B$ is Boltzmann’s constant, $T$ is the temperature of the solution and $\eta_s$ is the solvent viscosity.

The zero-shear viscosity of a (monodisperse) solution or dispersion of Brownian rigid rods can be used to calculate the average length to diameter ratio (aspect ratio of the rods). The zero shear viscosity (Kirkwood and Plock 1956) is

$$\eta_0 = \lim_{\dot{\gamma} \to 0} \eta(\dot{\gamma}) = \eta_s \left(1 + \frac{4}{5} k_B T \tau \nu \right)$$  \hspace{1cm} (2.32)

where $\eta_s$ is the solvent viscosity, $k_B$ is Boltzmann’s constant, $T$ is temperature, $\nu$ is the number of rods per unit volume, and

$$\tau = \frac{\zeta L^3}{72 k_B T}$$  \hspace{1cm} (2.33)

is the rotational relaxation time of the rods, and $\zeta$ is the perpendicular drag coefficient of the rods. The number concentration of rods is related to the volume fraction $\phi$ as $\nu = \phi / (\pi R^2 L)$ where $R$ is the rod radius and $L$ is the length. The perpendicular drag coefficient $\zeta$ on a slender cylinder (Batchelor 1970) is

$$\zeta = 4 \pi \eta_s \epsilon f(\epsilon)$$  \hspace{1cm} (2.34)

where,
\[ \varepsilon = \frac{1}{\ln(L/R)} \] (2.35)

\[ f(\varepsilon) = \frac{1 + 0.64\varepsilon}{1 - 1.5\varepsilon} + 1.659\varepsilon^2 \] (2.36)

This yields the relationship

\[ \frac{\eta - \eta_s}{\eta_s \phi} = \frac{2}{45} \left[ \ln \left( \frac{L}{R} \right) \right]^2 \left[ \frac{1 + 0.64}{\ln(L/R)} \right] + \frac{1.659}{\left( \ln(L/R) \right)^2} \] (2.37)

In the polydisperse case, the viscosity contributions of each subpopulation of length are additive and the intrinsic viscosity is related to the ratio of the third and first moments of the distribution of length.

### 2.6.2 Semidilute solutions

The dilute regime requires that the volume fraction be sufficiently low that the rods can rotate freely without interacting with one another. Once this criteria can not be met, the solution is called semidilute. The term semidilute reflects the fact that the static properties of the solution remain very similar to those of the dilute solution. The rods' rotations may be impeded, but additional rods can be inserted into the solution with negligible probability that they will intersect other rods. The volume swept by a single rod is approximately \( L^3 \), so the concentration where the solution transitions from dilute to semidilute would be expected to be proportional to \( L^{-3} \) (Larson 1999, pp. 285-286). However, due to the ability of the rods to “dodge” one another, experimentally the transition concentration occurs at a volume fraction

\[ \phi = \alpha (R/L)^2 \] (2.38)
where \( r \) is the radius of the rod and \( \alpha \approx 30 - 40 \) for most rod like polymer systems (Larson 1990).

Doi and Edwards developed a model for the semidilute regime by considering each rod to be confined by a cylindrical cage into which other rods can not penetrate. The time required for a rod to escape its cage \( \tau_d \) is related to the rotational diffusion constant, \( D_{ro} = 1/\tau_d \) and

\[
D_r = \beta D_{ro} (vL^3)^{\gamma/2} \propto \phi^{-2} L^{-7} \ln(L/D)
\]

(2.39)

The dimensionless constant \( \beta \) is around 1350 for perfectly rigid rods (Larson 1999). In this region the zero shear viscosity is proportional to \( \phi^3 \).

### 2.6.3 Isotropic concentrated

As the concentration is further increased, excluded volume interactions become appreciable and isotropic packing of the rods becomes difficult. This regime occurs at a volume fraction

\[
\phi = \frac{\pi D}{4L}
\]

(2.40)

Further increases in concentration result in alignment of the rods and in the formation of an anisotropic liquid crystalline phase in equilibrium with the isotropic concentrated phase. The rheological behavior of the solution depends on the relative amounts of each phase; rheological characteristics associated with liquid crystalline polymer solutions become more apparent as the anisotropic phase becomes dominant.
2.7 Rheological Characteristics of Rod-like Polymer Solutions

Theories and models for liquid crystalline polymer rheology are still being developed; yet, several experimental characteristics which are known to be indicative of a liquid crystalline polymer solution:

- the viscosity versus concentration curve goes through a maximum;
- viscosity versus shear rate shows three distinct regions, often including a yield stress;
- with increasing shear rate, the first normal stress difference (N1) changes sign from positive to negative and back to positive;
- in transient shearing tests the shear stress and first normal stress difference oscillate for ~100 shear units or more before reaching steady state;
- the Cox-Merz rule is not obeyed.

It should be noted that the profound effect of shear history can cause rheological studies of lyotropic liquid crystalline polymers to be plagued by reproducibility problems. Moreover, the solvents are frequently corrosive and hygroscopic. In addition, edge fracture and expulsion of the sample from the gap often limit the range of shear rates that can be tested.

While each of the above behaviors is indicative of liquid crystallinity, the absence of one or more of them does not preclude the existence of a liquid crystalline state. For example, the three region viscosity versus flow rate curve has only been proven to exist for a few systems (Wissbrun 1981), and some systems never show a negative first normal stress difference (Wissbrun 1981; Kiss and Porter 1998). To date, the reasons behind each of these behaviors are still only partially understood.
2.7.1 **Maximum in viscosity versus concentration curve**

In non-nematogenic polymer solutions, the viscosity increases with concentration. In nematogenic systems, the relationship between viscosity and concentration goes through a maximum (Figure 2.11). Viscosity increases with concentration in the isotropic regime; however, the creation of an anisotropic phase results in a decrease in viscosity as a lower shear stress is required to orient an anisotropic phase than individual molecules in an isotropic phase. The maximum in the viscosity curve is not necessarily equal to the concentration where the system becomes a single phase liquid crystal. Generally concentrations near the maximum are still biphasic with the anisotropic phase being dominant. The onset of a single liquid crystalline phase is generally somewhere along the right shoulder of the curve in the region of decreasing viscosity (Wissbrun 1981). The critical concentration where the liquid crystalline phase forms, estimated from Flory’s theory, is generally found to only slightly under-predict the transition to liquid crystallinity for rod-like polymer systems. For example, the predicted value of $\phi$ only slightly underestimates the concentration corresponding to the maximum in viscosity for helical polypeptides in m-cresol (Kiss and Porter 1978; Kiss 1979; Kiss and Porter 1980; Lin, Jho et al. 1993; Kiss and Porter 1998). For less rigid systems, the difference between the predicted and actual value becomes more significant (Qin, Brydon et al.; Wissbrun 1981).
Figure 2.11. Viscosity of PBG (M_{w} = 335000) in m-cresol as a function of concentration for different shear rates (Kiss and Porter 1998).

Figure 2.11 also shows that at higher shear rates, the steady shear viscosity maximum shifts to lower values and the magnitude of the maximum is depressed. At higher shear rates, the ordering resulting from shear stress becomes approximately the same as that caused by alignment due to packing effects. The dynamic viscosity measured during oscillatory shear has similar behavior to the steady shear viscosity; but the location of the maximum does not depend on frequency (Kiss and Porter 1998).

Imperfections in the ordering of anisotropic solutions are evidenced by their shear thinning behavior; shear induced orientation enhances alignment causing a decrease in viscosity with increasing shear rate. Also, the viscosity measured at a fixed shear rate may continue to decrease with concentration after the critical concentration is reached. This indicates that for a limited concentration range greater than \( \phi_{N} \), the statistical ordering becomes more perfect with increasing concentration (Kiss 1979). For many systems, the viscosity versus concentration curve goes through a minimum as well as a
maximum. Once the best packing has been achieved, further increases in concentration will increase viscosity, often dramatically. This is due to the increasing importance of viscous and texture stresses (Larson 1999). Figure 2.12 shows that in PPTA in sulfuric acid, a two to three percent increase in concentration after the viscosity minimum resulted in such a dramatic increase in viscosity such that it was almost impossible to obtain homogeneous solutions (Papkov, Iovleva et al. 1973). Papkov also found that the viscosity of a given concentration of PPTA in $\text{H}_2\text{SO}_4$ was dependent on the acid concentration (Figure 2.13). In the 4 % and 6 % isotropic solutions, the viscosity reached a maximum at 98% sulfuric acid. For the 7 % solution, the viscosity went through a minimum at 98% sulfuric acid. For the anisotropic 11 % solution, the viscosity increased with sulfuric acid concentration up to 100% sulfuric acid and then increased rapidly at higher concentrations (as the amount of free $\text{SO}_3$ was increased). This rheological behavior is likely related to the role of acid strength and protonation in rod-like polymer dispersal. Rod-like polymers are typically insoluble in common organic solvents, but are soluble in protic sulfonic acids of the form $\text{RSO}_3\text{H}$ where $\text{R}$ includes $\text{HO}^−$, $\text{CH}_3^−$, $\text{Cl}^−$, $\text{CF}_3^−$, and $\text{C}_6\text{H}_5^−$. Solvation of polymers such as PBO (poly ($p$-phenylene benzo-$bis$-oxazole) and PBT (poly ($p$-phenylene benzo-$bis$-thiazole)) involves protonation of the polymer ($P$)

\[
P + n\text{RSO}_3 \leftrightarrow \text{PH}^+_{n} + n\text{RSO}_3^− \tag{2.41}
\]

Dissolution of the charged polymer is facilitated by the resulting electrostatic repulsion between the charged molecules. The degree of protonation for rigid rod polymers has historically been measured by measuring freezing point depression of the polymers in $\text{H}_2\text{SO}_4$ (Berry, Cotts et al. 1981)
Figure 2.12. Viscosity versus concentration of PPTA in sulfuric acid at a shear stress of $2 \times 10^3$ dyne/cm$^2$ (Papkov, Iovleva et al. 1973).

Figure 2.13. Relative viscosity of PPTA solutions of various concentrations as a function of free SO$_3$ content (Papkov, Iovleva et al. 1973).
2.7.2 Viscosity versus shear rate

For some lyotropic liquid crystals, the viscosity versus shear rate curve has been found to exist of three regions (Onogi and Asada 1980). Examples include hydroxypropylcellulose (HPC) in water, and poly(1,4-phenylene-2,6-benzobisthiazole) (PBZT or PBT) in methane sulfonic acid. It is not known whether the lack of a three region curve in most systems is due to differences between liquid crystalline polymer (LCP) systems or experimental limitations such as the lower shear limit of most commercial equipment and the tendency of liquid crystals to eject out of the gap at high shear rates.

![Graph showing three region flow curve for liquid crystalline polymers proposed by Onogi and Asada (Onogi and Asada 1980).](image)

Figure 2.14. Three region flow curve for liquid crystalline polymers proposed by Onogi and Asada (Onogi and Asada 1980).

In isotropic polymer solutions, the viscosity versus shear rate curve generally consists of two parts: 1) a low shear rate Newtonian plateau where the flow does not significantly change the distribution of molecular orientations and conformations and 2) a shear
thinning region that starts when the shear rate becomes strong enough to change the molecular orientation distributions. These two regions can be considered analogous to Region II and Region III of the liquid crystalline polymer viscosity versus shear rate curve. It is therefore Region I behavior which distinguishes the curve of liquid crystalline polymer solution from that of an isotropic system. However, Region I is rarely observed; generally Region I is only found in high viscosity, “tumbling” nematics were the shear viscosity in Region II exceeds ~ 10 Pa s and the characteristic texture length scale is on the order of 1 μm. In lyotropic systems, the presence of Region I can depend on polymer concentration (Walker and Wagner 1994). Region I can also depend on shear history; for example, 40% PBLG (MW=238,000) in m-cresol shows evidence of a weak Region I in initial testing. However, in tests after preshearing at critical shear rate of about 3 s⁻¹ a much more prominent Region I was found (Walker, Wagner et al. 1995). Even when Region I is experimentally apparent, its origin not well understood; three mechanisms have been proposed for Region I behavior (Wissbrun 1981):

1. Shear thinning results from competition between orientation of molecules at a boundary and in the shear field. The yield stress is the static stress required to deform the director field to one in equilibrium with the imposed flow.

2. Shear thinning results from the texture of the liquid crystal and the yield stress results from “plastic flow of piled domains” whose submicron texture is insensitive to shear rate.

3. Shear induced phase separation results in a yield stress.
In Region I and II, the polydomain structure is preserved in spite of the shear stress; no net orientation of the director is induced (Marrucci 1991). Many believe the “tumbling” behavior of Region I transitions to “wagging” in Region II and the director begins to oscillate about a steady value (Larson 1990). An alternative cause of Region II behavior is alignment of the rods in the vorticity direction over a limited range of shear rates (Montesi, Pena et al. 2003). At a molecular level, a polymeric nematic is at equilibrium when the Deborah number, $De$, is small

$$De = \frac{\tau_0}{\dot{\gamma}}$$  \hspace{1cm} (2.42)

However, on a larger scale the director pattern is only close to equilibrium when the Ericksen number, $Er$, is small

$$Er = \frac{\eta \dot{\gamma} h^2}{K}$$  \hspace{1cm} (2.43)

Due to the high viscosity of liquid crystalline polymers, the Ericksen number is usually high even when the Deborah number is low. At high Ericksen number, a disordered flowing state called director turbulence results from the disclinations that occur for both flow-aligning and tumbling nematics. These distortions of the nematic director or textures become finer with increasing shear rate.

In Region III, the shear rate is sufficient to change the order parameter $S$ through flow alignment; this results in shear thinning. Typically, the slope of viscosity versus shear rate in Region III is lower in magnitude than that of Region I. Shear alignment during processing is used to help produce highly aligned macroscopic structures from liquid crystalline dispersions.
2.7.3 Changing Sign of the First Normal Stress Difference N1

A third rheological characteristic of liquid crystals that can be used to distinguish them from isotropic solutions is the negative normal stress effect. In rheological measurements using cone and plate geometry, the first normal stress difference N1 is simply the total thrust on the cone. For many lyotropic liquid crystals, the first normal stress difference changes sign with shear rate (Figure 2.15). At low shear rates, N1 is positive and increases with shear rate as would be expected for an isotropic polymer solution. At intermediate shear rates, N1 suddenly decreases and changes to a negative value. As shear rate is further increased, N1 becomes positive once again (Kiss 1979; Grizzuti, Cavella et al. 1990; Baek, Magda et al. 1994; Kiss and Porter 1998). The origin of negative N1 has been the subject of considerable research and is still not completely understood (Chaffey and Porter 1985; Marrucci and Maffetone 1989; Larson and Doi 1991; Kiss and Porter 1998; Larson 1999). Essentially, negative N1 is believed to be a consequence of director tumbling. For systems where negative N1 is observed, the change from positive to negative occurs near the onset of Region III in the viscosity versus shear rate curve; this is believed to be a consequence of the transition from "tumbling" to "wagging." The negative maximum occurs at the transition from "wagging" to steady state (Larson 1990). Negative N1 has also been observed once in highly concentrated suspensions (Laun 1994), once recently in emulsions (Montesi, Pena et al. 2003), occasionally in electrorheological suspensions under electric fields (Larson 1999), and also, in flocculated dispersions of multi-walled carbon nanotubes in toluene thickened with low-molecular weight polyisobutylene (Lin-Gibson, Pathak et al. 2004).
2.7.4 Long oscillatory transients

Another liquid crystalline polymer characteristic is the behavior at the start-up of shear flow. In non-nematogenic polymer melts and solutions, start up of flow at low shear rates results in both the stress and the first normal stress difference $N_1$ growing monotonically with time, until they reach a steady state value. At higher shear rates, the shear stress overshoots the steady state value and then decays to a steady state and $N_1$ grows monotonically until it reaches the steady state value. At even higher shear rates, $N_1$ also shows a small overshoot (Marrucci 1991). This transient response occurs for a few shear units at most (a shear unit is the product of shear rate and time). For large molecule liquid crystals, the transient response is more complex and much longer in duration, and can last more than 100 shear units. Dispersions of flexible anisotropic
materials such as fibers also exhibit long oscillatory transients, but for these systems the viscosity quickly increases to a pseudoplateau prior to the viscosity overshoot (Ramazani, Ait-Kadi et al. 2001). At all shear rates, both shear stress (and therefore viscosity) and first normal stress difference oscillate prior to reaching steady state (see Figure 2.16). At shear rates in Region II of the viscosity versus shear rate curve, the oscillation period is fairly regular and roughly inversely proportional to shear rate. As a result, when the transient stress responses obtained at different shear rates within Region II are plotted against shear units the maximum and the minimum of all curves will overlap (Moldenaers and Mewis 1986; Picken, Aerts et al. 1991; Mortier, Moldenaers et al. 1996; Walker, Mortier et al. 1996). Such behavior is also seen in tumbling small molecule nematics, suggesting that this behavior in polymeric liquid crystals is also due to tumbling (Larson 1999).

Similar scaling behavior has also been seen after the cessation of shear. The time for the strain to be recovered grows with the previously applied shear rate. This indicates that an elastic microstructure is created during shearing of the LCP; the texture relaxation time is inversely proportional to the experienced shear rate (Larson 1999). The transient phenomena seen in liquid crystalline polymers are due to the distortions of the nematic director under shear. These distortions (textures) can be seen with an optical microscope or by measuring the scattering dichromism during shear. This implies that the transient behavior is due to structures or domains whose size are near the wavelength of light, on the order of microns. The annealing or healing time, $t_a$, for the spontaneous disappearance of a disclination texture from a nematic of viscosity $\eta$ and thickness $h$ is

$$t_a \approx \frac{\eta h^2}{K}$$

(2.44)
where $K$ is the characteristic Frank constant (Larson 1999, p. 516). For small molecule nematics, the viscosity is low and textures heal relatively quickly. Conversely, polymeric nematics have high viscosity can which cause the textures to persist for days, or even longer. The effective "director diffusivity" $K/\eta$, of small molecule nematics is on the order of $10^{-6}$ cm$^2$/s, while for polymeric nematics $K/\eta \sim 10^{-8}$ to $10^{-10}$ cm$^2$/s. Therefore, for a typical rheological sample 500 μm in thickness, a small molecule nematic would only take minutes to heal itself of disclinations resulting from sample loading and any other prior shear history. In contrast, a similar sample composed of polymeric nematic could take anywhere from a few days to nearly one year to heal. Since it is impractical to wait so long between sample loading and testing, reproducible transient rheological data for liquid crystalline polymers has come to rely on preshear protocols in which each sample is subjected to a prescribed shear history before any data is recorded.

![Graph](image)

Figure 2.16. Start-up of shear flow of 40 % wt. HPC in acetic acid at a shear rate of 0.27 s$^{-1}$. First normal stress difference (upper curve) and shearing stress (lower curve) upon start-up of shear (Metzner and Prilutski 1986).
2.7.5 The Cox-Merz rule is not obeyed

A final rheological distinguishing feature of liquid crystalline polymer solutions is that steady and dynamic viscosities do not exhibit the same behavior as a function of shear rate. In other words, the Cox-Merz rule is not obeyed. This empirical rule states that at a given frequency \( \omega \) and shear rate \( \dot{\gamma} \) the dynamic viscosity \( \eta^*(\omega) \) and steady shear viscosity \( \eta(\dot{\gamma}) \) are equal at all \( \omega = \dot{\gamma} \). An example of this behavior, reported by Grizzutti, Cavella, and Cicarelli (1990) is shown in Figure 2.17. In addition to not obeying the Cox-Merz rule, measurements of \( \eta^*(\omega) \) suffer reproducibility problems. Dynamic tests probe the microstructure of the sample. As described in the previous section, the initial material response is based on its history extending a significant amount of time into the past. As with transient testing applying a preshear before the experiment can reduce the effects of the uncontrolled past history (Donald and Windle 1992).

![Figure 2.17](image)

Figure 2.17. Complex viscosity (upper curve) and steady shear viscosity (lower curve) for 50 % wt. HPC in water (Grizzuti, Cavella et al. 1990).
2.7.6 Optical microscopy

Optical microscopy is often used to study the morphology of lyotropic nematic liquid crystalline polymers and to complement rheological information on phase behavior. In fact, birefringence is a necessary, albeit not sufficient, criteria for establishing liquid crystallinity. Nematic liquid crystals are so named for their “threaded” textures. These can typically be seen in optical microscopy by using phase contrast in the absence of cross polarizers, typically with low magnification objectives of low numerical aperture. Where microscope attachments for phase contrast are not used, the thread like texture can be obtained from the aperture restriction in the back-focal plane. Another characteristic of a nematic phase is the Schlieren texture which can be viewed between cross polarizers. This texture was described by Friedel as structures à noyaux (nuclei). The dark regions occur where one of the principal axes of the domain (within the section plane) is parallel to the analyzer or the polarizer. Rotation of the crossed polarizer, or the sample, causes the dark regions to move. A clear indication of a nematic phase is the presence of point singularities which appear as centers to either two or four radiating dark bands called “brushes.” As the polarizer, or sample, is rotated, the brushes rotate giving a rotating propeller like appearance. Representative microscope images are shown in Figure 2.18.
Following shear, a banded texture perpendicular to the direction of shearing is typically seen in nematic liquid crystalline polymers. This can be observed in both polarized microscopy and electron microscopy. Figure 2.19 shows the effect of shear rate on the banded structure of dried films of 15% PBLG in dioxane.
2.8 Comparison of Criteria for Assessing Liquid Crystallinity

Since no single criteria can perfectly predict the transition to a single phase liquid crystal $\phi_N$, several criteria are often compared. For example, Kiss (1979) compared values of $\phi_N$ based on the following: birefringence, maximum in steady shear viscosity at low shear rate with concentration, maximum in the dynamic viscosity at low frequency with concentration, maximum in elastic modulus with concentration, maximum in the first normal stress difference with concentration, and Flory theory (Table 2.1). For 335,000 MW PBG (equal weights of poly-$\gamma$-D-glutamate and poly-$\gamma$-L-glutamate with equal amounts of both enatiomers) in m-cresol, the various criteria placed the onset of liquid crystallinity between 8 and $11 \text{ wt}\%$.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>% wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical anisotropy</td>
<td>9.9</td>
</tr>
<tr>
<td>Maximum in $\eta_{\gamma,0}$ vs. concentration</td>
<td>11.0</td>
</tr>
<tr>
<td>Maximum in $\eta_{\alpha,0}$ vs. concentration</td>
<td>11.0</td>
</tr>
<tr>
<td>Maximum in $G'$ vs. $C$</td>
<td>9.9</td>
</tr>
<tr>
<td>Maximum in $\tau_{11} - \tau_{12}$ vs. concentration</td>
<td>8.1</td>
</tr>
<tr>
<td>Flory theory</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Table 2.1. Indication of liquid crystalline order in PBG ($M_w = 335,000$) in m-cresol (Kiss 1979).
2.9 Fiber Spinning

This section provides a general overview of fiber spinning and the interrelationship between rheology, phase behavior and solution spinning of fibers. A history of SWNT fiber spinning can be found in Davis and Pasquali 2005. Several research groups are making regular breakthroughs in the production of macroscopic SWNT fibers; these groups include the Poulin and Bernier groups at CNRS, the Baughman group at the University of Texas at Dallas, the Windle group at Cambridge University, and the Smalley group at Rice University.

2.9.1 General Overview of Fiber Spinning

Commodity polymer fibers, such as carpet fiber, are usually produced from polymer melts. However, when the polymer does not form a melt that is thermally stable or does not have a viscosity suitable for fiber formation, a more complex process termed solution spinning is usually employed. Solution spinning is commercially used to produce fibers from lyotropic nematic liquid crystals of rigid rod polymers such as PPTA and semi-rigid polymers such as cellulose acetate (CA), hydroxypropylcellulose (HPC) and acetoxypropylcellulose (APC). Cellulose xanthate in NaOH is used to produce Rayon fibers and cellophane films. Examples of organic rigid rod polymers used to produce fibers are shown in Figure 2.20. Of these the best known is PPTA, which is sold under the DuPont trade name, Kevlar®.
Solution spinning can be divided into two main categories: dry solution spinning and wet solution spinning. In both cases, the spinning solution consists of the polymer dissolved in a solvent. Typically, the polymer content is less than 30% wt. and sometimes less than 10% wt. In many, but not all, cases the solution is formed at the molecular level. Dry spinning is used where the solvent is volatile and can be evaporated from the fiber during its formation. Wet spinning is used when the polymer is dissolved in a non-volatile solvent. A key example of a wet solution spun fiber is DuPont Kevlar, produced from poly (p-phenylene terephthalamide) (PPTA) dissolved in sulfuric acid. In wet solution spinning, (Figure 2.21), the solution is extruded through one or more small orifices in the spinneret. Typically, the solution goes through an air gap and then enters the coagulation bath. In this case, the process is termed “dry jet wet spinning.” The air gap allows elongation and cooling of the spinning solution prior to entering the bath. The
presence and length of the air gap depends on the ability of the polymer solution exiting the spinneret to withstand surface forces prior to entering the coagulation bath. For PPTA air gaps are less than 2 cm, and a gap of 0.5 to 1.5 cm is considered optimal (Rakas 1990). Longer distances cause the surface forces to break the fiber line before it can be coagulated. In contrast, higher viscosity PBZT/poly (phosphoric acid) and PBO/poly (phosphoric acid) spinning solutions allow air gaps of up to 20 cm without fiber line breakage (Rakas 1990). If no air gap can be tolerated, the spinneret is immersed directly into the coagulation bath and the process is termed “wet jet wet spinning.”

Upon entering the coagulation bath, mass transfer occurs between the coagulant (non-solvent) in the bath and the solvent in the spinning solution, which can now be considered as the “protofiber” (Paul 1968; Ziabicki 1976). The goal of the coagulation process is to freeze protofiber structure and solidify the fiber. The final properties of the resulting fiber depend on the initial polymer solution, processing conditions, the coagulation process (Hancock, Spruiell et al. 1977; Berry, Wong et al. 1979; Hancock 1981; Chenevey and Wadhwa 1982; Rakas 1990), drawing of the fiber, and post-processing steps such as secondary washings (Chenevey and Wadhwa 1982; Rakas 1990) or drying (Pottick 1986).
2.9.2 Implications of Phase Behavior and Rheology on Fiber Spinning

The rheology and phase behavior profoundly influence the selection of the spinning solution concentration, spinning and coagulation process variables, and alignment in the as spun fibers. Neglecting disruptions in orientation occurring during spinning and coagulation, the following would be expected for fibers made from solutions of a given molecular weight (aspect ratio) solution at increasing concentration (Kiss 1979). The same behavior would also be expected for a given concentration at increasing molecular weight (increasing aspect ratio).

1. At low concentration, the solution is predominantly isotropic, it is very viscous and difficult to spin. Spinning results in an unoriented weak as-spun fiber.

2. At intermediate concentration, the solution is predominantly anisotropic but still contains some isotropic phase, the viscosity is reduced easing processing and a partially oriented somewhat stronger as-spun fiber results.
3. At higher concentration, the solution is almost entirely anisotropic, the viscosity is still lower further easing processing and the as-spun fiber will be better oriented and stronger. For a completely ordered solution with few packing defects, the as-spun fibers should be almost perfectly ordered and post-treatment will result in minimal gains in properties.

4. At still higher concentrations, higher mass fractions will facilitate coagulation, but the resulting increase in viscosity can result in inhomogeneous mixing and difficulties in processing during spinning.

Understanding rheological properties is important for selecting processing conditions. For example, shear thinning can be useful in reducing viscosity enough to facilitate flow through the spinneret. However, it is undesirable to spin in the range of shear rates where the liquid is yielding and slight changes in applied shear rate (or shear stress) result in a significant change in viscosity and flow rate out of the spinneret. Knowing the effect of temperature on rheological properties is also critical. Polymer melts generally become less viscous with increasing temperature facilitating processing. However, this is not necessarily the case for liquid crystalline solutions. The increase in entropy with increasing temperature can cause the liquid crystalline structure to disintegrate resulting in an increase in viscosity (Figure 2.22). In addition, higher temperatures can result in degradation reactions.
Figure 2.22. Effect of temperature on PBA/DMAC viscosity (Papkov, lovleva et al. 1973).

Understanding rheological properties is also useful for determining if an air gap can be used choosing the coagulant, and designing the coagulation and drawing system, air gap and spinning rate (Berry, Wong et al. 1979). For example, spinning at shear rates where the first normal stress difference is negative should be avoided. Just as positive normal stresses typically result in die swell negative normal stresses can result in protofiber contraction at the spinning outlet. Contraction can also result from too rapid coagulation in wet-jet wet spinning. In spinning of PBO and PBT solutions, protofiber contraction allowed the coagulant to flow up into the spinneret along the inner wall asymmetrically. This premature and unsymmetric coagulation prevented significant drawing of the fiber and obtaining a high stretch ratio (Berry, Wong et al. 1979).
Chapter 3

Experimental Details

Developing new experimental methods was a necessary and challenging part of this research. This was one of the first projects requiring gram quantities of SWNTs as well as SWNT dispersal in liquids at concentrations > 0.5 % wt. One challenge was the difficulty of mixing the high viscosity nanotube dispersions; initially a series of commercially available mixers were used but ultimately new mixers had to be designed. Additional challenges were the moisture sensitivity, corrosivity and carcinogenicity of the superacids; protocols were developed to minimize the risk of moisture ingress, equipment corrosion and researcher injury. Still more challenges were related to the limited characterization methods that could be used due to the SWNT-superacid dispersions’ corrosivity, optical opacity, high viscosity, and polydispersity. Most dispersion characterization focused on assessing SWNT-superacid phase behavior and flow characteristics through the use of rheology and optical microscopy, but even these standard methods had to be adapted to handle the SWNT-superacid dispersions. The following sections describe materials and methods related to preparation of nanotubes and superacids, mixing dispersions, spinning fibers and characterizing dispersions and fibers. The evolution of both the starting materials and experimental protocols during the course of this research is also described.
3.1 Single-Walled Carbon Nanotube (SWNT) Preparation

The SWNTs used in this work were produced in a HiPco (Bronikowski, Bradley et al. 2000) research reactor at Rice University. Reactor conditions were frequently varied as part of HiPco process and reactor design research. Prior to late 2003, all of the purified batches had a similar average length to diameter ratio, and reactor variations did not have a significant impact on the phase behavior, rheology or fiber spinning experiments. However, between late 2003 and 2005 numerous changes in reactor conditions, reactor design and purification protocols resulted in appreciable batch to batch variation. In order to minimize the impact of these variations, each set of experiments was performed either from a single batch or batches produced under similar conditions.

The bulk of this research used nanotubes purified by the “soft-bake HCl process” to remove amorphous carbonaceous material, fullerenes, and residual iron catalyst. This process consisted of the following steps: heating the SWNTs at 250°C for 15 hrs in the presence of moisture, soaking them in hydrochloric acid for eighteen hours, rinsing the SWNTs with water until neutral, exchanging the water with methanol, and finally vacuum drying the SWNTs and storing them in a sealed container (Chiang, Brinson et al. 2001). The soft-bake HCl process resulted in 95% pure SWNTs; the remaining impurities were due to residual iron catalyst. However, this process also caused oxidative damage to the SWNTs; the SWNTs were shortened and the smaller diameter SWNTs tended to be destroyed. In addition, the final purified material was in the form of large hard granules; prior to use these granules had to be ground into a medium grain powder with a mortar and pestle. The grinding was not believed to damage the SWNTs, but was very time consuming.
This research was able to take advantage of two key improvements to the purification process. First, in late 2003, the hexane purification process was developed. This technique did not significantly improve purity or reduce oxidation, but resulted in easily handled spheres of SWNTs called “bucky-pearls” that did not require grinding. Second, in 2004, Xu et al. (2005) developed an improved purification technique using multistage oxidation in the presence of fluorine. SWNTs purified using this technique have less oxidative damage and higher purity compared to SWNTs purified using the soft-bake HCl process, and the material is an easily handled powder.

Due to concerns that the soft-bake HCl process damaged tubes and increased bundle formation, a small amount of rheology and fiber spinning work was conducted on raw, unpurified, tubes. These studies found that the high level of impurities (20 – 30 % wt.) made unpurified SWNTs unsuitable for fiber spinning. More recently, rheological characterization of unpurified SWNT-superacid dispersions was conducted as part of a parametric study on the impact of HiPco reactor conditions on SWNT purity, average length, and average diameter. In both cases, the extremely low bulk density of raw SWNTs (~ 1 g/l) made them very difficult to handle; the bulk density was increased by wetting the SWNTs with a volatile non-solvating liquid such as methanol, ethanol or propanol and then evaporating the solvent. After densification the raw SWNTs were handled and dried in the same manner as the purified SWNTs.
3.2 Acid Preparation and Titration

Oleum, triflic acid, concentrated sulfuric acid, and chlorosulfonic acid were taken directly from the bottles supplied by Sigma Aldrich without any additional drying. The 102 % sulfuric acid used was prepared by mixing the concentrated (96 % wt.) sulfuric acid with oleum inside an anhydrous glove bag or glove box. Initially, the mixing ratio was determined by assuming equimolar reaction between the excess SO₃ in the oleum and the water in the oleum; the concentrations of water and excess SO₃ were estimated based on the initial bottle specifications and how often the bottles had been opened outside of the glove box. This method was too inexact to enable investigation of the impact of SO₃ content on phase behavior. Therefore, in late 2003, the American Chemical Society (ACS) titration method for quantifying excess SO₃ content in fuming sulfuric acid was implemented (American Chemical Society 2000). This method requires filling a 2 ml capacity Dely weighing tube (Welcher 1963) in the glovebox, weighing the acid, and transferring it to a 250 ml flask containing 50 ml of nanopure water and eight drops of 1% phenolphthalein solution (indicator range pH 8.2 to 10). The concentration of the acid was then calculated according to the ACS specification formula (American Chemical Society 2000)

\[
\% \text{H}_2\text{SO}_4 = \frac{(mL \times N \text{ NaOH} \times 4.904)}{\text{Sample weight (g)}}
\] (3.1)

3.3 Dispersion Preparation

Strict avoidance of moisture was the most critical aspect of dispersion preparation; even low moisture levels increased corrosivity, resulted in the evolution of acidic fumes, and
significantly changed the phase behavior of the system. To prevent moisture contamination, the nanotubes, the mixing apparatus, and all sampling tools were thoroughly dried. Nanotubes were either dried in a vacuum oven overnight at > 80 °C or under vacuum at 110 °C in the assembled apparatus. All mixing components and tools were either flame dried or vacuum dried at > 80 °C overnight and then cooled in an anhydrous atmosphere. In addition to drying all components before use, an anhydrous environment was maintained through the mixing and characterization process.

For comparing SWNT phase behavior to theoretical models, it was necessary to determine the SWNT volume fraction \( \phi \). Since the true average density of HiPco SWNTs is unknown, the density was estimated based on the calculated density of 1.45 g/ cm\(^3\).

\[
\phi = \frac{\text{volume SWNTs}}{\text{volume solvent} + \text{volume SWNTs}} = \frac{\rho_{\text{rel}} w}{1 + (\rho_{\text{rel}} - 1) w}
\] (3.2)

where,

\[
\begin{align*}
 w & = \text{SWNT weight fraction} \\
 \rho_{\text{rel}} & = \frac{\text{SWNT density}}{\text{solvent density}} = \frac{\rho_{\text{SWNT}}}{\rho_{\text{Acid}}} \\
 \rho_{\text{SWNT}} & = 1.45 \text{ g/cm}^3 \\
 \rho_{102\%\text{H}_2\text{SO}_4} & = 1.88 \text{ g/cm}^3 \\
 \rho_{120\%\text{H}_2\text{SO}_4} & = 1.92 \text{ g/cm}^3 \\
 \rho_{\text{CISO}_3\text{H}} & = 1.76 \text{ g/cm}^3 
\end{align*}
\]

### 3.3.1 Low concentration mixing

Low concentration (< 0.5 % wt.) SWNT dispersions were mixed with Teflon covered magnetic stir bars. Room temperature mixing was conducted in sealed glass flasks and vials inside a glove box maintained at ~ 50 °C dewpoint (approximately 0 % relative
humidity). For safety reasons, mixing at elevated temperatures up to 120 °C was generally conducted in a fume hood with the apparatus maintained under positive argon pressure. All samples were mixed for more than twenty-four hours, and typically for between three and seven days.

3.3.2 High concentration mixing

The viscosity of samples > 0.5 % wt. SWNT necessitated using more powerful and complex mixers. In the initial stages of the project, it was unknown whether inhomogeneities in high concentration dispersions were the result of solvent quality or mixer design. Several generations of mixers were used in this investigation.

The first mixer used for > 0.5 % wt. dispersions was a Trubore mixer (Ace Glass, Vineland, NJ) consisting of a Teflon blade on a glass rod connected to a flexible shaft motor (Figure 3.1). For mixing at temperatures above ambient, the mixer was immersed in a silicon oil heating bath. Uniform dispersion could not be achieved in the Trubore for SWNT concentrations greater than or equal to 4 % wt. For example, thermal gravimetric analysis revealed that the SWNT concentration of one sample removed from a nominal 4 % wt. mixture was 7 % wt. SWNT. Several attempts were made to improve mixing with modifications to the mixing paddle and glassware design, but these were not successful. An additional problem with the Trubore was that its minimum volume was approximately 12 ml. For these reasons, the Trubore mixer was only used for oleum and triflic acid samples between 1 and 4 % wt. All samples mixed in the Trubore were mixed under an argon blanket at temperatures ranging from 70 to 120 °C for a minimum of three days.
The second mixer design was a Daca Double Helix Mixer (Daca Instruments, Goleta, CA). This mixer (Figure 3.2) was of interest because it had been used for Kevlar™ research; and it proved useful for making numerous SWNT-superacid dispersions for rheology and fiber spinning experiments. Concentrations of up to 8 wt% SWNT were mixed in the Daca at temperatures between 25 and 120 °C. However, the Daca had three key drawbacks. First, vertical concentration gradients existed for dispersions greater than 5 % wt.; these gradients resulted from the large normal stresses of the liquid crystalline dispersions (Chapter 4.6.2). Second, the outer screw often rubbed against the glass wall resulting in contamination measurable by both energy dispersive spectroscopy (EDS) and thermal gravimetric analysis (TGA). Third, the Daca could not be directly integrated with a spinning apparatus, creating the risk of moisture contamination prior to fiber spinning.
The third mixer tested was a Haake MiniLab (Thermo Electron, Karlsruhe, Germany) recirculating co-rotating twin screw extruder. Prior to acquiring the MiniLab, limited tests were performed with a Haake Rheomix 600 mixer at Georgia Institute of Technology (Ericson and Davis 2001). Mixtures of up to 10 % wt. SWNT in oleum were produced, but the mixtures were contaminated with moisture due to inadequate argon purge. Major disadvantages of the Rheomix 600 were the large sample volume and that the torque was very low regardless of concentration and mixing speed; this was an indication of slip and mixer not being transferred to the dispersion. It was hoped that the Haake MiniLab (Figure 3.3) could be used not only to overcome these problems but to also spin fibers directly from the mixer. However, low torque was also a problem in the MiniLab; it was not possible to create enough pressure in the apparatus to spin fibers. A possible explanation for the low torque was that the free superacid coated the agitator blades resulting in slip (Ericson and Davis 2001).
Due to the problems with commercially available mixers, and the desire to be able to mix and spin from a single apparatus, the Spinning Bob Mixer (SBM) was designed and built at Rice (Ericson 2003). The SBM requires approximately 8 ml of sample and was successfully used to mix concentrations up to 10 % wt. SWNT and to spin greater than 100 m of continuous 40 μm to 100 μm fibers. The modularity of the SBM has allowed ongoing refinements to processing conditions as well as to mixing element and spinneret design. In general, the SWNT-superacid dispersions were premixed using a spatula in an anhydrous glove box and then further mixed by being forced through mixing elements along the horizontal axis of the apparatus (Figure 3.4). After mixing, the sample was extruded through one of several interchangeable spinnerets at the bottom of the mixer.
Figure 3.4. Photograph (top) and schematic (bottom) of the Spinning Bob Mixer (SBM). SWNTs soaked in superacid were injected into the SBM using a syringe and mixed by being forced through mixing elements along the horizontal axis. For fiber extrusion, one side of the mixer was blocked and the other piston was used to force material through the central chamber and out a spinneret at the bottom of the mixer (Ericson 2003).
The final mixer design used in this investigation was a custom design paddle mixer developed for producing small volumes for rheology and phase behavior studies (Figure 3.5). The "mini-mixer" (Kittrell 2005) combined the high shear of the Daca with the all glass and Teflon construction of the Trubore. Small Teflon paddles were angled to move the dispersion vertically as well as radially; the clearance between the paddles and between the paddles and the wall created high shear. This mini-mixer was used to produce between 3 and 8 ml samples, and it was the only one of the mixers capable of withstanding the extreme corrosivity of chlorosulfonic acid (ClSO$_3$H).

![Figure 3.5. Photograph of the mini-mixer used to mix 3 to 8 ml samples for phase behavior and rheology studies.](image)

### 3.3.3 Mixer sampling and sample handling

Significant effort was made to minimize sample exposure to atmospheric moisture during sampling. Whenever possible, the mixer was transferred to a glove box prior to sampling. When it was necessary to acquire a sample outside the glove box, the sample was extracted through a septum using 14 to 20 gauge stainless steel syringe needles attached to gas-tight syringes. Immediately upon removal from the mixer, the syringe
needles were plunged through the septums of vials containing desiccant, and the backs of the syringes were wrapped with Parafilm. For high viscosity mixtures that could not be extracted using a syringe, the argon flow was increased to maintain the dry blanket over the sample, the mixer was opened, and the sample was rapidly extracted.

All samples were stored in an anhydrous glove box to prevent moisture contamination. Prior to removal from the glove box, they were sealed and placed in portable dry environments. Rheology samples were kept in glass gas-tight syringes with the needle tip inserted into a septum-sealed glass vial containing desiccant. Microscope slides were either vacuum or flame dried prior to preparation in an anhydrous glove box, sealed with Teflon and/or aluminum duct tape after preparation, and transported to the microscope in dried sealed containers.

3.4 Fiber Spinning

The initial SWNT fibers were produced as part of this research and SWNT-superacid phase behavior and rheology directly impacts the spinning process and fiber morphology. However, as fiber spinning and fiber properties are not the main emphases of this dissertation, the process is described only briefly. Detailed information on the Rice fiber spinning protocols can be found in the works of Ericson (Ericson 2003; Ericson, Fan et al. 2004).

All fibers were produced by solution spinning SWNT-superacid dispersions into a liquid coagulation bath. However, as was the case for mixer design, fiber spinning equipment and protocols evolved with time. Initial experiments were performed by manually extruding the fiber out of a glass gas-tight syringe with a small orifice diameter
needle attached. This procedure resulted in fibers with wavy edges because of the difficulty of maintaining perfectly constant extrusion rate. Next, a KD Scientific (Holliston, MA) Model-100 Syringe pump was used. At concentrations above 4 % wt. (5.4 % vol.) SWNT in oleum, this pump was incapable of supplying sufficient pressure to expel the high viscosity paste through the needle. For this reason, a higher pressure Harvard Apparatus (Holliston, MA) Remote 44 syringe pump was acquired. Ultimately, most of the fibers were spun using the Spinning Bob Mixer, but manual extrusion and syringe pumps continued to be used for small volume screening experiments.

In general, the syringe was mounted vertically and the coagulant was in a vertical column approximately two feet in length. Spinneret diameters ranged from less than 100 μm to 500 μm. Several types of spinnerets were used including 100 to 300 μm syringe needles, Teflon tubing and drawn glass capillaries between 0.5” and 12” in length. Coagulation baths included diethyl ether, aqueous sulfuric acid, and water. Coagulation had a significant impact on fiber macrostructure; as for solution spun liquid crystalline polymer fibers (Ziabicki 1976) rapid coagulation resulted in irregular fiber shapes (Ericson 2003). For concentrations less than 6 % wt. (7.6 % vol.) SWNT, attempts to provide extensional flow by having an air gap between the needle and coagulant were unsuccessful, so fibers were produced by wet-jet wet spinning where the needle tip is in contact with the coagulant. Fiber spun from > 6wt% SWNT were spun with a one to two centimeter air gap.
3.5 Characterization Methods

3.5.1 Rheology

Rheological testing was performed to evaluate dispersion flow characteristics, phase transitions, and liquid crystallinity. Tests were performed using Advanced Rheometry System (ARES) 100 and 2000 FRTs with LS air bearing motors and a RDA III strain controlled rheometer (TA Instruments, Wilmington, DE). The test geometries were a Couette with a 34 mm bob diameter and a 35 mm cup diameter, 25 mm and 50 mm parallel plates and two sets of 25 mm cones and plates with angles of 0.04 and 0.10 radians. Gaps for the parallel plates ranged from 0.3 mm to 1.0 mm, and gaps for the cones were 0.058 mm for the 0.04 radian cone and 0.051 for the 0.10 radian cone.

Rheological characterization required overcoming three key challenges. First, testing fixtures had to be corrosion resistant, either Hastelloy C or 316 stainless steel. Second, the hygroscopic nature of the acids and the formation of aggregates upon exposure to moisture required that sample loading and testing be conducted in an anhydrous environment. On the ARES, an anhydrous environment was achieved by enclosing the fixtures in a custom-built desiccant chamber continuously purged with ultra high purity argon (Figure 3.6). Samples were loaded from a syringe through a side port in the chamber. For most samples, the added precaution of a layer of 3M Flourinert® FC-77 (density = 1.78 g/cm³, viscosity = 1.3 mPa s) or 10 to 100 mPa s silicon oil was used to prevent the possibility of any moisture ingress. On the RDA III (Figure 3.7), an anhydrous environment was achieved by enclosing the fixtures in a nitrogen purged chamber during loading and purging the oven with nitrogen during testing. Again, Flourinert or silicon oil was typically used for added protection.
Figure 3.6. Ares 100 FRT rheometer, with circulating temperature bath and Argon flowing to a desiccant chamber (left). Close-up of desiccant chamber surrounding fixture (right).

Figure 3.7. RDA III rheometer with nitrogen purged loading chamber and oven. The red tubing connects to the ultra high purity nitrogen tank.

The third challenge was testing samples with a broad range of viscosities (26 mPa s to 100,000 Pa s) over a wide range of temperatures (25 °C to 150 °C). The ARES with its air transducers and motor, was the more sensitive of the two instruments, but was initially limited to a torque of 0.004 to 100 g cm, and a normal force of 100 g. In mid-2002, the ARES was replaced with a new model capable of torques from 0.004 to 2000 g, and normal forces up to 2000 g. This enabled testing the full range of concentrations and viscosities on the ARES. However, loading dispersions containing more than 6 % wt. was still problematic; the samples did not self-center and the high normal forces coupled with long relaxation times made loading take as much as six hours. For these reasons, the
majority of testing was conducted in parallel plate geometry where a larger gap could be used and a specific gap did not have to be achieved. While the ARES 2000 FRT was able to test a broader range of viscosities than the 100 FRT, its capabilities were still limited by the temperature bath which could operate only between 10 and 80 °C. The RDA III was used for tests above 70 °C; the RDA III measured torques from 2 to 1500 g cm, and normal forces from 2 to 1500 g at temperatures ranging from ambient to 600 °C.

3.5.2 Optical microscopy

Optical microscopy was used to obtain morphological data to complement the rheological data. A Zeiss Axioplan microscope was used; it was capable of imaging samples in transmission, dark field reflection or bright field reflection with or without cross polarizers and differential interference contrast (DIC). Key challenges were the optical opacity of the samples, consistent slide preparation, and preventing moisture contamination during slide preparation and imaging. Samples containing up to 4 % wt. SWNT were imaged in transmission; however, it was necessary to prepare very thin samples. Thicker samples appeared homogeneous simply due to the blockage of light. Samples containing greater than 4 % wt. SWNT were imaged using the microscope's cross polarized reflected dark field capabilities. For these samples, thickness was not an issue, but it was difficult to get consistent domain sizes because of the influence of the sample's top surface morphology and its contact with the coverslip. Consistent slide preparation was important because shearing the sample affected birefringence. Additionally, for lower viscosity samples less than (1 % wt. SWNT), phase separation and concentration gradients could be induced because the superacids wet the slides. Hydrophobically treated slides and coverslips (Wen and Papadopoulos 2000) were tested,
but while this prevented phase separation, the drops did not spread sufficiently to allow clear imaging of the sample’s microstructure. Therefore, untreated, hydrophilic slides were used almost exclusively.

3.5.3 Raman spectroscopy

A Renishaw Polarized Micro-Raman System 1000 with rotating stage was used to characterize liquid and quenched dispersions, fibers, and alewives. A 782 nm laser was used to probe semiconducting SWNTs and a 514 nm laser was used to probe metallic SWNTs. The Raman spectra of SWNTs have several key features (Figure 3.8). The radial breathing modes at approximately 200 cm\(^{-1}\) are indicative of SWNT diameters. The peak at approximately 1330 to 1360 cm\(^{-1}\) is due to the axial breathing of sp\(^3\) hybridized carbons and is commonly referred to as the disorder (D) peak as it indicates a disruption to the perfect chemical structure of a pristine SWNT. Large D peaks are obtained for sidewall functionalized nanotubes (Liang, Sadana et al. 2004). The G peak corresponds to the tangential mode of the sp\(^2\) hybridized carbons; it is the most dominant peak in the spectrum and is centered at 1594 cm\(^{-1}\) for pristine SWNTs. A smaller second order peak for the tangential mode occurs at approximately 2600 cm\(^{-1}\) and is called the G’ peak.

The position of the dominant G peak shifts to higher wave numbers when the SWNTs are protonated. This behavior, called the Eklund shift, was used to determine the number of carbons sharing each positive charge in a variety of acidic solvents using a factor of 320 cm\(^{-1}\)/hole/C (Sumanasekera, Allen et al. 1999). Raman spectra of dispersions rapidly quenched in ether or alcohols were also useful in determining whether
SWNT protonation was reversible and whether mixing in any of the solvents had a permanent impact on SWNT structure.

Figure 3.8. Key features of the Raman spectra of a single-walled carbon nanotube. RBM = radial breathing modes at ~ 200 cm\(^{-1}\), D = disorder peak due to tangential mode of sp\(^3\) hybridized carbons at 1330 to 1360 cm\(^{-1}\), G = tangential mode of sp\(^2\) hybridized carbons at 1594 cm\(^{-1}\), and G' = second order tangential mode of sp\(^2\) hybridized carbons at 2600 cm\(^{-1}\). The G peak shifts to the right with increasing nanotube protonation.

Raman spectroscopy was also used to determine alignment in quenched SWNT structures, namely fibers and tactoid shaped crystal solvates called alewives (Chapter 4.7). Several spectra were taken along the sample with its primary axis aligned to the incident laser; this process was repeated with the primary axis of the alewife or fiber aligned perpendicular to the incident laser. Comparison of the intensity of the G peaks provided an indication of the relative degree of alignment within the sample. Raman does not probe as deeply into the sample as x-ray scattering techniques, but does provide an easy screening of the relative degree of alignment. WAXD results which probe the cross section of the fiber were in good agreement with Raman results (Zhou, Vavro et al.; Zhou, Winey et al. 2002).
3.5.4 Scanning Electron Microscopy (SEM)

A Phillips FEI XL30 ESEM with EDAX energy dispersive spectroscopy (EDS) system was used for imaging quenched solutions and fiber samples at up to 100,000 times magnification without any coating. The samples were prepared by immersing the SWNT-superacid mixture into diethyl ether, evaporating the ether and attaching the remaining solid to SEM mounts with double-sided carbon tape. The morphology of the quenched samples was indicative of the morphology of the nanotubes in the mixture. Fiber imaging focused on the exterior surface along the length of the fiber samples, but some visualization of the fiber cross section was performed by threading the fibers through holes drilled into standard SEM mounts and affixing them with silver paint from Ted Pella (Redding, CA). Several techniques for eliminating artifacts from breaking of the fibers were attempted. Initially, the technique reported by Hancock for use with rod-like polymer fibers (Hancock, Spruiell et al. 1977) was adapted for use with SWNT fibers. The exposed end of the fiber was frozen in liquid nitrogen and fractured approximately 3 mm (1/8") above the surface. This method significantly reduced artifacts resulting from cutting or manually breaking the fiber and enabled visualization of the fiber cross-section. However, due to SWNTs mechanical strength, it did not provide a perfectly flat surface. Later, a laser cutting and etching technique was developed; this technique resulted in a perfectly flat surface useful not only for fiber characterization but also the continued growth of SWNTs from SWNT fiber scaffolds (Wang 2004).
3.5.5 Determination of the maximum concentration in the isotropic phase

The maximum concentration of SWNTs that could exist in the isotropic phase was determined using a procedure developed by Rai (Rai, Pinnick et al. submitted). 0.15 % wt. SWNTs were mixed in superacid for three days and centrifuged for fourteen hours on a Fisher Centriflic 225 Centrifuge at 5100 ppm. The isotropic top phase was extracted, and its UV-vis-nIR absorption spectra was measured on a Shimadzu UV3101PC spectrophotometer using 1 mm pathlength quartz cells with teflon caps. Comparison of the sample absorption at 500 nm to that of a calibration curve developed for that batch of SWNTs in that superacid enabled determination of the concentration in the isotropic phase (Rai in preparation). For superacids where the solubility exceeded 0.15 % wt., 0.5 % wt. SWNTs were mixed and the sample was diluted by a factor of ten prior to absorption measurements.
Chapter 4

Phase Behavior and Rheology of SWNTs in Superacids

This chapter summarizes the results of extensive investigation into the rheology and phase behavior of SWNTs in a variety of superacids including 102% sulfuric acid ($\text{H}_2\text{SO}_4$ with 2% excess $\text{SO}_3$), oleum (120% $\text{H}_2\text{SO}_4$), and triflic acid. The primary focus of this research has been the rheology and phase behavior of SWNTs in 102% $\text{H}_2\text{SO}_4$; all the results in this chapter are for SWNTs in 102% $\text{H}_2\text{SO}_4$ unless otherwise noted. Chapter 5 describes the impact of acidity on phase behavior, with particular emphasis on the phase behavior of SWNTs in chlorosulfonic acid ($\text{CISO}_3\text{H}$), and mixtures of 102% $\text{H}_2\text{SO}_4$ and $\text{CISO}_3\text{H}$.

Superacids are generally defined as acids which have a protonating ability greater than that of 100% sulfuric acid (Gillespie 2001). While 100% sulfuric acid is the least aggressive of the superacids, it is still $10^{13}$ times as acidic as a 0.1 N solution of sulfuric acid in water. SWNTs mixed with acids weaker than 100% $\text{H}_2\text{SO}_4$ did not disperse well (Ramesh, Ericson et al. 2004); most experiments were conducted with 102 % $\text{H}_2\text{SO}_4$ to provide a margin for accidental ambient moisture contamination. The choice of 100 – 102% $\text{H}_2\text{SO}_4$ was also attractive in terms of commercial scalability. Sulfuric acid is one of the world’s most widely produced industrial chemicals; in 2000 US production alone was 44 kT compared to 55kT for ethylene and 31kT for propylene (Chemical and
Engineering News 2001). Sulfuric acid is primarily used in the production of fertilizers; however, it is also used in the production of solution spun fibers such as DuPont Kevlar™. Therefore, developing a sulfuric acid based SWNT solution spinning process is attractive in terms of raw material availability and the existence of solution spinning equipment capable of handling sulfuric acid's corrosivity.

4.1 Dispersion of SWNTs in Superacids

During the course of this research it was discovered that the protonation of SWNTs in acidic solvents results in a delocalization of positive charge along the entire nanotube. The formation of the SWNT carbocation can be viewed as

\[
C_x + yAH \rightarrow \left[ C_x^{\delta^+} + H_y^{(1-k\delta^+)} \right] + yA^- \quad (4.1)
\]

Where \( k = x/y \) and \( \delta^+ \) is the fractional charge carried by each carbon atom (Ramesh, Ericson et al. 2004). This dispersion by protonation mechanism is analogous to that for rod-like polymers in acidic solvents; the key difference is that in the case of nanotubes the charge is delocalized while in the case of rod-like polymer molecules there are very specific protonation sites. The SWNT dispersion by protonation mechanism has been supported by numerous experimental results including: uv-VIS-NIR absorption shifts (Ramesh, Ericson et al. 2004), Raman shifts in the G peak in the Raman spectra (Davis, Prieto et al. in preparation), swelling of fibers immersed in sulfuric acid and oleum (Ericson, Fan et al. 2004), differential scanning calorimetry of SWNTs in sulfuric acid and oleum (Zhou 2005; Zhou, Fischer et al. 2005) and SWNT templating of sulfuric acid crystallization (Zhou, Heiney et al. 2005).
As shown by Raman and rheological studies, the protonation of SWNTs in superacids is non-destructive and reversible. The G peak in the Raman spectra corresponds to the tangential vibrational mode of the SWNTs' sp² hybridized carbons and is centered at 1594 cm⁻¹ for carbon nanotubes in the solid, uncharged state. With increasing protonation, the G peak shifts in the upward direction; this shift (referred to as the Eklund shift) corresponds to 320 cm⁻¹ per hole per carbon (Sumanasekera, Allen et al. 1999). For SWNTs dispersed in 102% H₂SO₄ and excited with a 514 nm laser the G band is centered at 1611 cm⁻¹ corresponding to an Eklund shift of 17 cm⁻¹. This equates to twenty carbons sharing each positive charge, or a fractional charge positive per carbon δ⁺ = 0.053. Excitation with a 780 nm laser, which is in resonance with ν₁ → c₁ transitions, results in only background scattering as the ν₁ valence electrons are depleted during the protonation process (Ramesh, Ericson et al. 2004). When the SWNT – 102% H₂SO₄ dispersions are quenched, rinsed with ethanol, and dried, the location of the G peak is restored to the original 1594 cm⁻¹ position. The restoration of the G peak, in conjunction with the absence of a D band resulting from sp³ hybridized carbons, shows that the mechanism of dispersion is one of reversible protonation and not sidewall functionalization. Furthermore, exposure to the superacids does not result in significant SWNT damage or cutting at ambient conditions. The rheologically determined average length of SWNTs in superacids (Section 4.3) corresponds well to the average length obtained by AFM even after two weeks of mixing at ambient conditions (Parra-Vasquez, Stepanek et al. in preparation) and no change in aspect ratio was measured by rheology after five weeks of mixing at ambient conditions.
4.2 Dilute Regime

Steady shear measurements of successive dilutions of SWNT – 102% H₂SO₄ dispersions show that below ~ 90 ppm vol. the SWNTs behave as non-interacting dilute Brownian rods (Chapter 2.5.1). Similar results were obtained for SWNTs in 120% H₂SO₄. Figure 4.1 shows data from dilutions of a representative batch (HPR 106.2) of purified SWNTs. The intrinsic viscosity \([\eta_\gamma] = (\eta - \eta_s)/\eta_s\phi\) versus shear rate \(\dot{\gamma}\) curves for 54 ppm, and 81 ppm vol. collapse almost perfectly; data for 27 ppm vol. agree less well because the dispersion viscosity was only about 10% higher than the solvent viscosity. This behavior of the intrinsic viscosity is in accordance with the theory of dilute Brownian rods (Kirkwood and Auer 1951): the viscosity depends linearly on concentration and the relaxation time is independent of concentration. Data for concentrations above 90 ppm vol. collapse onto a different curve (Figure 4.3). Therefore, the transition from dilute to semidilute occurs at ~ 90 ppm vol.; below this critical concentration the tubes are dissolved as individuals and do not interact. An alternative method for estimating the critical volume fraction for the transition from dilute to semidilute is taking the reciprocal of the intrinsic viscosity; this yields a value of 120 ppm vol. which compares well to the value of 90 ppm obtained from the mastercurves. In terms of number of rods per unit sphere swept by a rod, the transition concentrations are estimated to be \(vL^2 = (4/\pi)\phi (L/d)^2 = 25\) to 33, which compares well with literature values (Larson 1999).
Dilute dispersions of SWNTs in superacids behaving as Brownian rods was not an obvious result for two reasons. First, the frequent appearance of curved SWNTs in transmission electron micrograph (TEM) and atomic force microscopy (AFM) images of dispersed SWNTs dried onto substrates has created the perception that dispersed SWNTs should be treated as semi-flexible, not rigid rods. The curvature often seen in images is most likely the result of defects in the SWNT sidewalls and artifacts induced by the drying process. Second, the size of SWNTs approaches that where non-Brownian behavior would be expected (Chapter 2.6).

As described in Chapter 2.6, the aspect ratio of a solution of Brownian rods can be determined from the zero shear viscosity using
\[
\frac{\eta - \eta_r}{\eta_r \phi} = \frac{2(L/R)^2}{45 \ln (L/R)} \left[ \left( 1 + \frac{0.64}{\ln (L/R)} \right) + \frac{1.659}{\left( \ln (L/R) \right)^2} \right] 
\]

(4.2)

In the polydisperse case, the viscosity contributions of each subpopulation of length are additive and the intrinsic viscosity is related to the ratio of the third and first moments of the distribution of length. Using the viscosity measured at the lowest accessible shear rate \(0.3 \, \text{s}^{-1}\) as the approximate value of the zero-shear viscosity (Figure 4.1), the extrapolated value of the intrinsic viscosity is

\[
[\eta_0] = \lim_{\dot{\gamma} \to 0} \frac{(\eta(\dot{\gamma}) - \eta_r)}{(\eta_r \phi)} = 8300 \pm 830
\]

(4.3)

Taking this extrapolated value, Equation 4.2 yields an average aspect ratio \((L/D)_{\text{KAB}} = 470 \pm 30\). The subscript KAB reflects the fact that the aspect ratio was obtained using the Kirkwood-Auer-Batchelor Equation (KAB). Numerous determinations of aspect ratio in both 102\% H\textsubscript{2}SO\textsubscript{4} and 120\% H\textsubscript{2}SO\textsubscript{4} between May 2001 and September 2003 all yielded aspect ratios in the range of 400 to 500. Subsequent to September 2003, aspect ratio became highly batch dependent due to research into the impact of reactor conditions on length and changes in the purification process; average aspect ratios measured on purified SWNTs ranged from 300 to 1000 between September 2003 and April 2005.

Rods shear thin when the product of the longest rotational relaxation time \(\tau\) and shear rate \(\dot{\gamma}\) exceeds \(\sim 0.2\) (i.e., the Weissenberg number \(Wi = \tau \dot{\gamma} > 0.2\)); because shear thinning starts at \(\dot{\gamma} \approx 0.3 \, \text{s}^{-1}\), the longest rotational relaxation time is approximately 0.7 s. This estimated value of the longest relaxation time together with the relationship between rotational relaxation time and length (Equation 2.33) yields 1.5 \(\mu\text{m}\) as the estimated length for the longest entities present in the HiPco sample (the diameter is nearly
immaterial for the determination of the relaxation time). Figure 4.1 shows that shear thinning is incipient at 0.3 s\(^{-1}\), near the lowest shear rates that can be measured within the limit of the torque transducer.

The specific intrinsic viscosity of typical SWNTs (Figure 4.1) is \([\eta_0] = \eta_0/\rho \approx 5.7 \text{ m}^3/\text{kg} = 57 \text{ dl/g}\). This value is comparable to or greater than the highest reported values for high molecular weight poly(p-benzamide) (PBA) in sulfuric acid (Mark 1999) (\([\eta_0]_c = 12.5 \text{ dl/g}\) for \(M_w = 64400 \text{ g/mol}\), i.e., \(L \approx 400 \text{ nm}\)), poly(benzobisthiazole) (PBT) in methane sulfonic acid (Berry, Wong et al. 1979) (\([\eta_0]_c = 26.5 \text{ dl/g}\) for \(M_w = 37000 \text{ g/mol}\), i.e., \(L \approx 190 \text{ nm}\)), large poly(benzobisoxazole) (PBO) in methane sulfonic acid (Roitman, Wessling et al. 1993) (\([\eta_0]_c = 50 \text{ dl/g}\) for \(M_w \approx 230000 \text{ g/mol}\), i.e., \(L \approx 390 \text{ nm}\)), and for very large molecules of xanthan (Takada, Sato et al. 1991) (\([\eta_0]_c = 71 \text{ dl/g}\) for \(M_w \approx 5.4 \text{ Mg/mol}\), i.e., \(L \approx 2.78 \mu\text{m}\)).

The measured aspect ratio, \((L/D)_{KAB} = 470 \pm 30\) and maximum length \(L \approx 1.5 \mu\text{m}\) compared well with viscosity (Parra-Vasquez, Stepanek et al. in preparation) and AFM (Islam, Rojas et al. 2002) measurements of individual tubes stabilized in pluronic surfactants; this provided the first suggestion that SWNTs in superacids dissolve as individuals instead of small bundles as originally hypothesized. Individual dissolution of SWNTs in superacids was proven through the use of two additional techniques: small angle neutron scattering (SANS) and atomic force microscopy (AFM). SANS of SWNTs in 102\% D\(_2\)SO\(_4\) showed that below 130 ppm vol. the SWNTs acted as dispersed rods (Zhou 2005). In addition, AFM images of SWNTs in 102\% H\(_2\)SO\(_4\) spin coated onto
silica wafers and rinsed with isopropanol and water, contained individual SWNTs (Figure 4.2).

Figure 4.2. AFM height image of individual SWNT (height less than 2 nm) obtained from 73 ppm vol. sample of SWNTs in 102% H₂SO₄. The batch used in this experiment was produced during attempts to produce longer SWNTs using the HiPco process.

4.3 Applications of Dilute Phase Behavior

Establishing that SWNTs in superacids dissolve as individuals and behave as Brownian rods resulted in two new techniques: functionalization of individualized SWNTs in superacids (Hudson, Casavant et al. 2004) and determination of the average aspect ratio of bulk samples of unpurified or purified SWNTs (Pasquali, Davis et al. 2005; Parra-Vasquez in preparation). Hudson et al. (2004) produced water soluble SWNTs by exploiting the individual solubility of SWNTs to functionalize large quantities of individual SWNTs with aromatic hydrocarbons. Prior to the discovery that SWNTs dissolve as individuals in superacids, they could only functionalize the outer surface of SWNT bundles or functionalize small quantities of individual SWNTS obtained through the time consuming surfactant stabilization process (Moore, Strano et al. 2003).
4.3.1 Motivation for rheological determination of SWNT length

SWNT diameter determination has long been possible through TEM and spectroscopic measurements. However, length determination has relied solely on AFM measurements. Rapid, reproducible measurement of the length of a statistically significant sample of SWNTs is important to understanding the impact of reactor conditions, purification, and proposed methods for cutting SWNTs. Since SWNT diameter varies only slightly (0.8 to 1.6 nm) compared to length (50 nm to 10 μm), the rheological measurement of SWNT aspect ratio provides a reasonable estimate of SWNT length.

Historically, determining average SWNT aspect ratio has relied on AFM measurements of dried samples of surfactant stabilized SWNTs. Such measurements neglect both the possible changes in length distribution resulting from sonication during SWNT dispersion as well as the possible exclusion of longer more difficult to debundle SWNTs during centrifugation. In addition, the reliability of historical AFM results was hindered by the small sample size (hundreds of SWNTs), and potential sample bias during sample deposition or imaging. More recently, dodecylated SWNTs (Liang, Sadana et al. 2004) have been used for AFM length determination. This results in less bias since the functionalization process itself does not appear to affect SWNT length, the bath sonication steps are much milder than the horn sonication needed to obtain surfactant dispersions, and no centrifugation is performed. In addition, dodecylated SWNTs provide higher coverage of the AFM sample resulting in more statistically significant sample sizes (thousands of SWNTs). In addition, recently developed software makes quantification more objective than the old technique of each researcher using his or her own criteria to determine which SWNTs were truly individuals and
which and how many SWNTs to measure. However, even using dodecylated SWNTs may give inaccurate results as longer SWNTs or more defected SWNTs may still undergo some breakage during the functionalization process. In contrast, rheological determination of the average length provides and unbiased measurement of a much larger quantity ($10^{13}$ SWNTs).

The primary advantage of AFM is that it provides detailed information on the SWNT length distribution. However, progress in refining the relationship between rheological behavior and length to account for polydispersity has made it possible to determine the length distribution from rheological measurements. As described in Chapter 2.5.1, the contributions of SWNTs of different lengths to the dispersion viscosity are additive and equivalent to the ratio of the third and first moments of the length distribution

$$\frac{L}{D} = \frac{1}{D} \sqrt{\frac{\langle L^3 \rangle}{\langle L \rangle}}$$  \hspace{1cm} (4.4)

Both raw and purified HiPco SWNTs have a log normal length distribution; therefore it has been possible to fit the rheological data to obtain length distributions in good agreement with AFM data (Parra-Vasquez, Stepanek et al. in preparation).

4.3.2 Rheological measurement of unpurified SWNT length

The viscosity average lengths of several batches of unpurified SWNTs dispersed in 102% $\text{H}_2\text{SO}_4$ were measured as part of a parametric study on the impact of HiPco catalyst flow rate on SWNT length, diameter, production rate and impurities. This effort differed from the previous length measurements in that unpurified SWNTs were significantly longer.
than the previously studied purified SWNTs and contained as much as 30 % wt. impurities (Carver, Robert L. Carver et al. 2005).

The longer lengths made it more difficult to precisely determine the average length; longer rods have a longer rotational relaxation time and shear thin at lower shear rates. All samples exhibited shear thinning behavior at 0.1s⁻¹, the lowest experimentally accessible shear rate for all samples. Therefore, the zero shear viscosity could not be obtained. Since the onset of shear thinning occurs when the product of the longest rotational relaxation time $\tau$ and shear rate $\dot{\gamma}$ exceeds $\approx 0.2$ (i.e., the Weissenberg number $Wi = \tau \dot{\gamma} > 0.2$), SWNTs greater than 2 $\mu$m in length were present in all samples. This contrasts with the purified SWNT samples (Chapter 4.2) in which the longest SWNTs were less than 1.5 $\mu$m (Davis, Ericson et al. 2004).

Table 4.1 compares the rheologically determined lengths ($L_{KAB}$) for unpurified SWNTs produced at different catalyst concentrations to the equivalent average length measured by AFM. As the zero shear viscosity plateau could not be accessed for any of the samples, the viscosity at 0.1 s⁻¹ was used in lieu of the zero shear viscosity; therefore the rheologically measured lengths are likely to be somewhat lower than the actual values. For all but the 50 mtorr sample, the rheologically determined average lengths were lower than the AFM average lengths. The effective diameter $D_{eff}$ used to calculate the rheologically measured $L_{KAB}$ from the aspect ratio was the average diameter determined by TEM plus 0.35 to account for the van der Waals distance around the SWNTs. The reported $L_{KAB}$ measured by AFM represents the square root of the ratio of the third and first moments of the distribution calculated from a lognormal fit of the data. Any SWNTs with frequencies less than 0.02 were not included in the data. This
prevented long SWNTs falling well outside the distribution from having a significant influence on the data; the viscosity average length is influenced much more by long SWNTs than the number average length. For example, in (Parra-Vasquez, Stepanek et al. in preparation) the inclusion of one additional SWNT changed the number average length by a mere 3%, but \( L_{KAB} \) by 16%.

<table>
<thead>
<tr>
<th>Catalyst Partial Pressure (mtorr)</th>
<th>Total Reactor Pressure (atm)</th>
<th>Rheo (L/D)_{KAB}</th>
<th>( D_{eff} )</th>
<th>Rheology ( L_{KAB} )</th>
<th>AFM fit ( L_{KAB} )</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>30</td>
<td>1270</td>
<td>1.55</td>
<td>1970 ± 400</td>
<td>2330</td>
<td>16%</td>
</tr>
<tr>
<td>22</td>
<td>30</td>
<td>1360</td>
<td>1.43</td>
<td>1940 ± 340</td>
<td>2030</td>
<td>4%</td>
</tr>
<tr>
<td>52</td>
<td>30</td>
<td>1280</td>
<td>1.44</td>
<td>1840 ± 200</td>
<td>1450</td>
<td>22%</td>
</tr>
<tr>
<td>91</td>
<td>30</td>
<td>1014</td>
<td>1.40</td>
<td>1420 ± 80</td>
<td>1550</td>
<td>10%</td>
</tr>
<tr>
<td>22</td>
<td>10</td>
<td>1200</td>
<td>1.49</td>
<td>1790 ± 90</td>
<td>2240</td>
<td>20%</td>
</tr>
</tbody>
</table>

Table 4.1. Comparison of unpurified SWNT length as measured by rheology and atomic force microscopy (AFM).

The average lengths \( L_{KAB} \)’s determined by rheology are significantly higher than in previous studies where the measured aspect ratios were less than 500 (\( L_{KAB} < 700 \)). The measurement error was also significantly greater, as high as ± 400 nm, compared to previous studies where the error was ± 30 nm or less in all cases (Davis, Ericson et al. 2004; Pasquali, Stepanek et al. filed 2 May 2003; Parra-Vasquez, Stepanek et al. in preparation). The higher error is primarily the result of the longer tubes preventing measurement of the zero shear viscosity; in fact, the error increased with increasing average length. The high impurity levels (20 to 30%) are not thought to have had a significant impact on the results. The impurities themselves should have little to no impact on the rheological measurement as they are small roughly spherical particles
which experience little viscous drag relative to that of the anisotropic SWNTs. However, errors in the quantification of impurities directly impacted the calculated volume fraction of SWNT in the rheology samples and therefore the measured aspect ratio.

4.4 Semidilute Regime

For SWNTs with an average aspect ratio \((L/D)_{KAB} = 470 \pm 30\) (Chapter 4.2), dispersed in 102% \(\text{H}_2\text{SO}_4\), concentrations between 94 ppm and 600 ppm vol. can be collapsed onto a master curve of reduced viscosity versus shear rate (Figure 4.3) that is distinct from that obtained for concentrations in the dilute regime. At low shear rates, these data depart from the dilute mastercurve (Figure 4.1) because the relaxation time is now concentration-dependent and thus the viscosity starts shear thinning at lower shear rates (below the sensitivity of the rheometer’s torque transducer). In the range of 94 to 600 ppm vol. the delay time between successive transient tests required to obtain reproducible data was higher at higher concentrations providing further support of semidilute behavior. Figure 4.3 shows data for an additional batch (HPR 105) demonstrating that the behavior was consistent between batches. The vertical offset between the two batches may have been due to the combination of initial volumetric dilution error as well as differences in the length distribution.
Figure 4.3. Reduced viscosity, \( (\eta - \eta_b)/(\eta_0 \phi) \) versus shear rate for 94 to 452 ppm vol. SWNTs in 100% H\(_2\)SO\(_4\). Filled symbols 94 to 454 ppm vol. SWNT batch HPR 105 September 2002, hollow symbols February 2003 103 to 407 ppm vol. SWNT batch HPR 106.2. Slope of -0.5 is drawn for reference and agrees with the theory of Kirkwood and Plocek. Vertical offset between HPR 105 and HPR 106.2 may be partly due to small differences in the initial volumetric dilution or slight differences in the length distribution.

The semidilute concentration range determined by steady shear rheology contrasts with that obtained by optical microscopy and oscillatory rheology measurements. Based on optical microscopy, a small amount of liquid crystalline phase forms between 100 to 300 ppm vol. (Chapter 4.5). Similarly, oscillatory rheology suggests that the semidilute regime extends to only about 300 ppm vol.; concentrations between 440 and 1170 ppm show different rheological behavior consistent with the transition to a biphasic system (Figure 4.30 and Figure 4.31). These slight discrepancies are likely due to the volume fraction of anisotropic phase that forms at hundreds of ppm SWNTs is too low to appreciably alter that the rheological behavior under steady shear. Measurements of the critical concentration at which the anisotropic phase first forms \( \phi_t \) using UV-vis-nIR the technique (Chapter 5) suggest that the liquid crystalline phase forms at approximately 100 ppm vol. However, these results are not directly comparable to the rheology studies;
due to SWNT availability, the SWNTs used in these studies were two to three times longer than the SWNTs used in the rheology studies.

4.5 Biphasic Regime

Optical microscopy shows that between 100 and 300 ppm vol. (0.01 to 0.03 % vol.) the system becomes biphasic; the SWNTs self-assemble into seemingly endless strands of supramolecular aggregates (Figure 4.4). The total volume fraction of strands increases with concentration, but the morphology of the strands appears to be constant, although at higher concentrations overlap between strands makes clear visualization impossible. The strands are in equilibrium with the isotropic phase and are termed hereafter “SWNT spaghetti.” The SWNT spaghetti are nematic liquid crystalline domains where tubes are free to translate along the length of the strand (Figure 4.4). Imaging successive z-planes shows that the strands continue through multiple focal planes and fails to reveal any ends. The constant optical density along the length of the strand suggests that the spaghetti have a uniform diameter below 600 nm (part of the measured diameter is due to diffraction). The “spaghetti morphology” of the biphasic region is markedly different from the globular morphology seen in the biphasic region for rigid rod polymers. This difference is due to a combination of factors: 1) solvent quality, 2) SWNT persistence length, and 3) the log-normal distribution of SWNTs. These factors are discussed in more detail in Chapter 5. In addition, the morphology may be related to the perfectly cylindrical geometry and the attractive forces between SWNTs.
Figure 4.4. SWNT spaghetti in 0.32 % vol. (0.25 % wt.) solution of SWNTs in 102% H₂SO₄ imaged on a Zeiss Axioplan microscope with 63x DIC, 1.4 NA oil immersion objective with 2.5x magnification in front of the camera; the scale bar is 20 μm (left). A digitally enhanced, magnified section of the image at left, showing the size and uniformity of the spaghetti; the scale bars is 10 μm (right).
4.6 Single-Phase Nematic Liquid Crystal

The behavior of SWNTs in superacids was compared to the known criteria for liquid crystalline species described in Chapter 2. The results of optical microscopy, steady shear rheology and formation of solid aligned species experiments are described below. The viscoelasticity data presented in Section 4.8 provide additional proof of the formation of a single-phase nematic liquid crystal.

4.6.1 Optical microscopy

Optical microscopy shows that the fraction of the SWNT spaghetti phase increases as the bulk concentration of SWNTs is raised, until only the SWNT spaghetti is present - a single phase polydomain lyotropic nematic liquid crystal exists above 5.1 % vol. (4 % wt.) SWNTs in 102% H₂SO₄. The transition to a single phase was determined by the absence of a meniscus of SWNT-poor liquid in the sample. The liquid crystalline dispersions are highly birefringent and the domains go bright and dark as the sample is rotated based on their relative alignment between their director and the polarization vector of the light.

The polydomain structure in Figure 4.5 is believed to be the result of spaghetti strand coalescence. On large length scales (~100 μm), the domains are randomly oriented with respect to each other. Characteristic Schlieren textures are visible in Figure 4.5 as a result of the defects between domains. As discussed in Chapter 2, the healing time for defects at the boundaries of the spaghetti strands is expected to be quite long, this contributes to the large number of domains.
Figure 4.5. 5.1 % vol. (4 % wt.) SWNT under cross polarized light on a Nikon E600 microscope with 20 x NA 0.5 objective. The domains become bright and dim as the sample is rotated. The circle shows a characteristic Schlieren texture arising from defects between domains.
4.6.2 Steady shear rheology

The nematogenic nature of SWNT-superacid solutions is further evidenced by key rheological signatures unique to lyotropic liquid crystals formed by high-molecular weight rod-like molecules: 1) in transient shearing tests the shear stress and first normal stress difference oscillate for approximately 100 shear units or more before reaching steady state, 2) the viscosity-concentration curve has a maximum, 3) the viscosity versus shear rate curve often shows three distinct regions, usually termed Regions I, II, and III, 4) with increasing shear rate, the first normal stress difference N₁ changes sign from positive to negative and back to positive, and 5) the Cox - Merz rule is not obeyed.

The first criteria, the shear stress and first normal stress difference oscillation for approximately 100 or more shear units (a shear unit is the product of shear rate and time), had a direct impact on all the steady shear rheology experiments. This behavior is quite different from that of isotropic suspensions and polymer solutions, where oscillatory transients last a few shear units at most (Marrucci 1991). Long oscillatory transients were displayed by all concentrated samples ($\phi > 4.5 \%$ vol.). For example, Figure 4.6 shows that the response of 7.6 \% vol. SWNT - superacid to start-up of steady shearing at shear rate 5 s⁻¹. Both the shear viscosity and the first normal stress difference oscillate for over 800 shear units. In other words, obtaining a single true steady state measurement would require more than 80,000 s (22 hours) at a shear rate of 0.01 s⁻¹, 8000 s (2.2 hrs) at a shear rate of 0.1 s⁻¹, and 800 s (0.2 hrs) at a shear rate of 1 s⁻¹. As a result, obtaining very accurate data, particularly first normal stress difference data, at low shear rates was problematic. For this reason, while low shear behavior was explored for some samples, most samples were not tested at shear rates below 0.1 s⁻¹.
Figure 4.6. Response of 7.9 % vol. (6 % wt.) SWNT in 102 % H_2SO_4 to start up of shear flow in 25 mm parallel plates at a shear rate of 5 s^-1. Solid diamonds represent viscosity; open triangles represent N_1.

The approximate time to steady state determined by the response to the start-up of shear (transient test) was used to determine what the shearing and measurement times to input into the rheometer software's 'steady rate sweep' test protocol where viscosity is measured at a series of increasing shear rates. The delay time was chosen to obtain a steady shear viscosity within about 10 % of the viscosity obtained during the transient test; the measurement time was chosen to obtain an average over one oscillation. Comparison of transient tests conducted on multiple loadings to the 'steady rate sweep' tests shows that the viscosity was not significantly influenced by measurement of the same sample at multiple shear rates. For example, the transient and steady rate sweep data for a 5.1 % vol. (4 % wt.) sample compare very well even at low shear rates (Figure 4.7).
Figure 4.7. Comparison of steady shear and transient data for 5.1% vol. (4.0 % wt.) SWNT in 102% H₂SO₄. Solid diamonds represent results obtained during continuous measurement at increasing frequency and triangles represent individual measurements of the steady state reached after the start-up of shear.

The adherence of SWNT - superacid dispersions to the second criteria, a non-monotonic relationship between viscosity and concentration, is depicted in Figure 4.8. The transition from a biphasic system to a single phase liquid crystal occurs in the concentration range between the maximum and the minimum in viscosity (Kiss 1979); thus, based on the steady shear rate data, the single phase nematic liquid crystal forms at a critical concentration φₙ between 3.5 and 5.1 % vol.%, a higher concentration than that estimated by Onsager (3.34 D/L ~ 1 % vol. for an number average aspect ratio of 350). As discussed in Chapter 5, this discrepancy is largely the result of SWNT polydispersity.
Figure 4.8. Relationship between viscosity and concentration for SWNTs in 102% H₂SO₄ at a shear rate of 0.1 s⁻¹. The system transitions to a single phase liquid crystal between the maximum at ~3.5 % vol. and the minimum at ~5.1 % vol. The error bars represent the standard deviation obtained by measuring three different samples.

The yield stress of the SWNT - superacid dispersions also exhibits non-monotonic relationship with concentration (Figure 4.9). The yield stresses, the stresses at which the viscosity decrease by greater than an order of magnitude, for the 1.9 and 5.1 % vol. dispersions are nearly equivalent. In contrast, the yield stress for the 3.5 % vol. dispersion is higher than that of the 7.6 % vol. dispersion. Many polymeric and mineral lyotropic liquid crystals formed by high-molecular weight rod-like molecules exhibit a yield stress (Marrucci 1991; Davidson, Gabriel et al. 1993; Wierenga, Philipse et al. 1998). However, yield stress alone is not a hallmark of liquid crystallinity; many systems such as concentrated suspensions and emulsions (e.g. paints, toothpaste, and mayonnaise) also exhibit a yield stress. Characterization of the yield stress is important to the design of fiber spinning or other SWNT-superacid processing equipment as the yield stress must be overcome for processing.
Figure 4.9. Dispersions greater than 1.9 \% vol. display a significant yield stress. The 1.9 and 5.1 \% vol. data have a similar yield stress in agreement with being on either side of the maximum of the viscosity concentration curve. However, the 7.9 \% vol. sample has a higher yield stress.

The third and fourth criteria, the three region viscosity versus shear rate curve and the first normal stress difference N1 changing sign with increasing shear rate and are depicted in Figure 4.10. At 4.5 \% vol., the dispersion is predominantly anisotropic. Notably, the viscosity decreases at low shear rates, seems to plateau at shear rate $\dot{\gamma} \approx 1 \text{ s}^{-1}$, and then shear thins at $\dot{\gamma} > 3 \text{ s}^{-1}$ (Figure 4.10). The narrowness of the plateau makes it difficult to conclusively state that the viscosity versus shear rate curve exhibits three region behavior. However, the reproducibility of the small plateau and the fact that N1 becomes negative at a similar shear rate strongly suggest the presence of three region behavior (Larson 1999). In addition, the onset of Region III (shear aligning behavior) at very modest shear rates $\approx 3 \text{ s}^{-1}$ is consistent with the facile alignment of SWNT-superacid dispersions. As the shear rate exceeds a critical value (about 10 s$^{-1}$ for 4.5 \% vol.), the
SWNT - superacid dispersion ejects itself from the rheometer gap. Figure 4.10 also shows that at low shear rates, N1 is positive and increases with shear rate; this behavior is also observed in polymer solutions. At a critical shear rate, N1 suddenly drops and switches to a large negative value. As shear rate is increased further, N1 begins to become positive once again (Kiss 1979; Grizzuti, Cavella et al. 1990; Baek, Magda et al. 1994; Kiss and Porter 1998); whether or not positive values were reached for a given sample depending on sample loading and the shear rate at which the sample was expelled from the gap.

![Graph showing viscosity vs. shear rate](image)

Figure 4.10. Viscosity (triangles) versus shear rate for 4.5 % vol. (3.5 % wt.) SWNT in 102 % H₂SO₄ measured on 25 mm cone and plate (cone angle = 0.04 radians). N1 (circles) is the thrust on the plate divided by the plate area. The behavior is indicative of the three region behavior seen with some liquid crystalline polymers and shear alignment at shear rates > 3 s⁻¹. The sign changes in first normal stress difference are also characteristic of liquid crystallinity.

The facile alignment of SWNTs at low shear rates is manifested in the high degrees of collective alignment in SWNT fibers produced by simply pushing the SWNT - superacid dispersion through a syringe needle into a coagulation bath (Ericson; Vavro, Llaguno et al. 2003; Ericson, Fan et al.) as shown in Figure 4.13. In addition, the ability
of the ropes to align under shear was directly seen in a nearly solid sample, removed from
the top of the Daca screw. The sample was dried under ambient conditions (without
quenching in ether). SEM of the uncoated sample showed clear alignment of ropes along
the direction of rotation which could have only resulted from the shear experienced
during mixing Figure 4.11.

Figure 4.11. A sample of 6 % wt. in 102% H₂SO₄ from the top of the Daca screw at two different
magnifications showing alignment of ropes resulting from mixing.

The fifth rheological signature demonstrated by liquid crystalline SWNT -
superacid dispersions is that the steady and complex viscosities do not exhibit the same
behavior as a function of shear rate and frequency (Grizzuti, Cavella et al. 1990;
Marrucci 1991) — i.e., the Cox - Merz rule is not obeyed (Figure 4.12). For
concentrations at which there is an appreciable, but not predominant, portion of liquid
crystalline phase, the Cox - Merz rule is obeyed, but it is not obeyed at higher
concentrations. For example, at 0.32 % vol. (0.25 % wt.) SWNT in 102% H₂SO₄, the
steady and oscillatory data overlay well with the exception of minor deviations at low
shear rates. For concentrations greater than 1.9 % vol. (1.5 % wt.), the data did not
overlay as shown in for 7.6 % vol. (6 % wt.) SWNT in 102% H₂SO₄ (Figure 4.12).
Figure 4.12. Comparison of steady and dynamic shear viscosity for 0.34 % vol. (top) and 7.6 % vol. (bottom) SWNTs in 102% H₂SO₄. Except for a slight deviation at low shear, the Cox – Merz rule is obeyed for the 0.34 % sample; the steady and dynamic shear viscosities overlay almost perfectly. The Cox – Merz rule is obeyed for the 7.6 % vol. dispersions. Triangles: dynamic viscosity, \( \eta^\ast \), versus frequency, \( \omega \). Squares: steady shear viscosity \( \eta \) versus shear rate \( \dot{\gamma} \).
4.6.3 Formation of solid aligned species

In addition to optical and rheological signatures in the liquid state, the nematic structure of SWNT - superacid dispersions is evident in scanning electron microscopy of materials quenched from the high concentration dispersions. Scanning electron microscopy of ether-quenched SWNT - superacid dispersions shows that the SWNTs are free to rearrange into a variety of aligned species (Figure 4.13). Bucky-papers prepared from SWNT - superacid dispersions show the typical mat of entangled ropes. The introduction of moisture into the system deprotonates the nanotubes, reduces the electrostatic stabilization, and causes the precipitation of tactoid structures similar in shape to those formed by inorganic liquid crystals such as vanadium pentoxide (Davidson, Bourgaux et al. 1995; Davidson, Batal et al. 1997; Sonin 1998). In the absence of moisture, the same starting concentration can be used to make highly aligned fibers with 20:1 axial to perpendicular alignment even in the absence of drawing (Ericson 2003; Smalley, Saini et al. 2003; Ericson, Fan et al. 2004) as well as well-ordered sheets (Bhattacharyya, Sreekumar et al. 2003).

4.6.4 Bucky-paper ropes

Scanning and transmission electron microscopy (SEM and TEM) show that SWNTs form bundles in the production process. These so-called “primordial” ropes are roughly 15 nm in diameter. Dried dispersions of SWNTs individually dispersed in surfactants show similar ropes on the order of 14 nm diameter (Figure 4.14). In contrast, SWNTs dispersed in superacids, quenched in ether and filtered show the formation of much larger
Figure 4.13. Rearrangement of SWNTs into aligned species. A 5.4 vol. (4 wt.) dispersion (a) can be quenched into ether and filtered resulting in a Bucky-paper of entangled ropes, (b) introduced to moisture resulting in the formation of aligned tactoids called alewives which have 14:1 alignment along their axis as measured by Raman, (c) extruded as an anhydrous dispersion through a syringe needle resulting in the formation of an aligned fiber with 20:1 alignment as measured by Raman.
ropes up to hundreds of nm in diameter (super-ropes). Within each rope the SWNTs are aligned, but the ropes themselves are entangled. This shows that SWNTs in superacids are not a crystal, they are free to rearrange into aligned species. The formation of SWNT ropes is very similar to what is seen for sols of $V_2O_5$, one of the more studied mineral liquid crystals, showing that while SWNT superacid dispersions have similar characteristics with lyotropic polymeric liquid crystals, they also share characteristics with lyotropic mineral liquid crystals.

![Image](a)

![Image](b)

![Image](c)

Figure 4.14. a) Bucky - paper from 6 % wt. SWNT in 102% H$_2$SO$_4$: rope diameter ~ 200 nm (Davis, Parra-Vasquez et al. 2003). b) Typical Bucky - paper from SWNT surfactant solution rope diameter ~ 14 nm c) Blitz sol of vanadium pentoxide rope diameter ~ 14 nm (Sonin 1998).

### 4.6.5 Alewives

The exposure of SWNTs dispersed in 100 to 123% sulfuric acid to moisture results in the formation of highly aligned tactoids which are relatively monodisperse in size for a given
concentration of SWNTs; lower concentrations result in smaller tactoids (Smalley, Hauge et al. 2001; Davis, Ericson et al. 2004; Ramesh, Ericson et al. 2004). These tactoids are highly birefringent and clearly visible by optical microscopy (Figure 4.15). Potential alewife applications include transportation of bulk quantities of aligned SWNTs, and incorporation into nanotube based devices as well as polymer - nanotube composites (Smalley, Hauge et al. 2001). For 5.4 % vol. SWNTs in 102 – 123% H₂SO₄, slow moisture contamination, such as exposure to ambient moisture (particularly above ambient temperatures) results in the formation of tactoids approximately 20 μm in length and 5 μm in diameter. The tactoids form as the result of OH⁻ causing the SWNTs to partially deprotonate (Ramesh, Ericson et al. 2004). The nanotubes rearrange into a highly aligned bundled tactoid structure to minimize their surface to volume ratio. The fact that tactoid structures result from the rearrangement of SWNTs and are not the result of deviations from the initial dispersion process is supported by Figure 4.16; this SEM image of a dispersion of SWNTs inadvertently exposed to moisture shows both the presence of tactoids and ropes. The forces governing the exact size and shape of the tactoids are not well understood, but are clearly related to concentration; lower concentration SWNT dispersions result in smaller tactoids. In addition, there is a time scale for rearrangement particularly for high concentration, high viscosity dispersions. Figure 4.16 depicts alewives of various lengths and diameters, but all other studies of have shown a fairly monodisperse size (Figure 4.15, Figure 4.17, Figure 4.18).
Figure 4.15. Alewives from 5.1 % vol. (4 % wt.) SWNT in 100 % H₂SO₄ observed without (left) and with (right) cross polarized light. Scale bars represent 100 µm.

The high degree of alignment within the alewives is visually apparent. Alewives in superacid are highly birefringent (Figure 4.15); in addition, SEM of ether quenched samples of alewives show a high degree of alignment along their axes. The dimensions of the solid alewive are are approximately the same as that of alewives in sulfuric acid suspensions; this implies that alewives are not a liquid crystalline phase but a crystal solvate phase where the nanotubes become fixed in a lattice with little to no free solvent between them. The relative degree of alignment was quantified by comparing the intensity of the G peak with the laser aligned parallel to an alewive’s long axis to the intensity with the laser aligned perpendicular the long axis. Probing the metallic and semiconducting SWNTs with 514 and 782 nm lasers respectively suggests the semiconducting SWNTs are more highly aligned (Figure 4.18). SWNTs at the interior of the alewives are more highly aligned than those at the exterior; therefore the Raman data suggests that the semiconducting SWNTs are in the interior and are shielded from the solvent by metallic SWNTs. This is consistent with the hypothesis that metallic SWNTs are more soluble in superacids than semiconducting SWNTs.
Figure 4.16. Alewives surrounded by ropes in moisture-contaminated Bucky - paper made from 7.6 % vol. (6 % wt.) SWNT in 102 % H₂SO₄ mixed in the Daca at 110 °C for thirteen days. The contamination is believed to have come from moisture entering the outlet of the syringe.
Figure 4.17. Ether quenched 4wt% SWNT – 120% H₂SO₄ samples containing alewives under the SEM (Pasquali, Davis et al. 2001).

Figure 4.18. Raman spectroscopy of alewives. The alewives as seen in the image screen (top). The intensities of the G peaks parallel and perpendicular to the alewife axis using 782 nm (left) and 514 nm (right) lasers. Both spectra show a high degree of alignment, but the alignment is more pronounced in the spectra obtained using the 782 nm laser which primarily probes semiconducting SWNTs (Pasquali, Davis et al. 2001).

Just as anisotropic species capable of forming mineral liquid crystals such as vanadium pentoxide showed similar rope structures as SWNTs in superacids, they also form tactoid structures upon changes to their chemical environment. Figure 4.19 shows tactoids formed from vanadium pentoxide sols.
4.6.6 Fiber Spinning

The liquid crystallinity of SWNT superacid dispersions directly impacts the production of pure highly aligned SWNT fibers. Even the very first fibers produced by forcing 5.2 % vol. (4 % wt.) SWNT-120% H₂SO₄ dispersions through a 25S (ID=150 μm) HPLC syringe needles had a remarkable degree of alignment; a relative alignment of 12:1 in the axial to perpendicular direction was measured by Raman spectroscopy; the alignment is visually apparent in SEM images. The fibers consist of a hierarchical structure of SWNT bundles; SEM images show that the fiber surface consists of well-aligned ropes of carbon nanotubes approximately 1 μm in diameter (Figure 4.20). Imaging of the cross section of fibers shows that the highly aligned bundle structure persists throughout the cross section of the fiber (Figure 4.21). This contrasts with fibers produced by the CNRS spinning process which possess a skin - core morphology in which the outer surface of the fiber has a high degree of shear alignment while the core of the fiber has little alignment (Vigolo, Penicaud et al. 2000; Vigolo, Poulin et al. 2002; Neimark, Ruetsch et al. 2003).
Figure 4.20. SEM image of a 75 µm diameter fiber from 5.2 % vol. (4 % wt.) SWNT – 120 % H$_2$SO$_4$ dispersion. Scale bar is 20 µm top and 2 µm bottom (Davis, Ericson et al. 2001).
Figure 4.21. Cross sections of fiber spun from a 5.1 % vol. (4 % wt.) SWNT in 102 % H₂SO₄ dispersion and coagulated in dilute sulfuric acid. The bundled structure persists across the fiber cross section. Scalebars are 20 μm (top) and 10 μm (bottom).
As shown in the higher magnification image in Figure 4.20, the early fibers had a significant void fraction. Rough measurements of fiber density gave a result of approximately 0.6 g/cc which is roughly one third of the theoretical value. The voids in the early fibers were due to the combination of spinning from a biphasic dispersion, limited extensional flow, and a lack of drawing. The coagulation process also had a significant impact: the diethyl ether channeled into the fiber and prevented complete fiber densification by creating multiple coagulation fronts and occupying volume. Many of the fibers visibly shrank when removed from the bath to air, as a result of ether evaporating from the fiber. The fibers’ irregular dogbone shape (Figure 4.22 and Figure 4.23) provides further evidence diethyl ether resulted in too rapid coagulation (Ziabicki 1976; Ericson 2003). Interestingly, the tendency for SWNTs to align is so strong that they generally align even along macroscopic changes in the SWNT’s outer diameter, in some case giving an appearance reminiscent of rings in a tree (Figure 4.24).

![Image of fiber structure](image)

**Figure 4.22.** Macrostructure of fiber extruded from 5.2 % vol. (4 % wt.) SWNT in 120% H₂SO₄. The early fibers had non-uniform diameters due to the difficulty of manually controlling flow rate through the syringe. The dogbone structure is due to too rapid coagulation.
Figure 4.23. Dogbone structure of 5.2 % vol. SWNTs in 120% H₂SO₄ coagulated in diethyl ether. Scalebar is 20 µm.

Figure 4.24. Microscopic SWNT alignment follows the macroscopic curvature of a fiber like rings in a tree. The fiber was spun from 5.2 % vol. (4 % wt.) SWNT in 120 % H₂SO₄ and coagulated in diethyl ether and has a clear hierarchical bundle structure. Scalebar is 10 µm.

The major focus of SWNT fiber research has been removing the defects between fiber bundles such as breaks between ropes (Figure 4.25). This has largely been achieved by optimizing the entire spinning process: dispersion, mixing and spinning conditions,
coagulation and post processing. This optimization process has included spinning from fully liquid crystalline dispersions, slower coagulation in water at ambient and sub-ambient temperatures, and drying the fibers on spools. These efforts have resulted in fibers with fewer breaks between ropes and promising properties such as a Young’s Modulus of 120 GPa. More details on the production of fibers from SWNT liquid crystalline dispersions can be found in Ericson 2003 and 2004.

Figure 4.25. Breaks between SWNT bundles created defects in the early fibers. Eliminating the defects has been the major focus of SWNT fiber spinning research and largely has been achieved through optimization of the dispersion, fiber spinning and coagulation processes (Ericson, Fan et al. 2004). Scalebar is 2 μm.

4.7 Effect of Temperature on Rheology and Phase Behavior

Understanding the impact of temperature on SWNT-superacid rheology and phase behavior is critical to determining optimum fiber spinning conditions. For lyotropic polymeric liquid crystals, increasing temperature typically improves solvent quality and reduces viscosity enabling easier processing. However, for polymers and for SWNTs,
processing at increased temperatures not only results in increased energy costs but an increased likelihood of oxidation and other degradation reactions. Therefore, temperature studies are an important part of characterizing a lyotropic nematogenic system.

Optical microscopy studies of SWNT-superacid phase behavior showed temperature had little to no impact on phase behavior between ambient and approximately 100 °C. Mineral liquid crystals, which like SWNTs are much more rigid (higher persistence length) objects than rod-like polymers display a similar temperature insensitivity (Gabriel and Davidson 2003). For such systems, phase behavior can only be controlled by changing the chemical nature of the solvent. The impact of the solvent on the phase behavior of SWNT - superacid dispersions is discussed in Chapter 5.

In terms of rheology, an increase in temperature is usually equivalent to a decrease in the viscoelastic time scale. This well known time - temperature superposition principle is commonly used to generate master curves for polymer melts and isotropic polymer solutions. For a solution of rods, time - temperature superposition has been shown to be valid as long as the order parameter is not a strong function of temperature (Huang, Magda et al. 1999). Figure 4.26 shows how this principle can be applied to a dilute solution of SWNTs (102 ppm vol. in 102% H$_2$SO$_4$). The overall solution viscosity decreases with temperature, but rescaling the x and y axes to account for the temperature dependence of solvent viscosity and SWNT relaxation time results in a master curve. The effect of solvent viscosity temperature dependence is eliminated by plotting the specific viscosity $(\eta - \eta_s(T))/\eta_s(T)$, and the temperature dependence of relaxation time is accounted for by plotting the Weissenberg number $\tau\dot{\gamma}$. The mean relaxation time $\tau$ was determined by fitting the raw data (Parra-Vasquez, Stepanek et al. in preparation).
Similar behavior was seen in the semidilute regime (Figure 4.27). However, since models have not yet been developed to calculate the relaxation time in the semidilute regime, a shift factor of $\eta_s L^3/k_B T$ was used to nondimensionalize the x-axis; this semi-empirical procedure resulted in near perfect collapse onto a master curve.

In contrast, between 25 and 70°C the viscosity of a 0.19 % vol. dispersion is nearly independent of temperature, with some slight deviations at very low and high shear rates (Figure 4.28). This concentration is slightly higher than the concentration at which the spaghetti have percolated to form a continuous structure (Chapter 4.8.2) resulting in the stresses being transmitted through the SWNT spaghettis instead of the solvent. Rescaling the data in the same manner as for the semidilute solution removes the inflection points in the curve, but increases the spread in the data; this is likely due to the multiple relaxation times inherent in a biphasic system or polydisperse rods.

For 2.6 % vol. (2.0 % wt.) SWNTs in 102% H$_2$SO$_4$, the viscosity was sufficiently high to be able to perform characterization on the RDA III at temperatures up to 100 °C (Figure 4.29). The higher error in viscosity measurements at this concentration make the impact of temperature somewhat more difficult to discern. At 25 °C the viscosity is somewhat higher than at the other temperatures, particularly between 1.7 and 7.9 s$^{-1}$. In addition, at 100 °C the viscosity appears to decrease more rapidly at low shear rates than for the other temperatures, and the Region II plateau is slightly more apparent. However, in general there appears to be little temperature dependence; this is consistent with the stress being conducted by the liquid crystalline phase. Applying the same shift factors used for the other concentrations improves the overlap for all but the 100 °C sample Figure 4.29.
Figure 4.26. The viscosity of 104 ppm vol. (80 ppm wt.) HPR 123.1 in 102% H$_2$SO$_4$. The solution viscosity decreases with temperature (top). Replotting the data as specific viscosity $(\eta-\eta_s)/\eta_s$ versus Weissenberg number $\tau_m \dot{\gamma}$ accounts for the temperature dependence of solvent viscosity and rotational relaxation time resulting in a master curve (bottom).
Figure 4.27. The viscosity of 390 ppm vol. (300 ppm wt.) HPR 123.1 in 102% H₂SO₄. The solution viscosity decreases with temperature between 25 and 70 °C (top). Rescaling the data by plotting specific viscosity \((\eta - \eta_s)/\eta_s\) against a shift factor time the shear rate \(\dot{\gamma}\) again results in a master curve. Since the rotational relaxation time at this semidilute concentration is not known, the Weissenberg number could not be calculated and the x-axis was made dimensionless by using the shift factor \(\eta_s L^3/k_B T\) to obtain a master curve.
Figure 4.28. The viscosities of the biphasic dispersions of 0.19 % vol. (0.15 % wt.) in 102% H₂SO₄ overlap almost perfectly between 25 and 70 °C (top). As for the 300 ppm dispersion, the axes were made dimensionless by plotting specific viscosity (η−ηₛ)/ηₛ against the shear rate γ times the shift factor ηₛL²/k₅T.
Figure 4.29. The viscosity of 2.6 % vol. (2.0 % wt) in 102% H₂SO₄. The error in viscosity measurements at this concentration is large because it is near the maximum in the viscosity versus concentration curve. The data overlap reasonably well although the 100 °C data has a more pronounced plateau (Region II behavior). Making the axes dimensionless by plotting the specific viscosity (η−η₀)/η₀ against the shear rate ɣ times the shift factor η₅L³/κ₀T yielded better overlap than for the 0.19 % vol. biphasic dispersion.
4.8 Viscoelasticity of SWNTs in 102% $\text{H}_2\text{SO}_4$

The viscoelasticity of SWNT-102% $\text{H}_2\text{SO}_4$ dispersions was investigated by conducting oscillatory shear tests on the dispersions. The results provided additional support to the liquid crystalline phase behavior described in the previous sections.

4.8.1 Determination of the linear viscoelastic region

The extent of the linear viscoelastic region was determined by measuring the response of the system to increasing strain rate. Concentrations greater than 3000 ppm vol. were tested at 6.28 rad/s in the small or large parallel plate geometries, and concentrations less than 3000 ppm vol. were generally tested at frequencies between 12.56 and 62.8 rad/s using the large Couette fixture. The frequency and geometries were chosen to obtain sufficient torque to get measurable values at low strain. Several concentrations were tested in different geometries, and at different frequencies, to verify that these variations did not significantly impact results.

As for many complex fluids, SWNT-102% $\text{H}_2\text{SO}_4$ dispersions have a linear viscoelastic region where the elastic ($G'$) and viscous ($G''$) modulus are constant below a critical strain $\gamma_c$. Above $\gamma_c$ the elastic and viscous moduli decrease with frequency; larger values of $\gamma_c$ are indicative of a more stable microstructure. Since $\tan(\delta) = G''/G'$ it provides a useful means of comparing $\gamma_c$ at different concentrations (Figure 4.30). The differences in critical strains at different concentrations provide further support to the phase boundaries described earlier in this chapter. For the 0.005 % vol. samples, $\tan(\delta)$ was approximately 6.4 across the range of 1 to 100 % strain; the entire measured range of strains was within the linear viscoelastic region. This provides further support that at
Figure 4.30. The ratio of the viscous to elastic modulus tan(\(\delta\)) versus % strain for 0.005 % vol. < \(\phi\) < 12.59 % vol SWNTs in 102% H\(_2\)SO\(_4\). The significantly smaller \(\gamma_c\) for 0.34 – 12.59 % vol. is in agreement with the formation of a significant amount of anisotropic domains.
0.005 % vol. SWNT in 102% H₂SO₄ is a dilute isotropic structureless fluid. For 0.024 and 0.030 % vol. SWNT, tan(δ) was 3.5 up to γᵣ = 10%; it then increased indicating the increasing dominance of the viscous modulus at higher strains. This is consistent with the previous assessment that concentrations in this range are semidilute. In the linear viscoelastic region for concentrations between 0.044 and 0.117 % vol., γᵣ = 2.5 % and the value of tan(δ) decreases with increasing concentration reaching a value of 1.5 for the 0.044 % vol. sample. The decrease in γᵣ indicates a more easily perturbed structure; the lower values of tan(δ) indicate that while the viscous contribution is still dominant, elastic contributions become increasingly significant with increasing concentration. Finally, at concentrations, greater than 0.34 % vol., tan(δ) is less than one and γᵣ decreases to approximately 0.1 % strain. The marked decrease in γᵣ is consistent with the emergence of numerous anisotropic domains. The finding that, for SWNTs in 102% H₂SO₄, γᵣ is dependent on phase boundaries is consistent with the system being analogous to a polymeric liquid crystal (Donald and Windle 1992); the finding contrasts with the results of Hough et al. (2004) for a network of SWNTs dispersed in NaDDBS (C₁₂H₂₅C₆H₄SO₃Na). Hough et al. found that above the percolation threshold, γᵣ was a function of concentration and could be normalized by the difference between the absolute and percolation concentrations (Hough, Islam et al. 2004). This difference is likely due to the different inter-SWNT forces in the two systems. Also, in Hough et al., 25 to 45% of the tubes were dispersed as small bundles (diameter less than 5nm) not individual SWNTs. Even for the individually dispersed SWNTs the aspect ratio was L/D < 165 and the study extended only to 3 % vol. SWNT.
4.8.2 Response to oscillatory shear of increasing frequency

Oscillatory shear measurements over a range of frequencies and at a constant strain within the linear viscoelastic region provided additional support to the proposed phase boundaries. For all samples, the maximum strain which was clearly within the linear viscoelastic regime was chosen to maximize the accessible range of frequencies. As in the previous section, $\tan(\delta)$ reveals the phase boundaries of the system (Figure 4.31). Four distinct regimes exist. Region A comprises $0.004 < \phi < 0.005$ % vol.; $\tan(\delta)$ has a plateau value of approximately 15 at low frequencies and then decreases sharply with increasing frequency. In this region, frequencies less than 1 rad/s were not experimentally accessible due to low torque. Region B includes $0.024 < \phi < 0.030$ % vol. where $\tan(\delta)$ is greater than one at all frequencies and goes through a maximum at approximately 10 rad/s. The break between Region A and B is consistent with the transition from dilute to semidilute observed by both the steady shear measurements and the measurements at constant frequency and increasing strain. In Region C comprises $0.044 < \phi < 0.120$ % vol. where $\tan(\delta)$ is less than one at frequencies below about 2.0 rad/s and reaches a maximum at a frequency of approximately 25 rad/s. The break between Region B and C is consistent with optical microscopy measurements of the onset of the biphasic region and the rheological measurements at constant frequency and increasing strain; however, this transition was not apparent in steady shear rheological measurements. Therefore, Region C can be considered as the predominantly isotropic portion of the biphasic region. In Region D ($0.32 < \phi < 12$ % vol.), $\tan(\delta)$
Figure 4.31. The ratio of the viscous to elastic modulus ($\tan(\delta) = G''/G'$) versus frequency for SWNTs in 102% H$_2$SO$_4$ for $0.004 < \phi < 12\%$ vol. Along the horizontal line $\tan(\delta) = 1$ indicating the viscous and elastic moduli are equal. A: the dilute regime $0.004 < \phi < 0.005\%$ vol., B: the semidilute regime $0.024 < \phi < 0.030\%$ vol., C: the predominantly isotropic portion of the biphasic region $0.044 < \phi < 0.120\%$ vol., and D: the appreciably biphasic to fully liquid crystalline region $0.32 < \phi < 12\%$ vol.
goes through a minimum between at frequencies between one and five radians per second, and \( \tan(\delta) \) is less than one at all measured frequencies. This indicates that the longest relaxation time of the dispersion is longer than experimentally accessible and is consistent with thermal fluctuations having little impact on structural relaxation (Hough, Islam et al. 2004). The transition between Region C and D is consistent with the optical microscopy and steady shear rheological findings that in this range the dispersions are predominantly to entirely liquid crystalline. Similar phase boundaries can be discerned by looking at \( G' \) and \( G'' \) versus frequency individually (Figure 4.32 and Figure 4.33). However, in this case the 0.32 % vol. data is separated from the bulk of the predominantly liquid crystalline data.

The data in Figure 4.32 can also be used to estimate the percolation concentration; the greater than two order of magnitude jump in \( G' \) between 0.117 and 0.32 % vol. is an indication of percolation. Near the percolation threshold,

\[
G'_0 \propto (\phi - \phi^*)^\nu
\]

(4.5)

where, \( G'_0 \) is the plateau value of the elastic modulus, \( \phi \) is the volume concentration of the nanotubes, \( \phi^* \) is the percolation threshold, and \( \nu \) is the percolation exponent. For the SWNT-102% H2SO4 dispersions, the values of \( \phi^* \) and \( \nu \) were determined by varying \( \phi^* \) to obtain the best linear fit of a plot of \( G'_0 \) versus \( (\phi - \phi^*) \). The values of \( \phi \) used to estimate \( \phi^* \) ranged from 0.117 % vol. to 3.54 % vol.; lower values were clearly below the percolation threshold and higher values contained such a high fraction of anisotropic phase that \( G' \) began decreasing with \( \phi \). Based on Equation 4.5, \( \phi^* = 0.113 \% \) vol. and \( \nu = 1.6 \) (Figure 4.34). For physical gels such as silica in water where chemical reactions
Figure 4.32. Elastic (storage) modulus $G'$ as a function of frequency.

Figure 4.33. Viscous (loss) modulus $G''$ as a function of frequency.
play no role, \( v \approx 3.8 \) (Sahimi and Arbabi 1993). The value of \( v = 1.6 \) is indicative of a chemical association between the SWNTs; values of 2.1 \pm 0.2 have been observed for cross linked gels of hydrolyzed polyacrylamide (Sahimi and Arbabi 1993) and suspensions of SWNTs in NaDDBS (\( \text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_{3}\text{Na} \)) (Hough, Islam et al. 2004). The slightly lower value obtained in the SWNT superacid system may be due to weaker associations between SWNTs than in NaDDBS. The value of \( \phi^* = 0.113 \% \text{ vol.} \) must represent percolation of the spaghetti network and not individual rods; optical microscopy (Chapter 4.5) and the centrifuge UV-vis-nIR data (Chapter 5.3) both show that percolation of the individual SWNTs in 102\% \( \text{H}_2\text{SO}_4 \) occurs at a much lower concentration (approximately 0.01 \% vol.). It is therefore surprising that the experimentally determined value of \( \phi^* = 0.113 \% \text{ vol.} \) compares favorably with the theoretical estimate for non-interacting polydisperse rods:

\[
\phi^* \approx R \frac{\langle L \rangle}{\langle L^2 \rangle}
\] (4.6)

The exact length distributions for the batches used in these experiments are not known, but typical values for batches produced and purified under similar conditions are \( R = 0.54 \) nm, \( \langle L \rangle = 348 \) nm, and \( \langle L^2 \rangle = 1.93 \times 10^5 \). This results in a theoretical \( \phi^* \approx 0.098 \% \text{ vol.} \) which is within 15\% of the observed \( \phi^* = 0.113 \% \text{ vol.} \). For a monodisperse system, percolation would be the upper limit of the isotropic region where the rods become interconnected.
4.8.3 Transition to a single phase liquid crystal ($\phi_N$)

The relationship between $G'$, $G''$ and the dynamic viscosity ($\eta^*$) versus concentration at low frequencies can be used to assess when the SWNT-102% H$_2$SO$_4$ dispersions are predominantly to fully liquid crystalline. As for the steady shear viscosity ($\eta$), $G'$, $G''$ and $\eta^*$ go through a maximum with increasing concentration. For predominantly isotropic dispersions, $G'$, $G''$ and $\eta^*$ all increase with increasing concentration. However, once the system is predominantly anisotropic all three parameters decrease with increasing concentration liquid crystalline packing is perfected. For all three parameters as well as the steady shear viscosity (Figure 4.8), the maximum is at $\sim 3.75$ % vol. (Figure 4.35). However, in contrast to the steady shear results a clear minimum is not obtained until $> 8$ % vol. For all three parameters, the 12.6 % vol. data (not plotted) was
approximately twenty times greater than the value at 8 % vol. This in suggests that the critical concentration for the formation of a single phase liquid crystal is higher than the 5.4 % vol. estimated from steady shear results, and most likely about 8 % vol. This is in close agreement with differential scanning calorimetry (DSC) results which showed that SWNTs form a single phase liquid crystal at a approximately 9 % vol. SWNT (Zhou submitted). The fact that oscillatory shear data is apparently a better indicator of $\phi_N$ than stead shear data is likely due to two reasons. First, oscillatory shear data is generally a better probe of sample microstructure. Second, there is evidence that SWNT-superacid dispersions are exigenic and some solvent may be pushed out of the sample at high strain rates. The low strains the samples experience during oscillatory testing are much less likely to disrupt the microstructure. It was not possible to systematically explore the possible exigenic nature of the system and whether slip was occurring in the steady shear tests because of the difficulties loading the sample to a series of prescribed gaps and the significant amount of SWNTs that would have been required. The use of DSC to determine the transition to a single phase liquid crystal is further discussed in Chapter 5.
Figure 4.35. $G'$ (top), $G''$ (middle) and $\eta^*$ as function of concentration. The maximum at 3.75 % vol. is consistent with the steady shear data, but the minimum occurring at greater than 7.64 % vol. is higher than observed in steady shear data and more consistent with differential scanning calorimetry.
4.9 Summary of Phase Boundaries

Single-walled carbon nanotubes (SWNTs) disperse in superacids via a protonation mechanism. Their phase behavior is generally that expected for rods in solution. However, the critical concentration at which the nematic phase first forms is an order of magnitude lower than what Onsager theory predicts for monodisperse rods interacting solely through hard rod repulsion. Likewise, the transition to a single phase liquid crystal occurs at a concentration many times the predicted value.

Table 4.2 provides the phase boundaries measured by the experimental methods used in this chapter. The wide biphasic region can be explained by two complications frequently encountered in experimental systems; polydispersity and solvent quality. The impact of each of these is discussed in Chapter 5.

<table>
<thead>
<tr>
<th>Method</th>
<th>( \phi_I ) % vol.</th>
<th>( \phi_N ) % vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Onsager Theory (Onsager 1949)</strong></td>
<td>~ 0.7</td>
<td>~ 1.0</td>
</tr>
<tr>
<td>Monodisperse ( \frac{L}{D} )_{KAB} = 500</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Onsager Theory (Onsager 1949)</strong></td>
<td>~ 0.3</td>
<td>~ 1.6</td>
</tr>
<tr>
<td>Monodisperse ( \frac{&lt;L&gt;}{\bar{D}} ) = 350</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Optical Microscopy</strong></td>
<td>0.01 - 0.03</td>
<td>~ 6</td>
</tr>
<tr>
<td>(Davis, Ericson et al. 2004)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Steady Shear Rheology</strong></td>
<td>0.01 - 0.04</td>
<td>~ 5</td>
</tr>
<tr>
<td>(Davis, Ericson et al. 2004)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Oscillatory Rheology</strong></td>
<td>0.03 - 0.04</td>
<td>~ 9</td>
</tr>
<tr>
<td><strong>Neutron Scattering</strong></td>
<td>0.01 - 0.03</td>
<td>N/A</td>
</tr>
<tr>
<td>(Zhou unpublished data)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2. Comparison of theoretical and experimentally observed phase transitions for SWNTs in 102 % H\(_2\)SO\(_4\).
4.10 Conclusions

The results provided in this chapter prove that SWNTs in superacids form lyotropic nematogenic phases. The direct protonation of single wall carbon nanotubes in superacids allows them to be dispersed at high concentration, more than an order of magnitude higher than typical concentrations achieved in surfactants or organic solvents. The phase behavior of SWNTs in superacids shows many parallels with that of lyotropic nematogenic rod-like polymer solutions. The notable distinction is that in the biphasic region the anisotropic phase consists of extremely long self-assembled strands. At sufficiently high concentrations, approximately 6 % vol. in 102% H₂SO₄, a single phase nematic liquid crystal is formed. The nematic structure of SWNT - superacid solutions is evidenced by the ability to form aligned species, birefringence, and rheological signatures including a maximum in the viscosity versus concentration curve, changes in sign of the first normal stress difference, and long oscillatory transients. In addition, the viscosity versus shear rate curve is suggestive of the three region behavior associated with many lyotropic nematic polymeric liquid crystals. This phase behavior is key to the production of highly aligned macroscopic articles consisting solely of SWNTs. The next chapter discusses the impact of acidity on controlling the phase boundaries and microstructure of the system and the role of polydispersity.
Chapter 5

Controlling SWNT - Superacid Phase Behavior

The data presented in Chapter 4 proved that SWNTs in superacids form lyotropic nematic liquid crystals: their rheology and phase behavior is characteristic of macromolecular liquid crystals including polymeric liquid crystals and inorganic (mineral) liquid crystals. However, SWNTs in 102% H₂SO₄ have an exceptionally broad biphasic region which contains an unusual liquid crystalline domain structure. This chapter explores the causes of the broad biphasic region observed in the SWNT-102% H₂SO₄ system, the methods for controlling the critical concentration at which the nematic phase first forms ϕ₁, and the critical concentration at which the system becomes completely nematic ϕₙ. For both polymeric and mineral liquid crystals, there are two possible causes of a broad biphasic region: high polydispersity, and relatively poor solvent quality. In polymeric systems, polymer chain flexibility also contributes to the breadth of the biphasic region. The persistence length Lₚ of SWNTs is tens of micrometers and their length L is typically below 1 μm (Yakobson and Smalley 1997; Yakobson and Couchman 2004; Duggal 2005; Duggal and Pasquali in preparation); therefore chain flexibility is not a reasonable explanation for the breadth of the biphasic region in the SWNT-102% H₂SO₄ system.

This chapter explains that polydispersity is likely the chief reason the biphasic to nematic transition ϕₙ occurs at a high value while solvent quality is the primary reason the isotropic to biphasic transition ϕ₁ occurs at such a low value. Solvent quality is shown
to be a function of the ability of the solvent to protonate the nanotube. In addition to controlling $\phi$, the protonating ability of the solvent has a significant impact on liquid crystal and fiber morphology.

### 5.1 Role of polydispersity

Experimental studies of lyotropic liquid crystals frequently cite polydispersity as a cause of broad biphasic regions (Donald and Windle 1992); in polydisperse systems longer rods preferentially enrich the nematic phase and it is possible for two distinct nematic phases to exist in equilibrium with an isotropic phase (I-N1-N2) (Speranza and Sollich 2003; Wensink and Vroege 2003). Phase coexistence can also result from attractive interactions between rods; this can result in coexisting isotropic phases (I1-I2-N) (Khokhlov 1991; Lacoste, Lau et al. 2002).

Explicit studies of the impact of polydispersity on phase behavior have been hindered by both the limited experimental control on polydispersity and the mathematical complexity of models capable of handling continuous distributions of lengths. Although the issue of polydispersity was initially addressed by Onsager (1949), most models still allow for only discrete distributions of length (i.e. a mixture of rods of lengths $L_1$ and $L_2$) or small perturbations about a mean length (Khokhlov 1991; Wensink and Vroege 2003). Solving the phase equilibrium conditions for a continuous distribution of lengths (e.g. Schulz, lognormal) is considerably more complicated. Continuous distributions can have a nearly infinite number of components (lengths) and simultaneous solution of an equally large number of equations is required (Wensink and Vroege 2003). For these reasons, detailed investigation of the effects of “a continuous distribution of rod lengths on the
Onsager theory remains an open problem” (Speranza and Sollich 2003). The additional complication of diameter polydispersity remains largely unaddressed.

In the case of HiPco produced SWNTs, significant progress has been made on tailoring the average aspect ratio (Carver, Robert L. Carver et al. 2005; Ziegler, Gu et al. 2005). However, the ability to control polydispersity remains elusive. Purified HiPco SWNTs have a log-normal distribution of lengths and diameters with diameter polydispersity of 0.18 and a length polydispersity of 0.6 to 0.75, where the polydispersity \( \sigma \) is defined by

\[
\sigma = \sqrt{\frac{\langle a^2 \rangle - \langle a \rangle^2}{\langle a \rangle^2}}
\] (5.1)

with \( a \) representing either the length or diameter of the rod.

The known models capable of calculating the phase behavior of such a highly polydisperse system with a log-normal distribution of lengths are the \( P_2 \) Onsager model developed by Sperenza and Sollich (2002, 2003) and the Gaussian Orientational Distribution Function (Gaussian ODF Ansatz) model developed by Wensink and Vroege (2003). Both models assume hard rod repulsion of spherocylinders based solely on the length of the cylinder; the diameter is assumed to be monodisperse. In both models, fractionation of the longer rods into the nematic phase results in the formation of cloud and shadow phases (also known as parent and daughter phases). A cloud point marks the concentration at which the cloud or parent phase splits off an infinitesimal amount of a new shadow phase. Figure 5.1 provides an example of a phase diagram showing cloud and shadow phases; in contrast to the monodisperse case, the concentration of rods in the isotropic and nematic phase is not uniform throughout the coexistence region. In this
dissertation, the critical concentration for the onset of the biphasic region is generally referred to as $\phi_1$, except where it is necessary to distinguish between experimentally measured concentrations of the isotropic cloud phase $\phi_I^{IC}$ and the coexisting nematic shadow phase $\phi_I^{NS}$. Similarly, $\phi_N$ will be used to denote the nematic cloud point.

![Phase Diagram](image)

Figure 5.1. General phase diagram for a lognormal distribution of rods. Adapted from Wensink and Vroege (2003). For the monodisperse case $\sigma = 0$, $\phi_I^{IC} = \phi_I^{NS}$ and $\phi_N^{NC} = \phi_N^{IS}$. I and N represent isotropic and nematic phases respectively.

Both the $P_2$ Onsager and Gaussian ODF models focused on locating the isotropic cloud point, the concentration at which the nematic shadow phase first forms, and obtained similar results. The $P_2$ Onsager Model (Speranza and Sollich 2002, 2003) is an approximate version of Onsager's original model. It simplifies the angular dependence of the excluded volume term in the free energy, truncating a series expansion of even Legendre polynomials $P_{2n}$ after the first nontrivial term. Critics of the $P_2$ Onsager Model model state that this approximation is only valid for weakly aligned nematic phases (Wensink and Vroege 2003) and therefore is not appropriate because the fractionation effect in highly polydisperse systems favors the formation of highly aligned nematics.
On the other hand, the Gaussian ODF model (Wensink and Vroege 2003) uses the full Onsager model which may provide a more accurate calculation of the isotropic and nematic cloud points, but limits detailed exploration of additional coexisting phases in the generally biphasic region (Wensink and Vroege 2003).

Comparison of the results of the two models is complicated by their different treatment of the maximum cut-off length. In the case of the \( P_2 \) Onsager model, the length was rendered dimensionless by a factor \( L_0 \) chosen such that the first moment of the length distribution \( <L> = 1 \). Model predictions were published for maximum dimensionless lengths \( (L_{\text{max}}) \) of 100 to 600; no minimum cutoff length was explicitly stated. For the Gaussian ODF model, predictions were published for maximum cut off lengths \( (L_{\text{max}}) \) of 10 or 100 with a minimum cutoff length \( (L_{\text{min}}) \) of 0.01. Effectively the range of dimensionless lengths for the Gaussian ODF model were \( L_{\text{max}}/L_{\text{min}} = 1000 \) or 10000. The two models compare reasonably well for the monodisperse case; at the isotropic cloud point the results of the \( P_2 \) Onsager model for \( L_{\text{max}} = 600 \) are similar to those obtained using \( L_{\text{max}} = 10 \) \( (L_{\text{max}}/L_{\text{min}} = 1000) \) in the Gaussian ODF Model.

To investigate the potential impact of polydispersity on SWNTs, the dilute data for SWNTs in Chapter 4 were fit with a model being developed at Rice University (A. Nicholas G. Parra-Vasquez, Ingrid Stepanek et al. in preparation). The model resulted in the following moments of the length distribution: \( <L> = 348 \text{ nm}, \ <L^2> = 1.9 \times 10^5, \ <L^3> = 1.7 \times 10^8, \) and \( \sigma = 0.75 \). This results in an estimated \( (L/D)_{\text{KAB}} = 550 \) versus the experimentally measured value of \( (L/D)_{\text{KAB}} = 470 \pm 30 \text{ nm} \) (Chapter 4); the slight difference between the two values is likely due to the limited ability to experimentally determine the zero shear viscosity. For monodisperse SWNTs with \( L = 348 \text{ nm} \) and \( D = \)}
1.27 nm, Onsager theory predicts $\phi_1 = 1.53$ % vol. using the original model (Onsager 1949) and 1.64 % vol. using subsequent numerical calculations (Khokhlov 1991). Table 5.1 compares this estimate to the values predicted by the $P_2$ Onsager and the Gaussian ODF models. For the monodisperse case ($\sigma = 0$), both models predict identical results. The results for polydisperse rods with a long normal length distribution are also similar. For $0.6 < \sigma < 0.8$, the models predict $0.31 < \phi_1 < 0.44$ % vol.; more than an order of magnitude higher than the experimentally determined value of $0.01 < \phi_1 < 0.03$ % vol. Using the unrealistic criteria of $L_{\text{max}}/L_{\text{min}} = 10,000$, the Gaussian ODF model predicts $\phi_1 = 0.08$ % vol which is still several times greater than the experimentally observed transition. Therefore, while polydispersity may contribute to the low value of $\phi_1$, it cannot be the sole cause of liquid crystalline domains forming at 0.01 to 0.03 % vol.

<table>
<thead>
<tr>
<th>$\phi_1$ % vol.</th>
<th>$\sigma = 0$</th>
<th>$\sigma = 0.6$</th>
<th>$\sigma = 0.8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onsager Original (4.19 D/L) (Onsager 1949)</td>
<td>1.53</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Onsager Numerical (4.49 D/L) (Khokhlov 1991)</td>
<td>1.64</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$P_2$ Onsager (Speranza and Sollich, 2002)</td>
<td>1.27</td>
<td>0.39</td>
<td>0.31</td>
</tr>
<tr>
<td>Gaussian ODF $L_{\text{max}}/L_{\text{min}} = 1000$ (Wensink and Vroege 2003)</td>
<td>1.27</td>
<td>0.44</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Table 5.1. Predicted values for the critical concentration at which liquid crystalline domains first form $\phi_1$ based on $<L> = 348$ and $D_{\text{eff}} = 1.27$. Polydispersity in diameter is neglected.

In contrast to their similar predictions for $\phi_1$, the $P_2$ Onsager and Gaussian ODF models predict significantly different results for the minimum concentration at which the system is completely liquid crystalline. As shown in Table 5.2, the predicted values even differ for the monodisperse case. More importantly, the Gaussian ODF model predicts that $\phi_N$ increases rapidly with increasing polydispersity while the $P_2$ Onsager Model
predicts only a slight increase. The $P_2$ Onsager model estimates a value of 1.5 % vol. < $\phi_N < 1.7$ % vol. for the same parameters used to estimate $\phi_l$. In contrast, the Gaussian ODF model estimates 11 % vol. < $\phi_N < 15$ % vol., even higher values than the experimentally observed 8 % vol. < $\phi_N < 11$ % vol. Therefore, based on the Gaussian ODF model polydispersity could be the cause of the high values of $\phi_N$ obtained for the SWNT-102 % H$_2$SO$_4$ system.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma = 0$</th>
<th>$\sigma = 0.6$</th>
<th>$\sigma = 0.8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onsager Original (4.19 D/L) (Onsager 1949)</td>
<td>1.5</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Onsager Numerical (4.49 D/L) (Khokhlov 1991)</td>
<td>1.6</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$P_2$ Onsager (Speranza and Sollich, 2002)</td>
<td>1.4</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Gaussian ODF $L_{max}/L_{min} = 1000$ (Wensink and Vroege 2003)</td>
<td>1.9</td>
<td>11</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 5.2. Predicted values for the critical concentration at which the system is completely liquid crystalline $\phi_N$ based on $<L> = 348$ and $D_{eff} = 1.27$. Polydispersity in diameter is neglected.

It is worth noting that both models allow for the possibility of an additional nematic phase within the biphasic region (I-N1-N2) but only over a limited and relatively low range of polydispersity. This raises the question of whether more than one nematic phase exists in the SWNT-102 % H$_2$SO$_4$ system. While the difficulty of visualizing microstructure details in highly concentration SWNT dispersions makes it impossible to rule out the possibility of I-N1-N2 coexistence, it is unlikely for two reasons. First, SWNT polydispersity is greater than that the range predicted to allow I-N1-N2 coexistence. Second, above the dilute regime SANS data scaled nearly exactly with concentration (Zhou 2005); it seems likely that the existence of a second nematic would have altered this relationship.
5.2 Effect of salt addition

The addition of electrolytes has been used to control phase behavior in colloidal systems including anisotropic mineral liquid crystals (Davidson, Gabriel et al. 1993; Davidson, Batail et al. 1997; Gabriel and Davidson 2003). The Derjaguin-Landau-Verwey-Overbeek (DLVO) model states that the potential between two colloidal objects is the sum of the van der Waals attraction and electrostatic repulsion between them. The van der Waals attraction between parallel cylinders scales with $r^{-1.5}$; therefore these attractions are significant over much longer distances than for atoms where the van der Waals attraction scales with $r^{-6}$ (Israelachvili 1992). In general, the addition of salts to a lyotropic nematogenic system has two competing effects: increasing the charge between the rods, while simultaneously shortening the screening length. In general, the addition of salts to mineral liquid crystals in aqueous solutions prevents flocculation while simultaneously stabilizing the nematic phase and decreasing $\phi_1$ (Gabriel and Davidson 2003). In this research, the impact of two salts with sulfate counter-ions were examined: potassium sulfate ($K_2SO_4$) and potassium persulfate ($K_2S_2O_8$).

5.2.1 Potassium sulfate addition

The addition of 50 to 250 mg/ml $K_2SO_4$ or $LiSO_4$ does not improve SWNT dispersion in 96 % $H_2SO_4$, nor does it appreciably change $\phi_1^{NS}$ (the lowest concentration at which the nematic phase is visible using optical microscopy) for SWNTs dispersed in 102 % $H_2SO_4$. Moreover, this additive has no measurable effect on Raman spectroscopy measurements of protonation; the Eklund shifts (Chapter 3.5.3) before and after salt addition are equivalent. However, as shown in Figure 5.2, potassium sulfate addition
Figure 5.2. The addition of 50 mg/ml to 0.19 % vol. (0.15 % wt.) SWNTs in 102 % H₂SO₄ (left) increases the diameter of the spaghetti strands by approximately 1.5 times.
increases the diameter of the liquid crystalline spaghetti strands in the biphasic by roughly 1.5 times. The estimated diameter change is based on the visibility of strands using the 50x objective and measurements of the apparent diameters. The diameter increase may simply be the result of the atomic radius of both potassium and lithium being significantly greater than that of hydrogen (243, 163, and 53 pm) respectively. Therefore, just a few potassium or lithium ions between the SWNTs in the spaghetti strands would increase the distance between them. This possibility would have to be proven by investigating the impacts of salts with differing cation diameters as well as different valencies. These experiments were not performed by the author as they were tangential to the primary goal of controlling $\phi_1$.

5.2.2 Potassium persulfate addition

In contrast to $K_2SO_4$ addition, the addition of $K_2S_2O_8$ has a marked impact on phase behavior. In 96% $H_2SO_4$, SWNTs disperse poorly with a significant number of large aggregates (Figure 5.3a and 2b). The addition of 50 mg/ml $K_2SO_4$ markedly improves dispersion (Figure 5.3c) and stabilizes the formation of the nematic phase resulting in the formation of the familiar nematic spaghetti morphology (Figure 5.3d). Reaction of the $K_2S_2O_8$ with water in the 96% $H_2SO_4$ can only partially account for this change; there were only 0.9 mmols of $K_2S_2O_8$ compared to 16 mmols of water in initial sample. In addition to the marked change in morphology, the Raman spectra indicates that the addition of $K_2S_2O_8$ increases SWNT protonation (Figure 5.4). Based on a factor of 320 cm$^{-1}$/hole/carbon (Sumanasekera, Allen et al. 1999), the fractional charge is $\delta = 0.07$ - even higher than that for SWNTS in 102 % $H_2SO_4$. 
Figure 5.3. 0.19 % vol. (0.15 % wt.) SWNTs in 96 % H₂SO₄ do not disperse well and no nematic phase forms (a and b). The addition of K₂S₂O₄ dramatically improves the degree of dispersion and results in the same liquid crystalline morphology as for SWNTs dispersed in 102 % H₂SO₄ (c and d). Scalebars represent 50 μm in (a and c) and 10 μm in (b and d).
Adding 50 mg/ml K₂S₂O₈ to SWNTs in 102 % H₂SO₄ significantly alters the chemistry and bulk morphology of the system. The system forms a free standing gel within a few hours of persulfate addition; the gel can be readily broken with shear and then reformed many times. Raman spectra of the system shows an increased Eklund shift indicating increased SWNT protonation. In addition, a strong disorder or D peak (Figure 5.5) is present; this indicates a marked increase in the number of sp³ hybridized carbons and is generally associated with functionalization. Interestingly, the majority of the D peak disappears upon quenching the system in either water, alcohol or ether; this suggests that bonding with the SWNTs is tenuous at best. Subsequent to this investigation it was discovered that SWNTs are shortened in H₂SO₄-K₂S₂O₈ mixtures. Therefore, the addition of K₂S₂O₈ to 102 % H₂SO₄ was not a suitable technique for trying to control phase behavior without SWNT modification.
Figure 5.5. (A) Raman spectrum of SWNTs in 102% H$_2$SO$_4$: G peak is centered at 1612 cm$^{-1}$. (B) Raman spectra of SWNTs in 102% H$_2$SO$_4$ with 50 mg/ml K$_2$S$_2$O$_8$: The center of the G peak increases to 1620 cm$^{-1}$ and a significant D peak nearly more than half the magnitude of the D peak. (C) Quenching the sample for B in water and rinsing it with ethanol removes the acid and persulfate causing the G peak to be restored to its 1594 cm$^{-1}$ position. Interestingly the D peak is minimal after rinsing suggesting that the sp$^3$ hybridization in (B) was mostly reversible.

5.3 Effect of SWNT Protonation on $\phi_1$

Given the key role of protonation in dispersal, as well as improved dispersion and increased Eklund shift upon K$_2$S$_2$O$_8$ addition to 96% H$_2$SO$_4$, the impact of acid strength on SWNT protonation and $\phi_1$ was investigated. Acid strength was varied by the adding either SO$_3$ to 96% H$_2$SO$_4$ or ClSO$_3$H to 102% H$_2$SO$_4$. The addition of a coacid to H$_2$SO$_4$ increases acidity according to

$$\text{HA} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{SO}_4^- + \text{A}^-.$$  \hspace{1cm} (5.2)

For example,

$$\text{HClSO}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{SO}_4^+ + \text{ClSO}_3^-.$$  \hspace{1cm} (5.3)
As discussed in Chapter 2.2, the strength of strong and superacids is typically measured in terms of the Hammett acidity. However, acidity is not a unique property of a solvent, but also depends on the solute (McNaught and Wilkinson 1997). In fact, markedly different Hammett acidity values have been measured for mixtures of H₂SO₄ and SO₃ even using the same solutes (Brand 1950; Gillespie, Peel et al. 1971). For these reasons, SWNT protonation, and not Hammett Acidity, was used as the basis for examining the impact of the superacid solvent on phase behavior. As in experiments on the effect of salt addition (Chapter 5.2), SWNT protonation was determined from the shift in the G peak in the Raman spectra (Chapter 3.5.3).

The impact of SWNT protonation on the transition to the biphasic region was examined by two methods. First, optical microscopy of dilutions of SWNT in superacids provided a qualitative measurement of the concentration in the nematic shadow phase $\phi_{NS}^N$. Second, centrifugation of SWNT-acid dispersions followed by UV-vis-nIR (Section 3.5.5) provided a quantitative measurement of the isotropic cloud point $\phi_{IC}^N$. The isotropic cloud point is the maximum concentration of SWNTs that can exist in the isotropic phase (Rai, Pinnick et al. submitted). Optical microscopy of several samples used to determine $\phi_{IC}^N$ confirmed that the samples obtained by this technique were isotropic. As with all other optical microscopy experiments, moisture incursion resulted in a significant change in morphology (Figure 5.7).
In the weakest acid studied, 96% H₂SO₄, the nematic phase does not form (Figure 5.3b); 100 ppm vol. SWNTs dissolve, but the majority of SWNTs form a coarse dispersion of irregularly shaped aggregates tens of microns in length (Figure 5.3a). For SWNTs in 102% H₂SO₄ (δ⁺ = 0.053), optical microscopy reveals a strand-like nematic phase (Davis, Ericson et al. 2004) which forms at 100 < φⁿˢ < 400 ppm vol. UV-vis-nIR
shows a similar result: $\phi_1^{IC} = 140$ ppm vol (Table 5.3). In 123% H$_2$SO$_4$ the excess SO$_3$ results in both increased SWNT protonation ($\delta^+ = 0.058$) and a higher concentration in the isotropic phase $\phi_1^{IC} = 350$ ppm vol; the concentration change could not be detected by optical microscopy. The addition of 10% vol. ClSO$_3$H to 102 % H$_2$SO$_4$ yields similar results and the morphology of the liquid crystalline phase appears similar to that for SWNTs in 102 – 123 % H$_2$SO$_4$ (Figure 5.8). Greater increases in SWNT protonation achieved through the addition of larger amounts of ClSO$_3$H in 102 % H$_2$SO$_4$ result in significant changes in the critical concentration at which nematic domains appear (Table 5.3).

<table>
<thead>
<tr>
<th>Acid</th>
<th>Coacid % vol</th>
<th>G cm$^{-1}$</th>
<th>dG cm$^{-1}$</th>
<th>$\delta^+ / C$</th>
<th>$\phi_1^{IC}$ ppm vol.</th>
<th>$\phi_1^{NS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>96% H$_2$SO$_4$</td>
<td></td>
<td>1607.0</td>
<td>13.0</td>
<td>0.041</td>
<td>100</td>
<td>N/A</td>
</tr>
<tr>
<td>98% H$_2$SO$_4$</td>
<td></td>
<td>1610.0</td>
<td>16.0</td>
<td>0.050</td>
<td>140</td>
<td>N/A</td>
</tr>
<tr>
<td>102 % H$_2$SO$_4$</td>
<td></td>
<td>1611.0</td>
<td>17.0</td>
<td>0.053</td>
<td>169</td>
<td>0.01 &lt; $\phi_1^{NS}$ &lt; 0.04</td>
</tr>
<tr>
<td>123% H$_2$SO$_4$</td>
<td></td>
<td>1612.5</td>
<td>18.5</td>
<td>0.058</td>
<td>350</td>
<td>0.01 &lt; $\phi_1^{NS}$ &lt; 0.04</td>
</tr>
<tr>
<td>102 % H$_2$SO$_4$</td>
<td>10% ClSO$_3$H</td>
<td>1612.0</td>
<td>18.0</td>
<td>0.056</td>
<td>360</td>
<td>0.01 &lt; $\phi_1^{NS}$ &lt; 0.04</td>
</tr>
<tr>
<td>102 % H$_2$SO$_4$</td>
<td>30% ClSO$_3$H</td>
<td>1614.0</td>
<td>20.0</td>
<td>0.063</td>
<td>1240</td>
<td>0.01 &lt; $\phi_1^{NS}$ &lt; 0.04</td>
</tr>
<tr>
<td>102 % H$_2$SO$_4$</td>
<td>50% ClSO$_3$H</td>
<td>1614.5</td>
<td>20.5</td>
<td>0.064</td>
<td>2130</td>
<td>0.04 &lt; $\phi_1^{NS}$ &lt; 0.06</td>
</tr>
<tr>
<td>102 % H$_2$SO$_4$</td>
<td>70% ClSO$_3$H</td>
<td>1615.0</td>
<td>21.0</td>
<td>0.066</td>
<td>3400</td>
<td>0.20 &lt; $\phi_1^{NS}$ &lt; 0.40</td>
</tr>
<tr>
<td>100% ClSO$_3$H</td>
<td></td>
<td>1619.0</td>
<td>25.0</td>
<td>0.078</td>
<td>4970</td>
<td>0.40 &lt; $\phi_1^{NS}$ &lt; 0.60</td>
</tr>
</tbody>
</table>

Table 5.3. Impact of acid composition on fractional protonation ($\delta^+$), and the critical concentration at which the system becomes biphasic.
Figure 5.8. Optical micrographs of 0.15 wt\% (0.19 vol.\%) SWNTs dispersed in 10/90 vol. CISO$_2$H in 102 \% H$_2$SO$_4$ show the same nematic morphology as in pure 102 \% H$_2$SO$_4$. The birefringent strands become bright and dark as the analyzer is rotated.

Figure 5.9 further illustrates the impact of SWNT protonation on $\phi^\text{IC}_i$; the relationship is nearly sigmoidal. Below the superacid regime, where there is still free water, a very low concentration of SWNTs disperses in the isotropic phase; increasing the concentration results in the formation of large aggregates. In the superacid regime, $\phi^\text{IC}_i$ increases significantly with increasing SWNT protonation up to $\delta^+ \approx 0.066$. The increase in $\phi^\text{IC}_i$ with increasing protonation then becomes more gradual as $\phi^\text{IC}_i$ nears the Onsager limit of the volume fraction of rods that can be contained in an isotropic phase.
Figure 5.9. The maximum concentration in the isotropic phase $\phi_{I}^{ic}$ (ppm vol.) as a function of SWNT protonation. Error bars for concentration are 5 %; error bars for $\delta^+$ represent ± 1 to 1.5 cm$^{-1}$ in the Raman spectra.

5.4 Effect of SWNT Protonation on $\phi_N$

In Chapter 4, the critical concentration $\phi_N$ at which the SWNT-102 % H$_2$SO$_4$ transitions to a single phase liquid crystal was estimated to be $7 \pm 2$ % vol. This estimate was based on several experimental techniques: optical microscopy, steady shear rheological characterization under steady shear, and differential scanning calorimetry (DSC), and oscillatory shear rheological characterization. The values of $\phi_N$ were all in close agreement and significantly higher than predicted by Onsager's theory for monodisperse hard rods. Of all the techniques, differential scanning calorimetry was found to be the most efficient as it provides a quantitative result with minimal sample volume and
experiment time. Optical microscopy slightly under predicted $\phi_N$, but was surprisingly accurate given the qualitative nature of the technique. Estimated values of $\phi_N$ in 120% H$_2$SO$_4$ and ClSO$_3$H are described below, along with the experimental limitations encountered.

5.4.1 SWNTs in ~ 120 % H$_2$SO$_4$ ($\delta^+ \sim 0.58$)

Differential scanning calorimetry (DSC) of the same batch of SWNTs (HPR 152.2) mixed in the mini-mixer for five days at ambient temperatures, shows that the system transitions to a single phase at a slightly lower concentration for SWNTs in 120% H$_2$SO$_4$ than for SWNTs in 102 % H$_2$SO$_4$ (Figure 5.10). For this particular batch, at 3.5 % wt. SWNT (4.5 % vol. in 102% H$_2$SO$_4$ and 4.6 % vol. in 120% H$_2$SO$_4$) the enthalpies of melting are 57 J/g in 102% H$_2$SO$_4$ and 39 J/g in 120% H$_2$SO$_4$. For 6 wt% SWNT (7.6 % vol. in 102% H$_2$SO$_4$ and 7.8 % vol. in 120% H$_2$SO$_4$) a small endotherm of 15 J/g still exists in 102% H$_2$SO$_4$, but there is no endotherm in 120% H$_2$SO$_4$. This indicates that the transition to a single phase liquid crystal occurs somewhere between 3.5 and 6.0 % wt. (4.6 and 7.8 % vol.) for SWNTs in 120% H$_2$SO$_4$ and at a concentration greater than 6.0 % wt. (7.6 % vol.) for SWNTs in 102% H$_2$SO$_4$. Based on this and previous DSC studies, the enthalpy varies linearly with concentration, so the transition concentrations can be calculated. Therefore, based on the results shown in Figure 5.5 SWNTs in 120% H$_2$SO$_4$, $\phi_N = 6.9$ % vol. whereas $\phi_N = 8.8$ % vol. for SWNTs in 120% H$_2$SO$_4$. 
Figure 5.10. Comparison of phase transitions for SWNT batch HPR 152.2 in 102% H$_2$SO$_4$ and 120% H$_2$SO$_4$ (Zhou, Heiney et al. 2005).
The DSC data is consistent with earlier findings. In fact, the very first characterizations of SWNTs in superacids were conducted for SWNTs in 120% H$_2$SO$_4$, and it was this system that gave the first hope for the formation of a SWNT-superacid liquid crystalline phase. Much of this characterization was completed before acquisition of key equipment (e.g. the Ares 2000 FRT, RDA III, and Zeiss Axioplan microscope), but it still provides useful support to the DSC data. Figure 5.11 shows bright field microscopy images of SWNTs in oleum in the absence of cross polarized light. The increased connectivity between 4 and 7 % wt. and the ridges and slight extensional viscosity of 7 % wt. sample gave the first hope of a single phase LC (Davis 2001); such ridges or shear bands and extensional viscosity are characteristics associated with polymeric liquid crystals. Early rheological data also suggested that $\phi_N$ is lower in 120% H$_2$SO$_4$ than in 102% H$_2$SO$_4$ (Figure 5.12). Rheological characterization of the SWNT-120% H$_2$SO$_4$ system was not as detailed as that of the SWNT-102% H$_2$SO$_4$ system; as the preferred system for fiber spinning the SWNT-102 % system was the primary focus of this research. The viscosity in 102 % H$_2$SO$_4$ is almost an order of magnitude lower than in 120% H$_2$SO$_4$. This means that either SWNTs are less soluble in oleum than 102% H$_2$SO$_4$ or that there is more anisotropic phase in 120% H$_2$SO$_4$. The first possibility is inconsistent with the solubility data (Table 5.3) but the second possibility is consistent with a lower value of $\phi_N$ in 120% H$_2$SO$_4$. 
Figure 5.11. Bright field microscopy images of SWNT-120% H₂SO₄ dispersions 1.3 % vol. (1 % wt.), and 5.2 % vol. (4 % wt.) (middle) and 9.2 % vol. (7 % wt.) (right) (Davis 2001). The lighter regions in the 7 % wt. image were formed after pressing on the slide and were voids, no meniscus representing free solvent was visible. The blank squares in the middle of the images are artifacts from the imaging system. Scalebars in the lower left corner are 50 μm.
Figure 5.12. Comparison of the shear thinning behavior of concentrated solutions of 4 % wt. SWNT in 102 % H2SO4 (triangles) and 120% H2SO4 (diamonds). Filled triangles are for data collected during a continuous sweep of shear rates; open triangles are for data collected from individual tests at a fixed shear rate. The line represents literature data for viscosity at and 12% PPTA (Kevlar) in sulfuric acid. The power law indices are 0.2 for both SWNT dispersions and for 0.3 for Kevlar (Davis, Ericson et al. 2001).

5.4.2 SWNTs in ClSO3H (δ* = 0.78)

For SWNTs in ClSO3H, the transition to a single phase liquid crystal ϕN occurs at approximately 5 % vol. based on optical microscopy. At 4.2 % vol. (3.5 % wt.) a small amount of isotropic phase is still visible (Figure 5.13a). This isotropic phase is darker than the both background (Figure 5.13a) and the voids in the sample. Rheology was not performed because efforts to design a chamber capable of preventing ClSO3H fumes from corroding the rheometer during loading and unloading were not successful. Differential scanning calorimetry was attempted. However, even for the pure acid, the freezing point, was below the lower temperature limit of the instrument. As optical microscopy proved a reliable indicator of ϕN in 102 – 120 % H2SO4, the estimate of ϕN ~
5 % vol. in ClSO$_3$H is considered reliable. The modest decrease in \( \phi_N \) for SWNTs in ClSO$_3$H indicates that solvent quality is not the dominant factor controlling \( \phi_N \); this provides further support that \( \phi_N \) is predominantly a function of polydispersity (Section 5.1).

![Images](a) (b)

Figure 5.13. Optical microscopy of 3.5 % wt. SWNT (4.2 % vol.) in ClSO$_3$H is predominantly liquid crystalline, however isotropic liquid can be seen. Image (a) was taken with non polarized light; the edge of the sample clearly shows isotropic phase which is lighter than the bulk of the sample but not as light as the background (upper left corner of a). The nanotube rich region shows marked birefringence under partially cross-polarized light (b). The voids in both images and pronounced alignment along the diagonal of (b) were likely due to slide preparation although no shear was intentionally applied. The scalebars are 100 \( \mu \)m.

### 5.5 Effect of SWNT Protonation on Liquid Crystal Morphology

In addition to markedly increasing \( \phi_i \), SWNT protonation has a significant impact on liquid crystal morphology. For dispersions containing more than 70% ClSO$_3$H \( (\delta^+ \geq 0.66) \), optical microscopy reveals a significantly different morphology than less protonating solvents. Therefore, the strand-like nematic phase observed for SWNTs in 102 % - 123% H$_2$SO$_4$ (Davis, Ericson et al. 2004) is not solely the result of SWNT persistence length and polydispersity; the solvent also plays a role. Near \( \phi_i \) (6000 ppm
vol. SWNT), the morphology of the liquid crystalline phase is more anisotropic than the globular structure seen in polymeric lyotropic liquid crystals (Donald and Windle 1992), but the domains are larger and less strand-like than seen in the 102 % H₂SO₄ system (Figure 5.14). Near $\phi_N$ (4.2 % vol.), SWNTs in ClSO₃H have a larger domain size with fewer defects and smoother boundaries between domains than seen in the weaker acids (Figure 5.15).

Figure 5.14. Morphology near the onset of the biphasic region for (top) SWNTs in ClSO₃H (0.6 % vol.), and (bottom) SWNTs in 102 % H₂SO₄ (0.01 % vol.). The morphology in ClSO₃H appears broader and more contiguous than that in 102 % H₂SO₄. Scalebars are 20 $\mu$m.
Figure 5.15. Comparison of liquid crystalline morphology 3.5 % wt. (4.2 % vol.) SWNTs in ClSO₃H (a) and 4 % wt. (5.4 % vol.) SWNTs in 102 % H₂SO₄ (b). Scalebars are 100 μm.

The impact of the addition of nonsolvents (coagulants) such as moisture is also significantly different in the more protonating solvents. In 102% - 123% H₂SO₄, slow moisture ingress results in deprotonation of the nanotubes and the breakup of the liquid crystalline structure into discrete monodisperse tactoid structures called alewives (Smalley, Hauge et al. 2001; Davis, Ericson et al. 2004; Ramesh, Ericson et al. 2004). In contrast, slow moisture ingress into 70/30 vol. ClSO₃H / 102% H₂SO₄ results in a coalescence of the liquid crystalline structure and expulsion of the free solvent. This results in the formation of large aligned fibrillar domains (Figure 5.16). There are two key reasons for this difference in behavior. First, the nanotubes in the ClSO₃H system are more highly protonated so they can more easily remain as solvated domains. Second, the viscosity of dispersion is lower, so it is easier for the SWNTs to rearrange on a larger scale. In fact, the SWNTs are so much better solvated in the high ClSO₃H content systems that even the addition of 102% H₂SO₄ to SWNTS dispersed in 70/30 ClSO₃H/102% H₂SO₄ can result in structural coalescence (Figure 5.17).
Figure 5.16. Rearrangement of 0.15 wt% (0.19 vol %) SWNTs 70/30 ClSO$_3$H/102% H$_2$SO$_4$ during introduction of ambient moisture. Scalebar is 50 μm.

Figure 5.17. Coalescence of SWNTs in 70/30 ClSO$_3$H/H$_2$SO$_4$ upon introduction of 102% H$_2$SO$_4$. Scalebar is 50 μm.
5.6 Impact of SWNT Protonation on Fiber Morphology

Liquid crystalline phase behavior and morphology as well as the response of the dispersion to coagulants directly impacts the morphology of solution spun pure SWNT fibers. Fibers solution spun from 102 – 123% H₂SO₄ have a hierarchical structure where small bundles of nanotubes (primordial ropes) comprise larger bundles which in turn comprise the fiber (Figures 4.22 to 4.25). Defects have the appearance of tapered bundle ends; similar to the morphology of alewives (Ericson, Fan et al. 2004). In contrast, just as slow moisture ingress resulted in a fine fibrillar structure during phase behavior studies, fibers solution spun from 4.2 % vol. (3.5 % wt.) SWNTs in ClSO₃H have a uniform microstructure of fine fibrils and few defects (Figure 5.18 and Figure 5.19). The fibers spun from SWNT-ClSO₃H dispersions were produced by manual extrusion through a 400 μm syringe needle into 96% H₂SO₄ inside an argon blanketed glove box. The fibers were subsequently rinsed with deionized water. The fibers’ gathered macrostructure (Figure 5.20) is likely the combined result of flow instabilities during manual extrusion and a rapid axial contraction upon exposure to the 96% H₂SO₄ coagulation bath. For the fibers that spun directly into water, the dominant characteristic is numerous holes resulting from the violent reaction between ClSO₃H and H₂O (Figure 5.21). Previous studies showed that for fibers spun from SWNT-120% H₂SO₄ dispersions coagulated in water, bubbles formed and disrupted the fiber microstructure. These bubbles were believed to result as the result of localized vaporization of water resulting from the reaction of 120% H₂SO₄ with water. The reaction between SWNT-ClSO₃H dispersions and water was significantly more violent resulting in a vapor cloud.
Figure 5.18. SEM of fiber spun from 4.2% vol. (3.5 % wt.) SWNTs in ClSO$_3$H coagulated in 96% H$_2$SO$_4$. The undulating macrostructure results from coagulation, but the fine uniform fibrillar (top left) microstructure results from the better solvent quality of ClSO$_3$H. This structure corresponds to the fibrillar fine microstructure seen in phase behavior studies.
Figure 5.19. Additional SEM of fibers spun from 4.2 % vol. (3.5 % wt.) SWNTs in ClSO$_3$H showing that defects between fibrils are rare.
Figure 5.20. Macroscopic pleating of SWNT fibers spun from 4.2 % vol . (3.5 % wt.) SWNT in CISO\(_2\)H and coagulated in 96% H\(_2\)SO\(_4\).
Figure 5.21. Fiber spun from 4.2 % vol (3.5 % wt.) SWNTs in CISO₂H coagulated in water. The porous structure is the result of the violent reaction between CISO₂H and water.

resulting in a vapor cloud that filled the glove box thereby preventing any efforts to visualize the protofiber-water interface.

To ensure that the morphology of fibers spun from the SWNT-CISO₂H dispersion was not due to the SWNT batch, mixing or spinning, SWNT-102 % H₂SO₄ and 120% H₂SO₄ dispersions were spun under the same conditions. The difference in chemical potentials between 96% and 100 - 120% H₂SO₄ was insufficient to achieve significant coagulation so the fibers were coagulated in ether. The fiber morphology was not one of highly aligned uniform gathered fibrils; typical SEM images (Figure 5.22) show an overall dog bone macrostructure and the microstructure consists of aligned. In fact, the fibers looked very similar to the fibers produced in the very early experiments using manual extrusion of biphasic dispersion through a syringe and an ether coagulant (Figure 4.22).
Figure 5.22. Scanning electron micrographs (SEMs) of 3.5 % wt. (4.5 % vol.) SWNTs in 102 % H₂SO₄ spun into ether using the same batch, mixing and spinning procedure as for the fibers produced from SWNT-CISO₃H dispersions.

5.7 Conclusion

Figure 5.23 shows the results presented in this chapter in the form of a typical phase diagram for lyotropic nematic dispersions. The concentration at which the nematic phase first forms φ₁ is largely controlled by SWNT protonation; polydispersity also appears to have an impact. Figure 5.24 shows the phase diagram with both Onsager’s predictions for monodisperse hard-rods and Wensink and Vroege’s (2003) Gaussian ODF model. The marked impact of SWNT protonation on φ₁ provides new support to the proposed protonation mechanism for SWNT dispersal in superacids. The similarity between the Gaussian ODF prediction and the experimental value for φ₁ in CISO₃H (δ⁻ = 0.078), suggests that CISO₃H may be nearly an athermal solvent; the narrow biphasic chimney predicted by Onsager theory is not feasible given the broad lognormal distribution of SWNT lengths.

The concentration at which the system becomes fully liquid crystalline φₙ is only somewhat affected by SWNT protonation; based on theoretical models φₙ appears to be controlled by polydispersity. Wensink and Vroege’s (2003) Gaussian ODF model predict
an even higher value of $\phi_N$, than measured for SWNTs in ClSO$_2$H; this also suggests ClSO$_2$H may be nearly an athermal solvent.

For SWNT protonation below $\delta^+ = 0.053$, a small concentration of SWNTs will disperse isotropically, but at higher concentrations large agglomerates form instead of a nematic phase. SWNTs dispersed in more protonating acids, form crystal solvates or fine fibrilliar structures when they are deprotonated by the introduction of another liquid.

In addition to being the primary determinant of $\phi_1$, SWNT protonation also affects liquid crystalline morphology and the response to coagulants. More protonated SWNTs form larger domains with fewer defects. In addition, for more protonated SWNTs, the introduction of coagulants results in structural coalescence instead of the formation of discrete tactoid structures. The phase behavior described in this chapter directly translates into the microstructure of solution spun fibers; this highlights the importance of understanding and controlling phase behavior in the production of highly aligned macroscopic three dimensional SWNT structures.
Figure 5.23. Phase diagram for SWNTs in super acids. The isotropic to biphasic boundary $\phi_i$ is strongly dependent on SWNT protonation, the biphasic to liquid crystalline boundary is only slightly affected by protonation. Below a critical level of protonation $-0.053$ SWNTs do not disperse well enough to form a liquid crystalline phase. When the protonation of already dispersed biphasic or liquid crystalline SWNTs is decreased the dispersions form either a tactoid crystal solvate phase (alewives) or fibrillar structures.
Figure 5.24. Phase diagram for SWNTs in superacids showing phase transitions predicted by theoretical models. Both the Onsager and Gaussian ODF models are for rods in athermal solvents; the placement of their predictions on the y-axis is arbitrary. A much narrower biphasic region is predicted by Onsager theory (1949). However, the Gaussian ODF model for a log normal distribution of rods (Wensink and Vroege 2003) predicts suggest that the breadth of the biphasic region in ClSO₃H (δ' = 0.78) could be solely the result of polydispersity and ClSO₃H may be nearly an athermal solvent.
Chapter 6

Conclusions

The protonation of SWNTs in superacids overcomes the van der Waals attraction between SWNTS and enable their dispersal at up to 10 % wt. (12.6 % vol.); this is an order of magnitude higher concentration than has been achieved in other solvents. Steady shear and oscillatory rheology, optical and electron microscopy, and differential scanning calorimetry have proven that SWNTs in superacids are a lyotropic nematogenic system; above a critical concentration the system forms a single phase nematic liquid crystal forms. Solution spinning the liquid crystalline phase results in highly aligned pure macroscopic SWNT fibers.

Rheological characterization has shown that SWNTs in 102% H₂SO₄ are individually dispersed and behave as dilute Brownian rods at concentrations up to approximately 100 ppm vol. As a result, the intrinsic viscosity of dilute SWNTs in conjunction with the Kirkwood-Auer-Batchelor equation can be used to determine the average aspect ratio \((L/D)_{KAB}\) of a bulk quantity of SWNTs; this value was approximately 500 for the majority of SWNTs used in this research. As the range of SWNT diameters is much less significant than the range of SWNT lengths, rheological determination of aspect ratio provides a new alternative to atomic force microscopy measurement of SWNT length. At slightly higher concentration, the system is semidilute where SWNT rotation, but not SWNT translation is inhibited. At 100 to 300 ppm vol., the SWNT-
102% H₂SO₄ system becomes biphasic; a liquid crystalline phase forms in equilibrium with the isotropic phase. The liquid crystalline phase is comprised of self-assembled seemingly endless strands of highly aligned solvated SWNTs called SWNT spaghetti. At a concentration of approximately 1100 ppm vol., the concentration of spaghetti strands becomes high enough to result in percolation. Above the spaghetti percolation concentration, the viscosity of the SWNT-superacid dispersions is independent of temperature. At even higher concentration, the system becomes fully liquid crystalline and can be rearranged into a variety of aligned species including ropes, tactoid shaped crystal solvates called alewives, and highly aligned fibers. Liquid crystalline dispersions of SWNTs in superacids exhibit the rheological characteristics of polymeric lyotropic liquid crystals: long oscillatory transients, a maximum in the viscosity versus concentration curve, a three region viscosity versus shear rate curve, first normal stress difference changing sign with increasing shear rate, and the Cox-Merz rule not being obeyed.

The critical concentration at which the nematic phase first appears φ₁ is largely controlled by SWNT protonation. In 102 % H₂SO₄ δ⁺ = 0.053 protons/carbon, and the maximum concentration in the isotropic phase is φ₁ = 170 ppm vol.; in ClSO₃H, δ⁺ = 0.078 protons/carbon and φ₁ = 4970 ppm vol. SWNT protonation also affects liquid crystalline morphology and fiber microstructure; dispersion of SWNTs in more protonating superacids results in larger domains with fewer defects and fibers comprised of a uniform fibrillar structure; this contrasts with the small domains hierarchical bundle structures seen in fibers spun from SWNTs in 102 to 120 % H₂SO₄.
In contrast to the significant effect SWNT protonation has on $\phi_l$, liquid crystal morphology and fiber microstructure, SWNT protonation only has a slight effect on the transition to a single phase liquid crystal $\phi_N$. This transition appears to be largely controlled by polydispersity; this hypothesis would have to be experimentally proven once SWNTs with controlled polydispersities become available. The impact of polydispersity on $\phi_N$ could have significant implications for future research on processing SWNT liquid crystals into macroscopic structures. Efforts to reduce the length polydispersity of HiPco produced SWNTs in conjunction with efforts to dramatically increase their average length of SWNT could drastically reduce $\phi_N$. This in turn could necessitate spinning from dispersions that are significantly lower in concentration, but not necessarily less viscous. In addition, efforts to produce a single diameter of SWNTs may cause the system to form a layered smectic phase instead of a nematic phase.

This research is an example of the resurgence of lyotropic liquid crystalline science created by the development of new anisotropic nanomaterials. Although the foundations of liquid crystalline science are independent of the chemical nature of anisotropic materials, they have been almost exclusively applied to polymeric materials. The discovery of SWNT liquid crystals, their rheological similarities to lyotropic polymeric liquid crystals, and their utility in producing highly aligned macroscopic SWNT structures, is likely to become just one of the first in a growing list of nanomaterial liquid crystals and liquid crystal applications.
References


