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Polyacrylonitrile Copolymers: Effects of Molecular Weight, Polydispersity, Composition, and Sequencing on Thermal Ring-Closing Stabilization

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POLYACRYLONITRILE COPOLYMERS: EFFECTS OF MOLECULAR WEIGHT,
POLYDISPERSITY, COMPOSITION, AND SEQUENCING ON
THERMAL RING-CLOSING STABILIZATION

by

Jeremy Daniel Moskowitz

A Dissertation
Submitted to the Graduate School
and the School of Polymers and High Performance Materials
at The University of Southern Mississippi
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

December 2015

ABSTRACT

POLYACRYLONITRILE COPOLYMERS: EFFECTS OF MOLECULAR WEIGHT, POLYDISPERSITY, COMPOSITION, AND SEQUENCING ON THERMAL RING-CLOSING STABILIZATION

by Jeremy Daniel Moskowitz

December 2015

Controlled polyacrylonitrile (PAN)-based carbon fiber precursors with defined molecular weights, polydispersities, compositions, and architectures have been prepared for their study on thermal ring-closing stabilization behavior. PAN and its copolymers of number average molecular weights exceeding 170,000 g/mol were successfully synthesized via low temperature reversible addition-fragmentation chain transfer (RAFT) polymerization. RAFT polymerizations of PAN-based precursors were compared to conventional free radical solution polymerizations with a focus on the effects of molecular weight and polydispersity on structural evolution and cyclization efficiency. When RAFT polymerization was extended to copolymers, it was found that RAFT copolymers achieved greater cyclization intensities and improved thermal stability as compared to analogous uncontrolled free radical copolymers. The greater thermal stability was attributed to the more controlled polymerization method and the reduction of chain transfer and small molecule defects.

New comonomers were introduced for PAN-based precursors and explored in relation to traditional comonomers. N-isopropylacrylamide (NIPAM) was found to be a promising comonomer by simultaneously serving as a mediator to thermal cyclization as well as a plasticizer to facilitate processing and spinning. Utilizing RAFT polymerization

in combination with a semibatch reaction technique the copolymer sequencing of p(AN-co-NIPAM) was systematically investigated. Results suggest that adjusting the feed rate of each comonomer affects the comonomer distribution along the backbone by offering tunable cyclization behaviors.

Attempts were made to mediate tacticity of PAN to study effects of tacticity on cyclization. A series of Lewis acids and fluoroalcohols were employed as additives in the polymerization, but no changes in tacticity were observed.

A 98/2 p(acrylonitrile-co-NIPAM) fiber was prepared from conventional free radical solution polymerization. The fiber morphology, characterized by Transmission Electron Microscopy (TEM), displayed minimal defects at the nanoscale with a characteristic ribbon-like wavy pattern. The degree of orientation in the fibers was found to exceed that of a commercial-grade PAN-based precursor. The thermo-oxidative stability of the lab-produced fiber shared similar characteristics to commercial fibers and has set the benchmark for future designs of PAN-based carbon fiber precursors.

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DEDICATION

This dissertation is dedicated to my family for their constant love and support. To my parents, Barry and Tammy Moskowitz, for teaching me invaluable life lessons and making me the person I am today. To my brothers and sisters, Josh, Kelsey, Jessica, and Stan, for always being at my side providing advice, and leading the way. To Rachel, for her motivation, pushing me to constantly better myself, and for believing in me and loving me.

ACKNOWLEDGMENTS

I would like to acknowledge my advisor, Dr. Jeffrey S. Wiggins, for providing me the opportunities to grow as a professional. I am sincerely grateful for his selfless devotion towards my success as a graduate student. Dr. Wiggins put me in the driver seat from day one and allowed me to make the most of my graduate school experience. My confidence as a polymer scientist emanated through his hands-off management style and intellectual freedom. I would also like to acknowledge my committee members: Dr. Derek Patton, Dr. Charles McCormick, Dr. Sarah Morgan, and Dr. Robson Storey, whom all have given academic guidance and insight. I am thankful to Dr. Bronwyn Fox and her research group and Dr. Matthew Weisenberger for their collaboration.

I would like to thank Dr. William Jarrett and David Delatte for their assistance with laboratory instrumentation throughout the years. I am also appreciative of Dr. Richard Liang and his research group at FSU to allow me to use their X-Ray Scattering instrument. I would also like to recognize Jody Wiggins, Stephanie Patton, and Charlene McMillin for all their help with lab supplies and organizing events. I would like to thank industry partners Rob Maskell, Al Thomas, Longgui Tang, Matt Jackson, and Steve Christensen for providing direction in my research.

I would like to thank my peers for making me a more well-rounded scientist and teaching me throughout my graduate career: Brooks Abel, Chris Childers, Mark Early, Phil Pickett, and Robert Peterson. Finally, I would like to acknowledge all of the current and past members from Wiggins Research Group, in particular John Misasi and Brian Greenhoe, for sticking together and making graduate school more enjoyable, and also my undergraduates for their contributions in the lab: Jonathan, Cade, and Anthony.

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CHAPTER I

INTRODUCTION

Carbon Fiber Composites

Global research initiatives continue to push the limits of materials performance as society strives for more fuel efficient automobiles, lighter aircrafts, higher performing sports equipment, improved construction materials, alternative sources of energy and new materials for general infrastructure. Fiber reinforced polymer matrix composites have rapidly proliferated over the past several decades due to favorable strength to weight ratios as compared to traditional materials such as wood, metals, and ceramics. Carbon fiber reinforced polymers (CFRPs) represent the highest performance polymer-matrix composites due to the high strength, high modulus, low density and economics of carbon fibers. Additionally, CFRPs retain high tensile moduli and high strengths at elevated temperatures and extreme environments, offer excellent electrical and thermal conductivity, and display a relatively low coefficient of thermal expansion.¹⁻³

To date, state-of-the-art carbon fibers have an ultimate tensile strength of around 7 GPa (1000 ksi), which greatly underestimates their theoretical potential.^{4,5} Advancing carbon fiber properties has proven to be a difficult task because carbon fiber production is quite complex including the design and synthesis of precursor polymers, the conversion of these polymers into white fibers, and the ultimate conversion of white fiber into carbon fiber. It is well accepted that ultimate carbon fiber performance relies on the appropriate design of the precursor chemistry and structure.^{1,5}

In the last five years research efforts have stimulated carbon fiber development including those by the Department of Energy's Institute for Advanced Composites

Manufacturing Initiative (IACMI) through the University of Tennessee and Oak Ridge National Laboratories,⁶ the Deakin University/CSIRO Carbon Nexus, and TU Munich led MAI Carbon. The overall goal is to better understand fundamental aspects which link carbon fiber precursor morphology and chemical composition with ultimate carbon fiber morphology and properties.

Polyacrylonitrile (PAN)-Based Carbon Fiber Precursors

Carbon Fiber Precursors

Thomas Edison was the first person to be credited for developing a carbon fiber filament in 1878 by pyrolyzing cotton and bamboo fibers into carbon fibers for use in incandescent lamps.⁵ During the mid- to late 20th century, carbon fiber production received renewed interest for use as a high strength polymer reinforcement. Initially, the military developed high-temperature resistant carbon fibers pyrolyzed from regenerated cellulosic fibers (rayon) for use in missile applications.⁵ Polyacrylonitrile (PAN)-based carbon fiber precursors were introduced in the 1960s and displayed fibers with a higher carbon content leading to substantial improvements in strength and modulus.

Nowadays, carbon fiber precursors are derived from three sources: synthetic PAN copolymers, coal or petroleum based mesophase-pitch, and regenerated cellulosic fibers. Polyacrylonitrile (PAN)-containing copolymers are the leading precursor materials for carbon fiber production, comprising approximately 90% of all production world-wide.⁷ PAN-based precursors yield the highest tensile strength due to a higher two dimensional molecular orientation of graphitic sheets as compared to pitch- and cellulose-based fibers.^{1,3,5,8} During the decade of 2000 to 2010, global carbon fiber consumption more than doubled from 16,600 to over 35,000 tons per year.⁹ PAN-based carbon fibers are

generally recognized as “the most important and promising precursors for manufacture of high strength carbon fibers.”⁵

Structure and Properties of PAN

Carbon fibers by definition contain a minimum of 92 wt. % carbon, while those containing >99% carbon are termed graphite fibers.^{1,3} The covalently bonded carbon atoms within these fibers are arranged in sp^2 hybridized hexagonal patterns set in planes of graphene sheets which stack via van der Waals and non-bonded interactions. Fibers made from PAN precursors form turbostratic layered structures where the planes are slightly off parallel and irregularly stacked. The irregular stacking results in larger interlayer spacings than those of graphite.⁸ Johnson and coworkers published a morphological model for the microstructure of PAN-based carbon fibers in 1987 based on X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis (Figure 1).^{10,11} This model suggests a ribbon-like outer sheath of graphene sheets scattered with needle-shaped voids (1-2 nm) surrounding a core of highly disordered and folded layer planes. Huang and Young confirmed a sheath-core structure using Raman spectroscopy in 1995.¹² Furthermore, Diefendorf and Tokarsky found that the modulus of PAN-based fibers varies throughout its cross-section, which reinforces the concept of a core-sheath morphology. Although the core-sheath morphology is generally accepted, there are very few studies which correlate the PAN precursor composition to morphological development.^{13,14}

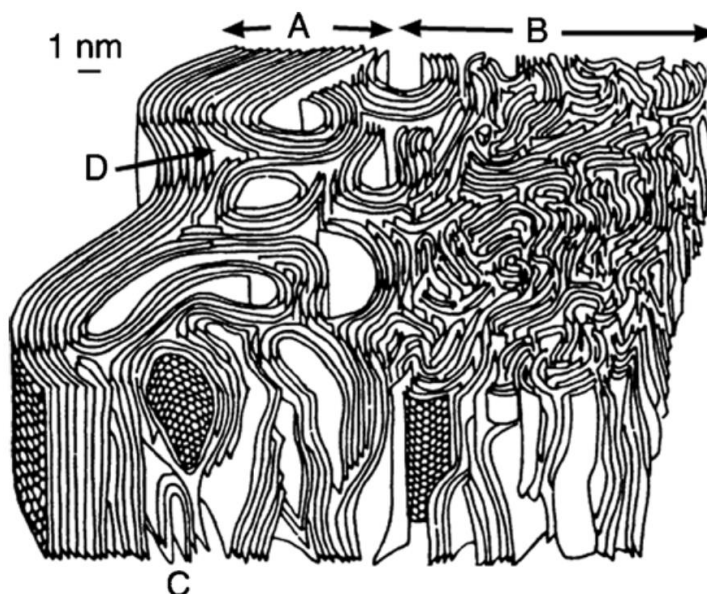


Figure 1. Microstructure of PAN-derived carbon fiber: (A) skin region, (B) core region, (C) hairpin defect, (D) wedge disclination. Reproduced by permission of the Society of Chemical Industry/London from reference number 10.

The morphology of PAN is driven by the crystal structure and the packing of polymer chains. PAN is virtually completely atactic, but still contains a considerable amount of crystallinity (>10%) with typical crystallite thicknesses of 10 monomer units.¹⁵ The conformation of atactic PAN is predominantly planar zigzag within a pseudohexagonal crystal lattice and occasional kinks arising from isotactic segments.¹⁶ The hexagonal crystal structure has characteristic (100) and (110) diffraction planes centered c.a. $2\theta = 17$ and 29° for X-ray scattering, respectively, with a broader diffraction peak c.a. 25° related to irregular structure.¹⁷ The irregular structure and crystalline disorder of PAN is responsible for improved compressive strength as compared to other carbon fiber precursors.¹⁸ To advance PAN-based precursors it is necessary to understand how changes in precursor composition influence crystal structure and crystallinity.

PAN-Based Copolymers

PAN homopolymer is seldom used for carbon fiber manufacturing due to its low solubility and poor processability from strong interactions and close packing of polymer chains.^{13,19} Typically, 3-10 wt. % of various comonomers are copolymerized with acrylonitrile to improve solubility, spinnability, drawability, hydrophilicity, and assist in the stabilization of the fibers during pyrolysis.^{3,8,20,21} Comonomers reduce interaction forces between polymer chains, resulting in larger crystallite thicknesses (L_c) for copolymers than PAN homopolymer.²²

Generally, PAN-based precursors are designed with more than one comonomer.²³ For example, the commercially available Bluestar® fiber contains 6% methyl methacrylate and 1% itaconic acid.²⁴ Acidic comonomers, such as acrylic acid (AA) and itaconic acid (IA), facilitate cyclization and increase hydrophilicity of PAN,^{25,26} while neutral comonomers like methyl acrylate (MA) and methyl methacrylate (MMA) improve solubility and processability.^{19,27} However, comonomers also influence polymerization kinetics, where unequal reactivities of each comonomer results in a heterogeneous distribution of comonomers, or non-uniform sequencing, along the chain.²³ Typically, neutral comonomers possess higher reactivity than acidic comonomers for terpolymers with acrylonitrile.^{28,29} If the amount of acidic comonomer in the feed increases during polymerization, the molecular weight decreases and results in poor carbon fiber performance. To overcome these challenges, a copolymer would be better suited for PAN-based precursors than conventional terpolymers. Recently, novel comonomers have been synthesized as itaconic acid derivatives to serve both the purpose of acidic comonomer and neutral comonomer.^{26,29,30} Therefore, a great interest is

emerging in comonomer design and future copolymers that could replace the traditional terpolymer precursors.

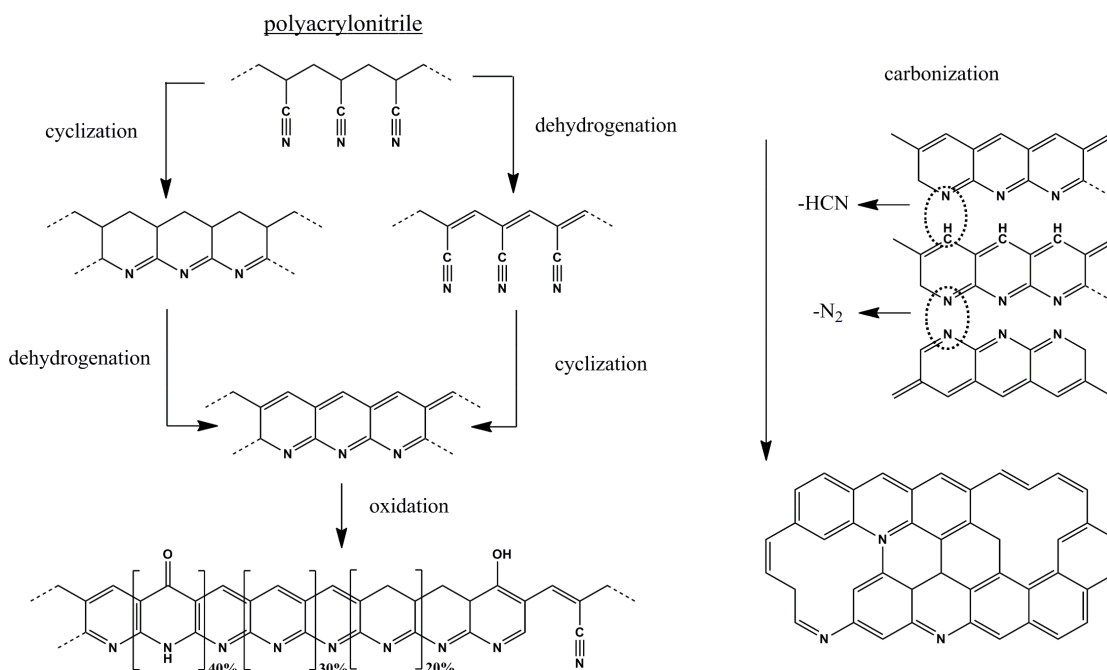
Processing of PAN-based Precursors

PAN-based precursors undergo a series of processing stages in the conversion of PAN to carbon fiber including: spinning, drawing, thermo-oxidative stabilization, and carbonization. Spinning and drawing are critical for establishing morphology of the fibers through mass transfer of solvent to form the fiber skin as well as the molecular orientation.⁸ Spinning and drawing heavily depend on the PAN precursor composition, since composition dictates macromolecular regularity, crystal orientation, and dimensional stability.³¹ Thermo-oxidative stabilization is also highly dependent on the precursor structure and properties as will be discussed in the following section. Carbonization occurs between 800 –1600 °C under nitrogen.^{7,8} During carbonization hydrogen and heteroatoms are volatilized into hydrogen gas, nitrogen gas, water, and carbon compounds: methane, hydrogen cyanide, carbon monoxide, carbon dioxide, etc. as large graphitic sheets are formed.⁸ Byproducts equate to over 40 wt.% of the starting mass.^{7,8}

Thermo-oxidative Stabilization of PAN-based Precursors

Thermo-oxidative stabilization or more simply, stabilization, is an essential and time-consuming step, which forms the cyclic polyimine, or “ladder polymer”, and sets the foundation for graphitic structures.^{7,32,33} Stabilization typically occurs between 200–300 °C in the presence of air.^{7,8} The time and temperature of stabilization can greatly affect the mechanical properties of the resulting carbon fibers.³⁴ It is suggested that a greater degree of stabilization allows the polymers to withstand higher temperature

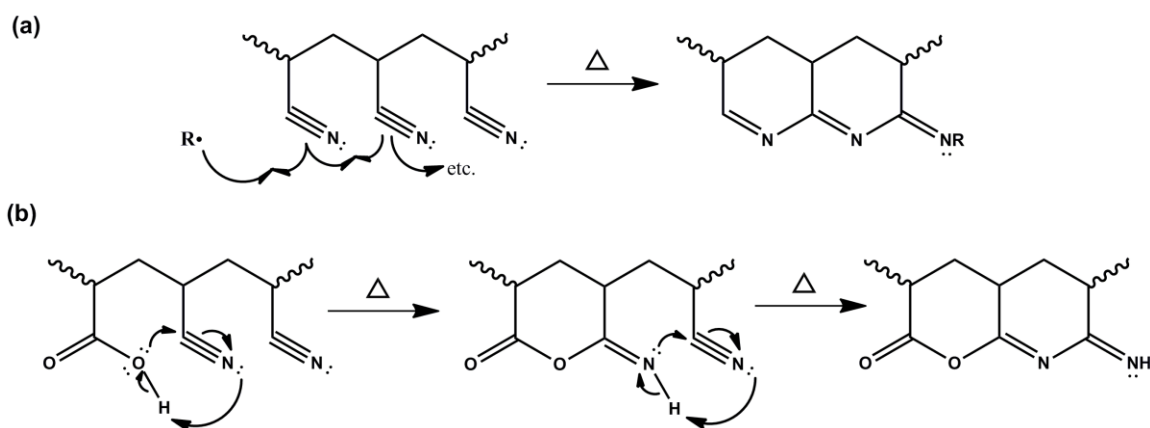
carbonization and yield better mechanical properties.^{13,21,35} Stabilization consists of four principle reactions: oxidation to form carbonyl and hydroxyl moieties, dehydrogenation to form conjugation along the backbone, intramolecular cyclization of nitriles, and intermolecular cross-linking between chains.^{7,32,36} The order and kinetics of these reactions are still disputed in the literature,^{37–39} but the general reaction scheme²³ is shown in Scheme 1 with composition of the given ladder structure as proposed by Bansal and Donnet.²¹ During stabilization, the “ladder polymer” undergoes a series of tautomerization and isomerization events from the polyimine to polyenamine.^{40–42} Stabilization is also characterized by the release of various byproducts such as hydrogen cyanide, ammonia, water, carbon dioxide, carbon monoxide, and methane.^{8,43} Relating these volatiles to precursor composition is a necessary step for the development of precursor architectures.



Scheme 1. General reaction scheme for PAN conversion to graphitic carbon structures.

Oxidation typically complicates stabilization by incorporating many compounds into the precursor structure such as ketones, nitrones, epoxides, and lactones.³² Oxygen can either promote cyclization acting as a site for initiation,^{23,44} or it can retard cyclization by scavenging radical intermediates.^{45,46} Thermal oxidation can also lead to relaxation of internal stresses with a decrease in strain of bonds and angles, but it is unclear whether the relaxation promotes or hinders cyclization.⁴⁷

While an oxygen atmosphere is necessary for dehydrogenation, it is not a prerequisite for cyclization. Cyclization follows first order kinetics,^{25,45} and can be initiated by impurities, end groups, radicals, the presence of ketonitriles, or other nucleophiles.^{7,48} More specifically, it is accepted that cyclization is initiated through a free-radical mechanism for homopolymer PAN, but when an acidic comonomer is present it is initiated via an ionic pathway^{25,42} as demonstrated in Scheme 2. Free radical cyclization is characterized by a very rapid exothermic reaction in which the heat released can destroy molecular chains causing structural flaws.⁴⁹ On the other hand, ionic cyclization occurs over a broader temperature range obviating the exothermic reactions taking place simultaneously and avoids a central heat release.²⁵



Scheme 2. (a) Radical cyclization of PAN and (b) ionic cyclization of p(AN-co-AA).

Cyclization is arguably the most important reaction in the stabilization phase of processing. Improving PAN-based carbon fibers hinges on the reduction of defects and disclinations present during this step, which generally spread through carbonization. A greater extent of cyclization would result in a higher carbon yield and fewer volatile byproducts. Thus, a better understanding of how composition correlates to the extent of cyclization will enable the future design of PAN-based precursors.

Polymer Precursor Properties and Their Effects on Carbon Fiber Processing

Effect of Molecular Weight and Polydispersity

Polymers are often identified by their molecular weight and molecular weight distribution. Typical carbon fiber precursors range between 70,000–200,000 g/mol with polydispersities (PDIs) (M_w/M_n) between 2–3.¹ High molecular weight fractions can cause issues during fiber spinning and filtration such as gelation and insolubility.^{23,50} In the carbon fiber manufacturing process, molecular weight and its distribution govern final carbon fiber properties.^{42,51–53} Increasing molecular weight leads to increased crystallite size and smaller void sizes as well as changes in the fiber morphology such as circular to bean-shaped cross sections and grooved surfaces along the skin.^{51,53} Moreover, increasing molecular weight has been shown to influence which small volatiles are released during thermo-oxidative stabilization of PAN-based precursors with higher molecular weights releasing more hydrogen cyanide and lower molecular weights giving off more ammonia.⁴¹

Although cyclization is recognized as one of the most important prerequisites for high performing carbon fiber, little is known about the effect of molecular weight and its distribution on the cyclization of PAN. Tsai et al. claim that cyclization onset temperature

increases with higher molecular weight, but samples in their study had high polydispersity (>1.8).⁵¹ Chernikova et al. asserted the same finding for a series of low molecular weight samples ($< 3,000$ g/mol), yet cyclization exotherms yielded several unresolved and overlapping peaks.⁵² Other reports in the literature make similar claims,⁵³ but lack hard evidence due to unreported polydispersities or conflicts within the data. Thus, the literature would benefit from a comprehensive study on the effects of cyclization wherein molecular weight and polydispersity are precisely controlled.

Effect of Polymerization Mechanism

Equally important to molecular weight is the polymerization mechanism. Since the first report of PAN-based carbon fibers by Shindo in 1961,⁵⁴ PAN precursors have been polymerized primarily by solution and suspension polymerization, with solution polymerization being most favorable due to immediate manufacture of spinning dopes.^{23,55} The two main drawbacks to solution polymerized precursors are that monomer conversion is typically only 50–70%, and that conventional solvent systems are characterized by high transfer constants leading to undesirable side reactions during polymerization.²³ Bol'bit and coworkers demonstrated that emulsion polymerization at low temperature (22 °C) led to a smaller proportion of long chain branches than solution polymerization at higher temperature (50 – 60 °C), even though the solution-formed polymer had a lower polydispersity.⁵⁶ Long chain branches present in conventional free radical solution polymers hinder reptational motion of the macromolecule. Therefore, the polymerization mechanism can significantly influence precursor properties.

Effect of Crystallinity

Oxidation and cyclization are thought to initiate in the amorphous region, where diffusion of small molecules are easier along with greater structural relaxation.^{7,31,32,57} Copolymer composition dictates crystallinity, wherein a greater content of comonomers lead to a greater amorphous content. Comonomers facilitate oxygen uptake and provide molecular passages due to their bulky size.²⁵ However, an excessive amount of comonomer can lead to structural defects in the polymer for cyclization,⁴⁴ while excessively high crystallinity can also lead to high stress during fiber stretching.⁵⁸ Additionally, solvent effects are important to consider as residual solvents from polymerization, such as N,N-dimethylformamide, can plasticize PAN and reduce the crystallinity.⁵⁹

Effect of Tacticity

Highly isotactic PAN (wherein the nitrile groups are in a meso configuration) could be advantageous, from a positional point of view, for cyclization of adjacent nitrile groups compared to other stereo structures.^{36,40,41,60,61} It was suggested that atactic PAN forms primarily isolated pyridine units in early stages of stabilization as opposed to long ladder sequences, whereas the formation of ladder structure could be expedited by isotactic PAN.⁶² Stabilization of atactic PAN is presumed to lead to defects such as olefinic and aliphatic units due to partial cyclization.⁵⁹ Moreover, the hexagonal plane layer that should form during carbonization of isotactic PAN should be larger than in conventional atactic PAN, resulting in higher mechanical strength.⁶⁰

Few studies evaluated the effect of tacticity on the cyclization mechanism of PAN. Zhang et al. found that cyclization of isotactic PAN has a higher activation energy

than atactic PAN.¹⁷ Similarly, Burkanudeen et al. showed that cyclization of isotactic PAN has a higher onset temperature and more gradual mass loss as compared to atactic PAN.⁶³ Yet, there are no known reports on how the tacticity plays a role in the final properties of carbon fiber, nor is there evidence that supports greater extent of stabilization for isotactic PAN.

Issues Regarding Past Research Methods

To date, most research on the cyclization of PAN-based precursors disregards information about the polymerization mechanism or the chemical and physical properties of the PAN precursor. Without answers to basic polymer properties and polymerization history, the results of the experiments are left open-ended. Griбанov and Sazanov discuss in detail the issues concerning the steric organization and long cyclic sequences of pyridine.⁴⁷ As a rule, only macrochains consisting of three to ten conjugated nitrogen-containing rings can be obtained, and more typically only five to seven in real PAN samples.⁴⁷ In the past, researchers attributed the short sequences to the lack of tacticity, but the authors explain that even in the case of 100% isotactic PAN (which is impossible) the amount of ring strain in the nitrogen-containing cyclic sequences and non-uniform electron density would limit their stability. The bond lengths of pyridine rings are non-equivalent as compared to benzene. To demonstrate ring strain, a sequence of 8 nitrogen-containing rings with the minimized energy (via Chem3D Pro Software) is shown in Figure 2. As can be seen, the ladder structure concaves towards the side with nitrogen atoms creating tension in the cyclic structure.

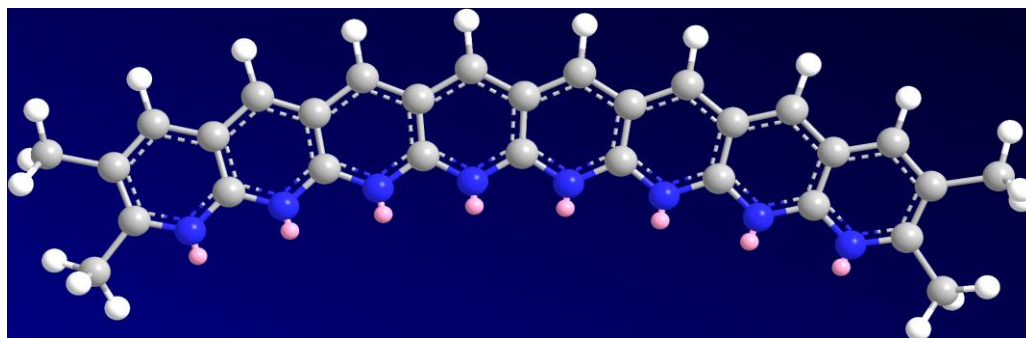


Figure 2. Ring strain for 8-membered cyclic sequence of nitrogen-containing rings. Gray atoms are carbon, blue atoms are nitrogen, white atoms are hydrogen, and the pink spheres represent lone electron pairs.

Moreover, the current literature base typically employs only a single thermal analysis method when investigating extent of stabilization or stabilization kinetics.⁶⁴ Recently, new methods for evaluating stabilization of PAN-based precursors have been developed^{58,65,66} and combining these techniques would elucidate the effects of polymer composition on stabilization behavior of PAN-based precursors.⁶⁷ Thus, a controlled study wherein the polymer properties are precisely identified in conjunction with comprehensive thermal analytical techniques would elucidate behaviors of PAN precursor stabilization.

Controlled/Living Radical Polymerization (CLRP) of PAN

With the advent of contemporary controlled/living radical polymerization (CLRP) methods, several attempts have been reported to control the polymerization of AN and its comonomers utilizing atom transfer radical polymerization (ATRP),^{68–71} activators regenerated by the electron transfer (ARGET) ATRP,⁷² and reversible addition-fragmentation chain transfer (RAFT) polymerization.^{50,52,73–78} Despite these efforts, there has been limited success in obtaining high molecular weight PAN with low polydispersities (PDIs). Controlling molecular weight and PDI of PAN is essential before

considering other precursor properties, such as comonomer selection and tacticity, to avoid confounding variables.

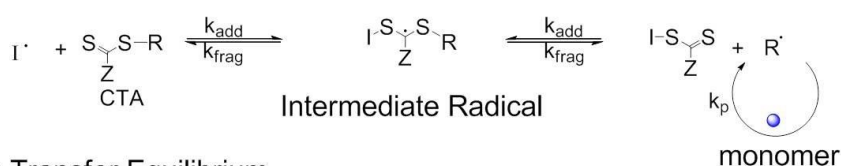
Dong et al.⁷² utilized ARGET ATRP at long reaction times (>90 hours) to prepare PAN with molecular weights above 200,000 g/mol (SEC-MALLS) with relatively high PDIs of 1.45. Yet, at shorter reaction times (<90 hours) conversions remained below 60% and molecular weights below 100,000 g/mol. Also, ATRP necessitates the use of a metal catalyst, which can be difficult to remove and the residual metal ions are detrimental to carbon fiber fabrication.⁷⁸ Pan et al.⁷⁹ recently reported on the photoinduced metal-free ATRP of acrylonitrile, but the resulting polymers were of low molecular weight (<15,000 g/mol) and broad PDI (>1.5).

Alternatively, RAFT polymerization is a versatile CLRP technique with excellent functional group tolerance⁸⁰ and shows promise for the production of carbon fiber precursor materials with controlled molecular weights and polydispersities. The general mechanism for RAFT polymerization is shown in Scheme 3. RAFT polymerization of PAN was first reported by Matyjaszewski et al. in 2003.⁷³ In 2012, Niu et al.⁷⁸ utilized a bifunctional dithiocarbamate to achieve relatively high molecular weight (>100,000 g/mol) and low PDI (< 1.4) PAN using RAFT. More recently, Spörl et al.^{50,81} demonstrated high conversion (> 80%) of AN in less than 7 hr with the use of 2-cyano-2-propyl dodecyltrithiocarbonate (CPDT) at 90 °C. However, references [50, 78, and 81] report molecular weights relative to polymethylmethacrylate (PMMA) standards, which overestimate the molecular weight of PAN.⁷² Additionally, these studies show non-linear kinetics for reaction times beyond 8 hours. Moreover, it is not uncommon to observe

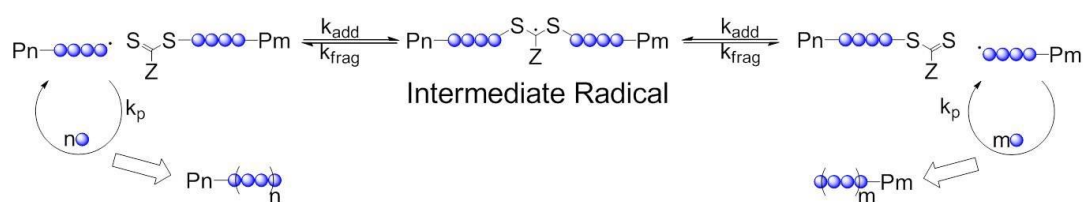
reduced conversions and molecular weights when acrylonitrile is copolymerized,^{50,76,77} and, therefore polymerization methods must be modified to overcome these challenges.

I. Initiation

II. Addition to CTA



III. Chain Transfer Equilibrium



Scheme 3. Schematic of RAFT mechanism. I. Initiation by thermolysis or photoinitiation to form radicals. II. Addition of the radical initiator to the chain transfer agent (CTA) to form dynamic equilibrium with intermediate radical. III. Chain transfer equilibrium with polymer chains.

Low Temperature Polymerization

It was first shown in 1995 by Kim et al.⁸² that the low decomposition temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (V-70), could be used to polymerize acrylonitrile under conventional free-radical solution conditions at 30 °C. Higher molecular weights were indicated by increased inherent viscosities as compared to those initiated by 2,2'-azobis(isobutyronitrile) (AIBN) at 50 °C. Similarly, high conversions and low polydispersities have been achieved during the room temperature RAFT polymerizations of acrylamide, N,N-dimethylacrylamide, and N-isopropylacrylamide using V-70 as the initiator.^{83,84} Additionally, Dong et al. demonstrated that lowering the temperature of the ATRP of AN from 65 °C to 40 °C resulted in lower polydispersities.⁷²

Thus, low temperature polymerizations could increase molecular weights and improve control in the RAFT polymerization of acrylonitrile and its copolymers.

Copolymer Sequencing

Evident from previous discussion, copolymer sequencing may hold significant value as the distribution of comonomer can affect crystallinity, thermal properties, and final carbon fiber properties. As mentioned, the maximum sequence length of heterocyclic, fused pyridine rings is about 5–7 rings. Also, ionic initiation of cyclization is the preferred mechanism due to the slower liberation of heat release. In theory, controlling the placement of comonomer to mediate cyclization by the ionic mechanism while optimizing crystallinity and structural characteristics would improve the efficacy of stabilization and increase the mechanical properties of carbon fibers. This concept was first investigated by Tsai et al. in 1991,⁸⁵ wherein methyl acrylate (MA), itaconic acid (IA), and 2-ethyl hexyl acrylate (EHA) were introduced at controlled feed rates and copolymerized with acrylonitrile. They found that slowing the feed rate of comonomer resulted in decreased crystallite size and crystallinity while neutral comonomers (MA and EHA) increased cyclization onset temperature and the acidic comonomer (IA) lowered cyclization temperature.

Hou et al.⁸⁶ used reactivity ratios for comonomers (IA, acrylic acid, and n-vinyl pyrrolidone) and acrylonitrile to simulate number average sequence lengths of the monomers. They found that the number average sequence length of acrylonitrile is sensitive to the composition of the feed and small changes significantly impact the precursor properties. For example, increasing IA content from 2 to 8 mol% results in a 4-fold decrease in the average sequence length of acrylonitrile (62.8 to 16.8). Thus,

comonomer content cannot be neglected when considering sequence distribution of the copolymer.

It is known that in batch copolymerization, varying reactivity ratios lead to compositional drift and yield copolymers with a compositional gradient along the backbone. CLRP techniques slow down the polymerization rate and thereby provide time to design and control the chain structure by a semibatch approach. Recently, Luo and Wang introduced the theory of a semibatch reaction design in conjunction with CLRP techniques.⁸⁷ In their study, they performed simulations of model semibatch reactions in which an optimum feeding profile could result in a uniform distribution of comonomers along the backbone. Successful demonstration of this theoretical method was then applied to RAFT copolymers of styrene and butyl acrylate,⁸⁸ as well as more exotic comonomer distributions such as linear gradient, hyperbolic tangent gradient, and triblock gradient profiles.⁸⁹ These results validate the possibility of precisely controlled copolymer architectures for PAN-based copolymers utilizing semibatch reactions in conjunction with RAFT polymerization.

Tacticity Control of PAN

As mentioned, tacticity could play a significant role in the cyclization of PAN-based precursors. There have been many attempts to synthesize isotactic PAN including: anionic polymerization, γ -ray irradiation, and utilization of zeolites.⁹⁰⁻⁹² The most promising method for controlling tacticity on a large scale is the use of Lewis acids, which have been employed in the synthesis of other vinyl polymers.⁹³⁻¹⁰⁰ Lewis acids are proposed to mediate polymerization by a bidentate chelation with the pendant group in

the monomer and the growing chain end, and they are compatible with controlled radical polymerization techniques.^{93–95}

It is proposed that strong Lewis acids with a high coordination number and a relatively large atomic radius induce isospecific chain growth.^{61,95} Metal triflates [Mt(OTf)₃; Mt=Y, Sc, Yb, etc.; OTf = OSO₂CF₃] can exhibit the necessary interactions and strongly interact with pendant groups of the polymer terminus or the monomer.⁹⁴ Aluminum chloride was shown to improve the isotacticity of PAN by about 7% when synthesized by ATRP.⁷¹ In the same experiment, no polymer was obtained when Y(OTf)₃ was used due to the Lewis acid interacting with the ligand. However, when Y(OTf)₃ was added to solution polymerization of N-isopropylacrylamide (NIPAM) at low temperature, the isotacticity increased as much as 35%.⁶¹ MgCl₂ in monomeric concentrations has mediated isotactic chain growth by acting as a geometric host for the bulk polymerization acrylonitrile.⁹⁴

Alternatively, it is worth pursuing syndiotactic PAN for the fundamental purposes of demonstrating tacticity effects on the cyclization mechanism. Isobutyraldehyde has been reported as an effective stereoregulator of syndiotactic vinyl chloride,¹⁰¹ and has been suggested as a possible stereoregulator for acrylonitrile.¹⁰² Also, fluoroalcohols have been shown to mediate syndiotactic-specific chain growth for vinyl esters.¹⁰³ Fluoroalcohols are proposed to create steric repulsion around the terminal chain end and the pendant group of the incoming monomer, facilitating racemic addition.¹⁰³

Moreover, RAFT polymerization is a robust controlled/living radical polymerization method and exhibits tolerance to functionalities including alcohols, amines, and acids.⁹⁴ Currently, there is only one known report which employs RAFT

polymerization of acrylonitrile in the pursuit of tacticity changes, but only an 8% increase in isotacticity was achieved.⁷⁸

Research Overview

The purpose of this dissertation is to build a platform for which the deliberate control of PAN-based precursors can be used for model studies relating precursor composition directly to carbon fiber stabilization behavior and kinetics. The central hypothesis being that higher control of PAN copolymer architecture such as comonomer structure, comonomer sequencing, and tacticity, will lead to increased cyclization efficiency and reduction in ladder structure disclinations. The motivation for this research stems from the renewed academic interest in creating higher performing CFRPs. With the advent of contemporary polymerization methods it is now possible to build and design new PAN-based precursor architectures. Thus, linking precursor composition to stabilization behaviors will lead to future generations of carbon fiber.

Currently, the literature focus is either on novel synthetic techniques or the characterization of PAN-based copolymers, but seldom is research conducted on both. Combining the controlled synthesis of PAN-based precursors with a widespread characterization of their structure and thermal stabilization behavior will elucidate the poorly understood effects of molecular weight, polydispersity, tacticity, and copolymer composition on the cyclization and stabilization of PAN-based precursors.

Herein, a straightforward method for producing high molecular weight and low polydispersity PAN via RAFT-mediated polymerization is demonstrated (Chapter III). The stabilization behavior and structure of RAFT-mediated polymerization is compared to conventional free radical polymerization of PAN (Chapter IV). The utilization of the

RAFT-mediated polymerization method is successfully extended to PAN-based copolymers in Chapter V. Copolymers of acrylonitrile with N-isopropylacrylamide (NIPAM), a new comonomer for the purpose of PAN-based carbon fiber precursors, were evaluated as compared to traditional PAN-based copolymers. Chapter VI presents a semibatch reaction procedure for the investigation of sequencing effects of NIPAM-containing PAN copolymers. Steps toward mediating tacticity of PAN homopolymer are introduced in Chapter VII. Finally, Chapter VIII explores the scale-up and spinning of a PAN-co-NIPAM white fiber precursor and its morphology in relation to commercial precursors.

CHAPTER II

MATERIALS, METHODS, AND PROCEDURES

Materials

Acrylonitrile (AN, 99%, 35-45 ppm monomethyl ether hydroquinone inhibitor (MEHQ), Sigma-Aldrich Chemical Co.) was passed through a neutral aluminum oxide (50-200 μm) column to remove the inhibitor immediately prior to use. Ethylene carbonate (EC, 99%, Alfa Aesar), dimethylformamide (DMF, 99%, Fisher Chemical Co.), dimethylsulfoxide (DMSO, 99%, Fisher Chemical Co.), and dimethylformamide were used as received. Tetrahydrofuran (THF, 99%, 250 ppm BHT inhibitor, Sigma Aldrich Chemical Co.) was vacuum distilled prior to use.

Selected Comonomers

Acrylic acid (AA, 99%, 180-200 ppm MEHQ inhibitor) was vacuum distilled to remove inhibitor. Methyl acrylate (MA, 99% 100 ppm MEHQ inhibitor), N,N-dimethylacrylamide (DMAM, 99%, 500 ppm MEHQ inhibitor), and methyl methacrylate (MMA, 99%, 30 ppm MEHQ as inhibitor) were passed through a neutral aluminum oxide (50-200 μm) column to remove the inhibitor immediately prior to use. N-isopropylacrylamide (NIPAM, 99%), fumaronitrile (FAN, 98%), maleic anhydride (MAD, 95%), isobornyl acrylate (IBA, 98.5%), acrylamide (AM, 98.5%, Acros Organics Chemical Co.), and itaconic acid (IA, >99%) were used as received. All comonomers were purchased from Sigma Aldrich Chemical Co. unless otherwise denoted and are shown in Figure 3.

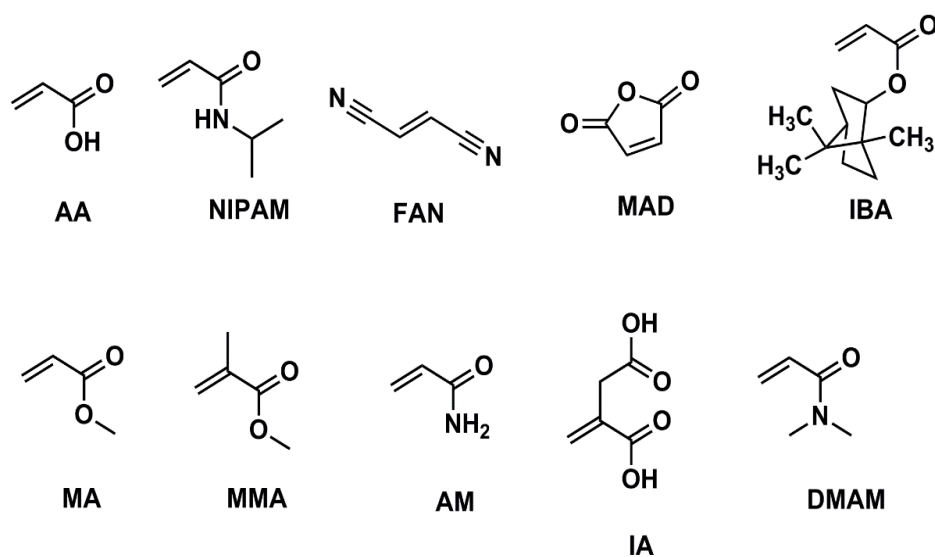


Figure 3. Structures of comonomers.

RAFT agents

2-cyano-2-propyl dodecyl trithiocarbonate (CPDT, 97%, Sigma Aldrich Chemical Co.) and cyanomethyl dodecyl trithiocarbonate (CMDT, 98%, Sigma Aldrich Chemical Co.) were used as received. Cyanoethyl dodecyl trithiocarbonate (CEDT) and 4-cyano-4-((thioethoxy)sulfanyl)pentanoic acid (CTSPA) were synthesized according to literature procedures as described below.^{104,105} Potassium ethyl xanthate (96%, Sigma-Aldrich Chemical Co.), iodine (99.8%, Sigma-Aldrich Chemical Co.), potassium iodide (99+%, Sigma-Aldrich Chemical Co.), anhydrous diethyl ether (Acros Organic), sodium thiosulfate pentahydrate (99.5%, Fisher Scientific), anhydrous magnesium sulfate (Fisher Scientific), 1-dodecanethiol (98%, Sigma Aldrich Chemical Co.), carbon disulfide (99.9%, Sigma Aldrich Chemical Co.), potassium phosphate tribasic (98%, Sigma Aldrich Chemical Co.), 2-bromopropionitrile (97%, Sigma Aldrich Chemical Co.), ethyl acetate (99+% extra pure, Acros Organics), absolute ethanol (99.5+%, Acros Organics),

hexane (Acros Organics), and acetic acid (99.7%, Sigma-Aldrich Chemical Co.) were used as received. The structures of the RAFT agents used are shown in Figure 4.

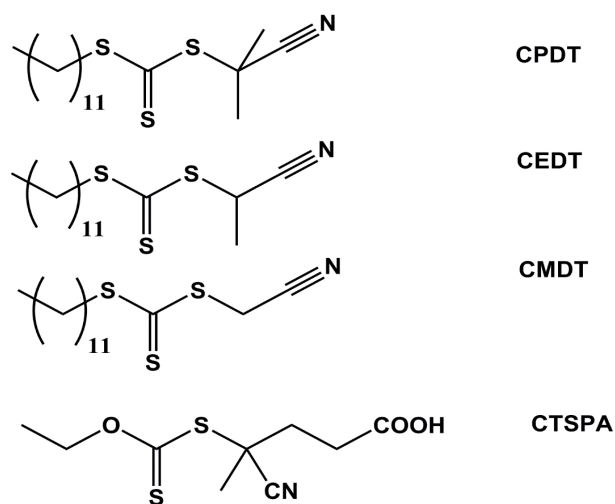
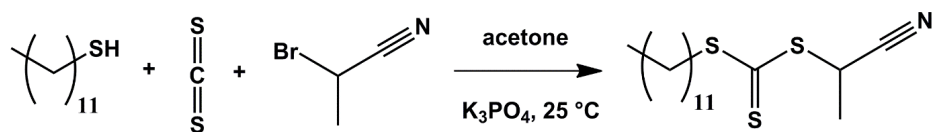


Figure 4. Structures of the RAFT agents used.

Synthesis of Cyanoethyl Dodecyl Trithiocarbonate (CEDT) (Scheme 4)

1-Dodecanethiol (1.76 g) and potassium phosphate tribasic (2.02 g) were dissolved in acetone (23.5 mL) in a 50 mL round bottomed flask equipped with magnetic stir bar. The solution was stirred at room temperature for 2 hours before carbon disulfide (1.97 g) was added dropwise via addition funnel over 10 mins and the reaction stirred an additional hour at room temperature. Then 2-bromopropionitrile (1.16 g) was added dropwise over 5 minutes via addition funnel and the solution stirred overnight. The salts were filtered and the solvent removed via rotary evaporation yielding a viscous yellow oil. Purification via column chromatography (silica gel, 60:40 hexane:ethyl acetate R_f = 0.59) yielded the product as a slightly yellow, waxy solid. The nuclear magnetic resonance (NMR) spectrum confirmed the structure of CEDT as shown in Figure 5.



Scheme 4. Synthesis of cyanoethyl dodecyl trithiocarbonate (CEDT).

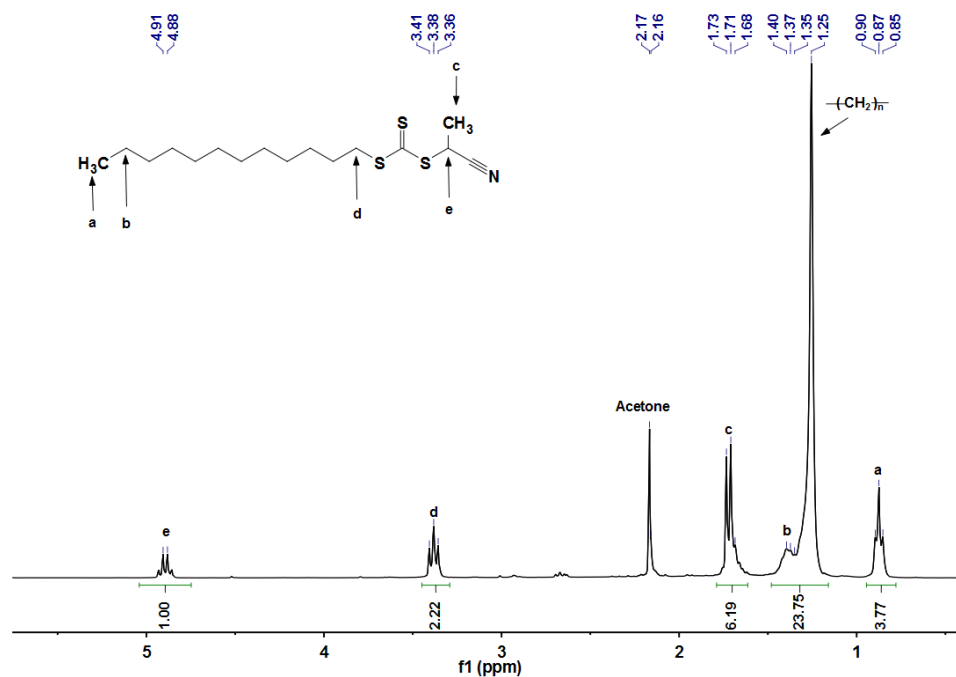
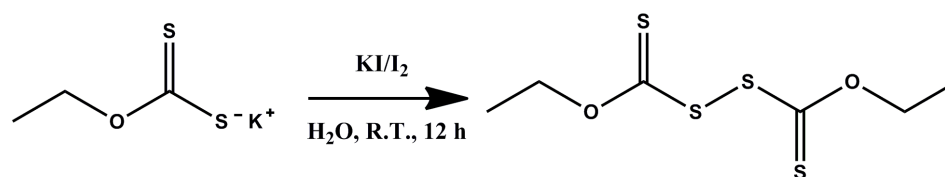


Figure 5. NMR spectrum of cyano ethyl dodecyl trithiocarbonate (CEDT).

Synthesis of Bisethylxanthate (BEX) (Scheme 5)

Potassium ethylxanthate (10.11 g) was dissolved in H₂O (50 mL) in a 250 mL round bottomed flask equipped with magnetic stir bar. A solution of I₂ (8.84 g) and KI (11.50 g) in H₂O (100 mL) was added dropwise via addition funnel over 30 mins and the reaction stirred overnight at room temperature. The solution was subsequently transferred to a separatory funnel, extracted three times with diethyl ether (100 mL), and the ether fractions combined, washed with aqueous sodium thiosulfate (5 wt. %, 100mL) and brine (100 mL) before drying over MgSO₄. The salts were filtered and the solvent

removed via rotary evaporation yielding a viscous yellow oil. The NMR spectrum confirmed the structure of BEX (Figure 6).



Scheme 5. Synthesis of bisethylxanthate (BEX).

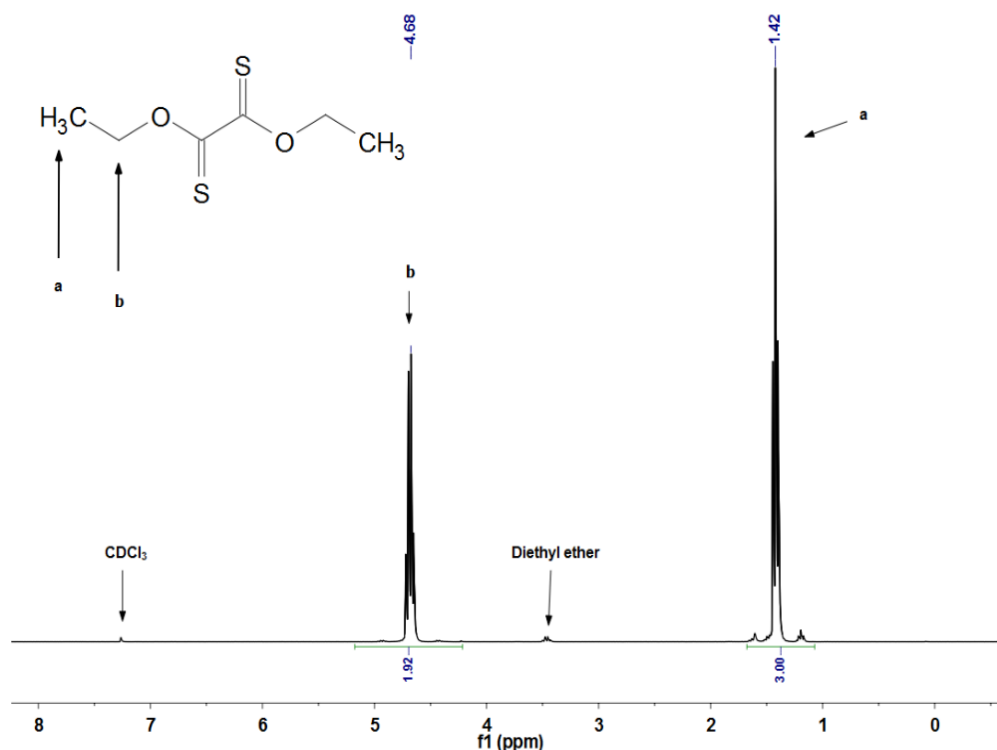


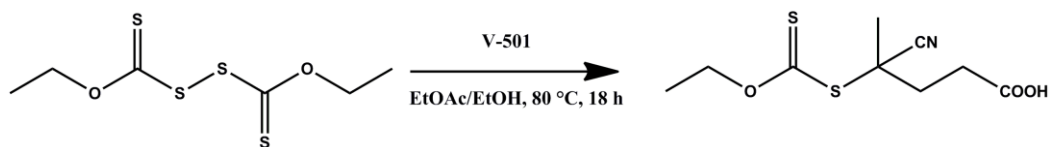
Figure 6. NMR spectrum of bisethylxanthate (BEX).

Synthesis of CTSPA (Scheme 6)

Bisethylxanthate (3.10 g) and V-501 (5.37 g) were dissolved in a 1:1 (v:v) mixture of ethyl acetate and absolute ethanol (200 mL) in a 3-necked round bottom flask equipped with magnetic stir bar and reflux condenser. The solution was purged with nitrogen for 40 mins and then heated to reflux overnight (18 h), upon which the reaction

was cooled to room temperature and the solvent removed via rotary evaporation.

Purification via column chromatography (silica gel, 60:39:1 hexane:ethyl acetate:acetic acid, $R_f = 0.3$) yielded the product as a slightly yellow, waxy solid. The NMR spectrum confirmed the structure of CTSPA (Figure 7).



Scheme 6. Synthesis of 4-cyano-4-((thioethoxy)sulfanyl) pentanoic acid (CTSPA).

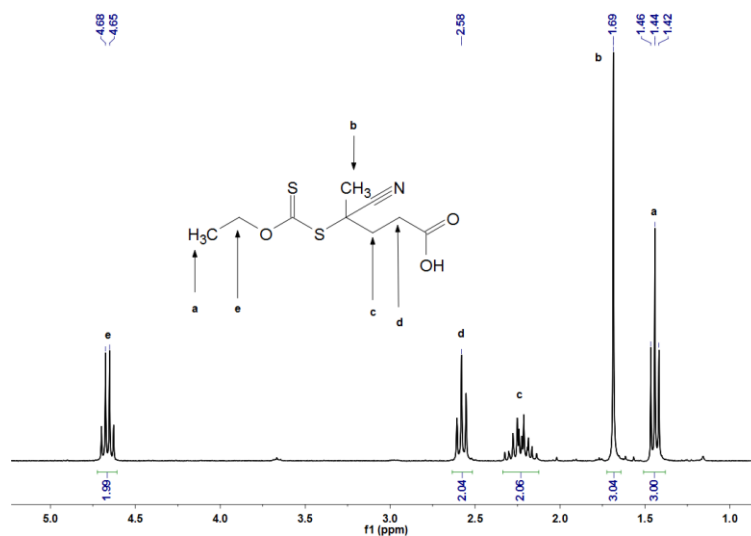


Figure 7. NMR Spectrum of 4-cyano-4-((thioethoxy)sulfanyl) pentanoic acid (CTSPA).

Initiator Structures

Azobisisobutyronitrile (AIBN, 99%, Sigma-Aldrich Chemical Co.), 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako Pure Chemical Industries, Ltd.), and 4,4'-azobis(4-cyanopentanoic acid) (V-501, 99%, Sigma-Aldrich Chemical Co.) were used as received. The structures of the initiators used are shown in Figure 8.

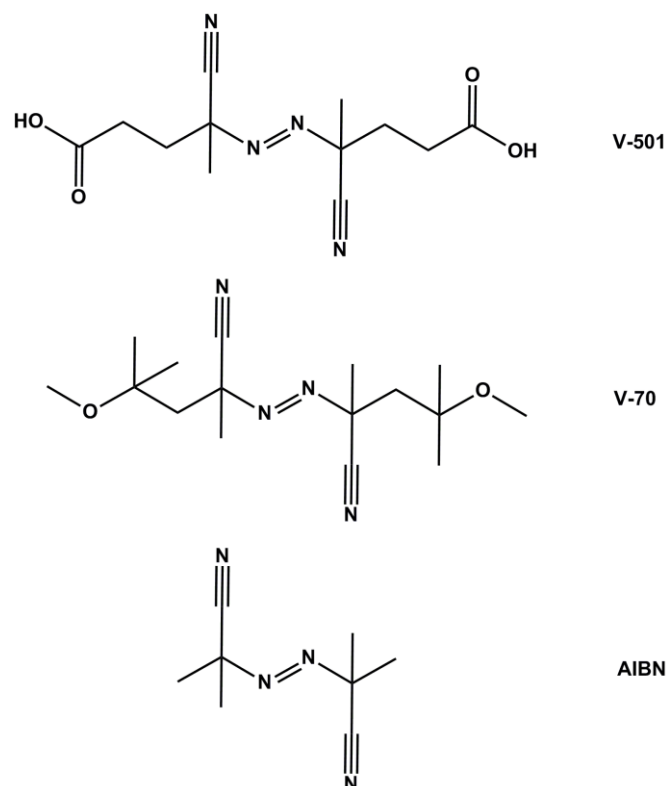


Figure 8. Structures of the initiators.

Lewis Acids, Fluoroalcohols, and Tacticity Modifiers

Lewis acids and fluoroalcohols were purchased from Sigma Aldrich Chemical Co. unless otherwise denoted. Isobutyraldehyde (99%, Acros Organics), 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene (BHFB, 97%, Matrix Scientific), Perfluoro-tert-butyl alcohol (PHTB, 99%, Acros Organics), 1,1,1,3,3,3-hexafluoro-2-propanol (HFP, 99.9%, Acros Organics), yttrium (III) trifluoromethanesulfonate ($\text{Y}(\text{OTf})_3$, 98%), ytterbium (III) trifluoromethanesulfonate ($\text{Yb}(\text{OTf})_3$, 99.99%), ytterbium chloride (YbCl_3 , 99.99%, anhydrous powder), zinc chloride (ZnCl_2 , 99.999%), aluminum chloride (AlCl_3 , 99.99%, anhydrous powder), and magnesium chloride (MgCl_2 , 98%) were used as received. The structures of the Lewis acids and fluoroalcohols are shown in Figure 9.

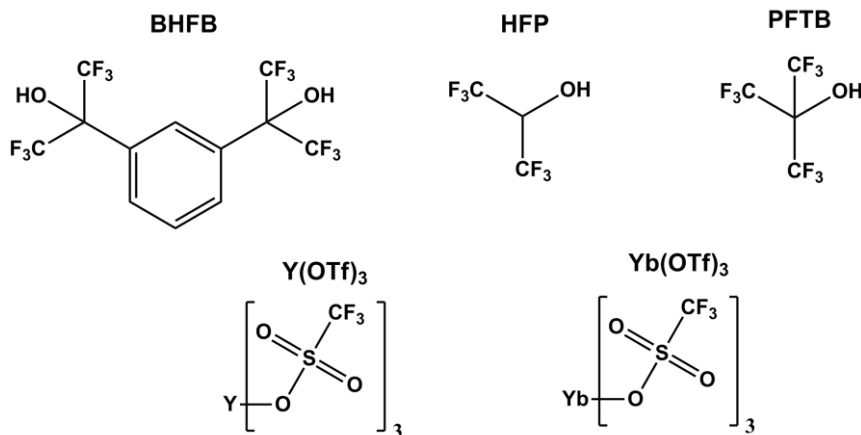


Figure 9. Structures of Lewis acids and fluoroalcohols.

Synthesis of Polyacrylonitrile and its Copolymers

Conventional Free Radical Solution Polymerization

A typical solution radical polymerization was as follows: ethylene carbonate (32.0 g), acrylonitrile (7.99 g, 151 mmol, 20 wt.%), and V-70 (9.5 mg, 0.031 mmol, stock solution in tetrahydrofuran (THF) 20 mg/mL) were charged to a 100 mL round bottom flask equipped with a magnetic stir bar. The reaction flask was capped with a rubber stopper and cooled to 0 °C and subsequently purged with N₂ for 60 min prior to heating in an oil bath 30 °C for 8 hours. When AIBN or V-501 were used as the initiator the oil bath was set to 65 °C and 70 °C, respectively (the initiator half-life temperatures), and stock solutions of similar concentration were prepared in DMF. Polymer isolation was achieved by precipitation into a 1 L bath of approximately 70:30 (v:v) deionized water and methanol followed by isolation via filtration and drying for 30 minutes under nitrogen. The polymer was then re-dissolved in DMF at 20 to 25 weight percent polymer, and the solution poured over aluminum foil and allowed to spread into a film. The film was coagulated by soaking in deionized water for 3-4 hour followed by a 24 hr

Soxhlet extraction in methanol to remove residual solvent. The polymer film was then dried in a vacuum oven at 60 °C overnight.

RAFT Polymerization

A representative RAFT polymerization of $[AN]_0:[CPDT]_0:[V-70]_0 = 10,000:1:0.67$ was as follows: ethylene carbonate (32.0 g), acrylonitrile (7.99 g, 151 mmol, 20 wt.%), CPDT (5.2 mg, 0.015 mmol, stock solution in dimethylformamide (DMF) 20 mg/mL), and V-70 (3.1 mg, 0.010 mmol, stock solution in tetrahydrofuran (THF) 20 mg/mL) were charged into a 100 mL round bottom flask equipped with a magnetic stir bar. The flask was capped with a rubber stopper and purged for 1 hour under nitrogen gas being held in an ice bath before being transferred to an oil bath set to 30 °C for 24 to 48 hours. Polymers were precipitated in and dried in the same manner as the uncontrolled free radical polymers. Theoretical number average molecular weights were determined by Equation 1:¹⁰⁶

$$M_{n,theor} = \frac{M_{MW} \cdot [M]_0 \cdot conversion}{[CTA]_0} + CTA_{MW} \quad (1)$$

in which $[M]_0$ and $[CTA]_0$ are the initial monomer and chain-transfer agent concentrations, respectively. M_{MW} and CTA_{MW} correspond to the molecular weights of the monomer and chain-transfer agent, respectively.

Kinetics of RAFT Polymerization

At timed intervals, 1 mL aliquots were drawn and analyzed by ¹H-NMR (DMSO-d₆) by comparing the relative integral areas of ethylene carbonate (δ (ppm): s, 4.50, CH₂) to the vinyl protons of AN (δ (ppm): d, 6.22; d, 6.36, CH₂; quad, 6.00, CH) as shown in Figure 10 for a polymerization with $[AN]_0:[CPDT]_0:[V-70]_0 = 10,000:1:0.67$. Size

exclusion chromatography (SEC) (DMF 20 mM LiBr) was used to monitor molecular weight progression and polydispersity during each polymerization.

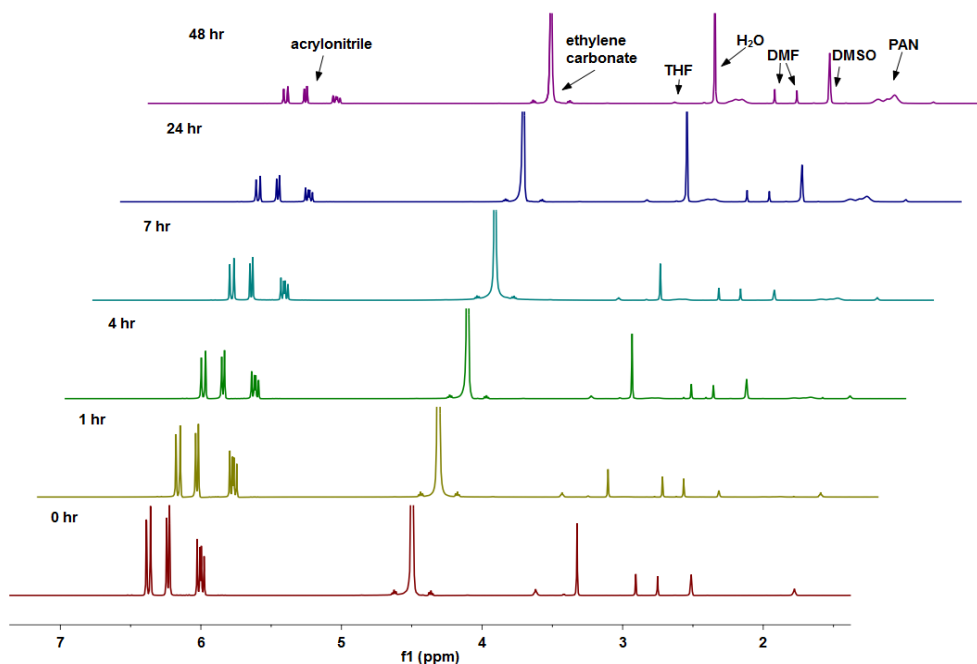


Figure 10. Representative NMR-spectra for timed intervals during RAFT polymerization of AN with $[AN]_0:[CPDT]_0:[V-70]_0 = 10,000:1:0.67$.

Scale-Up Polymerizations

A representative scale-up copolymerization of 98/2 p(AN-co-NIPAM) at $[AN]_0:[NIPAM]_0:[CPDT]_0:[V-70]_0 = 9,800:200:1:0.67$ was as follows: AN (80.00 g, 1.51 mol), NIPAM (3.34 g, 0.03 mol), CPDT (50.9 mg, 0.15 mmol, stock solution in dimethylformamide (DMF) 20 mg/mL), V-70 (30.3 mg, 0.10 mmol) stock solution in tetrahydrofuran (THF) 20 mg/mL) and ethylene carbonate (600 g, 80 wt%) were charged into a 1 liter round bottom, 2-neck reactor equipped with a magnetic stir bar. For free radical scale-up polymerizations, AIBN was utilized as the initiator and the reaction was performed at 65 °C with a reflux condenser. The flask was capped with a rubber stopper and purged for 1 hour under nitrogen gas being held in an ice bath before being

transferred to an oil bath set to 65 °C for 8 hr. The polymer was then precipitated in a 20 L bath of deionized water and allowed to dry. The polymer was then re-dissolved in dimethylsulfoxide (DMSO) at c.a. 15 wt. % weight percent polymer and re-precipitated in deionized water and soaked in methanol for 3-4 hours before drying in a vacuum oven at 60 °C overnight.

Methods of Characterization

Oxidation Treatment

Selected polymer films (50 mg) were subjected to an oxidation treatment in a Thermo Scientific Lindberg Blue M programmable oven by ramping to 225 °C at 5 °C/min air and holding at 225 °C for set time intervals.

Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H-NMR experiments were recorded with a Bruker Acend™ 600 MHz spectrometer. ¹H-NMR experiments were conducted at 30 °C with 5 wt% solutions in DMSO-d₆ using 32 scans and a 1 second relaxation delay. Monomer conversion was followed throughout the reaction by tracking the relative monomer concentration (δ (ppm): d, 6.22; d, 6.36; quad, 6.00) with respect to the ethylene carbonate (δ (ppm): s, 4.50). Quantitative ¹³C-NMR experiments (proton decoupler turned off) were also recorded at 30 °C using 1280 scans and a 45 second relaxation delay. Tacticity could be determined from the peak splitting of the methine carbon from PAN (c.a. 28 ppm) and the nitrile carbon (c.a. 120 ppm).¹⁰⁷

Size Exclusion Chromatography with Multi- Angle Laser Light Scattering (SEC-MALLS)

Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) of the polymer materials were measured using a GPC

system consisting of a Waters Alliance 2695 separation module, online multi-angle laser light scattering (MALLS) detector fitted with a gallium arsenide laser (20 mW power) operating at 690 nm (MiniDAWN Wyatt Technology Inc.), an interferometric refractometer (Optilab DSP, Wyatt Technology Inc.), and two Agilent PLgel mixed-C columns connected in series. HPLC grade N,N'-dimethylformamide (DMF) with 0.02 M LiBr served as the mobile phase and was delivered at a flow rate of 0.5 mL/min while operating at 60 °C. Sample concentrations were prepared at approximately 5 mg/mL with an injection volume of 100 μ L. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology Inc.). The dn/dc for PAN (0.084 mL/g) in the above eluent was determined offline from the slope of the refractive index vs. polymer concentration plot generated from refractive index measurements made at 4 polymer concentrations between 1 and 10 mg/mL (Figure 11). The measured dn/dc value was in excellent agreement with the dn/dc value calculated from the response of the interferometric refractometer, assuming 100% mass recovery (0.086 mL/g). Molecular weights were also determined relative to polymethyl methacrylate (PMMA) standards.

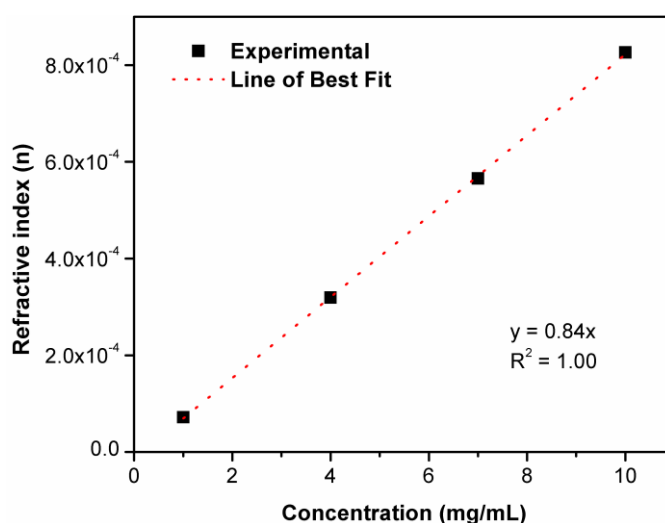


Figure 11. Determination of dn/dc (0.084 mL/g) for PAN.

Ubbelohde Viscometry

Viscosity average molecular weight, M_η , was measured using the intrinsic viscosity, $[\eta]$, in accordance with the Mark-Houwink equation from the relationship between molecular weight and viscosity (Eqn. 2):

$$[\eta] = K \cdot M_\eta^\alpha \quad (2)$$

The Mark-Houwink parameters, K and α , are constants for a given system where $K = 24.3 \cdot 10^{-3}$ mL/g and $\alpha = 0.75$ for polyacrylonitrile in DMF at 25 °C.¹⁰⁸ To measure $[\eta]$, solutions of known concentration (c) were prepared and the flow times of the neat solvent (t_0) and solutions (t) were measured using an Ubbelohde viscometer. Flow times were repeated in triplicate and five concentrations were prepared between 2 and 10 mg/mL. The reduced viscosity, η_{red} (Eqn. 3), and the inherent viscosity, η_{inh} (Eqn. 4), are both extrapolated to the zero concentration limits, where the average of the two ordinates is taken as the intrinsic viscosity (Eqn. 5):

$$\eta_{red} = \frac{\left(\frac{t - t_0}{t_0} \right)}{c} \quad (3)$$

$$\eta_{inh} = \frac{\ln\left(\frac{t}{t_0} \right)}{c} \quad (4)$$

$$[\eta] = \text{average} \left[\left(\lim_{c \rightarrow 0} \eta_{red} \right), \left(\lim_{c \rightarrow 0} \eta_{inh} \right) \right] \quad (5)$$

UV-Vis Spectroscopy

UV-Vis spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer. Samples were prepared using a stock solution of polymer in DMF in a glass quartz

cuvette. Excitation was carried out between 250–700 nm with a 0.5 nm slit width, 1 nm resolution, and 480 nm/min scan speed.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) Spectroscopy

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed using a Bruker Microflex LRF MALDI-TOF mass spectrometer equipped with a nitrogen laser (337 nm) possessing a 60 Hz repetition rate and a 50 μ J energy output. Polyacrylonitrile samples were prepared using a pre-mixed droplet method. A 10 mg/mL solution of matrix (4-hydroxybenzylidenemalonitrile) (4HBM) and THF, a 1 mg/mL solution of polyacrylonitrile and DMSO, and a 2 mg/mL solution of silver trifluoroacetate (AgTFA) and 50/50 (v:v) mixture of acetonitrile and water were all mixed in a volumetric ratio of 1:1:1 (10 μ L of each). Following, a 1 μ L aliquot was deposited onto a stainless steel MALDI sample target for analysis. All spectra were obtained in the positive ion mode utilizing the linear mode micro-channel plate detector and are the sum of 1000 shots.

Differential Scanning Calorimetry (DSC)

DSC was performed on a TA Instruments DSC Q200 equipped with a nitrogen purge gas. Heating ramp rates of 2, 5, 10, and 20 $^{\circ}$ C/min were employed from 30–320 $^{\circ}$ C. Sample sizes ranged from 2–6 mg in hermetic aluminum pans.

Cyclization activation energy was determined from the Flynn-Wall-Ozawa (FWO) and Kissinger methods, displayed in Equations 6 and 7, respectively, where E_a is the activation energy, R is the universal gas constant, T_p is the peak exotherm temperature in Kelvin, and ϕ is the temperature ramp rate in Kelvin. In both cases the activation energy is calculated by a series of temperature ramps for these systems and

both methods have seen wide employment in a variety of disciplines.^{25,59,109–111} The pre-exponential frequency factor, A, otherwise known as ‘collision frequency’, was determined from Equation 8 for both cases.²⁵

$$-\frac{E_a}{R} = 0.951 \bullet \frac{d(\ln \phi)}{d\left(\frac{1}{T_p}\right)} \quad (6)$$

$$-\frac{E_a}{R} = \frac{d\left[\ln\left(\frac{\phi}{T_p^2}\right)\right]}{d\left(\frac{1}{T_p}\right)} \quad (7)$$

$$A = \frac{\phi E_a}{RT_p^2} e^{\frac{E_a}{RT_p}} \quad (8)$$

The cyclization index (CI) was calculated using heat released related to exotherm DSC peaks by Equation 9,^{67,112–114} where H_v and H_o are the heat released for the virgin and stabilized polymers, respectively:

$$CI = \frac{H_v - H_o}{H_v} \bullet 100\% \quad (9)$$

The H_v and H_o were calculated by integrating the total area under the exothermic peak related to cyclization.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra in transmission mode were recorded using a Thermo Scientific Nicolet 6700 FTIR in the range of 4000-400 cm^{-1} . An infrared source was used in conjunction with a KBr beam splitter and a DTGS KBr detector. Samples were prepared by dissolving about 5-10 wt.% polymer in DMF and then solution cast onto a polished 25mm x 4mm NaCl salt disc. The samples were then placed in a vacuum oven at 60 °C

overnight. The samples were monitored in real-time in a Simplex Scientific Heating Cell where 32 scans at 4 cm^{-1} resolution were acquired every 5 minutes during the cyclization reaction. The sample chamber was purged with nitrogen throughout the duration of the reaction (unless otherwise noted) as the temperature was raised to $225\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C}/\text{min}$ and then held at $225\text{ }^{\circ}\text{C}$ for 5 hours. The unreacted nitrile fraction was determined by Equation 10,⁴⁵ while the extent of stabilization, E_s , was determined by Equation 11,²⁵ where $A_{2240\text{cm}^{-1}}$ is the absorption of the nitrile ($-\text{C}\equiv\text{N}$), $A_{1590\text{cm}^{-1}}$ is the absorption of the imine ($-\text{C}=\text{N}-$), and f is the ratio of the absorptivity constants (0.29):³⁸

$$-CN\text{ unreacted} = \frac{A_{2240\text{cm}^{-1}}}{A_{2240\text{cm}^{-1}} + (f \bullet A_{1590\text{cm}^{-1}})} \quad (10)$$

$$E_s = \frac{A_{1590\text{cm}^{-1}}}{A_{2240\text{cm}^{-1}}} \quad (11)$$

Thermogravimetric Analysis (TGA)

TGA results were recorded on a TA Instruments Discovery Thermogravimetric Analyzer. The TGA was utilized to determine mass loss of the PAN samples in a nitrogen atmosphere ramped at $10\text{ }^{\circ}\text{C}/\text{min}$ to $700\text{ }^{\circ}\text{C}$. In an attempt to simulate conditions similar to industrial processing of carbon fiber, select samples were also heated in air at $10\text{ }^{\circ}\text{C}/\text{min}$ and held at a series of 4 temperatures in one of two conditions, before subsequently ramping to $700\text{ }^{\circ}\text{C}$ in nitrogen:

- Pre-oxidation 1 (Pre-ox 1): isotherms at 230, 245, 253, and $265\text{ }^{\circ}\text{C}$, for 15 minutes each
- Pre-oxidation 2 (Pre-ox 2): isotherms at 245, 260, 268, and $280\text{ }^{\circ}\text{C}$, for 15 minutes each

Raman Spectroscopy

Raman spectroscopy was carried out on a Thermo Scientific DXR Confocal Raman Microscope using a 532 nm excitation laser. The laser power was set to 5 mW with a 10x magnification objective lens, and the aperture selected was a 0.25 μm pinhole. Spectra were recorded until 1 cm^{-1} resolution was achieved. The ratio of the D-band (defect-induced) intensity (I_D) c.a. 1350 cm^{-1} and the G-band (sp^2 -hybridized carbon in graphite planes) intensity (I_G) c.a. 1600 cm^{-1} was used to determine the lateral crystallite domain size, L_a , from Equation 12:^{115–117}

$$L_a = \frac{4.4}{I_D / I_G} \quad (12)$$

Wide Angle X-Ray Scattering (WAXS)

Wide angle X-ray scattering measurements were performed on a Brüker NanoSTAR system with an Incoatec I μ S microfocus X-ray source operating at 45 kV and 650 mA with a wavelength of Cu $K\alpha$ = 0.1542 nm. The primary beam was collimated with cross-coupled Göbel mirrors and a pinhole of 0.1 mm in diameter. The sample to detector distance was 5.2 cm and a 20 min exposure time was used to collect the WAXS pattern on a Fuji Photo Film image plate with a Fuji FLA-7000 Scanner. Diffraction peaks and integral areas were acquired via a peak fitting method by the software Origin 8.0 as shown in Figure 12.

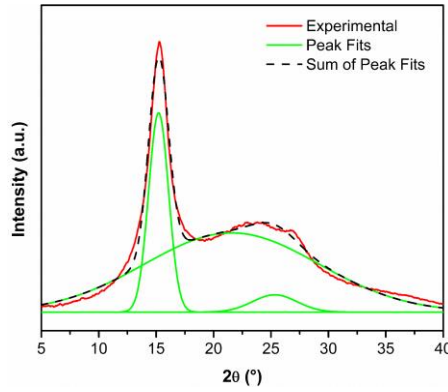


Figure 12. Example of Origin 8.0 peak fitting for 2θ vs. Intensity of 5 mol% p(AN-co-AA) copolymer.

The lateral crystallite thickness (L_c) of the pseudohexagonal crystal lattice¹¹⁸ was determined by the Scherrer equation (Equation 13) for the (100) reflection at $2\theta = 17^\circ$, in which $\lambda = 0.154$ nm is the wavelength of CuK α X-ray, θ is the Bragg diffraction angle, B is the full width at half maximum intensity in radians, and K is a constant and is equal to 0.9:¹¹⁹

$$L_c = \frac{K \lambda}{B \cos(\theta)} \quad (13)$$

The percent crystallinity (χ_c) was determined by the Bell and Dumbleton method¹²⁰ (Equation 14), in which A_c and A_a are the integral areas of the crystalline zone around the $2\theta = 17^\circ$ and the amorphous zones, respectively:

$$\chi_c = \frac{A_c}{A_c + A_a} \bullet 100\% \quad (14)$$

The stabilization index (SI) was used to evaluate the quantitative changes in structural order related to the formation of cyclic structure by Equation 15, in which I_0 and I_i are the intensities of the $2\theta = 17^\circ$ peak for the virgin and heat treated polymers, respectively:⁶⁵

$$SI = \frac{I_0 - I_i}{I_0} \bullet 100\% \quad (15)$$

CHAPTER III

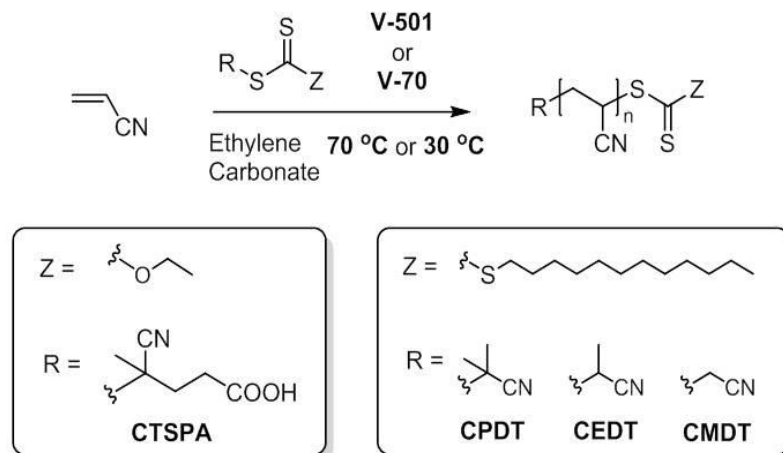
HIGH MOLECULAR WEIGHT AND NARROW POLYDISPERSITY

POLYACRYLONITRILE VIA LOW TEMPERATURE RAFT POLYMERIZATION

Abstract

High molecular weight polyacrylonitrile (PAN) with low polydispersity has been successfully synthesized utilizing reversible addition-fragmentation chain transfer (RAFT) polymerization. A comprehensive study was performed to understand the influence of reaction temperature, RAFT agent structure, and $[M]_0:[CTA]_0[I]_0$ on the polymerization kinetics and the molecular weight as well as polydispersity. Enhanced control is attributed to reduction of side reactions by conducting the polymerization at lower temperature, and optimizing the radical exchange between active and dormant states via appropriate selection of RAFT agent and initiator. A size exclusion chromatograph equipped with a multi angle laser light scattering (SEC-MALLS) detector allowed direct measurement of the absolute weight average molecular weight and polydispersity of the resulting polymers. Ultimately, PAN of molecular weight $\approx 170,000$ g/mol (SEC-MALLS) and $M_w/M_n = 1.25$ was obtained at 70% conversion. Such well controlled polymers are excellent model precursors for further study of in situ carbon fiber production of PAN-based carbon fibers.

Results and Discussion



Scheme 7. General RAFT polymerization of acrylonitrile.

The general RAFT polymerization of AN is outlined in Scheme 7. Ethylene carbonate was utilized as the solvent to minimize chain transfer to solvent.^{76,121} The effects of RAFT agent structure, $[\text{M}]_0:[\text{CTA}]_0:[\text{I}]_0$, and polymerization temperature on molecular weight, polydispersity, and polymerization rate were investigated. Judicious selection of the RAFT agent is necessary to achieve successful polymerization control of a given monomer. The free radical leaving R-group determines the fragmentation efficiency,¹²² while the Z-group modifies the reactivity of the thiocarbonylthio compound and the derived adduct radical.¹²³ There are established classes based on R- and Z-groups of suitable RAFT agents for select monomers^{80,124}, and the homopolymerization of AN has been conducted using dithiobenzoates^{73,74,76}, trithiocarbonates^{50,74,81}, as well as dithiocarbamates⁷⁸. However, to date there are no reported examples of xanthate-mediated RAFT polymerizations of AN, which have radical stabilities between those of trithiocarbonates and dithiocarbamates. Thus, we first investigated xanthate-mediated RAFT polymerization of AN. Furthermore, we wanted to explore the effects of R-group,

$[M]_0:[CTA]_0:[I]_0$, and temperature on the reaction conditions to reach controlled, high molecular weight PAN by RAFT polymerization.

RAFT Polymerizations of AN at 70 °C

We first compared the effect of Z-group on the RAFT polymerization of AN using the xanthate, CTSPA, and the commercially available trithiocarbonate, CPDT, which has been shown to successfully control the RAFT polymerization of AN.⁵⁰ The Z-group controls intermediate radical stability by altering the ground state energy as shown in Figure 13. The oxygen on the xanthate is more electron donating than the sulfur on the trithiocarbonate, which lowers the intermediate radical stability of the former. The concentration of ‘active’ propagating radicals increases as the intermediate radical stability decreases, thus, we expect to observe a faster rate of polymerization for the xanthate-mediated polymerization as compared to the trithiocarbonate-mediated polymerization.

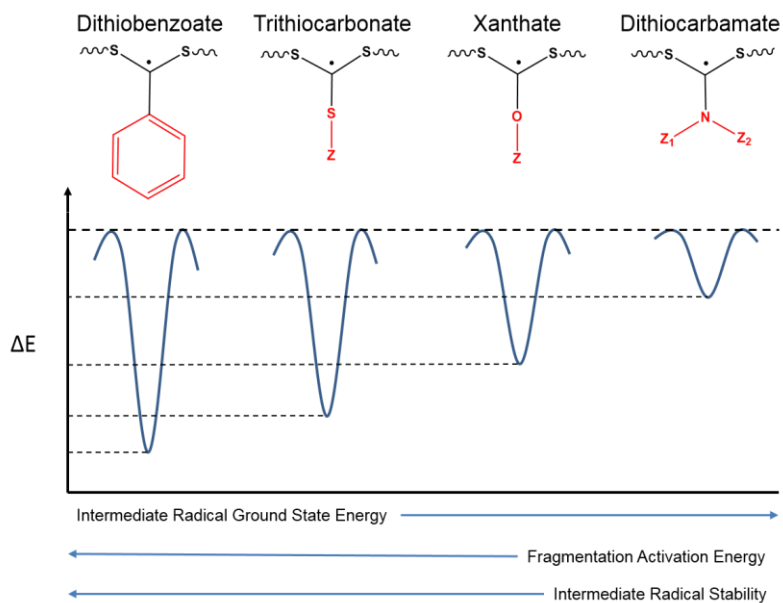
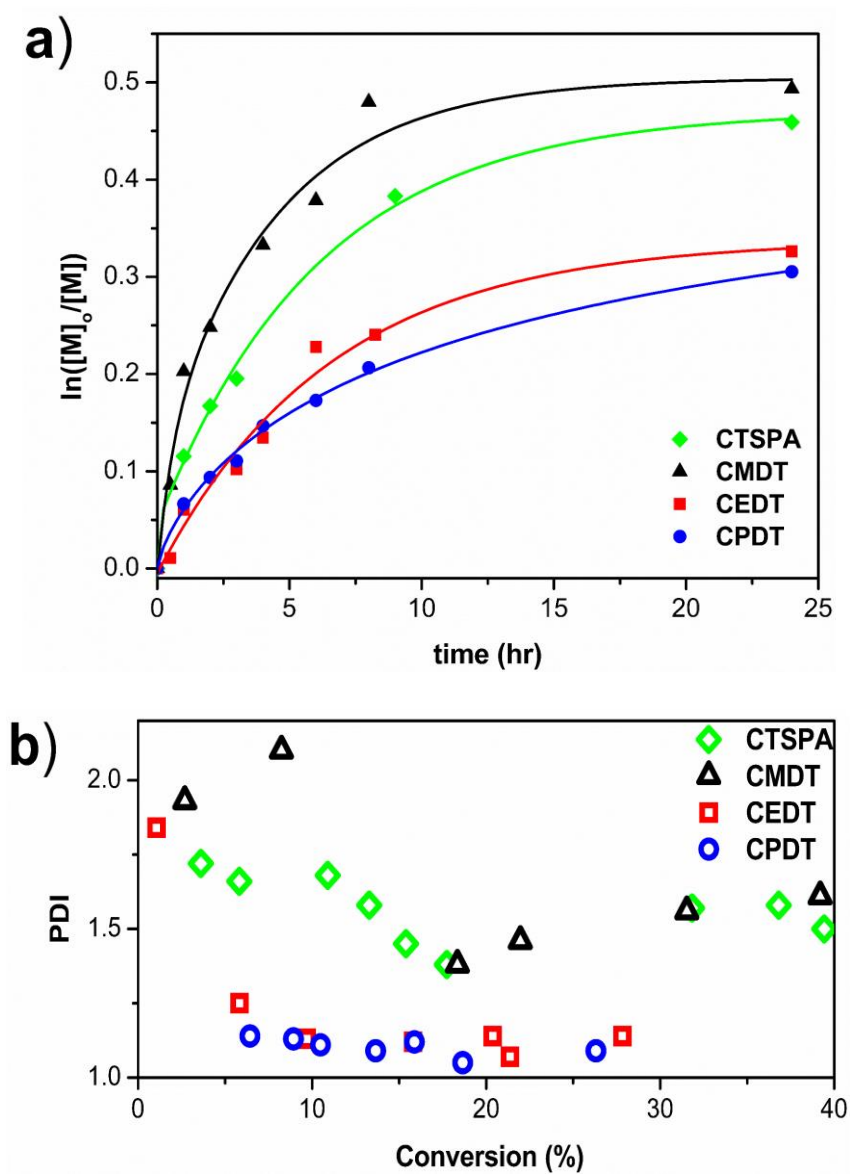


Figure 13. Transition state energy (ΔE) for various RAFT agent Z-groups.

Figure 14 shows $\ln([M]_0/[M])$ vs. time (Figure 14a), polydispersity vs. conversion (Figure 14b), and M_n vs. conversion (Figure 14c) plots for the CTSPA- and CPDT-mediated polymerizations of AN in ethylene carbonate at 70 °C ($[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.4$).



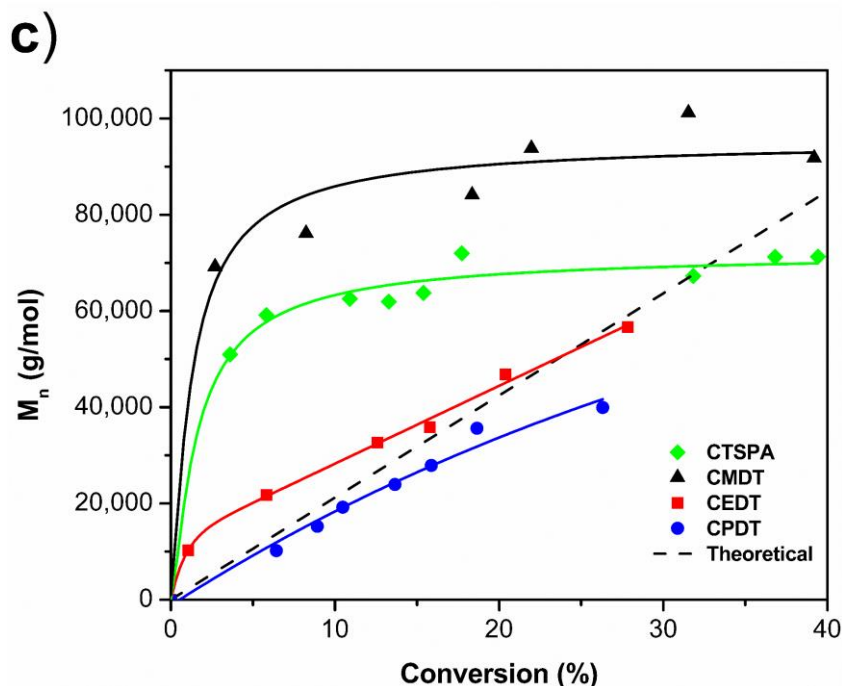


Figure 14. (a) Kinetic plots, (b) polydispersity vs. conversion, and (c) M_n (SEC-MALLS) vs. conversion plots for selected RAFT agents at 70 °C and $[M]_0:[CTA_0]:[I]_0 = 4,000:1:0.4$.

As observed in Figure 14a, the kinetic plots for both the CTSPA- and CPDT-mediated polymerizations of AN deviate significantly from pseudo-first-order behavior beyond approximately 4 hr. The slope of the kinetic plot is linear when the rate of polymerization (R_p) is first order with respect to $[M]$, and $k_p[P\cdot]$ is constant where k_p is the propagation rate constant and $[P\cdot]$ is the concentration of propagating radicals.¹²⁵ Deviation from linearity indicates that the propagating radical concentration is diminishing over time due to deleterious chain transfer and/or radical termination events. Furthermore, limited monomer conversion was observed beyond 10 hr which has been attributed to the reduced radical flux observed as initiator concentration decreases after prolonged reaction times.¹⁰⁶ Figures 14b and 14c show the influence of RAFT agent Z-group on molecular weight progression during the CPDT- and CTSPA-mediated

polymerizations of AN at 70 °C. The CPDT-mediated polymerization of AN showed a linear progression in molecular weight with conversion while the experimentally determined molecular weights ($M_{n_{exp}}$) were in good agreement with the theoretical molecular weights ($M_{n_{theory}}$) calculated based upon monomer conversion (Figure 14c, dashed line). In addition, the polydispersities remained low ($PDI < 1.20$) throughout the CPDT-mediated polymerization of AN at 70 °C (Table 1. Entries 5a-c). In contrast, the CTSPA-mediated polymerization of AN resulted in $M_{n_{exp}}$ values greatly exceeding the $M_{n_{theory}}$ values at low monomer conversions while polydispersities increased as the polymerization progressed ($PDI > 1.50$) (Table 1. Entries 1a-c). The poor control exhibited during the CTSPA-mediated polymerization of AN is likely due to the lower chain transfer constant of xanthates as compared to analogous trithiocarbonates, which gives a higher probability for the propagating chain to add to monomer than for addition back to the CTA.¹²³ The difference in molecular weight control is further exhibited by Figure 15, where the progressive refractive index (RI) traces from SEC analysis are plotted for CPDT- (Figure 15a) and CTSPA- (Figure 15b) mediated polymerizations.

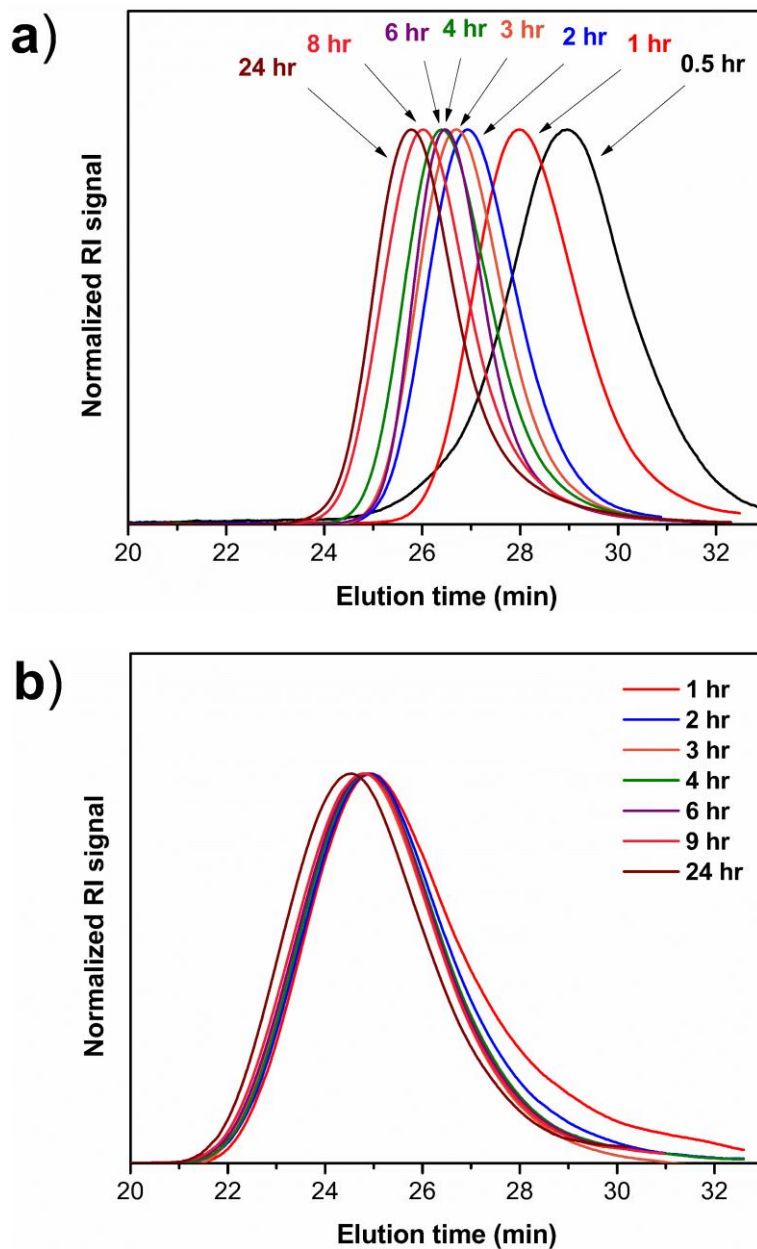


Figure 15. RI traces for the polymerization of AN using CPDT (a) and CTSPA (b) at 70 °C with $[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.4$.

The SEC chromatogram overlay for the CPDT-mediated polymerization of AN (Figure 15a) shows a shift in the RI peaks toward shorter elution times as the reaction progresses, consistent with the RAFT process in the absence of significant termination and/or undesirable chain transfer events. However, beyond 8 hr, a minimal increase in

monomer conversion and molecular weight is observed, indicating a loss in the “livingness” of the polymerization at longer reaction times. In comparison, the CTSPA-mediated polymerization of AN results in a rapid increase in molecular weight at low conversions (Figure 14c) with almost no change in the elution time of the SEC chromatogram RI traces (Figure 15b) which suggests that CTSPA does not adequately mediate the polymerization of AN under the chosen polymerization conditions.

Based upon the better molecular weight control afforded by the trithiocarbonate CPDT as compared to the xanthate CTSPA, we chose to only utilize the trithiocarbonate CTAs in our attempts to achieve high molecular weight, low polydispersity PAN by RAFT polymerization. We first scanned the effect of the trithiocarbonate R-group on the RAFT polymerization of AN at 70 °C. An earlier study by Donovan et al. had shown that the R-group can have a significant role in the re-initiating ability of N,N-dimethylacrylamide utilizing dithiobenzoates.¹²⁶ In this part of the study we explored three different cyanoalkyl R-groups ranging from primary radical (CMDT) to tertiary radical (CPDT) leaving groups (Scheme 7, Table 1, Entries 2-3). The kinetic plot (Figure 14a) for CEDT-mediated polymerization of AN exhibits very similar behavior to that of CPDT in that they both show rapid monomer conversion early in the reaction, followed after about 4 hr by a decreased rate of monomer consumption due to undesirable chain termination events. The greatest difference is in the CMDT-mediated polymerization which shows a faster rate of polymerization (Figure 14a), a lack of control with higher polydispersities (Figure 14b), and non-ideal molecular weight growth (Figure 14c) as compared to the CEDT- and CPDT-mediated polymerizations. This is attributed to the poor fragmentation and, thus slow, reinitiation by the primary cyanomethyl radical, thus

increasing likelihood of monomer propagation before complete initialization of the RAFT agent.¹²⁷ This effect is also observed to some extent during the CEDT-mediated polymerization of AN, which shows an initial overshooting of $M_{n,exp}$ relative to $M_{n,theory}$ but a linear progression in $M_{n,exp}$ that tends towards the theoretical values at higher conversions (Figure 14c). The CPDT-mediated polymerization of AN offered promising molecular weight control, prompting our investigation into the effect of $[CTA]_0:[I]_0$ on the molecular weight progression (Figure 16, Table 1. Entries 4-6).

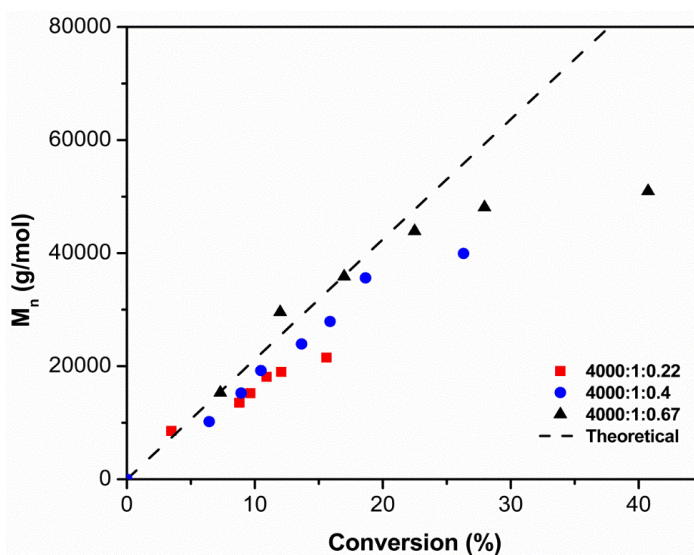


Figure 16. M_n (SEC-MALLS) vs. conversion for the CPDT-mediated RAFT polymerization of AN at 70 °C at various $[M]_0:[CTA]_0:[I]_0$ ratios.

Typically, an increase in initiator concentration results in a higher concentration of initiator-derived polymer chains, which leads to deviation from pseudo-living behavior and an increased PDI.⁷⁶ In this case, Equation 1 should be rewritten to yield Equation 16, in which $[P_n\cdot]$ are chains derived from the initiator species:

$$M_{n,th} = \frac{M_{MW}[M]_0 \bullet \rho}{[CTA]_0 + [P_n\cdot]} + CTA_{MW} \quad (16)$$

$[P_n\cdot]$ increases as $[CTA]_0:[I]_0$ decreases due the lower probability of initiator adding to CTA and establishing the RAFT equilibrium. However, when the $[CTA]_0:[I]_0$ is suitably large, $[P_n\cdot]$ is expected to be negligible. Interestingly, increasing the $[CTA]_0:[I]_0$ to 1:0.67 under these reaction conditions resulted in minimal deviation from $M_{n,th}$ while conversion increased to over 40% after 24 hr. The results for polymerizations at 70 °C are summarized in Table 1.

Table 1

Conversion, Molecular Weight, and Polydispersity Data for the RAFT Polymerization of AN Conducted at 70 °C

Entry ^a	RAFT agent	$[M]_0:[CTA]_0:[I]_0$	Time (hr)	Conv. ^b (%)	M_n (Theor.) ^c	M_n (MALLS) ^d	M_n (PMMA) ^e	PDI ^d
1a	CTSPA	4 000:1:0.4	3	18	38 200	72 000	214 300	1.38
1b	CTSPA	4 000:1:0.4	6	32	67 900	67 300	207 300	1.57
1c	CTSPA	4 000:1:0.4	24	37	78 800	74 600	191 000	1.58
2a	CMDT	4 000:1:0.4	3	22	46 400	93 800	365 800	1.46
2b	CMDT	4 000:1:0.4	6	32	67 600	83 400	330 900	1.81
2c	CMDT	4 000:1:0.4	24	36	76 700	77 300	310 200	1.42
3a	CEDT	4 000:1:0.4	3	10	20 900	35 900	117 700	1.13
3b	CEDT	4 000:1:0.4	6	20	43 600	46 800	144 300	1.14
3c	CEDT	4 000:1:0.4	24	28	59 400	56 700	152 300	1.14
4a	CPDT	4 000:1:0.22	3	9	19 500	15 200	47 400	1.24
4b	CPDT	4 000:1:0.22	6	12	25 900	18 100	49 300	1.08
4c	CPDT	4 000:1:0.22	24	16	33 200	21 500	54 300	1.10
5a	CPDT	4 000:1:0.4	3	10	22 600	22 300	58 500	1.09
5b	CPDT	4 000:1:0.4	6	16	34 000	27 900	81 300	1.08
5c	CPDT	4 000:1:0.4	24	26	56 200	39 900	113 600	1.14

Table 1 (continued).

Entry ^a	RAFT agent	[M] ₀ : [CTA] ₀ : [I] ₀	Time (hr)	Conv. ^b (%)	M _n (Theor.) ^c	M _n (MALLS) ^d	M _n (PMMA) ^e	PDI ^d
6a	CPDT	4000:1:0.67	3	12	25 800	29 600	81 700	1.12
6b	CPDT	4000:1:0.67	6	22	48 100	43 900	117 500	1.08
6c	CPDT	4000:1:0.67	24	41	86 800	51 000	143 500	1.18

^aPolymers synthesized in ethylene carbonate at 20 wt.% monomer concentration under a nitrogen atmosphere with V-501 as the initiator.

^bConversions were determined by ¹H-NMR spectroscopy recorded in DMSO-d₆. ^cTheoretical number average molecular weights were calculated according to the following equation: $M_n = (\rho \cdot MW_{mon} \cdot [M]_0 / [CTA]_0) + MW_{CTA}$ where ρ is the fractional monomer conversion, MW_{mon} is the molecular weight of the monomer, and MW_{CTA} is the molecular weight of the CTA. ^dNumber average molecular weight (M_n) as determined by SEC (0.5 mL/min, 60 °C, Polymer Labs PL gel 5 μ m mixed-C column, DMF with 0.02 M LiBr eluent) equipped with RI and MALLS detectors. ^e M_n relative to PMMA standards.

Evident from Table 1, the polymerization of AN mediated by CTAs CPDT and CEDT exhibited lower PDIs than the polymerizations mediated by CTSPA and CMDT. Also, the conversions for entries 1-5 remained below 40% after 24 hr of polymerization. It was found that conversion and molecular weight could be increased by more than 10% at the expense of increasing PDI (Entry 6). Molecular weights were reported relative to PMMA standards for comparison with literature reported values due to the issues of performing SEC on PAN.⁷²

Thus far, our efforts to achieve high molecular weight and low PDI PAN by varying the CTA structure and [M]₀: [CTA]₀: [I]₀ were unsatisfactory. It has been shown that conversion and molecular weight of conventional solution polymerization of AN can be increased by utilizing lower temperature polymerizations.^{82,128} Moreover, other issues commonly associated with polymerization of acrylamides, such as broad PDIs, have been

addressed with low temperature RAFT polymerization.^{83,84} Therefore, we explored the effects of lowering the reaction temperature on achieving high molecular weights while maintaining low PDI.

RAFT Polymerizations of AN at 30 °C

The kinetic chain length, ν , is expressed as R_p/R_t , where R_p is the rate of propagation and R_t is the rate of termination. R_p decreases with decreasing temperature, however, R_t typically decreases at a much faster rate than R_p .¹²⁹ This suggests that even with a slower propagation, the termination and chain transfer events should be even further reduced as illustrated in Figure 17.¹²⁹

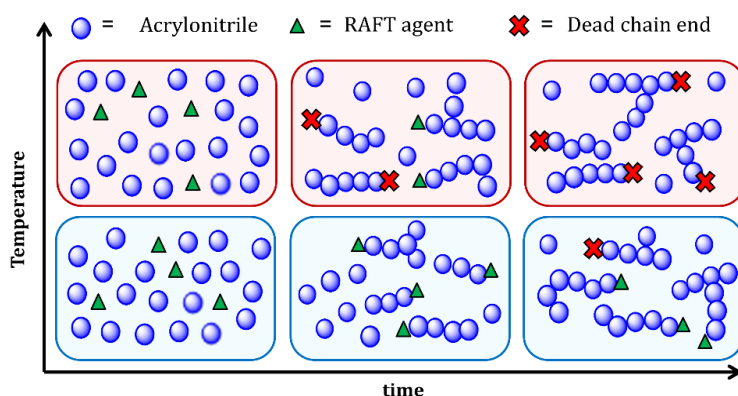


Figure 17. At higher temperatures polymer chains grow faster, but also have more chain termination and branching events while at low temperatures chain termination and chain branching are suppressed.

The polymerization temperature of 30 °C was selected based on the decomposition temperature of the initiator, V-70, which has the same initiator efficiency as V-501 at 70 °C. The RAFT polymerization conditions for AN at 30 °C were otherwise analogous to those at 70 °C. The kinetic plots, polydispersity vs. conversion, and M_n vs. conversion plots at $[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.22$ are shown in Figure 18(a-c).

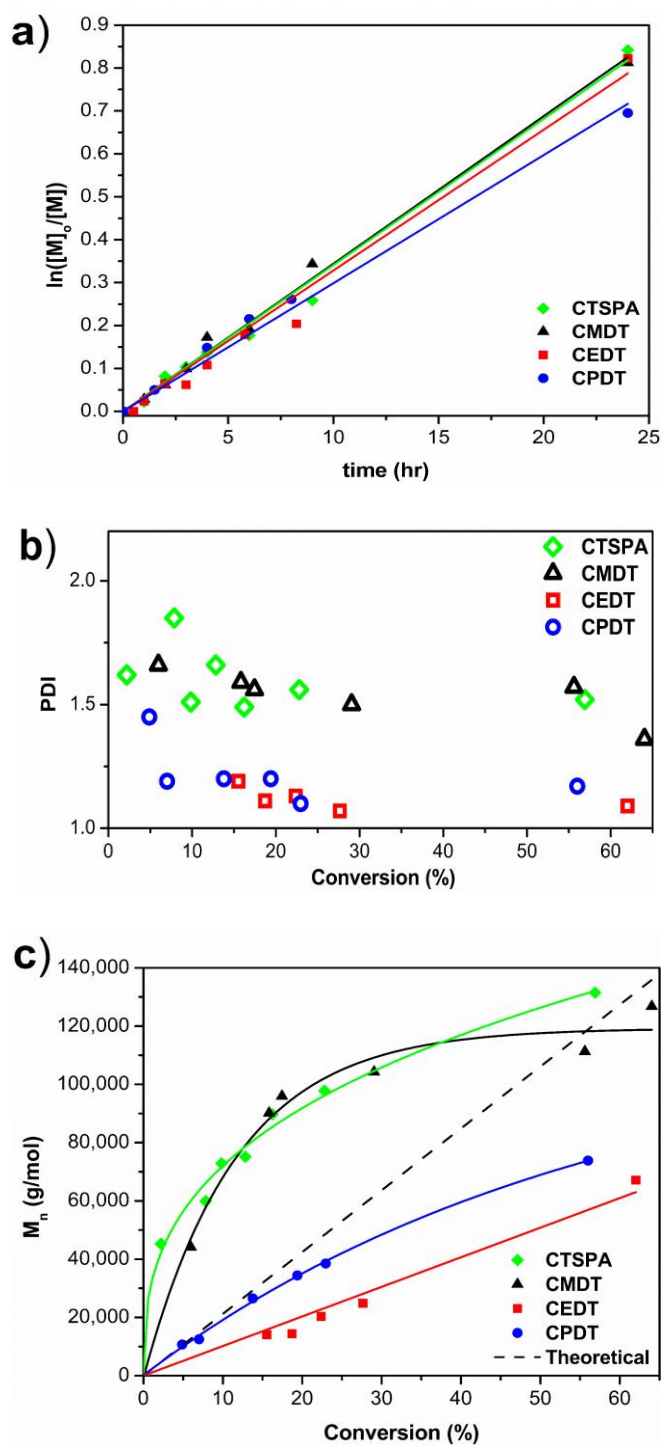


Figure 18. (a) Kinetic plots, (b) polydispersity vs. conversion, and (c) molecular weight (SEC-MALLS) vs. conversion for selected RAFT agents at 30 °C and $[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.4$.

As seen in Figure 18a, the kinetic plots for all CTAs exhibit a linear relationship, which indicates a constant radical concentration, $[P\cdot]$, throughout the duration of the reaction. This suggests that chain termination reactions are reduced at 30 °C and that monomer is still being consumed at long reaction times. Figures 18b and 18c are consistent with the 70 °C results showing that CEDT and CPDT are the most effective CTAs in controlling molecular weight and polydispersity. Most importantly, at 24 hr the conversion reaches about 60% and molecular weight exceeds 60,000 g/mol at the given $[M]_0:[CTA]_0:[I]_0$. The RI traces for the CPDT-mediated polymerization of AN at 30 °C are shown in Figure 19. SEC-RI traces are unimodal and continue to shift to lower elution times with increasing conversion even for reaction times up to 24 hr. The CTAs and $[M]_0:[CTA]_0:[I]_0$ were varied the same as in Table 1 at 30 °C and the results are summarized in Table 2.

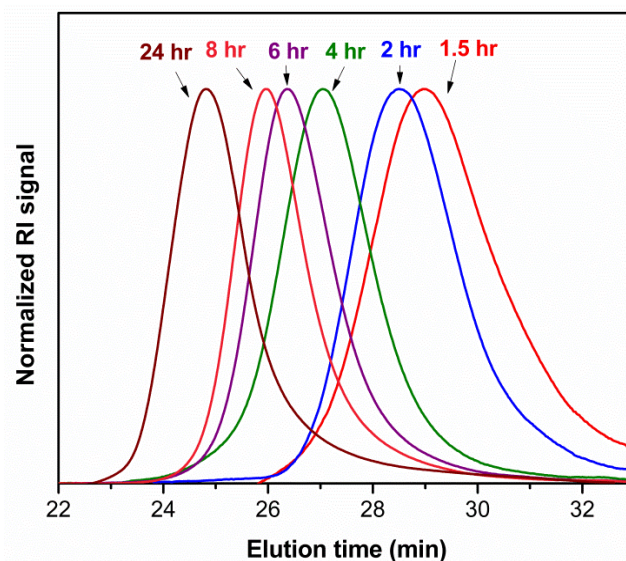


Figure 19. RI traces for the polymerization of AN using CPDT at 30 °C with $[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.4$.

Table 2

Conversion, Molecular Weight, and Polydispersity Data for the RAFT Polymerization of AN Conducted at 30 °C

Entry ^a	RAFT agent	[M] ₀ : [CTA] ₀ : [I] ₀	Time (hr)	Conv. ^b (%)	M _n (Theor.) ^c	M _n (MALLS) ^d	M _n (PMMA) ^e	PDI ^d
7a	CTSP	4 000:1:0.4	4	13	27 600	75 200	254 200	1.66
7b	CTSP	4 000:1:0.4	6	16	34 000	89 700	273 700	1.49
7c	CTSP	4 000:1:0.4	24	57	121 000	131 500	237 800	1.52
8a	CMDT	4 000:1:0.4	4	16	33 600	90 200	309 500	1.59
8b	CMDT	4 000:1:0.4	6	18	37 900	96 000	342 200	1.56
8c	CMDT	4 000:1:0.4	24	64	136 200	126 600	318 070	1.36
9a	CEDT	4 000:1:0.4	4	19	40 000	20 300	68 800	1.13
9b	CEDT	4 000:1:0.4	6	28	59 000	24 900	54 600	1.07
9c	CEDT	4 000:1:0.4	24	62	131 900	70 300	196 200	1.09
10a	CPDT	4000:1:0.22	4	12	25 800	21 000	54 000	1.11
10b	CPDT	4000:1:0.22	6	18	38 500	25 800	71 700	1.11
10c	CPDT	4000:1:0.22	24	40	84 800	69 000	183 300	1.07
11a	CPDT	4 000:1:0.4	4	14	29 300	27 700	69 000	1.47
11b	CPDT	4 000:1:0.4	6	19	41 200	36 000	96 300	1.20
11c	CPDT	4 000:1:0.4	24	57	121 300	73 900	201 900	1.17
12a	CPDT	4000:1:0.67	4	19	41 100	34 400	93 600	1.08
12b	CPDT	4000:1:0.67	6	24	50 900	43 300	128 100	1.11
12c	CPDT	4000:1:0.67	24	63	134 200	84 800	301 500	1.24

^aPolymers synthesized in ethylene carbonate at 20 wt.% monomer concentration under a nitrogen atmosphere with V-70 as the initiator.

^bConversions were determined by ¹H-NMR spectroscopy recorded in DMSO-d₆. ^cTheoretical number average molecular weights were calculated according to the following equation: $M_n = (\rho \cdot MW_{mon} \cdot [M]/[CTA]) + MW_{CTA}$ where ρ is the fractional monomer conversion, MW_{mon} is the molecular weight of the monomer, and MW_{CTA} is the molecular weight of the CTA. ^dNumber average molecular weight (M_n) as determined by SEC (0.5 mL/min, 60 °C, Polymer Labs PL gel 5 μ m mixed-C column, DMF with 0.02 M LiBr eluent) equipped with RI and MALLS detectors. ^e M_n relative to PMMA standards.

Data in Table 2 show that low temperature reactions maintain control for longer reaction times and that higher molecular weight can be achieved. Entries 10-12, which parallel entries 4-6, show that as $[CTA]_0:[I]_0$ decreases greater conversion can be achieved at the cost of increasing polydispersity. Also, beyond 6 hr, the molecular weight tends to deviate from those theoretically predicted due to the existence of irreversible chain termination at long reaction times in entries 11 and 12. Figure 20 shows the respective kinetic and molecular weight vs. conversion plots of the CPDT-mediated polymerizations of AN at 30 °C and 70 °C. Figure 20a shows that the conversion at 30 °C surpasses that of the polymerization at 70 °C at about 6 hr. Figure 20b shows that higher conversion and molecular weight is achieved at 30 °C as compared to the analogous polymerization conducted at 70 °C.

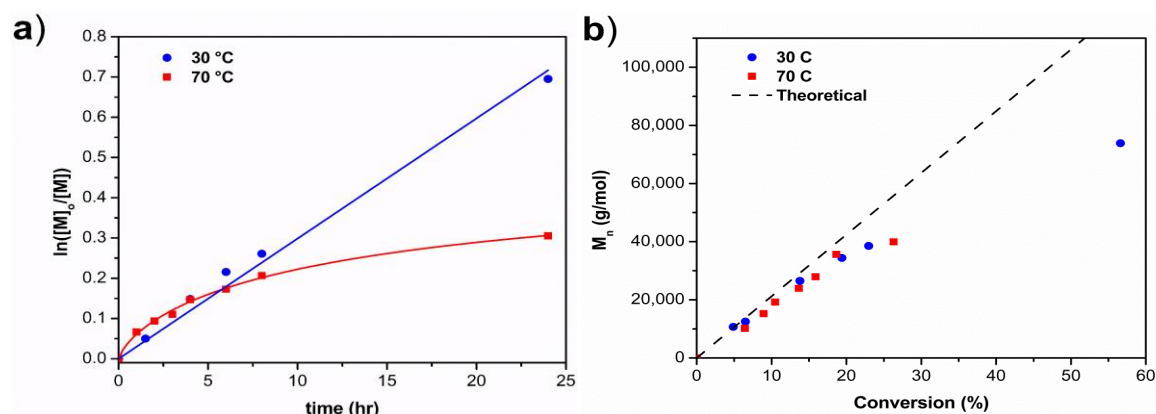


Figure 20. (a) Kinetics plots as a function of reaction time, (b) molecular weight (SEC-MALLS) vs. conversion for polymerization of AN with CPDT at $[M]_0:[CTA]_0:[I]_0 = 4,000:1:0.4$ for both 30 and 70 °C.

High Molecular Weight RAFT Polymerizations of AN at 30 °C

The above results show that AN polymerizations mediated by CPDT or CEDT at 30 °C facilitate controlled and predictable molecular weights while maintaining low

polydispersities up to 8 hr. Beyond 8 hr the polymerization deviates from ideal behavior, but still shows much greater conversion as compared to the analogous 70 °C reactions at 24 hr. Commercially used PAN-based carbon fiber precursors traditionally have molecular weights above 100,000 g/mol. Therefore, we investigated the effect of $[M]_0:[CTA]_0:[I]_0$ to achieve molecular weights above 100,000 g/mol and the results are summarized in Table 3.

Table 3

Conversion, Molecular Weight, and Polydispersity Data for the RAFT Polymerization of AN Conducted at 30 °C and Higher $[M]_0:[CTA]_0$ Ratios

Entry ^a	RAFT agent	$[M]_0:[CTA]_0:[I]_0$	Time (hr)	Conv. ^b (%)	M_n (Theor.) ^c	M_n (MALLS) ^d	M_n (PMMA) ^e	PDI ^d
13a	CPDT	1 333:1:0.22	4	25	17 300	17 000	43 100	1.05
13b	CPDT	1 333:1:0.22	6	33	23 000	23 200	54 500	1.04
13c	CPDT	1 333:1:0.22	24	59	42 100	42 000	88 100	1.06
14a	CPDT	8 000:1:0.22	6	10	40 800	29 800	81 300	1.11
14b	CPDT	8 000:1:0.22	24	24	102 600	77 900	193 900	1.08
14c	CPDT	8 000:1:0.22	48	31	130 100	97 600	234 200	1.06
15a	CPDT	10 000:1:0.22	6	12	64 000	53 400	144 000	1.12
15b	CPDT	10 000:1:0.22	24	22	153 400	131 100	320 100	1.06
15c	CPDT	10 000:1:0.22	48	38	202 900	137 900	330 100	1.06
16a	CPDT	2 000:1:0.4	3	14	14 500	16 800	60 300	1.05
16b	CPDT	2 000:1:0.4	6	32	33 600	27 000	110 500	1.10
16c	CPDT	2 000:1:0.4	24	49	52 300	34 500	121 100	1.09
17a	CPD	8 000:1:0.4	6	10	42 100	31 200	102 000	1.21
17b	CPD	8 000:1:0.4	24	31	131 200	73 000	220 300	1.19
17c	CPD	8 000:1:0.4	48	51	216 100	125 000	274 800	1.12

Table 3 (continued).

Entry ^a	RAFT agent	[M] ₀ : [CTA] ₀ : [I] ₀	Time (hr)	Conv. ^b (%)	M _n (Theor.) ^c	M _n (MALLS) ^d	M _n (PMMA) ^e	PDI ^d
18a	CPD	6 667:1:0.67	3	31	109 300	34 800	99 600	1.1
18b	CPD	6 667:1:0.67	6	39	137 600	47 100	143 810	1.12
18c	CPD	6 667:1:0.67	24	54	190 700	55 100	170 730	1.19
19a	CPD	10 000:1:0.67	7	27	142 900	50 500	165 000	1.09
19b	CPD	10 000:1:0.67	24	49	259 700	108 600	365 600	1.21
19c	CPD	10 000:1:0.67	48	71	377 100	131 400	423 100	1.27
20a	CPD	13 333:1:0.67	7	37	261 400	70 000	195 800	1.11
20b	CPD	13 333:1:0.67	24	53	374 600	138 200	433 900	1.19
20c	CPD	13 333:1:0.67	48	70	495 600	168 600	564 800	1.25

^aPolymers synthesized in ethylene carbonate at 20 wt.% monomer concentration under a nitrogen atmosphere with V-70 as the initiator.

^bConversions were determined by ¹H-NMR spectroscopy recorded in DMSO-d₆. ^cTheoretical number average molecular weights were calculated according to the following equation: $M_n = (\rho \cdot MW_{\text{mon}} \cdot [M]/[CTA]) + MW_{CTA}$ where ρ is the fractional monomer conversion, MW_{mon} is the molecular weight of the monomer, and MW_{CTA} is the molecular weight of the CTA. ^dNumber average molecular weight (M_n) as determined by SEC (0.5 mL/min, 60 °C, Polymer Labs PL gel 5 μ m mixed-C column, DMF with 0.02 M LiBr eluent) equipped with RI and MALLS detectors. ^e M_n relative to PMMA standards.

As shown in Table 3, the [CTA]₀: [I]₀ was retained at the previous ratios of 1:0.22, 1:0.4, and 1:0.67 in entries 13-15, 16-17, and 18-20, respectively. It may be seen that lower target molecular weights (Entries 13 and 16) agree well with the theoretical molecular weights due to the lower [M]₀: [CTA]₀ ratios. In particular, the lowest polydispersities and best matches to theoretical molecular weights are observed in entries 13-15, while the highest conversions (above 70% at 48 hr) are represented by entries 18-20. Entry 15 shows conditions for synthesizing PAN with M_n of 137,900 g/mol and PDI of 1.06 at 38% conversion. Decreasing [CTA]₀: [I]₀ led to conversions above 70% and a

slight increase in PDI (1.27) with a similar M_n of 131,400 g/mol as seen in Entry 19. These results demonstrate conditions for preparing high molecular weight and low PDI PAN. As an example of these high $[M]_0:[CTA]_0$ polymerizations, the kinetic plot and molecular weight vs. conversion plots are shown for entry 15 in Figure 21.

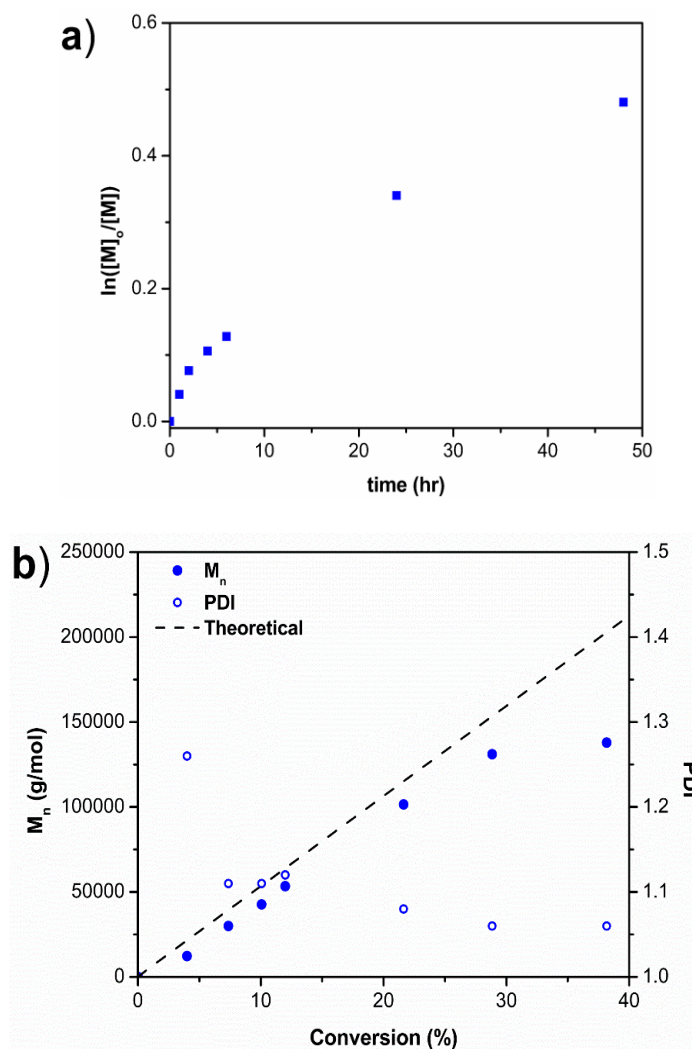


Figure 21. (a) Kinetics plots and (b) molecular weight and polydispersity (SEC-MALLS) vs. conversion for polymerization of AN with CPDT at $[M]_0:[CTA]_0:[I]_0 = 10,000:1:0.22$.

Figure 21a exhibits continued monomer conversion for up to 48 hr, which suggests that radical concentration is preserved. Moreover, Figure 21b shows that ideal

chain growth continues up to 30% conversion at 24 hr, indicating the existence of living chain ends for long reaction times, followed by non-linear behavior beyond 24 hr.

Additionally, the progressive RI traces obtained from SEC for Table 3, Entry 19 are shown in Figure 22, which show the continued shifts in elution time for 48 hr of reaction time. These plots denote the reduction of chain transfer and chain termination events even at high $[M]_0:[CTA]_0$ ratios.

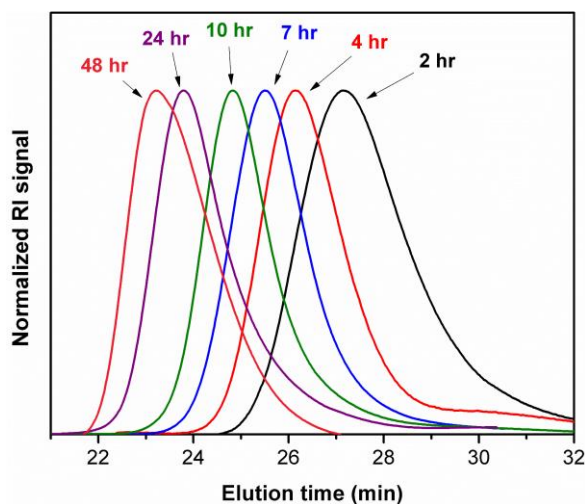


Figure 22. Progressive RI traces for the polymerization of AN using CPDT at 30 C with $[M]_0:[CTA]_0:[I]_0 = 10,000:1:0.67$.

Verification of Molecular Weight Determination

The ability to accurately determine the molecular weight of polyacrylonitrile has been questioned in the literature⁷² and has, therefore, prompted further verification of molecular weight through the use of UV-Vis Spectroscopy as well as MALDI-TOF for Table 3, Entry 13c. Following a literature method,¹³⁰ the molar absorptivity of the $\pi \rightarrow \pi^*$ transition of CPDT was determined to be 9,900 L/(mol*cm) at 300 nm as shown in Figure 23. Molar absorptivity is determined by the slope of concentration vs. max absorbance at $\lambda_{\max}=300$ nm multiplied by the molar mass of CPDT (343 g/mol).

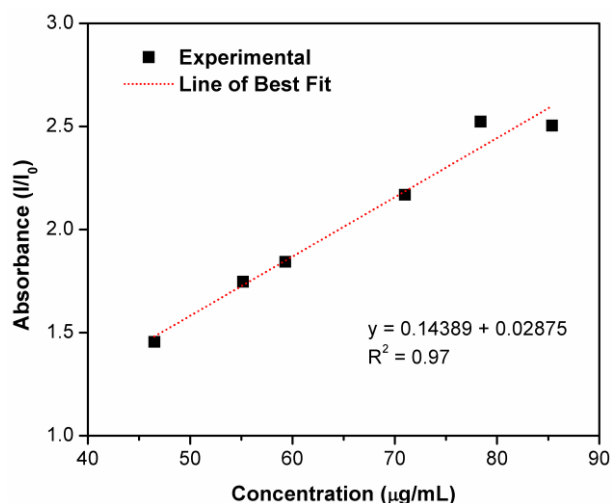


Figure 23. Molar absorptivity of CPDT.

Assuming that all polymer chain ends are capped with CPDT, the molecular weight of the polymer can be determined by Equation 17, in which c is concentration of polymer, ϵ is the molar absorptivity of CPDT, and A_{polymer} is the measured absorbance of the polymer at $\lambda_{\text{max}}=300$ nm.

$$M_n = \frac{c}{\left(\frac{A_{\text{polymer}}}{\epsilon_{\text{CPDT}}} \right)} \quad (17)$$

Using Equation 17, the average molecular weight for a series of three concentration measurements was determined to be 41,200 g/mol, which agrees very well with Table 3, Entry 13c determined by SEC-MALLS (42,000 g/mol). This also demonstrates that the assumption that all chains are capped by CPDT is valid.

Even further validation was taken by measuring the molecular weight of the same polymer with MALDI-TOF mass spectroscopy. The number average molecular weight was determined to be 44,500 g/mol with a polydispersity of 1.06 (Figure 24), which is also in excellent agreement with the values obtained by SEC-MALLS.

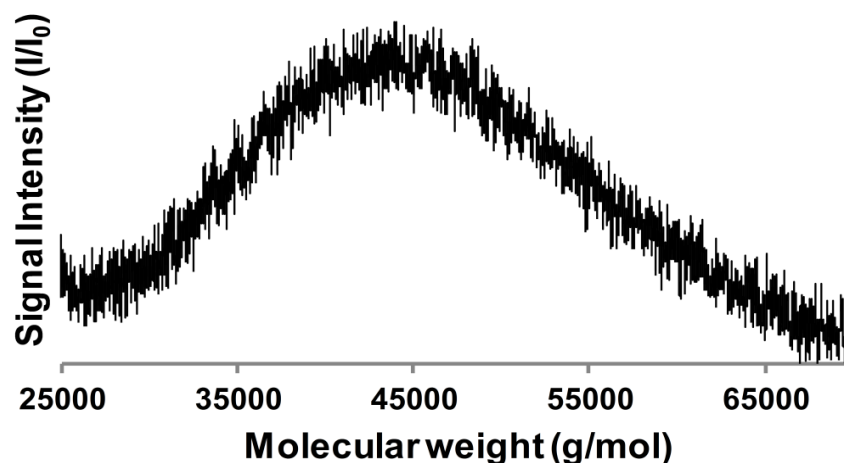


Figure 24. MALDI-TOF mass spectroscopy of PAN (Table 3, Entry 13c).

Summary

Polymerization of AN has been performed in the presence of a series of RAFT agents at various temperatures and reactant concentrations with the purpose to synthesize PAN with high molecular weight and low polydispersity. It was found that:

- (1) neither CTSPA nor CMDT provided adequate control for RAFT-mediated polymerization of AN as compared to CEDT and CPDT,
- (2) decreasing the $[CTA]_0:[I]_0$ ratio in CPDT-mediated polymerizations yields higher molecular weight and higher conversion at the cost of broader molecular weight distributions and larger deviations from $M_{n,theory}$, and
- (3) lowering the polymerization temperature to 30 °C is an effective for increasing molecular weight and conversion.

It is suggested that chain termination reactions are suppressed at 30 °C, permitting monomer conversion up to 48 hr. Utilizing CPDT as the RAFT agent at $[M]_0:[CTA]_0:[I]_0 = 10,000:1:0.67$ and 30 °C in ethylene carbonate, PAN of molecular weight $\approx 170,000$

g/mol and $M_w/M_n = 1.25$ was obtained at 70% conversion. On the contrary, at $[M]_0:[CTA]_0:[I]_0 = 10,000:1:0.22$, PAN of molecular weight $\approx 137,000$ g/mol and $M_w/M_n = 1.06$ was obtained at 38% conversion.

CHAPTER IV

STABILIZATION OF POLYACRYLONITRILE: CONVENTIONAL FREE RADICAL
VERSUS CONTROLLED RAFT POLYMERIZATIONS

Abstract

Careful control of polyacrylonitrile (PAN) precursor properties and, in particular, the polymerization method and ensuing molecular weight and molecular weight distribution are important considerations for mitigating defects and enhancing processability of carbon fibers. Herein, a comprehensive study was performed to understand the influence of molecular weight, molecular weight distribution, and polymerization method between reversible addition-fragmentation chain transfer (RAFT) and conventional free radical (FR) solution polymerization on the cyclization behavior and structural evolution of stabilized PAN. The kinetic parameters of activation energy (E_a) and pre-exponential factor (A) were determined along with the cyclization index (CI) by differential scanning calorimetry (DSC) and the extent of stabilization (E_s) was measured via fourier transform infrared spectroscopy (FTIR). Thermogravimetric analysis (TGA) was used to determine the degradation differences in the polymers. Structural characterization of graphitic content was determined by Raman spectroscopy and crystallite properties and stabilization index (SI) by wide-angle X-ray scattering (WAXS). Significantly, it was found that cyclization initiated at lower temperature as well as proceeded at a more moderate pace for FR polymers as compared to RAFT homopolymers.

Results and Discussion

RAFT and FR Polymerization of Acrylonitrile

Six polyacrylonitrile samples were selected of varying molecular weight and polydispersity. The PAN samples were subdivided into two groups: samples prepared by conventional uncontrolled free-radical solution polymerization (FR-1, FR-2, FR-3), and those prepared by RAFT polymerization (RAFT-1, RAFT-2, RAFT-3). The results are summarized in Table 4. The molecular weights of the FR (free radical) samples ranged between 25,000 – 260,000 g/mol, and PDIs ranged from 1.59 – 2.09. FR-2 was synthesized utilizing the initiator, AIBN, at 65 °C to give the same end groups (2-cyano-2-propyl) as the RAFT polymers to mitigate end group effects.^{41,48} The RAFT samples had molecular weights ranging between 42,000 – 135,000 g/mol (SEC-MALLS) and PDIs from 1.06 – 1.27. These RAFT molecular weights were confined within the lower and upper limits of the FR polymers. The SEC-chromatograms of all six samples are portrayed in Figure 25, where the normalized refractive index (RI) traces are plotted verse elution time. All of the RAFT chromatograms (blue) are within the bounds of the FR-1 and FR-3 traces (red). Furthermore, the RI traces of the RAFT polymers are much narrower than all three FR polymers.

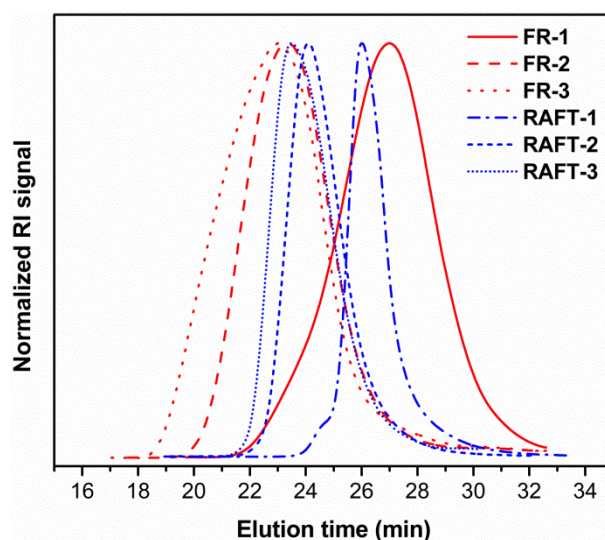


Figure 25. RI traces for the FR polymers (red) and RAFT polymers (blue).

Table 4

Summary of RAFT and FR PAN Samples

Entry ^a	[M] ₀ : [CTA] ₀ : [I] ₀	T (°C) ^b	Time (hr)	Conv. (%) ^c	M _n (Theor.) ^d	M _n (MALLS) ^e	M _n (PMMA) ^f	PDI ^e
FR-1	130:0:1	30	8	-	-	25,900	71,400	1.88
FR-2	3,260:0:1	65	8	-	-	173,400	447,000	1.59
FR-3	4,900:0:1	30	8	-	-	257,800	546,300	2.09
RAFT-1	1,333:1:0.22	30	24	59	42,100	42,000	88,100	1.06
RAFT-2	6,667:1:0.67	30	48	67	236,700	90,000	281,000	1.23
RAFT-3	10,000:1:0.67	30	48	71	377,100	131,400	423,100	1.27

^aPolyacrylonitrile synthesized in ethylene carbonate at 20 wt.% monomer concentration under a nitrogen atmosphere. ^bReactions at 30 °C used V-70 as the initiator and reactions at 65 °C used AIBN as the initiator. ^cConversions were determined by ¹H-NMR spectroscopy recorded in DMSO-d₆. ^dTheoretical number average molecular weights were calculated according to the following equation: $M_n = (\rho \cdot MW_{mon} \cdot [M]_0 / [CTA]_0) + MW_{CTA}$ where ρ is the fractional monomer conversion, MW_{mon} is the molecular weight of the monomer, and MW_{CTA} is the molecular weight of the CTA. ^eNumber average molecular weight (M_n) as determined by SEC (0.5 mL/min, 60 °C, Polymer Labs PL gel 5 μ m mixed-C column, DMF with 0.02 M LiBr eluent) equipped with RI and MALLS detectors. ^f M_n relative to PMMA standards.

To verify the molecular weight of the FR and RAFT polymers, we determined the viscosity average molecular weight via intrinsic viscosity measurements (example shown in Figure 26). The results are summarized in Table 5.

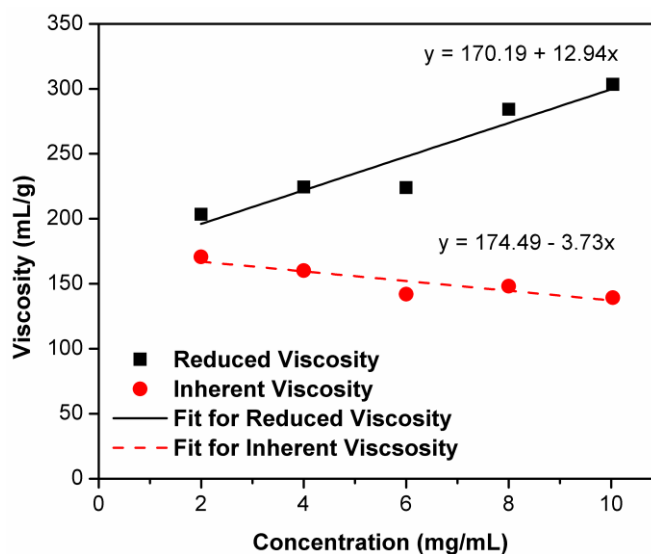


Figure 26. The intrinsic viscosity of RAFT-2 in DMF at 25 °C.

Table 5

Intrinsic Viscosity, $[\eta]$, and Viscosity Average Molecular Weight, M_η , of RAFT and FR PAN Homopolymers Determined by Ubbelohde Viscometer Method at 25 °C in DMF

Entry	$[\eta]$ (mL/g)	M_η (g/mol) ^a
FR-1	63	35,700
FR-2	243	215,800
FR-3	500	563,500
RAFT-1	65	37,300
RAFT-2	172	136,300
RAFT-3	188	152,900

^aViscosity average molecular weight was determined from the following equation: $[\eta] = K \cdot M_\eta^\alpha$ where K and α are the Mark-Houwink constants (K=0.0243 and α =0.75).

Table 5 shows that the intrinsic viscosity has a large spread across all of the samples ranging from 63 to 500 mL/g. Moreover, FR-3 has a very high viscosity average molecular weight, which is expected due to the high polydispersity and high molecular weight tail seen in the SEC trace (Figure 25). Despite FR-1 having a broad chromatogram (Figure 25), the viscosity average molecular weight is still the lowest in the set of polymers.

Influence of Molecular Weight and Polydispersity on the Cyclization of PAN

Although studies have shown that there is a molecular weight dependence on the formation of the final fibers⁵³ and during the pyrolysis of PAN,^{41,52} it is not clear how polydispersity and molecular weight affect the cyclization temperature, the extent of cyclization, and the structural changes that occur through the stabilization phase of PAN-based carbon fibers. This prompted our investigation into comparing the progress of thermal stabilization between polymers of varying molecular weights and polydispersities.

DSC Exotherms, Activation Energies, and Cyclization Index

The DSC method is one of the most prominent methods for characterizing the event of cyclization.^{27,67,112} DSC gives a very narrow peak for the exothermic cyclization reaction for homopolymer PAN due to the rapid free radical ring-closing mechanism of adjacent nitriles along the polymer chain.^{25,27} Figure 27 shows the overlaid DSC curves for the PAN samples for 5 °C/min in nitrogen. The RAFT homopolymers exhibit very narrow exotherms with peaks centered between 274–279 °C, while the FR homopolymers show exothermic peaks in the range of 260–265 °C. Additionally, the RAFT polymer peaks are sharper and have heat flows c.a. 30 W/g, which is high

compared to values for the FR polymers with heat flows c.a. 10–15 W/g. Notably, the RAFT polymers exhibit unconventional cyclization exotherms that appear inverted at the base (inward bending of the peak), which could be due to the heat evolution exceeding the sensitivity of the instrument. This massive amount of energy that is released over a narrow temperature range would be detrimental to carbon fiber fabrication and it could prematurely degrade the polymer backbone.

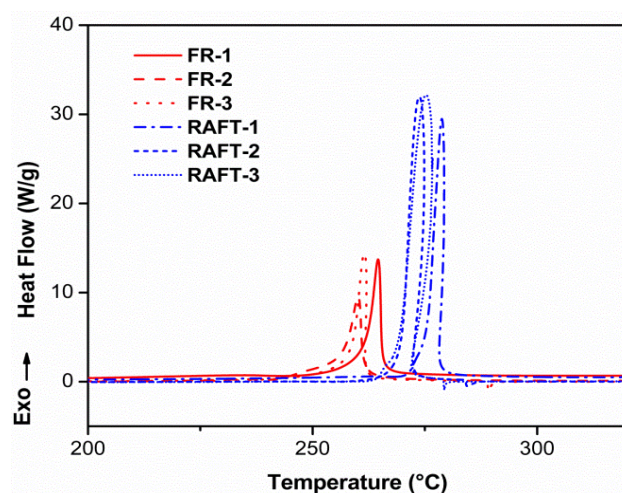


Figure 27. DSC curves of RAFT and FR PAN homopolymer samples at 5 °C/min.

Interestingly, both FR-1, possessing the lowest M_n , and FR-3, owning the highest M_n , have lower peak cyclization temperatures than any of the RAFT polymers (Fig. 27). Because the end groups of the FR-2 polymer are the same as the RAFT polymers (2-cyano-2-propyl), which still has a lower peak cyclization temperature, end group effects are expected to be negligible. This indicates that polydispersity and polymerization mechanism could have a profound effect on the cyclization exotherm. Moreover, RAFT-1 has a higher peak cyclization temperature than the RAFT-2 and RAFT-3 polymers, which contradicts literature claims that higher M_n leads to higher T_p .^{51–53}

To further examine this behavior, we determined the peak exotherm temperature at several ramp rates (2, 5, 10, and 20 °C/min) (example in Figure 28) and the results are listed in Table 6. The exotherm temperature increases with increasing ramp rate as shown in Figure 28. We see that with increasing ramp rate the max heat flow increases. As shown in Table 6, all peak exotherms are higher for the RAFT samples than the analogous FR samples for a given ramp rate.

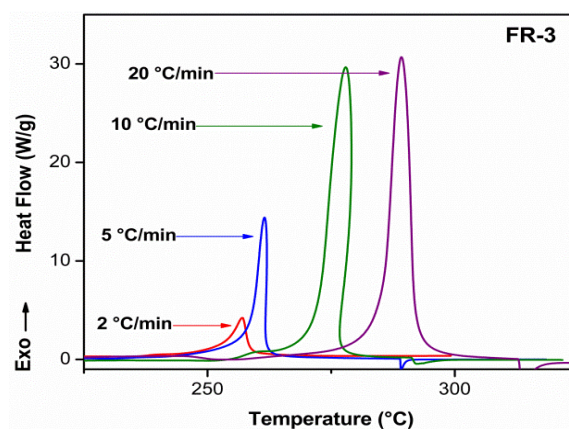


Figure 28. DSC curves for FR-3 at 2, 5, 10, and 20 °C/min.

Table 6

DSC Peak Maxima for RAFT and FR PAN Homopolymer Samples

Entry	Peak Temperature (°C)			
	2 °C/min	5 °C/min	10 °C/min	20 °C/min
FR-1	252	265	272	286
FR-2	249	260	268	276
FR-3	257	261	278	289
RAFT-1	261	279	291	312
RAFT-2	262	274	288	310
RAFT-3	261	275	290	307

Applying the Ozawa and Kissinger equations, we can obtain activation energy.

The Ozawa and Kissinger plots are shown in Figure 29.

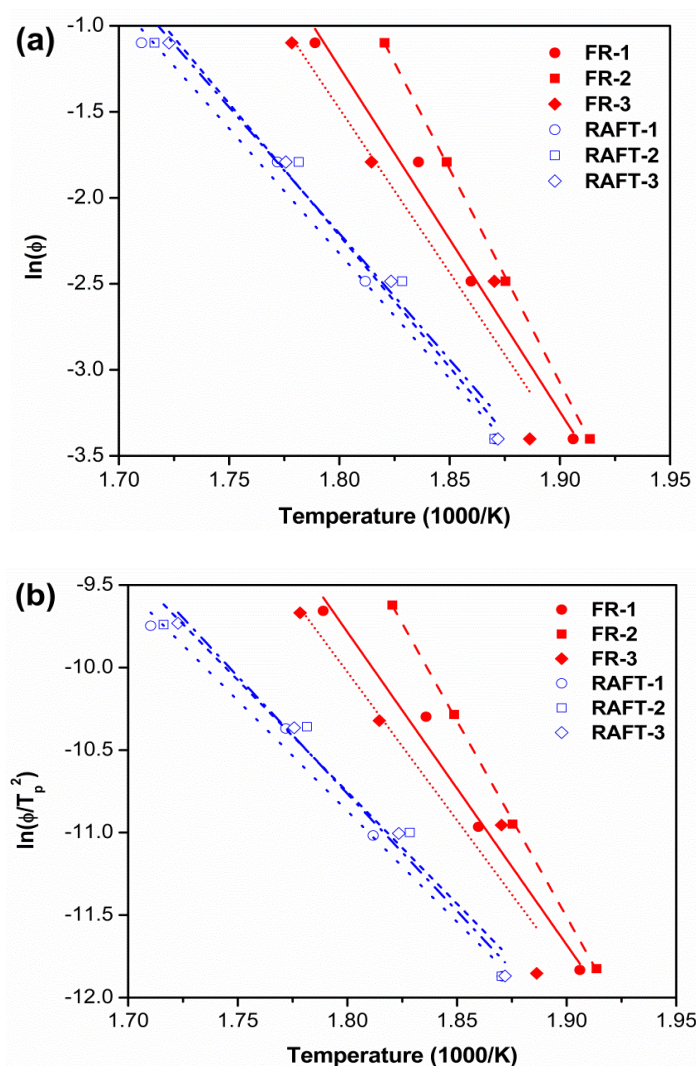


Figure 29. Plots of $1000/T_p$ vs. (a) $\ln(\phi)$ according to the Ozawa method and (b) $\ln(\phi/T_p^2)$ according to the Kissinger method.

Shown in Figure 29 the Ozawa and Kissinger slopes are steeper for the FR polymers than the RAFT polymers. Yet, all of the fits for the RAFT polymers are shifted to the left due to higher peak temperatures. The activation energies and pre-exponential factors are compiled in Table 7 along with the summarized data from the 5 °C/min ramp rate.

Table 7

Activation Energies of RAFT and FR PAN Homopolymers

Entry	Ozawa Method ^a		Kissinger Method ^b		5 °C/min			
	E _a (kJ/mol)	A (sec ⁻¹)	E _a (kJ/mol)	A (sec ⁻¹)	T _p ^c (°C)	T _p Breadth ^d (°C)	Intensity ^e (J/g)	Heat Flow ^f (W/g)
FR-1	158.3	1.32x10 ¹³	157.6	1.11x10 ¹³	265	15	512	13.5
FR-2	196.0	1.10x10 ¹⁷	197.3	1.47x10 ¹⁷	260	19	671	9.6
FR-3	150.6	2.76x10 ¹²	149.3	2.07x10 ¹²	261	13	589	13.7
RAFT-1	114.8	2.78x10 ⁸	111.5	1.31x10 ⁸	279	7	563	29.4
RAFT-2	115.9	4.59x10 ⁸	112.7	2.18x10 ⁸	274	6	591	31.9
RAFT-3	121.1	1.39x10 ⁹	118.2	7.10x10 ⁸	275	9	531	32.1

^aActivation energy determined from Ozawa method. ^bActivation energy determined by Kissinger method. ^cThe peak exotherm temperature was determined as the temperature with the maximum heat flow via DSC. ^dThe peak exotherm breadth was determined by the onset and end of the peak exotherm temperature. ^eThe intensity was calculated by the integral area under the peak exotherm. ^fThe heat flow was taken as the maximum heat flow at the peak temperature.

As shown in Table 7, the activation energies of the three polymers prepared by RAFT polymerization are lower than the respective FR polymers. The exotherm intensities for all six samples are similar. Interestingly, the collision frequency (A) is 4–9 orders of magnitude higher in the case of the polymers prepared by conventional free radical polymerization. We can rationalize that FR polymers have more defect sites and impurities from residual polymerization products that provide more opportunities for cyclization to occur.⁷ Also, the frequency factor increases in order of molecular weight for the RAFT polymers, which suggests that high molecular weight PAN has an

increased statistical probability of nitriles sterically orienting. Moreover, the RAFT polymers exhibit peak breadths ranging from 6–9 °C compared to the FR polymers with peak breadths between 13–19 °C. This could be directly related to the lower activation energy of the RAFT polymers. We can reason that a low PDI with fewer impurities leads to all of the chains initiating cyclization simultaneously. In general, the higher the A -value then the lower the peak exotherm temperature, but the higher the E_a the broader the exotherm for homopolymer PAN.

In-situ FTIR Analysis of Extent of Stabilization

Real-time FTIR spectra were recorded in a heating cell at 225 °C for 5 hours as shown in Figure 30. The stabilization temperature of 225 °C was selected to be below the peak exotherm temperature in order to observe quantitative differences in cyclization rate. In general, stabilization leads to a decreased intensity of the narrow band at 2240 cm^{-1} related to the nitrile stretching and an increased intensity of the broad band centered around 1590 cm^{-1} corresponding to vibrations of $-\text{C}=\text{C}-$ and $-\text{C}=\text{N}-$ linkages in the aromatic rings.^{25,32,67} The other band assignments are as follows: 1452 cm^{-1} from the polymer backbone ($-\text{CH}_2-$ bend), 1672 cm^{-1} due to oxygen uptake ($-\text{C}=\text{O}-$ stretch) or termination by disproportionation ($-\text{C}=\text{C}-$ stretch), 2939 cm^{-1} from the polymer backbone ($-\text{CH}_2-$ stretch), 3212 and 3360 cm^{-1} due to tautomerization and isomerization of the imine into enamine and hanging amines⁴¹ ($-\text{NH}-$ stretch). Additionally, a small peak at about 2220 cm^{-1} forms, which could be due to the isomerization of the ladder structure or dehydrogenation resulting in α,β -unsaturated nitrile groups.^{25,32} The noise c.a. 2300 cm^{-1} is presumed to be from carbon dioxide in the background.

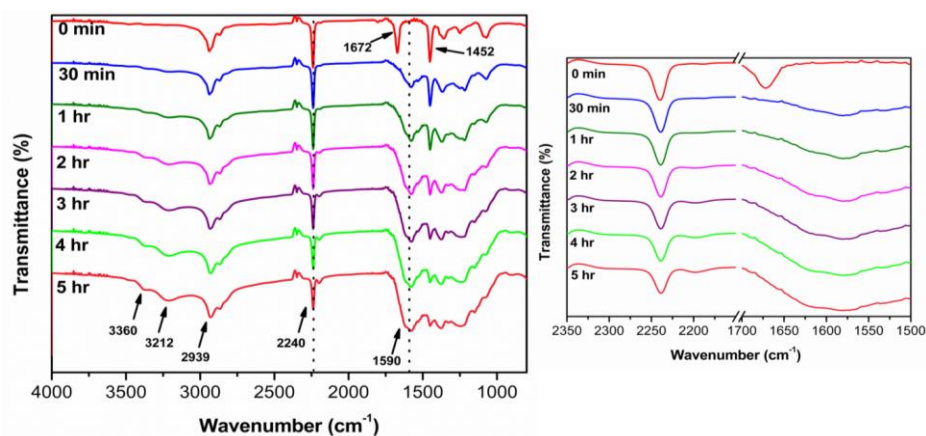
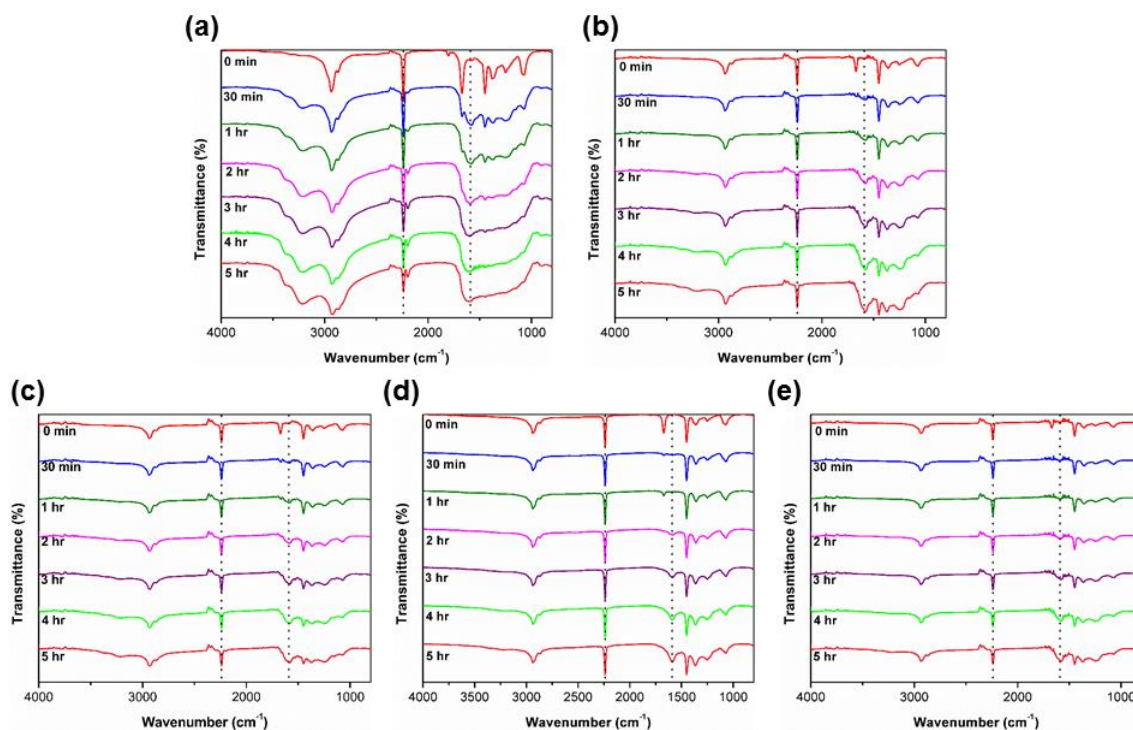


Figure 30. FTIR spectra of FR-2 heated at 225 °C for 5 hr in nitrogen (left) and zoomed in around 2240 and 1590 cm^{-1} (right). Times shown are with respect to post ramp to 225 °C at 5 °C/min.

The real-time FTIR spectra for the other samples are shown in Figure 31. Evident from Figures 30, 31a, and 31b, the FR homopolymers exhibit the peak resembling imine structure after 30 min, while this peak appears in the RAFT polymers after 1–2 hr (Figures 31c-e). Furthermore, the FR-1 and FR-2 polymers have strong signals c.a. 3200 cm^{-1} , resembling amine and alcohol formation, which are almost absent in the RAFT polymers. The integrated signals for the nitrile and imine were recorded and the plots for the determined unreacted nitrile content and E_s are shown in Figure 32. In accordance with the DSC results, the FR polymers begin cyclization prior to the RAFT polymers and reach a greater extent of stabilization at 225 °C over the course of 5 hours as seen in Figure 32. Specifically, RAFT-1 does not begin conversion of nitrile groups until about 45 min of heat treatment (Fig. 32a), while the FR polymers exhibit the greatest nitrile conversions. Interestingly, FR-1 shows that E_s increases quickly, but then seems to level off over time (Fig. 32b). This could be due to the low molecular weight, but high PDI, of this polymer, which could cause a slope change due to unequal reactivity of the varying polymer chain sizes.



- (1) The plateau between 200–270 °C represents the cyclization period which forms the ladder structure and should have minimal weight loss.²⁷
- (2) Rapid weight loss between 270–300 °C due to dehydrogenation and the heat liberated from the cyclization, which is accompanied by release of small volatiles.²³
- (3) Steady weight loss between 300–450 °C due to removal of small impurities as volatile by-products that were residuals from the cyclized ladder structure such as methane, ammonia, hydrogen cyanide, water, and carbon dioxide.⁷
- (4) The plateau between 450–600 °C, which encompasses the stabilized structure before further release of hydrogen cyanide, nitrogen, and hydrogen through carbonization.⁴¹

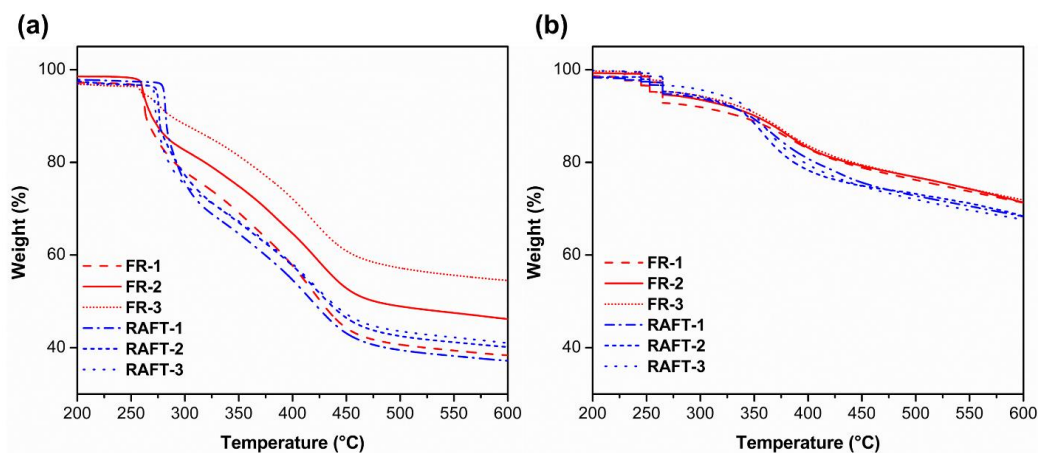


Figure 33. TGA plots of (a) untreated PAN polymers ramped at 10 °C/min to 600 °C in N₂ and (b) polymers ramped at 10 °C/min in air and held at isotherms of 230, 245, 253, and 265 °C for 15 min each and then ramped at 10 °C/min to 600 °C in N₂.

Apparent in Figure 33a, the FR polymers begin weight loss (c.a. 270 °C) before the RAFT polymers (c.a. 280 °C). Furthermore, the rapid weight loss between 270–300 °C of the RAFT polymers is steeper (> 20% mass loss) due to the greater heat flow

generated during cyclization as compared to the more gradual slope change of the FR polymers, especially FR-3. The final plateaus (450–600 °C) coincide with the order of molecular weight, which may suggest that higher molecular weights lead to greater residual mass. Figure 33b demonstrates that a pre-oxidation treatment greatly increases stability of the ladder structures and minimizes rapid mass loss post cyclization, while nearly eliminating the effect of molecular weight.

Oxidative Stabilization and Structural Changes With Respect to Molecular Weight and Polydispersity

To complement the differences in thermal cyclization and degradation we investigated the structural changes that occur through oxidation of these polymers by heat treating them at 225 °C in air for 30 min and for 5 hr. The degree of cyclization was determined via the cyclization index (CI) by DSC.

Cyclization Index (CI) via DSC

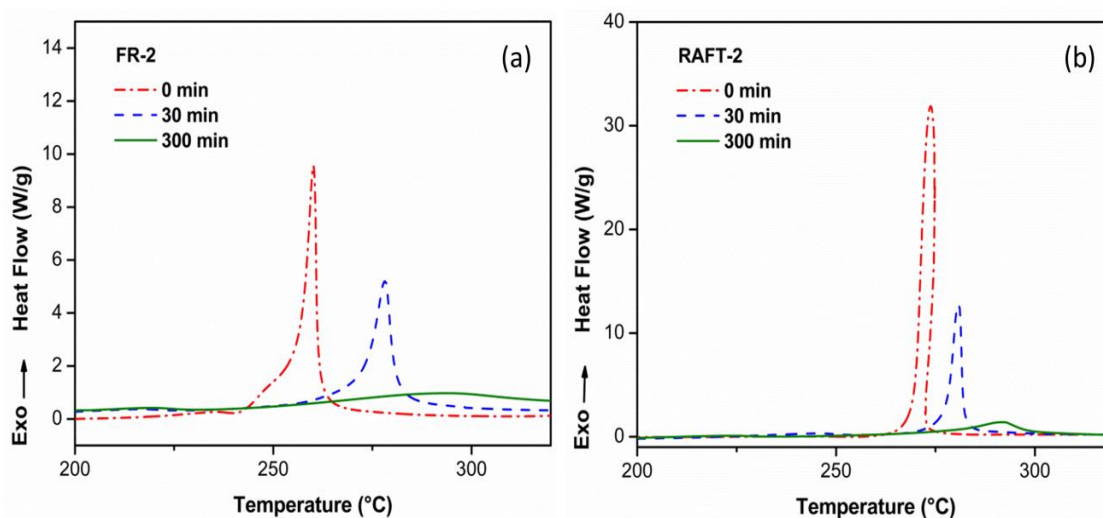


Figure 34. DSC curves of pre-oxidized PAN treated at 225 °C in air for 30 min and 5 hr (a) FR-2 and (b) RAFT-2.

Figure 34 shows an example of the DSC curves of the heat treated polymers. The exotherm peaks shift to a higher temperature indicating a higher degree of stability in the polymer architecture with a longer pre-oxidation time. The cyclization reaction is mostly completed by 5 hr at 225 °C noted by the significant decline in exotherm intensity. The CI was determined for each polymer at 30 min and 5 hr and the results are summarized in Table 8. The CI is consistent with the previous data showing that cyclization progresses more at 225 °C for the FR polymers. After 30 min of oxidation at 225 °C, FR polymers reach 15-20% completion of cyclization, while RAFT polymers reach only 5-10% completion.

Table 8

Cyclization Index (CI) of RAFT and FR Homopolymers as a Function of Time at 225 °C in air

Entry	CI (%)	
	30 min	5 hr
FR-1	18.5	88.6
FR-2	20.1	81.5
FR-3	16.0	87.8
RAFT-1	6.7	62.2
RAFT-2	8.1	63.1
RAFT-3	8.5	75.0

CI = $100 \cdot (H_v - H_o) / H_v$, where H_v is the exotherm intensity of the untreated virgin polymer and H_o is the intensity of the pre-oxidized polymer.

Raman D/G Ratios and Lateral Crystal Size

An example of the Raman spectra of FR-2 heat treated at 225 °C for 30 min and 5 hr in air along with the sample recovered from TGA analysis ramped to 800 °C in N₂ for FR-2 is depicted in Figure 35.

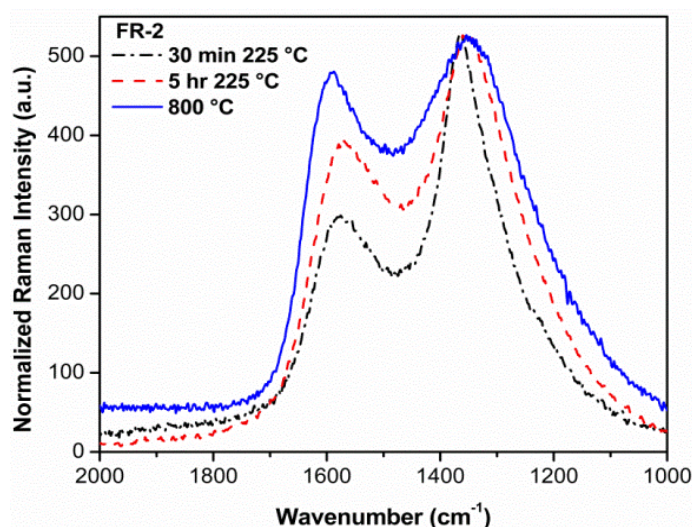


Figure 35. Raman spectra of FR-2 polymer heat treated in air at 225 °C for 30 min and 5 hr and also ramped to 800 °C in N₂.

The band located c.a. 1600 cm⁻¹ presents a main first order sp²-hybridized C–C stretching mode (G mode, E_{2g2}) while the band c.a. 1350 cm⁻¹ is due to less ordered or “defect induced” carbonaceous material (D mode).^{115–117} This D mode band is probably due to carbon atoms in the immediate vicinity to the edge of a graphene layer or other lattice disturbances.¹³¹ It is well known that the ratio between the intensity of the D-band and the G-band is indicative of the degree of graphitization and alignment of the graphitic planes, where the lower the ratio then the higher the amount of order in the structure.^{116,117} In Figure 35, it is seen that the G-band increases relative to the D-band from 30 min to 5 hr and then further when ramped to 800 °C. The I_D/I_G ratios of all the polymer samples are shown in Figure 36.

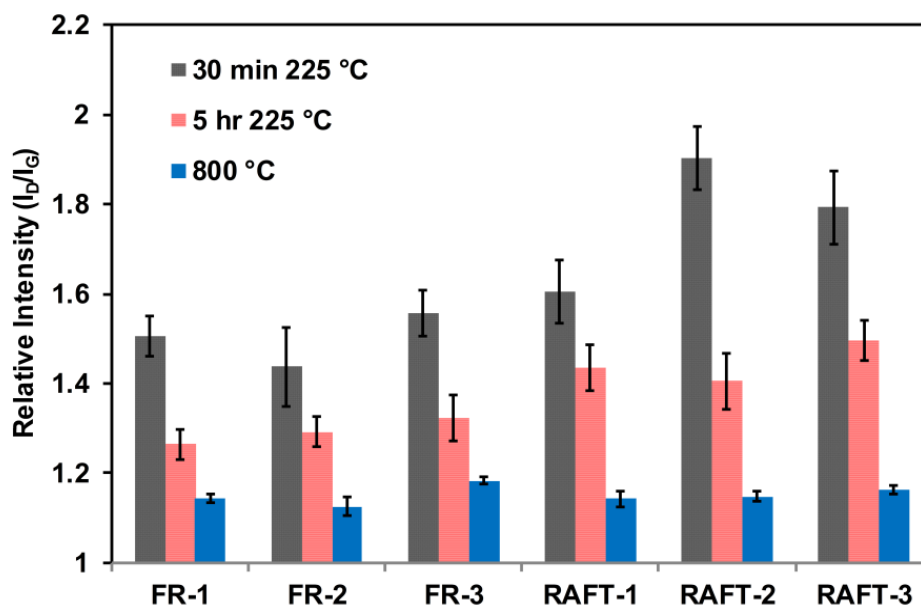


Figure 36. Relative intensity (D-band/G-band) for Raman spectra of PAN polymers treated to 225 °C in air for 30 min and for 5 hr and also ramped to 800 °C in N₂. Error bars represent one standard deviation from the mean of 5 spots measured and are estimates of the uncertainty of the measurement.

From Figure 36, the greatest contrast between the D/G intensities of RAFT and FR polymers is after 30 min of heat treatment at 225 °C, but for 5 hr at 225 °C and after a ramp to 800 °C the I_D/I_G ratio seems to converge at a common value of about 1.15.

Knight and White developed an empirical formula that relates this ratio to the crystalline domain size, L_a , of graphite (Chapter II, Equation 12).¹¹⁵ The I_D/I_G ratios and determined L_a values are summarized in Table 8. The domain size is larger for the FR polymers after 30 min at 225 °C, but then all of the polymers meet at about 3.80 nm when ramped to 800 °C. This indicates that the FR polymers begin forming ordered graphitic structure before the RAFT polymers, but ultimately the polymers reach a common structure of similar size given the polymers are all polyacrylonitrile homopolymers.

Table 9

Relative Intensities of D-band to G-band and Crystalline Domain Size (L_a (nm) = $4.4/(I_D/I_G)$) Determined at Various heat Treatment Conditions

Entry	30 min at 225 °C in air		5 hr at 225 °C in air		Ramp to 800 °C in N ₂	
	I_D/I_G	L_a (nm)	I_D/I_G	L_a (nm)	I_D/I_G	L_a (nm)
FR-1	1.51	2.91	1.26	3.49	1.14	3.86
FR-2	1.44	3.06	1.29	3.41	1.13	3.89
FR-3	1.56	2.82	1.32	3.33	1.18	3.73
RAFT-1	1.61	2.75	1.44	3.06	1.14	3.86
RAFT-2	1.90	2.32	1.41	3.12	1.15	3.83
RAFT-3	1.79	2.46	1.50	2.93	1.16	3.79

WAXS Diffraction Patterns and Crystallite Properties

The structural differences were also characterized by WAXS as shown in Figure 37. Remarkably, there are no evident structural differences between the untreated polymers despite the vastly different stabilization characteristics. Apparent in Figure 37, after 30 min of oxidation treatment, the peak c.a. $2\theta = 17^\circ$ (100) becomes more pronounced as compared to the untreated polymers. In addition a new band appears, which is attributed to the (110) planes.³¹ Sharper bands and the formation of new bands with heat treatment are not uncommon in the literature.^{24,32,33} This phenomenon is a result of thermal relaxation and an increase in flexibility of the molecular chain and a consequent orientation of polymer chains into a higher crystalline order.³³ Most obvious from Figure 37 are the differences between the samples at 5 hr of pre-oxidation treatment, which show that the scattering patterns in the FR samples become much more diffuse, especially for FR-1 and FR-2.

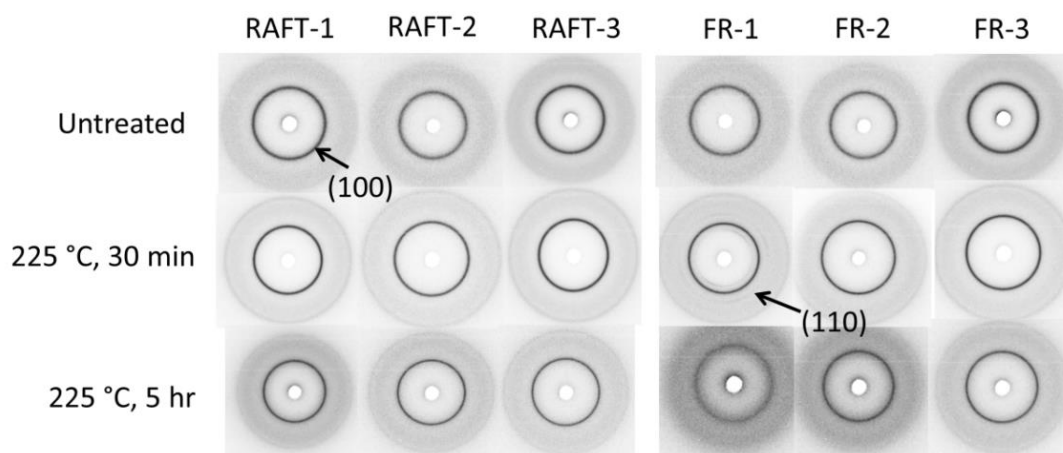


Figure 37. WAXS patterns for PAN samples at given heat treatment conditions in air.

Examples of the 2θ vs. intensity plots for FR-2 and RAFT-2 are demonstrated in Figure 38. From Figure 38, the formation of the new (110) band appears c.a. $2\theta = 29^\circ$ peak after 30 min. After 5 hr, a broad halo appears between $15\text{--}30^\circ$ after 5 hr, for the FR-2 polymer (Figure 38a) indicating amorphitization of the crystal structure.

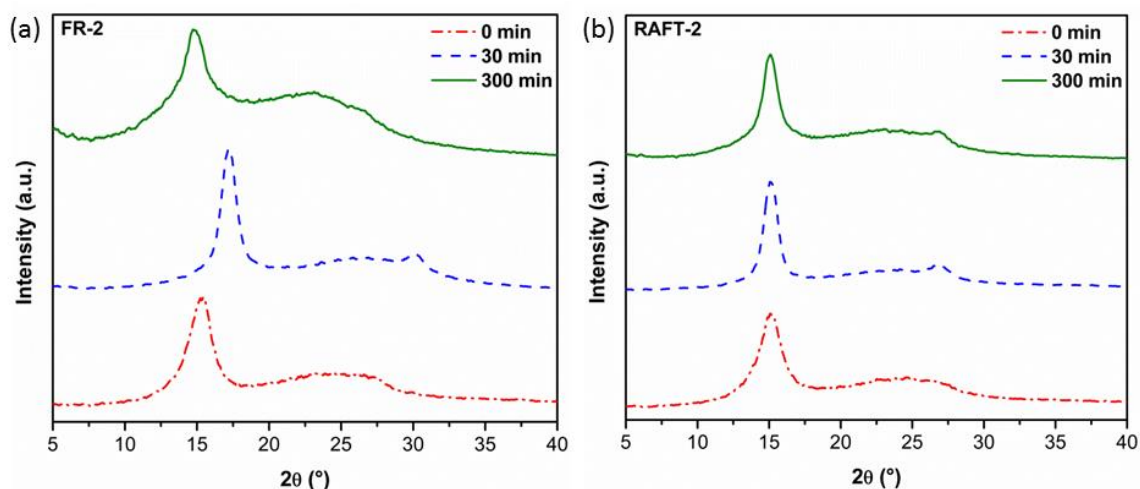


Figure 38. 2θ vs. intensity of (a) RAFT-2 and (b) FR-2 at 225°C in air for various times.

The crystallite thicknesses, L_c , stabilization indices, SI, and crystallinities, χ_c , of each polymer sample are compiled in Table 10. The L_c for all samples increases after 30 min of oxidation treatment, while the SI is shown to decrease after 30 min of heat

treatment. After 5 hr of oxidation at 225 °C, the L_c then decreases and the SI increases dramatically, especially for FR polymers. Noted in Table 10, the FR polymers reach a higher SI than the analogous RAFT polymers, consistent with thermal characterization.

Table 10

WAXS Data Summarized for RAFT and FR PAN Homopolymer Samples

Entry	Untreated		30 min at 225 °C in air			5 hr at 225 °C in air		
	χ_c (%)	L_c (nm)	χ_c (%)	L_c (nm)	SI (%)	χ_c (%)	L_c (nm)	SI (%)
FR-1	37.6	3.58	24.2	5.97	-27.4	10.5	2.48	53.3
FR-2	44.4	3.91	28.6	5.89	-33.1	18.2	3.80	39.8
FR-3	32.3	4.41	32.7	6.45	-4.64	21.1	5.28	27.9
RAFT-1	37.6	4.82	38.1	6.95	-25.7	23.4	5.66	19.4
RAFT-2	44.0	3.83	43.9	6.46	-28.1	29.0	5.66	-6.2
RAFT-3	34.3	3.67	33.0	6.26	-26.8	30.4	4.46	25.7

Summary

We have demonstrated the difference between stabilization behavior of PAN homopolymers produced by conventional free radical polymerization and those by controlled RAFT polymerization. Polymerization mechanism along with polydispersity have apparent effects on both the onset and extent of cyclization in PAN. It appears that narrow polydispersities via RAFT polymerization lead to (1) higher exotherm temperatures, (2) faster liberation of heat released during the cyclization exotherm, and (3) lower activation energy with narrow windows for cyclization. The initiation temperature of cyclization for homopolymers strongly correlates to collision frequency (A), with FR homopolymers having higher probability for cyclization to occur due to

more defects and radical sources. Meanwhile, RAFT homopolymers have lower activation energies, which leads to narrower exotherm temperatures and greater evolution of heat that prematurely degrades the polymers. The WAXS results complement these thermal differences with greater stabilization indices and reduced crystallinities seen in the FR polymers as compared to RAFT polymers post oxidation at 225 °C in air. These findings will be useful when designing precursors for next generation carbon fibers with RAFT polymerization methods.

CHAPTER V

AN INVESTIGATION OF N-ISOPROPYLACRYLAMIDE CONTAINING PAN-
COPOLYMERS AND THE STABILIZATION BEHAVIOR OF PAN-BASED RAFT
COPOLYMERS

Abstract

The viability of N-isopropylacrylamide (NIPAM) as a novel comonomer for PAN-based precursors has been demonstrated. As compared to traditional comonomers such as acrylic acid (AA), NIPAM-containing PAN copolymers reveal a similar extent of stabilization and residual nitrile fraction through thermal Fourier transform infrared (FTIR) spectroscopy studies. Differential scanning calorimetry (DSC) of NIPAM-containing PAN copolymers exhibit monomodal exothermic peaks related to cyclization, which are broad and reduced as compared to homopolymer PAN. Meanwhile, NIPAM as a comonomer offers structural benefits similar to that of methacrylate (MA) and methyl methacrylate (MMA), which disrupts the crystalline packing of PAN and should provide better polymer processing for solubility, spinnability, and drawability as shown through Raman spectroscopy and wide-angle X-ray scattering (WAXS).

This study is the first to demonstrate a route to preparing high molecular weight, controlled PAN-based copolymers via reversible addition-fragmentation chain transfer (RAFT) polymerization with molecular weights exceeding 165,000 g/mol (SEC-MALLS) and polydispersity (M_w/M_n) < 1.35. The thermo-oxidative stabilization of these high molecular weight, narrow polydispersity PAN-based RAFT copolymers are extensively studied. Selected RAFT copolymers significantly show an increase in mass retention during thermo-oxidative stabilization as compared to conventional free radical

copolymers. These RAFT copolymers exhibit promising properties as next generation carbon fiber precursors.

Results and Discussion

Investigation of Novel Comonomers for PAN-based Precursors by DSC

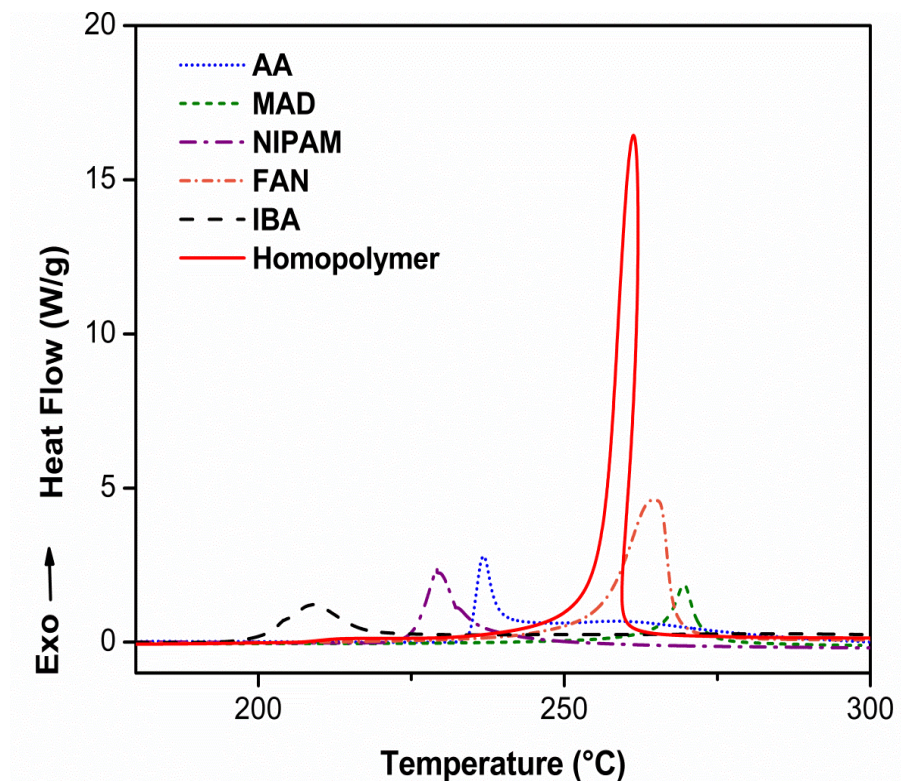


Figure 39. DSC curves (5 °C/min ramp rate) of 95/5 PAN-based copolymers prepared by FR polymerization.

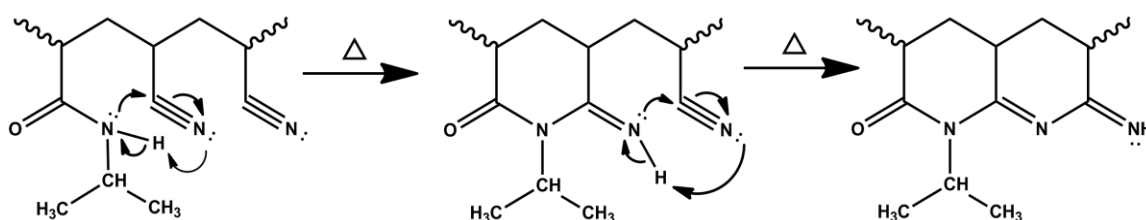
Several novel PAN-based copolymer precursors (95/5: AN/comonomer) were screened by DSC using acrylic acid as a traditional comonomer for comparison. The results are shown in Figure 39. The copolymers were prepared by conventional free radical (FR) polymerization at 65 °C using 0.02 mol% AIBN as the initiator. Fumaronitrile (FAN) was selected because of its dual nitrile functionality, which was expected to enhance the number of cyclized rings. Interestingly, the FAN-containing copolymer exhibited a broad monomodal exotherm at a higher temperature than

homopolymer, which suggests that cyclization is inhibited relative to homopolymer. This could be caused by an increase in polarity of the nitrile groups and hydrogen bonding between chains, which further stabilizes the semi-crystalline structure.¹³² Maleic anhydride (MAD) was chosen on the basis that the anhydride would hydrolyze forming two acid moieties similar to that of itaconic acid, which is a common comonomer in the literature.^{25,26} The 95/5 MAD-copolymer also showed an unexpected temperature increase in the cyclization exotherm, perhaps due to favoring the anhydride form over the maleic acid form.

The only two copolymers to exhibit lower cyclization temperatures as compared to the AA-containing copolymer were those containing isobornyl acrylate (IBA) and *n*-isopropylacrylamide (NIPAM). It was expected that the isobornyl acrylate with a very bulky side group would increase the cyclization temperature, similar to other bulky comonomers like methyl acrylate, which disrupts the crystalline packing and means for free radical cyclization to occur.^{114,133} However, it is possible that IBA can provide chain flexibility, allowing parallelization between chains.¹³⁴ Also, IBA should increase the amorphous content providing ease for diffusion of oxygen into the less dense regions of the polymer, thus allowing oxidation to promote cyclization.^{7,31,57} Nonetheless, at 5 mol% IBA, the reduction in exothermic peak intensity is dramatic and the extent of cyclization was assumed to be negatively impacted by such a bulky comonomer.

On the other hand, NIPAM also lowered the peak exotherm temperature without compromising the peak intensity presumably because of its ability to initiate ionic cyclization by the amide group (Scheme 8). Moreover, NIPAM is a promising comonomer selection because of its bulkiness to improve plasticity of the PAN precursor.

Other studies have incorporated similar comonomers that simultaneously benefit the plasticity and processability of PAN precursors while also mediating the cyclization exotherm through the introduction of an acid or amide moiety.^{29,30} However, these studies required synthetic steps to create analogues of itaconic acid while NIPAM is a common and commercially available monomer, which can be readily scaled for PAN precursors. As discussed in the Introduction, the advantage to utilizing a single comonomer over traditional terpolymers is that terpolymers have unequal reactivities of the added comonomers resulting in decreased performance of the carbon fiber.²⁸ As seen in Figure 39, the NIPAM-containing copolymer exhibits both a reduced and broad cyclization exotherm. The activation energies determined by Ozawa and Kissinger methods (5, 10, 15, and 20 °C/min ramp rates) along with the exotherm behavior from the 5 °C/min ramp rate are tabulated in Table 11.



Scheme 8. Cyclization of p(AN-co-NIPAM).

Table 11

Activation Energies of Novel PAN-based (95/5) Copolymers by FR Polymerization

Entry	Ozawa Method ^a		Kissinger Method ^b		5 °C/min			
	E _a (kJ/mol)	A (sec ⁻¹)	E _a (kJ/mol)	A (sec ⁻¹)	T _p ^c (°C)	T _p Breadth ^d (°C)	Intensity ^e (J/g)	Heat Flow ^f (W/g)
Homo	150.6	2.83x10 ¹²	149.3	2.09x10 ¹²	261	12	589	16.4
AA	92.4	1.24x10 ⁷	88.5	4.71x10 ⁶	233	52	251	2.3
FAN	107.6	1.09x10 ⁸	104.0	4.69x10 ⁷	264	15	481	4.1
MAD	105.5	5.02x10 ⁷	101.7	2.09x10 ⁷	270	10	117	1.5
IBA	78.0	9.49x10 ⁵	73.8	3.15x10 ⁵	209	17	143	1.2
NIPAM	54.5	9.82x10 ²	48.6	2.14x10 ²	230	24	320	1.7

^aActivation energy determined from Ozawa method. ^bActivation energy determined by Kissinger method. ^cThe peak exotherm temperature was determined as the temperature with the maximum heat flow via DSC. ^dThe peak exotherm breadth was determined by the onset and end of the peak exotherm temperature. ^eThe intensity was calculated by the integral area under the peak exotherm. ^fThe heat flow was taken as the maximum heat flow at the peak temperature.

As seen in Table 11, the NIPAM-containing copolymer has the lowest activation energy as well as a lower peak cyclization temperature as compared to the AA-containing PAN. The max heat flow, breadth, and intensity of the exotherm all indicate the velocity of heat release and the range of temperature for cyclization. As expected, all of the copolymers demonstrate moderate intensity and heat flows relative to the PAN homopolymer with p(AN-co-FAN) being the most similar to homopolymer. The NIPAM-containing copolymer, which exhibits an increased intensity and decreased max heat flow as compared to the AA-containing copolymer, was selected for further study.

Synthesis of PAN-Based RAFT Copolymers

Based on the above findings, we prepared RAFT copolymers (30 °C for 48 hr, $[M_a+M_b]_0:[CPDT]_0:[I]_0 = 10,000:1:0.67$) containing 2 and 5 mol% NIPAM in comparison to similar and traditional comonomers for PAN-precursors: AA, methyl acrylate (MA), methyl methacrylate (MMA), acrylamide (AM), dimethylacrylamide (DMAM), and itaconic acid (IA). The conversions, molecular weights, polydispersities, and compositions of the copolymers are summarized in Table 12. The results indicate that the same low temperature CPDT-mediated polymerization conditions employed for homopolymer resolve the low-conversion issues encountered with RAFT copolymerizations of acrylonitrile.^{50,76,77}

Table 12

Summary of RAFT Copolymers

Comonomer ^a	Comonomer content (%)		Conv. (%) ^d	M _n (Theor.) ^e	M _n (MALLS) ^f	PDI ^f
	Feed	Copolymer ^c				
AA	2	1.9	71	379 300	168 400	1.33
NIPAM	2	3.4	65	352 700	142 100	1.38
AM	2	3.2	68	363 200	128 500	1.21
MA	2	5.1	64	343 800	130 800	1.22
MMA	2	6.9	58	313 200	138 700	1.21
DMAM ^g	2	-	63	340 000	162 100	1.41
IA ^g	2	-	41	224 000	53 300	1.18
AA	5	4.5	78	421 100	197 500	1.23
NIPAM	5	8.2	64	358 700	154 700	1.40

Table 12 (continued).

Comonomer ^a	Comonomer content (%)		Conv. (%) ^d	M _n (Theor.) ^e	M _n (MALLS) ^f	PDI ^f
	Feed	Copolymer ^c				
AM	5	7.3	72	388 100	161 300	1.39
MA	5	6.8	65	355 600	139 700	1.36
MMA	5	12.0	66	360 800	118 400	1.17
DMAM ^g	5	-	57	315 600	188 700	1.27
IA ^g	5	-	30	170 900	45 400	1.26
Homopolymer ^b	0	0	71	377 100	131 400	1.27

^aPolyacrylonitrile copolymers synthesized in ethylene carbonate at 20 wt.% monomer concentration under a nitrogen atmosphere at 30 °C using V-70 as the initiator and [M]₀: [CPDT]₀: [I]₀ = 10,000:1:0.67, in which [M]₀ = [M_{AN}]₀ + [M_{Comonomer}]₀. Homopolymer PAN repeated at same concentration of [M]₀: [CPDT]₀: [I]₀ = 10,000:1:0.67. ^cCopolymer composition determined by ¹H-NMR for MA, MMA, and NIPAM-containing copolymers and by quantitative ¹³C-NMR for AA and AM- containing copolymers. ^dConversions were determined by ¹H-NMR spectroscopy recorded in DMSO-d₆. ^eTheoretical number average molecular weights were calculated according to the following equation: $M_n = (\rho \cdot MW_{mon} \cdot [M]/[CTA]) + MW_{CTA}$ where ρ is the fractional monomer conversion, MW_{mon} is the molecular weight of the monomer, and MW_{CTA} is the molecular weight of the CTA. ^fNumber average molecular weight (M_n) as determined by SEC (0.5 mL/min, 60 °C, Polymer Labs PL gel 5 μ m mixed-C column, DMF with 0.02 M LiBr eluent) equipped with RI and MALLS detectors. ^gThese copolymers were removed from the following studies.

PAN-based copolymers of molecular weight > 165,000 g/mol with polydispersity (M_w/M_n) < 1.35 at > 70% conversion were achieved. In the case of IA-containing copolymers the molecular weight was much lower, which could be due to chain transfer with IA. Due to the difficulty of drying and isolating 5 mol% DMAM copolymers and the low conversions of IA-containing RAFT copolymers, DMAM and IA-containing copolymers were removed for the remaining precursor studies.

As an example, the kinetic plots and conversion vs. molecular weight are shown for 2 mol% NIPAM and 5 mol% AA copolymers in Figures 40 and 41. The kinetic plots in Figures 40 and 41 show continued monomer conversion out to 48 hr and molecular weights increase linearly with conversion.

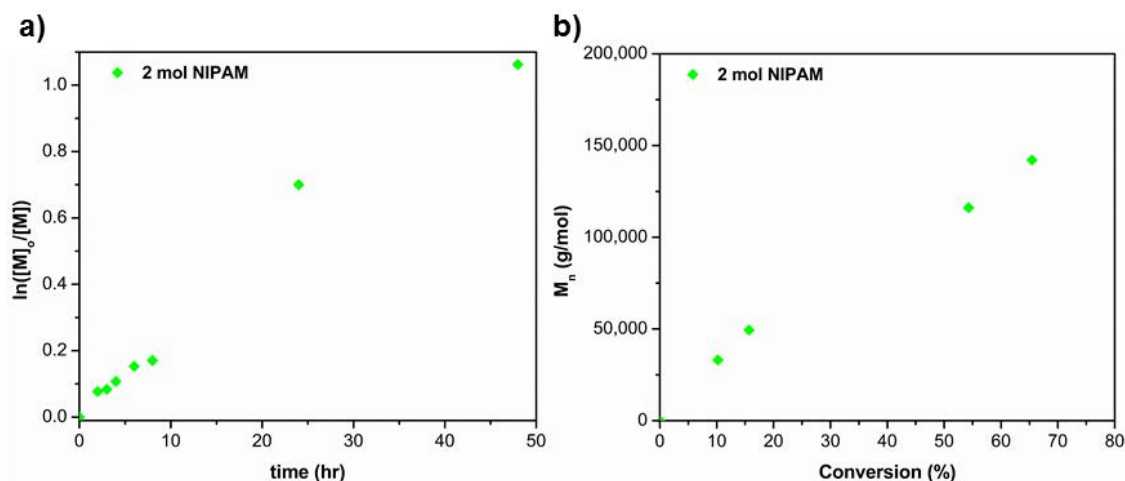


Figure 40. (a) Kinetic plot and (b) molecular weight vs. conversion for 98/2 p(AN-co-NIPAM) CPDT-mediated RAFT Polymerization at 30 °C and $[M]_0:[CPDT]_0:[I]_0 = 10,000:1:0.67$, in which $[M]_0 = [M_{AN}]_0 + [M_{NIPAM}]_0$.

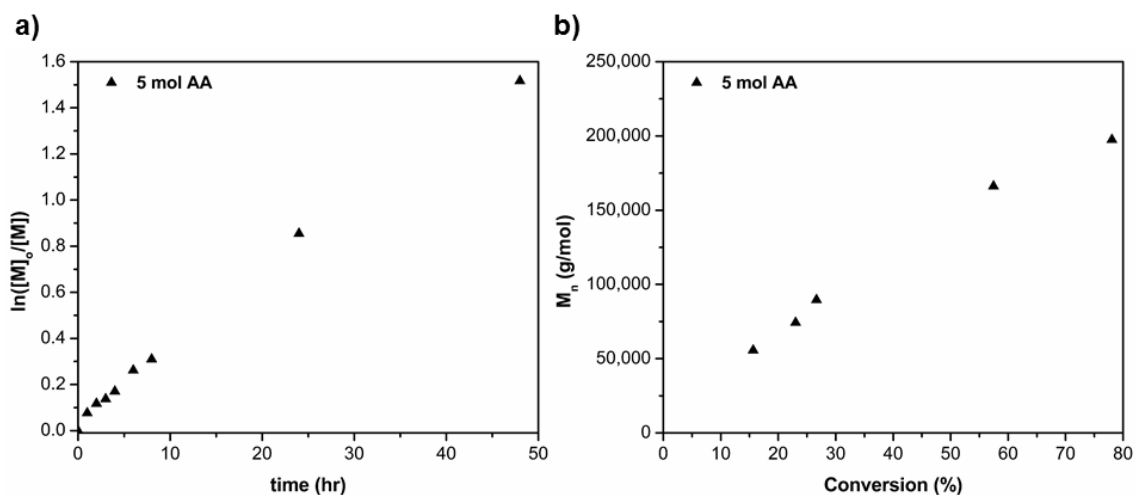


Figure 41. (a) Kinetic plot and (b) molecular weight vs. conversion for 95/5 p(AN-co-AA) CPDT-mediated RAFT Polymerization at 30 °C and $[M]_0:[CPDT]_0:[I]_0 = 10,000:1:0.67$, in which $[M]_0 = [M_{AN}]_0 + [M_{AA}]_0$.

Table 12 also shows that the only polymer which has less comonomer incorporated into the composition than in the feed are the AA-containing copolymers. This result is consistent with previous work wherein acidic comonomers have lower reactivity toward acrylonitrile than neutral comonomers such as MA and MMA.^{28,29} Consequently, the AA-containing copolymers reach the highest conversions and highest molecular weights as compared to the other copolymers. On the other hand, the copolymer with 5 mol% MMA in the feed actually incorporates 12% of the comonomer into the copolymer, which is more than double that of AA. This further exemplifies the difficulties in achieving a uniform distribution of monomers in a terpolymer system with acrylonitrile, one acidic comonomer, and one neutral comonomer.

Structural Characterization of PAN-based RAFT Copolymers (WAXS)

WAXS results of the diffraction patterns for the selected copolymers are shown in Figure 42. The main qualitative differences are seen in the AA-containing copolymers and the MMA-containing copolymers. The scattering angle at the (100) diffraction plane in the 5 mol% MMA sample has a much more diffused and broader band than the sharp and defined band in the 5 mol% AA sample. This is due to the higher amount of MMA incorporated into the structure (12 mol%) and also the bulkiness of the comonomer.

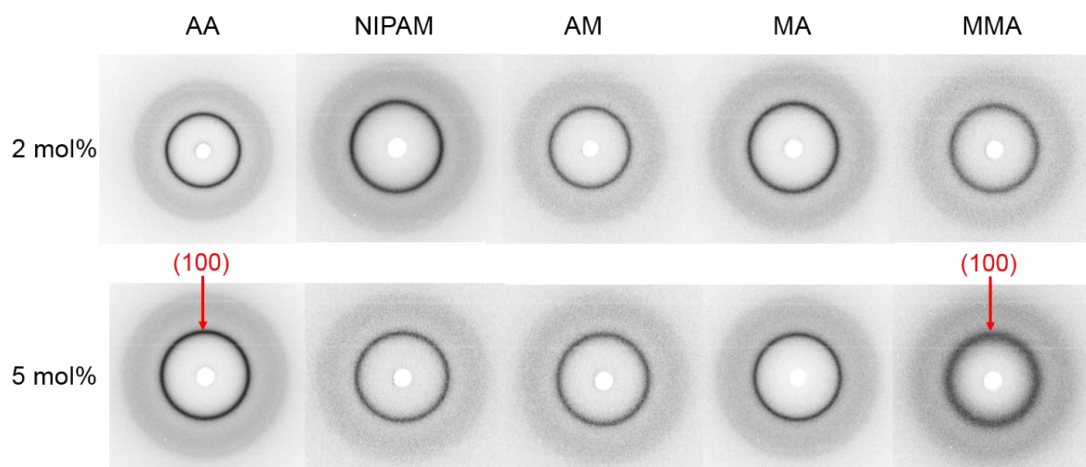


Figure 42. WAXS Patterns for RAFT Copolymers.

The 2-theta vs. intensity plots for 2 and 5 mol% AA, MMA, and NIPAM copolymers are shown in Figures 43a and 43b, respectively. As shown in Figure 43a, the 2 mol% NIPAM copolymer has a similar (100) diffraction peak c.a. $2\theta = 17^\circ$ to the 2 mol% MMA copolymer, while the 2 mol% AA copolymer has a much narrower crystalline peak. Meanwhile, the (100) peak in the 5 mol% MMA copolymer is much broader probably due to the significantly high MMA content in the composition (12 mol%). All of the copolymers exhibit a characteristic broad reflection c.a. $2\theta = 25^\circ$, which has been previously reported in copolymer structures and ascribed to the (200) plane relating to preliminary sheet-like structures.^{19,50,65} Also noted, the AA-containing copolymers exhibit a weak diffraction peak c.a. $2\theta = 29^\circ$, which is attributed to the (110) diffraction plane^{17,34,65} and is absent in the NIPAM and MMA-containing copolymers. The apparent crystallinities and crystallite thicknesses are summarized in Table 13.

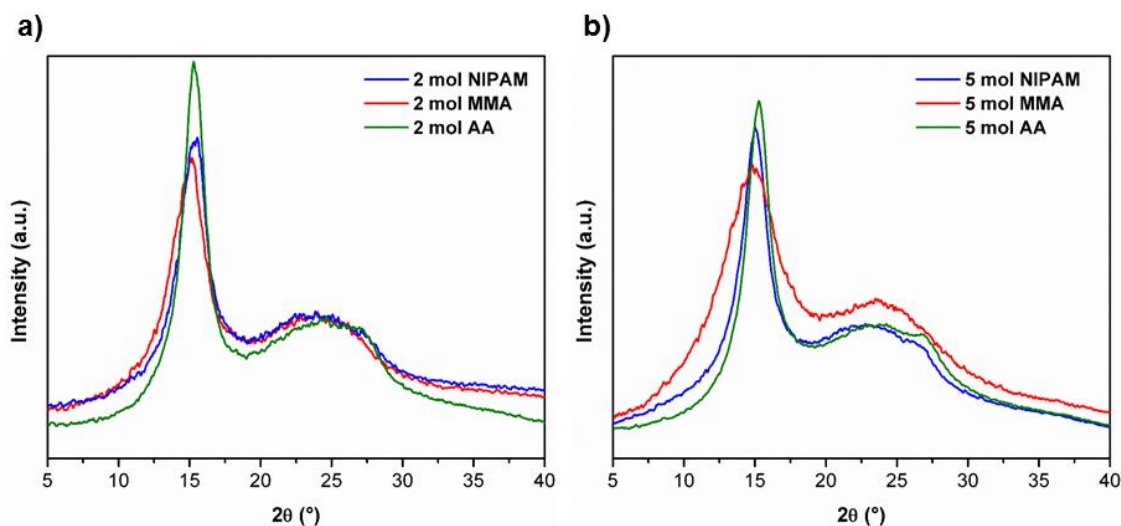


Figure 43. 2-theta vs. Intensity for (a) 2 mol% and (b) 5 mol% NIPAM, AA, and MMA copolymers.

Table 13

Crystallite Thickness and Crystallinity of RAFT Copolymers

Entry	Comonomer content (%)	Molar Mass (g/mol)	Comonomer density (g/cm ³)	van der Waals Volume (x10 ²² cm ³ /molecule) ^a	χ_c (%) ^b	L _c (nm) ^c	“CF” ($\chi_c \cdot L_c$)
AA	2	72	1.05	1.14	32.2	4.08	131.4
NIPAM	2	113	1.10	1.71	34.2	3.04	104.0
AM	2	71	1.13	1.04	33.9	3.28	111.2
MA	2	86	0.95	1.50	24.4	3.58	87.4
MMA	2	100	0.94	1.77	18.0	3.02	54.4
AA	5	72	1.05	1.14	25.6	3.87	99.1
NIPAM	5	113	1.10	1.71	18.6	3.66	68.1
AM	5	71	1.13	1.04	35.6	3.03	107.9
MA	5	86	0.95	1.50	21.7	3.72	80.7
MMA	5	100	0.94	1.77	24.2	1.94	46.9

^aVan der Waals volume determined by comonomer molar mass/($\rho \cdot N_A$). ^b χ_c determined by the integral area of the crystalline peaks in the 2 θ vs. intensity plots divided by the total area. ^cL_c determined by Scherrer’s equation.

Table 13 also shows the comonomer molar mass, comonomer density, van der Waals volume (Equation 18), and “CF”, or the “crystallinity factor”. CF is a new term defined in Equation 19, in which ρ is the density of the comonomer, N_a is Avogadro’s number, χ_c is the percent crystallinity, and L_c is the crystallite thickness.

$$\text{van der Waals volume} = \frac{\text{Comonomer molar mass}}{\rho * N_a} \quad (18)$$

$$CF = \chi_c * L_c \quad (19)$$

Evident from Table 13, the percent crystallinity tends to decrease with bulkier comonomers. The AA-containing copolymers yield the highest L_c values while the MMA-containing copolymers have the lowest L_c values. Moreover, the determined CF values coincide excellently with the estimated van der Waals volume. In general, the larger the comonomer the smaller the CF. The CF decreases from 2 to 5 mol% copolymers, and thus the introduction of a greater content of comonomer further disrupts the crystalline packing of chains. Most importantly, the NIPAM-containing copolymers have structural similarities to MA- and MMA-containing copolymers, which means that NIPAM could provide processability to PAN-based carbon fiber precursors.

Influence of Comonomer on the Cyclization and Stability of PAN-based RAFT

Copolymers

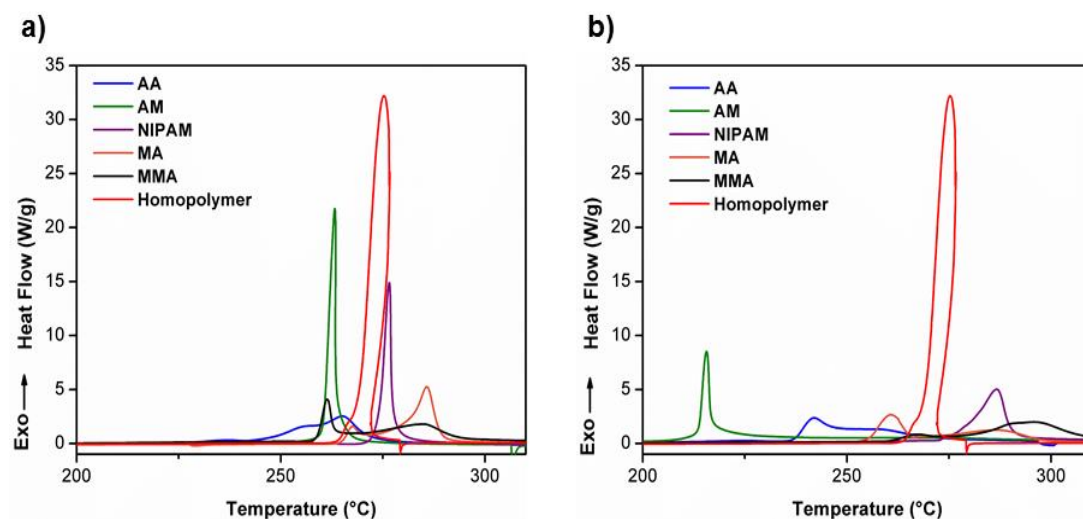
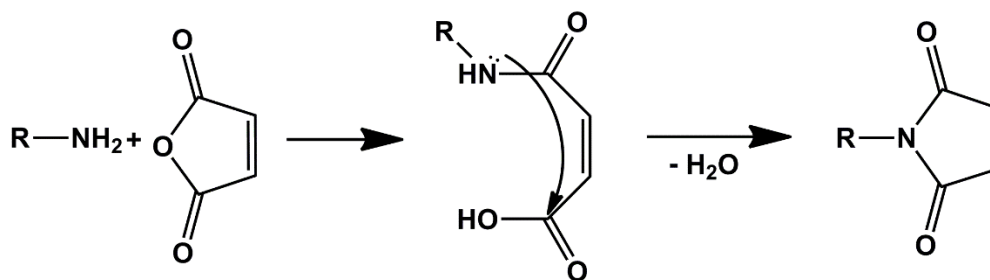


Figure 44. DSCs of RAFT copolymers at 5 °C/min relative to PAN homopolymer at (a) 2 mol% and (b) 5 mol%.

The cyclization behaviors of the RAFT copolymers characterized by DSC are shown in Figure 44 relative to PAN homopolymer. Figure 44a shows that 2 mol% copolymers resemble the homopolymer exotherm closely with large exotherms and peaks centered near the exotherm of the homopolymer. At 5 mol% (Figure 44b), the peaks shift away from the homopolymer exotherm and the max heat flows are further reduced. Notably, the AM- and AA-copolymers shift to lower temperatures, while the NIPAM-, MA-, and MMA-copolymers shift to a higher temperature. The increased exotherm temperature is attributed to disruption in ordered packing of the chains.^{114,133} On the other hand, the AA- and AM- monomers do not disrupt the packing and ionic cyclization has a lower initiation temperature as compared to the free radical mechanism of homopolymer.^{25,26,66,67}

Shown in Figure 44a and 44b, MMA, MA, and AA-copolymers exhibit bimodal peaks. Typically, neutral comonomers display only one peak because they do not initiate cyclization through the ionic pathway, however, we attribute the second peak to hydrolyzed MMA and MA units along the backbone partaking in ionic cyclization. Contrarily, the amide-containing copolymers were expected to have bimodal peaks, but instead, the apparent monomodal peaks are more narrow and pronounced, which could be due to the strong nucleophilicity of the amide moiety. Amines are known to be stronger nucleophiles as compared to acids as witnessed by the synthesis of maleimides (Scheme 9).¹³⁵ Additionally, fast cyclization rates for acrylamide have been reported relative to methacrylic acid due to tautomerization of the α -proton on the amine initiating cyclization in two directions, although this theory has not been verified.^{136,137}



Scheme 9. Synthesis of maleimides demonstrating the nucleophilicity of the amine relative to the acid.

The activation energies were determined by the Ozawa and Kissinger methods. The Ozawa method fits for the AA-, AM-, and NIPAM- containing copolymers are shown in Figure 45. For the purposes of this study, the copolymers with two DSC peaks were split into separate peaks (peak 1 and peak 2). Interestingly, the slope of the 2 mol% NIPAM copolymer parallels the 2 mol% AM copolymer, but the 5 mol% NIPAM

copolymer shows a slope more similar to the 5 mol% AA copolymer peaks. The results are summarized in Table 14.

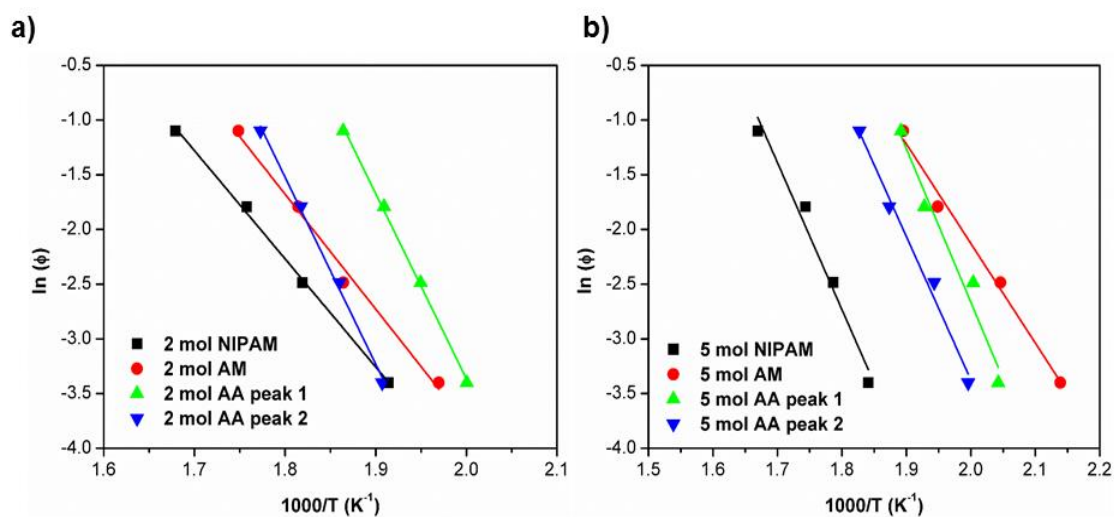


Figure 45. Ozawa plots for RAFT copolymers for (a) 2 mol% and (b) 5 mol%.

Table 14

Activation Energies and Exotherm Behavior of RAFT Copolymers

Comonomer	Com. content (mol %)	Ozawa Method ^a		Kissinger Method ^b		5 °C/min			
		E _a (kJ/mol)	A (sec ⁻¹)	E _a (kJ/mol)	A (sec ⁻¹)	T _p ^c (°C)	T _p Breadth ^d (°C)	Intensity ^e (J/g)	Heat Flow ^f (mW)
NIPAM	2	78.2	1.2x10 ⁵	73.0	3.4x10 ⁴	276	10	464	14.6
MMA1	2	68.1	1.1x10 ⁴	62.4	2.7x10 ³	261	6	-	4.1
MMA2	2	86.0	3.0x10 ⁵	80.9	9.6x10 ⁴	285	24	498	1.8
MA1	2	75.2	4.7x10 ⁴	70.1	1.4x10 ⁴	268	7	-	1.6
MA2	2	120.0	6.3x10 ⁸	116.7	3.0x10 ⁸	286	21	576	4.8
AA1	2	133.8	2.1x10 ¹¹	132.1	1.4x10 ¹¹	240	13	-	1.6
AA2	2	135.1	6.3x10 ¹⁰	133.1	3.9x10 ¹⁰	265	14	561	2.5

Table 14 (continued).

Comonomer	Com. content (mol %)	Ozawa Method ^a		Kissinger Method ^b		5 °C/min			
		E _a (kJ/mol)	A (sec ⁻¹)	E _a (kJ/mol)	A (sec ⁻¹)	T _p ^c (°C)	T _p Breadth ^d (°C)	Intensity ^e (J/g)	Heat Flow ^f (W/g)
AM	2	83.04	2.1x10 ⁶	78.4	6.5x10 ⁵	220	13	572	21.7
NIPAM	5	106.1	2.7x10 ⁷	102.1	1.1x10 ⁷	287	18	475	4.8
MMA1	5	79.4	1.3x10 ⁵	74.4	4.0x10 ⁴	267	9	-	0.9
MMA2	5	100.2	4.8x10 ⁶	95.8	1.8x10 ⁶	296	29	532	2.0
MA1	5	119.4	2.1x10 ⁹	116.8	1.2x10 ⁹	260	12	-	1.3
MA2	5	131.1	7.0x10 ⁹	128.6	4.0x10 ⁹	287	27	522	2.8
AA1	5	110.9	7.5x10 ⁸	108.2	3.9x10 ⁸	241	10	-	2.5
AA2	5	103.6	5.4x10 ⁷	100.3	2.5x10 ⁷	259	25	461	1.3
AM	5	71.9	1.5x10 ⁵	67.4	4.5x10 ⁴	216	10	459	8.3
Homo	0	121.1	1.4x10 ⁹	118.2	7.10x10 ⁸	275	9	531	32.1

^aActivation energy determined from Ozawa method. ^bActivation energy determined by Kissinger method. ^cThe peak exotherm temperature was determined as the temperature with the maximum heat flow via DSC. ^dThe peak exotherm breadth was determined by the onset and end of the peak exotherm temperature. ^eThe intensity was calculated by the integral area under the peak exotherm. ^fThe heat flow was taken as the maximum heat flow at the peak temperature.

As seen in Table 14, the NIPAM-containing RAFT copolymers have lower activation energies than the RAFT PAN homopolymer. Additionally, all of the 5 mol% copolymers show reduced heat flows compared to the analogous 2 mol% copolymers. In general, the copolymers that exhibit two peaks yield a higher activation energy for the latter of the two peaks. The first peak is attributed to the ionic mechanism, which is

expected to have a lower activation energy,²⁵ while the second peak is ascribed to the free radical mechanism. Notably, the AA- and acrylate-containing copolymers have broader overall exotherms and reduced max heat flows as compared to the amide-containing copolymers. Significantly, the NIPAM copolymers exhibits similar activation energy to the traditional AA copolymers, despite the increased exotherm temperature of the NIPAM copolymers. To further elucidate differences in the cyclization behavior of the RAFT copolymers, the cyclization reaction was monitored by FTIR in a heating cell at 225 °C for 5 hours in nitrogen as shown in Figure 46 for the 2 mol% copolymers.

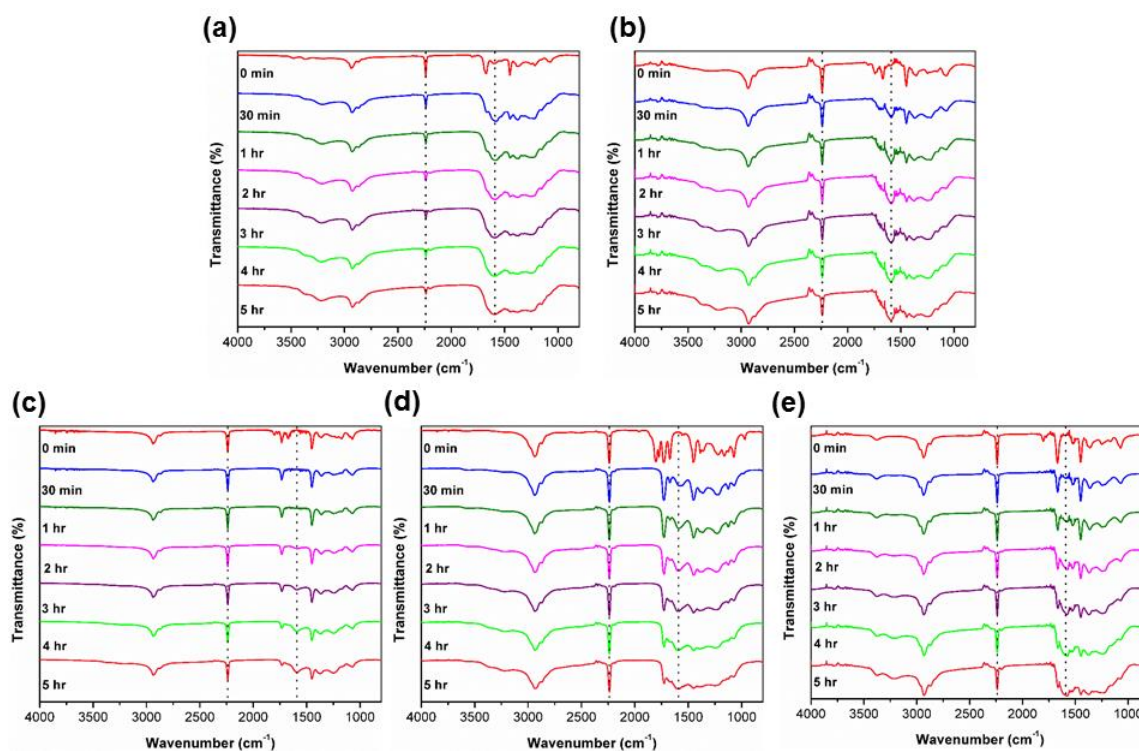


Figure 46. Real-time FTIR spectra of RAFT copolymers at 225 °C in nitrogen for 2 mol % (a) AM, (b) AA, (c) MA, (d), MMA, and (e) NIPAM (dotted lines represent IR bands for nitrile (2240 cm^{-1}) and imine (1590 cm^{-1}) functionalities).

It is clear from Figure 46a that cyclization is fastest in the AM-containing copolymers at 225 °C with the significant increase in the imine peak and reduction in the

nitrile after 30 min. On the other hand, the 2 mol% MA and MMA copolymers (Figure 46c and 46d) exhibit insignificant increases in the imine band in the first hour of heat treatment. Also, all copolymers except for the AM reveal a new series of peaks c.a. 1800 cm^{-1} (0 min) as compared to homopolymer (Chapter IV, Figures 30 and 31), attributed to the carbonyl moieties on the comonomers, which disappear after the first 30 min of heat treatment. Due to the rapid cyclization of AM-containing copolymers the carbonyl is presumed to be already vacant during the ramp to 225 °C. Significantly, the NIPAM-containing copolymer reveals a new band c.a. 3200 cm^{-1} which grows with reaction time (Figure 46e), indicating the presence of bonded amines and alcohols in the stabilized ring structure similar to those of AM and AA (Figures 46a and 46b). The presence of this band suggests that the NIPAM does participate in some capacity of ionic cyclization. The nitrile and imine peaks were integrated as described in Chapter IV to determine the residual nitrile fraction and extent of stabilization and the results are shown in Figures 47 and 48.

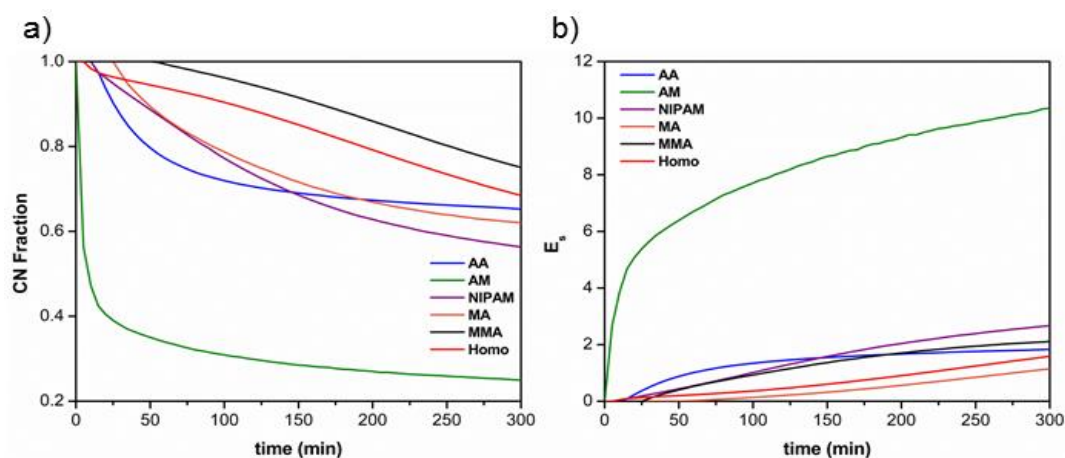


Figure 47. 2 mol% RAFT copolymers heated in FTIR at 225 °C for hours plotted for (a) residual nitrile fraction and (b) extent of stabilization (E_s).

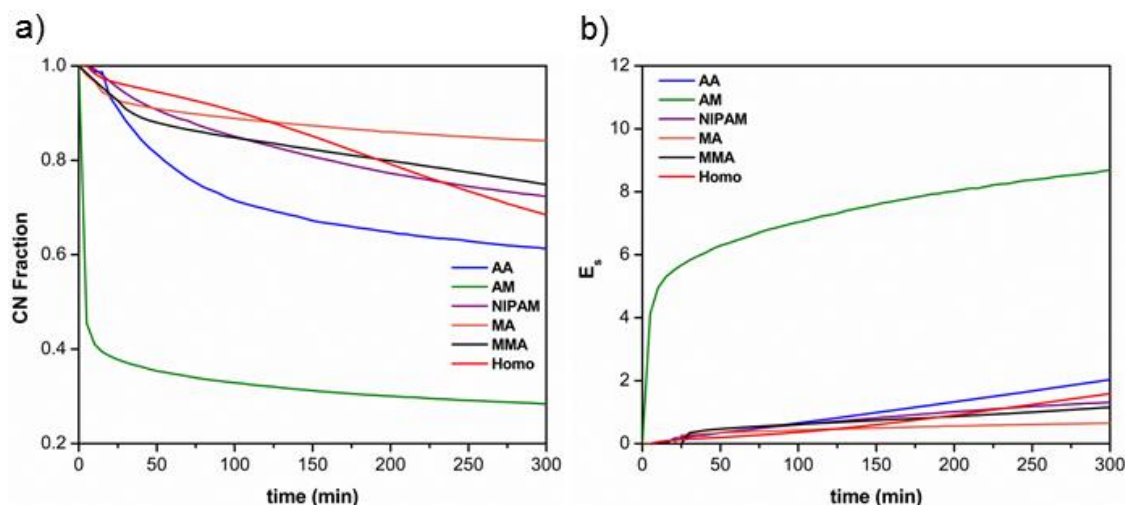


Figure 48. 5 mol% RAFT copolymers heated in FTIR at 225 °C for hours plotted for (a) residual nitrile fraction and (b) extent of stabilization (E_s).

Figures 47 and 48 demonstrate that the AM-containing copolymers achieve the greatest extent of stabilization. Interestingly, the extent of stabilization for all copolymers except for PAN-co-AA is decreased from the 2 to the 5 mol% samples. This suggests that 5 mol% comonomer is above the critical concentration for optimal cyclization behavior. Moreover, 5 mol% copolymers containing MA, MMA, and NIPAM, suppress cyclization as compared to the homopolymer. This can be more clearly seen in Table 15, which lists the final extent of stabilization and residual nitrile fractions of the polymers at the end of the heat treatment. Table 15 shows that the MA-, MMA-, NIPAM- and AA-copolymers end with more than 55% of residual nitriles, while AM-containing copolymers result in less than 30% of nitriles remaining. The conversion of nitriles to rings is critical to reduce the amount of hydrogen cyanide released during stabilization.

Table 15

Final Residual Nitrile Fraction and Extent of Stabilization for RAFT Copolymers Treated at 225 °C for 5 hours in Nitrogen

Polymer	Comonomer Content (%)	Residual CN Fraction (%)	Extent of Stabilization
NIPAM	2	56	2.67
MMA	2	75	2.11
MA	2	62	1.15
AA	2	65	1.83
AM	2	25	10.35
NIPAM	5	72	1.32
MMA	5	76	1.16
MA	5	84	0.65
AA	5	61	2.03
AM	5	28	8.69
Homopolymer	0	68	1.59

As Beltz and coworkers have shown that oxygen can affect cyclization reactions during stabilization,⁴⁵ we studied the cyclization reaction of the 2 mol% AA, AM, and NIPAM copolymers in relation to homopolymer in the presence of dried air and the results are shown in Figure 49. The oxygen atmosphere can promote cyclization, cross-linking, and aromatization reactions, by introducing –OH, C=O, and some N–O groups.⁵⁹ These groups are necessary for dehydrogenation along the polymer backbone by the liberation of water molecules and can also act as initiating centers for cyclization.^{7,43,138} Shown in Figures 49a and 49b, the AM- and AA-copolymers form strong imine bands at 30 min of treatment in oxygen. Contrarily, oxygen can scavenge radicals, which inhibits

free radical cyclization as noted by the delayed imine peak formation (> 2 hr) for the homopolymer (Figure 49d). The residual nitrile fractions and extents of stabilization shown in Figure 50 (solid lines in air and dashed lines in N_2).

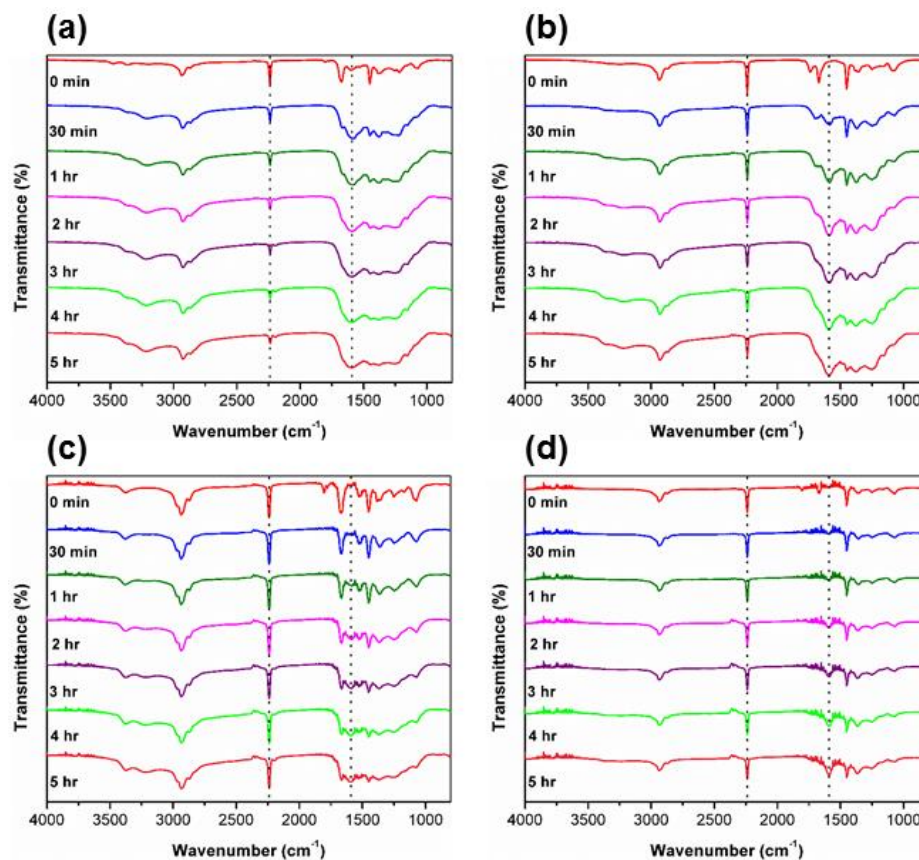


Figure 49. Real-time FTIR spectra recorded in the presence of dried air at 225 C for PAN copolymers with 2 mol% (a) AM, (b) AA, (c), NIPAM, and (d) homopolymer.

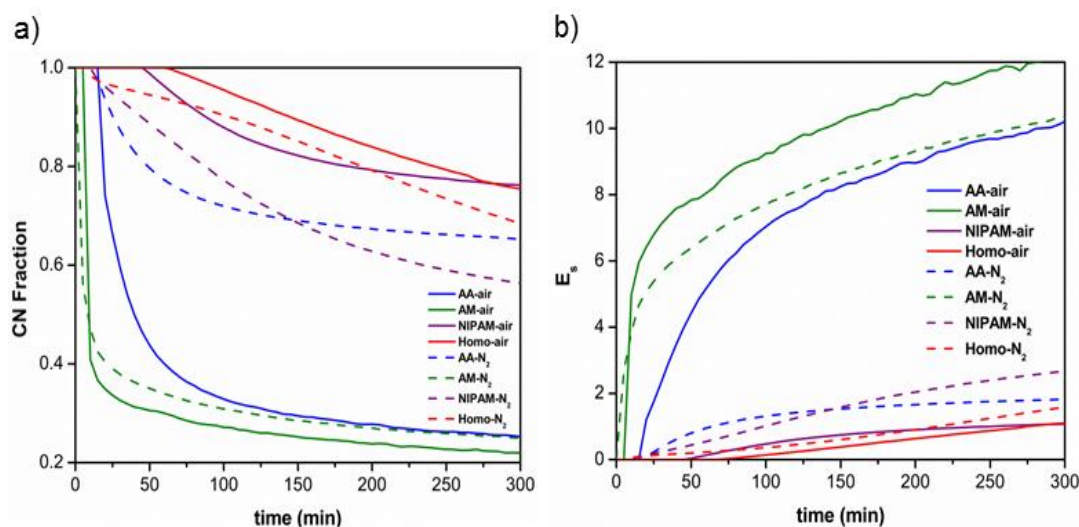


Figure 50. 2 mol% RAFT copolymers treated in air and nitrogen at 225 °C for 5 hr plotted for (a) residual nitrile fraction and (b) extent of stabilization.

Seen in Figure 51, the cyclization of 2 mol% AA copolymer is largely promoted and the 2 mol% AM copolymer is slightly promoted by the presence of oxygen. The 2 mol% AA copolymer samples treated in nitrogen and air are shown in Figure 51. It is clear that oxygen accelerated cyclization by the dark brown color of the air-treated sample over the golden-yellow color of the nitrogen-treated sample.



Figure 51. FTIR salt plates of 2 mol% AA treated at 225 °C in nitrogen (left) and air (right).

On the other hand, the 2 mol% NIPAM copolymer and the homopolymer appear to be inhibited by the presence of oxygen and both exhibit inhibition periods by the presence of delayed onset of cyclization (Figure 50). The nitrile conversion of the 2 mol% NIPAM copolymer sample begins earlier than the homopolymer sample, but the residual nitrile content after 5 hr is nearly equal to that of the homopolymer. This is also noted by the nitrile band in the 2 mol% NIPAM sample (Figure 49c), which is still much stronger than the AM- and AA-copolymers after 5 hr. Eluding to the Introduction, cyclization typically occurs in the amorphous regions before the crystalline regions,^{32,57} which could also be the cause of earlier cyclization in the 2 mol% NIPAM sample compared to homopolymer. Likewise, the bulky NIPAM should permit a greater uptake of oxygen, which reduces the oxidation gradient throughout the polymer sample.

The mass retention of the RAFT copolymers treated at 10 °C/min in nitrogen to 700 °C by TGA are shown in Figure 52. In general, the 2 mol% copolymers have less water bound to the surface as compared to the 5 mol% copolymers evident from the mass loss around 100–150 °C. The onset of degradation c.a. 280 °C follows the DSC and FTIR results by which the polymers that exotherm and form cyclized rings first also begin degradation first. In particular, the NIPAM-containing copolymers yield a steep mass loss between 300–350 °C and the TGA curve is absent of a “bump” c.a. 400 °C, which is present in the rest of the copolymers. To further understand the differences in degradation, TGA equipped with a mass spectrometer will be used in the future. All of the copolymers retain a similar mass ratio (38–44%) at 700 °C.

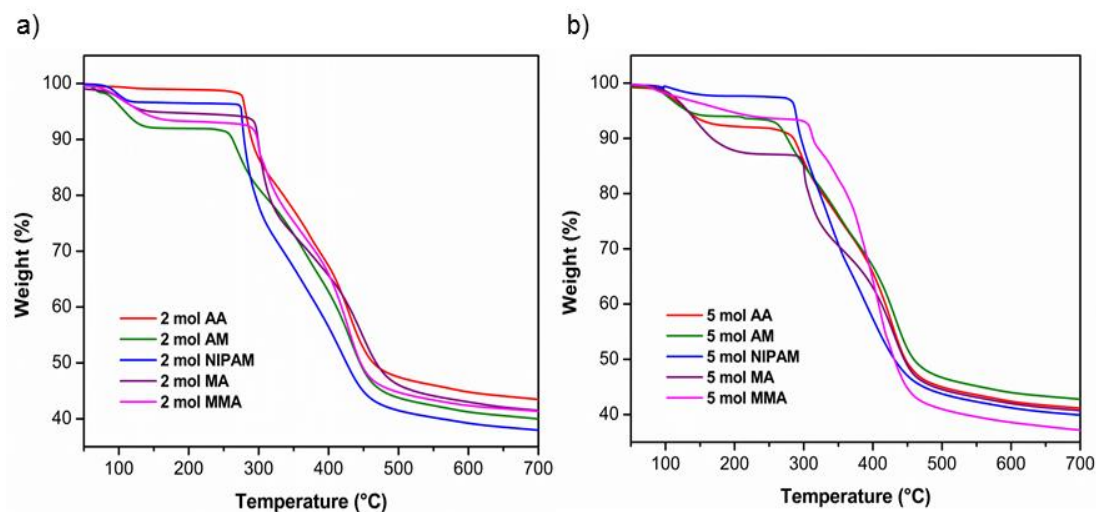


Figure 52. TGA of RAFT (a) 2 mol % and (b) 5 mol% RAFT Copolymers in nitrogen at 10 °C/min.

Thermo-oxidative Stabilization of PAN-based RAFT Copolymers

As discussed previously, the atmosphere plays an important role in the cyclization behavior of the PAN-based precursors. Therefore, the RAFT copolymers were pre-treated in air at 225 °C for 30 min and for 5 hr. The cyclization index (CI) was determined by DSC of the treated samples as shown in Figure 53 for 2 mol% NIPAM. The DSC curves shift to higher temperatures and the exotherm intensities are reduced with long oxidation treatments. The results are summarized in Table 16.

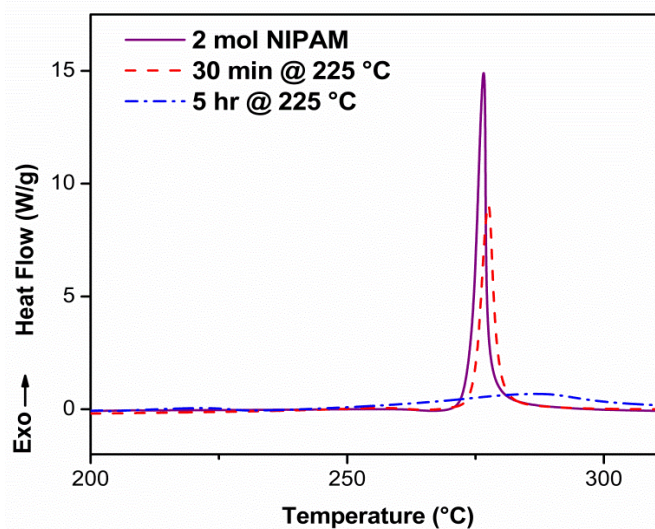


Figure 53. DSC curves for 2 mol% NIPAM RAFT copolymer pre-treated in air at 225 °C for 30 min and for 5 hr.

Table 16

Cyclization Index of RAFT Copolymers Pre-Treated in O₂-rich Atmosphere at 225 °C

Polymer	Comonomer Content (%)	CI (%) after 30 min ^a	CI (%) after 5 hr ^a
NIPAM	2	18	61
MMA	2	6	67
MA	2	8	53
AA	2	27	65
AM	2	28	76
NIPAM	5	8	66
MMA	5	4	54
MA	5	4	44
AA	5	84	93
AM	5	29	88
Homopolymer	0	9	75

^aCI determined by $(I_v - I_o)/I_v \times 100\%$ where the intensity of the virgin sample, I_v , and the intensity of the oxidized sample, I_o , are determined by integrated area under the exotherm.

Table 16 shows that the CI index is greatest for the copolymers containing AA and AM, and in particular the 5 mol% AA sample, which is almost completely cyclized by 30 min of pre-treatment. The samples with MA, MMA, and 5 mol% NIPAM display reduced CI values as compared to homopolymer, which is consistent with the previous data as these comonomers have higher peak cyclization temperatures. Similar to the FTIR results, the 2 mol% NIPAM copolymer appears to assist cyclization initially, but ultimately reaches a lower CI than homopolymer. The heat treated films of 2 mol% AA, AM, and NIPAM copolymers are shown in Figure 54. The 2 mol% AA and AM copolymers are dark brown after 30 min and then black after 5 hours of heat treatment. Meanwhile, the 2 mol% NIPAM takes on a beige color after 30 min and then dark brown after 5 hours of heat treatment.

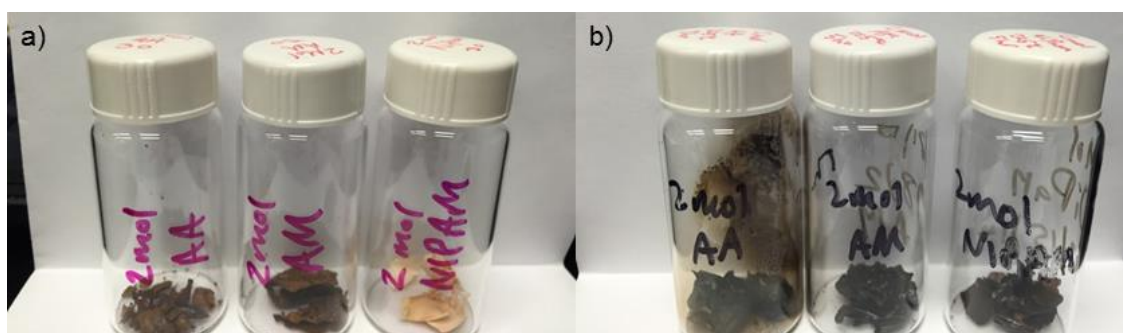


Figure 54. Films of RAFT copolymers pre-treated in oxygen-rich atmosphere at 225 °C for (a) 30 min and for (b) 5 hrs. Left to right: 2 mol% AA, 2 mol% AM, 2 mol% NIPAM.

The pre-treated films were then characterized by Raman Spectroscopy as in Chapter IV by analyzing the ratio of the intensity of the D- and G- bands. The D- and G-bands could not be resolved for the NIPAM, MA, and MMA copolymers after 30 minutes of treatment. Therefore, results for the 5 hours of treatment at 225 °C are presented in Figure 55. The D/G intensity ratio is smallest for the copolymers with AA and AM and then largest for the NIPAM-containing copolymers. Interestingly, the 2 and 5 mol%

copolymers show no statistical difference between the D/G intensity ratios. This means that the crystalline planar size (L_a) is more dependent on comonomer selection rather than comonomer content. Even if there is a greater degree of cyclization between the 2 and 5 mol% samples, the sizes of the graphitic basal planes are the same.

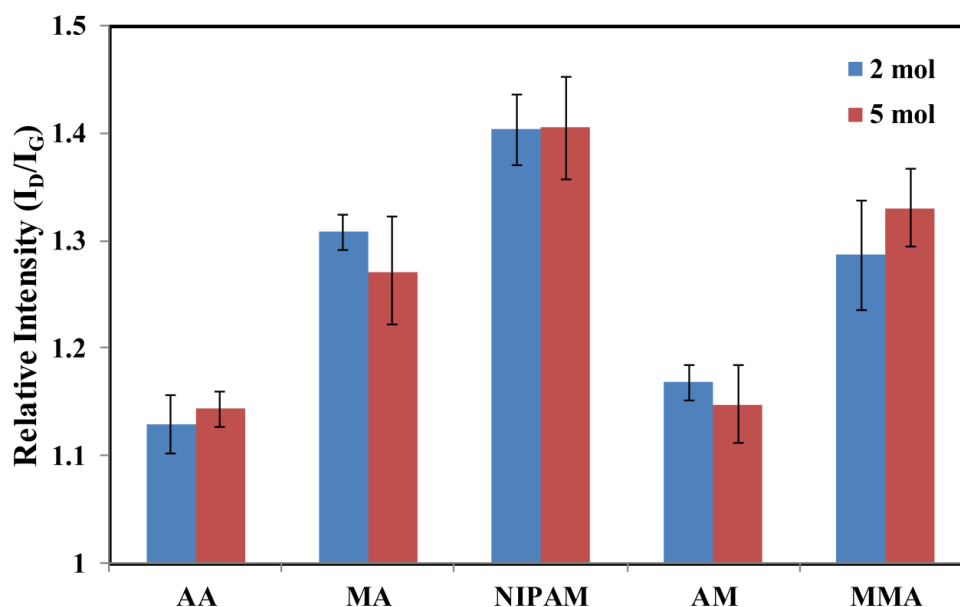


Figure 55. I_D/I_G ratios for RAFT Copolymers treated at 225 °C in air for 5 hours. Error bars represent +/- 1 standard deviation of 5 spots measured via Raman spectroscopy.

The determined D/G intensity ratios and the calculated crystalline planar sizes are summarized in Table 17. Notably, L_a is greater for all of RAFT copolymers at 225 °C for 5 hr than the homopolymer. Even though the copolymers with acrylates had lower CI values than homopolymer, the sizes of the ladder structures are larger. In theory, increased crystalline planar sizes would exhibit improved graphitization degree and increased grain sizes, but it has been shown that increasing the L_a actually correlates to reduced tensile strength in practice.^{139,140} This could be partially related to smaller crystalline planes being easier to draw fibers and process the fibers. To understand this phenomenon, more studies correlating precursor structure to end fiber need to be

performed. Noted in Table 17, the L_a of the NIPAM copolymers is the smallest of the copolymers and most similar to the homopolymer.

Table 17

Summary of I_D/I_G Ratios and L_a Values of RAFT Copolymers

Entry	Comonomer Content (mol%)	30 min at 225 °C in air		5 hr at 225 C in air	
		I_D/I_G	L_a (nm)	I_D/I_G	L_a (nm)
AA	2	1.55	2.84	1.13	3.90
NIPAM	2	-	-	1.40	3.14
AM	2	1.62	2.71	1.17	3.77
MA	2	-	-	1.31	3.36
MMA	2	-	-	1.29	3.42
AA	5	1.31	3.36	1.14	3.85
NIPAM	5	-	-	1.41	3.13
AM	5	1.62	2.71	1.15	3.83
MA	5	-	-	1.27	3.46
MMA	5	-	-	1.33	3.31
Homopolymer	0	1.79	2.46	1.50	2.93

Stabilization of $p(\text{AN-co-AA})$ and $p(\text{AN-co-NIPAM})$: RAFT vs. Free Radical (FR)

Here we explored the differences between 5 mol% NIPAM and AA copolymers prepared by RAFT and FR methods as was done for PAN homopolymer in Chapter IV. The RAFT polymers were synthesized utilizing CPDT as the RAFT agent at 30 °C with $[M]_0:[\text{CPDT}]_0:[\text{V-70}]_0 = 10,000:1:0.67$, while the FR polymers were synthesized at 65 °C with 0.02 mol% AIBN. The selected copolymers were characterized by SEC-MALLS as shown in Figure 56. The RAFT copolymers exhibit much narrower chromatograms as

compared to the FR copolymers, which have low molecular weight tails at longer elution times. The molecular weights and PDIs are reported in Table 18, which confirms that the RAFT polymers have higher molecular weights and lower polydispersities.

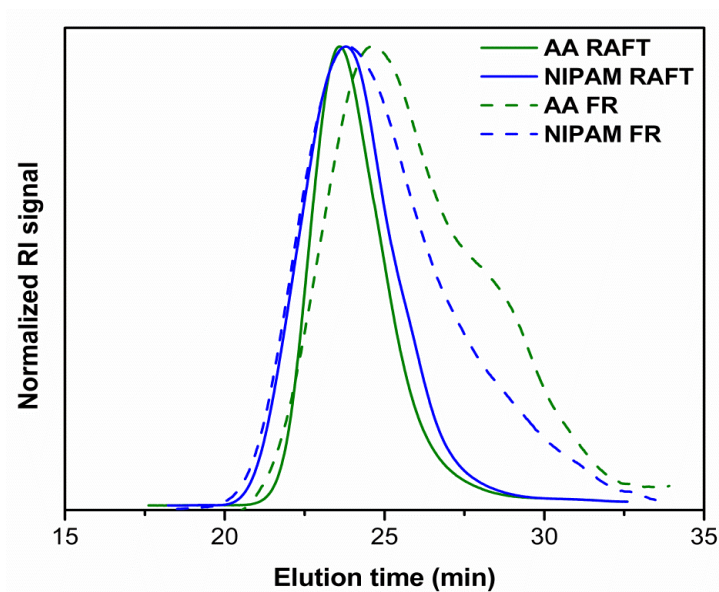


Figure 56. SEC chromatograms of 5 mol% RAFT and FR copolymers (AA and NIPAM).

Table 18

Molecular Weight and PDI of 5 mol% RAFT and FR Copolymers (AA and NIPAM)

Polymer ^a	M_n (SEC-MALLS) ^c	Conversion (%) ^b	PDI ^c
5 mol% AA	197 500	78	1.23
5 mol%	154 700	64	1.40
5 mol% AA FR	89 500	-	1.73
5 mol%	78 900	-	2.10

^aRAFT copolymers synthesized in ethylene carbonate at 20 wt.% monomer concentration under a nitrogen atmosphere at 30 °C and V-70 as the initiator for 48 h and FR copolymers synthesized at 65 °C with 0.02 mol% AIBN as the initiator for 8 h. ^bConversions were determined by ¹H-NMR spectroscopy recorded in DMSO-*d*₆. ^cNumber average molecular weight (M_n) as determined by SEC (0.5 mL/min, 60 °C, Polymer Labs PL gel 5 μ m mixed-C column, DMF with 0.02 M LiBr eluent) equipped with RI and MALLS detectors.

The PAN-based copolymers characterized by DSC are shown in Figure 57. Consistent with FR homopolymers, the onset of the exotherm occurs at a lower temperature for the FR copolymers. The FR copolymers should have more chain ends and more defects for initiation of cyclization to occur as compared to the RAFT copolymers. Additionally, the cyclization exotherms of the RAFT copolymers are narrower with greater max heat flows, which was shown in the case of homopolymers. The exotherm properties are summarized in Table 19. Unique from the homopolymers, the RAFT copolymers display much greater intensities and higher activation energies than the analogous FR copolymers. The increased intensity could be related to a higher extent of reaction, which would suggest a more complete ladder structure.

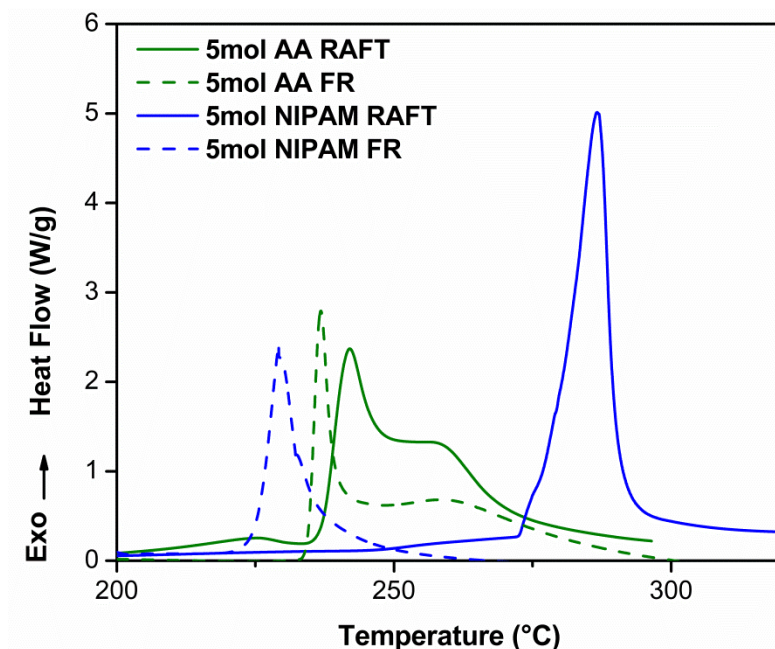


Figure 57. DSC curves of 5 mol% RAFT and FR copolymers at 5 °C/min (AA and NIPAM).

Table 19

Activation Energy and DSC Exotherm Behavior of 5 mol% RAFT and FR Copolymers (AA and NIPAM)

Polymer	Ozawa Method		Kissinger Method		$T_p(^{\circ}\text{C})$	T_p Breadth ($^{\circ}\text{C}$)	Intensity (J/g)	Max Heat Flow (W/g)
	E_a (kJ/mol)	A (s^{-1})	E_a (kJ/mol)	A (s^{-1})				
NIPAM_RAFT	106.1	2.7×10^7	102.1	1.1×10^7	287	18	475	4.8
AA_RAFT*	110.9	7.5×10^8	108.2	3.9×10^8	241	35	461	2.5
NIPAM_FR	54.5	9.8×10^2	48.6	2.1×10^2	230	24	320	1.7
AA_FR*	92.4	1.2×10^7	88.5	4.7×10^6	233	52	251	2.3

*Only the peak maximum considered and not the shoulder peak.

The differences in mass retention through pyrolysis were characterized by TGA as shown in Figure 58. The RAFT copolymers show a higher stability to degradation up to about 280 $^{\circ}\text{C}$, likely because there are fewer low molecular weight impurities (Figure 58a). Furthermore, the RAFT copolymers yield a higher mass retention at 600 $^{\circ}\text{C}$. Unlike the RAFT homopolymers, which have extreme heat flows and rapid mass loss, the RAFT copolymers exhibit more gradual mass loss due to the alternative pathway for cyclization. Thus, the greater mass retention of the RAFT copolymers post pyrolysis supports the idea that RAFT copolymers lead to a greater extent of ladder structure formation as compared to FR copolymers. More intriguingly, Figure 58b shows that mass loss between the RAFT and FR copolymers is even more accentuated when the copolymers are pre-oxidized. Between 350–400 $^{\circ}\text{C}$ (post cyclization), the FR copolymers lose about 10–20% more mass than the RAFT copolymers.

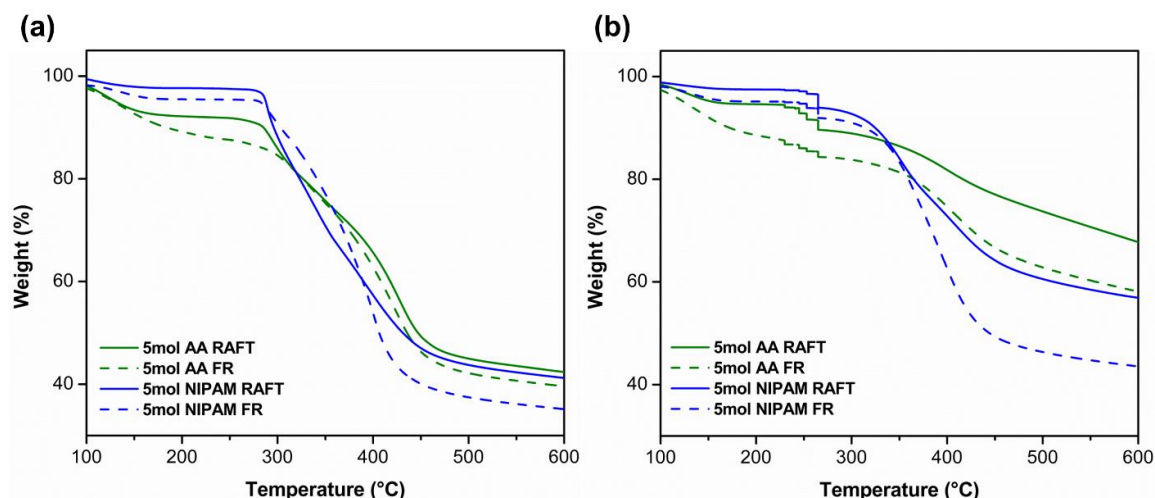


Figure 58. TGA plots of 5 mol% RAFT and FR copolymers (AA and NIPAM) (a) ramped at 10 °C/min to 700 °C in N₂ and (b) ramped at 10 °C/min in air and held at isotherms of 230, 245, 253, and 265 °C for 15 min each and then ramped at 10 °C/min to 700 °C in N₂.

These findings led us to further investigate the copolymers containing NIPAM by adding a second pre-oxidation treatment (Pre-ox 2, Chapter II) as shown in Figure 59.

Pre-ox 2 was selected with a higher temperatures because of the higher cyclization temperatures of NIPAM-containing copolymers. The results show that the 2 mol% NIPAM RAFT copolymer yields the greatest stability after pre-oxidation treatment, which confirms that the 2 mol% NIPAM copolymer reaches a greater extent of cyclization. As expected, Pre-ox 2 yields a better residual mass content as compared to the Pre-ox 1 treatment, with further optimization left for future study. Impressively, the 2 mol% copolymer yields about 70% residual mass post stabilization to 600 °C.

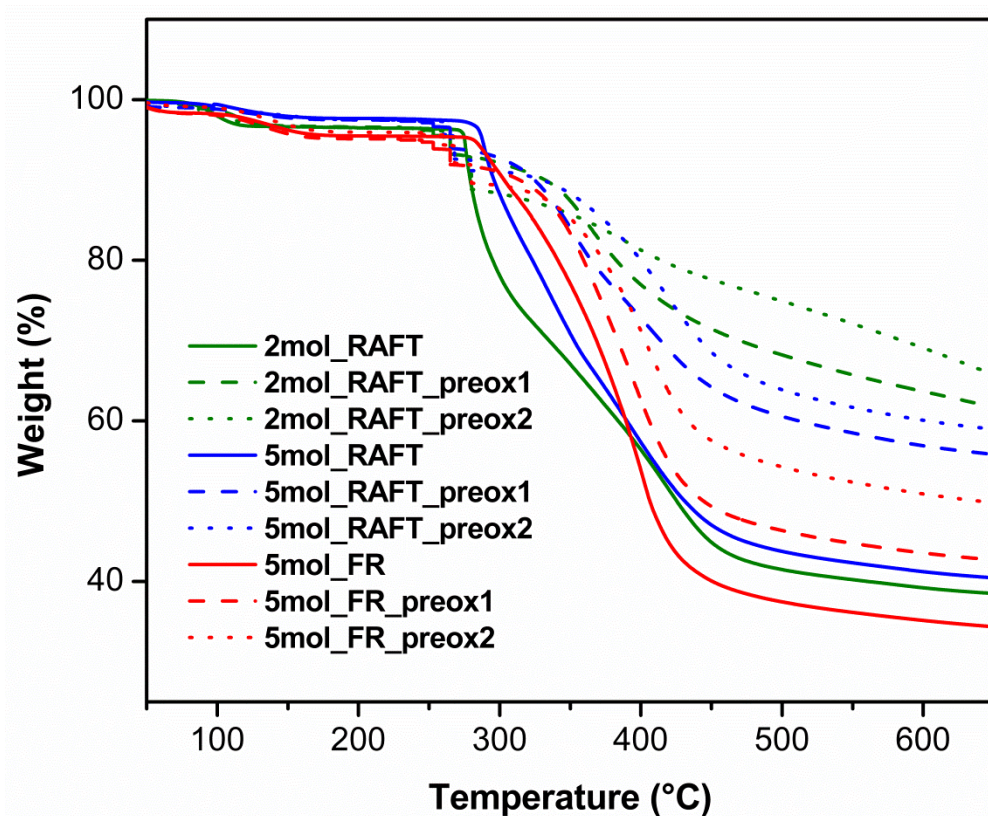


Figure 59. TGA plots of NIPAM-containing copolymers ramped at 10 °C/min to 700 °C in N₂, Preox1: ramped at 10 °C/min in air and held at isotherms of 230, 245, 253, and 265 °C for 15 min each and then ramped at 10 °C/min to 700 °C in N₂, and Preox2: ramped at 10 °C/min in air and held at isotherms of 245, 260, 268, and 280 °C for 15 min each and then ramped at 10 °C/min to 700 °C in N₂.

Summary

NIPAM-containing copolymers posed several interesting characteristics including: (1) monomodal DSC exotherms with reduced heat flow, (2) lower crystallinity and smaller crystalline planar size compared to p(AN-co-AA), (3) as well as impressive thermo-oxidative stability. The use of a single comonomer, such as NIPAM, that provides both processability as well as an aid to the cyclization process would benefit carbon fiber properties substantially over the use of a conventional terpolymer system. Furthermore, the route used to synthesize the RAFT copolymers led to unprecedented

molecular weights above 160,000 g/mol (SEC-MALLS) with polydispersities (M_w/M_n) < 1.35. It was shown that these RAFT copolymers, with greater cyclization intensities than the FR counterparts, led to a greater extent of cyclization by an increased mass yield post thermo-oxidative stabilization and fewer small volatile byproducts.

CHAPTER VI

SEMI-BATCH RAFT POLYMERIZATION OF POLY(ACRYLONITRILE-CO-N-ISOPROPYLACRYLAMIDE) AND ITS STABILIZATION BEHAVIOR

Abstract

Utilizing reversible addition-fragmentation chain transfer (RAFT) polymerization, the composition profile of PAN-based copolymers becomes a tunable parameter in preparing carbon fiber precursors. In this work, poly(acrylonitrile-co-N-isopropylacrylamide) copolymers were prepared via a semi-batch process mediated by 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT). The monomer reactivity ratios were determined by the Fineman-Ross (FR), Kelen-Tüdös (KT), and non-linear least squares (NLLS) models. The number average sequence length of acrylonitrile (AN) was found to be highly dependent on the comonomer content. NIPAM was introduced at a controlled rate into a reaction vessel in attempts to facilitate comonomer distribution. These semibatch copolymers were evaluated based on their ring-closing cyclization behavior, which was characterized by differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). Significantly, DSC exotherms were reduced and cyclization occurred much faster reaching a greater thermal stability when NIPAM was introduced at slow feed rates.

Results and Discussion

Copolymer Reactivity Ratios

Copolymers of acrylonitrile (AN) and n-isopropylacrylamide (NIPAM) were prepared utilizing 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) in ethylene carbonate at 30 °C, with $[AN+NIPAM]_0:[CTA]_0:[I]_0 = 10,000:1:0.67$ and $[AN+NIPAM]_0$

= 20 wt.%. The concentrations of NIPAM and AN were varied to determine the reactivity ratios by three methods: the Fineman-Ross (FR),¹²⁵ the Kelen-Tüdös (KT),¹⁴¹ and the non-linear least squares (NLLS)¹⁴² methods. The Mayo-Lewis equation, or the instantaneous copolymerization equation,¹²⁵ is given in Equation 20:

$$F_1 = G(f_1, r_1, r_2) = \frac{r_1 f_1^2 + f_1(1 - f_1)}{r_1 f_1^2 + 2 f_1(1 - f_1) + r_2(1 - f_1)^2} \quad (20)$$

where F_1 is the mole fraction of monomer 1 in the final copolymer, f_1 is the mole fraction of monomer 1 in the feed, and r_1 and r_2 are the reactivity ratios of monomers 1 and 2, respectively. The reactivity ratios are defined as:

$$r_1 = \frac{k_{11}}{k_{12}}, \quad r_2 = \frac{k_{22}}{k_{21}} \quad (21)$$

in which k_{11} , k_{12} , k_{22} , and k_{21} , are the rate constants for a monomer y to add to a chain with terminal monomer x , k_{xy} . The classical FR method is expressed as follows:

$$G = r_1 H - r_2 \quad (22)$$

where G and H are defined as:

$$G = X(Y - 1)/Y, \quad H = X^2/Y \quad (23)$$

in which X and Y are the molar fraction ratios in the feed and in the final copolymer, respectively:

$$X = f_1 / f_2, \quad Y = F_1 / F_2 \quad (24)$$

The plot of G versus H gives a straight line with the slope as r_1 and the intercept of the y -axis as r_2 .

The KT model defines new parameters to approximate a linear relationship from the Mayo-Lewis equation as follows:

$$\eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_2}{\alpha} \quad (25)$$

where η and ξ are represented by:

$$\eta = G/(\alpha + H), \quad \xi = H/(\alpha + H) \quad (26)$$

and α is a constant defined as:

$$\alpha = (H_m \bullet H_M)^{-1/2} \quad (27)$$

in which H_m and H_M are the lowest and highest values calculated for H from the series of measurements. The plot of η versus ξ gives a straight line with extrapolation to $\xi = 1$ as r_1 and to 0 gives r_2/α .

The NLLS method is the most accurate method, which fits Eqn. 28 to the composition data seeking to minimize the difference between the fitting function and the real data by iteratively changing the fitting parameters to find the global minimum in the weighted sum of squares error defined by:¹⁴²

$$SSE(r_1, r_2) = \sum_{i=1}^n \left(\frac{F_{1i} - G(f_{1i}, r_1, r_2)}{\sigma} \right)^2 \quad (28)$$

where n is the number of data points and σ is the standard deviation of the error distribution in the measured value of F_1 .

The copolymer compositions were determined by ^1H -NMR as shown for a 5 mol% NIPAM copolymer in Figure 60.

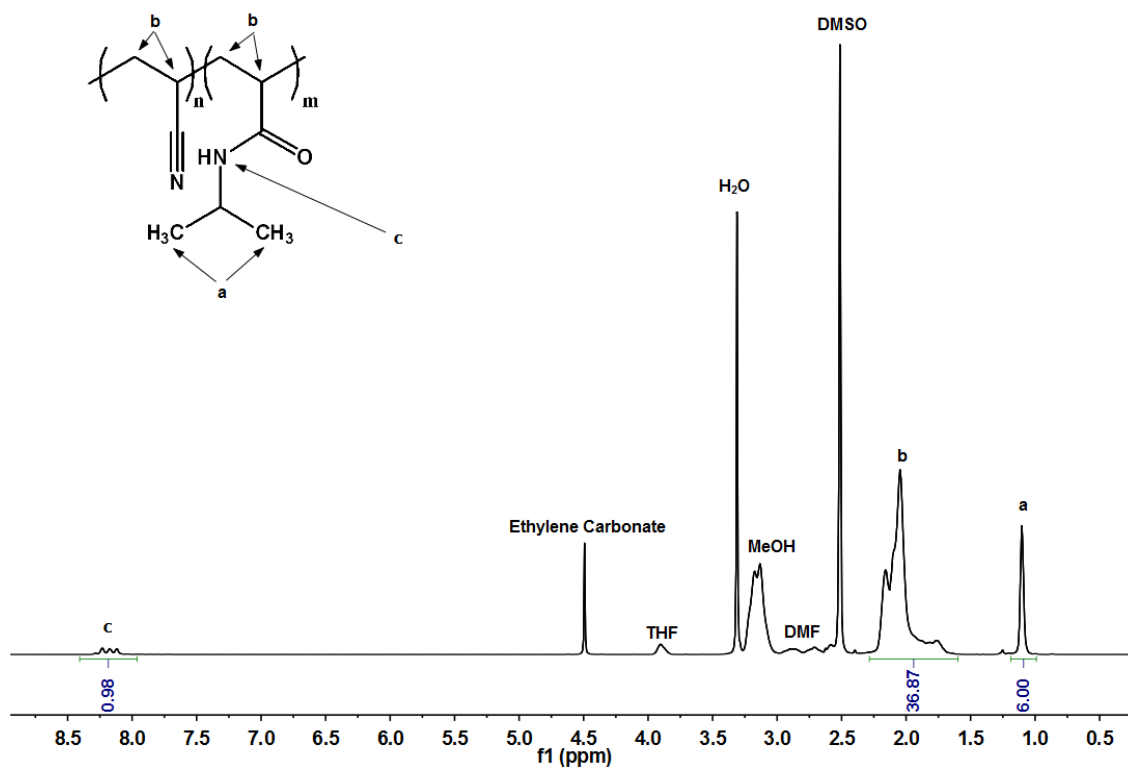


Figure 60. ^1H -NMR of 95/5 p(AN-co-NIPAM).

The polymer peaks (Figure 60, 'b') c.a. 2 ppm, corresponding to backbone protons, were integrated and normalized to the methyl groups on the NIPAM monomer (Figure 60, 'a') c.a. 1.1 ppm. The composition of the 5 mol% NIPAM copolymer was then determined as follows:

$$a = 6m = 6.00, \quad b = 3n + 3m = 36.87 \quad (29)$$

where m is the normalized number of NIPAM units per a chain and n is the normalized number of acrylonitrile units per a chain. Solving for m and n , the mole fraction of AN in the copolymer, F_{AN} , is given:

$$F_{\text{AN}} = \frac{n}{n + m} \times 100\% \quad (30)$$

The monomer mole fractions in the feed and in the final copolymer composition under low conversion are reported in Table 20. Copolymer conversion was experimentally limited by quenching the reaction in liquid nitrogen after 2 hours ($\approx 10\%$ conversion) in order to prevent compositional drift associated with depletion of the more reactive monomer with increasing conversion.¹⁴³ Polymers were then purified by precipitation into water (repeated twice) before being collected by filtration.

Table 20

Comonomer Mole Fractions in the Feed and the Final Copolymer for AN and NIPAM

f_{AN}	f_{NIPAM}	F_{AN}	F_{NIPAM}
0.98	0.02	0.932	0.068
0.95	0.05	0.880	0.120
0.85	0.15	0.769	0.231
0.65	0.35	0.566	0.434
0.45	0.55	0.347	0.653
0.25	0.75	0.311	0.689

The reactivity ratios were then determined by the FR and KT methods as shown in Figure 61. These results along with those determined by the NLLS method are compiled in Table 21. The reactivity ratios calculated by these three methods are in good agreement and the reactivity ratio of NIPAM is larger than that of AN, indicating that NIPAM possesses higher reactivity than AN. The correlation coefficients (r^2 values) are all very close to 1, which suggests the fits correlate well with the experimental results. However, both reactivity ratios are less than 1, which suggests that both monomers favor

cross-propagation leading to an alternating copolymer. Therefore, it is expected that the NIPAM content will be richer in the copolymer than in the feed for polymers with 2–5 mol% NIPAM. The composition profiles predicted by the three methods are shown in Figure 62.

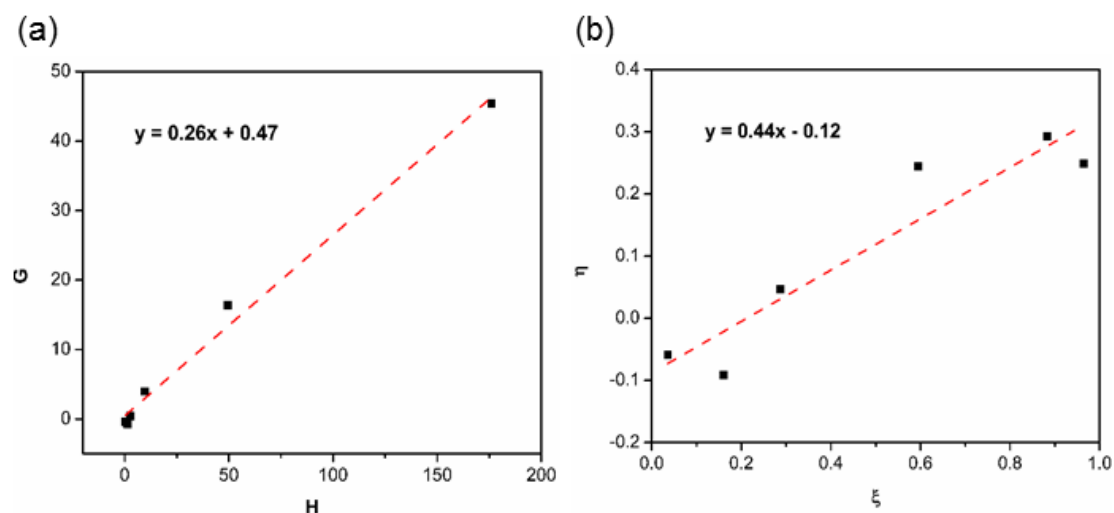


Figure 61. Reactivity ratios determined by the (a) Fineman-Ross and (b) Kelen-Tüdös methods.

Table 21

Reactivity Ratios for AN and NIPAM

Method	r_{AN}	r_{NIPAM}	r^2
NLLS	0.39	0.72	0.951
FR	0.26	0.47	0.947
KT	0.32	0.78	0.963

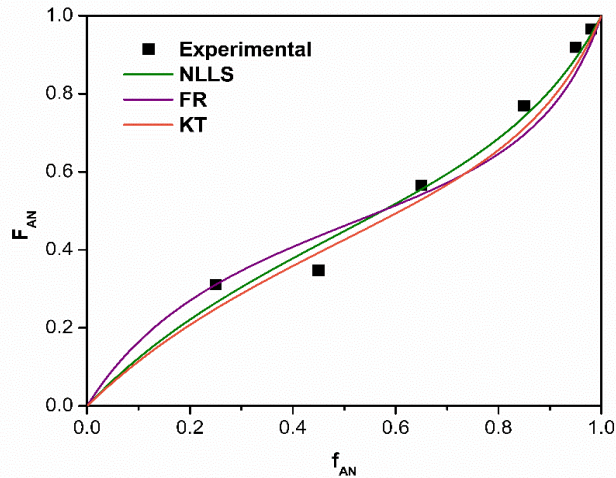


Figure 62. Composition profiles based on model predictions and experimental data for p(AN-co-NIPAM) copolymers.

Statistical Analysis

The reactivity ratios determined by NLLS were employed for the following statistical analysis. Assuming the Alfrey-Mayo model (1st order Markov model) to be valid for these low conversion copolymers the number fraction of acrylonitrile (A) and n-isopropylacrylamide (N) triads can be predicted by the following set of equations:¹⁴⁴

$$\begin{aligned}
 F_{AAA} &= [1 - p(N/A)]^2 \\
 F_{AAN} &= F_{NAA} = 2p(N/A)[1 - p(N/A)] \\
 F_{ANA} &= p(N/A)^2 \\
 F_{NNN} &= [1 - p(A/N)]^2 \\
 F_{NNA} &= F_{ANN} = 2p(A/N)[1 - p(A/N)] \\
 F_{NAN} &= p(A/N)^2
 \end{aligned} \tag{31}$$

where $p(N/A) = 1/(1+r_{AN}/q)$, $p(A/N) = 1/(1+r_{NIPAM}q)$ and $q = f_{NIPAM}/f_{AN}$ is the instantaneous feed ratio. F represents the number fraction of triads normalized to unity, and $p(M_1/M_2)$ represents the probability of a growing chain, having M_2 as the chain end to add to monomer M_1 . Varying the feed ratio, the weighted triad sequences are plotted in Figure 63.

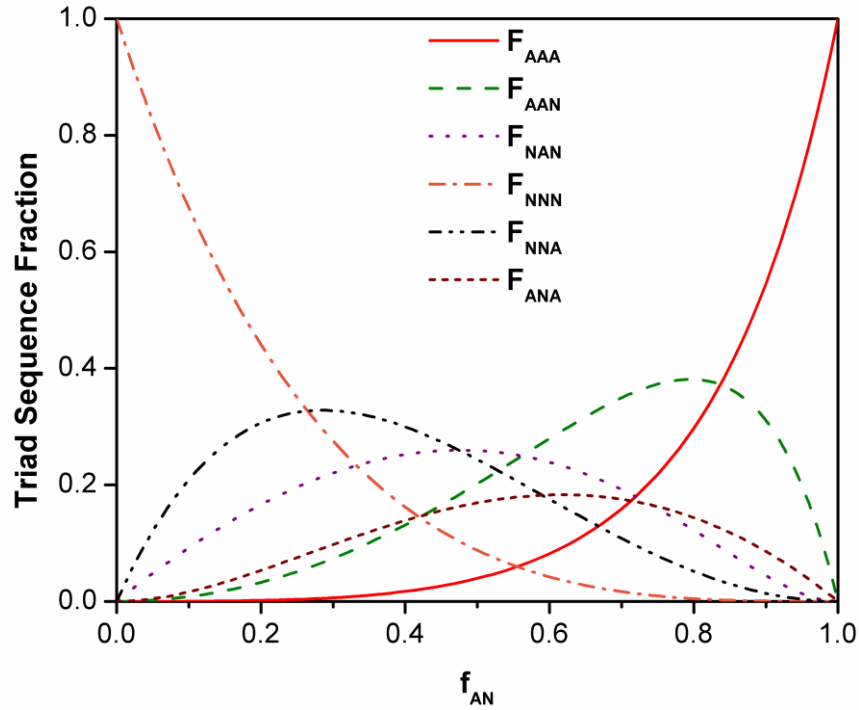


Figure 63. Number fraction of triad sequences for p(AN-co-NIPAM) copolymer.

Let p_{AA} be the probability that chain terminus AN adds to an AN monomer:

$$p_{AA} = \frac{r_{AN} f_{AN}}{f_{AN} (r_{AN} - 1) + 1} \quad (32)$$

Then, the instantaneous number-average sequence length of acrylonitrile, $\langle N_A \rangle_n$, is expressed as:¹⁴⁵

$$\langle N_A \rangle_n = \frac{1}{1 - p_{AA}} \quad (33)$$

Specifically, we consider the 95/5 and 98/2 AN/NIPAM copolymers, which are common molar ratios for PAN-based carbon fiber precursors. The triad sequences and number-average sequence lengths for these two copolymers are reported in Tables 22 and 23, respectively.

Table 22

Triad Sequences for 98/2 and 95/5 p(AN-co-NIPAM) Copolymers

Triad Sequence	98/2 p(AN-co-	95/5 p(AN-co-
F_{AAA}	88.50	73.75
F_{AAN}	9.26	19.91
F_{NAN}	0.24	1.34
F_{NNN}	0.00	0.01
F_{NNA}	0.06	0.35
F_{ANA}	1.94	4.64

Table 23

Number-Average Sequence Lengths for 98/2 and 95/5 p(AN-co-NIPAM) Copolymers

Number Avg. Seq.	98/2 p(AN-co-	95/5 p(AN-co-
AN	20.11	8.41
NIPAM	1.01	1.04

Considering the cyclization of PAN, the longest consecutive pyridine sequence lengths are capped at about 5–7 adjacent rings.⁴⁷ Therefore, a high fraction of F_{AAA} triads correlate to long AN sequences in the backbone which are unnecessary and could potentially lead to unrestrained heat release during free radical initiated cyclization. Seen in Table 22, F_{AAA} increases by about 15% from the 5 to 2 mol% NIPAM copolymer. On the other hand, the concern with the 5 mol% NIPAM copolymer is that triads containing two NIPAM units would disrupt the cyclic sequences and act as disclinations in the

ladder structure. The F_{NAN} sequence is still greater than 1% of the triads in the copolymer at $f_{\text{AN}}=0.95$. Triads which contain two NIPAM units ($F_{\text{NAN}}, F_{\text{NNA}}$) decrease by about 3–7 times from the 5 mol% copolymer to the 2 mol% copolymer. Also noted, is that the instantaneous number-average sequence length of AN more than doubles from the 5 mol% copolymer to the 2 mol% copolymer (Table 23).

The current issue is that 2 mol% NIPAM copolymers tend to form long sequences of AN, which should result in narrower cyclization exotherms and poorer solubility. However, introducing a greater content of NIPAM (5 mol%) leads to increased disclinations in the backbone and a lower extent of stabilization, or ladder structure formation. In a conventional batch reaction with a low NIPAM content, NIPAM is consumed much faster than AN due to the higher reactivity and leads to compositional drift at high conversions. This presents a gradient in the copolymer backbone as shown in Figure 64a. In theory, ideal PAN-based precursors would have both (1) a low content of triad sequences with multiple comonomer units and (2) a uniform distribution of comonomer along the chain to break up long AN sequences as shown in Figure 64b.

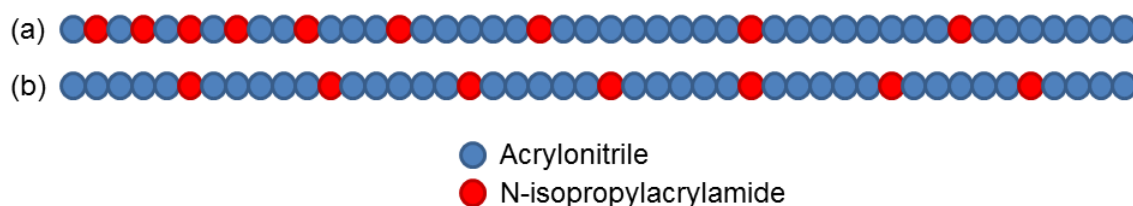


Figure 64. Copolymer sequence of alternating PAN-based copolymers with (a) compositional drift and (b) uniform distribution of comonomer.

Semibatch reactions

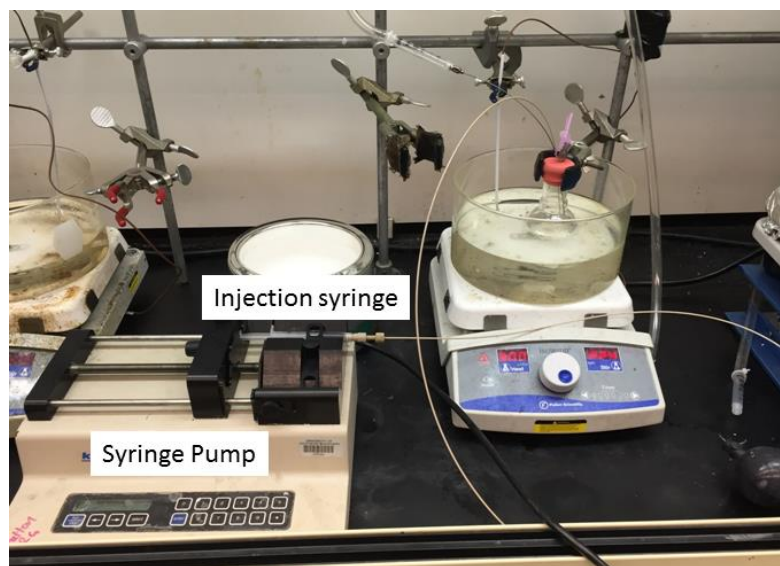


Figure 65. Semibatch reaction setup.

Herein, we investigate whether starving the reaction of the more reactive NIPAM results in a more uniform distribution along the copolymer backbone as evidenced by changes in the cyclization behavior. Semibatch reactions were prepared as shown in Figure 65. Following the same procedure as the batch reactions at 30 °C, V-70 (0.010 mmol, 3 mg), CPDT (0.015 mmol, 51 mg), and a predetermined concentration of each monomer (20 wt. % solution) were added to a 100 mL round bottom flask. The reaction vessel was purged with nitrogen for 1 hour at 0 °C and then transferred to an oil bath at 30 °C and continued purging throughout the duration of the reaction. Utilizing a syringe pump, a 20 wt. % solution of NIPAM dissolved in a mixture of 50/50 (w:w) of ethylene carbonate and DMF was injected at a predetermined rate into the reaction vessel. The apparent “ t_0 ” concentration is defined as the initial concentration of NIPAM in the reaction vessel, and “ t_f ” is the final concentration after the syringe pump has completed the injection. A total of three semibatch reactions (SB) and a control “Batch”

copolymerization were prepared and are summarized in Table 24. The batch copolymerization was quenched after 8 h of reaction to give comparable molecular weights to the SB copolymers. The final compositions of the copolymers were determined via $^1\text{H-NMR}$.

Table 24

Semibatch Reaction Parameters.

Entry ^a	t_0 (mol%) ^b	t_f (mol%) ^c	Injection Volume (mL)	Injection Rate (mL/hr)	Duration of Injection	F_{AN} (%) ^d	F_{NIPAM} (%) ^d
SB-1	0	2	1.4	0.058	24	97.2	2.8
SB-2	0	2	1.4	0.029	48	97.5	2.5
SB-3	0	4	2.8	0.058	48	93.6	6.4
Batch ^e	2	2	-	-	-	96.3	3.7

^aSemibatch copolymers of AN and NIPAM were prepared utilizing 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) in ethylene carbonate at 30 °C, with $[\text{AN+NIPAM}]_0:[\text{CTA}]_0:[\text{I}]_0 = 10,000:1:0.67$ and $[\text{AN+NIPAM}]_0 = 20$ wt.% for 48 h. ^bThe initial amount of NIPAM charged to the reaction vessel. ^cThe amount of NIPAM in the reaction vessel post injection. ^dThe final copolymer composition determined by $^1\text{H-NMR}$. ^eBatch copolymerization was quenched at 8 h to give similar molecular weight to semibatch copolymerizations.

We have previously shown that copolymerizations of p(AN-co-NIPAM) maintain pseudo-first-order kinetics for reaction times up to 48 h and, therefore, we initially we elected to use injection durations of 24 and 48 h to obtain varying degrees of comonomer distribution (SB-1 and SB-2). Expectedly, a slower injection rate and longer injection duration of NIPAM leads to a lower percentage of NIPAM in the copolymer composition with SB-2 having a lower NIPAM concentration than SB-1. Furthermore, the batch copolymerization has an even greater composition of NIPAM than SB-1 or SB-2 due to

the higher initial amount in the reaction. Upon these observations, SB-3 was amended to the study in order to increase the concentration of NIPAM in the copolymer composition. The number average molecular weights (SEC-MALLS) and polydispersities (PDIs) are reported in Table 25.

Table 25

Molecular Weight and Polydispersity of Semibatch Copolymers

Entry ^a	M _n (g/mol) ^b	PDI ^b
SB-1	66,500	1.10
SB-2	57,200	1.19
SB-3	50,800	1.17
Batch	68,100	1.18

^aPolymers synthesized in ethylene carbonate at 20 wt.% monomer concentration under a nitrogen atmosphere with V-70 as the initiator.

^bNumber average molecular weight (M_n) as determined by SEC (0.5 mL/min, 60 °C, Polymer Labs PL gel 5 µm mixed-C column, DMF with 0.02 M LiBr eluent) equipped with RI and MALLS detectors.

As seen in Table 25, SB-1 has the greatest molecular weight and SB-3 has the lowest molecular weight of the SB copolymers. Because the rate of polymerization is proportional to monomer concentration, [M], it is expected that molecular weights decrease with greater concentrations in the syringe pump and with slower feed rates. Another possibility for the reduced molecular weights is that the reactions are purged with nitrogen throughout the duration of the reaction, which could lower the internal temperature of the reaction vessel. The batch copolymerization was prepared with similar molecular weight to the SB copolymers to mitigate molecular weight effects. Noted in Table 25, all of the molecular weight distributions are narrow, which highlights the controlled behavior of the RAFT copolymerization.

Stabilization Behavior of Semibatch Copolymers

To evaluate the semibatch reactions, the efficacy of cyclization was investigated via DSC, FTIR, and TGA. The results of the DSC exotherms at 5 °C/min are shown in Figure 66. Most significantly, the semibatch copolymers have broader and reduced exotherms as compared to the batch copolymer. SB-1 behaves most similar to the batch copolymer perhaps due to the closest composition and the shorter feed duration. SB-3 also yields a decreased exotherm temperature and an even broader peak. Of particular interest is SB-2, which contains the lowest concentration of NIPAM, displays a bimodal DSC exotherm. Bimodal DSC exotherms are common for acidic copolymers wherein the ionic cyclization pathway occurs at a lower temperature and then at a higher temperature the free radical pathway is activated similar to PAN homopolymer.²⁵ While the batch copolymer initiates cyclization above 260 °C, all three of the SB copolymers initiate cyclization below 245 °C, despite the final composition of NIPAM in the copolymer. This result importantly suggests that cyclization temperature can be manipulated by controlling the feed rate of NIPAM. We presume that controlling the feed of NIPAM allows for a greater distribution of the comonomer throughout the copolymer, thereby promoting a greater extent of ionic cyclization and lowering the exotherm temperature. The properties of the exotherms at 5 °C/min are summarized in Table 26.

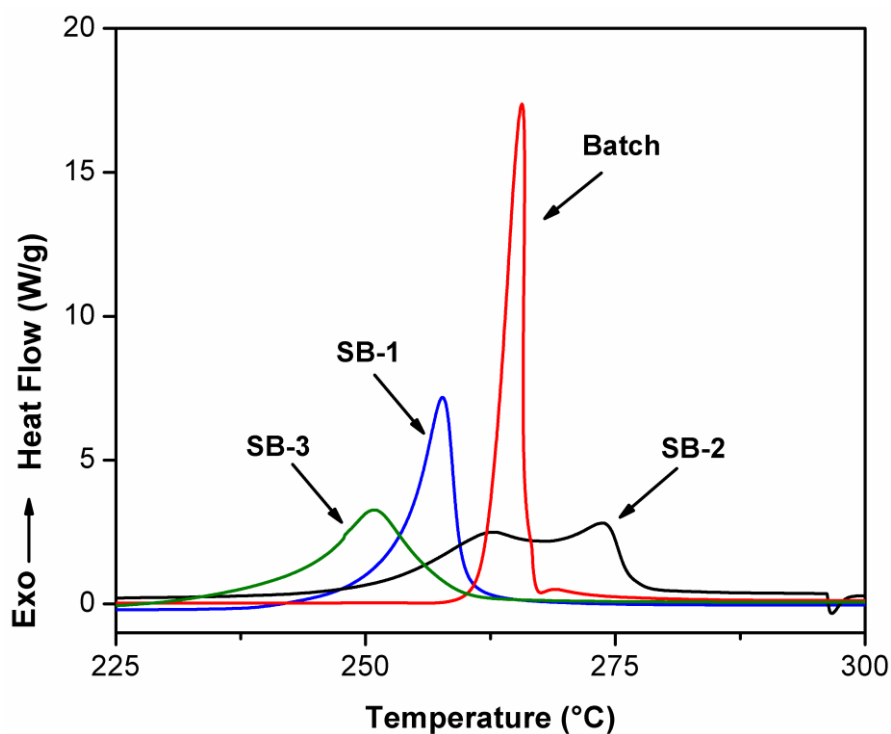


Figure 66. DSC exotherms of semibatch copolymers at a 5 °C/min ramp rate.

Table 26

Peak Exotherm Behavior at 5 °C/min for Semibatch Copolymer.

Entry	5 °C/min			
	T_p (°C) ^a	T_p Breadth (°C) ^b	Intensity (J/g) ^c	Heat Flow (W/g) ^d
SB-1	258	16	528	7.2
SB-2 ^e	262, 274	29	537	2.5, 2.8
SB-3	251	32	482	3.3
Batch	266	7	487	17.4

^aPeak temperature determined as the temperature for maximum heat flow. ^bThe breadth determined as the difference of the onset and offset of the peak. ^cThe intensity is taken as the area under the curve. ^dThe maximum heat flow at the given peak temperature. ^eSB-2 displays bimodal peaks, breadth and intensity given as the sum of both peaks.

Table 26 clearly demonstrates the differences in peak breadth of the SB copolymers in comparison to the batch copolymer. All of the peak intensities, which indicate the overall heat of reaction, are nearly equal suggesting a similar extent of reaction. Most critically, the amount of heat that is emitted at the peak exotherm temperature is decreased from 17.4 W/g to below 7.2 W/g from the batch copolymer to the SB copolymers. Limiting the amount of centralized heat release is important to prevent premature chain degradation when processing of PAN-based copolymers into carbon fiber.

The semibatch copolymers were treated at 225 °C for 5 hr in nitrogen using a heating cell and studied real-time via FTIR as shown in Figure 67. The residual nitrile fractions and extents of stabilization, E_s , are shown in Figures 68 and 69, respectively. In agreement with the DSC results, SB copolymers have a faster rate of cyclization at 225 °C. In particular, SB-3 with the lowest peak exotherm temperature demonstrates the fastest rate of cyclization at 225 °C, noted by the prominence of the imine peaks (c.a. 1590 cm^{-1}) (Figure 67c). Also, recalling from Chapter V, the residual nitrile fractions of the batch copolymers containing acrylic acid were greater than 60%; SB-3 impressively displays a residual nitrile fraction below 40% after 5 hr of heating at 225 °C (Figure 68). Furthermore, SB-1 and SB-2 exhibit similar behavior to the batch copolymer up to about 75 min while E_s increases linearly (Figure 69). After 75 min the batch copolymer exhibits a kink in the curve as though the cyclization has been exhausted while SB-1 and SB-2 continue to increase.

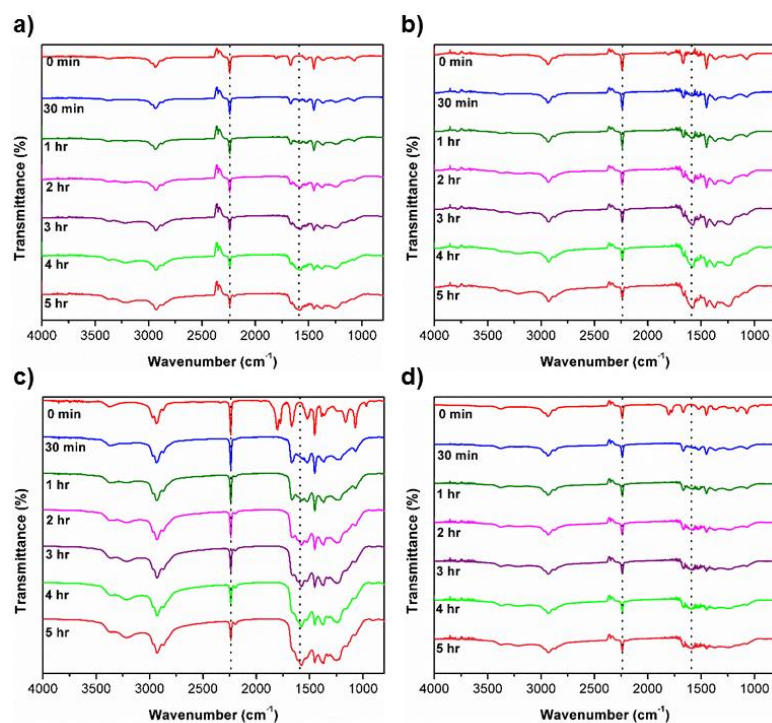


Figure 67. Real-time FTIR spectra recorded at 225 °C for 5 hr in nitrogen for (a) SB-1, (b) SB-2, (c) SB-3, and (d) Batch (dotted lines represent IR bands for nitrile (2240 cm^{-1}) and imine (1590 cm^{-1}) functionalities).

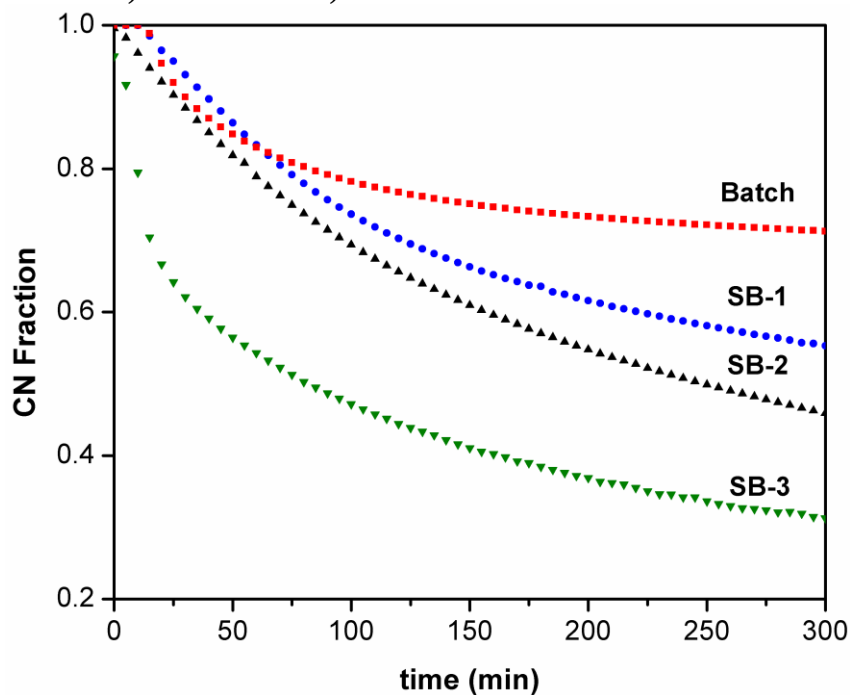


Figure 68. Residual nitrile fraction for semibatch copolymers treated at 225 °C for 5 hr in nitrogen.

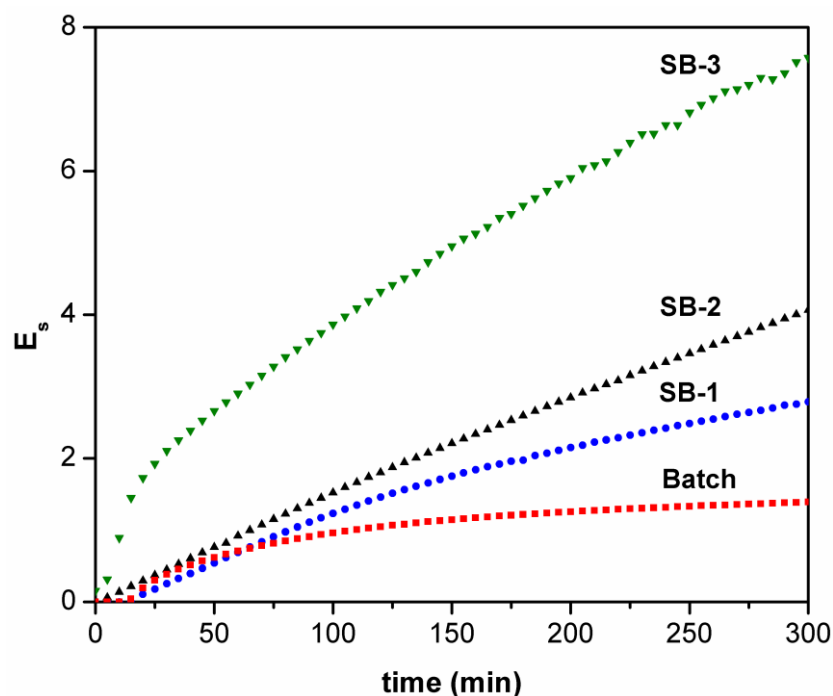


Figure 69. Extent of stabilization for semibatch copolymers treated at 225 °C for 5 hr in nitrogen.

Thermal stabilities were studied via TGA by ramping in nitrogen at 10 °C/min as shown in Figure 70. Post cyclization, all copolymers exhibit gradual mass loss c.a. 270–450 °C in the form of small molecule volatiles such as ammonia, hydrogen cyanide, methane, water, carbon monoxide, and carbon dioxide.^{7,8,43} It is suggested that a more complete ladder structure would result in fewer impurities, less small volatile formation, and greater mass stability to during carbonization (temperatures above 800 °C). Evident from Figure 70, SB-2 and SB-3 portray the greatest thermal stability by the lowest mass loss up to 700 °C, while the batch copolymer results in the lowest mass retention at 700 °C. Furthermore, the SB-2 and SB-3 exhibit lower degradation temperature onsets and more gradual mass loss between 300–350 °C, which is beneficial to carbon fiber processing.

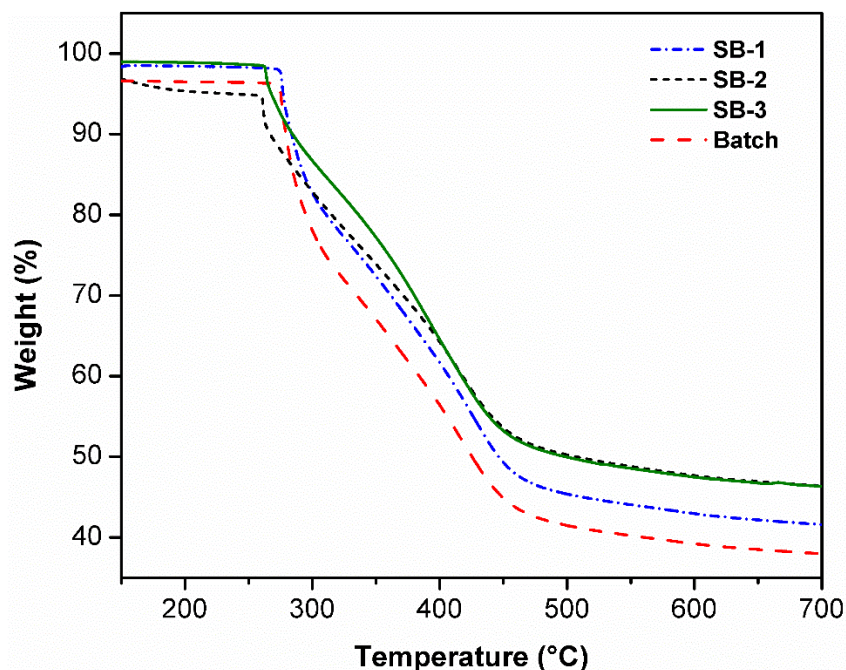


Figure 70. TGA curves for semibatch copolymers ramped at 10 °C/min in nitrogen to 700 °C.

The semibatch copolymers were evaluated by the Pre-ox 2 method as shown in Figure 71. Interestingly, all of the copolymers result in a similar final mass percentage after the thermo-oxidative temperature ramp to 700 °C. However, the SB-1 and SB-3 copolymers preserve a greater mass up to 350 °C, unlike SB-2 and the batch copolymer. Post 350 °C, SB-1 and SB-3 copolymers begin to degrade and lose a significant mass percentage. The SB-3 copolymer loses the greatest amount of mass above 400 °C, which was characteristic of the higher compositions of the 5 mol% NIPAM copolymers in Chapter V. Therefore, this mass loss is currently attributed to degradation of the NIPAM units, but further study is required.

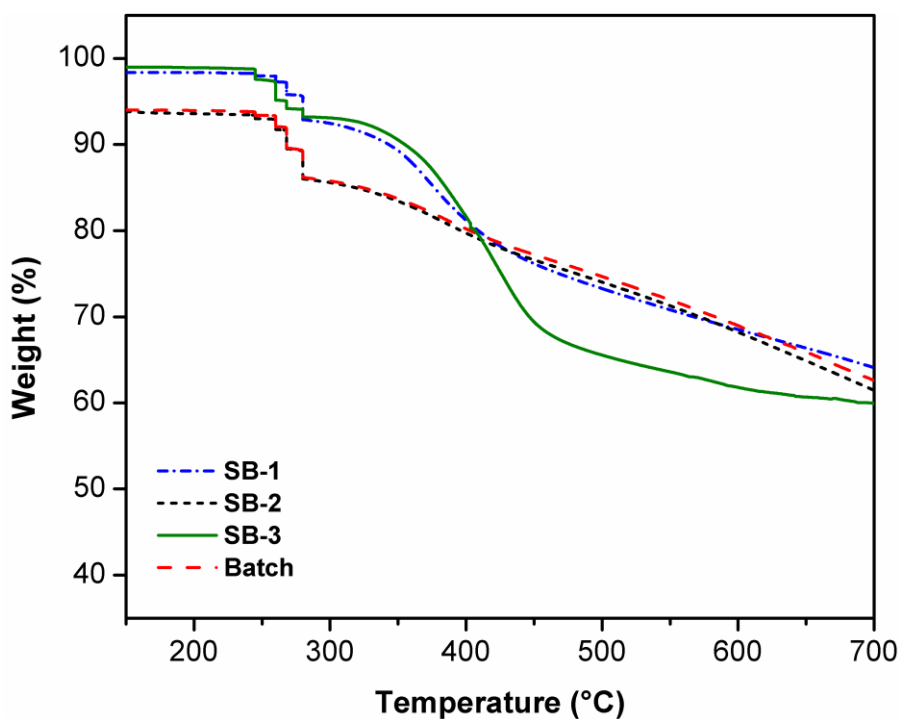


Figure 71. TGA curves for semibatch copolymers treated in air at 230, 245, 253, and 265 °C for 15 min each before ramping in nitrogen at 10 °C/min to 700 °C.

Summary

Reactivity ratios were successfully determined for p(AN-co-NIPAM) at 30 °C in ethylene carbonate and in the presence of CPDT. The reactivity ratios reveal that NIPAM has a higher reactivity as compared to AN, which results in compositional drift and gradient copolymers. The effect of compositional drift and comonomer sequencing on the cyclization were investigated by a semibatch RAFT copolymerization wherein NIPAM was injected into the reaction vessel at predetermined rates. The cyclization was characterized by DSC, FTIR, and TGA. It was found that the slower addition of NIPAM and greater amounts of the NIPAM led to more reduced exotherm temperatures and broader exotherm peaks. Furthermore, copolymers SB-2 and SB-3, with presumably the greatest distribution of NIPAM along the backbone, present (1) the lowest peak onset

temperatures, (2) the fastest rates of cyclization, and (3) the greatest thermal stability in nitrogen up to 700 °C. This study has significantly demonstrated the ability to tune PAN-based copolymer stabilization behavior through the utilization of novel semibatch reaction techniques in conjunction with RAFT polymerization.

CHAPTER VII

ATTEMPTS TO CONTROL TACTICITY IN POLYACRYLONITRILE

Abstract

The tacticity of polyacrylonitrile is proposed to influence cyclization behavior and efficiency. In this study, several methods were employed in attempt to simultaneously control the molecular weight and tacticity of PAN via RAFT polymerization in conjunction with the use of isobutyraldehyde, fluoroalcohol solvents, and Lewis acid additives. Herein, the triad tacticity of modified PAN samples were compared to a baseline PAN sample ($mm = 0.28$, $rr = 0.21$, $mr = 0.51$), but no statistically significant change in tacticity was observed.

Results and Discussion

Both isotactic and syndiotactic PAN should be considered when investigating tacticity effects on cyclization. Previously, isotactic PAN has been reported to have a higher activation energy¹⁷ and a higher cyclization initiation temperature⁶³ than conventional atactic PAN. Although these studies suggest tacticity dependence on the cyclization of PAN, it is worth investigating tacticity effects in a controlled polymerization system to avoid confounding variables. Additionally, there are no reports on how syndiotactic PAN impacts cyclization efficiency. Thus, we also consider syndiotactic-mediated polymerization of acrylonitrile.

The “baseline” PAN was synthesized in the presence of cyano-2-isopropyl dodecyl trithiocarbonate (CPDT) at 30 °C with $[M]_0:[CPDT]_0:[V-70]_0=10,000:1:0.67$, and 20 wt. % monomer in ethylene carbonate. The triad tacticity was determined by quantitative ¹³C-NMR as shown in Figures 72 and 73. Both the nitrile carbon (δ (ppm):

120.1, rr; 120.5, mr; 120.8, mm) and the methine carbon (δ (ppm): 27.2, mm; 27.9, mr; 28.4, rr) can be assessed, where 'r' and 'm' are racemic linkages and meso linkages, respectively.¹⁰⁷ For the purposes of this study, the methine carbons were used for comparison of triad sequences.

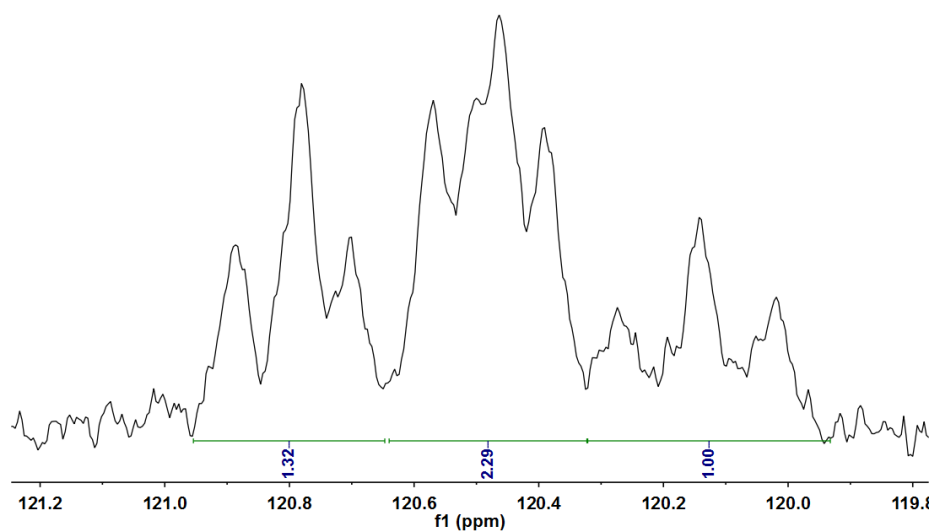


Figure 72. Tacticity assignments of baseline PAN for the nitrile carbon via ^{13}C -NMR (δ (ppm): 120.1, rr; 120.5, mr; 120.8, mm).

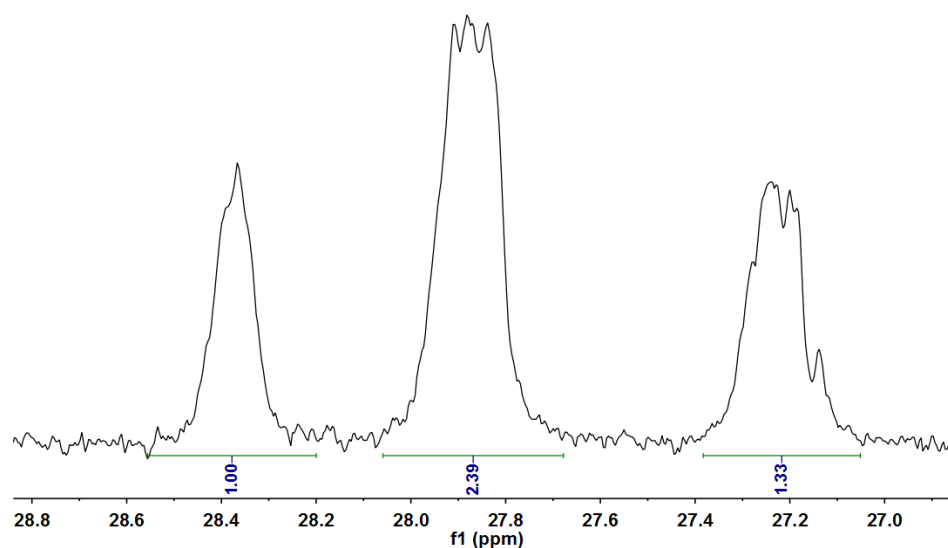


Figure 73. Tacticity assignments of baseline PAN for the methine carbon via ^{13}C -NMR (δ (ppm): 27.2, mm; 27.9, mr; 28.4, rr).

The “syndiotactic-directing” additives chosen were isobutyraldehyde and fluoroalcohol solvents. The fluoroalcohols selected have varying degrees of bulkiness as shown in Figure 9 (Methods, Chapter II). Specifically, perfluoro-tert butyl alcohol (PFTB) and hexafluoro-2-propanol (HFP) have been shown to interact strongly with proton acceptors such as dimethyl ether and acetonitrile.^{146,147} The bulky 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene (BHFB) has been reported as an effective syndiotactic-director for polymethylmethacrylate.¹⁴⁸ In the present study, the highly acidic bulky alcohol is suspected to coordinate with the nitriles on the growing polymer chain end and the monomer to cause steric repulsion around the polymer chain terminal,⁹⁴ resulting in stereospecific growth (Figure 74).

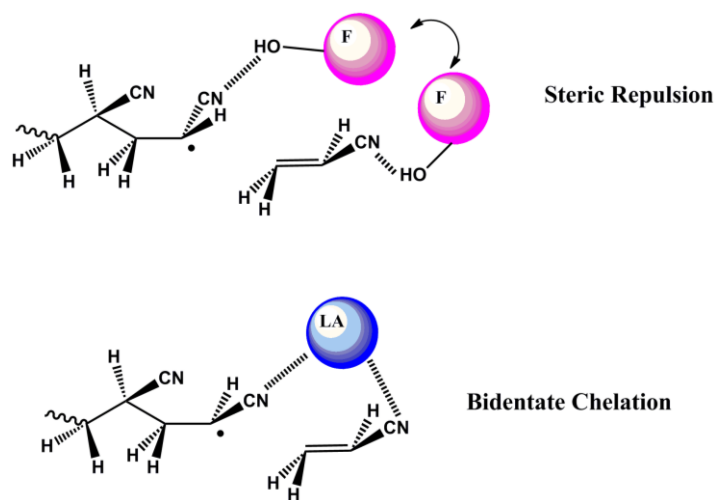


Figure 74. Stereoregulating mechanisms of fluoroalcohols (top) and Lewis acids (bottom) (F = fluoroalcohol, LA= Lewis acid).

On the other hand, the “isotactic-directing” additives chosen were Lewis acids, which have had success with acrylamides.^{93,149,150} Although it is known that Lewis acids can affect reactivity and polymerization kinetics,^{61,96} the focus of this study was to determine tacticity changes prior to other effects. The Lewis acids selected ($Y(OTf)_3$,

Yb(OTf)₃, YbCl₃, ZnCl₂, AlCl₃, and MgCl₂) have varying degrees of acidity and atomic radii. The literature suggests that larger atomic radii and stronger acids with a higher coordination number are the most effective for acrylamide-based monomers.^{96,150} The Lewis acids are expected to form a bidentate chelation with the nitriles on the growing chain end and the incoming monomer to mediate meso-addition,⁹⁴ resulting in isotactic growth (Figure 74). To obey the bidentate chelation in acrylamides, only a catalytic amount of Lewis acid was utilized.⁶¹ Alternatively, fairly large quantities of MgCl₂ and NiCl₂ have been used for polyacrylonitrile, forming 1:1 complexes with the monomer in a “solid state template-assisted” polymerization,^{60,63} which led us to consider larger quantities of Lewis acids in the polymerizations. The triad tacticities of the polymerizations with the added stereoregulators are summarized in Table 27.

Table 27

Triad Tacticities of PAN polymers with Stereoregularity Additives

Entry ^a	Additive	Concentration [Additive]:[I]	rr (%) ^b	mr (%) ^b	mm (%) ^b
1. Control	none	none	21.3	50.7	28.0
2	Isobutyraldehyde	7,000:1	21.7	50.5	27.7
3 ^c	Isobutyraldehyde	7,000:1	22.1	50.6	27.3
4	HFP	15:1	22.1	51.0	26.9
5	HFP	150:1	20.8	51.3	27.9
6	HFP	2,700:1	21.8	50.7	27.5
7	PFTB	15:1	21.8	51.3	26.9
8	PFTB	250:1	21.5	51.8	26.7
9	BHFB	15:1	21.4	51.0	27.6

Table 27 (continued).

Entry ^a	Additive	Concentration [Additive]:[I]	rr (%) ^b	mr (%) ^b	mm (%) ^b
10	BHFB	500:1	21.4	41.1	27.5
11	YbCl ₃	15:1	21.4	51.1	27.5
12	ZnCl ₂	15:1	21.4	51.8	26.9
13	ZnCl ₂	150:1	21.0	51.2	27.8
14	ZnCl ₂	500:1	21.1	51.2	27.7
15	ZnCl ₂	5,000:1	21.3	50.4	28.4
16	AlCl ₃	15:1	21.2	51.2	27.7
17	AlCl ₃	150:1	20.4	51.5	28.1
18 ^d	AlCl ₃	500:1	-	-	-
19 ^d	AlCl ₃	5,000:1	-	-	-
20	Y(OTf) ₃	15:1	20.6	51.8	27.7
21	Y(OTf) ₃	150:1	21.1	51.7	27.2
22	Y(OTf) ₃	750:1	20.4	52.2	27.4
23	Yb(OTf) ₃	15:1	20.9	51.3	27.8
24	Yb(OTf) ₃	150:1	22.5	49.7	27.8
25	Yb(OTf) ₃	500:1	21.1	51.1	27.8
26 ^e	ZnCl ₂	500:1	20.2	50.0	29.8
27 ^e	Yb(OTf) ₃	500:1	23.3	50.8	25.9
28 ^e	Y(OTf) ₃	500:1	-	-	-
29 ^e	AlCl ₃	500:1	-	-	-
30 ^e	MgCl ₂	500:1	-	-	-

^aPolymers prepared at 30 °C in the presence of CPDT at a [M]₀: [CPDT]₀: [V-70]₀ = 10,000:1:0.67 in ethylene carbonate. ^bTriad tacticities determined via ¹³C-NMR in d₆-DMSO by the peak splitting of the methine carbon. ^cConcentration of ethylene carbonate reduced to 70 wt.%. ^dEntries 18 and 19 turned yellow during polymerization and resulted in low polymer yield. ^eEntries 26-30 were conducted in bulk with no ethylene carbonate.

PAN was found to be highly insoluble in isobutyraldehyde and fluoroalcohols, which could be cause for minor interactions with these syndiotactic-directing solvents. Thus, we tried reducing the amount of ethylene carbonate in Table 27, Entry 3, but the tacticity changes were negligible. Lewis acids were prepared in stock solutions of acrylonitrile in a dry box prior to weighing out in the reaction vessel due to sensitivity with oxygen. Still, Entries 18 and 19 turned yellow probably due to oxidation of the aluminum chloride resulting in low polymer yield.

Literature shows that the solvent selection has a very important role in the efficacy of the Lewis acids,^{96,149} and indicates that the solvent should not be more polar than the monomer as this could make the Lewis acid coordinate more with the solvent than the monomer. This led us to attempt bulk polymerization of acrylonitrile (Table 27, Entries 26-30) since most solvents for acrylonitrile are very polar, including ethylene carbonate. Entry 26 did show the greatest difference from the baseline polymer, however, the conversions of Entries 28-30 were very low and not a sufficient amount polymer could be filtered from the polymerization for NMR analysis. Seen in Table 27, there is no significant statistical change in triad tacticity for any of the polymer samples with additives as compared to the baseline sample, Entry 1.

Summary

Stereoregulation of PAN by fluoroalcohol and Lewis acid additives proves to be a difficult task. Many different additives were examined at various concentrations in attempt to modify the triad tacticity, but efforts were to no avail. Most likely, the additives are coordinating with the high concentration of ethylene carbonate in the

polymerization. Less polar solvent substitutes for ethylene carbonate or bulk polymerization may help to achieve tacticity changes in the RAFT polymerization of AN.

CHAPTER VIII

SCALE-UP REACTIONS AND CARBON FIBER PROPERTIES

Abstract

The conventional free radical solution copolymerization of 98 mol% acrylonitrile (AN) and 2 mol% N-isopropylacrylamide (NIPAM) was successfully scaled and spun into fiber filaments. The morphology of the precursor fibers were then characterized by transmission electron microscopy (TEM), optical microscopy, and X-ray diffraction (XRD). The thermal behavior was compared to commercial white fiber precursors by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The morphology and thermal properties of the produced fiber serve as a benchmark for the future design of precursor compositions and architectures.

Results and Discussion

Scale Up Copolymerization and Fiber Spinning

The copolymerization of 98/2 p(AN-co-NIPAM) was prepared as described in Chapter II. The polymer solution was poured into a separation funnel heated at 80 °C by heating tape. The solution was then discharged at a steady flow into a 20 L container of deionized water while being mechanically stirred as shown in Figure 75a. The polymer was then washed and re-precipitated forming white fibrous material as shown in Figure 75b.

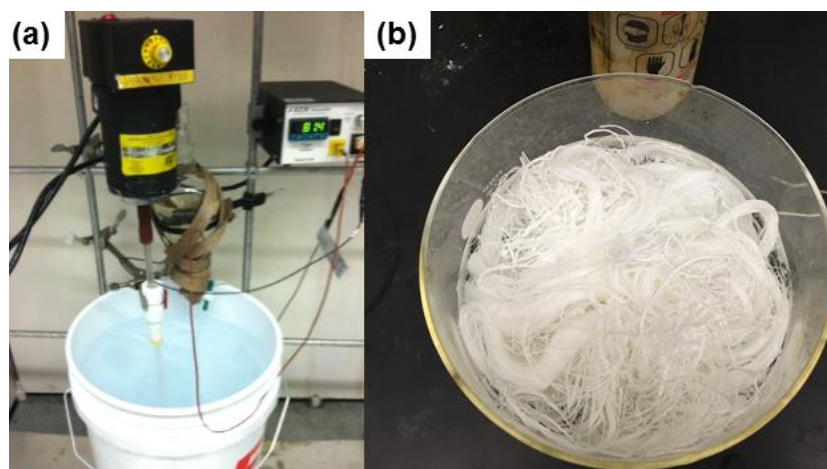


Figure 75. (a) Precipitation of scale up reaction and (b) fibrous material from the precipitation.

The PAN-based copolymer was successfully spun into a fiber bundle by Dr. Matthew Weisenberger from the University of Kentucky into a 500 count tow as shown in Figure 76. Copolymer composition was determined via $^1\text{H-NMR}$ NIPAM as shown in Figure 77. The number of protons in the backbone associated with AN is calculated $[(87.10-3)/3]=28.03$ and then the content of AN is $[28.03/(28.03+1)]=96.6 \text{ mol\%}$ and NIPAM content is $3.4 \text{ mol\%}$.



Figure 76. Fiber spool of 98/2 p(AN-co-NIPAM) copolymer.

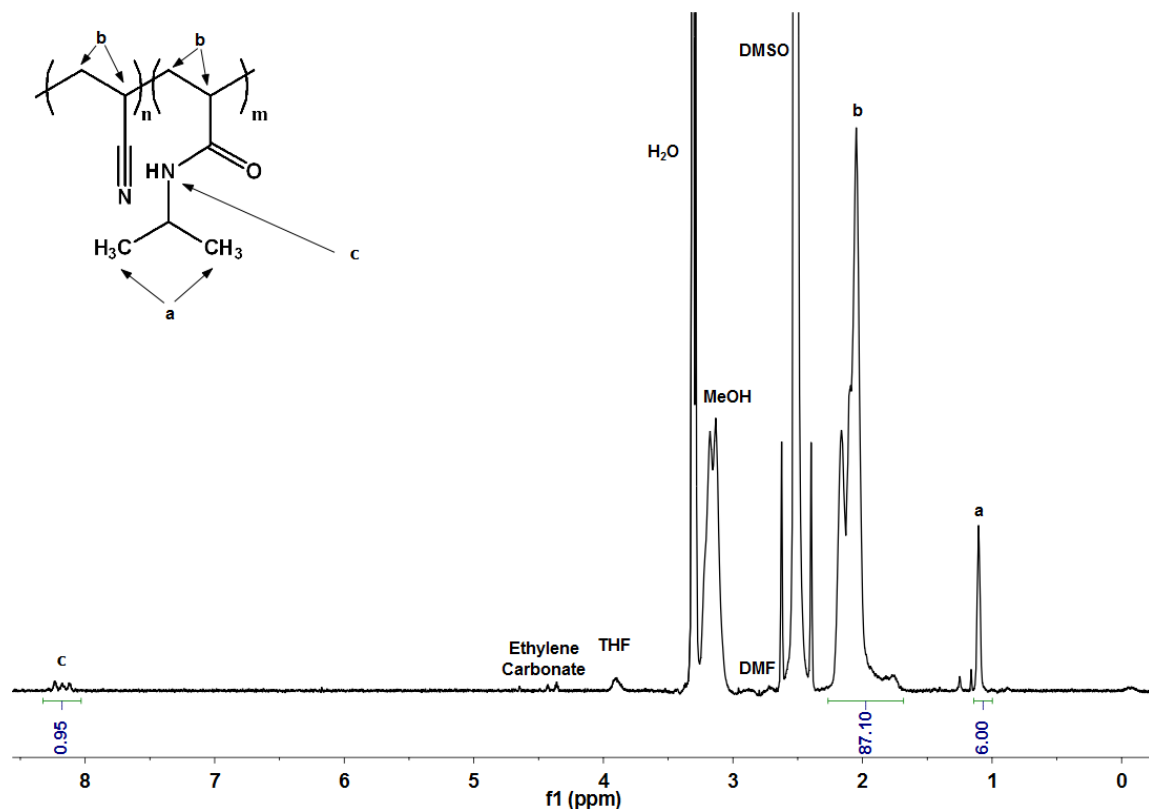


Figure 77. ^1H -NMR of 98/2 p(AN-co-NIPAM) fiber sample.

The lab-produced NIPAM fiber was compared to commercially available fibers (Bluestar from China (BS), and Jilin from Korea (JL)). It is known that the primary comonomer in the BS fiber is methyl acrylate with a minor amount of itaconic acid and the primary comonomer in the JL fiber is vinyl acetate with a minor amount of an unknown acidic comonomer. The molecular weights of the NIPAM fiber and two commercial white fiber precursors determined by SEC-MALLS are reported in Table 28. Notably, the molecular weight of the experimental fiber (NIPAM) is much greater than those of the commercial fibers.

Table 28

Molecular Weights and Polydispersities of White Fiber Precursors

Fiber Sample	M_n (MALLS) g/mol	PDI (M_w/M_n)
98/2 p(AN-co-NIPAM) (NIPAM)	147,400	1.71
Bluestar Chinese Fiber (BS)	74,400	1.48
Jilin Korean Fiber (JL)	87,200	1.93

Fiber Morphology

The NIPAM fiber precursor was converted to carbon fiber at Deakin University in Geelong, Australia, in connection with the Carbon Fiber Nexus. The fiber was stabilized in a series of oxidation ovens at 245, 260, 268, and 280 °C before passing through high temperature ovens up to 1550 °C. Transmission Electron Microscopy (TEM) was performed on cross-sections of the carbon fiber samples. TEM samples were prepared at Deakin University (Dr. Bronwyn Fox's research group) by embedding fiber bundles in a copper wire and setting them with an epoxy matrix material. Samples were polished by a precision ion polishing system at low voltage for 23 hr. High magnification TEM images from the carbon fiber samples (Figures 78 and 79) demonstrate the characteristic ribbon-like wavy planes of graphitic sheets as described in the model by Johnson and coworkers.¹¹ Surprisingly, the high magnification images show very few needle-shaped voids or defects in the wavy patterns.

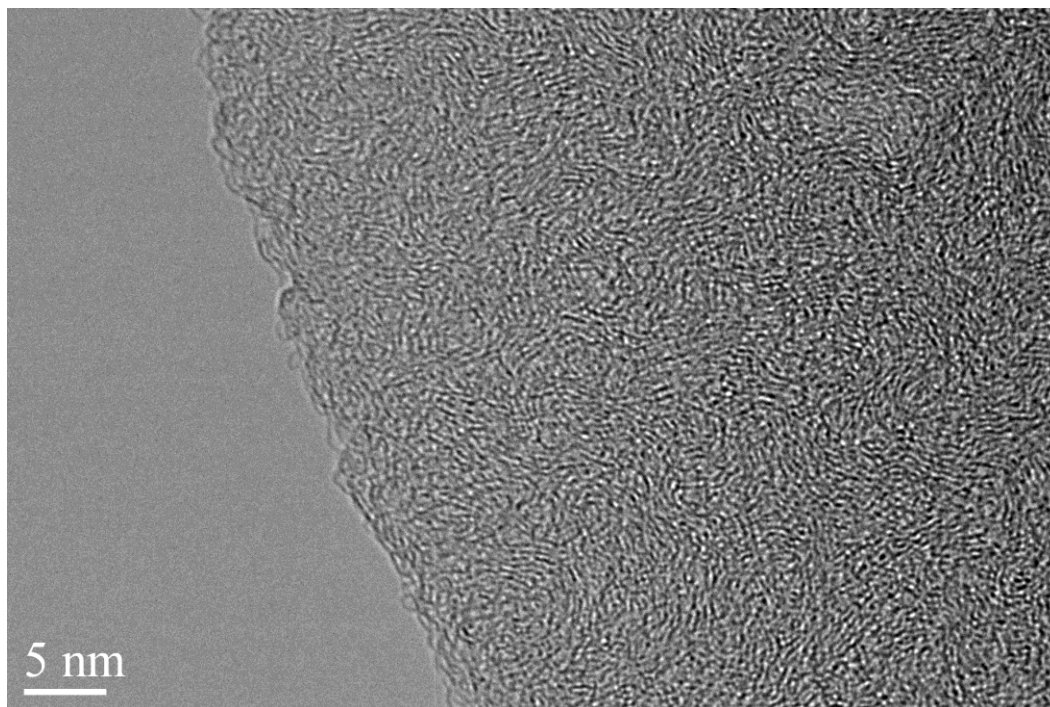


Figure 78. TEM image of cross-section of 98/2 p(AN-co-NIPAM) fiber treated up to 1450 °C.

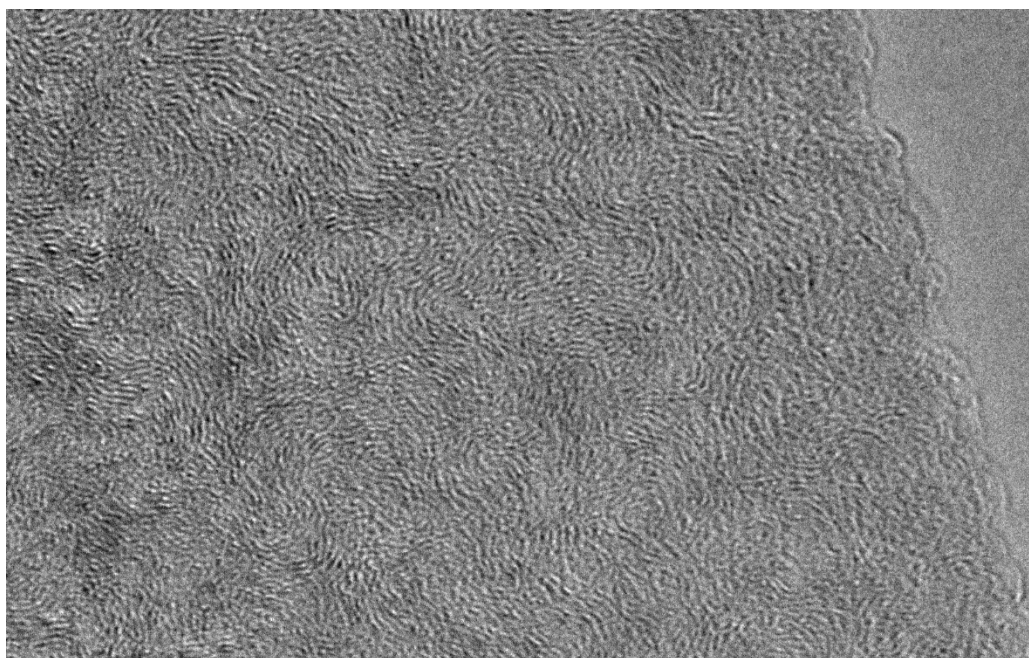


Figure 79. TEM image of cross-section of 98/2 p(AN-co-NIPAM) fiber treated up to 1550 °C.

The optical microscopy images of the NIPAM fiber from white fiber through to carbon fiber are shown in Figure 80. The fiber cross-sections are round and exhibit a distribution of sizes with diameters ranging from about 5-10 μm in size. Also, some fibers display micron sized pores, which are apparent from the white fiber through to the carbon fiber. These defects could be residue from the polymerization or from the spinning process. More work needs to be done to investigate the formation of these voids. Most importantly, these experimental fibers are absent of the characteristic ‘core-shell’ morphology, or a gradient through the fiber cross-section.²³ This could be beneficial to carbon fiber performance.

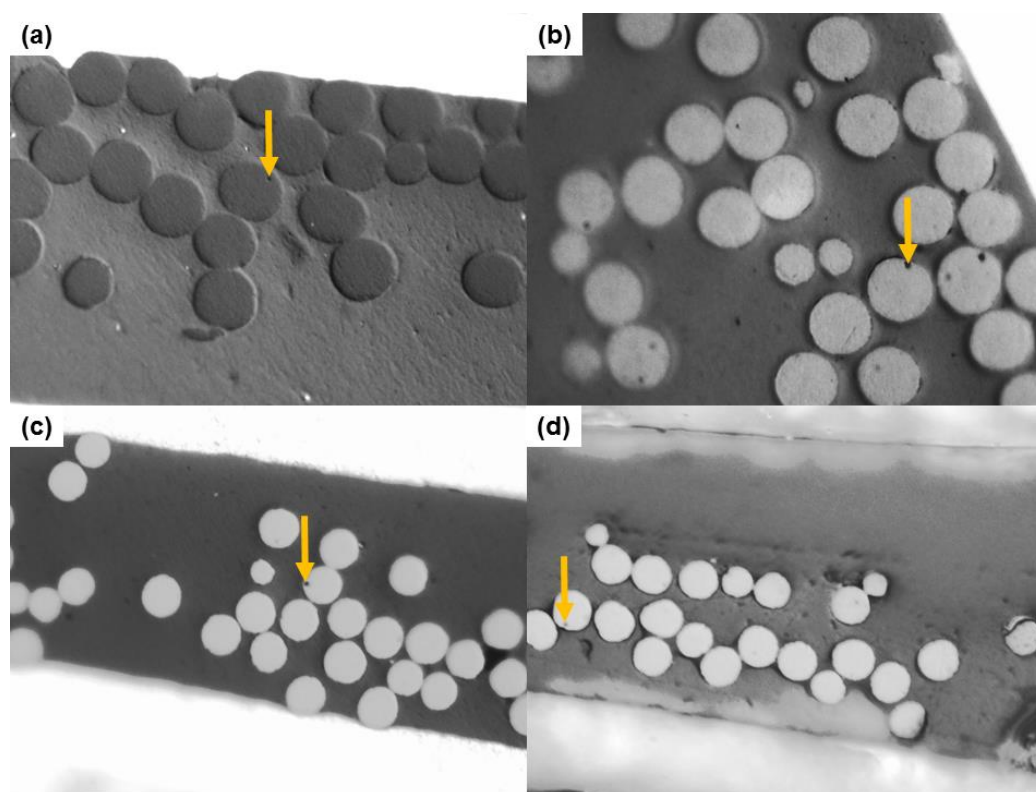


Figure 80. Optical microscopy of 98/2 p(AN-co-NIPAM) (a) white fiber precursor, (b) post oxidative stabilization up to 280 °C, (c) heating to 1450 °C, and (d) heating to 1550 °C (yellow arrows indicate micro porous defects).

The orientation a bundle of 20 monofilament white fibers were qualitatively determined by azimuthal analysis using X-ray Diffraction (XRD) as compared to commercial-grade BS fiber in Figure 81. The images display two concentric arcs, or ‘lobes’, at the top and bottom which denote the alignment of fibers with smaller arcs indicating a greater orientation of fibers. As demonstrated in Figure 81, the NIPAM fibers have narrower arcs, which resembles are greater alignment of the fibers as compared to BS fibers. Alignment of the fibers is critical in maximizing carbon fiber performance and yielding high strength materials.

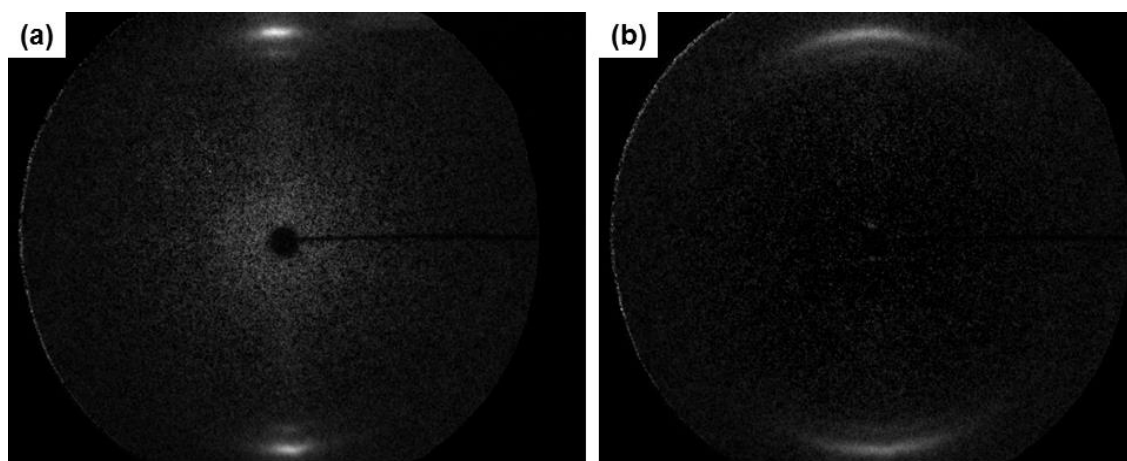


Figure 81. Azimuthal analysis by XRD for (a) 98/2 p(AN-co-NIPAM) precursor white fibers and (b) BS white fiber.

Thermal Properties

The cyclization exotherm behavior of the NIPAM fiber precursor was compared to BS and JL commercial fibers through heat treatment in DSC at 5 °C/min as shown in Figure 82. Evident from the DSC exotherms, the NIPAM fiber has a lower peak exotherm temperature, but also a much narrower exotherm and a greater peak intensity. The NIPAM fiber has a greater max heat flow relative to the commercial-grade fibers. The exotherm behavior from DSC is summarized in Table 29.

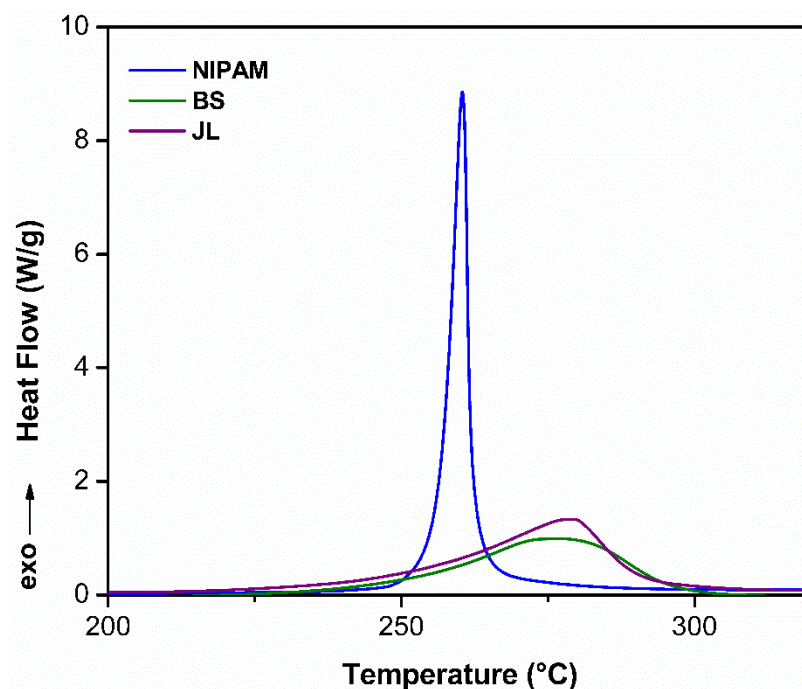


Figure 82. DSC exotherms of white fiber precursors heated at 5 °C/min.

Table 29

Exotherm Behavior of White Fiber Precursors Heated at 5 °C/min

Sample	Peak Temp (°C)	Peak Breadth (°C)	Intensity (J/g)	Max Heat Flow (W/g)
NIPAM Fiber	260	14	473.9	8.85
BS Fiber	277	67	417.9	0.99
JL Fiber	280	63	422.8	1.33

Thermogravimetric analysis (TGA) was used to evaluate mass retention of the fibers by heat treating up to 700 °C. The fibers were treated at 10 °C/min in nitrogen as shown in Figure 83a and they were stabilized in air according to Pre-ox 2 (Chapter II) before ramping in nitrogen at 10 °C/min in Figure 83b. As seen in Figure 83a, the NIPAM precursor has a greater mass loss through the stabilization of the carbon fiber in

nitrogen. However, Figure 83b displays that the experimental NIPAM fiber resembles very similar mass loss behavior to commercial-grade fiber precursors. This significantly demonstrates the ability of a lab produced copolymer to exhibit behavior to industry leading precursors. Using this simple copolymer composition as a benchmark, the opportunity for advanced copolymer structures and utilization of RAFT polymerization methods allows for further advancement of PAN-based carbon fiber precursors.

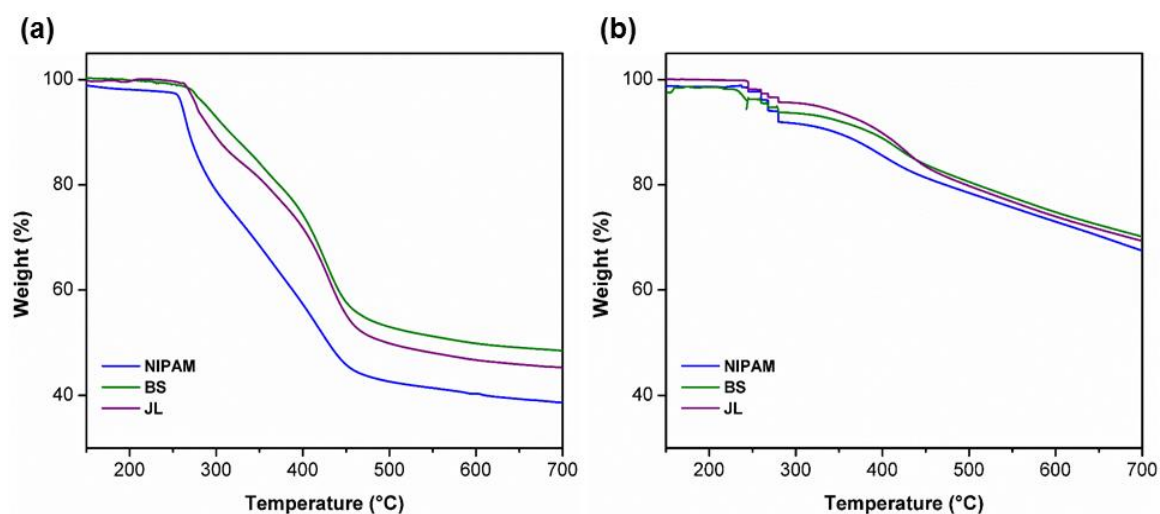


Figure 83. TGA plots of white fiber precursors (a) ramped at 10 °C/min to 700 °C in N₂ and (b) ramped at 10 °C/min in air and held at isotherms of 245, 260, 268, and 280 °C for 15 min each and then ramped at 10 °C/min to 700 °C in N₂.

Summary

Polyacrylonitrile with 2 mol% NIPAM was successfully spun into a white fiber precursor. The fiber precursor morphology was characterized by TEM, XRD, and optical microscopy. The fiber shows minimal defects and the absence of the typical core-shell morphology of PAN-based carbon fibers. The nano-scale TEM images yield ribbon-like wavy planes characteristic of the graphitic sheets. The orientation of the experimental NIPAM-containing fibers are better than analogous commercial-grade BS fibers as evidence by azimuthal analysis. The thermal properties show that the NIPAM fibers have

greater exotherm intensities and narrower temperatures as compared to commercial fibers, but the mass retention is almost identical to commercial fibers when oxidatively stabilized prior to pyrolysis. These findings will serve as the benchmark for future designs and compositions of precursor architectures with more advanced RAFT polymerizations.

CHAPTER IX

CONCLUSIONS AND FUTURE WORK

PAN-based precursors represent more than 90% of the market for carbon fibers, yet, only a small fraction of the theoretical strength of an ideal carbon fiber has been achieved since their inception in 1961. This is in part due to the lack of disseminated research on these highly proprietized materials, but also due to the ability to link precursor composition all the way through to carbon fiber in an academic setting. Historically, reports on PAN-based precursors have ignored fundamental polymer characteristics such as molecular weight and polydispersity and disregard polymerization history. To fully understand the evolution of carbon fiber and the structure-property relationships involved with carbon fiber performance, research efforts herein have taken a focus on finely tuning PAN-based polymer properties to better understand how these properties influence conversion towards carbon fiber.

In Chapter III, the RAFT polymerization of AN was systematically investigated to reach high molecular weight with low polydispersity. High molecular weight (above 100,000 g/mol) is essential for mechanical performance of carbon fiber. Upon exploration of low temperature CPDT-mediated polymerization, molecular weights above 170,000 g/mol can be achieved or polydispersities below 1.1 depending on the ratio of reactants. The reactions displayed continued monomer conversion for up to 48 hr, which has been unprecedented in the literature. It is suggested that lowering polymerization temperature from 70 to 30 °C decreases the relative number of chain transfer and chain termination events with respect to propagation. Significantly, this

result was extended to PAN-based copolymers in Chapter V, where several RAFT copolymers exhibited controlled behavior with high molecular weights.

The effects of molecular weight, polydispersity, and polymerization were then explored through RAFT polymerization and conventional FR solution polymerization (Chapter IV). The low polydispersity and control exhibited by RAFT polymers clearly demonstrated differences to the FR polymers beyond molecular weight dependences. The RAFT homopolymers led to higher exotherm temperatures and faster liberation of heat during cyclization. When broadened to copolymers (Chapter V), it was found that RAFT copolymers exhibit greater thermo-oxidative stability and enhanced exotherm intensities. It is suggested that RAFT polymerization yields fewer defects to initiate cyclization, but also retains more mass and a higher carbon yield post cyclization when a comonomer is present.

A series of new comonomers were introduced in Chapter V, of which NIPAM displayed characteristics resembling traditional comonomers. Particularly, NIPAM offers benefits to both cyclization of PAN, but also the spinning and subsequent processing of carbon fibers. The NIPAM-containing copolymers yield reduced heat flows in the exothermic cyclization as compared to methyl methacrylate, lowered crystallinity as compared to acrylic acid, and showed impressive thermo-oxidative stability. The use of a single comonomer as compared to traditional terpolymers is beneficial for the production of carbon fibers.

PAN-co-NIPAM copolymers were further investigated in Chapter VI, wherein the reactivity ratios were determined and the sequencing of comonomers were altered by the use of a syringe pump continuously injecting NIPAM into the reaction vessel. The

distribution of NIPAM along the backbone is theoretically optimized when the NIPAM unit is placed between every 8-10 acrylonitrile units. Yet in a batch reaction, NIPAM being a more reactive comonomer is consumed faster than acrylonitrile leading to a gradient of NIPAM in the copolymer composition. It was clearly demonstrated that changes in the injection rate of NIPAM led to unique copolymer behavior suggesting that cyclization can be tuned. When NIPAM was injected at a slow feed rate over 48 hr (SB-2 and SB-3), the peak onset temperature of cyclization shifted to a lower temperature, faster rates of cyclization were realized, and greater thermal stability in nitrogen was achieved.

Of great interest to the academic community is the effect of polymer tacticity on the evolution of carbon fiber and its significance. Literature suggests that isotactic-PAN should be ideal for promoting cyclization of pendant nitrile groups. Facile methods to alter tacticity of PAN are necessary to explore the differences in cyclization. In Chapter VII, Lewis acids as well as fluoroalcohols were explored extensively in hopes to mediated isotactic or syndiotactic polymerization, respectively. However, it was found that tacticity was largely unaffected by these additives, despite their reported success with other polymer systems. It is recommended that future studies attempt bulk polymerizations or substitute ethylene carbonate, which is probably coordinating with these polar additives, with a less polar solvent.

Finally, Chapter VIII presents the scale-up of a conventional solution copolymerization of 98/2 p(AN-co-NIPAM). The copolymer was successfully spun into a 500 count tow of white fiber. The fiber morphology and thermal behavior were compared to commercial-grade carbon fiber precursors. The experimental fiber showed minimal

voids and defects along with greater orientation in respect to the commercial BS fiber. The NIPAM-containing fiber did, however, display increased heat flows during cyclization with lower cyclization temperatures. The NIPAM fiber ultimately showed very similar thermo-oxidative stability and near-parallel behavior to the commercial fibers, which benchmarks this copolymer composition with commercial-grade white fiber properties. This copolymer composition can be used as a baseline for design of future copolymer architectures and their scale-up towards carbon fiber.

In the future, scale-up reactions with RAFT copolymers would help bridge the gap between morphology of RAFT and FR polymerization methods. Furthermore, new comonomers with structures similar to NIPAM, but perhaps less acidic and less bulky, would further obviate exothermic cyclization reactions. Also, characterization techniques such as solid-state NMR and TGA equipped with mass-spectroscopy will help connect copolymer composition and molecular weight dependences to degradation pathways. Additionally, average hole size free volume and fractional free volume would be interesting attributes to correlate to copolymer architecture via Positron Annihilation Lifetime spectroscopy (PALS) and Pressure Volume Temperature (PVT) change experiments, respectively. Finally, optimizing thermo-oxidative stabilization protocols for various copolymers through FTIR studies should increase the cyclization efficiency of precursors.

APPENDIX
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