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POLY (ACRYLONITRILE-CO-1-VINYLMIDAZOLE): A NEW MELT PROCESSABLE CARBON FIBER PRECURSOR

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POLY (ACRYLONITRILE-*CO*-1-VINYLMIDAZOLE): A NEW MELT
PROCESSABLE CARBON FIBER PRECURSOR

A Dissertation
Presented to
the Graduate School of
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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
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December 2010

Accepted by:

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ABSTRACT

Carbon fiber polymer composites have attracted worldwide interest in sporting goods and aerospace industries due to their excellent specific strength, stiffness and lightweight. The replacement of solution-spinning process by melt-spinning process is one of the major approaches to make cost effective carbon fiber. In recent years, researchers have explored the possibilities to synthesize melt processable carbon fiber precursors, but their thermal stabilization is still a challenge. The goal for this research project is to prepare melt processable carbon fiber precursors which have the capability of thermal stabilization. Acrylonitrile/1-vinylimidazole (AN/VIM) copolymers containing various mol% of VIM were synthesized by free radical solution polymerization. The copolymers were characterized by Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy, ^1H -NMR spectroscopy, gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). 82/18 mol percent of AN/VIM copolymer based carbon fiber precursor was processed by melt spinning at 192 °C and thermal stabilization of the melt-spun fiber was achieved by heating in air at 250 °C for 5 hrs. The change of fiber structure during stabilization process was confirmed with ATR-IR spectra. Tan Delta value of the stabilized fiber is 0.17, which is much lower than that of as-spun fiber, about 2.12. The oxidized fiber (250 °C / 5 h) did keep its shape after carbonization at 1000 °C for 2 h, which indicates that poly (acrylonitrile-*co*-1-vinylimidazole) melt-spun fiber after thermal stabilization can be carbonized. A novel dispersion polymerization of poly (acrylonitrile – *co* -1-

vinylimidazole) by using small amount of protonated copolymer itself as a stabilizer was also introduced in this study.

Poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) were synthesized for gas separation membranes. Terpolymers of methyl methacrylate, methyl acrylate and furfuryl methacrylate (MMA/MA/FMA) were synthesized successfully by solution polymerization and emulsion polymerization and were characterized by ^1H NMR, ATR-IR and DSC. The thermo-reversible property of MMA/MA/FMA and BMI cross-linked polymer was confirmed by solubility test. The MMA/MA/FMA and BMI cross-linked polymer emulsion can be applied for making thermally re-moldable carbon fiber composite.

DEDICATION

I dedicate this work to my parents. I am blessed for being their daughter.

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CHAPTER ONE

SYNTHESIS AND CHARACTERIZATION OF POLY (ACRYLONITRILE-CO-1-VINYLMIDAZOLE) CARBON FIBER PRECURSORS

Introduction

Carbon fiber polymer composites have attracted worldwide interest in sporting goods and aerospace industries due to their excellent specific strength, stiffness and lightweight [1-3]. A single carbon fiber filament is thin with a diameter of 5–8 μm and consists almost exclusively of carbon. **Figure 1.1** shows a carbon filament (6 μm diameter) compared to a human hair [3, 4]. Carbon fiber has high strength and light weight. Carbon fiber is about 4.5 times less dense than steel, but has a tensile strength almost 3 times greater than that of steel (**Table 1.1**) [5]. Thousands of these filaments are placed together to form tow, which then can be used to form various composite matrix materials for varied applications ranging from aerospace, automobile to sporting goods [1].

Figure 1.1 Photograph of a carbon filament (6 μm diameter) compared to a human hair (carbon filament runs from bottom left to right) (Reprinted with permission from W.J. Cantwell, J. Morton, Composites 1991; 22(5): 347-362, Copyright © 1991, Elsevier under the license number 2550921045990) [3]

Table 1.1 Tensile strength and density comparisons of carbon fiber and steel [5]

Property	Carbon fiber	Steel
Tensile strength	3.50 GPa	1.30 GPa
Density	1.75 g/cm ³	7.90 g/cm ³

Carbon fiber can be prepared from several precursors such as pitch, cellulose, lignin and polyacrylonitrile (PAN) copolymers. The pitch-based precursors have several advantages compared with PAN-based precursors: a 40 to 50% cheaper raw material, less energy required to be converted to carbon fiber, and about 75% high carbon yield [74]. The pitch-based precursor is a good alternative to the PAN-based precursor. However, currently **90%** of all commercial carbon fibers are produced from PAN-based precursors, which mostly because PAN-based precursors are more suitable to produce high modulus and high tensile strength carbon fibers [25]. The synthesis [6-8], structural characterization [9-21], and cyclization studies [21] of polyacrylonitrile based precursors have been received a great deal of attention in recent years. PAN based carbon fibers are usually produced by the following steps: 1) Spinning of precursors; 2) oxidative stabilization and carbonization of fiber precursors. Solution spinning of the precursors is carried out at different drawing rates while stabilization typically occurs around 200-300 °C in air, which leads to the formation of a ladder polymer necessary to obtain a high quality carbon fiber. The step of forming ladder polymers is very important, as it

influences the physical properties and the microstructure of the resultant carbon fibers. Subsequently, carbonization is carried out at temperature of 1000-1400 °C in an inert atmosphere which removes nearly all of the non-carbon elements. **Figure 1.2** shows the manufacture process from monomer to carbon fiber [22]. When higher modulus of carbon fiber is required, graphitization above 2000 °C would be carried out in an inert atmosphere.

Figure 1.2 Manufacture process from monomer to carbon fiber (Toho Tenax: Japanese company, the world's leading C-fiber manufacturer) [22]

The resulting carbon fibers are used to produce the reinforced polymer composites which are known to give high strength, high modulus, light weight and high heat resistance [3]. Popular applications include the commercial aircrafts (up to 50% of the structure uses carbon fiber), recreational units (golf and fishing pole), and industrial materials. The growth rate for the last 23 years was about 12% per year. The marketing research company, Lucintel is estimating that the carbon fiber market will reach \$2.4 billion in 2014 [23]. The major carbon fiber manufacturers include Toray Industries, Inc, Toho Tenax Co Ltd, SGL Carbon Group, Zoltek Companies Inc, Nippon Graphite Fiber Corp and Cytec Industries Inc [24]. There is a business unit of Cytec Industries Inc in Greenville, SC.

The traditional PAN precursors are the copolymers of acrylonitrile (AN) with approximately 3-5 % other comonomers including methyl acrylate, vinyl acetate, acrylic acid, etc [26]. In general, commercial PAN precursors degrade before they melt therefore, the precursor fibers are commonly solution-spun (20–30 wt% solution) from polar solvents [28]. However, the solution spinning process requires solvent recovery and higher processing costs which restricts their applications. There is a need to prepare cost effective carbon fibers to expand their applications including automotive industries.

The replacement of solution-spinning by a melt-spinning process is one of the major approaches which can help in producing cost effective carbon fiber precursors. In recent years, researchers have explored the possibilities to synthesize melt processable carbon fiber precursors [28, 29]. Melt-processable PAN copolymers in combination with other comonomers such as methyl acrylate [30], methacrylic acid [14], and itaconic acid

[31] are commercialized but their thermal stabilization is still a challenge. Recently McGrath et al., has reported the melt-processable carbon fiber precursors based on terpolymers of acrylonitrile, methyl acrylate and acryloyl benzophenone (ABP) (**Figure 1.3**) [30]. These precursors can be stabilized by UV light, which sometimes is not sufficient enough for cross-linking (~ 65 % gel fraction) [30, 32] and again add cost specialized technique. Insufficient cross-linking means the stabilized precursor did not form good three dimensional networks, which would not enable it to withstand the high temperature treatment (> 1000 °C) during carbonization process.

Figure 1.3 Structure of photocrosslinkable terpolymer reported by McGrath's group [30]

The objective of our study is to synthesize melt processable carbon fiber precursors which have the capability of thermal stabilization in air which would make them cost-effective and widen their applications. AN/VIM copolymers [33, 34] have been reported by several researchers, but to the best of our knowledge none of AN/VIM copolymer compositions has been reported for carbon fiber applications. VIM comonomer can disrupt PAN crystallinity to make it melt-processable, while the unsaturated pendant imidazole groups enable the precursor to be thermally cross-linkable.

Also, VIM will help in balancing the atomic ratio of nitrogen to carbon (N/C) which is related to microstructure of these precursors and further affects the structure and mechanical properties of carbon fibers [35-37]. The nitrogen-rich carbon fiber precursors can be carbonized at high temperature, which leads to the high modulus and high tensile strength of final carbon fiber product. The gel fraction, char yield and rheological properties of these copolymers were studied. Here, based on rheological studies and optimum char yield, 82/18 AN/VIM composition was chosen for melt spinning and has been discussed in detail. Thermal and structural characterization of successful melt spun fiber was also studied.

Synthesis and characterization of AN/VIM copolymers

The solution polymerization of AN and VIM by varying feed molar ratio was carried out at 70 °C. The schematic representation for the synthesis of AN with VIM is shown in **Scheme 1.1**. The copolymer obtained was shown in **Figure 1.4**.

Scheme 1.1 Free radical copolymerization of AN with VIM

Figure 1.4 Photograph of 82/18 AN/VIM copolymer **CF33**

Addition of monomers was carried out by two different methods: “one pot” method and “starve-fed addition” method to synthesize these copolymers. In “one pot” method, VIM content of the copolymer measured by ^1H NMR was almost twice the feed molar ratio. The higher composition of VIM in “one pot” copolymers can be very well understood based on the reactivity ratios of these two monomers as $r_{\text{AN}} = 0.24$ and $r_{\text{VIM}} = 0.12$ [33]. It was observed that this polar donor –acceptor (AN-VIM) pair intended to form alternating copolymer [33, 39-40]. In order to better control the composition drifts, we have used “starve-fed addition” method to synthesize AN/VIM copolymers. The “starve-fed addition” is a monomer addition method where the monomers are added gradually to the reaction vessel (drop by drop in lab) at a rate allows most monomers to be consumed before more are added. This method generally used to control the distribution of monomers with different reactivity ratios into the copolymers. The copolymer composition determined by ^1H NMR (**Table 1.2**), shows the feed molar ratio

of copolymer was reasonably represented in the copolymer structure prepared by “starve-fed addition” method. In this study we have used feed molar ratio to describe the results unless otherwise NMR measured composition ratio is stated.

Table 1.2 Feed and copolymer compositions of AN/VIM copolymers by starve-fed addition*

Sample	In Feed (mol%)		In Copolymer ^a (mol%)	
	VIM	AN	VIM	AN
CF16	0	100	0	100
CF28	10	90	14	86
CF26	12	88	16	84
CF33	18	82	22	78
CF39-3	21	79	27	73
CF35-2	25	75	37	63

^a Determined by ¹H NMR

* Solution polymerization of AN and VIM in DMF initiated by AIBN at 70 °C for 16 h

A typical ¹H NMR spectrum of 82/18 AN/VIM copolymer is shown in **Figure 1.5**. ¹H NMR signals at δ 2.0 represent the backbone CH₂ from VIM and AN linkages. Signals at δ 3.1 indicate backbone CH units from AN enchainment, while signals at δ 4.4 represent backbone CH of VIM and signals ranging δ 7.8- 6.8 describe the unsaturated CH groups in VIM. **Figure 1.6** depicts the ATR-FTIR spectrum of 82/18 AN/VIM copolymer **CF33**. Backbone CH₂ stretching for the AN unit occurs at 2922 cm⁻¹ and CN stretching signals are clearly visible at 2243 cm⁻¹. For the VIM unit, C-H ring stretching was observed at 3117 cm⁻¹, backbone CH₂ stretching at 2922 cm⁻¹, C-N ring stretching at 1229 cm⁻¹, C-H ring in-phase bending at 1082 cm⁻¹ and C-N= ring stretching at 665 cm⁻¹.

Figure 1.5 ^1H NMR of 82/18 AN/VIM copolymer **CF33** (in $\text{DMSO-}d_6$)

Figure 1.6 ATR-FTIR spectrum of 82/18 AN/VIM copolymer **CF33**

Relative molecular weights of AN/VIM copolymers to polystyrene standards were determined using size exclusion chromatography in DMF. A bimodal distribution in GPC curve was observed for all copolymer compositions. The bimodal distribution curve of 82/18 AN/VIM copolymer ($\overline{M}_n = 31,734$ g/mol, $\overline{M}_w = 82,508$ g/mol, PDI = 2.6) is shown in **Figure 1.7**. For the current study, the molecular weight is reported for the larger fraction, which corresponds to the bigger peak occurring around 18 min elution time, since the smaller fraction (corresponding to the smaller peak occurring around 14 min elution time) exceeds the calibration range (maximum 3,390,000 g/mol). Particle size and distribution curves (three repeated tests) of the copolymer solution were

observed in the DLS (**Figure 1.8**). This bimodal distribution in GPC could possibly be due to chain transfer of copolymer [41] or due to attack on the other polymerization site of pendant imidazole group [42] which may lead to branching.

Figure 1.7 Gel permeation chromatogram of 82/18 AN/VIM copolymer **CF33** in DMF

Figure 1.8 Particle size of 82/18 AN/VIM copolymer **CF33** in DMF solution by DLS

Figure 1.9 shows the DSC curves of polyacrylonitrile and AN/VIM copolymers from 60 to 200 °C. No T_g signal was observed in the case of acrylonitrile homopolymer [35] but copolymers exhibited T_g values *i.e.* T_g of 87/13 AN/VIM copolymer at 117 °C; T_g of 84/16 AN/VIM copolymer at 106 °C. For 81/19 AN/VIM copolymer, two T_g were exhibited, T_{g1} at 93 °C and T_{g2} at 160 °C. Other researchers have also observed these two transitions and were attributed to the onset of backbone chain mobility and intermolecular bonding associated with the nitrile groups [44-46]. The decrease in transition temperatures T_{g1} and T_{g2} with the increase of VIM molar ratio can be attributed to the disrupted long-range order of the acrylonitrile structure by the introduction of the comonomer with bulky side substituent hence resulting in reduction in dipole-dipole

interactions. However, no clear melting peak was observed by DSC curve for the copolymers, which is consistent with the other reports [47]. For the polymers with high acrylonitrile content, a first-order phase transition is typically not observed due to interchain interactions between polar nitrile substituents as reported by Hutchinson *et al* [48].

Figure 1.9 DSC thermograms of (a) AN homopolymer; (b) 87/13AN/VIM; (c) 84/16 AN/VIM; and (d) 81/19 AN/VIM copolymers (10 °C/min, in N₂)

TGA studies were performed to determine the initial decomposition temperature and char yield of the copolymers. The initial decomposition temperature of the

copolymers was 300-310 °C. A representative TGA curve of 82/18 AN/VIM copolymer **CF33** is shown in **Figure 1.10**. All the copolymers showed rapid weight loss when the temperature is higher than approximately 310 °C.

Figure 1.10 TGA curve of 82/18 AN/VIM copolymer **CF33** (10 °C/min, in N₂)

Carbon yield of precursor polymers

Char yields of various AN/VIM copolymers (**Table 1.3**) were obtained by TGA under the similar conditions as was reported by McGrath *et al.* [28]. The average char yields of AN/VIM copolymers were found to be in the range of 40-48% depending upon the composition of copolymers. The copolymers with 10-18% VIM have the char yields of 47-48%, which are comparable with that of commercial PAN fibers *i.e.* 50% [49]. This led us to conclude that VIM concentration 10- 18 mol% can be effectively used for carbon fiber precursors. We also have examined several its terpolymers, AN/VIM/IP,

AN/VIM/St and AN/VIM/MA, which shows lower char yield, **Table 1.4**, and limit their application as carbon fiber precursors.

Table 1.3 Char Yield of Various AN/VIM Copolymers

AN/VIM copolymer (Feed mol%)	Char yield Wt (%)
90 / 10	47
88 / 12	48
82 / 18	47
79 / 21	40
75 / 25	40

Table 1.4 Char yield of terpolymers

Terpolymer (feed mol%)	Char yield (%)
AN/VIM/IP (82/12/6)	40
AN/VIM/St (82/12/6)	38
AN/VIM/MA (79/18/3)	40
AN/VIM/MA (84/10/6)	38

Gel fraction of AN/VIM copolymer precursors

Cross-linking ability of AN/VIM copolymer precursors was determined by using their gel fraction after heating at 210 °C/2 h or 250 °C/5 h in air. The color of copolymers

changed from white to brown and then black during stabilization as expected. The stabilized black copolymers were insoluble in dimethylformamide (DMF), showing good cross-linking ability (**Figure 1.11**). The average gel fraction of 88/12 AN/VIM copolymer was about 99% while average gel fraction of 82/18 AN/VIM copolymers was ~ 90% at 210 °C/2h in the air. However, at higher temperature and longer time (250 °C/5h), the gel fraction of 82/18 AN/VIM copolymer increased to 99%. The requirement of higher temperature with increasing VIM concentration to get high gel fraction may be due to presence of comonomers with bulky side groups which introduces a slower step in the stabilization [47]. Bulky imidazole group needs higher temperature and longer time to undergo intra-molecular cyclization or inter-molecular cross-linking reaction than that of nitrile group.

The gel fractions of these thermally stabilized copolymers are better than the gel fraction (~ 65%) of melt-spun carbon fiber precursor which is stabilized by UV light [50]. Both gel fraction and char yield results support that AN/VIM copolymers can be thermally cross-linked in air, which makes it a promising carbon fiber precursor.

Figure 1.11 Photographs of copolymers before and after oxidation during gel fraction experiment (Oxidized copolymer retained its shape in DMF even after 7 days.)

Conclusions

AN/VIM copolymers with various molar ratio of VIM were successfully prepared and characterized. DSC results show that T_g decreases with the increasing VIM content, which suggests the VIM helped to disrupt interchain interactions of AN unites. High gel fraction and char yield of the copolymer shows its thermally cross-linking ability.

Experimental

Materials

2,2'-Azobis(2-methylpropionitrile) (AIBN), 1-vinylimidazole (VIM), acrylonitrile(AN), isoprene(IP), styrene(St), N,N-dimethylformamide (DMF), dimethyl

sulfoxide (DMSO) and 1-Dodecanethiol were purchased from the Aldrich Chemical Co. All reagents were used as received.

Synthesis of carbon fiber precursor copolymer CF4-42

The solution polymerization of AN and VIM by varying feed ratio was carried out in a 250 mL flask fitted with a thermocouple probe, condenser, addition funnel and nitrogen inlet. The flask was charged with 60 mL DMF and purged with nitrogen for 30 min. Then the monomers, AIBN and chain transfer agent, 1-dodecanethiol were added drop wise into the flask over a period of 2-5 h. The polymerization reactions were carried out at 70 °C with continuous stirring. The polymer was precipitated in excess de-ionized water, filtered and washed with methanol and hexane to remove residual monomers and then dried in vacuum oven for two days till constant weight was obtained.

Characterization of copolymer precursors

¹H NMR spectrum was obtained with JEOL ECX-300 spectrometer using DMSO-*d*₆ as solvent. Size exclusion chromatography (SEC) was used to determine the molecular weights of polymers in *N,N*-dimethylformamide (DMF) at 50 °C at 1 mL/min flow rate on a Waters SEC instrument equipped with two Waters Styragel HR5E (DMF) columns, a Waters 717 plus autosampler, a Waters 2414 differential refractive index detector and a Wyatt Technologies miniDAWN multiangle laser light scattering (MALLS) detector. Malvern Zetasizer Nano was used for dynamic light scattering of polymer solution (1mg/mL, 25 °C) and three test cycles were carried out.

Attenuated total reflectance Fourier transform infrared (ATR–FTIR) analysis of copolymers was performed on a Thermo-Nicolet Magna 550 FTIR spectrophotometer with a high endurance diamond ATR attachment. The thermal stability and char yield of all the copolymers were performed by using Mettler-Toledo 851 thermogravimetric analyzer at controlled conditions of temperature and time conditions to simulate the similar conditions as those used in conversion of precursors into carbon fibers [28]. Differential scanning calorimetry (DSC) was performed on a TA Q1000 instrument in nitrogen at a heating rate of 10 °C min⁻¹. The glass transition temperature (T_g) was obtained from a second heating cycle using TA Universal Analysis 2000 software suite.

Char yield and gel fraction testing

Char yields of the copolymers were obtained by heating at 10 °C/min from ambient temperature to 220 °C in air followed by isothermal at 220 °C for 3 h with increase in temperature from 220 to 550 °C in N₂ and again isothermal at 550 °C for 3 h in N₂ [28]. In order to calculate the gel fraction, these copolymers were first stabilized by heating at 210 °C for 2 h or 250 °C for 5 h respectively in an oven under air and then they were immersed in DMF solvent for 3 days. The gels were dried in vacuum for 7 days till constant weight.

CHAPTER TWO

MELT PROCESSING OF POLY (ACRYLONITRILE-*CO*-1-VINYLMIDAZOLE) CARBON FIBER PRECURSOR

Introduction

Polymers show a combination of elastic and viscous behavior known as viscoelasticity [51-55]. Dynamic oscillatory shear study is a useful method to evaluate viscoelastic property of the polymer [56-66], which provides important information for processing the polymer. Dynamic oscillatory shear studies of 1-vinylimidazole and acrylonitrile terpolymers with isoprene (IP) and styrene (St) respectively have not been reported. In this research, 1-vinylimidazole (VIM) as a comonomer was introduced to disrupt the PAN crystallinity in order to make it melt processable; and the double bonds in the pendant 1-vinylimidazole ring capable of being activated by heat make it thermally cross-linkable during stabilization process. Dynamic viscosity of 1-vinylimidazole and acrylonitrile polymer with different composition was examined to determine the suitable one chosen for melt-spinning. The dynamic temperature sweeps of polymers were studied at 0.1 rad/s and 0.1% strain, which showed the amount of VIM in polymer clearly affected its storage modulus (G'), loss modulus (G'') and complex viscosity (η^*). One critical temperature exists for all the polymers, above which, the η^* , G' and G'' all increased instead of continuing to decrease with temperature rise due to the reactions between active pendant groups. Viscoelastic properties of 1-vinylimidazole and acrylonitrile with isoprene and styrene respectively were also examined by dynamic oscillatory shear experiments. Successful melt spinning of 82/18 AN/VIM copolymer

precursor was carried out at 192 °C and the resulting melt-spun fiber was characterized by XRD, DSC and ATR-IR.

Dynamic oscillatory shear properties of acrylonitrile and 1-vinylimidazole copolymers

Dynamic strain sweep of 82/18 AN/VIM copolymer CF33

Viscosity is an important parameter for polymer processing and low viscosity is desirable for the melt-spinning process. To ensure that dynamic oscillatory measurements were made in the linear viscoelastic region for 82/18 AN/VIM **CF33** (feed molar ratio) polymer in this study, strain sweeps were performed at 200 °C (**Figure 2.1**) which is well below the cross-linking and degradation temperature of these copolymers. The storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) was found to be constant up to a strain of 10% for all the AN/VIM copolymer compositions. In this research, viscosity of AN/VIM copolymer with varying VIM composition was measured by dynamic temperature sweep at 0.1 rad/s and 0.1% strain.

Figure 2.1 Dynamic strain sweep of 82/18 AN/VIM copolymer **CF33** (200 °C, 10 rad/sec)

Dynamic temperature sweep of various AN/VIM copolymers

A significant dependence of the dynamic melt viscosity on the copolymer composition was observed. The dependence of G' , G'' and η^* of AN/VIM copolymer on temperature was reported here. It was found that properties varied with change in concentration of VIM while keeping all other components constant. The polymers used in this research have a M_n around 30,000-40,000, which is required by its melt-spinning process. The viscosity of polyacrylonitrile homopolymer was so high that the rheometer was overloaded and there is no data that can be obtained. While AN/VIM copolymers showed lower viscosities, the data obtained are shown in **Figure 2.2-2.5**.

Viscosities of AN/VIM copolymers with VIM amount in the range of 10-16% are not low enough for melt-spinning. Dynamic temperature sweep of 86/14 AN/VIM copolymer **CF28** is shown in **Figure 2.2**. At 161 °C, the copolymer had a high viscosity value of 120,000 Pa-s, and G' and G'' were also high. With the temperature raise, η^* , G' and G'' all decreased. At 188 °C, G' and G'' had their lowest values of 3201 and 2044 Pa, respectively. At 192 °C, its viscosity reached the lowest value around 55,060 Pa-s. Above that, the η^* , G' and G'' all started to increase with temperature, which showed certain reactions took place around 192 °C. Tan delta is the ratio of loss modulus to storage modulus. High tan delta value indicates the material has good flexibility; while low tan delta means the material is stiff. Tan delta values less than 1 showed that 86/14 AN/VIM copolymer had more solid character during 160-230 °C, except for 192 °C. The dynamic oscillatory shear property indicates crystallinity of 86/14 AN/VIM copolymer has not been disrupted in long-range order.

Figure 2.2 Dynamic temperature sweep of 86/14 AN/VIM copolymer **CF28** (0.1 rad/s, 0.1% strain)

Viscosities of AN/VIM copolymers with VIM amount in the range of 18-32% shows much lower viscosity. VIM amount in this range effectively disrupted PAN crystallinity. Dynamic temperature sweep of 74/26 AN/VIM copolymer **CF27** is shown in **Figure 2.3**. At 162 °C, the copolymer had a high viscosity value of 41,700 Pa-s, also G' and G'' were high. With the increase of the temperature, all of them decreased. At 200 °C, the η^* , G' and G'' all reached their lowest values of 6650 Pa-s, 366 and 554 Pa, respectively. These values are much lower than that of 86/14 AN/VIM copolymer. Tan delta values higher than 1 showed that 74/26 AN/VIM copolymer had more liquid character during 170-200 °C. Above 206 °C, the η^* , G' and G'' of 74/26 AN/VIM copolymer all increased with temperature and tan delta values changed to be less than 1, which suggests certain reactions took place at higher temperature. This happened due to the reactions between active pendant groups, which would be useful for stabilization process of carbon fiber manufacture.

Figure 2.3 Dynamic temperature sweep of 74/26 AN/VIM copolymer **CF27** (0.1 rad/s, 0.1% strain)

Higher viscosity was observed for the copolymer with VIM amount higher than 35%. Dynamic temperature sweep of 63/37 AN/VIM copolymer **CF39** is shown in **Figure 2.4**. At 166 °C, the copolymer had a high viscosity value of 132,000 Pa-s, also G' and G'' were high. With temperature increase, η*, G' and G'' all decreased. At 203 °C, G' reached its lowest value, 1092 Pa. At 212 °C, the η* and G'' researched their lowest values of 32,038 Pa-s and 2960 Pa, respectively. Above that, the η*, G' and G'' all started to increase with temperature, which showed certain reactions took place around 212 °C. Tan delta value of 3 showed it had clear liquid property at 203 °C. Above 219 °C, tan delta values less than 1 indicated it started to show more solid property. 63/37

AN/VIM copolymer showed higher viscosity than that of 74/26 AN/VIM copolymer, which is possibly because of the large and bulky pendant group of VIM preventing the polymer chains from sliding past each other easily.

Figure 2.4 Dynamic temperature sweep of 63/37 AN/VIM copolymer **CF39** (0.1 rad/s, 0.1% strain)

Dynamic temperature sweep of 55/45 AN/VIM copolymer **CF35** is shown in **Figure 2.5**. At 165 °C, the copolymer had a very high viscosity value of 358,000 Pa-s, also G' and G'' were very high. With temperature raise, all of them decreased. At 213 °C, the η^* , G' and G'' all reached their lowest values of 55,453 Pa-s, 3644 and 4179 Pa, respectively. Above that, they all increased with temperature, which showed the

reactions happened around 219 °C. Tan delta values higher than 1 showed it had more liquid character at 184-225 °C. The reactions between active pendant groups took place at higher temperature when VIM amount in AN/VIM copolymer increased. This suggests VIM can introduce slower stabilization for carbon fiber manufacture.

Figure 2.5 Dynamic temperature sweep of 55/45 AN/VIM copolymer **CF35** (0.1 rad/s, 0.1% strain)

AN/VIM copolymer with different composition showed different viscoelastic property. But there is one thing in common for all the AN/VIM copolymers, which is, at certain temperature, the η^* , G' and G'' all increased instead of continuing decrease with temperature raise. This is due to the reactions between active pendant groups of AN/VIM copolymer, which is important for stabilization process of carbon fiber manufacture and make it a promising carbon fiber precursor.

Dynamic frequency sweep of 74/26 AN/VIM copolymer

The lowest viscosity was observed in the range including 18-32% VIM, which makes it the interesting candidate for melt-spinning, other experiments were designed to better understand the rheological property of the copolymer with 18-32% VIM. 74/26 AN/VIM copolymer was chosen to investigate the dependence of viscoelastic property on frequency. Dynamic frequency sweep ranging between 0.1-100 rad/s was performed at 0.1% strain and 180 °C (**Figure 2.6**). With the frequency increase, G' and G'' both increased, while its viscosity decreased from 41,000 Pa-s at 0.05 rad/s to 895 Pa-s at 79 rad/s. At lower frequency (< 0.7 rad/s), 74/26 AN/VIM copolymer showed more liquid property ($\tan \delta > 1$). While at 0.79 rad/s, the G' value (9600 Pa) started to be higher than the G'' value (8797 Pa). $\tan \delta$ values decreased with frequency increased. The copolymer showed more solid character at higher frequency. The frequency-dependent viscoelastic property of AN/VIM copolymer was observed. The copolymer viscosity decreased sharply when the frequency increased.

Figure 2.6 Dynamic frequency sweep of 74/26 AN/VIM copolymer (180 °C, 0.1% strain)

Dynamic time sweep of 82/18 AN/VIM copolymer CF33

The viscosity of copolymer precursor is required to be stable at the melt-spinning temperature for a certain time for fiber drawing. Dynamic time sweep was used to determine the viscosity stability of 82/18 AN/VIM copolymer **CF33** precursor. At 205 °C, the viscosity of copolymer precursor was relatively steady for 25 min, while at 210 °C the viscosity increased sharply after 20 min (**Figure 2.7**). The high jump in viscosity observed is likely due to the intermolecular cross-linking. In order to ensure a steady copolymer viscosity for an easy processability in 25 min, the melt-spinning temperature of 82/18 AN/VIM copolymer should be lower than 210 °C.

Figure 2.7 Dynamic time sweep viscosity of 82/18 AN/VIM copolymer **CF33** at 0.1% strain, 1 rad/s, at 205 °C and 210 °C.

Dynamic oscillatory shear properties of AN/VIM/St and AN/VIM/IP terpolymers

Dynamic temperature sweep of AN/VIM/St (CF42) and AN/VIM/IP (CF29) terpolymers

For melt-spinning, low and stable viscosity of molten polymer at drawing temperature is required. Therefore, a third monomer was introduced to synthesize with acrylonitrile and 1-vinylimidazole to form the terpolymer for possible better property suited for melt-spinning. Acrylonitrile, 1-vinylimidazole and isoprene terpolymer was synthesized at feed molar ratio of 82/12/6 (AN/VIM/IP). Dynamic temperature sweep of 82/12/6 (AN/VIM/IP) **CF29** terpolymer was examined and shown in **Figure 2.8**. Acrylonitrile, 1-vinylimidazole and styrene terpolymer was also synthesized at feed

molar ratio of 82/12/6 (AN/VIM/St **CF42**). Dynamic temperature sweep of 82/12/6 AN/VIM/St terpolymer is shown in **Figure 2.9**.

At 160 °C, 82/12/6 AN/VIM/IP terpolymer **CF29** had a high viscosity value of 49,835 Pa-s, G' and G'' were also high. With the temperature increase, all of them decreased. At 188 °C, G' had its lowest values of 1513 Pa. At 194 °C, its η^* and G'' reached the lowest values of 17,907 Pa-s and 569 Pa, respectively. Above that, the η^* , G' and G'' all started to increase with temperature, which showed the reactions took place around 202 °C. Tan delta values less than 1 showed it had more solid character during 160-217 °C, only except for 188 °C. Dynamic temperature sweep of 82/12/6 AN/VIM/IP terpolymer showed that isoprene added did not effectively lower the viscosity of the polymer.

Figure 2.8 Dynamic temperature sweep of 82/12/6 AN/VIM/IP terpolymer **CF29** (0.1 rad/s, 0.1% strain)

In **Figure 2.9**, 82/12/6 AN/VIM/St terpolymer **CF42** had a high viscosity value of 59,404 Pa-s, also G' and G'' were high at 165 °C. With temperature increase, η^* , G' and G'' all decreased. At 202 °C, its η^* , G' and G'' reached the lowest values of 7122 Pa-s, 638 and 316 Pa, respectively. Above 210 °C, the η^* , G' and G'' increased with temperature, where the reactions took place. 82/12/6 AN/VIM/St terpolymer showed low viscosity similar as 74/26 AN/VIM copolymer, so we are interested to know if it is more stable than AN/VIM copolymer at high drawing temperature.

Figure 2.9 Dynamic temperature sweep of 82/12/6 AN/VIM/St terpolymer **CF42** (0.1 rad/s, 0.1% strain)

Dynamic time sweep of AN/VIM/St terpolymer CF42

We have discussed that 82/18 AN/VIM (feed molar ratio) copolymer can be stable at 205 °C, but can not be stable at 210 °C for 25 min. While 82/12/6 AN/VIM/St terpolymer **CF42** can be stable at 210 °C shown in **Figure 2.10**. The starting η^* , G' and G'' of 82/12/6 AN/VIM/St terpolymer are 8879 Pa-s, 4858 and 7433 Pa, respectively. After 30 min, its η^* , G' and G'' increased gradually to 10,374 Pa-s, 7224 and 7446 Pa, respectively. Its G'' almost did not change at all. On the contrary the G' increased about 44% and the viscosity increased 16% after 30 min. Its tan delta values decreased from 1.5 at the beginning to 1.0 after 30 min. But higher than 1 indicates 82/12/6 AN/VIM/St terpolymer shows more liquid character at 210 °C.

Figure 2.10 Dynamic time sweep of 82/12/6 AN/VIM/St terpolymer **CF42** (210 °C, 1 rad/s, 0.1% strain)

It seemed styrene could help to stable the polymer at higher temperature. But unfortunately, including Styrene damaged its carbon yield. The carbon yield of 82/12/6 AN/VIM/St terpolymer was only 38%, while the value of 82/18 AN/VIM copolymer was 47%. The low carbon yield of AN/VIM/St terpolymer limits its application as carbon fiber precursor.

Characterization of the melt spun fiber

The materials used for melt-spinning should be able to withstand the high stretching during drawing process under the high draw ratio, which requires certain molecular weight and cohesive energy of the polymers. If the molecular weight of the polymer is too low, or the polymer does not have high enough cohesive energy, the fiber can not be drawn continuously. 82/18 AN/VIM copolymer **CF27** has a low Mw of 23,000, which showed discontinuity in the melt-spinning process while 82/18 AN/VIM copolymer **CF33** has a high Mw of 32,000, which showed continuity. The AN/VIM copolymer **CF33** was used for melt-spinning. The copolymer **CF33** with 82/18 AN/VIM (feed molar ratio) composition, which has low viscosity and good char yield of 47%, was selected for further studies.

Fiber spinning was performed by Dr. Alexander Lobovsky at Advanced Fiber Engineering, LLC, West field, NJ. 82/18 AN/VIM copolymer precursor ($[\eta] = 0.59$ dL/g) was ground into coarse granules in a grinder and these copolymer granules were vacuum dried at 65 °C for 3 hrs. In a typical trial, ~ 9 g of copolymer was loaded in

preheated rheometer at 180 °C under nitrogen atmosphere and left there to heat up for 10 min, after that drawing temperature was raised to 192 °C. Melt spun fiber was collected by winding on 3 inches diameter bobbin rotating at 84 rpm. Successful melt-spun fiber of 82/18 AN/VIM copolymer **CF33** drawn at 192 °C is shown in **Figure 2.11** and characterized by ATR-IR, DSC and X-ray diffraction.

Figure 2.11 Photograph of melt spun fiber of 82/18 AN/VIM **CF33** (by Dr. Alexander Lobovsky at Advanced Fiber Engineering, LLC, Westfield, NJ)

The X-ray diffraction spectrum of melt spun fiber of 82/18 AN/VIM copolymer **CF33**, **Figure 2.12** was used to determine the preferred orientation of carbon layers and degree of crystallinity. A sharp reflection peak at 5.8 Å was observed (**Figure 2.12**), which is comparable to that reported by Bashir et al. [67]. The author has mentioned that the PAN chains adopts a rod-like conformation and may undergo packing in lateral domains which could lead to clusters of nitrile dipoles in interchains and lead to

conjugated -CN groups without a cyclic structure. The degree of crystallinity in melt spun fiber was about 35%, which is the ratio of the sharp peak area to the total area.

Figure 2.12 X-ray diffraction spectrum of melt-spun fiber of 82/18 AN/VIM CF33 (Cnt time: 1. 300 sec; Step scan rate: 0.02 deg/min; Range: 5.00 – 70.00 (Deg))

The ATR-IR spectrum is shown in **Figure 2.13** where N-H stretching at 3373 cm^{-1} , C-H ring stretching at 3117 cm^{-1} , backbone C-H stretching at 2923 cm^{-1} , $\text{C}\equiv\text{N}$ stretching at 2242 cm^{-1} , C=C stretching at 1662 cm^{-1} , C=N ring stretch at 1496 cm^{-1} , and imidazole ring vibrations at 1229 , 1083 , 664 cm^{-1} are observed in the copolymer as well as its melt-spun fiber. This indicates that no significant cross-linking was observed even after processing at $192\text{ }^{\circ}\text{C}$. The T_g of 82/18 AN/VIM copolymer as well as its melt-spun

fiber ((**Figure 2.14**) was around 108 °C, which is in good agreement with above mentioned result.

Figure 2.13 ATR-FTIR spectrum of (a) 82/18 AN/VIM copolymer **CF33** before melt processing, (b) melt spun fiber of 82/18 AN/VIM **CF33**

Figure 2.14 DSC thermograms of (a) 82/18 AN/VIM copolymer **CF33** before melt processing; (b) melt spun fiber of 82/18 AN/VIM **CF33** (10 °C/min, in N₂)

Conclusions

Dynamic oscillatory shear experiments showed the amount of VIM in AN/VIM copolymer clearly affected its G' , G'' and η^* . The lowest viscosity was observed in the range including 18-26% VIM. There is one critical temperature existing for each 1-vinylimidazole and acrylonitrile polymer, above which, the η^* , G' and G'' all increased instead of continuing decrease with temperature rise, which is due to the reactions between active pendant groups. This property is useful for stabilization process of carbon fiber manufactur. Successful melt spinning of the 82/18 AN/VIM (feed molar ratio)

copolymer precursor was carried out at 192 °C and the resulting melt-spun fiber was characterized by XRD, DSC and ATR-IR.

Experimental

Materials

2,2'-Azobis(2-methylpropionitrile) (AIBN), 1-vinylimidazole (VIM), acrylonitrile (AN), isoprene(IP), styrene(St), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and 1-Dodecanethiol were purchased from the Aldrich Chemical Co. All reagents were used as received.

Synthesis of the polymers CF27-42

The solution polymerization of the polymer by varying feed ratio was carried out in a 250 mL flask fitted with a thermocouple probe, condenser, addition funnel and nitrogen inlet. The flask was charged with DMF and purged with nitrogen. Then the monomers, AIBN and chain transfer agent, 1-dodecanethiol were added drop wise into the flask over a period of 2-5 h. The polymerization reaction was carried out at 70 °C with continuous stirring. The polymer was precipitated in excess de-ionized water, filtered and washed with methanol to remove residual monomers and then dried in vacuum oven for two days till constant weight was obtained.

Melt-spinning of AN/VIM copolymer precursor CF33

Fiber spinning was performed at Advanced Fiber Engineering, LLC, West field, NJ. 82/18 AN/VIM copolymer CF33 precursor ($[\eta] = 0.59 \text{ dL/g}$) was ground into coarse granules in a grinder and these copolymer granules were vacuum dried at 65°C for 3 hrs. An Instron 3211 capillary rheometer (capillary diameter, $D = 0.030$ inches) was used to draw the fibers. In a typical trial, $\sim 9 \text{ g}$ of copolymer was loaded in preheated rheometer at 180°C under nitrogen atmosphere and left there to heat up for 10 min, after that drawing temperature was raised to 192°C . Melt spun fiber was collected by winding on 3 inches diameter bobbin rotating at 84 rpm.

Characterization of the polymer precursors and melt spun fiber

^1H NMR spectrum was obtained with JEOL ECX-300 spectrometer using $\text{DMSO-}d_6$ as solvent. The VIM content of copolymer was measured by ^1H NMR. In this study we have used NMR measured composition ratios to describe the results unless otherwise feed molar ratio is stated. Attenuated total reflectance Fourier transform infrared (ATR–FTIR) analysis of copolymers was performed on a Thermo-Nicolet Magna 550 FTIR spectrophotometer with a high endurance diamond ATR attachment. Differential scanning calorimetry (DSC) was performed on a TA Q1000 instrument in nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$ to 200°C . The glass transition temperature (T_g) was obtained from a second heating cycle using TA Universal Analysis 2000 software suite. Size exclusion chromatography (SEC) was used to determine the molecular weights of polymers in *N,N*-dimethylformamide (DMF) at 50°C at 1 mL/min flow rate on a Waters

SEC instrument equipped with two Waters Styragel HR5E (DMF) columns, a Waters 717 plus autosampler, a Waters 2414 differential refractive index detector and a Wyatt Technologies miniDAWN multiangle laser light scattering (MALLS) detector.

Dynamic oscillatory shear properties of 1-vinylimidazole polymers were determined by well calibrated TA instruments ARES LS/M LS001-270i (Rheometric Scientific) in N₂ atmosphere. Cone-and-plate, oscillatory shear mode and strain control were applied. Strain sweep was conducted at 10 rad/s and 200 °C in order to determine the linear viscoelastic region of these copolymers. The dynamic temperature sweep of polymers was studied at 0.1 rad/s and 0.1% strain. Dynamic frequency sweep ranging between 0.1-100 rad/s was performed at 0.1% strain and 180 °C. The dynamic time sweep was carried out at 0.1% strain and angular frequency of 1 rad/s at 205 °C and 210 °C. Ostwald Viscometer was used to measure the intrinsic viscosity ($[\eta]$) of copolymer in (0.01 g/mL polymer in DMSO at 25 °C) by using following equation [38]:

$$[\eta] = \left(\frac{\sqrt{2}}{c} \right) (\eta_{sp} - \ln \eta_{rel})^{0.5}$$

Where $[\eta]$ is intrinsic viscosity, c = concentration of polymer solution (g/dL); η_{sp} = specific viscosity; η_{rel} = relative viscosity. The Scintag XDS 2000 x-ray diffractometer was used for X-ray diffraction analysis of melt-spun fiber.

CHAPTER THREE

THERMAL STABILIZATION OF POLY (ACRYLONITRILE-CO-1-VINYLMIDAZOLE) MELT-SPUN FIBER

Introduction

Thermal treatment of commercial carbon fiber generally involves stabilization, carbonization and graphitization processes [68-70]. The oxidative stabilization of the fiber is to form ladder structure, which enables it withstand higher temperature. The carbonization of the fiber is to remove all the non-carbon atoms. Then graphitization of the fiber would improve its orientation and stiffness [71]. During the manufacture process, obvious color change of the fiber can be observed. The white as-spun fiber changes its color to yellow, brown, then dark brown, finally become black [71].

Commercial carbon fiber precursors are stabilized first at 200-300 °C in air [72, 73], which breaks many of the hydrogen bonds and oxidizes the precursors. There are several dominant reactions during oxidative stabilization including the intra-molecular nitrile reaction with the formation of cyclized C=N containing structures (the ladder polymer) (**Figure 3.1**) [73], the hydrogen elimination leading to the formation of conjugated C=C structures on the chain back-bone (**Figure 3.2**) [71], oxidation of the ladder polymer (**Figure 3.3**) [74] and the inter-molecular nitrile reaction forming cross-linking to prevent fiber fusion (**Figure 3.4**) [74]. HCN can be released by condensation reactions between ladder structures [74].

Figure 3.1 Intra-molecular nitrile reaction with the formation of C=N containing ladder Structure (Reprinted with permission from Bashir Z. Carbon 1991; 29(8): 1081-1090 Copyright © 1991, Elsevier under the license number 2551531154163) [73]

Figure 3.2 The dehydrogenation eliminations during stabilization process (Reprinted with permission from Rahaman M S A, Ismail A F, Mustafa A. J Polym Degrad and Stab 2007; 92(8): 1421-1432 Copyright © 1991, Elsevier under the license number 2551540066692) [71]

Figure 3.3 Oxidation of ladder polymer a) Ladder polymer b) Oxidation to hydro peroxide c) Keto-formation by loss of water d) Tautomeric change to hydroxy-pyridine structure e) Tautomeric change to pyridone structure [74]

Figure 3.4 Cross-linking of ladder polymer by loss of H_2 [74]

The oxidized PAN precursor is subjected to heat above $1000\text{ }^{\circ}\text{C}$ in inert atmosphere, which induces the carbonization and graphitization of the precursor by changing the molecular bond structure (**Figure 3.5**) [74]. When heated in the right conditions, these chains bond side-to-side, forming graphene sheets. The resulting fibers usually contain 93–95% carbon [68, 75-83].

Figure 3.5 Cross-linking of layers by loss of N_2 [74]

Stabilization is an essential step to form cross-linking chains and prepare a structure which can withstand high temperature [84-87]. Poor stabilization can cause

excessive weight-loss during carbonization and graphitization processes and lead to carbon fiber product with poor properties [69]. Thermal stabilization of melt processable carbon fiber precursor [88-91] is still a challenge. UV light is required to enhance stabilization [92], which is an expensive affair and limits their applications. In this study, thermal stabilization of poly (acrylonitrile-co-1-vinylimidazole) melt-spun fiber was discussed. This new carbon fiber precursor introduced the commercially available 1-vinylimidazole (VIM) as a comonomer to make it melt processable by disrupting the PAN crystallinity; while the double bonds in pendant 1-vinylimidazole ring capable of being activated by heat make it thermally cross-linkable during stabilization process. In the present paper, the thermal, mechanical and morphological characterization techniques including TGA, DMA and SEM were employed for analyzing stabilized melt-spun fiber. The change of fiber structure during stabilization process was confirmed by ATR-IR spectra.

Effect of oxygen (O₂) on stabilization of 82/18 AN/VIM CF33 melt-spun fiber

Stabilization of 82/18 AN/VIM **CF33** melt-spun fiber was carried under air or N₂ to examine the effect of oxygen (O₂). Char yields were used to evaluate the effect of O₂ on the stabilization. The procedure is described in section 2.5. The different stabilization conditions led to different char yield results. The melt-spun fiber stabilized in O₂ showed high char yield of 46%; while those stabilized in N₂ had a char yield value of 37%. The decrease of char yield from 46% to 37% shows that O₂ was involved in the stabilization of AN/VIM melt-spun fiber and gave it important assistance. Stabilization without O₂

resulted in poor stabilization, caused more weight-loss at 550 °C and led to lower char yield. Based on better stabilization in O₂, all the following stabilization experiments in this study were performed in air.

Conditions of oxidative stabilization

Oxidative stabilization is an exothermic process therefore, temperature control is very important. If the stabilization temperature is too high, fusion and chain scission, even burning would happen; while if the temperature is too low, incomplete stabilization and poor carbon yield might be caused. Oxidative stabilizations of 82/18 AN/VIM **CF33** melt-spun fiber were carried under different temperatures ranging from 210-250 °C by varying the time from 80 to 300 minutes in air (**Table 3. 1**) to observe the structure change during stabilization and determine the optimum condition. The stabilization temperatures were chosen based on the rheological study of 82/18 AN/VIM precursor, which showed the high jump in viscosity due to the intermolecular cross-linking occurred above 210 °C. **Figure 3.6 (left)** shows the filaments of 82/18 AN/VIM as-spun fiber were lined up at the fixed length and stabilized under the conditions shown in **Table 3.1**. After the oxidative stabilization, the color of filaments changed from yellow to black (**Figure 3.6 right**), which is believed to be due to the formation of a ladder ring structure [93]. The change in structure during stabilization was also confirmed by using ATR-IR.

Table 3.1 Conditions of oxidative stabilization of 82/18 AN/VIM **CF33** melt-spun fiber*

Reaction	Temperature (°C)	Oxidation time (min)
1	210	80
2	210	120
3	220	120
4	230	90
5	230	120
6	250	120
7	250	300

* in air

Figure 3.6 Photos of melt-spun fiber of 82/18 AN/VIM copolymer **CF33**: as-spun fiber color is yellow (left); oxidized fiber color is black (right)

ATR-IR spectra of oxidized melt-spun fibers

ATR-IR spectra of oxidized melt-spun fibers were applied to examine the change of fiber structure during the stabilization process. The ATR-IR of oxidized fiber stabilized at different conditions is shown in **Figure 3.7**. The ATR-IR spectrum of oxidized melt-spun fiber of 82/18 AN/VIM **CF33** precursor (210 °C / 80 min) is shown in **Figure 3.7 (b)**, where O-H and N-H stretching at 3351 cm⁻¹, backbone C-H stretching at 2926 cm⁻¹, C≡N stretching at 2241 cm⁻¹, and imidazole ring vibrations at 1229, 1083, 664 cm⁻¹ are observed in this oxidized fiber as well as its as-spun fiber (**Figure 3.7(a)**). A new peak 1618 cm⁻¹ appeared, which may be attributed to the conjugated C=N-C=C stretching.

ATR-IR spectrum of oxidized melt-spun fiber of 82/18 AN/VIM precursor (220 °C/ 2h) is shown in **Figure 3.7 (c)** where O-H, N-H stretching at 3352 cm⁻¹, C-H ring stretching at 3118 cm⁻¹, backbone CH₂ stretching at 2926 cm⁻¹, C≡N stretching at 2241 cm⁻¹, C-N ring stretching at 1229 cm⁻¹, C-H ring in-phase bending at 1083 cm⁻¹ and C-N= ring stretching at 664 cm⁻¹ were observed, but not as sharp as that shown in **Figure 3.7 (a & b)**. The peaks are becoming much broader.

On further increase in temperature and time, ATR-IR spectrum of oxidized melt-spun fiber of 82/18 AN/VIM precursor (250 °C / 5h) is shown in **Figure 3.7 (d)**. Absorptions of 2920 cm⁻¹ (backbone C-H stretching) and 2242 cm⁻¹ (C≡N stretching) decreased a lot. Peaks belonging to imidazole ring are not shown. Two very broad peaks are clearly shown. The one ranged from 2500 to 3600 cm⁻¹ includes O-H, N-H stretching at 3352 cm⁻¹, C-H ring stretching at 3197 cm⁻¹ and backbone C-H stretching at 2920 cm⁻¹. Another broad absorption ranged from 1000 to 1700 cm⁻¹ includes nitrone absorption

around at 1600 and 1380 cm^{-1} and conjugated $\text{C}=\text{N}-\text{C}=\text{C}$ stretching at 1618 and 1580 cm^{-1} . These two broad peaks are similar to those of oxidized polyacrylonitrile (heated 7 hr at 220 $^{\circ}\text{C}$ in air) [94].

ATR-IR spectra of oxidized melt-spun fibers clearly show the obvious change of the fiber structure during the stabilization process. The absorptions of $\text{C}\equiv\text{N}$ group and imidazole ring decreased with the increase of temperature and time of the oxidative stabilization, which indicates both of the functional groups contributed to the stabilization.

Figure 3.7 ATR-IR spectra of 82/18 AN/VIM **CF33** fibers: (a) as spun fiber; (b) oxidized fiber (210 $^{\circ}\text{C}$ / 80 min); (c) oxidized fiber (220 $^{\circ}\text{C}$ / 2 h); (d) oxidized fiber (250 $^{\circ}\text{C}$ / 5h)

Morphology study of oxidized melt-spun fibers

SEM micrographs of Cross-sections of the melt-spun fibers of 82/18 AN/VIM **CF33** precursor are taken to observe the uniformity of core and shell areas of the fibers during the stabilization processes. If the stabilization temperature is not high enough, or stabilization time is not long enough, or the diffusion of O₂ is not fast enough, the core area of the fiber would not be stabilized properly, the difference of the core and shell areas would be shown in SEM micrographs. SEM micrographs of the melt-spun fibers of 82/18 AN/VIM precursor are shown in **Figure 3.8**. SEM micrographs of cross-sections of the melt-spun fibers stabilized at 210 °C / 80 min (**Figure 3.8 b**) and 220 °C / 2 h (**Figure 3.8 c**) are not uniform, which indicates the two fibers stabilized under these conditions would result in incomplete stabilization. **Figure 3.8 (d)** is a SEM micrograph of the cross section of the melt-spun fiber stabilized at 250 °C for 5 h, which is uniform, showing a better stabilization. But a few other fiber filaments still showed the difference between core and shell areas even after being stabilized at 250 °C for 5 h, which suggest high temperature and enough time are needed for full stabilization of the melt-spun fiber. This observation shows the oxidative stabilization took place faster at the shell area of the fiber than the core area, which might be affected by the diffusion rate of O₂. Careful control is needed to avoid incomplete stabilization or chain scission/burning of these precursors.

Figure 3.8 SEM micrographs of oxidized 82/18 AN/VIM CF33 melt-spun fiber: a) as-spun fiber; b) oxidized fiber (210 °C / 80 min); c) oxidized fiber (220 °C / 2 h); d) oxidized fiber (250 °C / 5h)

The diameter of commercial carbon fiber filaments is about 5-8 μm . Due to the fact that the diameter of the fibers is shrinking during the heat treatment process, the diameter of as-spun fiber needs to be about 15-20 μm , while right now our melt-spun fiber diameter is still big. To decrease the fiber diameter, lower viscosity of precursor polymer is required for the melt-spinning process. Since a certain range of high M_w and

cohesive energy are also required for melt-spinning (as described in page 34), we are still working on to decrease the fiber diameter.

Thermal and dynamic mechanical analysis of 82/18 AN/VIM CF33 oxidized fiber

82/18 AN/VIM **CF33** melt-spun fiber oxidized at 250 °C for 5 h shows the best stabilization, which was chosen for thermal and dynamic mechanical analysis by TGA and DMA. The TGA thermogram of the fibers is shown in **Figure 3.9**. Decomposition temperature of 82/18 AN/VIM oxidized fiber (250 °C/5h) examined by TGA is 352 °C (onset point), which is much higher than that of 82/18 AN/VIM as-spun fiber, about 317 °C (onset point). This suggests the oxidized fiber (250 °C/5h) is changed to a more stable structure. DSC data in **Figure 3.12** also suggests the structure change.

Figure 3.9 Thermogram of as-spun & oxidized fibers of 82/18 AN/VIM copolymer **CF33** by TGA (10 °C/min, in N₂)

Dynamic mechanic analysis (DMA) was used to examine the mechanical properties of 82/18 AN/VIM oxidized fiber (**Figure 3.10**). Tensile storage moduli of as-spun and the oxidized fibers at low temperature of 0-15 °C are about 30,000 and 40,000 MPa, respectively. Both of them decreased with temperature increase. As-spun fiber of 82/18 AN/VIM has a low T_g. When the temperature is above the T_g, the fiber became so soft that it stretched very much and showed very high displacement in DMA. The oxidized fiber, has a T_g around 166 °C, however, was more resistant to a higher temperature.

Figure 3.10 Tensile storage moduli of as-spun & oxidized fibers of 82/18 AN/VIM CF33 copolymer by DMA (2 °C/min, in N₂)

Tensile loss modulus of as-spun fiber 82/18 AN/VIM **CF33** peaks at 2971 MPa at 101 °C; while the highest E'' value of the oxidized fiber is 1860 MPa at 139 °C (**Figure 3.11**). Tan delta values of as-spun and oxidized fibers are 2.12 and 0.17, respectively (**Figure 3.12**). High tan delta value of as-spun fiber showed its good flexibility. Much lower tan delta value of the oxidized fiber shows it is changed to a much stiffer material after thermal stabilization.

Figure 3.11 Tensile loss moduli of as-spun & oxidized fibers of 82/18 AN/VIM **CF33** copolymer by DMA (2 °C/min, in N₂)

No glass transition was observed up to 170 °C in DSC curve of 82/18 AN/VIM CF33 oxidized fiber, which was probably because the signal was too weak. But it did show a T_g around 166 °C by DMA (**Figure 3.12**). Compared with as-spun melt-spun fiber with a glass transition at 127 °C in DMA, oxidized fiber is changed to a more rigid structure.

Figure 3.12 Tan delta values of as-spun & oxidized fibers of 82/18 AN/VIM copolymer CF33 by DMA (2 °C/min, in N₂)

Preliminary carbonization study

After oxidative stabilization process, carbonization trial experiment was carried out to study the property of the oxidized fiber. The carbonization procedure is described

in section 2.6. The oxidized fiber (250 °C / 5 h) did keep its shape after carbonization at 1000 °C for 2 h (**Figure 3.13**), which indicates that 82/18 AN/VIM **CF33** melt-spun fiber after thermal stabilization can be carbonized. The lateral surface of carbonized fiber is smooth, but cross-section showed some defects. More research needs to be done to confirm the carbonization property.

Figure 3.13 Photograph (left) and SEM image (right) of carbonized 82/18 AN/VIM **CF33** melt-spun fiber

Conclusion

Thermal stabilization of the melt-spun fiber of 82/18 AN/VIM copolymer **CF33** was achieved in air at 250 °C for 5 hrs. Change in fiber color from yellow to brown and finally black can suggest the formation of ladder ring structure. The change of fiber structure during stabilization process was confirmed with ATR-IR spectra. Glass transition temperature of the stabilized fiber was observed at 166 °C by dynamic

mechanic analysis (DMA). Tan Delta value of the stabilized fiber is 0.17, which is much lower than that of as-spun fiber, about 2.12. The oxidized fiber (250 °C / 5 h) did keep its shape after carbonization at 1000 °C for 2 h, which indicates that poly (acrylonitrile-*co*-1-vinylimidazole) melt-spun fiber after thermal stabilization can be carbonized.

Experimental

Materials

2,2'-Azobis(2-methylpropionitrile) (AIBN), 1-vinylimidazole (VIM), acrylonitrile(AN), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and 1-Dodecanethiol were purchased from the Aldrich Chemical Co. All reagents were used as received.

Synthesis of 82/18 AN/VIM CF33 carbon fiber precursor

The solution polymerization of AN and VIM was carried out in a 250 mL flask fitted with a thermocouple probe, condenser, addition funnel and nitrogen inlet. The flask was charged with DMF and purged with nitrogen for 30 min. Then the monomers (AN and VIM with molar ratio of 82 to 18), AIBN and 1-dodecanethiol were added drop wise into the flask for 5 h. The polymerization was carried out at 70 °C with continuous stirring. The copolymer **CF33** was precipitated in de-ionized water, filtered and washed with methanol and hexane and then dried in vacuum oven for two days till constant weight was obtained.

82/18 AN/VIM copolymer precursor was selected for melt-spinning based on the rheological study, which shows the copolymer with 18% VIM (feed molar ratio) has the lowest viscosity and good stability at high temperature.

Melt-spinning of AN/VIM copolymer precursor CF33

82/18 AN/VIM copolymer CF33 precursor ($[\eta] = 0.59$ dL/g) was ground into coarse granules in a grinder and dried in vacuum at 65 °C for 3 hrs. Instron 3211 capillary rheometer (capillary diameter, $D = 0.030$ inches) was used to draw the fibers of copolymer. ~ 9 g of copolymer was loaded in preheated rheometer at 180 °C under nitrogen atmosphere and left there to heat up for 10 min, after that drawing temperature was raised to 192 °C. Melt spun fiber was collected by winding on 3 inches diameter bobbin rotating at 84 rpm. The melt-spun fiber was drawn by our collaborator Advanced Fiber Engineering, LLC, Westfield, NJ.

Characterization of CF33 melt-spun fiber

Attenuated total reflectance Fourier transform infrared (ATR–FTIR) analysis of the polymers was performed on a Thermo-Nicolet Magna 550 FTIR spectrophotometer with a high endurance diamond ATR attachment. The decomposition temperature and char yield of the fibers were obtained by using mettler TGA/SDTA851 thermogravimetric analyzer and Hi-Res TGA 2950 Thermogravimetric Analyzer at a heating rate of 10 °C /min from 0 - 550 °C in N₂ atmosphere. TA Q1000 DSC instrument was used to determine the glass transition temperature in inert atmosphere at a heating

rate of 10 °C/min. Hi-Res TGA 2950 Thermogravimetric Analyzer was used for carbonization at 1000 °C. TA Instruments Q800 DMA was used for temperature sweep tensile testing, which was under strain control (0.126% strain, 15 µm amplitude). The DMA samples were heated at a rate of 2 °C/min and vibrated at a frequency of 1 Hz. SEM 3400 S-3400N (electron beam energy 5.0 keV) and FESEM- Hitachi S4800 (electron beam energy 20.0 keV) were used to study morphology of melt-spun fibers.

Char yield testing

To study the effect of environment on stabilization, the char yields of the melt-spun fibers were determined by TGA under two different conditions:

A. Stabilization of melt-spun fiber in air: (1) room temperature to 220 °C at 10 °C /min in air; (2) 220 °C for 3h in air; (3) 220 to 550 °C at 10 °C /min in nitrogen (N₂); (4) 550 °C for 3h in N₂.

B. Stabilization of melt-spun fiber in N₂: (1) room temperature to 220 °C at 10 °C /min in N₂; (2) 220 °C for 3h in N₂; (3) 220 to 550 °C at 10 °C /min in N₂; (4) 550 °C for 3h in N₂.

Preliminary carbonization study by TGA

Preliminary carbonization experiment was performed in Nitrogen (N₂) under the following carbonization procedure: (1) Ramp 10 °C /min to 700 °C; (2) Isothermal at 700 °C for 20 min; (3) Ramp 10 °C /min to 1000 °C ; (4) Isothermal at 1000 °C for 2 h.

CHAPTER FOUR

DISPERSION POLYMERIZATION OF POLY (ACRYLONITRILE-*CO*-1-VINYLMIDAZOLE)

Introduction

The copolymerization of acrylonitrile (AN) and 1-vinylimidazole (VIM) has been reported by a few researchers. Poly (acrylonitrile – *co* -1-vinylimidazole) prepared by ^{60}Co - γ – irradiation of AN/VIM monomer mixture was reported by Pekel et al [95]. Monomer reactivity ratios of the solution polymerization of acrylonitrile and 1-vinylimidazole have been determined [96]. However, water-based dispersion polymerization of acrylonitrile and 1-vinylimidazole has not been reported. Compared with organic solvents, water has some attractive properties such as non-flammability, non-toxicity and low cost. Water used as a medium is considered an environmentally friendly polymerization process [97]. Unlike in emulsion polymerization, the polymerization medium is not a solvent for the monomers; in dispersion polymerization, the polymerization medium is a solvent for the monomers, but not a solvent for the polymer [98].

Among those several heterogeneous polymerizations, dispersion polymerization is a relatively new technology started in mid 1970's [99]. Dispersion polymerization starts as a homogeneous solution, and becomes heterogeneous during the polymerization process, which is similar to precipitation polymerization except that the polymer product is stabilized by the stabilizer to form controlled-size particles between 0.1-15 μm [100].

In general, monomers, stabilizer and initiator used in water-based dispersion polymerization are water soluble. The location of dispersion polymerization is the water medium, which is different from emulsion polymerization where micelle is the polymerization location. Produced polymers nucleated together to form particle, which is stabilized in water by stabilizer. The mechanism of particle nucleation in the dispersion polymerization is shown in **Figure 4.1** [101].

Figure 4.1 Mechanism of particle nucleation in the dispersion polymerization [101]

Stabilizers are very important to provide colloidal stability in dispersion polymerization. A number of block and graft copolymers were popularly used as stabilizers [102-110]. But random copolymers become more attractive in industry because they are synthesized more easily and affordably [111-114]. There are also

several homopolymers [115], such as poly (vinyl pyrrolidone) [116], hydroxyl propyl cellulose and poly (acrylic acid) have been successfully applied as stabilizers in dispersion polymerization [100, 117-118]. Random copolymers of acrylonitrile and 1-vinylimidazole used as stabilizers in dispersion polymerization have not been reported.

In this study, water-based dispersion polymerization of acrylonitrile and 1-vinylimidazole is discussed. Small amount of protonated random copolymer of acrylonitrile and 1-vinylimidazole was used as stabilizer for synthesizing itself in dispersion polymerization. For this application, the protonation of stabilizer copolymer of acrylonitrile and 1-vinylimidazole is very crucial, which bring it amphiphilic nature necessary to stabilize AN/VIM copolymer particles formed by dispersion polymerization in water. It also overcome one drawback to remove the stabilizer incorporated in the final product. Various copolymers with different 1-vinylimidazole content were studied as stabilizer in acidic water of pH 1.5. The effects of stabilizer concentration and monomer concentration on the properties of ultimate polymer particle dispersions also have been discussed in this study.

Effect of VIM content in stabilizer on properties of the ultimate copolymer particle prepared by dispersion polymerization

Acrylonitrile and 1-vinylimidazole were initiated by potassium persulfate ($K_2S_2O_8$). Water-based dispersion polymerization of acrylonitrile and 1-vinylimidazole is shown in **Scheme 4.1**.

Scheme 4.1 Dispersion polymerization of AN/VIM copolymer

The statistic random copolymers of acrylonitrile and 1-vinylimidazole were protonated in the acidic water to form stabilizers with amphiphilic nature (**Scheme 4.2**). The protonation process is crucial to form valid stabilizers for the dispersion polymerization. The protonated copolymer of acrylonitrile and 1-vinylimidazole has the amphiphilic property, whose hydrophilic part would secure good salvation from water. The copolymers with VIM content lower than 16% can not be dissolved well in acidic water of pH 1.5, while the copolymers with VIM content higher than 22% can be dissolved well. These phenomena suggest that vinylimidazole pendant group is the location for protonation and certain amount of vinylimidazole group is necessary for forming the valid stabilizer.

Scheme 4.2 Protonation reaction of forming AN/VIM copolymer stabilizer with amphiphilic nature

Table 4.1 shows the effect of VIM content in stabilizer on the particle size and polydispersity index of the ultimate particles by dispersion polymerization. The higher the polydispersity index (P.I) value, the wider the particle size distribution. Since stabilizer and monomer concentration are also the key factors for particle properties, they were kept constant in all the dispersion polymerizations shown in **table 4.1**, where the ratio of monomer to water (% w/w) is 15% and stabilizer to monomer (% w/w) is 6.8%. With the increase of the VIM content in stabilizer from 24% to 47%, the particle size of the dispersion polymer particles decreased from 11.3 μm to 0.11 μm , and the polydispersity index of the ultimate particles decreased from 1.44 to 1.21. The dramatic decreasing of particle size shows protonated vinylimidazole pendant group is the key factor for stabilizing the particles formed by dispersion polymerization in water.

Table 4.1 Effect of VIM content in stabilizer on the ultimate particles prepared by dispersion polymerization

Sample	Stabilizers*	VIM content in stabilizer (mol%) ^a	Particle size Dn (μm) ^b	P.I. ^b
CF68	P(AN-co-VIM)(76:24)	24	11.3	1.44
CF66	P(AN-co-VIM)(69:31)	31	6.9	1.31
CF62	P(AN-co-VIM)(53:47)	47	0.11	1.21
CF67	PVIM	100	0.26	0.17

Reaction condition: 15% monomer/water (w/w), 6.8% stabilizer/monomer (w/w), 60 °C for 16h

^a Determined by ¹H NMR

^b Determined by Dynamic light scattering (DLS)

1-vinylimidazole homopolymer was also investigated in this study. In **table 4.1**, very low polydispersity index 0.17 suggests almost monodispersed particles formed by using poly (1-vinylimidazole) as a stabilizer in dispersion polymerization. The average particle size of the ultimate particles is 0.26 μm by using poly (1-vinylimidazole) as a stabilizer in dispersion polymerization, while the average particle size of the ultimate particles is 0.11 μm by using P(AN-co-VIM)(53:47) as a stabilizer. Stable and fine polymer particles were formed in both dispersions, which showed both random copolymers of acrylonitrile and 1-vinylimidazole and 1-vinylimidazole homopolymer can be stabilizers for dispersion polymerization in acidic water.

Effect of stabilizer concentration on properties of the ultimate copolymer particle prepared by dispersion polymerization

At the early stage of the dispersion polymerization of acrylonitrile and 1-vinylimidazole, homogeneous nucleation took place in the acidic water. As the propagation continued, the growing polymer chains exceeding a soluble critical chain length started to form heterogeneous nucleation particles. At this stage, stabilizer molecules were absorbed on the surface of growing copolymer particles because the amphiphilic stabilizer tended to locate at the interface between hydrophobic polymer surface and hydrophilic water medium. Without the amphiphilic stabilizer, the ultimate polymer particles are not stable, having an average particle size about 29.1 μm shown in table 4.2.

Table 4.2 Effect of stabilizer concentration on the ultimate particles prepared by dispersion polymerization

Sample	Stabilizer concentration (% w/w to monomers)	Particle size Dn (μm) ^a	P.I. ^a
CF53	0	29.1	1.46
CF55	6.8	2.6	1.74
CF61	10	0.082	0.67
CF56	13	0.063	0.47

Reaction condition: 7% monomer/water (w/w), P (AN-co-VIM) (74:26) as stabilizer (26% VIM), 60 °C for 16h

^a Determined by Dynamic light scattering (DLS)

The effect of stabilizer concentration on the particle size and polydispersity index of the ultimate particles by dispersion polymerization is shown in **table 4.2**. With the increase of the ratio of stabilizer to monomer from 6.8% to 13%, the particle size of the dispersion polymer particles decreased from 2.6 μm to 0.063 μm , and the polydispersity index of the ultimate particles decreased from 1.74 to 0.47. The sharp decreasing of particle size and polydispersity index shows the concentration of stabilizer is very important for forming stable polymer particles during dispersion polymerization. Small size particles have higher surface area in total than that of bigger particles, which requires higher amount of stabilizer molecules absorbed on their surfaces to be stabilized in water. For the dispersion of higher ratio of stabilizer to monomer, the growing polymer particles have enough stabilizer molecules on its surface to form fine small particles.

Since VIM content in stabilizer and monomer concentration are also the key factors for particle properties, they were kept constant in all the dispersion polymerizations shown in **table 4.2**, where the VIM content in stabilizer is 26% and the ratio of monomer to water (% w/w) is 7%. The DLS curve of the ultimate AN/VIM copolymer **CF55** particles (P(AN-*co*-VIM) (74:26) as stabilizer, 6.8% stabilizer/monomer (w/w), 7% monomer/water (w/w)) is shown in **Figure 4.2**.

Figure 4.2 DLS curve of the ultimate AN/VIM copolymer **CF55** particles (P(AN-*co*-VIM) (74:26) as stabilizer, 6.8% stabilizer/monomer (w/w), 7% monomer/water (w/w), 60 °C for 16h)

Effect of monomer concentration on properties of the ultimate copolymer particle prepared by dispersion polymerization

Enough solvation from medium in dispersion polymerization is also crucial to form stable fine polymer particles. In the dispersion with low ratio of monomer to water, the formed polymer particles were surrounded with enough water molecules, which keep them away from each other, so fine small particles could form. While in the dispersion with high ratio of monomer to water, the particles did not have enough water molecules to separate them, so the collision between polymer particles took place.

The effect of monomer concentration on the particle size and polydispersity index of the ultimate particles by dispersion polymerization is shown in **table 4.3**. With the increase of the ratio of monomer to water from 15% to 35%, the particle size of the dispersion polymer particles increased from 0.11 μm to 16.3 μm . The dramatic change of particle size shows the ratio of monomer to water is crucial to form stable polymer particles during dispersion polymerization. Since VIM content in stabilizer and stabilizer concentration are also the key factors for particle properties, they were kept constant in all the dispersion polymerizations shown in **table 4.3**, where the VIM content in stabilizer is 47% and the ratio of stabilizer to monomer (% w/w) is 6.8%.

Table 4.3 Effect of monomers concentration on the ultimate particles prepared by dispersion polymerization

Sample	Monomer concentration (% w/w to water)	Particle size Dn (μm) ^a	P.I. ^a
CF62	15	0.11	1.21
CF63	25	0.28	0.27
CF65	30	10.8	0.65
CF64	35	16.3	0.33

Reaction condition: 6.8% stabilizer/monomer (w/w), P (AN-*co*-VIM) (53:47) as stabilizer (47% VIM), 60 °C for 16h

^a Determined by Dynamic light scattering (DLS)

Characterization of poly (acrylonitrile – *co* -1-vinylimidazole) synthesized by dispersion polymerization

Poly (acrylonitrile – *co* -1-vinylimidazole) synthesized by dispersion polymerization was confirmed by ^1H NMR and ATR-FTIR spectra. A typical ^1H NMR spectrum of AN/VIM copolymer **CF53** is shown in **Figure 4.3**, Where signal δ 2.0 represents backbone CH_2 from VIM and AN linkages, signal δ 3.1 represents backbone CH from AN unit), signal δ 4.4 represents backbone CH from VIM unit and signals δ 6.9, 7.3 and 7.7 represent CH groups in imidazole ring. **Figure 4.4** shows the ATR-FTIR spectrum of AN/VIM copolymer **CF53** synthesized by dispersion polymerization. Backbone CH_2 stretch at 2923 cm^{-1} and CN stretching at 2242 cm^{-1} are from AN unit. Backbone CH_2 stretching at 2923 cm^{-1} , C-N ring stretching at 1229 cm^{-1} , C-H ring in-phase bending at 1082 cm^{-1} and C-N= ring stretching at 665 cm^{-1} are from VIM unit.

Figure 4.3 ^1H NMR spectrum of 82/18 AN/VIM copolymer **CF53** (in $\text{DMSO-}d_6$) synthesized by dispersion polymerization

Figure 4.4 ATR-FTIR spectrum of AN/VIM copolymer **CF53** synthesized by dispersion polymerization

High molecular weight of poly (acrylonitrile – *co* -1-vinylimidazole) synthesized by dispersion polymerization was obtained by using the recipe in experimental section and P(AN-*co*-VIM) (74:26) as stabilizer, 6.8% stabilizer/monomer (w/w), 7% monomer/water (w/w). Gel permeation chromatogram of AN/VIM copolymer **CF53** (**Figure 4. 5**) shows the number average molecular weight (M_n) is 880,839 and polydispersity index of molecular weight is 3.6. The AN/VIM copolymer synthesized by dispersion polymerization has a decomposition temperature around 300 °C detected by TGA.

Figure 4.5 Gel permeation chromatogram of AN/VIM copolymer **CF53** synthesized by dispersion polymerization (polystyrene standard, in DMF)

Conclusions

Poly (acrylonitrile – *co* -1-vinylimidazole) was successfully synthesized by dispersion polymerization, which was confirmed by ^1H NMR and ATR-FTIR spectra. Controlled-size particles were obtained by using random copolymer of acrylonitrile and 1-vinylimidazole as a stabilizer in dispersion polymerization in acidic water of pH 1.5. The vinylimidazole pendant group is the location for protonation and above 22% VIM in copolymer is necessary for forming a valid stabilizer. The effects of stabilizer concentration and monomer concentration on the particle size and polydispersity index of the ultimate particles by dispersion polymerization have been studied. With the increase

of the ratio of stabilizer to monomer from 6.8% to 13%, the particle size of the dispersion polymer particles decreased from 2.6 μm to 0.063 μm , and the polydispersity index of the ultimate particles decreased from 1.74 to 0.47. With the increase of the ratio of monomer to water from 15% to 35%, the particle size of the dispersion polymer particles increased from 0.11 μm to 16.3 μm . The protonated poly (acrylonitrile – *co* -1-vinylimidazole) can be a novel stabilizer for dispersion polymerization.

Experimental

Materials

Potassium persulfate, 1-vinylimidazole (VIM), acrylonitrile (AN), acetic acid, 2,2'-Azobis(2-methylpropionitrile) (AIBN), N,N-dimethylformamide (DMF) and 1-Dodecanethiol were purchased from the Aldrich Chemical Co. All reagents were used as received.

Synthesis of polymeric stabilizers

Random copolymers of acrylonitrile and 1-vinylimidazole were prepared as stabilizers for dispersion polymerization. The solution polymerization of AN and VIM by varying feed ratio was carried out in a reaction flask fitted with a thermocouple probe, condenser, addition funnel and nitrogen inlet. The flask was charged with solvent DMF and purged with nitrogen for 30 min. Then the monomers, AIBN and chain transfer agent, 1-dodecanethiol were added drop wise into the flask over a period of 2-5 h. The polymerization reactions were carried at 70 $^{\circ}\text{C}$ with continuous stirring. The copolymer

was precipitated in excess de-ionized water, filtered and washed with methanol and hexane to remove residual monomers and then dried in vacuum oven for two days till constant weight was obtained. ^1H NMR spectrum ($\text{DMSO-}d_6$) of AN/VIM copolymer stabilizer: δ 2.0 (backbone CH_2 from VIM and AN linkages), δ 3.1 (backbone CH from AN unit), δ 4.4 (backbone CH from VIM unit) and δ 7.8- 6.8 (CH groups in imidazole ring).

Dispersion polymerization of acrylonitrile and 1-vinylimidazole copolymers CF52-67

The pH of de-ionized water was adjusted to 1.5 by acetic acid. Stabilizers were dissolved in the acidic water in the reaction flask fitted with a thermocouple probe, condenser, addition funnel and nitrogen inlet at 60 °C. Potassium persulfate (0.014 g) was added into the flask. Then acrylonitrile (2.2 g) and 1-vinylimidazole (0.85 g) mixture was added drop wise into the flask within 1 h. The dispersion polymerization was carried at 60 °C with continuous stirring for 16 h. The copolymer dispersion was neutralized by potassium hydroxide. The precipitated copolymer was filtered and washed with methanol and hexane to remove residual monomers and then dried in vacuum oven for two days till constant weight was obtained.

Characterization of AN/VIM copolymers

^1H NMR spectrum was obtained by JEOL ECX-300 spectrometer using $\text{DMSO-}d_6$ as solvent. Size exclusion chromatography (SEC) was used to determine the molecular weights of polymers in *N,N*-dimethylformamide (DMF) at 50 °C at 1 mL/min flow rate on

a Waters SEC instrument equipped with two Waters Styragel HR5E (DMF) columns, a Waters 717 plus autosampler, a Waters 2414 differential refractive index detector and a Wyatt Technologies miniDAWN multiangle laser light scattering (MALLS) detector. Coulter N4MD Sub-Micron Particle Analyzer was used to determine particle size and distribution of the copolymer dispersion and the data shown in the table is the average of three repeated test values. Attenuated total reflectance Fourier transform infrared (ATR–FTIR) analysis of the copolymer was performed on a Thermo-Nicolet Magna 550 FTIR spectrophotometer with a high endurance diamond ATR attachment. The thermal stability of the copolymer was performed by using Mettler-Toledo 851 thermogravimetric analyzer.

CHAPTER FIVE

POLY (ACRYLONITRILE-*CO*-1-VINYLMIDAZOLIUM TETRAFLUOROBORATE) AND POLY (ACRYLONITRILE-*CO*-1-VINYLMIDAZOLIUM HEXAFLUOROPHOSPHATE) FOR GAS SEPARATION MEMBRANES

Introduction

The most commercially utilized membranes in separation industry are made of polymers [119, 120]. The polymer has to be a suitable membrane former in terms of its chain rigidity, chain interactions and polarity [121, 122]. The polymer also needs to be able to form stable, thin and low-cost membrane. Polysulfone, polyimide, cellulose acetate, polyphenylene oxide and silicone rubber are the principle commercially used polymer membrane materials [123]. **Figure 5.1** shows the structure of a typical anisotropic gas separation membrane. The top selective layer is very thin (less than 5 μm) and has fine pores with the size in range of 100-200 Å [123].

Figure 5.1 The structure of a typical anisotropic gas separation membrane (Reprinted with permission from Baker R W. Ind Eng Chem Res 2002; 41: 1393-1411, Copyright © 2002 American Chemical Society under the license number 2550960473514) [123]

Closely packed polymer chains tend to give better selectivity, at the cost of permeability (P). Robeson has illustrated the inverse selectivity/permeability relationship of polymer membranes in 1991. The plot of oxygen/nitrogen selectivity as a function of oxygen permeability for polymer membranes is shown in **Figure 5.2** [123]. It depicts the trade off between selectivity and permeability. There are also cobalt carrier facilitated transport membranes in the plot showing one promising type of membranes. The structure of cobalt carrier membrane polymer is shown in **Figure 5.3** [123]. The cobalt complex is chemically bond to the polymer backbone and functions as the oxygen carrier to improve both permeability and selectivity of oxygen.

Figure 5.2 Robeson plot of oxygen/nitrogen selectivity as a function of oxygen permeability for polymer membranes (Reprinted with permission from Baker R W. Ind Eng Chem Res 2002; 41: 1393-1411, Copyright © 2002 American Chemical Society under the license number 2550960473514) [123]

Figure 5.3 Structure of cobalt carrier membrane polymer (Reprinted with permission from Baker R W. Ind Eng Chem Res 2002; 41: 1393-1411, Copyright © 2002 American Chemical Society under the license number 2550960473514) [123]

Permeability and selectivity of polymeric membranes still low and need to be improved. For example, polyimides are one type of widely used polymers for gas separation membranes. Membranes made of polyimides with different structures show different permeabilities and selectivities of gases. One research showed $P(\text{CO}_2)$ of the polyimide membrane is 42.7 barrer and selectivity $\alpha(\text{CO}_2/\text{N}_2)$ is 16 [124]. Another research showed $P(\text{CO}_2)$ of the polyimide membrane is 27 barrer and selectivity $\alpha(\text{CO}_2/\text{N}_2)$ is 33 [125]. Whereas, certain imidazolium-based supported ionic liquid membranes (SILMs) have shown CO_2 permeabilities near 1000 barrers and selectivities for CO_2/N_2 greater than 50 [126].

SILMs are a class of supported liquid membranes composed of room-temperature ionic liquids (RTILs) encapsulated within a polymeric support. SILMs show higher permeabilities and selectivities than polymeric membranes. However, SILMs lack robust

stability and are subject to break under moderate pressures [126]. Polymerized room-temperature ionic liquids (poly(RTILs)) are developed to overcome the limitations of supported ionic liquid membranes (SILMs). Imidazolium cations are bound to the polymer backbone while anions not covalently bound to the polymer. Poly(RTILs) are more stable and can be performed under higher pressures. In this study, poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) and poly (acrylonitrile – *co*-1-vinylimidazolium hexafluorophosphate) membranes were applied for gas separation, which has not been reported.

Synthesis and characterization

The schematic representation for the synthesis of poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) is shown in **Scheme 5.1**.

Scheme 5.1 Synthesis of poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate)

Poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) synthesized were confirmed by ATR-FTIR and ^{19}F NMR spectra. **Figure 5.4** shows the ATR-FTIR spectrum of Poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) **IL4**. Backbone CH_2 stretch at 2929 cm^{-1} and CN stretching at 2240 cm^{-1} are from AN unit. C-H ring stretching at 3109 cm^{-1} , backbone CH_2 stretching at 2929 cm^{-1} , C-N ring stretching at 1229 cm^{-1} , and C-N= ring stretching at 665 cm^{-1} are from VIM unit. The peak at 1057 cm^{-1} is corresponding to the $\nu(\text{BF}_4)$ vibration [127, 128].

Figure 5.4 ATR-IR spectrum of poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) **IL4**

Figure 5.5 ATR-IR spectrum of poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) **IL6**

Figure 5.5 shows the ATR-FTIR spectrum of Poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) **IL6**. Backbone CH₂ stretch at 2962 cm⁻¹ and CN stretching at 2242 cm⁻¹ are from AN unit. C-H ring stretching at 3118 cm⁻¹, backbone CH₂ stretching at 2962 cm⁻¹, C-N ring stretching at 1229 cm⁻¹, and C-N= ring stretching at 665 cm⁻¹ are from VIM unit. The peak at 837 cm⁻¹ is corresponding to the v(PF₆) vibration [129].

Figure 5.6 ^{19}F NMR of poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) **IL4** in $\text{DMSO-}d_6$

A ^{19}F NMR spectrum of poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) **IL4** is shown in **Figure 5.6**. In ^{19}F NMR spectra ($\text{DMSO-}d_6$), signal at $\delta -148.0$ ppm represents 4F from BF_4 [130]. A ^{19}F NMR spectrum of poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) **IL6** is shown in **Figure 5.7**. In ^{19}F NMR spectra ($\text{DMSO-}d_6$), signals at $\delta -68.7$ and -71.2 ppm represent 6F from PF_6 . The splitting is due to the spin-spin coupling of ^{19}F and ^{31}P [131].

Figure 5.7 ^{19}F NMR of poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) **IL6** in $\text{DMSO-}d_6$

Gas separation performances of poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) membranes

Photos of poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) **IL4** and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) **IL6** membranes used for gas separation are shown in **Figure 5.8**. They are transparent thin films.

Figure 5.8 Poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) **IL4** membrane used for gas separation (left); poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) **IL6** membrane used for gas separation (right) . Both were made by Adam T. Haldeman in Tetramer Technologies, L.L.C)

Permeabilities of poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) **IL4** and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) **IL6** membranes were tested by Adam T. Haldeman in Tetramer Technologies, L.L.C and shown in **table 5.1**. The low selectivities indicate that the permeance measured primarily through micro-voids rather than intermolecular free volume. And it also indicates the intrinsic permeabilities of the polymers are low.

Table 5.1 Gas separation performances of permeabilities of poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) **IL4** and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) membranes **IL6**

Membrane	Permeabilities (Barrer)					Selectivities			Thickness (cm)
	N ₂	O ₂	CH ₄	H ₂	CO ₂	O ₂ /N ₂	CO ₂ /CH ₄	H ₂ /CO ₂	
CF47 (reference)									
	21525	20694	27802	81208	17057	1.0	0.6	4.8	0.0045
	178659	198510	282688	920922	N/A	1.1	0.6	5.2	0.0025
	21375	20654	29776	97009	18806	1.0	0.6	5.2	0.0015
	10136	11812	16571	47563	11079	1.2	0.7	4.3	0.004
CF47-BF₄ (IL4)	N/A	N/A	N/A	N/A	N/A				0.00535
	9.7	10.8	15.6	31.8	16.3	1.1	1.0	2.0	0.0023
CF47-PF₆ (IL6)	N/A	N/A	N/A	2505	618			4.1	0.004
	702	591	871	2246	400	0.8	0.5	5.6	0.004
	469	155	392	468	89	0.3	0.2	5.2	0.0013

Conclusions

Poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) were successfully synthesized and confirmed by ATR-FTIR and ¹⁹F NMR spectra. Membranes made of them were applied for gas separation.

Experimental

Materials

1-Chlorobutane, Potassium tetrafluoroborate (KBF_4), Potassium hexafluorophosphate (KPF_6), acetonitrile (MeCN), 2,2'-Azobis(2-methylpropionitrile) (AIBN), 1-vinylimidazole (VIM), acrylonitrile (AN), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and 1-Dodecanethiol were purchased from the Aldrich Chemical Co. All reagents were used as received.

Synthesis of poly (acrylonitrile – co -1-vinylimidazolium tetrafluoroborate) IL4 and poly (acrylonitrile – co -1-vinylimidazolium hexafluorophosphate) IL6

The solution polymerization of AN and VIM was carried out in a 250 mL flask fitted with a thermocouple probe, condenser, addition funnel and nitrogen inlet. The flask was charged with DMF and purged with nitrogen for 30 min. The monomers (AN and VIM with molar ratio of 82 to 18), AIBN and 1-dodecanethiol were added drop wise into the flask for 5 hrs. The polymerization was carried out at 70 °C with continuous stirring for 16 h. Then 1-Chlorobutane and acetonitrile were added in the polymer solution. The reaction was carried out at 75 °C for 48 hrs. Poly (acrylonitrile – co -1-vinylimidazolium chloride) was precipitated in toluene, filtered and washed with methanol and hexane and then dried in vacuum oven for two days till constant weight was obtained.

Potassium tetrafluoroborate (KBF_4) and poly (acrylonitrile – co -1-vinylimidazolium chloride) were added in the flask charged with DMSO. The ion exchange reaction was carried out at 60-65 °C for 8 hrs. Poly (acrylonitrile – co -1-vinylimidazolium tetrafluoroborate) **IL4** was precipitated in excess de-ionized water,

filtered and washed with methanol and hexane and then dried in vacuum oven for two days till constant weight was obtained.

Potassium hexafluorophosphate (KPF_6) and poly (acrylonitrile – *co* -1-vinylimidazolium chloride) were added in the flask charged with DMSO. The ion exchange reaction was carried out at 60-65 °C for 10 hrs. Poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) **IL6** was precipitated in excess de-ionized water, filtered and washed with methanol and hexane and then dried in vacuum oven for two days till constant weight was obtained.

Characterization

Thermo-Nicolet Magna 550 FTIR spectrophotometer was used for ATR-IR analysis of polymers. ^{19}F NMR spectra were obtained with JEOL ECX-300 spectrometer using $\text{DMSO-}d_6$ as solvent.

Procedure for making poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) membranes (Adam T. Haldeman, Scientist in Tetramer Technologies, L.L.C)

Poly (acrylonitrile – *co* -1-vinylimidazolium tetrafluoroborate) and poly (acrylonitrile – *co* -1-vinylimidazolium hexafluorophosphate) membranes were made by Adam T. Haldeman in Tetramer Technologies, L.L.C. ~10wt% polymer solution (DMF as solvent) was used for casting membrane onto a silicon wafer. The wafer was then covered with a lid with a small hole on the top to limit solvent evaporation rate. The

wafer was then heated to 80 °C for 4 hrs to slowly evaporate the solvent. Then the membrane was washed by CHCl_3 and put in an oven at 80 °C overnight in order to drive off residual solvent.

Gas separation experiment

Figure 5.9 A photo of the gas permeance testing panel showing the test cell in the center of the panel and the bubble-flow meter to the right of the panel (in Tetramer Technologies, L.L.C)

Gas separation experiments were performed by Adam T. Haldeman in Tetramer Technologies, L.L.C. A homemade measurement panel (**Figure 5.9**) was used to characterize membranes in order to identify promising polymers for further investigation

and optimization. The system applied a gas at a given pressure to the feed side of the membrane, and as gas passed through the membrane, it pushed a bubble through a flow meter on the opposite side (permeate side) of the membrane. The testing temperature is 25 °C. Circular stamps with 1.5 inch diameters were first cut from each membrane for testing in the gas permeance panel. Once a stamp was sealed in the instrument's cell, nitrogen at 100 psi was applied to the testing cell. The system was given 10 minutes to equilibrate at that pressure before any measurements were taken in order to ensure steady-state conditions. The selectivity of one gas over another was taken as the relative ratio of their permeances.

CHAPTER SIX

UV-CURABLE OPTICAL FIBER COATINGS

Introduction

Silica-based optical fibers are widely used in telecommunication systems [132-135]. A polymeric coating is applied to optical fibers to shield glass from scratches which can result in fiber damage. The elastomeric coatings provide mechanical protection to the pristine surface of the glass fiber. The acrylate coatings can be cured at high speeds by ultraviolet (UV) light, which provides high production rates. Also the coatings have properties ranging from soft and elastic to hard and tough [136, 137]. Acrylic coated fibers are durable, providing years of high performance service [138, 139]. **Figure 6.1** shows the drawing, coating and UV curing processes of the optic fiber.

Figure 6.1 The drawing, coating and UV curing processes of the optical fiber

However, as fibers used in extreme environments, such as down-hole monitoring of oil wells, the greater thermal stability of optical fiber is required. There is a growing need for coatings that withstand higher temperature and does not change (much) their existing process. In this study, the method of improving the thermal stability of optical fiber is to add a multi-fuctional monomer (penta-acrylate in **Figure 6.2**) to increase the cross-linking of the polymeric coating. I worked with Stephen Budy on this project.

Figure 6.2 Structure of dipentaerythritol penta-acrylate (purchased from Aldrich Chemical Co.)

Thermal stability

Thermal stability of the polymeric coating was examined by TGA at a heating rate of 10 °C /min in N₂ and air. Degradation temperature increased as DeSolute coating #3471-3-14 was added with dipentaerythritol penta-/hexa-acrylate. **Figure 6.3** shows the thermogram of blended UV coatings of DeSolute #3471-3-14 with different percentage of dipentaerythritol penta-/hexa-acrylate in N₂ [140]. DSM DeSolute #3471-3-14 coating has an early degradation around 140 °C, and sharp degradation at 248 °C in N₂. As dipentaerythritol penta-/hexa-acrylate added in DSM DeSolute #3471-3-14, even 1%, the early degradation disappeared. The sharp degradation of blended DeSolute #3471-3-14 and 1% dipentaerythritol penta-/hexa-acrylate started at 287 °C. With the increase of weight percentage of dipentaerythritol penta-/hexa-acrylate in the blended coating, the degradation temperature increased. The blended coatings with 40% and 60% dipentaerythritol penta-/hexa-acrylate began to degrade at 305 °C and 312 °C, respectively, and the degradations are much slower than that of DeSolute #3471-3-14. At

450 °C, the blended coating of DeSolite #3471-3-14 with 60% dipentaerythritol penta-/hexa-acrylate had a weight loss around 20%.

Figure 6.3 Thermogram of UV coatings of DeSolite #3471-3-14 with different percentage of dipentaerythritol penta-/hexa-acrylate (10 °C/min, in N₂)

Figure 6.4 is the thermogram of UV coatings of DeSolite #3471-3-14 with different percentage of dipentaerythritol penta-/hexa-acrylate in air. DSM DeSolite #3471-3-14 coating has an early degradation around 137 °C, and sharp degradation at 231 °C in air. As dipentaerythritol penta-/hexa-acrylate added in DSM DeSolite #3471-3-14, the early degradation also disappeared in air. The sharp degradation of blended DeSolite #3471-3-14 and 1% dipentaerythritol penta-/hexa-acrylate started at 285 °C in air. With the increase of weight percentage of dipentaerythritol penta-/hexa-acrylate in

the blended coating, the degradation temperature increased. The blended coatings with 40% and 60% dipentaerythritol penta-/hexa-acrylate began to degrade at 296 °C and 307 °C in air, respectively.

Figure 6.4 Thermogram of UV coatings of DeSolite #3471-3-14 with different percentage of dipentaerythritol penta-/hexa-acrylate (10 °C/min, in air)

Figure 6.5 shows the dependence of degradation temperature of UV coatings on weight percentage of dipentaerythritol penta-/hexa-acrylate in N₂ and in air. The coatings intended to decrease at lower temperature in air than in N₂. Even with 1% dipentaerythritol penta-/hexa-acrylate added in DeSolite #3471-3-14, the degradation temperature increased 39 °C in N₂ and 54 °C in air. Dipentaerythritol penta-/hexa-

acrylate has high cross-linking functionality, which would increase the cross-linking degree of the system, and result in better thermal stability of commercial DSM DeSolite #3471-3-14.

Figure 6.5 Dependence of degradation temperature of UV coatings on weight percentage of dipentaerythritol penta-/hexa-acrylate (10 °C/min)

Flexibility

Fiber coatings need to exhibit greater thermal stability without damaging other properties. In some cases, high functional cross-linker would damage the flexibility when increase cross-linking. In this study, spin coated films of DeSolite #3471-3-14 with different percentage of dipentaerythritol penta-/hexa-acrylate on transparency were bent 180 degree. The films with 5-25% dipentaerythritol penta-/hexa-acrylate showed good

flexibility with no fracture (**table 6.1**). But the film with 40% dipentaerythritol penta-/hexa-acrylate showed some fracture. So lower than 25% dipentaerythritol penta-/hexa-acrylate can be added in DeSolute #3471-3-14 to form good flexible fiber coatings.

Table 6.1 Flexibility of UV coatings of DeSolute #3471-3-14 with different percentage of dipentaerythritol penta-/hexa-acrylate

Weight percentage of the high functional acrylate	Flexibility
5	Good
8	Good
10	Good
12	Good
15	Good
18	Good
20	Good
25	Good
40	Bad

Conclusion

UV-curable DeSolute #3471-3-14 with 1-25% dipentaerythritol penta-/hexa-acrylate exhibits great thermal stability and good flexibility, which are very useful in the extreme environments, where fiber coatings withstand high temperature is required.

Experimental

Materials

DeSolite coating #3471-3-14, a UV-curable acrylate resin, was purchased from DSM DeSolite, Inc. Dipentaerythritol penta-/hexa-acrylate was purchased from Aldrich Chemical Co. and used as received.

Experimental

DeSolite coating #3471-3-14 was blended with different weight percentage of Dipentaerythritol penta-/hexa-functional acrylate to form uniform mixture. Spin coating was used to make the film of the mixture. The film was cured under a UV lamp. Thermal stability of the polymeric coating was examined by Hi-Res TGA 2950 Thermogravimetric Analyzer at a heating rate of 10 °C /min in N₂ and air.

CHAPTER SEVEN

THERMO-REVERSIBLE METHYL METHACRYLATE-METHYL ACRYLATE-FURFURYL METHACRYLATE (MMA/MA/FMA) AND BISMALIMIDE (BMI) CROSS-LINKED POLYMER

Introduction

Cross-linking brings good mechanical property, heat and chemical resistances to polymers. However, one major drawback of cross-linked polymers is lack of re-fabrication ability [141]. Polymers that can be reversibly cross-linked through covalent bonds are of much current research interest from the standpoints of recycling, processability, self-repairing and re-fabrication [142-144]. The Diels-Alder (DA) reaction is one, which is known to generate thermo-reversible cross-linking. The covalent bond (adduct) formed by DA reaction can be easily broken down to diene and dienophile [145-148]. DA reaction in polymer cross-linking brings a new class of thermally-reversible cross-linked polymers [149-158].

The DA reaction of maleimide and Furan-functionalized polymer bringing thermo-reversible cross-linking ability to product has been discussed by some researchers [159-161]. But to the best of our knowledge, emulsion polymerization of methyl methacrylate - methyl acrylate - furfuryl methacrylate (MMA/MA/FMA) terpolymer has not been reported so far. In this research, terpolymers of methyl methacrylate, methyl acrylate and furfuryl methacrylate were synthesized successfully by solution polymerization and emulsion polymerization and were characterized by ^1H NMR, ATR-

IR and DSC. Emulsion polymerization is a type of radical polymerization which is widely used in industry, which generally starts with an emulsion incorporating water, monomer, and surfactant [163]. **Figure 7.1** shows the general mechanism of the emulsion polymerization. There are several advantages of using it: low cost process, nonflammable, and environmentally friendly water. Also, excessive exothermic effects can be minimized by the dispersing medium [164]. This polymer emulsion used as resin can low its cost and widen its application.

Figure 7.1 General mechanism of emulsion polymerization (Reprinted with permission from its author Firesine for free license under the Creative Commons Attribution-ShareAlike License) [163]

The MMA/MA/FMA terpolymer showed tunable T_g by adjusting feed molar ratio of soft monomer MA and stiffer monomer MMA, which is useful for the prosthetic

application. The furfuryl methacrylate unit in MMA/MA/FMA terpolymer can be cross-linked with bismaleimide (BMI) and generate the thermo-reversible cross-linked polymer by DA chemistry. It can be applied for making thermally re-moldable carbon fiber composite. In current prosthetic technology, when body heals and limb adding to the discomfort to the patient, the carbon fiber composite must be replaced by new one, which leads to high cost. The MMA/MA/FMA and BMI cross-linked polymer emulsion can be used as resin to replace the current epoxy and amine system.

Characterization of MA/MMA/FMA terpolymer

In this research, terpolymers of methyl methacrylate, methyl acrylate and furfuryl methacrylate (MMA/MA/FMA) were synthesized successfully by solution polymerization and emulsion polymerization. The furan-functionalized terpolymer was thermally cross-linked with bismaleimide (BMI) at low temperature 55 °C; while thermally reversible uncrosslinking was accomplished at 130 °C (**Scheme 7.1**).

Scheme 7.1 Diels-Alder and retro Diels-Alder reactions of MA/MMA/FMA terpolymer with BMI

^1H NMR (300MHz, $\text{DMSO}-d_6$) of MA/MMA/FMA terpolymer **TR1** is shown in **Figure 7.2** where signals at δ 6.4 and δ 7.2 represent furfuryl protons, signal at δ 3.5

represents -OCH₃ protons in MMA and MA. **Figure 7.3** shows the ATR-FTIR spectrum of MA/MMA/FMA terpolymer **TR1**. C-C stretch (in-ring) at 1435 cm⁻¹ and C-H out-of-plane bend at 750 cm⁻¹ from FMA unit were observed; C=O stretch at 1724 cm⁻¹, C-O stretch at 1139 cm⁻¹, and C-H stretch at 2950-2990 cm⁻¹ from MA, MMA and FMA were clearly shown. The molecular weight of MA/MMA/FMA terpolymer **TR1** determined by GPC showed a broad distribution. A typical GPC curve of MA/MMA/FMA terpolymer **TR1** is shown in **Figure 7.4**, which has an average number molecular weight of 27,022 and weight distribution index (PDI) of 4.1. **Figure 7.5** shows the decomposition temperature of MA/MMA/FMA terpolymer **TR1** is around 337 °C in N₂; while 310 °C in air. It is one-step sharp decomposition, having a weight loss of 95% at about 440 °C in N₂; while 90% at 445 °C in air. Oxygen in air could accelerate the decomposition of this MA/MMA/FMA terpolymer.

Figure 7.2 ¹H NMR of MA/MMA/FMA terpolymer **TR1** (in DMSO-*d*₆)

Figure 7.3 ATR-IR spectrum of MA/MMA/FMA terpolymer **TR1**

Figure 7.4 Gel permeation chromatogram of MA/MMA/FMA terpolymer **TR1** (polystyrene standard, in THF)

Figure 7.5 TGA thermograms of MA/MMA/FMA and BMI cross-linked polymer **CR1** and MA/MMA/FMA terpolymer **TR1** (10 °C/min, in N₂ and air)

Previous research indicated that high amount of FMA would lead to insoluble polymer [148], and even 3-5% furfuryl functional group can bring effective cross-linking property [149]. Based on these previous results, 15% molar ratio of FMA was chosen to be fed in all the polymerizations of terpolymer in this research. Molar ratio of MMA and MA was adjusted to tune the glass transition temperature (T_g) of MA/MMA/FMA terpolymer. **Table 7.1** shows three typical glass transition temperatures of the terpolymer with three different feed molar ratios of MA and MMA. High amount of MA added would decrease T_g of the terpolymer due to the soft nature of MA; while high amount of MMA added would raise T_g of the terpolymer because MMA is a stiff monomer. Tunable T_g of the terpolymer was obtained by adjusting the feed molar ratio of soft monomer MA and stiffer monomer MMA, which is useful for the prosthetic application.

Table 7.1 Composition and glass transition temperature of MA/MMA/FMA terpolymer

MA (Feed mol %)	MMA (Feed mol %)	FMA (Feed mol %)	T_g of MA/MMA/FMA terpolymer (°C) *
55	30	15	57
45	40	15	82
30	55	15	103

*TA Q1000 DSC (10 °C/min, in N₂)

Characterization of MA/MMA/FMA and BMI cross-linked polymer

MA/MMA/FMA and BMI cross-linked polymer emulsion **CR4** has a particle size around 5870 nm and polydispersity index (P.I.) about 1.06 (**Figure 7.6**); while MA/MMA/FMA terpolymer emulsion **TR4** has a particle size of 119 nm and P.I. about 0.051 (**Figure 7.7**). The sharp increase of particle size of the cross-linked polymer emulsion is due to the DA reaction of FMA and BMI, which linked the terpolymer particles together to form bigger cross-linked polymer particles. Thermal characterization of MA/MMA/FMA and BMI cross-linked polymer showed different properties from that of MA/MMA/FMA terpolymer. The cross-linked polymer **CR1** has an earlier decomposition started around 136 °C in air & N₂ in TGA thermogram (**Figure 7.5**), and a new transition at 139 °C in DSC thermogram (**Figure 7.8**), which can be uncross-linking of the polymer caused by retro-DA reaction.

Figure 7.6 Particle size and distribution of MA/MMA/FMA and BMI cross-linked polymer emulsion **CR4** by DLS

Figure 7.7 Particle size and distribution of MA/MMA/FMA terpolymer emulsion **TR4** by DLS

Figure 7.8 DSC thermogram of MA/MMA/FMA and BMI cross-linked polymer **CR1** (10 °C/min, in N₂)

Thermo-reversible property of MA/MMA/FMA and BMI cross-linked polymer

Attenuated total reflectance Fourier transform infrared (ATR–FTIR) was used to observe the thermo-reversible property of MA/MMA/FMA and BMI cross-linked polymer. ATR-IR spectrum of the cross-linked polymer **CR1** (**Figure 7.9 b**) has a peak at 1674 cm^{-1} , from C=C in adduct of cross-linked polymer, which indicates that (4+2) cycloaddition took place between furfuryl group in MA/MMA/FMA terpolymer and BMI. This peak disappeared after the cross-linked polymer being heated at high temperature and quenched by liquid N_2 to freeze its structure (**Figure 7.10 a**). The disappearance of peak 1674 cm^{-1} is due to the uncross-linking by retro Diels-Alder (rDA) reaction. Once the uncross-linked polymer was heated again and cooled slowly by air, the peak 1677 cm^{-1} was shown again in ATR-IR spectrum (**Figure 7.10 b**), which indicates that (4+2) cycloaddition took place again by DA chemistry. Cross-linked MA/MMA/FMA and BMI polymer can be easily uncross-linked and recross-linked by DA and retro-DA reactions.

Figure 7.9 ATR-IR spectra of: a) MA/MMA/FMA terpolymer **TR1**; b) MA/MMA/FMA and BMI cross-linked polymer **CR1**

Figure 7.10 ATR-IR spectra of: a) uncross-linked MA/MMA/FMA terpolymer with BMI; b) MA/MMA/FMA and BMI recross-linked polymer

Thermo-reversible properties of MA/MMA/FMA and BMI cross-linked polymers **CR1** and **CR4** were also confirmed by solubility test. MA/MMA/FMA and BMI cross-linked polymer **CR1** would be uncross-linked after being heated at 130-136 °C in DMF for 2 h and shown as a clear solution (**Figure 7.11 a**); While the cross-linked polymer gel was insoluble in DMF at room temperature even after one month (**Figure 7.11 b**). This experiment showed Diel-Alder (DA) and retro Diels-Alder (rDA) reactions did take place between MA/MMA/FMA terpolymer and BMI.

Figure 7.11 (a) Cross-linked polymer **CR1** (left) and uncross-linked polymer solution after being heated at 130 °C in DMF (right); (b) Insoluble cross-linked polymer gel after one month in DMF at room temperature.

Remolding experiments

Cross-linked MA/MMA/FMA and BMI polymer **CR1** would become very soft after being heated about 2 min by heat gun. It could be easily molded to various shapes when it was hot. When cooling down, the polymer became stiff, and maintained its shape at room temperature. This heating and cooling process could be repeated 7 cycles without damaging the polymer. But after 9 cycles, the polymer color became darker. **Figure 7.12** shows various shapes of cross-linked MA/MMA/FMA and BMI polymer **CR1** after being heated and remolded. The property is very useful for making thermo-remoldable carbon fiber composite.

Figure 7.12 Re-molding experiment of MA/MMA/FMA and BMI cross-linked polymer **CR1**

MA/MMA/FMA and BMI cross-linked polymer emulsion **CR4** was used as resin to produce thermo-remoldable carbon fiber composite in this study. Carbon fiber cloth was filled with MA/MMA/FMA and BMI cross-linked polymer emulsion **CR4** and heated at 70 °C to form carbon fiber composite. The composite obtained could be molded to various shapes when it was hot. After cooling down, the composite maintained its shape at room temperature. **Figure 7.13** shows various shapes of carbon fiber composite after being heated and remolded. This MA/MMA/FMA and BMI cross-linked polymer emulsion has the potential application as the resin to replace epoxy and amine system for carbon fiber composite and lower the cost in prosthetic industry.

Figure 7.13 Re-molding experiment of MA/MMA/FMA and BMI resin **CR4** carbon fiber composite

Conclusions

A novel MA/MMA/FMA terpolymer was synthesized by solution polymerization and emulsion polymerization. Thermo-reversible cross-linking via DA and retro-DA reactions between the terpolymer and BMI was confirmed by ATR-IR and solubility tests. The cross-linked polymer showed a quick remolding ability. MA/MMA/FMA and BMI cross-linked polymer emulsion has the potential to replace epoxy and amine system for carbon fiber composite and lower the cost in prosthetic industry.

Experimental

Materials

Methyl acrylate (MA), Methyl methacrylate (MMA), furfuryl methacrylate (FMA), 2,2'-Azobis(2-methylpropionitrile) (AIBN), N,N'-1,3-phenylenedimaleimide

(BMI), Ammonium persulfate, Sodium dodecylbenzenesulfonate, Dihexyl sulfosuccinate sodium salt solution were purchased from the Aldrich Chemical Co. All reagents were used as received.

Synthesis of MA/MMA/FMA terpolymers

a) Solution polymerization of MA/MMA/FMA terpolymers TR1-3

MA/MMA/FMA terpolymers **TR1-3** were prepared by free radical polymerization. 250 ml three necks round bottom flask equipped with magnetic stir-bar was charged with furfuryl acrylate, methylmethacrylate and methacrylate in different molar ratio in toluene and isopropanol. The ratio of monomer/solvent was 1/4 (v/v). The polymerization was initiated by azobisisobutyronitrile (AIBN) under nitrogen atmosphere. The flask was purged with N₂ gas, sealed with a rubber septum, and placed in 70 °C temperature oil bath. The reaction was carried out for 16 h with continuous stirring. The terpolymers were precipitated with excess de-ionized water, then washed and dried in vacuum oven for two days till constant weight was obtained.

b) Emulsion polymerization of MA/MMA/FMA terpolymers TR4-8

The emulsion polymerization of MA/MMA/FMA terpolymer **TR4-8** by varying feed molar ratio was carried out in a 250 mL flask fitted with a thermocouple probe, condenser, addition funnel and nitrogen inlet. The flask was charged with 2 g Sodium dodecylbenzenesulfonate, 4.5 g Dihexyl sulfosuccinate sodium salt and ammonium persulfate in 90 mL water and purged with nitrogen for 30 min. Then MA, MMA and

FMA mixture was added drop wise into the flask over a period of 1 h. The polymerization reaction was carried at 70 °C with continuous stirring. The terpolymers were precipitated in 1% MgSO₄ solution, then washed and dried in vacuum oven for two days till constant weight was obtained.

Characterization of MA/MMA/FMA terpolymers

¹H NMR spectrum was obtained with JEOL ECX-300 spectrometer using DMSO-*d*₆ as solvent. Attenuated total reflectance Fourier transform infrared (ATR–FTIR) analysis of copolymers was performed on a Thermo-Nicolet Magna 550 FTIR spectrophotometer with a high endurance diamond ATR attachment. The thermal stability of the polymer was performed by using Mettler-Toledo 851 thermogravimetric analyzer. Differential scanning calorimetry (DSC) was performed on a TA Q1000 instrument in nitrogen at a heating rate of 10 °C min⁻¹. The glass transition temperature (*T*_g) was obtained from a second heating cycle using TA Universal Analysis 2000 software suite. Size exclusion chromatography (SEC) was used to determine the molecular weights of polymers in chloroform at 35 °C at 1 mL/min flow rate on a Waters SEC instrument equipped with a Waters 2695 separations module and a Waters 2410 refractive index detector. Coulter N4MD Sub-Micron Particle Analyzer was used for Dynamic light scattering of polymer solution (25 °C).

Diels-Alder (DA) and retro Diels-Alder (rDA) reactions

a) Diels-Alder (DA) reactions

Cross-linker N, N'-1, 3- phenylenedimaleimide (BMI) in DMF solution was prepared. Cross-linker solution was added drop wise into DMF solution of MA/MMA/FMA terpolymer at 55 °C and stirred overnight in N₂ atmosphere. The cross-linked MA/MMA/FMA and BMI polymer was washed by methanol and dried in vacuum oven for a few days till constant weight was obtained.

And also Cross-linker N, N'-1,3- phenylenedimaleimide (BMI) solution was added drop wise into MA/MMA/FMA terpolymer emulsion at 55 °C and stirred overnight in N₂ atmosphere. The cross-linked MA/MMA/FMA and BMI polymer precipitated from emulsion was washed by methanol and dried in vacuum oven for a few days till constant weight was obtained.

b) retro Diels-Alder (rDA) reactions

A 250 mL reaction flask fitted with a thermocouple probe, condenser, addition funnel and nitrogen inlet was charged with DMF. The cross-linked MA/MMA/FMA and BMI polymer obtained from solution polymerization or emulsion polymerization was added in the flask. The uncross-linking reaction was carried at 130-136 °C with continuous stirring.

Procedure of making carbon fiber composite

Carbon fiber cloth was filled with MA/MMA/FMA and BMI cross-linked polymer emulsion and heated in oven at 70 °C overnight.

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APPENDICES

Appendix A
Selected NMR Spectra

Figure A-1: ^1H NMR of 82/12/6 AN/VIM/IP terpolymer **CF29**

Figure A-2: ^1H NMR of 82/12/6 AN/VIM/St terpolymer **CF42**

Appendix B

Selected DLS Spectra

Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coeff (m ² /s)	Counts/s	Baseline Error	Overflow
Rept.1	2462.4	1.751	1.99e-13	4.39e+05	4.00%	0
Rept.2	2592.3	1.709	1.89e-13	4.62e+05	7.21%	0
Rept.3	2734.9	1.770	1.79e-13	4.58e+05	4.23%	0
Average	2596.6 ± 111.29	1.743 ± 0.026

Figure B-1: DLS curve of AN/VIM copolymer **CF55** prepared by dispersion polymerization (7% w/w monomer to water, 26% VIM copolymer stabilizer, 6.8% stabilizer concentration)

Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coeff (m ² /s)	Counts/s	Baseline Error	Overflow
Rept.1	82.5	0.747	5.95e-12	7.83e+04	4.98%	5
Rept.2	82.0	0.647	5.98e-12	7.75e+04	3.02%	3
Rept.3	81.5	0.619	6.02e-12	7.65e+04	2.61%	3
Average	82.0 ± 0.40	0.671 ± 0.055

Figure B-2: DLS curve of AN/VIM copolymer **CF54** prepared by dispersion polymerization (7% w/w monomer to water, 26% VIM copolymer stabilizer, 10% stabilizer concentration)

Unimodal Results Summary

Rept.#	Mean (nm)	P.I.	Diff.Coeff (m ² /s)	Counts/s	Baseline Error	Overflow
Rept.1	9840.3	1.044	4.98e-14	1.80e+05	20.72%	0
Rept.2	5199.1	1.456	9.43e-14	1.15e+05	4.26%	0
Rept.3	5790.0	1.437	8.47e-14	1.29e+05	7.99%	0
Average	6943.2 ± 2062.75	1.312 ± 0.190

Figure B-3: DLS curve of AN/VIM copolymer **CF66** prepared by dispersion polymerization (15% w/w monomer to water, 31% VIM copolymer stabilizer, 6.8% stabilizer concentration)

Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coeff (m ² /s)	Counts/s	Baseline Error	Overflow
Rept.1	24437.7	-0.428	2.01e-14	8.43e+05	29.97%	0
Rept.2	29109.4	1.459	1.69e-14	8.41e+05	35.18%	0
Rept.3	22795.8	-0.126	2.15e-14	9.48e+05	21.97%	0
Average	25447.6 ± 2674.64	0.301 ± 0.828

Figure B-4: DLS curve of AN/VIM copolymer **CF53** prepared by dispersion polymerization (7% w/w monomer to water, 26% VIM copolymer stabilizer, 0% stabilizer concentration)

Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coeff (m ² /s)	Counts/s	Baseline Error	Overflow
Rept.1	125.9	1.435	3.90e-12	3.25e+04	7.50%	12
Rept.2	98.1	1.068	5.00e-12	3.34e+04	0.29%	0
Rept.3	101.3	1.112	4.84e-12	3.50e+04	0.19%	0
Average	108.4 ± 12.43	1.205 ± 0.164

Figure B-5: DLS curve of AN/VIM copolymer **CF62** prepared by dispersion polymerization (15% w/w monomer to water, 47% VIM copolymer stabilizer, 6.8% stabilizer concentration)

Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coeff (m ² /s)	Counts/s	Baseline Error	Overflow
Rept.1	261.1	0.160	1.88e-12	1.30e+06	0.01%	0
Rept.2	261.5	0.184	1.88e-12	1.29e+06	0.02%	0
Rept.3	260.7	0.176	1.88e-12	1.29e+06	0.00%	0
Average	261.1 ± 0.34	0.173 ± 0.010

Figure B-6: DLS curve of AN/VIM copolymer **CF67** prepared by dispersion polymerization (15% w/w monomer to water, 100% VIM copolymer stabilizer, 6.8% stabilizer concentration)

Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coeff (m ² /s)	Counts/s	Baseline Error	Overflow
Rept.1	125.9	1.435	3.90e-12	3.25e+04	7.50%	12
Rept.2	98.1	1.068	5.00e-12	3.34e+04	0.29%	0
Rept.3	101.3	1.112	4.84e-12	3.50e+04	0.19%	0
Average	108.4 ± 12.43	1.205 ± 0.164

Figure B-7: DLS curve of AN/VIM copolymer **CF62** prepared by dispersion polymerization (15% w/w monomer to water, 47% VIM copolymer stabilizer, 6.8% stabilizer concentration)

90.0° Unimodal Distribution
Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coeff (m ² /s)	Counts/s	Baseline Error	Overflow
Rept.1	287.6	0.289	1.71e-12	1.76e+06	0.07%	0
Rept.2	282.7	0.281	1.74e-12	1.72e+06	0.01%	0
Rept.3	283.0	0.252	1.73e-12	1.72e+06	0.01%	0
Average	284.4 ± 2.26	0.274 ± 0.016

Figure B-8: DLS curve of AN/VIM copolymer **CF63** prepared by dispersion polymerization (25% w/w monomer to water, 47% VIM copolymer stabilizer, 6.8% stabilizer concentration)

Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coeff (m ² /s)	Counts/s	Baseline Error	Overflow
Rept.1	9840.3	1.044	4.98e-14	1.80e+05	20.72%	0
Rept.2	5199.1	1.456	9.43e-14	1.15e+05	4.26%	0
Rept.3	5790.0	1.437	8.47e-14	1.29e+05	7.99%	0
Average	6943.2 ± 2062.75	1.312 ± 0.190

Figure B-9: DLS curve of AN/VIM copolymer **CF66** prepared by dispersion polymerization (30% w/w monomer to water, 47% VIM copolymer stabilizer, 6.8% stabilizer concentration)

90.0° Unimodal Distribution
Unimodal Results Summary

Rept#.	Mean (nm)	P.I.	Diff.Coeff (m ² /s)	Counts/s	Baseline Error	Overflow
Rept.1	16396.1	0.248	2.99e-14	5.77e+05	7.42%	0
Rept.2	19890.9	-0.089	2.47e-14	4.91e+05	18.48%	0
Rept.3	16284.8	0.334	3.01e-14	5.60e+05	6.52%	0
Average	17524.0 ± 1674.31	0.164 ± 0.182				

17.5 μ m

Figure B-10: DLS curve of AN/VIM copolymer **CF64** prepared by dispersion polymerization (35% w/w monomer to water, 47% VIM copolymer stabilizer, 6.8% stabilizer concentration)

Appendix C

Selected DSC Spectra

Figure C-1: DSC curve of 85/15 AN/VIM copolymer **CF4**

Figure C-2: DSC curve of 85/15 AN/VIM copolymer **CF7**

Figure C-3: DSC curve of 85/15 AN/VIM copolymer **CF8**

Figure C-4: DSC curve of 85/15 AN/VIM copolymer **CF9-2**

Figure C-5: DSC curve of 85/15 AN/VIM copolymer **CF9-3**

Figure C-6: DSC curve of 95/5 AN/VIM copolymer **CF17**

Figure C-7: DSC curve of 90/10 AN/VIM copolymer **CF18-3**

Figure C-8: DSC curve of 90/10 AN/VIM copolymer **CF18-2**

Figure C-9: DSC curve of 75/25 AN/VIM copolymer **CF12**

Figure C-10: DSC curve of 85/14/1 AN/VIM/BA terpolymer **CF14**

Figure C-11: DSC curve of 85/12/3 AN/VIM/BA terpolymer **CF13**

Figure C-12: DSC curve of 85/9/6 AN/VIM/BA terpolymer **CF15**