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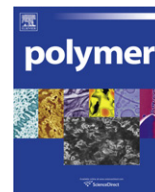
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Poly (acrylonitrile – co -1-vinylimidazole): A new melt processable carbon fiber precursor

Wenjin Deng^a, Alexander Lobovsky^b, Scott T. Iacono^{a,2}, Tianyu Wu^d, Neetu Tomar^a, Stephen M. Budy^{a,3}, Timothy Long^d, Wesley P. Hoffman^c, Dennis W. Smith Jr.^{a,*,1}

^a Department of Chemistry, Clemson University, Clemson, SC 29634, USA

^b Advanced Fiber Engineering, LLC, 8 Floral Ct, Westfield, NJ 07090, USA

^c AFMC AFRL/RZSM, US Air Force Research Lab, Edwards AFB, CA 93524, USA

^d Department of Chemistry, Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24061, USA

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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). Char yields of the copolymers were 40–48% as determined by thermogravimetric analysis (TGA) while gel fractions were found to be 90–99% depending upon the composition, temperature and time. The complex viscosity of the precursor copolymers was measured as a function of composition and temperature. 82/18 mol% of AN/VIM copolymer based carbon fiber precursor was successfully processed by solvent-free melt spinning at 192 °C and the melt-spun fiber was characterized by DSC, ATR-IR, and X-ray Diffraction (XRD).

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1. 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]. Thus the synthesis [4–6], structural characterization [7–19], and cyclization studies [19] of PAN based precursors have 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. 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].

In general, commercial PAN precursors degrade before they melt therefore, the precursor fibers are commonly solution-spun (20–30 wt% solution) from polar solvents [20]. 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 [20,21]. Melt processable PAN copolymers in combination with other comonomers such as methyl acrylate [22], methacrylic acid [12], and itaconic acid [23] 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) [22].

* Corresponding author. Tel.: +1 864 207 0661.

E-mail address: dwsmith@utdallas.edu (D.W. Smith).

¹ Present address: The University of Texas at Dallas, 800 W Campbell Rd. BE26, Richardson, TX 75080-3021, USA.

² Present address: Department of Chemistry, United States Air Force Academy, USAF Academy, CO 80840, USA.

³ Present address: Department of Chemistry & Biochemistry, University of Arizona, Tucson, AZ 85721, USA.

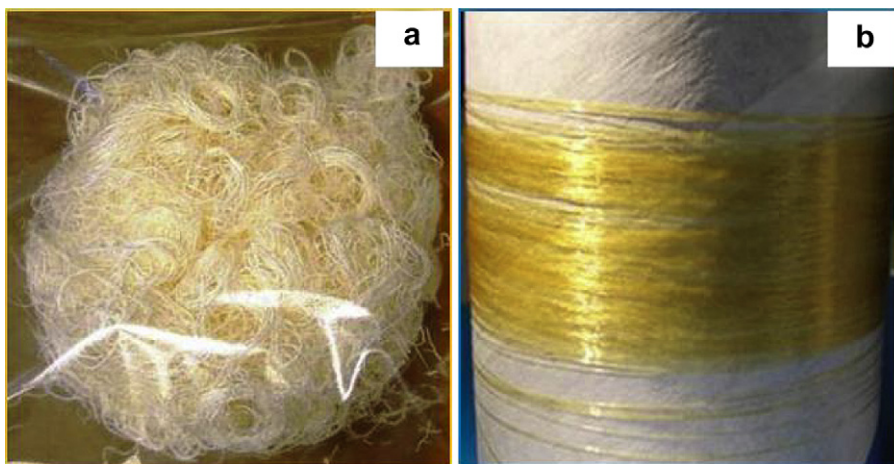


Fig. 1. Photograph of (a) 82/18 AN/VIM copolymer; (b) melt-spun fiber of 82/18 AN/VIM.

These precursors can be stabilized by UV light, which sometimes is not sufficient enough for cross-linking (~65% gel fraction) [22,24] and again add cost specialized technique.

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 [25,26] 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 [27–29]. 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.

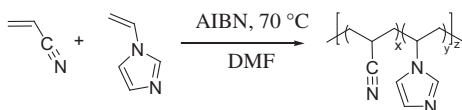
2. Experimental

2.1. 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.

2.2. Synthesis of carbon fiber precursor

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.



Scheme 1. Free radical copolymerization of AN with VIM.

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 copolymer was precipitated in 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 (Fig. 1a).

2.3. Characterization of copolymer precursors and melt-spun fiber

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 (1 mg/mL, 25 °C) and three test cycles were carried out. An 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 [30]:

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

where $[\eta]$ is intrinsic viscosity, c = concentration of polymer solution (g/dL); η_{sp} = specific viscosity; η_{rel} = relative viscosity.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analysis of copolymers was performed on a Thermo-Nicolet

Table 1

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

In feed (mol%)		In copolymer ^a (mol%)	
VIM	AN	VIM	AN
0	100	0	100
10	90	14	86
12	88	16	84
18	82	22	78
21	79	27	73
25	75	37	63

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

^a Determined by ¹H NMR.

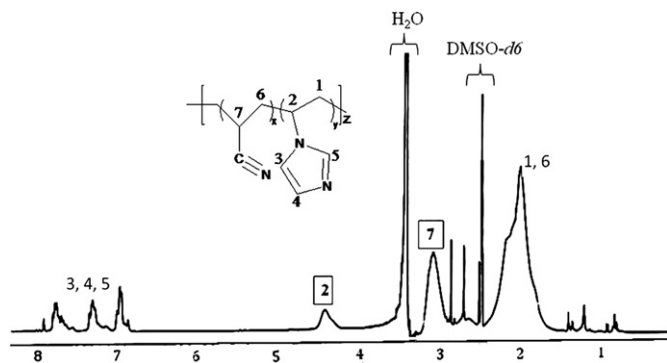


Fig. 2. ^1H NMR of 82/18 AN/VIM copolymer.

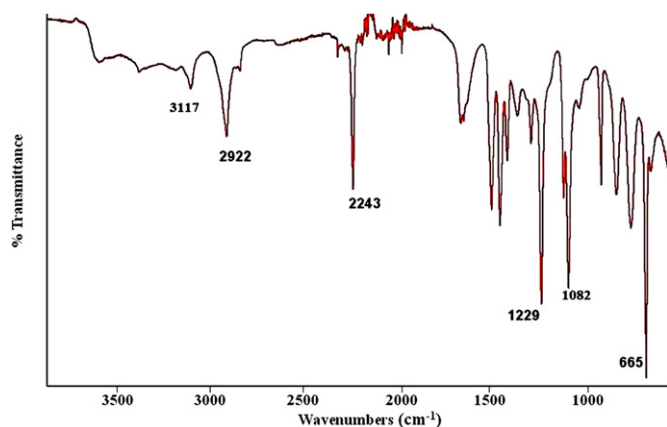


Fig. 3. ATR-FTIR spectrum of 82/18 AN/VIM copolymer.

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 [20].

Differential scanning calorimetry (DSC) was performed on a TA Q1000 instrument in nitrogen at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The glass transition temperature (T_g) was obtained from a second heating cycle using TA Universal Analysis 2000 software suite.

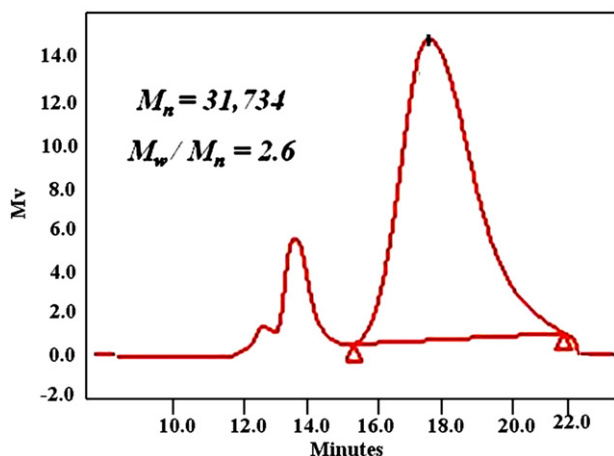


Fig. 4. Gel permeation chromatogram of 82/18 AN/VIM copolymer in DMF.

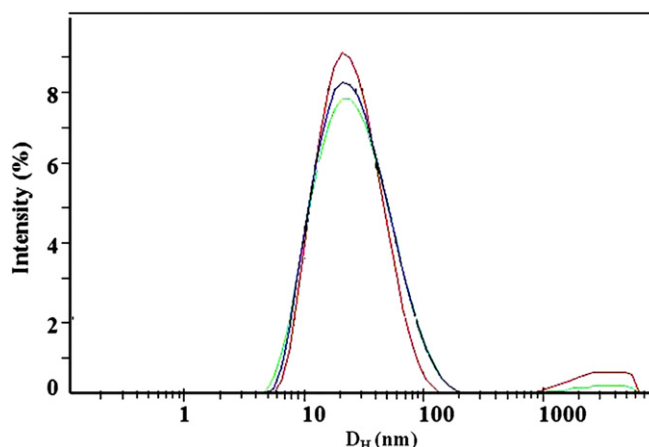


Fig. 5. Particle size of 82/18 AN/VIM copolymer in DMF solution by DLS.

The Scintag XDS 2000 X-ray diffractometer was used for X-ray diffraction analysis of melt-spun fiber. The count time is 1.300 s, step scan rate is $0.02\text{ }^\circ/\text{min}$ and the range is $5.00\text{--}70.00^\circ$. Dynamic oscillatory shear properties of the copolymers were determined by well calibrated TA instruments ARES LS/M LS001-270i (Rheometric Scientific) in N_2 atmosphere. Frequency sweep ranging between 0.1 and 100 rad/s was performed by using cone-plate at 0.1% strain and $200\text{ }^\circ\text{C}$. Strain sweep was conducted at 10 rad/s and $200\text{ }^\circ\text{C}$ in order to determine the linear viscoelastic region of these copolymers. Dynamic time sweeps were carried out at 0.1% strain and angular frequency of 1 rad/s at $205\text{ }^\circ\text{C}$ and $210\text{ }^\circ\text{C}$ for 25 min. Dynamic temperature sweeps of 88/12 and 82/18 AN/VIM copolymers were studied at $2\text{ }^\circ\text{C/min}$ from 160 to $220\text{ }^\circ\text{C}$ at 0.1 rad/s and 0.1% strain.

2.4. Melt-spinning of AN/VIM copolymer precursor

Fiber spinning was performed at Advanced Fiber Engineering, LLC, Westfield, NJ. 82/18 AN/VIM copolymer precursor ($[\eta] = 0.59\text{ dL/g}$) was ground into coarse granules in a grinder and these copolymer granules were vacuum dried at $65\text{ }^\circ\text{C}$ for 3 h. An Instron 3211 capillary rheometer (capillary diameter, $D = 0.030\text{ inches}$) was used to draw the fibers. In a typical trial, $\sim 9\text{ g}$ of copolymer was loaded in preheated rheometer at $180\text{ }^\circ\text{C}$ under nitrogen atmosphere and left there to heat up for 10 min, after that drawing temperature was raised to $192\text{ }^\circ\text{C}$. Melt-spun fiber (Fig. 1b) was collected by winding on 3 inches diameter bobbin rotating at 84 rpm.

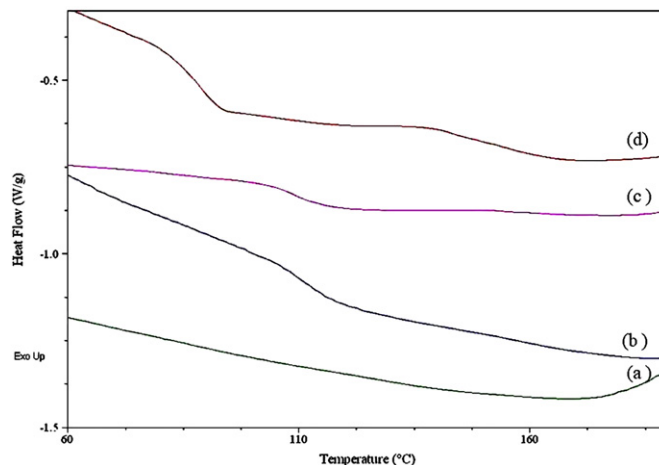


Fig. 6. DSC thermograms of (a) AN homopolymer; (b) 87/13 AN/VIM; (c) 84/16 AN/VIM; and (d) 81/19 AN/VIM copolymers.

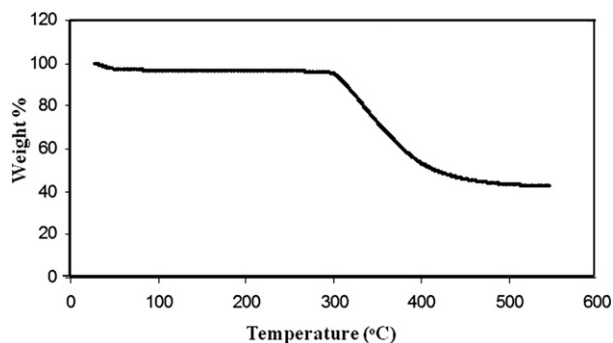


Fig. 7. TGA curve of 82/18 AN/VIM copolymer in N_2 .

Table 2

Char yields of various AN/VIM copolymers.

AN/VIM copolymer (feed mol%)	Char yield ^a wt (%)
90/10	47
88/12	48
82/18	47
79/21	40
75/25	40

^a Determined by TGA.

2.5. 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 N_2 and again isothermal at 550 °C for 3 h in N_2 [20]. In order to calculate the gel fraction, the copolymers were first stabilized by heating at 210 °C for 2 h or 250 °C for 5 h respectively in an oven in air and then immersed in DMF solvent for 3 days. The gels were filtered, washed with methanol, and dried in vacuum for 7 days till constant weight.

3. Results and discussion

3.1. Composition of the copolymer precursor

The schematic representation for the synthesis of AN with VIM is shown in Scheme 1. Addition of monomers was carried out by two different methods: “one pot” method and “starve-fed addition” method. In the “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 $r_{1\text{ AN}} = 0.24$ and $r_{2\text{ VIM}} = 0.12$ [25]. It was observed that this polar donor–acceptor (AN–VIM) pair intended to form alternating copolymer [25,31,32]. In order to better control the composition drifts, we have used “starve-fed addition” method to synthesize AN/VIM copolymers. The copolymer composition determined by 1H NMR (Table 1), 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.

A typical 1H NMR spectrum of 82/18 AN/VIM copolymer is shown in Fig. 2. 1H NMR signals at δ 2.0 represent the backbone CH_2 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. Fig. 3 depicts the ATR–FTIR spectrum of 82/18 AN/VIM copolymer. Backbone CH_2 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 CH_2 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} .

3.2. GPC and DLS of AN/VIM copolymer precursor

Relative molecular weights of AN/VIM copolymers to polystyrene standards were determined using size exclusion chromatography in DMF. A bimodal distribution was observed for all copolymer compositions. The bimodal distribution curve of 88/12 AN/VIM copolymer ($\bar{M}_n = 31,734\text{ g/mol}$, $\bar{M}_w = 82,508\text{ g/mol}$, PDI = 2.6) is shown in Fig. 4. 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 (Fig. 5). This bimodal distribution in GPC could possibly be due to chain transfer of copolymer [33] or due to attack on the other polymerization site of the pendant imidazole group [34] which may lead to branching.

3.3. Glass transition temperatures of AN/VIM copolymer precursor

Fig. 6 shows the DSC curves of polyacrylonitrile and AN/VIM copolymers from 60 to 200 °C. No T_g signal was observed in the case

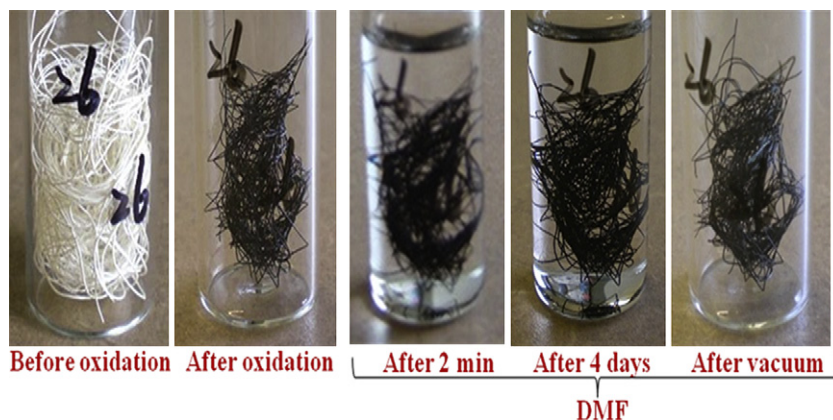


Fig. 8. Photographs of copolymers before and after oxidation during gel fraction experiment (oxidized copolymer retained its shape in DMF even after 7 days.).

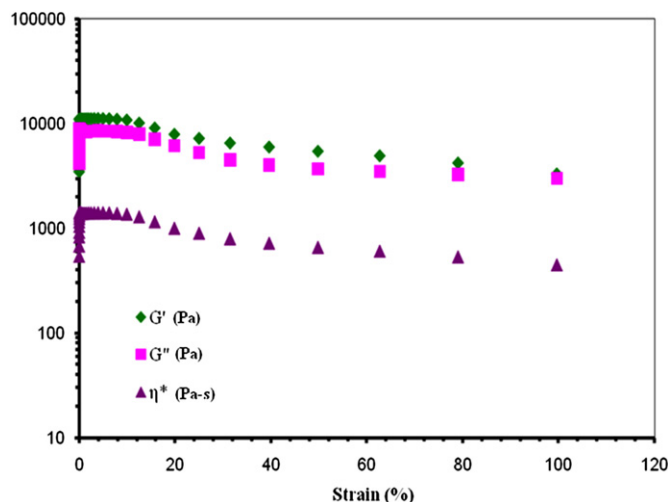


Fig. 9. Dynamic strain sweep of 82/18 AN/VIM copolymer (200 °C, 10 rad/s).

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 [36–38]. The decrease in transition temperatures 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 [39]. For the polymers with high acrylonitrile content, a first-order phase transition (melting) is typically not observed due to the inter-chain interactions between polar nitrile substituents as reported by Hutchinson [40].

3.4. Decomposition temperature and char yield of AN/VIM polymer

TGA studies were performed to determine the initial decomposition temperature and char yield of the copolymers. The initial decomposition temperature for the copolymers was 300–310 °C. A representative TGA curve of 82/18 AN/VIM copolymer is shown in

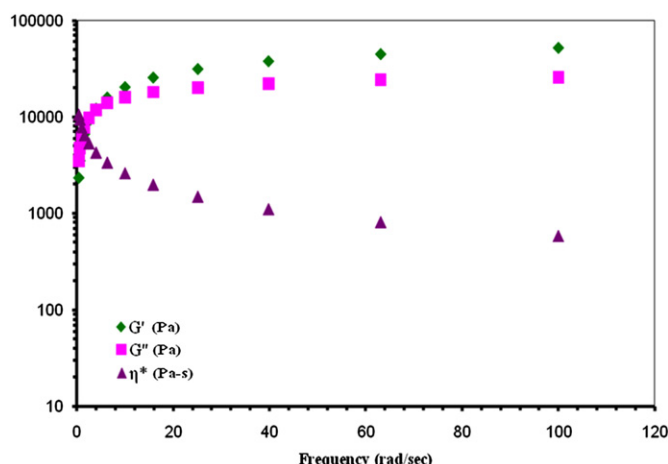


Fig. 10. Dynamic frequency sweep of 82/18 AN/VIM copolymer (200 °C, 0.1% strain).

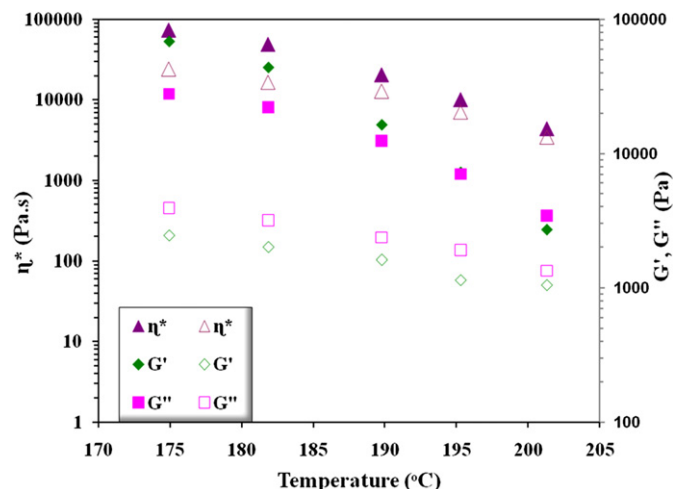


Fig. 11. Dynamic temperature sweep of 82/18 AN/VIM copolymer (open symbol) and 88/12 AN/VIM copolymer (closed symbol) at 0.1 rad/s, 0.1% strain.

Fig. 7. All the copolymers showed rapid weight loss when the temperature is higher than approximately 310 °C.

Char yields of various AN/VIM copolymers (Table 2) were obtained by TGA under the similar conditions as was reported by McGrath et al. [20]. 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% [41]. This led us to conclude that VIM concentration 10–18 mol% can be effectively used for carbon fiber precursors.

3.5. 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 the copolymers changed from white to brown and then black during stabilization as expected. The stabilized black copolymers were insoluble in DMF, showing good cross-linking ability (Fig. 8). The average gel fraction of 88/12 AN/VIM copolymer was about 99% while average gel fractions of 82/18 AN/VIM copolymers was ~90% at 210 °C for 2 h in the air. However, at higher temperature and longer time (250 °C for 5 h), the gel fraction of 82/18 AN/VIM copolymer increased to 99%. The requirement of higher temperature with increasing VIM concentration to get high

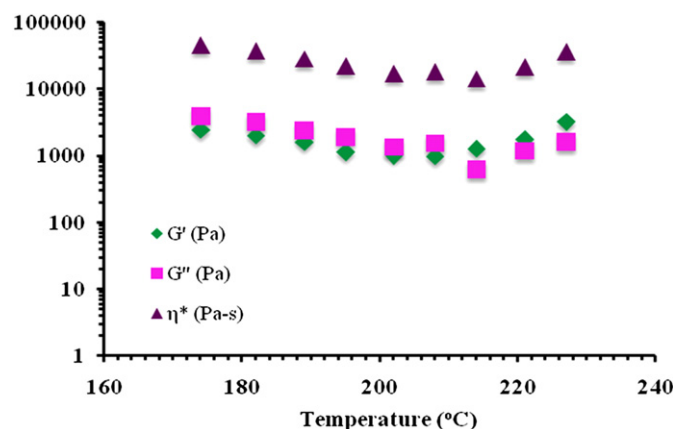


Fig. 12. Dynamic temperature sweep of 82/18 AN/VIM copolymer (0.1 rad/s, 0.1% strain).

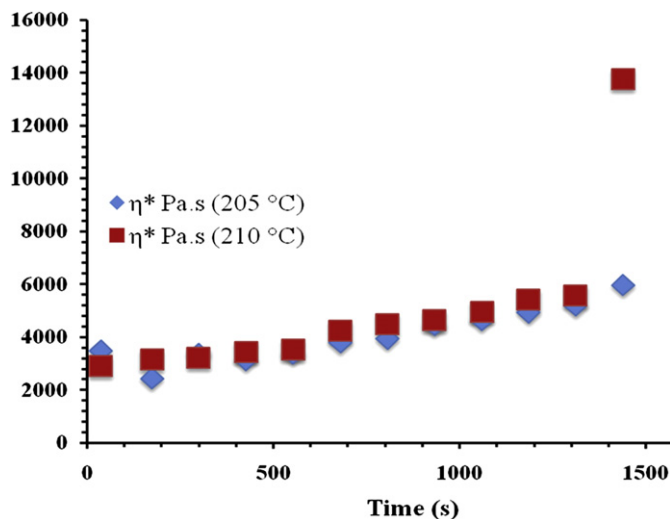


Fig. 13. Dynamic time sweep viscosity of 82/18 AN/VIM copolymer CF33 at 0.1% strain, 1 rad/s, at 205 °C and 210 °C.

gel fraction may be due to presence of comonomers with bulky side groups which introduces a slower step in the stabilization [39]. These results are consistent with the rheological data (discussed in Section 3.6).

The gel fractions of these thermally stabilized copolymers are better than the gel fraction (~65%) of melt-spun carbon fiber precursor which are stabilized by UV light [42]. 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.

3.6. Rheology study of AN/VIM copolymer precursors

The melt processability of the various copolymers was assessed by rheological measurements as melt processing windows depend upon the copolymer composition. To ensure that dynamic oscillatory measurements were made in the linear viscoelastic region for the polymers, strain sweeps were performed at 200 °C, 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 the various AN/VIM copolymer compositions. The strain sweep curve of 82/18 copolymer is shown in Fig. 9, where the

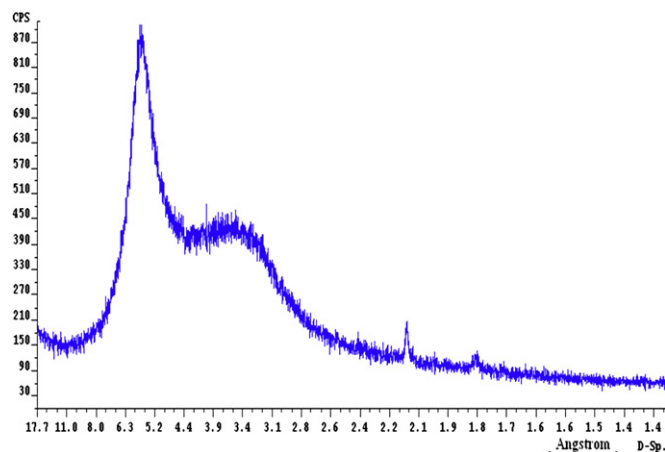


Fig. 14. 1D X-ray spectrum of melt-spun fiber of 82/18 AN/VIM (Count time: 1300 s; Step scan rate: 0.02 °/min; Range: 5.00–70.00 (°)).

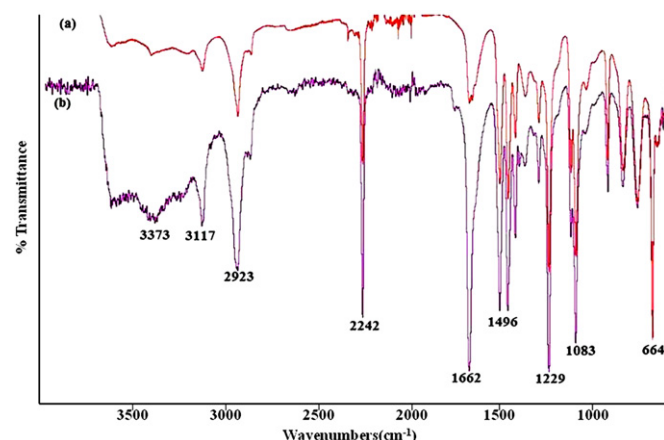


Fig. 15. ATR-FTIR spectrum of (a) 82/18 AN/VIM copolymer before melt processing, (b) melt-spun fiber of 82/18 AN/VIM.

viscosity kept constant at the low strain range. A strain of 0.1% was chosen for further dynamic viscosity testing in this study. Fig. 10 shows the frequency-dependent viscoelastic property of 82/18 AN/VIM copolymer. The viscosity of AN/VIM copolymer decreased sharply when the frequency increased.

The dynamic temperature sweep of AN/VIM copolymer was determined at 0.1% strain and 0.1 rad/s frequency in N_2 atmosphere. A significant dependence of the dynamic viscosity on the copolymer composition was observed. The homopolymer of acrylonitrile was too viscous to measure the viscosity at these testing conditions, while AN/VIM copolymers showed much lower viscosities. Viscosities of 88/12 and 82/18 AN/VIM copolymer are presented in the Fig. 11. The viscosity of 82/18 AN/VIM copolymer was lower by ~45% as compared to that of 88/12 AN/VIM copolymer. Viscosities of AN/VIM copolymer with higher VIM contents were also examined, yet no appreciable change in viscosity was observed with increase in VIM content. The 82/18 AN/VIM copolymer registered the lowest value of viscosity and good char yield of 47%, therefore, this composition was selected for further studies.

Fig. 12 is the dynamic temperature sweep of 82/18 AN/VIM copolymer (0.1 rad/s, 0.1% strain), which shows one critical temperature exists for the copolymer, 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. The viscosity of the copolymer precursor is required to be stable at the melt-spinning temperature for a certain time for fiber drawing. Dynamic time sweep was

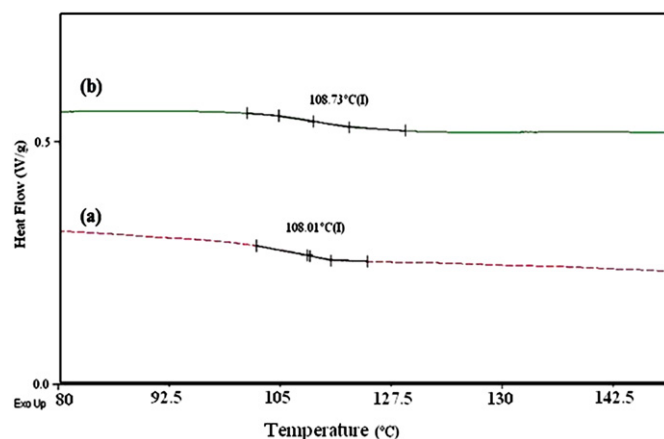


Fig. 16. DSC thermograms of (a) 82/18 AN/VIM copolymer before melt processing; (b) melt-spun fiber of 82/18 AN/VIM.

used to determine the viscosity stability of the 82/18 AN/VIM copolymer. At 205 °C, the viscosity was relatively steady for 25 min, while at 210 °C the viscosity increased sharply after 20 min (Fig. 13). The high jump in viscosity observed is likely due to intermolecular cross-linking. In order to ensure a stable copolymer viscosity for 25 min, the melt-spinning temperature should be lower than 210 °C.

3.7. Characterization of the melt-spun fiber

Successful melt-spun fiber of 82/18 AN/VIM copolymer drawn at 192 °C is shown in Fig. 1b and characterized by ATR-IR, DSC and X-ray diffraction.

The X-ray diffraction spectrum of melt-spun fiber of 82/18 AN/VIM copolymer, Fig. 14 was used to determine the preferred orientation of carbon layers and degree of crystallinity. A sharp reflection peak at 5.8 Å was observed (Fig. 14) which is comparable to that reported by Bashir [43]. The degree of crystallinity was about 35%. The ATR-IR spectrum is shown in Fig. 15 where N–H stretching at 3373 cm⁻¹, C–H ring stretching at 3117 cm⁻¹, backbone C–H stretching at 2923 cm⁻¹, C≡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 °C. The *T_g* of 82/18 AN/VIM copolymer as well as its melt-spun fiber (Fig. 16) was around 108 °C, which is in good agreement with above mentioned result.

4. 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 that the VIM helped to disrupt interchain interactions of AN units. The VIM content also greatly reduced the melt viscosity thus improving processability of the precursor. Successful melt spinning of the 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. High gel fraction and char yield of the copolymer shows its thermal cross-linking ability.

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