



ELSEVIER

Polymer 43 (2002) 4841–4850

polymerwww.elsevier.com/locate/polymer

Synthesis and characterization of acrylonitrile methyl acrylate statistical copolymers as melt processable carbon fiber precursors

V.A. Bhanu, P. Rangarajan, K. Wiles, M. Bortner, M. Sankarpandian, D. Godshall, T.E. Glass, A.K. Banthia, J. Yang, G. Wilkes, D. Baird, J.E. McGrath*

Department of Chemistry, Chemical Engineering and Materials Research Institute, Virginia Polytechnic Institute and State University, 2108 Hahn Hall, Blacksburg, VA 24061, USA

Received 18 January 2002; received in revised form 17 May 2002; accepted 17 May 2002

Abstract

Statistical (random) copolymers of acrylonitrile (AN) and methyl acrylate (MA) have been synthesized by free radical homogeneous (solution) and heterogeneous (suspension) methods. Selected compositions can be fabricated by environment friendly, solvent-free melt spinning and are of interest as precursors for carbon fibers. The dynamic and steady state melt viscosities of these copolymers were studied as a function of molecular weight and copolymer composition. Melt processability at 200–220 °C depends on the copolymer composition, and also on the molecular weight, which was controlled by chain transfer agent concentration and reaction temperature. Copolymers of controlled molecular weight containing 10 or more mol% of methyl acrylate show good melt processability, which can be further enhanced by stabilizers. This thermoplastic behavior is supported by a significant increase in temperature by the cyclization exotherm. Thermal analysis (differential scanning calorimetry, dynamic mechanical analysis) further illustrates that the comonomers retarded the cyclization, which permits thermoplastic processing. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Acrylonitrile–methyl acrylate copolymers; Melt processability; Carbon fiber precursors

1. Introduction

Polyacrylonitrile-based textile fibers are well known and, indeed, currently account for a nearly \$6 billion pound per year worldwide effort [1]. A small fraction (~30 million pounds) of these materials is used as a precursor to carbon fibers. The latter are widely used to produce high performance polymer matrix composites, characterized by high strength, stiffness, and lightweight [2,3]. It is well known that the free radically produced polyacrylonitrile displays a T_g of around 105 °C and a melting point of around 300 °C [2]. The complex reaction of Intra- and intermolecular cyclization, which is referred to as ‘stabilization’ in the carbon fiber community, occurs at 220 °C or higher and prevents thermoplastic fabrication by economical and environmentally attractive melt spinning processes. Commercial copolymers contain just a few mol% of comonomers, such as methyl acrylate (Scheme 1) and do not significantly disrupt the ‘long-range order’ or paracrystallinity (which is present in these atactic polymers) [2,4].

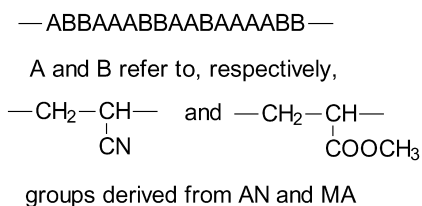
It was postulated that suitable comonomers could also be used to reduce the long-range order, simply by increasing their concentration. It has been demonstrated that solvent-free melt spinning can be conducted successfully [5–7]. The literature, while implying a great deal of interest in such behavior, has been very limited with respect to providing detailed information, even in the patent literature [8–16] and certainly not in many publications [17–30]. This study has investigated the role of polymerization processes, chemical composition and molecular weight on the melt viscosity and capability of melt fabrication/spinning of these copolymers. The results discussed in this paper have been based upon various synthetic strategies, as well as characterization by spectroscopy, chromatography, thermal analysis, melt viscosity measurements, and preliminary melt spinning experiments [6].

2. Experimental

2.1. Materials

The monomers, AN, MA, initiators AIBN (2,2'-azo-bis-isobutyronitrile) and BPO (benzoyl peroxide) and chain

* Corresponding author. Tel.: +1-540-231-4457; fax: +1-540-231-8517.
E-mail address: jmcgrath@vt.edu (J.E. McGrath).



Scheme 1. Typical carbon fiber precursor made from acrylonitrile.

transfer agent dodecyl mercaptan (abbreviated as mercaptan) were obtained from Aldrich. The solvent, *N,N*-dimethylformamide (DMF) was obtained from EM Sciences and was used as received. The monomers were passed over activated alumina prior to use to remove inhibitor. Suspension aids were principally hydrolyzed polyvinyl alcohols (M_w 85,000 and 31,000, degree of hydrolysis about 87%), obtained from Aldrich and are referred to, respectively, as PVA1 and PVA2. Polyvinylpyrrolidone, PVP, (M_w 55,000) was also obtained from Aldrich. The inorganic salts, calcium sulphate dihydrate, calcium phosphate, magnesium sulphate (anhydrous), potassium persulphate (KSP) and sodium bisulphite (SBS) were all purchased from Aldrich.

2.2. Copolymerization

Free radical copolymerizations were conducted under both homogeneous (solution) or heterogeneous (suspension) conditions. The latter were initiated by either an organic soluble (AIBN) or by water-soluble oxidation/reduction (redox) initiator. The abbreviations 85/15 and 90/10 for the copolymers made with AN and MA, refers to the molar% feed concentration of AN and MA, respectively.

Solution polymerization. A typical polymerization procedure is illustrated below for polymer 4 in Table 1. The major reaction variables were temperature, initiator and mercaptan concentrations (Tables 1 and 2). The reactor was a 500 ml 3-necked flask fitted with a condenser, glass stirrer, nitrogen inlet tube, and thermocouple probe. Firstly, the flask was charged with 100 ml DMF and purged with dry nitrogen for 15 min. Next, the mixture of 640 mmol AN,

113 mmol MA, 3.75 mmol AIBN (0.49 mol% based on total monomer concentration) and 0.375 mmol mercaptan (0.05 mol% based on total monomer concentration) was introduced and polymerized at 65 °C for 6 h. The copolymer was purified by precipitation from 50-fold excess of de-ionized water. It was then filtered, washed with water and methanol and dried under vacuum at 70 °C for 24 h, affording a yield of 85%.

Aqueous redox initiated polymerization. A literature procedure described above [31] was followed. The typical procedure for an 85/15 AN/MA copolymer is described here.

The reaction assembly used was same as above for solution polymerization. The flask was charged with 340 ml of de-ionized water and purged with dry nitrogen for 30 min while heating to the reaction temperature (40 °C). The mixture of 327 mmol AN, 57 mmol MA, 1 mmol mercaptan (2.0 mol% of total monomer concentration) was then added followed by 4.20 g (6 mmol) of the sodium bisulphite (SBS, 1.05 wt% with respect to total water) in 10 ml de-ionized water. After 5 min, 4.33 g (16 mmol) of the potassium persulphate (KSP, 1.08 wt% with respect to the total water) dissolved in 50 ml de-ionized water was added and the reaction was allowed to proceed for 3 h at 40 °C. The product was then directly filtered and washed with large amounts of de-ionized water and dried as described above; recovered yield = 88%.

Organic soluble initiator suspension polymerization. A reported procedure [32] was used as a guideline. A typical procedure used for all the copolymers reported here is described for a 90/10 AN/MA copolymer.

The reaction assembly was the same as described above for solution polymerization. The suspending agent PVA1, 0.20 g, was dissolved in 150 ml water previously purged with dry nitrogen for 30 min, and then 400 mg calcium sulphate and 80 mg calcium phosphate were added. The mixture of 632 mmol AN, 70 mmol MA, 2.74 mmol AIBN initiator (0.39 mol% based on the total monomers) and 4.2 mmol mercaptan (0.59 mol% based on the total monomers) was next added. Finally, a solution of 0.1 g magnesium sulphate in 50 ml de-ionized water was added

Table 1
Effect of various reaction parameters on the molecular weight of 85/15 AN/MA solution copolymers

Polymer no. ^a	Reaction temperature (°C)	Initiator (mol%) ^b	CTA (mol%)	Intrinsic viscosity (NMP/25 °C)	M_n (GPC data)	M_w (GPC data)
1	80	A/0.49	0.70	0.18	11,600	18,500
2	75	A/0.49	0.33	0.33	14,300	22,000
3	80	A/0.49	0.05	0.45	21,000	34,300
4	65	A/0.49	0.05	0.65	39,000	58,300
5	60	A/0.49	0.00	0.73	39,700	59,200
6	90	B/0.55	0.05	0.36	17,400	24,900
7	75	B/0.55	0.05	0.75	34,600	59,400
8	65	B/0.55	0.00	0.86	—	—

^a Molar feed ratio of AN/MA is 640/113 mmol.

^b A and B stand for AIBN and BPO, respectively, initiator and CTA mol% figures are with respect to total monomer concentration.

Table 2
Effect of reaction parameters on intrinsic viscosity and molecular weight of various AN/MA solution copolymers

Polymer no.	AN/MA feed ratio	AN/MA molar feed ratio (mmol)	Reaction temperature (°C)	Initiator (mol%) ^a	CTA (mol%)	Intrinsic viscosity (NMP/25 °C)	M_n (GPC)	M_w (GPC)
9	98/2	740/15	80	A/0.49	0.70	0.25	–	–
10	95/5	717/38	80	A/0.49	0.70	0.25	–	–
11	93/7	702/53	80	A/0.49	0.70	0.26	–	–
12	90/10	680/75	80	A/0.49	0.70	0.25	–	–
13	90/10	680/75	60	A/0.49	0.05	0.82	36,400	53,700
14	90/10	680/75	70	A/0.49	0.05	0.63	23,600	37,400
15	90/10	680/75	70	A/0.49	0.10	0.55	–	–
16	90/10	680/75	80	B/0.55	0.05	0.63	26,400	45,200
17	90/10	680/75	70	B/0.55	0.05	0.84	–	–
18	100/0	755	70	A/0.49	0.05	0.60	–	–
19	88/12	680/93	70	A/0.49	0.05	0.50	23,700	44,000

^a A and B stand for AIBN and BPO, respectively, initiator and CTA mol% figures are with respect to total monomer concentration.

and the suspension was heated to 65 °C for 5 h. This reaction temperature was limited by boiling points of the monomers. At the end of the reaction, the suspension was cooled and the product was filtered, washed with de-ionized water and dried as above to afford a yield of 85%. Magnesium sulphate was not mentioned in the above mentioned reference [32], but it was found very useful in obtaining suspension particles of fairly uniform and smaller size, which also allows faster filtration. The 85/15 copolymer was prepared using higher quantities of PVA1 and calcium sulphate (Table 5) but calcium phosphate quantity was same as above.

2.3. Characterization

¹H NMR spectra were obtained with a Varian UNITY 400 MHz spectrometer using DMSO-d₆ as solvent (5%, w/v polymer solutions). Intrinsic viscosity (IV) measurements were performed in NMP at 25 °C using a Cannon Ubbelohde viscometer. Infrared spectra were recorded on copolymer films using a FTIR instrument (Nicolet impact 400). Thermogravimetric analysis (TGA) was performed using a Seiko 400 instrument. The TGA utilized programmed heating in an attempt to closely simulate heating conditions that are used during conversion of the polymer precursor in to a carbon fiber [2,3]. Thus, the copolymer was initially heated in air to 220 °C at 10 °C/min, then held at that temperature for 3 h in air. It was next heated at 10 °C/min up to 550 °C and held at that temperature for 3 h in a nitrogen atmosphere. The mass remaining at the end was considered to be the 'char yield' for that polymer. Differential scanning calorimetry (DSC) was performed using a Perkin Elmer model 7 instrument, in nitrogen atmosphere at a heating rate of 10 °C/min. Absolute molecular weight measurements from gel permeation chromatography (GPC) were conducted at 60 °C with a Water 2690 Separation Module equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek T60A) coupled in parallel. NMP

containing 0.02 M P₂O₅ was used as a solvent [33]. The melt viscosity was measured using a RMS 800 Dynamic Spectrometer. Sample preparation consisted of compression molding circular disks of 25.0 mm diameter and 1 mm thickness at 200 °C. A dynamic frequency sweep was employed to determine the melt viscosities using parallel plates at 0.1% strain and 220 °C. The dynamic runs were expected to provide a quick indication of the melt processability of these precursors. The steady shear melt viscosity experiments were conducted at 220 °C in air at steady shear frequency of 0.1 s⁻¹ over a time period of 30 min. Dynamic mechanical analysis (DMA) was performed on compression molded films at -150 to 200 °C using a DMS 210 Seiko instrument. The samples had a span length of 10 mm and a cross-sectional area of 0.5 mm². The measurements were conducted from -150 to 200 °C at a rate of 2 °C/min and vibrated in the tension mode at a frequency of 1 Hz under nitrogen.

3. Results and discussion

3.1. Copolymer synthesis

The AN/MA copolymers were prepared using three different methods namely, solution, aqueous redox and organic soluble initiated aqueous suspension. This allowed careful comparison of copolymer microstructure and its implication to melt processability. Detailed analysis of the reactivity ratios for the AN/MA solution copolymerization has been conducted using in situ infrared and a non-linear analysis method [34]. Reactivity ratio values were r_{AN} : 1.29 ± 0.2 and r_{MA} : 0.96 ± 0.2 , at the 95% confidence level. The copolymers obtained were characterized by ¹H NMR and IR spectra. A typical proton NMR spectrum is shown in Fig. 1. The ratio of integrations of the ester methyl protons and the methylene protons of both comonomers (shown as A and B, respectively, in Fig. 1) was used to calculate the compositions. The high conversion copolymer

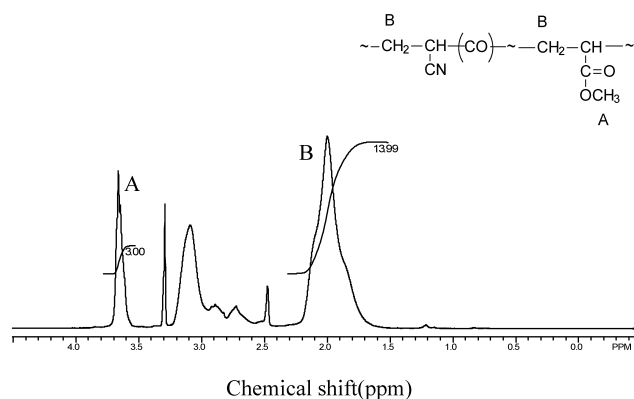


Fig. 1. Proton NMR spectrum of a typical 85/15 AN/MA copolymer.

compositions agreed well with the monomer feed compositions for all copolymers. A representative FTIR spectrum (Fig. 2) indicates the presence of nitrile CN and ester CO functionalities, further confirming the copolymer structure. The GPC curve for a typical AN/MA solution copolymer follows a symmetric, unimodal distribution with a modest dispersity index of about 1.6 (Fig. 3).

Molecular weights necessary to develop mechanical strength and to spin very fine fibers for subsequent stabilization step were defined. Empirically, an intrinsic viscosity (IV) value of about 0.5 dl/g in NMP at 25 °C proved to be a general target for a 85/15 copolymer that corresponds to the M_w of about 35,000 g/mol. Accordingly, various combinations of reaction parameters that would afford IV in the range of 0.3–0.6 dl/g were investigated. The results obtained for the three copolymerization systems are discussed below separately.

Solution copolymerization. Homogeneous synthesis of the copolymers in amide solvents such as DMF eliminates aqueous solubility concerns with the AN and MA monomers. Only dodecyl mercaptan was used as a chain transfer agent (CTA) in these experiments. The major reaction variables were the type and concentration of the initiator (AIBN or BPO), reaction temperature, CTA concentration and chain transfer to the solvent. The IV data for the 85/15

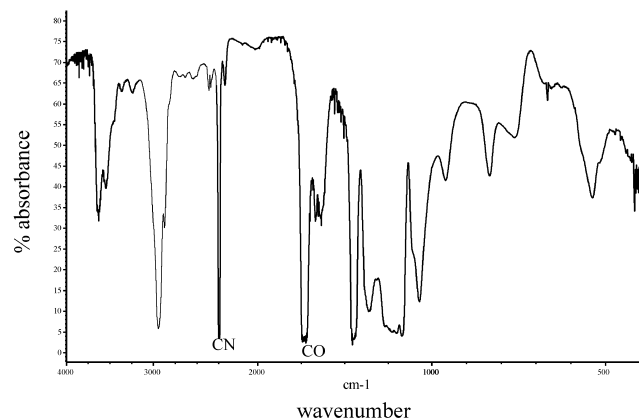


Fig. 2. IR spectrum of typical AN/MA 90/10 copolymer film.

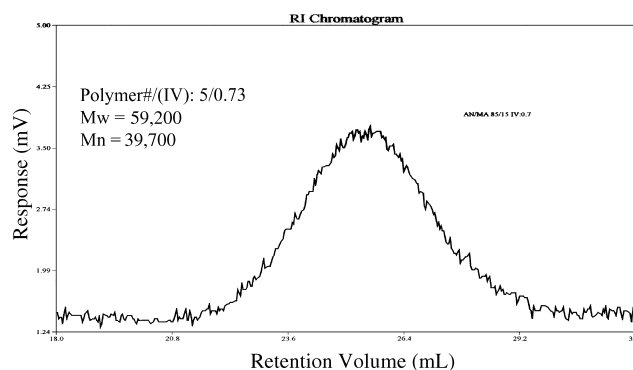


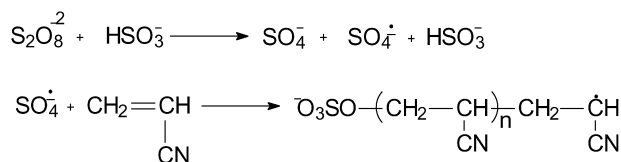
Fig. 3. Typical GPC molecular weight distribution data for an AN/MA 85/15 copolymer in NMP(0.025M P_2O_5) at 60 °C.

AN/MA system are shown in Table 1. The reaction temperature and CTA concentration both can be used as process variables. As expected, lowering the reaction temperature and dodecyl mercaptan (CTA) concentration increases the IV. BPO afforded higher IV copolymers than AIBN in the temperature range of 65–75 °C but the color of the solution turned very dark, implying side reactions. The IV was only slightly higher with no CTA for both initiators, demonstrating the importance of the DMF solvent chain transfer constant [29]. The recovered yields in all the cases were about 85%, irrespective of the detailed reaction conditions and the initiator type.

Copolymers with higher content of AN (>85%) are desirable precursors for carbon fibers. Table 2 shows the effect of various reaction parameters on the IV of copolymers obtained for the 90/10 and higher AN compositions. Reaction temperature and dodecyl mercaptan concentration are again the major factors controlling the IV. Only low viscosity copolymers for compositions containing more than 90 mol% AN were synthesized as discussed below.

Redox copolymerization. The redox method is a solvent-free, water based process (Scheme 2) which utilizes mild reaction conditions, short time, and yet afforded high conversion [35].

Isopropanol (IPA) was investigated as a water soluble CTA instead of dodecyl mercaptan, since it is economical and a known chain transfer agent for PAN synthesis [36]. Unfortunately, even with very high amounts of IPA high intrinsic viscosity values, e.g. 1.32 dl/g, were still obtained. Synthesis of 85/15 AN/MA copolymers with the target value of 0.5 dl/g was not attempted though it may be possible to make it by using known combinations of redox initiators [31]. Table 3 shows redox polymerization data for



Scheme 2. Aqueous redox initiated polymerization of acrylonitrile.

Table 3
Effect of various reaction parameters for 85/15 redox copolymerization

Polymer no. ^a	Amount of KSP (g%)	Amount of SBS (g%)	CTA (mol%)	Intrinsic viscosity (NMP/25 °C)	M_n (GPC)	M_w (GPC)
20	1.08	1.05	2.00	0.95	26,400	64,200
21	1.08	1.05	2.56	0.90	14,300	41,300
22	0.20	0.10	1:1 ^b	1.32	–	–

^a Molar feed ratio of AN/MA is 320/57; 400 ml water used in all experiments.

^b Refers to molar ratio of total monomers/IPA, using procedure of Ref. [36].

experiments conducted with dodecyl mercaptan as CTA, it is evident from the data that significantly higher CTA concentration is required to obtain 85/15 copolymers of desired IV.

The 95/5 and 90/10 AN/MA copolymers were also prepared using dodecyl mercaptan as CTA (Table 4). These copolymers prepared under similar conditions have progressively lower IV values than the 85/15 copolymer at the same CTA concentration, e.g. 0.90 (85/15), 0.55 (90/10) and 0.46 (95/5). Same trend was confirmed from the weight average molecular weight values (M_w) for 85/15, 90/10 and 95/5 copolymers, namely, 64,200, 38,700 and 31,900 g/mol, respectively (Tables 3 and 4). The IV can be controlled to some extent by varying the monomer and water concentrations and hence indirectly by varying initiator concentration (Table 4).

Suspension polymerization. This method has a potential to provide a almost ready to use product, like the redox method, if the various suspending aids are used in a bare minimum quantity. We could get such products using PVA1 as the suspending agent. The 85/15 copolymer required much higher suspending aid for stabilizing the suspension probably because the lower T_g of this composition tends to coagulate the suspension at the reaction temperature (Table 5). The suspension polymerization was also found to require higher mercaptan concentration to control molecular weight since; again the DMF chain transfer contribution was

absent. The other suspending agents namely, PVA2 and PVP, form very unstable suspension under similar conditions, indicating that the choice of the suspending agent also appears to be critical for controlling IV. The suspension copolymerization with BPO initiator surprisingly afforded unattractive yield (<10%), and hence was not pursued further.

To summarize, reaction temperature and dodecyl mercaptan concentration both are inversely related to IV in homogeneous solution polymerization but the situation is more complicated for heterogeneous polymerizations. For aqueous redox polymerization, much higher mercaptan concentration was required to produce copolymers of similar IV. The copolymer composition also has an effect on IV, e.g. lower AN correlates with high IV copolymers, perhaps reflecting an interesting polymer solvent interaction. Furthermore, variation in mercaptan concentration at this high level does not significantly influence the IV (or indirectly the molecular weight); controlling the IV is possible to some extent by reducing the water content. For the suspension polymerization method, the suspending agent, initiator and mercaptan concentration are very important variables.

3.2. Melt processability

Melt processability of the copolymers was assessed by rheology measurements. Fig. 4 shows the dynamic melt viscosities of different AN/MA copolymer compositions (prepared in solution) as a function of frequencies. The melt viscosity of the copolymers was found to be a function of copolymer compositions. The copolymers with MA content 10 mol% or higher appear to be melt processable, as evidenced by low melt viscosity values corresponding to frequency of 0.1 s^{-1} (100,000 Pa s or less). Lower content of MA resulted in very high melt viscosities, implying that these copolymers are not melt processable. Also, as seen from Fig. 4, the melt viscosity is very sensitive to variation in composition, just a 3% increase in MA content from 7 to 10 causes a 4-fold drop in the melt viscosity values corresponding to the frequency of 0.1 s^{-1} (referred to as LSV in the following discussion). The copolymer with MA content of 10 mol% may be on the borderline for processability. We have also assumed a LSV of 100,000 Pa s as an upper limit for melt viscosity of our

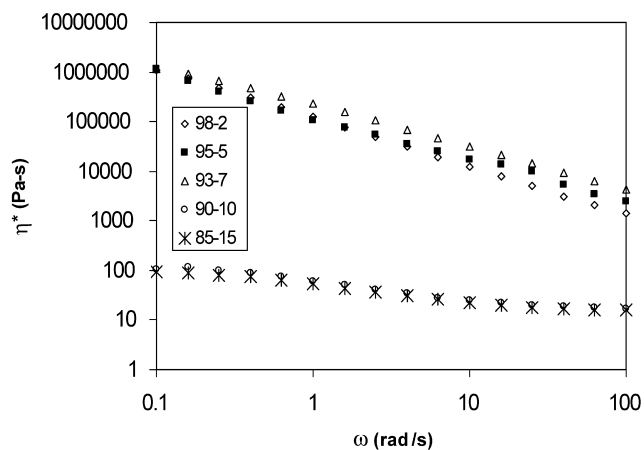


Fig. 4. Melt viscosity as a function of ω copolymer composition at 220 °C; AN/MA ratio (polymer number) are: 98/2 (#9), 95/5 (#10), 93/7 (#11), 90/10 (#12) and 85/15 (#1).

Table 4
Effect of reaction parameters for various AN/MA compositions made by redox copolymerization

Polymer no.	AN/MA feed ratio ^a (mmol)	Amount of water (ml)	Amount of KSP (g%)	Amount of SBS (g%)	CTA (mol%)	Intrinsic viscosity (NMP/25 °C)	M_n (GPC)	M_w (GPC)
23	95/5	400	1.08	1.05	2.56	0.46	15,400	31,900
24	90/10	400	1.08	1.05	2.56	0.55	20,600	38,700
25	90/10	400	1.08	1.05	3.00	0.53	–	–
26	90/10	400	1.50	1.50	2.56	0.53	32,200	86,400
27	90/10 ^b	320	1.09	0.42	2.56	0.42	13,400	33,000
28	90/10 ^b	220	1.59	0.61	2.56	0.39	12,100	78,700

^a Feed ratios for 95/5 and 90/10 compositions are 359/19 and 340/38, respectively.

^b AN/MA feed ratio 160/18 mmol.

precursors for the processing temperature range of 200–220 °C, based on the experience with a number of samples and a semi-commercially available melt-spinnable precursor. A similar dependence of melt viscosity on the copolymer composition was found for the copolymers synthesized by redox and suspension methods (Figs. 5 and 6); since the LSV values appear to be very high for 92/8 and even the 90/10 suspension compositions, one might speculate that this indicates the grafting of high molecular weight suspending agent on the copolymer being formed. Nevertheless, the data suggests that the relation between the melt viscosity and copolymer composition is fairly independent of the method of polymerization. Although the existence of such a ‘critical comonomer concentration’ required to significantly influence a particular property of acrylonitrile copolymers is well known [4,23,37], it is very conspicuously manifested in this correlation. Furthermore, it elegantly demonstrates that a practically important bulk property (melt viscosity) is directly controlled at molecular level by the copolymer composition. We would like to add some more comments on this observation, in the light of some interesting results available in the literature. It is well known [4] that strong interactions exist between adjacent nitrile groups in polyacrylonitrile (PAN). This renders the amorphous, atactic PAN to display considerable crystallinity [4]. The same is most probably true for the copolymers containing up to about 10 mol% MA; Bang et al. [27] have reported similar X-ray patterns for copolymers containing 2–8 mol% MA. Further, it is believed that comonomer like MA, because of its flexibility, is able to penetrate the crystal lattice as a defect [4], producing a characteristic morphology, which is described as amorphous with a high degree of ‘lateral bonding’ [4].

Beyond the MA content of about 10 mol%, the comonomer is probably present in excess quantity than that required to retain the ordered structure. Consequently, the morphology characterized by the long-range order observed for the copolymers containing less than this critical MA content is completely disrupted. And this probably results in very significant drop in the melt viscosity as observed in the dynamic rheology experiments. Similar results have been reported by various groups for the copolymers of AN, on the basis of X-ray, DSC and DMA studies, and these have been reviewed recently [4].

Further experiments show the notable dependence of a melt processability window on the copolymer composition. LSV values below 20,000 Pa s were obtained for 85/15 solution copolymers having IV over a range of 0.20–0.88 dl/g. On the other hand, in case of the 90/10 solution copolymers, LSV increases more rapidly with IV. Thus, e.g. 85/15 copolymers with IV of 0.45 and 0.65 have LSV values of about 800 and 8000 Pa s, respectively (Fig. 7). In contrast, 90/10 copolymer of IV 0.55 has the LSV value of about 8000 (Fig. 8), while LSV value for 90/10 copolymer of IV 0.82 is too high to be of any interest. Thus, the processability window is narrower for the 90/10 composition as compared to the 85/15 composition. This is understandable because the long-range order becomes more dominant as AN concentration in the copolymer increases and hence such copolymers are difficult to flow. A similar narrower window of processability most probably exists for 90/10 AN/MA copolymers made by redox and suspension methods (Fig. 9). Furthermore, the LSV crosses the limiting value of 100,000 Pa s in case of suspension polymer #30 of IV 0.55.

Melt processability of the various copolymers was also

Table 5
Intrinsic viscosity data for suspension copolymerization of various AN/MA copolymers

Polymer no.	AN/MA feed ratio	AN/MA molar feed ratio	PVA (wt%)	CaSO ₄ (wt%)	CTA (mol%)	AIBN (mol%)	Intrinsic viscosity (NMP/25 °C)
29	85/15	283/51	0.34	0.55	2.88	0.50	0.39
30	90/10	632/70	0.10	0.20	0.59	0.39	0.55
31	92/8	644/56	0.10	0.20	0.66	0.39	0.43
32	88/12	618/84	0.10	0.20	0.59	0.39	0.49

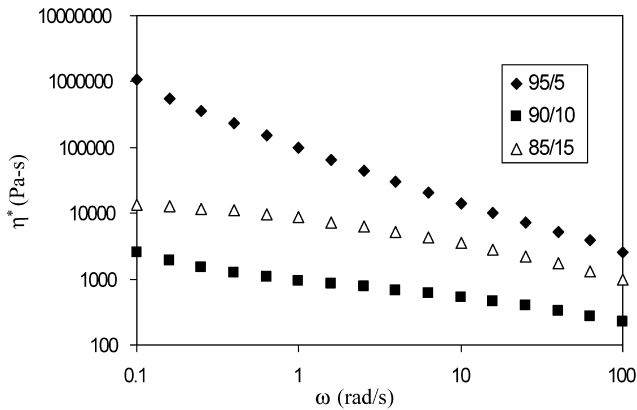


Fig. 5. Melt viscosity at 220 °C as a function of copolymer composition for polymers made by redox method; AN/MA ratio(polymer number) are: 95/5(#23), 90/10(#27), 85/15(#20).

studied using capillary rheometer and a lab scale extruder [38]. From these studies it appears that thermal behavior of the precursors can be best predicted from accelerated melt viscosity measurements conducted at low steady shear viscosity (about 0.1 s^{-1}) conditions. This is probably because the accelerated test so conducted more closely simulates the practical extruding conditions. We have therefore assessed the melt stability by studying the steady shear melt viscosity of different copolymers for a time of 30 min. The comparative time sweep data in Fig. 10 for the 85/15, 88/12 and 90/10 solution copolymers shows that copolymer composition has a significant influence on the steady state melt viscosity. The melt viscosity of 85/15 copolymer is fairly stable for 30 min (typical dwell time in an extruder) at 220 °C but in contrast, it starts to rise within 10 min for the 90/10 composition. Interestingly, the 88/12 copolymer shows a much more stable viscosity up to 20 min, which can be extended to 30 min by adding stabilizers like boric acid [39]. This implies that the 12 mol% MA content probably represents the critical comonomer concentration at and above which the copolymers can have good melt stability and melt processability. Thus, fine fibers can be melt extruded with ease only from

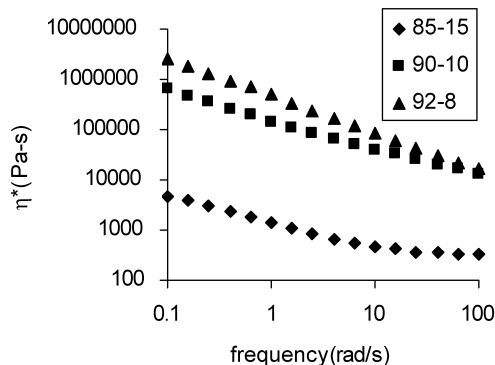


Fig. 6. Melt viscosity at 220 °C as a function of copolymer composition for polymers made by suspension method; AN/MA ratio(polymer number) are: 85/15(#29), 90/10(#30), 92/8(#31).

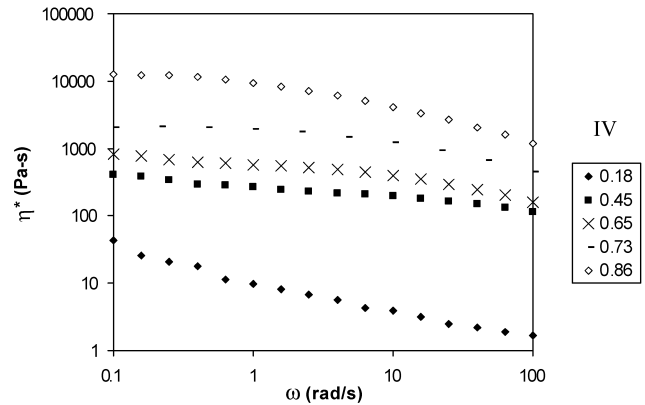


Fig. 7. Melt viscosity as a function of IV at 220 °C for various AN/MA 85/15 copolymers made by solution method; the IV(polymer numbers) are: 0.18(#1), 0.45(#3), 0.65(#4), 0.73(#5), 0.86(#8).

copolymers containing <88 mol% AN in the precursor, which has been successfully verified in bench scale experiments for 85/15 and 88/12 solution copolymers [38]. Further work on the stabilization of melt-spun precursors is in progress; these experiments are expected to be useful in optimizing the exact composition of the precursors for carbon fiber applications.

The stability of 88/12 copolymer as compared to the 90/10 can be explained as follows: Firstly, probability of the exothermic cyclization reaction (stabilization) involving the pendant nitrile groups is decreased at higher comonomer content due to the hindrance provided by the comonomer; similar observation was reported in the case of AN/Vinyl acetate copolymer [4]. The shift in the peak exotherm to higher temperature for 85/15 copolymers compared to PAN (AN homopolymer) as observed by DSC (Fig. 11) is consistent with this contention, and also with similar reports on AN/vinyl acetate copolymers [4]. Secondly, the cyclization reaction can take place both intra- and inter-molecularly in the polymeric chains. The melt viscosity would be expected to rise significantly even after few inter-molecular bonds are formed. The long-range order which favors cyclization is most probably absent above the critical comonomer content in the copolymer since the steady shear

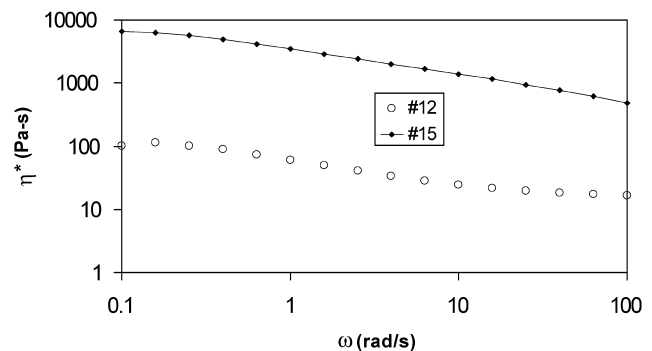


Fig. 8. Melt viscosity as a function of IV at 220 °C for 90/10 AN/MA copolymers made by solution method; the IV(polymer numbers) are: 0.25(#12), 0.55(#15).

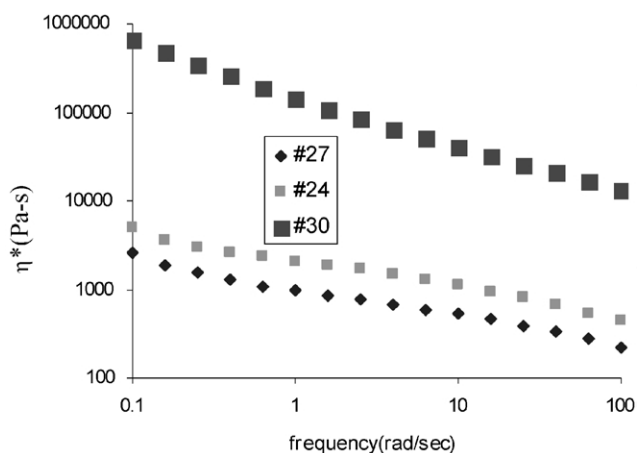


Fig. 9. Melt viscosity as a function of IV at 220 °C for 90/10 AN/MA copolymers made by redox and suspension methods; the IV (polymer number) are: redox- 0.42(#27), 0.55(#24); suspension-0.55(#30).

viscosity remains much lower in the case of 88/12 and 85/15 copolymers as compared to the 90/10 copolymer (Fig. 10). Hence no significant rise in melt viscosity is observed for a 88/12 copolymer as compared to the 90/10 copolymer. Thirdly, the presence of higher comonomer content that causes a breakdown of the ordered structure with simultaneous decrease the melt viscosity further reduces the probability of the cyclization reaction, as the polymer chains possess better mobility at lower melt viscosity. This is supported by a peak $\tan \delta$ transition at lower temperature of about 100 °C for 88/12 and 88/15 AN/MA copolymers (Fig. 12), with respect to a reported $\tan \delta$ transition value in the range of 110–115 °C for AN homopolymer. The DMA $\tan \delta$ transitions does not appear to be sensitive to the change in AN/MA copolymer composition from 88/12 to 85/15. The DMA storage modulus data in Fig. 13, however, also indicates that both the copolymers (88/1 and 85/15) behave more like thermoplastics, and also shows that 88/12 composition has a modestly higher modulus than the 85/15 copolymer, which is consistent with its higher AN content and possibly higher inter-molecular interactions.

Thus, the above data shows that melt viscosity is significantly influenced by the copolymer composition

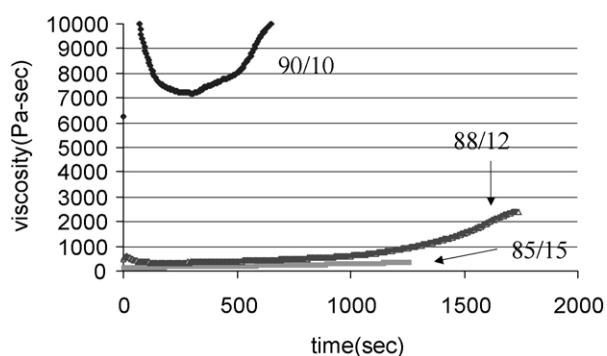


Fig. 10. Comparative time sweep data at 220 °C for various AN/MA copolymers (polymer #): 90/10(15), 88/12(19) and 85/15(3).

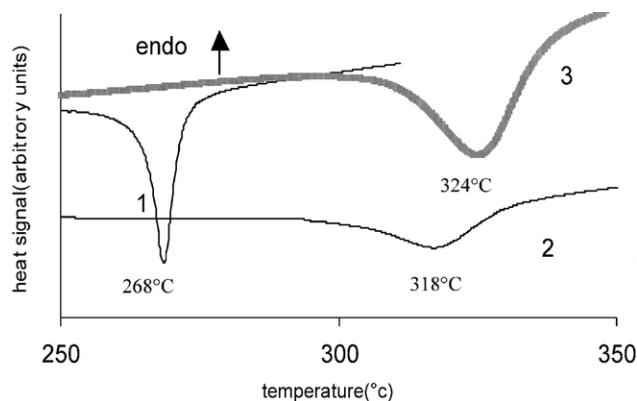


Fig. 11. DSC thermograms for (1) AN homopolymer (2) AN/MA 85/15 solution copolymer #4 and (3) AN/MA 85/15 suspension copolymer #29.

even at likely comparable molecular weights. Further, the optimum IV value of the melt processable AN/MA copolymer will unfortunately vary with the composition. More specifically, melt processable precursors can be made with about 12 mol% or higher MA. Finally, the steady shear viscosity data, in conjunction with the dynamic runs data suggests that higher comonomer content not only decreases the melt viscosity of the copolymers, but also helps to improve their melt stability.

3.3. Thermal analysis

The TGA was conducted under specially chosen conditions to simulate heating conditions used for converting an acrylic precursor into a carbon fiber. The TGA data (Fig. 13) for copolymers containing varying MA content indicates that copolymers initially degrade at a faster rate than PAN, but all afford a char yield similar to PAN (about 50%). Thus, the higher quantity of comonomer used to make melt processable precursors does not affect the char yield significantly as evident from TGA residual weights.

That the exothermic degradation is controlled by the comonomer is more clearly evident from the DSC data

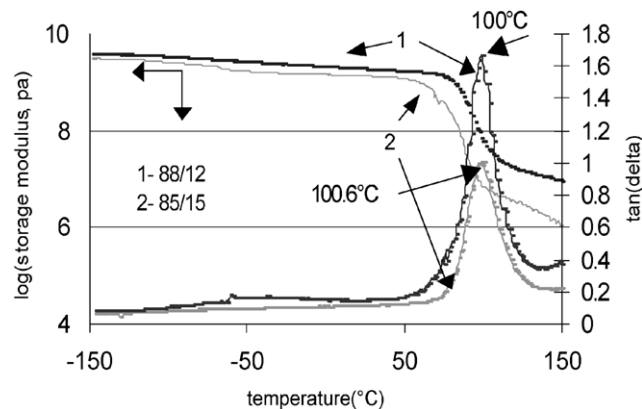


Fig. 12. Dynamic mechanical behaviour (1 Hz) of two solution copolymers (polymer #): 85/15(#3) and 88/12(#19).

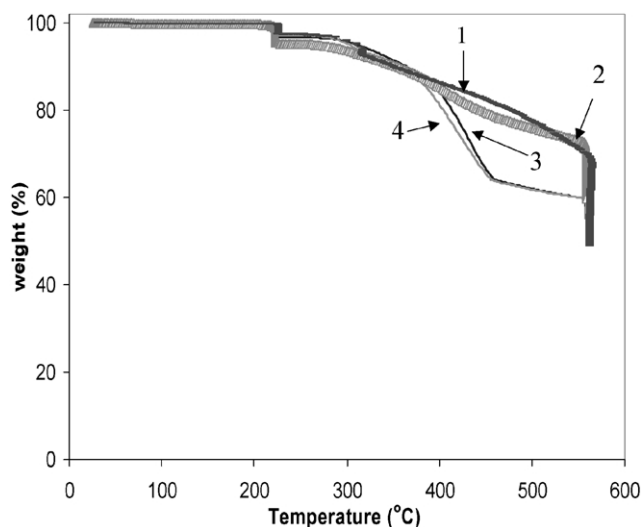


Fig. 13. TGA data for AN homopolymer and copolymers made by solution method; number(composition): 1(homopolymer), 2(95/5), 3(90/10), 4(85/15). Atmosphere: air(up to 220 °C)/nitrogen(220–550 °C)

(Fig. 11). The DSC thermograms show that AN homopolymer exhibits a sharp exothermic cyclization peak at 268 °C while the AN/MA 85/15 copolymers beneficially reduce the rate of this process, and hence exhibit a broader exotherm in accordance with the literature [4,24,25]. Consequently, the peak exotherm is shifted to higher temperature values of 318 and 324 °C for the solution and suspension copolymers, respectively.

4. Conclusions

Melt processable AN/MA copolymers were synthesized by solution, redox and suspension methods. The study showed that copolymers containing about 15 mol% MA are potential carbon fiber precursors. The role of different variables useful in regulating the intrinsic viscosity of the precursor copolymers has been demonstrated for both homo- and heterogeneous polymerization methods. These copolymers exhibit two interesting correlations. The first relation correlates melt viscosity with composition and shows that melt processable precursors are obtained when MA content in the copolymers is 10 mol% or more; the corresponding drop in melt viscosity is nearly 4-fold for only a few mol% change in MA content. The second relation of melt viscosity and molecular weight (in terms of IV) at a particular composition is important from a process design viewpoint. It indicates that a processable viscosity window is broader for 85/15 composition and narrower for the 90/10 composition. Both the correlations are consistent with the generally accepted view that comonomers like MA can get incorporated in the crystal lattice of AN up to a critical comonomer content and disrupt the characteristic morphology beyond the critical limit (observed at about 12 mol% MA content). Thus the copolymer composition

seems to have a decisive influence on the processability of the precursors, which in turn is related to the long-range order present in AN-based polymers. Hence, it appears that it is the elusive long-range order in AN based polymers which dictates the processability of these precursors. It will be therefore interesting to study how effectively different comonomers can influence the disruption of the long-range order in predominantly AN-based copolymers. Such a study will contribute to a broader fundamental understanding of developing a method to convert simple linear polymers into morphologically complex but easily melt processable useful products.

Acknowledgments

We thank the Department of Energy for the funding under the contract 4500011036. We also thank Dr H.K. Shobha and Dr Yu Sueng Kim for GPC analysis, and Prof. D. Edie and his group at Clemson University for conducting the melt spinning trials, which will be discussed separately.

References

- [1] Tullo AH. C&E News 2000;78:11.
- [2] Bahl OP. In: Donnet JB, Wang TK, Rebouillat S, Peng JCM, editors. Carbon fibers, 3rd ed. New York: Marcel Dekker; 1998. p. 1–84. Chapter 1.
- [3] Edie DD. Carbon 1998;36:345.
- [4] Frushover BN. In: Masson JC, editor. Acrylic fiber technology and applications. New York: Marcel Dekker; 1995. p. 197–258. Chapter 7.
- [5] Yang J, Banthia AK, Godshell D, Rangarajan P, Glass TE, Wilkes GL, Baird DG, McGrath JE. Polym Prepr 2000;41:59.
- [6] Bhanu VA, Wiles KB, Banthia AK, Mansuri A, Sankarpandian M, Rangarajan P, Glass TE, Baird DG, Wilkes GL, McGrath JE. Polym Prepr 2001;42:663.
- [7] Rangarajan P, Yang J, Bhanu VA, Godshall D, Wilkes GL, McGrath JE, Baird DG. J Appl Polym Sci 2002; 85:69.
- [8] Ball LE, Jorkasky RJ, Uebele CE, Wu MM. Eur Patent Appl EP 780, 498, 1996; Chem Abstr 127:110258p.
- [9] Smierciak RC, Wardlow E, Ball LE. US Patent US 5,618,901, 1995; Chem Abstr 126:317827e.
- [10] Daumit GP, Ko YS, Slater CR, Venner JG, Young CC, Zwick MM. US Patent US 4,933,128, 1988; Chem Abstr 113:174006y.
- [11] Sugimori T, Sakanaga K, Fukahori N. Jpn Kokai Tokkyo Koho JP 6, 285,012, 1985; Chem Abstr 107:79382k.
- [12] Asahi Chem. Industry Co. Ltd. Jpn Kokai Tokkyo Koho JP 6,094,615, 1984; Chem Abstr 103:89014y.
- [13] Asahi Chem. Industry Co. Ltd. Jpn Kokai Tokkyo Koho JP 59,163, 413, 1981; Chem Abstr 101:212592y.
- [14] Mitsubishi Rayon Co. Ltd. Jpn Kokai Tokkyo Koho JP 6,359,409; 1988.
- [15] Shido H. Jpn Kokai Tokkyo Koho JP 8,199,422, 1996; Chem Abstr 125:250269p.
- [16] Daumit GP, Ko YS, Slater CR, Venner JG, Young CC. US Patent US 5,168,004.
- [17] Aturelia SK, Bashir Z. Polymer 1993;34:5116.
- [18] Liu XD, Ruland W. Macromolecules 1993;26:3030.
- [19] Rizzo P, Auriemma F, Guerra G, Petraccone V, Corradini P. Macromolecules 1996;29:8852.

- [20] Hobson RJ, Windle AH. *Macromolecules* 1993;26:6903.
- [21] Rizzo P, Auriemma F, Guerra G, Petraccone V. *Macromolecules* 1996;29:1830.
- [22] Andreeva UA, Burkova LA, Basok MO. *Vysokomol Soedin Ser A* 1995;37:591.
- [23] Groblny J, Sokol M, Turska E. *Polymer* 1989;30:1187.
- [24] Bajaj P, Sreekumar TV, Sen K. *Polymer* 2001;42:1707.
- [25] Dalton S, Heatley F, Budd PM. *Polymer* 1999;40:5531.
- [26] Kakida H, Tashiro K. *Polym J (Tokyo)* 1997;9:557.
- [27] Bang YH, Lee S, Cho HH. *J Appl Polym Sci* 1998;68:2205.
- [28] Davidson JA, Jung HT, Hudson SD, Percec S. *Polymer* 2001;42:3357.
- [29] Gupta AK, Paliwal DK, Bajaj P. *JMS Rev Macromol Chem Phys* 1991;31:1.
- [30] Grove D, Daga V, Desai P, Abhiraman AS. In: Vigo TL, Kinzig BJ, editors. *Composite applications: the role of matrix, fiber, and interface*. Weinheim: VCH Inc; 1992. p. 107–31. Chapter 5.
- [31] Ebdon JR, Huckerby TN, Hunter TC. *Polymer* 1994;34:4659.
- [32] Arshady R, Kenner GW, Ledwith A. *J Polym Sci, Polym Chem Ed* 1974;12:2017.
- [33] Konas M, Moy TM, Rogers ME, Schultz AR, Ward TC, McGrath JE. *J Polym Sci, Polym Phys Ed* 1995;33:1441.
- [34] Wiles KB, Bhanu VA, Pasquale AJ, Long TE, McGrath JE. In preparation.
- [35] Sarac AS. *Prog Polym Sci* 1999;24:1095.
- [36] Minagawa M, Iwamatsu T. *J Polym Sci, Polym Chem Ed* 1980;18:481.
- [37] Gupta AK, Singhal RP. *J Polym Sci, Polym Phys Ed* 1983;21:2243.
- [38] Edie D. Private communication. Clemson University; 2001.
- [39] Bhanu VA, Wiles KB, Rangarajan P, Baird DG, McGrath JE. *SAMPE Proc* 2001;33:1499.