

Effect of Comonomers on Melt Processability of Polyacrylonitrile

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Received 23 April 2001; accepted 9 October 2001

ABSTRACT: This work is concerned with the feasibility of achieving melt-processable polyacrylonitrile copolymer systems as precursors for the manufacture of carbon fibers. Identification of suitable comonomers and achieving the optimum content of the comonomer were some of the main objectives of this investigation. It was seen that methyl acrylate (MA) was found to be suitable for enabling the melt processing of polyacrylonitrile (PAN), in terms of melt viscosity, time stability, and char yield. Below 10 mol % of MA, the PAN copolymer exhibited no flowability, even at very low molecular weights ($\sim 20,000$). The long-range order inherently present in PAN is speculated to be broken down at a critical value of about 10% MA at 220°C in the PAN-based system, enabling its melt flowability. It was also seen that the incorporation of MA was seen to improve the temperature and molecular weight window of processability of the PAN system. The molecular weight cutoff for the 90/10 mol % acrylonitrile/methyl acrylate (AN/MA) system was about 50,000 at 220°C, whereas it was increased to about 100,000 in the presence of 15 mol % MA comonomer. Feasibility studies on the use of other comonomers such as higher acrylates and acrylamides were also conducted. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 69–83, 2002

Key words: melt processability; polyacrylonitrile; comonomers; carbon fibers; methyl acrylate

INTRODUCTION

Carbon fibers are finding a wide variety of applications in the industrial sector, which encompasses the high-tech aerospace and defense areas and, increasingly, the shipping, sporting, and medical fields as well.¹ They have excellent mechanical properties, good chemical inertness, a low weight-to-volume ratio, and good weatherability properties and thus are very attractive structural materials in composites as reinforcing

agents. One of the major shortcomings that limit the potential widespread use of carbon fibers in commercial applications is their prohibitive cost comparison with that of other structural materials. As an illustration, carbon fibers could be up to 10 to 20 times the cost of glass fibers on a weight basis, although this ratio is lowered when normalized on a modulus basis. Hence, the use of carbon fibers is currently limited to those applications where the cost of the part is outweighed by the utility of the part, that is, mainly in defense and aerospace applications. To make them competitive structural materials in the commercial industry, their cost of manufacture needs to be reduced considerably. Current industrial manufacturing routes mainly use melt-spinnable me-

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Contract grant sponsor: U.S. Department of Energy; contract grant number: 4500011036.

Journal of Applied Polymer Science, Vol. 85, 69–83 (2002)
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sophase pitch fibers or solution-spun polyacrylonitrile fibers as precursors, which result in an expensive end product (carbon fibers). The overall goal of this work is to identify a credible path for producing low-cost carbon fibers, with specific application as an automotive structural material.

Carbon fibers are generally produced by crosslinking carbonaceous precursor fibers in a thermooxidative stabilization procedure and then converting them into carbon fibers in a carbonization step at a high temperature and inert atmosphere. The two principal precursors commonly used are polyacrylonitrile (PAN) and mesophase pitch. Carbon fibers made from PAN-based precursors tend to have lower tensile moduli but higher tensile and compressive strengths and higher elongation at break compared to the properties of those made from mesophase pitch blends. Edie² reported that the tensile strengths of carbon fibers made from PAN-based precursors are about three times the value of the pitch-based carbon fibers, whereas their moduli reach about 50% of the pitch-based fibers. Also, the mesophase pitch is more expensive than acrylonitrile monomer. In the automotive industry, where low-cost carbon fibers could find a major commercial application, structural materials with high tensile modulus and high tensile strengths are being sought. This is typically achieved by carbon fibers made from PAN-based precursors. Based on a review of the literature, it seems that, although a lot of work has been reported on optimization of the stabilization and carbonization treatments for PAN-based systems, very little work on the optimization and manufacture of the PAN precursor fiber itself has been reported.² Hence, the remainder of this communication will be devoted to the efforts undertaken to develop the melt-processable PAN precursors with an aim to lowering the cost of the final carbon fiber product.

Because PAN begins to degrade at a temperature lower than its melting point, the precursor fibers are generally solution-spun (20–30 wt % solution) in polar solvents, such as dimethyl acetate. Two of the disadvantages of this process include the use of toxic, environmentally unfriendly solvents, and the need for a solvent-recovery unit, which leads to higher capital and operating costs. Furthermore, significant capital costs are involved in the equipment required for the drawing step used to develop fibers with high molecular orientation and relatively free of voids, which is favorable for stabilization and carboniza-

tion. It is in this regard that melt spinning of PAN precursors seems to be the better alternative for reducing the cost of the final carbon fiber product. In the latter case, we are dealing with higher amounts of PAN concentration (100 wt % of the PAN copolymer) as opposed to 20–30 wt % typically used in solution spinning. The solvent-recovery process is eliminated (lowering the capital costs), which reduces the downstream processing costs and makes the PAN precursor manufacturing process an environmentally benign one. Moreover, it is believed that the melt-spun PAN fibers, as opposed to the conventional solution-spun fibers, would be essentially void-free, leading to less severe conditions and lesser times for the stabilization and carbonization steps, which translates to better savings for the entire process. Hence, the focal point of this work is to develop PAN copolymers of appropriate molecular weight and MA/AN ratio that can lead to a melt-processable PAN system. It is to be noted that this approach of environmentally friendly melt-spinnable PAN systems has another application in the area of textile fibers, which is a huge market for the more predominant and conventional solution-spun PAN.

Some of the literature discusses the melt spinning of acrylic fibers by mixing the polymer with additives such as water, acetonitrile,³ propylene carbonate,⁴ lower molecular weight PAN, and water-soluble polyethylene glycol.⁵ These additives plasticize the polymer and lower its melting point, thereby enabling the melt spinning without significant degradation. The reduction in melting temperatures of PAN attributed to the use of water as a plasticizer is particularly well documented in literature.⁴ Because of its small size and molecular weight, water is able to penetrate the two-dimensional paracrystalline PAN, thus leading to the breakage of nitrile–nitrile interaction, which is the actual binding force in the homopolymer. The amounts of solvents (acetonitrile/water and propylene carbonate) used varied from 20 to 50 wt % in the references cited and, hence, they were not truly melt-processable PAN systems. The morphology of the melt-spun fibers was comparable to that of fibers obtained from wet and dry spinning. However, more surface defects and internal voids were observed in the plasticized melt-spun system, which decreased the final mechanical properties of the resulting carbon fibers. Furthermore, plant-scale operations presented many challenges, such as when using water as a plasticizer, the extrusion of the PAN

filaments into a heated pressurized chamber was required to allow water to escape without flashing and foaming the matrix. Similarly, toxic expensive plasticizers would involve a cumbersome solvent-recovery unit. Both of these processes would increase the cost of manufacture of the PAN precursor and the carbon fibers. What is needed is a true melt-spinning process in which solvents or plasticizers are not present, at least in large volumes.

PAN-based precursor fibers are generally produced as a copolymer of PAN with a low percentage of comonomer such as methyl acrylate (MA), itaconic acid, methacrylic acid (2–7 mol %), and so forth.⁶ These comonomers help in the stabilization reactions of the precursor fibers and improve the mechanical properties of the resulting carbon fibers. As an illustration, acidic comonomers change the mechanism of stabilization from a free-radical reaction to an ionic reaction and help in initiating the cyclization reaction at a lower temperature and slower rate. Because the cyclization reaction is exothermic and PAN homopolymer is a bad conductor of heat, these comonomers help to provide a uniform heat transfer in the PAN system, leading to better precursor fiber properties. On the other hand, ester comonomers have a different effect on PAN processability. Because they are randomly polymerized with the acrylonitrile comonomer, the acrylate comonomer acts as defects and helps to reduce the dipole–dipole interactions and long-range order present in PAN systems. On adding about 2–5 mol % of MA, the mobility of the PAN system is sufficiently increased so as to improve the orientation of the PAN fibers, and thereby improve the final mechanical properties of the carbon fibers.

We propose to study the feasibility of melt-processing PAN systems with MA as comonomer. The use of MA would further disrupt the order found in the PAN system, thereby reducing its glass-transition temperature and lowering its processability temperature, thereby facilitating the melt extrusion/spinning of the PAN copolymer. Also, the effects of other comonomers on PAN melt processability were investigated. At the same time, we want to ensure that the PAN fibers that are melt-spun and drawn can be suitably stabilized and converted into carbon fibers. Hence, identifying the right type and the optimum amount of comonomer was one of the main objectives of this work. In particular, we studied the effect of comonomer type, content, estimated temperature of processing, the stability, and mo-

lecular weight on the melt processability of the PAN systems. Although the overall goals of this study were geared toward the production of carbon fibers with good mechanical properties, this report focuses primarily on the feasibility of achieving melt-processable PAN-based systems.

EXPERIMENTAL

Materials

An extrudable-grade AN/MA copolymer standard, Barex, containing 65 mol % AN, 25 mol % MA, and 10 mol % elastomer, was obtained from BP/Amoco. A solution-spun PAN precursor containing about 3 mol % MA was also obtained from BP/Amoco for characterization standard. Acrylonitrile (AN), MA, isobutyl acrylate (IBA), acrylamide (AM), dimethyl acrylamide (DMAA), AIBN (2,2'-azobisisobutyronitrile), and 1-dodecanethiol [chain-transfer agent (CTA)] were obtained from Aldrich (Milwaukee, WI). GR-grade *N,N*-dimethylformamide (DMF) solvent was obtained from EM Science (Fort Washington, PA) and was used as received. The monomers were passed over activated alumina before use. Potassium persulfate (KSP) and sodium bisulfite (SBS) were purchased from Aldrich and used as received. Deionized water was used for aqueous polymerization using redox initiator.

Synthesis

Copolymerization was carried out using two different methods.

Solution Polymerization

This was carried out using a 500-mL three-neck flask fitted with a condenser, glass stirrer, nitrogen inlet tube, and thermocouple probe. First, the flask was charged with 100 mL DMF and it was purged with dry nitrogen for 15 min. Next, the mixture of AN, MA, AIBN, and CTA was introduced and the content was polymerized at 70°C for 6 h. The polymer so obtained was purified by precipitation from 50-fold excess of deionized water. It was then filtered and dried under vacuum at 70°C for 24 h. As an illustration, for AN/MA mol ratios of 85/15 and 90/10, the quantities of monomers used are as follows: 85/15 (AN 0.640 mol, MA 0.110 mol): CTA and AIBN (0.05 and 0.5% mol of total monomers, respectively); 90/10 (AN 0.684 mol, MA 0.080 mol): CTA and AIBN

(0.05 and 0.5% mol of total monomers, respectively). PAN homopolymer and the other AN/MA copolymers were also synthesized by this technique.

Redox Polymerization

The procedure given in the literature⁷ was used as a guideline in these experiments. The reaction was carried out using an assembly similar to that above. The water (400 mL) was flushed with dry nitrogen for about 20 min, after which the reactants were added. The polymerization was carried out for 3 h at 40°C and the product was directly filtered, washed with copious amounts of deionized water, and dried as above. For AN/MA ratios of 85/15 and 90/10, the quantities of monomers used were as follows: 85/15: AN (17 g, 0.340 mol), MA (4.87 g, 0.060 mol), CTA (1.62 g, or 2% mol of total monomers as given), KSP (4.33 g, 1.08% g of volume of water), SBS (4.20 g, 1.05% g of volume of water); 90/10: AN (17 g, 0.340 mol), MA (3.27 g, 0.038 mol) (or the other comonomers), CTA (1.62 g, or 2% mol of total monomers as given), KSP, and SBS (as above for the 85/15 system).

Molecular Weight Analyses

Absolute molecular weight measurements from gel-permeation chromatography (GPC) were conducted at 60°C with a Waters 2690 separation module (Waters Associates, Milford, MA), equipped with a differential refractometer detector and an online differential viscometric detector (Viscotek T60 A) coupled in parallel. NMP containing 0.02M P₂O₅ was used as a solvent.

Thermal Analysis

Thermal analysis of the samples was studied mainly using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Powder samples in the weight range of 6–10 and 10–20 mg were used for the DSC and TGA, respectively. The glass-transition temperatures (T_g) of the PAN samples were evaluated using a Perkin–Elmer differential scanning calorimeter DSC 7 (Perkin Elmer Cetus Instruments, Norwalk, CT). The heating rate employed was 10°C/min and the sample was heated from room temperature to 200°C, cooled back to room temperature at the same heating rate, and reheated again to 200°C. The gravimetric thermal analysis was studied using a Perkin–Elmer thermogravimetric analyzer TGA 7. Two kinds of heating cycles were studied. In the first case, the sample (10–20 mg)

was heated in an inert atmosphere (N₂) from room temperature to 550°C at 10°C/min. The second experiment consisted of simulating a thermooxidative stabilization reaction for the PAN copolymer. The system was heated in air at 10°C/min to 220°C, maintained in air for 3 h, and then heated from 220 to 550°C at 10°C/min in N₂ and heated at 550°C in a nitrogen atmosphere for 3 h.

The temperature dependency of the viscoelastic behavior of the PAN samples was studied using a Seiko DMS 2310 dynamic mechanical analyzer (Seiko Instruments, Tokyo, Japan). The samples had a span length of 10 mm and a cross-sectional area of 0.5 mm². They were heated from 0 to 200°C at a rate of 2°C/min and vibrated in the tension mode at a frequency of 1 Hz with N₂ as purge gas.

Morphology

Wide-angle X-ray scattering was employed to detect the long-range order or crystallinity in the PAN copolymer system. A CuK_α radiation with a wavelength of about 1.54 Å at 40 kV and 20 mA with a Warhaus camera and pinhole colimation was used. Powdered samples were investigated.

Rheology

Sample preparation consisted of compression-molding circular discs of 1-in. diameter and 1 mm thickness at 200°C. The linear viscoelastic properties of the PAN copolymer samples were determined using an RMS 800 mechanical spectrometer (Rheometrics Scientific). Frequency sweeps were carried out using parallel plates (25-mm diameter), at 0.1% strain and 220°C, unless specified otherwise. Strain sweeps were conducted to verify that the material behaved in a linear viscoelastic manner under given strains. The time sweeps were carried out at 0.1% strain and angular frequency of 10 rad/s at 220°C for 30 min. In this study, we used the magnitude of the complex viscosity η^* as representative of the viscosity (Cox–Merz relation⁸). The melt rheology here refers to the complex viscosity η^* , storage modulus G' , and loss modulus G'' of the samples at the temperature of analysis.

RESULTS AND DISCUSSION

In this section, the effect of various parameters on the melt processability of the synthesized PAN

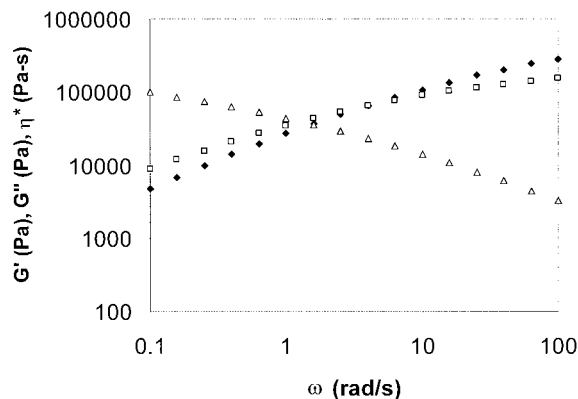


Figure 1 Dynamic frequency sweep of Barex (standard) at 180°C. G' (◆), G'' (□), η^* (△).

copolymers is investigated. These variables include the comonomer content, molecular weight of the copolymer, temperature, and time stability of viscosity of the AN/MA copolymer system. The effect of changing the comonomer on the flowability and char yield of the PAN system is also explored.

To get a better perspective of the melt spinnability of these synthesized PAN samples, a standard melt-extrudable commercially available polyacrylonitrile sample, Barex (65 mol % AN, 25 mol % MA, and 10 mol % elastomer), was studied for its melt viscosity properties. Figure 1 shows the frequency sweep at 180°C, the temperature found useful for extruding Barex. The zero-shear viscosity value at 180°C is around 70,000 Pa s⁻¹. Because the system was melt extrudable at 180°C and formed fine fibers, this zero-shear viscosity was taken as the value we aimed for in the synthesized PAN copolymer samples. Barex was found to be highly stable at 180°C (<0.1% viscosity rise in 30 min). It needs to be mentioned that Barex is a barrier polymer used in packaging applications and not used as a carbon-fiber precursor.

Effect of Amount of MA on T_g and Melt Processability of PAN

The amount of MA in the PAN copolymer is crucial in tailoring the melt processability of the system. A minimum amount is needed to disrupt the long-range order sufficiently to melt-process the copolymer. Increasing the amount of MA beyond this threshold value could give us better maneuverability in terms of melt processability of the system but it would decrease the theoretical yield

of carbon in the copolymer and could also make the process of stabilization/cyclization more difficult to achieve. Therefore, determining the optimum amount of MA needed to achieve a melt-processable system is crucial. At the threshold value of MA needed to disrupt the long-range order of PAN, there could be significant changes in the thermal-transition behavior and flow properties of the system, which would be interesting to observe and record. Hence, a series of copolymers of AN/MA with identical sequence and method of synthesis and similar intrinsic viscosities (0.25 dL/g in NMP at 25°C), but differing in the amount of MA in the polymer chain, was studied for their thermal-transition behavior and melt rheology.

The DSC plots of the various AN/MA copolymer samples are shown in Figure 2. PAN homopolymer was found to have a T_g of about 106.4°C. It can be seen that as the amount of MA increases, the T_g drops progressively, but the change in T_g is gradual, and not much inference can be drawn regarding the extent of long-range order disruption in the PAN copolymer system. Hence, any evidence of the minimum required MA quantity to break the long-range order, which would be characterized by a large drop in T_g at the threshold value, was not observed for this range of MA (2–15 mol %). The shape of the plots shows that the glass transition becomes better defined with increasing amounts of MA, because the order decreases and the amorphous region increases.

AN/MA copolymers exhibited a very striking dynamic melt-viscosity variation with varying amounts of MA. A temperature of 220°C was chosen for studying the melt-viscosity values. This value represents the temperature that is typically employed as the lower limit for conducting stabilization reactions industrially.⁵ Because we want to melt-process the PAN copolymer systems below the stabilization temperatures, 220°C seems to be a suitable temperature for conducting feasibility studies on their melt processability. At low MA contents (2–7 mol %), the order in the PAN system is very large because of the dipole–dipole interaction of the nitrile groups, and the melt viscosity is very high (>100,000 Pa s⁻¹) at 220°C (Fig. 3). At 10 mol % MA content, the long-range order is broken down, which is evidenced by a substantial drop of about four orders of magnitude in the dynamic melt viscosity at low shear rates. A subsequent increase in MA content to 15 mol % did not significantly reduce the dynamic melt viscosity at 220°C. This trend was also ob-

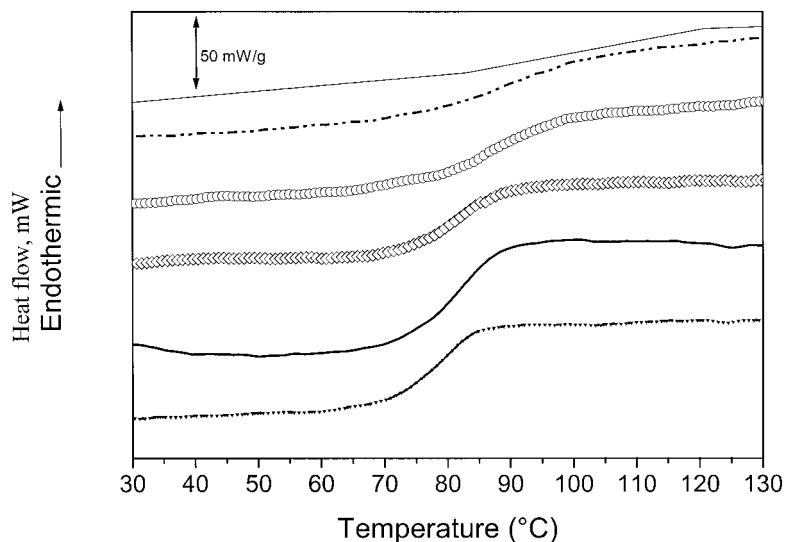


Figure 2 Effect of content of MA (mol %) on T_g of copolymer. AN/MA ratio and T_g (in $^{\circ}\text{C}$), respectively, are: 100/0, 106.4 (—); 98/2, 92.5 (— · — ·); 95/5, 85.8 (\circ); 93/7, 82.7 (\diamond); 90/10, 81.8 (—); and 85/15, 80.8 (\blacktriangledown); heating rate: $10^{\circ}\text{C}/\text{min}$.

served for the storage (G') and loss moduli (G''). Figure 4 shows the G' variation with frequency for different amounts of MA. This seems to confirm the speculation that there is a critical amount of comonomer concentration required that serves as a defect to destroy the crystal structure of PAN. Other investigators previously proposed this speculation.⁹ WAXS studies did provide some evidence of long-range order, but we could not determine a significant breakdown in the order with increased amounts of MA (Fig. 5).

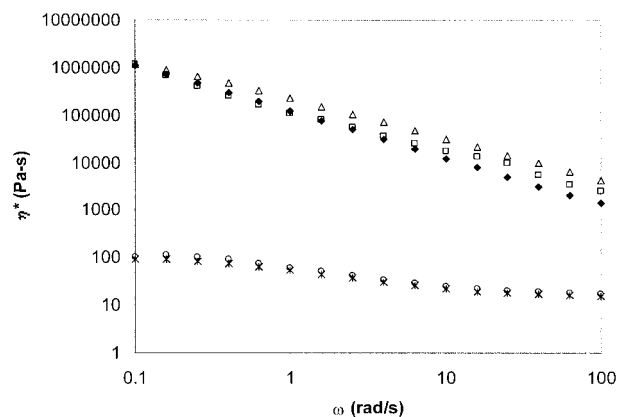


Figure 3 Effect of amount of MA on dynamic viscosity of AN/MA copolymers at 220°C . Frequency sweep AN/MA ratios are: 98/2 (\blacklozenge); 95/5 (\square); 93/7 (\triangle); 90/10 (\circ); and 85/15 (\ast); intrinsic viscosity: 0.25 dL/g in NMP at 25°C .

Neither three-dimensional ordering nor crystallinity was seen in these patterns for either the PAN homopolymer or the AN/MA copolymer. Compared to the ring pattern observed for the PAN homopolymer, the scattering pattern of the AN/MA copolymer was more diffuse, indicating some disruption of the long-range order. However, a quantitative estimation was not obtained in this study. More work is being undertaken in terms of characterization of this behavior by dynamic mechanical analysis (DMA) and nuclear magnetic resonance studies and will be the subject of another study.

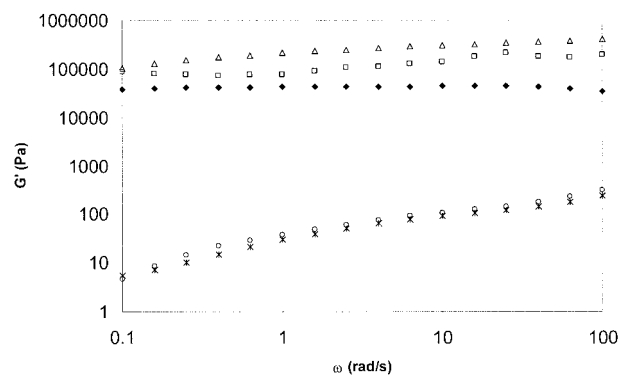
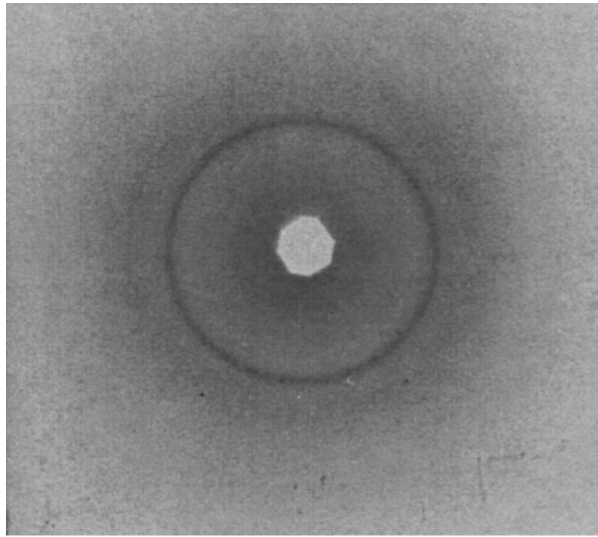
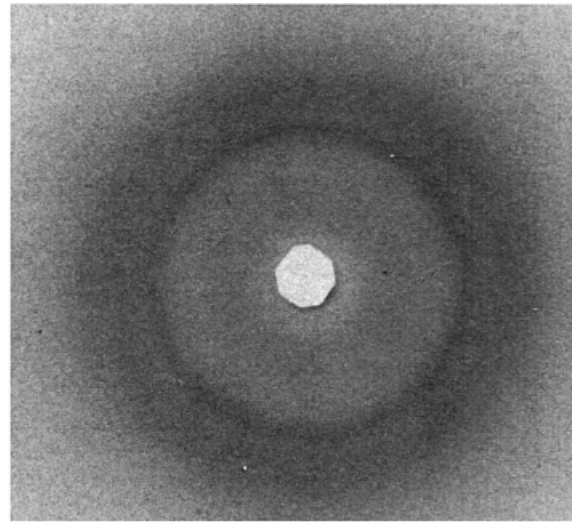


Figure 4 Effect of amount of MA on storage modulus of PAN/MA copolymers at 220°C . Frequency sweep AN/MA ratios are: 98/2 (\blacklozenge); 95/5 (\square); 93/7 (\triangle); 90/10 (\circ); and 85/15 (\ast); intrinsic viscosity: 0.25 dL/g in NMP at 25°C .



PAN Homopolymer

(a)


 $M_n=40,600, M_w=143,800$ g/gmol
AN/MA Copolymer (85/15 mol%)

(b)

Figure 5 Wide-angle X-ray scattering of PAN copolymers: (a) PAN homopolymer; (b) AN/MA copolymer (85/15 mol %; $M_n = 40,600, M_w = 143,800$ g/gmol).

Samples containing 10 and 15 mol % comonomer (of MA) exhibited very similar complex viscosity plots at 220°C. However, we wanted to determine whether this behavior is also seen at lower temperatures. Hence, the variation in the complex viscosity of 10 and 15 mol % MA samples was studied as a function of temperature (be-

tween 160 and 220°C) and time (Figs. 6 and 7). Neither sample exhibited a zero shear viscosity plateau at any temperature studied. Based on a comparison of the viscosity with that of Barex at low shear rates, temperatures of 160°C and approximately 195°C were found suitable for extruding AN/MA 85/15 and 90/10% copolymers, respectively. Thus, it can be clearly seen that at

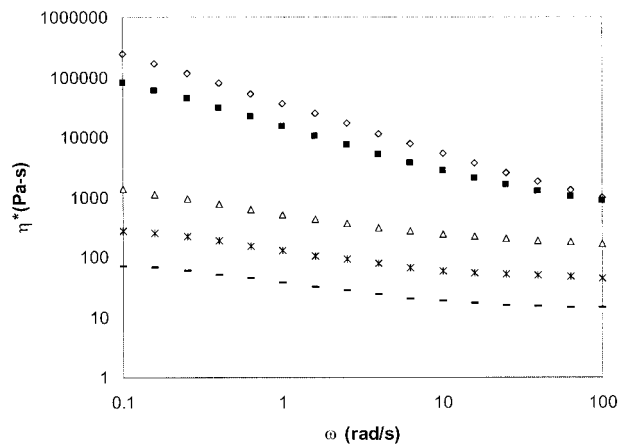


Figure 6 Dynamic viscosities of AN/MA copolymer (85/15 mol %) at varying temperatures: 180°C (◇), 190°C (■), 200°C (△), 210°C (*), 220°C (-); intrinsic viscosity of AN/MA sample: 0.25 dL/g in NMP at 25°C.

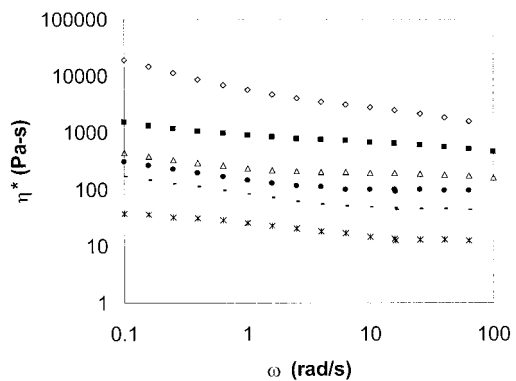


Figure 7 Dynamic viscosities of AN/MA copolymer (90–10 mol %) at varying temperatures: 160°C (◇), 170°C (■), 180°C (△), 190°C (●), 200°C (-), 220°C (*); intrinsic viscosity of AN/MA sample: 0.25 dL/g in NMP at 25°C.

Table I Activation Energies of Flow for AN/MA Copolymers and Barex

Sample	ΔE (kcal/mol)
Barex (65 mol % AN, 25 mol % MA, 10% elastomer)	7.36
AN/MA (85/15%)	17.44
AN/MA (90/10%)	42.50

lower temperatures, the rise in viscosity for the 10 mol % samples is higher than that for 15 mol % MA. This result seems to corroborate the hypothesis that MA acts as a defect in the PAN chain and improves the mobility of the PAN chains, in agreement with observations of previous workers.^{5,9,10} Therefore, increasing the amount of MA widens the temperature range over which the AN/MA copolymer is melt processable. Time sweeps also indicated that below 200°C, the rise in viscosity was less than 10% for 30 min for both samples. From the temperature plots, and based on the shift-factor approach, the activation energy (AE) for flow of the samples was computed (Table I) using equations from the literature.⁸ It can be seen that the AE for Barex (containing 25 mol % MA) is the lowest, whereas it is highest for the sample containing 10 mol % MA. As the AE for flow increases, the change brought by temperature on the flow property of the polymer increases. Thus, we can see that for two AN/MA copolymers of the same $I-V$, the minimum temperature at which the sample containing 15 mol

% MA is potentially extrudable is about 160°C, whereas this increases to 195°C for the sample containing 10 mol % MA. We conclude that the addition of MA helps to improve the melt flowability of the system. The higher the amount of MA, the larger the temperature window over which the PAN system is melt processable. Hence, the inference that we can draw from these studies employing various amounts of MA in otherwise similar AN/MA copolymer systems is that there is an optimum concentration of MA that is suitable for disrupting the order of PAN and thereby making the system melt processable.

To confirm the long-range order disruption of PAN by MA beyond 10 mol %, the thermal-transition behavior of the PAN copolymer was also studied by means of dynamic mechanical testing methods. Previous work on DMA of PAN homopolymer showed two thermal transitions corresponding to the paracrystalline region and the amorphous regions.¹¹ The lower transition corresponded to the molecular motion in the paracrystalline region, whereas the higher transition corresponded to the intermolecular dipole-dipole dissociation of the nitrile groups in the amorphous regions. In the sample of PAN homopolymer synthesized in this work, a single transition was observed (Fig. 8). The reason for this discrepancy can be explained as follows. The method of synthesis employed was different from that used in our work. Also, the samples reported in the literature were PAN fibers, which could possess higher order and orientation than those of the powder samples used in our experiments. Fur-

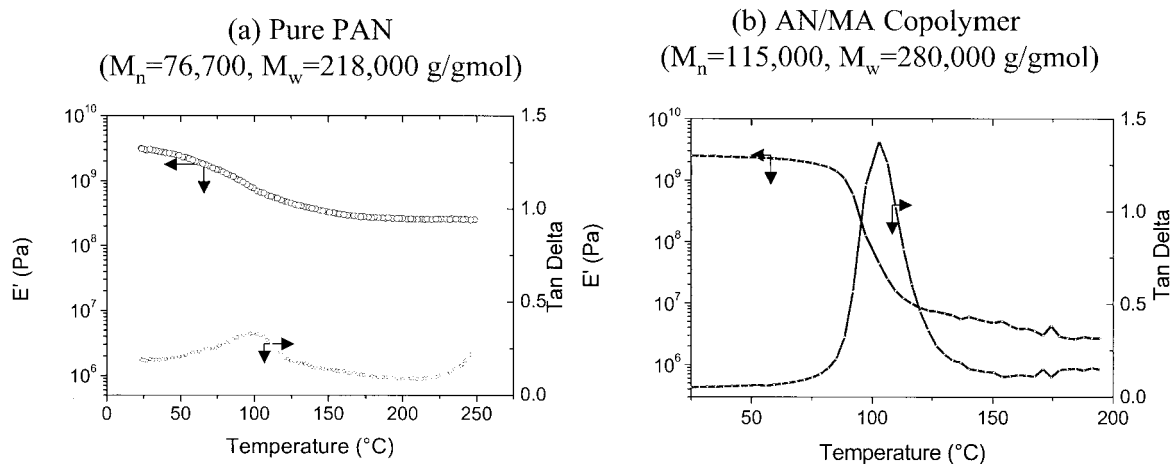


Figure 8 DMA of (a) pure PAN (homopolymer; $M_n = 76,700$, $M_w = 218,000$ g/gmol) and (b) AN/MA copolymer (85/15 mol %; $M_n = 115,000$, $M_w = 280,000$ g/gmol).

thermore, our sample was heated at 2°C/min, which is higher than the value used by the previous investigators (1°C/min). Also, in our case, we had formed a film by compression molding at 200°C. Although this heat treatment is for a short duration (typically 3–5 min), the temperature is above the T_g of PAN, and this could have an effect on the PAN transitions observed, which could also explain the discrepancy observed between the experimental data observed in our case and data reported in the literature.⁹ The DMA plot was compared with that of a high molecular weight (MW) copolymer of AN/MA (15 mol % MA) to qualitatively understand the difference in the thermal-transition behavior and to see evidence of long-range order disruption by inclusion of MA. In the synthesized AN/MA copolymer (15 mol %), a single transition corresponding to the glass transition of the PAN amorphous region was observed. A comparison of the peaks and transitions of the PAN homopolymer and AN/MA copolymer reveals two distinct differences. The $\tan \delta$ of the PAN copolymer, which is the ratio of the tensile loss modulus (E'') to the tensile storage modulus (E'), is much higher than that of the PAN homopolymer. Also, the E' drops less than an order of magnitude at the thermal transition for the PAN homopolymer, whereas the E' corresponding to the AN/MA copolymer drops over two orders at the identical thermal transition. Both of these differences in behavior are attributed to the disruption of long-range order resulting from paracrystallinity by the comonomer addition in the PAN system and a corresponding increase in the amount of amorphous phase of the copolymer. Such behavior was previously reported for other PAN copolymer systems.¹²

Effect of Molecular Weight on Glass Transition and Melt (Complex) Viscosity of AN/MA Copolymer System

We have established that a certain minimum amount of MA is needed to disrupt long-range order in the AN/MA system. Increasing the MA beyond this amount improves the melt processability by increasing the temperature window, but it would also reduce the theoretical char yield during stabilization/carbonization stages. The other parameter that could be crucial for optimum processability would be the molecular weight of the PAN copolymer system. Higher molecular weight systems give better mechanical properties in the final carbon fibers because bet-

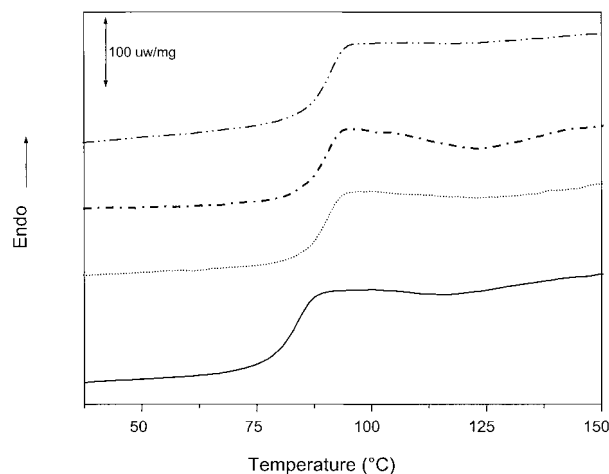


Figure 9 Effect of MW on T_g of AN/MA copolymers (85/15 mol %). M_n (in g/mol) and T_g (in °C) are, respectively: 40,600 and 91.4 (— · —); 34,700 and 90.7 (— · · —); 31,700 and 90.2 (· · ·); 8700 and 83.9 (—); heating rate: 10°C/min.

ter orientation could be imparted to the precursor fibers as a result of longer relaxation times. The viscosity of a sample tends to depend on MW raised to a power law (3.4–3.6) beyond the critical entanglement molecular weight (which is reported to be about 3000 for the PAN system¹³). A very high melt viscosity of the polymer system could make the processing more difficult. Thus, the effect of molecular weight variation on the melt processability of the AN/MA system was investigated. The molecular weights studied ranged from $M_n = 115,000$ and $M_w = 280,000$ to $M_n = 8700$ and $M_w = 22,400$, respectively, for an AN/MA copolymer (85/15 mol %), as shown in Figures 9 and 10. Normally, the conventional solution-spun samples used in the manufacture of carbon fibers have molecular weights in the range of about 100,000.⁵ Solution-spun samples have only about 20–30 wt % concentration of the polymer and, hence, they need to have high MW to achieve high orientation during drawing. In the melt-spun samples, it is believed that lower molecular weight samples could give carbon fibers with mechanical properties comparable to those made from solution-based PAN precursors. The T_g 's of the AN/MA copolymer samples were studied for a wide range of molecular weights. The DSC curves showed that the T_g 's decreased with a decrease in the molecular weight of the sample (Fig. 9).

The magnitude of complex viscosities (η^*) of the different MW AN/MA copolymers (85/15 and

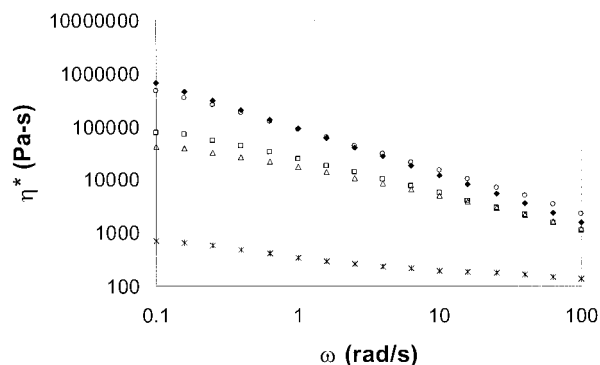


Figure 10 Effect of MW on dynamic viscosity of AN/MA copolymers (85/15 mol %) at 220°C. M_n and M_w (in g/gmol) are, respectively: 115,000 and 280,000 (◆); 40,600 and 143,800 (○); 34,900 and 97,900 (□); 31,700 and 94,900 (△); and 8700 and 22,400 (*).

90/10) as a function of angular frequency (ω) was studied, to obtain an estimate of their melt processability at 220°C (Figs. 10 and 11). The frequency sweeps show that the higher molecular weight samples, as one would expect, have much higher viscosity than that of Barex (70,000 Pa s⁻¹ measured for the Barex standard) at 220°C. A flattening of the curves was not observed at lower frequencies, suggesting the materials possess a distinct zero shear melt viscosity only at very low shear rates.

It can be seen from Figure 11 that the sample with $M_n = 35,000$ and $M_w = 100,000$ has a high low-shear rate viscosity at 220°C ($\sim 100,000$ Pa s⁻¹), compared to that of Barex, the reference material, at 180°C. Note that we are assuming that the low-shear η^* is taken to represent the

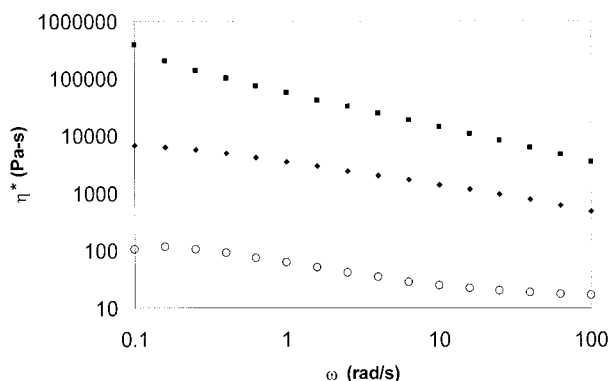


Figure 11 Effect of MW on dynamic viscosity of AN/MA copolymers (90/10 mol %) at 220°C. M_n and M_w (in g/gmol) are, respectively: 9000 and 15,000 (○); 19,400 and 26,700 (◆); and 36,400 and 53,700 (■).

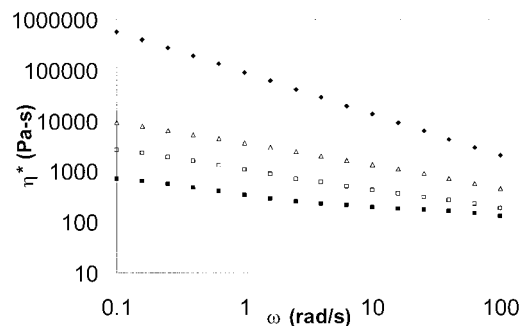


Figure 12 Dynamic frequency sweep of a mixture of low and high MW AN/MA copolymers (85/15 mol %) at 220°C. Ratio of high ($M_n = 35,000$, $M_w = 100,000$ g/gmol) and low ($M_n = 8700$, $M_w = 22,400$ g/gmol) MW samples: 50 : 50 (△); 25 : 75 (□); 0 : 100 (●); 100 : 0 (◆).

zero-shear viscosity. On the other hand, very low values of the low-shear rate viscosity were observed for the sample with $M_n = 8700$ and $M_w = 22,400$. Both MW samples would not be melt-spinnable at 220°C, the former having too high a viscosity and the latter most likely having too low a melt strength. Hence, mixtures of 50 : 50 and 25 : 75% wt % of the high/low molecular weight samples were prepared by dry blending. The lower MW sample serves to dilute or plasticize the system, thereby bringing about a viscosity reduction.⁵ We wanted to get a melt-processable system that had a zero-shear viscosity at 220°C, close to that obtained with a standard melt-processable system such as Barex at 180°C. The frequency sweeps of these mixtures are shown in Figure 12. As can be observed from the plot, both the 50/50 and 25/75 wt % samples showed a melt-viscosity curve similar to that of Barex, indicating systems that seem amenable to melt spinning.

The time stability of these samples is extremely crucial in determining their processability. In a large-scale extruder, the mean residence time of a polymer is less than 5 min. However, some of the polymer has a longer residence time and can remain for much longer times. Hence, we used a time sweep of about 30 min to measure the stability of these samples. The results are shown in Figure 13. As the molecular weight of the system increases, it begins to degrade faster and the rate of increase of viscosity is much more rapid. Although the rapid rise in viscosity is very favorable during the stabilization reaction, the viscosity buildup needs to be minimized in the extruder at the processing temperature. The buildup of viscosity for the 50/50 and 25/75 wt % samples was seen to be about 60%, relative to the initial

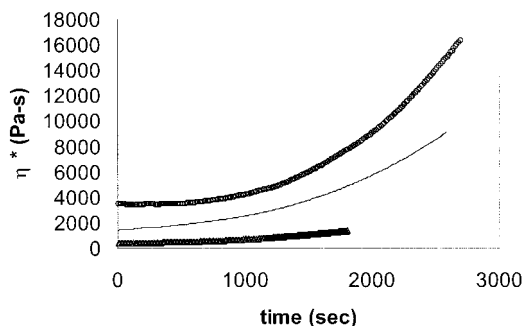


Figure 13 Time stability sweep of a mixture of low and high MW AN/MA copolymers (85/15 mol %) at 220°C. Ratio of high ($M_n = 35,000$, $M_w = 100,000$ g/gmol) and low ($M_n = 8700$, $M_w = 22,400$ g/gmol) MW samples: 25 : 75 (—); 50 : 50 (○); 0 : 100 (△).

value after 30 min, suggesting that they would be suitable for extrusion and thus fiber spinning at 220°C.

Figure 11 shows the effect of molecular weight on the dynamic melt viscosity of a 90/10 (mol %) AN/MA copolymer system. Compared with the melt viscosity of Barex, it is clear that the sample having a M_w of 53,700 would be most likely too viscous at 220°C to be extruded. For the 85/15 mol % AN/MA copolymer, under otherwise similar conditions of synthesis and processing, the corresponding M_w value was closer to 100,000. Thus, increasing the amount of MA in the PAN copolymer helps to increase the range of MWs over which the system is melt processable.

Based on these results, it is concluded that, although both 90/10 and 85/15 mol % systems of AN/MA copolymer are melt processable, a broader range of MWs over which the system is melt processable is achievable with 85/15 mol % systems. Thus, it is concluded from these results that increasing MA in the PAN copolymers has the effect of enhancing the range of MWs and temperatures over which the system is melt processable. Bhanu and coworkers¹⁴ have shown

that the experimental char yield of 85/15 and 90/10 AN/MA copolymer systems is similar. Therefore, based on these results, it seems that 85/15 systems are more suitable for conducting further studies on the feasibility of using them as carbon-fiber precursors. Hence, the remainder of this work is focused toward studying PAN systems having 15 mol % comonomers. Although the threshold value for long-range order disruption (and hence melt processability) would be dependent on the nature of the comonomer, a 15 mol % comonomer system seems to be a good starting point for studying the feasibility of their melt processing.

Effect of Comonomer Nature on Thermal-Transition Behavior

After investigation of MA comonomer systems, the effect of changing comonomers on thermal transitions and melt rheological behavior was investigated. Three different kinds of comonomers were studied: methyl acrylate (MA), isobutyl acrylate (IBA), and acrylamide (AM). The reason these comonomers were chosen is that these are commonly used in small amounts (2–7 mol %) in commercial-grade PAN systems and solution-spun fibers to improve the precursor fiber properties and processing and, in some cases, the final carbon fiber properties. All the results reported in this subsection correspond to a comonomer content of 15% (mol) in the PAN copolymer. The molecular weights and glass-transition temperatures of the copolymers synthesized are shown in Table II. Fairly high molecular weight samples have been synthesized that are in the range of molecular weights used in solution-spun PAN precursor systems. All the samples shown here were synthesized by redox reaction, as explained in the Experimental section. The PAN homopolymer synthesized had a T_g of 106.4°C, in good agreement with some of the values reported in the

Table II Effect of Comonomer Type on T_g and Yield of PAN Copolymers (Comonomer: 15 mol %)

Sample	Molecular Weight (g/gmol)		T_g (°C)	Char Yield (%)	
	M_n	M_w		In N ₂	With Stabilization
PAN	76,700	218,000	106.4	47	48
AN/MA	115,000	280,000	90.7	44	56
AN/IBA	219,000	385,000	80.2	29	45
AN/AM	46,300	128,000	113.3	54	65

literature for PAN systems.³ The DSC of AN/AM (97/3 mol %) copolymer fibers obtained from BP/Amoco and used as a reference indicated that the sample had a T_g of about 105°C. It can be seen from Table II that the incorporation of the acrylate (MA and IBA: 15 mol %) comonomers in the PAN chain leads to a drop in the T_g values. This is indicative of the disrupting of the order in PAN homopolymer attributed to the random inclusion of the comonomer, leading to an increase in the free volume of the chains and thereby lowering the T_g . This is seen despite an increase in the molecular weights of the copolymers compared to that of the PAN homopolymer.

The change in T_g of the PAN copolymer was found to be dependent on the nature and size of the comonomer (Table II). In the case of the acrylate copolymers, IBA is a bulkier molecule than MA, and the disruption in the long-range order is expected to be greater in the PAN copolymer for the same amount of comonomer addition, and thus the decrease in T_g would be greater. Alternatively, comonomers have a diluting effect on the copolymer system.¹⁵ Because the acrylate polymers have a lower T_g than that of the acrylonitrile polymer (T_g of polymers: MA = -10°C; IBA = -58°C¹⁶), they tend to decrease the T_g of the copolymer. On the other hand, the inclusion of acrylamide has an adverse effect on the T_g of the copolymer, increasing it by approximately 10°C over that of the homopolymer. Again, the T_g of acrylamide polymer (~ 165°C) is higher than that of polyacrylonitrile, which could increase the T_g of the copolymer. Thus, we can see from the results that the depression of T_g ascribed to the inclusion of the comonomer is dependent on both the nature and the size of the comonomer.

Effect of Comonomer on Char Yield

Because our primary aim is to produce a PAN copolymer that is melt processable, we need a window of processability, whereby the system is melt processable at a given temperature and, on a slight increase of temperature, the crosslinking reactions proceed at a very fast rate, leading to the stabilization of the fiber.⁶ It is to be noted that the term *stabilization* refers to the thermooxidative step, during which the PAN chains undergo fusion and form a ladderlike structure. This leads to a three-dimensional network system on carbonization at a higher temperature with the elimination of all atoms except carbon. The theoretical amount of carbon in a PAN homopolymer, which

is the maximum attainable carbon yield after stabilization and carbonization, is about 50 wt %.⁵ The TGA of the samples was done to obtain the thermal stability and get an estimate of the carbon yield, which was achievable with each of the copolymers synthesized. As the sample undergoes heating, it starts to actively cyclize at temperatures greater than 220°C (typically between 300 and 400°C), leading to char formation at the end of the heat cycle of the TGA.⁶ This gives us a preliminary estimate of the carbon yield of the copolymer. Two kinds of heat cycles were studied using the TGA. In the first cycle, the sample weight loss was monitored as it was heated from room temperature to about 800°C in an inert atmosphere (N₂) at a heating rate of 10°C/min. The results are tabulated in Table II. It can be seen that in the presence of MA, the char yield is similar to that of homo PAN (~ 45 wt %), whereas it was considerably lower for IBA, suggesting that the acrylate comonomer inhibits the cyclization reactions of the PAN polymer to a certain degree, depending on its nature and size. Because the MA units act as defects in the PAN chain, the ladder-structure formation, which the PAN typically exhibits during the thermooxidative stabilization process, is more difficult to achieve, resulting in slightly lower char yields. This sacrifice in lower char yield, which could translate into lower carbon yield,¹⁴ is offset by the potential of melt processability of the copolymer. This experiment was carried out in nitrogen and without oxidation/stabilization; hence, the copolymers tend to show a weight loss greater than that found for the homopolymer.

There was, however, a weight increase for AN/AM copolymer (~ 54 wt %) and this can be attributed to the crosslinking reaction found in the polyacrylamide copolymer itself.^{17,18} To determine the char yield, which could provide a more realistic indication of the final carbon content (for conversion to carbon fiber under actual test conditions), the stabilization reaction carried out in air/oxygen during the real carbon fiber manufacture was simulated using the TGA. It was previously seen from literature⁵ that oxygen acts in two opposing ways during stabilization. On the one hand, it initiates the formation of activated centers for cyclization, whereas, on the other hand, it retards the reactions by increasing the activation energy. Despite this, the use of oxygen is preferred because it results in the formation of oxygen-containing groups in the backbone of the

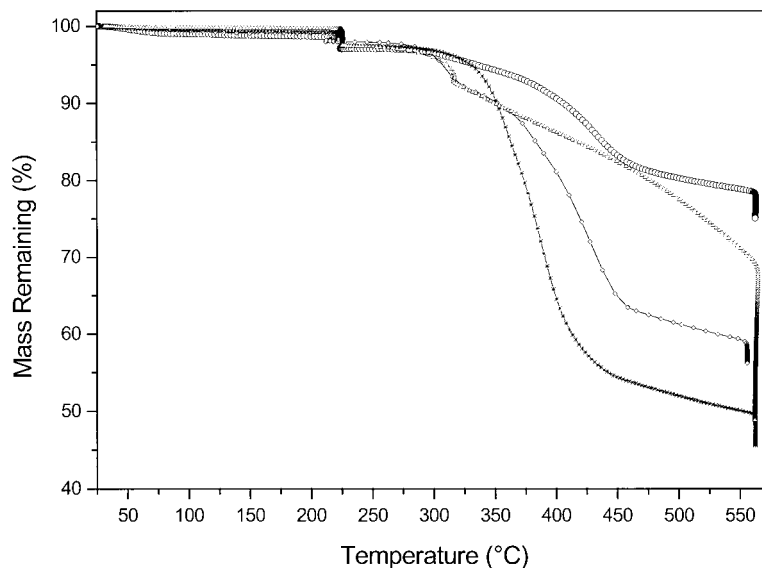


Figure 14 Char yields of PAN copolymers (15 mol % comonomer): PAN (Δ), AN-MA (\diamond), AN-IBA (---x---), AN-AM (\circ). Heat treatment: (1) room temperature to 220°C at 10°C/min in air; (2) 220°C for 3 h in air; (3) 220 to 550°C at 10°C/min in N_2 ; (4) 550°C for 3 h in N_2 .

ladder polymer, which help in fusion of the ladder chains during the carbonization reactions.

Hence, in the second type of heat cycle employed in the TGA, the PAN copolymer was stabilized by heating a small sample to 220°C in air, maintaining it at 220°C in air for 3 h, then heating it to 550°C and heating in N_2 at 550°C for 3 h. This is similar to the stabilization treatment for a PAN precursor fiber before carbonization for conversion to carbon fibers. The results are shown in Table II and Figure 14. It can be seen from the TGA plot in Figure 14 that up to 325°C, the weight-loss curve is fairly similar for all four systems. Above 325°C, the AN/IBA copolymer starts degrading rapidly until about 420°C and loses up to 55% of its original weight at 550°C after the stabilization treatment. This is lower than that of the PAN homopolymer, which typically loses up to 50% of its initial weight in a gradual decline from 325 to 550°C. The AN/MA copolymer has a fairly rapid drop in weight until about 450°C, after which the drop was more gradual and the sample was found to lose about 44% of its initial mass after heat stabilization at 550°C. The dissipation of heat is more difficult in a PAN homopolymer because it is a poor conductor of heat. Hence, excessive localized heating can lead to chain scission and lower the char yield in the TGA.⁵ Thus, inclusion of MA and IBA could help in better chain mobility as a result of higher free

volumes, thereby leading to more uniform heat transfer and better stabilization. This translates into a higher char yield for AN/MA copolymers compared to that for PAN homopolymer (Table II). In the case of AN/IBA copolymer, however, the bulky comonomer IBA has sufficiently disrupted the order in the PAN system. This tends to have a detrimental effect on the cyclization/crosslinking reaction and leads to a lower char yield at the end of stabilization.

Acrylamide copolymers gave the best char yield of about 65%. This would translate to a high carbon content precursor, and AN/AM copolymer appears very attractive as a potential candidate for a precursor material. One of the main reasons that the acrylamide copolymer gives high carbon yield is because of the faster onset of cyclization in the presence of acrylamide.^{17,18}

It must be cautioned here that the TGA analysis used to assess the char yield of the PAN copolymer is only a preliminary test. The test results would vary with the heating rate, polymer physical form, and so forth. Hence, this is not a truly accurate test procedure for ascertaining the true carbon values in the precursor or final fiber.

AN/AM Copolymer Systems

We have investigated the optimum MA content and MW ranges for the melt processability of the

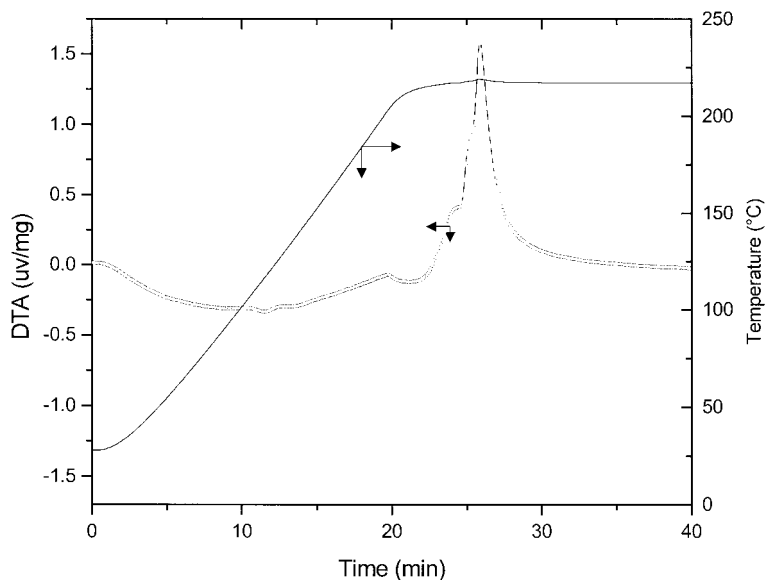


Figure 15 Effect of heating on AN/AM (85/15 mol %) copolymers.

AN/MA copolymer system. Because the char yield analysis of AN/AM system looks promising from TGA results, it would be an interesting system to study. Hence, the AN/AM system was studied for melt processability for a variety of molecular weights and different amounts of acrylamide comonomer (2–19 mol %). An extremely rapid buildup of viscosity occurred almost instantaneously after reaching 200°C. Because of the extremely large normal force, it was not found possible to evaluate the viscosities of these samples. The exothermic reaction was observed to occur within 5 min on reaching 220°C (as seen from the exothermic peak observed on the DSC when heated isothermally at 220°C). This is clearly shown in Figure 15, where the AN/AM sample was heated from 25 to 220°C, and held isothermally for about 15 min. It can be seen that an exothermic cyclization peak is observed within 5 min of reaching 220°C. Therefore, it was not possible to measure the viscosity. Hence, although AN/AM copolymer looks very promising in terms of char yield, it is most likely not suitable for melt spinning.

In AM, it has been speculated that the presence of hydrogen on the amide group facilitates the crosslinking reactions, leading to high melt viscosities. If the hydrogen atoms are replaced by methyl groups, these reactions would not be promoted and we would get a system that is potentially melt processable. To prove our hypothesis, a system containing 15 mol % dimethyl acrylamide as comonomer was studied for its melt flowability,

shown in Figure 16. It is observed that the viscosity is similar to that obtained for AN/MA systems containing 15 mol % MA. This result corroborates the speculation that AM serves to increase the crosslinking characteristics in the PAN system ascribed to the labile hydrogen atom present on the amide group.^{17,18} Although this leads to increased char yield, it is also detrimental to the melt processability of the system.

CONCLUSIONS

Three comonomers were studied for improving the melt processability of PAN system. Based on

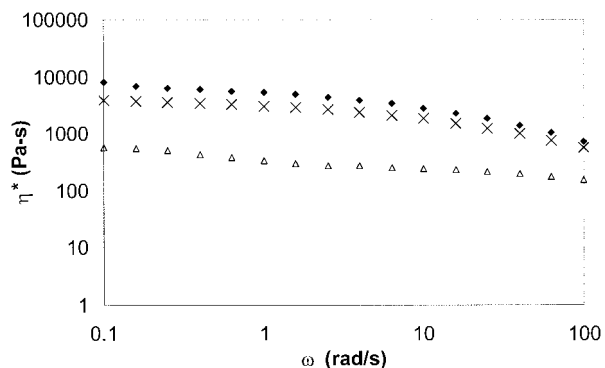


Figure 16 Comparison of dimethyl acrylamide versus methyl acrylate as comonomer (15 mol %) in PAN copolymer systems. Type of comonomer and intrinsic viscosity are, respectively: MA, 0.44 (Δ); MA, 0.65 (\times); DMAA, 0.58 (\blacklozenge); intrinsic viscosity in *n*-methyl pyrrolidone at 25°C.

our experiments, it has been concluded that MA is a good comonomer for generating melt processable PAN copolymer systems based on a suitable melt viscosity and char yield. Characterization was done in terms of the MW of the copolymer, amount of MA, and temperature to get the ideal sample for extruding/melt spinning. About 10 mol % of MA was found to be the critical amount needed to disrupt the long-range order of PAN and it caused a dramatic drop of four orders of magnitude in the complex viscosity at low angular frequencies at 220°C. PAN copolymers containing less than 10 mol % MA were found to exhibit no flowability, even at molecular weights as low as 20,000. Increasing the amount of MA beyond 10 mol % improved the melt processability of the PAN system and processing flexibility in terms of temperature and/or molecular weight, but had a negative impact on the theoretical carbon yield of the system. It was seen that the incorporation of MA improved the temperature and molecular weight window of processability of the PAN system. The molecular weight cutoff for 90/10 mol % (AN/MA) system was about 50,000 at 220°C, whereas it was increased to about 100,000 in the presence of 15 mol % MA comonomer. Hence, about 10–15 mol % of MA is seen as ideal for melt processing of PAN copolymers. It was also shown that acrylamide comonomer was not found to improve the melt processability of the PAN system because of extensive crosslinking.

The authors acknowledge the support of the U.S. Department of Energy through UT-Battelle LLC, under subcontract no. 4500011036 for the funding of this work. The authors also thank Dr. H. K. Shobha for the GPC analysis; Dr. Banthia, K. Wiles, and A. Mansuri for some of the synthesis work; and Dr. Sankarapandian for consultation.

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