

Modification of Polyacrylonitrile Precursors for Carbon Fiber via Copolymerization of Acrylonitrile with Ammonium Itaconate

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Received 28 October 2005; accepted 16 January 2006

DOI 10.1002/app.24256

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Ammonium-modified polyacrylonitrile was prepared by free-radical solution copolymerization of acrylonitrile (AN) with ammonium itaconate (AIA), and then it was spun into precursor fibers in this study. Effects of AIA and itaconic acid on the characteristics of the copolymers and precursor fibers were studied in contrast. It has been found that the ammonium modification could obviously increase the hydrophilicity of the copolymer. And in the spinning processes, modified copolymer can withstand higher total draw-ratio of 12.6 folds, while unmodified copolymer only 8.5 folds. The void volume, fineness, tenacity,

and elongation at-break of the ammonium-modified precursors are all improved and enhanced. WAXD test manifested that the modified precursors had higher degree of orientation. DSC test showed that the thermal properties of the modified and unmodified precursor fibers were almost the same. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2175–2179, 2006

Key words: carbon fiber precursor; PAN; ammonium itaconate (AIA)

INTRODUCTION

Carbon fibers are well known for their high tensile strength and modulus and lightweight. The properties of the final carbon fibers are determined to a great extent by the nature of the precursor fibers. Among the precursors available for producing carbon fibers, polyacrylonitrile (PAN) fibers are the most commonly used and promising precursors. But, PAN homopolymer as precursor results in carbon fiber of poor quality because of its low thermal property.¹ So PAN precursor is usually modified by incorporation of suitable comonomer during polymerization.

The selection of a suitable comonomer is an important step, which has been a hot subject of study.^{1–8} With acidic monomers acting as the comonomers, such as methacrylic acid or itaconic acid (IA), PAN copolymers possess high thermal property because the acidic groups in the PAN copolymer can catalyze the cyclization of nitrile groups during the heat stabilization treatment of PAN precursors. IA is the most commonly used comonomer.^{9–11} But, several key physical properties of P(AN-IA) copolymers, such as void volume, fineness, tenacity, and degree of orientation, are still not satisfying because the drawn-ratio

of P(AN-IA) fibers can not reach high enough.¹¹ There are reports^{12,13} on ammonium itaconate (AIA) acting as the comonomers, but the effects of AIA on the thermal and physical properties of the final PAN precursor fibers are not discussed.

In this experiment, AIA was prepared by the neutralization of IA with NH₃. Then, acrylonitrile (AN) and AIA were copolymerized to synthesize the ammonium-modified copolymer P(AN/AIA). The P(AN/AIA) acquired was spun into fibers through a wet spinning process. The control tests with IA acting as the comonomer were taken. Effects of AIA and IA on the characteristics and properties of the copolymers and precursor fibers were studied in contrast after.

EXPERIMENTAL

Materials

Monomer AN was of industrial polymerization-grade and distilled to remove inhibitors before use. Comonomer IA was re-crystallized from acetone. Azobisisobutyronitrile (AIBN) was re-crystallized from ethanol. Dimethyl sulfoxide (DMSO) was distilled to remove moisture. NH₃ was used as received.

Neutralization

IA was firstly charged into a flask and dissolved in ethanol. Then, the NH₃ gas was slowly blown into the

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solution. Neutralization took place and IA turned into AIA. AIA precipitated when there was enough NH_3 blown in. Precipitated AIA was filtered and dried under vacuum.

Polymerization

AN and AIA were copolymerized using DMSO as solvent and AIBN as radical initiator in this study. First, AN, AIA (or IA), AIBN, and DMSO were precisely measured out. Every measured ingredients were charged in the flask, which was continuously flushed with ultra-pure nitrogen. The flask was wholly immersed in a temperature-controlled water bath of 60°C and was shaken from time to time. After a definite reaction time, the resultant mixture was poured into a large amount of methanol for precipitation, washed with methanol several times, dried at 80°C under vacuum, and then weighed. The total concentration of monomers (including AN and AIA (or IA)) was controlled at 20 wt %, with the concentrations of the comonomers (AIA or IA) changing from 0.0 to 2.1 wt % according to respective experiment. The copolymer composition was determined by elemental analysis.

Wet spinning

A 18% solution of copolymer in DMSO (dope) was spun on a laboratory-made wet-spun apparatus. First, the dope was deaerated *in vacuo* at 60°C and filtered through a stainless steel mesh before spinning. Then, the dope was extruded under pressure through a capillary tube of 0.06 mm diameter and was passed through three coagulating baths to get gel fibers. Subsequently, the gel fibers were thoroughly washed with water and were drawn through three drawing processes including hot-water drawing, boiling-water drawing, and high-pressure-steam drawing. Following drawing, the filaments were finished, dried, and collapsed, and then prepared into the precursor fibers.

Characterization

Conversion and the rate of polymerization were calculated from the weight of polymer obtained. The molecular weight (M_w) of the purified polymers was determined by viscosities. Viscosities of the polymers were measured at 35°C in dimethyl formamide by using an Ubbelohde viscometer, and the molecular weight was calculated from the following equation¹⁴:

$$[\eta] = 2.78 \times 10^{-4} M_w^{0.76}$$

Hydrophilicity of the copolymer was determined by the contact angle. The contact angle can be calculated by the following equation,¹⁵

$$\cos \theta = 1 - \rho g h_m^2 / 2\sigma_l$$

where θ is the contact angle, h_m is the maximal height of the liquid, σ_l is the surface tension, ρ is the liquid density, and g is a constant.

The void volume of the precursor fibers was calculated from the density of the fiber sample. Density was measured with a density gradient column consisting of a mixture of *n*-heptane and carbon tetrachloride at 25°C. And the void volume of the bulk homopolymer, whose density is 1.18 g/cm³, was considered 0.

X-ray diffraction (WAXD) of the powdered specimens was obtained on a Phillips PW1710 X-ray diffractometer with nickel-filtered Cu K α radiation at a 1° scan rate. For orientation measurements, the fiber sample was wound on an aluminum sample holder in such a manner that the individual filaments were parallel. The 2θ set at 16.9°, an azimuthal scan, was taken. The width in degrees of the half-maximum intensity ($\beta_{1/2}$) of the peak obtained from an azimuthal scan was used to calculate the degree of orientation. The lower $\beta_{1/2}$ is, the higher the degree of orientation will be.

DSC curves of the precursors were recorded on NETZSCH DSC404C thermal analyzer in air flow using a heating rate of 5°C/min in the temperature range from 30 to 450°C.

TG curves of AIA and IA were recorded on NETZSCH TG209C thermal analyzer in air flow using a heating rate of 5°C/min in the temperature range from 30 to 135°C and keeping 135°C for 30 min.

RESULTS AND DISCUSSION

Effect of ammonium modification on the copolymerization reaction

Solution polymerization technique was used to synthesize AN/AIA copolymer. Effect of time on copolymerization rate was studied. Figure 1 shows the variation in percentage conversion as a function of reaction time. According to the results summarized in Figure 1, it is clear that conversion increases quickly before reaction time reaches 8 h. Induction period of copolymerization of modified copolymer becomes shorter when compared with that of unmodified copolymer. During the whole polymerization period, the values of the conversions of both unmodified copolymer and modified copolymer are almost equivalent, with the maximum conversion difference of 7.3% at 6 h. The changes of conversion of copolymerization become less prominent when the reaction time is above 8 h, with conversion difference only 2.6%. Generally, the copolymerization rate of modified copolymer is slower and smoother than that of the unmodified copolymer. The possible reason is that AIA has

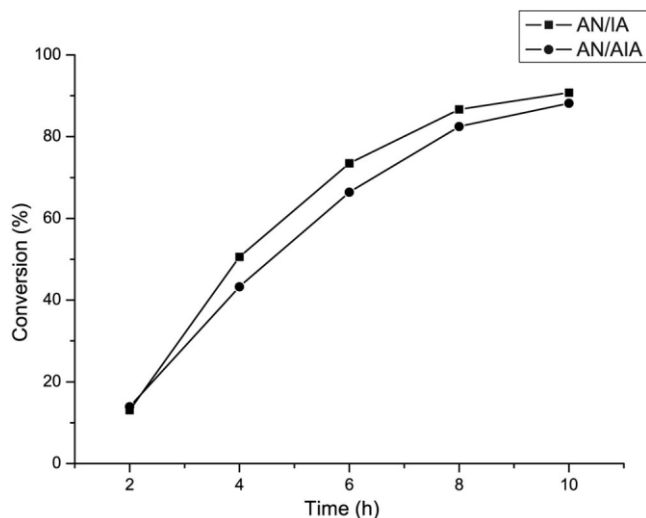


Figure 1 Relationship between conversion and time.

bigger space volume than IA and the steric hindrance of AIA decreases its reactivity.

Meanwhile, as shown in Figure 2, the average of the molecular weights of P(AN/AIA) copolymers acquired in this research is 13.8×10^4 , only a bit lower than the 14.4×10^4 of the P(AN/IA) copolymers. That is to say, the effect of ammonium modification on the molecular weights is less obvious when the comonomer concentration is below 2.1 wt %.

Effect of ammonium modification on the hydrophilicity of the copolymer

The contact angle between a polymer layer and water can be used to demonstrate the hydrophilicity of the polymer.¹⁵ The lower the contact angle is, the higher the hydrophilicity will be. The relationship between

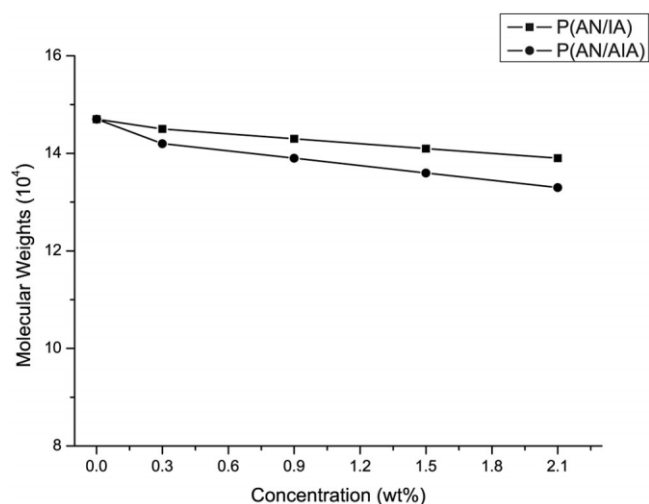


Figure 2 Effect of ammonium modification on molecular weights.

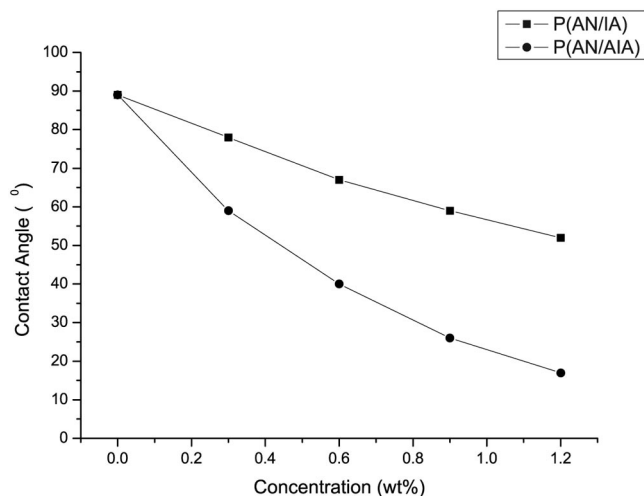


Figure 3 Relationship between hydrophilicity and the comonomers concentration.

the hydrophilicity of the discussed copolymers and the concentrations of the comonomers (IA or AIA) is shown in Figure 3. From the changes of the contact angle value, we can find that the hydrophilicity of P(AN/AIA) and P(AN/IA) both show a trend of increase on the increase of IA or AIA concentration. But AIA is much more efficient than IA in improving the hydrophilicity. The improvement of ammonium modification on copolymer hydrophilicity is obvious.

The increase of the copolymer hydrophilicity gives advantages to the precursor fibers in spinning processes, namely in the coagulation and stretching processes. First, in the coagulation process where the polymer solution (dope) is converted into gel fibers because of the phase separation, the hydrophilic AIA segments in the polymer chain can improve the micro-environment where the micro-phase separation is taking place. Second, it is easier for ammonium-modified precursors to infuse with water, which can act as the plasticizer of molecular section movement. And when water plays as plasticizer in the stretching process of spinning, the draw-ratio of precursor fibers can be higher and the orientation of the fibers can be increased. Therefore, with the increase of hydrophilicity, the physical properties of the precursor fibers can be improved, which will be discussed later.

Effect of ammonium modification on physical properties of the precursor fibers

It is very important to study the physical properties of the precursor fibers. The comonomers (AIA or IA) play a key role in the factors that affect the physical properties of the precursor fibers. Table I shows effects of AIA or IA on physical properties of the precursor fibers.

TABLE I
Physical Properties of the Precursor Fibers

Fiber	Optimized draw-ratio	Fineness (dtex)	Tenacity (cN/dtex)	Elongation at break (%)	Void volume (%)
Unmodified precursor	8.5	1.0	6.0	9	2.3
Modified precursor	12.6	0.8	7.8	11	1.0

From Table I, it can be shown that the ammonium-modified precursor fibers give an attractive hand. In the spinning processes, the optimized draw-ratio of modified copolymer was 12.6 folds, while of unmodified copolymer only 8.5 folds. So the modified copolymer can withstand higher total draw-ratio. The void volume, fineness, tenacity, and elongation at-break of the modified precursors are all improved and enhanced. In addition, there are no fluffs, broken and adhered fibers in them. The reason of the physical property improvements is the preferable hydrophilicity of the ammonium-modified copolymers and fibers, as analyzed in the last section. The infused water in ammonium-modified fibers acts as plasticizer in the stretching processes of spinning. And when water plays as plasticizer, the extent of the stretching of precursor fibers can be higher.

What is more, the hydrophilicity increase of the ammonium-modified copolymers made the micro-phase separation more homogeneous in the coagulation process of spinning. That is to say, hydrophilicity improves the homogeneity of the fiber structure by reducing the incidence of larger voids. So, the void volume of the ammonium-modified precursor fibers is 1.0%, much lower than the 2.3% of unmodified. In addition, the orientation of the ammonium-modified precursor fibers is also increased, which can be shown in Figure 4. For the peak at $2\theta = 16.9^\circ$, the $\beta_{1/2}$ value of ammonium-modified precursor fibers is 1.03° ,

lower than the 1.47° of the unmodified precursor fibers.

Thus, the structure and physical properties of the ammonium-modified precursor fibers can satisfy the requirements for high-tenacity carbon fibers.

Thermal properties

To study the effect of ammonium modification on the thermal properties of precursor fibers, the DSC curves of the P(AN/AIA) copolymer, P(AN/AIA) precursor fibers, and P(AN/IA) precursor fibers were recorded and shown in Figure 5. Table II shows some important DSC parameters of the curves. It is noted that the DSC curves of P(AN/AIA) fibers and P(AN/IA) fibers are almost doubling. That is to say, the fibers made from P(AN/AIA) copolymer have the same exothermic reactions as P(AN/IA) fibers. From Figure 5 and Table II, we can see that the DSC curve of P(AN/AIA) copolymer is quite different from that of the fibers, which similar observation had been reported by Zhang et al.¹³

From the characteristics of the DSC curves, we can conclude that P(AN/AIA) changed into P(AN/IA) in the processes of spinning. The reason is that AIA is an ammonium salt and ammonium salts will decompose when heated. The drying and high-pressure steam-stretching processes of spinning are both taken place at high temperature. After going through these high-temperature processes, the ammonium groups in

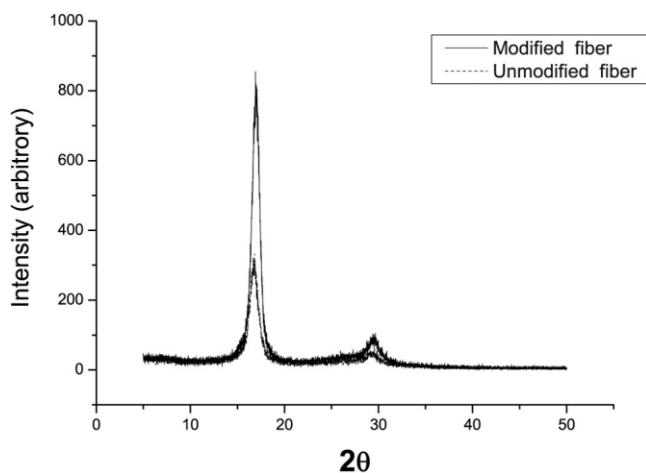


Figure 4 WAXD patterns of precursor fibers.

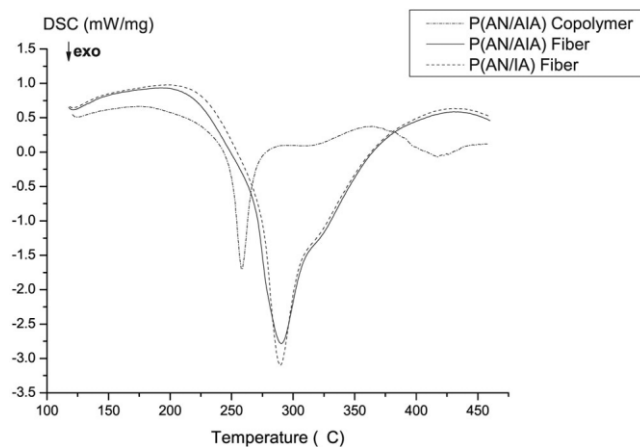


Figure 5 DSC plot of copolymer and fibers.

P(AN/AIA) decomposed into carboxyl groups and NH_3 gas, so the P(AN/AIA) turned into P(AN/IA). The decomposition of AIA was justified by TG test shown in Figure 6. From Figure 6, it was observed that the decomposition temperature of AIA is about 135°C . Above all, ammonium modification does not change the thermal properties of the final precursor fibers because P(AN/AIA) turned back into P(AN/IA) in the spinning processes through the thermal decomposition.

CONCLUSIONS

Laboratory studies of ammonium modification of PAN precursors for carbon fiber have shown that there are little differences in reaction rates and molecular weights when IA was replaced by AIA in the copolymerization with other condition being the same. But, the ammonium modification could obviously increase the hydrophilicity of the copolymer. And in the spinning and stretching processes, modified copolymer can withstand higher total draw-ratio of 12.6 folds, while unmodified copolymer can withstand only 8.5 folds, with other conditions being the same. The void volume, fineness, tenacity, and elongation at-break of the modified precursors are all improved and enhanced. WAXD manifested the modified precursors have structure of higher degree of orientation. The differences of thermal properties between the modified and unmodified precursor fibers are very small.

TABLE II
Important DSC Parameters of Copolymer and Fibers

	T_i ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	ΔT ($^\circ\text{C}$)	ΔH (J/g)
(AN/AIA) copolymer	221.2	275.3	255.8	54.2	372
P(AN/AIA) fiber	216.2	366.0	290.6	149.8	3981
P(AN/IA) fiber	226.3	368.5	289.6	142.2	4032

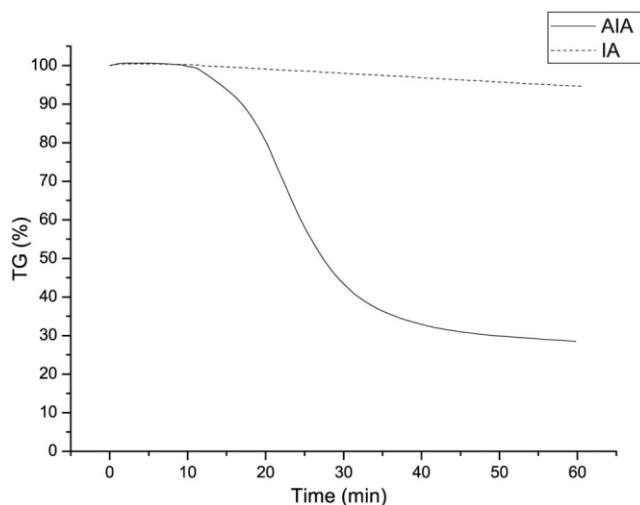


Figure 6 TG plot of AIA and IA.

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