

The Degradation and Prestabilization of Acrylonitrile Copolymers

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ABSTRACT: The degradation and prestabilization of polyacrylonitrile (PAN) were investigated with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR). The initial temperature, initial loss-weight temperatures, and loss-weight were significantly lowered when ammonium itaconate (AIA) was used as comonomer. One exothermal peak of PAN (homopolymer) was shown in the DSC curves, while there were four exothermal peaks of poly(AN-AIA). FTIR spectra results confirm the degradation process

of NH_4^+ groups. During the heating process, NH_4^+ groups (3030 cm^{-1}) were changed into NH_3^+ (2955 cm^{-1}) and then NH_2^+ groups (2920 cm^{-1}). The dissociated H^+ could initiate the cyclization reactions of $\text{C}\equiv\text{N}$ accompanied with heat released. The effect of ammonia on degradation and prestabilization of PAN was also studied. It was found that ammonia could accelerate prestabilization of acrylic precursors. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1596–1600, 2010

Key words: degradation; prestabilization; acrylonitrile

INTRODUCTION

Acrylonitrile (AN) polymers-based precursors are emerging as one of the best materials for making carbon fibers. Superior mechanical properties of carbon fiber are reported when some comonomers are usually used, such as itaconic acid (IA), acrylic acid (AA), and acrylamide (AM).^{1–4}

Bhat et al.⁵ had investigated acrylic fibers prestabilization in ammoniac atmosphere. They deemed that the final spinning dope treated by ammonia or the acrylic fiber prestabilization in ammoniac atmosphere can increase the reactive rate of cyclization and improve the properties of preoxidated fibers. Their studies almost focused on the polyacrylonitrile (PAN) copolymers treatment. However, the treatments of comonomers were usually neglected.

In our experiments, IA was treated by ammonia, and it would be formed an ammonium salt of IA, namely ammonium itaconate (AIA). The structure of poly(AN-AIA) copolymer is given in Scheme 1. According to the contact angle of copolymer, it was found that poly(AN-AIA) had excellent hydrophilicity compared with poly(AN-IA). The final fibers made by poly(AN-AIA) had lower residuary solvent and better properties than other fibers.⁶

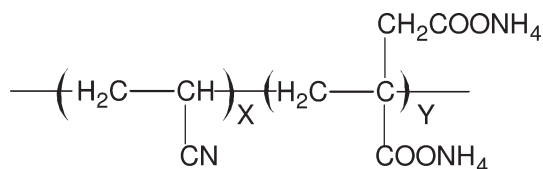
Chen et al. had studied the degradation of poly(AN-AIA) in air^{7,8}; however, the abnormal exothermal peaks in the DSC curves were neglected. In this article, the degradation and prestabilization of the copolymers were determined by DSC and TGA. Compared with poly(AN-IA), poly(AN-AIA) had different thermal behaviors. According to FTIR, it was found that the cyclization reaction mechanisms of poly(AN-AIA) were different from poly(AN-IA). Treated by ammonia, poly(AN-IA) copolymers had lower initial (T_i) and final temperature (T_f) of nitrile cyclization reactions than those of untreated.

EXPERIMENTAL

Polymerization

AN was purified by alkali washing followed by distillation. AIA was recrystallized in methanol. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was used as initiators and also refined before use. Deionized water was adopted as the polymerization medium. Required amounts of AN, AIA, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and deionized water were placed in closed glass bottles. Ultrapure nitrogen was flushed into the bottle. After a defined reaction time, the resultant mixture was poured into a large amount of methanol for precipitation, washed with methanol several times, dried at 60°C under vacuum, and then weighed. The details of copolymers are given in Table I.

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Scheme 1 The chemical structure of AN/AIA copolymer.

Treatment

Sample AI was treated by the following three methods. First, using DMSO as solvent, plenty of ammonia gas was flushed into the solution of sample AI and closed the bottle for 1 h. Then, the copolymer was filtered and purified by large amount of deionized water, dried under vacuum at 50°C for 5 h, and determined by DSC in air (sample AI1). Second, sample AI was determined by DSC in ammoniac (sample AI2). Third, sample AI was dipped in aqueous ammonia for 10 h, then filtered, washed by large amount of deionized water, dried, and determined by DSC in air (sample AI3).

Characterization

Viscosities of the copolymers were measured at 30°C in DMF using an Ubbelohde viscometer, and the number-average molecular weights (M_n) of the purified copolymers were calculated from eq. (1),¹⁰

$$[\eta] = 3.92 \times 10^{-4} M_n^{0.75}. \quad (1)$$

Elemental analysis of the copolymers was carried out using a Vario EL III elemental analyzer to determine oxygen content in these copolymers.

DSC measurements were carried out in nitrogen, air, or ammoniac with DT40 thermal analyzer (Japan SHIMADZU). These DSC studies were performed at a heating rate of 5°C min⁻¹ with sample weights of about 2.5 mg. The time conversion data were obtained using TA Instruments "Universal Analyzer" software.

TGA studies of samples were carried out on a DT40 thermal analyzer from 50 to 390°C in air atmosphere at a heating rate of 5°C min⁻¹. A sample

weight of about 4–5 mg in the form of powder samples was used.

Fourier transform infrared (FTIR) measurements were made by loading samples on KBr disks (0.5 mg sample with 200 mg KBr) for the specimens, which were selected from samples after different heat temperatures, by the use of a Nicolet 750 spectrometer.

RESULTS AND DISCUSSION

DSC study of poly(AN-AIA) copolymers

DSC exotherms of PAN copolymers in nitrogen with different contents of AIA are shown in Figure 1, and the details of the DSC exotherms are given in Table II. First, with increasing the ratio of molar fractions of the AIA and AN in the copolymers, the initial temperatures (T_i) were gradually reduced. The decrease of T_i became less prominent, when AIA concentrations were more than 1.5 wt %. Second, the exothermic peak width ($\Delta T = T_i - T_f$), liberated heat (ΔH), and heat liberated rate (\emptyset , $\Delta H/\Delta T$) were increased, but all the amplitudes became decreasing. Third, the final temperature (T_f) of S2, S3, and S4 had hardly any changes. Therefore, poly(AN-AIA) copolymers could obtain lower T_i , ΔH , \emptyset . According to these thermal properties, it was indicated that poly(AN-AIA) copolymers were more suitable for use as the precursors of carbon fiber.

Two distinct exothermic peaks during the dynamic DSC/TGA studies of poly(AN-IA) had been reported.^{9,11} However, four exothermic peaks were shown in the DSC exotherms of poly(AN-AIA), which were not separate distinctly but overlapped with each other, and the fourth peak was least, followed by the first. When the concentration of AIA was low (as S1), the four peaks overlapped and almost turned into a peak. And, S1 had higher T_i , T_f , \emptyset , and ΔT , compared with sample AI, which may be attributed to low concentration of comonomer. The cyclization reactions of S1 were similar to those of PAN homopolymers, which contained both free radical and ion initial.¹²

FTIR was used to investigate the structure changes of PAN. According to the four exothermic peak

TABLE I
Parameters of PAN Copolymers

Sample ^a	Ratio of molar fractions AN/comonomer (g/g)	$[\eta]$ (mL/g)	$M_v^b \times 10^4$	Oxygen concentration in copolymers (wt %)	AIA concentration in copolymers (mol %)
AI	99.1 : 0.9	5.039	40.51	0.3797	0.022
S1	99.7 : 0.3	4.868	38.71	0.226	0.01
S2	99.1 : 0.9	4.874	38.77	0.3810	0.028
S3	98.5 : 1.5	4.756	37.54	0.4453	0.048
S4	96.5 : 3.5	4.524	35.14	0.5111	0.107

^a AI is poly(AN-IA); S1, S2, S3, and S4 are poly(AN-AIA) copolymers.

^b M_v is calculated by $[\eta] = 2.83 \times 10^{-4} M_v^{0.758}$.

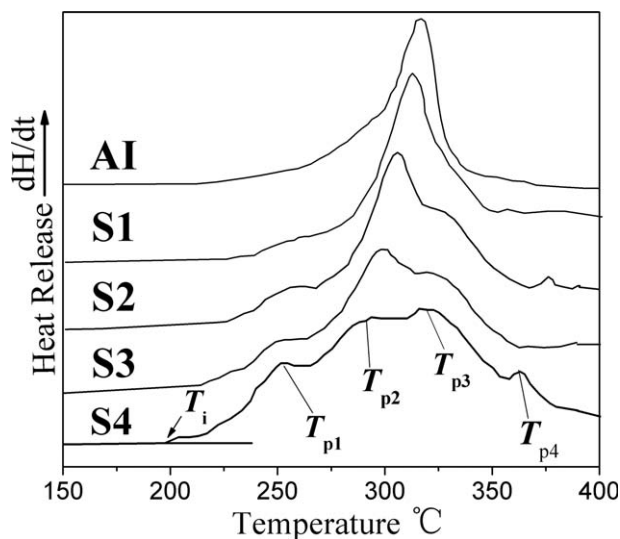


Figure 1 Dynamic DSC exotherms of PAN copolymers in air.

temperatures in DSC, the sample S4 was heated up in air, and then the samples were determined by FTIR, respectively. The data are plotted in Table III and Figure 2 to get information for the structural changes related to the thermal history of the process of prestabilization. In the prestabilization process, the most prominent structural changes were the decrease in the intensities of the 2241–2243 cm^{-1} , which attributed to $\text{C}\equiv\text{N}$ band, and increase of a shoulder-like peak in 1718 cm^{-1} (due to cyclic $\text{C}=\text{O}$), the band in 1597 cm^{-1} (due to $\text{C}=\text{N}$, $\text{C}=\text{C}$, $\text{N}-\text{H}$ mixed), and the band in 802 cm^{-1} (due to $\text{C}=\text{C}-\text{H}$).^{13,14} These spectroscopic results had shown that some chemical processes occurred in the stages of prestabilization. First, reaction of nitriles results in conjugated $\text{C}=\text{N}$ containing structures, which result from intramolecular cyclization or intermolecular crosslinking. Second, hydrogen elimination leads to the formation of conjugated $\text{C}=\text{C}$ structures on the chain backbone, which then undergo further reaction. Third, introduction of oxygen leads to the formation of carboxyl groups. It had also been noted that a low peak at about 2330 cm^{-1}

was present due to CO_2 , which resulted from the thermal degradation of PAN precursor.

In the region 2900–3100 cm^{-1} , there was a strong absorbance peak, and the band of the peak was decreased with the treatment temperatures of S4 increased. In the FTIR curve of sample 1, the peak was at 3030 cm^{-1} , which was due to the NH_4^+ groups. Then in samples 2 and 3, the peak was at 2955 and 2920 cm^{-1} , which was due to the NH_3^+ and NH_2^+ groups, respectively. The peak almost disappeared when the treatment temperature was more than 321 °C. These changes showed that the thermal degradation of NH_4^+ groups occurred during the heating process. According to the previous data, it was shown that H^+ was dissociated from NH_4^+ step by step. Dissociated H^+ could initiate the cyclization reactions of $\text{C}\equiv\text{N}$ accompanied with heat released, which presented as four distinct exothermic peaks in DSC exotherms of poly(AN-AIA). And also, the samples did not dissolve over 301 °C, which indicated that the degree of cyclization and crosslinking were quite high.

TGA study of poly(AN-AIA) copolymers

In prestabilization process, loss-weight behaviors of PAN copolymers would take place. The weight loss was multistage reactions and taken place at different temperatures.⁹ To investigate the behaviors, TGA scans of samples AI, S1, and S2 were performed in air at a heating rate of 5 °C min^{-1} , as shown in Figure 3. The lowest initial loss-weight temperature was sample S2 (at 225 °C), followed by AI (230.8 °C) and S1 (248.3 °C). Under initial loss-weight temperatures, the weight loss was very slow (1.2–1.8%), which attributes to the water of samples. Thereafter, the rate of loss-weight became very intense. Loss-weight reactions were accompanied by nitrile cyclization reactions.^{9,14} Theoretically, the nitrile cyclization reactions should not bring about any weight loss. However, if the rate of the reaction and heat liberating was very high, fragmentation of polymer chains may occur producing volatile particles leading to weight loss. During the prestabilization in air,

TABLE II
Parameters Obtained from DSC Exotherms (Rate of Heating 5 °C)

Samples ^a	T_i (°C) ^b	T_p (°C)				T_f (°C)	ΔT (°C)	ΔH (J g^{-1})	$\Delta S = \Delta H / \Delta T$ (J g^{-1} °C ⁻¹)
		1	2	3	4				
AI	227.2	–	295.5	–	–	314.1	86.9	362.4	4.17
S1	234.3	–	308.7	–	–	327.4	93.1	408.2	4.38
S2	220.0	262.3	307.0	324.3	370.2	377.2	157.2	385.7	2.45
S3	209.1	260.4	299.9	319.8	367.5	377.8	168.2	378.9	2.25
S4	207.3	257.8	300.3	320.8	364.6	377.5	170.2	374.3	2.20

^a AI is poly(AN-IA); S1, S2, S3, and S4 are poly(AN-AIA) copolymers.

^b T_i is the lowest starting exothermic temperatures of copolymers in DSC exotherms.

TABLE III
Parameters of S4 Treatment (Rate of Heating 5°C min⁻¹)

Samples	Treatment temperature (°C) ^a	Treatment time (min)	Dissolubility ^b
1	25	5	Soluble
2	258	5	sparingly soluble
3	301	5	Insoluble
4	365	5	Insoluble
5	378	5	Insoluble

^a Treatment temperatures were the four exothermic peak temperatures of S4.

^b The dissolubility of simples in DMF.

some micromolecules (e.g., H₂, HCN, CO₂, and H₂O) were got rid of from PAN, and oxygen was linked forming carbonyl groups (C=O),¹⁵ which finally brought about the total weight decreasing.

From 230.8 to 249.5°C, sample AI had strong loss-weight reactions and its weight lost from 1.88 to 13% (the average loss-weight rate: 0.595%/°C). And, it was indicated that the structure of copolymers chains was damaged, which would lead to following results: part of the formation of cyclized C=N and conjugated C=C hardly taken place in short time, amount of vacancies formed in chains, the molecular rearrangements progressed deficiently, and so on. These factors would make the final carbon fiber properties reduce.¹⁶ Thus, the rate of loss-weight reactions should be controlled.

From Figure 3, S1 had higher initial loss-weight temperature (>248°C) and loss-weight (at 390°C > 19%), which may be attributed to low concentration of comonomer. The loss-weight reactions of S1 were similar to those of PAN homopolymer, which was intense at higher temperature. And, it was also

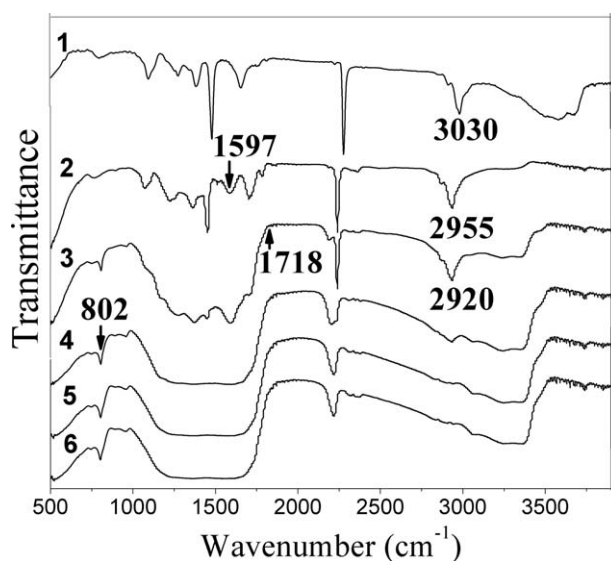


Figure 2 The FTIR spectra of S4 samples at different temperatures.

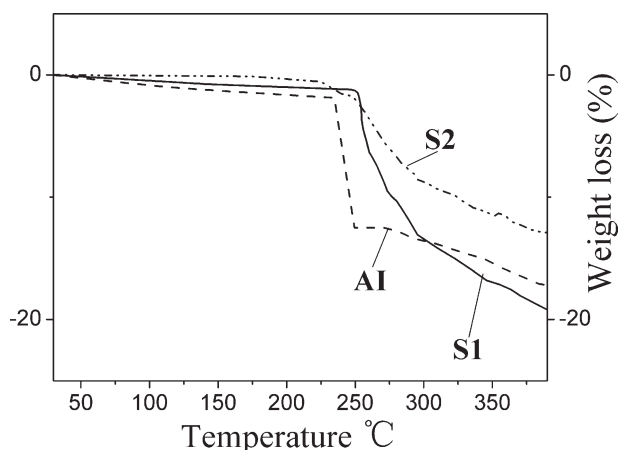


Figure 3 TGA curves of PAN copolymers.

found that the initial loss-weight temperature and loss-weight reaction of poly(AN-AIA) were lower than those of poly(AN-IA), at the same concentration of comonomer. Therefore, AIA was more suitable for comonomer of carbon fiber precursor.

Effect of ammonia on thermal behaviors of poly(AN-IA) copolymers

To study the effect of ammonia on thermal behaviors of poly(AN-IA) copolymers, the sample AI was treated by the methods described in section "treatment" and then determined by DSC. The DSC exotherms of samples are shown in Figure 4, and the parameters are given in Table IV. From Figure 4 and Table IV, the shapes of DSC exotherm were similar to those untreated. However, the T_i and ΔH of treated samples were decreased, and the changes were less prominent than those of poly(AN-AIA).

From Table IV, it was also found that AI1 obtained the lowest T_i , ΔH , which could be explained

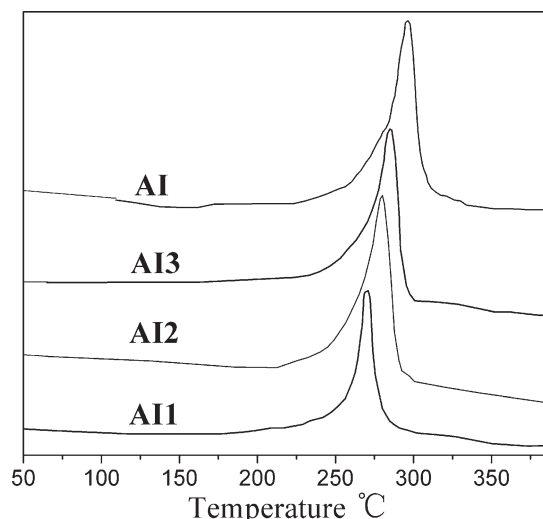


Figure 4 DSC curves of PAN copolymers.

TABLE IV
DSC Parameters of Poly(AN-IA) Treated by Ammonia

Samples	T_i (°C)	ΔT (°C)	$\Delta H/\Delta T$ (J g ⁻¹ °C ⁻¹)
AI	227.2	86.9	4.17
AI1	222.3	93.7	3.83
AI2	224.1	90.5	3.97
AI3	226.8	87.7	4.14

by FTIR data. According to FTIR, it was shown that there were only a few of NH_4^+ groups in AI1, which indicated that only a small amount of IA had reacted with ammonia. While there were hardly any NH_4^+ groups in AI3. And so, because of the low concentrations of NH_4^+ groups, the shapes of DSC exotherm had hardly any changes compared with that of PAN homopolymer.

Therefore, these three methods could improve the thermal behaviors of poly(AN-IA) copolymers. In the formation of carbon fibers, poly(AN-IA) copolymers treated by ammonia obtained rapid disruption of lateral order in morphology and produced a significant enhancement in the prestabilization rate.

CONCLUSIONS

To improve the performance of preoxidized fiber, AIA was used as the comonomer of PAN precursors. From DSC, TGA, and FTIR curves, it was found that the thermal characteristics of copolymers were highly influenced by AIA. The poly(AN-AIA) obtained lower T_i , ΔH , ΔT , E_a , loss-weight, and higher T_f , ΔT . There were four exothermal peaks in the DSC curves of poly(AN-AIA) copolymers, which

were attributed to the nitrile cyclization reactions. The reactions were initiated by the hydrogen ions in NH_4^+ , and it could be confirmed by FTIR spectra.

The effect of ammonia on degradation and prestabilization of poly(AN-IA) copolymers shows that ammonia can accelerate the prestabilization reactions of poly(AN-IA) copolymers, but different treatment methods had different effects on the copolymers.

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