

# Determination of Degradation Rate of Acrylonitrile Polymers

Chen Hou,<sup>1</sup> Rongjun Qu,<sup>1</sup> Wang Qun,<sup>1</sup> Liang Ying<sup>2</sup>

<sup>1</sup>College of Chemistry and Materials Science, Yantai Normal University, Yantai 264025, China

<sup>2</sup>Office of Science and Technology, Yantai Normal University, Yantai 264025, China

Received 11 December 2004; accepted 28 January 2005

DOI 10.1002/app.22290

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

**ABSTRACT:** Low-temperature degradations of acrylonitrile homopolymers and acrylonitrile/acrylamide copolymers in air were investigated by IR and thermogravimetry. The degradation rates of acrylonitrile polymers were determined by measurement of normalized absorbance of  $-\text{C}\equiv\text{N}$  band and effects of the degradation temperature, time, and comonomer on the rate of degradations were discussed. It was found that the polymers start to degrade as the temperature increased to 150°C. In the temperature range of 180–210°C, values of the rate of polymer degradation were maximal and the rate of degradation of acrylonitrile/acrylamide

copolymers was higher compared with that of acrylonitrile homopolymers. At 150°C, acrylonitrile homopolymers had an induction period of about 0.5 h. The rate of degradation of acrylonitrile/acrylamide copolymers showed an obvious trend of increase along with acrylamide concentration, and changes of the rate became less prominent as the weight ratio of acrylamide/acrylonitrile went beyond 5/95. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1511–1514, 2006

**Key words:** degradation; kinetics (polym.); copolymerization; acrylamide; homopolymers

## INTRODUCTION

Conversion of polyacrylonitrile fibers to good-quality carbon fibers requires an essential low-temperature thermal stabilization step before carbonization. Low-temperature degradations of acrylonitrile polymers have proved to be an interesting area of investigation.<sup>1,2</sup> A large number of patents and publications have thus been devoted mainly to a basic understanding of the exothermic behavior of polyacrylonitrile and several reaction mechanisms have been proposed.<sup>3–6</sup> In the studies published, the authors have presented the results obtained intermittently in nitrogen. It is very difficult to track instantaneously the small changes of polymer structure and property along with the minuscule changes of experimental conditions. There are a great many differences between experimental conditions and polyacrylonitrile precursor thermal stabilization. Selection of a suitable comonomer for synthesis of an acrylic polymer that satisfies the requirements for carbon fibers is an important step. The interaction of a few percent of

comonomers generally depresses the onset of cyclization temperature during oxidation. To our knowledge, there is almost no published report on acrylamide (AM) as a comonomer. The present study was thus undertaken to carry out degradation of acrylonitrile (AN) polymers performed in the same way as the process of polyacrylonitrile precursor thermal stabilization at low temperature, and to ascertain the influence of the degradation temperature and time on the rate of degradation of AN polymers. Studies have been further extended to ascertain the influence of AM on the degradation of AN/AM copolymers. In this study, aqueous suspension polymerization techniques were used to synthesize AN polymers. The results of IR and thermogravimetry (TG) of low-temperature degradation of acrylonitrile polymers in air are reported.

## EXPERIMENTAL

### Copolymerization

AN monomer was of industrial polymerization grade and distilled to remove inhibitors before use. AM was supplied as extrapure grade. Azobisisobutyronitrile (AIBN) was used as the initiator and recrystallized from ethanol before use. Polyvinyl alcohol (PVA) was used as the suspending agent. Deionized water was adopted as the polymerization media.

Required amounts of AN, AM, PVA, AIBN, and deionized water were placed in a glass flask, which

Correspondence to: C. Hou (sdchenhou@hotmail.com).

Contract grant sponsor: Youth Science Foundation, Department of Science and Technology, Shandong Province; contract grant number: 2005BS11010, Y2005F11.

Contract grant sponsor: Natural Science Foundation, Yantai Normal University, contract grant number: 042920, 032912, 20052901.

was continuously flushed with purified nitrogen. The flask was wholly immersed in a temperature-controlled water bath 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 60°C under vacuum until attaining a constant weight, and then weighed.

### Characterization

Viscosities of the copolymers were measured at 30°C in dimethylformamide (DMF) using a Ubbelohde viscometer, and the number-average molecular weights ( $M_n$ ) of the purified copolymers were calculated from the following equation:<sup>7</sup>  $[\eta] = 3.92 \times 10^{-4} M_n^{0.75}$ , where  $[\eta]$  is the intrinsic viscosity.

Elemental analysis of the copolymers was carried out using a PE 2400 elemental analyzer (Perkin-Elmer Cetus Instruments, Norwalk, CT) to determine the oxygen in these copolymers.

Nuclear magnetic resonance (NMR) measurements were carried out using a DPX300 spectrometer (Bruker, Rheinstetten, Germany) operating at 75 MHz. Analysis was made according to the manner of Inoue and the isotacticity discussed here is defined by three monomer units (triad tacticity).

IR spectra of the sample were recorded on a model 750 Magna-IR (Nicolet Instrument Technologies, Madison, WI) using the KBr-pellet method, covering the range 400–4000  $\text{cm}^{-1}$ . Thin films of AN polymers used for IR degradation studies were prepared by evaporation of a 3% dimethyl sulfoxide solution. The solvent was removed by stirring in water for several days and subsequently dried under high vacuum. The films were then transferred to KBr discs and placed in a specially designed cell contained in the spectrometer that allows continuous monitoring at elevated temperatures in air. Particular care was made to ensure that temperature control of degradation of AN polymers was performed in the same way as the process of polyacrylonitrile precursor thermal stabilization. To ensure the accuracy of IR signals of AN polymers, the degradation was observed for 5 min to reach the steady state.

TG curves of AN polymers were recorded on DT 40 thermal analyzer (Shimadzu, Kyoto, Japan) in air and the heating rate was the same as that of precursor thermal stabilization. To ensure the weight loss of polymers could reach steady state, the degradation was observed for 5 min.

## RESULTS AND DISCUSSION

### Synthesis of polymers

AN homopolymers (PAN) and AN/AM copolymers [poly(AN-AM)] were prepared by aqueous suspen-

TABLE I  
Important Parameters of Polymerization<sup>a</sup>

AN/AM (w/w)	$M_n \times 10^{-4}$	Oxygen concentration in copolymer (wt %)	AM concentration in copolymer (wt %)	Triad isotacticity
100/0	43.2	0	0	0.375
98/2	40.8	0.45	1.99	0.346
97/3	39.9	0.67	2.97	0.329
95/5	41.4	1.12	4.97	0.311
92/8	36.7	1.78	7.90	0.299
90/10	37.9	2.25	9.98	0.275

<sup>a</sup> Conditions:  $C_{\text{AN}} = 4.15 \text{ mol/L}$ ,  $C_{\text{AIBN}} = 0.008 \text{ mol/L}$ ,  $C_{\text{PVA}} = 0.22 \text{ g/L}$ ,  $T = 60^\circ\text{C}$ ,  $t = 50 \text{ min}$ .

sion polymerization. Some important parameters and polymerization conditions of the polymers are listed in Table I, which shows that pure AN polymers can be synthesized by this technique. The composition of [poly(AN-AM)] was determined from the oxygen concentration in the copolymer.

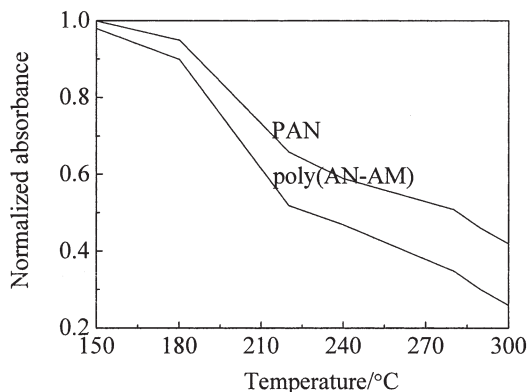
### Determination of the rate of polymer degradation

IR spectra of AN polymers were previously studied and analyzed by several workers.<sup>8,9</sup> The typical spectrum of polymers shows a characteristic peak, at 2400  $\text{cm}^{-1}$ , attributed to  $-\text{C}\equiv\text{N}$  band-stretching frequency. The spectral features observed upon the thermal degradation of AN polymers were previously described in detail.<sup>10,11</sup> A brief description of the essential points relevant to this current study are presented. When AN polymers are heated in air, the peak at 2400  $\text{cm}^{-1}$  starts to decrease as a result of initiation of the cyclization reaction. As the degradation reaction proceeds, there is a continuous reduction in the absolute intensities of  $-\text{C}\equiv\text{N}$  band at 2400  $\text{cm}^{-1}$ . By measuring the absorbance of this band as a function of time at the degradation temperature, the fraction of AN units that have reacted can be estimated. Measurements of the relative absorbance of  $-\text{C}\equiv\text{N}$  band at 2400  $\text{cm}^{-1}$  as a function of degradation time are revealing. To compare the relative rate of degradation of AN polymers, normalized absorbance of  $-\text{C}\equiv\text{N}$  band at 2400  $\text{cm}^{-1}$  as a function of time was used in this study. Normalized absorbance is readily obtained for AN polymers from measurement of the peak height or area of this band.

The weightlessness ratio of AN polymers as a function of degradation time from TG results of the degradation of AN polymers in air was used to estimate the rate of degradation.

### Effect of degradation temperature on the rate of degradation

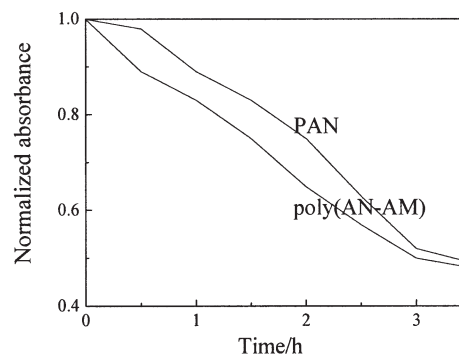
Effects of degradation temperature on the rate of degradation of PAN and [poly(AN-AM)] were discussed



**Figure 1** Graph of normalized absorbance of  $-C\equiv N$  band against degradation temperature.

when the weight ratio of AN/AM was controlled at 98/2. To ensure the accuracy of IR signals of AN polymers, the degradation was observed for 5 min to reach the steady state. Figure 1 shows the normalized absorbance of  $-C\equiv N$  band as a function of temperature. It is evident from Figure 1 that the normalized absorbance of  $-C\equiv N$  band of polymers starts to decrease when polymers are heated above  $150^{\circ}\text{C}$  and normalized absorbance of  $-C\equiv N$  band substantially decreased in the temperature range of  $180\text{--}210^{\circ}\text{C}$ , which means that values of the rate of polymer degradation are maximal and the rate of degradation of [poly(AN-AM)] is higher than that of PAN. It is reported that the cyclization reaction of AN polymers in air is initiated in the amorphous parts of the polymers because of ease of diffusion of oxygen into the less dense amorphous phase compared to the more dense crystalline phase and then spread to the crystalline component.<sup>12</sup> For [poly(AN-AM)], the cyclization reaction can be initiated by an ionic mechanism of comonomers at a lower temperature because of the reaction of exocyclic imine group contained in the comonomer with oxygen.<sup>13</sup> Initiation by AM units of cyclization reaction of adjacent AN units is a relatively rapid reaction, as is the propagation of the cyclization of subsequent AN units down the chain, so the rate of degradation is high.

Comparison of the weight loss ratio of the polymers in Table II shows that the thermal stability of PAN is much better than that of [poly(AN-AM)]. With respect to weight loss, the rate of [poly(AN-AM)] shows a



**Figure 2** Graph of normalized absorbance of  $-C\equiv N$  band against degradation time at  $150^{\circ}\text{C}$ .

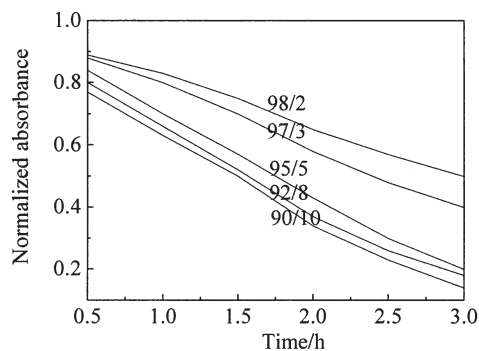
significant increase compared with that of PAN in the temperature range of  $180\text{--}220^{\circ}\text{C}$ , which confirms the theory that the normalized absorbance of  $-C\equiv N$  band at  $2400\text{ cm}^{-1}$  can be used to determine the rate of degradation of AN polymers. The initial weight loss below  $100^{\circ}\text{C}$  may have resulted from the small amount of moisture absorbed during the sample preparation and also from the interaction between functional groups on the polymer surface and oxygen.

#### Effect of degradation time on the rate of degradation

Effects of degradation time on the rate of degradation of PAN and [poly(AN-AM)] were discussed by varying degradation time from 0 to 3.5 h when the weight ratio of AN/AM was controlled at 98/2 while keeping the degradation temperature at  $150^{\circ}\text{C}$ . Figure 2 shows a graph of the normalized absorbance of  $-C\equiv N$  band at  $2400\text{ cm}^{-1}$  as a function of degradation time. It is apparent that, in the case of [poly(AN-AM)], the initiation of the degradation reaction occurs almost immediately. Conversely, the degradation reaction for PAN appears to require an induction period of about 0.5 h, after which the degradation reaction propagates at a faster rate and is more extensive at times, exceeding that of PAN by 2 h. This implies that initiation of the degradation of [poly(AN-AM)] occurs more rapidly, although this is offset by a more rapid degradation of PAN upon initiation. This can be explained on the basis of the two different mechanisms suggested for these two copolymers.<sup>14</sup> Propagation of the cy-

**TABLE II**  
Relationship Between the Ratio of Weight Loss and Temperature

Sample	Weight loss ratio (%)						
	$90^{\circ}\text{C}$	$180^{\circ}\text{C}$	$200^{\circ}\text{C}$	$220^{\circ}\text{C}$	$240^{\circ}\text{C}$	$280^{\circ}\text{C}$	$320^{\circ}\text{C}$
PAN	0.94	5.8	15.7	22.7	24.5	28.8	31.8
Poly(AN-AM)	1.05	9.9	19.4	27.8	29.1	34.2	40.2



**Figure 3** Effect of the weight ratio of AN/AM on normalized absorbance of  $-\text{C}\equiv\text{N}$  band at  $150^\circ\text{C}$ .

clization reaction may occur on either side of the AM unit in [poly(AN-AM)] from the exocyclic imine and hydroxyl groups formed at the degradation temperature. In contrast, for PAN, propagation can occur only after diffusion of oxygen into the less dense amorphous phase.

#### Effect of AM concentration on rate of degradation

The effect of AM concentration on the rate of degradation of [poly(AN-AM)] was also studied while keeping the degradation temperature at  $150^\circ\text{C}$ . Different [poly(AN-AM)] samples were synthesized by using the aqueous suspension polymerization technique, which is given in Table I. It is clear from Figure 3 that the rate of degradation shows an obvious trend of increase along with acrylamide concentration, and changes of the rate become less prominent as the weight ratio of AM/AN is  $>5$  wt %, which show a few disagreements with the values of reported.<sup>15</sup> There are a number of factors that appear to limit the extent of cyclization reaction of AN units, the most important of which are tacticity, sequence distribution, stereochemistry of AN and AM units in the copolymer chain, and spatial considerations. AM is directly involved in the initial cyclization of AN units at relatively low temperature. When the weight ratio of AM/AN goes be-

yond 5/95, the extent of isotacticity of AN units in [poly(AN-AM)] is affected and begins to decrease (Table I). The changes of the rate of [poly(AN-AM)] then become correspondingly less.

#### CONCLUSIONS

Laboratory studies of degradation of acrylonitrile homopolymers and acrylonitrile/acrylamide copolymers in air have shown that polymers start to degrade as the temperature increases to  $150^\circ\text{C}$ . The theory that the normalized absorbance of  $-\text{C}\equiv\text{N}$  band at  $2400\text{ cm}^{-1}$  as a function of time can be used to determine the rate of AN polymers has been confirmed. In the temperature range of  $180$ – $210^\circ\text{C}$ , values of the rate of polymer degradation are maximal. Acrylonitrile homopolymers have an induction period of about 0.5 h at  $150^\circ\text{C}$ . The rate of degradation shows an obvious trend of increase along with acrylamide concentration, and changes of the rate become less prominent as the weight ratio of AM/AN goes beyond 5/95.

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