

Determination of the Degradation Apparent Activation Energy of Acrylonitrile/Acrylic Acid Copolymers

Chen Hou,¹ Junshen Liu,¹ Chunnuan Ji,¹ Chengguo Wang²

¹College of Chemistry and Materials Science, Yantai Normal University, Yantai 264025, People's Republic of China

²College of Materials Science and Engineering, Shandong University, Jinan 250061, People's Republic of China

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ABSTRACT: Acrylonitrile/acrylic acid copolymers were prepared by H₂O/dimethyl formamide suspension polymerization technique. Differential scanning calorimetry was used to investigate the degradation of acrylonitrile/acrylic acid copolymers in air. The apparent activation energy of degradation of the copolymer was calculated with the Kissinger method. Effects of copolymerization conditions on the apparent activation energy of copolymer were studied. It has been found that increasing the dimethyl formamide concentration in the solvent mixture led to a gradual in-

crease (97.3–149.4 kJ mol⁻¹) in the apparent activation energy of degradation of the acrylonitrile/acrylic acid copolymers. The apparent activation energy decreases with increase in acrylic acid concentration, and this change became less prominent as the acrylic acid/acrylonitrile weight ratio is more than 5/95. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4668–4671, 2006

Key words: degradation; kinetics; apparent activation energy

INTRODUCTION

Carbon fibers from acrylonitrile polymers are usually prepared through the following three steps: (a) stretching to get raw oriented acrylic fibers, (b) stabilization in air at moderately high temperatures between 200 and 300°C, and (c) finally, carbonization of the stabilized fibers between 900 and 1500°C.¹ To increase the industrial productivity of carbon fibers, the optimization of the thermal treatment, especially during the step (b), is critical. The selection of a suitable comonomer for synthesis of the acrylic polymer satisfying the requirements for acrylic precursors is an important step. Interaction of a few percent of comonomers generally enhances the spinnability and depresses the onset of cyclization temperature during the thermal stabilization process of carbon fibers. Low temperature degradation of acrylic copolymer is an interesting area,^{2,3} and several reaction mechanisms have been proposed.^{4–6} In the published studies, the authors have presented the results obtained intermittently in nitrogen. It is very difficult to track instantaneously the small changes in the polymer structure

and properties along with the small changes in the experimental conditions.⁷ There are many differences between the experimental conditions and polyacrylonitrile precursor thermal stabilization.⁸ To our knowledge, there is almost no report on acrylic acid (AA) as a comonomer. In this study, different suspension polymerization techniques were used to synthesize acrylonitrile (AN)/AA copolymer. The results of differential scanning calorimetry (DSC) of the degradation of AN/AA copolymers performed in the same way as the process of polyacrylonitrile precursor thermal stabilization are reported. The apparent activation energy of degradation (ΔE_a) of AN/AA copolymers was determined with the Kissinger method.⁹ Effects of different copolymerization conditions on the apparent activation energy of AN/AA copolymers were examined in contrast and thus the degradation information obtained in this study in turn can be used to elucidate the optimum copolymerization conditions of AN/AA copolymers.

EXPERIMENTAL

Materials

Monomer AN was of industrial polymerization-grade, which was distilled to remove inhibitors before use. Comonomer AA was supplied as extra pure grade by Tianjin Chemical Resin Industry (Tianjin, China). Azobisisobutyronitrile (AIBN) was used as the initiator, and was recrystallized from ethanol before use. Polyvinyl alcohol (PVA) was used as the suspending

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

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TABLE I
Effects of Solvent Mixture on Copolymerization System

H ₂ O/DMF (w/w)	AN/AA (W/W)	M_n (10^{-4})	Oxygen concentration in the copolymer (wt %)	AA concentration in the copolymer (wt %)
100/0		46.7	0.809	1.82
90/10		40.3	0.818	1.84
80/20		36.5	0.831	1.87
60/40		32.6	0.822	1.85
50/50	98/2	28.7	0.840	1.89
40/60		25.6	0.858	1.93
20/80		20.2	0.849	1.91
10/90		14.5	0.871	1.96
0/100		10.2	0.884	1.99

Conditions: concentration of AN = 4.5 mol/L; concentration of AIBN = 0.008 mol/L; concentration of PVA = 0.22 g/L; temperature = 60 °C; time = 20 min.

agent. Deionized water and dimethyl formamide (DMF) supplied as extra pure grade by Shanghai Chemical Resin Industry (Shanghai, China) were adopted as the polymerization media.

Copolymerization

Required amounts of AN, AA, PVA, AIBN, deionized water, and DMF were placed in a glass flask, which 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 *in vacuo* until constant weight, and then weighed.

Characterization

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

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

where η is the intrinsic viscosity.

Elemental analysis of the copolymers was carried out using a Vario EL III elemental analyzer (German) to determine their oxygen concentrations.

The triad tacticities [(*mm*), (*mr*), (*rr*); *m* and *r* mean *meso* and *racemo* diad sequences, respectively] of AN/AM copolymers were determined, on the basis of the Schaefer's assignment¹¹, from the ratio of intensities for the three nitrile carbon peaks in the ¹³C NMR spectra. ¹³C NMR spectra were recorded on a Bruker-DPX300 spectrometer (Germany) in 2.5 wt % solution in deuterated dimethylsulfoxide (DMSO-*d*₆) at 80 °C under the following operating conditions: complete

decoupling mode—pulse delay time, 1.745 s; acquisition time, 0.655 s; pulse width, 5.5 μs (45° pulse); accumulation—more than 3000 times.

DSC curves of AN/AA copolymer were recorded on DSC 204 F1 Phoenix thermal analyzer (German) in air. Particular care was taken to ensure that the heating rate was the same as that of the precursor thermal stabilization process used in the production of carbon fibers. The apparent activation energy of degradation of the copolymers was calculated with the Kissinger method

$$-\frac{\Delta E_a}{R} = \frac{d \ln\left(\frac{F}{T_m^2}\right)}{d\left(\frac{1}{T_m}\right)} \quad (2)$$

where ΔE_a is the apparent activation energy of degradation, F is the heating rate, T_m is the highest temperature of exothermic peak, and R is the gas constant. ΔE_a was determined from the slope of a linear plot of $\ln\left(\frac{F}{T_m^2}\right)$ versus $\frac{1}{T_m}$.

TABLE II
DSC Parameters of AN/AA Copolymer Synthesized by the Aqueous Suspension Technique

φ (k min ⁻¹)	T_m (K)	$\ln\left(\frac{\varphi}{T_m^2}\right)$	$10^3 \times \frac{1}{T_m}$ (K ⁻¹)
5	528	-10.929	1.8940
10	544	-10.295	1.8382
15	553	-9.923	1.8083
20	560	-9.660	1.7857

Conditions: concentration of AN = 4.5 mol/L; [AN]/[AA] = 98.2 (w/w); concentration of AIBN = 0.008 mol/L; concentration of PVA = 0.22 g/L; temperature = 60 °C; time = 20 min.

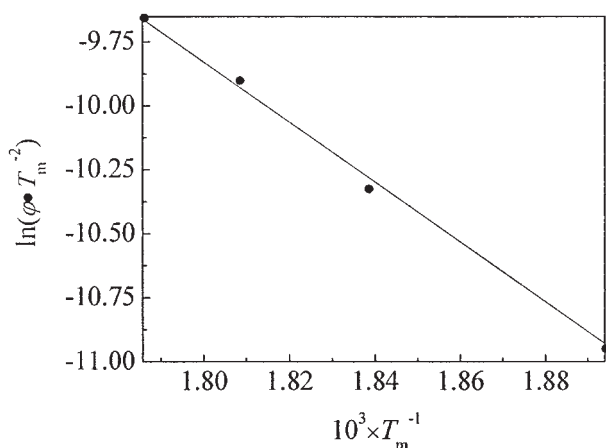


Figure 1 Plot of $\ln\left(\frac{\phi}{T_m^2}\right)$ versus $\frac{1}{T_m}$

RESULTS AND DISCUSSION

Effect of solvent mixture on copolymerization

H₂O/DMF suspension polymerization technique was used to synthesize AN/AA copolymers. Effects of reaction media on copolymerization were shown in Table I. The pure AN/AA copolymers were synthesized with this technique. The composition of AN/AA copolymer was determined from the oxygen concentration in the copolymer. The molecular weights of the copolymers decreased with an increase in the DMF concentration in the reaction media and the oxygen concentration in the copolymer increases with an increase in DMF content in the copolymerization reaction media, which was due to the high chain transfer coefficient of DMF (2.8×10^{-4} at 50°C)¹² and the greater solubility of Nathan than that of AN in DMF.

ΔE_a of the copolymer synthesized by the aqueous suspension technique

Table II shows some important DSC parameters and polymerization conditions. ΔE_a , calculated from a linear plot, was 97.3 kJ mol⁻¹ (Fig. 1) and served as a criterion for judging other results.

Effect of solvent mixture on ΔE_a of the copolymers

ΔE_a of AN/AA copolymers prepared by H₂O/DMF suspension polymerization technique was also calculated with the Kissinger method. The experimental results are given in Table III. ΔE_a of the copolymer synthesized in a DMF solution, which was the largest, was 146.5 kJ mol⁻¹. With an increase in the DMF concentration in the reaction media, ΔE_a rose rapidly. ΔE_a was determined by the energy needed to initiate the intramolecular cyclization of AN/AA copolymer.¹³ There were a number of factors that appeared

to limit the extent of cyclization reaction of AN units, the most important of which were tacticity, sequence distribution, stereochemistry of AN and AA units in the copolymer chain, and special considerations.¹⁴ The initiation by AA units of cyclization reaction of adjacent isotactic AN units was a relatively rapid reaction, as was the propagation of the cyclization of subsequent isotactic AN units down the chain, and so the value of ΔE_a was small.¹⁵ From the point of view of oxidative stabilization, solvent water suspension polymerization technique was substantially effective in lowering the onset of exotherm, in comparison with solution polymerization.

When AN/AA copolymer was synthesized with the solvent water suspension technique, oligomeric radicals may have formed in the initial stages of polymerization, precipitated out after a certain critical molecular weight was attained, and then acted as primary particles. Propagation then occurred either in the water phase, in the DMF phase, in the oligomeric radical phase, or at the DMF–water–oligomer mixture interface, depending on the solubility of monomers.^{16,17} In water-rich reaction media (H₂O/DMF > 80/20), because of the insolubility oligomeric radicals, propagation followed the suspension polymerization technique more. A two-locus polymerization mechanism was assumed (i.e., water phase and oligomeric radicals phase). Propagation then mostly occurred in the oligomeric radicals phase. AN units were more easily absorbed by polymer radicals than by AA units. The value of ΔE_a was small. In DMF-rich reaction media (DMF/H₂O > 60/40), copolymerization followed the solution polymerization technique more. The extent of chain transfer reaction grew. The value of the high chain transfer coefficient of DMF was 2.8×10^{-4} at 50°C.¹² The solubility of AA was greater than that of AN in DMF. The impacting opportunities between AA units and polymer radicals rose, and this led to a random array of AA units in the copolymer chain. The

TABLE III
 ΔE_a of Copolymer Synthesized in H₂O/DMF Solvent Mixture

H ₂ O/DMF (w/w)	Triad isotacticity	ΔE_a (kJ mol ⁻¹)
100/0	0.357	97.3
90/10	0.347	102.6
80/20	0.333	108.2
60/40	0.311	114.1
50/50	0.293	119.9
40/60	0.287	127.3
20/80	0.279	134.4
10/90	0.259	139.2
0/100	0.241	146.5

Conditions: concentration of AN = 4.5 mol/L; [AN]/[AA] = 198/2 (w/w); concentration of AIBN = 0.008 mol/L; concentration of PVA = 0.22 g/L; temperature 60°C; time = 20 min.

TABLE IV
Effect of Monomer Ratio on ΔE_a of Degradation

AN/AA (w/w)	Triad isotacticity	ΔE_a (kJ mol ⁻¹)
100/0	0.375	132.5
99/1	0.361	118.6
98/2	0.357	97.3
95/5	0.342	91.2
94/6	0.321	87.8
93/7	0.299	88.3
92/8	0.279	87.8
90/10	0.256	87.4

Conditions: concentration of AN = 4.5 mol/L; H₂O/DMF = 100/0 (w/w); concentration of AIBN = 0.008 mol/L; concentration of PVA = 0.22 g/L; temperature = 60°C; time = 20 min.

extent of isotacticity of AN units in the copolymers decreased (Table III). The molecular weights of the copolymers decreased with an increase in the DMF concentration in the reaction media, but the extent of isotacticity of AN units in the copolymers decreased more prominent, thus ΔE_a rose with an increase in the DMF concentration.

Effect of AA concentration on ΔE_a of the copolymers

To study the effect of AA on ΔE_a , AN/AA copolymers of different monomer ratios were synthesized, which was given in Table IV. ΔE_a decreased quickly as AA concentration rose; when the weight ratio was greater than 5/95, the changes in ΔE_a became less prominent. This can be explained on the different mechanisms suggested for these copolymers. AA was directly involved in the initial cyclization of AN units at a relatively low temperature. The propagation of the cyclization reaction may have occurred either on the side of hydroxyl groups formed at the degradation temperature or on the side of imino groups formed by the water absorbability of AA units.¹⁸ When the weight ratio of AA/AN is more than 5/95, the extent of isotacticity of AN units in the copolymers was affected and began to decrease (Table IV). The changes of the apparent activation energy then became correspondingly less. The degraded copolymers became increasingly colored as the AA concentration increased. The

extent of precursors thermal stabilization was affected by AA concentration.

CONCLUSIONS

Laboratory studies of degradation of AN/AA copolymer in air showed that the apparent activation energy of degradation increased rapidly with an increase in the DMF concentration in DMF/H₂O mixture solutions. AA comonomer could directly initiate and accelerate the intramolecular cyclization, and the apparent activation energy of degradation then decreased quickly as the AA concentration rose. When the weight ratio of AA/AN was greater than 5/95, the changes of the apparent activation energy of degradation became less prominent. Furthermore the idea that the extent of tacticity of AN units in copolymer chain played a major role in limiting the size of the apparent activation energy of degradation was confirmed.

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