Degradation of Acrylonitrile–Ammonium Itaconate Copolymers

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ABSTRACT: Acrylonitrile–ammonium itaconate copolymers were prepared by H_2O/dimethyl formamide suspension polymerization technique. Differential scanning calorimetry results of the degradation of acrylonitrile–ammonium itaconate copolymers in air are presented. The apparent activation energy of degradation of the copolymer was calculated using the Kissinger method. Effects of copolymerization conditions on the apparent activation energy of copolymer were studied. Increasing the dimethyl formamide concentration in the solvent mixture leads to a rapid increase in the degradation apparent activation energy of acrylonitrile–ammonium itaconate copolymer. The value of the degradation apparent activation energy of the copolymer synthesized in dimethyl formamide solvent increases up to 168.3 kJ mol^{-1}. The apparent activation energy decreases quickly along with an increase in ammonium itaconate concentration, and this change becomes less prominent as the weight ratio of ammonium itaconate/acrylonitrile goes beyond 6/94, $\Delta E_a = 89.4 \pm 2.0$ kJ mol^{-1}. The apparent activation energy shows a trend of increase with increasing copolymerization temperature. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1708–1711, 2005

Key words: degradation; kinetics; apparent activation energy

INTRODUCTION

Carbon fibers from acrylonitrile polymers are ordinarily 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) final 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 step (b) is critical. 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 has been an interesting area,[2,3] and several reaction mechanisms have been proposed.[4–6] In the studies published, 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 tiny changes of

experimental condition. There are many differences between the experimental conditions and polyacrylonitrile precursor thermal stabilization. To our knowledge, there is almost no report on itaconate as a comonomer. In this study, different suspension polymerization techniques were used to synthesize acrylonitrile (AN)–ammonium itaconate (AIA) copolymer. The results of differential scanning calorimetry (DSC) study of the degradation of AN–AIA copolymers performed in the same way as the process of polyacrylonitrile precursor thermal stabilization are reported. The apparent activation energy of degradation of AN–AIA copolymers was determined by the Kissinger method.[7] Effects of different copolymerization conditions on the apparent activation energy of AN–AIA copolymers were discussed in contrast and thus the degradation information obtained in this study in turn can be used to elucidate the optimum copolymerization conditions of AN–AIA copolymers.

EXPERIMENTAL

Copolymerization

Monomer AN was of industrial polymerization grade and distilled to remove inhibitors before use. Copolymer AIA was obtained by neutralization of itaconic acid supplied as extrapure grade by Tianjin Chemical Resin Industry (Tianjin, China) and NH3. Azobi-

TABLE I
Effects of Solvent Mixture on Copolymerization System

H$_2$O/DMF/(w/w)	AN-AIA/(w/w)	$M_n \times 10^{-4}$	Oxygen concentration in copolymer/wt%	AIA concentration in copolymer/wt%
100/0		41.3	0.696	1.79
90/10		35.4	0.706	1.81
80/20		30.9	0.714	1.83
60/40		23.2	0.718	1.84
50/50	98/2	21.7	0.734	1.88
40/60		22.1	0.730	1.87
20/80		19.2	0.753	1.93
10/90		16.8	0.757	1.94
0/100		11.4	0.773	1.98

Note. Condition: C_{AN} = 4.15 mol/L, C_{AIBN} = 0.008 mol/L, C_{PVA} = 0.22 g/L, T = 60 °C, t = 20 min.

sisobutyronitrile (AIBN) was used as the initiator and recrystallized from ethanol before use. Polyvinyl alcohol (PVA) was used as the suspending agent. Deionized water and dimethyl formamide (DMF) supplied as extrapure grade by Shanghai Chemical Resin Industry (Shanghai, China) were adopted as the polymerization media.

Required amounts of AN, AIA, 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 vacuum until constant weight, and then weighed.

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),[8]

$$[\eta] = 3.92 \times 10^{-4} M_n^{0.75}, \tag{1}$$

where η is the intrinsic viscosity.

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

Nuclear magnetic resonance measurements were carried out using a Bruker-DPX300 spectrometer (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).

DSC curves of AN–AM copolymer were recorded on DSC 204 F1 Phoenix thermal analyzer 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 carbon fiber production. The apparent activation energy of degradation of the copolymers was calculated by the Kissinger method[7] from eq. (2),

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

where ΔE_a is the apparent activation energy of degradation, ϕ is the rate of temperature rising, 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 $\ln\left(\frac{\phi}{T_m^2}\right)$ vs. $\frac{1}{T_m}$.

RESULTS AND DISCUSSION

Effect of solvent mixture on copolymerization

H$_2$O/DMF suspension polymerization technique was used to synthesize AN–AIA copolymers. Effects of reaction medium on copolymerization are shown in Table I. Table I shows that pure AN–AIA copolymer can be synthesized by this technique. The molecular weights of copolymers decrease with an increase in the DMF concentration in the reaction medium. The composition of AN–AIA copolymer was determined from the oxygen concentration in the copolymer. The oxygen concentration in the copolymer increases with an increase of DMF content in the copolymerization reaction medium.

Apparent activation energy of degradation of copolymer synthesized by the aqueous suspension technique

Aqueous suspension polymerization technique was used to synthesize AN–AIA copolymer. Table II

$\phi/k \cdot min^{-1}$	T_m/K	$\ln\left(\dfrac{\phi}{T_m^2}\right)$	$10^3 \times \dfrac{1}{T_m}/K^{-1}$
5	530	−10.936	1.8868
10	545	−10.299	1.8349
15	554	−9.926	1.8051
20	561	−9.664	1.7825

Note. Condition: $C_{AN} = 4.15$ mol/L; [AN]/[AIA] = 98/2(w/w); H_2O/DMF(w/w) = 100/0; $C_{AIBN} = 0.008$ mol/L; $C_{PVA} = 0.22$ g/L; $T = 60$ °C; $t = 20$ min.

shows some important DSC parameters and polymerization conditions. The value of apparent activation energy of degradation, calculated from linear plot is 101.4 kJ mol^{-1} (Fig. 1), which is a criterion to judge other results.

Effect of solvent mixture on apparent activation energy of degradation of copolymer

ΔE_a of AN–AIA copolymers prepared by H_2O/DMF suspension polymerization technique was also calculated by the Kissinger method. The experimental results are given in Table III. The value of ΔE_a of copolymer synthesized in DMF solution, which is the largest, is 168.3 kJ mol^{-1}. With an increase of DMF concentration in the reaction medium, the apparent activation energy of degradation rises rapidly. The degradation apparent activation energy is determined by the energy needed to initiate intramolecular cyclization of AN–AIA copolymer.[9] 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 AIA units in the copolymer chain, and spatial considerations.[10] Initiation by AIA units of cyclization
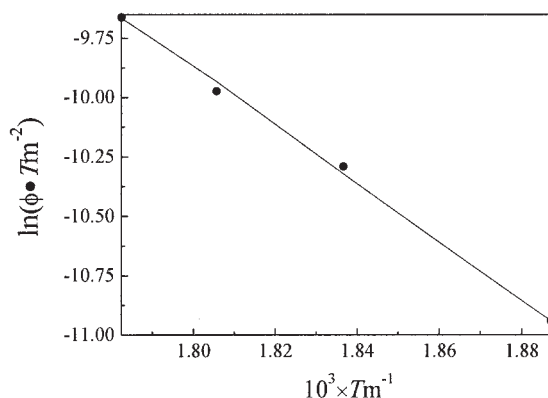

Figure 1 Plot of $\ln\left(\dfrac{\phi}{T_m^2}\right)$ vs. $\dfrac{1}{T_m}$.

H_2O/DMF(w/w)	Triad isotacticity	ΔE_a/kJ $\cdot$ mol^{-1}
100/0	0.359	101.4
90/10	0.345	105.6
80/20	0.331	112.2
60/40	0.307	123.1
50/50	0.294	128.9
40/60	0.285	138.3
20/80	0.276	151.4
10/90	0.256	158.2
0/100	0.247	168.3

Note. Condition: $C_{AN} = 4.15$ mol/L; [AN]/[AIA] = 98/2(w/w); $C_{AIBN} = 0.008$ mol/L; $C_{PVA} = 0.22$ g/L; $T = 60$ °C; $t = 20$ min.

reaction of adjacent isotatic AN units is a relatively rapid reaction, as is the propagation of the cyclization of subsequent isotatic AN units down the chain, so the value of ΔE_a is small.[11] From the point of view of oxidative stabilization, solvent water suspension polymerization technique is substantially effective in lowering the onset of exotherm compared to solution polymerization. Precursors prepared by solvent water suspension polymerization technique show better mechanical properties.

When AN–AIA copolymer is synthesized by solvent water suspension technique, oligomeric radicals may be formed in the initial stages of polymerization, which precipitate out after a certain critical molecular weight is attained and then act as primary particles. Propagation would then occur in the water phase, the DMF phase, the oligomeric radicals phase, or at the interface of DMF–water–oligomer mixture depending on the solubility of monomers.[12,13] In water-rich reaction medium (H_2O/DMF > 80/20), because of the insolubility oligomeric radicals, propagation follows more of the suspension polymerization technique. A two-loci polymerization mechanism is assumed, i.e., water phase and oligomeric radicals phase. Propagation would then mostly occur in oligomeric radicals phase. AN units are more easily absorbed by polymer radicals than AIA units. The value of ΔE_a is small. In DMF-rich reaction medium (H_2O/DMF < 80/20), copolymerization follows more that of the solution polymerization technique. The extent of chain transfer reaction is growing. The value of the high chain transfer coefficient of DMF is 2.8×10^{-4} at 50 °C.[14] Solubility of AIA is greater than AN in DMF. The impacting opportunities between AIA units and polymer radicals are rising, which leads to the random array of AIA units in the copolymer chain. The extent of isotacticity of AN units in copolymer decreases (Table III), so ΔE_a rises with an increase of DMF concentration.

Effect of AIA concentration on apparent activation energy of degradation of copolymer

To study effect of AIA on ΔE_a, AN–AIA copolymers of different monomer ratios were synthesized, which is given in Table IV. It is clear from the table that ΔE_a reduces quickly with rising AIA concentration; when the weight ratio is more than 6/94, changes of ΔE_a become less prominent. This can be explained on the basis of different mechanisms suggested for these copolymers. AIA is directly involved in the initial cyclization of AN units at relatively low temperature. Propagation of cyclization reaction may occur either on the side of hydroxyl groups formed at the degradation temperature or the side of imino groups formed by the water absorbability of AIA units.[15] When the weight ratio of AIA/AN is more than 6/94, the extent of isotacticity of AN units in copolymer is affected and begins to decrease (Table IV). The changes of the apparent activation energy then become correspondingly less. The degraded copolymers become increasing colored as AIA concentration increases at the same time. The extent of precursors thermal stabilization is affected by AIA concentration.

Effect of temperature on apparent activation energy of degradation of copolymer

Effect of temperature on the apparent activation energy of degradation of AN–AIA copolymer was also studied. AN–AIA copolymer was synthesized using the aqueous suspension polymerization technique. According to the results summarized in Table V, values of ΔE_a increase gradually with an increase of temperature. The extent of chain transfer reaction increases and the impacting opportunities between AIA units and polymer radicals are also rising. Polymer-

TABLE IV
Effect of Monomer Ratio on ΔE_a of Degradation

AIA/AN/(w/w)	Triad isotacticity	ΔE_a/kJ · mol^{-1}
0/100	0.388	127.6
1/99	0.375	114.5
2/98	0.359	101.4
5/95	0.332	97.7
6/94	0.301	89.4
7/93	0.284	88.1
8/92	0.265	91.3
10/90	0.226	87.4

Note. Condition: C_{AN} = 4.15 mol/L; H$_2$O/DMF(w/w) = 100/0; C_{AIBN} = 0.008 mol/L; C_{PVA} = 0.22 g/L; T = 60 °C; t = 20 min.

TABLE V
Effect of Copolymerization Temperature on ΔE_a of Degradation

T/°C	ΔE_a/kJ · mol^{-1}	T/°C	ΔE_a/kJ · mol^{-1}
55	82.8	63	120.3
58	92.1	65	130.8
60	101.4	70	149.4

Note. Condition: C_{AN} = 4.15 mol/L; [AN]/[AIA] = 98/2(w/w); H$_2$O/DMF(w/w) = 100/0; C_{AIBN} = 0.008 mol/L; C_{PVA} = 0.22 g/L; t = 20 min.

ization becomes violent and dangerous at polymerization temperature above 65 °C. AN–AIA copolymers are usually synthesized at about 60 °C.

CONCLUSIONS

Laboratory studies of degradation of acrylonitrile–ammonium itaconate copolymer in air have shown that the apparent activation energy of degradation increases rapidly with an increase of DMF concentration in DMF–water mixture solution. AIA comonomer can directly initiate and accelerate intramolecular cyclization, the apparent activation energy of degradation, and then reduces quickly with rising AIA concentration, when the weight ratio of AIA/AN is higher than 6/94, the changes of the apparent activation energy of degradation become less prominent. Furthermore, the theory that the extent of tacticity of AN units in copolymer chain plays a major role in limiting the size of the apparent activation energy of degradation has been confirmed.

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