

Degradation kinetics of Acrylonitrile/Ammonium Acrylate Copolymers

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ABSTRACT: acrylonitrile (AN)/ammonium acrylate (AAT) copolymers were prepared by H₂O/dimethyl formamide suspension polymerization technique. Differential scanning calorimetry results of the degradation of AN/AAT copolymers in air are presented. The apparent activation energy of degradation of the copolymer was calculated by using Kissinger method. Effects of copolymerization conditions on the apparent activation energy of copolymer were studied. It has been found that increasing dimethyl formamide concentration in the solvent mixture leads to a rapid increase in the degradation apparent activation energy of AN/AAT copolymer. The value of the degradation apparent activation

energy of the copolymer synthesized in dimethyl formamide solvent increases up to 141.7 kJ mol⁻¹. The apparent activation energy decreases quickly, along with increase in AAT concentration, and this change becomes less prominent as the weight ratio of AAT/AN goes beyond 6/94. The apparent activation energy shows a trend of increase with increasing copolymerization temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4649–4653, 2006

Key words: degradation; kinetics; apparent activation energy

INTRODUCTION

Carbon fibers from acrylonitrile (AN) 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) 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 the step (b) is critical. Selection of a suitable comonomer for the 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, but the small changes of polymer structure and property along with the tiny changes of experimental conditions were not tracked

instantaneously and there are many differences between the experimental conditions and polyacrylonitrile precursor thermal stabilization. To our knowledge, there is almost no report on degradation kinetics of AN/AAT copolymers. in this study, AAT was firstly used as a comonomer and different suspension polymerization techniques were used to synthesize AN/AAT copolymer. The results of differential scanning calorimetry (DSC) study of the degradation of AN/AAT copolymers performed in the same way as the process of polyacrylonitrile precursor thermal stabilization are reported. The apparent activation energy of degradation of AN/AAT copolymers was determined by Kissinger method.⁷ The effects of different copolymerization conditions on the apparent activation energy of AN/AAT 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/AAT copolymers.

EXPERIMENTAL

Materials

Monomer AN was of industrial polymerization-grade, and was distilled to remove inhibitors before use. Comonomer AAT was obtained by neutralization of acrylic acid (supplied as extra pure grade by tianjin chemical resin industry, tianjin, china) and NH₃. Azobisisobutyronitrile (AIBN) was used as the initiator

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TABLE I
Effects of Solvent Mixture on Copolymerization System

H ₂ O/DMF (w/w)	AN/AAT (w/w)	M _n (10 ⁻⁴)	Oxygen concentration in the copolymer (wt %)	AAT concentration in the copolymer (wt %)
100/0		47.9	0.665	1.85
90/10		41.2	0.669	1.86
80/20		37.6	0.662	1.84
60/40		33.5	0.680	1.89
50/50	98/2	29.7	0.676	1.88
40/60		24.8	0.701	1.95
20/80		19.9	0.712	1.98
10/90		13.9	0.726	2.02
0/100		11.1	0.737	2.05

Condition: C_{AN} = 4.5 mol/L, C_{AIBN} = 0.008 mol/L, C_{PVA} = 0.22 g/L, T = 60°C, t = 20 min.

and recrystallized from ethanol before use. Polyvinyl alcohol (PVA) was used as the suspending 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, AAT, 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 copolymerization was terminated by cooling the flask in the ice water and 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

intrinsic viscosities of the copolymers were measured at 30°C in DMF using an Ubbelohde viscometer,⁸ and the number-average molecular weights (M_n) of the purified copolymers were calculated from the following equation

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

where $[\eta]$ is the intrinsic viscosity.

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

The triad tacticities [(*mm*), (*mr*), (*rr*); *m* and *r* mean *meso* and *racemo* diad sequences, respectively] of AN/AAT copolymers were determined 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 (german) in 2.5 wt % so-

lution in deuterated dimethylsulfoxide (dmsO-d₆) 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.

Differential scanning calorimetry (DSC) spectra of AN/AAT copolymers were determined on a 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 fibers production. The apparent activation energy of degradation of the copolymers was calculated by the Kissinger method from equation

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

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

RESULTS AND DISCUSSION

Effect of solvent mixture on copolymerization

H₂O/DMF suspension polymerization technique was used to synthesize AN/AAT copolymers. effects of reaction media on copolymerization were shown in Table I. It shows that pure AN/AAT copolymers can be synthesized by this technique. The molecular weights of copolymers decrease with an increase in the DMF concentration in the reaction media. The composition of AN/AAT copolymer was determined from the oxygen concentration in the copolymer. The oxygen concentration in the copolymer increases with

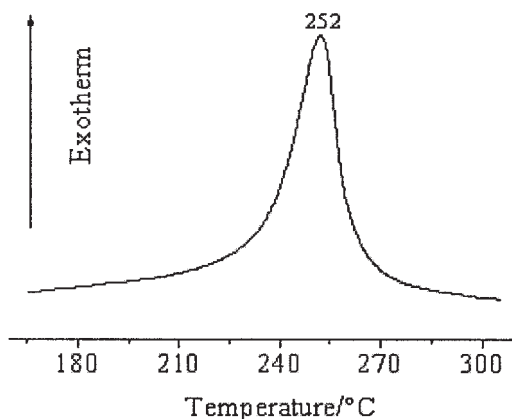


Figure 1 DSC curve of AN/AAT copolymer with the rate of temperature rising at 5 k min^{-1} .

an increase in DMF content in the copolymerization reaction media.

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

Aqueous suspension polymerization technique was used to synthesize AN/AAT copolymers. Figure 1 is a DSC curve of AN/AAT copolymer with the rate of temperature rising at 5 k min^{-1} . Table II shows DSC parameters and polymerization conditions of AN/AAT copolymers at the different temperature rising rates. The value of apparent activation energy of degradation, calculated from linear plot is 89.8 kJ mol^{-1} (Fig. 2), which is a criterion to judge other results.

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

ΔE_a of AN/AAT copolymers prepared by $\text{H}_2\text{O}/\text{DMF}$ suspension polymerization technique was also calculated by Kissinger method. The experimental results are given in Table III. The value of ΔE_a of the copolymer synthesized in DMF solution, which is the largest,

TABLE II

DSC Parameters of AN/AAT Copolymer Synthesized by the Aqueous Suspension Technique

ϕ (k min^{-1})	T_m (K)	$\ln\left(\frac{\phi}{T_m^2}\right)$	$10^3 \times \frac{1}{T_m}$ (K^{-1})
5	525	-10.917	1.9048
10	542	-10.288	1.8450
15	552	-9.919	1.8116
20	559	-9.657	1.7889

Condition: $C_{\text{AN}} = 4.5 \text{ mol/L}$, $[\text{AN}]/[\text{AAT}] = 98/2$ (w/w), $C_{\text{AIBN}} = 0.008 \text{ mol/L}$, $C_{\text{PVA}} = 0.22 \text{ g/L}$, $T = 60^\circ\text{C}$, $t = 20 \text{ min}$.

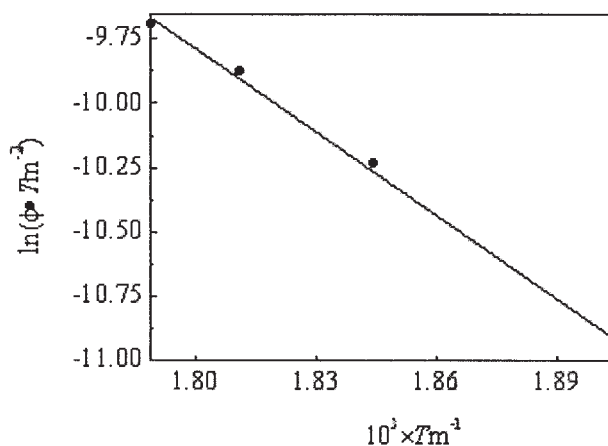


Figure 2 plot of $\ln\left(\frac{\phi}{T_m^2}\right)$ versus $\frac{1}{T_m}$.

is $141.7 \text{ kJ mol}^{-1}$. With an increase in DMF concentration in the reaction media, 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/AAT 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 AAT units in the copolymer chain, and spacial considerations.¹⁰ cyclization of adjacent isotactic AN units in AN/AAT copolymers is initiated by AAT units with an ionic mechanism, and this initiation is a relatively rapid reaction, as is the propagation of the cyclization of subsequent isotactic AN units down the chain, so the value of ΔE_a is small.¹¹

When AN/AAT copolymer is synthesized by $\text{H}_2\text{O}/\text{DMF}$ suspension polymerization technique, oligomeric radicals may be formed in the initial stages of polymerization, which precipitate out after attaining a certain critical molecular weight and then act as pri-

TABLE III

Values of ΔE_a of Copolymer Synthesized in $\text{H}_2\text{O}/\text{DMF}$ Solvent Mixture

$\text{H}_2\text{O}/\text{DMF}$ (w/w)	Triad isotacticity	ΔE_a (kJ mol^{-1})
100/0	0.365	89.8
90/10	0.349	94.9
80/20	0.327	101.7
60/40	0.313	112.2
50/50	0.298	117.9
40/60	0.282	121.3
20/80	0.272	131.5
10/90	0.249	136.2
0/100	0.231	141.7

Condition: $C_{\text{AN}} = 4.5 \text{ mol/L}$, $[\text{AN}]/[\text{AAT}] = 98/2$ (w/w), $C_{\text{AIBN}} = 0.008 \text{ mol/L}$, $C_{\text{PVA}} = 0.22 \text{ g/L}$, $T = 60^\circ\text{C}$, $t = 20 \text{ min}$.

TABLE IV
Effect of Monomer Ratio on ΔE_a of Degradation

AAT/AN (w/w)	Triad isotacticity	ΔE_a (kJ mol ⁻¹)
0/100	0.388	131.5
1/99	0.374	120.6
2/198	0.365	89.8
5/95	0.321	85.9
6/94	0.308	82.8
7/93	0.292	81.9
8/92	0.279	82.1
10/90	0.265	82.4

Condition: $C_{AN} = 4.5$ mol/L, $H_2O/DMF = 100/0$ (w/w), $C_{AIBN} = 0.008$ mol/L, $C_{PVA} = 0.22$ g/L, $T = 60^\circ\text{C}$, $t = 20$ min.

mary particles. Propagation would then occur either in 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 media ($H_2O/DMF > 80/20$), because of the insolubility oligomeric radicals, propagation follows the suspension polymerization technique more. 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 AAT units. The value of ΔE_a is small. In DMF-rich reaction media ($H_2O/DMF < 80/20$), copolymerization follows the solution polymerization technique more. 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 AAT is greater than AN in DMF. The impacting opportunities between AAT units and polymer radicals are rising, which leads to the random array of AAT units in the copolymer chain. The extent of isotacticity of AN units in copolymer decreases (Table III), so ΔE_a rises with an increase in DMF concentration.

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

To study the effect of AAT on ΔE_a , AN/AAT 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 the increase in AAT concentration, when the weight ratio is more than 6/94, changes of ΔE_a become less prominent. Bajaj¹⁵ also reported that the activation energy of AN/itaconic acid copolymers shows a trend of decrease with addition of itaconic acid. This can be explained on the basis of different mechanisms suggested for these copolymers. AAT 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 on the side of imino groups formed by the water absorbability of AAT units.¹⁶ When the weight ratio of AAT/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.

Effect of polymerization temperature on apparent activation energy of degradation of copolymer

Effect of polymerization temperature on the apparent activation energy of degradation of AN/AAT copolymer was also studied. AN/AAT copolymer was synthesized using the aqueous suspension polymerization technique. According to the results summarized in Table V, values of ΔE_a increase gradually with the increase in polymerization temperature. The extent of chain transfer reaction increases and the impacting opportunities between AAT units and polymer radicals are also found to increase. Polymerization becomes violent and dangerous beyond 65°C . AN/AAT copolymers are usually synthesized at about 60°C .

CONCLUSIONS

Laboratory studies of degradation of AN/AAT copolymer in air have shown that the apparent activation energy of degradation increases rapidly with an increase in DMF concentration in DMF–water mixture solution. AAT comonomer can directly initiate and accelerate intramolecular cyclization, the apparent activation energy of degradation then reduces quickly with the AAT concentration rising, when the weight ratio of AAT/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.

TABLE V
Effect of Copolymerization Temperature on ΔE_a of Degradation

T (°C)	ΔE_a (kJ mol ⁻¹)
55	78.9
58	82.1
60	89.8
63	97.5
65	110.2
70	126.4

Condition: $C_{AN} = 4.5$ mol/L, $[AN]/[AAT] = 98/2$ (w/w), $C_{AIBN} = 0.008$ mol/L, $C_{PVA} = 0.22$ g/L, $t = 20$ min.

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