

Kinetic Study of the Degradation of Acrylonitrile–Acrylamide Copolymers

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ABSTRACT: Differential scanning calorimetry was used to investigate the degradation of acrylonitrile–acrylamide copolymers in air. The apparent activation energy of degradation of the copolymers was calculated with the Kissinger method. The effects of the copolymerization conditions on the apparent activation energy of the copolymers were studied. Increasing the dimethylformamide concentration in the solvent mixture led to a rapid increase in the apparent activation energy of degradation of the acrylonitrile–acryl-

amide copolymers. The apparent activation energy decreased quickly as the comonomer acrylamide concentration increased, and this change became less prominent as the acrylamide/acrylonitrile weight ratio increased beyond 5/95. The apparent activation energy increased as the copolymerization temperature increased. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1017–1020, 2005

Key words: degradation; kinetics (polym.); synthesis

INTRODUCTION

The selection of a suitable comonomer for the synthesis of an acrylic polymer satisfying the requirements for acrylic precursors is an important step. The interaction of comonomers at a concentration of a few percent generally enhances the spinnability and depresses the onset of the cyclization temperature during oxidation. The low-temperature degradation of acrylic copolymers is an interesting area,^{1,2} and several reaction mechanisms have been proposed.^{3–5} In the published studies, the authors have presented 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. There are many differences between the experimental conditions and polyacrylonitrile precursor preoxidation. To our knowledge, there are almost no reports on acrylamide (AM) as a comonomer. In this study, different polymerization techniques were used to synthesize acrylonitrile (AN)–AM copolymers. The results of a differential scanning calorimetry (DSC) study of the degradation of the copolymers performed in the same way as the process of preoxidation are reported. The apparent activation energy of degradation (ΔE_a) of the copolymers was calculated with the Kissinger method.⁶ The effects of different copolymerization

conditions on the apparent activation energy of the copolymers were examined as well.

EXPERIMENTAL

Copolymerization

Monomer AN was industrial-polymerization-grade and was distilled before use for the removal of inhibitors. AM was extra-pure-grade. Azobisisobutyronitrile (AIBN) was used as the initiator and was recrystallized from ethanol before use. Poly(vinyl alcohol) (PVA) was used as the suspending agent. Deionized water and dimethylformamide (DMF) were adopted as the polymerization media.

Required amounts of AN, AM, 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 a constant weight, and then weighed.

Characterization

The viscosities of the copolymers were measured at 30°C in DMF with an Ubbelohde viscometer, and the number-average molecular weights (M_n 's) of the purified copolymers were calculated as follows:⁷

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TABLE I
Effects of the Solvent Mixture on the Copolymerization System

H ₂ O/DMF (w/w)	AN-AM (w/w)	$M_n \times 10^{-4}$	Oxygen concentration in the copolymer (wt%)	AM concentration in the copolymer (wt%)
100/0		43.3	0.407	1.81
90/10		36.9	0.412	1.83
80/20		31.2	0.416	1.85
60/40		24.8	0.421	1.87
50/50	98/2	22.9	0.425	1.89
40/60		23.1	0.423	1.88
20/80		18.7	0.437	1.94
10/90		16.9	0.439	1.95
0/100		11.6	0.448	1.99

Conditions: concentration of AN = 4.15 mol/L; concentration of AIBN = 0.008 mol/L; concentration of PVA = 0.22 g/L; temperature = 60°C; time = 15 min.

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

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

The elemental analysis of the copolymers was carried out with a PE 2400 elemental analyzer (PerkinElmer, Inc., Shelton, CT) to determine their oxygen concentrations.

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

DSC curves of the AN-AM copolymers were recorded on a shimadzu (Kyoto, Japan) DT 40 thermal analyzer in air. Particular care was taken to ensure that the heating rate was the same as that of the precursor preoxidation process used in carbon-fiber production. ΔE_a of the copolymers was calculated with the Kissinger method:⁶

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

where ϕ is the rate at which the temperature rises, T_m is the highest temperature of the exothermic peak, and R is the gas constant. ΔE_a was determined from the slope of a linear plot of $\ln(\phi/T_m^2)$ versus $1/T_m$.

RESULTS AND DISCUSSION

Effect of the solvent mixture on the copolymerization

A water/DMF suspension technique was used to synthesize AN-AM copolymers. The effects of the reaction media on the copolymerization are shown in Table I. The pure AN-AM copolymers was synthesized

with this technique. The molecular weights of the copolymers decreased with an increase in the DMF concentration in the reaction media. The compositions of the AN-AM copolymers were determined from the oxygen concentrations in the copolymers. The oxygen concentrations in the copolymers increased with the DMF content in the copolymerization reaction media.

ΔE_a of the copolymers synthesized by the aqueous suspension technique

The aqueous suspension polymerization technique was used to synthesize AN-AM copolymers. Table II shows some important DSC parameters and polymerization conditions. ΔE_a , calculated from a linear plot, was 95.6 kJ mol⁻¹ (Fig. 1) and served as a criterion for judging other results.

Effect of the solvent mixture on δE_a of the copolymers

ΔE_a of AN-AM copolymers prepared by the solvent water suspension polymerization technique was also calculated with the Kissinger method. The experimental results are given in Table III. ΔE_a of the copolymer

TABLE II
DSC Parameters of AN-AM Copolymers Synthesized in the Aqueous Suspension Copolymerization System

ϕ (k/min)	T_m (K)	$\ln\left(\frac{\phi}{T_m^2}\right)$	$10^3 \times \frac{1}{T_m}$ (K ⁻¹)
5	532	-10.94	1.880
10	548	-10.31	1.825
15	558	-9.94	1.792
20	565	-9.68	1.770

Conditions: concentration of AN = 4.15 mol/L; [AN]/[AM] = 98/2 w/w; H₂O/DMF 00/0 w/w =; concentration of AIBN = 0.008 mol/L; concentration of PVA = 0.22 g/L; temperature = 60°C; time = 15 min.

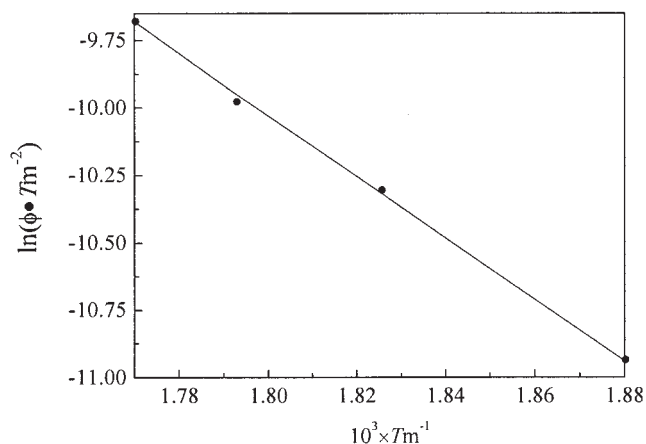


Figure 1 Plot of $\ln(\phi/T_m^2)$ versus $1/T_m$.

synthesized in a DMF solution, which was the largest, was $162.2 \text{ kJ mol}^{-1}$. 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 the AN-AM copolymers.⁸ There were a number of factors that appeared to limit the extent of the cyclization reaction of the AN units, the most important of which were the tacticity, sequence distribution, stereochemistry of AN and AM units in the copolymer chain, and spatial considerations.⁹ The initiation by the AM units of the cyclization reaction of the adjacent isotactic AN units was a relatively rapid reaction, as was the propagation of the cyclization of subsequent isotactic AN units down the chain, so the value of ΔE_a was small.¹⁰ From the point of view of oxidative stabilization, the solvent water suspension polymerization technique was substantially effective in lowering the onset of the exotherm, in comparison with solution polymerization. Precursors prepared by the solvent water suspension polymerization technique showed better mechanical properties.

TABLE III
 ΔE_a of Copolymers Synthesized in the H₂O/DMF Solvent Mixture Medium

H ₂ O/DMF (w/w)	Triad isotacticity	ΔE_a (kJ/mol ⁻¹)
100/0	0.363	95.6
90/10	0.352	103.4
80/20	0.332	110.3
60/40	0.310	121.2
50/50	0.302	126.7
40/60	0.291	133.2
20/80	0.271	144.4
10/90	0.262	151.2
0/100	0.253	162.2

Conditions: concentration of AN = 4.15 mol/L; [AN]/[AM] = 98/2 w/w; concentration of AIBN = 0.008 mol/L; concentration of PVA = 0.22 g/L; temperature = 60°C; time = 15 min.

When the AN-AM copolymers were synthesized with the solvent water suspension technique, oligomeric radicals may have formed during the initial stages of the polymerization, precipitated after a certain critical molecular weight was attained, and then acted as primary particles. Propagation then occurred 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 the monomers.^{11,12} In water-rich reaction media (water/DMF > 80/20), because of the insolubility of the oligomeric radicals, propagation followed the suspension polymerization technique more. A two-locus polymerization mechanism was assumed (i.e., a water phase and an oligomeric radical phase). After half an hour, propagation then mostly occurred in the oligomeric radical phase. AN units were more easily absorbed by the polymer radicals than AM units. The value of ΔE_a was small. In DMF-rich reaction media (water/DMF < 80/20), copolymerization followed the solution polymerization technique more. The extent of the chain-transfer reaction grew. The high chain-transfer coefficient of DMF was 2.8×10^{-4} at 50°C.¹³ The solubility of AM was greater than that of AN in DMF. The opportunities for impact between the AM units and polymer radicals rose, and this led to a random array of AM units in the copolymer chain. The extent of the isotacticity of the AN units in the copolymers decreased (Table III), so ΔE_a rose with an increase in the DMF concentration.

Effect of the AM concentration on δE_a of the copolymers

To study the effect of comonomer AM on ΔE_a , we synthesized AN-AM copolymers of different monomer ratios, which are listed in Table IV. ΔE_a decreased quickly as the AM concentration rose; when the weight ratio was greater than 5/95, the changes in ΔE_a became less prominent ($\Delta E_a = 89.2 \pm 0.9 \text{ kJ mol}^{-1}$). This can be explained by different mechanisms sug-

TABLE IV
Effect of the Monomer Ratio on ΔE_a

AM/AN (w/w)	Triad isotacticity	ΔE_a (kJ/mol)
0/100	0.383	121.8
1/99	0.372	110.9
2/98	0.363	95.6
5/95	0.303	88.3
7/93	0.273	87.9
8/92	0.254	90.1
10/90	0.223	89.2

Conditions: concentration of AN = 4.15 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 = 15 min.

TABLE V
Effect of the Copolymerization Temperature (I) on ΔE_a

T (°C)	ΔE_a (kJ/mol)	T (°C)	ΔE_a (kJ/mol)
55	85.6	63	112.2
58	90.8	65	125.7
60	95.6	70	145.2

Conditions: concentration of AN = 4.15 mol/L; [AN]/[AM] = 98/2 w/w; H₂O/DMF 100/0 w/w =; concentration of AIBN = 0.008 mol/L; concentration of PVA = 0.22 g/L; time = 15 min.

gested for these copolymers. AM was directly involved in the initial cyclization of the 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 AM units.¹⁴ When the AM/AN weight ratio was greater than 5/95, the extent of isotacticity of the AN units in the copolymers was affected and began to decrease (Table IV). The changes in the apparent activation energy then became correspondingly less. The degraded copolymers became increasingly colored as the AM concentration increased. The extent of the precursor preoxidation was affected by the AM concentration.

Effect of the temperature on δE_a of the copolymers

The effect of the temperature on ΔE_a of the copolymers was also studied. AN-AM copolymers were synthesized with the aqueous suspension polymerization technique. According to the results summarized in Table V, ΔE_a increased gradually with an increase in the temperature. The extent of the chain-transfer reaction increased, and the opportunities for impact between the AM units and polymer radicals also rose.

The polymerization became violent and dangerous at polymerization temperatures greater than 65°C. The AN-AM copolymers were usually synthesized at about 60°C.

CONCLUSIONS

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

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