Degradation Kinetics of Acrylonitrile/Methyl Vinyl Ketone Copolymers

Chen Hou,[1] Zhenliang Guo,[1] Junshen Liu,[1] Liang Ying[2]

[1]*College of Chemistry and Materials Science, Yantai Normal University, Yantai 264025, China*
[2]*Scientific Research Department, Yantai Normal University, Yantai 264025, China*

ABSTRACT: Methyl vinyl ketone (MVK) was first used to successfully copolymerize with acrylonitrile (AN). This was achieved by using azobisisobutyronitrile as the initiator. Differential scanning calorimetry results of the degradation of AN/MVK copolymers in air are presented. The apparent activation energy of degradation of the copolymers was calculated with Kissinger method. Effects of copolymerization conditions on the apparent activation energy of the copolymers were studied. It has been found that increasing dimethyl sulfoxide concentration in the solvent mixture leads to a rapid increase in the degradation apparent activation energy of AN/MVK copolymers. The apparent activation energy decreases quickly along with increase in the comononer MVK concentration, and this change becomes less prominent as the weight ratio of MVK/AN goes beyond 7/93. The apparent activation energy shows a trend of increase as the copolymerization temperature increases. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1386–1390, 2007

Key words: degradation; kinetics; apparent activation energy

INTRODUCTION

Carbon fiber composites are important construction materials in applications where high strength and modulus, high thermal and corrosion resistance, and light weight are the prime requirements.[1] It is well known that the properties of the final carbon fibers are determined by the nature of the acrylic precursor fibers. Selection of a suitable comonomer for synthesis of an acrylic polymer satisfying the requirements for acrylic precursors is an important step. The interaction of a few percent of comonomers generally enhances the spinnability and depresses the onset of cyclization temperature during oxidation. Low-temperature degradation of acrylic copolymer has been an interesting area,[2,3] and several reaction mechanisms have been proposed.[4,5] In the studies published, the authors have presented the results obtained intermittently in nitrogen.[6-8] 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 a great many differences between experimental conditions and polyacrylonitrile precursor preoxidation. To our knowledge, there is almost no report on methyl vinyl ketone (MVK) as a comonomer. In this study, different polymerization techniques were used to synthesize acrylonitrile (AN)/MVK copolymer. The results of differential scanning calorimetry (DSC) study of the degradation of the copolymer performed in the same way as the process of preoxidation are reported. The apparent activation energy of degradation of AN/MVK copolymer was calculated by Kissinger method.[9] Effects of different copolymerization conditions on the apparent activation energy of the copolymer were discussed in contrast.

EXPERIMENTAL

Copolymerization

Acrylonitrile (AN) (Shanghai Chemical Reagents Co., A.R. grade) was vacuum distilled from CaH_2 just before polymerization. Methyl vinyl ketone (MVK) (Shanghai Chemical Reagents Co., A.R. grade) was used as a comonomer. Azobisisobutyronitrile (AIBN) was used as an initiator and recrystallized from ethanol before use. Polyvinyl alcohol (PVA) was used as a suspending agent. Deionized water and dimethyl sulfoxide (DMSO) were adopted as the polymerization medium.

TABLE I
Effects of Solvent Mixture on Copolymerization System

H_2O/DMSO (w/w)	AN/MVK (w/w)	M_n (10^{-4})	Oxygen concentration in copolymer (wt %)	MVK concentration in copolymer (wt %)
100/10		53.2	0.432	1.89
90/10		45.7	0.441	1.93
80/20		32.1	0.448	1.96
60/40		24.5	0.455	1.99
50/50	98/2	20.6	0.478	2.09
40/60		18.9	0.533	2.33
20/80		14.3	0.606	2.65
10/90		12.5	0.681	2.98
0/100		10.9	0.713	3.12

Condition: C_{AN} = 4.15 mol/L; C_{AIBN} = 0.008 mol/L; C_{PVA} = 0.22 g/L; T = 60°C; t = 15 min.

A typical example of the general procedure was as follows. Required amounts of AN, MVK, PVA, AIBN, deionized water, and DMSO 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 under vacuum until constant weight, and then weighed.

Characterization

Viscosities of the copolymers were measured at 30°C in DMSO using an Ubbelohde viscometer, and the number-average molecular weights (M_n) of the purified copolymers were calculated from the following eq. (1).[10]

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

where [η] is the intrinsic viscosity.

Elemental analysis of the copolymers was carried out using a PE 2400 elemental analyzer (PerkinElmer, Shelton, CT) to determine the oxygen in these copolymers.

Nuclear magnetic resonance measurements were carried out using a Bruker-DPX300 spectrometer (The Bruker Companies, German) 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/MVK copolymer were recorded on DSC 204 F1 Phoenix thermal analyzer (Netzsch Geratebau GmbH, German) in air. Particular care was taken to ensure that the heating rate was the same as that of precursor preoxidation process used in carbon fibers production. The apparent activation energy of degradation of the copolymers was calculated by the Kissinger method[7] from eq. (2).

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

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_2O/DMSO suspension technique was used to synthesize AN/MVK copolymers. The effects of reaction media on copolymerization were shown in Table I. It shows that AIBN successfully initiates the free radical copolymerization of AN with MVK. The molecular weights of AN/MVK copolymers decrease with an increase in the DMSO concentration in the reaction media. The composition of AN/MVK copolymer was determined from the oxygen concentration in the copolymer. The oxygen concentration in the copolymer increases with an increase of DMSO content in the copolymerization reaction media.

Apparent activation energy of degradation of AN/MVK copolymer synthesized by aqueous suspension technique

Aqueous suspension polymerization technique was used to synthesize AN/MVK copolymer. Table II shows some important DSC parameters and copolymerization conditions. The value of apparent activa-

TABLE II
DSC Parameters of AN/MVK Copolymer Synthesized in Aqueous Suspension Copolymerization System

ϕ (k·min^{-1})	T_m (K)	$\ln\left(\dfrac{\phi}{T_m^2}\right)$	$10^3 \dfrac{1}{T_m}$ (K^{-1})
5	540	−10.97	1.852
10	559	−10.35	1.789
15	568	−9.98	1.761
20	578	−9.72	1.730

Condition: C_{AN} = 4.15 mol/L; [AN]/[MVK] = 98/2 (w/w); H$_2$O/DMSO (w/w) = 100/0; C_{AIBN} = 0.008 mol/L; C_{PVA} = 0.22 g/L; T = 60°C; t = 15 min.

TABLE III
Values of ΔE_a of Copolymer Synthesized in H$_2$O/DMSO Solvent Mixture Medium

H$_2$O/DMSO (w/w)	Triad isotacticity	ΔE_a (kJ·mol^{-1})
100/0	0.374	85.6
90/10	0.361	94.5
80/20	0.340	100.4
60/40	0.321	110.3
50/50	0.309	117.6
40/60	0.298	121.2
20/80	0.265	130.5
10/90	0.254	142.3
0/100	0.243	151.4

Condition: C_{AN} = 4.15 mol/L; [AN]/[MVK] = 98/2 (w/w); C_{AIBN} = 0.008 mol/L; C_{PVA} = 0.22 g/L; T = 60°C; t = 15 min.

tion energy of degradation, calculated from the linear plot is 85.6 kJ mol^{-1} (Fig. 1), which is a criterion from which to judge other results.

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

ΔE_a of AN/MVK copolymers, prepared by solvent water suspension polymerization technique, was also calculated by Kissinger method. The experimental results are given in Table III. The value of ΔE_a of copolymer synthesized in DMSO solution, which is the largest, is 151.4 kJ mol^{-1}. With an increase of DMSO 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/MVK copolymer.[11] 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 MVK units in the copolymer chain, and spacial considerations.[12] Initiation by MVK units of cyclization reaction of adjacent isotatic AN units is a relatively rapid reaction, as is the propagation of the cy-
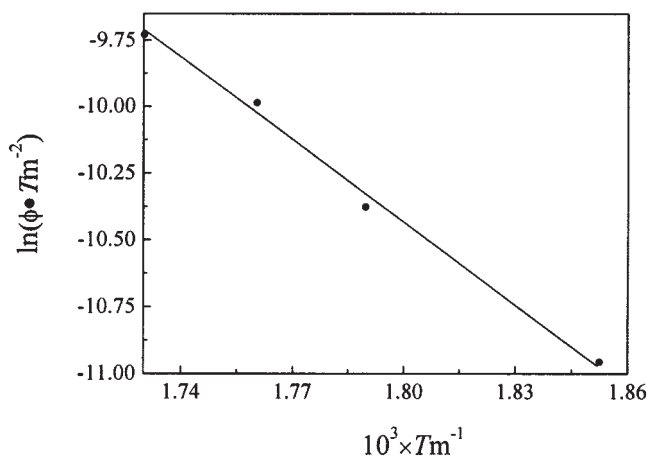
clization of subsequent isotatic AN units down the chain, so the value of ΔE_a is small.[13] From the point of view of oxidative stabilization, solvent water suspension polymerization technique is substantially effective in lowering the onset of exotherm, compared with solution polymerization. Precursors prepared by solvent water suspension polymerization technique show better mechanical properties.

When AN/MVK copolymer is synthesized using solvent water suspension 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 primary particles. Propagation would then occur either in water phase, the DMSO phase, the oligomeric radicals phase or at the interface of DMSO/water/oligomer mixture depending on the solubility of monomers.[14,15] In water-rich reaction media (H$_2$O/DMSO > 80/20), propagation follows more of the suspension polymerization technique. A two-loci polymerization mechanism is assumed, water phase and oligomeric radicals phase. Propagation would then mostly occur in oligomeric radicals phase. AN units are more easily ab-

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

TABLE IV
Effect of Monomer Ratio on ΔE_a of Degradation

MVK/AN (w/w)	Triad isotacticity	ΔE_a (kJ·mol^{-1})
0/100	0.396	113.5
1/99	0.383	105.8
2/98	0.374	85.6
5/95	0.332	82.4
7/93	0.271	76.8
8/92	0.253	78.4
10/90	0.234	77.9

Condition: C_{AN} = 4.15 mol/L; H$_2$O/DMSO (w/w) = 100/0; C_{AIBN} = 0.008 mol/L; C_{PVA} = 0.22 g/L; T = 60°C; t = 15 min.
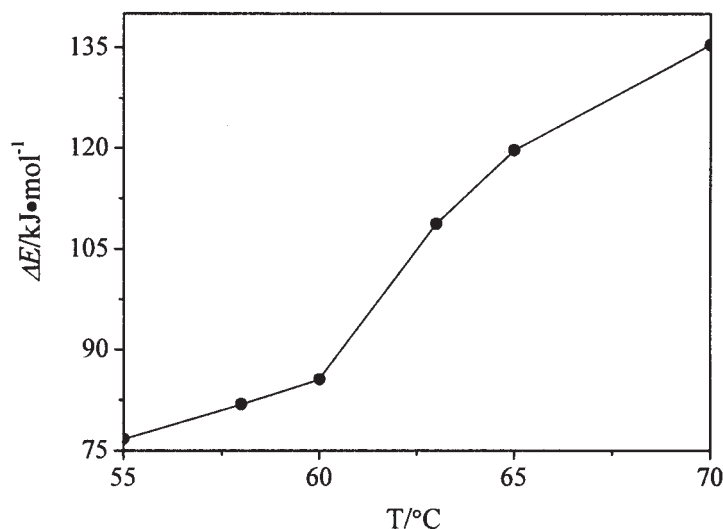
Figure 2 Effect of copolymerization temperature on ΔE_a of Degradation. Condition: $C_{AN} = 4.15$ mol/L, [AN]/[MVK] = 98/2 (w/w), H_2O/DMSO (w/w) = 100/0, $C_{AIBN} = 0.008$ mol/L, $C_{PVA} = 0.22$ g/L, $t = 15$ min.

sorbed by polymer radicals than MVK units. The value of ΔE_a is small. In DMSO-rich reaction media (DMSO/H_2O > 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 DMSO is 7.95×10^{-5} at 50°C.[16] Solubility of MVK is greater than AN in DMSO. The impacting opportunities between MVK units and polymer radicals are rising, which leads to the random array of MVK 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 DMSO concentration.

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

To study the effect of comonomer MVK on ΔE_a, AN/MVK copolymers of different monomer ratios were synthesized, which is given in Table IV. It is clear from the following table that ΔE_a reduces quickly with the MVK concentration rising, when the weight ratio goes beyond 7/93, the changes of ΔE_a becomes less prominent, $\Delta E_a = 77.6 \pm 0.8$ kJ mol^{-1}. This can be explained on the basis of different mechanisms suggested for these copolymers. MVK is directly involved in the initial cyclization of AN units at relatively low temperature. Propagation of cyclization reaction may occur on the side of hydroxyl groups formed at the degradation temperature.[17] When the weight ratio of MVK/AN is more than 7/93, 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 MVK concentration increasing at the same time.

Effect of temperature on apparent activation energy of degradation of copolymer

Effect of temperature on apparent activation energy of degradation of copolymer was also studied. AN/MVK copolymer was synthesized using the aqueous suspension polymerization technique. According to the results summarized in Figure 2, the value of ΔE_a increases gradually with an increase of temperature. The extent of chain transfer reaction increases and the impacting opportunities between MVK units and polymer radicals are also rising. Polymerization becomes violent and dangerous when the polymerization temperature is above 65°C.

CONCLUSIONS

Laboratory studies of degradation of AN–MVK copolymer in air have shown that the apparent activation energy of degradation increases rapidly with an increase of DMSO concentration in DMSO–water mixture solution. MVK comonomer can directly initiate and accelerate intramolecular cyclization, the apparent activation energy of degradation then reduces quickly with the MVK concentration rising, when the weight ratio of MVK/AN is higher than 7/93, 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 value of the apparent activation energy of degradation has been confirmed.

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