

Copolymerization of Acrylonitrile with Methyl Vinyl Ketone

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ABSTRACT: Methyl vinyl ketone (MVK) was first used to successfully copolymerize with acrylonitrile (AN). This was achieved with azobisisobutyronitrile as the initiator. The kinetics of the copolymerization of AN with MVK were investigated in a H₂O/dimethyl sulfoxide (DMSO) mixture between 50 and 70°C under N₂ atmosphere. The rate of copolymerization was measured. The kinetic equation of the copolymerization system was obtained, and the overall activation energy for the copolymerization system was deter-

mined. The values of the monomer apparent reactivity ratios were calculated by the Kelen–Tudos method. In a DMSO-rich reaction medium (DMSO/H₂O > 80/20), the monomer apparent reactivity ratios were similar to those in the solution polymerization system. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1940–1944, 2006

Key words: copolymerization; kinetics (polym.); 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 precursor fibers. It is important to select a suitable technique and to optimize the conditions of polymerization for the synthesis of an acrylic polymer that satisfies the requirements for high-tenacity acrylic fibers.^{2,3} Several polymerization techniques have been successfully used to synthesize homopolymers and copolymers of acrylonitrile (AN) for high-tenacity fibers. Solution, aqueous suspension, and solvent–water suspension are the most common useful techniques.⁴ The solvent–water suspension method is a new and promising technique that may be used in the production of high-performance acrylic fibers; it cleverly combines the advantages of a solution and those of an aqueous suspension. Various comonomers are used to copolymerize with AN to obtain specialty fibers for various applications.^{5–8} The interaction of a few percentage points of comonomers generally enhances the spinnability and depresses the onset of the cyclization temperature during oxidation.⁹ It was reported that carbon fiber

prepared from AN/methyl vinyl ketone (MVK) copolymer precursors has an average tensile strength of about 6500 MPa.¹⁰ To our knowledge, there are only a few reports on MVK as a comonomer,¹¹ but there are fewer on the kinetic study of the copolymerization of AN with MVK in H₂O/dimethyl sulfoxide (DMSO) mixture systems. In this study, a H₂O/DMSO suspension technique was used to synthesize AN/MVK copolymers. To estimate polymerization rates (R_p 's), copolymerization experiments were terminated at less than 10% conversion.¹² The conversion was controlled and determined by gravimetric measurements. The kinetics of copolymerization of AN/MVK were studied between 50 and 70°C under a N₂ atmosphere, and a suitable kinetic scheme is proposed. Furthermore, the overall activation energy was evaluated. The values of the monomer apparent reactivity ratios were calculated by the Kelen–Tudos method.¹³

EXPERIMENTAL

Materials

AN (analytical reagent grade, Shanghai Chemical Reagents Co., Shanghai, China) was vacuum-distilled from CaH₂ (analytical reagent grade, Shanghai Chemical Reagents Co.) just before polymerization. MVK (analytical reagent grade, Shanghai Chemical Reagents Co.) was used as a comonomer and was distilled to remove hydroquinone. Azobisisobutyronitrile (AIBN) (analytical reagent grade, Shanghai Chemical Reagents Co.) was used as an initiator and was recryst-

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tallized from ethanol before use. Poly(vinyl alcohol) (PVA; polymerization degree = 1800; analytical reagent grade, Tianjin Chemical Reagents Co., Tianjin, China) was used as a suspending agent. Deionized water (self-made) and dimethyl sulphoxide (DMSO) supplied by Shanghai Chemical Resin Industry (Shanghai, China) were adopted as the polymerization medium.

Copolymerization

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 flask, which was continuously flushed with ultrapure nitrogen. The flask was wholly immersed in a temperature-controlled water bath and was shaken from time to time. All of the experimental conditions are provided in the tables. After a definite reaction time, we terminated the copolymerization at less than 10% conversion by cooling the flask in the ice water. 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 was reached, and then weighed.

Characterization

Conversion and R_p values were calculated from the weight of the polymer obtained. The weight-average molecular weight (M_w) of the purified polymers was determined by viscosity ($[\eta]$) measurements. $[\eta]$ of the polymers were measured at 35°C in dimethylformamide with an Ubbelohde viscometer,¹⁴ and M_w was calculated from¹⁵

$$[\eta] = 2.78 \times 10^{-4} M_w^{0.76} \quad (1)$$

Elemental analyses of the copolymers were carried out with a PE2400 microanalyzer (PerkinElmer, Inc., Shelton, CT) to determine the oxygen content of these copolymers. The monomer reactivity ratios for the copolymerization of AN and MVK (r_{AN} and r_{MVK} , respectively) were determined from the monomer feed ratios and the copolymer composition. r_{AN} and r_{MVK} were calculated by the Kelen-Tudos method from

$$\frac{x(y-1)}{ay+x^2} = \frac{(r_{AN} + r_{MVK}/a)x^2}{ay+x^2} - \frac{r_{MVK}}{a} \quad (2)$$

$$x = \frac{M_{AN}}{M_{MVK}} \text{ (mol/mol)}, \quad y = \frac{dM_{AN}}{dM_{MVK}} \text{ (mol/mol)}$$

where x is the ratio of the molar fractions of the monomers AN and MVK in the monomer feed, y is the

TABLE I
Effect of Initiator Concentration on Copolymerization

Initiator concentration (mol/L)	Conversion (%)	$M (\times 10^4)$
0.0050	6.03	59.3
0.0065	7.31	49.8
0.0075	8.04	37.6
0.0095	9.43	29.5

Conditions: AN concentration = 4.15 mol/L; MVK concentration = 0.04 mol/L; PVA concentration = 0.22 g/L; H₂O/DMSO (w/w) = 80/20; temperature = 60°C; time = 15 min.

ratio of the molar fractions of the monomers AN and MVK in the copolymer, M_{AN} and M_{MVK} are the concentrations of the monomers AN and MVK in the monomer feed, respectively, and a is an equation parameter. a can be computed according to

$$a = \frac{x_{\min}x_{\max}}{\sqrt{y_{\min}y_{\max}}} \quad (3)$$

where x_{\min} and x_{\max} are the minimum and maximum molar fractions, respectively, in the monomer feed and y_{\min} and y_{\max} are the minimum and maximum molar fractions, respectively, in the copolymer.

Equation (2) transforms into the form

$$\tau = (r_{AN} + r_{MVK}/a)\delta - \frac{r_{MVK}}{a} \quad (4)$$

$$\tau = \frac{x(y-1)}{ay+x^2}, \quad \delta = \frac{x^2}{ay+x^2}$$

The plot of τ versus δ produced a straight line. Extrapolation of the line to $\delta = 1$ gave r_{AN} and that of $\delta = 0$ gave r_{MVK}/a .

RESULTS AND DISCUSSION

Kinetic equations of different copolymerization systems

The solvent-water suspension technique was used to synthesize the AN/MVK copolymer.¹⁶ The effect of initiator concentration on the copolymerization was studied. Table I shows the variation in percentage conversion and M_w as a function of initiator concentration. According to the results summarized in Table I, conversion increased quickly, and M_w decreased quickly as the initiator concentration increased. R_p was calculated from the slope of a plot of conversion versus time. Figure 1 is a logarithmic plot of R_p versus [AIBN]. The reaction order estimated from the slope was 0.698.

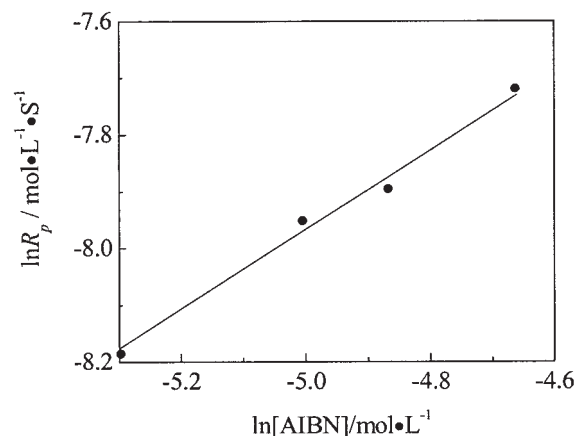


Figure 1 Relationship between $\ln R_p$ and $\ln [AIBN]$.

The effect of AN and MVK concentrations on R_p was also studied. The reaction orders from the slope of the plot were 1.75 and 1.34, respectively. The overall rate of copolymerization was $R_p \propto [AIBN]^{0.698} [AN]^{1.75} [MVK]^{1.34}$. This was different from the reaction order reported. Pan¹⁷ revealed that reaction orders of initiator and monomer were 0.5 and 1 when the solution technique was used to synthesize polyacrylonitrile. Zhou¹⁸ also studied the kinetics of polymerization of AN initiated by a redox system with the aqueous suspension technique, and the kinetic equation $R_p \propto [Initiator]^{0.7} [AN]^2$ was proposed.

AIBN cannot dissolve in water easily. When the AN/MVK copolymer is synthesized with the solvent-water suspension technique,^{19,20} oligomeric radicals may form quickly in the initial stages of polymerization. The oligomeric polymers precipitate out at different critical molecular weights depending on the solvent/water ratio and then act as primary particles. In a water-rich reaction medium ($H_2O/DMSO > 80/20$), the propagation of oligomeric polymers is more likely to follow the way of suspension polymerization because of the insoluble primary radicals. The chain

TABLE III
Solution Copolymerization Parameters of AN
with MVK in DMSO

x (mol/mol)	Conversion (wt %)	Content of oxygen (mol %)	y (mol/mol)
100	6.48	0.016	60.5
60	7.64	0.027	32.4
30	8.29	0.053	17.2
10	9.91	0.173	4.78

Conditions: AN concentration = 4.15 mol/L; AIBN concentration = 0.075 mol/L; temperature = 60°C; time = 15 min.

termination mainly results from a one-radical reaction so that the reaction order of the initiator tends to be 1. The rate of initiation is influenced by the monomer concentration, so the reaction order of the monomer is much larger than 1. The solubility and reactivity of MVK was greater than AN in DMSO, so the departure from 1 of the reaction order was smaller. In a DMSO-rich reaction medium ($DMSO/H_2O > 80/20$), there were no oligomeric polymers precipitating out, and the copolymerization followed the way of solution polymerization. The kinetic equation was $R_p \propto [AIBN]^{0.546} [AN]^{1.24} [MVK]^{1.05}$ when the ratio of $H_2O/DMSO$ was 10/90 (Table II). The extent of active free radicals embedded became less prominent. The chain termination mainly resulted from a two-radical reaction so that the reaction order of the initiator was close to 0.5. The efficiency of the initiator increased, and almost of all the radicals were used to initiate the monomers. The reaction order of the monomers tended to be 1.

Effect of the copolymerization systems on the monomer reactivity ratios

The solution polymerization technique was used to synthesize the AN/MVK copolymer in DMSO. For the estimation of the monomer reactivity ratios, Table III

TABLE II
Effect of the $H_2O/DMSO$ Ratio on the Kinetic Equation

$H_2O/DMSO$ (w/w)	R_p (mol L ⁻¹ s ⁻¹) \propto
100/0	$[AIBN]^{0.763} [AN]^{1.99} [MVK]^{1.41}$
90/10	$[AIBN]^{0.742} [AN]^{1.83} [MVK]^{1.39}$
80/20	$[AIBN]^{0.698} [AN]^{1.75} [MVK]^{1.34}$
70/30	$[AIBN]^{0.673} [AN]^{1.68} [MVK]^{1.22}$
60/40	$[AIBN]^{0.649} [AN]^{1.59} [MVK]^{1.19}$
50/50	$[AIBN]^{0.635} [AN]^{1.48} [MVK]^{1.16}$
40/60	$[AIBN]^{0.626} [AN]^{1.42} [MVK]^{1.12}$
30/70	$[AIBN]^{0.619} [AN]^{1.38} [MVK]^{1.09}$
20/80	$[AIBN]^{0.582} [AN]^{1.32} [MVK]^{1.08}$
10/90	$[AIBN]^{0.546} [AN]^{1.24} [MVK]^{1.05}$
0/100	$[AIBN]^{0.521} [AN]^{1.16} [MVK]^{1.02}$

Conditions: temperature = 60°C; time = 15 min.

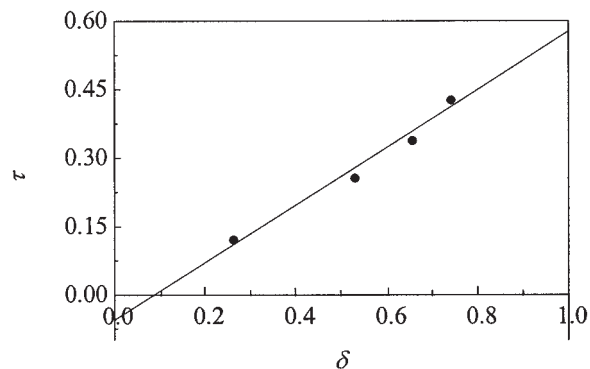


Figure 2 Relationship between τ and γ .

TABLE IV
Reactivity Ratio Parameters in the H₂O/DMSO
Mixture Solvent Medium

H ₂ O/DMSO (w/w)	r_{AN}	r_{MVK}
100/0	0.792	2.78
90/10	0.788	2.84
80/20	0.765	2.87
60/40	0.706	3.02
50/50	0.675	3.13
40/60	0.626	3.21
20/80	0.571	3.29
10/90	0.575	3.31
0/100	0.576	3.32

Conditions: AN concentration = 4.15 mol/L; AIBN concentration = 0.0075 mol/L; temperature = 60°C; time = 15 min.

shows some important parameters and polymerization conditions of the copolymer. The Kelen-Tudos method gave values of $r_{AN} = 0.576$ and $r_{MVK} = 3.32$ (Fig. 2), which were criteria used to judge other results. The higher r_{MVK} confirmed its high reactivity compared with that of AN. The polymer radical with a MVK unit at the chain end was considerably more active than that with an AN unit, and the probability of MVK entry into the chain was greater than that of AN entry, which led to an increase in the polymerization conversion with the addition of MVK comonomer (Table III).

The effect of the mixture solution on the apparent reactivity ratios of the monomers was also studied. AN/MVK copolymer was synthesized by the H₂O/DMSO suspension polymerization technique. According to the results summarized in Table IV, in the DMSO-rich reaction medium (DMSO/H₂O > 80/20), the values of the monomer reactivity ratios were similar to those in the solution polymerization system; copolymerization followed more of the solution polymerization technique.²¹

Determination of the activation energy

The effect of the temperature on polymerization was also studied, which is given in Table V. The AN/MVK

TABLE V
Effect of Temperature (T) on Copolymerization

T (°C)	Conversion (%)	M_w ($\times 10^4$)
50	3.19	64.1
55	4.81	54.9
60	8.04	37.6
65	12.2	32.7
70	18.3	22.8

Conditions: AN concentration = 4.15 mol/L; MVK concentration = 0.04 mol/L; AIBN concentration = 0.0075 mol/L; H₂O/DMSO (w/w) = 80/20; PVA concentration = 0.22 g/L; time = 15 min.

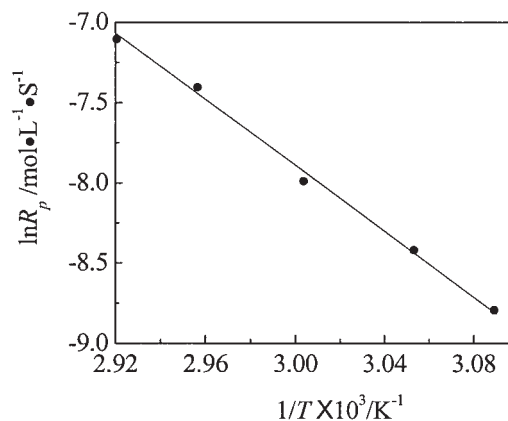


Figure 3 Relationship between R_p and T .

copolymer was synthesized at 50, 55, 60, 65, and 70°C. R_p of the copolymer increased, and the molecular weight decreased as temperature increased. The drop in the molecular weight may have been due to the swift termination rate, which resulted from the high chain-transfer coefficient. It was reported that the high chain-transfer coefficient of DMSO was 7.95×10^{-5} at 50°C²² and that the extent of the chain-transfer reaction increased with temperature. The overall activation energy of polymerization, calculated from the slope of a linear Arrhenius plot (Fig. 3), was 85.6 kJ/mol. Moreover, the overall activation energy computed was 82.3 kJ/mol when the AN concentration was 4.35 mol/L instead of 4.15 mol/L; the overall activation energy computed was 83.1 kJ/mol when the MVK concentration was 0.05 mol/L instead of 0.04 mol/L. From these experiments, we concluded that the influence of the monomer concentration on the overall activation energy was less obvious. The overall activation energy was mainly determined by the activation energy of the pyrolytic reaction of the initiator.

CONCLUSIONS

Laboratory kinetic studies of different copolymerization systems revealed that AIBN successfully initiated the free-radical copolymerization of AN with MVK. Kinetic schemes were proposed. In a DMSO-rich reaction medium, values of the monomer apparent reactivity ratios were similar to those in a solution copolymerization system. The overall activation energy was mainly determined by the activation energy of the pyrolytic reaction of the initiator.

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