Monomer Apparent Reactivity Ratios for Acrylonitrile/Methyl Vinyl Ketone Copolymerization System

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ABSTRACT: Methyl vinyl ketone was firstly used to successfully copolymerize with acrylonitrile. This was achieved by using azobisisobutyronitrile as the initiator, and dimethyl sulfoxide as the solvent. Effect of copolymerization systems on monomer apparent reactivity ratios for copolymer of acrylonitrile with methyl vinyl ketone was studied for contrast. Values of monomer apparent reactivity ratios were calculated by Kelen–Tudos method. It has been found that the apparent reactivity ratios in aqueous suspension polymerization system were similar to those in solution polymerization system at polymerization conversion less than 20%. Beyond 50% of conversion, the changes of monomer apparent reactivity ratios become less prominent. In water-rich reaction medium [(H$_2$O/dimethylsulfoxide (DMSO)>80/20), monomer apparent reactivity ratios were approximately equivalent to those in aqueous suspension polymerization system. In DMSO-rich reaction medium (DMSO/H$_2$O > 80/20), apparent reactivity ratios were similar to those in solution polymerization system. Values of apparent reaction ratios both decreased when AN/MVK copolymer was synthesized in DMF and DMAc. The values of apparent reaction ratios gradually tend to 1 with increasing the copolymerization temperature. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4045–4048, 2006

Key words: copolymerization; kinetics; reactivity ratio; fibers

INTRODUCTION

Knowledge of copolymer's composition is an important factor in the evaluation of its utility. The theory of radical copolymerization leads to the conclusion that the copolymer composition and its distribution are dependent on the monomer reactivity ratios. Reactivity ratio values may be evaluated by various procedures: linear procedures, nonlinear procedures, and other copolymer composition equations.[1–3] Kelen–Tudos method has been widely used.[4] Suitable comonomers are used to synthesize acrylic polymers that satisfy the requirements for high-tenacity acrylic fibers. The interaction of a few percentage points of the comonomers generally enhances the spinnability and depresses the onset of cylization temperature during oxidation.[5–7] To our knowledge, there are only a few reports on methyl vinyl ketone (MVK) as a comonomer, but there are almost no reports on monomer apparent reactivity ratios for copolymer of acrylonitrile (AN) with MVK in different copolymerization systems. In this study, different polymerization techniques were used to synthesize AN/MVK copolymer. To estimate the monomer reactivity ratios, copolymerization experiments were terminated at less than 10% conversion. The conversion was controlled and determined by gravimetric measurements. Elemental analyses were carried out by a PE2400 microanalyzer. Kelen–Tudos method was also employed. Effects of different copolymerization conditions on monomer apparent reactivity ratios for AN/MVK copolymer were studied for contrast.

EXPERIMENTAL

Materials

AN (Shanghai Chemical Reagents Co., A.R. grade) was vacuum distilled from CaH$_2$ just before polymerization. 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 suspending agent. Deionized water and di-

TABLE I
Solution Copolymerization Parameters
of AN/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

Condition: [AN] = 4.15 mol/L; [AIBN] = 0.008 mol/L; time: 20min; temperature: 60°C.

methyl sulfoxide (DMSO) or dimethyl formamide (DMF) were adopted as the polymerization medium.

Polymerization

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. 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, and then weighed.

Characterization

Elemental analyses of the copolymers were carried out with PE2400 microanalyzer to determine the oxygen content of these copolymers. The monomer reactivity ratios for copolymerization of AN and MVK were determined from the monomer feed ratios and the copolymer composition. The apparent reactivity ratios of AN and MVK were calculated from the following equation, using Kelen–Tudos method

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

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

where x is the ratio of molar fractions of monomer AN and monomer MVK in the monomer feed, y is the ratio of molar fractions of monomer AN and monomer MVK in the copolymer, and a is an equation parameter. The equation parameter can be computed according to the following equation

$$a = \frac{x_{min}x_{max}}{\sqrt{y_{min}y_{max}}} \quad (2)$$

where x_{min}, x_{max} are minimal and maximal molar fractions in the monomer feed, respectively. y_{min}, y_{max} are minimal and maximal molar fraction in the copolymer.

Equation (1) can be transformed into

$$\tau = (r_{AN} + r_{MVK}/a)\delta - \frac{r_{MVK}}{a} \quad (3)$$

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

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

RESULTS AND DISCUSSION

Reactivity ratios in solution polymerization system

Solution polymerization technique was used to synthesize AN/MVK copolymer. Table I shows some important parameters and the polymerization conditions of the copolymer. It has been found that pure AN/MVK copolymers have been obtained successfully. Kelen–Tudos method gave monomer apparent reactivity ratios for AN and MVK of $r_{AN} = 0.576$, $r_{MVK} = 3.32$ (Fig. 1), which is a criteria to judge other results. The higher reactivity ratio value of MVK confirms its high reactivity when compared with that of AN. The polymer radical with a MVK unit at the chain end is considerably more active than with an AN unit, and the probability of MVK entry into the chain is greater than that of AN entry, which leads to an increase in polymerization conversion with the addition of MVK comonomer.

Reactivity ratios in aqueous suspension polymerization system

Apparent reactivity ratios of AN and MVK in aqueous suspension polymerization system was also calculated by Kelen–Tudos method. The experimental results are
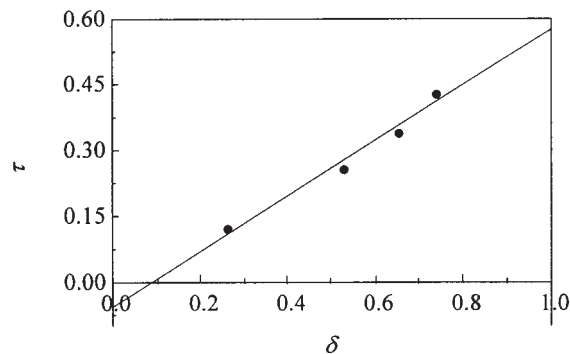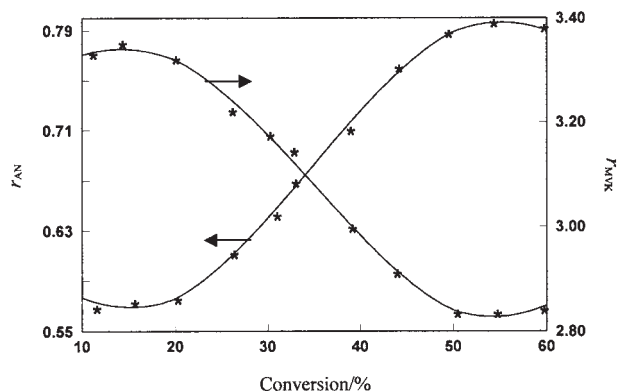

Figure 1 Relationship between τ and δ.

Figure 2 Effect of conversion on monomer reactivity ratios in aqueous suspension polymerization system. Condition: [AN] = 4.15 mol/L; [AIBN] = 0.008 mol/L; [PVA] = 0.22 g/L; temperature: 60°C.

given in Figure 2. When the monomer conversion is less than 20%, the values of monomer apparent reactivity ratios in aqueous suspension polymerization system are similar to those in solution polymerization system, r_{AN} = 0.576 ± 0.002, r_{MVK} = 3.32 ± 0.02. With an increase in monomer conversion, reactivity ratio for AN rises rapidly and that for MVK reduces quickly. When conversion is more than 50%, the changes of monomer reactivity ratios become less prominent, r_{AN} = 0.789 ± 0.002, r_{MVK} = 2.84 ± 0.01. When AN/MVK copolymer is synthesized using aqueous 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 or the oligomeric radicals phase.[8,9] As polymerization conversion goes beyond 20%, propagation would then mostly occur in oligomeric radicals phase. AN units are more easily absorbed by polymer radicals than MVK units. The value of reactivity ratio for AN rises rapidly.

Effect of mixture solution on reactivity ratios

Effect of mixture solution on apparent reactivity ratios of monomers was also studied. AN/MVK copolymer was synthesized by solvent water suspension polymerization technique. According to the results summarized in Table II, in water-rich reaction medium (H$_2$O/DMSO > 80/20), values of monomer apparent reactivity ratios are similar to those in aqueous suspension polymerization system; in DMSO-rich reaction medium (DMSO/H$_2$O > 80/20), values of monomer reactivity ratios are similar to those in solution polymerization system. When AN/MVK copolymer is synthesized using solvent water suspension technique, after a definite time, 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.[10,11] In water-rich reaction medium, propagation would then occur either in water phase or the oligomeric radicals phase. In DMSO-rich reaction medium, propagation would then occur in DMSO phase.

Effect of solvent polarity on reactivity ratios

To study the effect of solvent polarity on apparent reactivity ratios of monomers, AN/MVK copolymer was synthesized in N,N-dimethyllformamide (DMF) and N,N-dimethylacetamide (DMAc) by solution polymerization technique, respectively. Previous articles reported that effect of solvent polarity on reactivity ratios may be not obvious.[12,13] But in this study, different conclusions are drawn, r_{AN} = 0.495, r_{MVK} = 2.98 in DMF; and r_{AN} = 0.506, r_{MVK} = 3.12 in DMAc. Both r_{AN} and r_{MVK} decrease when compared with those in DMSO. Solubility and activity of monomer AN, MVK, and the polymer radicals are different in different polar solvents. The concentrations of AN and MVK in local area are lower than those in the monomer feed. The reactivity ratios of AN and MVK were calculated using concentrations in the monomer feed instead of those in local area. In fact, what we calculated are called the apparent reactivity ratios.

Effect of polymerization temperature on reactivity ratios

Effect of polymerization temperature on comonomer reactivity ratios was also examined, which is given in Table III. AN/MVK copolymer was synthesized in DMSO at different temperatures by solution polymerization technique. According to the characterizing definition of reactivity ratio,[13] the values of reactivity ratios tend to 1 and copolymerization tends to ideal copolymerization as polymerization temperature rising. Table III shows that r_{AN} increases from 0.562 to

TABLE II
Reactivity Ratios Parameters in H2O/DMSO Mixture Solvent Medium

H$_2$O/DMSO (w/w)	r_{AN}	r_{NVP}
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

Condition: [AN] = 4.15 mol/L; [AIBN] = 0.008 mol/L; [PVA]= 0.22 g/L; time: 20 min; temperature: 60°C.

TABLE III
Effect of Polymerization Temperature
on Reactivity Ratio

Temperature (°C)	r_{AN}	r_{NVP}
58	0.562	3.46
60	0.576	3.32
65	0.589	3.17
70	0.605	2.98
75	0.617	2.81

Condition: [AN] = 4.15 mol/L; [AIBN] = 0.008 mol/L; time: 20 min.

0.617 and r_{MVK} decreases from 3.46 to 2.81 when polymerization temperature rises from 58 to 75°C, which is consistent with theoretic derivation.

CONCLUSIONS

Laboratory studies of different copolymerization systems of AN with MVK have shown that monomer apparent reactivity ratios in a system depend on the method of polymerization and the medium and temperature of polymerization. Monomer apparent reactivity ratios in aqueous suspension polymerization system were similar to those in solution polymerization system when polymerization conversion is less than 20%. When conversion was more than 50%, the changes of monomer reactivity ratios became less prominent. In water-rich reaction medium, monomer reactivity ratios were about equivalent to those in aqueous suspension polymerization system. Values of both reaction ratios decreased when AN/MVK copolymer was synthesized in DMF by solution polymerization technique. The copolymerization tended toward ideal copolymerization and values of reaction ratios gradually tended toward 1 as the copolymerization temperature increased.

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