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Determination of monomer apparent reactivity ratios for acrylonitrile-acrylamide copolymerization system

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Effect of copolymerization systems on monomer apparent reactivity ratios for copolymer of acrylonitrile with acrylamide 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 18% [reactivity ratio of acrylonitrile (r_{AN}) = 0.398 ± 0.004, reactivity ratio of acrylamide (r_{AM}) = 2.61 ± 0.02]. As conversion of more than 60%, the changes of monomer apparent reactivity ratios become less prominent ($r_{AN} = 0.651 \pm 0.008$, $r_{AM} = 1.98 \pm 0.01$). In water-rich reaction medium [(H_2O/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_2O > 80/20), apparent reactivity ratios were similar to those in solution polymerization system. With an increase of polarity of solvent, values of apparent reaction ratios both decreased. The values of apparent reaction ratios gradually tend to 1 with increasing the copolymerization temperature. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Knowledge of copolymer's composition is an important factor in the evaluation of its utility. The theory of radical copolymerization leads 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. To our knowledge, there are only a few reports on acrylamide (AM) as a comonomer, but there are almost no reports on monomer apparent reactivity ratios for copolymer of acrylonitrile (AN) with AM in different copolymerization systems. In this study, different polymerization techniques were used to synthesize AN/AM copolymer. To estimate themonomer reactivity ratios, copolymerization experiments were terminated at less than 15% 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. The effects of different copolymerization conditions on monomer apparent reactivity ratios for copolymer of AN with AM were studied for contrast. The most optimum copolymerization conditions and AN/AM copolymer composition for high-tenacity acrylic fibers can be obtained by the monomer apparent reactivity ratios.

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2. Experimental

2.1. Materials

Monomers AN was industrial polymerization grade and distilled to remove inhibitors before use. AM was analytic grade and 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 dimethyl sulphoxide (DMSO) or dimethyl formamide (DMF) were adopted as the polymerization medium.

2.2. Polymerization

Required amounts of AN, AM, PVA, AIBN, deionized water, DMSO or DMF 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.

2.3. 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 AM were determined from the monomer feed ratios and the copolymer composition. The apparent reactivity ratios of AN and AM were calculated by Kelen-Tudos method from Equation 1.

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

$$x = \frac{M_{\mathrm{AN}}}{M_{\mathrm{AM}}}(\mathrm{mol/mol}), \qquad (1)$$

$$y = \frac{\mathrm{d}M_{\mathrm{AN}}}{\mathrm{d}M_{\mathrm{AM}}}(\mathrm{mol/mol})$$

where x is the ratio of molar fractions of monomer AN and monomer AM in the monomer feed, y is the ratio of molar fractions of monomer AN and monomer AM in the copolymer, and a is an equation parameter. The equation parameter can be computed according to Equation 2:

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

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.

Transform Equation 1 into the form:

$$\tau = (r_{\mathrm{AN}} + r_{\mathrm{AM}}/a)\xi - \frac{r_{\mathrm{AM}}}{a}$$

$$\tau = \frac{x(y-1)}{ay+x^2}, \quad \xi = \frac{x^2}{ay+x^2} \qquad (3)$$

TABLE I Solution copolymerization parameters of AN with AM in DMSO

AN/AM (w/w)	x (mol/mol)	Conversion (wt%)	Content of oxygen (wt%)	y (mol/mol)
98/2	102.62	9.6	0.721	40.52
95/5	39.79	10.8	1.773	15.69
92/8	24.08	12.2	2.788	9.487
90/10	18.85	14.3	3.447	7.418

Condition: (AN) = 4.15 mol/L; (AIBN) = 0.008 mol/L; temperature 60°C.

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

3. Results and discussion

3.1. Reactivity ratios in solution polymerization system

Solution polymerization technique was used to synthesize AN/AM copolymer. Table I shows some important parameters and the polymerization conditions of the copolymer. Kelen-Tudos method gave monomer apparent reactivity ratios for AN and AM of $r_{\mathrm{AN}} = 0.395$, $r_{\mathrm{AM}} = 2.60$ (Fig. 1), which is a criteria to judge other results. The higher reactivity ratio value of AM confirms its high reactivity compared with that of AN. The polymer radical with a AM unit at the chain end is considerably more active than with an AN unit, and the probability of AM entry into the chain is greater than that of AN entry, which leads to an increase of polymerization conversion with the addition of AM comonomer (Table I).

3.2. Reactivity ratios in aqueous suspension polymerization system

Apparent reactivity ratios of AN and AM in aqueous suspension polymerization system was also calculated by Kelen-Tudos method. The experimental results are given in Fig. 2. At polymerization conversion less than 18%, the values of monomer apparent reactivity ratios in aqueous suspension polymerization

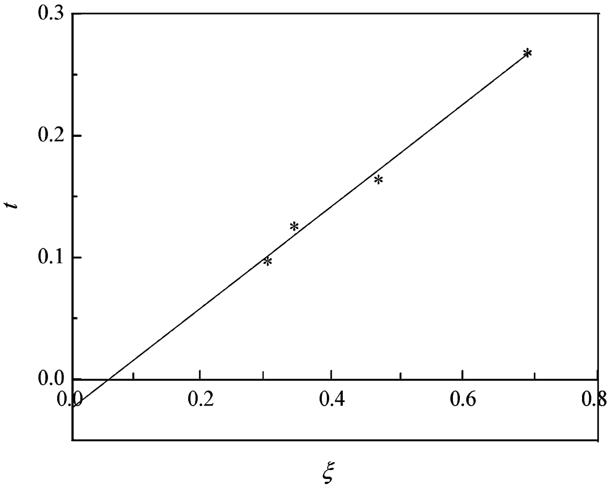

Figure 1 Relationship between τ and ξ.

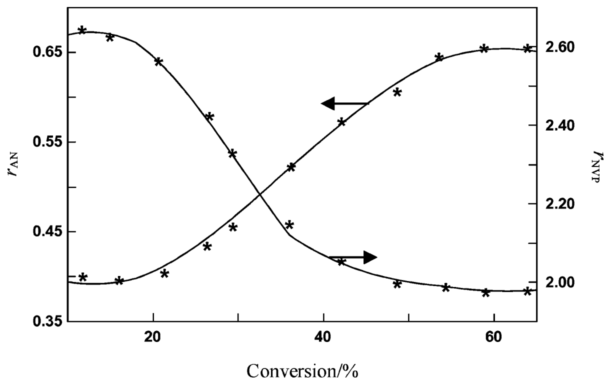

Figure 2 Relationship between reactivity ratios and conversion in aqueous suspension polymerization system. (Condition: (AN) = 4.15 mol/L; (AIBN) = 0.008 mol/L; (PVA) = 0.22 g/L; temperature 60°C).

system are similar to those in solution polymerization system, $r_{AN} = 0.398 \pm 0.004$, $r_{AM} = 2.61 \pm 0.02$. With an increase of polymerization conversion, reactivity ratio for AN rises rapidly and that for AM reduces quickly. When conversion is more than 60%, the changes of monomer reactivity ratios become less prominent, $r_{AN} = 0.651 \pm 0.008$, $r_{AM} = 1.98 \pm 0.01$. Apparent reactivity ratios of monomners in a system depend on the technique of polymerization. When AN/AM 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 [5, 6]. When conversion is less than 18%, polymerization follows more of the solution polymerization technique, reactivity ratios calculated are similar to those in solution polymerization system. As polymerization conversion increasing, propagation would then mostly occur in oligomeric radicals phase. AN units are more easily absorbed by polymer radicals than AM units. The value of reactivity ratio for AN rises rapidly.

3.3. Effect of mixture solution on reactivity ratios

Effect of mixture solution on apparent reactivity ratios of monomers was also studied. AN/AM copolymer was synthesized by solvent water suspension polymerization technique. According to the results summarized in Table II, in water-rich reaction medium (H_2O/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_2O > 80/20), values of monomer reactivity ratios are similar to those in solution polymerization system. When AN/AM 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 [7, 8]. In water-rich reaction medium, because of the insolubility oligomeric radicals, Propagation follows the suspension polymerization technique more. In DMSO-rich reaction medium, copolymerization follows the solution polymerization technique more.

TABLE II Reactivity ratios parameters in H_2O/DMSO mixture solvent medium

H_2O/DMSO (w/w)	r_{AN}	r_{NVP}
90/10	0.650	1.96
80/20	0.647	1.94
60/40	0.601	2.05
50/50	0.535	2.21
40/60	0.488	2.38
20/80	0.403	2.59
10/90	0.398	2.62

Condition: (AN) = 4.15 mol/L; (AIBN) = 0.008 mol/L; (PVA) = 0.22 g/L; temperature 60°C.

3.4. Effect of solvent polarity on reactivity ratios

In order to study the effect of solvent polarity on apparent reactivity ratios of monomers, AN/AM copolymer was synthesized in DMF by solution polymerization technique. Previous articles reported that effect of solvent polarity on reactivity ratios may be not obvious [9, 10]. But in this study, different conclusions are drawn, $\mathrm{r}_{AN} = 0.377$, $r_{AM} = 2.31$. Both r_{AN} and r_{AM} decrease compared with those in DMSO. Solubility and activity of monomer AN, AM and the polymer radicals are different in different polar solvent. The concentrations of AN and AM in local area are lower than those in the monomer feed. The reactivity ratios of AN and AM 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.

3.5. 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/AM copolymer was synthesized in DMSO at different temperature by solution polymerization technique. According to the characterizing definition of reactivity ratio [10], 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 0.384 to 0.512 and r_{AM} decreases from 2.71 to 1.87 when

TABLE III Effect of polymerization temperature on reactivity ratio

Temperature(°C)	r_{AN}	r_{NVP}
58	0.384	2.71
60	0.395	2.60
65	0.421	2.44
70	0.452	2.08
75	0.512	1.87

Condition: (AN) = 4.15 mol/L; (AIBN) = 0.008 mol/L.

polymerization temperature rises from 58 to 75°C, which is consistent with theoretic derivation.

4. Conclusions

Laboratory studies of different copolymerization systems of AN with AM 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 as polymerization conversion less than 18%. When conversion was more than 60%, 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. With an increase of polarity of solvent, values of reaction ratios both decreased. The copolymerization tended toward ideal copolymerization and values of reaction ratios gradually tended toward 1 as the copolymerization temperature increased.

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