

Determination of the Reactivity Ratios for Acrylonitrile/*N*-Vinylpyrrolidone Copolymerization Systems

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Received 20 June 2002; accepted 7 August 2002

ABSTRACT: The effects of the copolymerization system on the monomer reactivity ratios for a copolymer of acrylonitrile with *N*-vinylpyrrolidone was studied for contrast. The values of the monomer reactivity ratios were calculated by the Kelen–Tudos method. The reactivity ratios in the aqueous suspension polymerization system were similar to those in the solution polymerization system at polymerization conversions of less than 6% [reactivity ratio of acrylonitrile (r_{AN}) = 0.438 ± 0.015 , reactivity ratio of *N*-vinylpyrrolidone (r_{N-VP}) = 2.28 ± 0.02]. As conversion of more than 12%, the changes in the monomer reactivity ratios became less prominent (r_{AN} = 0.651, r_{N-VP} = 1.98). In the water-rich

reaction medium [H_2O /dimethylsulfoxide (DMSO) > 60/40], the monomer reactivity ratios were approximately equivalent to those in the aqueous suspension polymerization system. In the DMSO-rich reaction medium (DMSO/ H_2O > 60/40), the reactivity ratios were similar to those in the solution polymerization system. With an increase in the polarity of the solvent, the values of the reaction ratios both decreased. The values of the reaction ratios gradually tended toward 1 with increasing copolymerization temperature. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 422–425, 2003

Key words: copolymerization; kinetics; fibers

INTRODUCTION

Knowledge of a copolymer's composition is an important factor in the evaluation of its utility. A copolymer's composition and its distribution are dependent on its reactivity ratios. Reactivity ratio values may be evaluated by various procedures: linear procedures, nonlinear procedures, and other copolymer composition equations.^{1–3} The 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 the cyclization temperature during oxidation. It was reported in a Japanese special permission bulletin 48-28986 that carbon fiber prepared from the acrylonitrile (AN)/*N*-vinylpyrrolidone (*N*-VP) copolymer precursors has an average tensile strength of about 6800 MPa.⁵ To our knowledge, there are only a few reports on *N*-VP as a comonomer, but there are almost no reports on monomer ratios for copolymers of AN with *N*-VP in different copolymerization systems. In this study, different polymerization techniques were used to synthesize AN/*N*-VP copolymers. To estimate the monomer reactivity ratios, we terminated the copoly-

merization experiments at less than 15% conversion. The conversion was controlled and determined by gravimetric measurements. Elemental analyses were carried out with a PE2400 microanalyzer. The Kelen–Tudos method was used. The effects of different copolymerization conditions on the monomer ratios for copolymers of AN with *N*-VP were studied for contrast.

EXPERIMENTAL

Materials

AN and *N*-VP monomers were industrial polymerization grade and distilled to remove inhibitors before use. Azobisisobutyronitrile (AIBN) was used as initiator and was recrystallized from ethanol before use. Poly(vinyl alcohol) (PVA) was used as a suspending agent. Deionized water and dimethylsulfoxide (DMSO) or dimethylformamide (DMF) were used as the polymerization media.

Polymerization

Required amounts of AN, *N*-VP, PVA, AIBN, deionized water, DMSO, and 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 defined reaction time, the resultant mixture was poured into a large amount of methanol for

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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 oxygen content. The monomer reactivity ratios for the copolymerization of AN and *N*-VP were determined from the monomer feed ratios and the copolymer composition. The reactivity ratio of acrylonitrile (r_{AN}) and the reactivity ratio of *N*-vinylpyrrolidone (r_{N-VP}) were calculated by the Kelen–Tudos method [eq. (1)]:

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

where x is the ratio of the molar fractions of the AN and *N*-VP monomers in the monomer feed, y is the ratio of molar fractions of the AN and *N*-VP monomers in the copolymer, and a is an equation parameter. The equation parameter can be computed according to eq. (2):

$$a = x_{\min} x_{\max} / (y_{\min} y_{\max})^{0.5} \quad (2)$$

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

Eq. (1) transforms into the form:

$$\eta = (r_{AN} + r_{N-VP}/a)\xi - r_{N-VP}/a \quad (3)$$

where η is equal to $x(y - 1)/(ay + x^2)$ and ξ is equal to $x^2/(ay + x^2)$. The plot of η versus ξ gives a straight line. Extrapolation of the line to $\xi = 1$ gives r_{AN} , and $\xi = 0$ gives r_{N-VP}/a .

RESULTS AND DISCUSSION

Reactivity ratios in the solution polymerization system

The solution polymerization technique was used to synthesize the AN/*N*-VP copolymer. Table I shows some important parameters and the polymerization

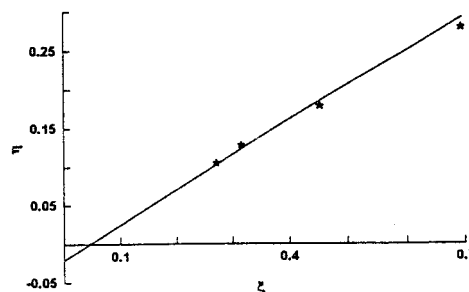


Figure 1 Relationship between η and ξ .

conditions of the copolymer. The Kelen–Tudos method gave monomer reactivity ratios of $r_{AN} = 0.446$ and $r_{N-VP} = 2.29$ (Fig. 1), which were used as criteria to judge other results. The higher reactivity ratio value of *N*-VP confirms its high reactivity compared with AN. The polymer radical with a *N*-VP unit at the chain end is considerably more active than that with an AN unit, and the probability of *N*-VP entry into the chain is greater than that of AN entry, which leads to an increase in the polymerization conversion with the addition of *N*-VP comonomer (Table I).

Reactivity ratios in the aqueous suspension polymerization system

The reactivity ratios of AN and *N*-VP in the aqueous suspension polymerization system were also calculated by the Kelen–Tudos method. The experimental results are given in Figure 2. At polymerization conversions less than 6%, the values of monomer reactivity ratios in the aqueous suspension polymerization system were similar to those in the solution polymerization system ($r_{AN} = 0.438 \pm 0.015$ and $r_{N-VP} = 2.28 \pm 0.02$). With increasing polymerization conversion, the reactivity ratio for AN rose rapidly, and that for *N*-VP decreased quickly. When conversion was more than 12%, the changes in the monomer reactivity ratios became less prominent ($r_{AN} = 0.651$ and $r_{N-VP} = 1.98$). The reactivity ratios of the monomers in a system depend on the polymerization technique. When the AN/*N*-VP copolymer was synthesized with the aqueous suspension technique, oligomeric radicals may have formed in the initial stages of polymerization, which precipitated out after a certain critical

TABLE I
Solution Copolymerization Parameters of AN with *N*-VP in DMSO

AN/ <i>N</i> -VP (w/w)	x (mol/mol)	Conversion (%)	Oxygen content (wt %)	y (mol/mol)
98/2	102.62	9.6	0.6808	42.25
95/5	39.79	10.8	1.5881	16.91
92/8	24.08	11.2	2.1336	12.05
90/10	18.85	12.3	2.882	8.38

Conditions: [AN] = 4.15 mol/L; [AIBN] = 0.008 mol/L; temperature = 60°C.

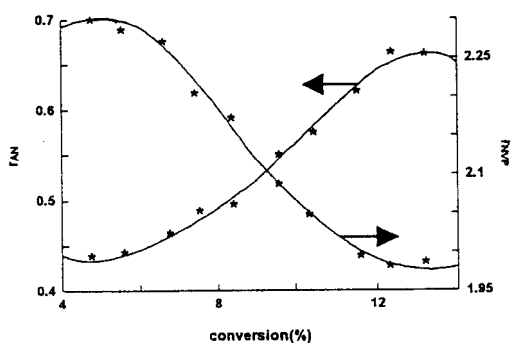


Figure 2 Relationship between reactivity ratios and conversion in the aqueous suspension polymerization system. Conditions: $[AN] = 4.15 \text{ mol/L}$, $[AIBN] = 0.008 \text{ mol/L}$, $[PVA] = 0.22 \text{ g/L}$, and temperature = 60°C .

molecular weight was attained and then acted as primary particles. Propagation would have then occurred either in the water phase or in the oligomeric radicals phase.^{6,7} When conversion was less than 6%, polymerization followed more of the solution polymerization technique; the reactivity ratios we calculated were similar to those in the solution polymerization system. As polymerization conversion increased, propagation then mostly occurred in the oligomeric radicals phase. AN units are more easily absorbed by polymer radicals than *N*-VP units. The value of reactivity ratio for AN rose rapidly.

Effect of the mixture solution on the reactivity ratios

The effect of the mixture solution on the reactivity ratios of the monomers was also studied. The AN/*N*-VP copolymer was synthesized by the solvent water suspension polymerization technique. According to the results summarized in Table II, in the water-rich reaction medium ($\text{H}_2\text{O}/\text{DMSO} > 60/40$), the values of the monomer reactivity ratios were similar to those in the aqueous suspension polymerization system; in the DMSO-rich reaction medium ($\text{DMSO}/\text{H}_2\text{O} > 60/40$), the values of the monomer reactivity ratios were similar to those in the solution polymerization system. When the AN/

TABLE II
Reactivity Ratio Parameters in the $\text{H}_2\text{O}/\text{DMSO}$
Mixture Solvent Medium

$\text{H}_2\text{O}/\text{DMSO}$ (v/v)	r_{AN}	r_{N-VP}
90/10	0.672	1.96
80/20	0.661	2.05
60/40	0.634	2.13
50/50	0.523	2.15
40/60	0.487	2.21
20/80	0.451	2.27
10/90	0.441	2.32

Conditions: $[AN] = 4.15 \text{ mol/L}$; $[AIBN] = 0.008 \text{ mol/L}$; $[PVA] = 0.22 \text{ g/L}$; temperature = 60°C .

TABLE III
Effect of Polymerization Temperature
on the Reactivity Ratios

Temperature ($^\circ\text{C}$)	r_{AN}	r_{N-VP}
58	0.424	2.35
60	0.446	2.29
65	0.489	2.04
70	0.573	1.88
75	0.704	1.57

Conditions: $[AN] = 4.15 \text{ mol/L}$; $[AIBN] = 0.008 \text{ mol/L}$; temperature = 60°C .

N-VP copolymer is synthesized with the solvent water suspension technique, after a defined time propagation occurs either in the water phase, in the DMSO phase, in the oligomeric radicals phase, or at the interface of the DMSO–water–oligomer mixture, depending on the solubility of monomers.^{8,9} In the water-rich reaction medium ($\text{H}_2\text{O}/\text{DMSO} > 60/40$), because of the insolubility of oligomeric radicals, propagation followed the suspension polymerization technique more. In the DMSO-rich reaction medium ($\text{DMSO}/\text{H}_2\text{O} > 60/40$), copolymerization followed the solution polymerization technique more.

Effect of the solvent polarity on the reactivity ratios

To study the effect of the solvent polarity on the reactivity ratios of the monomers, the AN/*N*-VP copolymer was synthesized in DMF by the solution polymerization technique. Previous articles reported that effect of the solvent polarity on the reactivity ratios may be not obvious.^{10,11} However, in this study, we drew different conclusions ($r_{AN} = 0.427$ and $r_{N-VP} = 1.85$). Both r_{AN} and r_{N-VP} decreased compared with those in DMSO. The solubility and activity of the AN and *N*-VP monomers and the polymer radicals were different in different polar solvents. The concentrations of AN and *N*-VP in the local area were lower than those in the monomer feed. The reactivity ratios of AN and *N*-VP were calculated with concentrations in the monomer feed instead of those in local area. In fact, what we calculated are called the apparent reactivity ratios.

Effect of the polymerization temperature on the reactivity ratios

The effect of the polymerization temperature on the comonomer reactivity ratios was also examined (see Table III). The AN/*N*-VP copolymer was synthesized in DMSO at different temperatures by the solution polymerization technique. According to the characterizing definition of *reactivity ratio*,¹¹ values of reactivity ratios tend toward 1, and copolymerization tends toward the

ideal copolymerization as the polymerization temperature rises. Table III shows that r_{AN} increased from 0.424 to 0.704 and r_{N-VP} decreased from 2.35 to 1.57 when the polymerization temperature rose from 58 to 75°C, which was consistent with the theoretic derivation.

CONCLUSIONS

Laboratory studies of different copolymerization systems of AN with N-VP showed that the monomer reactivity ratios in a system depend on the method of polymerization, the medium, and the temperature of polymerization. Monomer reactivity ratios in aqueous suspension polymerization system were similar to those in the solution polymerization system at polymerization conversion of less than 6%. When the conversion was more than 12%, the changes in the monomer reactivity ratios became less prominent. In the water-rich reaction medium ($H_2O/DMSO > 60/40$), the monomer reactivity ratios were about equivalent to those in the aqueous suspension polymerization system. With increasing polarity of the solvent, the

values of the reaction ratios both decreased. The copolymerization tended toward ideal copolymerization, and values of the reaction ratios gradually tended toward 1 as the copolymerization temperature increased.

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