

Monte Carlo Simulation of Sequence Distributions of Acrylonitrile Copolymers

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ABSTRACT: A Monte Carlo simulation examining the effect of monomer ratios on the composition and sequence distribution of acrylonitrile (AN) copolymers with *N*-vinyl pyrrolidone (NVP), itaconic acid (IA), and acrylic acid (AA) as comonomers has been developed. The Kelen–Tudos method was used to estimate monomer reactivity ratios. The results of the simulation are consistent with the academic conclusion and are as foreseen by the experimental data. The average number of NVP identical monomers in a sequence length of AN/NVP copolymer chain increases continuously and the average number of AN identical monomers in a

sequence length shows a prominent decrease with an increase of NVP concentration in the feed. Changes in the monomer average number of AN/IA and AN/AA copolymers in a sequence length were the same as those of AN/NVP copolymer with an increase of comonomer concentration in the feed. The optimum weight ratio of AN with comonomers for manufacturing carbon fibers is 98/2. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 483–488, 2005

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INTRODUCTION

Knowledge of copolymer composition is an important step in the evaluation of their utility. Copolymer composition and its distribution are dependent on monomer reactivity ratios.¹ Reactivity ratio values may be evaluated by various procedures: linear, nonlinear, and other copolymer composition equations.^{2–4} The Kelen–Tudos method has been widely used.⁵ The properties of the final carbon fibers are determined by the nature of the acrylic precursor fibers.⁶ Selection of a suitable comonomer for synthesis of acrylic polymers satisfying the requirements for acrylic precursors is very important. The interaction of a few percent of the comonomers generally enhances the spinnability and depresses the onset of cyclization temperature during oxidation.^{7–10} The Monte Carlo method is advanced and has been widely used in polymer science.¹¹ To our knowledge, early studies were just empirical attempts to correlate copolymerization variables with the final properties of acrylonitrile (AN) copolymers,^{12,13} with a little investigation into the kinetics of AN copolymerization by the Monte Carlo method,¹⁴ and there are almost no reports on Monte Carlo simulation of composition and sequence

distribution of AN copolymers. In this study, *N*-vinyl pyrrolidone (NVP), itaconic acid (IA), and acrylic acid (AA) were used as comonomers, respectively. The dimethyl sulfoxide (DMSO) solution copolymerization technique was used to prepare AN copolymers. Many possible designs of monomer ratios in copolymerization process were applied. The Kelen–Tudos method was used to estimate monomer reactivity ratios. The Monte Carlo simulation was first used to examine the effect of monomer ratios on the composition and sequence distribution of AN copolymer.

EXPERIMENTAL

Materials

Monomer AN was industrial polymerization grade and distilled to remove inhibitors before use. Comonomers NVP, IA, and AA were analytical grade. Azo-bis(isobutyronitrile) (AIBN) was used as initiator and recrystallized from ethanol before use. DMSO was adopted as the polymerization medium.

Copolymer preparation

Required amounts of AN, NVP (or IA, AA), AIBN, and DMSO were placed in a glass 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.

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The resultant mixture was poured into a large amount of methanol for precipitation, washed with methanol several times, and dried at 60°C under vacuum until it reached a constant weight. Copolymer samples were then obtained.

Elemental analysis

Elemental analysis of AN copolymers was carried out using a PE2400 elemental analyzer to determine oxygen content in these copolymers. The copolymer composition can be calculated with regard to oxygen content in these copolymers.

Determination of monomer reactivity ratios

Reactivity ratio values may be evaluated by various procedures: linear, nonlinear, and other copolymer composition equations. The Kelen–Tudos method has been widely used and the operation is easy.¹⁵ In this method, the monomer reactivity ratios for copolymerization of AN and comonomer were determined from the monomer feed ratios and the copolymer composition. The reactivity ratios of AN and comonomer were calculated using the Kelen–Tudos method from Eq. (1),

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

$$x = \frac{M_{AN}}{M_{comonomer}} \text{ (mol/mol)}, y = \frac{dM_{AN}}{dM_{comonomer}} \text{ (mol/mol)}, \quad (1)$$

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

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

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

Transform Eq. (1) into the form

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

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

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

Monte Carlo simulation

According to the binary copolymerization with end effect, the composition and sequence distribution of AN copolymers were systematically investigated using the Monte Carlo method. A working hypothesis must be established that copolymerization of AN with

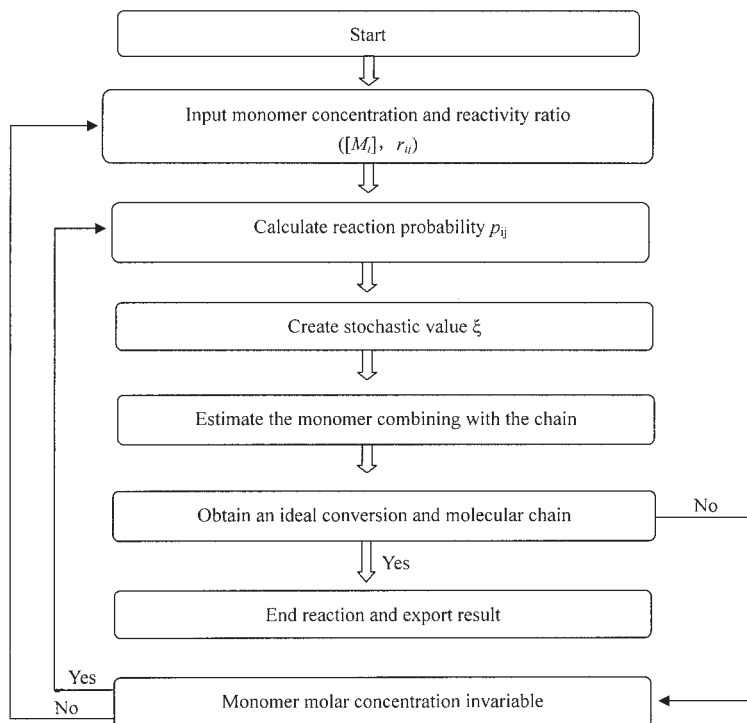


Figure 1 Flow chart of the Monte Carlo simulation program.

TABLE I
Copolymerization Parameters of AN with NVP

AN/NVP/(w/w)	x/(mol/mol)	Conversion/wt %	Content of oxygen/wt %	y/(mol/mol)
98/2	102.62	9.6	0.708	40.52
95/5	39.79	10.8	1.697	15.69
92/8	24.08	12.2	2.607	9.487
90/10	18.85	14.3	3.174	7.418

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

NVP, IA, and AA is steady and irreversible. Another assumption that is taken into account is that the rate of propagation of copolymer chain length is directly proportional to the monomer concentration to the one power. For Monte Carlo simulation, copolymerization experiments were terminated at less than 10% conversion.

Propagation of the reaction will proceed through the successive addition of monomer to the radicals.¹⁶ The type of process can be expressed in the following form,



where the free radical that is propagating is denoted by $\sim M_i\cdot$, and the rate constant of reaction is denoted by k_{ij} . If this is the case, p_{11} p_{12} is equal to the proportion of $\sim M_1\cdot$ combining with M_1 and M_2 , respectively. p_{21} p_{22} is equal to the proportion of $\sim M_2\cdot$ combining with M_1 and M_2 , respectively,

$$p_{11} = \frac{k_{11}[M_1\cdot][M_1]}{k_{11}[M_1\cdot][M_1] + k_{12}[M_1\cdot][M_2]} = \frac{r_1[M_1]}{r_1[M_1] + [M_2]} \quad (8)$$

$$p_{12} = 1 - p_{11} \quad (9)$$

$$p_{21} = \frac{[M_1]}{[M_1] + r_2[M_2]}, \quad (10)$$

$$p_{22} = 1 - p_{21} \quad (11)$$

where $[M_i]$ is the monomer molar concentration in the feed, and r_i is the monomer reactivity ratio.

Figure 1 shows a flow chart of the Monte Carlo simulation program using the computer. The Monte Carlo simulation program is composed of the following steps:

(a) Assume that the first unit of the copolymer molecular chain that is propagating is $\sim M_i\cdot$, p_{ij} is calculated based on $[M_i]$ and r_i .

(b) A stochastic value ξ is generated in a unit range.

(c) According to $p_{i1} + p_{i2} = 1$, if ξ is in the range of $\xi < p_{i1}$, the copolymer molecular chain which is propagating combines M_1 ; if ξ is in the range of $p_{i1} = \xi < 1$, the copolymer molecular chain which is propagating combines M_2 . If the monomer molar concentration in the system does not undergo any change during the process, simulation continues from step b; but if the monomer molar concentration in the system varies along with the process, and the monomer molar concentration $[M_i]$ in the system is calculated over again, simulation continues from step a.

(d) The above steps are executed by repetition until an ideal conversion and copolymer molecular chain length is obtained. The obtained data are analyzed statistically.

The above simulation is carried out 10,000 times and the average value with regard to the results simulated is obtained. The maximal, minimal, and average numbers of the identical monomer in a sequence length of the AN copolymer chain are also simulated by the Monte Carlo method.

Academic calculation of copolymer composition

AN copolymer composition is directly related to monomer concentration in the feed and also to the

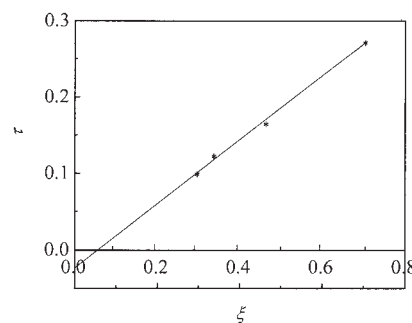


Figure 2 Relationship between τ and ξ .

TABLE II
Reactivity Ratios of AN and Comonomers

AN/NVP		AN/IA		AN/AA	
r_{AN}	r_{NVP}	r_{AN}	r_{IA}	r_{AN}	r_{AA}
0.395	2.60	0.575	2.05	0.495	2.50

monomer reactivity ratios by the classical polymerization theory.¹⁷ To calculate AN copolymer composition, the steady state is normally employed. Therefore, a steady-state concentration is assumed for both species $\sim M_1^\bullet$ and $\sim M_2^\bullet$, separately. The interconversion between the two species must be equal in order for the concentrations of each to remain constant, and hence the rates of reactions, Eqs. (5) and (6), must be equal. Another working hypothesis must be established that copolymerization of AN with NVP, IA, and AA is irreversible and the chemical activity of the free radical propagating chain is determined not by the chain length but by the end unit. Another assumption is that degree of polymerization of AN copolymer is so great that the effect of the two main kinetic steps, initiation and termination, during polymerization on copolymer composition is less obvious.

The most familiar form of the copolymer composition equation is obtained as

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \quad (12)$$

The copolymer composition equation can also be expressed in mole fractions instead of concentrations, which helps to make the equation more useful for experimental studies. To put the equation into these terms, F_1 and F_2 are the mole fractions of M_1 and M_2 in the copolymer, and f_1 and f_2 are the mole fractions of monomers M_1 and M_2 in the feed. Therefore,

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \quad (13)$$

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad (14)$$

Then, combining Eqs. (12), (13), and (14) gives

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (15)$$

This form of the copolymer equation gives the mole fraction of AN in the copolymer.

RESULTS AND DISCUSSION

Monomer reactivity ratios

The solution polymerization technique was used to synthesize AN/NVP copolymer. For estimating monomer reactivity ratios, copolymerization experiments were terminated at less than 15% conversion. The conversion was controlled and determined by gravimetric measurements. Table I shows some important parameters and polymerization conditions of the copolymer. The Kelen-Tudos method gave monomer reactivity ratios for AN and NVP of $r_{AN} = 0.395$, $r_{NVP} = 2.60$ (Fig. 2). The higher reactivity ratio value of NVP confirms its high reactivity compared with that of AN. The polymer radical with a NVP unit at the chain end is considerably more active than with an AN unit. Monomer reactivity ratios in the AN/IA, AN/AA copolymerization systems, which are shown in Table II, were also determined using the Kelen-Tudos method.

Results of Monte Carlo simulation

Relationship between monomer ratios and copolymer composition

The effect of monomer ratios on AN copolymer composition was discussed. AN copolymer composition was calculated by the copolymer chain structure sim-

TABLE III
Comparison of the Results of Simulation with Academic Conclusions and the Experimental Data in Different Copolymerization Systems

System	Monomer ratio/(w/w)	f_1 /mol %	F_1 /mol %		
			Simulation	Academic conclusion	Experimental data
AN/NVP	98/2	0.990	0.978	0.975	0.976
	95/5	0.975	0.936	0.939	0.940
	92/8	0.960	0.902	0.904	0.905
AN/IA	98/2	0.992	0.985	0.986	0.984
	95/5	0.979	0.961	0.964	0.966
	92/8	0.966	0.937	0.942	0.940
AN/AA	98/2	0.985	0.968	0.970	0.968
	95/5	0.963	0.928	0.927	0.926
	92/8	0.940	0.884	0.883	0.885

TABLE IV
Effect of the Ratio of AN/NVP on Numbers of Monomers in a Sequence Length

Monomer ratio/ (w/w)	98/2		95/5		92/8	
	AN	NVP	AN	NVP	AN	NVP
Maximal number	139	2	93	2	91	4
Minimal number	1	1	1	1	1	1
Average number	41.5	1.0	15.7	1.1	10.6	1.2

ulated by the Monte Carlo method. The copolymer composition was also calculated by the academic theory. The experimental data of the copolymer composition were also obtained with regard to the oxygen content of these copolymers determined by a PE2400 elemental analyzer. It is evident from Table III that the results of the simulation are consistent with the academic conclusion and are as foreseen by the experimental data. The Monte Carlo simulation is actually a numerical implementation of the copolymerization theory, which leads to the good match observed between theory and simulation in Table III.

Effect of monomer ratios on sequence length distribution of AN copolymers

Another advantage of the Monte Carlo simulation is that there is more detailed information on the sequence distribution. The sequence length distribution is an important parameter for characterizing the properties of AN copolymers. The higher average sequence length indicates a larger number of the identical monomer in a sequence length and leads to high-performance carbon fibers. According to practical polymerization, the degree of polymerization is controlled at 1000 and the magnitude of copolymer chains simulated is 10,000. The sequence length distribution of copolymers AN/NVP, AN/IA, and AN/AA was simulated by the Monte Carlo method. Maximal, minimal, and average numbers of the identical monomer in a sequence length are shown in Tables IV, V, and VI, respectively.

From Table IV, the average number of NVP identical monomer in a sequence length of AN copolymer chain increases continuously and the average number

TABLE V
Effect of the Ratio of AN/IA on Numbers of Monomers in a Sequence Length

Monomer ratio/ (w/w)	98/2		95/5		92/8	
	AN	IA	AN	IA	AN	IA
Maximal number	101	1	99	2	65	3
Minimal number	1	1	1	1	1	1
Average number	62.8	1.0	26.9	1.1	16.8	1.1

TABLE VI
Effect of the Ratio of AN/AA on Numbers of Monomers in a Sequence Length

Monomer ratio/ (w/w)	98/2		95/5		92/8	
	AN	AA	AN	AA	AN	AA
Maximal number	134	2	96	3	79	4
Minimal number	1	1	1	1	1	1
Average number	32.0	1.1	13.9	1.1	8.8	1.2

of AN identical monomers in a sequence length shows a prominent decrease with an increase of NVP concentration in the feed. It is evident from Tables V and VI that changes in average number of AN and IA, AA in a sequence length are in the same mode with those of AN and NVP.

It is feasible to enhance the spinnability and depress the onset of cyclization temperature during oxidation of AN polymers by selecting a suitable comonomer, but AN average number in a sequence length always shows a prominent decrease with an increase in the comonomer concentration, which reduces the properties of the resulting carbon fibers. When the weight ratio of AN with comonomer is 98/2, the average numbers of AN and comonomer in a sequence length are relatively ideal for manufacturing carbon fibers.

CONCLUSIONS

AN copolymers with NVP, IA, and AA as comonomers were synthesized using the DMSO solution polymerization technique. Monomer reactivity ratios in the different copolymerization systems were determined using the Kelen-Tudos method. The composition and sequence distribution of AN copolymers were simulated by the Monte Carlo method. The effect of monomer ratios on the composition and sequence distribution of AN copolymers was discussed. The Monte Carlo simulation is confirmed as being valid by comparison with academic conclusions and the experimental data. With an increase of NVP concentration in the feed, NVP average number in a sequence length increases continuously and AN average number in a sequence length shows a prominent decrease. Changes of average number of AN and IA, AA in a sequence length were in the same mode with those of AN and NVP with an increase of comonomer concentration in the feed. When the ratio of AN with comonomer is 98/2, the average numbers of AN and comonomer in a sequence length are relatively ideal for manufacturing carbon fibers.

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