Monte Carlo Study of Binary Copolymerizations. 1. Ultimate and Penultimate Effect, Applications

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Monte Carlo Study of Binary Copolymerizations.
1. Ultimate and Penultimate Effect, Applications

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ABSTRACT

The Monte Carlo models of binary irreversible copolymeriza-
tion with ultimate and penultimate effect are applied to the
copolymerization of acrylic acid and methyl acrylate, and
styrene and benzylidene malononitrile, respectively. The
agreement with available experimental data is quite good.
A comparative study between the formal kinetics model and
the Monte Carlo model reveals that statements concerning the
copolymer composition are robust, but statements concerning
the sequence distribution are not always robust.

INTRODUCTION

In previous papers we have proposed and tested Monte Carlo
models for binary irreversible copolymerization reactions with ulti-
mate [1, 2] and penultimate [3, 4] effects kinetics (for a recently
published review on Monte Carlo applications to study the polymers
microstructure, see Ref. 5).
The Monte Carlo models are easy to formulate and to implement.
They have at least two important advantages: they take into account

the conversion in a quite simple manner and visualize the relative distribution of the mers in macromolecule.

The quality of Monte Carlo computations strongly depends upon the size of the used sample (in our case polymerization degree, N; $N \simeq 1000$ assures statistical stationarity) and the quality of the random number generator used. Our programs use the ALEAT subroutine to generate random numbers with uniform repartition. The best sequence of a thousand random numbers obtained by means of ALEAT is the sequence 6000-7000, and it was used in computations. ALEAT (IRIS-50 mathematical library) and RANDOM (IBM mathematical library) are about of the same quality. We have proved [6] that by rejecting the first 6000 random numbers generated by ALEAT, the results obtained do not depend on the particular sequence of random numbers used in the computations.

The results reported here were obtained by means of our computer programs MEMØRY-3 (ultimate effect) and MEMØRY -5 (penultimate effect).

The copolymerization with ultimate effect was also studied using an analytic model [7]:

$$W_1 = Nw_{21}/(w_{12} + w_{21}); \qquad w_2 = Nw_{12}/(w_{12} + w_{21}) \qquad (1)$$

$$n_1(1) = NW_1(1 - w_{11})^2 ; \qquad n_1(k) = n_1(1)w_{11}^{k-1} \qquad (2)$$

$$n_2(1) = NW_2(1 - w_{22})^2 ; \qquad n_2(k) = n_2(1)w_{22}^{k-1} \qquad (3)$$

where W_1 and W_2 stand for the number of M_1 and M_2 mers, respectively, in the macromolecule with polymerization degree N. $n_1(k)$ and $n_2(k)$ represent the number of blocks $+M_1+_k$ and $+M_2+_k$, respectively, in the macromolecule, $k = 1, 2, \ldots$.

w_{ij} stands for the probability of the reaction

$$\sim\sim M_i^{\bullet} + M_j \longrightarrow \sim\sim M_j^{\bullet}, \qquad i, j = 1, 2$$

Among the Monte Carlo models (based on a numerical method) and the analytic models (derived using the methods of formal kinetics), there is a principal distinction: the former are models at the molecular level, while the latter are models at the macroscopic level.

Using MEMØRY-3 and the above model, the following conclusions have been reached: statements concerning copolymer composition are robust, but those concerning sequence distribution are not always robust (according to Ref. 8, a statement is robust if it does not depend on the details of the model; if contrary, the statement is fragile).

The results detailed in the next section will argue the above statements.

TABLE 1. Composition of Acrylic Acid (M_1)/Methyl Acrylate (M_2) Copolymers

No.	M_1 in feed (mole %)	M_1 in copolymer (mole %)		
		Experimental	Eq. (1)	Monte Carlo
1	88	91.1	90.8	92.0
2	81	85.7	84.9	85.4
3	72.4	77.2	77.2	76.7
4	71.6	75.6	76.4	75.5
5	58.9	61.5	63.9	61.2
6	58.7	62.2	63.7	61.1
7	51	56.1	55.6	53.4
8	45.8	49.1	50.0	46.6
9	34	41.1	36.9	33.0
10	30.5	32.6	33.0	28.7
11	20.2	25.1	21.5	20.2

ULTIMATE EFFECT: COPOLYMERIZATION OF ACRYLIC ACID AND METHYL ACRYLATE

The necessary experimental data ($r_1 = 1.4$, $r_2 = 1.0$) concerning copolymerization of acrylic acid (M_1) with methyl acrylate (M_2) are taken from Ref. 9. The experiments were carried out at 6% conversions; thus it is justified to perform the computations for stationary conditions.

Table 1 collects the computed and experimental compositions of 11 acrylic acid/methyl acrylate copolymers.

The agreement between experimental and computed compositions is expressed by the following least-squares equations:

$$M_{1,exp} = 7.658 + 0.904 M_{1,MC} \qquad (4)$$

r	s	F	EV
0.998	1.371	981.779	0.995

$$M_{1,exp} = 2.854 + 0.957 M_{1,Eq. (1)} \tag{5}$$

r	s	F	EV
0.996	1.759	594.962	0.993

where r is the correlation coefficient, s is the standard deviation, F is Fisher statistics, and EV is the explained variance.

Equations (4) and (5) need no further comment. In Tables 2, 3, and 4 the sequence distribution for Copolymers 2, 3 and 4 is shown. n(k) computed according to Eqs. (2) and (3) is given with one decimal digit and only $n(k) \geq 1$ are recorded.

Inspecting Tables 2, 3, and 4, one concludes that statements concerning the sequence distribution are fragile.

Thus the computed sequence distribution strongly depends on the details of the model used. Because experimental data are not available, one cannot discriminate between the two models.

PENULTIMATE EFFECT: COPOLYMERIZATION OF STYRENE WITH BENZYLIDENE-MALONONITRILE

In the case of copolymerization of styrene (M_1) and benzylidene malononitrile (M_2), two sets of reactivity ratios were used: $r_1 = 0.125$, $r_2 = 0.000$, $r_1' = 1.250$, $r_2' = 0.000$ (Kreisel et al. [10]); and $r_1 = 1.00$, $r_2 = 0.00$, $r_1' = 1.44$, $r_2' = 0.00$ (Borrows et al. [11]).

The compositions of the copolymers studied are displayed in Table 5.

Equations (6) and (7) argue that one cannot discriminate between the two sets of reactivity ratios using only composition data:

$$M_{1,exp} = 1.158 + 1.013 \, M_{1,a} \tag{6}$$

r	s	F	EV
0.996	0.593	179.745	0.989

$$M_{1,exp} = -14.649 + 1.220 \, M_{1,b} \tag{7}$$

r	s	F	EV
0.997	0.457	247.580	0.998

Table 6 systematizes the sequence distribution in Copolymers 3 and 4 of Table 5.

TABLE 2. Sequence Distribution in Acrylic Acid (M_1)/Methyl Acrylate (M_2) Copolymer No. 1

Length of the sequence (L)	No. of sequences of length L			
	Monte Carlo		Eqs. (2) and (3)	
	M_1	M_2	M_1	M_2
1	3	72	7.15	70.95
2	5	4	6.52	8.51
3	6		5.94	1.02
4	8		5.41	
5	3		4.93	
6	5		4.49	
7	4		4.09	
8	4		3.73	
9	1		3.40	
10	3		3.10	
11	2		2.82	
12	1		2.57	
13	2		2.34	
14	-		2.14	
15	1		1.95	
16	5		1.77	
17	6		1.62	
18	1		1.47	
19	1		1.34	
20	1		1.22	
21	-		1.11	
22	3		1.01	
23	2			
24	2			
25	-			

(continued)

TABLE 2 (continued)

Length of the sequence (L)	No. of sequences of length L			
	Monte Carlo		Eqs. (2) and (3)	
	M_1	M_2	M_1	M_2
26	3			
27	1			
28	1			
34, 38	2, 1			

TABLE 3. Sequence Distribution in Acrylic Acid (M_1)/Methyl Acrylate (M_2) Copolymer No. 2

Length of the sequence (L)	No. of sequences of length L			
	Monte Carlo		Eq. (3)	
	M_1	M_2	M_1	M_2
1	15	103	17.49	98.74
2	11	20	14.98	18.76
3	14	1	12.83	3.56
4	13		10.99	
5	6		9.41	
6	15		8.06	
7	6		6.90	
8	7		5.91	
9	3		5.06	
10	5		4.34	
11	5		3.72	
12	6		3.18	
13	5		2.73	
14	2		2.33	
15	5		2.00	
16	2		1.71	

TABLE 3 (continued)

| Length of the sequence (L) | No. of sequences of length L | | | |
| | Monte Carlo | | Eq. (3) | |
	M_1	M_2	M_1	M_2
17	1		1.47	
18	-		1.25	
19	1		1.08	
20	-			
21	-			
22	-			
23	1			
24	-			
25	1			
26	-			

TABLE 4. Sequence Distribution in Acrylic Acid (M_1)/Methyl Acrylate (M_2) Copolymer No. 3

| Length of the sequence (L) | No. of sequences of length L | | | |
| | Monte Carlo | | Eq. (3) | |
	M_1	M_2	M_1	M_2
1	43	133	35.35	119.59
2	27	34	27.78	33.01
3	24	8	21.84	9.11
4	16	2	17.16	2.51
5	18		13.49	
6	15		10.60	
7	8		8.33	
8	7		6.55	
9	5		5.15	

TABLE 4 (continued)

| Length of the sequence (L) | No. of sequences of length L | | | |
| | Monte Carlo | | Eq. (3) | |
	M_1	M_2	M_1	M_2
10	4		4.05	
11	4		3.18	
12	-		2.50	
13	2		1.96	
14	-		1.54	
15	3		1.21	
16	-			
17	1			
18	-			
19	-			
20	-			
21	-			
22	-			
23	-			
24	-			
25	1			
26	-			

TABLE 5. Composition of Styrene (M_1)-Benzylidene Malononitrile (M_2) Copolymers

| No. | M_1 in feed (mole %) | M_1 in copolymer (mole %) | | |
| | | Experimental[c] | Monte Carlo | |
			a	b
1	92.9	76.9	77.8	-
2	89.4	74.5	74.5	73.1
3	85.8	72.5	72.2	71.1

(continued)

TABLE 5 (continued)

No.	M_1 in feed (mole %)	M_1 in copolymer (mole %)		
		Experimental[c]	Monte Carlo	
			a	b
4	81.5	69.5	69.9	69.4
5	69.1	66.7	66.3	66.2
6	59.8	63.3	-	64.3
7	34.3	58.7	59.7	60.0

[a]Reactivity ratios from Ref. 10.
[b]Reactivity ratios from Ref. 11.
[c]Data taken from Ref. 10.

TABLE 6. Sequences Distribution in Styrene (M_1)-Benzylidene Malononitrile (M_2) Copolymers

k	Sequence distribution			
	Copolymer no. 3		Copolymer no. 4	
	$n_1(k)^a$	$n_1(k)^b$	$n_1(k)^a$	$n_1(k)^b$
2	153	150	184	163
3	49	51	52	62
4	30	31	20	16
5	11	9	6	9
6	5	4	3	4
7	1	1	-	1
8	1	1		
9	-	-		
10	2	1		
11	2	2		

[a]Results obtained with reactivity ratios from Ref. 10.
[b]Results obtained with reactivity ratios from Ref. 11.

CONCLUSIONS

This paper applied the previously developed Monte Carlo models of binary irreversible copolymerizations with ultimate and penultimate effect to concrete cases. The examples studied argued the advantages of the Monte Carlo models. The ultimate effect copolymerization calculations were compared with the corresponding results obtained with the formal kinetics model. The comparison emphasized that the statements concerning compositions are robust (i.e., they do not depend on the model details), while the statements concerning sequence distribution are fragile (i.e., they strongly depend on model details).

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