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Monte Carlo Study of Binary Copolymerizations. 2. The Determination of Reactivity Ratios, Applications

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ABSTRACT

This paper discusses an improved and efficient version of the MEMØRY-7 computer program described in a previous paper. The program, called MEMØRY-7/1, implements a Monte Carlo algorithm to compute reactivity ratios in binary irreversible copolymerizations. For the copolymerization of acrylic acid and methyl acrylate, the computed r_1, r_2 values (r_1 = 1.374, r_2 = 1.038) compare quite well with experimentally determined ones (r_1 = 1.4, r_2 = 1.0; Eldridge and Treloar).

INTRODUCTION

In the previous paper dedicated to this problem [1], we proposed interpreting the sequence distribution as a chemical *dictionary*:

$$\begin{array}{ccccccc} \text{mers} & \longrightarrow & \text{blocks } \{\text{M}\}_1, \{\text{M}\}_{n>1} & \longrightarrow & \text{macromolecule} \\ \downarrow & & \downarrow \quad\quad \downarrow & & \downarrow \\ \text{letters} & \longrightarrow & \text{punctuations,} \quad \text{words} & \longrightarrow & \text{sentence, grammar} \\ & & & & \text{(chemical dictionary)} \end{array} \qquad (1)$$

The chemical features of the monomers are properly taken into account through grammar. We feel that the diagram (1) is commutative,

i.e., one can reverse the direction of the arrows. In this case the chemical dictionary can be used to determine the reactivity ratios which are memorized by the macromolecule and are "written" in the corresponding sentence.

It seems to be right to interpret the blocks $\overrightarrow{(M_1)_1}$, $\overrightarrow{(M_2)_1}$ as punctuations and the blocks $\overrightarrow{(M_1)_{n\geq 2}}$, $\overrightarrow{(M_2)_{n\geq 2}}$ as words because our Monte Carlo simulations [2, 3] of copolymerization pointed out that the monads are very sensitive to the perturbations of r_1, r_2 values, while longer blocks are stable. Thus the meaning of the sentence lies in the blocks with $n \geq 2$, and the variability of the blocks with $n = 1$ can be regarded as spelling mistakes.

We note that similar ideas are used in molecular biology [4, 5].

In order to obtain the reactivity ratios for a pair of monomers which copolymerize following the irreversible, ultimate effect kinetics, we have developed the following strategy: one computes all r_1, r_2 pairs which generate the macromolecules with the same composition F_1 or F_2 for a given feed composition f_1 or f_2. One selects the appropriate r_1, r_2 values using one of the following two methods:

1. One takes into account the information concerning the sequence distribution, knowing that the macromolecules discriminate quite well in the sequence distribution space [6].
2. One considers the composition of the copolymers in a manner detailed below.

Monte Carlo algorithms were previously used to study the reactivity in polymer modification reactions (see Ref. 7 and the references cited therein).

THE MEMØRY - 7/1 PROGRAM

The previous version of the program [1] took about 2 hr to study a macromolecule. The present version of the program significantly improves the computing efficiency: 20 min/macromolecule.

The input data are as follows: N (polymerization degree), NA (the number of M_1-type mers), NB (the number of M_2-type mers in the macromolecule), and $C = f_2/f_1$.

The computing scheme uses the Monte Carlo model of binary irreversible copolymerization [8].

Briefly, the algorithm implemented by MEMØRY-7/1 is:

1. An α and β pair is considered ($\alpha = r_1/(r_1 + C)$, $\beta = r_2/(r_2 + C^{-1})$).
2. With the considered α and β values, a macromolecule is simulated and characterized by composition (A = number of M_1 mers, B = number of M_2 mers) and sequence distribution.

3. If A ± 5 = NA and B ± 5 = NB, information concerning the generated macromolecule is stored; otherwise it is not.

4. The β value is advanced by an amount 10/N while α is kept fixed; the algorithm is continued with Point 2. When $\beta = 1$, the algorithm is continued with Point 5.

5. The α value is advanced by an amount 10/N, β is set $\beta = 1/N$, and the algorithm is continued with Point 2. When $\alpha = 1$, the computing procedure is stopped.

The flow chart of MEMØRY 7/1 is shown in Fig. 1.

Observation

The program computes α and β with an accuracy of 20/N. Because α and β are handled with three decimal digits and random numbers with eight decimal digits, the MEMØRY 7/1 results differ slightly when compared with the same results obtained by means of the MEMØRY 3 program.

APPLICATIONS: ACRYLIC ACID/METHYL ACRYLATE COPOLYMERS

In order to illustrate the method described, the copolymerization of acrylic acid and methyl acrylate is studied. The necessary experimental data are taken from Ref. 9 and collected in Table 1.

The representative r_1, r_2 values obtained by means of MEMØRY 7/1 are collected in Table 2.

In order to select the appropriate reactivity ratios for the acrylic acid/methyl acrylate pair, the following strategy is used.

For each pair of compositions $(f, F)_I$, the set S_I is computed:

$$S_I = \{(r_1, r_2)_{J,I}\} \qquad \begin{matrix} I = 1, 2, \ldots, N \\ J = 1, 2, \ldots, N_I \end{matrix}$$

I indexes the different feed compositions used to synthesize the copolymer considered (the other conditions are fixed), and J indexes the reactivity ratio pairs which gave the same copolymer composition.

Due to an error of experimental composition and to the simplification of the mathematical model, we must consider as definitions that

$$(r_1, r_2)_I = (r_1', r_2')_{I'}$$

if and only if

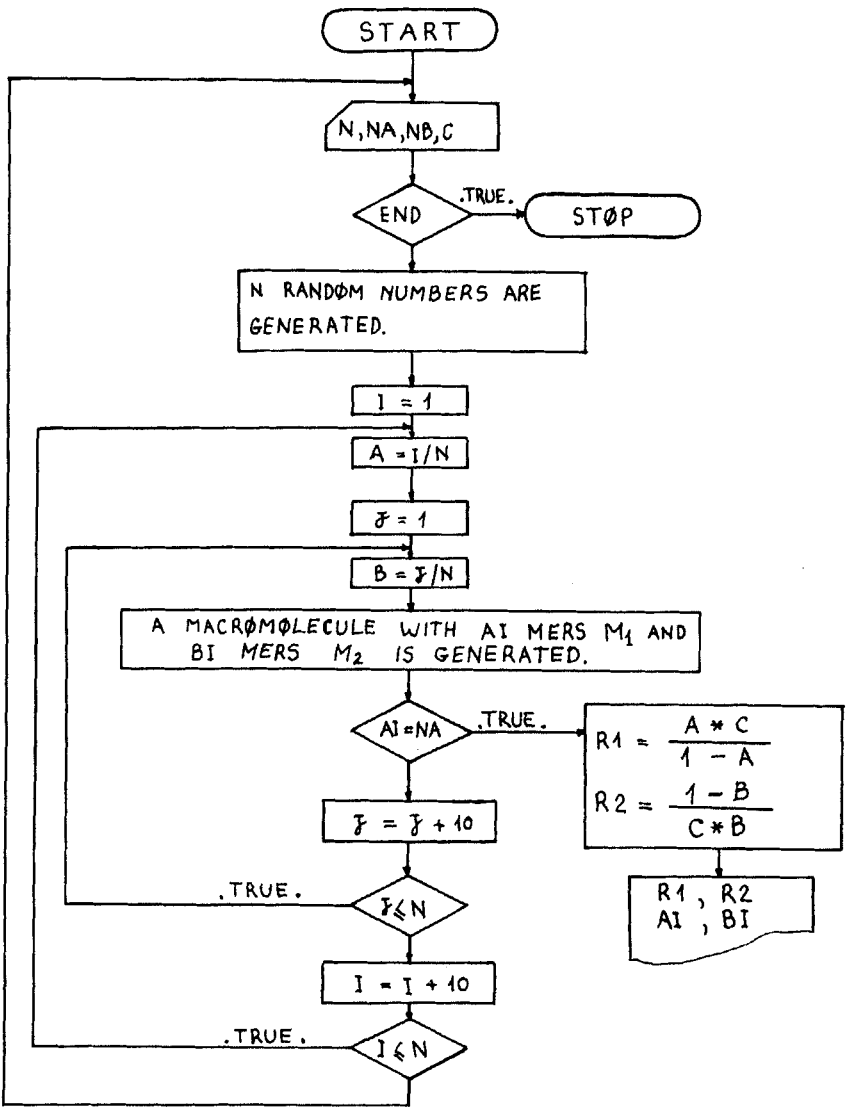

FIG. 1. Flow chart of MEMØRY - 7/1 program.

TABLE 1. The Input Data (N = 1000)

No.	C	NA	NB
1	19.0/81.0	857	143
2	27.6/72.4	772	228
3	28.4/71.6	756	244
4	41.1/58.9	615	385
5	59.0/51.0	561	439
6	54.2/45.8	491	509
7	66.0/34.0	411	589
8	69.5/30.5	326	674

$$r_1 \pm \epsilon_1 = r_1' \quad \text{and} \quad r_2 \pm \epsilon_2 = r_2', \qquad 0 \leq \epsilon_1, \epsilon_2 \leq a \tag{2}$$

$(r_1, r_2)_I$ were computed using the $(f, F)_I$ pair, and $(r_1', r_2')_{I'}$ using the pair $(f, F)_{I'}$.

The value of a is of the order of magnitude of 3s, s being the standard error of the experimental copolymer composition.

Using Definition (2), we perform the intersections (3):

$$\bigcap_{I=1}^{N} S_I = \{ (r_1, r_2)_K \}, \qquad K = 1, \ldots, L \tag{3}$$

K indexes the reactivity ratio pairs which obey Relation (2).

The desired r_1, r_2 values are obtained as an average of the r_1, respectively r_2, values common (according to Relation 2) to the N sets of computed reactivity ratios which gave the same copolymer compositions. Thus

$$r_1 = \frac{1}{L} \sum_K r_1 \quad \text{and} \quad r_2 = \frac{1}{L} \sum_K r_2 \tag{4}$$

In the case of acrylic acid/methyl acrylate copolymers, the elements of the set $\bigcap S_I$ are in the areas marked by the dashed line in Table 2. r_1 and r_2 values computed according to Relations (4) are

TABLE 2. r_1, r_2 Values Com-

Copoly-

1		2		3		4	
r_1	r_2	r_1	r_2	r_1	r_2	r_1	r_2
1.076	0.173	0.894	0.051	0.809	0.075	0.361	0.043
1.153	0.806	0.938	0.106	0.847	0.246	0.507	0.251
1.241	1.175	0.985	0.256	0.887	0.341	0.701	0.426
1.340	1.490	1.036	0.354	0.930	0.407	0.822	0.555
1.453	1.733	1.091	0.459	0.976	0.441	0.926	0.703
1.584	2.493	1.150	0.652	1.025	0.513	1.008	0.768
1.737	2.830	1.214	0.779	1.078	0.588	1.143	0.951
1.917	3.617	1.283	0.965	1.135	0.707	1.302	1.034
2.135	4.419	1.359	1.066	1.196	0.836	1.423	1.266
2.401	5.404	1.443	1.286	1.263	0.976	1.490	1.318
2.735	5.404	1.534	1.742	1.335	1.127	1.717	1.486
3.165	7.228	1.636	1.892	1.415	1.293	1.996	1.744
3.741	10.387	1.748	2.053	1.501	1.674	2.222	2.141
5.780	14.198	1.874	2.317	1.597	1.973	2.488	2.650
		2.016	2.226	1.702	2.227	2.641	2.770
		2.177	3.325	1.819	2.318	2.994	3.492
		2.361	3.918	1.950	2.614	3.985	4.771
		2.574	4.262	2.098	3.069	4.711	6.070
		2.822	4.850	2.265	3.766	5.704	7.448
		3.116	5.549	2.457	4.096	7.143	11.478
		3.469	6.391	2.678	4.662	11.129	26.667
		3.902	6.712	2.937	4.872		
		4.444	7.056	3.242	5.855		
		5.144	10.427	4.060	8.393		
		6.080	14.749	4.624	8.393		
		9.394	23.349	5.352	11.222		
				9.774	25.184		

puted by Means of MEMØRY 7/1

mer no.

5		6		7		8	
r_1	r_2	r_1	r_2	r_1	r_2	r_1	r_2
0.212	0.009	0.090	0.114	0.126	0.276	0.174	0.556
0.414	0.212	0.244	0.223	0.242	0.328	0.314	0.629
0.520	0.275	0.397	0.343	0.373	0.403	0.374	0.656
0.617	0.345	0.440	0.414	0.488	0.420	0.405	0.684
0.758	0.444	0.510	0.473	0.519	0.420	0.470	0.713
0.822	0.488	0.728	0.635	0.616	0.493	0.538	0.744
0.965	0.558	0.860	0.717	0.797	0.579	0.646	0.848
1.132	0.782	0.972	0.746	0.836	0.602	0.981	0.972
1.388	0.966	1.142	0.912	0.960	0.627	1.077	1.019
1.447	0.966	1.287	1.071	1.004	0.653	1.127	1.019
1.643	1.076	1.395	1.116	1.145	0.738	1.463	1.123
1.960	1.319	1.452	1.211	1.411	0.837	1.590	1.180
2.149	1.555	1.512	1.211	1.560	0.953	1.872	1.243
2.364	1.691	1.641	1.316	1.799	0.996	2.029	1.382
2.611	1.765	1.710	1.316	1.949	1.041	2.288	1.461
3.059	2.202	2.024	1.562	2.111	1.090	3.033	1.744
3.426	2.417	2.113	1.562	2.382	1.196	3.579	2.128
4.123	3.278	2.526	1.872	2.584	1.255	4.443	2.467
4.724	4.408	2.774	1.962	2.924	1.318	5.096	2.674
5.082	5.046	2.911	2.059	3.785	1.537	5.889	3.188
6.487	5.424	3.386	2.273	3.959	1.622	6.519	3.515
7.854	6.904	3.984	2.661	4.341	1.715	9.778	4.979
11.201	11.809	4.763	4.097	5.016	2.182	10.451	5.742
15.324	24.345	5.428	4.404	5.554	2.331	13.015	8.166
		6.759	6.139	6.536	2.685	14.115	8.116
		7.330	6.139	7.813	3.742		
		10.770	11.057	8.330	4.126		
				10.267	5.146		

TABLE 3. Sequence Distribution[a]

	1				2					
	a		b		a		b		c	
k	$n_1(k)$	$n_2(k)$	$n_1(k)$	$n_2(k)$	$n_1(k)$	$n_2(k)$	$n_1(k)$	$n_2(k)$	$n_1(k)$	$n_2(k)$
1	24	135	21	110	264	174	126	81	14	7
2	18	6	13	20	30	74	52	48	10	6
3	19		14	1	3	32	21	29	3	1
4	12		12		-	12	7	18	5	5
5	10		12		-	4	1	6	3	4
6	14		15		1	1	1	9	5	2
7	8		5			-	1	6	4	2
8	2		6			1		4	4	2
9	3		2					2	2	1
10	8		6					3	-	4
11	4		4						2	1

[a]The reported values were obtained by means of MEMØRY-3 and they are slightly different when compared with those obtained by MEMØRY-7/1:

1-a: $r_1 = 1.07$, $r_2 = 0.173$; 2-a: $r_1 = 0.24$, $r_2 = 0.33$

1-b: $r_1 = 1.24$, $r_2 = 1.17$; 2-b: $r_1 = 1.41$, $r_2 = 0.84$

2-c: $r_1 = 10.27$, $r_2 = 5.15$

$r_1 = 17.857/13 = 1.374$ and $r_2 = 13.492/13 = 1.038$, and compare very well with those determined by Eldridge and Treloar [9], $r_1 = 1.4$ and $r_2 = 1.0$ (these values are reliable, for they were calculated by the method of Fineman and Ross and checked by the methods of Tidwell-Mortimer and Tüdös).

Because information concerning the sequence distribution is not available, we could not use Method 1 mentioned above. In order to argue the statement that macromolecules discriminate well in sequence distribution space, the corresponding data for two copolymer compositions are collected in Table 3.

To conclude, the present paper proposed and applied with satisfactory results an original method to compute the reactivity ratios in binary irreversible copolymerization. With some technical improvements the method may be of practical value. We note that the

method described satisfies the conditions pointed out by Behnken [10] and Tidwell and Mortimer [11], i.e., the method does not transform the error structure in the observed copolymer composition (for an elegant study of this problem, see Refs. 12 and 13).

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