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COMPUTER MONTE CARLO MODEL OF THE MONOMER REACTIVITY IN BINARY IRREVERSIBLE COPOLYMERIZATION

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Abstract. The paper describes a method based upon the Monte Carlo tehnique for computing the reactivity ratios in binary irreversible copolymerization with ultimate effect. The method is applied with very good results to the methyl methacrylate / chloroprene copolymerization : r_1 = 0.08, r_2 = 5.1 (experimentally determined values), and r_1=0.073, r_2=5.852 (here computed values). A brief discussion on the stability of some Monte Carlo algorithms used in Polymer Chemistry is also included.

1. Introduction

The Monte Carlo computation of the monomer reactivity ratios has two important advantages : i) the easy usage of the sequence distribution data, and ii) the method does not change the error structure observed in the original data (this problem has been discussed by Behnken[1], Tidwell and Mortimer[2], McFarlane, Reilly and O'Driscoll[3]; for an up-to-date review of Monte Carlo applications in Polymer Science one may consult ref. 4).

Our Monte Carlo method[5-7] was developed to compute the reactivity ratios in binary irreversible copolymerization with ultimate effect.

$$\sim\sim M_I^* + M_J \xrightarrow{k_{IJ}} \sim\sim M_J^* \qquad ; \qquad I,J = 1,2$$

where $\sim\sim M_I^*$ denotes the macroradical or macroion, M_J stands for the monomer, and $r_I = k_{II}/k_{IJ}$, $I \neq J$, defines the reactivity ratios.

This method is presented and applied to the copolymerization of methyl methacrylate with chloroprene.

We note that it is not difficult to extend the method to copolymerizations which follow other reaction mechanisms, i.e., penultimate effect, reversible copolymerization, etc.

2. Monte Carlo Computation of the Reactivity Ratios

Briefly, our Monte Carlo method for computing the reactivity ratios consists in the following : one generates, using the Monte Carlo model[8] of binary irreversible copolymerization with ultimate effect, all the macromolecules possessing the same specified composition, F_1, for a given feed composition , f_1. The resulted r_1, r_2 values are recorded and used within the strategy described below.

For a given (f_i, F_i) pair one obtains n_i doublets (r_1, r_2). Let us denote the set S_i by :

$$S_i = \left\{ (r_1, r_2)_{ij} \right\} \quad , \quad \begin{matrix} i = 1,2,\ldots,n \\ j = 1,2,\ldots,n_i \end{matrix} \qquad (1)$$

Because the monomer reactivity depends on its chemical identity, the desired r_1, r_2 values must exist within every set S_i , $i = 1,2,\ldots,n$, and one obtains them performing the intersections :

$$\bigcap_{i=1}^{n} S_i = S \qquad (2)$$

Because both the experimental data, i.e., (f,F), and the computing method, i.e., the Monte Carlo model, are mortaged by errors and simplifications, respectively, the intersections (2) are performed according to the rule that two pairs of reactivity ratios are equal if they coincide within chosen tolerances as :

$(r_1, r_2)_{ip} = (r_1, r_2)_{jq}$, if and only if

$$(r_1)_{ip} \pm x = (r_1)_{jq} \quad \text{and} \quad (r_2)_{ip} \pm y = (r_2)_{jq}$$

with

$$0 \leqslant x \leqslant a \ , \ 0 \leqslant y \leqslant b$$

where a and b are the chosen tolerances, and $(r_1, r_2)_{ip} \in S_p$, $(r_1, r_2)_{jq} \in S_q$.

The intersections (2) result in the set S :

$$S = \left\{ (r_1, r_2)_k \right\} \quad , \quad k = 1,2,\ldots,m$$

and the desired values r_1, r_2 of the reactivity ratios are obtained as arithmetic means :

$$r_1 = \frac{1}{m} \sum_{k=1}^{m} (r_1)_k \quad , \quad r_2 = \frac{1}{m} \sum_{k=1}^{m} (r_2)_k \qquad (3)$$

3. Application : Copolymerization of Methyl Methacrylate with chloroprene

The experimental data displayed in Table 1 are taken from ref. 9 ; M_1 refers to methyl methacrylate and M_2 to chloroprene.

Table 1. The input data (the polymerization degree N is 1000)

No.	f_2/f_1	$F_1 \times 10^3$	$F_2 \times 10^3$
1	2/98	860	140
2	3/97	770	230
3	4/96	710	290
4	5/95	640	360
5	10/90	480	520

Table 2. Reactivity ratios (r_1, r_2 values) computed by means[4] of MEMORY - 7.

1		2		3		4		5	
r_1	r_2	r_1	r_2	r_1	r_2	r_1	r_2	r_1	r_2
0.094	1.463	0.068	0.633	0.057	0.732	0.036	0.585	0.004	1.101
0.100	5.994	0.072	0.976	0.061	1.816	0.042	1.915	0.005	1.333
0.108	12.174	0.075	1.326	0.064	2.394	0.045	3.164	0.006	1.453
0.117	16.246	0.079	3.996	0.067	3.309	0.055	4.568	0.023	2.984
0.126	19.917	0.083	5.274	0.070	4.290	0.058	4.869	0.043	5.041
0.138	25.130	0.088	6.176	0.076	4.632	0.060	5.179	0.053	6.228
		0.092	8.116	0.080	5.710	0.063	5.496	0.060	6.762
		0.097	9.703	0.083	7.277	0.071	7.584	0.063	7.043
		0.103	12.021	0.091	8.563	0.084	8.765	0.068	7.334
		0.116	16.753	0.096	9.481	0.095	11.962	0.071	7.636
		0.123	21.687	0.100	9.959	0.104	14.135	0.078	7.949
		0.131	24.543	0.105	11.477	0.126	17.311	0.091	8.964
				0.111	12.565	0.132	18.756	0.099	10.108
				0.117	14.327	0.154	22.014	0.121	12.378
				0.123	16.265	0.172	28.089	0.148	14.018
				0.130	17.669			0.182	17.393
				0.137	19.965			0.217	19.037
				0.146	20.786			0.335	26.857
				0.164	27.517				

The elements of the sets S_i, i = 1,2,...,5, are collected in Table 2 (copolymer number corresponding to Table 1). The elements of the S set are in the area marked by dashed lines in Table 2. By means of relations (3), one obtains :

$$r_1 = 0.587/8 = 0.073, \quad r_2 = 46.819/8 = 5.852 \qquad (4)$$

The values (4) compare very well with those obtained by Braun et al.[10] (i.e., $r_1 = 0.08$, $r_2 = 5.1$) using usual methods.

4. The Precision and the Stability of the Monte Carlo Models.

The Monte Carlo models are relatively widely used in Physics[11], Chemistry[12] and Polymer Science[4] because they allow to construct the state history (in chronological order) of the real system. The value of the Monte Carlo experiments is conditioned by the precision and the stability of the results one obtains.

It is well known[13] that the precision of the Monte Carlo computations is proportional to $(D/N)^{1/2}$, where D is a constant and N stands for the number of trials. For the purpose of the Polymer Chemistry (i.e., simulation of polymerization reactions) one assures an acceptable precision considering a polymerization degree $N \geqslant 500$. The following results, obtained using our MEMORY-3 program[8], support the above statement :

N	10	50	100	200	300	400	500	600	700	800	900	1000
$\%M_1$	90	60	57	57	56.67	56.00	56.00	56.17	56.17	56.25	56.33	56.31

Table 1. The stability of the Monte Carlo results (MEMORY - 5 type computations[15]) [a],[b]

No.	$\%M_1$	No.	$\%M_1$	No.	$\%M_1$	No.	$\%M_1$
1	66.7	26	66.1	51	65.2	76	65.2
2	67.1	27	66.7	52	66.2	77	66.7
3	66.2	28	66.3	53	66.8	78	66.6
4	65.9	29	65.2	54	67.0	79	66.9
5	67.3	30	67.6	55	67.8	80	66.8
6	67.6	31	65.7	56	67.6	81	66.9
7	67.7	32	66.9	57	66.3	82	66.2
8	65.7	33	66.6	58	67.0	83	67.3
9	67.3	34	66.2	59	67.1	84	67.6
10	65.3	35	67.0	60	67.7	85	66.4
11	66.6	36	65.9	61	64.6	86	66.5
12	66.7	37	67.0	62	67.3	87	66.8
13	66.8	38	65.9	63	67.7	88	67.3
14	67.3	39	65.4	64	67.3	89	65.8
15	65.9	40	65.5	65	66.4	90	66.3
16	66.6	41	66.3	66	65.3	91	66.6
17	66.5	42	66.7	67	66.7	92	65.4
18	66.1	43	66.1	68	66.6	93	66.7
19	67.5	44	67.1	69	66.9	94	66.4
20	66.0	45	66.2	70	67.2	95	66.3
21	65.9	46	67.1	71	66.1	96	66.9
22	66.3	47	67.2	72	66.1	97	66.1
23	68.4	48	66.1	73	66.9	98	66.5
24	67.7	49	66.2	74	67.3	99	67.0
25	67.4	50	65.9	75	66.1	100	67.1

[a] The total computing time is 5 min. 1 sec. on the IRIS 50 computer.

[b] No. 1 means that one has used the sequence 6000 - 7000, No. 2 the sequence 7000 - 8000 etc.

$\%M_1$ stands for the molar percent of the M_1 - mer in the macromolecule with polymerization degree N :

$$\sim\sim M_I^* + M_J \xrightarrow[\text{effect}]{\text{ultimate}} \sim\sim M_J^*$$

Concerning the stability of Monte Carlo results, we note that they are very senzitive to the statistical quality of the random numbers sequence between 6000 and 7000 is the best sequence of 1000 random numbers furnished by ALEAT (i.e., C.I.I. random numbers generator). Working with the best sequence, one may credit the results obtained in <u>one</u> rum. In this way, one gets the important advantage to visualize some molecular features of the macromolecule. In order to study if the results depend upon the random numbers sequence, we "synthetized" 100 macromolecules (N=1000) using 100,000 random numbers (i.e., the sequences 6000 - 7000, 7000 - 8000 etc) :

$$\sim\sim M_I - M_J^* + M_K \xrightarrow[\text{effect}]{\text{penultimate}} \sim\sim M_J - M_K^* \; ; \; I,J,K=1,2$$

(r_1=0.325, r_1'=1.330, r_2=r_2'=0.000, M_1 in feed, molar fraction is 0.6). The results displayed in Table 3 clearly show the dependence upon the statistical quality of the random number sequences which we used.

Because the standard deviation, s, of $\%M_1$ values collected in Table 3 compares well with the experimental accuracy, one may conclude that the variability of the Monte Carlo results is not very important :

$$s = \left[\sum_{i=1}^{n}(x_i - \bar{x})^2/(n-1)\right]^{1/2} = \left[\sum_{i=1}^{100}(\%M_{1,i} - \overline{\%M_1})^2/99\right]^{1/2} =$$

$$= 0.693 \quad \text{where } \overline{\%M_1} = \sum_{i=1}^{n}x_i/n = \sum_{i=1}^{100}\%M_{1,i}/100 = 66.574 .$$

References

1. P.W.Behnken, J.Polym.Sci., A2, 645 (1964).
2. P.W.Tidwell and G.A.Mortimer, J.Polym.Sci., A3, 369 (1965).
3. R.C. McFarlane, P.M.Reilly and K.F.O'Driscoll,J.Polym.Sci., (in press).

4. W.Bruns, I.Motoc and K.F.O'Driscoll, "Monte Carlo Applications in Polymer Science", Lecture Notes in Chemistry,Springer, Berlin, 1981 (in press).
5. I.Motoc,Math.Chem., 11 (in press).
6. I.Motoc and I.Muscutariu, J.Polym.Sci.,Chem.Ed., 18, 757 (1980).
7. I.Motoc,J.Macromol.Sci.-Chem., A15, 85 (1981).
8. I.Motoc, St.Holban and D.Ciubotariu,J.Polym.Sci., 15, 1465 (1977).
9. J.R.Ebdon,Polymer, 15, 782 (1974).
10. D.Braun, W.Brendlein and G.Mott, Eur.Polym.J., 9, 1007 (1973).
11. K.Binder,ed., "Monte Carlo Methods in Statistical Physics", Springer, Berlin, 1979.
12. P.Lykos,ed., "Computer Modeling of Matter", ACS Symp.Series, Washington, 1978.
13. J.M.Hammersley and D.C.Handscomb, "Monte Carlo Method", Wiley, New York, 1964.
14. G.W.Evans, G.F.Wallance and G.L.Sutherland "Simulation Using Digital Computers", Prentice-Hall, Englewood Cliffs, N.J., 1967.
15. I.Motoc,R.Vancea and St.Holban, J.Polym.Sci., 16, 1587 (1978).