Sequence Distribution in Copolymers: A Chemical Dictionary. II. Application to Copolymerization of α-Methylstyrene and Styrene

In an earlier article[1] the interpretation of sequence distribution in copolymers was proposed in the form of a chemical dictionary. Using the macromolecule as the "entry" and the chemical dictionary, we can "read" reactivity ratios. The computer program[1] MEMØRY-7 was developed to prove this statement. MEMØRY-7 needed about 2 hr per macromolecule. The improved version of the program (MEMØRY-7/1) which was used in this article is much more efficient, for it required only about 20 min per macromolecule. The program made use of Monte Carlo techniques and solved the inverse of the problem from ref. 2 (apherent programs were published in refs. 3 and 4).

To obtain the reactivity ratios for a given pair of monomers all macromolecules with the same composition and obtained with the same feed composition are generated. To discriminate among macromolecules, two strategies can be used:

(1) The sequence distribution information (if available) can be taken into account, knowing that macromolecules discriminate quite well in the sequence distribution space.[2,5]

(2) Copolymer composition can be described in the following manner: let s be the standard error of the copolymers composition (F_1 or F_2). Using the 3σ rule, we can estimate the confidence interval $\pm a$ for the r values. With feed compositions $f_{1,1}, \ldots, f_{1,N}$ we obtain copolymers $F_{1,1}, \ldots, F_{1,N}$ according to

$$\text{wwM}_I + \text{M}_J \xrightarrow{r_1, r_2} \text{wwM}_J, \qquad I, J = 1,2$$

where M_1 and M_2 are the monomers. We proceed as follows: with MEMØRY-7/1 we compute all pairs (r_1, r_2) that generate macromolecules with the same F_1 for a given f_1. We then obtain the sets

$$S_I = \{(r_1, r_2)_{IJ}\}, \qquad I = 1, \ldots, N; J = 1, \ldots, N_I \tag{1}$$

which correspond to the pairs (f_I, F_I).

Assuming that the reactivity of monomers depends on their chemical identity and not on feed composition, the desired reactivity ratios would be given by the intersections $\cap_I S_I$. Because the experimental data (F) and the theoretical model are not error free, $\cap_I S_I$ has more than one element:

$$\bigcap_{I=1}^{N} S_I = S_0 = \{(r_1, r_2)_k\}, \qquad k = 1, \ldots, L \tag{2}$$

TABLE I
The Input Data ($N = 1000$)[a]

No.	C[b]	F_1 (mole %)	F_2 (mole %)	Initial solution viscosity (cP)
1	1.353/3.588	800	200	0.447
2	1.353/3.588	794	206	0.767
3	3.194/1.541	462	538	0.464
4	3.194/1.541	452	548	0.792
5	1.045/2.773	806	194	0.436

[a] In all cases initiator concentration is [I] = 0.0143M.
[b] $C = f_2/f_1$.

TABLE II
Sequence Distribution[a]

k	1						3					
	A		B		C		A		B		C	
	$n_1(k)$	$n_2(k)$	$n_1(k)$	$n_2(k)$	$n_1(k)$	$n_2(k)$	$n_1(k)$	$n_2(k)$	$n_1(k)$	$n_2(k)$	$n_1(k)$	$n_2(k)$
1	50	176	8	47	1	8	453	373	185	146	75	56
2	31	17	11	33	1	3	—	70	65	66	43	32
3	27	2	11	14	—	4	1	9	25	42	26	22
4	20		12	11	—	3	—	1	5	14	17	24
5	16		10	—	3	4			2	4	10	9
6	18		10	—	2	3			1	4	3	8
7	8		6	—	2	2			1	3	1	10
8	8		5	1	—	2			—	2	1	3
9	5		4	—	—	2				1	—	4
10	5		6	1	3	2					—	5
11	2		5	—	1	2					1	1
12	1		4	1	1							—
13	1		4		1							—
14	1		3		1							1
15	2		3		—	1				1		—
16	—		2		2							1
17	1		2		1							—
18			1									1

19	—	1
20	— 3	1
21	— 2	1
22	1 1	
23	1 1	
24	1 1	1
25	— 1	
26	1	
27	1	
28	—	
29		
30	— 1	
31	—	
33,35,39,47,59	2	
	1	
41	2	

^{a} The reported values were obtained with MEMORY −3 and differ slightly in comparison with those obtained with MEMORY 7/1.

1-A $r_1 = 1.270$ 3-A $r_1 = 0.002$
     $r_2 = 0.464$ $r_2 = 0.105$
1-B $r_1 = 2.336$ 3-B $r_1 = 1.121$
     $r_2 = 2.748$ $r_2 = 0.462$
1-C $r_1 = 7.319$ 3-C $r_1 = 3.256$
     $r_2 = 12.856$ $r_2 = 1.020$

TABLE III
Values of r_1, r_2 Computed by MEMØRY 7/1

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
1.270	0.464	1.137	0.197	0.002	0.091	0.002	0.105		
1.345	0.618	1.201	0.428	0.089	0.112	0.089	0.120	1.269	0.325
1.427	0.788	1.270	0.618	0.135	0.120	0.135	0.135	1.344	0.502
1.518	1.078	1.345	0.744	0.233	0.143	0.233	0.169	1.426	0.701
1.618	1.242	1.427	0.927	0.340	0.169	0.340	0.206	1.517	0.976
1.730	1.551	1.518	1.186	0.428	0.206	0.428	0.237	1.617	1.079
1.854	1.761	1.618	1.360	0.623	0.259	0.623	0.320	1.728	1.301
1.994	2.075	1.730	1.618	0.893	0.378	0.893	0.409	1.853	1.620
2.336	2.749	1.854	1.912	0.980	0.393	1.025	0.426	1.993	1.836
2.564	3.228	1.995	2.250	1.025	0.409	1.121	0.462	2.334	2.539
3.082	4.308	2.154	2.538	1.121	0.426	1.276	0.500	2.544	3.103
3.432	5.125	2.336	3.101	1.276	0.444	1.388	0.542	2.790	3.364
3.860	6.461	2.546	3.501	1.388	0.462	1.446	0.564	3.080	3.964
4.396	6.461	2.792	3.961	1.446	0.481	1.635	0.587	3.430	4.906
6.014	11.232	3.082	4.902	1.635	0.500	1.921	0.691	3.857	6.162
7.319	12.856	3.432	5.609	1.921	0.637	2.166	0.751	4.393	6.162
9.292	16.156	3.860	6.461	2.166	0.721	2.443	0.818	6.010	11.240
		6.014	12.856	2.443	0.751	2.874	0.975	7.314	12.864
		9.292	16.156	2.874	0.932	3.256	1.021	9.286	13.828
				3.256	0.975	3.866	1.175		
				3.860	1.069	4.425	1.234		
				4.227	1.175	5.099	1.440		
				5.356	1.440	5.356	1.519		
				5.930	1.606	6.251	1.701		
				6.978	1.918	7.392	2.183		
				7.392	2.044	8.894	2.939		
				8.343	2.713	10.963	3.864		
				9.507	2.939	16.943	6.313		
				10.192	3.200				
				11.838	4.294				
				16.943	5.474				
				27.966	11.285				

The desired r_1, r_2 values are given by

$$r_1 = \sum_{k=1}^{L} r_{1,k}/L \quad \text{and} \quad r_2 = \sum_{k=1}^{L} r_{2,k}/L \tag{3}$$

To perform the intersections (2) the following rule is used

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

if and only if

$$r_{1,I} \pm \epsilon_1 = r_{1,I'} \quad \text{and} \quad r_{2,I} \pm \epsilon'_1 = r_{2,I'} \tag{4}$$

or

$$r_{1,I'} \mp \epsilon_1 = r_{1,I} \quad \text{and} \quad r_{2,I'} \mp \epsilon_2 = r_{2,I}, \qquad 0 \le \epsilon'_1, \epsilon'_1 \le a$$

Using definitions (4), we have

$$\bigcap_{I}^{N} S_I = \{(r_1, r_2)_k\}$$

if and only if

$$(r_1 \pm \epsilon_1, r_2 \pm \epsilon'_1)_1 = \ldots = (r_1 \pm \epsilon_I, r_2 \pm \epsilon'_I)_I = \ldots = (r_1 \pm \epsilon_N, r_2 \pm \epsilon'_N)_N$$
$$= (r_1, r_2)_k, \quad k = 1, 2, \ldots, L, 0 \le \epsilon_1, \epsilon'_1, \ldots, \epsilon_N, \epsilon'_N \le a \tag{5}$$

Relations (5) assume that each $F_1, \ldots, F_N$ has the standard error s.

We note that the method described satisfies the conditions pointed out by Behnken[6] and Tidwell and Mortimer[7]; that is, the method does not transform the error structure in the observed copolymer compositions (for an elegant study of this problem see refs. 8 and 9).

Monte Carlo algorithms were previously used to study the reactivity in polymer analogous reactions (see ref. 10 and the references cited therein).

We apply the method described in this article to the copolymerization of styrene (M_1) and α-methylstyrene (M_2). The necessary experimental data are taken from an article by Rudin and Chiang.[11] These authors pointed out that the simple copolymerization theory accounts quantitatively for reported experimental data and the more complicated reaction models considered by other workers result from systematic losses of low-molecular-weight copolymer species (Rudin and Chiang used gas chromatography to monitor the rate of consumption of monomers).

The input data used in MEMØRY-7/1 computations are listed in the Table I.

Table II lists the sequences distribution in some polymers. These figures argue the statement that the macromolecules with the same composition discriminate well in the sequence distribution space.

The computed r_1, r_2 values are given in Table III (copolymers are indexed according to Table I). The elements of the set $\cap S_I$ are in the areas marked by the dashed line in Table III.

Values of r_1 and r_2 computed according to the relations (3) are $r_1 = 17.395/14 = 1.243$ and $r_2 = 7.045/14 = 0.503$, and they compare well with those determined by Rudin and Chiang, $r_1 = 1.12$ and $r_2 = 0.63$.

To conclude, this article proposed and applied, with satisfactory results, an original method to compute the reactivity ratios in binary irreversible copolymerizations. With some technical improvements this method may be of practical value (in order to save computer time, the probabilities[2] α and β are handled with only three decimal digits).

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