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Copolymer Microstructure by High-Resolution NMR Studies

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Summary

The monomer and configurational sequences of several radical copolymers between substituted styrenes and acrylates have been examined by analyzing the high-resolution NMR spectra with the previously reported treatment of the styrene–methyl methacrylate system. The analyses have led to the conclusion that the monomer sequence distribution is just as expected from the usual copolymerization theory with r_1 and r_2. The coisotacticity, σ, which is a probability of the alternating styrene and acrylate units taking the same configurations, was shown to depend particularly upon the nature of α-substituent, decreasing from 0.8 for styrene–methyl acrylate to about 0.25 for α-methylstyrene–methyl methacrylate, via about 0.5 for styrene–methyl methacrylate and α-methylstyrene–methyl acrylate. In view of these results, the copolymerization process on the plausible steric courses giving rise to the cotactic placements and on the interactions between substituents of different monomers is discussed.

INTRODUCTION

Recently high-resolution nuclear magnetic resonance (NMR) spectroscopy has found considerable use and importance for the studies of copolymer analyses and, in favorable cases (*1–20*), provided rather unambiguous information on the chain microstructure, permitting direct examination of propagation sequences.

In the system of styrene and methyl methacrylate (*1–6*), several authors have shown that the methoxy proton resonance consists of three main peaks as a result of diamagnetic shielding by benzene-ring current. Although the peak assignments were necessarily complicated by the presence of configurational sequences, we have recently performed a quantitative analysis by introducing a single stereochemical parameter, coisotacticity, besides the monomer reactivity ratio which was assumed to give the desired monomer distributions of methyl methacrylate-centered triads (*6*).

This paper is intended to examine several related systems with the same treatment and to discuss the radical copolymerization process in view of the monomer and configurational sequence distributions.

EXPERIMENTAL

Monomers were supplied as commercial products or prepared by the usual procedures. Copolymers were obtained in low conversions (< 10 wt.%) with radical initiators (benzoyl peroxide or azobisisobutyronitrile at 60 to 108°C or under irradiation of γ-ray or UV light at −25 or 0°C.

NMR spectra were measured at 60 to 100°C with about 10% solutions in carbon tetrachloride with a Japan Electron Optics Model JNM-C-60 spectrometer working at 60 Mc. Tetramethylsilane was used as an internal standard.

RESULTS

Peak Assignments and Analytical Procedure

Let us first consider the analysis of the methoxy proton resonance of the styrene–methyl methacrylate system (*6*). In contrast with a sharp single peak at 6.4τ in poly(methyl methacrylate), three main peaks are observed in a copolymer; X at 6.4 to 6.8τ, Y at 7.1 to 7.3τ, and Z at about 7.8τ (overlapped with methyne and methylene peaks). Bovey (*1*) and Kato et al. (*3*) have suggested that both the sequence distribution and the configuration of the methacrylate-centered triads were important to account for the resolved peak areas. Based on these proposals, our analysis (*6*) assumed that such peak separations were brought about only by the nearest-neighbor styrene units which had the same configurations as the methyl methacrylate unit of interest, so that

$$F_X = F_{MMM} + 2(1-\sigma)F_{MMS} + (1-\sigma)^2 F_{SMS} \qquad (1)$$

$$F_Y = 2\sigma F_{MMS} + 2\sigma(1-\sigma)F_{SMS} \qquad (2)$$

$$F_Z = \sigma^2 F_{SMS} \qquad (3)$$

where F_{MMM}, etc., are the corresponding triad fractions, with M and S standing for methyl methacrylate and styrene units, respectively. σ represents a probability of alternating M and S units taking the same (coisotactic) configurations, referred to as coisotacticity hereafter, with the assumption that σ is constant regardless of the sequence of addition, i.e., $\sigma = \sigma_{12} = \sigma_{21}$.

Triad fractions have been obtained from monomer reactivity ratio by assuming the usual terminal model of copolymerization theory (*1,21*):

$$F_{MMM} = (1 - P_{MS})^2 \qquad (4)$$

$$F_{MMS} = F_{SMM} = P_{MS}(1 - P_{MS}) \qquad (5)$$

$$F_{SMS} = (P_{MS})^2 \qquad (6)$$

where P_{MS}, the probability of a given M unit being followed by an S unit, is given kinetically by

$$P_{MS} = 1/(1 + r_M/x) \qquad (7)$$

with the monomer reactivity ratio of M, $r_M = k_{MM}/k_{MS}$, and the molar ratio in feed, $x = [S]/[M]$.

Then σ was obtained from the relative peak areas by substituting these calculated triad fractions in Eq. (1). Harwood and Ritchey (*4,5*) have independently supported the above treatment with the NMR spectra measured in carbon tetrachloride.

It is one of the theses of the present paper that substitution of Eqs. (4) to (6) in Eqs. (1) to (3) produces the simple relations that permit explicit examination of this treatment:

$$F_X = (1 - \sigma P_{MS})^2 \qquad (8)$$

$$F_Y = 2\sigma P_{MS}(1 - \sigma P_{MS}) \qquad (9)$$

$$F_Z = (\sigma P_{MS})^2 \qquad (10)$$

The given natures of X, Y, and Z will then be clear, because σP_{MS} represents the probability of a given M unit being followed by a coisotactic S unit.

The following equations are readily derived from Eqs. (7) to (10), and appear to be conveniently used for the determination of σ and check of the assumptions:

$$F_Y^2 = 4F_X F_Z \tag{11}$$

$$1 - F_X^{1/2} = \sigma P_{MS} \tag{12}$$

$$1/(1 - F_X^{1/2}) = 1 + 2F_X/F_Y = 1/\sigma + (r_M/\sigma)(1/x) \tag{13}$$

Determination of σ according to Eq. (12), with P_{MS} calculated from r_M, is essentially the same as the previous procedure according to Eq. (1). Equation (11) may provide a method for checking the justifiability of the assumptions made. However, since F_Z is usually accompanied by a large error due to its very small value, the first equality of Eq. (13) would take the place of this purpose. Therefore, the linear plots of $1/(1 - F_X^{1/2})$ or $1 + 2F_X/F_Y$ against $1/x$ according to Eq. (13) not only provide σ and r parameters but would justify the present treatment as well. In the absence of configurational problems, the plots should have an intercept of unity with a slope of r_M. Deviation from linearity would be expected if the copolymerization did not obey the above assumptions.

In a strict sense, however, it might be pointed out that the linear relation alone, say, of Eq. (13), is insufficient to prove wholly the present treatment, because of a number of underlying assumptions, including the peak assignment, the terminal model of copolymerization, and the random (Bernoullian) formation of cotactic sequence. However, we believe the treatment will be reasonably justified when several independent checks of the analytical procedures and assumptions are consistent with each other, and then perhaps when the results of a number of related systems can be treated by the same procedure. These considerations will be discussed in detail using the results of the α-methylstyrene–methyl acrylate system below. Indeed, all the assumptions will be shown to be reasonable enough to explain the present experimental results.

Styrene (S)–Methyl Methacrylate (M)

The plots of the previous data (6) according to Eqs. (12) and (13) are shown in Figs. 1 and 2. The calculated lines correspond to the previously determined parameters; $r_M = 0.50$ (independently determined from the copolymer composition by the line-intersection method) and $\sigma = 0.48$ [determined from F_X by Eq. (1) or (12)]. The agreements between experiment and theory are also quite satisfactory in these plots, justifying the present treatment.

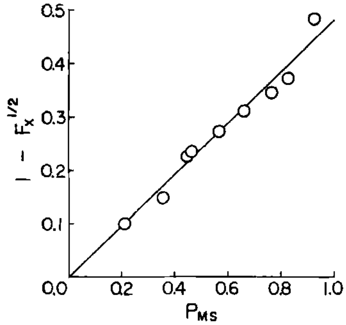


FIG. 1. Plots according to Eq. (12) for the system of styrene-methyl methacrylate. The theoretical line is given by $r_M = 0.50$ and $\sigma = 0.48$.

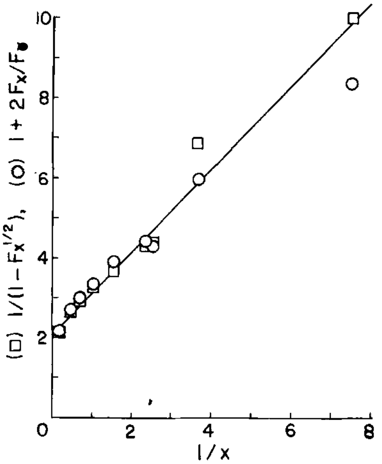


FIG. 2. Plots according to Eq. (13) for the system of styrene-methyl methacrylate. The theoretical line is given by $r_M = 0.50$ and $\sigma = 0.48$.

α-Methylstyrene (S)-Methyl Acrylate(M)

Typical NMR spectra are shown in Fig. 3. The three main peaks are clearly observed in the region of methoxy proton resonance; X at 6.4 to 6.7τ, Y at 6.9 to 7.1τ, and Z at 7.5τ (now not overlapped with the broad peak due to methyne and methylene protons at higher field). To check the justifiability of the present treatment, this system was examined in detail.

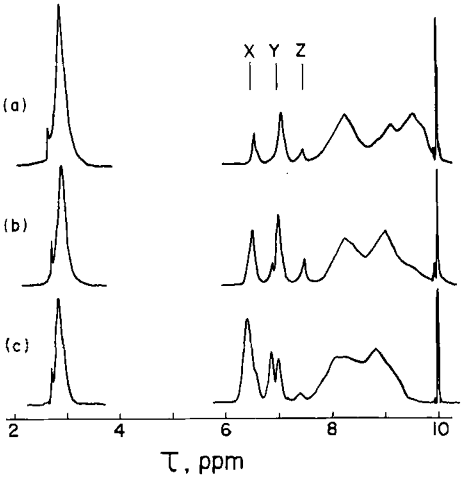


FIG. 3. NMR spectra of α-methylstyrene-methyl acrylate copolymers. Polymer composition (S/M in molar ratio): (a) 70.9/29.1 (sample 1), (b) 50.1/49.9 (sample 5), (c) 32.7/67.3 (sample 7).

The analytical details are shown in Table 1. $P_1\{M\}$ is the mole fraction of all methyl acrylate units in the copolymer, which was obtained as the average between the composition determined from the phenyl proton peak and that from the total methoxy proton peaks. F_X, F_Y, and F_Z are the measured relative peak areas of the respective methoxy proton resonances, with measurement errors less than 5%. The triad fractions, F_{MMM}, etc., in Table 1 were calculated according to Eqs. (4) to (6) using the methyl acrylate reactivity ratio. Apparently there is no direct correspondence between these triad fractions and the observed F_X, F_Y, F_Z, suggesting again that the relative configurations are also responsible for the peak separations. Then σ was calculated from the respective peak areas by solving Eqs. (1) to (3) or (8) to (10).

TABLE 1

Analytical Data of α-Methylstyrene–Methyl Acrylate System

	Experimental					Calculated						
										σ from[c]		
Sample	x	$P_1\{M\}$	F_X	F_Y	F_Z	P_{MS}[a]	F_{MMM}[b]	$2F_{MMS}$[b]	F_{SMS}[b]	F_X	F_Y	F_Z
1	9.12	0.291	0.303	0.486	0.211	0.995	0.000	0.010	0.990	0.45	0.42	0.46
2	4.14	0.370	0.306	0.484	0.210	0.985	0.000	0.030	0.970	0.45	0.42	0.47
3	1.86	0.434	0.298	0.481	0.221	0.968	0.001	0.063	0.936	0.47	0.42	0.49
4	0.995	0.461	0.362	0.456	0.182	0.941	0.004	0.109	0.887	0.43	0.37	0.45
5	0.543	0.499	0.358	0.459	0.183	0.900	0.010	0.180	0.810	0.45	0.39	0.48
6	0.242	0.556	0.437	0.454	0.109	0.799	0.040	0.322	0.638	0.42	0.43	0.42
7	0.0599	0.673	0.587	0.354	0.059	0.495	0.255	0.500	0.245	0.47	0.46	0.49

[a] From Eq. (7) with $r_M = 0.061$.

[b] From Eqs. (4) to (6) with $r_M = 0.061$.

[c] From Eqs. (1) to (3) or (8) to (10) with $r_M = 0.061$.

First of all, it is apparent that σ is reasonably constant throughout the range of x investigated, independent of the peak and equation used for determination. Since the parameter of monomer reactivity ratio used was independently obtained from the copolymer composition, this fact points to the self-consistent nature of the assumptions of the treatment. This is also clear in the plots of Eq. (13) in Fig. 4, where the theoretical line was drawn using the r and σ parameters thus determined separately. This check was satisfactorily performed in every system investigated.

Next, some independent checks for the respective assumptions can be performed on this system as follows:

1. With increasing x (accordingly with increasing S units in

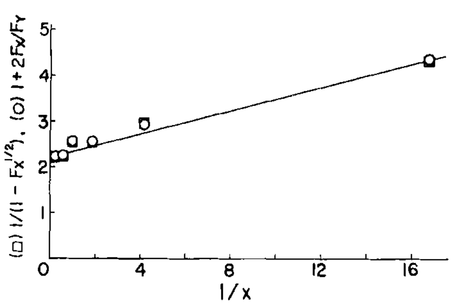


FIG. 4. Plots according to Eq. (13) for the system of α-methylstyrene–methyl acrylate. The theoretical line is given by $r_M = 0.061$ and $\sigma = 0.45$.

copolymer), relative peak areas F_X, F_Y, and F_Z are observed to approach certain limiting values which are no longer dependent on the feed composition x, as shown in the sample numbers 1 to 3 in Table 1. This fact must be necessarily accounted for by the constant monomer and configurational sequence distributions of some M-centered sequence(s). Calculated triad fractions in Table 1 support the present peak assignment, because the SMS triads predominate almost exclusively in these samples; consequently, the observed peak separations of these samples [Fig. 3(a)] are attributed almost only to the difference in the configurational sequences, such that

$$F_X = (1-\sigma)^2 \tag{14}$$

$$F_Y = 2\sigma(1-\sigma) \tag{15}$$

$$F_Z = \sigma^2 \tag{16}$$

assuming the random (Bernoullian) formation of the cotactic sequences. Calculation of σ by Eqs. (14 to 16), of course, produced essentially the same values as those obtained from the general equations [Eqs. (8) to (10)] in Table 1. Any other peak assignments in terms of the longer sequences such as the M-centered pentads appear to be improbable, because they should be still strongly dependent upon such a range of x; for example, the pentad fraction of MSMSM varies from 0.526 to 0.152 and that of SSMSS from 0.059 to 0.365 by changing x from 1.86 (sample 3) to 9.12 (sample 1).

2. The assumption of random (Bernoullian) statistics of the cotactic sequence distributions can also be checked using the results of samples 1 to 3, because almost all M units are present in the triads SMS, as discussed above, so that peaks X, Y, and Z correspond substantially to the coisotactic (I), coheterotactic (H), and cosyndiotactic (S) SMS triads, respectively. Then, for example, according to the general treatment of Coleman and Fox (22), the persistence ratio

$$\rho = \frac{2(\mathrm{I}+\mathrm{H}/2)(\mathrm{S}+\mathrm{H}/2)}{\mathrm{H}} = \frac{2(F_X+F_Y/2)(F_Z+F_Y/2)}{F_Y} \tag{17}$$

can be used for this check. This parameter was calculated to be nearly equal to unity (1.020, 1.023, 1.033 with samples 1, 2, 3, respectively). This means almost random distributions of the configurational sequences. Furthermore, the assumption that $\sigma_{12} = \sigma_{21}$

can also be supported as follows. If $\sigma_{12} \neq \sigma_{21}$, then Eqs. (14) to (16) should be replaced by

$$F_X = (1 - \sigma_{12})(1 - \sigma_{21}) \tag{18}$$

$$F_Y = \sigma_{12}(1 - \sigma_{21}) + \sigma_{21}(1 - \sigma_{12}) \tag{19}$$

$$F_Z = \sigma_{12}\sigma_{21} \tag{20}$$

and the quantity of $[(\sigma_{12} + \sigma_{21})^2 - 4\sigma_{12}\sigma_{21}]$ should have a positive value. If $\sigma_{12} = \sigma_{21}$, this should be zero. Calculation showed this quantity to be nearly zero (−0.018, −0.024, and −0.033 with samples 1, 2, and 3).

3. The assumption of the terminal model of copolymerization could then be checked by the linearity of the plots according to Eq. (13), because the other copolymerization model such as the penultimate model should change the monomer reactivity ratio, say, of Eq. (13), depending upon the feed composition (*21*). Direct evidence for this assumption was obtained by use of 1,1-diphenylethylene in place of α-methylstyrene (*16*); indeed, Eqs. (4) to (6) by the terminal model directly interpreted the peak areas of the resolved methoxy proton resonances, because the presence of a 1,1-diphenylethylene unit as a neighbor to a methyl acrylate unit should always produce a diamagnetic shielding effect upon the methoxy protons. In other words, σ in Eqs. (1) to (3) or (8) to (10) was effectively unity, as it should be. This fact also supports the present peak assignment.

Combining all these considerations, we can now say that the present treatment and assumptions are reasonably justified to explain and further discuss the experimental results.

However, we must also point out some subtle problems concerning the peak assignments for these systems. First the cosyndiotactic S unit may be somewhat responsible for an up-field shielding effect, resulting in the slight difference in the chemical shifts of the respective terms in Eqs. (1) and (2). This appears to be why the peak position and shape of X and Y depend upon the copolymer composition, as shown in Fig. 3. Second, more remote S units other than the nearest-neighbor ones may also exert a slight shielding effect, because fine structures are also observed in each of the separated methoxy proton peaks of 1,1-diphenylethylene–methyl acrylate copolymers (*16*). This also appears to be why the peak position generally shows a slight up-field shift with increasing S content. Indeed, with the spectra of styrene–methyl methacrylate copolymers measured in aromatic solvents, Harwood and Ritchey (*4*) have tentatively proposed pentad assignments. These situations suggest that the pattern of these peak resolutions may be closely related with their chain conformations in solution. Some further discussions will be given later. In this investigation we have focused mainly on the three separated peaks in carbon tetrachloride which can be treated with the foregoing peak assignments.

α-Methylstyrene(S)–Methyl Methacrylate(M)

As seen in Fig. 5, the methoxy proton peaks, X and Y, are observed at about 6.3 and 6.7τ, respectively, but peak Z is almost obscure at about 7.0τ.

As in the previous system, the observed linear plot of Eq. (13) in Fig. 6 justified the usual monomer distributions. It will be noted that σ is quite small, as reflected in the weak peaks of Y and Z in Fig. 5.

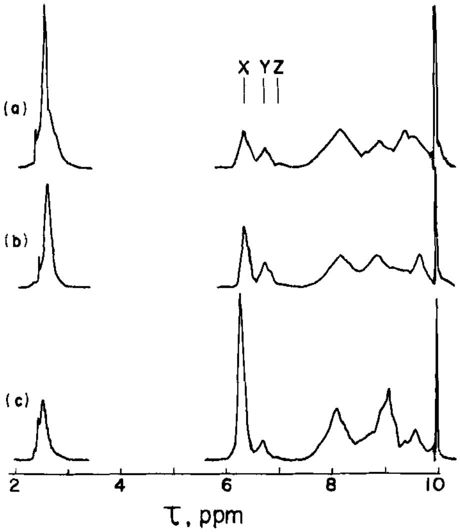


FIG. 5. NMR spectra of α-methylstyrene–methyl methacrylate copolymers. Polymer composition (S/M in molar ratio): (a) 70.0/30.0, (b) 46.4/53.6, (c) 19.4/81.6.

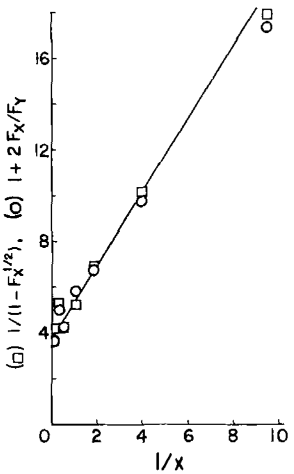


FIG. 6. Plots according to Eq. (13) for the system of α-methylstyrene–methyl methacrylate. The theoretical line is given by $r_M = 0.45$ and $\sigma = 0.27$.

Other Related Systems

Several other related systems were similarly examined and the results are summarized in Table 2, together with the systems described above. Satisfactory agreement between experiment and theory was obtained in all cases with the parameters given in the table. The details of the experimental and analytical data will be published elsewhere.

DISCUSSION

The above results show for all systems investigated that the sequence distributions, at least in terms of the acrylate-centered triads, are just as expected from the usual copolymerization theory. It seems reasonable to conclude that most radical copolymerizations are justifiably expressed by the usual copolymerization scheme of Mayo and Lewis type.

As to the parameters of coisotacticity, σ, it is interesting to note that σ varies from system to system, particularly depending upon the nature of α-substituents in styrene and acrylate. This is expected because σ would reflect any kind of interactions between the substituents of different monomer units. Table 3 summarizes these parameters as well as the differences in free-energy changes

TABLE 2

Summary of the Analyses of Ester Proton Resonances[a]

Sample	System[b] S-M	Protons	Peak position[c] (τ, ppm) X	Y	Z	Monomer reactivity ratio[d] r_S	r_M	σ	Ref.
1	St-MA	OCH_3	6.40	6.55	6.75	1.0 ± 0.1	0.16 ± 0.02	0.80 ± 0.05[e]	7
2	St-BzA	OCH_2Ph	5.05	5.17	5.3	0.90 ± 0.10	0.14 ± 0.05	0.8 ± 0.1[e]	
3	St-MMA	OCH_3	6.4–6.7	7.1–7.3	7.8	0.45 ± 0.10	0.50 ± 0.05	0.48 ± 0.04	6
4	*p*MeOSt-MMA	OCH_3	6.3–6.5	6.7–6.9	7.4	0.38 ± 0.05	0.45 ± 0.10	0.49 ± 0.08	
5	*p*MeSt-MMA	OCH_3	6.4–6.7	6.7–7.0	7.3	0.35 ± 0.10	0.43 ± 0.08	0.49 ± 0.05	
6	*p*ClSt-MMA	OCH_3	6.3–6.6	6.8–6.9	7.1	0.72 ± 0.15	0.45 ± 0.10	0.45 ± 0.02	
7	St-BzMA	OCH_2Ph	5.1	5.75	6.2	0.46 ± 0.05	0.62 ± 0.10	0.42 ± 0.04	8
8	St-MPA	OCH_3	6.3–6.4	6.9–7.0	7.5	0.72 ± 0.08	0.21 ± 0.06	0.57 ± 0.03	
9	αMeSt-MA	OCH_3	6.4–6.7	6.9–7.1	7.5	0.18 ± 0.02	0.061 ± 0.010	0.45 ± 0.02	
10	αMeSt–MMA	OCH_3	6.3	6.7	7.0	0.16 ± 0.05	0.45 ± 0.08	0.27 ± 0.03	

[a] Parameters r and σ are those of polymerizations at 60°C.

[b] St, styrene; *p*MeOSt, *p*-methoxystyrene; *p*MeSt, *p*-methylstyrene; *p*ClSt, *p*-chlorostyrene; αMeSt, α-methylstyrene; MA, methyl acrylate; BzA, benzyl acrylate; MMA, methyl methacrylate; BzMA, benzyl methacrylate; MPA, methyl α-*n*-propylacrylate.

[c] The Z-peak position is generally not very clear because of the overlaps with methyne and methylene peaks or because of very weak signals.

[d] Determined by line-intersection method.

[e] σ was obtained by trial and error as the most probable value to give the best fits to the observed spectra which show poor resolutions of X, Y, Z. See Ref. 7.

calculated according to

$$\Delta\Delta F^{\ddagger} = \Delta F_i^{\ddagger} - \Delta F_s^{\ddagger} = -2.3RT \log [\sigma/(1-\sigma)] \qquad (21)$$

where $\Delta F_i^{\ddagger}$ and $\Delta F_s^{\ddagger}$ correspond to the free-energy changes involved in the formation of coisotactic and cosyndiotactic placements, respectively. Now, it is reasonable to suppose that coisotactic or cosyndiotactic placement means the relative configuration with regard to the arrangements of the phenyl and carbomethoxy groups, as shown in the scheme below, insofar as the NMR peak assignments given above are the result of interactions between these substituents.

Before discussing the individual σ-value, it will be of value to discuss the plausible steric courses giving rise to these cotactic placements. For the radical polymerization of methyl methacrylate, Cram et al. (23,24) proposed a model of the transition state representing the least steric barrier to reaction which led to a syndiotactic placement. Tsuruta et al. (25) have recently considered an equilibrium between the rotational radical isomers which would

TABLE 3

Coisotacticity Parameters

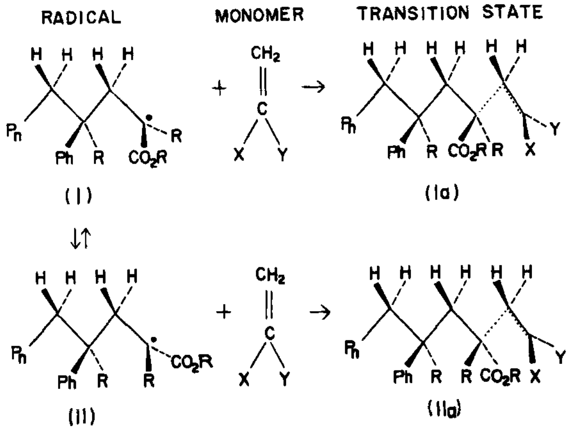
Sample	System[a]	Polymerization temp., °C	σ	$\Delta\Delta F^{\ddagger b}$, kcal/mole
1	St-MA	60	0.80 ± 0.05	−0.92
	St-MA	−25	0.85 ± 0.05	−0.86
2	St-BzA	60	0.8 ± 0.1	−0.92
3	St-MMA	108	0.49 ± 0.05	0.03
	St-MMA	60	0.48 ± 0.04	0.05
	St-MMA	0	0.44 ± 0.02	0.13
4	*p*MeOSt-MMA	60	0.49 ± 0.08	0.03
5	*p*MeSt-MA	60	0.49 ± 0.05	0.03
6	*p*ClSt-MMA	60	0.45 ± 0.02	0.13
7	St-BzMA	60	0.42 ± 0.04	0.21
8	St-MPA	60	0.57 ± 0.03	−0.19
9	αMeSt-MA	60	0.45 ± 0.02	0.13
10	αMeSt-MMA	100	0.25 ± 0.03	0.81
	αMeSt-MMA	60	0.27 ± 0.03	0.66
	αMeSt-MMA	0	0.21 ± 0.03	0.72

[a] See Table 1.

[b] With error of ±0.1 kcal/mole on the average.

lead to the isotactic and syndiotactic placements via Crams's transition states. Such rotation about the terminal bond in the radical state would properly account for the isotactic/syndiotactic product ratio, since Yoshino et al. (*26*) have very recently shown that the mode (front or back) of monomer approach is almost random with respect to the terminal radical in the radical polymerization of methyl acrylate.

Based on these proposals, the most plausible steric courses in the present copolymerization system could be written as in the following scheme.



The transition states Ia and IIa lead to coisotactic and cosyndiotactic placements, respectively. The entering monomer, whether it be M or S, is assumed to approach the radical along the least crowded direction, as indicated. Thus only interaction between substituents of the penultimate and terminal monomer units in the growing radical plays a role in the steric control. The assumption that $\sigma = \sigma_{12} = \sigma_{21}$ may therefore become a reasonable one, because the interactions should be almost the same by replacing the penultimate and terminal units in the above scheme.

A question then arises as to the kind of interaction that may operate in controlling the steric placements. Comparing the preference of syndiotactic placements in radical homopolymerizations [σ of about 0.2 for poly(methyl methacrylate) (*27*)] with σ of 0.8 for styrene–methyl acrylate suggests an attractive interaction operating between a benzene ring and a carbomethoxy group. It is noteworthy that similar weak interactions of about 1 kcal have been observed between aromatic rings and aldehyde groups from NMR studies (28). Substitution of one methyl group into the α-position of styrene or acrylate (system 3 or 9) results in the apparent disappearance of any interaction (σ of about 0.5). This might be a result of competition of some opposing interactions. Further α-methyl substitution (system 10) decreases σ to about 0.25, probably as a result of steric repulsion between the same α-methyl groups in both monomers.

The apparent absence of electronic effects, which might be deduced from the constant σ-values of *p*-substituted styrene–methyl methacrylate (systems 3 to 6), is not decisive, because styrene–methyl methacrylate already has a nearly random configuration (σ of about 0.5). At least the results of styrene–methyl and -benzyl acrylate systems must be attributed to an electronic interaction, because there can be no steric advantage of the coisotactic placement in these cases. However, because of the rather poor precision of σ in Table 3, it cannot be decided to what extent the coisotactic (or cosyndiotactic) predominance can be attributed to enthalpy or entropy factors.

At any rate, the magnitude of interactions would be very small, probably on the order of 1 kcal/mole at most, as visualized in $\Delta\Delta F^{\ddagger}$ in Table 3, and as expected from the scheme. Nonbonding interactions are concerned here between the substituents, which are separated by three carbon atoms from each other, and would be sensitive to the mutual orientation and distance of the substituents. A similar situation is found in the endo-exo competition in the Diels-Alder reactions between cyclopentadiene and acrylates (29), where the endo addition is preferred with methyl acrylate but exo is preferred with methyl methacrylate.

Finally, we must point out that the present treatment should apply to radical copolymers whose monomer distributions are justifiably described by the usual copolymerization theory. In some ionic copolymerization systems, departure from this treatment may be expected because the propagation process might often be controlled by various factors other than the nature of the growing chain end, such as penultimate units, or counterions which might be complexed with monomer or solvent molecules. For an extreme example, styrene–methyl methacrylate in an anionic system almost produced mixtures of homopolymers, as clearly demonstrated in the

NMR spectra (*30*). The assumption of a single σ to give the desired configurations may also be doubtful in ionic systems, as found in homopolymerizations (*27*).

Further, an unfavorable limitation at present comes from the fact that a substituent with a strong shielding effect, such as a benzene ring in the present cases, is required to produce sufficient peak separation, assuring such treatment. Other satisfactory examples were found in such rather limited cases as several fluorinated (^{19}F NMR) (*12–14,19*) and chlorinated copolymers (*9–11,17,20*). Even in those cases, some subtle situation occurs, as exemplified by the benzyl methacrylate–methyl methacrylate copolymers (*8*), whose benzyl methylene and methoxy protons give rise only to sharp singlets at 4.85 and 6.37τ, respectively, as found in the homopolymers. This is probably because the benzene ring of a benzyl methacrylate unit is too far separated to be sensitive to the chain configuration. The poor resolutions of X, Y, and Z in systems 1 and 2 (see Table 2) also show that these protons are not in very different magnetic circumstances, which we speculate to reflect more flexible polymer chains as compared with the α-methyl–substituted systems.

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Zusammenfassung

Die Monomerenfolge und konfigurative Sequenz verschiedener radikalisch gebildeter Copolymerer aus substituierten Styrolen und Acrylaten wurde durch Analyse der hochaufgelösten NMR• Spektren untersucht unter Anwendung der früher für das System Styrol-Methylmethacrylat berichteten Methoden. Die Analysen führten zu dem Schluss, dass die Sequenzverteilung der Monomeren sich wie erwartet im Sinne der üblichen Copolymerisationstheorie verhält, d.h. in Beziehung steht mit r_1 und r_2. Die Co-isotaktizität, σ, welche die Wahrscheinlichkeit ausdrückt, dass die alternierenden Styrol- und Acrylateinheiten dieselbe Konfiguration aufweisen, zeigte sich als besonders von der Art des α-Substituenten abhängig. Die numerischen Werte dieser Grösse vermindern sich von 0.8 für Styrol–Methylmethacrylat zu ca. 0.25 für α-Methylstyrol-Methylmethacrylat um für Styrol–Methylmethacrylat und α-Methylstyrol–Methylmethacrylat einen Wert von ca. 0.5 anzunehmen. Unter Berücksichtigung dieser Ergebnisse wird der Copolymerisationsprozess diskutiert und auch dessen sterischer Verlauf, der zu der co-taktischen Anordnung und der gegenseitigen Wechselwirkung zwischen den Substituenten der verschiedenen Monomeren führt.

Résumé

On a étudié le monomère et les séquences de configurations de plusieurs copolymères radicalaires des styrolènes substitués et des acrylates, par l'analyse des spectra de RNM à haute résolution, utilisant le traitement rapporté précédemment pour le système styrolène–méthacrylate de méthyle. Les analyses conduisent à la conclusion que la distribution des sequences du monomère est exactement comme prévue par la théorie habituelle de copolymérisation avec r_1 et r_2. La co-isotacticite, σ, qui représente la probabilité des unités alternantes de styrolène et d'acrylate prennant la même configuration, dépend particuliérement de la nature du substituant α, et diminue de 0.8 pour le styrolène-acrylate de méthyle jusqu'à environ 0.25 pour l'α-methylstyrolène-méthacrylate de méthyle, via environ 0.5 pour le styrolène-méthacrylate de méthyle et l'α-méthylstyrolène-acrylate de méthyle. Vue ces résulatats, on discute le processus de copolymérisation, les cours stériques plausibles donnant lieu à ces placements co-tactiques et les interactions entre les substituants de différents monomères.