and mutual interaction of short-chain radicals, especially if these occur in regions of high local radical concentration.

Acknowledgments. We wish to thank the Australian Institute of Nuclear Science and Engineering for supporting this project, the Australian Atomic Energy Commission, and particularly Mr. J. H. Bolton and Mr. B. M. O'Leary, for irradiation of samples, Professor L. E. Lyons for generously making the esr facilities available, and C.S.I.R.O. for providing a studentship for M. J. B.

Interactions in Solutions of Block and Statistical Copolymers of Styrene and Methyl Methacrylate

Lechoslaw A. Utracki[1a] **and Robert Simha**[1b]

Division of Polymer Science, Case Western Reserve University, Cleveland, Ohio 44106.

Received August 30, 1968

ABSTRACT: Intrinsic viscosities of block and statistical copolymers of styrene (S) and methyl methacrylate (M) are analyzed as a function of molecular weight and composition by means of relations recently applied to styrene–butadiene block polymers. The unperturbed dimensions of the block polymer are entirely determined by those of the individual blocks and the composition. In the statistical copolymers they depend on the placement probabilities of the various pairs along the chain, but the departure from the relation for block copolymers turns out to be small. The long-range interaction parameter can be expressed for both types of copolymers as a quadratic form in the composition. The polymer–polymer interaction factor varies with the polymerization conditions of the PMMA block, and a correlation with the heterotacticity index is shown to exist. In a series of samples with similar indices for heterotacticity the interaction parameter is independent of molecular weight, composition and number of blocks. Also, no systematic differences are observed between benzene and toluene at 25 and 30°.

The solution properties of block copolymers have been investigated for a number of years and the poly(methyl methacrylate) (PMMA)–polystyrene (PS) combination has been a preferred object of study. Frequently contradictory findings have been summarized at various occasions.[2–9]

We have recently measured the intrinsic viscosities and second virial coefficients of polystyrene–polybutadiene block copolymers[10] and given a description of the molecular weight and composition dependence. It is based on the concept of a θ temperature at which all long-range interactions vanish separately rather than on a mutual compensation which would make the θ temperature dependent on molecular weight and composition for a given solvent.[8,11,12] The purpose of this paper is to examine available experimental data on PS–PMMA di- and triblock copolymers on the basis of the relations developed previously.

Method of Analysis

Consider a block copolymer composed of a series of chemical species $i = 1, 2 \ldots n$. Let M_i be the molecular weight of species i, with a repeat unit of molecular weight M_{0i} (per one carbon bond of the backbone chain), unperturbed dimensions $\langle r_\theta^2 \rangle_i$, and short-range interaction parameter $A_i^2 = a_i^2/M_{0i} = \langle r_\theta^2 \rangle_i / M_i$. If x_i is the mole fraction and $B_i = \beta_i/M_{0i}^2$ the long-range interaction parameter, we write for the copolymer the averages[10] given in eq 1, where the subscript c refers to the copolymer. The second equation

$$
\begin{aligned}
M_{0c} &= \sum_i x_i M_{0i} \\
a_c^2 &= A_c^2 M_{0c} = \sum_i x_i a_i^2 \qquad (1) \\
\beta_c &= B_c M_{0c}^2 = \sum_i \beta_{ii} x_i^2 + 2 \sum_{i<j} \beta_{ij} x_i x_j
\end{aligned}
$$

expresses the Gaussian character of the chain at $T = \theta$, where all β_{ij} vanish. The third assumes that the fraction of i–j configurations characterized by an interaction parameter β_{ij} can be represented as a product of mole fractions. This, of course, is strictly valid only for a random distribution of segments, and should not be expected to hold if all the β's are sufficiently different from each other. In the styrene–butadiene system, eq 1 proved to be valid in solvents which are good for at least one of the components.[10] Equation 1 extends any two-parameter (A,B) relation developed for homopolymers to block copolymers by the introduction of additional quantities β_{ij}.

---

(1) (a) Research Center, Shawinigan Chemicals Ltd., Ste-Anne de Bellevue, Quebec. (b) To whom correspondence should be addressed.

(2) (a) G. M. Burnett, P. Meares, and C. Paton, *Trans. Faraday Soc.*, **58**, 737 (1962); (b) S. Krause, *J. Phys. Chem.*, **68**, 1948 (1964).

(3) J. R. Urwin and M. Stearne, *Makromol. Chem.*, **78**, 204 (1964).

(4) W. H. Stockmayer, L. D. Moore, Jr., M. Fixman, and B. N. Epstein, *J. Polym. Sci.*, **16**, 517 (1955).

(5) D. Froelich and H. Benoit, *Makromol. Chem.*, **92**, 224 (1966).

(6) A. Dondos, D. Froelich, P. Rempp, and H. Benoit, *J. Chim. Phys.*, **64**, 1012 (1967).

(7) D. Froelich, *ibid.*, **64**, 1311 (1967).

(8) H. Inagaki and Y. Miyamoto, *Makromol. Chem.*, **87**, 166 (1965).

(9) H. Inagaki, *ibid.*, **86**, 298 (1965).

(10) L. Utracki and R. Simha, *Amer. Chem. Soc., Div. Polym. Chem., Preprints*, **9**, 742 (1968); L. Utracki, R. Simha, and L. J. Fetters, *J. Polym. Sci., Part A-2*, in press. For the second virial coefficient of a statistical copolymer, a quadratic form in the composition (see eq 1) was given earlier by R. Simha and H. Branson, *J. Chem. Phys.*, **12**, 253 (1944).

(11) S. Schlick and M. Levy, *J. Phys. Chem.*, **64**, 883 (1960).

(12) T. Kotaka, H. Ohnuma, and Y. Murakami, *ibid.*, **70**, 4099 (1966).

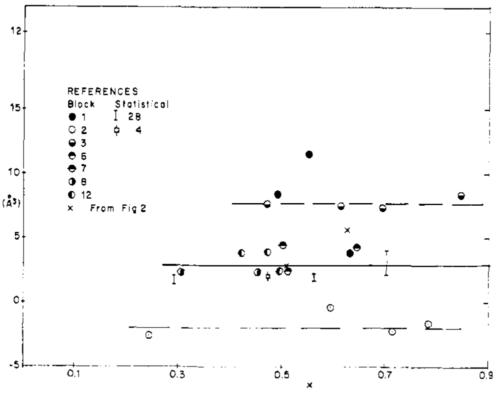


Figure 1. PS–PMMA interaction parameter β_{12} as a function of mole fraction of PS. Points and crosses represent values for block copolymers computed directly (see Table I) and interpolated from Figure 2, respectively. The bars indicate the range of β_{12} computed for statistical copolymers (see Table III) in three solvents. The square represents β_{12} for butanone solution with a standard deviation indicated by the bar.

The quantity of concern here will be the intrinsic viscosity and the basic equation to be used is[13]

$$[\eta]/M^{1/2} = 2.87 \times 10^{21}(A^3 + 0.51BM^{1/2}) \qquad (2)$$

This semiempricial reation has been observed to hold[14] for hompolymers in the range $[\eta]/[\eta]_\theta \leq 2.7$. When using M_n in eq 2, we found it to be valid also beyond this range.[10]

Discussion

A. Block Copolymers. We consider two series of data. In the first, the solvent and temperature, *viz.* toluene at 25 and 30°, and benzene at 30°, are very similar, especially in respect to polystyrene. In the second, the polymer samples were the same and the solvent was varied.

Table I summarizes the experimental material of the first series. In the sixth column are shown the β_{12}, where 1 and 2 represent styrene and methyl methacrylate, respectively, as computed for each polymer by means of eq 1 and 2, and the characteristic parameters for the two homopolymers, tabulated in Table II. These are derived from results on atactic polymers in the indicated solvents at the temperatures shown. As will be noted, β assumes the identical value for PS in toluene and benzene. Table III exhibits the numerical values of β_1, β_2 and β_{12} in five solvents for two polymer samples in each, one being fractionated, the other as polymerized.[6]

The variation of β_{12} with the mole fraction of PS, x, shown in Table I, is plotted in Figure 1. There is scatter in the results and the horizontal lines represent crude averages for three apparent groups of points. However, within each group we note the absence of any systematic variation in respect to x, M, numbers of blocks, solvent or temperature. The usual errors in $[\eta]$ and M_n are not sufficient to explain the differences in β_{12}. Since all polymers are fractions, differences in heterogeneity should be of minor importance. The only remaining explanation resides in the structure,

TABLE I

INTRINSIC VISCOSITIES AND NUMBER AVERAGE MOLECULAR WEIGHTS OF DI- (SM) AND TRI- (MSM) BLOCK COPOLYMERS

No.	$M_n \times 10^{-3}$	x	Solvent and temp[b]	$[\eta]/M_n^{1/2} \times 10^3$	β_{12}, Å^3	Ref
1	229	0.631	I	1.73	3.77	1[c]
2	259	0.550	I	2.83	11.38	1[c]
3	316	0.490	I	2.54	8.33	1[c]
4	278[a]	0.712	II	1.10	−2.33	2
5	529[a]	0.783	II	1.44	−1.64	2
6	1150[a]	0.591	II	1.56	−0.32	2
7	2170[a]	0.243	II	0.95	−2.65	2
8	187	0.470	I	2.05	7.57	3
9	225	0.611	I	2.18	7.45	3
10	302	0.692	I	2.32	7.27	3
11	390	0.845	I	2.40	8.30	3
12	400	0.641	III	2.11	4.29	6[c]
13	603	0.510	III	1.97	2.47	6[c]
14	345	0.500	III	2.03	4.47	7[c]
15	36	0.450	I	1.09	2.20	8
16	37.4	0.302	I	1.05	2.31	8
17	36	0.450	I	1.09	2.20	12
18	317	0.490	I	1.62	2.51	12
19	509	0.420	I	2.05	3.89	12
20	530	0.470	I	2.11	3.89	12

[a] M_{app} from light scattering. [b] I, toluene, 25.0°; II, toluene, 30°; III, benzene, 30°. [c] Diblocks.

TABLE II

SHORT- AND LONG-RANGE INTERACTION PARAMETERS FOR PS AND PMMA

No.	Polymer	Solvent	Temp, °C	a^2, Å^2	β, Å^3	Ref
1	PS	Toluene	25	25.5	2.84	*a*
2	PMMA	Toluene	25	20.5	1.70	*b*
3	PS	Benzene	30	25.5	2.84	*a*
4	PMMA	Benzene	30	20.5	2.28	*c*
5	PS	Butanone	22	25.5	0.46	*d*
6	PMMA	Butanone	25	20.5	1.20	*e*

[a] C. E. H. Bawn, R. J. F. Freeman, and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 1107 (1950). [b] S. N. Chinai, J. D. Matlack, A. L. Resnick, and R. J. Samuels, *J. Polym. Sci.*, **17**, 391 (1955). [c] H.-J. Cantow and G. V. Schul, *Z. Phys. Chem.* (Frankfurt am Main), **2**, 117 (1954). [d] P. Outer, C. I. Carr, Jr., and B. H. Zimm, *J. Chem. Phys.*, **10**, 830 (1954). [e] F. W. Billmeyer, Jr., and C. B. de Than, *J. Amer. Chem. Soc.*, **77**, 4763 (1955).

TABLE III

PARAMETERS β_1 (PS), β_2 (PMMA) AND β_{12} FOR BLOCK COPOLYMERS[6] IN VARIOUS SOLVENTS AT 25°

Solvent	β_1, Å^3	β_2, Å^3	β_{12},[a] Å^3	β_{12},[b] Å^3
Benzene	2.13	2.08	4.99	2.93
Chloroform	2.31	3.51	6.52	3.69
Dioxane	1.43	1.96	4.57	2.68
Tetrahydrofuran	1.78	1.39	4.37	2.50
p-Xylene	1.31	−1.25	1.24	0.62

[a] Calculated for unfractionated sample $M_c = 4 \times 10^5$, $x = 0.641$. [b] Calculated for a fraction $M_c = 6.03 \times 10^5$, $x = 0.507$.

---

(13) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **1**, 137 (1963).

(14) See, for example, H. Inagaki, T. Miyamoto, and S. Ohta, *J. Phys. Chem.*, **70**, 3420 (1966).

TABLE IV
POLYMERIZATION CONDITIONS OF PMMA BLOCKS AND THEIR ESTIMATED TACTICITIES

No.	Initiator	Solvent and temp, °C	Copolymerization	Ref	—Tacticity,[a] %—			Ref
					i	*h*	*s*	
1	PS-OOH	H_2O (emulsion), 8	PS-OOH purified and dried before second stage of polymerization	1	8	48	44	*b*
2	Na-PS-Na (initiated by sodium naphthalene)	THF, −78	MMA added to living PS. Gel formed	2	$i + h = 10$		90	*c*
3	Na-PS-Na (initiated by sodium biphenyl)	THF, −78	Living PS added to MMA. No gel reported	3	$i + h = 10$		90	*d*
4	PS-K (initiated by phenyl isopropyl potassium + α-methylstyrene tetramer)	THF, −78	MMA added slowly to living PS	6, 7	23	47	30	*d*
5	δ,δ′-Azobis(δ-cyanopentanol)	DMF, 100	Homopolymers purified and dried. Coupling by thionyl chloride	8	8	39	53	*e–g*
6	Anionic polymerization	?	?	12				

[a] Standard deviation ±5%. [b] Yu. B. Amerik, I. I. Konstantinov, and B. A. Krentsel, IUPAC Macromolecular Chemistry Symposium, Tokyo, Kyoto, Japan, Vol. I, 1966, p 30. [c] R. K. Graham, D. L. Dunkelberger, and E. S. Cohn, *J. Polym. Sci.*, **42**, 501 (1960). [d] R. K. Graham, D. L. Dunkelberger, and J. R. Panchak, *ibid.*, **59**, S43 (1962). [e] C. Walling and D. D. Tanner, *ibid.*, *Part A*, **1**, 2271 (1963). [f] F. A. Bovey and G. V. D. Tiers, *ibid.*, **44**, 173 (1960). [g] M. Reinmoller and T. G Fox, *Amer. Chem. Soc., Div. Polym. Chem., Preprints*, **7**, 999 (1966).

i.e., tacticity introduced by differences in the polymerization conditions. These are summarized in Table IV. It is well known that solution polymerization of PS, both radical and anionic, results in conventional atactic polymer, containing *ca.* 80% of syndiotactic diads.[15] In contrast, the tacticity of PMMA depends strongly on the method of synthesis.

The values of β_{12} appear to fall into three groups. The top and bottom lines represent the data of one laboratory each. In Table IV is listed information regarding tacticity as derived from high-resolution nmr spectroscopy of PMMA, prepared under similar conditions as the copolymers used to compute β_{12}. The tacticity of these polymers may be considered comparable to the tacticity of PMMA blocks in the copolymers. From the reported *i*, *h* and *s* indices we obtain a syndiotactic index $P(s) = s + {}^1/_2h$. A general correlation seems to emerge such that the top and bottom lines in Figure 1 correspond to $P(s) \simeq 90\%$ whereas for the center line $P(s)$ fluctuates between 54 and 80% with a standard error of ±5%. On the other hand, $h \simeq 5\%$ with the same experimental error for the two extremes, whereas it is distinctly different for the middle group, varying between 39 and 48%.

On the basis of these findings we should not have expected the pronounced difference between the top and the bottom line. The latter encompasses Krause's[2b] data and it is known from earlier work[16] that her polymers have high gel melting points, suggestive of relatively long tactic sequences. This is supported also by the observation[16] that gel forms after 30 min during the copolymerization of the very same samples. If aggregates favored by long-ordered sequences[17] occur intramolecularly, the intrinsic viscosity for a given M_w and β_{12} in eq 1 and 2 will be reduced. Actually β_{12} is negative in this case. From the difference in β_{12} between the top and the bottom line in Figure 1 we can estimate the change in intrinsic viscosity brought about by this internal aggregation. For molecular weights ranging between 2.8×10^5 and 2.2×10^6 and x between 0.24 and 0.78 one finds viscosity ratios between 1.9 and 3.5. In comparison, $[\eta]/[\eta]_\theta$ would vary between 2.5 and 5.1 in the absence of aggregation.

The results of Urwin and Stearne[3] are well approximated by the upper line. Judging from the conditions specified, namely, anionic initiation at −78° in THF, the PMMA block should be highly syndiotactic.[18] The absence of gel in this case may by inference be connected with an absence of long tactic sequences.

The center line groups together polymers initiated either by free radicals[2a,8] or potassium complex[6,7] (1, 4 and 5 in Table IV). As mentioned previously, the heterotactic contents *h* are very similar, and significantly larger then for the other systems. This similarity, however, does not hold in respect to the syndiotactic and isotactic indices. Two samples, namely, 2 and 3 in Table I, depart considerably from the pattern of the other free radical polymers. Both are fractions from a different batch than no. 1 of the same laboratory. We have no interpretation to offer for this apparent discrepancy.

A further correlation results from an examination of the measurements of Dondos, *et al.*,[6] of PS–PMMA copolymers in a series of solvents. The intrinsic viscosities are available for a fraction with $M_n = 6.03 \times 10^5$, $x = 0.507$, and for the original preparation with $M_n = 4.0 \times 10^5$ and $x = 0.641$. The authors also provide the intrinsic viscosities of the two homopolymers of a single molecular weight. Using the a_i^2 values in Table II we obtain β_1, β_2 and thus ultimately β_{12} for the five solvents at 25° shown in Table III. Figure 2 indicates a relation between β_{12} and β_2. The upper and lower lines refer to the unfractionated and fractionated copolymer, respectively, and a quite

---

(15) F. A. Bovey, *Polym. Eng. Sci.*, 7, 128 (1967).

(16) See Table IV, footnote *c*.

(17) H. Z. Liu and Kang-jen Liu, *Amer. Chem. Soc., Div. Polym. Chem., Preprints*, **8**, 982 (1967); A. M. Liquori, G. Anzuino, V. M. Coiro, M. D'Alagni, P. DeSantis, and M. Savino, *Nature*, **206**, 358 (1965).

(18) See Table IV, footnote *d*.

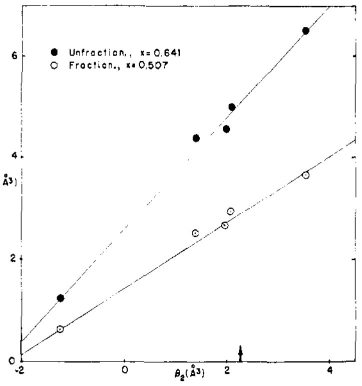
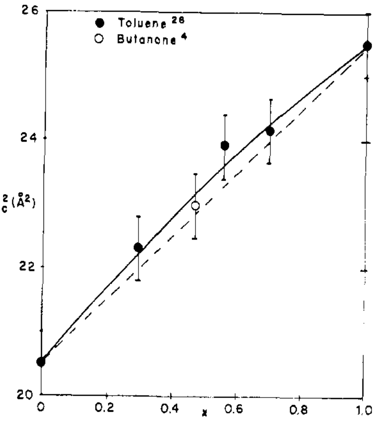


Figure 2. PS–PMMA interaction parameter β_{12} *vs.* PMMA–solvent interaction parameter β_2, computed from data of ref 6. Open and filled circles represent values for fraction and original unfractionated polymer, respectively. The arrow indicates β_2 for PMMA–benzene at 25° (see Table II).



Figures 3. Parameter a_c^2 of PS–PMMA statistical copolymer in toluene (filled circles) and butanone (open circle), 30°, as a function of the mole fraction of PS. The solid line was computed from eq 3 and ref 19. Bars indicate the standard deviation computed from the original [η] — data.[4,19]

accurate linear correlation is found. The differences between the two lines may be caused by the presence of homopolymer in the original batch, as suggested by the authors.[6] An analogous relationship with β_1 cannot be observed, since β_1 does not vary as much as β_2 (see Table III). A similar parallelism between β_{12} and β_2 is also noticeable from our styrene (1)–butadiene (2) data.[10]

The arrow marking the abscissa, $\beta_2 = 2.28$, corresponds to benzene at 30°, as shown in Table II and used to compute β_{12} in Figure 1. From the two lines we derive β_{12}'s indicated by crosses in Figure 1. The difference between the two points may be taken as a rough measure of the effect of compositional and size heterogeneity on the calculation of β_{12}.

B. Statistical Copolymers. Data in several solvents and compositions are at our disposal.[4,19] As before, we start with eq 2 and continue to use the relationship involving β_c (eq 1). However, a_c^2 cannot be expressed as a function of composition by eq 1 (see below). Since a series of molecular weights are available for each composition, least-square treatments of the data for $[\eta]/[\eta]_\theta \leq 2.7$ yield experimental values of $A_c^2 = a_c^2/M_{0c}$ and B_c as a function of composition. An analysis of these data has already been presented by the authors[19] themselves. However, they apply a more complicated relation between $[\eta]$ and M than eq 2 and assume the unperturbed dimensions to be identical in different solvents and independent of temperature. In Figure 1 are marked the minimum and maximum values of β_{12} for each composition taken from Table V, as well as the range of experimental error for butanone.[4] It is gratifying to note that β_{12} for the statistical copolymers is in the region mapped out by the block copolymers with atactic PMMA segments. Since the parameters a_1 and a_2 are known in toluene, see Table II, we can obtain the dependence of the effective segment length a_c on x. The result is shown in Figure 3.

Table V

Parameters Computed for Random SM Copolymers

Symbol	x	Solvent[a]	$a_c^{2\,b}$	β_{12}, Å^3	Ref
SM 3	0.291	I	22.3	1.98 ± 0.35	19
		II	20.7	2.08 ± 0.11	
		III	20.7	1.26 ± 0.12	
SM A[c]	0.474	Butanone	23.0	1.98 ± 0.30	4
SM 5	0.558	I	23.9	1.67 ± 0.11	19
		II	22.7	1.56 ± 0.13	
		II	22.8	2.08 ± 0.22	
SM 7	0.702	I	24.1	4.00 ± 0.07	19
		II	22.2	2.07 ± 0.09	
		III	22.5	3.25 ± 0.21	

[a] I, toluene; II, diethylmalonate; III, 1-chloro-*n*-butane, all at 30°. [b] Standard deviation ±0.5. [c] For a_i^2 and β_i values see Table II.

Alternatively a theoretical expression for a_i is derived from the equation[10]

$$a_c^2 = \sum_{i,j} X_{ij} a_{ij}^2$$

where a_{ij} refers to an effective segment length determined by an *i–j* pair and X_{ij} is the probability of occurrence of such a pair. The X_{ij} must be defined strictly in respect to both tactic and chemical placements in the chain. Thus two sets of nearest neighbor, if not higher order, conditional probabilities are involved. The experimental information available is too meager to warrant such a multiparameter effort. Moreover, judging from experimental results on the homopolymers,[20] tacticity appears to have a smaller influence on the unperturbed dimensions than chemical composition. Hence we shall consider only chemical placements, that is, the X_{ij} will be assumed to be determined entirely by the copolymer composition and the reactivity ratios r_1 and r_2. The authors[19] give the monomer compositions used in the copolymerization. Since the conversions do not exceed 10%, it is not necessary to use integrated monomer–polymer compositional relationships. For the binary system we write therefore with $a_{12} = a_{21}$, $a_{ii} = a_i$, $i = 1, 2$

$$(N_1 + N_2)a_c^2 = a_1^2 N_{11} + a_2^2 N_{22} + 2a_{12}^2 N_{12}$$

where N_{ij}, N_1, N_2 are the number of *i–j* pairs, 1's and

---

(19) T. Kotaka, Y. Murakami, and H. Inagaki, *J. Phys. Chem.*, **72**, 829 (1968). We are indebted to Professor H. Inagaki for a copy of the manuscript prior to publication.

(20) I. Sakurada, N. Nakajima, O. Yoshizaki, and K. Nakamae, *Kolloid Z.*, **186**, 41 (1962).

2's in the copolymer, respectively. We have[21] $N_{ij} = N_i p_{ij}$, where the conditional probabilities p_{ij} are given by

$$p_{ij} = 1 - p_{ii}$$

$$p_{ii} = r_i n_i/(r_i n_i + n_j)$$

where $i, j = 1, 2, i \neq j$. The monomer composition n_i is computed from N_i by means of the relationship

$$N_1/N_2 = n_1(r_1 n_1 + n_2)/[n_2(r_2 n_2 + n_1)] \tag{3a}$$

Hence

$$a_c^2 = a_1^2 x p_{11} + a_2^2(1 - x)p_{22} + 2x(1 - p_{11})a_{12}^2 \tag{3b}$$

with

$$x = N_1/(N_1 + N_2)$$

From Table I of ref 19 we have five sets of data for the determination of the r_i. In effect only three points are available, since some of the monomer feeds are identical, although the initiator concentration and reaction time were permitted to vary. From the appropriate linear plot of the compositional relationship we obtain $r_1 = 0.56$, $r_2 = 0.48$, which compares reasonably well with the tabulated[21] values of 0.52 ± 0.03, 0.46 ± 0.03, or more recently[22] $r_1 = 0.54 \pm 0.04$ and $r_2 = 0.42 \pm 0.1$.

From eq 3 and the values of a_c^2 quoted in Table V for toluene we find a_{12} to vary between 23.0 and 23.9 for the highest and lowest composition. Since the standard deviation for a_c^2 is ± 0.5, an average value of $a_{12} = 23.5$ is acceptable as a constant to be used in the computation of a theoretical relation between a_c^2 and x. The result is presented in Figure 3 and we conclude that our analysis, based on eq 3 and copolymerization statistics solely, accounts for the observations as well as can be expected. A nonlinear relationship between the conformational parameter $\sigma^2 \propto a_c^2$ and x has been observed previously.[19] Note that a_{12}^2 is close to the mean of $a_1^2 = 25.5$ and $a_2^2 = 20.5$, which may be indicative of particular relationships between the hindrance potentials.

Conclusion

Our treatment separates the short- and long-range interaction parameters. For block copolymers present experimental data do not permit a direct evaluation of the former from eq 2 and the additivity of the a_i^2, eq 1, is employed instead. In the statistical copolymer departures from additivity can be predicted from simple copolymerization theory, eq 3, and directly compared with experiment, using eq 2 for a series of polymers with constant composition. Figure 3 indicates that in the case of PS–PMMA, the deviations from additivity are small.

Having obtained a_c, one can extract β_c from experiment by means of eq 1. Therefrom the polymer–polymer interaction parameter β_{12} is derived, provided β_1 and β_2 are known. We have assumed throughout that β_1 and β_2 depend only on the solvent and temperature but not on the origin of the polymer. This assumption should be satisfactory in respect to β_1, since solution polymerization of styrene is supposed to yield an atactic product. However, there exists experimental evidence that the second virial coefficient in a given solvent is sensitive to tacticity and therefore to the polymerization conditions.[23] Thus variations in β_2 cannot be ruled out, but we have no way of estimating the magnitude of the effect in the absence of experimental information for PMMA. The value of β_2 adopted corresponds to heterotactic free radical initiated polymer. On this basis one separates three bands of β_{12} values, which could be related to the heterotactic content of the PMMA block. For highly tactic blocks we tentatively suggest an effect of sequence length on β_{12}.

The numerical magnitude of β_{12} for atactic blocks should be least affected by the uncertainties in β_2 mentioned above. In the same range are also found the interaction parameters for the statistical copolymers in different solvents. This supports the concept that β_{12} correlates with tacticity. We suggest that the difference between the upper and the center line in Figure 1 is an indication of an enhanced interaction between regularly placed groups. Such an increase would be expected for both syndio and isotactic blocks. Conversely, the position of the bottom line is characteristic of an enhanced interaction between relatively extended *s* and *i* sequences within the PMMA block.

Acknowledgment. This work was partially supported by Contract No. 951836 between the Jet Propulsion Laboratory, California Institute of Technology, and the University of Southern California and sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

---

(21) See, for example, R. Simha and L. A. Wall, *J. Res. Nat. Bur. Stand.*, **41**, 521 (1948); "Styrene Its Polymers, Copolymers and Derivatives," R. F. Boundy and R. F. Boyer, Ed., Reinhold Publishing Corp., New York, N. Y., 1952, Chapter 20.

(22) C. C. Price and J. G. Walsh, *J. Polym. Sci.*, **6**, 239 (1951).

(23) W. R. Krigbaum, J. E. Kurz, and P. Smith, *J. Phys. Chem.*, **65**, 1984 (1961); J. M. G. Cowie and S. Bywater, *J. Polym. Sci., Part A-2*, **6**, 499 (1968).