Conformation of Block Copolymers in Dilute Solution. The Molecular Dimension/Block Architecture Relationships

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ABSTRACT: Conformational properties of AB di- and BAB triblock copolymers in dilute solution were examined by three different methods including Monte Carlo calculations on a self-avoiding lattice walk, light-scattering measurements with solvents isorefractive for the B blocks, and intrinsic viscosity measurements in different solvents. Polymer samples used were a series of anionically prepared polystyrene (PS)–poly(methyl methacrylate) (PM) diblock and PM–PS–PM triblock copolymers. Emphasis was placed on elucidating the difference between the two copolymers in the effects of heterosegmental interactions on their molecular dimensions. The main conclusions obtained were: as opposed to the diblock copolymer case, the central A block in a BAB copolymer is appreciably more expanded than an identical A homopolymer; and the overall dimension of a triblock copolymer is generally larger than that of its diblock equivalent. Together with some calculative and experimental results on a random (statistical) copolymer, it was deduced that copolymer dimension generally becomes larger with the increase of block number when compared at common molecular weight and composition, thus a diblock copolymer having the smallest dimension, and a random copolymer the largest dimension. However, the molecular weight dependence of chain dimension was essentially different between random and block copolymers.

In view of the generally incompatible nature of two different homopolymers in solution[2] as well as in bulk, it is essential to clarify the effects of incompatible (repulsive) interactions on the conformation of an individual block copolymer chain in dilute solution and to understand the underlying rules which govern the relationships between properties and chain architecture. This necessarily requires the characterization of chain conformation in a quantitative manner rather than by ambiguously defined terms like "segregated" and "quasi-random coil" conformations. Of the enormous amount of work[3] having been done so far, little has been designed from such a standpoint. As a first step of such a study, we[4] recently proposed the characterization of the conformation of an AB diblock copolymer in terms of the two parameters γ_K and σ defined by

$$\gamma_K = \langle S^2\rangle_K/\langle S^2\rangle_{H\text{-}K} \qquad (K = A \text{ or } B) \tag{1}$$

$$\sigma = \langle G^2\rangle/(2\langle S^2\rangle_{H\text{-}A} + 2\langle S^2\rangle_{H\text{-}B}) \tag{2}$$

where $\langle S^2\rangle_K$ and $\langle S^2\rangle_{H\text{-}K}$ are the mean-square radii of gyration of the K block and of the K homopolymer identical with the K block, respectively, and $\langle G^2\rangle$ is the mean-square distance between the centers of mass of the two blocks. Monte Carlo calculations on self-avoiding lattice-walk and light-scattering measurements have revealed that γ is very close to unity in any case. This means that diblock copolymer conformation can be characterized practically by the single parameter σ. The indication of the calculations was that σ would range from unity to about 1.5, depending on the magnitude of the K–K and A–B interactions as well as on copolymer composition, but not on molecular weight, essentially. It should be noted that we do not necessarily mean the "dumbbell" model. As pointed out previously,[4] the increase of σ is achieved mainly by the increases of the end-to-end distances of the two blocks and of the angle that the two end-to-end vectors make. The "biellipsoidal" model of Bendler et al.[5] places emphasis on the "shape" of the molecule, and our expression here places emphasis on the experimentally determinable dimensions of the molecule.

The behavior of block copolymers with more than two blocks should be much more complicated, not allowing such a simple picture as for diblock copolymers. In this paper, we first examine the conformation of a BAB triblock copolymer by similar Monte Carlo calculations. In relation to experiments, particular attention is paid to the following two points: One is the value of γ_A defined anologously to eq 1. As to each B side block, the conclusion for diblock copolymers should be valid, i.e., $\gamma_{B'} \sim 1.0$ (in this paper, we attach a prime to the quantities related to an individual B side block to distinguish them from those related to the two B side blocks as a whole). The situation of the central A block is different, since it is perturbed by the two B blocks from *both* sides. The other question is whether or not there exists any singificant difference between the overall dimensions of di- and triblock copolymers when compared at common molecular weight and composition. Experiments were conducted on polystyrene (PS)–poly(methyl methacrylate) (PM) diblock and PM–PS–PM triblock copolymers and compared with the Monte Carlo results: The quantity γ_{PS} can be determined directly by light-scattering measurements with solvents isorefractive to PM, and the overall dimensions of the copolymers should be in close relation to the intrinsic viscosities $[\eta]$. Through such studies, we have obtained a fairly unified view on the relationships between conformation and copolymer architecture. The results will be reported herein.

(A) Monte Carlo Calculations on BAB Triblock Copolymer Systems

Model and Method. The mean-square radius $\langle S^2\rangle$ of an A–B binary copolymer is generally given by

$$\langle S^2\rangle = x\langle S^2\rangle_A + y\langle S^2\rangle_B + xy\langle G^2\rangle \tag{3}$$

where x $(= 1 - y)$ is the fraction of A segments, $\langle S^2\rangle_K$ is the mean-square radius of the K part, i.e., all K segments in a molecule (K = A or B), and $\langle G^2\rangle$ is the mean-square distance between the centers of mass of the A and B parts. To quantitatively describe the conformation of a symmetrical BAB triblock copolymer, we further define the following mean-square quantities; $\langle S^2\rangle_{B'}$ as the radius of a B′ side block, $\langle G'^2\rangle$ as the distance between the centers of mass of the A and B′ blocks, $\langle G''^2\rangle$ as the distance between the centers of mass of the two B′ blocks; and $\langle R^2\rangle$, $\langle R^2\rangle_A$, and $\langle R^2\rangle_{B'}$ as the end-to-end distance of the whole chain, of the A block, and of the B′ block, respectively. We now introduce the expansion factors α's given by

$$\alpha^2 = \langle S^2\rangle/\langle S^2\rangle_0 \tag{4a}$$

$$\alpha_R{}^2 = \langle R^2\rangle/\langle R^2\rangle_0 \tag{4b}$$

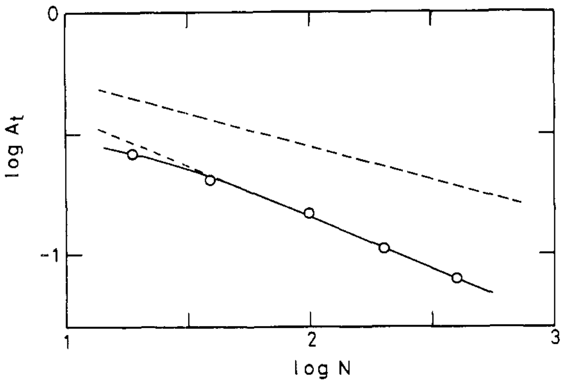

Figure 1. Plots of sample attrition At vs. chain size N for symmetrical triblock copolymers of equimolar composition on a simple cubic lattice. The upper broken curve is for diblock copolymers.[4]

$$\alpha_{G'}{}^2 = \langle G'^2\rangle / \langle G'^2\rangle_0 \qquad (4c)$$

$$\alpha_K{}^2 = \langle S^2\rangle_K / \langle S^2\rangle_{K,0} \qquad (K = A \text{ or } B') \qquad (4d)$$

$$\alpha_{RK}{}^2 = \langle R^2\rangle_K / \langle R^2\rangle_{K,0} \qquad (K = A \text{ or } B') \qquad (4e)$$

where the subscript 0 denotes the ideally unperturbed state.[4] Knowing the quantities in eq 4, one can calculate $\langle G^2\rangle$, $\langle G''^2\rangle$, and $\langle S^2\rangle_B$ from eq 3 together with the identities,

$$\langle S^2\rangle_B \equiv \langle S^2\rangle_{B'} + \langle G'^2\rangle - \langle G^2\rangle \qquad (5)$$

$$\langle G''^2\rangle \equiv 4(\langle G'^2\rangle - \langle G^2\rangle) \qquad (6)$$

We note that for diblock copolymers $\langle G'^2\rangle = \langle G^2\rangle$, $\langle S^2\rangle_{B'} = \langle S^2\rangle_B$, and $\langle R^2\rangle_{B'} = \langle R^2\rangle_B$ (or $\alpha_{G'} = \alpha_G$, $\alpha_{B'} = \alpha_B$, and $\alpha_{RB'} = \alpha_{RB}$) in accord with the previous notations.[4]

Our purpose here is to evaluate the α's by Monte Carlo calculations. The model and method were as described previously.[4] In brief, we generated, on a three-dimensional six-choice simple cubic lattice, samples of BAB triblock copolymer chains which have no pair of dissimilar segments occupying the same lattice site. Introducing the interaction parameter ξ_{AB} for a pair of dissimilar segments being in contact, i.e., occupying the nearest neighbor sites, we calculated the average $\langle X\rangle$ (= $\langle S^2\rangle$, $\langle S^2\rangle_A$, etc.) from[6]

$$\langle X\rangle = \sum_i X_i \exp(-\eta_i \xi_{AB}) / \sum_i \exp(-\eta_i \xi_{AB}) \qquad (7)$$

where η_i is the number of such heterocontacts in the ith chain. This model would represent a triblock copolymer chain in a common theta state, i.e., a state in which the excluded volume effects exist only between dissimilar segments. The chain size N (= $N_A + N_B$), where N_K is the number of K segments in a chain) ranged from 20 to 400, and the number of samples ranged from 1000 to 3000 for each block copolymer. For simplicity, the chains were assumed to be symmetrical, and the composition $x = N_A/N$ was fixed at $\frac{1}{2}$. To reduce computation time, the Wall–Erpenbeck method[7] of chain enrichment was applied for longer chains ($N > 50$).

Monte Carlo Results. In Figure 1, sample attrition At(N) is plotted against chain size N ($\xi_{AB} = 0$). As in the case of diblock copolymers, the relation,

$$\text{At}(N) = N^{-\lambda'} \qquad (8)$$

holds for large N, but with the constant $\lambda' = 0.43$ larger than the corresponding value of 0.28 for diblock coplymers. That is, sample attrition in triblock copolymers is heavier than that in diblock copolymers, although it is still trivial as compared with the exponentially decreasing function in completely self-avoiding (homopolymer) chains.[6,7] The result is quite understandable, since self-avoiding type segment interactions take place mostly among segments located nearby along the chain. Obviously, the distance along the chain between dissimilar segments is, on average, shorter in triblock copolymers than in diblock copolymers. Thus, we can expect that triblock copolymers are more seriously perturbed by the heterocontact interactions than diblock copolymers are. We shall see this below.

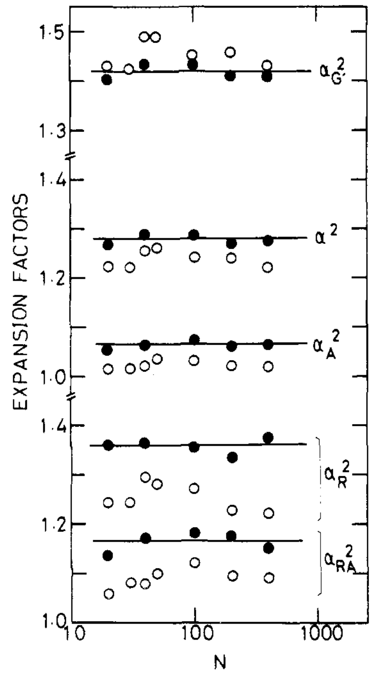

Figure 2. Plots of expansion factors α vs. chain size N for symmetrical triblock copolymers of equimolar composition on a simple cubic lattice with interaction parameter $\xi_{AB} = 0$ (filled circles). Open circles are for diblock copolymers.[4]

First, we consider the case of $\xi_{AB} = 0$. In Figure 2, α's are plotted against N. We see that all the α's are apparently independent of N and that the following relations hold for any not-too-small N:

$$\langle S^2\rangle = 1.28\langle S^2\rangle_0 \qquad (9a)$$

$$\langle R^2\rangle = 1.36\langle R^2\rangle_0 \qquad (9b)$$

$$\langle G'^2\rangle = 1.42\langle G'^2\rangle_0 \qquad (9c)$$

$$\langle S^2\rangle_A = 1.07\langle S^2\rangle_{A,0} \qquad (9d)$$

$$\langle R^2\rangle_A = 1.17\langle R^2\rangle_{A,0} \qquad (9f)$$

Naturally, the behavior of the B′ block (not shown in the figure) was almost the same as that of either block in a diblock copolymer with corresponding composition. The mean-square dimensions of the whole chain as well as of the individual portions show the same N dependence, i.e., proportional to N, as diblock copolymers. However, the differences in $\langle S^2\rangle$ or $\langle R^2\rangle$ and in $\langle S^2\rangle_A$ are especially noteworthy: Both the whole chain and A block of a triblock copolymer are significantly larger than those of a diblock copolymer (compare eq 9 with eq 7 in ref 4).

In Figure 3, we have shown the variation of α's with ξ_{AB} for a triblock copolymer with $N = 200$. We see that all the α's increase monotonously with ξ_{AB}. Above all, the behavior of $\alpha_A{}^2$ should be noted. It increases from 1.07 to 1.13 as ξ_{AB} increases from 0 to 0.25, in contrast with the behavior of a diblock copolymer for which $\alpha_K{}^2$ remained very close to unity over the entire range of ξ_{AB} examined (see Figure 4 in ref 4). Chains with different sizes behaved similarly.

At this stage, the results of the first-order perturbation

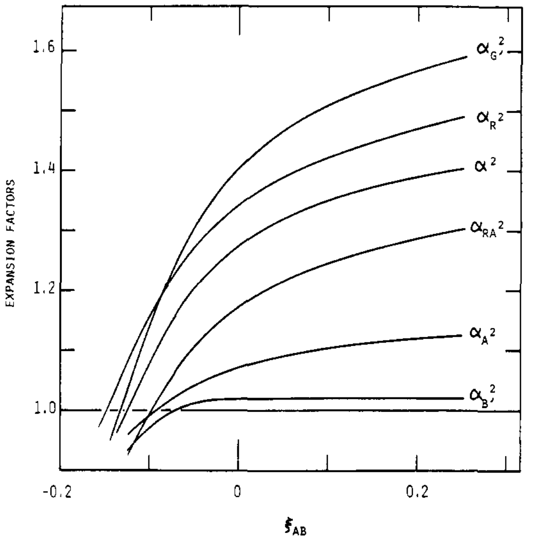

Figure 3. Variation of expansion factors α with interaction parameter ξ_{AB} for a symmetrical triblock copolymer on a simple cubic lattice; chain size N = 200 and composition x = ½.

theory[8-10] may be interesting to note. In a common theta state where both Z_{AA} and Z_{BB} are zero, the expansion factors for di- and triblock copolymers of equimolar composition are given by[10]

$$\alpha^2 = 1 + C_1 Z_{AB} + \ldots \qquad C_1 = 0.391\ (\mathrm{AB}) \qquad (10a)$$

$$= 0.408\ (\mathrm{BAB}) \qquad (10b)$$

$$\alpha_A^2 = 1 + C_{A,1} Z_{AB} + \ldots \qquad C_{A,1} = 0.267\ (\mathrm{AB}) \qquad (10c)$$

$$= 0.417\ (\mathrm{BAB}) \qquad (10d)$$

$$Z_{AB} = (2\pi b^2/3)^{-3/2} \beta_{AB} N^{1/2}$$

where β_{AB} is the (only nonzero) binary-cluster integral between dissimilar segments and b is the statistical length of the segments. The first-order theory expects that $\langle S^2 \rangle_A$ of triblock copolymers would be significantly larger than that of diblock copolymers, whereas their difference in overall dimension would be trivial. The former result is in qualitative agreement with the Monte Carlo result, but the latter is not necessarily so. The first-order theory alone is, of course, unable to predict the behavior of the chains with large Z_{AB} and to tell, for example, whether the expansion factors become constant for large N as the Monte Carlo results indicated. An answer might be obtained after calculating higher order coefficients of the perturbation expansions. At this stage, we should only like to point out that the two models as they stand now do not correspond with each other, since the β_{AB} close to the ideal "theta" situation, for example, can by no means be related to ξ_{AB}.

Another question concerns the "theta" point at which the expansion factors become unity. Figure 4 in ref 4 indicates that all the expansion factors become unity at a nearly single point of ξ_{AB}, whereas Figure 3 here indicates that the "theta" points for the different expansion factors may be different and that the ξ_{AB}'s are much larger (i.e., closer to zero) than that for the diblock copolymer. However, a definite conclusion on this point should be deferred, because the present data may not be sufficient in sample size as well as in chain size to discuss the behavior of chains with negative ξ_{AB}.

We now turn to our main subject. We have so far assumed a common theta state, wherein the parameter γ_A defined by eq 1 agrees with α_A^2. In there, γ_A is about 1.07 for $\xi_{AB} = 0$ and becomes somewhat larger as ξ_{AB} increases. If the excluded volume effects exist also between A–A segments, γ_A should become somewhat smaller than that in the common theta state. This must be so, since an expansion of the A block necessarily reduces the number of heterocontacts, with the A block remaining in a less perturbed state,[4] i.e., a smaller γ_A. Data of Alexandrowicz and Accad[11] on a self-avoiding homopolymer chain support this view. The effects of the B–B interactions are complicated. On the one hand, the interactions within the same B side block would result in a smaller γ_A by the same reason as for the A block. On the other hand, those between the two B side blocks would make themselves more apart from each other forcing the central A block to become more expanded, i.e., a larger γ_A. Hence it is not possible to predict a priori which way γ_A will move. To see this, calculations were made on the model in which the intersections of B–B type as well as of A–B type were prohibited. The results showed that γ_A remains almost unchanged from the value for the model with only A–B intersections being prohibited, presumably because the above two effects cancel out. In short, γ_A would become somewhat smaller as the solvent quality becomes better for the central A block, while the solvent quality for the B side blocks would have little effect on γ_A.[12]

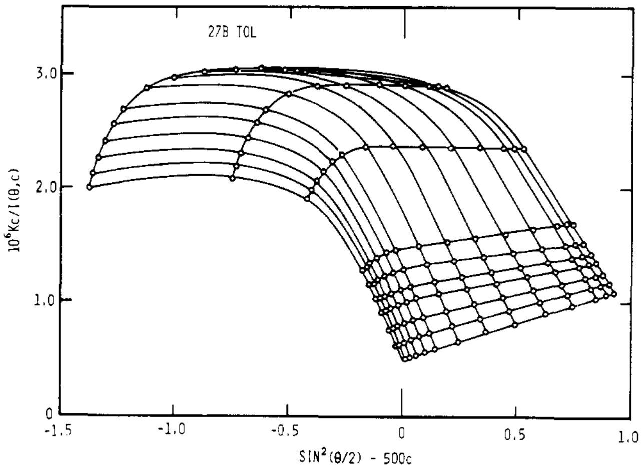

Figure 4. Zimm plot for PM–PS–PM triblock copolymer 27B in toluene at 30.0 °C.

Next we wish to predict which of the di- and triblock copolymers would have a larger overall dimension in general. The indication of the above calculations was that in a common theta solvent the A–B interactions expand a triblock chain more significantly than a diblock chain. Thus, we may legitimately assume that this would well be the case in common good solvents for the parent homopolymers. On the other hand, in selective solvents whose solvency is largely different for the two homopolymers, the dimensions of the two copolymers would differ from each other, even if the A–B interactions were absent. This can be seen in a crude manner from the behavior of random-flight block-copolymer chains comprised of two types of segments with different lengths. For an equimolar composition, the $\langle S^2 \rangle$ of such chains are[13]

$$\langle S^2 \rangle = \langle S^2 \rangle_{\mathrm{H\text{-}A}} + \langle S^2 \rangle_{\mathrm{H\text{-}B}} \qquad (\text{AB diblock}) \qquad (11a)$$

$$\langle S^2 \rangle = (11/8)\langle S^2 \rangle_{\mathrm{H\text{-}A}} + (5/4)\langle S^2 \rangle_{\mathrm{H\text{-}B'}} \qquad (\text{BAB triblock}) \qquad (11b)$$

with $\langle S^2 \rangle_{\mathrm{H\text{-}B}} = 2\langle S^2 \rangle_{\mathrm{H\text{-}B'}}$. The random-flight models are presumably too crude, but we believe they are good enough to describe the cases in selective solvents, in which $\langle S^2 \rangle_{\mathrm{H\text{-}A}} \gg \langle S^2 \rangle_{\mathrm{H\text{-}B}}$ or $\langle S^2 \rangle_{\mathrm{H\text{-}A}} \ll \langle S^2 \rangle_{\mathrm{H\text{-}B}}$. Equation 11 indicates that a qualitative feature of the A–B interaction-absent chains would be: if $\langle S^2 \rangle_{\mathrm{H\text{-}A}} > \langle S^2 \rangle_{\mathrm{H\text{-}B}}$, then $\langle S^2 \rangle_{\mathrm{triblock}} > \langle S^2 \rangle_{\mathrm{diblock}}$,

Table I
Refractive Index Increments of Polystyrene and Poly(methyl methacrylate) in Toluene and Toluene/*p*-Cymene Mixtures for 436-nm Light[a]

	TOL[b]			TOL/pCY[c] (wt ratio)	
				73.4/26.6	49.7/50.3
Temp, °C	30	50	70	30	30
PS	0.113	0.119	0.125	0.115	0.117
PM	0.004	0.009	0.014	0.006	0.008

[a] Toluene is a good solvent for both PS and PM; *p*-cymene is a good solvent for PS and a nonsolvent for PM. [b] For values at different temperatures see ref 4. [c] Values estimated from the Gladstone–Dale equation together with assumption of a linear relation between refractive index and solvent composition.

and if $\langle S^2\rangle_{\mathrm{H-B}} > \langle S^2\rangle_{\mathrm{H-A}}$, the inequality reverses. A previous first-order perturbation calculation[10] led to the same conclusion. From these and the Monte Carlo results, we may safely say that a triblock chain would be larger than a diblock chain in solvents which have solvency similar to the two homopolymers or better for the central block rather than for the side blocks. This may not be the case in solvents which are much better for the side blocks than for the central block. Unfortunately, it is not possible to give more quantitative descriptions with the presently available knowledge.

(B) Experimental Section

Light-Scattering Measurements on PM–PS–PM Triblock Copolymer Systems. Light-scattering measurements were made to evaluate γ_{A} (= γ_{PS}) of PM–PS–PM triblock copolymers using solvents in which PM blocks are almost "invisible". Polymer samples used were two anionically prepared PM–PS–PM block copolymers (coded 58B[14] and 27B[15]) of nearly equimolar composition and relatively high molecular weight ($>10^6$) plus their precursor PS's (58H and 27H, respectively) which should be identical with the PS blocks of the copolymers. The solvents used were toluene (TOL) and TOL/*p*-cymene (pCY) mixtures. The solvent characteristics are given in Table I. Details of measurements were given previously.[4,16] Here only one point should be made. The "low-angle anomaly"[16,17] which we often observed for the one-component-invisible block copolymer systems was less significant in the present triblock copolymer systems, in agreement with the previous theoretical prediction.[16] However, we observed a different type of anomaly: the $Kc/I(\theta,c)$ vs. $\sin^2(\theta/2)$ plots observed at relatively high concentrations showed downward rather than "usual" upward concavity at low angles.[14] The reason for this anomaly is not yet clear. Figure 4 shows an example. In the figure, we also notice that the $Kc/I(0,c)$ vs. c curve becomes significantly downward concave in the high concentration region ($c > 0.007$). The curve is quite similar to that for a PS–PM diblock copolymer reported previously (see Figure 4 in ref 16). The anomaly might be ascribed to the same cause as implied for the diblock copolymer systems, i.e., the formation of a certain ordered structure in solution.[16] However, the $KC/I(\theta,0)$ vs. $\sin^2(\theta/2)$ curves were normal, guaranteeing correct evaluation of apparent mean-square radius $\langle S^2\rangle_{\mathrm{app}}$. Values of $\langle S^2\rangle_{\mathrm{app}}$ obtained are listed in Table II.

Analysis of Light-Scattering Data. Previously we described a theoretical basis of interpreting light-scattering data from diblock copolymer systems and emphasized the importance of making suitable correction for the contribution from the almost but not perfectly "invisible" blocks.[4] Here we extend the analysis to the triblock copolymers. For this purpose, it may be convenient to express $\langle S^2\rangle_{\mathrm{app}}$ in the form,[18]

$$\langle S^2\rangle_{\mathrm{app}} = \mu_{\mathrm{A}}^2\langle S^2\rangle_{\mathrm{A}} + \mu_{\mathrm{B}}^2\langle S^2\rangle_{\mathrm{B}} + 2\mu_{\mathrm{A}}\mu_{\mathrm{B}}\langle S^2\rangle_{\mathrm{AB}} \qquad (12)$$

where μ_{A} (= $1 - \mu_{\mathrm{B}}$) is the optical weight factor[4] and $2\langle S^2\rangle_{\mathrm{AB}}$ is the mean-square distance between dissimilar segments (averaged over all pairs), which is for a BAB triblock copolymer chain equal to

$$2\langle S^2\rangle_{\mathrm{AB}} = \langle S^2\rangle_{\mathrm{A}} + \langle S^2\rangle_{\mathrm{B'}} + \langle G'^2\rangle \qquad (13)$$

Now we introduce parameter σ'' (which is analogous to σ' for diblock copolymers) given by

$$\sigma'' = \langle G'^2\rangle/(2\langle S^2\rangle_{\mathrm{A}} + 2\langle S^2\rangle_{\mathrm{B'}}) \qquad (14)$$

When $\mu_{\mathrm{B}} \sim 0$, we can neglect[19] the μ_{B}^2 terms and obtain from eq 12–14

$$\gamma_{\mathrm{A}} = \gamma_{\mathrm{app}}[1 - \mu_{\mathrm{B}}(2\sigma'' + 1)\langle S^2\rangle_{\mathrm{B'}}/\langle S^2\rangle_{\mathrm{app}}]/[1 + \mu_{\mathrm{B}}(2\sigma'' - 1)] \qquad (15)$$

$$\gamma_{\mathrm{app}} = \langle S^2\rangle_{\mathrm{app}}/\langle S^2\rangle_{\mathrm{H-A}}$$

The rhs of eq 15 includes two unknowns, i.e., σ'' and $\langle S^2\rangle_{\mathrm{B'}}$, which may be approximated as follows. In view of the fact that $\langle S^2\rangle_{\mathrm{K}}/\langle S^2\rangle_{\mathrm{H-K}}$ for diblock copolymers is very close to unity irrespective of composition and magnitude of heterocontact interactions, we may assume that $\langle S^2\rangle_{\mathrm{B'}} \sim \langle S^2\rangle_{\mathrm{H-B'}}$. This assumption would not be too serious, since the ratio of $\langle S^2\rangle_{\mathrm{B'}}/\langle S^2\rangle_{\mathrm{app}}$ should usually be quite small (see eq 15). In the same light, it would be reasonable to assume that σ'' ranges from 1.0 to 1.5 in accordance with the behavior of σ' for diblock

Table II
Estimation of Values of $\gamma_{\mathrm{PS}} = \langle S^2\rangle_{\mathrm{PS}}/\langle S^2\rangle_{\mathrm{H-PS}}$ for Styrene (*S*)–Methyl Methacrylate (M) PM–PS–PM Triblock Copolymers in Toluene, Toluene/*p*-Cymene Mixtures, and *p*-Xylene

Code	$\langle S^2\rangle_{\mathrm{app}}^{1/2}$, Å	$\langle S^2\rangle_{\mathrm{H-PS}}^{1/2}$,[a] Å	$\langle S^2\rangle_{\mathrm{H-PM'}}^{1/2}$[b], Å	γ_{app}	γ_{corr} $\sigma'' = 1.0$	γ_{corr} $\sigma'' = 1.5$
PM–PS–PM's in Toluene at 30.0 °C						
58B[c]	384	336	166	1.30	1.23	1.19
27B[d]	456	414	228	1.21	1.11	1.05
PM–PS–PM 58B[c] in Toluene at Different Temperatures (°C)						
20.2	368	338	166	1.19	1.16	1.15
25.0	372	337	166	1.22	1.17	1.14
35.1	377	336	166	1.26	1.17	1.12
40.3	378	335	166	1.27	1.17	1.10
44.9	389	335	166	1.35	1.23	1.15
50.1	390	334	166	1.36	1.22	1.13
59.7	391	333	166	1.38	1.20	1.11
70.3	397	331	166	1.44	1.23	1.10
PM–PS–PM 58B[c] in Toluene/*p*-Cymene (wt ratio) at 30.0 °C						
73.4/26.6	385	328	134	1.38	1.29	1.23
49.7/50.3	365	320	132	1.30	1.20	1.13
PM–PS–PM in *p*-Xylene at 30 °C (Previous Work[23])						
27B[d]	385	378	145	1.04	0.92	0.84

[a] Values for sample 58B were estimated by measuring $\langle S^2\rangle$ of sample 58H at eight different temperatures ranging from 14 to 65 °C and inter- or extrapolating the data to the desired temperature so as to eliminate data scattering arising from experimental artefacts. [b] Calculated from the intrinsic viscosity data[20,21] (see ref 4). [c] $10^{-6}M_{\mathrm{w}} = 1.10$ and $x_{\mathrm{PS}} = 0.50$; $10^{-6}M_{\mathrm{w,H-PS}} = 0.558$.[14] [d] $10^{-6}M_{\mathrm{w}} = 1.47$ and $x_{\mathrm{PS}} = 0.41$; $10^{-6}M_{\mathrm{w,H-PS}} = 0.671$.[15]

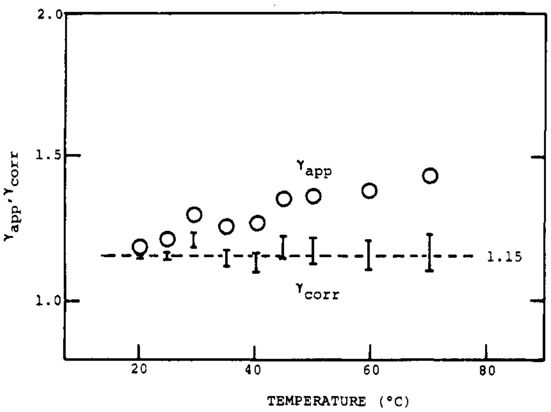

Figure 5. Plots of γ_{app} and γ_{corr} vs. temperature for PM–PS–PM triblock copolymer 58B in toluene; circles are measured γ_{app}, and vertical half-lines are γ corrected with σ'' varying from 1.0 (upper end) to 1.5 (lower end).

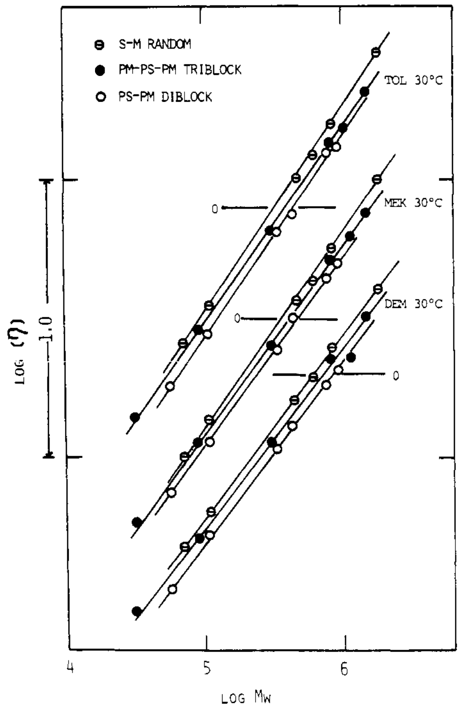

Figure 6. Plots of log $[\eta]$ vs. log M_w for PS–PM diblock (this work), PM–PS–PM triblock,[25] and S–M random[29] copolymers of nearly equimolar composition in toluene (TOL), 2-butanone (MEK), and diethyl malonate (DEM) at 30.0 °C.

copolymers.[4] Under these assumptions we have evaluated γ_{PS} from eq 15. The necessary $\langle S^2 \rangle_{H\text{-}PM'}$ values were estimated from the intrinsic viscosity data[20,21] in combination with suitable theories (see ref 4). The results are summarized in Table II.

As Table I shows, PM blocks in TOL become more easily visible as temperature is raised. Presumably reflecting this effect, γ_{app} observed for sample 58B increases with increasing temperature (Figure 5). In fact, the corrected value γ_{corr} can be regarded as a constant independent of temperature, giving $\gamma_{corr} = 1.15 \pm 0.05$. In the figure the upper end lower ends of vertical half-lines correspond to the assumption of $\sigma'' = 1.0$ and 1.5, respectively. Values of γ_{corr} obtained for the other systems are similar to this one (Table II). These results show that the central PS block is more expanded by 10 to 20% than the corresponding homopolymer. Earlier, similar results have been reported by Leng and Benoit[22] for the PM–PS–PM/benzene system. All these agree with the Monte Carlo results semiquantitatively.

In this connection, our previous results[23] for a PM–PS–PM in p-xylene (pXY) are interesting. pXY is a good solvent for PS but a theta solvent for PM (θ = 35.0 °C[24]). Hence at 30 °C, for example, the interactions operating within and between the PM side blocks should be attractive ones. The apparent value of γ_{PS} observed for sample 27B at 30 °C was 1.04. This value reduces to 0.88 ± 0.04, if corrected following the above scheme (see Table II). That is, γ_{PS} is considerably smaller in this system than in the above good solvent systems. This is no doubt caused by the attractive interactions between the PM side blocks in favor of themselves coming closer to each other, thus restricting the conformation of the central PS block toward a smaller γ_{PS}.[23,25,26]

Table III
Intrinsic Viscosities $[\eta]$ of Polystyrene–Poly(methyl methacrylate) Diblock Copolymers in Various Solvents at 30.0 °C[a]

			$[\eta]$, dL/g				
Sample	x[b]	$10^{-5}M_w$	TOL	MEK	DEM	pXY	nBC
39B	0.48	5.81	0.227	0.187	0.168	0.192	0.167
47B	0.42	10.9	0.351	0.286	0.264	0.295	0.234
46B	0.45	34.0	0.812	0.611	0.537	0.644	0.461
53B	0.51	44.0	0.94	0.794	0.648	0.694	0.546
63B50	0.49	76.4	1.58	1.108	0.916	1.077	0.842
54B	0.42	93.0	1.65	1.252	1.037	1.062	0.816

[a] Abbreviations: TOL = toluene, MEK = 2-butanone, DEM = diethyl malonate, pXY = p-xylene, and nBC = 1-chlorobutane. [b] Weight fraction of styrene.

Intrinsic Viscosity. Intrinsic viscosities $[\eta]$ of a series of anionically prepared PS–PM diblock copolymers[14,16] were measured in various solvents including TOL, 2-butanone (MEK), diethyl malonate (DEM), 1-chlorobutane (nBC), and pXY all at 30 °C. Here, TOL and MEK are good solvents for both PS and PM: TOL has solvency somewhat better for PS than for PM, while MEK has the opposite solvency. The rest are all theta solvents for either PS or PM but good or moderate solvents for the other: θ = 35.9 °C for PS in DEM[27] and 35.5 °C for PM in nBC.[24] Measurements were made with a Ubellohde dilution viscometer at four different concentrations. The results are listed in Table III. Here, it should be noted that block copolymers often undergo intermolecular association in selective solvents forming stable micelles.[28] In fact, we have observed that the present diblock copolymer samples, especially those with large molecular weight, underwent micelle formation in pXY[21,23] even in very dilute solutions under all experimentally feasible conditions.[17c] Hence, the values of $[\eta]$ in this solvent, if not all, will not represent the dimension of a single chain. Therefore, we will exclude the pXY data in the following discussion. On the other hand, the block copolymers are likely in the state of monomolecular dispersion in DEM and nBC at or above 30 °C.[14,21]

In Figure 6, values of $[\eta]$ for the PS–PM copolymers in TOL, MEK, and DEM are compared with those for the PM–PS–PM copolymers reported by us previously.[25] For the later discussion, our previous data[29] for styrene (S)–methyl methacrylate (M) random copolymers of azeotropic composition ($X_{PS} = 0.52$) are also included in the figure. In all these solvents, $[\eta]$ increases in the order of diblock < triblock < random, when compared at common molecular weight and composition ($x = 0.5 \pm 0.1$ for all the samples).

The results for the nBC system are somewhat different (see Figure 7). In the region of low molecular weight, the triblock copolymers have larger $[\eta]$ than the diblock copolymers, while the inequality appears to reverse in the high molecular weight region. The $[\eta]$ of the random copolymers is the largest as in the other systems.

Although no reliable relation is as yet known which quantitatively correlates the $[\eta]$ value of a block copolymer in, for example, a selective solvent with the $\langle S^2 \rangle$ (or $\langle R^2 \rangle$) value, we still believe that $\langle S^2 \rangle$ (or $\langle R^2 \rangle$) increases in the same order as $[\eta]$ does. As pointed out before, there would be two factors which may bring about a certain dimensional difference among block copolymers with different architecture: One is, of course, the effect of heterosegmental interactions, and the other is the effect of solvent solvency. As for the present systems, eq 11 expects that $\langle S^2 \rangle_{diblock} > \langle S^2 \rangle_{triblock}$ in DEM and MEK, while $\langle S^2 \rangle_{triblock} > \langle S^2 \rangle_{diblock}$ in TOL and nBC (if the former effect is absent). The indication of experiments was that $\langle S^2 \rangle_{triblock} > \langle S^2 \rangle_{diblock}$ in all these systems except for the nBC system with large molecular weight. This would mean that the effect of heterosegmental interactions predominates in these systems and that the effect appears more noticeably in triblock copolymers than in diblock copolymers. This, again, is in qualitative agreement with the Monte Carlo results. The inversion of the $[\eta]$ inequality found in the nBC system is rather unusual. We should again remember that the interactions in the nBC

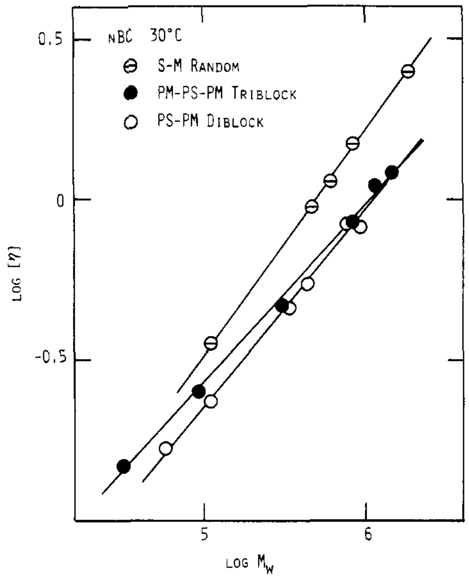

Figure 7. Plots of log [η] vs. log M_w for PS-PM diblock (this work), PM-PS-PM triblock,[25] and S-M random[29] copolymers of nearly equimolar composition in 1-chlorobutane (nBC) at 30.0 °C.

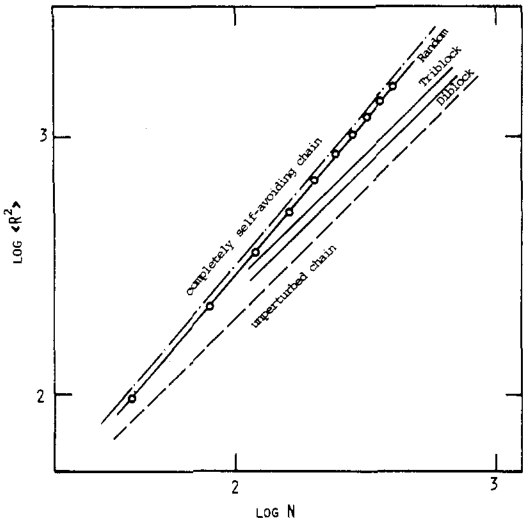

Figure 8. Plots of log ⟨R^2⟩ vs. log N for a random copolymer (R = 50, x = 0.50) on a tetrahedral lattice (open circles). Data for a completely self-avoiding (homopolymer) chain on a tetrahedral lattice[7] and for diblock[4] and triblock copolymers on a simple cubic lattice are as indicated in the figure.

30 °C system operating between the PM side blocks must be attractive ones as in the pXY 30 °C system. A PM-PS-PM chain is very likely to assume a conformation in this system also such that the PM side blocks come closer to each other with the average dimension of the whole chain being smaller than in the absence of the attractive interactions. Such an effect, if any, should become more and more significant with the increase of molecular weight,[23,26] thereby resulting in the inversion of the [η] inequality. Comments on the random copolymer data will be given later.

(C) Discussion

Two main conclusions have been obtained commonly by the Monte Carlo calculations and the experiments. One is that the mean square radius of gyration of an individual block of an AB diblock copolymer is almost the same as that of the corresponding homopolymer,[4] whereas that of the central A block of a BAB triblock copolymer is significantly larger than the homopolymer. The other is that the overall dimension of a triblock copolymer is generally larger than its diblock equivalent. As is evident from the Monte Carlo calculations, the different behavior of the two block copolymers can be satisfactorily explained by assuming repulsive interactions between dissimilar segments are strong as compared with those between similar segments.

From these results we may predict the behavior of block copolymers with more than three blocks. With the increase of block number, the average distance along the chain between dissimilar segments obviously becomes shorter, and hence the probability of heterosegmental intersections should become larger. This has been clearly observed in comparison of the Monte Carlo sample attrition At's for di- and triblock chains (Figure 1). A chain with more than three blocks should be perturbed by heterosegmental interactions more significantly than its triblock and hence diblock equivalents, presumably with the overall dimension being more expanded. This prediction can be verified by Monte Carlo calculations on similar block copolymer models with specified block numbers. Such calculations, however, would not be quite rewarding, since the corresponding (well-defined) block copolymer samples are hardly available at the moment, and without these this sort of calculation may be of little practical significance.

Instead, we refer to some calculative and experimental results obtained for random copolymers. A random copolymer can be, in a certain sense, regarded as a block copolymer with a large number of "blocks". If the above prediction is correct, its dimension must be larger than those of di- and triblock copolymers so far as the molecular weight and the number of blocks are not too small. Figure 8 shows a preliminary result of similar Monte Carlo calculations made on a random copolymer. On the calculations, we imposed, as before, nonintersecting interactions (ξ_{AB} = 0) only between dissimilar segments (i.e., a common theta state). Here, we tentatively identified a monomer unit as a segment. The so-called run number R[30] of the copolymer, i.e., the population of A-B linkages, was assumed to be 50, so that the average composition was 0.50.[31] A three-choice tetrahedral lattice was employed instead of the six-choice simple cubic lattice employed for the block copolymers. On the latter lattice, the interactions between dissimilar segments very close to each other along the chain are necessarily counted in, obviously resulting in a dependence of chain dimension on the sequential arrangement of segments, i.e., monomer units. This is too unrealistic, since the interactions between neighboring monomer units should be of *short-range* nature. Although such interactions may be important in discussing unperturbed dimensions of copolymers (see below), they should have nothing to do per se with the *long-range* interactions which we are discussing. The former lattice, on the other hand, is free at least from this apparent contradiction, since interactions thereon operate only between segments separated by four other segments or more along the chain, which appears to be reasonably far enough. In Figure 8, the behavior of di- and triblock copolymers predicted from the data on the cubic lattice are indicated by solid lines. The figure shows that ⟨R^2⟩ of the random copolymer varies with N almost in parallel to that of a completely self-avoiding (homopolymer) chain,[7] giving the relation

$$\langle R^2 \rangle \propto N^{\upsilon} \tag{16}$$

with the exponent υ as large as 1.2. In other words, a random copolymer in a common theta state behaves much like a homopolymer in a good solvent but essentially differently from the block copolymers whose υ values are of course unity as pointed out several times. Even if we employed the tetrahedral lattice also for the block copolymers, the results should not be essentially different. Thus, it is clear that the dimension

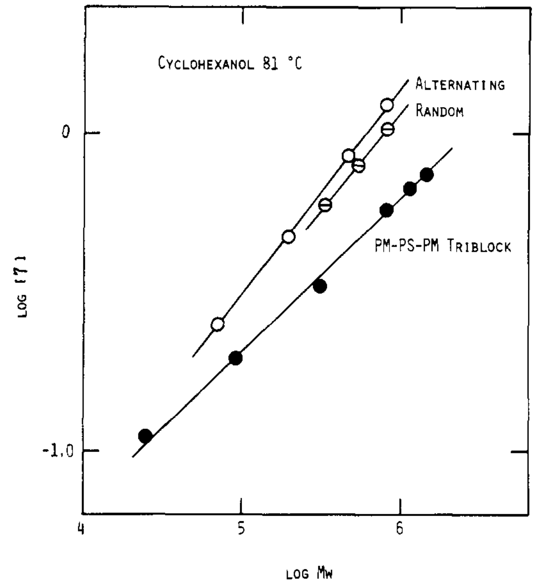

Figure 9. Plots of log [η] vs. log M_w for PM–PS–PM triblock,[36] S–M random,[29] and S–M alternating[29] copolymers in cyclohexanol (CHL) at 81.0 °C.

of a random copolymer becomes larger than those of the block copolymers ultimately for large N, as expected.

Here, it may be interesting to ask, "what is the critical number of blocks beyond which the proportionality of $\langle R^2 \rangle$ to N breaks?" To answer this question, we should note the following: in a random copolymer the (average) number of "blocks" obviously increases in proportion to molecular weight, which, of course, is not the case with "true" block copolymers. Thus, if chain dimension is to increase with block number at a fixed N as implied above, the dimensional difference between a random copolymer and a block copolymer (with the block number fixed) should become larger and larger with the increase of molecular weight. Consequently, the exponent υ of the random copolymer must be larger than unity, even though the υ values of block copolymers are unity. This, in turn, would qualitatively explain the large υ value of the random copolymer obtained above. On the other hand, there appears to be no obvious reason to believe that the υ value should suddenly deviate from unity when block number exceeds a certain number. It would be rather reasonable to assume that $\langle R^2 \rangle$ of any block copolymer chain (in which only A–B intersections are prohibited) is proportional to N for sufficiently large N, so far as the block number is definite.

We now turn to an experimental situation of random copolymers. We have already seen that the S–M random copolymer has a larger dimension than PS–PM and PM–PS–PM block copolymers in all the solvents examined (Figures 7 and 8), in apparent agreement with the Monte Carlo results. Similar results have been reported by other authors.[32-34] However, we should remember another factor which would also contribute to the dimensional difference between random and block copolymers. That is the short-range interactions which are closely related to the local structure of a chain. As for S–M copolymers, we have observed that the unperturbed dimension becomes larger with the increase of run number R, showing that the S–M linkages play an important role.[29] Hence the difference as appeared in Figures 7 and 8 should be ascribed partly to the short-range interactions. However, closer inspection of the figures reveals that the exponent a in the Mark–Houwink relation is slightly larger for the random copolymer than for the block copolymers, presumably reflecting the interactions of long-range nature.

A more definite answer will come if one examines a common theta solvent system. A theta state common to PS and PM is approximately realized in cyclohexanol (CHL) around 81 °C (θ = 81.8 and 79.4 °C for PS and PM, respectively[35]). In Figure 9, we have referred to the [η] data obtained for S–M alternating (R = 100),[29] S–M random (R = 67),[29] and PM–PS–PM block ($R \sim 0$)[36] copolymers in CHL at 81.0 °C. All these samples have nearly equimolar composition. The figure shows that the Mark–Houwink exponent a is about 0.5 for the block copolymer but it is much larger than 0.5 for the other two (0.62 and 0.65 for the random and the alternating copolymers, respectively). This is what the Monte Carlo calculations have predicted. Here it should be commented that we have previously given a somewhat different explanation to the above experimental results.[29] One will see, however, that the previous explanation is not necessarily in conflict with the present one. More detailed discussion on this particular system will be given elsewhere together with the data on PS–PM diblock copolymers which are presently lacking.

From all these results, we may conclude that the behavior of block and random copolymers as predicted from the lattice-walk model is essentially correct.

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Dipole Moments of Poly(*p*-chlorostyrene) Chains

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ABSTRACT: The mean-squared dipole moments $\langle \mu_x^2 \rangle$ of poly(*p*-chlorostyrene) (PPCS) chains have been calculated as a function of stereochemical composition using the rotational isomeric state analysis recently published for polystyrene. The dipole moment ratio $D_\infty \equiv \lim_{x\to\infty} (\langle \mu_x^2 \rangle / x\mu_0^2)$, where μ_x is the dipole moment of the x-meric chain and μ_0 is the dipole moment of the structural unit, is calculated to be less than unity at all stereochemical compositions: 0.59 for syndiotactic, ca. 0.55 throughout the atactic range, and 0.78 for isotactic. Unfavorable correlation of the individual dipoles is thus implied. The low value for syndiotactic is attributed to the approximate antiparallelism of the resultant moments for successive sequences $|\mathrm{tt}|_y$ of y trans,trans dyads. The mutual correlation of dipoles in sequences of the preferred $|\mathrm{tg}|$ conformation for the isotactic chain is poor, but the more favorable mutual orientation of resultant moments for successive sequences is responsible for the larger ratio D_∞. The calculations are in good agreement with the average, $D_\infty = 0.54 \pm 0.07$, of experimental results for atactic PPCS estimated to contain ca. 35% meso dyads. The temperature coefficient is calculated to be negative in agreement with available experiments.

The conformations accessible to a vinyl polymer chain $-(\mathrm{CHR{-}CH_2}-)_x$, in which the substituent is a planar group, can be adequately represented by two rotational states, trans (t) and gauche (g), for each bond of the chain skeleton.[2–4] The gauche-bar ($\bar{\mathrm{g}}$) state, in which the planar substituent is tilted inward with respect to the incident dyad, is effectively suppressed by steric interactions (see below). Conformational energy calculations on polystyrene[2b,3] (PS) with R = C_6H_5, on poly(methyl acrylate)[4] (PMA) with R = $COOCH_3$, and on the disubstituted homologue of PMA, poly(methyl methacrylate)[2a] (PMMA), show the energy of the $\bar{\mathrm{g}}$ conformation to be excessive, a conclusion that may be anticipated from critical examination of models.

The two-state scheme has been applied to stereochemical equilibria in oligomers of PS,[5] to the analysis of unperturbed dimensions expressed by the characteristic ratio $C_n = \langle r^2 \rangle_0 / nl^2$ of the PS chain,[2b] and to its optical anisotropy.[6] It has been employed also to treat the electric birefringence of poly(*p*-chlorostyrene) (PPCS) and poly(*p*-bromostyrene)[7] (PPBS). As was pointed out previously,[8] para substitution with Cl or Br does not materially affect the conformational energy. Hence, the conformational energies calculated for PS[2b] should be applicable also to the latter derivatives of this polymer. Advantages of the newer model over the three-state scheme used previously[9–11] accrue principally from refinements in the locations of rotational isomeric states for the meso and racemic dyads and in their relative energies. Apart from procedural simplifications resulting from reduction in the number of rotational states to be considered, rejection of conformations involving $\bar{\mathrm{g}}$ states for one or more bonds of the chain are of minor significance, inasmuch as the statistical weights previously employed[5,8–11] in the three-state model reduced $\bar{\mathrm{g}}$ conformations to low incidence.

The present study explores the use of the two-state scheme for treating the mean-square dipole moments $\langle \mu_x^2 \rangle$ of x-meric PPCS chains of variable stereochemical compositions. Calculations are carried out also on the dependences of the dipole moments on temperature. The results are directly relevant to the interpretation of the electrical birefringence of these chains,[7] as characterized by the molar Kerr constant, ${}_{\mathrm{m}}K$, which is determined principally by the configurationally averaged quantity $\langle \boldsymbol{\mu}^{\mathrm{T}} \hat{\alpha} \boldsymbol{\mu} \rangle$, where $\boldsymbol{\mu}^{\mathrm{T}}$ is the transpose of the dipole moment vector $\boldsymbol{\mu}$ for the molecule as a whole and $\hat{\alpha}$ is the anisotropic polarizability tensor of the molecule. A number of experimental studies[12–19] of the dipole moments of PPCS have been conducted over ranges of temperature. We compare these results with theoretical calculations.

Structural Geometry, Statistical Weights, and Computational Procedure

A planar substituent such as phenyl, represented as R in Figure 1, is restricted to an orientation about the C–R bond such that its plane is approximately perpendicular to the plane of the two skeletal bonds (e.g., bonds $i-1$ and i in Figure 1) flanking the substituted carbon.[2a,11,20] Steric repulsions by hydrogens of the adjoining methylene groups impose this constraint. In the $\bar{\mathrm{g}}$ conformation in which the C–R bond assumes the position of the methine C–H in Figure 1, the planar R group, oriented as stated, impinges on one of the groups, R, CH_2, or H, pendant to the neighboring substituted carbon of the dyad embracing the $\bar{\mathrm{g}}$ bond.[2,4] According to calculations of the conformational energy of PS,[2b] occurrence of a $\bar{\mathrm{g}}$ conformation entails an energy of at least 5 kcal mol^{-1}. Neglect of this state is well justified therefore, and we adopt the statistical weight matrices employed previously. These are[2b]

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \tag{1}$$

for a pair of bonds flanking a substituted carbon, irrespective of the configurations of the adjoining dyads, and

$$\mathbf{U}_{\mathrm{m}}'' = \begin{bmatrix} \omega'' & 1/\eta \\ 1/\eta & \omega/\eta^2 \end{bmatrix} \tag{2}$$

$$\mathbf{U}_{\mathrm{r}}'' = \begin{bmatrix} 1 & \omega'/\eta \\ \omega'/\eta & 1/\eta^2 \end{bmatrix} \tag{3}$$

for the bond pairs within a meso and a racemic dyad, respectively. The statistical weights are here normalized to unity for racemic,tt. The first-order parameter η measures the preference for trans over gauche. The second-order parameters ω,