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Conformation of Block Copolymers in Dilute Solution. 3. Determination of the Center-to-Center Distance between the Two Blocks by Light Scattering[1]

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ABSTRACT: The conformation of an AB diblock copolymer in dilute solution may be characterized by the mean-square radii $\langle S^2\rangle_A$ and $\langle S^2\rangle_B$ of the two blocks and the mean-square distance $\langle G^2\rangle$ between the centers of mass of them. It was previously established that $\langle S^2\rangle_K$ (K = A or B) is almost identical with the radius $\langle S^2\rangle_{H\text{-}K}$ of the equivalent K homopolymer, unless the A–B interactions are attractive. In such a situation, it is possible to determine $\langle G^2\rangle$ by light scattering with a solvent having large refractive index increments for the two homopolymers. Experiments were conducted on polystyrene–poly(methyl methacrylate) diblock copolymers in 2-butanone. The parameter σ representing the extent of "segregation" of the two blocks, $\sigma = \langle G^2\rangle/(2\langle S^2\rangle_A + 2\langle S^2\rangle_B)$, was evaluated with due regard to the sample heterogeneity. The influence of heterogeneity was found to be unexpectedly large even for a fairly homogeneous sample, say $M_w/M_n < 1.1$, and without adequate correction to this effect, the conclusion drawn from such an analysis could be misleading. It was found that σ lies very close to 1.2. This shows that the conformation of the block copolymer is almost the same as that of the homopolymers. Models like "segregated" and "core-in-shell" conformations are utterly at variance with reality.

Despite the enormous effort so far made to understand the chain conformation of block copolymers in dilute solution, the progress until recently has been highly unsatisfactory.[2a] This is due, on the one hand, to crucial difficulties of dealing with the problem theoretically[2b] and, on the other hand, to lack of effective experimental techniques which provide unequivocal information. This situation has given rise to considerable confusion regarding the simplest picture of block copolymer conformation, and thus various models, typified by the "quasi-random coil", "segregated", and "core-in-shell" conformations, have been proposed, without clear definitions for them.[1]

Very recently, considerable success has been gained by computer "experiments".[3-6] One of the important conclusions drawn thereby[3] was that the mean-square radius $\langle S^2\rangle_K$ (K = A or B) of the individual block in an AB diblock copolymer is almost the same as the radius $\langle S^2\rangle_{H\text{-}K}$ of the equivalent K homopolymer, insofar as the A–B interactions are assumed to be nonattractive. More precisely, it was shown that the ratio γ_K given by

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

ranges from 1.00 to 1.02 in a common good or Θ solvent for the two homopolymers.[7] Existing Monte-Carlo data on homopolymers[3] and those on block copolymers recently reported by Bendler et al.[5] are quite consistent with this conclusion.

Interestingly, an artificial "segregated" chain which was simulated by a random walk biased by the presence of an impermeable, noninteracting plane passing through the A–B junction was found to give a value of $\gamma_K = 1.03$.[8]

The parameter γ_K can be unambigously determined by light-scattering experiments: For a *homogeneous* diblock copolymer, the light-scattering apparent radius $\langle S^2\rangle_{app}$ is given by

$$\begin{aligned}\langle S^2\rangle_{app} &= \mu_A\langle S^2\rangle_A + \mu_B\langle S^2\rangle_B + \mu_A\mu_B\langle G^2\rangle \\ \mu_A &= 1 - \mu_B = x_A\nu_A/(x_A\nu_A + x_B\nu_B)\end{aligned} \tag{2}$$

where $\langle G^2\rangle$ is the mean-square distance between the centers of mass of the two blocks, and x_K and ν_K are the weight fraction and the refractive index increment of the *K* block, respectively. With a solvent in which $\nu_B = 0$, for example, we have $\langle S^2\rangle_A$ $(=\langle S^2\rangle_{app})$. Obviously, this method is applicable also to a heterogeneous block copolymer, for which the *z*-average radius of the A block is obtained. An analysis of existing light-scattering data of this kind led to the conclusion that γ_K is unity within an experimental uncertainty of, say, ±10%.[3] More recent neutron-scattering data of Benoit et al.[9,10] appear to be consistent with this conclusion. As far as we are aware, the only counterevidence for this is found in the paper of Han and Mozer.[11a] However, these experiments seem to leave room for criticism.[11b]

For all these reasons, it is firmly believed that γ_K is, in a practical sense, equal to unity for a block copolymer showing repulsive interactions between the two blocks. Under such a situation, eq 2 may be well approximated by

$$\langle S^2\rangle_{app} = \mu_A\langle S^2\rangle_{H\text{-}A} + \mu_B\langle S^2\rangle_{H\text{-}B} + \mu_A\mu_B\langle G^2\rangle \tag{3}$$

With independently determined values of $\langle S^2\rangle_{H\text{-}K}$, we can

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determine $\langle G^2 \rangle$ using a solvent having large ν's for the two homopolymers. In this paper, we will report the results of such a light-scattering study made on polystyrene (PS)–poly(methyl methacrylate) (PM) diblock copolymers in 2-butanone (MEK). The PS/PM pair is known as a fairly incompatible one. MEK has relatively large ν's and moderately good solvency for both PS and PM.

The results will be presented in terms of the "segregation index" σ introduced previously.[3]

$$\sigma = \langle G^2 \rangle / (2\langle S^2 \rangle_{\text{H-A}} + 2\langle S^2 \rangle_{\text{H-B}}) \tag{4a}$$

$$\sigma \approx \langle G^2 \rangle / (2\langle S^2 \rangle_{\text{A}} + 2\langle S^2 \rangle_{\text{B}}) \tag{4b}$$

This parameter is considered to be close to unity for the hypothetical chain with absent A–B interactions (and is exactly unity for the Gaussian block copolymer).[3] Only through this parameter will be detected the influence of heterosegmental interactions upon chain conformation. The previous Monte-Carlo results[3] have indicated that σ ranges from unity to about 1.5 depending on the magnitudes of the K–K and A–B interactions and copolymer composition, but not on molecular weight. This much of "segregation" of the two blocks is expected to occur even in a homopolymer chain in a good solvent. For example, a value close to 1.25 is obtained for a self-avoiding homopolymer chain on a lattice.[3] In this regard, these chains may be legitimately called "quasi-random coil" chains. On the other hand, the artificial "segregated" chain quoted above presents a value of $\sigma = 2.5$,[8] whereas one would expect a σ much smaller than unity for a model like the "core-in-shell" conformation proposed by Han and Mozer.[11a]

Before presenting the results, we will examine in some detail the influence of sample heterogeneity on the value of $\langle S^2 \rangle_{\text{app}}$ obtained from the conventional Zimm plot. As will be seen, the influence is not at all small even for a sample which is usually regarded as fairly homogeneous. Without adequate correction for this effect, the conclusions drawn from such an analysis can be misleading. We will propose a method of the correction and analyze the data on that basis.

Theoretical Section. Light Scattering from Heterogeneous Block Copolymers

According to Benoit et al.,[14] $\langle S^2 \rangle_{\text{app}}$ of a heterogeneous A–B binary copolymer is generally given by

$$M_{\text{app}}\langle S^2 \rangle_{\text{app}} = \nu^{-2}\sum_i w_i M_i \,(x_{\text{A},i}{}^2\nu_{\text{A}}{}^2\langle S^2 \rangle_{\text{A},i} + x_{\text{B},i}{}^2\nu_{\text{B}}{}^2\langle S^2 \rangle_{\text{B},i} + 2x_{\text{A},i}x_{\text{B},i}\nu_{\text{A}}\nu_{\text{B}}\langle S^2 \rangle_{\text{AB},i}) \tag{5}$$

where M_{app} is the apparent molecular weight, ν is the (average) refractive index increment of the copolymer given by $\nu = x_{\text{A}}\nu_{\text{A}} + x_{\text{B}}\nu_{\text{B}}$ with x_{K} being the average composition, and w_i is the weight fraction of the ith component with molecular weight M_i and composition $x_{\text{K},i}$ ($\sum w_i = 1$).

For a diblock copolymer, $\langle S^2 \rangle_{\text{app}}$ in eq 5 is given by

$$2\langle S^2 \rangle_{\text{AB},i} = \langle S^2 \rangle_{\text{A},i} + \langle S^2 \rangle_{\text{B},i} + \langle G^2 \rangle_i \tag{6}$$

$$\langle G^2 \rangle_i = 2\sigma_i(\langle S^2 \rangle_{\text{A},i} + \langle S^2 \rangle_{\text{B},i}) \tag{7}$$

The parameter σ here is different from the previous σ, eq 4a, but as we have already assumed that $\langle S^2 \rangle_{\text{K}} = \langle S^2 \rangle_{\text{H-K}}$, we will not distinguish them in this paper.[15] With eq 6 and 7, eq 5 reads

$$M_{\text{app}}\langle S^2 \rangle_{\text{app}} = \nu^{-2}\sum_i w_i M_i \,[x_{\text{A},i}{}^2\nu_{\text{A}}{}^2\langle S^2 \rangle_{\text{A},i} + x_{\text{B},i}{}^2\nu_{\text{B}}{}^2\langle S^2 \rangle_{\text{B},i} + x_{\text{A},i}x_{\text{B},i}\nu_{\text{A}}\nu_{\text{B}}(2\sigma_i + 1)(\langle S^2 \rangle_{\text{A},i} + \langle S^2 \rangle_{\text{B},i})] \tag{8}$$

The rhs of eq 8 includes the two types of summations, i.e., $\sum w_i M_i x_{\text{K},i}{}^2\langle S^2 \rangle_{\text{K},i}$ and $\sum w_i M_i x_{\text{A},i}x_{\text{B},i}(2\sigma_i + 1)\langle S^2 \rangle_{\text{K},i}$. The former is readily found to give the z-average mean-square radius of the K block, $\langle S^2 \rangle_{\text{K},z}$:

$$\sum_i w_i M_i x_{\text{K},i}{}^2\langle S^2 \rangle_{\text{K},i} = x_{\text{K}} M_{\text{K,w}}\langle S^2 \rangle_{\text{K,z}} \tag{9}$$

where $M_{\text{K,w}}$ is the weight-average molecular weight of the K block.

The latter type of summation cannot be performed without knowing w_i and σ_i as functions of M_i and $x_{\text{K},i}$. Here we make two assumptions: (i) the molecular weights of the two blocks of a given species are uncorrelated (the assumption of random coupling);[16,17] (ii) σ is independent of molecular weight and composition. The validity of these assumptions will be discussed later on. With these assumptions, the latter summation is found to give the weight-average mean-square radius $\langle S^2 \rangle_{\text{K,w}}$:

$$\sum_i w_i M_i x_{\text{A},i}x_{\text{B},i}(2\sigma_i + 1)\langle S^2 \rangle_{\text{A},i} \simeq x_{\text{A}} M_{\text{B},n}(2\sigma + 1)\langle S^2 \rangle_{\text{A,w}} \tag{10}$$

where $M_{\text{K,n}}$ is the number-average molecular weight of the K block.

Putting eq 9 and 10 into 8, we have

$$\langle S^2 \rangle_{\text{app}} = (1 + \mu_{\text{A}}{}^2 Y_{\text{A}} + \mu_{\text{B}}{}^2 Y_{\text{B}})^{-1}[(1 + Y_{\text{A}})\mu_{\text{A}}{}^2\langle S^2 \rangle_{\text{A,z}} + (1 + Y_{\text{B}})\mu_{\text{B}}{}^2\langle S^2 \rangle_{\text{B,z}} + \mu_{\text{A}}\mu_{\text{B}}(2\sigma + 1)(\langle S^2 \rangle_{\text{A,w}} + \langle S^2 \rangle_{\text{B,w}})]$$
$$Y_{\text{K}} = (M_{\text{K,w}}/M_{\text{K,n}}) - 1 \qquad \text{K} = \text{A or B} \tag{11}$$

where we have used the relation

$$M_{\text{app}}/M_{\text{n}} = 1 + \mu_{\text{A}}{}^2 Y_{\text{A}} + \mu_{\text{B}}{}^2 Y_{\text{B}} \tag{12}$$

which is valid for a "randomly coupled" block copolymer.[16,17] An equation equivalent to eq 11 with $\sigma = 1$ was recently obtained by Benoit and co-workers,[10] independently from us.[18]

It is noticed that eq 11 includes the weight-average as well as the z-average radii. The one can be calculated from the other if we know the molecular weight distribution $f(M)$ and the relation between $\langle S^2 \rangle$ and M for the relevant (monodisperse) homopolymers, the latter usually being given by

$$\langle S^2 \rangle = aM^b \tag{13}$$

For $f(M)$, we assume the Schulz distribution,[19a]

$$f_{\text{w}}(M) = y^{h+1}M^h \exp(-yM)/\Gamma(h + 1)$$
$$h^{-1} = Y = M_{\text{w}}/M_{\text{n}} - 1, \qquad y^{-1} = M_{\text{n}}Y \tag{14}$$

Then we have

$$\langle S^2 \rangle_z = aM_{\text{n}}{}^b Y^b \Gamma(2 + b + Y^{-1})/\Gamma(2 + Y^{-1}) \tag{15}$$

$$\langle S^2 \rangle_z / \langle S^2 \rangle_{\text{w}} = (1 + b + Y^{-1})/(1 + Y^{-1}) \tag{16}$$

where Γ is a Γ function. Equation 16 for $b = 1$ is the one conventionally used by other authors.[19b]

Figures 1 and 2 show the behavior of eq 11 with eq 16 for a simplest case with $\langle S^2 \rangle_{\text{A,z}} = \langle S^2 \rangle_{\text{B,z}}$, $Y_{\text{A}} = Y_{\text{B}}$, and $b = 1$. Figure 1 is the case with $\sigma = 1$ (Gaussian block copolymer chain). For a homogeneous copolymer ($Y_{\text{K}} = 0$), the curve $\langle S^2 \rangle_{\text{app}}/\langle S^2 \rangle_{\text{K,z}}$ vs. μ_{K} is given by a parabola, whereas with increase of Y_{K}, the curve becomes broader and broader, approaching the straight line passing through (0,1) and (1,1). Figure 2 shows the σ dependence of $\langle S^2 \rangle_{\text{app}}$ for the case with $Y_{\text{K}} = 0$. With decrease of σ, the curve becomes broader, approaching again the horizontal straight line for $\sigma = 0$. That is, a decrease of σ and an increase of Y_{K} bring about a similar effect on $\langle S^2 \rangle_{\text{app}}$. Quantitatively, the curves for $Y_{\text{A}} \neq Y_{\text{B}}$ become asymmetric with respect to $Y_{\text{K}} = {}^1/_2$,[10] and those for $b > 1$ become somewhat broader than those for $b = 1$.

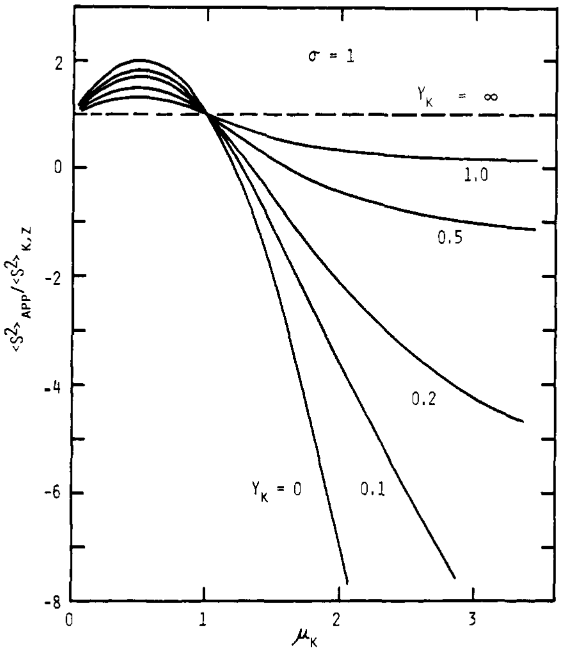

Figure 1. Plots of $\langle S^2\rangle_{app}/\langle S^2\rangle_{K,z}$ vs. contrast factor μ_K (K = A or B) for the case with $\sigma = 1.0$, $Y_A = Y_B$, $\langle S^2\rangle_A = \langle S^2\rangle_B$, and $b = 1$.

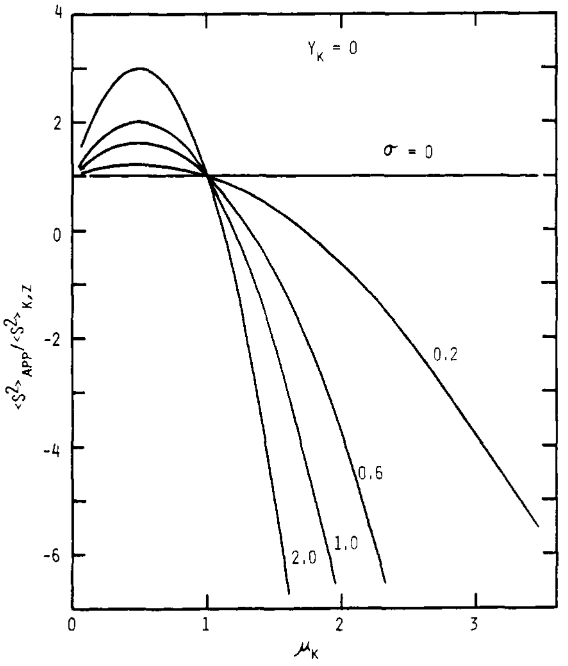

Figure 2. Plots of $\langle S^2\rangle_{app}/\langle S^2\rangle_{K,z}$ vs. contrast factor μ_K (K = A or B) for the case with $Y_A = Y_B = 0$, $\langle S^2\rangle_A = \langle S^2\rangle_B$, and $b = 1$.

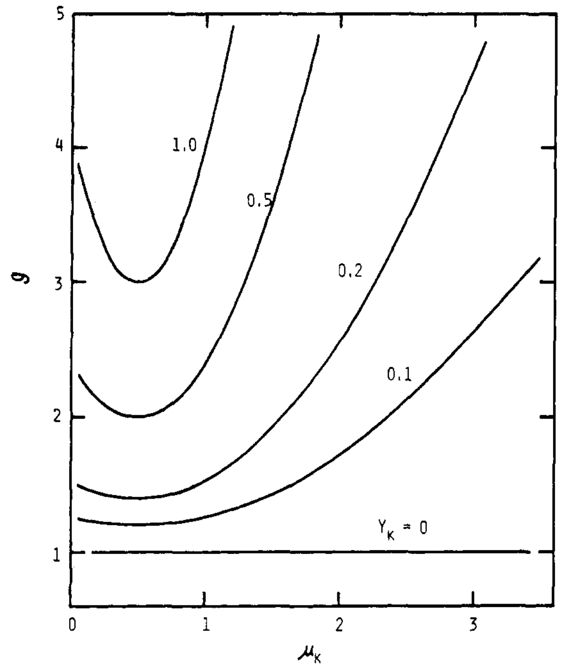

Figure 3. Plots of the correction factor g vs. contrast factor μ_K (K = A or B) for the case with $\sigma = 1.0$, $Y_A = Y_B$, $\langle S^2\rangle_A = \langle S^2\rangle_B$, and $b = 1$.

In Figure 3, the same data as in Figure 1 are looked at from a somewhat different angle: For a homogeneous block copolymer, σ is given by eq 1 and 4b, i.e.,

$$\sigma = (\langle S^2\rangle_{app}/\langle S^2\rangle_{K,z} - 1)/(4\mu_A\mu_B) \qquad (17)$$

whereas for a heterogeneous copolymer, the σ calculated from eq 17 is not correct but must be multiplied by a factor g to give the true σ (=1, in this case). In the figure, the correction factor g is plotted against μ_K for several values of Y_K. It can be seen that g becomes larger as Y_K increases when μ_K is fixed, and does so as $|\mu_K - {}^1/_2|$ increases when Y_K is fixed. Even for a copolymer with $Y_K = 0.1$ ($Y_{cop} = 0.05$), for example, which usually is regarded as a fairly homogeneous sample, g is 1.2 for $\mu_K = {}^1/_2$ and becomes as large as 4 for $\mu_K = -3$ (or +4). In this respect, most synthetic block copolymers available to date are *appreciably* heterogeneous, and an adequate correction to the heterogeneity is indispensable. In order to evaluate σ correctly, it is thus essential to use copolymers with as small heterogeneity as possible, second to characterize them as perfectly as possible, and third to use a solvent in which μ_K is as close to ${}^1/_2$ as possible.

Recently, small-angle neutron scattering is proving to be a valuable method for studying the conformational properties of polymer chains in solution as well as in bulk. The biggest advantage of this method as applied to block copolymers is said to be that the optical weight factor μ_K can be changed to a large extent without change of the thermodynamic state of the system. In fact, different μ_K's have been realized by deuterium labeling one of the two blocks and using solvents partially labeled by deuterium.[9-11a] Unfortunately, however, it is not possible to approach, with such a sample, a fairly wide region around $\mu_K = {}^1/_2$,[9,10] where the overall chain conformation can be least ambiguously known. Of course, one can realize $\mu_K \simeq 1$ with a fully deuterated sample in a protonic solvent or vice versa, but in this case μ_K cannot be largely changed. This is just the type of experiment that can be done by light scattering with more ease and, in certain cases, higher accuracy. The most comprehensive study that can be done at the present time would be to carry out both neutron and light scattering with a one-block-labeled sample. With suitable solvents, this combination realizes all $\mu_K \simeq 0$, 1, and ${}^1/_2$, so that $\langle S^2\rangle_K$'s and $\langle G^2\rangle$ can be determined with least interference from sample heterogeneity (even though certain technical problems such as the sample molecular weights feasible to the two methods will still remain). In addition, simultaneous neutron-scattering studies made in the regions of $\mu_K > 1$ and < 0 should provide the relevant information of sample heterogeneity.[10]

Experimental Section

Polymer Samples and Characterization. The preparation and characterization procedures of polystyrene (PS)–poly(methyl methacrylate) (PM) block copolymers were described previously.[12]

Table I
Characteristics of Homo-PS and -PM Samples and the Values of Mean-Square Radius $\langle S^2 \rangle$ (in 10^4 Å^2 unit) in MEK at 30.0 °C

code	$10^{-5} \cdot M_n$	$10^{-5} \cdot M_w$	M_w/M_n	M_w/M_n (GPC)	$\langle S^2 \rangle$
PS 53H	1.80	1.98	1.10	1.03	2.20
54H	3.64	3.95	1.09	1.07	4.59
74H	3.42	3.61	1.06	1.05	4.09
63H	3.54	3.96	1.12	1.09	4.32
27H	5.54	6.71	1.21	1.10	9.08
61H		15.9		1.23	22.7
PM 67M	2.21	3.12	1.41	1.48	4.47
78M	3.96	6.27	1.58	1.41	9.88
80M	9.16	11.1	1.22	1.21	17.6
75M		21.4		1.35	35.9

In brief, the preparation was carried out in tetrahydrofuran at −78 °C with either cumylpotassium or *n*-butyllithium as initiator. In each reaction, 1,1-diphenylethylene (DPE) was used as an intermediate to suppress grafting of the living PS to MMA units.[16] An aliquot of the living PS (coded H and having the same code number as the relevant block copolymer) was recovered for the convenience of later analysis. By thin-layer chromatography (TLC),[12,20] the block copolymers were found free from the homopolymers. Homo-PM samples (coded M) were also anionically prepared under the same conditions as for the block copolymers. For example, the initiator was treated with DPE prior to the polymerization of MMA. Gel permeation chromatography (GPC) and nuclear magnetic resonance showed no clear differences in molecular weight distribution and microstructure between the cumylpotassium- and butyllithium-initiated PM's, so that these PM's should have molecular characteristics similar to those of the PM blocks of the block copolymers. The homo-PS samples used in this study are the precursors of the block copolymers.

Figure 4 shows the GPC curves for PS–PM 63B50, PS 63H, and PM 80M. For comparison, the GPC curve for a Pressure Chemical PS ($M = 4.1 \times 10^5$, $M_w/M_n = 1.05$) is also shown. It can be seen that the PS sample has a fairly sharp distribution similar to that of the standard sample, while the PM sample has a rather broad distribution. The (apparent) broadness of the molecular weight distribution of the block copolymer is between the two. This was generally the case with the other samples.

The results of sample characterization are summarized in Tables I and II. The weight-average molecular weights M_w were determined by light scattering. The solvents used were 2-butanone (MEK), toluene (TOL), and 1,2-dichloroethane for the block copolymers,[12] and only MEK for both homopolymers. The number-average molecular weights M_n were determined by osmometry[12] by using TOL as the solvent. We notice that the M_n values obtained for the block copolymers are in good agreement with the values calculated from the M_n values of the precursor PS's and the known compositions. In the tables are also given the M_w/M_n ratios determined by GPC. Those values were obtained after being corrected for axial dispersion by the method of Hamielec and Ray.[21] The correction factors to multiply the apparent M_w/M_n ratios ranged from 0.92 to 0.94 for all the samples. For the homopolymers, the ratios determined by GPC are in good agreement with those determined by the absolute measurements (Table I), while for the block copolymers the agreement is somewhat less satisfactory (Table II). This may be due partly to the inadequacy of the GPC analysis for the block copolymers carried out here,[22] and partly to the difficulty of M_w determination for copolymers by the conventional light-scattering method.

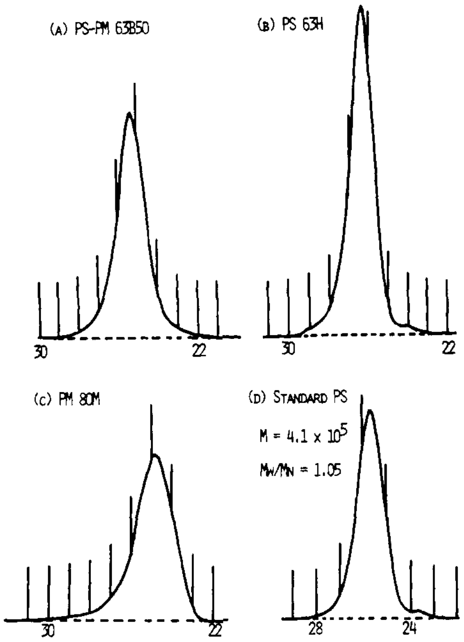

Figure 4. Gel permeation chromatograms for: (a) PS–PM diblock copolymer 63B50, (b) the precursor PS 63H, (c) PM 80M, and (d) Pressure Chemical Standard PS ($M = 4.1 \times 10^5$).

Light Scattering. Light-scattering measurements were made in MEK at 30.0 °C on a Fica photometer Model 50. Scattered light intensities were measured at 11 different angles ranging from 30 to 150° with vertically polarized light of 436-nm wavelength. The refractive index increments ν of the block copolymers were calculated from $\nu = x_{PS}\,\nu_{PS} + x_{PM}\,\nu_{PM}$ with $\nu_{PS} = 0.232$ and $\nu_{PM} = 0.113$ (mL/g). The details of measurements were as described previously.[12] Figure 5 shows typical examples of the Zimm plots. In the abscissa we employed $\sin^2(\theta/2) - [\text{constant} \times c]$ (in g/mL) instead of the conventional $\sin^2(\theta/2) + [\text{constant} \times c]$. Values

Table II
Characteristics of PS–PM Diblock Copolymers

sample	x_{PS}[a]	$10^{-5}M_n$	$10^{-5}M_w$[b]	M_w/M_n[b,c]	Y_{PS}	Y_{PM}[d]	Y_{PM}[e]
54B	0.42	8.61	9.30	1.08 (1.18)	0.09	0.3	
74B	0.47	7.39	7.65	1.04 (1.13)	0.06	0.38	
63B30	0.24	14.8[f]	15.0	1.02	0.12		0.4
63B50	0.49	6.89	7.64	1.11 (1.18)	0.12	0.37	0.4
63B70	0.69	5.10[f]	6.4	1.25	0.12		0.6

[a] Weight fraction. [b] Determined by the conventional light-scattering method with three different solvents (see text). [c] Values in parentheses by GPC. [d] Determined by light scattering with a solvent (bromobenzene) having zero ν (see text). [e] Determined by TLC analysis (see text). [f] Calculated from the M_n data for the precursor PS.

Table III
Summary of the Light-Scattering Results on PS–PM Diblock Copolymers in MEK at 30.0 °C ($\langle S^2 \rangle$ in 10^4 Å^2 unit)

sample	$\langle S^2 \rangle_{app}$	$\langle S^2 \rangle_{PS,z}$	$\langle S^2 \rangle_{PS,w}$	$\langle S^2 \rangle_{PM,z}$	$\langle S^2 \rangle_{PM,w}$	σ
54B	11.9	4.59	4.21	9.53	7.59	1.10
74B	10.2	4.09	3.85	8.09	6.20	1.13
63B30	24.9	4.32	3.87	26.7	20.3	0.76
63B50	9.67	4.32	3.87	7.03	5.41	1.28
63B70	6.10	4.32	3.87	3.80	2.68	1.19

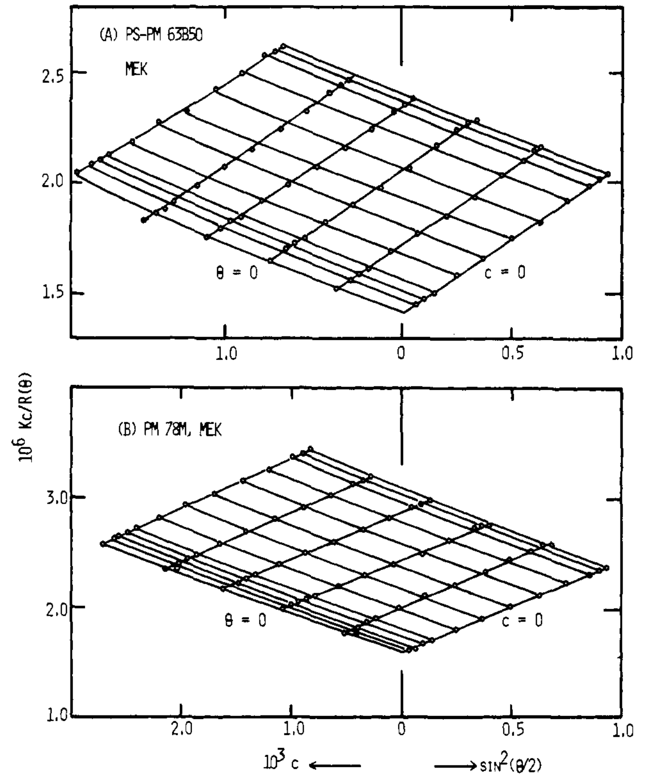

Figure 5. Zimm plots for: (a) PS–PM diblock copolymer 63B50, and (b) PM 78M. Measured in MEK at 30.0 °C.

of root-mean-square radius obtained are listed in Tables I and III.

Results and Discussion

As has been pointed out, adequate knowledge of the polydispersities of the two blocks is crucially important to determine σ correctly. The characterization of the PS block can be adequately done, since the precursor PS is available. These two should be identical insofar as any premature termination of the living PS did not take place. This, in fact, was the case as the TLC and osmometry results showed.

The second block (PM) is difficult to characterize in general. A direct method to determine Y_{PM} is to make light scattering in a solvent having zero ν_{PS}. Bromoform, for example, approximately meets this condition.[23] We have tried such measurements, but the results were not very satisfactory because of difficulty of handling this optically unstable solvent. Some other specially devised experiments are needed for estimating Y_{PM} precisely. Here we have employed the following two methods. These are both based on the assumption of random coupling,[16,17] i.e., that the chain has structure described by the random-coupling statistics. This assumption is quite plausible for the type of block copolymers under consideration. In fact, we have recently obtained a direct experimental verification for it.[24]

One method is, again, light scattering, but carried out in a solvent having zero refractive index increment ν for a copolymer. In this case, the forward scattering intensity reflects solely the sample heterogeneity.[25] It was confirmed that the parameter Q, related to the second moment of compositional distribution,[14] can be determined in this way much more precisely than in the conventional way of using solvents having finite ν. For a "randomly coupled" block copolymer, Q is proportional to $Y_A + Y_B$, and thus Y_{PM} can be determined with required accuracy. The details will be reported elsewhere.[26] The other method is TLC analysis.[27] As reported previously,[28] it is possible to separate a block copolymer into components differing only in composition and thus to construct a compositional distribution curve. Again for a randomly coupled block copolymer, the distribution is a function essentially of Y_A, Y_B, and x_K alone. Thus Y_{PM} can be estimated through comparison of the experimental and calculative curves. This method also seems effective, since block copolymer heterogeneity manifests itself much more markedly in composition distribution than in molecular weight distribution. Values of Y_{PM} estimated by one or both of the two methods are listed in Table II. These values are quite reasonable with regard to those for the homo-PM's prepared under the similar conditions (Table I). In addition, the consistency in the values for sample 63B50 obtained by the two methods confirms the reliability of these data.

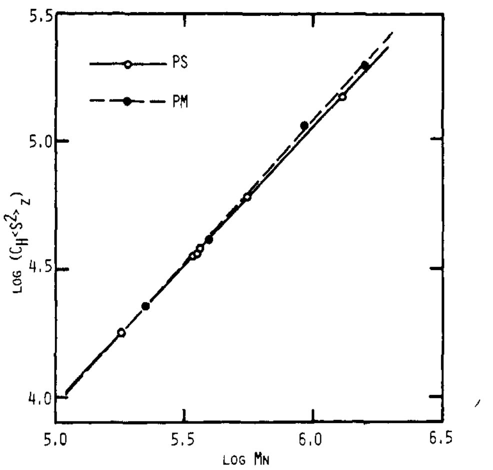

Figure 6. Plots of log $C_H\langle S^2\rangle$ vs. log M_n for PS and PM samples in MEK at 30.0 °C: $C_H = \Gamma(2 + Y^{-1})/[Y^b\,\Gamma(2 + b + Y^{-1})]$.

Now we turn to the light-scattering results. In Figure 6, values of $\langle S^2\rangle_z$ for the two homopolymers are plotted against M_n. Here, $\langle S^2\rangle_z$ has been multiplied by the correction factor C_H for the sample polydispersity, which according to eq 15 may be given by

$$C_H = \Gamma(2 + Y^{-1})/[Y^b\Gamma(2 + b + Y^{-1})] \tag{18}$$

Because the present samples have reasonably narrow distributions, this particular assumption of distribution function (the Schulz function) should not seriously affect the final results. As the figure shows, the data points for both homopolymers having different polydispersities nicely fall on the respective single lines. The exponents b used to calculate C_H were determined in an iterative manner so as to coincide with the slopes of the final curves. The following relations were found:

$$C_H\langle S^2\rangle_z = 3.77 \times 10^{-2}M_n^{1.08}(\text{PS}) \tag{19a}$$

$$C_H\langle S^2\rangle_z = 2.65 \times 10^{-2}M_n^{1.11}(\text{PM}) \tag{19b}$$

These relations correspond to the $\langle S^2\rangle$ vs. M relations for the monodisperse homopolymers, from which $\langle S^2\rangle_w$, $\langle S^2\rangle_z$, etc., of an unknown (polydisperse) homopolymer and hence of the equivalent block can be calculated with the known $M_{K,n}$ and Y_K values.

Table III lists the measured values of $\langle S^2\rangle_{app}$ for the block copolymers along with the relevant dimensions of the individual blocks calculated from eq 19. Values of σ computed from eq 11 are shown in the last column. For the samples of nearly equimolar composition (54B, 74B, and 63B50), σ is close to 1.2. This is the case also with sample 63B70, while σ is considerably smaller than unity for sample 63B30. However, it is noted that sample 63B30

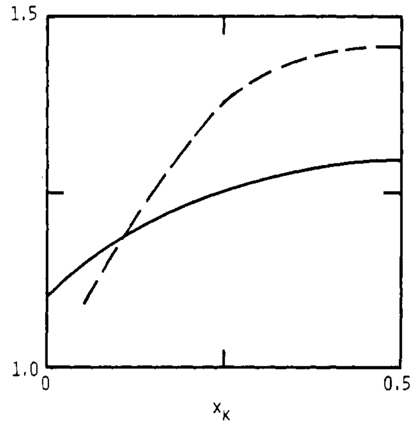

Figure 7. Plots of σ vs. composition x_K (K = A or B) estimated for a self-avoiding homopolymer chain (b = 1.20). The broken curve is for a self-avoiding block copolymer chain with absent K–K interactions.[3]

has a very long PM block relative to the PS block, and therefore the computed σ value depends strongly on the Y_{PM} value. If we assume that $Y_{PM} = 0.3$ instead of 0.4, σ is computed to be 1.1. This much of ambiguity in Y_{PM} must be expected in certain cases. As PM composition decreases, the computed value of σ becomes less and less sensitive to a supposed change in Y_{PM}. For sample 63B70 which has the lowest PM composition, the σ value shifts only ±5% with a change in Y_{PM} of ±0.1. Thus, the small value of σ found for sample 63B30 should be ascribed more to experimental accuracy (in Y_{PM} as well as in $\langle S^2\rangle$) rather than to a specific conformational property.

Here, it may be interesting to compare this result with the behavior of the homopolymers. As pointed out previously,[3] the relation $\langle S^2\rangle_K \simeq \langle S^2\rangle_{H\text{-}K}$ should be valid also for homopolymers (in a good or Θ solvent). That is, if we supposedly divide a homopolymer chain into two arbitrary "blocks" A and B, the radius of each block must be almost the same as that of the equivalent free chain. Since the relation $\langle S^2\rangle = aM^b$ generally holds, it is readily found that the σ of the homopolymer chain is given by

$$\sigma \simeq (1 - x_A^{b+1} - x_B^{b+1})/[2x_Ax_B(x_A^b + x_B^b)] \qquad (20)$$

For a self-avoiding chain on three-dimensional lattices[29] (and according to the Flory theory[30]), $b = 1.20$, for which case the σ calculated from eq 20 is shown in Figure 7. It can be seen that σ has the largest value of 1.30 for $x_K = {}^1/_2$ and decreases as x_K decreases, approaching the limiting value of $(1 + b)/2 = 1.10$ for vanishing x_K. In reality, the maximum value should be somewhat smaller than 1.30, because $\langle S^2\rangle_K$ is not exactly equal to $\langle S^2\rangle_{H\text{-}K}$. If we set $\langle S^2\rangle_K = 1.02\langle S^2\rangle_{H\text{-}K}$, we recover the previously estimated value of $\sigma = 1.25$.[3] It is not unreasonable that the value at $x_K = 0$ is larger than unity. This value corresponds to the ratio $\langle R_{0G}^2\rangle/2\langle S^2\rangle$, where $\langle R_{0G}^2\rangle$ is the mean-square distance between the end segment and the center of mass of the whole chain. Obviously, $\langle R_{0G}^2\rangle = 2\langle S^2\rangle$ for a Gaussian chain, but for a perturbed chain, the former should be somewhat larger than the latter.[3] Nevertheless, the similarity will be obvious between this behavior of the homopolymer and that of the self-avoiding block copolymer chain with absent K–K interactions simulated previously[3] (the broken curve), even though the absolute values of σ are different. In both examples, σ can be regarded as constant for not-too-small x_K and is obviously independent of molecular weight.[3] Thus even if there is a positive composition dependence of σ, it should be too small to be detected by the present technique. This, in turn, would justify the assumption we have made in the previous section that σ is independent of both molecular weight and composition. The values of b found for the present homopolymer systems were somewhat smaller than 1.20 (see eq 19), the corresponding values of σ being 1.11 (PS) and 1.16 (PM) for $x_K = {}^1/_2$. In any case, it is clear that the conformation of PS–PM block copolymers in MEK corresponds very closely to those of the parent homopolymers. Models like the "segregated" and "core-in-shell" conformations are highly unlikely. This conclusion essentially agrees with the Monte-Carlo results.[3] Thus, this should not be the feature particular to the PS–PM/MEK system.[31]

Conclusions

(I) In order to evaluate the mean-square distance between the centers of mass of the two blocks or, equivalently, the parameter σ, light-scattering data on PS–PM diblock copolymers in MEK were analyzed under the assumption that the mean-square radius of each block is the same as that of the equivalent homopolymer. This assumption has been amply justified.

(II) The importance of an adequate correction for sample heterogeneity was stressed. A method of correction was proposed, according to which the data were analyzed. The method includes the following assumptions or approximations: (i) The molecular weight of one block is independent of that of the other block. (ii) The molecular weight distribution of each block is given by a Schulz function. (iii) The parameter σ is independent of both molecular weight and composition. It was pointed out that none of these assumptions or approximations is unrealistic.

(III) The σ value for this system was found to be about 1.2. It is concluded that the block copolymer conformation corresponds very closely to that of the parent homopolymers. Models like the "segregated" and "core-in-shell" conformations are highly unrealistic. This should be generally true for a block copolymer (whose parent homopolymers show unfavorable compatibility) in a common good solvent for the two homopolymers.

Acknowledgment. We would like to thank Professor H. Benoit, University of Strasbourg, for his stimulating discussion on this subject. Thanks are also due to Professor T. Kotaka, Osaka University, for his valuable comments.

References and Notes

(1) Parts 1 and 2 of this series are ref 3 and 6, respectively.
(2) An accumulation of relevant papers can be found in ref 3 and 6; (b) A brief review on the theoretical achievements can be found in ref 5.
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(4) T. M. Birstein, A. M Skvortsov, and A. A. Sariban, *Macromolecules*, **9**, 888 (1976).
(5) (a) J. Bendler, K. Šolc, and W. Gobush, *Macromolecules*, **10**, 635 (1977); (b) J. Bendler and K. Šolc, *Polym. Eng. Sci.*, **17**, No. 8 (1977).
(6) T. Tanaka, T. Kotaka, K. Ban, M. Hattori, and H. Inagaki, *Macromolecules*, **10**, 960 (1977).
(7) In a selective solvent, i.e., a poor or nonsolvent for one of the two blocks, micelle formation usually takes place, and a molecular dispersion is realized only in a limited range of solvent solvency (see, e.g., T. Kotaka, T. Tanaka, M. Hattori, and H. Inagaki, *Macromolecules*, **11**, 138 (1978)). Recent Monte-Carlo results indicate that γ_K for such a molecularly dispersed diblock copolymer is still close to unity; T. Tanaka, to be published.
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(9) M. Duval, R. Duplessix, C. Picot, P. Rempp, H. Benoit, J. P. Cotton, G. Jannink, B. Farnoux, and R. Ober, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 585 (1976).
(10) H. Benoit, Lecture at the IUPAC Congress, 5E-13, Tokyo, 1977; M. Ionescu, Ph.D. Dissertation, Strasbourg University, 1976.

(11) (a) C. C. Han and B. Mozer, *Macromolecules*, **10**, 44 (1977). (b) In ref 11a, neutron and light scattering are made on a PS–PM diblock copolymer (with a deuterated PS block) and the relevant homopolymers in tolune. The authors conclude that $\gamma_{PS} \simeq 1$ and $\gamma_{PM} \ll 1$, according to which they propose a "partially segregated core-in-shell model". Since this is directly in opposition to our basic assumption that $\gamma_K = 1$, it is felt necessary to comment on their results in some detail. First, the neutron scattering measurements seem to be made in a range of Q (momentum transfer) apparently too high to correctly estimate $\langle S^2 \rangle$ and the second virial coefficient A_2 of those samples. This must be true especially for the block copolymer in the one-component-invisible system.[12] Second, the molecular weights of the PS and the PS block seem to be too low ($M < 10^5$) for light scattering to provide reliable data. In fact, some questions arise as to the reported data with regard to the previously published data on high molecular weight samples.[3,12,13] Third, their interpretation on the $\langle S^2 \rangle$ data for the block copolymer seems erroneous: As to the neutron experiments, for example, they remark that the scattering from the PS block is so small that $\langle S^2 \rangle_{app}$ is very close to $\langle S^2 \rangle_{PM}$. This certainly is not the case. With the numerical data presented therein, we have $\mu_{PS} = 1 - \mu_{PM} = -0.08$. Putting these and the measured values of $\langle S^2 \rangle_{app}{}^{1/2} = 85$ Å and $\langle S^2 \rangle_{PS}{}^{1/2} = 225$ Å into eq 11 of ref 3, we find $\langle S^2 \rangle_{PM}{}^{1/2} = 140$ to 170 Å corresponding to the assumption of $\sigma' = 1.0$ to 1.5 (see ref 3).

(12) T. Tanaka, T. Kotaka, and H. Inagaki, *Macromolecules*, **7**, 311 (1974).

(13) G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1960).

(14) See, e.g., H. Benoit and D. Froelich in "Light Scattering from Polymer Solutions", M. B. Huglin, Ed., Academic Press, New York, 1972.

(15) According to the previous notation,[3] the σ in eq 7 should be written as σ'.

(16) D. Freyss, P. Rempp, and H. Benoit, *J. Polym. Sci., Part B*, **2**, 217 (1964).

(17) T. Kotaka, N. Donkai, and T. I. Min, *Bull. Inst. Chem. Res., Kyoto Univ.*, **52**, 332 (1974).

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(22) In this analysis, the molecular weight M of a fraction of the block copolymer eluted at a elution volume V_e was assumed to be given simply by $\log M = x_{PS} \log M_{PS}(V_e) + x_{PM} \log M_{PM}(V_e)$.

(23) See, e.g., D. Rahlwes, J. E. L. Roovers, and S. Bywater, *Macromolecules*, **10**, 604 (1977).

(24) M. Omoto, T. Tanaka, S. Kadokura, and H. Inagaki, *Polymer*, in press.

(25) J. Vorliček and P. Kratochvîl, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 855, 1251 (1973).

(26) T. Tanaka, M. Omoto, and H. Inagaki, to be published.

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(28) T. Kotaka, T. Uda, T. Tanaka, and H. Inagaki, *Makromol. Chem.*, **176**, 1273 (1975).

(29) See, e.g., S. Windwer in "Markov Chains and Monte Carlo Calculations in Polymer Science", G. G. Lowry, Ed., Marcel Dekker, New York, 1970.

(30) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.

(31) Rahlwes and Kirste (*Makromol. Chem.*, **178**, 1793 (1977)) have reported light-scattering results on PS–poly(α-methylstyrene) (PMS) diblock copolymers with high homogeneity. The conclusion they reached is essentially the same as ours, i.e., the PS–PMS conformation in TOL corresponds very closely to that of PS and PMS. Since the PS/PMS pair is known as a fairly compatible one (see, e.g., D. G. H. Ballard, M. G. Rayner, and J. Shelten, *Polymer*, **17**, 640 (1976)), their conclusion and ours here for the two rather typically different polymer pairs certainly reinforces the conformational picture obtained from the Monte-Carlo calculations.[3,5]

Notes

The Valence Angle at the Bridge Oxygen Atom in Cellulose

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The results of the stereochemical analysis of polysaccharides depend significantly on the geometrical parameters used for the repeat unit.[1-3] Inherent in these calculations is the assumption that the geometry of the residue in the crystal structures of the mono- and disaccharides would remain the same when incorporated in the polymer. Using the geometries derived from various crystal structure reports on small molecules containing the β-D-glucose moiety, French and Murphy[3] found differences in the results of the structure analysis of cellulose.

In addition to the geometry of the monomer unit, the valence angle ∠COC (denoted here by τ) at the bridge oxygen atom is also an important parameter. In methyl glycosides it is of the order of 113°, whereas it increases to 116–118° in disaccharides.[2,4-6] It would thus seem that the angle τ increases with the size of the substituent on the sugar residues, as well as on the type of linkage between the units, in the crystal structure of the small molecules. Conventionally, values in the range of 116.5 to 117.5° (similar to those in disaccharides) have been used in the conformational calculations on cellulose. However, using the Arnott–Scott geometry for the residue,[6] Gardner and Blackwell[7] concluded that a lower value of 114.8° should be used for τ to achieve a distance of 2.75 Å for the O-3′- - -O-5 hydrogen bond. Use of $\tau = 117°$ leads to a shorter hydrogen bond distance. The calculations of French and Murphy[3] also led to similar results and they observed that neither a small glycosidic angle nor a short hydrogen bond distance should be considered improbable in cellulose structure.

In view of the preference shown in the above work for a lower value of τ, it is appropriate to examine the effect of the variation of τ in the conformational energies of the cellulose chain. The results of such an analysis are presented here.

When the repeat distance and the screw symmetry are known from diffraction data, the virtual bond method has proved useful for rapid analysis of the conformations of a polymer. The description of the virtual bond method was given before.[1,8,9] Essentially, it involves a rotation θ of the residue about its virtual bond or the end-to-end vector, thereby varying the disposition of the atoms of the residue with respect to the helix axis. In this process, the angle at the bridge atom varies with θ. For each value of θ, contiguous residues may be generated and the energy of interaction between contiguous residues or between remote residues can be calculated. From the coordinates of the residues along the helix thus generated, the angle τ as well as the torsion angles ϕ and ψ around the glycosidic bonds can be evaluated. It is thus a convenient method

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