Macromolecules **1985,** *18,* 651–657

Configurational Characteristics of Thermotropic Polymers Comprising Rigid Groups Connected by Polymethylene Spacers

Do Y. Yoon* and Sergio Bruckner†

IBM Research Laboratory, San Jose, California 95193. *Received June 14, 1984*

ABSTRACT: The distribution of chain sequence extension, calculated by using rotational isomeric state (RIS) models, is compared with isotropic–nematic transition characteristics for a number of thermotropic polymers comprising rigid groups connected by polymethylene (PM) spacers. This distribution depends strongly not only on the even–odd character of the number of methylene units of the spacers, but also on the specific groups (or atoms) connected at the ends of PM spacers. When PM spacers are attached to a linear rigid unit (LR) by LR—O—PM or LR—O(O=)C—PM linkage, chains having even-numbered methylene spacers exhibit a significant population of highly extended conformers, favorable for packing, which allow nearly parallel alignment of rigid units along the major extension axis; they also lower significantly the internal (conformational) energy below the average energy. Chains with odd-numbered methylenes attached in the same way offer few conformers in which the polymer as a whole is highly extended; furthermore, the energies of the relatively extended conformers are only slightly lower than the average and they place the rigid units tilted by ca. 30° from the major extension axis. When PM spacers are attached by LR—C(=O)O—PM linkage, on the other hand, the population of extended conformers is reduced significantly for the chains with even-numbered methylene spacers. When compared with those of odd-numbered methylene spacers linked in the same way, they exhibit even smaller fractions of relatively extended conformers and the lowering in the energy of extended conformers relative to the average energy is smaller, reversing the typical even–odd effects. These characteristics of chain sequence extension and extended conformers relate very closely to the experimental results of isotropic–nematic transition characteristics of these polymers. This finding therefore shows very clearly the critical importance of highly extended conformers and their preferential selection in forming nematic states and thus supports the view that emphasizes the steric repulsive forces in considering the stability of ordered states of chain molecules. Furthermore, the detailed conformational order of PM sequences in nematic states is then deducible by matching the experimental results of enthalpy and entropy changes with those estimated from the conformational selection on the basis of chain sequence extension.

Introduction

The mesomorphic state, or liquid crystalline state, of bulk polymers has been a subject of very intense investigations in recent years, in view of the scientific and technological importance associated with this class of polymers.[1,2] Among the various mesomorphic polymers, the thermotropic polymers comprising rigid groups connected by flexible spacer groups in the chain backbone have been studied most prominently due to the presence of well-defined isotropic–mesomorphic transitions that are easily accessible to most experimental studies.[3-11] Moreover, since the chemical structures of these polymers represent a small departure from conventional flexible polymers, the nature of their mesomorphic states is very closely related to the more general subject of disordered vs. ordered states of polymers in condensed states.

A large number of studies carried out on this class of polymers show unambiguously the critical importance of the spacer and the groups (or atoms) connecting it to a rigid group. When the polymethylene (PM) spacers are attached to a linear rigid group (LR) by LR—O—PM or LR—O(O=)C—PM linkage (see Figure 1a,b), the nematic states occur readily, and the enthalpies and the entropies of isotropic–nematic transitions of these polymers are much larger,[5,6,11] by 5–10 times, than those of the corresponding monomeric liquid crystals. Moreover, the enthalpy and entropy changes are much larger for the chains with even-numbered methylene spacers than those with odd-numbered methylenes.[3,5-7] On the other hand, when the PM spacers are attached by LR—C(=O)O—PM linkage (see Figure 1c), the tendency to form a nematic state is significantly suppressed.[8,9] Furthermore, when a nematic state occurs, the even–odd effect of the PM spacer is reversed; the enthalpies and the entropies of the transition are smaller for the chains having even-numbered methylene spacers than those with odd-numbered methylenes.[10]

These results indicate that flexible spacer groups do not play the role of solvents, but rather participate actively in the ordering process. However, how the specific details of the spacer and the connecting group contribute to the isotropic–nematic transitions and what are the conformations of PM spacers in the nematic state are not understood. Recently, Abe[12] pointed out that the orientational correlations of the two successive rigid groups depend strongly on the even–odd character of the intervening PM spacer between them, but not on the connecting group (i.e., LR—O(O=)C—PM vs. LR—C(=O)O—PM linkage). Moreover, the transition entropy estimated by selecting chain conformations on the basis of orientational correlations of rigid groups is found to be much smaller than the experimental results.[12] Therefore, orientational correlations of rigid groups, although they are undoubtedly important, do not seem to be the most predominant factor.

In this regard, it is important to note that the total partition function of a bulk system of chain molecules may be factorized into three contributions as[13]

$$Z_T = Z_{st}Z_{en}Z_{conf} \tag{1}$$

where Z_{st} denotes the steric exclusion (excluded volume effect), Z_{en} is the orientation-dependent (anisotropic) attraction, and Z_{conf} represents the configurational degrees of freedom. Here the contributions from the orientation-dependent steric exclusion and the anisotropic interactions may be expressed by[14]

$$-\ln Z_{st} \simeq X\left[\frac{4}{\pi}\langle\sin\Psi\rangle - \frac{4}{\pi}\langle\sin\Psi\rangle \ln\left(\frac{4}{\pi}\langle\sin\Psi\rangle\right)\right] \tag{2}$$

$$-\ln Z_{en} \simeq -\tfrac{1}{2}X(T^*/T)(1 - \tfrac{3}{2}\langle\sin^2\Psi\rangle)_r{}^2 \tag{3}$$

where X is the ratio between the contour length and the mean diameter of the chain, Ψ is the angle between a chain

---

† IBM World Trade Postdoctoral Fellow. Permanent address: Dipartimento di Chimica, Politecnico di Milano, Milan, Italy.

0024-9297/85/2218-0651$01.50/0

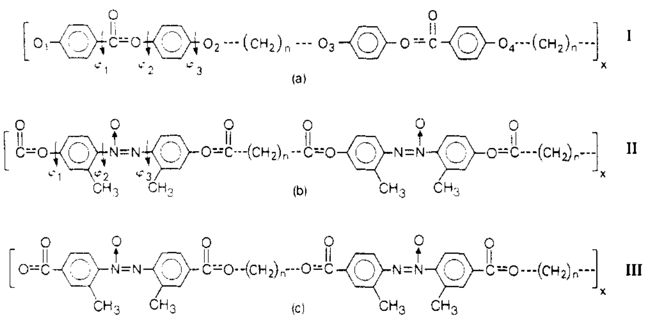


Figure 1. Schematic diagrams of the three types of thermotropic polymers comprising linear rigid groups connected by polymethylene spacers. They are distinguished by the groups (or atoms) attached at the ends of polymethylene sequences, as shown by the dashed lines in each diagram.

segment and the macroscopic orientation axis, and T^* denotes the magnitude of orientation-dependent attractions per chain length of unit axial ratio. The brackets in eq 2 denote averaging over all chain segments, whereas the brackets with subscript r in eq 3 represent averaging over rigid units only, which are the major source of anisotropic interactions.

The occurence of ordered states of chain molecules is thus driven by the reduced steric exclusion and more favorable intermolecular attractions, at the expense of decreased configurational degrees of freedom. In this regard, theoretical considerations[13,15] show that in the case of high molecular weight systems the steric contribution is most predominant owing to the difficulty of packing long-chain molecules in a disordered array. (For flexible polymers, of course, this packing difficulty is compensated by an enormous diversity in available chain configurations.[15]) Consequently, a stable ordered (nematic) state of long-chain molecules is subject to the condition that the value of $\langle \sin \Psi \rangle$ of the chain can be decreased substantially without causing an excessive reduction in the concomitant configurational partition function, according to eq 2.

The foregoing considerations then suggest that the tendency, or probability, of chain sequences to assume highly asymmetric extended configurations is most critical to forming a nematic state. In this paper we thus examine the distribution of chain sequence extension for the three types of polymers shown schematically in Figure 1. Since our main emphasis is to investigate the effect of even–odd character of the polymethylene (PM) spacer and the contribution of the connecting group at the ends of the PM spacer, the details of the linear rigid (LR) groups are not critical; they are chosen in consideration of available experimental results for a later purpose. In type I polymers the PM spacers are attached by -O- linkage to the LR group. The type II polymers have LR—O(O═)C—PM links, whereas in type III polymers the ester unit connection is reversed to LR—C(═O)O—PM. The average internal (conformational) energy and the orientational correlations of rigid units are also calculated as functions of chain sequence extension in order to obtain detailed characteristics of extended conformers.

Computational Method

Geometrical and Conformational Parameters. The bond geometries used here are taken mostly from the crystal structures of phenyl benzoate[16] and p-azoxyanisole[17] and are listed in Table I. The ester and the azoxy groups are in the trans conformation. In type I polymers (see Figure 1a), the torsional angles involving phenylene groups are taken to be $\phi_1 = 0$, $\phi_2 = \pm 65$, and $\phi_3 = 0$ or 180°.[16] The rotations of C_6H_4-O┼CH_2-CH_2 bonds in polymer I are assumed to be in the trans conformation in view of severe steric repulsions involving the phenylene and the methylene group in the gauche states. In type II polymers (see Figure 1b), the torsional angles involving the phenylene and the azoxy groups are taken to be $\phi_2 = 0$ and $\phi_3 = \pm 36°$, respectively, from the results of ^{1}H NMR spectra analyses of this polymer,[18] and $\phi_1 = \pm 65°$ from its correspondence to ϕ_2 in polymer I. The torsional angles involving the phenylene groups in type III polymers are taken from the corresponding angles in the type I and type II polymers.

The torsional angles of trans conformations involving spacer groups are taken to be zero, and the torsional angles of the various gauche states are designated in Table II. Also listed are the first-order interactions denoting the energies of gauche conformation relative to that of trans for the various bonds considered here. The second-order interactions denoting the extra energies in the double-gauche (gg) states of same and opposite signs, respectively, due to the interactions involving pairs of groups or atoms separated by four skeletal bonds are listed in Table III. All the values are taken from the recent investigations of Abe[12,19] by relating his energy parameters to this conventional form. In view of the critical importance of the first-order interaction of the O-CH_2┼CH_2-CH_2 bond (see below) in the case of polymer III, the two limiting values[20]

Table I
Bond Geometries

bond length, Å		bond angle, deg	
C^{ar}—C^{ar}	1.39	C^{ar}—C^{ar}—C^{ar}	120
C^{ar}—C	1.51	C^{ar}—C*—O	112
C^{ar}—N	1.49	C^{ar}—O—C*	116
C^{ar}—O	1.44	C^{ar}—O—C	112
C—C	1.53	C^{ar}—N(O)═N	112
C—O	1.44	C^{ar}—N═N(O)	115
C*[a]—O	1.35	C—C—C	112
N═N	1.22	C*—O—C	114
		O—C*—C	112
		O—C—C	112

[a] The asterisk denotes the carbon of the carbonyl group.

Table II
Torsional Angles and First-Order Interactions

bond[a]	gauche state, deg	first-order interaction, kcal mol^{-1}
O-C—C-C	120	0 (−0.40)[b]
C-C—C-C	112.5	0.50
C*-O—C-C[c]	104	0.35
O-C*—C-C	120[d]	1.02
C*-C—C-C	110	0.39

[a] The torsional angle denotes the rotations around the bond shown by long lines. [b] For polymer III, both values were used as the two limits.[20] The calculations of polymer I and II are carried out taking 0, since the results are scarcely dependent on this parameter. [c] The asterisk denotes the carbonyl carbon. [d] The three-state rotational isomeric state model of Abe[19] is adopted here.

Table III
Second-Order Interactions[a]

bond pair	second-order ineraction, kcal mol^{-1}	
	$g^{\pm}g^{\pm}$	$g^{\pm}g^{\mp}$
O-C—C—C-C	0.0	0.50
C-C—C—C-C	0.0	2.0
C*-O—C—C-C[b]	0.0	very large[c]
O-C*—C—C-C	−0.53	very large
C*-C—C—C-C	0.0	very large

[a] The two bonds around which the rotations occur are designated by long lines. [b] The asterisk denotes the carbonyl carbon. [c] These states are assigned a statistical weight of 0.

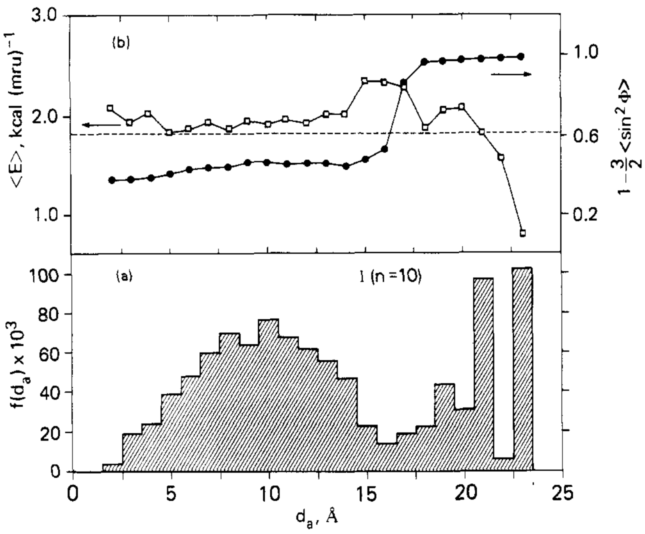


Figure 2. (a) Distribution of chain sequence extension calculated for polymer I with $(CH_2)_{10}$ spacer at $T = 500$ K. (b) Orientational correlations of rigid units with the major extension axis and the average internal (conformational) energy as function of chain sequence extension; the dotted line denotes the average energy of all conformers.

of 0 and −0.4 kcal mol^{-1} are considered in the calculations of polymer III. In the case of polymer I, the key results are scarcely dependent on this interaction, and it is taken to be 0.

Computational Procedure. In our calculations all the possible conformations are considered by enumeration of all the rotational isomeric states. For each conformation the major extension axis a is defined from the two vectors representing the two rigid groups attached at the ends of the spacer (e.g., O_1–O_2 and O_3–O_4 in Figure 1a) by diagonalizing the tensorial sum of the self-direct products of these vectors. The projection of the repeat unit vector (e.g., O_1–O_3 in Figure 1a) along this axis is defined as the repeat unit extension d_a, and the angle between the major extension axis and each rigid group vector is then defined by Φ. (The repeat unit here refers to a rigid group and a spacer sequence.) The distribution of d_a is then determined in the form of a histogram for each integer values of d_a by summing the statistical weights of all conformers with their repeat unit extensions in the interval between $d_a - 0.5$ Å and $d_a + 0.5$ Å and normalizing it with respect to the total. The average internal (conformational) energy and the average orientational correlation of rigid units along the major extension axis, $1 - 3/2\langle\sin^2 \Phi\rangle$, are also computed for each interval of d_a.

Numerical Results

Polymer I. The results obtained for polymer I with $(CH_2)_{10}$ spacer (see Figure 1a) are plotted in Figure 2. The repeat unit extension has a very striking distribution, exhibiting a well-defined peak at the maximum extension at $d_a = 23$ Å, which comprises ca. 10% of the total conformer populations. This group of fully extended conformers place the two rigid groups connected by the PM sequence parallel to the major extension axis, as shown by the values of $1 - 3/2\langle\sin^2 \Phi\rangle$ in Figure 2b. Furthermore, the average conformational energy of these conformers is substantially lower, by ca. 1.0 kcal per mole of repeat unit (mru), than the average energy denoted by the dotted line in Figure 2b.

The results of Figure 2 show that nearly all the conformers with $d_a \geq 18$ Å place the rigid groups parallel to each other. In terms of orientational correlations of rigid units, they are sharply distinguished from the remaining conformations for which the orientational correlation $(1 - 3/2\langle\sin^2 \Phi\rangle)$ is decreased to ca. 0.4. This is identical with the result found by Abe,[12] who observed a well-separated bimodal distribution in orientational correlations of two rigid groups connected by even-numbered methylene spacers. The results of Figure 2 also show, however, that the conformers allowing parallel alignment of rigid units can be further distinguished according to their chain sequence extensions, or shape anisotropies.

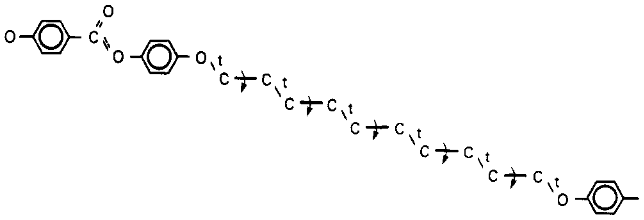


Figure 3. Schematic drawing of the set of conformers exhibiting the maximum extension ($d_a = 23$ Å) in Figure 2a. The bonds designated by t assume exclusively the trans conformation, and the bold lines with arrows indicate the bonds around which the trans, gauche$^+$, and gauche$^-$ states are allowed in proportion to their statistical weights.

Careful examination of the conformers with extreme extension ($d_a = 23$ Å) reveals that they are made up of a unique set of conformations that adopt exclusively the trans state at evey second bond starting from the O–CH_2 bond adjoining the phenylene, as shown schematically in Figure 3. The bonds between these exclusively trans bonds are free to adopt the normal trans, gauche$^+$, and gauche$^-$ conformations in proportion to their statistical weights. Because of the nearly tetrahedral bond geometries involved, all the conformers of this kind allow not only parallel alignment of rigid units, but also maximum extension of the chain sequence along this alignment axis.

The presence of this set of conformers, which offer high chain extension and parallel alignment of rigid groups without incurring excessive reduction in the configurational partition function, will help promoting a stable nematic state. It is also most likely that these conformers will be preferred over the others in a nematic state. The enthalpy of the resulting isotropic–nematic transition of the polymer will then have a significant contribution from this conformational selection owing to the large change in the internal (conformational) energy of the PM spacers. Consequently, the transition enthalpy of the polymer will be considerably larger than that of the monomeric liquid crystal. This deduction follows very closely, qualitatively at least, the experimental result of polymer I with $(CH_2)_{10}$ spacer in comparison with that of the corresponding monomer.[11]

The results of the chain sequence containing $(CH_2)_9$ spacer are shown in Figure 4. In sharp contrast to the results in Figure 2, the fraction of highly extended conformers is quite small. Furthermore, the relatively extended conformers place the rigid units tilted by ca. 30° with respect to the extension axis, with their orientational correlations falling in the range of ca. 0.6. The average energy of these relatively extended conformers, which make up an appreciable fraction, is only slightly lower than the average energy.

Polymer II. The conformer fraction, the orientational correlation of rigid groups, and the average conformational energy as function of repeat unit extension of polymer II with $(CH_2)_{10}$ spacer are plotted in Figure 5. The results are very close to those of polymer I shown in Figure 2; the fraction of the conformers with extreme extension is only slightly smaller and the difference in its energy compared with the average is somewhat less. The results of the

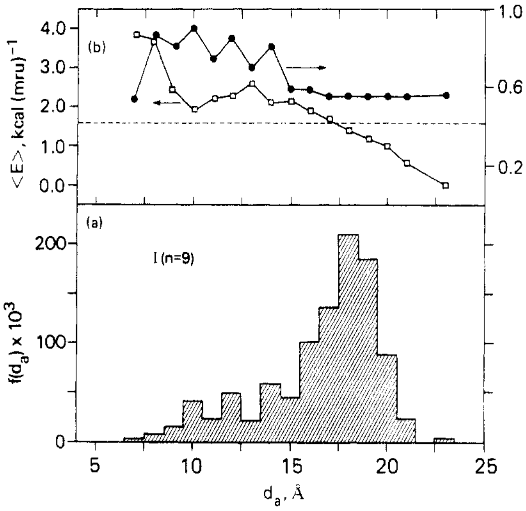


Figure 4. Distribution of chain sequence extension, and orientational correlations of rigid units and the internal energy as function of extension, calculated for polymer I with $(CH_2)_9$ spacer at T = 500 K; see the caption of Figure 2.

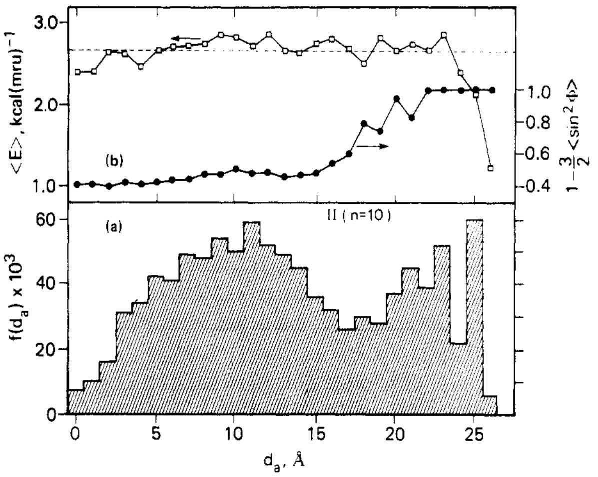


Figure 5. Distribution of chain sequence extension, and orientational correlations of rigid units and the internal energy as function of extension, calculated for polymer II with $(CH_2)_{10}$ spacer at T = 360 K; see the caption of Figure 2.

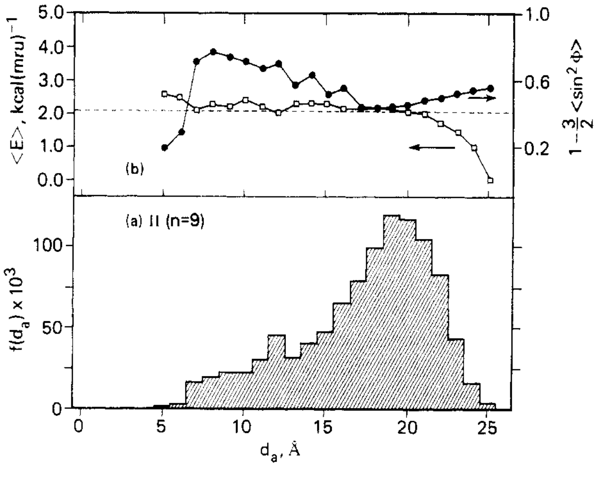


Figure 6. Distribution of chain sequence extension, and orientational correlations of rigid units and the internal energy as function of extension, calculated for polymer II with $(CH_2)_9$ spacer at T = 360 K; see the caption of Figure 2.

polymer with $(CH_2)_9$ spacer shown in Figure 6 are also very close to those of the corresponding polymer I in Figure 4; the distribution is only slightly broader.

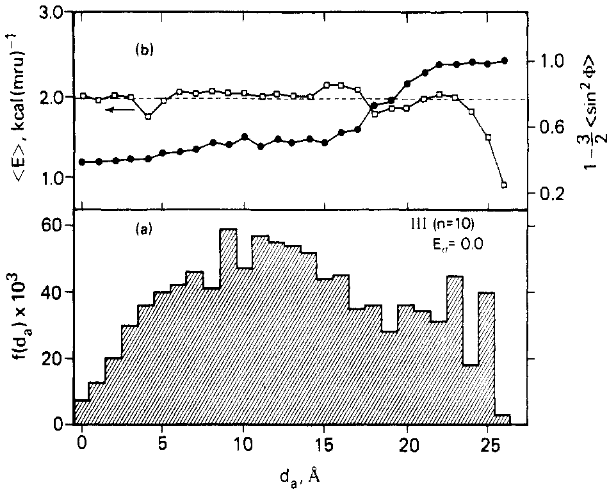


Figure 7. Distribution of chain sequence extension, and orientational correlations of rigid units and the internal energy as function of extension, calculated for polymer III with $(CH_2)_{10}$ spacer at T = 400 K. The first-order interaction E_σ denoting the energy of gauche relative to trans conformation of the O–CH_2ǂCH_2–CH_2 bond is taken to be 0; see also the caption of Figure 2.

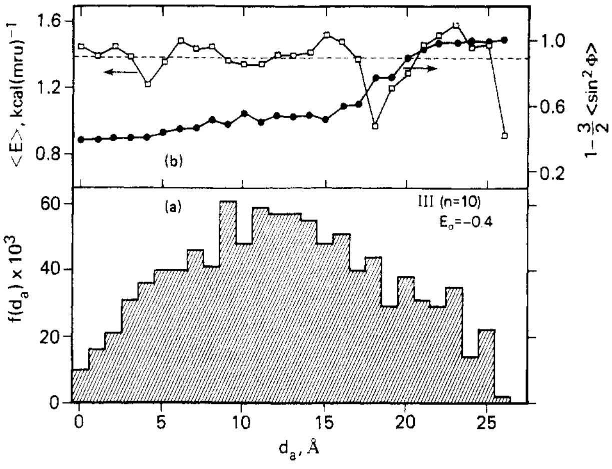


Figure 8. Distribution of chain sequence extension, and orientational correlations of rigid units and the internal energy as function of extension, calculated for polymer III with $(CH_2)_{10}$ spacer at T = 400 K taking E_σ = −0.4 kcal mol^{-1} for the O–CH_2ǂCH_2–CH_2 bond; see the caption of Figure 7.

The close similarity in the isotropic–nematic transition characteristics between polymer I and polymer II is thus followed by the similarity in their configurational characteristics of chain sequence extension. Furthermore, the strong dependence of the transition enthalpy of polymer II on the even–odd character of the PM spacer[6] is matched closely by the characteristics of the extended conformers, i.e., the energies of those extended conformers (that make up an appreciable fraction) relative to the average energy as well as the orientational correlations of rigid units with respect to the chain extension (or alignment) axis that determine the anisotropic attractions (see eq 3).

Polymer III. In this case the results are critically dependent on the first-order interaction energy E_σ denoting the energy of the gauche with respect to the trans conformation of the O–CH_2ǂCH_2–CH_2 bond. This energy falls between 0 and −0.4 kcal mol^{-1} according to the previous investigations of chain conformations of poly(trimethylene oxide).[20] Because of this uncertainty the two limiting values are considered in our calculations. The results of the polymer with $(CH_2)_{10}$ spacer computed taking E_σ = 0 and −0.4 kcal mol^{-1} at 400 K are shown in Figures 7 and

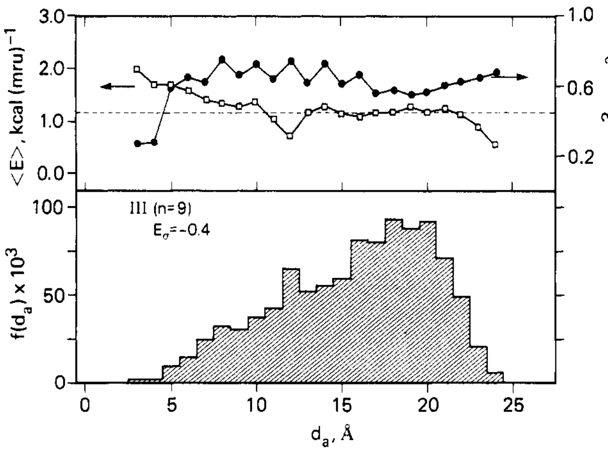


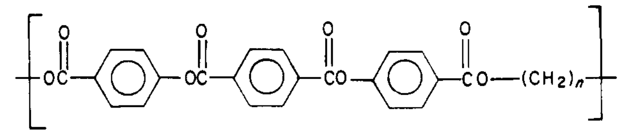
Figure 9. Distribution of chain sequence extension, and orientational correlations of rigid units and the internal energy as function of extension, calculated for polymer III with $(CH_2)_9$ spacer at $T = 400$ K taking $E_\sigma = -0.4$ kcal mol^{-1} for the $\mathrm{O{-}CH_2{\downarrow}CH_2{-}CH_2}$ bond; see the caption of Figure 7.

8, respectively. The distributions of chain sequence extension, especially the fraction of highly extended conformers, are critically dependent on the value of E_σ. However, it is evident that within the allowed range of E_σ the fraction of highly extended conformers is considerably smaller than that of the corresponding polymer II (see Figure 5). Moreover, as the results of Figure 8 demonstrate most strikingly, the average energy of relatively extended conformers might be even higher than the average energy. Lack of highly extended conformers of appreciable population therefore suggests that it will be less likely to form a nematic state of this type of polymer. Furthermore, when a nematic state occurs, the transition enthalpy will have a very small contribution, if any, from the conformational energy of the PM spacer.

This rather drastic consequence of LR—C(=O)O—PM linkage can be traced to the first-order interaction of the $\mathrm{O{-}CH_2{\downarrow}CH_2{-}CH_2}$ bond. That is, the highly extended conformers of the type shown in Figure 3 place the two $\mathrm{O{-}CH_2{\downarrow}CH_2{-}CH_2}$ rotations at both ends of the PM sequence in the trans state. As the negative sign of E_σ indicates, the energy of the trans conformation of this bond is higher than that of the gauche state. This situation is in sharp contrast to that of polymers I and II with even-numbered methylene spacers, where the energies of the trans bonds of highly extended conformers are always lower than those of alternate gauche states.

In the case of polymer III with $(CH_2)_9$ spacer, the results are only slightly dependent on E_σ within the allowed range. The values calculated taking $E_\sigma = -0.4$ kcal mol^{-1}, plotted in Figure 9, are rather close to those of the corresponding polymer II (Figure 5); the distribution is somewhat broader and the lowering in the energy of the relatively extended conformers from the average is slightly smaller. Therefore, in the case of PM spacers of odd-numbered methylenes the difference between the LR—O(O=)C—PM and LR—C(=O)O—PM linkages is much less pronounced than that of the even-numbered methylenes. For the chain sequences with odd-numbered methylene spacers, the average energy of relatively extended conformers is definitely lower than the average, while this may not be the case for the even-numbered methylenes.

Therefore, the enthalpies of the isotropic–nematic transition of type III polymers might become larger for the chains with odd-numbered methylenes than those with even methylenes, reversing the ordinary even–odd effect. This deduction, based on the characteristics of extended conformers, follows closely the experimental results reported for the isotropic–nematic transitions of the polymers comprising the repeat units of[10]



Moreover, the general difficulty of finding nematic states of type III polymers with even-numbered methylene spacers[8,9] relates very closely to the lack of extended conformers of chain sequences of this type.

Discussion

The results presented above indicate very clearly the critical importance of highly extended conformers and their preferential selection in forming nematic states of polymers and thus strongly support the view that emphasizes steric repulsive forces in considering the stability of ordered states of polymers. The tendency to favor highly extended conformers is dependent on the detailed conformational characteristics of the chain sequence, which in turn depends not only on the chemical structure of the spacer, but also on the groups (or atoms) connecting the spacer to the rigid group. Moreover, the enthalpy and the entropy (see below) of the isotropic–nematic transition seem to reflect strongly the conformational ordering of the spacer group in the nematic state.

The specific conformational order in the nematic state may then be inferred by matching the experimental results of the transition enthalpy and entropy. For polymer I with $(CH_2)_{10}$ spacer, it was pointed out previously[11] that the enthalpy of the isotropic–nematic transition is much larger than what can be expected from the orientational order alone, upon comparing the enthalpy change and the order parameter of the polymer with those of the corresponding monomer. Hence, an additional contribution to the enthalpy change from the increased trans bond fraction of the spacer in the nematic state was implied.

Specifically, the experimental results[11] show that $\Delta H \simeq 0.18$ kcal mol^{-1} and $s \simeq 0.37$ for the monomer, and $\Delta H \simeq 1.56$ kcal per mole of repeat unit (mru) and $s \simeq 0.75$[21] for the polymer. Therefore, the enthalpy change due to anisotropic interactions in the polymer is estimated to be ca. 0.74 kcal (mru)$^{-1}$ according to eq 3. This estimate is an upper bound, however, since it assumes that the enthalpy change of the monomer is entirely due to the orientational order and thus ignores any contribution from the conformational part. The enthalpy change due to conformational ordering in the polymer should then be ca. 0.82 kcal (mru)$^{-1}$ at a minimum. This estimate is matched closely by the difference in the energy of the fully extended conformers (with d_a = 23 Å) from the average, which corresponds to 0.98 kcal (mru)$^{-1}$ according to the results plotted in Figure 2.

In addition, the entropy change due to the restriction of chain conformations in the nematic state to this set of conformers can be estimated from

$$\Delta S_c = -k_B \ln f_N + \Delta h / T_{NI} \qquad (4)$$

where f_N is the fraction (in partition function) of the conformers allowed in the nematic state, Δh denotes the lowering in the energy of these conformers from the average energy, and T_{NI} is the transition temperature. The entropy contribution from the steric exclusion may be estimated from eq 2. For this calculation, the value of $\langle \sin \Psi \rangle$ is averaged over the rigid and spacer groups with weighting factors in proportion to their contour lengths.

Table IV
Calculated and Experimental Values of Enthalpy and Entropy Change at Isotropic–Nematic Transition of Polymer I with $(CH_2)_{10}$ Spacer

	conformations	anisotropic interactions	steric[c]	total (calcd)[a]	expt[b]
ΔH, kcal $(mru)^{-1}$	0.98	0.74		1.72	1.56
ΔS, cal $(mru)^{-1}$ K^{-1}	6.3		−3.3	3.0	3.2

[a] All the calculations are carried out at $T = 500$ K. [b] The values are taken from ref 11. [c] The axial ratio of the repeat unit is ca. 5.3.

Table V
Calculated and Experimental Values of Enthalpy and Entropy Change at Isotropic–Nematic Transition of Polymer I with $(CH_2)_9$ Spacer

	conformations	anisotropic interactions	steric[c]	total, (calcd)[a]	expt[b]
ΔH, kcal $(mru)^{-1}$	0.40	0.27		0.67	(0.60)
ΔS, cal $(mru)^{-1}$ K^{-1}	2.15		−0.63	1.52	(1.44)

[a] All the calculations are carried out at $T = 500$ K. [b] The values are taken from the corresponding polymer II in ref 6; see the text. [c] The axial ratio of the repeat unit is ca. 5.0.

The calculation for the spacer group is carried out by representing it as three linear segments with their ends placed at the two terminal oxygens and the fourth and eighth carbon from the initial oxygen; the contour length of each segment thus approximates the mean chain diameter of 4.6 Å.[12,14] The total entropy change calculated in this manner matches very closely the experimental result, as shown by the comparison in Table IV. (The negative value of the entropy change due to steric contribution reflects the more severe steric exclusion in the isotropic state.)

Hence, the experimental results of both enthalpy and entropy changes suggest strongly that, in the nematic state of type I and type II polymers with even-numbered methylene spacers, the PM sequences assume highly extended configurations; they adopt exclusively the trans conformation at every second bond starting from the first bond which is not collinear with the rigid group, as drawn schematically in Figure 3. Further confirmation of this model is provided by ^2H NMR measurements of polymer I with $(CD_2)_{10}$ spacer in the nematic state.[22] In the case of type III polymers, such conformers place the two $O{-}CH_2 \nmid CH_2{-}CH_2$ rotations in the trans conformation, which is not a favored state for this bond.[20] Consequently, the nematic state of type III polymers with even-numbered methylene spacers is less likely to form, and when it does, the conformations of the PM group will depart considerably from those represented by Figure 3.

The results of Table IV show that the entropy change is also due primarily to the restrictions on the spacer conformations in the nematic state. In this regard, the fact that entropy changes at the isotropic–nematic transition of polymer II with odd-numbered methylene spacers are significantly smaller than those with even-numbered methylenes suggests that the restriction on the spacer conformations of the nematic state is considerably less severe for the odd-numbered methylenes. The entropy changes estimated for polymer I with $(CH_2)_9$ spacer, assuming that only the conformers with the repeat unit extension $d_a \geq 18$ Å are allowed in the nematic state, are listed in Table V. The estimate of the corresponding enthalpy change, assuming that the orientational order parameter of chain extension axis a is identical with that of the polymer with $(CH_2)_{10}$ spacer, is also listed in the same table. The experimental results of this polymer are not available yet. However, the calculated values may be compared with the results of polymer II with $(CH_2)_9$ spacer, since the experimental results of ΔH and ΔS for polymer I with $(CH_2)_{10}$ are very close to those of the corresponding polymer II.[6] Both the enthalpy and entropy changes estimated in this manner seem to reproduce the experimental values.

All the conformers thus considered to exist in the nematic state of the polymer I (and polymer II) with $(CH_2)_9$ spacer are found to place the rigid units tilted by ca. 30° from the axis of chain extension (and hence chain alignment). Therefore, in the polymers with odd-numbered methylene spacers the degree of alignment of rigid units will be different from the orientational order of the chain sequences; the alignment of rigid units is expected to decrease to ca. 60% of that of chain sequences according to the results in Figure 4b.

Finally, we would like to point out that the idea of relating the characteristics of extended conformers to the enthalpy and entropy changes of polymers at their isotropic–nematic transitions suggests further interesting (and different) results when the PM spacers are replaced by other flexible groups, e.g., polyoxyethylene, poly(dimethyl siloxane), etc. Therefore, future investigations in this direction will be very helpful in establishing better understanding of the nature of liquid crystalline order in polymers.

Acknowledgment. We are indebted to Professor P. J. Flory for valuable comments and suggestions during the course of this work. We acknowledge that our work benefited a great deal from the results of Professor A. Abe. S.B. thanks IBM World Trade of Italy for granting a postdoctoral fellowship.

References and Notes

(1) Cifferi, A., Krigbaum, W. R., Meyers, R. B., Eds. "Polymer Liquid Crystals"; Academic Press: New York, 1982.
(2) Flory, P. J. *Adv. Polym. Sci.* **1984**, *59*, 1.
(3) Roviello, A.; Sirigu, A. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 455; *Eur. Polym. J.* **1979**, *15*, 61.
(4) Jackson, W. J., Jr.; Kuhfuss, H. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2043.
(5) Griffin, A. C.; Havens, S. J. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 951.
(6) Blumstein, A.; Thomas, O. *Macromolecules* **1982**, *15*, 1264. Blumstein, R. B.; Stickles, E. M.; Blumstein, A. *Mol. Cryst. Liq. Cryst. (Lett.)* **1982**, *82*, 205.
(7) Anton, S.; Lenz, R. W.; Jin, J. I. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1901.
(8) Krigbaum, W. R.; Astar, J.; Toriumi, H.; Ciferri, A.; Preston, J. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 109. Krigbaum, W. R.; Watanabe, J. *Polymer* **1983**, *24*, 1299.
(9) Blumstein, A.; Vilasagar, S.; Ponrathnam, S.; Clough, S. B.; Maret, G. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 877.
(10) Ober, C. K.; Jin, J. I.; Lenz, R. W. *Polym. J.* **1982**, *14*, 9.
(11) Sigaud, G.; Yoon, D. Y.; Griffin, A. C. *Macromolecules* **1983**, *16*, 875.
(12) Abe, A. *Macromolecules* **1984**, *17*, 2280.
(13) Ronca, G.; Yoon, D. Y. *J. Chem. Phys.* **1982**, *76*, 3295; **1984**, *80*, 925.
(14) Flory, P. J.; Ronca, G. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 289, 311.
(15) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 73; *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 4510.

Macromolecules **1985,** *18,* 657-665

(16) Harkema, S.; Gaymans, R. J.; van Hummel, G. J.; Zylberlicht, D. *Acta Crystallogr., Sect. B* **1979**, *35*, 506. Hummel, J. P.; Flory, P. J. *Macromolecules* **1980**, *13*, 479.
(17) Krigbaum, W. R.; Chatani, Y.; Barber, P. G. *Acta Crystallogr., Sect. B* **1970**, *26*, 97.
(18) Martins, A. F.; Ferreira, J. B.; Volino, F.; Blumstein, A.; Blumstein, R. B. *Macromolecules* **1983**, *16*, 279.
(19) Abe, A. *J. Am. Chem. Soc.* **1984**, *106*, 14.
(20) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969; p 173.
(21) This value is determined from both ^{1}H NMR and ^{2}H NMR measurements of the polymer with $(CD_2)_{10}$ spacer of a relatively low molecular weight.[22] It is somewhat larger than $s \sim 0.6$ obtained in ref 11 from the measurement of diamagnetic anisotropy of a high molecular weight polymer. This difference is most likely due to the difficulty in achieving complete alignment of the high molecular weight polymer under the applied magnetic field in the latter experiment.
(22) Bruckner, S.; Scott, J. C.; Yoon, D. Y.; Griffin, A. C., in preparation.

Theory of Micelle Formation in Block Copolymer–Homopolymer Blends

Mark Douglas Whitmore† and Jaan Noolandi*

Xerox Research Centre of Canada, 2660 Speakman Drive,
Mississauga, Ontario, Canada L5K 2L1. *Received April 23, 1984*

ABSTRACT: The structural parameters of monodisperse AB diblock copolymer micelles in homopolymer of type A are derived by minimizing a simple free energy expression. The core is found to consist almost entirely of B blocks of the copolymer molecules, with radius l_B depending primarily on the degree of polymerization of that block, Z_{CB}. l_B scales as $l_B \propto Z_{CA}^{\mu} Z_{CB}^{\nu}$, where Z_{CA} is the dp of the copolymer A block, $0.67 \lesssim \nu \lesssim 0.76$, and μ is small and negative, $-0.1 \lesssim \mu \lesssim 0$. Similarly the corona thickness l_A is found to depend primarily on the copolymer A block, varying as Z_{CA}^{ω}, with $0.5 \lesssim \omega \lesssim 0.86$. The physical origin of these exponents is discussed, and the stretching parameters of the polymer chains are obtained. The swelling of the corona by homopolymer of low molecular weight ($Z_{HA} \ll Z_{CA}$) is also described. The theory is applied to an analysis of recent small-angle neutron scattering data for the polystyrene/polybutadiene system, and excellent agreement with experiment is demonstrated. The critical micelle concentration is calculated and shown to be dominated by an exponential dependence on $\chi_{AB} Z_{CB}$, where χ_{AB} is the Flory–Huggins interaction parameter. As a general result, the importance of the copolymer composition is emphasized; every property of the system depends on either Z_{CA} or Z_{CB} or both, but never on just the total molecular weight.

1. Introduction

Recent experimental work[1] on the structure of block copolymer–homopolymer blends using small-angle neutron scattering (SANS) affords a unique opportunity to test modern theories of micelle formation in these systems. Previously we have developed a simple model of AB diblock copolymer micelles in selective small-molecule solvents.[2] In this paper our earlier work is generalized to include "dilute solid solutions" of diblock copolymers of arbitrary composition in a homopolymer matrix. Remarkably good agreement with the SANS measurements of Selb et al.[1] is obtained. There are no fitted parameters in our model.

Our model assumes that both the corona and core of the micelle are homogeneous, as shown in Figure 1, allowing us to write down the free energy density of the system quite simply without any integrals over density profiles. Minimization of the free energy with respect to the structural and compositional parameters of the micelle gives the optimum values of the core and corona radii, as well as the aggregation number of copolymer molecules per micelle. These quantities are shown to depend not only on the total molecular weight of the copolymer, but, more significantly, on the individual blocks CA and CB.

As an added result, we find that allowing for copolymer in solution between micelles has very little effect on the calculated size parameters, but it is important in determining the critical micelle concentration.[3]

In section 2 we begin with a detailed description of the model. The general trends with the molecular weights of each block of the copolymer and of the homopolymer are explored in section 3a. We find that the homopolymer is almost completely excluded from the core of the micelle for a wide range of molecular weights. The core radius and corona thickness are found to scale primarily with the molecular weights of the CB and CA blocks of the copolymer, respectively. The values of the important exponents are derived from the analytical expressions given in section 2. In particular the penetration and stretching of the A blocks of the corona by homopolymer of small molecular weight is discussed quantitatively. Section 3b and Tables I–V compare the results of our calculations for the system of polystyrene/polybutadiene copolymers in polybutadiene homopolymers with the SANS measurements of Selb et al.[1] The critical micelle concentration is discussed in section 4, and section 5 contains the conclusions.

2. Description of Model

Each micelle is modeled by a spherical core of radius l_B surrounded by a corona of thickness l_A, as indicated in Figure 1. The unit cell is a sphere of radius R and is defined as the volume which on average contains one micelle. Each of the three regions is assumed uniform throughout. The number fraction of copolymers which remain in solution in region 3 between the micelles is denoted by F_3^C, while $F_M^C = 1 - F_3^C$ is the fraction in the micelles. The copolymers which are in micelles are assumed to have their joints localized at the interface, with the polystyrene block, labeled CB, stretched in toward the center, and the polybutadiene, or CA block, in the corona. The core radius l_B and the corona thickeness l_A are proportional to the average end-to-end distances of the CB and CA blocks, respectively. Polybutadiene homo-

---

† Permanent address: Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7.

0024-9297/85/2218-0657$01.50/0 © 1985 American Chemical Society