Conformational Statistics of Polyisobutene by a Monte Carlo Study

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ABSTRACT: The Monte Carlo method has been utilized to investigate the conformational distribution in the central section of a polyisobutene (PIB) decamer at various temperatures. The Monte Carlo results are in excellent agreement with the experimental data on the average dimensions of PIB chains, as well as with the molecular scattering functions of this polymer in solution and in bulk. The average values of the backbone bond angles centered at the CH_2 and at the disubstituted C atom are 126° and 110°, respectively, at 400 K. The distribution of torsional angles is characterized by six distinct maxima centered at ±15°, ±130°, and ±105°. A six-state RIS model with states located in the latter positions constitutes a very good description of the conformational distribution in PIB, leading to calculated properties in good agreement with experiments. The Monte Carlo results are then at variance with the outcome of previous calculations based on constrained minimizations of the energy, which led to the inaccurate conclusion that torsional angles around ±105° are of negligible incidence in PIB. Therefore, this Monte Carlo based conformational analysis is shown to be particularly powerful in investigating chains with a number of highly interdependent conformational variables.

Introduction

The relationships between chemical constitution and spatial distribution of monomers in macromolecules have been traditionally investigated from the theoretical point of view by using internal energy calculations on short-chain model compounds. This approach, applied by Flory and co-workers to several polymers representative of various classes (see, for instance, refs 2–4), has led to our present understanding of the conformational statistics of polymer chains in solutions and in the amorphous state. For most of the polymers which have been studied, the conformations of minimum energy found for the short-chain models are not substantially different from the most abundant conformations of the corresponding segments embedded in the polymer chain. The overall conformations of the polymer can then be described as statistical sequences of rotational isomeric states (RIS) coincident with these minima. This approach cannot be utilized for crowded polymers like polyisobutene[5] (PIB) or poly(methyl methacrylate)[6] (PMMA), since both the location of the conformational states and their relative energies are strongly influenced in short-chain models by the presence of the chain ends. As a consequence, the conformational study of these two polymers has been performed using different techniques, involving minimizations of the energy for the central part of model oligomers in ref 5 and minimizations for infinite chains under the condition of conformational periodicity in ref 6.

The problem of locating the energy minima in the multidimensional configurational space of a given short-chain model has been usually tackled by building two-dimensional energy maps with respect to two consecutive backbone torsional angles, while all the other internal parameters (i.e., the backbone bond angles and the bond angles and torsional angles in the side groups) are held fixed at values which are believed to correspond to low-energy situations. In other words, it is assumed that correlations between the backbone torsional angles and the other internal parameters are negligible. Assumptions of this kind may be invalid. For instance, the first attempt to analyze the local conformations of PMMA led to inaccurate conclusions about the energy of one of the states because the plane of the ester group was assumed to be in a fixed orientation with respect to the adjoining backbone bonds.[7] It has been subsequently shown that the orientation of the ester group and the value of the backbone bond angle at the disubstituted carbon atom are coupled in PMMA with the torsional angles around the two adjoining backbone bonds.[6] A similar situation may exist for other polymers with conformationally flexible side groups. In order to circumvent this difficulty, several energy maps can be evaluated for various values of some of the latter internal parameters, or the energy can be optimized in each point of the maps with respect to one or more of them, all the others being still kept fixed.

Calculations of this kind may give useful information about the geometries and the relative internal energies of the stable conformations of a polymer chain, provided that a suitable force field is available for the polymer under study and that all the other assumptions on which the calculation is based are substantially correct. However, the resulting description of the conformational statistics of the polymer in disordered states is intrinsically approximated, since the relative frequencies of the various conformations in these states depend on free energy differences rather than on internal energy differences. As a consequence, the statistical weights deduced from the calculations for the various torsional states, as well as the exact location of these states, are usually treated as adjustable parameters in order to obtain a good agreement with the experimental values of conformation-dependent quantities such as the mean-square end-to-end distance and its temperature coefficient, the mean-square dipole moments, the depolarized Rayleigh scattering intensities, the electric Kerr constants, or the molecular scattering functions of the polymer.[2]

We utilize in this paper a different approach to the problem. In our method, the conformations permissible to a sufficiently long oligomer are sampled using the Monte Carlo technique. The oligomer is long enough such that the effect of the chain ends is negligible in its central portion but short enough such that the conformational distribution in this central portion is not perturbed by long-range excluded-volume interactions. The location of the conformational states and their probability of occurrence in the polymer chain are then deduced from the Monte Carlo sample by examining the behavior of the

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Table I
Values of Characteristic Ratios, C_∞, Evaluated for PIB According to Various Versions of the Four-State Model[a]

model	bond angles, deg		torsional states	C_∞
	C–CH$_2$–C	C–CMe$_2$–C		
ref 4, switched bond angles	109	123	+15°,−15°,+130°,−130°	6.8
ref 8, correct bond angles	123	109	+15°,−15°,+130°,−130°	4.7
ref 8, revised four-state model	124	110	+25°,−25°,+120°,−120°	6.6

[a] The experimental value at 300 K is 6.6–6.9.

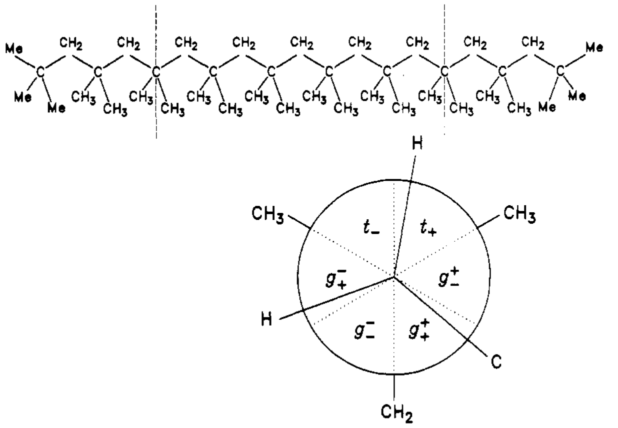

Figure 1. Schematic representation of the PIB decamer and notation used to classify the torsional states of the skeletal bonds in six domains. The vertical dashed lines delimit the central portion of the decamer used to represent a corresponding segment embedded in a long PIB chain.

central part of the model oligomer. At variance with the other methods, this approach does not require approximations other than those implicit in the set of potential functions adopted to model the intramolecular interactions. It is then generally applicable to polymers with various constitutions, including crowded polymers and those with flexible side chains. The computer time required to produce a meaningful Monte Carlo sample varies obviously with the total number of atoms in the model oligomer and with the number of independent variables. Although the calculation can be relatively long, especially for crowded polymers, the total time needed for these polymers is much smaller than that utilized in refs 5 and 6, with the important advantage that the calculation proceeds almost automatically after the potential field and the initial conformation of the model oligomer has been established.

As a first application of the method, we present in this paper the results obtained for PIB. The conformations of PIB chains in disordered states have been investigated by several groups over the past 3 decades.[5,8] However, both the location of the torsional states available to the bonds of a PIB chain and their probability of occurrence are still unclear. The four-state RIS model suggested by the conformational analysis in ref 5 predicted conformation-dependent properties in good agreement with the experiments (see Table I). Also, the molecular scattering functions of PIB chains calculated on the basis of this model were found to be in very good agreement with the results of X-ray and neutron scattering experiments.[9] However, it was later realized that the two distinct bond angles centered at the CH$_2$ and at the disubstituted C atom had been inadvertently switched in both calculations.[10] Properties evaluated using the location of the RIS states indicated in ref 5 and the correct bond angles were found to be unacceptably far from the experimental results. As a consequence, a revised version of the four-state model has been proposed in ref 10, with the value of the bond angles and the location of the torsional states modified with respect to the previous scheme (Table I).

Although the properties evaluated according to the revised four-state model are in very good agreement with experiments on PIB,[10] the proposed new locations of the states seem quite far from those of the energy minima deduced in ref 5. We show in this paper that, according to the results of our Monte Carlo calculations, a more accurate description of the conformational distribution of PIB requires the inclusion of torsional states which were considered to be negligible in ref 5.

System and Method of Calculation

The calculations reported in this paper have been performed on a segment of a PIB chain containing 19 backbone carbon atoms plus two terminal methyl groups. A schematic representation of this segment, denoted as *decamer* from now on, is shown in Figure 1. The two vertical dashed lines delimit the central portion of the decamer which has been used to deduce the conformations available to the backbone bonds in a long PIB chain. This central portion comprises five *diads*, that are two-bond sequences centered at the CH$_2$ groups, and four *interdiads*, that are two-bond sequences centered at the disubstituted C atoms. Figure 1 also shows the notation used throughout the paper to classify the torsional states of the skeletal bonds of PIB in six domains. The symbol $|\varphi, \varphi'|$ is used to denote the torsional state of the two consecutive bonds of a diad, while the symbol $\varphi'|\varphi$ is used for interdiads, the vertical bar representing the location of a disubstituted C atom.

All the atoms have been explicitly considered in our calculations (including the hydrogen atoms in the side groups), with the exception of the hydrogens bonded to the three terminal methyl groups at each end of the model decamer. These six methyl groups, denoted Me in Figure 1, have been treated as united atoms. Also, all the bond angles at the backbone carbon atoms and all the torsional angles have been varied independently. However, the geometry of the two terminal *tert*-butyl groups and of the side-chain methyl groups has been kept tetrahedral. This considerably reduces the number of independent variables and is expected to have no significant influcence on the resulting conformational distribution.

The method of calculation of the energies is identical to that described in ref 6. The potential functions and parameters utilized to evaluate the energy contributions deriving from distortions of bond angles and torsional angles and from interactions between nonbonded atoms are those proposed for oligmers of PIB by Suter, Saiz, and Flory[5] (see Table II). As in ref 6, the torsional energy for a given C–C bond is calculated as the sum of nine contributions from each one of the nine X–C–C–Y dihedral angles defined around that bond, the torsional barrier for each dihedral angle being $^1/_9$ of the overall barrier.

The conformational distribution was sampled using the well-known method suggested by Metropolis et al.[11] At each step, one of the independent variables (a bond angle or a torsional angle) was selected at random and varied at

Table II
Energy Functions and Parameters Used in the Calculations

Energy Functions

bond lengths	fixed
bond angles	$E(\theta) = 1/2k_\theta(\theta - \theta_0)^2$
torsional angles	$E(\varphi) = 1/2k_\varphi(1 - \cos 3\varphi)$
nonbonded interactions	$E_{ij}(d) = a_{ij}/d^{12} - b_{ij}/d^6$

Geometry and Energy Parameters

bond type	bond length, Å	torsional barrier, kcal mol^{-1}
C–C	1.53	2.8 (overall, see text)
C–H	1.10	

bond angle	10^3k_θ, kcal deg^{-2} mol^{-1}	θ_0, deg
C–C–C	35.1	111
C–C–H	26.7	109.5
H–C–H	22.3	107.9

interacting pair	$10^{-3}\alpha_{ij}$, kcal Å^{12} mol^{-1}	b_{ij}, kcal Å^6 mol^{-1}
C,C	398.3	366.0
C,H	56.8	127.9
H,H	7.3	47.1

random in a given interval centered at the current value of that variable. The new conformation was then accepted or discarded according to the outcome of a statistical test in which a random number, r, uniformly distributed in [0, 1] is compared with $\sigma = \exp(-\Delta E/RT)$, ΔE being the internal energy difference between the new and the old conformation. When the test failed (that is, $r > \sigma$), the old conformation was restored and counted once more in the Monte Carlo sample.

Whenever a bond angle was selected, its displacement from the current value was chosen at random in a relatively small interval, that is, between −5° and +5°. However, in order to overcome the barriers to conformational changes which are especially high in a crowded polymer like PIB, the displacement of the torsional angles was chosen in the full range [−180°, +180°]. Consider the sequence of atoms A–B–C(D,E,F), with D, E, and F being the three distinct atomic groups bonded to atom C. As specified before, all the bond angles and all the torsional angles can vary independently in our calculation, which implies that the three torsional angles identified by the sequences A–B–C–D, A–B–C–E, and A–B–C–F are considered as three distinct, independent variables (see ref 6). However, changing the value of one of them while the others are kept constant also changes the value of the bond angles centered at atom C, in such a way that only small torsional displacements could be accepted. For this reason, when the randomly selected displacement $\Delta\varphi$ was higher than 10° in absolute value, the three groups D, E, and F were simultaneously rotated around the bond B–C by the same angle $\Delta\varphi$. Even at the lowest temperature used in our calculations (400 K), we have found that this mechanism allows jumps between different torsional states for all the bonds in the decamer, including those in the central diad.

The Monte Carlo method used in our calculations is ergodic in principle; that is, any configuration of the model oligomer can be reached after a finite number of steps from any other configuration. However, owing to the fact that PIB is a crowded polymer, calculations performed at low temperatures could sample only a limited region of the configurational space in a reasonable amount of computer time. In order to understand the effects of the temperature, we have performed several calculations at various different temperatures, that is, 400 K and higher. The numerical results obtained at high temperatures can be only considered as indicative of general trends, being obviously limited by inadequacy of both the form of the potential functions and the values of the parameters adopted to evaluate the various contributions to the internal energy. Nevertheless, they can be used as a check for calculations performed at lower temperatures, indicating whether all the regions of the configurational space have been properly sampled in the latter case. Less than 20 000 Monte Carlo steps were required at 400 K to bring the (high) energy of the arbitrary initial conformation in the equilibrium range. The equilibrium was anyway continued for a total of 50 000 steps, after which the process of collecting the successively generated conformations was started. A typical run consisted of 500 000 total steps. In one case, at 400 K, we have also performed a longer calculation (10^6 total steps). Eight independent calculations were performed at 400 K, each calculation requiring approximately 12 h of CPU on a IBM 3090. The results shown in the next section are averaged over all the corresponding runs. Comparing the results obtained at 400 K with those obtained at higher temperatures indicates that all the regions of the configurational space of the model oligomer have been sampled at the lower temperature in each separate run. However, the computer time required to obtain statistically significant results increases with decreasing the temperature. For this reason, we did not attempt calculations at temperatures lower than 400 K.

Before starting the Monte Carlo runs, we have performed several preliminary calculations to check the general performance of our programs. For example, we have optimized the internal energy of a number of representative conformations of the decamer with respect to all the internal variables. In one of these calculations, in particular, the decamer was initialized in the helical $|t_+g_+^+|_n$ conformation with values of the bond angles and torsional angles identical to those reported in Table V of ref 5. Although the subsequent optimization was performed in the absence of constraints of any kind, the final values of the internal parameters in the central region of the decamer were remarkably independent from the exact location along the chain of the bonds considered. However, due to the different calculation scheme, the results are not identical to those of ref 5. The diad conformation in the central part of our model is |+17.9°, +128.3°|, while the backbone bond angles at the CH_2 and at the disubstituted C atoms are 124.5° and 110.3°, respectively. The corresponding values in ref 5, using a shorter model and imposing helical symmetry, were |+15.1°, +129.4°| for the torsional angles and 124.6° and 109.3° for the two bond angles, respectively. Both sets of values are in very good agreement with the experiments on crystalline PIB[12-14] indicating a 8_3 helical conformation with a 0.233-nm pitch per monomer unit. In particular, the rotation and the pitch calculated following Miyazawa[15] and using the set of parameters obtained from our calculation are 137° and 0.228 nm, respectively. In the rest of this paper, all the energies are reported with respect to the optimized $|t_+g_+^+|_n$ conformation, taken as the reference state.

Results and Discussion

The results of our calculations consist of several sets of conformations of the model decamer shown in Figure 1, with the various conformations distributed in each set according to the Boltzmann statistics at the given temperature. They contain all the information necessary to understand and describe the conformational characteristics of the central portion of the decamer. Since one of the fundamental assumptions of our calculation is that

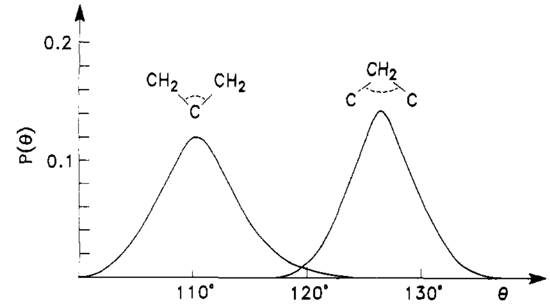

Figure 2. Distribution of the backbone bond angles in the central section of the model decamer as obtained from the Monte Carlo calculations at 400 K.

the backbone bonds in this central portion of the decamer are subject to the same intramolecular interactions that the backbone bonds in long (unperturbed) PIB chains experience, we want to show first that our results are in very good agreement with experiments on PIB. To this end, we have divided the [−180°, +180°] range of torsional angles around the backbone bonds into 72 intervals 5° wide and calculated the 72 × 72 matrix, $\mathbf{P}''_{72}$, of the probability $p(|\varphi,\varphi'|)$ that the sequence $|\varphi,\varphi'|$ is found in one of the five central diads in the decamer at 400 K. The corresponding matrix $\mathbf{P}'_{72}$, referring to the interdiads, has been obtained in a similar way. The equivalent positions in the two 72 × 72 matrices have been also averaged, taking into account the local symmetry of the PIB bonds; that is, $p(\varphi,\varphi') = p(\varphi',\varphi) = p(-\varphi,-\varphi') = p(-\varphi',-\varphi)$ for consecutive bonds both at diads and interdiads.

The two matrices have then been used to evaluate the mean-square end-to-end distance and the neutron and X-ray molecular scattering functions of long PIB chains. This calculation has been performed by generating a large number of conformations of a chain containing 240 monomer units according to the conditional probabilities implicit in $\mathbf{P}''_{72}$ and $\mathbf{P}'_{72}$. The two bond angles at the CH_2 and at the disubstituted C atoms have been set equal to 126° and 110°, respectively, that are the average values of these bond angles in the Monte Carlo samples at 400 K (see Figure 2). The coordinates of the central 200 monomer units have been used to calculate the contribution to the scattering functions from scattering centers separated by less than 400 skeletal bonds. The contribution from scattering centers separated in long PIB chains by more than 400 skeletal bonds, which is negligible for values of the scattering vector $q > 0.07$ Å^{-1}, has been added as in ref 16. The characteristic ratio of the chains generated according to this method was 6.7 ± 0.2, in excellent agreement with the experimental value 6.6–6.9 (see ref 5 and references therein). Properties calculated from the Monte Carlo results at 400 K are compared, here and in the following, with room temperature experimental data on the grounds that their temperature variation in this range is probably smaller than the uncertainty of both the experimental and theoretical values. For instance, the experimental value of the characteristic ratio is between 6.6 and 6.9 at room temperature, while its temperature coefficient is as small as $-(0.1\text{–}0.3) \times 10^{-3}$ K^{-1}.

The continuous line in Figure 3 shows the absolute-scale Kratky plot of the molecular scattering function obtained placing the scattering centers in the center of mass of the hydrogen atoms of the CH_2 backbone groups (with the scattering power $f = 2$) and of the hydrogens of the side-chain methyl groups (with $f = 3$). The analogous curve calculated with scattering centers in the side chains only is shown by the dashed line, while the dotted line has been obtained with scattering centers placed on the backbone disubstituted C atoms. The three calculated curves are directly comparable with the results of the experiments reported in ref 9. In particular, the continuous and the dashed curves can be compared with those obtained in neutron scattering experiments on PIB–H dispersed in fully deuterated PIB-d_8 and in PIB-d_6, respectively, while the dotted curve can be compared with the results of X-ray scattering by n-heptane solutions of PIB. The calculated curves are practically coincident with the experimental results obtained in ref 9, as far as the neutron scattering data are concerned. The high-q portion of the scattering function evaluated with scattering centers on the disubstituted C atoms (dotted curve in Figure 3) rises with increasing q slightly more than indicated by the experiments on n-heptane solutions of PIB. However, the exact location of the scattering centers for the X-ray scattering of PIB chains in n-heptane is much less clear than the location of the scattering centers in neutron scattering experiments. When it is considered that the molecular scattering functions in Figure 3 have been calculated using the torsional distribution directly obtained from the Monte Carlo runs and using values of the bond angles coincident with the averages in Figure 1 (the scattering curves, as well as the characteristic ratio, are usually sensitive to the values selected for the bond angles), it seems reasonable to conclude that the conformational distribution in the central part of the model decamer studied in this work is very similar to that in long PIB chains.

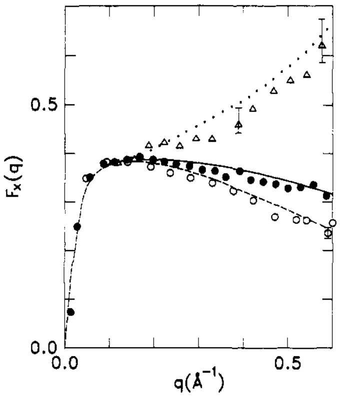

Figure 3. Calculated molecular scattering functions (in absolute-scale Kratky plots) for long PIB chains with scattering centers located on the following: the centers of mass of the hydrogen atoms of the CH_2 backbone groups and of the hydrogen atoms of the side-chain methyl groups (full line); the centers of mass of the hydrogens of the side-chain methyl groups only (dashed line); the disubstituted backbone C atoms (dotted line).

Having proved that all the assumptions which are the basis of our calculations are substantially correct, we proceed to examine the distribution of torsional angles around the backbone bonds. Figure 4 plots the probability, $p(\varphi)$, that the torsional angle around one of the bonds in the central portion of the decamer is found in a 5° interval centered at φ. The data in Figure 4 have been averaged over all the bonds in the central part of the model decamer and over the two equivalent (by symmetry) 5° intervals at $-\varphi$ and $+\varphi$. Figure 4 shows that the torsional distribution around the backbone bonds in PIB is characterized at 400 K by six maxima, approximately centered at +15° (t_+), −15° (t_-), +130° (g^+_+), +105° (g^+_-), −105° (g^-_+), and −130° (g^-_-), with the notation for the various domains as in Figure 1. The Monte Carlo results are then very similar to those of the energy optimizations reported in ref 5, as far as the locations of these maxima are concerned. In fact, exactly the same locations were

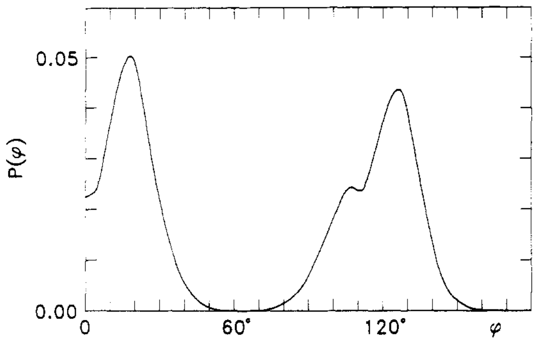

Figure 4. Distribution of torsional angles around the backbone bonds in the central section of the model decamer at 400 K.

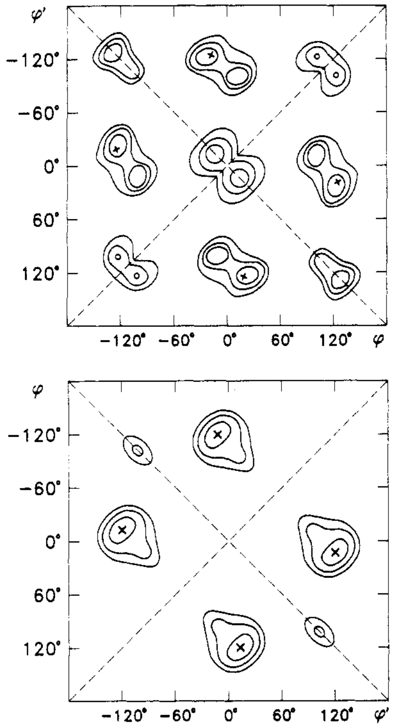

Figure 5. Distribution of torsional angles in two bond sequences in the central section of the model decamer at 400 K shown in the form of probability maps [(a) diads, (b) interdiads]. The absolute maxima are indicated by ×. Curves are drawn at values of the probability equal to the maximum for each map multiplied by $\exp(-\Delta G_i/RT)$, with $\Delta G_i = 1$, 2, and 3 kcal mol^{-1}.

assumed in ref 5 for the rotational isomers of a six-state RIS model of PIB. On the other hand, the presence of distinct maxima at ±105° and the abundance in the Monte Carlo results of conformations in the g_-^+ and g_+^- domains are somehow surprising, since the occurrence of conformations in these domains was considered negligible in ref 5. Furthermore, calculations at higher temperatures indicate that the principal effects of increasing the temperature are to coalesce the two maxima in the trans domains and to increase the fraction of high-energy conformations around 60° at the expenses of the maxima centered at ±130°. Varying the temperature has only minor effects on the abundance of conformations around ±105°, in such a way that the fraction of conformations in the g_-^+ and g_+^- domains is expected to be significant at room temperature also.

The distribution of torsional angles in two-bond sequences at 400 K is shown in Figure 5, in which the previous 72 × 72 matrices $\mathbf{P}''_{72}$ and $\mathbf{P}'_{72}$ are presented in the form of probability maps (diad (a), interdiad (b)). The absolute maxima, indicated in Figure 5 by ×, correspond to probabilities of 7.1×10^{-3} and 5.8×10^{-3} in the diad and interdiad maps, respectively. For comparison, the average value for a random distribution of two-bond sequences is 1.93×10^{-4}. Curves are drawn at values of the probability equal to the maximum value for each map multiplied by $\exp(-\Delta G_i/RT)$ with $\Delta G_i = 1$, 2, and 3 kcal mol^{-1}. The analogous maps calculated at 600 K and at higher temperatures are relatively uninteresting and are not shown here. However, it is useful to remark that all the features present in the high-temperature maps are present at 400 K as well. Taking into account that PIB is a crowded polymer, this is a good indication that the Monte Carlo method utilized in our calculations was indeed ergodic also at the lower temperature.

Figure 5 confirms the location of the most abundant conformations for the PIB bonds deduced from Figure 4. Several maxima are present in the maps, many of them related to others by symmetry (see before). The absolute maxima in the diad map (Figure 5a) are found in the $|t_+g_+^+|$ and symmetry-related domains, while the absolute maxima of the interdiad map (Figure 5b) are located in the $t_+|g_+^+$ and symmetry-related domains. These maxima, as well as all the other probability maxima present in the two maps, correspond to conformations in which the displacement from perfect staggering of the two consecutive bonds is of the same absolute sense. This feature of the PIB conformations is then in agreement with the analysis of ref 5. In most of the cases, however, the maxima in Figure 5 are broad enough to comprise a substantial amount of two-bond conformations with very small displacements from staggering or even with consecutive displacements of the opposite sense (see, for instance, the t|g and g|t domains in Figure 5b).

It is worth noting that distinct maxima with φ or φ' very close to ±105° are present in both maps of Figure 5. In particular, the maxima in the $|t_+g_+^-|$ and symmetry-related domains in the diad map (Figure 5a) are comparable in intensity and shape with the absolute maxima of this map. Furthermore, two consecutive gauche bonds are permissible at an interdiad junction (Figure 5b) only when they are both +105° or both −105°. Since this appears to be a point of substantial disagreement with the outcome of the energy minimizations of ref 5, where conformations of this kind were deduced to be negligible, we have examined in detail some of the decamer conformations contained in the Monte Carlo sample at 400 K. With respect to the optimized $|t_+g_+^+|_n$ conformation which is our reference state, the aveage energy at this temperature is ca. 50 kcal mol^{-1} (of decamer) and the most stable conformation included in the sample has an energy of 27 kcal mol^{-1}. After optimization, however, the energy of the latter decreases to −1.2 kcal mol^{-1} with only minor adjustements of all the variables. Starting from the bond C_3–C_4, this conformation is described by

$$|g_+^-t_+|g_+^+t_+|g_+^+t_+|g_+^+g_+^+|t_+g_+^+|t_+g_+^+|t_+t_+|$$

We have then examined all the conformations containing the ±105° states in the central diad of the decamer. The most stable of these conformations included in the Monte Carlo sample has an energy of 28.8 kcal mol^{-1}, well below the average and very similar to that of the most stable conformation in absolute. Furthermore, after optimization the energy decreases to −1.5 kcal mol^{-1} with only local changes of the variables. This conformation has two g_-^+ states in the central diads (with $\varphi = 106°$ in both cases) and corresponds to

$$|g_+^+t_+|g_+^+t_+|g_+^+t_+|g_-^+g_-^-|t_-g_-^+|t_+g_+^+|t_+t_+|$$

In conclusion, conformations containing the states at ±105° in the central part of the decamer are found to be among the most stable in our calculations. This is not in disagreement with the data in Table IV of ref 5, where one of the lowest energy hexad conformations (no. 54 in the table) contains the g_+^- state in the central diad. The question arises then why the two calculations provide a substantially different model of the local conformations in PIB chains. In our opinion, this is mainly due to the fact that the vast majority of the hexad conformations examined in ref 5 contained t|t sequences at the interdiad junctions. Sequences of this kind are very high in energy, however, and their occurrence in PIB is almost negligible, as found in ref 5 and confirmed by Figure 5 of this paper (also, see later). When the hexad conformations containing t|t interdiad sequences are exlcuded from the table, the remaining entries are inadequate to provide a reliable estimate of the energy parameters and preexponential factors needed for a six-state RIS model of PIB. In other words, the conclusions of ref 5 are inaccurate, inasmuch as they are based on the energies calculated for conformations which are of very low incidence in PIB.

We have already shown that the information contained in the two matrices $\mathbf{P}''_{72}$ and $\mathbf{P}'_{72}$ (see above) is consistent with a large body of experimental data on PIB. However, in order to provide a simpler description of the conformational distribution of this polymer, it is useful to compress this information into a more manageable RIS model. To this end, a natural choice of the location of the torsional states is in correspondence of the maxima in Figure 4, which identifies the allowed states with those torsional angles which occur more frequently. Dividing the [−180°, +180°] range of torsional angles around the central bonds of the model decamer in six domains (see Figure 1), the 6 × 6 diad ($\mathbf{P}''_6$) and interdiad ($\mathbf{P}'_6$) matrices of the a priori probabilities for two-bond sequences in PIB at 400 K are

$$\mathbf{P}_6'' = \begin{bmatrix} 0.056 & 0.012 & 0.072 & 0.029 & 0.054 & 0.004 \\ 0.012 & 0.056 & 0.004 & 0.054 & 0.029 & 0.072 \\ 0.072 & 0.004 & 0.036 & 0.007 & 0.019 & 0.001 \\ 0.029 & 0.054 & 0.007 & 0.015 & 0.011 & 0.019 \\ 0.054 & 0.029 & 0.019 & 0.011 & 0.015 & 0.007 \\ 0.004 & 0.072 & 0.001 & 0.019 & 0.007 & 0.036 \end{bmatrix}$$

$$\mathbf{P}_6' = \begin{bmatrix} 0.003 & 0.002 & 0.120 & 0.075 & 0.019 & 0.015 \\ 0.002 & 0.003 & 0.015 & 0.019 & 0.075 & 0.120 \\ 0.120 & 0.015 & 0.000 & 0.001 & 0.000 & 0.000 \\ 0.075 & 0.019 & 0.001 & 0.033 & 0.000 & 0.000 \\ 0.019 & 0.075 & 0.000 & 0.000 & 0.033 & 0.001 \\ 0.015 & 0.120 & 0.000 & 0.000 & 0.001 & 0.000 \end{bmatrix}$$

with states indexed in the order t_+, t_-, g_+^+, g_-^+, g_+^-, g_-^-. The relative error of the probability data in the two matrices, evaluated from the various independent calculations and from the probabilities of symmetry-related domains, is on the order of 5%. The percentage of bonds in the various states at 400 K is 23% for t_+ (or t_-), 14% for g_+^+ 13% for g_-^+ (or g_+^-). The total population of the trans states is then similar to that of the gauche states, the four gauche states being almost equally populated at 400 K. Also, sequences of two trans bonds at the interdiad junctions represent only 1% of all the possible interdiad sequences, which are mainly in the t|g and g|t domains (92%). On the contrary, sequences of two trans bonds are relatively frequent inside a diad (14%). In practice, a t_+ bond has approximately the same probability of being followed in a diad by a second t_+ bond or by a g_+^- bond, while the probability of being followed by a g_+^+ bond is somewhat higher. Another point of interest is the fact that more than 20% of all the diad conformations do not conform to the rule that the two bonds in a diad are displaced in the same sense with respect to perfect staggering.

We have checked that a six-state RIS model based on the two matrices $\mathbf{P}''_6$ and $\mathbf{P}'_6$ constitutes a description of the conformational distribution in PIB in very good agreement with experiments. With the values of the bond angles 126° and 110°, as before, and with the six torsional states placed in correspondence of the maxima in Figure 4, we have used the Monte Carlo method to generate the long PIB chains according to the probabilities dictated by $\mathbf{P}''_6$ and $\mathbf{P}'_6$ and to evaluate the characteristic ratio and the various molecular scattering functions predicted by the six-state model at 400 K. The results of the scattering functions are practically indistinguishable from those obtained using the matrices $\mathbf{P}''_{72}$ and $\mathbf{P}'_{72}$ (see Figure 3), the characteristic ratio being again 6.7 ± 0.2.

Conclusions

We have shown that the Monte Carlo method can be utilized to investigate the distribution of conformations available on a local scale for relatively long segments of a polymer chain, avoiding approximations other than those implicit in the set of potential functions adopted to model the intramolecular interactions. The method has been applied in this paper to investigate the conformational distribution in PIB. By examining the behavior of the central portion of a model decamer, we have obtained the distribution of the bond angles centered at the CH_2 groups and at the disubstituted C atoms in PIB and calculated the distribution of the probability of occurrence of two-bond sequences of torsional angles for both diads and interdiads in this polymer. Using the Monte Carlo results directly as they are, we have then generated long PIB chains and calculated their molecular scattering functions with scattering centers placed in various locations. The outcome of this calculation has been found to be in excellent agreement with the results of neutron scattering experiments on mixtures of deuterated and undeuterated PIB chains in bulk and with the X-ray scattering of an *n*-heptane solution of PIB. The characteristic ratio of the chains generated according to the Monte Carlo results was 6.7 ± 0.2, in excellent agreement with experimental results.

The distribution of torsional angles in the central portion of the model decamer at 400 K indicates that a RIS model appropriate for PIB is naturally characterized by six states located at ±15°, ±130°, and ±105°. We have shown that a six-state model based on the average probabilities indicated by the Monte Carlo calculations constitutes an accurate description of the PIB conformations, leading to calculated properties in good agreement with the experiments. According to our calculations, the states at ±105° are almost as populated as those at ±130°. Hence, the Monte Carlo results differ from those obtained by minimization of the conformational energy in ref 5. This explains why the four-state model of ref 5 was unable to provide calculated properties in good agreement with experiments[10] and why the torsional angles corresponding to all four states had to be altered substantially in ref 10 with respect to the locations of the energy minima in order to reproduce the experimental results.

In the hope of deriving a set of statistical weights appropriate for a six-state model of PIB, we have used the model of ref 5 to fit the probabilities in $\mathbf{P}''_6$ and $\mathbf{P}'_6$. We have found that no reasonable adjustment of the 10 parameters of the model can give a good agreement with the probabilities indicated by the Monte Carlo calculations. This is partly due to the fact that diad conformations like $|t_+g_-^+|$ are excluded a priori in the model of ref 5 and partly to the fact that the same second-order interaction parameters are used in ref 5 irrespective of the exact distance of the two interacting groups. A good fit to the Monte Carlo results could be obtained only by adding more parameters to the model.

In this regard, the Monte Carlo method does not readily provide the information on specific interactions defined by the statistical weight parameters. On the other hand, the total statistical weight for a given conformation of a long PIB chain, divided by the conformational partition function, coincides with the probability of occurrence of that conformation. Hence, the matrix multiplication methods to compute various conformation-dependent properties averaged over all possible conformations for long chains can be readily adapted by substituting the a priori probability matrix and the conditional probability matrices implicit in $\mathbf{P}''_6$ and $\mathbf{P}'_6$ for the corresponding statistical weight matrices. In this regard, the probability maps of parts a and b of Figure 5 may be regarded as representing the free-energy maps averaged over all the surrounding chain segments including correlations beyond the usual adjacent bond pairs. This is a definite advantage of the Monte Carlo method, since such computations are practically impossible by the conventional energy minimization method.

The good results obtained for PIB by use of the Monte Carlo method suggest that this approch could be used for other very crowded polymers (and for low molecular weight compounds as well). Furthermore, the method is well suited to analyze the conformational distribution whenever the number of relevant internal variables is greater than two or three. This is the case, for instance, of polymers with monomer units comprising several nonequivalent backbone bonds. A second case is that of polymers with conformationally flexible side groups, in which both the bond angles and the torsional angles in the main chains may be coupled strongly with those in the side groups.[17]

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Appendix

In spite of the fact that a six-state model is a natural choice for describing the conformational distribution in PIB chains, a simpler model can be obtained by labeling all the bond conformations in the domain [60°, 180°] and all those in the domain [−60°, −180°] with the symbols g^+ and g^-, respectively. This leads to a four-state model formally analogous to that of refs 5 and 10 but leaves the exact location of the gauche states undefined. In fact, there is no reason why the *efficient* location of these states (the one that gives calculated properties in agreement with experiments) should coincide with the average torsional angle inside the selected domains. On the contrary, the effect on the molecular dimensions of torsional angles around ±105° is expected to be larger than that of the corresponding torsional angles around ±130°, in such a way that the efficient location of the gauche states in the four-state RIS model should be at angles smaller than 120° in absolute value. With some simplification, the 4 × 4 diad ($\mathbf{P}''_4$) and interdiad ($\mathbf{P}'_4$) matrices of the a priori probabilities at 400 K are

$$\mathbf{P}_4'' = \begin{bmatrix} 0.068 & 0.000 & 0.101 & 0.058 \\ 0.000 & 0.068 & 0.058 & 0.101 \\ 0.101 & 0.058 & 0.065 & 0.050 \\ 0.058 & 0.101 & 0.050 & 0.065 \end{bmatrix}$$

$$\mathbf{P}_4' = \begin{bmatrix} 0.000 & 0.000 & 0.195 & 0.034 \\ 0.000 & 0.000 & 0.034 & 0.195 \\ 0.195 & 0.034 & 0.038 & 0.000 \\ 0.034 & 0.195 & 0.000 & 0.038 \end{bmatrix}$$

the states being indexed in the order t_+, t_-, g^+, g^-. We have found that a good agreement with the experimental molecular scattering functions and with the value of the characteristic ratio is obtained when the *efficient* location of the gauche states is assigned the value ±112°, all the other geometric parameters of the calculation being unchanged with respect to those for the six-state model. It may be useful to underline that the four-state model derived by the Monte Carlo calculations and the model proposed in ref 10 are substantially different with respect to both the geometry (bond angles and location of the states) and the probability of occurrence of the various two-bond sequences. On the other hand, a four-state RIS model constitutes a rough approximation to the conformational statistics of PIB chains, which is properly described instead by the much better six-state model.

References and Notes

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