Macromolecules **1992,** *25,* 6315–6321

Kinematics of Polymer Chains with Freely Rotating Bonds in a Restrictive Environment. 2. Conformational and Orientational Correlations

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Received February 13, 1992; Revised Manuscript Received June 17, 1992

ABSTRACT: The mathematical formulation developed in the preceding paper is used to study the kinematics of polymer chains in a restrictive environment. Conformational and orientational correlations along the chain are analyzed. Calculations are performed by generating an initial configuration for a 25-bond freely rotating chain, changing the dihedral angle for the middle bond, and studying the resulting changes in all of the degrees of freedom, internal and external. Results from Monte Carlo chains generated in this manner are averaged over a sufficient number of initial configurations. The following conclusions are reached: (i) A change in the dihedral angle of a given internal bond in small steps up to ±120° is accommodated by the spatial readjustments of about three neighboring bonds on each of its sides. Spatial configurations of more distant neighbors are negligibly affected. Thus, the conformational correlation length along the freely rotating chain extends over 6–8 bonds. (ii) In general, the rotational motion of a given bond is accompanied by counterrotations of its first neighbors. (iii) The response of second neighbors is lightly stronger than that of the first neighbors on the average, though occurring randomly in the positive or negative sense. (iv) The kinematics of motion imply the potential occurrence of transitions of the form $g^{\pm}tt \leftrightarrow ttg^{\pm}$ and $ttt \leftrightarrow g^{\pm}tg^{\mp}$, in agreement with previous predictions of Helfand. (v) Bonds in the close neighborhood of the rotating bond exhibit a broad distribution of angular displacements in space as a result of the compensating effect of the cooperative motions.

Introduction

The cooperative nature of the conformational transitions of chain units in a moving segment predominantly stems from the requirement to localize or compensate the original motion. The propositions of crankshaft[1] and 3- or 4-bond motions[2] as the mechanism of local relaxational processes in polymers conform with the idea of immobilizing the ends of a moving segment which, in turn, is of the smallest possible size compatible with the tetrahedral geometry. These motions involve simultaneous isomeric rotations of more than one skeletal bond. Later experimental observation of activation energies of about one rotameric barrier height[3] invalidates, however, this picture of highly localized motions.

A classification of local motions based on the spatial rearrangement of the so-called "tails" surrounding the mobile segment has found widespread use in describing local chain dynamics.[4,5] Accordingly, correlated motions giving rise to the translation of the tails are referred to as type II motions and appear from Brownian dynamics simulations[6,7] to be relatively favored. Gauche migration and pair gauche production/annihilation are the two major transitions belonging to this category. Their respective kinetic schemes are $g^{\pm}tt \leftrightarrow ttg^{\pm}$ and $ttt \leftrightarrow g^{\pm}tg^{\mp}$, where t, g^+, and g^- refer to the rotational isomeric states trans, gauche$^+$, and gauche$^-$. On the other hand, crankshaft motions and 3- or 4-bond jumps, which are classified as type I, are highly improbable, as confirmed by simulations. The third group of transitions, referred to as type III, constitutes the major fraction of operating transitions. Those are individual bond flips between rotational isomeric states, which are accommodated by the coordinated small-amplitude rearrangements of neighboring units. Thus, the concept of a kinetic segment of a few backbone bonds over which the new orientation resulting from the rotating bond is spread and dissipated without recourse to a coupled rotameric jump of a nearby unit is introduced as a probable mechanism of conformational relaxation.

In general, backbone bonds in real chains are expected to undergo several oscillatory motions about a given rotational energy minimum before eventually jumping to another rotational isomeric state. The magnitude of these oscillations depends both on the shape of the intramolecular potential well and on the immediate environment of the chain. Recent molecular dynamics studies of the isolated poly(methylene) chain[8] indicate that the oscillations are in the range of about ±15–30° about the minima. Molecular dynamics simulations in the bulk state[9] lead to similar results. In the case of chains with freely rotating bonds, identical to the model adopted in the present study, the simulations of Takeuchi and Roe[9] show that the oscillations in the dihedral angles may be much larger. Such oscillatory motions were first observed in ^{13}C-NMR in polymer melts[10] and more recently by two-dimensional NMR experiments of Spiess and collaborators[11–13] for chains in the bulk state at temperatures down to the glass transition temperature. In NMR experiments, the reorientation of the transition moment vector—along the C–H bond, for example—is expected to accompany the motion of the backbone bond on which it is rigidly attached. The experimentally observed broad distribution of angular reorientation in space for a given transition moment vector invites attention to the limits of the validity of rotational isomeric jumps of about 120° amplitude as the basic mechanism of local relaxation. Instead, cooperative small-amplitude motion of several adjoining units, smoothening to a large extent the distortions induced by individual jumps, is brought into consideration.

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The Brownian dynamics simulations of isolated polyisoprene and polyethylene chains by Adolf and Ediger[14,15] indicate the localization of conformational motions to about one repeat unit. Interpretation of dielectric relaxation experiments of polyisoprene,[16] on the other hand, leads to a length scale of two or three repeat units over which the motions in the bulk state are cooperative. The size of the chain cooperatively engaged in local relaxation processes as a function of the flexibility of the chain and the compliance of the environment is not known precisely. Also, the relative role and importance of steric effects and energetic interactions, either of intramolecular or of intermolecular character, in relation to the constraints imposed by chain connectivity, the influence of the heterogeneities of the environment associated with the free volume, or density fluctuations are some of the challenging aspects of local chain dynamics which await further elucidation.

The influence of short-range intramolecular conformational energetics on local chain dynamics has been investigated in a number of recent studies within the framework of the rotational isomeric state formalism.[17,18] In these studies, emphasis is placed on the real structural and conformational characteristics and the short-range interdependence of neighboring bonds. Constraints imposed by the chain connectivity effect and the environmental frictional drag are recognized[19,20] by the introduction of position-dependent friction resistance[21] in the rate expressions. Although this mean-field approximation asserts the gradual damping of the rate of motion away from the rotating bond and automatically restricts the range of transmission of reorientational motion along the chain, it does not distinguish between specific transitions, of type II for instance, which are observed from simulations to be more favorable. The mathematical treatment presented in the preceding paper[22] will be used for a possible understanding of the frequent occurrence of correlated transitions of type II and for the estimation of the length scale of cooperative motions participating in local relaxation processes. Minimization of the cumulative square displacements of chain atoms is adopted therein[22] as the fundamental criterion determining the choice of the optimal mechanism of relaxation for a given initial configuration. Orientational and conformational correlations between neighboring bonds, succeeding the rotameric transition of an internal bond, will be studied within this framework. The conventional freely rotating chain model[23] of equilibrium statistics is taken up. Thus, in contrast to the previous approach where the emphasis is put on intramolecular energetics,[17-20] the present model illustrates the case of a chain whose dynamics is exclusively dominated by intermolecular constraints, in addition to the inherent chain connectivity effect.

General Approach

The notation and formulation of the preceding paper, referred to hereafter as ref 22, will be adopted in the following. For a chain of n backbone bonds, $n + 4$ variables described in Figures 1 and 2 of ref 22 determine the overall configuration. Among them, the $n - 2$ internal degrees of freedom associated with bond torsional flexibilities are represented by the dihedral angles φ_j, $2 \leq j \leq n - 1$. The external degrees of freedom associated with the translation $\mathbf{R}_0 \equiv (X_0, Y_0, Z_0)$ of the first atom and rotation (Φ, ψ, χ) of the first bond constitute the remaining six variables. Atoms are indexed from 0 to n. The position vector of the ith atom with respect to the laboratory-fixed frame $OXYZ$ is denoted by $\mathbf{R}_i$.

A chain of 25 bonds is considered. This chain is sufficiently long to permit the internal reorganization of the atoms without substantial displacement of the tails, as will be presented below. Bonds are originally assigned three types of equally probably torsional states, trans, gauche$^+$, and gauche$^-$, by a random number generator subroutine. The original configuration of the chain segment is perturbed by introducing a small step change $\Delta\varphi_s$ in the dihedral angle of the middle bond s, and the induced changes in the other $n + 3$ variables are examined. The incremental changes in those variables are organized, for convenience, in the form of two arrays $\Delta\varphi \equiv \text{col}\,(\Delta\varphi_1\ \Delta\varphi_2 \ldots \Delta\varphi_{s-1}\ \Delta\varphi_{s+1} \ldots \Delta\varphi_{n-1})$ and $\Delta\mathbf{X} \equiv \text{col}\,(\Delta\psi\ \Delta\Phi\ \Delta X_0\ \Delta Y_0\ \Delta Z_0)$ and are computed from eq 42 of ref 22.

The present method may be regarded as a zero-temperature approach where a coordinate is forced and other coordinates respond according to the energy minimization principle. Thus the present approach differs from molecular dynamics or Brownian dynamics simulations in which the motions occur as a natural result of thermal fluctuations. In the present case, the driving term in the reaction coordinate is externally imposed.

Inasmuch as the above theory is a first-order approximation applicable to differential changes only, in either external or internal degrees of freedom, the incremental changes $\Delta\varphi_s$ of the rotational state of the middle bond are selected to be sufficiently small to avoid any nonlinear response. The occurrence of a nonlinear response, if any, may be monitored by observing the magnitude of the S function

$$S \equiv (n + 1)^{-1} \sum_{i=0}^{n} (\Delta \mathbf{R}_i)^2 \tag{1}$$

during a particular conformational rearrangement. An abrupt change in the latter is indicative of a major, large-amplitude change in the spatial distribution of atoms, which is beyond the range of the applicability of the theory. Incremental changes $\Delta\varphi_s$ of 0.05 rad have proven to be compatible with the present mathematical framework. For $\Delta\varphi_s \leq 0.05$ rad, the evolution of the dihedral angles of relevant bonds exhibits closely the same pattern as a function of φ_s, and hence the adoption of smaller size steps is unnecessary.

Illustrative Examples

Figure 1 illustrates some typical changes occurring in the dihedral angles of bonds in the close neighborhood of the bond $s = 13$, which undergoes a rotational transition of about 120° through a succession of 42 steps, each of 0.05-rad ($\sim$2.89°) amplitude. The particular sequence of isomeric states surrounding the middle bond prior to its rotation is indicated in the figure caption. The cumulative change in the dihedral angle of the central bond is shown by the filled squares as a function of step number in all of the figures. The accompanying cumulative changes in the dihedral angles of bonds 11 and 15 are shown by the filled circles and triangles, respectively. Those for bonds with even serial number, 12 and 14, are represented by the empty circles and triangles, respectively. $\Delta\varphi_k$ for the other bonds, remaining always lower than 25°, are not shown in the figures. The distribution of cumulative changes in dihedral angles $\Delta\varphi_k$ for k = 1–25 at the end of the rotational transition of the middle bond is displayed in Figure 2 for this particular example chain. Lines are drawn to guide the eye. It is observed that the new rotational state is accommodated by the torsional motions of a few bonds ($\sim$8) in the close neighborhood of the rotating bond.

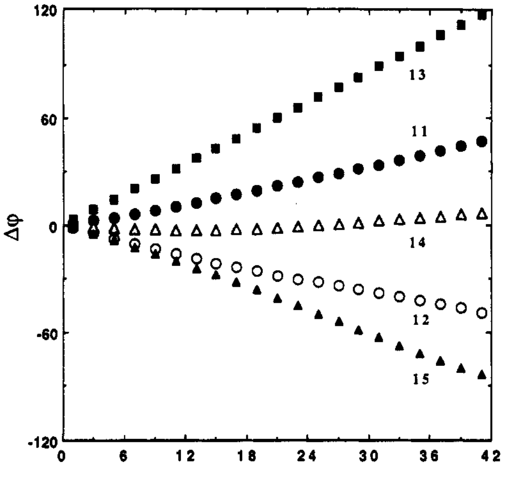

Figure 1. Cumulative changes in the dihedral angles of bonds 11 (●), 12 (○), 14 (△), and 15 (▲) following the successive changes of 0.05 rad in the dihedral angle of bond 13 (■) for an illustrative chain of 25 bonds with the central bonds 11–15 originally in configuration $g^+g^-g^-tg^-$. Bonds 11–15 approach the state $g^+g^-g^+tg^+$ in response to the rotation of the middle bond.

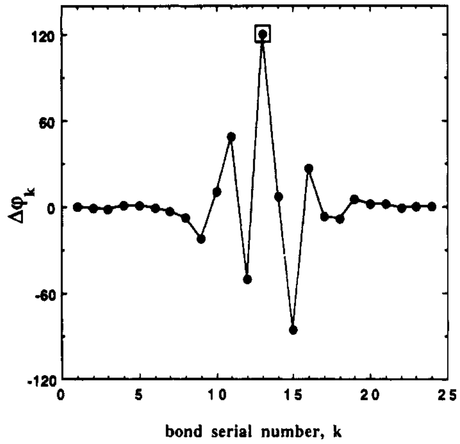

Figure 2. Distribution of changes in dihedral angles $\Delta\varphi_k$ for k = 1–25 at the end of the rotational transition of the middle bond for the example chain of Figure 1. Lines are drawn to guide the eye. The change in the dihedral angle of bond 13 is represented by a square around the circle to indicate that its rotation is externally imposed.

Examination of the response of chains with a variety of initial configurations shows in general that counterrotations of substantial amplitude (~90°) are effectuated by the first or second neighbors on either side of the rotating bond.

It is interesting to note that the response of the neighboring bonds does not occur in the form of random fluctuations in rotational angles eradicating thus the net change in dihedral angles, but as a smooth torsion developing along a given direction in general, so that the cumulative change in one or more dihedral angles at the end of the passage is of considerable magnitude. Another feature emerging from the study of chains with various configurations is the tendency of at least one of the first or second neighbors flanking the middle bond to undergo large-amplitude rotations of opposite sense compared to the middle bond, apparently to compensate the rotation of the adjoining bond. Also, some correlation between the rotational motion of bonds s and $s \pm 2$ is observed, which will be further exploited next.

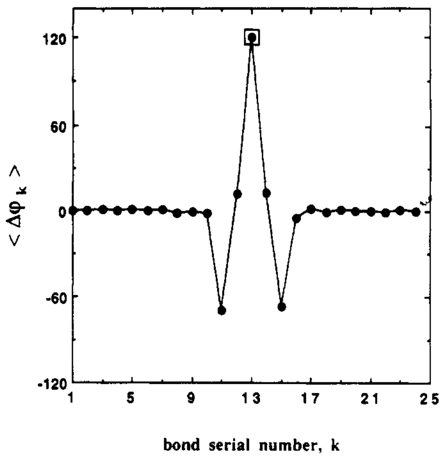

Figure 3. Effect of rotation of the central bond in a ttttt sequence for the t to g^+ state on the dihedral angles of neighboring bonds. The middle bond is rotated through 42 intermediate steps by a total amount of 120°. The accompanying rotations of bonds in the close neighborhood are presented as a function of bond serial number. The ordinate values represent $\langle\Delta\varphi_k\rangle$ for k = 1–25 obtained from 200 MC chains.

Comparison with Brownian Dynamics Simulations

The interdependence of bonds s and $s \pm 2$ brings into consideration the incidence of conformational transitions of the form (i) ttt ↔ g^+tg^- and (ii) $g^-tt \leftrightarrow ttg^-$, which Helfand points out to be of significant importance in Brownian simulations[6,7] and classifies as type II motions. In this respect, it seems interesting to follow up the coupled motion of sequences of bonds with those specific conformations to assess the origin of this type of transitions. To avoid any complications arising from the asymmetry of the generated configurations and to have a larger number of sample transitions, sequences of five bonds (instead of three) with a symmetric configuration with respect to the central bond are considered in a 25-bond chain. The central bond (s = 13) in each case is assumed to rotate following the above schemes.

First, the possible occurrence of the transition ttt ↔ g^+tg^- is searched by setting the five central bonds to the t state and rotating the middle bond through 42 intermediate steps from state t to g^+. The accompanying rotations of bonds in the close neighborhood are examined. This process is repeated for 200 Monte Carlo (MC) chains with a variety of configurations surrounding the middle five bonds. The resulting distribution of average changes in dihedral angles $\langle\Delta\varphi_k\rangle$ for k = 1–24 is shown in Figure 3. It is observed that bonds $s + 1$ and $s - 1$ exhibit small-amplitude distortions (of 12.2 ± 0.5°) in the same direction as the middle bond. On the other hand, bonds $s + 2$ and $s - 2$ are found to undergo large rotations (of 67.9 ± 1.3°) in the negative direction, in qualitative agreement with scheme i described above. A closer examination of the behavior of *each* individual MC chain indicates that the same distribution curve is closely reproduced, irrespective of the configurational state of the bonds flanking the middle segment of interest. It is noted that the $\langle\Delta\varphi_k\rangle$ values reached by bonds $k = s \pm 2$ exceed the angular displacement required to cross the saddles or high-energy barriers between rotamers of a polyethylene chain, for example. In the presence of intramolecular conformational energetics, it is clearly not favorable for a given bond to assume rotational states near the potential barrier (~60°). However, if the access to or the passage over the saddle is forced by effects such as chain connectivity and environmental constraints as presently demonstrated,

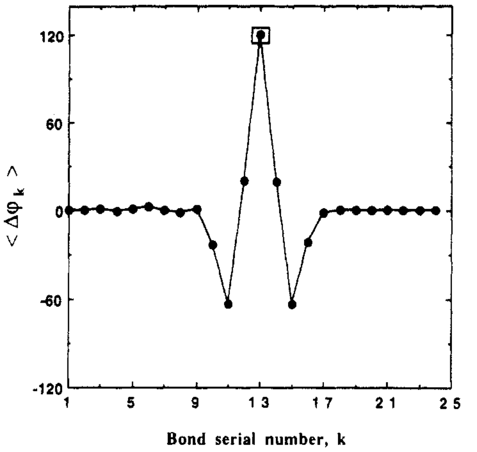

Figure 4. Effect of rotation of the central bond in a ttg$^-$tt sequence from the g$^-$ to t state on the dihedral angles of neighboring bonds. The middle bond is rotated through 42 intermediate steps by a total amount of 120°. The ordinate values represent average $\langle \Delta\varphi_k \rangle$ for bonds k = 1–25 obtained from 200 MC chains.

there is an enhanced chance that the isomeric transition of ~120° will be completed all the way down the intramolecular energy valley.

Similarly, for the investigation of the possible occurrence of the transition g$^-$tt ↔ ttg$^-$, the middle bond in a central segment with the original conformation ttg$^-$tt, is rotated by 120°. This motion is found to lead to the distribution depicted in Figure 4, which is closely reproduced in each of the 200 generated MC chains with various bond conformations surrounding the central segment. Thus, a 120° rotation of the middle bond is found to induce, invariably, a negative rotation of the second neighbors: The average values −63.1 ± 0.1° are obtained for the rotations of those bonds. It is observed that this motion is supplemented by the spatial rearrangements of the close neighbors, i.e., by systematic rotations of 19.8 ± 0.4° and −22.5 ± 0.5° from the parts of bonds $s \pm 1$ and $s \pm 3$, respectively. It is interesting to note that, in both Figures 3 and 4, the correlation between the motion of the central bond and its close neighbors does not extend beyond third neighbors. Although the remaining bonds undergo, in general, small-amplitude oscillatory torsions, as illustrated in Figure 2, no motion in a well-defined sense occurs so that their $\langle \Delta\varphi_k \rangle$ values become vanishingly small.

The two transitions (i) ttt ↔ g$^{\pm}$tg$^{\mp}$ and (ii) g$^{\mp}$tt ↔ ttg$^{\mp}$ account for more than 80% of the cooperative transitions observed in Brownian dynamics simulations.[7] Here, cooperative transitions refer to two successive rotational jumps undergone by the first and third bonds within a time interval shorter than a cutoff value. Other transitions are also listed[7] belonging to that category, though their probability of occurrence is substantially low. An example is the transition ttt ↔ g$^+$tg$^+$ in which two gauche bonds of the same sign are either created or annihilated. The application of the present mathematical formalism to a variety of MC chains with central sequences originally in the ttt state leads systematically to final configurations close to g$^{\pm}$tg$^{\mp}$ and not to g$^{\pm}$tg$^{\pm}$. Indeed, the final state g$^{\pm}$tg$^{\pm}$ is obtained only for some particular favorable configurations of the neighboring bonds. Similar behavior is observed for the other weakly cooperative transitions as well. Thus, except for the two most probable transitions presented above, changes in the dihedral angle of the second neighbor by more than 60° appears to necessitate suitable configuration of the nearest neighbors along the chain and cannot be ascribed uniquely to the geometric features of sequences of three bonds alone.

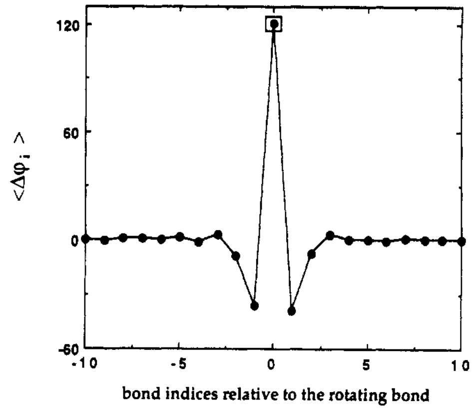

Figure 5. Average change $\langle \Delta\varphi_i \rangle$ in bond dihedral angles in response to 120° rotation of the middle bond evaluated from 1000 MC chains of various original configurations presented as a function of location relative to the central bond.

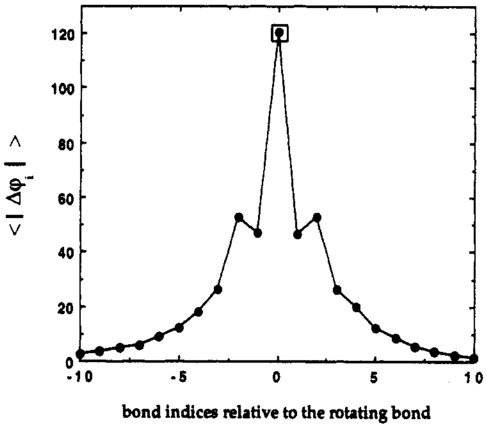

Figure 6. Dependence of $\langle |\Delta\varphi_i| \rangle$ on location i relative to the middle bond in response to 120° rotation of the middle bond evaluated from 1000 MC chains of various original configurations.

As a final remark concerning the relative probability of occurrence of the two transitions (i) ttt ↔ g$^+$tg$^-$ and (ii) g$^-$tt ↔ ttg$^-$ we might add that, on the basis of the mean-square displacement S of atoms, gauche migration appears to be more probable to gauche pair production/annihilation. This feature is in qualitative agreement with the results from Brownian simulations.

Correlations between Bond Rotational Motions

The correlation between the rotational motions of various bonds along the chain is analyzed by computing the change in the dihedral angle of each of the 25 bonds for an ensemble of 1000 MC chains in which the central bond rotates by 120°. Figures 5 and 6 display the resulting distributions of $\langle \Delta\varphi_i \rangle$ and $\langle |\Delta\varphi_i| \rangle$, respectively, as a function of bond index relative to the rotating bond. The weak asymmetries of the figure with respect to the central vertical line gives an estimate of the error bounds of the simulated results.

An interesting feature appearing from Figure 5 is the fact that the rotations of the first neighbors on both sides of the central rotating bond do not average out to zero but remains at about −40°. This indicates the strong tendency of bonds to undergo counterrotations in response to the rotation of their first neighbors. This feature evidently helps to compensate and localize the original motion. $\langle \Delta\varphi_i \rangle$ for the second neighbor is about −8°, and the values for the other bonds are vanishingly small, indicating no preference for bonds beyond second neighbors to undergo rotations along well-defined senses. On the other hand, if the magnitudes of the changes in dihedral angles are considered, irrespective of their sense, the response of

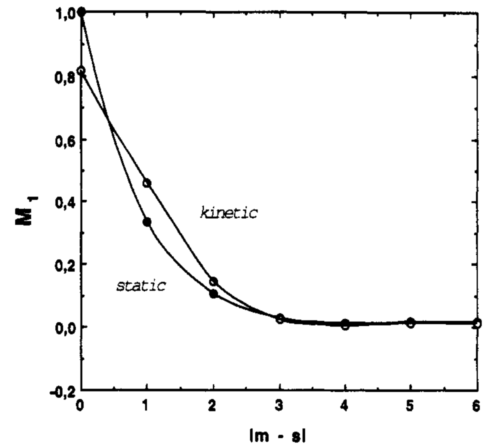

Figure 7. First orientational correlation function M_1 between the central bond s and the mth bond as a function of the absolute number $|m - s|$ of intervening bonds. The static correlation function represents calculations based on the initial configurations of 1000 MC chains. The kinetic M_1 represents the average correlations between the initial conformation of the central bond and the final configuration of the mth bond obtained after a 120° rotation of the central bond.

bonds $s \pm 2$ turns out to be stronger than that of bonds $s \pm 1$. This feature is illustrated in Figure 6. The respective $\langle|\Delta\varphi_i|\rangle$ values for bonds $s \pm 1$ and $s \pm 2$ are equal to 45 ± 1° and 51 ± 2°. A similar figure was first given by Adolf and Ediger[14,15] in their analysis of Brownian dynamics simulations. It should be pointed out that those two figures represent about half of the actual displacements observed in the majority of MC chains. This is due to the fact that a large-amplitude rotation occurs, in general, on one side of the middle bond only, while the other side is weakly perturbed. As a consequence, the average $\langle|\Delta\varphi_i|\rangle$ for a given bond on one side is diminished by approximately a factor of 2.

It should be added that calculations repeated for MC chains of $n = 39$ bonds lead, almost indistinguishably, to the same distribution curve as the one displayed in Figure 6 for the average absolute changes in dihedral angles in response to the rotation of the middle bond. Thus, the curve displayed in Figure 6 is representative of the kinematics of a freely rotating chain in a restrictive environment, irrespective of the size of the molecule.

Correlations between Bond Orientations

The first and the second orientational correlation functions M_1 and M_2 for the mth bond vector ℓ_m and the nth bond vector ℓ_n are defined respectively as

$$M_1 = \langle \ell_m \cdot \ell_n \rangle \qquad (2)$$

and

$$M_2 = (1/2)\langle 3(\ell_m \cdot \ell_n)^2 - 1 \rangle \qquad (3)$$

In Figure 7, values of M_1 between the mth bond and the central bond s are presented as a function of the difference $|m - s|$. Thus, the intercepts with the ordinate indicate the *autocorrelation* function for the middle bond, while the remaining points, which are connected to guide the eye, correspond to orientational *cross-correlations* between the middle bond and its neighbors. The curve labeled "static" is obtained from the initial configurations of 1000 MC chains and reflects the equilibrium orientational correlations among the central and different bonds along the chain.[24] The curve labeled "kinetic" is similarly obtained from 1000 MC chains and represents the correlations between the central bond s (in the initial configuration) and the bond m (in the final configuration), following a 120° rotation of the central bond. Orientational correlations are insignificant beyond the second neighbor. It is interesting to note that the orientational correlations between the central bond and its first and second neighbors are stronger in the kinetic case. This may be attributed to the cooperative rearrangements of these bonds so as to minimize the overall displacements of atoms. Results for M_2 are presented in Figure 8. Similar to the results for M_1, orientational correlations beyond the second neighbors of a given bond are negligibly small.

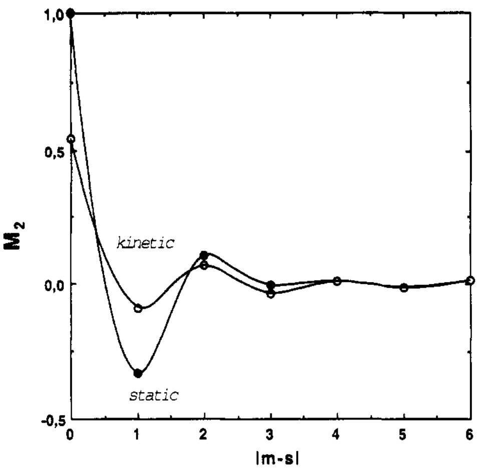

Figure 8. Second orientational correlation function M_2 between the central bond s and the mth bond as a function of the absolute number $|m - s|$ of intervening bonds. See legend for Figure 7.

It is interesting to observe from the intercepts in both figures that the orientational autocorrelation functions of the middle bond decay from 1 to some lower value (~0.8 for M_1 and ~0.5 for M_2) at the end of its torsional motion. This decrease indicates an axial reorientation in space of about 35° from the part of the middle bond in addition to its rotational motion about its own axis. Thus, the rotameric transition of a given bond is accommodated among various spatial readjustments by the axial reorientation of the rotating bond itself, which overrules the previously proposed on-lattice descriptions of local motions in polymers.

NMR experiments detect the spatial reorientation of transition moment vectors rigidly moving with the backbone bonds. In this respect, the motion of the first neighbor as a result of the rotation of a given bond is of interest. Let α denote the angle between the initial and final orientations of the first neighbor under study. In the absence of any cooperative internal and external rearrangements, an isomeric jump of 120° by a given bond in a tetrahedral chain is expected to induce a spatial reorientation of $\alpha = 109.5°$ on its first neighbor. On the other hand, cooperative rearrangements of the chain units surrounding the rotating bond are expected to minimize the angular displacement to a certain extent. For a quantitative understanding of the role of cooperativity in determining the spatial reorientation of the vector of interest, the probability distribution of the angle α has been calculated from 1600 MC chains of 25 bonds. Contrary to the expectations for on-lattice transitions, a wide variety of angular displacements, changing in the range $0 \leq \alpha \leq 95°$ is obtained, as shown in Figure 9. The distribution exhibits three peaks approximately centered about 20, 45, and 70. The mean value is calculated as 51.5°.

The broad range of angular displacements in Figure 9 might be attributed to the experimentally observed small-

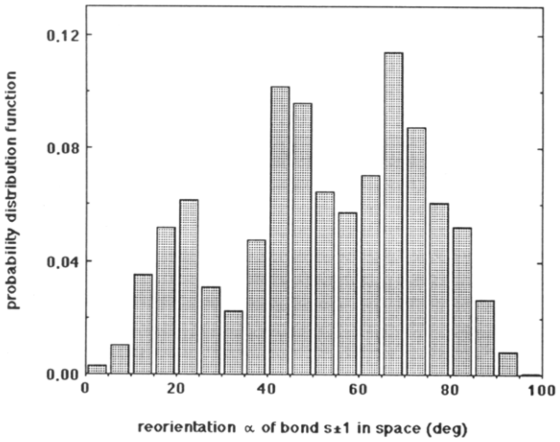

Figure 9. Probability distribution of angular displacement α of backbone bonds in response to the rotameric transition of their first neighbors along the chain. Results are obtained from 1600 MC chains of 25 bonds.

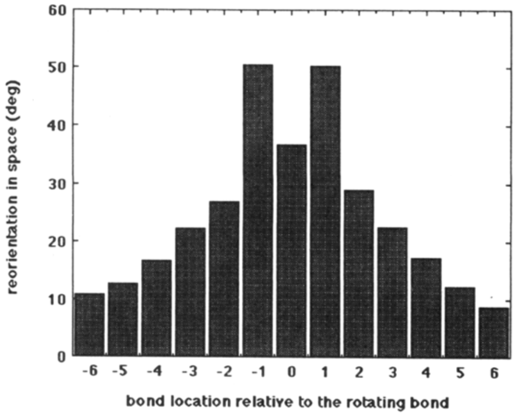

Figure 10. Mean angular displacements of backbone bonds in response to the rotameric transition of the central bond. The orientation of each bond is given as a function of its location relative to the rotating bond.

amplitude distortions which are generally identified as librational motions. The present calculations indicate that the observation of a wide range of small-amplitude reorientations does not necessarily imply the absence of jumps between rotational isomeric states. Thus, although a complete 120° rotation is undergone by a given bond, it is reflected upon its neighbors (including the first) in the form of relatively small-amplitude distortions in a restrictive environment. A visualization of the effect of bond rotation on the reorientation of the near neighboring bonds is possible from the examination of Figure 10. In this figure, the mean α values obtained for bonds up to the sixth neighbors of the rotating bond s are displayed. The rotating bond itself is also being reoriented as pointed out above. The angular displacement of the first neighbors is the highest. A relatively smooth distribution of angular displacements is observed for the remaining neighbors, again strengthening the argument of a large number of small-amplitude distortions associated with rotational isomeric transitions.

Displacement of Chain Atoms

The average displacement $\langle \Delta \mathbf{R}_i \rangle$ of chain atoms accompanying the rotation of the central bond is shown in Figure 11. The figure shows the averages obtained from 500 MC chains of various original configurations as a function of atom index. The asymmetry of the figure gives an estimate of the error bounds of the computations. It is noted that the two atoms belonging to the rotating bond undergo the largest displacement in space, and the displacements gradually decrease with separation from the rotating bond. Finite displacements remaining at the tails indicate the overall translation and reorientation of the chain in space. Calculations performed for longer chains indicate that the displacement of the tails approaches zero as the length of the chain increases.

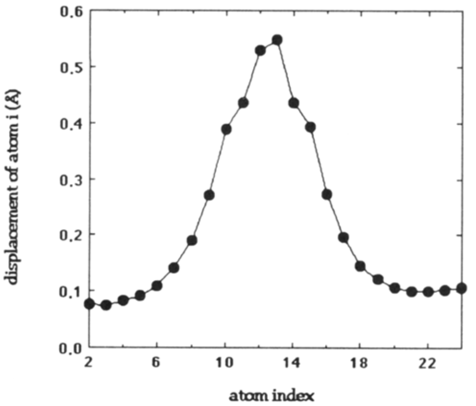

Figure 11. Mean spatial displacements $\langle \Delta \mathbf{R}_i \rangle$ of backbone atoms i in response to the rotameric transition of the central bond in freely rotating chains of 25 bonds. The length of each bond is taken as 1 Å. The displacement of each atom is given as a function of its atom index along the chain.

Concluding Remarks and Discussion

Results of calculations indicate that the correlation length for local orientational motions is less than 10 Å for a freely rotating chain model in a restrictive medium. The mobile unit is found to be of the order of 6–8 bonds. This result provides an estimation of the size of the kinetic segment involved in local conformational motions in a chain enjoying a high degree of intramolecular flexibility such as the freely rotating model but being severely restricted by intermolecular constraints. Thus, the freely rotating chain represents an extreme case, from the point of view of intramolcular potentials, in which no preference for a certain rotational isomeric state takes place. Interdependence of neighboring bonds through finite intramolecular potentials might increase the correlation length and/or the number of bonds cooperatively participating in local relaxation processes. An improvement of the present theory upon inclusion of energy changes during conformational transitions might be of interest as a future study.

Recent Brownian dynamics simulations of Adolf and Ediger[14,15] indicate that, for polyethylene and polyisoprene chains, distortions in atomic positions and bond dihedral angles accompanying a conformational transition are localized to about four carbon atoms along the main chain, in agreement with the correlation length observed in the present work. Second-neighbor torsional coupling is found[10] to be important for polyethylene but not for polyisoprene. The present work performed for perfect tetrahedral freely rotating chains leads to the torsional coupling distribution in Figure 6, which is very similar to that observed from Brownian dynamics simulations for polyethylene. Thus the occurrence of torsional coupling between second neighbors appears as a natural consequence of the approximate tetrahedral geometry of the backbone. We may conclude that second-neighbor cooperativity is an important and a general consequence of chain connectivity, irrespective of intramolecular energetics, provided that the backbone structure is approximately tetrahedral. Heterogeneities of the backbone structure such as double bonds, twofold symmetric potentials, may, on the other hand, weaken or hamper this effect, as observed[15] in polyisoprene.

In the present work, the kinematics of a segment succeeding a rotameric transition of a given bond was emphasized. However, not only the accommodation of the segment accompanying a complete isomeric jump but the coupled or concerted small-amplitude oscillatory motions—to minimize the energy dissipation under the constraints of chain connectivity and environmental resistance—are also described by the present mathematical model. Those highly correlated motions may be particularly important in the vicinity of the glass transition temperature where free volume limitations hinder large-amplitude rotations and superposition of fast librational motions predominantly operates in local relaxation.

The present analysis was carried out for a restrictive medium in which the spatial rearrangements of atoms are coupled so as to minimize the cumulative displacements of atoms during each small-amplitude perturbation, irrespective of the type and direction of motion. Recent molecular dynamics simulations of bulk amorphous polymers indicate, however, that reorientation of the chain axis may be strongly impeded compared to rotations about the chain axis, even in freely rotating chain models.[9,10] Thus, in addition to the chain connectivity effect inherently favoring rotational motions about the chain axis, as has been demonstrated by Brownian dynamics simulations[7] and by calculations based on dynamic rotameric states formalism,[25] the anisotropy of intermolecular interactions is also pointed out[9,10] as a factor responsible for the pronounced anisotropy of local motions. Flory's theoretical examination[26] of levels of order in amorphous polymers indicates the existence of anisotropic effects over short length scales. Extension of the present approach to include the heterogeneity of the environment and allow for the preferential mobility along well-defined directions might also be conceived.

An important feature demonstrated by the present mathematical formalism is the occurrence of a wide distribution of angular displacements of backbone bonds in response to the rotameric transition of their first neighbors. This phenomenon reconciliates the picture of the wide range of small-amplitude distortions observed in NMR experiments with the process of rotameric jumps as a mechanism involved in local chain relaxation. Another important feature related to dielectric relaxation experiments in particular is the absence of a torsional rotation along a preferred sense for the second neighbor of a rotating bond, as observed in Figure 9. This indicates that orientation cross-correlations beyond first neighbors are negligibly small, and the consideration of autocorrelations and first-neighbor cross-correlations is sufficient in practice for a reasonable interpretation of dielectric relaxation experiments.

Acknowledgment. This work was supported by NATO Grant CRG 910422. Partial support from Bogazici University Research Funds Project 91P0029 is gratefully acknowledged by I.B.

References and Notes

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