Cooperativity of Local Conformational Dynamics in Simulations of Polyisoprene and Polyethylene

David B. Adolf and M. D. Ediger*

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received July 22, 1991; Revised Manuscript Received September 25, 1991

ABSTRACT: Brownian dynamics computer simulations of polyethylene and *cis*-polyisoprene are analyzed to determine how various degrees of freedom cooperate in localizing conformational transitions. Changes in atomic positions, bond angles, and torsional angles are considered. For both polyethylene and polyisoprene the distortions in atomic positions accompanying a conformational transition are localized to about four carbons along the backbone. Second-neighbor torsional coupling is found to play an important role in localizing conformational transitions for polyethylene but not for polyisoprene. The motion which occurs in connection with a conformational transition in polyethylene is almost independent of whether a second conformational transition occurs cooperatively with the first. Several aspects of the polyethylene results are consistent with earlier calculations using multidimensional Kramers' theory.

I. Introduction

Computer simulations provide an important tool for the exploration of structure/property relationships in polymers. A microscopic analysis of a simulation may reveal insights into the origin of important properties which could not be obtained directly from experiments. The reliability of such insights is partially indicated by the extent to which the simulation can successfully model observable properties of a polymeric system.

We have recently reported Brownian dynamics simulations of *cis*-polyisoprene.[1] Several features of the simulations are in good agreement with NMR experiments on polyisoprene in dilute solutions. A new technique for examining the role of cooperativity in local polymer dynamics was utilized in analyzing these simulations. This technique allowed us to determine that distortions in atomic positions accompanying a conformation transition are localized to about one repeat unit in polyisoprene.

In the course of our work on polyisoprene we repeated Helfand and co-workers'[2,3] simulations of polyethylene. In this paper we apply our new technique for examining cooperativity to the polyethylene simulations and compare the local dynamics of polyethylene and polyisoprene. By this procedure, we take a small step toward increasing our understanding of structure/property relationships on a fundamental level.

Cooperativity is a widely used concept in the discussion of local conformational dynamics.[4-10] In addition, it is often used with different meanings. In some cases, two conformational transitions which occur simultaneously or sequentially are termed cooperative transitions. Schatzki's crankshaft[11] and Helfand's cranklike[12] motions are examples of these types of motions. We shall refer to this type of motion as a "cooperative transition pair".

There is also a broader sense in which conformational dynamics are cooperative. In this sense, *all* conformational transitions are cooperative. Even if only one conformational state changes in a given motion (sometimes called an "isolated" transition), other degrees of freedom must adjust to localize the transition.[13] Otherwise a significant section of the chain would have to rotate rigidly through space. The friction associated with this type of motion would be enormous. If this were the normal pathway for conformational transitions they could not occur on the picosecond and nanosecond time scale and would not be independent of molecular weight. Somehow other degrees of freedom must cooperate with the rotating bond in order to localize the portion of the chain which is required to move. These other degrees of freedom may be bond angles, torsional angles, or, more generally, atomic positions.

In this paper we examine cooperativity in both of these senses. We find that distortions in atomic positions accompanying a conformational transition in polyethylene are localized within about four carbons along the backbone. This is very similar to our result for polyisoprene. Consistent with previous work by Helfand,[12,13] second-neighbor torsional coupling is found to play an important role in localizing conformational transitions in polyethylene. This effect is not seen in polyisoprene. Surprisingly, the motion which occurs in connection with a conformational transition in polyethylene is almost independent of whether a second transition occurs cooperatively with the first. Thus cooperative transition pairs and isolated transitions are more similar than has been previously understood. Finally, we show that earlier calculations which used multidimensional Kramers' theory[14] to analyze polyethylene transitions are consistent with the results of our cooperativity analysis.

II. Description of Simulations

A complete description of the *cis*-polyisoprene[1] and polyethylene[1-3] simulations has been given elsewhere. In both cases, Brownian dynamics simulations were performed. In these simulations an individual polymer chain is modeled on a molecular level in a fairly realistic manner. Bond stretching and bending potentials are included in addition to torsional potentials. Random coil structures with 70–100 repeat units are utilized. Some structural simplifications were introduced for computational efficiency; e.g., certain groups of atoms were collapsed onto single united atoms. Hydrogens were collapsed onto their parent carbons and the fairly rigid $CH{=}C(CH_3)$ group was collapsed to a single unit. The simulated chain interacts with a viscous, structureless continuum (the bath). Stochastic forces allow for energy exchange between the chain and the bath. In this manner, the motion of a chain in dilute solution is approximately reproduced.

The polyethylene simulations were originally performed by Helfand and co-workers.[2,3] We reproduced this simulation for the purposes of extending the analysis and making comparisons with our polyisoprene simulations. As a check, we repeated the analysis of Helfand and co-workers on our polyethylene simulations and found

0024-9297/92/2225-1074$03.00/0

quantitative agreement with their results. These comparisons are discussed in ref 1.

In ref 1 we discuss the relationship between our polyisoprene simulations and experimental results. Several features of the simulations are in good agreement with ^{13}C NMR T_1 experiments on polyisoprene; e.g., the relative rates of motion of various C–H vectors within the repeat unit are correctly predicted by the simulation.

III. Cooperativity of Transitions in Polyethylene

Helfand and co-workers have analyzed Brownian dynamics simulations of polyethylene in terms of cooperative transition pairs.[2] They found that after a conformational transition occurred in polyethylene, a second transition occurred nearby along the chain within a very short time (3 ps at 425 K) in 29% of the cases. These are "cooperative" in the narrow sense discussed in the Introduction. The second transition always occurred about the second-neighbor torsion, relative to the initial transition. This second-neighbor coupling effect had been predicted previously by Helfand.[12] Seventy-one percent of all the transitions occurred without an accompanying transition. These are "isolated transitions".

In a previous paper we introduced a new method for examining cooperativity (broadly defined) in conformational transitions.[1] This method is well suited for determining (i) which degrees of freedom adjust in order to accommodate the transforming bond and (ii) over what length scales these adjustments occur. In our previous work, we applied this technique to polyisoprene simulations. Here we analyze conformational transitions in polyethylene in the same manner and compare to the polyisoprene results. We do this for all of the transitions and separately for only the cooperative transition pairs. This provides some insight into the differences between cooperative transition pairs and isolated transitions.

Conceptually, we examine cooperativity in conformational transitions by taking a snapshot of the atomic (or bead) positions on a section of a chain just before and just after a conformational transition. By averaging over thousands of transitions, we can determine the average atomic displacements accompanying a conformational transition.[15] Mathematically, we calculate the quantity

$$\langle|\vec{r}_i(t=\tau_{\text{trans}}+\Delta t) - \vec{r}_i(t=\tau_{\text{trans}}-\Delta t)|\rangle \qquad (1)$$

Here $\vec{r}_i$ represents the coordinates of the ith atom along the chain. The index i is the position of an atom along the chain contour relative to the position of the transforming bond; the transitions take place between atoms 0 and 1. We calculate the quantity shown for i = −20 to +20; i.e., we analyze the movements of 20 atoms on each side of the transforming bond. τ_{trans} is the time when the transforming bond crosses the torsional potential barrier and Δt is 0.5 ps (the average time between transitions for polyethylene at 425 K is 55 ps). The ensemble average is taken over all transitions occurring in the trajectory.

Figure 1 shows a plot of expression 1 for polyethylene at 425 K. The solid line is the result for all transitions while the dashed line represents only the cooperative transition pairs described above. As expected, the two atoms which define the transforming bond show the greatest change in position during the short time interval about τ_{trans}. The atomic position distortion drops off quickly as atoms farther from the transforming bond are considered. Six atoms away along the chain contour the displacement is no greater than 20 atoms away. This baseline simply reflects thermal motions which occur in any 1-ps interval regardless of whether a transition has occurred nearby. The fwhm of the peak is 3.5 atoms or about two repeat units. The results are very similar for the entire group of transitions and the subset of cooperative transition pairs.

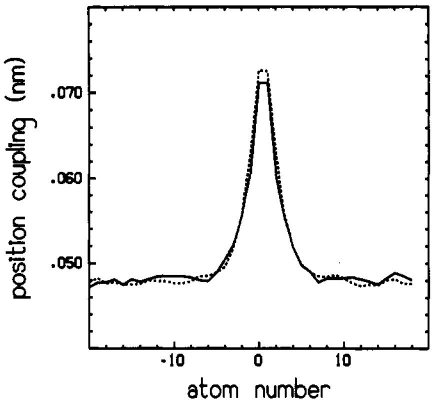

Figure 1. Distortion of atomic positions accompanying a conformational transition in simulated polyethylene (expression 1): (—) all transitions; (- - -) cooperative transitions. The conformational transition occurs between atoms 0 and 1. In each case, the distortion is limited to a few repeat units.

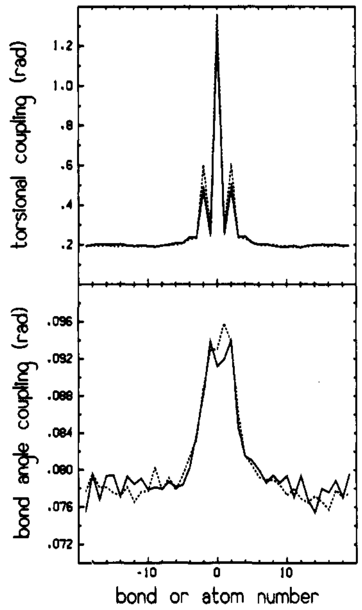

Figure 2. Distortions of torsional modes (top panel) and bond angles (bottom panel) accompanying a conformational transition in simulated polyethylene: (—) all transitions; (- - -) cooperative transitions. These plots are created from expression 2 and its analogue for bond angles. For the torsional modes, the transition occurs at bond 0; for the bond angles the transition occurs between atoms 0 and 1. The distortions are limited to a few repeat units. The bond angle coupling is small in magnitude (about 1°).

An analysis similar to expression 1 can be carried out for any degree of freedom in the simulation. We have analyzed coupling with neighboring torsions ϕ_i using the expression

$$\langle|\phi_i(t=\tau_{\text{trans}}+\Delta t) - \phi_i(t=\tau_{\text{trans}}-\Delta t)|\rangle \qquad (2)$$

We have also analyzed bond angle coupling with a similar expression. Figure 2 shows the torsional and bond angle coupling at 425 K for polyethylene. As in Figure 1, the solid lines represent all of the transitions while the dashed lines represent only the cooperative transition pairs. Both panels of the figure show maximum distortions at the position of the conformational transition; the distortion is negligible more than six atoms away from the transforming bond. Thus Figures 1 and 2 show a consistent

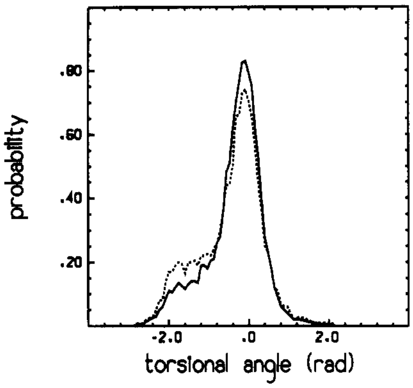

Figure 3. Probability that the second-neighbor torsion in polyethylene undergoes a given angular change during the 1 ps surrounding a conformational transition: (—) all transitions; (- - -) cooperative transitions.

picture of conformational transitions localized to about two repeat units. In both panels of Figure 2 the results for the subset of cooperative transition pairs are very similar to the results for the group of all transitions.

The peak in torsional coupling shown in Figure 2 for second neighbors is consistent with the hazard analysis of first passage times for polyethylene in ref 2. The hazard analysis indicated that an additional transition following an initial transition was most likely to occur at the second-neighbor position. Expression 2 is different from the hazard analysis in that it indicates cooperative motions whether or not they result in a second conformational transition.

To gain some additional insight into the torsional coupling process involving second neighbors, we have further analyzed the second-neighbor peak shown in the top panel of Figure 2. The value of about 0.5 rad for the second-neighbor coupling represents the average displacement of second-neighbor torsions in a short time surrounding a conformational transition. Any individual second neighbor may change more or less than this. The entire distribution of second-neighbor torsional adjustments is shown in Figure 3, i.e., the probability of a given torsional adjustment for bonds $i + 2$ and $i - 2$ during a 1-ps interval in which a conformational transition occurred at bond i. The solid line represents all the transitions while the dashed line shows the result for only the cooperative transition pairs. Figure 3 shows that many second neighbors move very little in the 1-ps time interval. About 25% of second neighbors counterrotate to a significant degree. Again we note that the cooperative transition pairs are only slightly different in character from the total group (cooperative transition pairs plus isolated transitions).

Superficially, Figure 3 seems inconsistent with the fact that 30% of the time a second-neighbor torsion undergoes a conformational transition. Only a very small fraction of second-neighbor torsional angles change by more than 120° (2.1 rad). Three important points must be kept in mind. First, Figure 3 includes second-neighbor torsions *on each side* of the transforming bond. Only rarely will both second-neighbor torsions make transitions. Second, Figure 3 examines angular motion during a 1-ps interval about τ_{trans}. The 30% fraction is calculated with a cutoff time of 3 ps. Thus Figure 3 emphasizes the character of the transition state more than the analysis of ref 2. Third, Helfand and co-workers[2] define a transition as going from the bottom of one well of the dihedral potential to the bottom of the next well. Only the last portion of this motion must occur within 3 ps of the initial transition in order for the second transition to count in the 30% fraction.

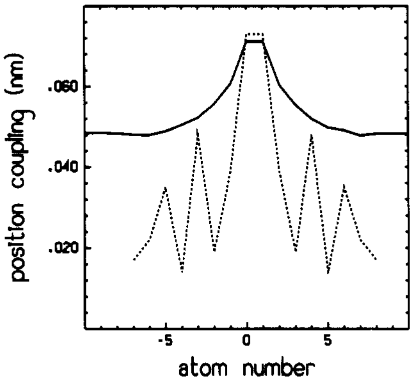

Figure 4. Distortion of atomic positions accompanying a conformational transition in polyethylene: (—) simulation; (- - -) multidimensional Kramers' theory.[14] The Kramers' calculations do not include random thermal motions.

Cooperative Transition Pairs vs Isolated Transitions. Figures 1–3 indicate that cooperative transition pairs and isolated transitions in polyethylene have very similar characteristics. We have performed the same analysis for a number of different values of Δt (0.5–10 ps) in expressions 1 and 2. In all cases, the cooperative transition pairs show very similar behavior to the group of all transitions. Reference 2 shows, in addition, that cooperative transition pairs and isolated transitions have the same activation energies.

We suggest that the difference between these two types of transitions has sometimes been overemphasized. When a conformational transition occurs, many degrees of freedom adjust in order to localize the distortion of atomic coordinates. Torsional angles are particularly important in this process. For polyethylene, second-neighbor torsions are the most important. Some fraction of the time a second-neighbor torsion adjusts enough to cause a second conformational transition. In terms of the types of cooperativity examined in this paper, whether a second transition occurs or not is not very important. It may be more insightful to view the displacements of the second-neighbor torsional angle as a continuous process instead of a two-state process.

IV. Comparison to Multidimensional Kramers' Theory

Helfand and co-workers[14,16,17] have used a multidimensional version of Kramers' rate theory to analyze conformational transitions in alkane chains of 32 carbons or less. With this procedure, the rate of a given conformational transition is calculated by examining the saddle point on the multidimensional potential surface which constitutes the effective barrier to the transformation. This calculation is performed in the spirit of the preceding paragraph; i.e., the influence of cooperative transition pairs is ignored. The potential used in their calculations was the same one used in the computer simulations of polyethylene.

Skolnick and Helfand have used this technique to calculate the differential displacements of various degrees of freedom during a given conformational transition.[14] These calculations (dashed lines) are compared in Figures 4 and 5 to the cooperativity analysis used for the polyethylene simulations (solid lines). The simulation results are for transitions of all types while the Kramers' calculation was performed for an all-trans 16-carbon alkane chain which undergoes a single t → g^+ transition about the central bond.

The differential displacements reported by Skolnick and Helfand would be best compared to expressions 1 and 2

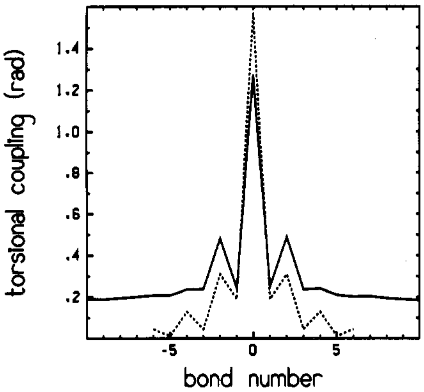

Figure 5. Distortion of torsional coordinate accompanying a conformational transition in polyethylene: (—) simulation; (- - -) multidimensional Kramers' theory.[14]

in the limit as $\Delta t \to 0$. As this cannot be done accurately with our simulation trajectories, we have made the comparison at a small value of $\Delta t = 0.5$ ps. We have directly plotted results from Table II of ref 14 against our results in Figures 4 and 5. The vertical scaling of this comparison is somewhat arbitrary (see eqs 4.3 and 5.4 in ref 14). It would be equally valid to compare the dashed and solid lines in Figures 4 and 5 after multiplying *both* dashed lines by some constant of order 1. For the torsional coupling comparison, the absolute values of the results from ref 14 are presented.

The torsional coupling from the Kramers' calculation shown in Figure 5 (dashed line) shows very similar features to that calculated from the simulation (solid line). The position coupling shown in Figure 4 shows good agreement between the simulations and the analytical calculations for the two atoms which define the transforming bond. For atoms further away along the chain contour the agreement is worse. The same trend is noted in Figure 5. The multidimensional Kramers' calculations do not consider displacements due to random thermal motions which occur in the simulation and in any real system. These motions are responsible for the nonzero, constant value of the displacement for atoms in the simulation which are at least five atoms away from the transforming bond. Given the absence of thermal motions in the Kramers' calculations, the results of those calculations are reasonably consistent with the simulation results.

The dashed curves in Figures 4 and 5 represent a calculation for only one initial configuration of a 16-carbon chain. While chain length had little effect on the results,[14] the starting configuration did have an effect on the calculated couplings. Although several other initial configurations gave results which were very similar to those shown in Figures 4 and 5, at least one[18] was quite different.

Figures 4 and 5 indicate that there is reasonable agreement between the multidimensional Kramers' calculations and our cooperativity analysis of the simulation results for polyethylene. These two methods are complementary for investigating polymer dynamics. Because the Kramers' calculations are closer to analytical theory, it is probably easier to examine the effect of individual variables on the dynamics in this context. On the other hand, it is probably easier to incorporate more complicated chain structures in the simulation approach. Also, an average over initial configurations is required with the Kramers' calculations.

V. Polyisoprene vs Polyethylene

In a previous paper we utilized expressions 1 and 2 to analyze the results of simulations on polyisoprene.[1] In many respects, the polyisoprene results are very similar to the polyethylene results. For all three types of coupling examined, distortions in the various degrees of freedom are limited to just a few atoms along the chain backbone, and the magnitudes of the distortions are very similar. The most striking difference between polyethylene and polyisoprene is observed for the torsional coupling. This is shown in Figure 6.

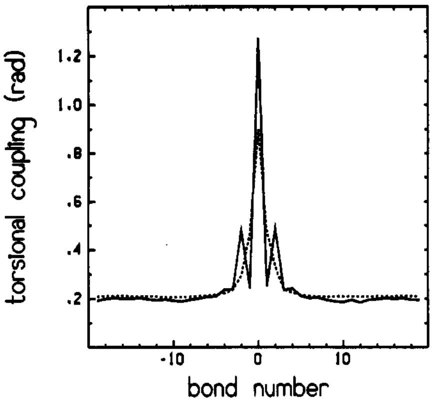

Figure 6. Comparison of the distortion of torsional coordinates accompanying conformational transitions in polyethylene (—) and polyisoprene (- - -). A significant difference is seen in the amount of second-neighbor coupling.

Why is the prominent second-neighbor torsional coupling observed for polyethylene but not for polyisoprene? Helfand has explained the second-neighbor torsional coupling for polyethylene.[12,13] If a first-neighbor bond to the transforming bond is trans, counterrotation of the second neighbor (which is collinear to the transforming bond) helps to localize the motion. Since the most common conformational state for polyethylene is trans, this explains the importance of second-neighbor torsional coupling. For *cis*-polyisoprene, the backbone structure is heterogeneous. A mixture of single bonds and double bonds is present, with both twofold and threefold potentials. In addition, since the barriers for the twofold potentials are low (2 and 9 kJ/mol),[1] large torsional fluctuations are possible with an energy input of only kT. All of these factors indicate that the simple picture of torsional cooperativity in polyethylene cannot be directly applied to polyisoprene.

VI. Concluding Remarks

The major goal of this paper has been to compare the local dynamics of polyethylene and polyisoprene. In terms of the number of chain atoms involved in conformational transitions, the two polymers are quite similar. In each case, only 3 or 4 backbone carbons need to adjust significantly their positions in order to localize a conformational transition.

These results need to be extended in two ways. First, a number of approximations in the simulations need to be improved so that more confidence can be placed in the results of the cooperativity analysis. Second, simulations of other polymers need to be analyzed in this manner. It may be that the length scale associated with conformational transitions correlates with the glass transition temperature of the polymers. A significant advantage of our cooperativity analysis is that chains of different structure can be easily and directly compared. The results are not forced into the basis set of rotational isomeric states. While a transition from one rotational isomeric state to another defines $t = 0$ in our analysis, the cooperativity of other degrees of freedom can be examined independent of whether further conformational transitions occur.

Acknowledgment. This work was supported by the National Science Foundation (DMR Polymers Program, Grant DMR-8822076). We gratefully acknowledge helpful discussions with Eugene Helfand and Alan English. We thank Wayne Mattice for a careful reading of the manuscript. D.B.A. is grateful for fellowship support from the American Chemical Society. M.D.E. thanks the Alfred P. Sloan Foundation for a research fellowship.

References and Notes

(1) Adolf, D. B.; Ediger, M. D. *Macromolecules* **1991**, *24*, 5834.
(2) Helfand, E.; Wasserman, Z. R.; Weber, T. A. *Macromolecules* **1980**, *13*, 526.
(3) Weber, T. A.; Helfand, E. *J. Phys. Chem.* **1983**, *87*, 2881.
(4) Anderson, J. E. *J. Chem. Phys.* **1970**, *52*, 2821.
(5) Boyd, R. H.; Breitling, S. M. *Macromolecules* **1974**, *7*, 855.
(6) Jones, A. A.; Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 847.
(7) Gronski, W. *Makromol. Chem.* **1977**, *178*, 2949.
(8) Bendler, J. T.; Yaris, R. *Macromolecules* **1978**, *11*, 650.
(9) Hall, C. K.; Helfand, E. *J. Chem. Phys.* **1982**, *77*, 3275.
(10) Mazur, S. *J. Chem. Phys.* **1989**, *91*, 7236.
(11) Schatzki, T. F. *J. Polym. Sci.* **1962**, *57*, 496.
(12) Helfand, E. *J. Chem. Phys.* **1971**. *54*, 4651.
(13) Helfand, E. *Science* **1984**, *226*, 647.
(14) Skolnick, J.; Helfand, E. *J. Chem. Phys.* **1980**, *72*, 5489.
(15) Following ref 2, a conformational transition is defined by a torsional coordinate passing from the bottom of one well of the dihedral potential to the bottom of the next well. We do not expect the results of our cooperativity analysis to be very sensitive to the definition of a transition.
(16) Helfand, E.; Wasserman, Z. R.; Weber, T. A.; Skolnick, J.; Runnels, J. H. *J. Chem. Phys.* **1981**, *75*, 4441.
(17) Helfand, E.; Skolnick, J. *J. Chem. Phys.* **1982**, *77*, 5714.
(18) Table VII of ref 14.

Registry No. Ethylene (homopolymer), 9002-88-4; isoprene (homopolymer), 9003-31-0.