Macromolecules **1991**, *24*, 2709–2714

Simulation by Molecular Dynamics of Poly(1,4-*trans*-butadiene) as an Inclusion Complex in the Channel of Crystalline Perhydrotriphenylene

Robert Dodge and Wayne L. Mattice*

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

Received September 13, 1990

ABSTRACT: A molecular dynamics simulation has been performed for a poly(1,4-*trans*-butadiene) chain, with a degree of polymerization of 10, confined to a channel produced by crystallization of 90 molecules of perhydrotriphenylene. All hydrogen atoms are treated explicitly in the simulation. The entire system contains 4422 atoms. No rotational isomerization is observed in the polymer if the perhydrotriphenylene matrix is artificially constrained to be rigid, with the geometry observed for the crystal. When this artificial constraint is removed, coupled rotational isomerizations at bonds i and $i + 2$ are observed in the polymer. These rotational isomerizations produce very little displacement of the tails, and in this respect they are similar to the transitions observed by Helfand and co-workers in the simulation by Brownian dynamics of a simple chain in a viscous environment. They can randomize the orientation of the C–H bond vectors within the time scale reported by Sozzani et al.[3] The coupled transitions can be written as $A^+TA^- \rightarrow A^-TA^+$, where $A^\pm$ and T denote anticlinal$^\pm$ and trans, respectively. The anticlinal states occur at $CH{-}CH_2$ bonds separated by a $CH{=}CH$ bond or a $CH_2{-}CH_2$ bond in a trans state.

Introduction

Macromolecules can exhibit surprising intramolecular dynamics when they are confined in unusual environments. Methods appropriate for the experimental observation of the dynamics naturally include those techniques, such as deuterium NMR, that are appropriate for the study of the motions of polymers in the solid state. The solid-state deuterium NMR line shapes for the motion of simple pendant groups, such as the rotation of a methyl group or the flip of a phenyl group, are well-known and easily calculated.[1] These motions are typically observed to be fast on the time scale of the deuterium NMR experiment ($<10^{-7}$ s). Molecular motions that entail rotational isomerism about a bond in the main chain from one stable rotational isomer to another may also occur on a time scale much less than 10^{-7} s. If different types of rotational isomerization can occur at internal bonds in the main chain, it is possible that these different molecular motions might not produce distinguishable deuterium NMR spectra. In such cases, the deuterium NMR spectra may provide accurate information about the time scale of the molecular dynamics of the main chain, but other techniques would be required to provide an accurate description of the local conformational transitions that are taking place on this time scale.

The molecular dynamics of poly(1,4-*trans*-butadiene) as an inclusion complex in the channel present in crystalline perhydrotriphenylene is simulated here, and the dynamics deduced from the trajectories is compared with the motions reported recently for this system by deuterium NMR.[3] Perhydrotriphenylene forms a stable channel that 1,3-butadiene can enter by diffusion, and irradiation induces polymerization of the monomer by a free-radical mechanism.[2] Due to the constraints imposed by the perhydrotriphenylene, the polymer contains the 1,4-trans isomer exclusively. The specific experiments of interest to us were performed with poly(1,4-*trans*-butadiene-*1,1,4,4-d*$_4$) prepared in this manner.[3] Deuterium NMR shows the poly(1,4-*trans*-butadiene-*1,1,4,4-d*$_4$) chain confined within the crystalline perhydrotriphenylene is sufficiently mobile so that the C–^{2}H bond vector, which makes an average angle of 75° to the chain axis, is completely averaged about the axis of the channel during the lifetime of the experiment.

Important information about the inclusion complexes with the monomer and with the polymer has been obtained from X-ray scattering.[4] Neither the monomer nor the polymer is observed directly in these experiments. Polymerization of the monomer does, however, produce an observable structural change in the perhydrotriphenylene lattice. The inability to observe the monomer directly has been attributed either to a repeat distance between 1,3-butadiene molecules that is identical with a repeat distance between perhydrotriphenylene molecules or to a disordered arrangement of the 1,3-butadiene molecules in the channels.[4] Similar explanations have been advanced for the inability to observe directly the poly(1,4-*trans*-butadiene) by X-ray scattering. Either the repeat distance in the macromolecule is indistinguishable from the repeat distance (4.78 Å) of the host perhydrotriphenylene containing the polymer or the polymer undergoes sufficient motion within the channel so that the scattering from it is dynamically averaged.

Precise identification of the conformational transitions responsible for the rapid motion of the C–^{2}H vector in the poly(1,4-*trans*-butadiene-*1,1,4,4-d*$_4$) in the channel formed by perhydrotriphenylene may have bearing on the behavior of poly(1,4-*trans*-butadiene) in the absence of this matrix. Poly(1,4-*trans*-butadiene) can exist in two crystalline forms.[5] A first-order solid–solid transition from a monoclinic phase to a pseudohexagonal condis crystal, designated the form II crystal, occurs at approximately 349 K.[6,7] ^{13}C NMR shows similar spin–lattice relaxation times for poly(1,4-*trans*-butadiene) in the form II crystal and in the channels of perhydrotriphenylene, and these spin–lattice relaxation times are faster than those of the low-temperature form I crystal of the polymer.[8] The possibility that the poly(1,4-*trans*-butadiene) chain may undergo similar motions in the form II crystal and in the channels formed by perhydrotriphenylene is suggested[8] by the similar ^{13}C spin–lattice relaxation times in these two environments and the inability to establish a clear conformation for the chain in form II.

Since the poly(1,4-*trans*-butadiene) can undergo rapid motion in the channel of perhydrotriphenylene and since this motion may be closely related to that which occurs in form II, motivation exists for establishing how this motion occurs. Possible motions for a chain trapped in

0024-9297/91/2224-2709$02.50/0

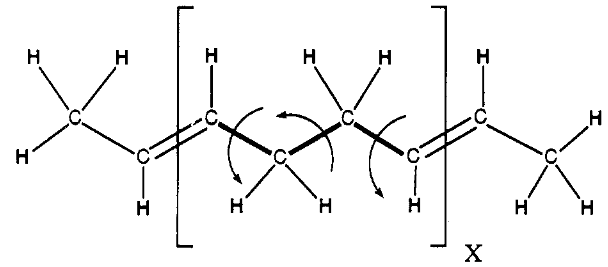

Figure 1. Segment of a chain of poly(1,4-*trans*-butadiene).

a channel include translation along the long axis, spinning of the entire polymer about the long axis, and local conformational transitions involving displacement of only a small portion of the molecule. Molecular dynamics methods have been used to successfully simulate the motions of large proteins[9] and polymers[10] on a time scale of tens to hundreds of picoseconds. When the computed trajectories can be shown to correctly reproduce the time scale of the dynamics observed by experiment, the wealth of data contained in the trajectories can provide valuable insight into the detailed mechanisms by which the motion occurs. We report here the results of a molecular dynamics simulation of poly(1,4-*trans*-butadiene) as an inclusion complex in the crystalline lattice of perhydrotriphenylene. After observing that the simulation reveals motions that occur on a time scale that is compatible with the experimental results of Sozzani et al.,[3] we then proceed to analyze the trajectories in order to determine the molecular origin of the motion.

Methodology for the Simulation of the Unconstrained Polymer

The molecular dynamics trajectory was calculated by using CHARMM[11] from Polygen.[12] The potential energy of the system, E, was calculated as

$$E = E_{\text{stretch}} + E_{\text{bend}} + E_{\phi} + E_{\text{improper}} + E_{\text{vdW}} \qquad (1)$$

where the terms on the right-hand side represent the contributions from bond stretching, bond angle bending, torsion potentials, improper dihedral contributions, and van der Waals interactions, using geometrical parameters adapted from DeRosa et al.[13] Pairs of atoms separated by less than 12 Å were included directly in the evaluation of E_{vdW}; for pairs separated by greater distances, a switching function[11] was adopted for increased efficiency in the lengthy computation.

Four bond angles were changed from the values supplied with CHARMM 2.1A to those described by DeRosa et al.[13] These changes are 100° → 109.47° for CH_2–CH_2–CH, 120° → 125° for CH_2—CH=CH, and 120° → 117.5° for H—C(=CH)—CH_2 and H—C(—CH_2)=CH. The location of the minimum for the torsion potential at the CH–CH_2 bond was shifted by 180° from the location supplied with the CHARMM 2.1A parameter table to the value used by DeRosa et al. (which is also the value found in Polygen's "Developmental parameters file"). The torsion potential used for the CH–CH_2 bonds in the simulation has minima at 0° and ±120°. The barrier height used for this torsion potential was 1.1 kcal/mol, which is similar to that supplied with CHARMM and found by DeRosa et al.[13] At the appropriate place in the description of the results, we will comment on the anticipated effect of using the slightly higher barrier height, 1.7 kcal/mol, observed for rotation about the internal C–C bond in 1-butene.[14]

A portion of a poly(1,4-*trans*-butadiene) chain is depicted in Figure 1. The conformations preferred by the three types of bonds in the main chain are summarized in Table I. Rotation about the CH–CH_2 bonds provides access to three rotational isomeric states denoted by cis and anticlinal$^{\pm}$. There are also three rotational isomers for rotation about the CH_2–CH_2 bond, and they are denoted by trans and gauche$^{\pm}$. The trans conformation is the only stable rotational isomer for the CH=CH bond. The conformation of the CH=CH bond will usually not be explicitly stated here because it is always trans. The calculations of DeRosa et al.[13] find a conformation of low energy for the sequence of rotational isomers $A^{\pm}TA^{\mp}$ for CH–CH_2–CH_2–CH, with the anticlinal states preferring dihedral angles of about ±116°. When propagated over a long chain, this conformation gives a calculated c axis in agreement with the one observed experimentally (4.83 Å)[15] for the low-temperature form I crystal of poly(1,4-*trans*-polybutadiene). Their calculations also find an energy minimum for $CTA^{\pm}$ that is approximately 1.1 kcal/mol above the energy for $A^{\pm}TA^{\mp}$, and a minimum for $A^{\pm}TA^{\pm}$ that is nearly of the same energy as the minimum for $A^{\pm}TA^{\mp}$. Inspection of the conformational energy surfaces published by DeRosa et al.[13] shows that the barrier to rotation from $A^{\pm}TA^{\mp}$ to $A^{\pm}TA^{\pm}$ is only slightly higher than the energy at the minimum for $A^{\pm}TC$.

Table I
Stable Conformations at the Bonds in the Main Chain

bond	conformn	abbrevn	dihedral angle, deg
CH–CH_2	cis	C	0
	anticlinal$^{\pm}$	$A^{\pm}$	~±116
CH_2–CH_2	trans	T	180
	gauche$^{\pm}$	$G^{\pm}$	~±60
CH=CH	trans	T	180

Several years ago Mark[16] and Abe and Flory[17] investigated rotational isomeric state models for poly(1,4-*trans*-butadiene) and compared them with the characteristic ratio, defined as the ratio of the mean-square unperturbed end-to-end distance to the value that would have been obtained for a freely jointed chain with bonds of the same number and lengths. Both Mark and Abe and Flory assigned low energies to the conformations $A^{\pm}TA^{\mp}$ and $CTA^{\pm}$. Abe and Flory assigned a conformational energy for $CTA^{\pm}$ that was higher by 0.3 kcal/mol than the energy assigned to $A^{\pm}TA^{\mp}$. The value for this energy difference found by DeRosa et al.,[13] and adopted in the present study, is 1.1 kcal/mol. This change in energies has little influence on the unperturbed dimensions. Abe and Flory showed that the calculated values of the characteristic ratio are not very sensitive to this energy difference. In fact, the small change in the characteristic ratio that does occur upon adopting the value of DeRosa et al. improves slightly the agreement between calculation and experiment. Figure 2 depicts the physical justification for the adoption of the results of DeRosa et al. The conformation $CTA^{\pm}$ causes the van der Waals radii of hydrogen atoms on consecutive repeat units to overlap slightly, resulting in a repulsive interaction that can be alleviated by changing the conformation to $A^{\pm}TA^{\mp}$.

A molecular dynamics simulation was performed for an unconstrained poly(1,4-*trans*-butadiene) chain of 10 monomer units in a vacuum. Starting from the $A^{\pm}TA^{\mp}$ conformation, the potential energy of the polymer was minimized by using a conjugate gradient method. A dynamic simulation was then performed by integrating the classical equations of motion for all atoms every 0.5 fs using the Verlet algorithm. All hydrogen atoms were included explicitly. The simulation was initiated with zero kinetic energy, and the temperature was increased at specified intervals by rescaling the velocities of all atoms, until the temperature reached 300 K. The simulation was then continued at constant energy. All conformations listed in Table I were visited during the trajectory.

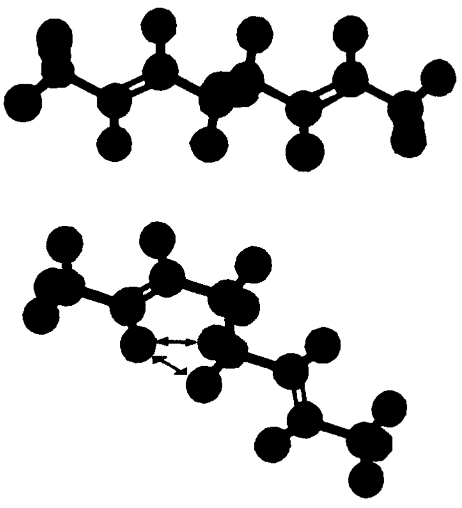

Figure 2. Dimers of poly(1,4-*trans*-butadiene) in the A$^{\pm}$TA$^{\mp}$ (top) and CTA$^{\pm}$ (bottom) conformations. Double-headed arrows in the CTA$^{\pm}$ conformation denote repulsive interactions between hydrogen atoms.

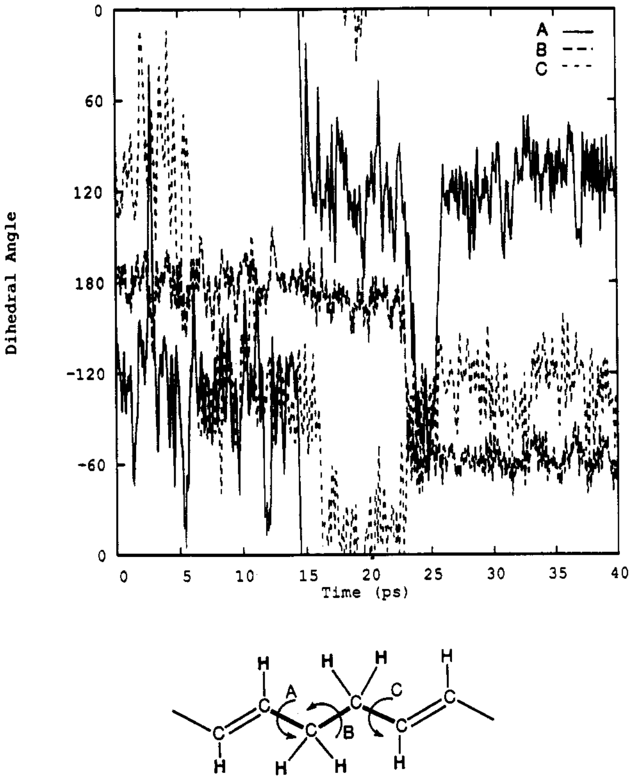

Figure 3. History of the dihedral angles at an internal CH–CH$_2$–CH$_2$–CH fragment during a 40-ps portion of the simulation of the isolated chain. The CH$_2$–CH$_2$ bond (longer dashes) undergoes a T → G$^-$ transition at about 23 ps. The CH–CH$_2$ bonds on either side (solid line and line with shorter dashes) experience several transitions between C and A$^{\pm}$, and between the A states, during the trajectory.

Transitions between T and G$^{\pm}$ are seen at the CH$_2$–CH$_2$ bonds, and transitions between C and A$^{\pm}$, and between the two A states, are seen at the CH–CH$_2$ bonds. The segment of the trajectory depicted in Figure 3 shows a T → G$^-$ transition at a CH$_2$–CH$_2$ bond, and several transitions between C and A$^{\pm}$, and also transitions between the A states, at the CH–CH$_2$ bonds on either side of the CH$_2$–CH$_2$ bond. This segment was chosen for illustration because it demonstrates the occurrence of several types of transitions occurring in a particular repeat unit. In general, conformational transitions in a repeat unit do not occur as frequently as this portion of the trajectory would suggest. Most of these conformational transitions are accompanied by large angular displacements of the tails on either side of the CH–CH$_2$–CH$_2$–CH fragment.

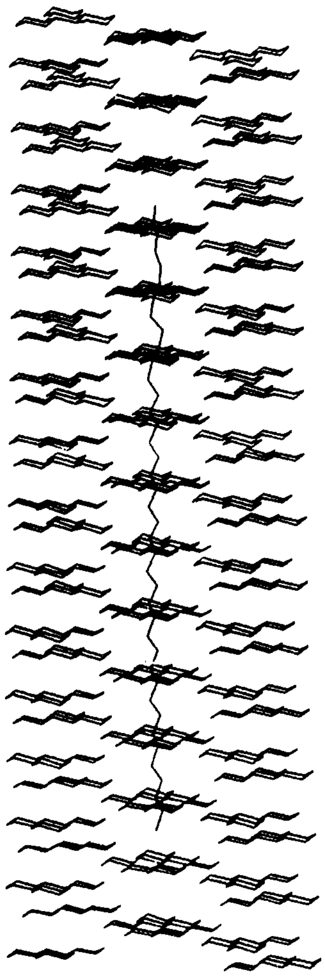

Figure 4. Side view of the system studied in the simulations. There are 90 molecules of perhydrotriphenylene, arranged in 6 stacks of 15 molecules each. A poly(1,4-*trans*-butadiene) chain consisting of 10 monomer units resides in the channel formed by the 6 stacks of perhydrotriphenylene molecules. For clarity, the figure depicts C–C bonds only. In the simulation itself, all pendant hydrogen atoms were considered explicitly.

Methodology for the Simulation of the Inclusion Complex

The crystal structure of the perhydrotriphenylene inclusion complex with poly(1,4-*trans*-butadiene) has been determined by X-ray analysis.[4] Figure 4 depicts the system that was simulated here. The crystalline matrix consists of 90 molecules of perhydrotriphenylene, arranged in 6 stacks of 15 molecules each. A poly(1,4-*trans*-butadiene) chain consisting of 10 monomer units is located in the channel formed by the 6 stacks of perhydrotriphenylene molecules. The conformation of each monomer unit in the polymer is A^{+}TA^{-}, consistent with the form I crystal. All hydrogen atoms are considered explicitly, both on the poly(1,4-*trans*-butadiene) and on all 90 of the molecules of perhydrotriphenylene. They are uniformly ^{1}H. Comparison of the results of the simulation with the result obtained experimentally with deuterium NMR carries with it the assumption that the most important motions on the time scale of interest are not strongly affected by substitution of ^{1}H for ^{2}H. The entire system contains 4422 atoms.

Two independent simulations were performed for the system depicted in Figure 4. In one case only the poly(1,4-*trans*-butadiene) was mobile, and the perhydrotriphenylene molecules were fixed in the geometry determined by X-ray analysis of the real system.[4] This simulation was rather uninteresting, because the only motions observed where oscillations about the starting conformation of the polymer. No rotational isomerism took place. In the other case, both the polymer and all of the perhydrotriphenylene molecules were mobile. This simulation was much more interesting. The results obtained from it will be presented and discussed in detail below. The strategy involved in heating the systems to 300 K was similar to that employed for the simulation of the isolated polymer. After reaching 300 K, the simulations were run for 70 ps. In the simulation in which all molecules were mobile, the average temperature for 70 ps was 297.3 K, with a root-mean-square fluctuation of 3.05 K, and the root-mean-square fluctuation in the energy was 0.09 kcal/mol.

A useful check on the validity of the simulation in which both polymer and matrix are mobile is provided by a comparison with the results of the crystal structure reported for this system.[18] For purposes of this comparison, the coordinates of all atoms were averaged over intervals of 5 ps during the simulation. The average coordinates of the perhydrotriphenylene molecules in the simulation gave a *c* axis of 4.8 Å and an $a = b$ axis between 14.2 and 14.6 Å. The numbers determined by experiment[18] are $a = b = 14.40$ Å and $c = 4.78$ Å. The agreement between the structure in the simulation and the real structure is quite good.

The dihedral angles for the central four monomer units of the poly(1,4-*trans*-butadiene) chain were monitored during the simulation. The three monomer units at either end of the chain were ignored in order to reduce any bias arising from end effects in the chain itself and in the perhydrotriphenylene matrix. The orientation of the C–H bond vectors in the four central monomer units was also monitored. Conformational transitions were much less frequent in the chain in the perhydrotriphenylene matrix than in the isolated chain. No transitions were observed at the CH_2–CH_2 bond during the trajectory of 70 ps. Transitions between C and $A^{\pm}$, which were observed at the CH–CH_2 bonds in the isolated chain, as shown in Figure 3, were also suppressed in the chain confined to the channel. Only one type of rotational isomerism was observed during the 70 ps of the simulation of the chain in the channel. This rotational isomerism involved the coupled rotation of a pair of dihedral angles from A^+XA^- to A^-XA^+, where X is either the trans CH=CH or the trans CH_2–CH_2. An example of this coupled transition is depicted in Figure 5. In contrast, the transitions between the A states in the isolated chain appear to occur at random, rather than as strongly correlated events at CH–CH_2 bonds *i* and *i* + 2.

In the simulation of length 70 ps for the chain confined to the channel, a total of 12 pairs of bonds at the internal four monomer units, or 24 dihedral angles, rotated from $A^{\pm}$ to $A^{\mp}$ and remained in the new state for at least 5 ps. These changes in dihedral angles are accompanied by large changes in the orientation of the C–H bond vectors. In absence of the rotational isomerism, there are fluctuations in the orientations of the C–H bond vectors, but these fluctuations are not likely to be the cause of the rapid motion detected by the deuterium NMR experiments of Sozzani et al.[3] It is the motion caused by the coupled rotational isomerisms, such as that depicted in Figure 5, that is the more likely molecular basis for the rapid motion detected in their experiments.

Results and Discussion

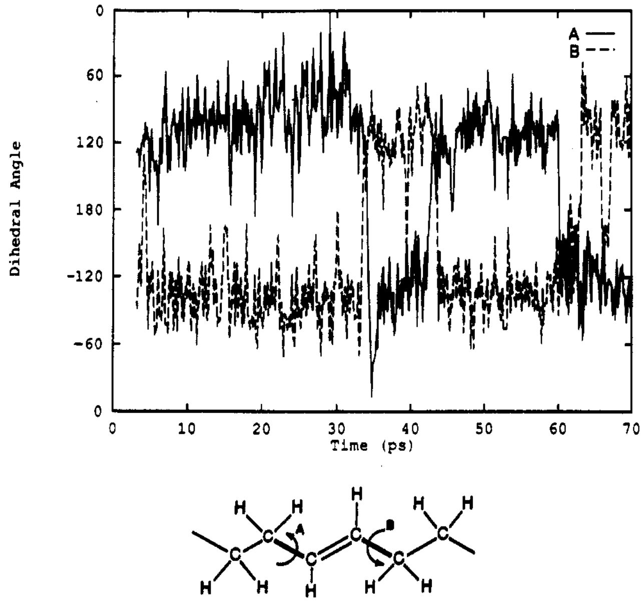

Figure 5. History of the dihedral angles denoted by A and B during the trajectory of 70 ps. Coupled transitions can be seen at about 35, 45, and 60 ps.

The poly(1,4-*trans*-butadiene) chain has very little room for lateral movement when it is confined within the channel provided by the six stacks of perhydrotriphenylene molecules. Nevertheless, the deuterium NMR experiments show that the C–^2H bond vectors, attached to the sp^3 carbon atoms of the chain and making an average angle of 75° with the cylinder axis, randomize their orientation about the cylinder within the time scale of the experiment ($\sim 10^{-7}$ s). When the conformation of the repeat unit of the polymer in the simulation is A^+TA^-, the average C–H bond at the sp^3 carbon atoms makes an angle of about 80° to the cylinder axis. The value of this angle is quite close to the value deduced from experiment. Simple spinning of the entire poly(1,4-*trans*-butadiene) chain about its long axis, if it were to occur, would randomize the orientation of the C–H vector, as demanded by experiment. However, this type of motion is not seen in the molecular dynamics simulation and is not considered to be a reasonable explanation for the experimental result. Simple translation of the poly(1,4-*trans*-butadiene) chain along the channel, if it were to occur, would not randomize the orientation of the C–H vectors. The simulation develops no evidence for simple translation of the polymer along the channel.

Conformational transitions of the type depicted in Figure 5 occur on a time scale that is appropriate for the motion detected by deuterium NMR, and these transitions alter the orientation of the C–H bond vectors. The coupled motion described in Figure 5 is a cranklike counterrotation by second-neighbor parallel bonds. The tails of the chain experience very little movement with this pair of coupled rotational isomerizations, as was also the case in the coupled transitions observed by Helfand[19] in Brownian dynamics simulations of simple chains. Experimental evidence for this type of motion has been developed from deuterium NMR studies of poly(butylene terephthalate) in the solid state, where a combination of Helfand mechanisms is suggested to explain the molecular motions that are observed.[20] While this type of coupled motion for dihedral angles *i* and *i* + 2 is favored in a frictional medium such as a solution or the solid state, it is crucial in a highly constrained environment such as the channel in crystalline perhydrotriphenylene.

In several of the correlated transitions seen in the polybutadiene chain in the channel, both dihedral angles simultaneously adopt values near 180°, which implies that the activation energy may be twice as large as the activation energy expected for a single transition in an isolated chain. In this respect the correlation of the transitions is stronger here than it was in the case of the Brownian dynamics simulations of Helfand and co-workers.[21] Presumably the stronger correlation in the present case arises from a lower torsional potential at the rotating bonds (1.1 vs ~3 kcal/mol) and the higher local viscosity provided by the crystalline matrix of perhydrotriphenylene.

Figure 6a depicts the positions of the four C–H bond vectors located on consecutive sp^3 carbon atoms in the center of the poly(1,4-*trans*-butadiene) chain when every repeat unit in the chain is in the A^+TA^- state. Figure 6b depicts, from the same perspective, the same four C–H bond vectors after a transition from A^+TA^- to A^-TA^+ at the repeat unit with the labeled C–H bonds. It is quite clear from the view along the long axis of the chain that this rotational isomerism produces a large alteration in the orientation of the labeled C–H bond vectors about the cylinder axis. This transition also reduces to 68°, the average angle that a labeled C–H bond makes with the cylinder axis.

While the molecular dynamics simulation was run for only a short time compared to the time scale of the deuterium NMR experiment, useful conclusions can be drawn nonetheless. From the rate of pairwise conformational transitions seen in the simulation, we conclude that on the order of 10^3 such transitions would occur for each eligible bond pair during the time of the deuterium NMR experiment. Repetition of 10^3 times the process depicted in Figure 6a,b would surely suffice to produce a randomization of the orientation of the $C-^2H$ bond vectors with respect to the cylinder axis. The frequency of these transitions might be reduced by 1 order of magnitude if the torsional barrier at the $CH-CH_2$ bonds were increased from 1.1 to 1.7 kcal/mol, but there would still be on the order of 10^2 transitions for each eligible bond pair in 10^{-7} s.

Figure 7 depicts fragments of a poly(1,4-*trans*-butadiene) chain in three different conformations. In the top picture, all monomer units adopt the conformation A^+TA^-, which produces a linear chain with a conformation corresponding to that found in form I crystals. The next two fragments in Figure 7 show, from different perspectives, the same chain after one of the monomer units changes conformation from A^+TA^- to A^-TA^+. This conformational change is achieved with very little swinging of the tails. The conformations depicted in the first three fragments in Figure 7 are the only conformations observed in the 70-ps simulation of the chain confined to the channels. The final two fragments in Figure 7 show, also from different perspectives, a chain in which one monomer unit is in the conformation CTA^-, the next monomer unit adopts the conformation A^+TC, and all other monomer units remain A^+TA^-. Comparison of the second and third fragments with the fourth and fifth fragments shows that the latter defect requires much more movement of the tails. The differences in movement are particularly apparent in the perspectives adopted in the third and fifth fragments. The conformations depicted in the last two fragments in Figure 7 are not observed in the simulation of the chain confined to the channel.

Two other local conformations deserve mention. The conformation CTC causes a relatively small displacement of the tails, but it is quite unfavorable on the basis of intramolecular short-range energies. It is not observed in the simulations. Recently Tonelli[22] has performed an equilibrium treatment of diene polymers in the channels formed by perhydrotriphenylene. He finds that repeat units with the conformation CTA^+ may fit into the inclusion complex if the diameter of the channel is 5.0 Å or greater. Nevertheless, we do not observe the CTA^+ conformation in the simulations. Part of the reason for the prediction of the CTA^+ conformation in the equilibrium treatment, and its absence in the simulation, may be

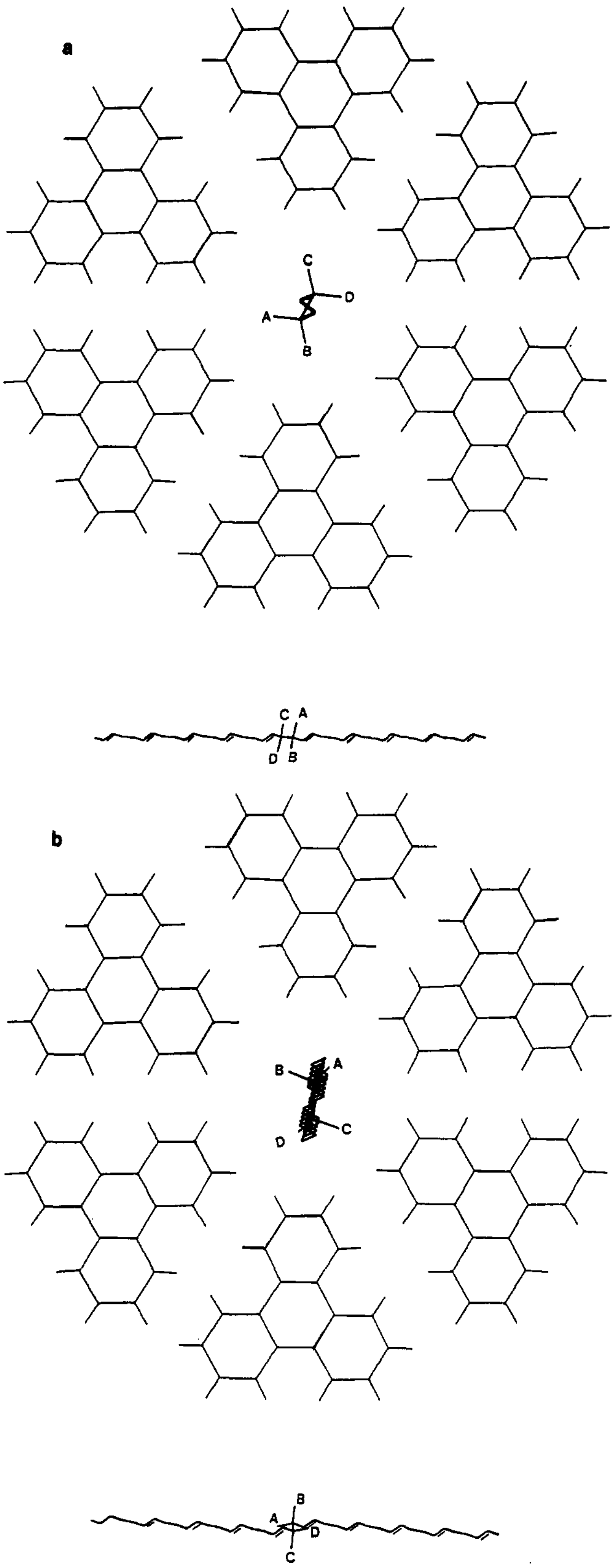

Figure 6. Top portion of both a and b presents a view down the axis of the chain confined in a channel of perhydrotriphenylene, and the bottom portion of both a and b presents a side view of the poly(1,4-*trans*-butadiene) chain only. Four hydrogen atoms at CH_2-CH_2 of one of the internal repeat units of the polymer are denoted by A–D. In Figure 6a all monomer units have the conformation A^+TA^-. In Figure 6b the monomer unit bearing hydrogen atoms A–D has changed its conformation to A^-TA^+.

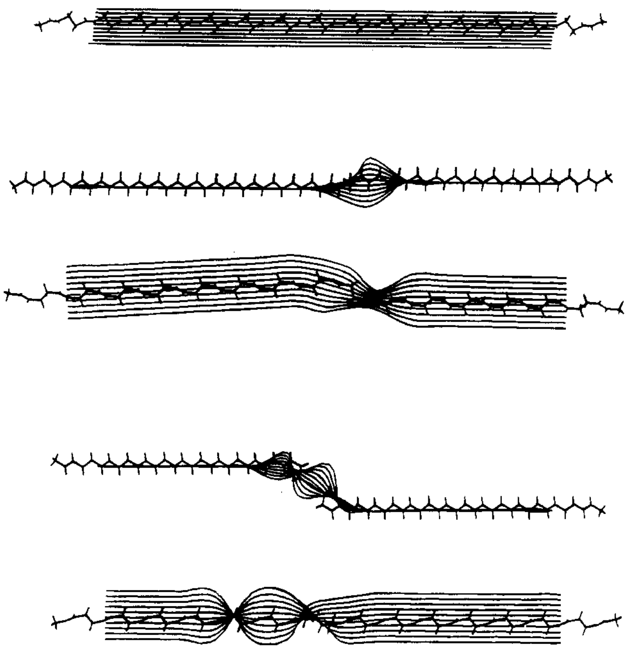

Figure 7. Fragments of a poly(1,4-*trans*-butadiene) chain in three conformations. In the top picture, all repeat units have the conformation A^+TA^-. The second and third pictures show, from different perspectives, a chain in which one monomer unit has changed its conformation to A^-TA^+, all remaining monomer untis being A^+TA^-. The bottom two pictures show, from different perspectives, a chain with the conformation CTA^- at one monomer unit, the conformation A^+TC at the next monomer unit, and the conformation A^+TC^- at all other monomer units.

attributed to differences in the van der Waals radii of the hydrogen atoms used. Tonelli used a radius of 0.5 Å, and we used a radius of 0.75 Å.

Sozzani et al.[8] measured ^{13}C chemical shifts and T_1 values for perhydrotriphenylene crystals with and without poly(1,4-*trans*-butadiene) as an inclusion complex. They observed different values for the chemical shifts for the two states of the perhydrotriphenylene molecules and attributed the differences to changes in the crystal lattice. They also observed significantly decreased spin–lattice relaxation times for the perhydrotriphenylene carbon atoms in the inclusion complex, as compared with those observed in the pure perhydrotriphenylene crystal. This difference was attributed to a higher molecular mobility of the perhydrotriphenylene molecules in the looser crystal packing of the inclusion complex, as opposed to the pure crystal. These results from NMR experiments yield a picture that is qualitatively similar to that extracted from the two different simulations of the same system. When the perhydrotriphenylene molecules were constrained to be motionless, no conformational transitions were observed in the poly(1,4-*trans*-butadiene) chain in the channel. The polymer experienced conformational transitions when the perhydrotriphenylene molecules were not artificially constrained to be rigid. In the latter simulation, the perhydrotriphenylene molecules undergo slight deviations in positions, although they remain at an average position that is very close to that determined for the crystal structure. The fact that some motion of the perhydrotriphenylene molecules is required in the simulations in order to see conformational transitions in the poly(1,4-*trans*-butadiene) is consistent with the ^{13}C NMR result suggesting increased mobility of the perhydrotriphenylene molecules in the presence of the polymer.

The results of this simulation also have implications for the form II crystal structure of poly(1,4-*trans*-butadiene). Solid-state ^{13}C NMR experiments on the form II crystal suggest a similar type of conformational mobility is present in the crystal and in the inclusion complex. The coupled conformational transitions observed in the simulation result in very little displacement of the chain's axis and only a slight decrease in the length along this axis. This type of static conformation for the form II crystal was suggested by Bautz et al.,[23] and dynamic transitions where this type, and other types, may occur were suggested by Moller[24] and by Corradini.[25]

Conclusions

We have observed molecular motions, consisting of coupled conformational transitions at bonds i and $i + 2$, to occur in the molecular dynamics simulations of poly(1,4-*trans*-butadiene) in a perhydrotriphenylene matrix. These motions occur with sufficient frequency to explain the randomization of the orientation of the C–^{2}H vectors in poly(1,4-*trans*-butadiene-*1,1,4,4*-d_4) that were observed by Sozzani et al.[3] The rotational isomerizations in the poly(1,4-*trans*-butadiene) backbone are suppressed if the perhydrotriphenylene matrix is artificially constrained to be rigid, with the geometry observed in the crystal.

Acknowledgment. This work was supported by research Grant DMR 89-15025 from the National Science Foundation. The stimulus for this simulation was provided by an excellent lecture by Dr. Lynn W. Jelinski at The University of Akron in 1989.

References and Notes

(1) Jelinski, L. W. *Annu. Rev. Mater. Sci.* **1985**, *15*, 359.
(2) Allegra, G.; Farina, M.; Immirzi, A.; Colombo, A.; Rossi, U.; Broggi, R.; Natta, G. *J. Chem. Soc. B* **1967**, 1020.
(3) Sozzani, P.; Behling, R. W.; Schilling, F. C.; Bruckner, S.; Helfand, E.; Bovey, F. A.; Jelinski, L. W. *Macromolecules* **1989**, *22*, 3318.
(4) Colombo, A.; Allegra, G. *Macromolecules* **1971**, *4*, 579.
(5) Natta, G.; Corradini, P. *J. Polym. Sci.* **1959**, *39*, 29.
(6) Wunderlich, B.; Grebowicz, J. *Adv. Polym. Sci.* **1984**, *60/61*, 1.
(7) Grebowicz, J.; Aycock, W.; Wunderlich, B. *Polymer* **1986**, *27*, 575.
(8) Sozzani, P.; Bovey, F. A.; Schilling, F. C. *Macromolecules* **1989**, *22*, 4225.
(9) Brooks, C. L., III; Karplus, M.; Pettitt, B. M. *Adv. Chem. Phys.* **1988**, *71*, 1.
(10) Zuniga, I.; Bahar, I.; Dodge, R.; Mattice, W. L., to be submitted for publication.
(11) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. *J. Comput. Chem.* **1983**, *4*, 187.
(12) Polygen Corporation, 200 Fifth Ave., Waltham, MA 02254.
(13) DeRosa, C.; Napolitano, R.; Pirozzi, B. *Polymer* **1985**, *26*, 2039.
(14) Kondo, S.; Hirota, E.; Morino, Y. *J. Mol. Spectrosc.* **1968**, *28*, 471.
(15) Iwayanagi, S.; Sakura, I.; Sakura, T.; Seto, T. *J. Macromol. Sci. Phys.* **1968**, *B2*, 163.
(16) Mark, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 6829.
(17) Abe, A.; Flory, P. J. *Macromolecules* **1971**, *4*, 219.
(18) Columbo, A.; Allegra, G. *Lincei-Rend. Sc. Fis. Mat. e Nat.* **1967**, *XLIII*, 41.
(19) Helfand, E. *Science* **1984**, *9*, 647.
(20) Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *Macromolecules* **1983**, *16*, 492.
(21) Helfand, E.; Wasserman, Z. R.; Weber, T. A. *Macromolecules* **1980**, *13*, 526.
(22) Tonelli, A. E. *Macromolecules* **1990**, *23*, 3129.
(23) Bautz, G.; Leute, U.; Dollhopf, W.; Hagele, P. C. *Colloid Polym. Sci.* **1981**, *259*, 714.
(24) Moller, M. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 107.
(25) Corradini, P. *J. Polym. Sci., Polym. Symp.* **1975**, *50*, 327.

Registry No. 1,4-*trans*-Butadiene (homopolymer), 9003-17-2; perhydrotriphenylene, 15074-91-6; perhydrotriphenylene·1,4-*trans*-butadiene (homopolymer), 29698-97-3.