Mobility of Polyethylene in the Inclusion Complex with Perhydrotriphenylene

Yongjian Zhan and Wayne L. Mattice*

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

Received February 20, 1992; Revised Manuscript Received April 29, 1992

ABSTRACT: Molecular dynamics simulations have been performed at 223, 300, and 373 K for polyethylene in the inclusion complex with perhydrotriphenylene. The system contains 90 molecules of perhydrotriphenylene, arranged in 6 stacks of 15 molecules each, and one molecule of *n*-tetracontane, $C_{40}H_{82}$. These 91 molecules have 4442 atoms. The internal CH_2–CH_2 bonds in the *n*-tetracontane have a strong preference for the trans state. However, the nearly complete suppression of trans → gauche transitions does not imply that the chain is quiescent in the channel. Instead it exhibits a high degree of internal flexibility via processes that have a low activation energy. The activation energy for rotation of a C–H bond vector about the long axis is less than 1 kcal mol^{-1}. The mobility of the C–H bond vectors is greater at the ends than in the middle of the chain. The angular distributions of the internal C–H bond vectors about the long axis of the channel are nearly randomized within 1 ns at 300 K.

Introduction

Molecular dynamics simulations of polymers as inclusion complexes provide a qualitative and quantitative means for understanding the behavior of chains isolated from each other. First, by playing back the trajectory file in graphic form, one can "watch" the motion of the chain in the narrow channel. Second, the quantitative features that characterize the conformation and mobility of the polymer, such as the time-averaged equilibrium properties, the dynamics expressed in an internal coordinate system defined by the chain, and the dynamics expressed in an external coordinate system defined by the lattice, are easily computed.

Molecular dynamics simulations have been used to study the conformation and mobility of poly(1,4-*trans*-butadiene) and poly(1,4-*trans*-isoprene) in the channel of crystalline perhydrotriphenylene and polyethylene in the channel of urea.[1-5] The results obtained with poly(1,4-*trans*-butadiene) in perhydrotriphenylene show that there are rapid conformational transitions between two anticlinal states and large fluctuations in the dihedral angles within an anticlinal state at the CH–CH_2 bonds. These internal motions rapidly randomize the angular distribution of a C–H bond vector about the axis of the channel.[1,2] This rapid randomization has been demonstrated experimentally by deuterium NMR of poly(1,4-*trans*-butadiene) with deuterated methylene groups.[6] The simulation shows that the conformational transitions can occur at CH–CH_2 bonds in the interior of the chain and at the ends of the chain. These transitions have a stronger tendency to be correlated with transitions at nearby bonds when they occur in the interior of the chain. Substitution of poly(1,4-*trans*-isoprene) for poly(1,4-*trans*-butadiene) shuts down the conformational transitions in the interior of the chain in the simulations,[4] as expected from the results obtained from the study of the inclusion complex of poly(1,4-*trans*-isoprene) in perhydrotriphenylene by NMR.[7]

The behavior of polyethylene in the inclusion complex is different from that of poly(1,4-*trans*-butadiene) and poly(1,4-*trans*-isoprene) in the same matrix. A view of this inclusion complex along the *c* axis is depicted in Figure 1. The study of the complex with ^{13}C NMR shows that the isolated chains of polyethylene strongly prefer an all-trans conformation similar to that of bulk crystalline polyethylene.[8] Although trans → gauche transitions were not observed, the chains undergo rapid local motion with an activation energy of only 1.1 kcal mol^{-1}. Several types of motions, such as the rotation of the chain about its long axis, librational motions of each CH_2–CH_2 bond, and the motion of a "twiston" along the chain, were considered in order to account for the high flexibility of the chain in the absence of rotational isomeric state transitions. A conformational analysis of polyethylene confined to a narrow channel finds that the chain strongly prefers the all-trans conformation, without the presence of bonds in gauche states or rapid interconversions between trans and gauche states.[9]

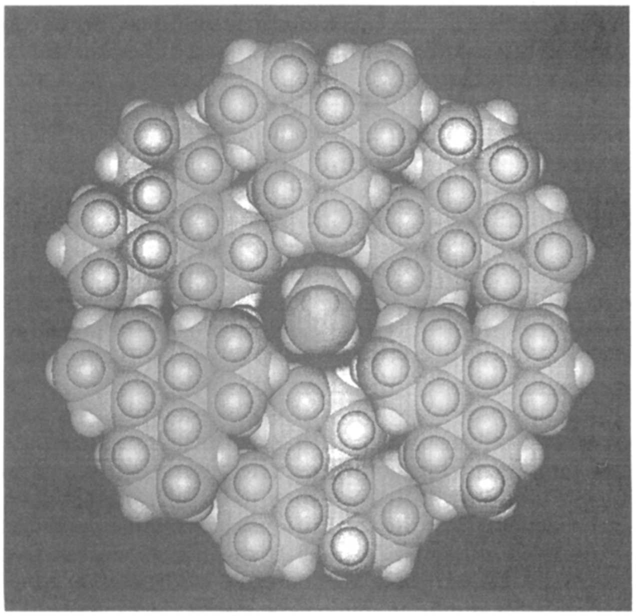

Figure 1. View along the *c* axis of a space-filling model of the inclusion complex, with the *n*-alkane in the perfect planar zigzag conformation.

Here we report simulations of the molecular dynamics of *n*-tetracontane, $C_{40}H_{82}$, in the channel of crystalline perhydrotriphenylene. The first objective is to determine whether the time-averaged conformation has an overwhelming preference for trans placements at the CH_2–CH_2 bonds. Then we will inquire how rapidly the angular distribution of a C–H bond vector is randomized about the long axis of the channel. We will determine whether the motions considered by Sozzani et al.[8] are detectable in the trajectory. Finally, by comparing results obtained from simulations performed at three temperatures (223, 300, and 373 K), we estimate the activation energies for the various types of motions and compare those numbers with the value of 1.1 kcal mol^{-1} determined by NMR measurements.

Methods

The molecular dynamics trajectory was computed using version 2.1 of CHARMm as provided by Polygen Corp., Waltham, MA.[10] The potential energy of the system, E, was calculated as

$$E = E_{\text{stretch}} + E_{\text{bend}} + E_{\text{dihedral}} + E_{\text{vdw}} \qquad (1)$$

without inclusion of any electrostatic contribution. The molecular dynamics of polyethylene chains in vacuo, as computed with the same algorithm, has been reported recently.[11]

The mobile *n*-tetracontane, $C_{40}H_{82}$, is constructed so that all of the CH_2–CH_2 bonds are initially in trans states. In one set of three simulations, this chain is placed in a rigid crystalline matrix consisting of 90 molecules of perhydrotriphenylene which are arranged in 6 stacks of 15 molecules each. The system contains 4442 discrete atoms. X-ray data are not yet available for the inclusion complex of polyethylene in perhydrotriphenylene. Therefore we assume the size of the unit cell of the channel is the same as in the inclusion complex of poly(1,4-*trans*-butadiene) with perhydrotriphenylene. That unit cell is $a = b = 14.25 \pm 0.01$ Å, $c = 4.78 \pm 0.01$ Å, and $\gamma = 120 \pm 0.5°$.[12,13] The potential energy of the system was first minimized using a conjugate gradient method. The simulation was then initiated with zero kinetic energy, and the temperature was increased to 223, 300, or 373 K in 1 ps, using a time step of 0.2 fs. After another 3 ps of equilibration, also with a time step of 0.2 fs, the simulation was performed at constant temperature with a time step of 0.5 fs. The length of these trajectories is 1 ns.

A fourth simulation, of duration 0.140 ns, was performed at 300 K. In this simulation, all 4442 atoms in the *n*-tetracontane and the 90 molecules of perhydrotriphenylene were dynamically active. The matrix retains its integrity at 300 K, but there are fluctuations of order 1% in the a and b dimensions and of order 0.1% in the c dimension.[1]

In all simulations, the instantaneous coordinates were recorded at intervals of 10^3 steps (0.5 ps) for subsequent analysis. When an external polar coordinate system is used for this analysis, the Z axis is parallel with the c axis of the crystal.

Results and Discussion

Trans vs Gauche States. The carbon atoms in *n*-tetracontane are labeled sequentially 1–40, and its C–C bonds are labeled sequentially 1–39. The dihedral angles at all of the internal CH_2–CH_2 bonds (bonds 2–38) in *n*-tetracontane were monitored during the simulations. The starting conformation had trans placements at all of these bonds in simulations performed in the rigid channel at 223, 300, and 373 K. No trans → gauche transition was observed at any of these bonds during the trajectory of 1 ns at the lower two temperatures. At 373 K, CH_2–CH_2 bonds 2 and 38 made few very brief excursions to a gauche state, as depicted in Figure 2, and bond 37 made one very brief visit to a gauche state. The CH_2–CH_2 bonds further removed from the ends remained in the trans state in the trajectory at 373 K.

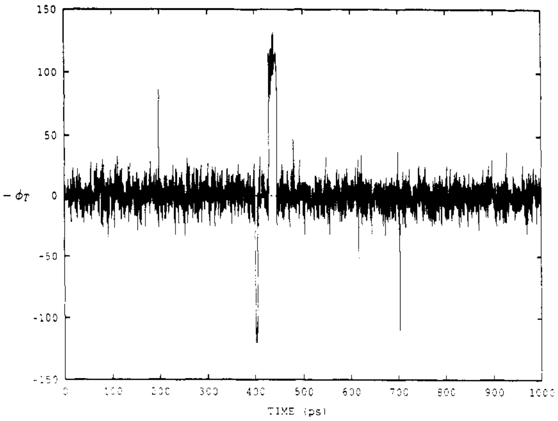

Figure 2. History of the dihedral angle at bond 38 in *n*-tetracontane in perhydrotriphenylene at 373 K. The dihedral angle for a trans placement is denoted by ϕ_T.

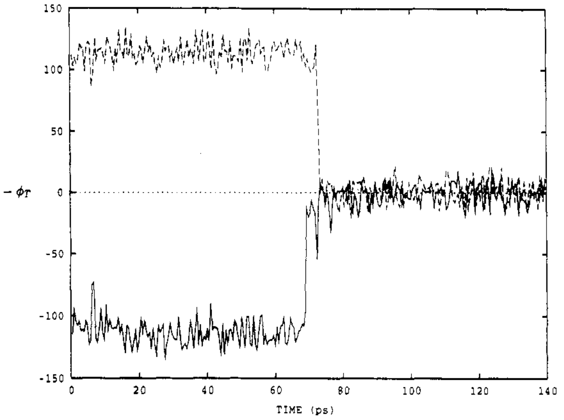

Figure 3. History of the dihedral angles at bonds 33 and 35 in *n*-tetracontane in the mobile channel of crystalline perhydrotriphenylene at 300 K.

Recently the rate constant defined by

$$\text{trans} \xrightarrow{2k_{gt}} \text{gauche}^{\pm} \qquad (2)$$

was evaluated for isolated *n*-alkanes at 300 K, using this same algorithm.[11] For $C_{10}H_{22}$ and $C_{50}H_{102}$, the values of $2k_{gt}$ were 4.0 and 2.5 ns^{-1}, respectively. Therefore, the half-life for the trans state at a CH_2–CH_2 bond in isolated *n*-tetracontane at 300 K would be about 0.20–0.25 ns. Hence, no more than 2 of the 37 internal CH_2–CH_2 bonds in an isolated chain of *n*-tetracontane would be expected to remain in the trans state for a period of 1 ns. The matrix provided by perhydrotriphenylene causes all 37 of these CH_2–CH_2 bonds to remain in the trans state for this length of time at 300 K. Even when the temperature is raised to 373 K, only the CH_2–CH_2 bonds near the ends of the *n*-tetracontane are able to undergo trans → gauche isomerization.

When the matrix was mobile, the conformations at CH_2–CH_2 bonds 33 and 35 in *n*-tetracontane change from trans to gauche during the process of heating the system to 300 K. The two gauche placements had opposite signs. Therefore, the trajectory at 300 K for *n*-tetracontane in the mobile channel began with the conformation ttt...tttg$^+$tg$^-$ttt. The time dependence of the dihedral angles at CH_2–CH_2 bonds 33 and 35 is depicted in Figure 3. The gauche states are maintained for about 70 ps, and then they revert to trans states in rapid succession. No other rotational isomeric state transitions are observed in the trajectory with the mobile channel.

Analysis of the NMR spectra of polyethylene in the inclusion complex in perhydrotriphenylene shows that only the trans conformation is present in significant amount.[8]

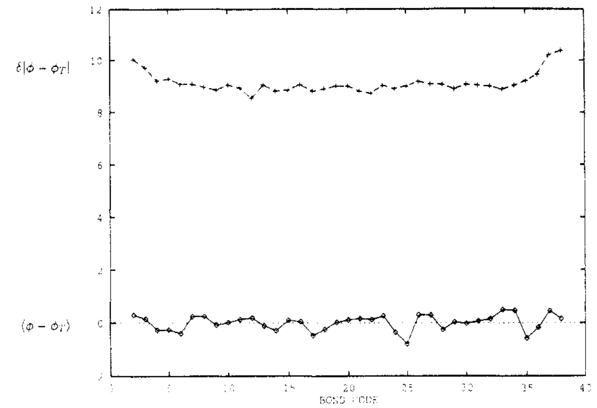

Figure 4. Values of $\langle\phi - \phi_T\rangle$ and $\delta|\phi - \phi_T|$ as a function of the bond index for *n*-tetracontane in rigid perhydrotriphenylene at 300 K.

Thus the time-averaged conformation deduced from the simulations is in agreement with experiment. A rotational isomeric state analysis of polyethylene indicates that the interconversion between stable conformers is possible in a concerted manner only if the channel has a diameter no smaller than 6.5 Å, which is well beyond the dimensions of the channel in perhydrotriphenylene.[9] The simulation shows that the rate of trans → gauche transitions at internal CH_2–CH_2 bonds is strongly suppressed by the channel. These transitions are allowed near the ends of the chain if sufficient thermal energy is present.

Fluctuations in the Trans State. The fluctuations in the trans state at 300 K were measured by evaluation of $\langle\phi - \phi_T\rangle$ and $\delta|\phi - \phi_T|$ for each internal CH_2–CH_2 bond.

$$\delta|\phi - \phi_T| = [\langle|\phi - \phi_T|^2\rangle - \langle|\phi - \phi_T|\rangle^2]^{1/2} \qquad (3)$$

Angular brackets denote the average of the enclosed quantity. The values of $\langle\phi - \phi_T\rangle$ and $\delta|\phi - \phi_T|$ for each internal CH_2–CH_2 bond at 300 K are depicted in Figure 4. None of the $\langle\phi - \phi_T\rangle$ has an absolute value that exceeds 1°, as expected. The fluctuations, $\delta|\phi - \phi_T|$, are about 10% larger for the two or three CH_2–CH_2 bonds near the end of the chain than for the internal CH_2–CH_2 bonds. The latter CH_2–CH_2 bonds have $\delta|\phi - \phi_T|$ of about 9°.

Randomization of C–H Bond Vectors about the *c* Axis. A recent NMR study has shown that the activation energy associated with the motion of polyethylene in perhydrotriphenylene is only 1.1 kcal mol^{-1}.[8] This low energy of activation suggests that the motions do not involve trans → gauche isomerization, for which the barrier height is about 3 kcal mol^{-1}, nor the translation of the buckled twist defect, for which the barrier is 4 kcal mol^{-1}.[8] The rotation of the entire chain about its axis might contribute strongly to the motion, if the activation energy for this process is substantially lower in perhydrotriphenylene than in the orthorhombic unit cell of crystalline polyethylene. In the latter environment, conformational energy calculations suggest that the activation energy is 1.2 kcal mol^{-1} per methylene unit for the rotation of the entire chain about its long axis.[14]

Rotation of the *n*-tetracontane was assessed using a polar coordinate system with the *Z* axis parallel to the channel. The angle between this axis and a selected C–H bond vector in *n*-tetracontane is denoted by θ, and ψ denotes the rotation of the selected C–H bond vector about the *Z* axis. The value of ψ can be affected by rotation of the chain about its long axis as a rigid body, by fluctuations in the dihedral angles at the C–C bonds, and by bending modes. The range of ψ sampled in 1 ns by a C–H bond vector in a centrally located methylene group is depicted in Figure 5. The instanteous value of θ determines the distance of a point from the intersection of the two dashed straight lines, and ψ determines the angle with the solid line. The values of θ are always close to 90°, and the values of ψ sample the entire accessible range within 1 ns. The density of points is not uniform over the entire range for ψ. The ratio of the highest and lowest densities is about 2 at 300 K. This fluctuation in density does not seem to be due to the finite length of the trajectory but may instead reflect a slight preference of the C–H bond vector for some orientations over other orientations.

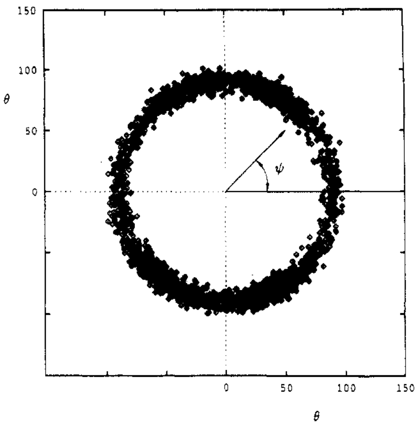

Figure 5. Instantaneous values of θ and ψ for a C–H bond vector in a centrally located methylene group in *n*-tetracontane in a rigid matrix of perhydrotriphenylene at 300 K, recorded at intervals of 0.5 ps over a trajectory of 1 ns. The distance of a point from the junction of the two straight dashed lines denotes θ, and ψ is given by the angle from the solid line.

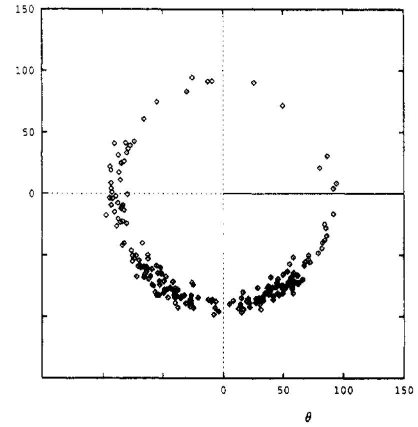

Figure 6. 200 points from Figure 5 that occur in the window from 0.6 to 0.7 ns of the 1-ns trajectory.

If the 2000 points depicted in Figure 5 were segregated into 10 similar plots, each containing 200 points that cover a time interval of 0.1 ns, each of these 10 plots contains points in all four quadrants. One of these 10 plots (for the period 0.6–0.7 ns in the trajectory) is depicted in Figure 6. Each of the other nine plots, for the other 0.1-ns time segments, shows at least as much randomization of ψ as does Figure 6.

A somewhat different picture is obtained in an equivalent analysis of the C–H bond vectors in the terminal methyl groups. This difference is most apparent in the behavior of θ, as depicted in the two panels in Figure 7. Here θ can sample two ranges, centered about 90° and 135° in one methyl group and about 90° and 45° in the other methyl group. The two ranges of θ for the C–H bond vectors in the methyl group arise from rotation about the CH_3–CH_2 bond, which lets the bond indicated by the long dash in *H*-CH_2—CH_2-CH_2 place the italicized H in either a trans or gauche orientation with respect to the

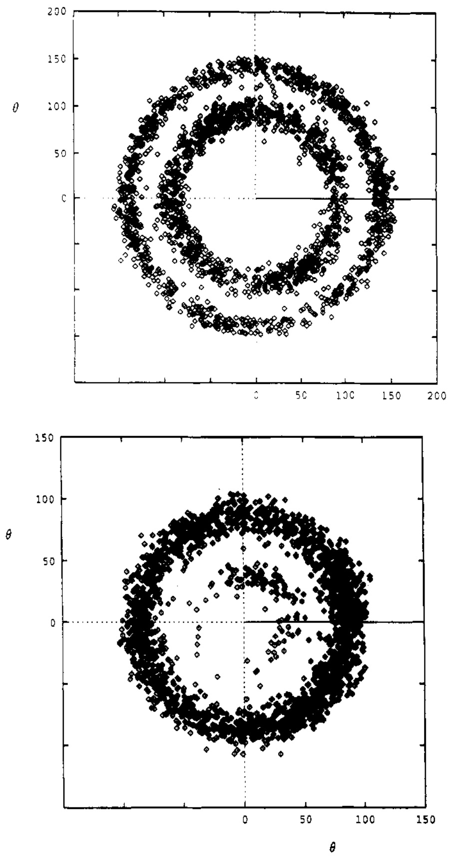

Figure 7. Instantaneous values of θ and ψ for a C–H bond vector in a methyl group in *n*-tetracontane in rigid perhydrotriphennylene at 300 K. The two panels depict results for methyl groups at either end of the chain.

italicized C. The rotation about the CH_3–CH_2 bond occurs on the time scale of 0.1 ns.

Rate of Rotation about the Long Axis. The rapid randomization of the values of ψ for the internal C–H bond vectors (Figures 5 and 6) is achieved without the assistance of trans → gauche transitions and with relatively small values of $\delta|\phi - \phi_T|$ (Figure 4). Somehow the chain must be able to achieve rapid rotation about its long axis. One method for detection of this motion is by examination of the time dependence of $\langle\psi\rangle_t$. Let $\psi(t,j)$ denote the angle between the X axis and the jth C–H vector at time t. (Figure 1 is oriented such that the X axis is horizontal and the Y axis is vertical.) Then the average value for M C–H vectors at that time is

$$\langle\psi\rangle_t = \frac{1}{M}\sum_{j=1}^{M}\psi(t,j) \qquad (4)$$

This averaging suppresses the influence of random fluctuations in dihedral angles and bond angles and yields a property that is sensitive to rotation of the chain as a rigid body. In the evaluation of eq 4, we ignore the C–H bonds attached to the five carbon atoms at either end of the chain. One C–H bond vector is chosen from each of the other 30 carbon atoms. These C–H bond vectors are selected so that successive pairs are in trans conformations in the fully extended chain.

For each vector, the reference for ψ is established by its orientation at $t = 0$. Therefore, by definition, $\langle\psi\rangle_0 = 0$. The sign of the rotation of a particular vector is retained throughout the trajectory, so that right-handed and left-handed rotations can be distinguished (and thus +360° is distinguished from −360°). The behavior of $\langle\psi\rangle_t$ during the trajectory is depicted in Figure 8. Based on $\langle\psi\rangle_t$, the chain experienced about 1.5 revolutions to the left early in the trajectory and several revolutions to the right during the middle portion of the trajectory and is rotating to and fro (by amounts that exceed a net change in $\langle\psi\rangle_t$ of 360°) during the last third of the trajectory.

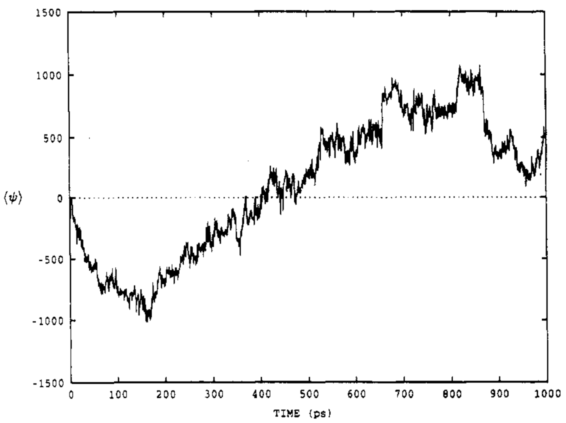

Figure 8. History of $\langle\psi\rangle_t$ over 1 ns at 300 K, using a rigid channel.

Table I
Rates for Three Motions of *n*-Tetracontane in Rigid Crystalline Perhydrotriphenylene

	rate[a]			
motion[b]	223 K	300 K	373 K	E_a, kcal mol^{-1}
rotation	28.9	35.2	40.7	0.37
twist	17.2	19.4	21.9	0.26
translation	0.552	0.587	0.694	0.24

[a] Rates in deg ps^{-1} for rotation and twist and in Å ps^{-1} for translation. [b] Rotation = $\langle|\Delta\psi|\rangle/\Delta t$, twist = $\langle|\Delta\phi|\rangle/\Delta t$, and translation = $\langle|\Delta Z|\rangle/\Delta t$.

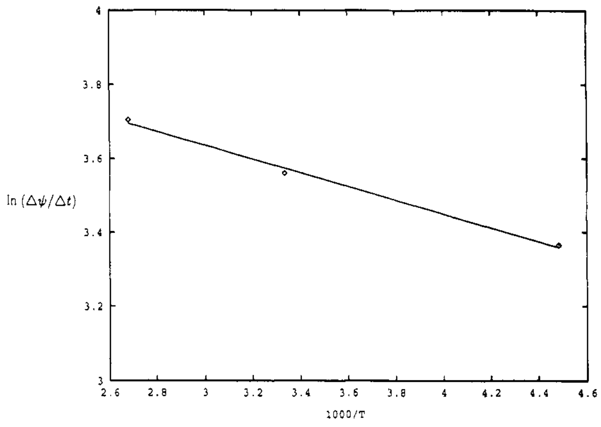

Figure 9. Arrhenius plot for $\langle|\Delta\psi|\rangle/\Delta t$.

The activation energy for this process can be estimated from the trajectories computed at 223, 300, and 373 K. The instantaneous rotational rate at time t in the trajectory is identified with

$$\frac{|\langle\psi\rangle_t - \langle\psi\rangle_{t-\Delta t}|}{\Delta t}$$

where Δt is the interval, 0.5 ps, at which the trajectory was recorded for subsequent analysis. The average rotational rate is identified with the simple average of the 1999 successive values of the instantaneous rate, using the 1999 successive records separated by Δt. This simple average is abbreviated as $\langle|\Delta\psi|\rangle/\Delta t$. The values of $\langle|\Delta\psi|\rangle/\Delta t$ extracted from the 1-ns trajectories at 223, 300, and 373 K are reported in Table I. When these three rates are plotted in the usual way (Figure 9), the slope of the best straight line specifies an activation energy of 0.37 kcal mol^{-1}. Both the molecular dynamics simulations and NMR measurements,[8] performed over the same range of tem-

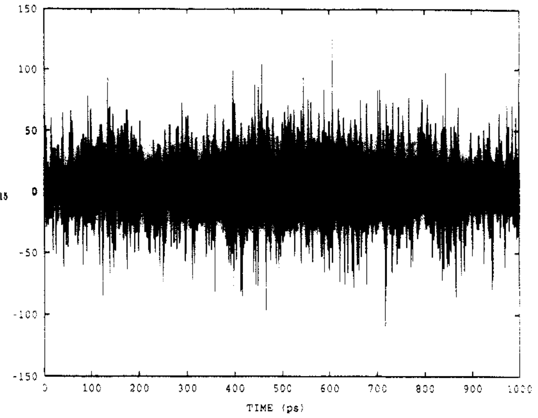

Figure 10. History of $\psi_{15} - \psi_{27}$ at 300 K, in the rigid channel.

peratures, find the randomization occurs by a process with an activation energy that is much smaller than the value (3 kcal mol^{-1}) associated with trans → gauche isomerization.

Influence of Internal Fluctuations. The foregoing analysis does not permit a distinction between rotation of the *n*-tetracontane as a rigid body or a time-dependent change in $\langle\psi\rangle$ as a consequence of internal fluctuations in the conformation of the *n*-alkane. The dihedral angles at all of the internal C–C bonds are subject to fluctuations, as shown in Figure 4. In order to assess the importance of the internal fluctuations, let $\phi(t,j)$ denote the instantaneous value of the dihedral angle at the *j*th internal CH_2–CH_2 bond at time *t*. Then the average value for *M* dihedral angles at that time is

$$\langle\phi\rangle_t = \frac{1}{M}\sum_{j=1}^{M}\phi(t,j) \qquad (5)$$

the instantaneous internal twisting rate at time *t* is identified with

$$\frac{|\langle\phi\rangle_t - \langle\phi\rangle_{t-\Delta t}|}{\Delta t}$$

and the simple average of this term over 1999 successive values, separated in time by $\Delta t = 0.5$ ps, is denoted by $\langle|\Delta\phi|\rangle/\Delta t$. (From this definition, we must obtain $\langle|\Delta\phi|\rangle/\Delta t = 0$ if *n*-tetracontane rotates as a rigid body, because every $\phi(t,j) - \phi(t-\Delta t,j)$ would then be zero.) The results deduced from the simulations are reported in Table I. The values of $\langle|\Delta\phi|\rangle/\Delta t$ are 60, 55, and 54% of $\langle|\Delta\psi|\rangle/\Delta t$ at 223, 300, and 373 K, respectively. The activation energy specified by the values of $\langle|\Delta\phi|\rangle/\Delta t$ is slightly smaller than the other specified by $\langle|\Delta\psi|\rangle/\Delta t$. Therefore, we conclude that the fluctuations of each dihedral angle within the trans state make an important contribution to the rapid randomization of the orientation of the C–H bond vectors in the methylene groups of the *n*-alkane.

Migration of a Conformational Twist along the Chain. Sozzani et al.[8] considered a conformational defect consisting of a small rotation from the idealized trans state at each of 10–14 consecutive bonds. If each such rotation were on the order of 15°, this arrangement introduces a twist of 180° into the chain. This defect has been labeled a "twiston". The results obtained from the simulations find that $\delta|\phi - \phi_T|$ is about 9° and the average of $\delta|\psi_i - \psi_{i-1}|$ is about 8.3°. Both of these measurements of fluctuations are a little smaller than 15°.

In order to show directly whether a twist of 180° might occur in 10–14 bonds, we depict in Figure 10 the time dependence of $\psi_{15} - \psi_{27}$ at 300 K. This quantity does indeed experience rapid fluctuations, but none of those fluctuations produces an absolute value of $\psi_{15} - \psi_{27}$ that is as large as 180°. The largest value is about 125°. If a larger number of bonds (more than 20) is involved, an instantaneous twist of 180° may occur.

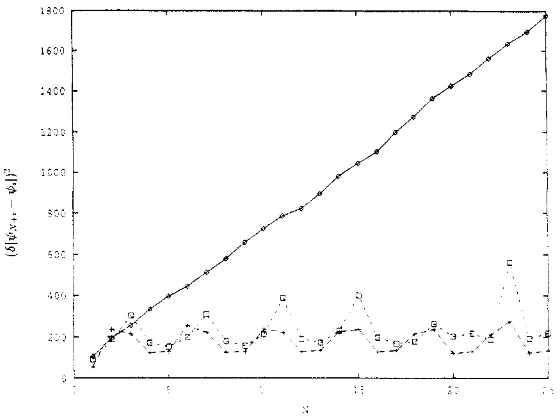

Figure 11. Relationship between $(\delta|\psi_{N+i} - \psi_i|)^2$ and *N* for (◇) *n*-tetracontane in perhydrotriphenylene at 300 K, in the rigid channel, (□) poly(1,4-*trans*-isoprene) in perhydrotriphenylene, and (+) poly(1,4-*trans*-butadiene) in form I.

Uncorrelated Fluctuations. The size of the fluctuation of $\psi_{15} - \psi_{27}$ emphasizes that the chain experiences internal motions that can produce large changes in conformation. It also shows that the chain does not rotate about its long axis as a rigid body. The random fluctuations of each dihedral angle are meausred by $\delta|\phi - \phi_T|$, which was depicted in Figure 4. Let us examine the consequences of the assumption that these fluctuations at bond *i* are uncorrelated with the fluctuations at bond *i* + 1. Our concern is with the cumulative fluctuations over a sequence of *N* bonds, as defined by

$$\delta|\psi_{N+i} - \psi_i| = [\langle|\psi_{N+i} - \psi_i|^2\rangle - \langle|\psi_{N+i} - \psi_i|\rangle^2]^{1/2} \qquad (6)$$

This term is sensitive to internal motions, such as fluctuations in the dihedral angle and bond angle, but is insensitive to rotation of the chain as a rigid body. The relationship between $\delta|\psi_{N+i} - \psi_i|$ and *N* is given by the model of the random walk

$$(\delta|\psi_{N+i} - \psi_i|)^2 = CN \qquad (7)$$

where *C* is the value of $(\delta|\psi_{N+i} - \psi_i|)^2$ when $N = 1$.

The validity of the simple model is tested against the simulation in Figure 11, in which $(\delta|\psi_{N+i} - \psi_i|)^2$ is plotted against *N*. The data for *n*-tetracontane in perhydrotriphenylene are a reasonable approximation to the straight line demanded by eq 7. The step size of the random walk is given by the square root of the slope of the best straight line in Figure 11. This procedure specifies a step size of 8.3°, which is very close to the value of $\delta|\phi - \phi_T|$ in Figure 4. If the nonzero values of $\delta|\psi_{N+i} - \psi_i|$ were produced entirely by the migration of a twiston, the data in Figure 11 would have shown positive curvature at small *N*.[15] The ratio of the limiting slope as $N \rightarrow \infty$ to the initial slope would have been $N_T/3$, where N_T denotes the number of bonds in the mobile twiston.

For comparison, Figure 11 also depicts data obtained from simulations of two systems where the chain is relatively immobile in its channel. These two systems are poly(1,4-*trans*-butadiene) in form I[2] and poly(1,4-*trans*-isoprene) in perhydrotriphenylene.[4] Neither system shows a linear increase in $(\delta|\psi_{N+i} - \psi_i|)^2$ as *N* increases. The local maxima in $(\delta|\psi_{N+i} - \psi_i|)^2$ for both systems occur when the two C–H bond vectors are on CH_2 and CH═. Figure 12 depicts the data for two systems in which rotational isomeric state transitions between anticlinal$^+$ and an-

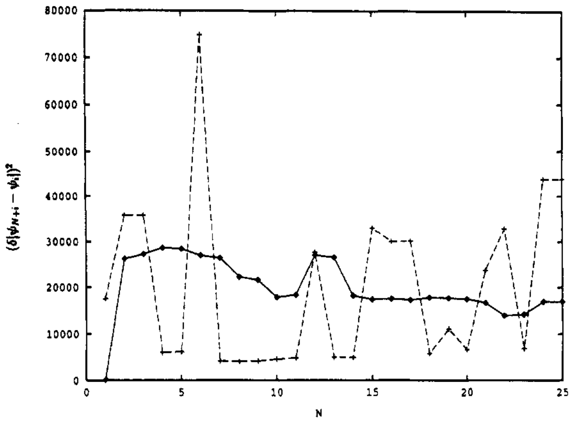

Figure 12. Relationship between $(\delta|\psi_{N+i} - \psi_i|)^2$ and N for poly(1,4-*trans*-butadiene) in (◇) perhydrotriphenylene and (+) form II.

ticlinal⁻ states contribute strongly to the randomization of the C–H bond vector. These two systems are poly(1,4-*trans*-butadiene) in perhydrotriphenylene[1-3] and in form II.[2,3] They also do not show a linear increase in $(\delta|\psi_{N+i} - \psi_i|)^2$ as N increases. Polyethylene in perhydrotriphenylene is the only one of these five systems in which the data describe a straight line with a positive slope. Therefore its adherence to the behavior predicted by eq 7 is unique among these five systems.

The success of this simple model for the motion of the C–H bond vectors in *n*-tetracontane in perhydrotriphenylene suggests that rapid fluctuations in ϕ, which are uncorrelated between nearest neighbors, contribute to the rapid randomization of ψ that was seen in Figures 5 and 6. Since each bond is fluctuating within a potential energy well, it has no activation energy to overcome insofar as intramolecular interactions are concerned. The small activation energy that is observed arises from the intermolecular interaction of the *n*-alkane with the walls of the channel as it twists internally in response to the uncorrelated fluctuations in the dihedral angles at each internal CH_2–CH_2 bond.

Translation of the Chain along Its Long Axis. Let Z_t denote the instantaneous value at time t of the coordinate on the Z axis of the center of mass of the 40 carbon atoms of *n*-tetracontane. Proceeding as with ψ and ϕ, we define an instantaneous translational rate for the center of mass as

$$\frac{|Z_t - Z_{t-\Delta t}|}{\Delta t}$$

and the simple average obtained from 1999 evaluations separated in time by $\Delta t = 0.5$ ps is denoted by $\langle|\Delta Z|\rangle/\Delta t$. The results, as reported in Table I, specify an activation energy for translation of 0.24 kcal mol^{-1}. A larger number might be expected for a longer *n*-alkane. This result might be affected somewhat if there were more than one *n*-alkane in the channel, but that effect should be small at the time scale studied here, because the displacement is small on that time scale.

Conclusion

Trans states are strongly preferred at the internal bonds in the *n*-alkane in the channel in perhydrotriphenylene. Gauche states are seen as a very minor constituent for the terminal CH_2–CH_2 bonds at 373 K. The simulations reveal contributions to the dynamics of the *n*-alkane from rigid-body rotation of the chain about its long axis and from uncorrelated fluctuations of internal degrees of freedom about their mean values. They provide no evidence for contributions from strongly correlated internal degrees of freedom, as would be required for the migration of a twiston. The rates for rotation as a rigid body and for displacements of C–H vectors as a consequence of random internal motion differ by no more than a factor of 2 at 300 K, with the former rate being the larger.

Acknowledgment. We thank Dr. Schilling for a preprint of ref 8. This research was supported by National Science Foundation Grant NSF DMR 89-15025.

References and Notes

(1) Dodge, R.; Mattice, W. L. *Macromolecules* **1991**, *24*, 2709.
(2) Zhan, Y.; Mattice, W. L. *Macromolecules* **1992**, *25*, 1554.
(3) Zhan, Y.; Mattice, W. L. *J. Chem. Phys.* **1992**, *96*, 3279.
(4) Zhan, Y.; Mattice, W. L. *Macromolecules*, in press.
(5) Lee, K.-J.; Mattice, W. L.; Snyder, R. G. *J. Chem. Phys.*, in press.
(6) Sozzani, P.; Behling, R. W.; Schilling, F. C.; Brückner, S.; Helfand, E.; Bovey, F. A.; Jelinski, L. W. *Macromolecules* **1989**, *22*, 3318.
(7) Schilling, F. C.; Sozzani, P.; Bovey, F. A. *Macromolecules* **1991**, *24*, 4369.
(8) Sozzani, P.; Bovey, F. A.; Schilling, F. C. *Macromolecules* **1991**, *24*, 6764.
(9) Tonelli, A. E. *Macromolecules* **1990**, *23*, 3134.
(10) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. *J. Comput. Chem.* **1983**, *4*, 187.
(11) Zúñiga, I.; Bahar, I.; Dodge, R.; Mattice, W. L. *J. Chem. Phys.* **1991**, *95*, 5348.
(12) Farina, M.; Natta, G.; Allegra, G.; Löffelholz, M. *J. Polym. Sci., Part C* **1967**, *16*, 2517.
(13) Colombo, A.; Allegra, G. *Macromolecules* **1971**, *4*, 579.
(14) Mansfield, M.; Boyd, R. H. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1227.
(15) Zhan, Y.; Mattice, W. L., submitted for publication in *Makromol. Chem., Makromol. Symp.*

Registry No. *m*-Tetracontane-perhydrotriphenylene, 141930-58-7; perhydrotriphenylene, 15074-91-6; tetracontane, 4181-95-7; polyethylene, 9002-88-4.