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Simulation of the Molecular Dynamics of Poly(1,4-*trans*-isoprene) and Isoprene as Inclusion Complexes in Crystalline Perhydrotriphenylene

Yongjian Zhan and Wayne L. Mattice*

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

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ABSTRACT: Simulations have been performed for the molecular dynamics of poly(1,4-*trans*-isoprene) and its monomer, isoprene, as inclusion complexes in the channel of crystalline perhydrotriphenylene. The system contains 90 molecules of perhydrotriphenylene and either 10 molecules of isoprene or a single methyl-terminated decamer of poly(1,4-*trans*-isoprene). The results are compared with previous simulations of the inclusion complex in which poly(1,4-*trans*-butadiene) is substituted for poly(1,4-*trans*-isoprene). Poly(1,4-*trans*-isoprene) interacts more strongly with the matrix of perhydrotriphenylene than does poly(1,4-*trans*-butadiene). Interaction between the methyl group and perhydrotriphenylene causes the poly(1,4-*trans*-isoprene) to distort the matrix so that the channel becomes elliptical in cross-section. The channel retained a circular cross-section in the inclusion complex with poly(1,4-*trans*-butadiene). Far from the ends of the chain, the conformation of the poly(1,4-*trans*-isoprene) in the inclusion complex is described by the repeating sequence TA$^{\pm}$TA$^{\mp}$, and the only motions on the nanosecond time scale are oscillations about these positions. Bonds near the ends of the chain are more mobile. They participate in coupled rotational isomeric state transitions represented by A$^{\pm}$TA$^{\mp}$ $\rightleftharpoons$ A$^{\mp}$TA$^{\pm}$ and A$^{\pm}$TA$^{\mp}$ $\rightleftharpoons$ TTT. Two types of motions are observed for the monomer, isoprene, on the nanosecond time scale. These motions are rotational diffusion of the monomer about the axis of the channel and translational diffusion of the monomer along this axis. No end-over-end flip by the monomer was observed on the time scale of the simulation.

Introduction

Slow cooling of a solution of poly(1,4-*trans*-isoprene) yields semicrystalline single lamellas or lamellar structures in one of two different crystal modifications.[1-3] The α form has a monoclinic unit cell with two chains, each contributing two repeat units, and the β form has an orthorhombic unit cell with four chains, each contributing one repeat unit. Partially crystalline poly(1,4-*trans*-isoprene) can be prepared from solution with only the α form, only the β form, or both crystal forms present.[2] The conformation of the chain in the α form is represented by a repeating pattern of eight bonds, TCTA$^{\pm}$TCTA$^{\mp}$, and the repeating pattern for the β form requires only four bonds, TA$^{\pm}$TA$^{\mp}$.[4] Here T denotes the trans placement at the C=C bond or at the CH_2–CH_2 bond, C denotes a cis placement at a $C(CH_3)$–CH_2 bond, and A$^{\pm}$ denotes anticlinal$^{\pm}$ placements at a CH–CH_2 or $C(CH_3)$–CH_2 bond.

High-resolution solid-state ^{13}C NMR spectroscopy has been used to investigate the dynamics of poly(1,4-*trans*-isoprene) in the crystalline states and as an inclusion complex in the channel of crystalline perhydrotriphenylene.[5,6] The chemical shifts and spin–lattice relaxation times show that the polymer in the inclusion complex has the conformation TA$^{\pm}$TA$^{\mp}$, as in the β form. The local internal dynamics of the chain is also similar in the inclusion complex and in the β form. When confined to the channel, the monomer, isoprene, can undergo end-to-end flipping and rotation about the long axis.[6] However, motions of the monomer in the channel are restricted when compared to their occurrence in neat isoprene.

Tonelli has examined the conformations of poly(1,4-*trans*-isoprene) in the channels of crystalline perhydrotriphenylene, and he has inferred the internal dynamics of this polymer from a study of static conformations.[7] He enumerated all of the stable rotational isomeric states of the isolated chain and determined which of these conformations could fit in the channel. The only conformations that fit in cylinders of the diameter of the channel in the inclusion complex are those conformations that have the repeating pattern of the β form. None of the conformations compatible with existence in the channel contained C placements. The internal dynamics of the chain was inferred by testing whether or not it could convert between two of these conformations while confined by the channel. The only paths for interconversion between two such conformations would require significant expansion of the constraining cylinders formed by the stacks of perhydrotriphenylene.

Here we report the results of a simulation of the internal dynamics of poly(1,4-*trans*-isoprene) as an isolated chain and in the constrained environment provided by the channel of crystalline perhydrotriphenylene, using the method of molecular dynamics.[8] Strongly correlated next-nearest-neighbor rotational isomeric state transitions are observed but only for bonds near the ends of the chain. In contrast, these correlated rotational isomeric state transitions can occur in the interior of the chain in the inclusion complex containing poly(1,4-*trans*-butadiene).[9,10] We also examine the behavior of the monomer in the channel.

Methods

The computational method is the same as the one used previously for the study of poly(1,4-*trans*-butadiene).[9,10] The molecular dynamics trajectories were computed using version 2.1 of CHARMm,[8] provided by Polygen Corp. The parameters changed by us from those supplied with version 2.1 of CHARMm in our investigations of poly(1,4-*trans*-butadiene)[9,10] were also changed in the present investigation of poly(1,4-*trans*-isoprene). The inclusion compounds were constructed initially with the assumptions that they are not affected by the substitution of isoprene for butadiene or the substitution of poly(1,4-*trans*-isoprene) for poly(1,4-*trans*-butadiene).

Before initiating the computation of the molecular dynamics, the potential energy was minimized using a conjugate gradient method. The simulation of the molecular dynamics was then initiated with zero kinetic

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Table I
Distribution of Dihedral Angles in the Internal Six Monomer Units

bond	system	$\langle|\phi - \phi_T|\rangle$, deg	$\delta|\phi - \phi_T|$, deg
CH–CH$_2$	rigid channel	94	12
	mobile channel	68	14
	isolated chain	62	27
C(CH$_3$)–CH$_2$	rigid channel	89	10
	mobile channel	66	12
	isolated chain	81	27
CH$_2$–CH$_2$	rigid channel	6	5
	mobile channel	8	6
	isolated chain	57	56
C=C	rigid channel	6	5
	mobile channel	7	6
	isolated chain	11	9

energy, and the temperature was raised to 300 K in 0.6 ps (in the mobile channel) or 1.0 ps (in vacuo and in the rigid channel), using a time step of 0.2 fs. After equilibration for another 2.2 ps (in the mobile channel) or 3.0 ps (in vacuo and in the rigid channel), also with a time step of 0.2 fs, the simulation was performed at constant temperature with the time step of 0.5 fs. The lengths of the trajectories are 75 ps (in the mobile channel) or 1 ns (in vacuo and in the rigid channel). The Z axis of the coordinate system used in the analysis of the trajectories is parallel with the c axis of the crystal. All hydrogen atoms were considered explicitly in every simulation.

Isolated Chain. The isolated chain, $C_{50}H_{82}$, contained 10 monomer units and was terminated by methyl groups. The initial conformation of the chain was constructed with all internal dihedral angles in the backbone in trans states.

Polymer in the Channel. The atomic composition of the entire system is $C_{1670}H_{2782}$. The atoms occur in 91 molecules, one of which is the mobile chain of poly(1,4-*trans*-isoprene) and the other 90 of which are perhydrotriphenylene. The mobile chain, $C_{50}H_{82}$, has the same composition and initial conformation as the isolated chain described above. It is placed in the channel formed by a hexagonal array of six stacks, each with 15 molecules of perhydrotriphenylene. The size of the unit cell is $a = b = 14.26 \pm 0.01$ Å, $c = 4.78 \pm 0.01$ Å, and $\gamma = 120 \pm 0.5°$.[9,11,12] Simulations were performed with a rigid matrix of perhydrotriphenylene and with a matrix that was mobile. The mobile matrix was treated in the same way as in the recent simulation of the inclusion complex in which poly(1,4-*trans*-butadiene) replaces poly(1,4-*trans*-isoprene).[9] In that work, the nonbonded interactions between the 90 molecules of perhydrotriphenylene were sufficient to hold the matrix close to the structure determined for the crystal, even without the imposition of artificial constraints. Thermal motion produced fluctuations of about 1% in the dimensions denoted by a and b and about 0.5% in the dimension denoted by c, when the channel contains a methyl-terminated decamer of poly(1,4-*trans*-butadiene).

Monomers in the Channel. The atomic composition of the channel was as in the simulation described above, but the structure is changed so that the unit cell is $a = 13.35 \pm 0.01$ Å, $b = 14.72 \pm 0.01$ Å, $c = 4.78 \pm 0.01$ Å, and $\gamma = 115.3 \pm 0.5°$.[4,12] The chain of poly(1,4-*trans*-isoprene) was replaced by 10 molecules of isoprene. Therefore the system contains 100 molecules and has the overall composition $C_{1670}H_{2800}$. Simulations were performed with a rigid matrix and with a mobile matrix.

Results and Discussion

Distribution Functions for Dihedral Angles. The C=C bonds are confined to T states. No C or G (gauche) states are observed at any bonds for the chain in the channel, but they do occur in the isolated chain. The CH$_2$–CH$_2$ bonds are confined to T states in the channel. The remaining bonds CH–CH$_2$ and C(CH$_3$)–CH$_2$, prefer the A$^\pm$ states in the internal six monomer units.

Figure 1. End-on view of poly(1,4-*trans*-isoprene) in the rigid channel of perhydrotriphenylene.

The quantitative comparison of the distribution functions for the dihedral angles will be made using two properties deduced from the trajectories. The mean dihedral angle is denoted by $\langle|\phi - \phi_T|\rangle$, where the broken brackets denote the average of the enclosed property and ϕ_T denotes the dihedral angle for a T placement. The fluctuation is defined as

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

These properties are presented in Table I for the internal six monomer units. The A$^\pm$ states for the CH–CH$_2$ bonds in the chain in the channel have values of $\langle|\phi - \phi_T|\rangle$ that are 32° larger than the values seen in the isolated chain. The A$^\pm$ states for the C(CH$_3$)–CH$_2$ bonds in the chain in the channel also have values of $\langle|\phi - \phi_T|\rangle$ that exceed those found in the isolated chain. The introduction of mobility into the matrix causes the A$^\pm$ states at both types of bonds to adopt smaller values of $\langle|\phi - \phi_T|\rangle$, due to the relief of a repulsive steric interaction between the matrix and the methyl group in the polymer.

The change in the conformation of the polymer is accompanied by movement of the matrix, as depicted in Figures 1 and 2. Figure 1 shows a projection down the rigid channel. A methyl group from the polymer extends from the chain to the left. Figure 2 shows an equivalent projection after relaxation of the channel and the polymer. The channel, which had a circular cross-section in Figure 1, becomes elliptical, with the long axis of the ellipse in the direction of the projection of the C–CH$_3$ bond. The projection of this bond also changes, due to the change in the conformation of the chain of poly(1,4-*trans*-isoprene). The distortion of the channel seen in Figures 1 and 2 was not observed in the simulation of the inclusion complex in which poly(1,4-*trans*-butadiene) replaces poly(1,4-*trans*-isoprene),[9] thereby conclusively identifying the methyl group as the source of the repulsive interaction.

The fluctuations of the dihedral angles about the mean are nearly identical in the rigid and mobile matrices and

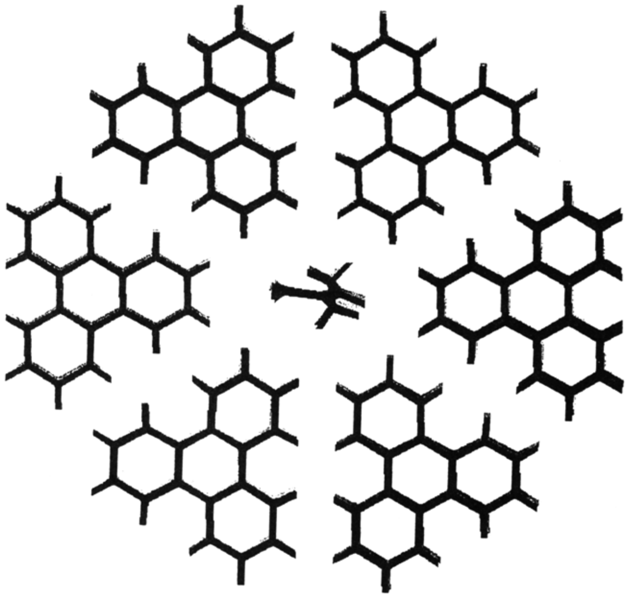

Figure 2. End-on view of poly(1,4-*trans*-isoprene) in the mobile channel of perhydrotriphenylene.

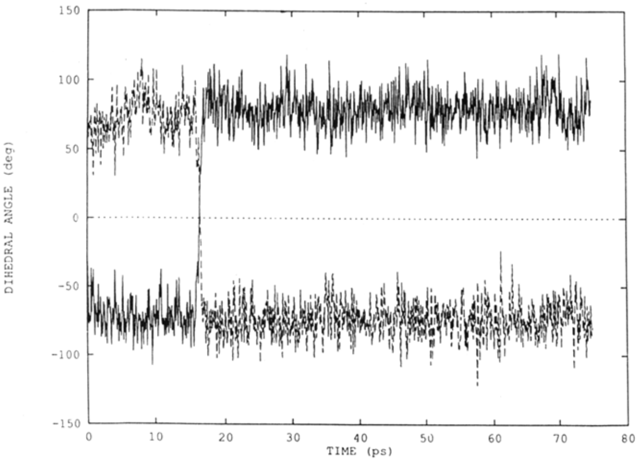

Figure 3. Conformational transition of the type $A^{\pm}TA^{\mp} \rightleftharpoons A^{\mp}TA^{\pm}$ near the end of the chain in the mobile channel.

very much smaller than the result seen in the isolated chain. The larger value of $\delta|\phi - \phi_T|$ in the isolated chain arises for two reasons. First, the wings of the distribution for the $A^{\pm}$ states are more prominent in the isolated chain, and, second, the C placements occur as a minor constituent of the distribution function in the isolated chain.

The magnitude of the restriction by both the rigid and the solid matrix on the dihedral angles at the CH_2-CH_2 bonds is most readily apparent in the comparison of the values of $\delta|\phi - \phi_T|$ for this bond and for the C=C bond. The fluctuations are virtually indistinguishable at these two types of bonds in the matrix. Of course, the CH_2-CH_2 bond experiences much greater fluctuation in the isolated chain, due to the population of G states and to a broadening of the distribution in the T state. The properties of the CH_2-CH_2 bond in Table I are similar to those evaluated for the same bond in poly(1,4-*trans*-butadiene).[10]

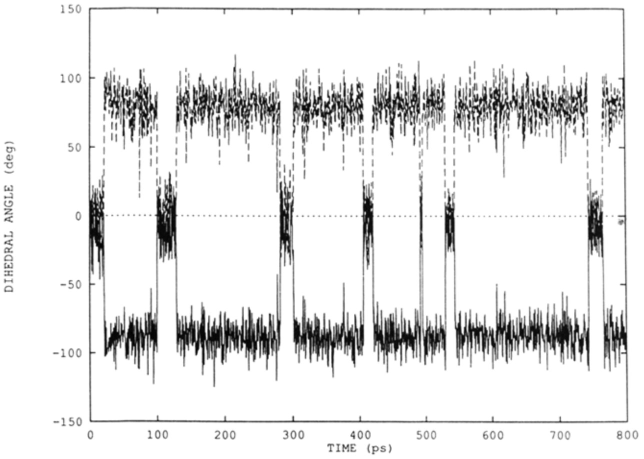

Figure 4. Correlated conformational transitions of the type $A^{\pm}TA^{\mp} \rightleftharpoons TTT$ near the end of the chain in the rigid channel.

Transitions between Rotational Isomeric States. The initial conformation of the chain in the channel had T placements at all internal C–C bonds. The conformation of the chain changed into $TA^{\pm}TA^{\mp}$ after the heating and equilibrium process. During the remainder of the simulation, there were no rotational isomeric state transitions at the $CH-CH_2$ and $C(CH_3)-CH_2$ bonds in the internal four monomer units of the chain, either in the mobile channel or in the rigid channel. Instead there were rapid fluctuations of the dihedral angles about their mean positions, with the magnitude of these fluctuations having been presented in Table I. The observation in the simulations that poly(1,4-*trans*-isoprene) in the channel adopts the $TA^{\pm}TA^{\mp}$ conformation of the β crystalline form is consistent with the conclusions derived from solid-state ^{13}C NMR measurements.[6]

By an evaluation of the dimensions of static conformations of the chain, Tonelli concluded that a channel with a diameter less than 6 Å would force the isoprene repeat unit into the $TA^{\pm}TA^{\mp}$ conformation, and conformational transitions of the type $A^{\pm} \rightarrow A^{\mp}$ would be forbidden.[7] The current study using molecular dynamics is in agreement with this prediction, if attention is confined to the internal four monomer units in the chain. However, the monomer units closer to the ends of the chain have more mobility. Figure 3 depicts a correlated transition, represented by

$$A^{\pm}TA^{\mp} \rightarrow A^{\mp}TA^{\pm} \qquad (2)$$

at $CH-CH_2CH_2-C(CH_3)$ for the chain in the mobile channel. The $CH-CH_2$ bond is located in unit 8, and its index is 31; the $CH_2-C(CH_3)$ bond is located in unit 9, and its index is 33. Figure 4 depicts more numerous transitions, represented by

$$A^{\pm}TA^{\mp} \rightleftharpoons TTT \qquad (3)$$

at $CH-CH_2CH_2-C(CH_3)$ for the chain in the rigid channel. The $CH-CH_2$ bond is located in unit 9, and its index is 35; the $CH_2-C(CH_3)$ bond is located in unit 10, and its index is 37. Correlated rotational isomeric state transitions, on the nanosecond time scale, are possible at next-nearest-neighbor bonds if both bonds lie within three monomer units of the end of a chain that is terminated with methyl groups.

Motions of the Monomers in the Channel. Three types of motions were monitored for the molecules of isoprene in the channels. There is rotation of the isoprene about its long axis in the mobile channel, an example of which is depicted in Figure 5. A rotational diffusion coefficient, defined as $\langle(\Delta\psi)^2\rangle/6\Delta t$, was estimated from the time dependence of the projection of a $C-CH_3$ bond onto the XY plane in a Cartesian coordinate system where the Z axis is parallel with the long axis of the channel. The rotational diffusion coefficients obtained by this method are on the order of 10^{11} s^{-1}. In the rigid matrix, the translational motion of the isoprene is best described as

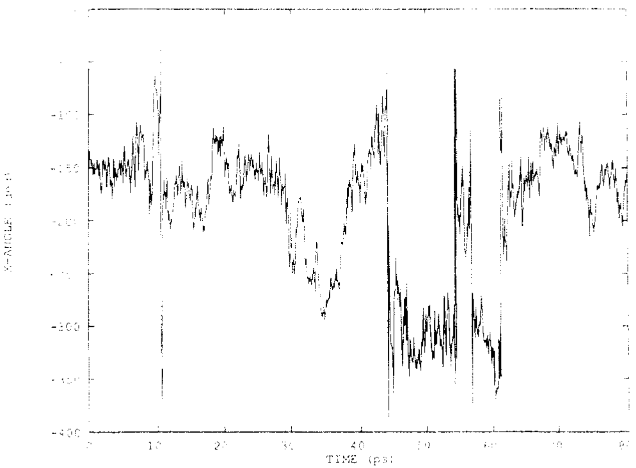

Figure 5. Illustrative rotation of isoprene about its long axis in the mobile channel. "*X*-ANGLE" is the angle between the *X*-axis and the projection of a C–CH_3 bond onto the *XY* plane. The Cartesian coordinate system has its *Z* axis parallel with the long axis of the channel.

minor fluctuations (δZ on the order of 0.2–0.3 Å) about a stable position. In the mobile matrix, these motions become larger in the direction of the channel. They can be converted to an estimate of a translational diffusion coefficient, defined here as $\langle(\Delta Z_{cm})^2\rangle/6\Delta t$, where Z_{cm} denotes the position along the *Z* axis of the center of mass of the five carbon atoms. The translational diffusion coefficients estimated by this method are on the order of 3×10^{-6} cm^2 s^{-1}. Thus isoprene undergoes rapid translational diffusion in the channel.

End-to-end flips of isoprene have been inferred from the temperature dependence of the microstructure of the polymers prepared in the channels.[13] However, no end-to-end flips of isoprene were observed on the nanosecond time scale of the simulations.

Conclusion

Poly(1,4-*trans*-isoprene) interacts more strongly with the matrix of perhydrotriphenylene than does poly(1,4-*trans*-butadiene). The former polymer tends to distort the matrix so that the cross-section of the channel becomes elliptical, but the channel retains a circular cross-section in the inclusion complex of the latter polymer. Far from the ends, the conformation of the poly(1,4-*trans*-isoprene) in the inclusion complex is described by the repeating sequence $TA^{\pm}T^{\mp}$, and the only motions on the nanosecond time scale are oscillations about these positions. Bonds near the ends of the chain are more mobile. They participate in coupled rotational isomeric state transitions represented by $A^{\pm}TA^{\mp} \rightleftharpoons A^{\mp}TA^{\pm}$ and $A^{\pm}TA^{\mp} \rightleftharpoons TTT$. Two types of motions are observed for the monomer, isoprene, on the nanosecond time scale. These motions are rotational diffusion of the monomer about the axis of the channel and translational diffusion of the monomer along this axis. End-over-end flips by the monomer are not observed on the time scale of the simulation.

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