Traveling Defects in 1,4-*trans*-Polybutadiene as an Inclusion Complex in Perhydrotriphenylene Canals and a Comparison with Molecular Motions in the Crystalline Solid State

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ABSTRACT: 1,4-*trans*-Polybutadiene in perhydrotriphenylene (PHTP) canals provides a model system for studying the behavior of a single polymer molecule in a highly hydrophobic environment. Solid-state deuterium NMR spectroscopy was used to obtain explicit molecular level information about the motions of 1,4-*trans*-*1,1,4,4*-d_4-polybutadiene in the polybutadiene–PHTP complex. These results were compared to the mobility of deuterated polybutadiene when the PHTP matrix had been removed and to the mobility of recrystallized polybutadiene in the solid state. The isolated molecules of deuterated 1,4-*trans*-polybutadiene in PHTP canals undergo rapid ($\tau_c \leq 10^{-7}$ s) diffusional motions about the long axis of the polymer chain. These motions are consistent with a traveling defect that produces rapid and complete conformational averaging of the C–D bond vector about a cylindrical axis. These motions are not completely frozen out ($\tau_c \leq 10^{-3}$ s) even at −160 °C, suggesting that the hydrophobic canals of the PHTP molecules provide a highly unusual environment for polybutadiene. In contrast, when the PHTP matrix is removed, the deuterated polybutadiene demonstrates motional properties that are very similar to those of recrystallized polybutadiene. At ambient temperature (i.e., form I) the crystalline regions are static on the deuterium NMR time scale, whereas the amorphous connections between these regions undergo rapid ($\tau_c \leq 10^{-7}$ s) tetrahedral jumps. Above the form I–form II solid–solid transition but below the melt temperature, the chains in the crystalline regions of this material undergo the rapid diffusional motions observed for polybutadiene in the PHTP canals. These results show that polybutadiene in PHTP canals is similar to form II material, but that the solid–solid transition to form I is prohibited by the canals.

As devices continue to move toward molecular dimensions, increased attention is being focused on a fundamental understanding of the physical properties of individual molecules, in an attempt to delineate the differences between individual molecules and their bulk properties. Individual or highly dilute molecules occur in many situations, perhaps the most familiar being the gas phase. Other examples include substrate molecules in the active sites of enzymes, chromophores such as retinal in their proteins, dilute catalytic sites on surfaces, and molecules trapped in zeolites. In this report we describe molecular level motions of individual 1,4-*trans-1,1,4,4*-d_4-polybutadiene chains that are prevented from associating with like molecules because they are entrained in perhydrotriphenylene (PHTP) canals (Figure 1). These canals are held together by van der Waals forces rather than by hydrogen bonding as in clathrates of urea, thiourea, or cyclodextrin and therefore provide appropriate models for hydrophobic pockets.

Many PHTP inclusion complexes have been studied extensively by Farina and co-workers.[1] The included molecules range from small molecules such as $CHCl_3$ and *n*-heptane to polymers such as polyethylene and poly(oxyethylene). In most cases the physical properties of both the PHTP and the entrained molecule change dramatically, with the melting point of the matrix and of the included molecule increasing significantly over the normal temperatures.

It has long been recognized that inclusion complexes can be used to produce highly stereoregular polymers.[2] In the simplest procedure, gaseous or liquid monomers are diffused into the canals, and these confined monomers are then irradiated to produce polymer chains of high molecular weight. In the case of PHTP, the polymerization propagates inside the PHTP crystal, linking together the monomers while reducing side reactions that would lead to polymer defects.[3] No amorphous phase is present because polymerization cannot occur outside the crystals. After polymerization the polymer obtained by selective dissolution of the matrix material is usually highly crystalline and stereoregular.

X-ray crystallography[4] and ESR spectroscopy[3b] have been used to study the polymerization of *trans*-1,3-butadiene in PHTP canals. This polymerization involves a transformation from a crystal inclusion complex of PHTP with the monomer to a crystal complex with the polymer. The PHTP crystal structure is not destroyed during the polymerization process, and the polymerization proceeds through a living radical mechanism.[3b] However, the inclusion complex undergoes significant changes in its lattice parameters upon irradiation. Furthermore, the polybutadiene molecules are not evident in the X-ray diffraction pattern after polymerization. This latter observation was attributed to one of two possible causes: either the polymer repeat distance was identical with the matrix repeat (4.78 Å), or the polymer was disordered and produced diffuse scattering.[4] Similar results were observed for 1,4-*trans*-polybutadiene in urea channels.[5] This latter observation was explained by assuming freely rotating polymer chains, but the data could not distinguish between time-averaged or space-averaged chains.

The results presented here serve to clarify these points. In this report we describe solid-state deuterium NMR experiments that provide explicit information on the molecular motion of 1,4-*trans-1,1,4,4*-d_4-polybutadiene as an inclusion complex in PHTP canals. Solid-state deuterium NMR spectroscopy is especially well-suited for probing molecular motions over a wide frequency range,[6] and in this work we have taken particular advantage of the temperature dependence of the phase transitions in polybutadiene.[7] We then compare the molecular motion of the individual polybutadiene molecules in the PHTP canals to that of the molecules after the canals have been

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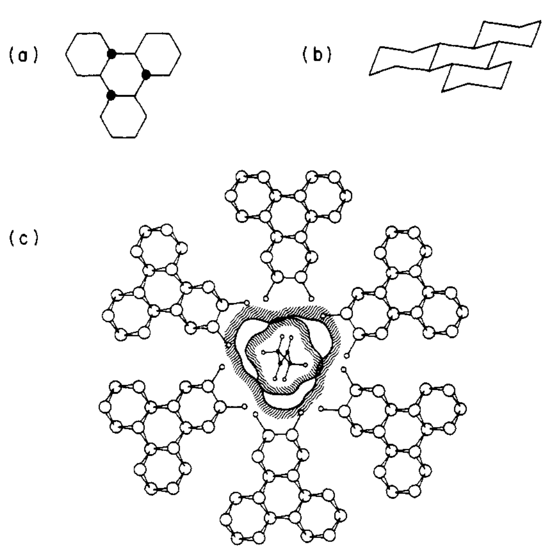

Figure 1. (a) Chemical structure of the equatorial form of perhydrotriphenylene (PHTP) used in these experiments; (b) structure showing the chair arrangement of the cyclohexane rings in PHTP; (c) positions of the atoms and van der Waals surfaces of the PHTP canals and 1,4-*trans*-polybutadiene at $z = c/4$. (Figure 1c has been adapted from Figures 3b and 5b of ref 4.)

removed and also to 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene that has been crystallized from solution.

Materials and Methods

Samples. The sample of 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene as an inclusion complex in PHTP was prepared according to literature methods[3] by using *1,1,4,4-d*$_4$-1,3-butadiene and the fully anti-trans isomer of perhydrotriphenylene.[9]

The PHTP matrix was removed from the entrained 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene by extracting the complex for 7 days in refluxing methanol. The sample was dried in vacuo prior to NMR measurements.

The recrystallized material was obtained by dissolving in chlorobenzene the 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene that had been removed from the PHTP matrix. This sample was heated and stirred overnight and then poured into a 3-fold excess of methanol at −78 °C. The sample was filtered and dried in vacuo. Approximately 30 mg of this material was used for NMR measurements.

NMR Measurements. Solid-state deuterium NMR spectra were obtained on 100-mg samples (unless noted otherwise) contained in 5 mm × 15 mm (o.d.) sample tubes by using a home-built spectrometer operating at 55.25 MHz for ^{2}H (360 MHz for ^{1}H). The spectrometer has been described previously.[8] Temperatures were regulated to ±1 °C and are considered accurate to ±2 °C. The standard quadrupole echo pulse sequence employed 3.2-μs 90° pulses, an echo delay time of 30 μs unless noted otherwise, and digitization rates of either 200 or 500 ns/point for 4K of data, depending on the width of the powder pattern. A pulse sequence using a presaturation series of 5 pulses that were separated by 2 ms was used to observe selectively those deuterons residing in amorphous regions. A delay of 100 ms was used after the presaturation pulse train to allow the amorphous deuterons to relax prior to obtaining the spectrum with the quadrupole echo pulse sequence.

Results and Discussion

Differential scanning calorimetry (DSC) traces are shown in Figure 2 for 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene as an inclusion complex in PHTP, for deuterated polybutadiene obtained from methanolic extraction of the PHTP matrix, and for recrystallized, deuterated polybutadiene. These traces show that the deuterated polybutadiene–PHTP adduct melts at 183 °C, much higher than the 133 °C melting point of pure 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene (Figure 2a). The endotherm at 125 °C corresponds to pure PHTP, and the DSC trace shows that approximately 20% of the PHTP does not contain polybutadiene in its channels. Above 67 °C 1,4-*trans*-polybutadiene undergoes a solid–solid transition from a monoclinic form (form I) to a pseudohexagonal modification (form II). The DSC traces in Figure 2b,c show the expected form I–form II transition at 67 °C and the melting transitions at 133 and 128 °C, respectively. No DSC transitions were observed for the polybutadiene–PHTP sample down to −130 °C (data not shown).

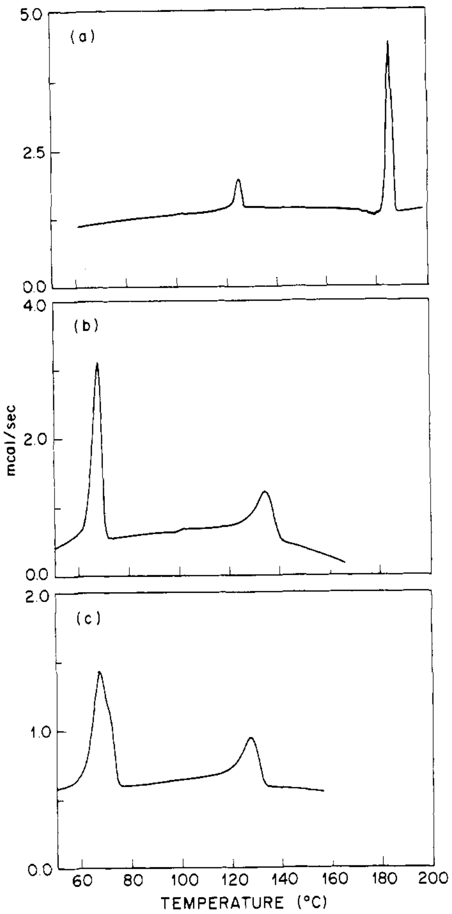

Figure 2. DSC traces of the materials used in this study: (a) 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene–PHTP adduct; (b) deuterated polybutadiene after the PHTP matrix has been removed by methanolic extraction; (c) deuterated polybutadiene that has been recrystallized. The heating rate for the sample in (a) was 10 °C/min; for (b) and (c) it was 20 °C/min.

Figure 3 shows a comparison of the solid-state deuterium NMR spectra of the samples whose DSC traces are shown in Figure 2. The striking difference between the spectrum in Figure 3a (the polybutadiene–PHTP complex) and the spectra in Figure 3b,c (polybutadiene with the matrix removed and recrystallized polybutadiene, respectively) is readily apparent. (A spectrum similar to that of Figure 3c has been reported by Möller for solution-crystallized 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene.[10,11]) Although a classic Pake pattern is observed in Figure 3a, the quadrupolar splitting ($\Delta\nu_q$ or $^3/_4(e^2qQ/h)$) is 50 kHz, substantially narrower than the ca. 125-kHz splitting expected for a static C–D bond. This narrowed pattern is consistent with rapid ($\tau_c \leq 10^{-7}$ s) and complete averaging over a cyclinder of a C–D bond vector that makes a 75° angle with the cylinder axis. It is well-known from X-ray crystal data that 1,4-*trans*-polybutadiene in its form I modification exists in a skew$^+$–trans–skew$^-$ conformation about the single bonds.[12,13] One can calculate that the C–D bonds form approximately 75 and 80° angles with the chain axis. Thus, the NMR results for deuterated polybutadiene in

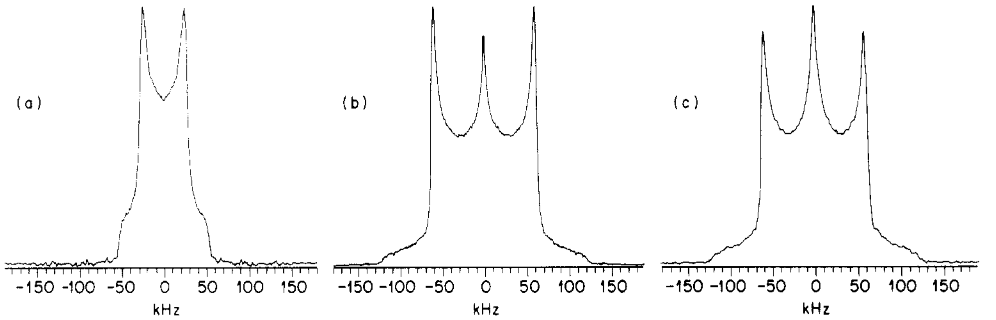

Figure 3. Comparison of the fully relaxed solid-state ^{2}H NMR spectra of (a) the 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene–PHTP inclusion complex, (b) deuterated polybutadiene after the PHTP matrix has been removed by treatment with methanol, and (c) recrystallized deuterated polybutadiene. All spectra were obtained at 18 °C and at 55.25 MHz for ^{2}H.

the PHTP channels are entirely consistent with the known structure of 1,4-*trans*-polybutadiene but require that diffusive motions average the C–D bond vectors about the chain axis. However, it is unreasonable to expect that the *entire* polymer chain, many hundreds of angstoms in length, is spinning about its long axis.

To explain the complete averaging of the C–D bond vectors about the chain axis, we take advantage of conformational energy calculations performed by De Rosa and co-workers,[13] who find that for form II there is a very small energy difference (4.9 kJ/mol) between the skew$^-$–trans–skew$^+$ conformation and a cis–trans–skew$^-$ conformation. These cis conformations are statistically distributed along the chain with a 25% probability.[12] However, an isolated cis defect displaces the axis of the chain, so the occurrence of such a defect must be accompanied by a concomitant rearrangement of the vicinal bond conformations. Therefore, a motional mechanism involving these conformations is consistent with our NMR results, providing that the polymer in the PHTP channels (at room temperature) is in the high-temperature (form II) modification.

We now examine the low-temperature behavior of the polybutadiene–PHTP complex and then compare it to the motions of polybutadiene alone. Figure 4 shows representative solid-state deuterium NMR spectra of the polybutadiene–PHTP complex obtained at low temperatures. (The NMR line shapes are fully reversible with temperature.) Although at −159 °C the motional averaging is much slower on the deuterium NMR time scale, the pattern is still not static. Such low-temperature behavior is very unusual. For example, methyl group rotation in deuterated alanine becomes slow on the deuterium NMR time scale at approximately −140 °C.[14,15] Phenyl ring flips in the peptide enkephalin become slow at −20 °C[16] and in the amorphous regions of polybutylene terephthalate at slightly below −20 °C.[17] Tetrahedral jumps in polybutylene terephthalate become static below −90 °C.[8] That the diffusive motion of the polybutadiene chains is unusually facile at low temperatures in these inclusion complexes suggests that the energy barrier for propagation of these defects is very low. This result is direct evidence of the unique and unusual environment in the PHTP canals.

Figure 5a shows the solid-state deuterium NMR spectrum of 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene after the PHTP matrix has been removed by treatment with methanol. The fully relaxed line shape is a complex pattern that can be decomposed into two main components by using a pulse sequence that takes advantage of the large differences in the spin–lattice relaxation times between the crystalline ($T_1 \simeq 5$ s) and amorphous ($T_1 \simeq 0.3$ s) regions of polybutadiene. Under these conditions, the signal from the crystalline component is greatly attenuated, and the spectrum representing solely the amorphous component is obtained (Figure 5c). The spectrum corresponding to the crystalline component alone (Figure 5b) was obtained by subtracting the data in 5c from those in 5a. The percent crystallinity determined from these NMR data is 82%, in

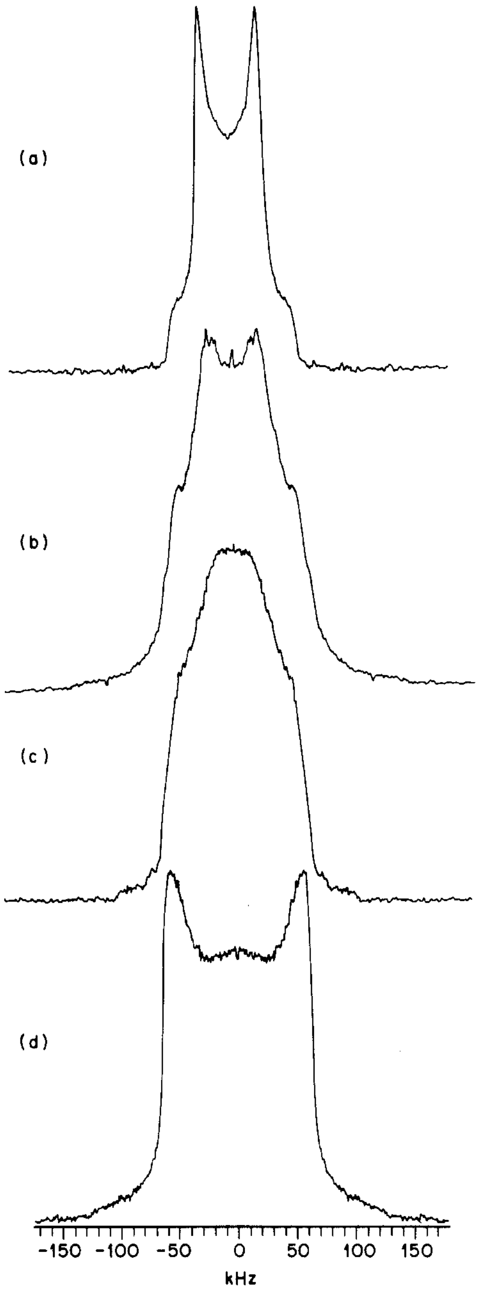

Figure 4. Low-temperature solid-state ^{2}H NMR spectra of 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene in PHTP canals: (a) 18; (b) −106; (c) −138; (d) −159 °C.

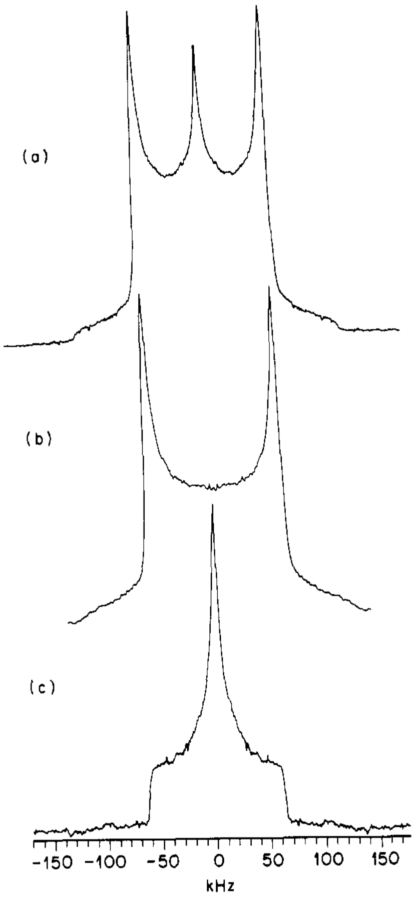

Figure 5. Solid-state ^2H NMR spectra of deuterated polybutadiene after the PHTP matrix has been removed by methanolic extraction: (a) a fully relaxed spectrum showing the complete line shape; (b) the component of the line shape that corresponds to the crystalline regions, obtained by subtracting the spectrum in (c) from the spectrum in (a); (c) a spectrum that represents the amorphous regions only. The spectrum in (c) was obtained by applying five 90° pulses separated by 2 ms to saturate the crystalline component and then waiting 100 ms for the amorphous component to relax before detecting it with the quadrupole echo pulse sequence. All spectra were obtained at 55.25 MHz for ^2H NMR and at 18 °C.

good agreement with the DSC results that indicate that the sample is 80% crystalline.[18] (Similar experiments for the recrystallized polybutadiene sample give 72% crystallinity by DSC and 77% by NMR measurements.)

The spectrum of the amorphous component (Figure 5c) is indicative of tetrahedral jumps that are rapid ($\tau_c \leq 10^{-7}$ s) on the time scale of the electric quadrupolar coupling. This spectrum can be understood as follows. Consider a deuterium that hops between two tetrahedral sites. The frequency of the perpendicular, or z, component of the electric field gradient tensor (ω_z) is unchanged by the motion and occurs at 63 kHz. The x component is averaged through the tetrahedral angle, half of which is the magic angle. This averaged component (ω_x) occurs at zero frequency. By symmetry, the third principal value must occur at $\omega_y = -\omega_z$, thus accounting for the line shape shown in Figure 5c.

Although this is the first time that tetrahedral jumps have been observed in polybutadiene, motions such as these have been observed in a number of polymers, including polybutylene terephthalate,[8] polyethylene,[19] and a number of lipids and liquid-crystalline polymers.[20] In polybutylene terephthalate, the mechanism of these tetrahedral jumps has been established as counterrotation about second-neighbor parallel bonds, as proposed theoretically by Helfand.[21,22]

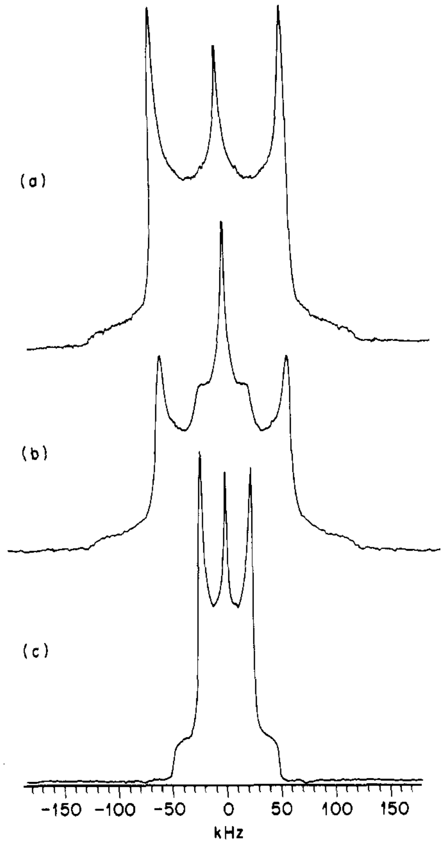

Figure 6. High-temperature solid-state ^2H NMR spectra of deuterated polybutadiene after the PHTP matrix has been removed by methanolic extraction: (a) 18, (b) 58, and (c) 79 °C.

By analogy to the solid-state ^{13}C NMR work of Schilling and Bovey on solution-crystallized 1,4-*trans*-polybutadiene[12] and to the spectrum of recrystallized 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene shown in Figure 3c, the amorphous regions that undergo these tetrahedral jumps are assigned to connections or loops between crystalline stems, while the static regions correspond to the crystal stems.

When the sample of polybutadiene without the PHTP matrix is heated to temperatures above the form I–form II, solid–solid transition (>67 °C), the molecular motion of the sample changes dramatically (Figure 6). The spectrum goes from one in which the crystalline regions are static and the amorphous regions are undergoing tetrahedral jumps to a spectrum in which the once-static chains undergo large-amplitude diffusive motions about the long axis of the chain. The quadrupolar splitting at 79 °C (Figure 6c) becomes 46 kHz, similar to that observed at room temperature and below for deuterated polybutadiene in the PHTP canals. The sharp line in the center of the spectrum is attributed to the amorphous regions. (Similar spectra were observed by Möller;[10,11] however, in these papers he incorrectly assumed that the C–D bond vector makes a 90° angle with the chain axis and therefore arrived at somewhat different conclusions.)

Conclusions

The results presented here provide explicit information about rapid ($\tau_c \leq 10^{-7}$ s) molecular motions of 1,4-*trans-1,1,4,4-d*$_4$-polybutadiene. As an isolated molecule in a PHTP inclusion complex, the C–D bond vectors of deuterated polybutadiene undergo rapid diffusional motions about the chain axis. These motions are interpreted in terms of conformational defects with very low barriers to propagation that diffuse rapidly along the polymer chain. These motions explain anomalies previously observed by

X-ray crystallography.[4,5] They are also consistent with the motions observed for form II (the high-temperature form) of recrystallized deuterated polybutadiene. These results are in agreement with a related ^{13}C MAS NMR study that shows that the chemical shifts and relaxation times of the polymer in the inclusion complex are very close to those of the polymer in form II.[23] The model proposed here is reasonable in view of the reduced mobility of polypentadiene (compared to polybutadiene) in PHTP channels as observed by deuterium NMR, due to steric hindrance by the methyl groups on the polymer chain.[24] This different behavior was also detected by ESR for the growing polymer chain end.[3b] The diffusive motions in the deuterated polybutadiene–PHTP complex are not completely frozen out ($\tau_c \leq 10^{-3}$ s) even at −160 °C, suggesting that the hydrophobic canals of the PHTP molecule provide a highly unusual environment for polybutadiene.

When the PHTP matrix is removed by methanolic extraction, polybutadiene demonstrates thermal properties that are very similar to those obtained for recrystallized polybutadiene. The experiments presented here show that polybutadiene is now comprised of crystalline and amorphous components, consistent with form I. [**Note added in proof**: Other, lower temperature methods for removing the PHTP produces a material whose amorphous region is somewhat more restricted in its motions than the material described in Figure 5c.] The amorphous components, presumably those parts of the chains forming the connections between crystallites or the loop regions, undergo rapid ($\tau_c \leq 10^{-7}$ s) tetrahedral jumps. As the temperature is raised beyond the solid–solid phase-transition and polybutadiene assumes its form II identity, the nature of the molecular motion changes abruptly. Above the form I–form II transition temperature, all of the chains undergo rapid motions that average the C–D bonds over a cylinder.

We conclude that the PHTP canals provide appropriate models for observing isolated molecules in a highly hydrophobic environments. Such models could be extended to study the motion of molecules or chromophores entrained in channel-forming proteins.

Registry No. PHTP, 119817-63-9.

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