Macromolecules **1991,** *24,* 4369–4375

Chain Conformation and Dynamics of Crystalline 1,4-*trans*-Polyisoprene and Its Inclusion Compound with Perhydrotriphenylene

Frederic C. Schilling,*,† Piero Sozzani,‡ and Frank A. Bovey†

AT&T Bell Laboratories, Murray Hill, New Jersey 07974, and Department of Organic and Industrial Chemistry, University of Milan, Milan, Italy

Received January 24, 1991; Revised Manuscript Received March 22, 1991

ABSTRACT: Crystalline 1,4-*trans*-polyisoprene and its inclusion compound with perhydrotriphenylene (PHTP) have been studied by high-resolution solid-state carbon-13 NMR spectroscopy. The chemical shift data and spin-lattice relaxation times are reported for the α- and β-polymorphs and the polymer in the inclusion compound. The results demonstrate that the polymer chains in the inclusion compound adopt a fixed skew–trans–skew conformation similar to that of the β-crystal structure. A similarity in local chain motions is observed for the polyisoprene chains of the inclusion compound and the β-form. The inclusion compound formed with PHTP and monomer isoprene has also been examined. The data indicate that isoprene adopts the same molecular conformation in the channels of the inclusion compound and in the neat liquid. While the molecules of isoprene are more restricted in the channels compared to those of neat isoprene, they do undergo rapid end-to-end flipping and rotation about the long molecular axis. This freedom of motion within the channel is reflected in the microstructure of the polymer formed by polymerization of the isoprene within the inclusion compound. The spin–lattice relaxation times of the PHTP in the inclusion compound are reduced compared to those of pure PHTP crystals and are similar to those previously reported for the 1,4-*trans*-polybutadiene/PHTP inclusion compound.

Introduction

Morphology and structure have a great influence in determining the properties of synthetic polymers. Recent advancements in solid-state characterization using NMR techniques have provided new descriptions of the intra- and intermolecular structures and chain dynamics of polymers in the bulk.[1] These techniques can examine the entire bulk sample or selectively probe individual phases possessing a wide range of order and mobility. The crystalline, amorphous, and interfacial regions of polymers have been characterized by this method.

Our interest in this field is part of a program to develop an understanding of the behavior of polymers in the solid state both in the bulk and as inclusion compounds (ICs). The analysis of polymer inclusion compounds provides an opportunity to examine the structure and mobility of polymer chains isolated from one another. Among the polymers under study are polybutadiene, polypentadiene, polyisoprene, polyethylene, polypropylene, and poly(oxyethylene). We wish to consider the following questions: (1) Is the stability of ordered aggregations of crystalline polymer chains the result of *intra*molecular or *inter*molecular forces? (2) Is it possible to induce unusual conformational structures and chain mobility by the isolation of individual polymer chains in inclusion compounds? (3) In the inclusion compound, where the polymer–polymer packing interactions are removed, is the chain structure determined by the intrinsic conformational energy, by the channel dimensions, or by both? In order to address these questions we have synthesized polymer inclusion compounds by direct solid-state polymerization and by cocrystallizing the polymer and the organic host from the melt state. These adducts and the "native" polymer were then compared to the bulk polymers of well-defined structures.[2–4] "Native" polymer is that polymer obtained directly from the removal of the organic host by extraction without any further treatment. The unique morphology of this native polymer is of special interest in that it can retain the extended chain structure of the inclusion compound. This has been observed to result in improved properties such as increased melting point.[5]

We have found the fully trans–anti isomer of perhydrotriphenylene (PHTP) to be the most versatile host for the formation of the inclusion compounds with hydrocarbon materials. Our NMR and ESR work[2–4] on the 1,4-*trans*-polybutadiene/PHTP inclusion compound (TPBD/PHTP-IC) demonstrated that the polymer chain conformation and chain dynamics were similar to that of the conformationally disordered, high-temperature form of crystalline 1,4-*trans*-polybutadiene (TPBD). In the proposed structure for this form the allylic bond samples both the cis and skew conformation, with a probability of 25 and 75%, respectively.[6] In the inclusion compound conformational averaging about this bond was observed to persist even at −160 °C, suggesting a very low energy barrier for this process and reflecting the unusual environment of the inclusion complex.[3]

In order to consider the effect of steric hindrance in determining the chain conformation and mobility within the channels of the inclusion compounds we are examining methyl-substituted TPBDs. In this report we describe the characterization of the 1,4-*trans*-polyisoprene/perhydrotriphenylene inclusion compound (TPI/PHTP-IC) and make comparisons to the two crystalline forms of bulk 1,4-*trans*-polyisoprene (TPI). In addition we compare the chain dynamics of TPI/PHTP-IC to that of TPBD/PHTP-IC.

Experimental Section

The racemic fully trans–anti isomer of PHTP was synthesized in heptane by hydrogenation of dodecahydrotriphenylene under severe conditions (295 °C, 120 atm, Pd/C catalyst, 1 week).[7] The desired isomer was recovered from the mixture of isomers by routinely precipitating the inclusion compound formed with heptane and equilibrating the residue. Heptane was removed from the inclusion compound by drying it for ca. 3 days at 10^{-4} Torr. PHTP was further purified by sublimation (80 °C, 10^{-5} Torr)

---

† AT&T Bell Laboratories.
‡ University of Milan.

and found to be >99% pure by GLC, NMR, and DSC. Crystalline PHTP was irradiated under vacuum (10^{-6} Torr) by γ-rays (^{60}Co source; 45 min, for a total dose of 0.8 Mrad). Stable radicals are formed in the solid state[2,8] and are used later to initiate the isoprene polymerization.

Isoprene (2-methyl-1,3-butadiene; bp 34 °C) was obtained from Aldrich Chemical Co. (99% pure). In order to obtain a PHTP inclusion compound containing isoprene monomer we followed two procedures. In the first, the isoprene was dried, degased, and transferred under reduced pressure over the preirradiated PHTP crystalline powder to form the isoprene/PHTP inclusion compound (I/PHTP-IC)[2] (sample 1). After several minutes the powder was transferred under nitrogen to the NMR rotor. In an alternate procedure the I/PHTP-IC was formed in situ by adding a drop of isoprene to 150 mg of PHTP that was packed in the NMR rotor. The sample was permitted to equilibrate for 5 min in air, after which time the volatile, free isoprene has escaped from the sample. Spectra were then collected on the resulting I/PHTP-IC (sample 2). The signals of the guest monomer molecules disappear in about 20 min due to the volatility of isoprene.

In order to obtain a TPI/PHTP-IC with a high conversion of monomer to polymer, an excess of isoprene is transferred under vacuum to a vial containing preirradiated PHTP; the monomer is put in contact with the PHTP at +70 °C and the monomer inclusion compound forms immediately.[9] This inclusion compound is held under the atmosphere of isoprene at +70 °C as the polymerization proceeds. At this temperature the optimum filling of the channels with polymer is achieved. After 2 days an 80% conversion of monomer to polymer is obtained. The extraction with boiling methanol of the PHTP from the TPI/PHTP-IC leads to pure, native TPI, which has been completely characterized by solution-state ^{13}C NMR analysis.[9] Molecular weights of the polyisoprene were kept low in order to avoid solubility problems and range from 3000 to 5000.[9] The molecular weight is controlled by varying the time for polymerization. Samples of the TPI/PHTP-IC were also prepared without preirradiation of the PHTP material. In this case initiation of the polymerization is accomplished by direct irradiation of the I/PHTP-IC. DSC analysis of the inclusion compounds was performed on a Perkin-Elmer DSC-4 calorimeter equipped with a Model 3600 data station.

The 50.3-MHz solid-state ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. The cross-polarized (CP), magic-angle spinning (MAS), dipolar-decoupled (DD) spectra were recorded by using a Doty Scientific probe with sapphire rotors spinning at rates ranging from 3 to 4 kHz. Spectra were recorded with a 20-kHz sweep width in 8K data points. The spin–lattice relaxation times were recorded by using a CPT$_1$ pulse sequence.[10] Chemical shifts were referenced to TMS by recording the spectrum of poly(oxymethylene) (POM) (89.1 ppm versus TMS) before and after the accumulation of each spectrum.

Results and Discussion

PHTP. We have examined a number of host matrices for the preparation of synthetic polymers and have selected perhydrotriphenylene (PHTP) as the most versatile for our purposes. PHTP inclusion polymerization is a well-established synthetic method for obtaining polymers and copolymers of well-defined structure.[11] Pure crystalline PHTP adopts a monoclinic structure and does not contain any channels.[12] Upon exposure of PHTP to small organic molecules a solid-state transformation occurs during which the channels containing the organic guest molecules are formed. Polymer/PHTP inclusion compounds are formed by the polymerization of monomers within an inclusion compound or by cocrystallizing PHTP and polymer from solution or the melt state.

In the inclusion compounds the molecules of PHTP form a cylindrical arrangement about the guest molecules as shown in Figure 1. The six molecules of PHTP that form the channel exist in two groups on different planes. The channels of PHTP are held together by van der Waals forces rather than by hydrogen bonding as in the clathrates of urea, thiourea, or cyclodextrin, which are also popular matrices for polymerization. The outline of the van der Waals surfaces of the channel is seen in Figure 1. The crystal structures of PHTP inclusion compounds were defined in a number of cases by X-ray diffractometry. The cross section of the channels was determined to be about 5.5 Å for most structures.[12,13] The average thickness of the crystals is in the range 1–1000 μm, producing channels that are much longer than an extended chain polymer of high molecular weight. The polymer represents about 10–15% by weight of the inclusion compound.

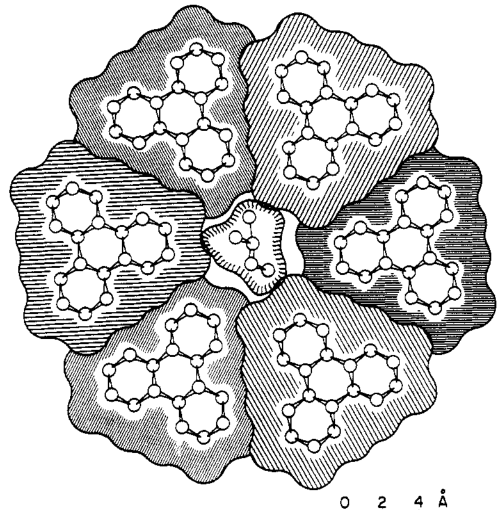


Figure 1. Schematic representation of 1,4-*trans*-polyisoprene chain in the PHTP inclusion compound as determined by X-ray diffraction.[12,13]

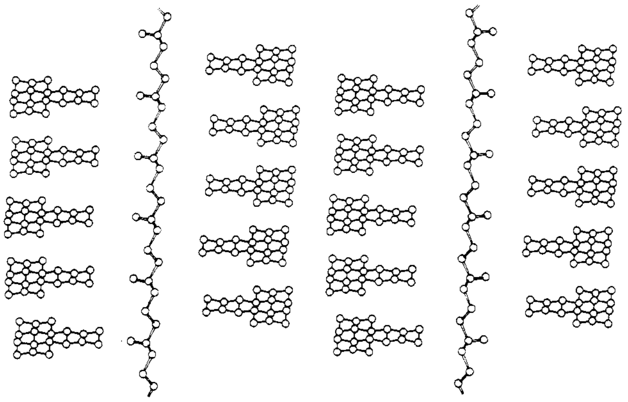


Figure 2. Side view of the TPI/PHTP-IC showing only the carbon nuclei.

A side view of the TPI/PHTP-IC is shown in Figure 2. For clarity only the carbon nuclei are illustrated. The orientation of the chain about its long axis and the vertical positioning within the channel is arbitrary as X-ray data of this particular IC are not available. The repeat distance of a single isoprene unit[14] is 4.72 Å in the β-form of TPI and 4.39 Å in the α-form compared to a separation of 4.78 Å betwen the PHTP molecules along the channel of an IC.[12,13] Therefore, if the polymer adopts the conformation of the α-form in the IC, the similarity of the polymer and matrix repeat would make identification of the polymer by X-ray very difficult. In contrast, if the polymer chain in the IC adopts the conformation of the β-form, we would expect identification of the polymer by X-ray to be feasible.

Monomer Inclusion Compounds. In order to study the I/PHTP-IC we characterized the adduct of preirradiated PHTP with the monomer (sample 1) before

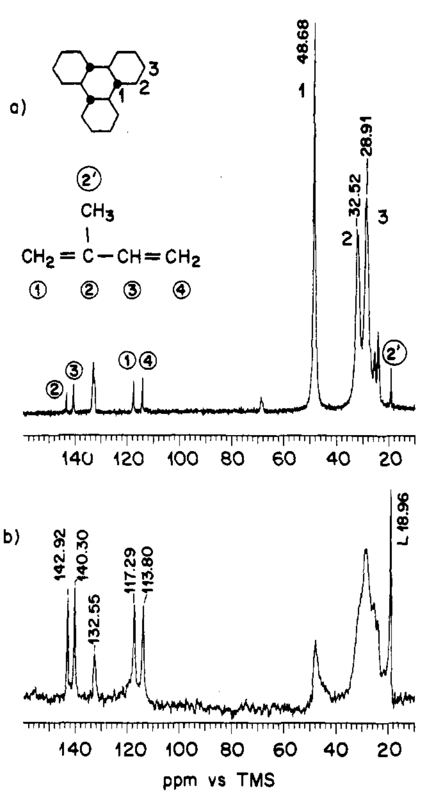


Figure 3. 50.3-MHz ^{13}C solid-state NMR spectra of isoprene monomer in PHTP matrix (I/PHTP-IC) at 23 °C: (a) CPMAS/DD and (b) MAS/DD.

significant polymerization can occur. The results were compared and confirmed with those obtained from sample 2, prepared with nonirradiated PHTP. The solid-state ^{13}C NMR spectra of sample 1 are shown in Figure 3. The cross-polarization technique used in recording the spectrum in Figure 3a enhances the resonances of the PHTP carbon nuclei relative to the carbon signals of the isoprene molecule. We obtained the assignment of the chemical shifts of isoprene from a two-dimensional heteronuclear correlation experiment. The chemical shift pattern of PHTP in the I/PHTP-IC differs from that observed for pure PHTP crystals.[4] After the volatile isoprene monomer escapes from the matrix the chemical shift pattern (not shown) reverts back to that of pure PHTP, reflecting the transformation from the inclusion compound to PHTP crystals.

The unlabeled resonances at 24, 26, and 132 ppm in Figure 3a are attributed to a small amount of dodecahydrotriphenylene that is produced during the γ-irradiation of the PHTP. In dodecahydrotriphenylene the center ring is aromatic. These chemical shifts are within 0.9 ppm of the values we observe for dodecahydrotriphenylene in solution. The resonances in question are not observed in the spectrum (not shown) of sample 2, the I/PHTP-IC formed without preirradiation of the PHTP.

The spectrum in Figure 3b is recorded without cross-polarization and with a pulse interval of 10 s. A significant suppression of the resonances (28–32 and 48 ppm) associated with the PHTP is observed relative to the signal strength recorded under conditions of cross-polarization. Although mobile compared to the PHTP portion of the matrix, the isoprene is not as mobile as in the neat liquid. This is reflected in the change of carbon spin–lattice relaxation times, T_1, that range from 20 to 40 s in neat isoprene but are reduced to 3–10 s in the inclusion compound. The X-ray data for the butadiene/PHTP inclusion compound indicate that the cross section of the channels are markedly elongated in order to accommodate the included butadiene molecules.[13] Following the butadiene polymerization the channels are observed to become nearly cylindrical.[13] X-ray data are not yet available for the isoprene/PHTP inclusion compound. However, if we assume that the channels of the I/PHTP-IC are also elongated, then molecular motion of isoprene will be limited to end-to-end flipping and rotation about its long axis within the channel. The length of the isoprene molecule is ca. 5.5 Å including the van der Waal surfaces of the protons. In addition, the channels prohibit translational motions of isoprene molecules. Thus the observed reduction in the value of the carbon T_1 in isoprene reflects the change in the nature of the molecular motion and the resultant increase in the correlation time. As shown in Table I the chemical shifts of the isoprene carbon nuclei in the inclusion compound and the neat liquid differ by only a few tenths of a ppm. This similarity in chemical shift demonstrates a similarity in the average molecular conformation. Rapid molecular reorientation of isoprene within the channels is also consistent with the microstructure of polyisoprene synthesized in the matrix at different temperatures (see below).[9]

Table I
^{13}C Chemical Shifts (ppm) of Isoprene at +23 °C

carbon[a]	neat liquid	I/PHTP-IC
2	143.1	142.9
3	140.7	140.3
1	117.3	117.3
4	113.9	113.8
2′	18.5	19.0

[a] See Figure 3a for designations.

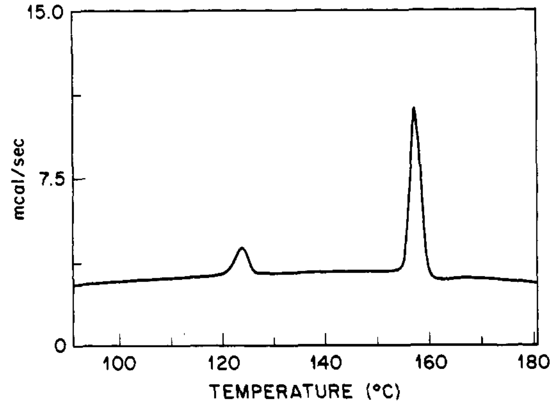
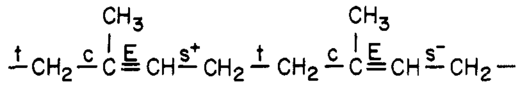


Figure 4. DSC thermogram of the inclusion compound formed by PHTP and 1,4-*trans*-polyisoprene (TPI/PHTP-IC).

Polymer Inclusion Compounds. The TPI/PHTP-IC is formed by holding the preirradiated I/PHTP-IC at 70 °C for 1 h. Evidence for the formation of the polymer inclusion compound is seen in the DSC thermogram of the TPI/PHTP-IC shown in Figure 4. The larger endotherm at 157 °C is the melting of the TPI/PHTP-IC and the smaller endotherm at 123 °C is the melting of pure PHTP, which represents about 15% of the total sample.

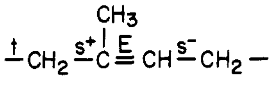
The NMR spectrum of this polymer inclusion compound is shown in Figure 5a. These data are recorded with cross-polarization and, as expected, the carbon resonances of the PHTP molecules are very strong. The PHTP signals are the truncated resonances at ca. 30 and 48 ppm. Four of the five resonances associated with the repeat unit of the polyisoprene chain are identified in the figure, with the C_4 methylene peak lost beneath a large PHTP resonance. Unreacted monomer that is trapped in the inclusion compound produces the five resonances labeled "m". These volatile isoprene molecules cannot diffuse from the solid-state complex becaues they are trapped between the ends of polymer chains. We think that this is the first example of volatile monomer molecules trapped by the polymer chains within an inclusion compound.

In order to determine the conformation of the polyisoprene chain within the channels of the inclusion compound we have compared the NMR data of the TPI/PHTP-IC to the chemical shift data that we have recorded for the two known crystalline conformers of pure 1,4-*trans*-polyisoprene. The conformations of the α- and β-polymorphs are as follows:



$$\overset{t}{-}CH_2\overset{c}{-}\overset{CH_3}{\overset{|}{C}}\overset{E}{=}CH\overset{s^+}{-}CH_2\overset{t}{-}CH_2\overset{c}{-}\overset{CH_3}{\overset{|}{C}}\overset{E}{=}CH\overset{s^-}{-}CH_2-$$

α - FORM



$$\overset{t}{-}CH_2\overset{s^+}{-}\overset{CH_3}{\overset{|}{C}}\overset{E}{=}CH\overset{s^-}{-}CH_2-$$

β - FORM

The α-form is adopted by the polymer under normal crystallization conditions from solution or the melt, and the β-form is obtained by quenching from the melt. The difference between these two structures is the conformation at the CH_2–CCH_3 bond, which is cis in the α-form[14] and skew in the β-form. The conformation of the β-form is the same as that for the low-temperature structure (form 1) of 1,4-*trans*-polybutadiene.[15] The sensitivity of the chemical shift of carbon nuclei to differences in specific bond conformation is the result of changes in the relationships of nuclei separated by three bonds, called the γ-gauche effect.[16] In the case of the α- and β-forms the difference in conformation at the CH_2–CCH_3 bond will affect the methyl, methine, and C_4 methylene carbons (see Figure 5a for designations). The carbon chemical shift data for these two polymorphs of TPI are given in Table II together with the data for TPI/PHTP-IC. The last two columns in Table II indicate the absolute difference in ppm for each resonance of the inclusion compound compared to the α- or β-polymorph. As indicated earlier the C_4 methylene resonance for the inclusion compound is obscured by a resonance of the PHTP molecule. For the 2′-methyl carbon the difference between the IC and the β-form is 0.3 ppm while the difference for the α-form is 2.3 ppm. Similarly, the difference between the IC and the β-form is only 0.5 ppm for the C_3 methine carbon compared to a difference of 3.5 ppm versus the α-form. On the basis of these comparisons we conclude that the polyisoprene chains in the channels of the PHTP matrix adopt the skew–trans–skew conformations of the β-form of crystalline TPI.

Of course, in addition to the chemical shift differences resulting from conformational variations, some differences in chemical shift are expected to result from the variations in crystal packing of the polymer chains of the α- and β-forms or from the lack of such packing in the inclusion compound. We attribute the differences in chemical shift for carbons 1 and 2 of the inclusion compound, the α-form, and the β-form to crystalline packing effects.

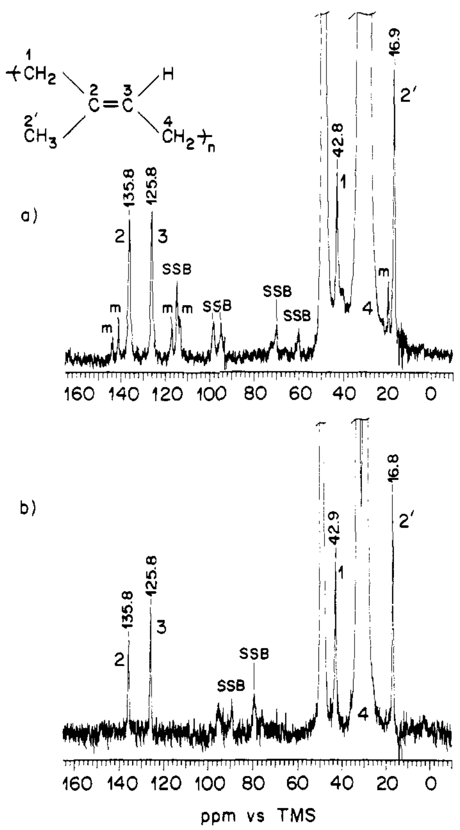


Figure 5. 50.3-MHz ^{13}C NMR CPMAS/DD spectra of TPI/PHTP-IC at 23 °C: (a) polyisoprene synthesized in PHTP and (b) polyisoprene cocrystallized with PHTP from the melt ("m" indicates resonance of residual monomer and "ssb" indicates spinning side band).

Table II
^{13}C Chemical Shifts (ppm) of 1,4-*trans*-Polyisoprene (TPI) at +23 °C

carbon[a]	TPI/ PHTP-IC	TPI β-form	TPI α-form	Δ IC − β	Δ IC − α
2	135.8	137.4	136.5	1.6	0.7
3	125.8	126.3	122.3	0.5	3.5
1	42.8	43.4	40.4	0.6	2.4
4		30.8	28.3		
2′	16.9	17.2	19.2	0.3	2.3

[a] See Figure 5a for designations.

The TPI/PHTP-IC can also be formed by cocrystallizing polyisoprene with PHTP from the melt. We have prepared an inclusion compound by this method using Balata, a pure head-to-tail 1,4-*trans*-polyisoprene. The ^{13}C NMR spectrum is shown in Figure 5b, where the chemical shifts of the polymer are observed to be nearly identical with those recorded for the polymer synthesized in the PHTP matrix (Figure 5a). This demonstrates that the polymer chains of the inclusion compound formed by cocrystallization also adopt the the conformation of the β-form.

The similarity of the polymer chains in TPI/PHTP-IC and the β-form of TPI is also observed in the local chain motions as reflected in the ^{13}C spin–lattice relaxation times (T_1) for the polymers. The T_1 values for the carbon nuclei of the inclusion compound, the α-form, and the β-form are given in Table III. The values for most of the carbons in the TPI/PHTP-IC and β-form are similar and somewhat shorter than those found in the α-form. This probably results from somewhat greater mobility of the chains in the TPI/PHTP-IC and β-form compared to the α-form. In making this comparison of relaxation data we must

Table III
^{13}C T_1 Values[a] (s) of 1,4-*trans*-Polyisoprene (TPI) at +23 °C

carbon[b]	TPI/PHTP-IC	TPI β-form	TPI α-form
2	70	50	100
3	50	50	100
1	80	80	120
4		90	110
2′	60, 10	40, 10	40, 7

[a] ±10%. [b] See Figure 5a for designations.

consider the potential contribution of the perhydrotriphenylene protons to the relaxation of the carbon nuclei in the polymer chains. In our earlier studies of the TPBD/PHTP-IC we observed a similarity of carbon T_1 data for the inclusion polymer and bulk TPBD in form II.[4] We also observed a similar deuterium coupling pattern for deuterated polymer in the channels and in the bulk form II.[3] The similarity of coupling patterns is direct evidence that the nature of the polymer chain motions is the same in the channel and in the bulk polymer. These observations demonstrated that in TPBD/PHTP-IC the near static protons of the perhydrotriphenylene molecules do not make a significant contribution to the relaxation of the carbon nuclei in the polymer. We assume that the same situation occurs in the TPI/PHTP-IC and that the similarity of relaxation times suggests a similarity of chain motions.

The relaxation times for the TPI/PHTP-IC also indicate that the polymer chains are much more restricted in local motion compared to the 1,4-*trans*-polybutadiene chains[4] in the PHTP matrix for which the T_1 values are 8–10 s. The relaxation curves for some of the carbon nuclei of the polymer in TPI/PHTP-IC do not follow a simple exponential decay. A two-component curve is necessary to fit the data of the methyl carbon. This suggests two distinct environments for these nuclei. It is possible that there are two types of methyl carbons within the channel and that they differ in their proximity to the number three carbons of the PHTP molecules (see Figure 3a for designation). The C_3 carbons of PHTP, which are closest to the guest molecules in the channel, also have distinct, two-component relaxation curves (see below).

The experimental observation of a fixed conformation and a lack of local chain mobility for polyisoprene in the inclusion compound is consistent with Tonelli's calculation of possible TPI conformers in the PHTP channels.[17] For a channel of <6 Å the isoprene repeat unit can only adopt the skew–trans–skew conformations of the β-form and interconversion between conformations (e.g., skew$^+$ to skew$^-$) is prohibited by the channel dimensions. However, neighboring monomer units may differ in the signs of the skew conformations. For example, the following conformational sequences of the carbon–carbon single bonds can be adopted by the polymer chain: s$^+$–t–s$^-$; s$^+$–t–s$^+$; s$^-$–t–s$^-$; s$^-$t–s$^+$.[17] In β-TPI the conformation is regular in the sign of the skew conformations in order to maximize interchain packing within the crystal. No such requirement exists for the isolated polyisoprene chain in the inclusion compound. Therefore, we expect that such chains will adopt a random distribution of the possible conformers that differ only in the sign of the skew conformation. Unfortunately, the chemical shift data will not show a difference between a regular or random distribution of these skew–trans–skew conformations.

The conformation of the β-form is slightly lower in energy than the skew–trans–cis conformation of the α-form;[18] however, the α-form is adopted in the normal crystallization of polyisoprene, probably the result of better interchain packing as suggested by conformational and packing energy calculations.[19] The study of methyl-substituted polybutadienes in channels with larger dimensions is planned in order to determine the conformations adopted when the geometric constraints permit conformers differing significantly in energy.

Native 1,4-*trans*-Polyisoprene. The crystals of PHTP inclusion compounds are very thick, with dimensions on the order of many micrometers.[12] Since the average polyisoprene chain in our sample contains ca. 60 monomer units, each channel of the matrix will contain many polymer molecules. Native polyisoprene is obtained from the inclusion compound by complete dissolution of the PHTP host molecules with boiling methanol. The native polymer, if crystalline, will have a unique morphology due to the preservation of the extended chains in the inclusion structure.

The degree of crystallinity of 1,4-*trans*-polyisoprene isolated from PHTP depends on the polymerization temperature, being inversely proportional to the content of head-to-head defects. The native polymer synthesized at −60 °C melts at +40 °C and, after annealing, shows an endotherm of 40 J g^{-1}.[9] For comparison the melting point of high molecular weight 1,4-*trans*-polyisoprene without head-to-head defects is +74 °C.[20] Our DSC traces of the inclusion compounds prepared at +70 °C show no transition in the 0–80 °C region, indicating that the materials are amorphous. Our solid-state NMR data for this polymer indicate a head-to-head, tail-to-tail content of 12%, in agreement with a solution NMR analysis[9] that found inverted unit concentrations of 7–16% for inclusion compounds prepared at −60 to +70 °C. It was determined that the succession of opposite units along the polymer chain is purely random[9] and only polymers synthesized at −40 and −60 °C show evidence of crystallinity.

The change in concentration of defects with temperature[9] and the random placement of the inverted monomer units in the inclusion compounds[9] suggest that the reactivity of the growing chain radicals controls the regioregularity of the polymer chain as in solution polymerizations of isoprene. In fact, at a given temperature the amount of reaction between the growing radical on carbon 1 (versus carbon 4) and the approaching monomer is the same in polymers obtained by free radical polymerization in solution and by the inclusion polymerization.[9] This interpretation requires that the monomer molecules rapidly flip end to end as the polymerization proceeds, since we presume that there is no directional bias in how the monomer molecules fill the channels of the I/PHTP-IC. While we cannot rule out the possibility of a temperature-dependent bias during channel filling, the coincidence of the defect content between solution and inclusion polymerization data over a wide temperature range strongly suggests rapid averaging of monomer orientation within the inclusion compound. The NMR relaxation times we have observed for the monomer molecules in the channels of the PHTP inclusion compound are consistent with our description. Support is also offered by the ESR observation of the dominance of the radical on carbon C_4 compared to the radical on carbon C_1 in the propagation step.[2]

The amorphous nature of the native polyisoprene from our inclusion compound prepared at +70 °C is reflected in a dramatic reduction in carbon T_1 values, which range from 0.1 to 1.3 s, compared to the 40–120-s values observed for the crystalline portion of bulk polyisoprene (see Table III). We also observe similarly short T_1 values for the amorphous portions of the pure polyisoprene samples in the α- and β-forms.

Table IV
^{13}C T_1 Values[a] (s) of Perhydrotriphenylene (PHTP) at +23 °C

carbon[b]	PHTP	TPBD/PHTP-IC	TPI/PHTP-IC	I/PHTP-IC
1	390	180	180	160
2	320	160	160	120
3	260	110	180, 20	120, 25

[a] ±10%. [b] See Figure 3a for designations.

Native polymer obtained from the inclusion compound prepared by the cocrystallization method shows a level of crystallinity of ca. 30% with a melting point of +60 °C, about 15 °C below that of solution-crystallized 1,4-*trans*-polyisoprene. The low degree of crystallinity and low melting point for this native polyisoprene are attributed to difficulties experienced in extracting the PHTP from the inclusion compound.

PHTP Dynamics. Our NMR relaxation studies also indicate a change in the motional characteristics of the PHTP molecule when an inclusion compound is formed. The T_1 values for the three carbons of PHTP are given in Table IV. In the pure monoclinic crystalline PHTP the relaxation times are ca. 250–400 s, as would be expected for a rigid lattice structure. After TPBD or TPI is polymerized within the PHTP matrix, we observe about a 50% reduction in the carbon relaxation times of PHTP. A similar effect is observed in the I/PHTP-IC. One possible explanation for these observations is that the protons of the more mobile polymer chains or monomer molecules moving within the channels of the inclusion compound reduce the relaxation times of the nuclei in the PHTP molecules. However, we should then expect the mobile isoprene molecules in the I/PHTP-IC and the mobile polybutadiene chains in the TPBD/PHTP-IC to generate a larger reduction in relaxation times than the rigid, conformationally fixed polyisoprene chains in the TPI/PHTP-IC. This is not observed. Also, in the structure of the inclusion compounds only the C_3 carbon of PHTP is close to the protons of the monomer or polymer molecules, yet the reduction in the major component of the relaxations times is uniform for the three carbon types. Therefore, this interpretation of the data would require substantial proton spin diffusion within the PHTP matrix. An alternative explanation for the observed reduction in the values of T_1 for the PHTP is that the inclusion compound is a less rigid structure than the pure crystalline PHTP. The increase in motion of the PHTP molecules within the matrix results in more efficient dipolar interactions between the carbons and proton nuclei. Relaxation measurements of the PHTP molecules in the presence of perdeuterated polymers are planned in order to provide the necessary evidence to resolve this issue.

There is only a single relaxation time for carbons 1 and 2 of PHTP in the I/PHTP-IC and TPI/PHTP-IC. In contrast, the relaxation data for the number 3 carbon in these structures has two components (Table IV). The shorter component represents 35 and 43% of the nuclei in the monomer and polymer inclusion compounds, respectively. This suggests that there are two distinct environments that differ in the proximity of carbon 3 of PHTP to the methyl group of isoprene. Consistent with this interpretation, the data in Table IV also show that only a single relaxation time is found for carbon 3 of PHTP in the TPBD/PHTP-IC and PHTP itself.[4]

Conclusion

We have examined the PHTP monomer isoprene inclusion compound and the PHTP polyisoprene inclusion compounds formed by polymerization within the organic matrix or by cocrystallizing polymer and PHTP. The I/PHTP-IC can be studied under an atmosphere of isoprene. The channels of this matrix are probably elongated as in the butadiene inclusion compound. This will restrict the motion of isoprene to end-to-end flipping and rotation about the long molecular axis. Molecular rotation about an axis parallel to the channel and translational motions will be prohibited. These changes in motion are reflected in a decrease in the carbon relaxation times for isoprene in the channel compared to pure liquid isoprene. Consistent with this observation, a microstructural analysis of the polymer prepared from the I/PHTP-IC indicates that the monomer molecules flip rapidly end to end within the PHTP channels, permitting the regioregularity of the chain to be determined by the reactivity of the growing chain radicals.

The solid-state NMR characterization of the TPI/PHTP-IC shows that unreacted monomer becomes trapped between the ends of polymer molecules within the channels of the polymer inclusion compound. Each channel of the inclusion compound is sufficiently long to contain many polymer molecules. The polymer chains in these channels adopt a fixed skew–trans–skew conformation similar to that of the β-form of crystalline 1,4-*trans*-polyisoprene. This conformation has been calculated to be the lowest energy conformation for an isolated chain of polyisoprene. However, in the inclusion compound it is not necessary for the signs of the skew conformations along the chain to alternate in a regular manner as in β-TPI. The local chain motions of the polymer in the inclusion compound are also similar to those of the polymer in the β-form and much reduced compared to those of the polymer in the TPBD/PHTP-IC where conformational averaging occurs. The polymer chain in the TPI/PHTP-IC formed by cocrystallization has the same conformational and motional properties as polymer synthesized within the inclusion compound.

Because of the large amount of regioirregularity, the native polyisoprene from the inclusion compound synthesized at +70 °C is amorphous. Native polymer obtained from the inclusion compound prepared by the cocrystallization method shows a level of crystallinity of ca. 30% with a melting point of +60 °C, about 15 °C below that of solution-crystallized 1,4-*trans*-polyisoprene. This reduction in melting point is attributed to difficulties in the extraction of the TPI/PHTP-IC.

The PHTP molecules of the inclusion compounds are observed to have reduced carbon spin–lattice relaxation times compared to that of pure PHTP. This can be attributed to either increased motion of the PHTP molecule within the inclusion compound or a specific dipolar interaction between the protons of the guest molecules in the channels and the PHTP molecule. Carbon 3 of PHTP, which is in close proximity to the guest molecules, has a short and long relaxation component as do the methyl carbons of the guest isoprene and polyisoprene molecules. This probably results from two environments that differ in the distance between carbon 3 of PHTP and the methyl carbon.

In future work we will examine methyl-substituted polybutadienes in channels of larger dimension to determine the conformations adopted by such polymers in an environment of reduced geometric constraints.

Acknowledgment. We thank Dr. G. G. Torri for obtaining the two-dimensional heterocorrelated spectrum of isoprene.

References and Notes

(1) *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH Publishers: Deerfield Beach, FL, 1986.

(2) Sozzani, P.; Di Silvestro, G.; Gervasini, A. *J. Polym. Sci., Part A, Polym. Chem. Ed.* **1986**, *24*, 815.

(3) Sozzani, P.; Behling, R. W.; Schilling, F. C.; Brückner, S.; Helfand, E.; Bovey, F. A.; Jelinski, L. W. *Macromolecules* **1989**, *22*, 3318.

(4) Sozzani, P.; Bovey, F. A.; Schilling, F. C. *Macromolecules* **1989**, *22*, 4225.

(5) Farina, M.; Di Silvestro, G. *Makromol. Chem.* **1982**, *183*, 241.

(6) Schilling, F. C.; Gómez, M. A.; Tonelli, A. E.; Bovey, F. A.; Woodward, A. E. *Macromolecules* **1987**, *20*, 2954 and references therein.

(7) Farina, M.; Pedretti, U.; Gramegna, M. T.; Audisio, G. *Macromolecules* **1970**, *3*, 475.

(8) Sozzani, P.; Scotti, R.; Morazzoni, F. *J. Chem. Soc., Faraday Trans 1* **1989**, *85*, 2581.

(9) Di Silvestro, G.; Sozzani, P.; Farina, M. *Macromolecules* **1987**, *20*, 999.

(10) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.

(11) Di Silvestro, G.; Sozzani, P. In *Comprehensive Polymer Science*; Eastmond, G. C., et al., Eds.; Pergamon Press: Oxford, 1988; Vol. 4, p 303.

(12) Allegra, G.; Farina, M.; Immirzi, A.; Columbo, A.; Rossi, U.; Broggi, R.; Natta, G. *J. Chem. Soc. (B)* **1967**, 1020.

(13) Colombo, A.; Allegra, G. *Macromolecules* **1971**, *4*, 579.

(14) Takahashi, Y.; Sato, T.; Tadokoro, H.; Tanaka, Y. *J. Polym. Sci.; Polym. Phys. Ed.* **1973**, *11*, 233.

(15) Natta, G.; Corradini, P.; Porri, L. *Atti. Accad. Naz. Lincei* **1956**, *20*, 728.

(16) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.

(17) Tonelli, A. E. *Macromolecules* **1990**, *23*, 3129.

(18) Flory, P. J. In *Statistical Mechanics of Chain Molecules*; Wiley-Interscience: New York, 1969; Chapter 5.

(19) Napolitano, R.; Pirozzi, B. *Makromol. Chem.* **1986**, *187*, 1993.

(20) Wunderlich, B. In *Macromolecular Physics*; Academic Press: New York, 1973; Vol. 1, p 388.