Characterization of Isolated Polyethylene Chains in the Solid State

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ABSTRACT: The study of polyethylene (PE) in the perhydrotriphenylene inclusion compound permits a characterization of the conformation and chain motions of the isolated polymer chain. Our solid state ^{13}C NMR results indicate that isolated chains of PE adopt an all-trans planar zigzag conformation similar to that of bulk crystalline PE. Variable-temperature spin-lattice relaxation measurements demonstrate that PE in the inclusion compound undergoes considerable local motion compared to the chains of the bulk material. The activation energy associated with this motion is 1.1 kcal/mol. This low-energy barrier suggests that the solid-state motions are not the result of trans-gauche conformational averaging. Several chain motions with low barriers are proposed to account for the increased flexibility of the isolated chains. These include rigid-rod rotation about the long axis of the molecule, librational motions at each carbon-carbon bond, and the translational movement of a "twiston", a conformational arrangement of ca. 12 bonds that introduces a 180° twist into the polymer chain. These motions are not identified in crystalline polyethylene at room temperature but may be related to the α_c relaxation process that occurs in crystalline polyethylene at elevated temperatures.

Introduction

Recently we proposed a new methodology for studying the conformation and the mobility of polymer chains that are segregated from one another in the solid state. This involves the application of solid-state magnetic resonance techniques (^2H NMR, ^{13}C NMR, and ESR) in the characterization of inclusion compounds that contain channels with appropriate dimensions for guest polymer chains.[1-5]

This approach has led to the observation of unusual conformational arrangements for some polymer chains that are confined in a tubular space. Depending on the relative dimensions of the polymer chain and the channel of the host matrix, the nonspecific environment of an inclusion compound can either produce constraints on the degree of freedom of the polymer chain or provide increased mobility about specific bonds of the macromolecule.

We have found the all-trans isomer of perhydrotriphenylene (PHTP), a hydrocarbon matrix, to be most suitable for our current studies. PHTP rapidly forms inclusion compounds (ICs) with many important polymers.[6] Some of these polymer inclusion compounds can be obtained by direct synthesis, starting from the monomer inclusion compounds.[7] A cross-sectional view of the typical structure of a crystalline adduct of PHTP with a polymer, as deduced from crystallographic data, is shown in Figure 1.[8] The cylindrical packing arrangement consists of two groups of three PHTP molecules that are packed on different planes, as indicated by the line drawings in the figure. The PHTP typically represents 90% by weight of the IC.

Polymers with differences in chain mobility and conformational arrangements compared to the same polymer in the bulk crystalline state have been identified in a series of 1,4-*trans*-polydiene/PHTP inclusion compounds. A solid-state ^2H and ^{13}C NMR study has demonstrated that the room-temperature conformation and chain dynamics of 1,4-*trans*-polybutadiene (TPBD) in the channels of the PHTP matrix are the same as those observed in the high-temperature crystal modification (form II) of the bulk TPBD.[3,4] The chain motion is still present at low temperature (−160 °C) and has been attributed to the presence of conformational defects with very low barriers to propagation that travel rapidly along the polymer chain.[3]

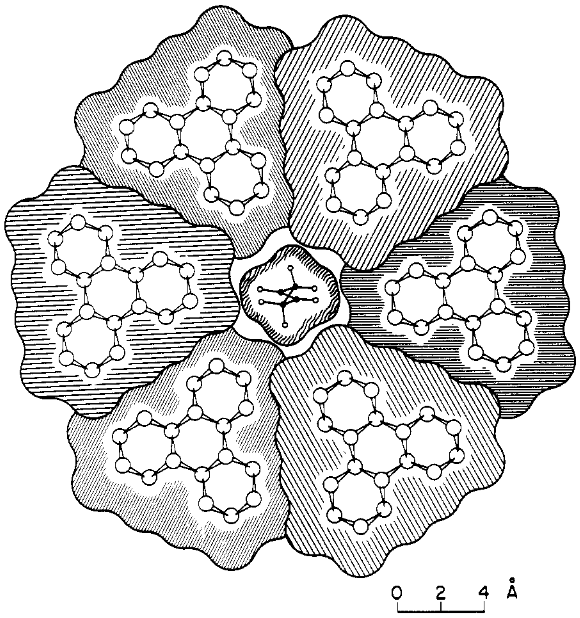

Figure 1. Schematic representation of a polymer chain in the PHTP inclusion compound, as determined by X-ray diffraction.[8] In this cross-sectional view the polymer is contained in a channel perpendicular to the plane of the paper. The projections of the van der Waals limiting surface of the polymer and PHTP molecules are shown.

The substitution of a methyl group for the hydrogen atom on the double bond transforms TPBD into 1,4-*trans*-polyisoprene (TPI). This structural change generates sufficient steric hindrance to substantially reduce the motion of the polymer molecules within the 5.5-Å channel of PHTP and is confirmed by variable-temperature ESR measurements of the chain ends.[1] The ^{13}C NMR chemical shift data demonstrate that the TPI chain in the inclusion

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compound adopts a conformational arrangement similar to the less stable β polymorph of crystalline TPI.[5,9]

An intermediate degree of mobility was observed by ^{2}H NMR spectroscopy in isotactic 1,4-*trans*-polypentadiene (TPPD).[2] The motion results from localized jumps to higher energy conformations at specific bonds along the macromolecule. Our observation of a decrease in chain mobility as a result of an increase in the steric hindrance of groups along the diene polymer chain agrees with Tonelli's rotational isomeric state (RIS) calculations on polymer chains confined in straight cylinders with the diameter of the PHTP channels.[10]

We now shift our attention to the saturated analogues of these diene molecules, i.e. the two commercially important polymers, polyethylene (PE) and polypropylene. Urea inclusion compounds containing alkanes of different length have been studied by carbon[11] and deuterium[12] NMR techniques, but we are not aware of any published work related to the NMR characterization of the polyethylene/perhydrotriphenylene inclusion compound (PE/PHTP-IC). We describe here our solid-state ^{13}C NMR study of PE/PHTP-IC. The polypropylene/PHTP-IC will be described in a subsequent report. On the basis of our studies of diene polymer inclusion compounds, the isolation of single chains of polyethylene in the noninteracting and "large" channels of the PHTP matrix may be expected to introduce some new conformational and motional properties to the polymer.

IR studies have suggested that the chain mobility in the high-temperature phase of crystalline *n*-alkanes results from "conformational solitons"[13] or *gtg′* type conformational defects[14] that propagate rapidly along the chain. The subject of solitons in polyethylene has generated much debate. An examination of isolated polyethylene chains in the solid state may provide an opportunity to identify solitons by a spectroscopic technique. The α_c relaxation process in PE is thought to require a rotational-translational motion of the polymer chains in the crystalline phase. A number of mechanisms have been suggested that could give rise to this type of motion.[15] The study of isolated PE chains in the solid state may provide information about these motions.

Experimental Section

Materials. The racemic trans–anti–trans–anti–trans–anti isomer of PHTP was synthesized, as described elsewhere,[16] precipitated as an inclusion compound with heptane, and purified by sublimation at 10^{-4} Torr and 80 °C. It was checked by GLC, NMR, and DSC methods and found to be >99% pure. The polyethylene used in the preparation of the polymer inclusion compound was synthesized from diazomethane according to standard procedure.[17] The synthesis yields a linear, high-density polyethylene that has a melting point of 137 °C. The molecular weights, M_n and M_w, as determined by GPC, were 1.75×10^4 and 7.49×10^4, respectively. Inclusion compounds of polyethylene with PHTP were formed by melting mixtures of the components (PE:PHTP ratio of ca. 1:10 w/w) in vials sealed under vacuum. The vials were held at 190 °C for 3 h and then cooled slowly (0.5 °C/min) to room temperature. The formation of the IC in each sample was monitored by DSC analysis.

Methods. Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer DSC-4 equipped with a Model 3600 data station. Solid-state NMR spectroscopy was performed at 50.3 and 100.5 MHz on Varian XL-200 and Unity-400 spectrometers, respectively. The cross-polarized (CP), magic angle spinning (MAS), dipolar decoupled (DD) spectra were measured on Doty Scientific, Inc., probes using Al_2O_3 rotors at spinning rates of 3–6 kHz. High-power proton decoupling was performed at ca. 10–12 G. The carbon spin–lattice relaxation times were obtained with the inversion–recovery and CPT$_1$ pulse sequences. Chemical shifts are referenced to TMS by recording the chemical shift of external poly(oxymethylene) (89.1 ppm) or the crystalline phase of external polyethylene (33.63 ppm)[18] before and after the NMR measurement of each sample.

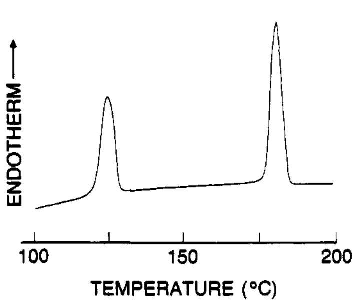

Figure 2. DSC thermogram of the PE/PHTP-IC sample used in the NMR analysis.

Results and Discussion

Formation of the IC. The inclusion compound of PE in PHTP can be obtained either by melting the two components together under vacuum (see Experimental Section) or by crystallization from a saturated solution of PHTP and PE. A third method that has been recently demonstrated is the direct polymerization of ethylene in the channels of PHTP.[19] This method has been excluded from the present study because the resultant polymer is of low molecular weight and a detailed characterization of the microstructure is not yet completed.

As has been previously reported,[20] the rapid formation of the IC by the melting process is demonstrated by calorimetric measurements on mixtures of the components in the stoichiometric ratio. In the first heating, one observes the melting of both the PHTP and PE at ca. 125 °C followed by the immediate formation of the PE/PHTP-IC that subsequently melts at ca. 180 °C. In the second heating, only the melt of the pure IC is observed.[20] As shown in Figure 2, the DSC data for the large sample of the IC prepared for our NMR analysis show an absorption of heat (8.0 cal/g) at 125 °C, reflecting excess PHTP not involved in the formation of the IC and a larger absorption of heat (11.4 cal/g) at 181 °C from the melt of the PE/PHTP-IC. Each of the endotherms constitutes about 50% of the heat evolved in the melting of the pure components (PHTP[4] and IC[20]). Therefore, virtually all of the sample is in the crystalline form. The DSC data give no indication of free, crystalline polymer (mp 137 °C). Similar DSC traces are obtained for the PE/PHTP-IC formed by precipitation from chloroform solution and careful drying. The solution-prepared samples typically contain smaller amounts of excess PHTP. Samples of the IC prepared from the either the melt or solution are therefore suitable for characterization by solid-state NMR spectroscopy, the presence of free PHTP presenting no problem in the interpretation of the NMR data.

NMR Spectroscopy of PHTP in PE/PHTP-IC. The ^{13}C NMR CPMAS/DD spectrum of the PE/PHTP-IC is presented in Figure 3. The three carbon resonances of the PHTP structure are labeled, and their chemical shift pattern corresponds to that of other polymer/PHTP inclusion compounds.[4,9] This pattern differs considerably from that of pure crystalline PHTP. In Figure 4 comparison is made between the spectrum of the 1,4-*trans*-polybutadiene/PHTP-IC (TPBD/PHTP-IC) and that of pure crystalline PHTP. The loss of multiplicity in the C_1 resonance is a good indicator of the crystal–crystal transition from pure PHTP to the IC.

The ^{13}C NMR spin–lattice relaxation times (T_1) for PHTP in PE/PHTP-IC, TPBD/PHTP-IC, and TPI/PHTP-IC and in the pure crystalline form are given in

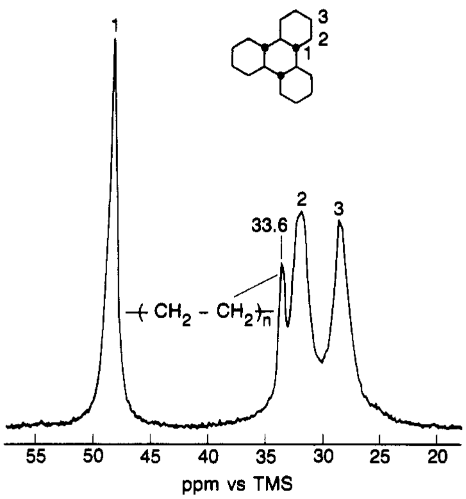

Figure 3. ^{13}C CPMAS/DD NMR spectrum at 100.5 MHz of the PE/PHTP-IC at 22 °C. The projection is of PHTP with the black dots representing the axial hydrogens.

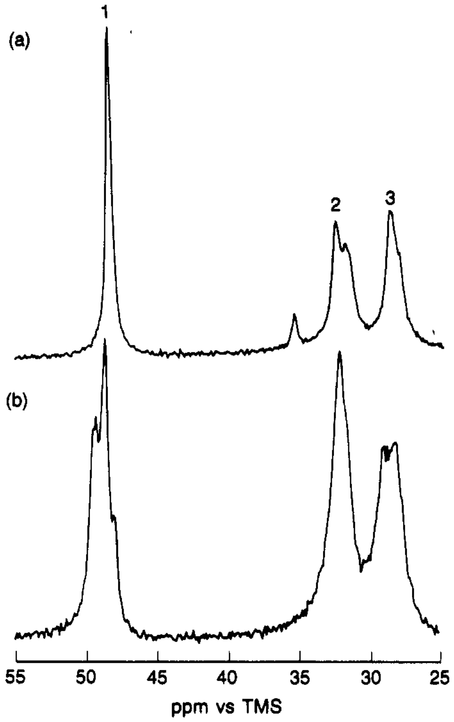

Figure 4. ^{13}C CPMAS/DD NMR spectrum at 50.3 MHz of (a) the PHTP matrix included with 1,4-*trans*-polybutadiene and (b) pure crystalline PHTP. The small resonance at 35.6 ppm in a is that of the polymer CH_2. See Figure 3 for designation of the carbons in PHTP.

Table I
^{13}C T_1's (s) of Perhydrotriphenylene (PHTP) at +23 °C

carbon[a]	PHTP	PE/PHTP-IC	TPBD/PHTP-IC	TPI/PHTP-IC
1	390	150	180	180
2	320	120	160	160
3	260	70	110	180, 20

[a] See Figure 3 for designations.

Table I. A substantial decrease in the value of T_1 is observed in each of the ICs, although there is some variation in the size of the decrease.[4] The reduction in the value of T_1 for the carbons of the host molecule has been attributed to a looser molecular packing (i.e. increased molecular motion) in the ICs. Only the C_3 carbon (see Figure 3 for designation) of the PHTP molecule appears sensitive to the nature of the included polymer molecule.

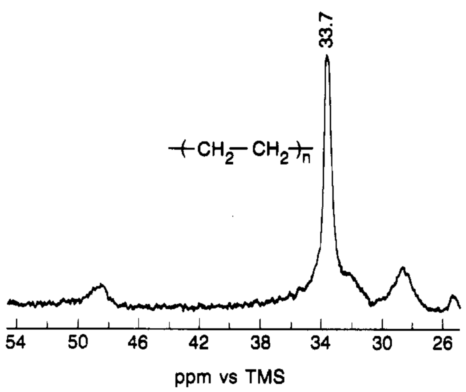

Figure 5. ^{13}C MAS/DD NMR spectrum at 100.5 MHz of the PE/PHTP-IC at 22 °C: delay time, 5 s.

For example, in the 1,4-*trans*-polyisoprene/PHTP-IC (TPI/PHTP-IC), the relaxation data of C_3 shows a complex exponential decay as does the methyl group of the included polyisoprene chain.[5,9]

NMR Spectroscopy of PE in PE/PHTP-IC. 1. Polymer Conformation. One of the difficulties in obtaining NMR data for a hydrocarbon polymer in the PHTP matrix is the possible overlap of the strong PHTP signals with the much weaker signals from the included polymer. In the spectrum of the PE/PHTP-IC obtained with CP (Figure 3), the resonance of the carbon nuclei in PE is not completely resolved from the C_2 resonance of PHTP. Variation of the cross-polarization contact time provides little improvement. The chemical shift of the PE resonance is 33.6 ppm with respect to external poly(oxymethylene) at 89.1 ppm. We have measured the carbon T_1 of the PE using the inversion–recovery method and find a value of 6.4 s at +22 °C. The large difference in the relaxation times for PHTP and PE in the IC (70–150 s vs 6.4 s, respectively) makes possible a significant reduction in the intensity of the resonances of PHTP relative to that of PE by recording a MAS/DD spectrum with a short delay (5 s), as shown in Figure 5. The signals of PHTP are extremely weak compared to the PE signal occurring at 33.7 ppm, in close agreement with the data of the CP experiment.

We have recorded, under the same conditions as for the ICs, the spectra of bulk crystalline PE. We have obtained data with and without CP at several delay times, including relaxation measurements. We have found the chemical shift of the crystalline phase at 33.6 ppm and that of the amorphous phase at 31.8 ppm. The chemical shift data for the included PE are therefore coincident with that of the crystalline phase of the bulk polymer. In crystalline PE the chains are packed in the fully extended all-trans conformation of the single bonds, as demonstrated by X-ray diffraction.[21] Since the carbon chemical shifts are sensitive to differences in conformational arrangements,[22] we can conclude that PE in the channels of PHTP prefers to adopt the same conformation, i.e. trans, as in the stems of the lamellae of crystalline PE. This was already suggested by Allegra et al. on the basis of the observed repeat period of PE included in PHTP.[23] A limited degree of motion along the polymer chain was observed in the TPBD/PHTP-IC, accompanied by a considerable increase in the population of cis bonds.[4] However, the NMR data of the PE/PHTP-IC indicate that only the trans conformation is present in significant amounts.

2. Molecular Motion. In contrast to the similarity of conformational arrangements in crystalline PE and the PE/PHTP-IC, a large difference is observed in the carbon spin–lattice relaxation times. For the crystalline phase of bulk PE we find a carbon T_1 of 320 s at +22 °C. This long relaxation time is typical of a rigid, crystalline structure, and similarly long values of T_1 have been previously reported for PE.[24] The very long T_1 demonstrates that there is little local motion in the megahertz regime at room temperature. In contrast, the short T_1 of the isolated PE chain (6.4 s) in the IC suggests a flexibility in the chain that must involve substantial local motion. How can such flexibility be compatible with a PE chain that adopts the all-trans conformation? Are these motions related to the molecular motions that give rise to the α_c relaxation process in crystalline PE? There are three types of motion possible for the PE chain within the PHTP channels that could contribute to a reduction in the carbon T_1: (1) rotation of the entire molecule about its long axis, (2) migration of a conformational kink or twist along the chain, and (3) libration about the trans conformation.

The rigid-chain rotation of the entire extended PE molecule about its long axis may appear improbable. Conformational energy calculations have shown that the activation energy per CH_2 unit for such rotation in the orthorhombic unit cell of crystalline polyethylene is 1.2 kcal/mol.[15] However, this activation energy results entirely from interactions between neighboring polymer chains in the crystal structure. Therefore, these calculated energy levels are probably not relevant for an isolated PE chain in the PHTP inclusion compound, and the actual barrier to rigid rotation may be substantially lower.

Our NMR chemical shift data cannot rule out the possibility of a small amount (<5%) of gauche conformations in the chain. The most probable arrangement would be a ttg^+tg^-tt sequence, where the gauche conformations of opposite sign minimize the displacement of the polymer chain. A "buckled twist" conformational defect has also been suggested as a defect in crystalline PE.[25] This involves twisting the molecule by 180° about the chain axis and incorporating one extra $-CH_2-$ unit in the compressed portion of the chain. Thus five methylene groups are accommodated in the distance that would normally be occupied by four methylene groups.[25] The conformational structure of this defect is either $-g^-tg^+g^+g^+g^+-$ or $-g^-tg^+g^+g^+-$.[26] An activation energy would be associated with the formation and translation along the PE chain of either of these two conformational defects. If such defect conformations moved rapidly through the channel, they would be expected to reduce the carbon T_1, with the size of the reduction related to the defect concentration and the rate of defect diffusion. However, an RIS analysis of the PE/PHTP-IC by Tonelli indicates that while certain conformers of polyethylene containing gauche bonds will fit within a 5-Å channel, conversion between conformers is only possible in a concerted manner in a 6.5-Å channel, well beyond the PHTP channel dimension.[27] The presence of a small amount of fixed conformational defects will not reduce the carbon relaxation times.

A second type of conformational defect is a rotation from the trans arrangement at each of 10–14 consecutive bonds. If each bond rotation is of the order of 15°, the carbon chemical shift would be expected to remain unchanged. This arrangement of bonds will introduce a twist of 180° into the polymer chain and has been labeled a "twiston".[13] The activation energy for formation of a twiston would be expected to be low, and translation would be independent of temperature since the twist can move without overcoming any local energy barriers. It has been described as a transition state rather than a defect that hops along the polymer chain.[15] Movement of the twiston conformation along the chain would produce a reduction in the carbon relaxation time.

In the third type of motion each bond along the chain simply librates about the trans arrangement. The carbon chemical shift data would be unaffected by the libration; however, such motion would affect the carbon T_1. Since this motion is unrelated to any energy barrier, its effect on the relaxation process would be expected to be independent of temperature.

In order to estimate the activation energy associated with the observed polymer chain motions in the PE/PHTP-IC, we have measured the carbon relaxation times at several temperatures. The values of T_1 are 4.0, 6.4, and 11.1 s at −50, +22, and +100 °C, respectively. This indicates an activation energy of only 1.1 kcal/mol. The low-energy barrier suggests that the motions do not involve gauche–trans conformational averaging where the barrier is ca. 3.5 kcal/mol.[28] The translation of the buckled twist defect is calculated to have a barrier of 4 kcal/mol.[26] This amount of energy should be further increased by the above-mentioned channel constraints, and therefore the buckled twist defect is not responsible for the carbon relaxation in the polyethylene chain of the inclusion compound.

There remain three possible motions for the polymer chain in the inclusion compound. The libration about each bond, the traveling twiston defect, and the rigid-rod rotation of the entire molecule about its long axis. Each motion is expected to be associated with only a small energy barrier, if any at all. In order to discriminate between such motions, an analysis of perdeuterated polyethylene in the channels of PHTP is in progress. Each of the three motions described above should produce a unique deuterium coupling pattern that will yield a precise description of the motion of the C–D vector.

Conclusions

Our solid-state ^{13}C NMR data indicate that an isolated polyethylene chain in the PE/PHTP-IC adopts an all-trans planar zigzag conformational arrangement very similar to that of the bulk crystalline PE. However, the spin–lattice relaxation time for the methylene carbon is 320 s in the PE crystal and only 6.4 s in the inclusion compound. This indicates considerable mobility of the polymer chain within the confines of the PHTP channel and reflects the absence of interactions with neighboring polymer chains. The dramatic drop in the value of T_1 is probably the result of librational motions at each bond or translational movement of a twiston defect. Such motions are unlikely events in the crystalline lattice of the bulk polymer at room temperature but are very likely in the IC since they have no associated energy barriers and do provide entropy to the system. These motions may also be related to the α_c relaxation process in crystalline PE. A less probable motion in the IC is the rotation of the entire molecule along its long axis. The exact nature of the molecular motion of PE will be determined in future studies using ^2H NMR spectroscopy.

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