Registry No. Polyisobutylene, 9003-27-4.

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Chain Mobility of Isotactic 1,4-*trans*-Poly(penta-1,3-diene) Included into Perhydrotriphenylene. A Broad-Line ^2H NMR Study

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ABSTRACT: Deuteron NMR offers the possibility of studying local motions of polypentadiene chains included into a crystalline perhydrotriphenylene matrix. Results show the copresence of a rigid and a mobile fraction of C–D bonds, mobility ranging over a wide temperature interval, from 150 K up to 360 K (close to the melting point of the host compound). The relatively scarce effect of temperature is in agreement with a model where the chain mobility is primarily governed by steric interactions with a rigid host structure. A T_1 relaxation analysis indicates that a simple two-fraction model is an oversimplification, a better description requiring a more complex distribution of correlation times. A complete characterization of the samples assures for the absence of unreacted monomers and for the structure of the inclusion compound.

Introduction

Inclusion polymerization can be considered as a unique method for obtaining highly stereoregular polymers. The explanation is that they retain the crystal state ordering features of the inclusion adduct with the monomers. On this basis most works were oriented toward the detection of intramolecular and supermolecular order in the polymer, both native and after dissolution.[1]

In recent years more attention has been focused on the presence of disorder phenomena in crystalline polymers and in inclusion compounds as well. For example, in the case of inclusion polymerization, a considerable amount of monomer unit inversion has been detected in poly(isoprene) as obtained in perhydrotriphenylene (PHTP);

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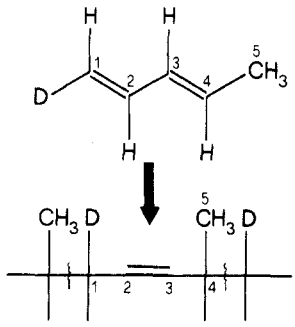
Chart I
Monomer to Polymer Transformation and Numbering Scheme Adopted



the energy involved in such disordering phenomena was determined with considerable accuracy[2] and may be the measure of the mobility in the inclusion compound (IC) with the monomer. Moreover, copolymers starting from far different monomers can be obtained with a statistical distribution of monomer units.[3-5] In other cases, such as butadiene in PHTP, the degree of conformational freedom of the propagating chain end within the channel was determined by ESR spectroscopy at different temperatures.[6]

In the present work we want to give an idea of the chain mobility of a polymer in the IC. In this respect the polymerization of pentadiene in PHTP seemed to give rise to an unfavorable case because the crystalline packing is expected to freeze molecular motions, as revealed by the high stereoregularity of the polymer obtained in the presence of this crystalline matrix.[7] On the other hand, previous X-ray diffraction analyses[8,9] and conformational energy calculations[10] have shown that isotactic 1,4-*trans*-poly(penta-1,3-diene) (IPP) can assume two different conformations in the crystalline state, and this affords the possibility of conformational changes being present whenever favorable surrounding conditions occur.

Mobility phenomena are likely to be observed in the IC's due to the scarce specificity of the interactions involved in the adduct formation. The idea of investigating molecular motions in IC's has already found a number of interesting applications,[11] we recall in particular a ^{1}H NMR broad-line analysis on urea and thiourea adducts.[12] In order to monitor molecular mobilities over a wide range of correlation times, however, ^{2}H NMR is the method of choice.[13] It affords dynamic information through the anisotropic parts of the spin Hamiltonians; in particular the quadrupole interaction of a deuteron nucleus, a single particle interaction, has the great advantage of being almost independent of the molecular environment. This approach obviously requires a selective deuteriation of the molecular fragment whose mobility is to be studied; this was performed by synthesizing (1*E*,3*E*)-[1-^{2}H]-1,3-pentadiene and by polymerizing it in the inclusion state (see Chart I).

Experimental Section

Sample Preparation. The synthesis of PHTP was performed as described before.[14] The synthesis of the deuteriated monomer was carried out as already reported by some of the authors.[15] The monomer was 99.5% pure (1*E*,3*E*)-[1-^{2}H]-1,3-pentadiene. The synthesis by inclusion polymerization of poly(1-deuteriopentadiene) (IPDP) took place in the IC by direct irradiation with γ-rays (source ^{60}Co, dose 1 Mrad). The procedure has already been described.[16] Ziegler–Natta polymerizations were carried out with the catalyst VCl_3–$AlEt_3$ in order to obtain a trans erythro diiso product and a tarns threo diiso product starting respectively from *cis*-pentadiene and *trans*-pentadiene.[15]

NMR and Calorimetric Measurements. Solution ^{13}C and ^{1}H NMR spectra were run on a Varian XL200 instrument operating at 50.3 and 200 MHz, respectively. Typically 15 000 transients were accumulated overnight at 60 °C in $CDCl_3$ in the case of ^{13}C NMR measurements. Other NMR spectra required room temperature and 5000 transients. Additional conditions: acquisition time, 1.5 s; delay time, 2 s; sweep width, 10 kHz. Cosy spectra were run on a 512 × 512 data set with the following parameters: sweep width, 1.4 kHz; delay time, 1 s; acquisition time, 0.5 s.

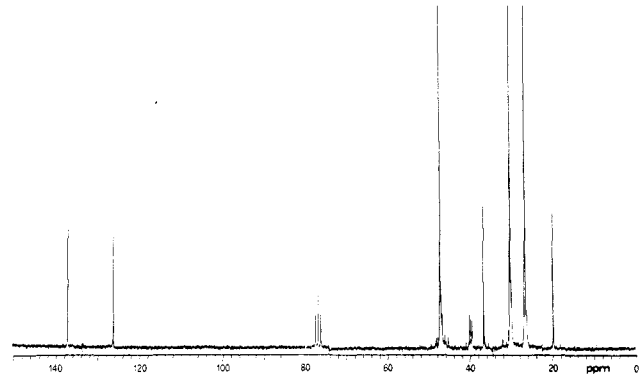


Figure 1. ^{13}C NMR spectrum run at 50.3 MHz of PHTP (out of scale) and IPDP as from the dissolution of IC without any separation.

DSC analyses were performed on a Mettler TA 3000 system in the temperature range 50–250 °C at a scanning rate of 5–10 K/min.

^{2}H NMR measurements were performed at 46.07 MHz with a Bruker CXP-300 spectrometer. The spectra were obtained by using the solid echo pulse technique with a pulse delay τ_1 of 30 μs and quadrature phase detection. Typically 2048 transients were accumulated prior to Fourier transformation. Spin–lattice relaxation time was monitored by determining the intensity I as the height of the solid echo generated at time τ^0 after the end of a 5 × 90° saturation pulse sequence;[17] I_∞ is the height of the fully relaxed echo. Typically 512 transients were accumulated for each τ_0 value in the range 0.5 ms < τ_0 < 20 s.

Results

The goal of studying polypentadiene mobility in the inclusion state in PHTP may be reached only after a very accurate characterization of the system under investigation.

The most important points to be established prior to any attempt of interpreting experimental data obtained from included polypentadiene are listed in the following section.

Characterization. The first requirement is to obtain the inclusion compound in a form as clean as possible. This is practicable only by forming the polymer itself in the inclusion state. Any attempt of including polypentadiene previously formed always leaves out a fraction of "free" polymer in the form of connections between microcrystals. This difference is well testified by the presence of an "extended chain" morphology when the high molecular weight polymer, obtained in situ, is separated from PHTP by boiling methanol.[18] This morphology cannot be obtained again, even with the same polymer, when the IC is built up with a preformed polymer. DSC analysis shows that IPDP has the same morphology as the nondeuteriated polymer, for which a single phase was demonstrated by low-angle X-ray experiments.[18]

In our experiments we used the pure polymerization product as jet included in PHTP.

The presence of unreacted monomers is ruled out by ^{13}C NMR analysis performed directly on the dissolved IC without any purification procedure (Figure 1). Besides the main peaks (out of scale in the figure) due to PHTP, minor signals are present, coincident with those given for isotactic head-to-tail 1,4-*trans*-polypentadiene:[19] 19.9 (CH_3), 36.8 (CH), 126.4 (CH(2)), and 137.2 ppm (CH(3)) and finally a triplet centered at 40.3 ppm which was as-

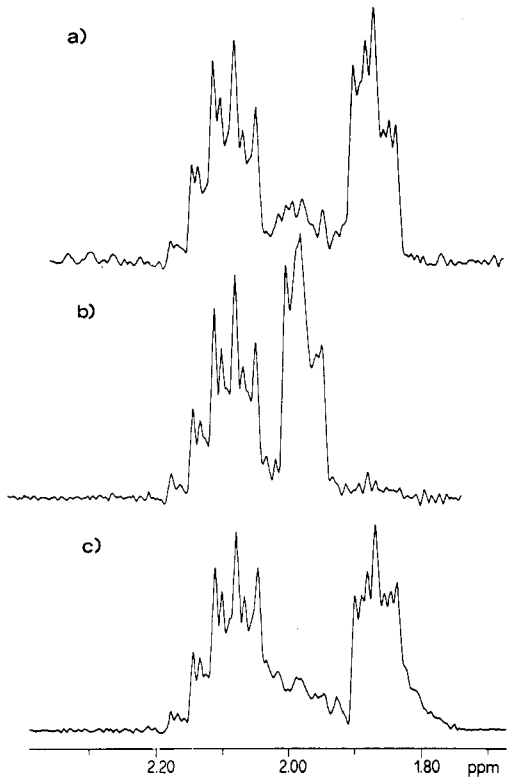


Figure 2. ^{1}H NMR spectrum run at 200 MHz, expansion of methylene and methyne zone: (a) IPDP; (b) threo sample; (c) erythro sample.

signed to the CHD group in position 1 (for the numbering scheme, see Chart I). No further peaks were detected. This evidence states (i) that monomers or oligomers are absent, at least within the limit of ca. 5%; (ii) that deuteriation is consistent with the monomer and the polymer structure, is quantitative, and is specific; and (iii) that the chemical shifts of the polymer do not differ from those of isotactic polypentadiene[19] even at extreme expansion and resolution enhancement where no further splitting was observed at 50.3 MHz. The structural results were confirmed on the polymer as analyzed after purification.

In addition to this necessary characterization we want also to point out that the introduction in the polymer of a deuteron atom starting from a trans deuterio monomer gives a better insight into the understanding of the specificity of the addition and in particular of the steric relationship toward the next methyl group. In fact it is not enough to know how regular the stereochemical arrangement is on carbon 4 to deduce the same stereoregularity on carbon 1. As a matter of fact polyhexadiene, as obtained in PHTP, contains ca. 30% stereochemical disorder of erythro/threo type.[20] The most sensitive tool to investigate this structural point is the high-field ^{1}H NMR analysis, since the ^{13}C chemical shift is virtually insensitive to erythro/threo configurational differences. In figure 2 the most significant part of the ^{1}H NMR spectrum of IPDP is compared with those obtained from samples synthetized with Ziegler–Natta catalysts, in pure erythro and threo form. The assignment of these reference compounds was previously established by analysis of the ozonation products consisting of erythro and threo methylsuccinic acid.[15]

It is apparent that IPDP contains ca. 80% of erythro configurations. The sensitive group of signals in the ^{1}H NMR spectrum is due to CHD as proved by 2D homocorrelated spectroscopy (Figure 3). It is not our intention to discuss in this context the implications for the mechanism of polymerization of pentadiene in the included state

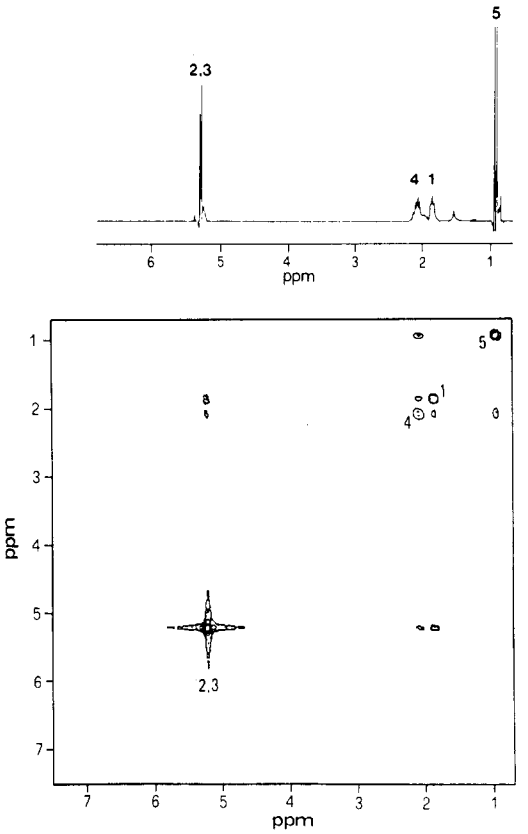


Figure 3. Homocorrelated 2D ^{1}H NMR spectrum run at 200 MHz of erythro 1,4-*trans*-polypentadiene compared to the monodimensional ^{1}H NMR spectrum (assignments are given following the numbering scheme indicated in Chart I).

due to the erythro/threo disorder, we only want to point out that this configurational uncertainty on carbon 1 does not imply any difference in the appearance of the ^{2}H NMR spectra. In fact, as will be discussed later in more detail, conformational mobility of C–D bonds is equally monitored despite the presence of an erythro or a threo configuration of the methylene group.

The ^{1}H NMR spectrum of the dissolved IC as from polymerization gives the host/polymer ratio, i.e., 3 mol of PHTP per mol of polypentadiene monomer unit. It corresponds to the yield of polymer as washed by boiling MeOH (90 mg of polymer per g of PHTP) and indicates a fulfilling of the channels. In spite of the good yield, the deuteron content in the sample is relatively small, thus explaining the low signal-to-noise ratio present in all the following ^{2}H NMR experiments.

Molecular Mobility. In Figure 4 we report ^{2}H NMR spectra of the IC collected at four different temperatures from 150 to 360 K under conditions reported in the Experimental Section. In Figure 5 results of T_1 measurements at room temperature are shown in the form of a progressive evolution towards the fully relaxed spectrum as τ_0 is increased from 0.1 to 20 s. In Figure 6 we summarize results of T_1 measurements, at three different temperatures, in terms of $(I_\infty - I_t)/I_\infty$ vs τ_0, I_∞ being the height of the fully relaxed echo.

A quick inspection of these figures is sufficient to draw the conclusion that considerable motion of C–D bonds still exists even at very low temperatures. This is supported by the two small peaks in the center of the spectrum collected at 150 K (Figure 4). This contribution from mobile C–D bonds increases, of course, with temperature, as is shown by spectra collected at 300 and 360 K (the substantial similarity of the spectra collected at 150 and 250 K is, in our opinion, only apparent and probably due

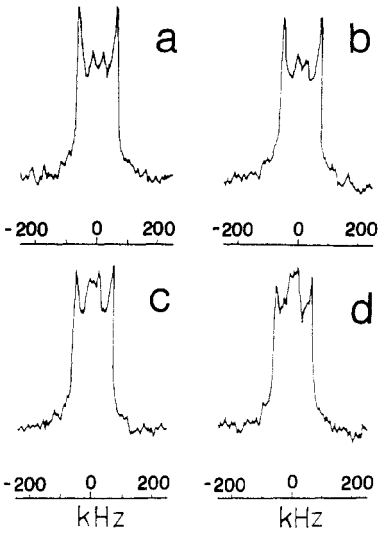


Figure 4. ^{2}H NMR spectra of the IC collected at four different temperatures: (a) 150; (b) 250; (c) 300; (d) 360 K.

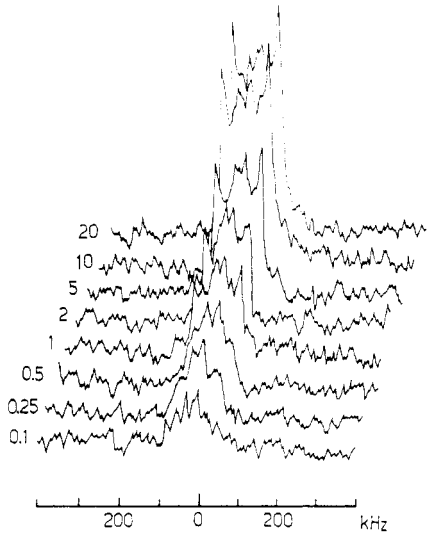


Figure 5. ^{2}H NMR T_1 relaxation measurements, at room temperature, reported in the form of a progressive evolution toward the fully relaxed spectrum as τ_0 is increased from 0.1 to 20 s.

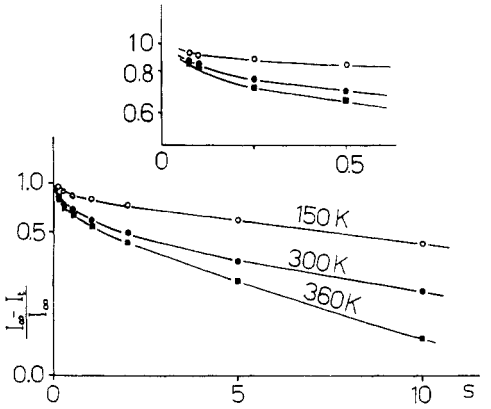


Figure 6. Summary of T_1 measurements at three different temperatures in terms of $(I_\infty - I_t)/I_\infty$ vs τ_0, I_∞ being the height of the fully relaxed echo. Data referring to the shortest values of τ_0 are reported separately.

to the fact that a τ_0 = 20 s is not long enough to allow for a complete relaxation of the magnetization). On the other hand, even at this temperature there is still a considerable fraction of C–D bonds that, on a time scale of the order of 10^{-5} s, can be considered rigidly oriented within the

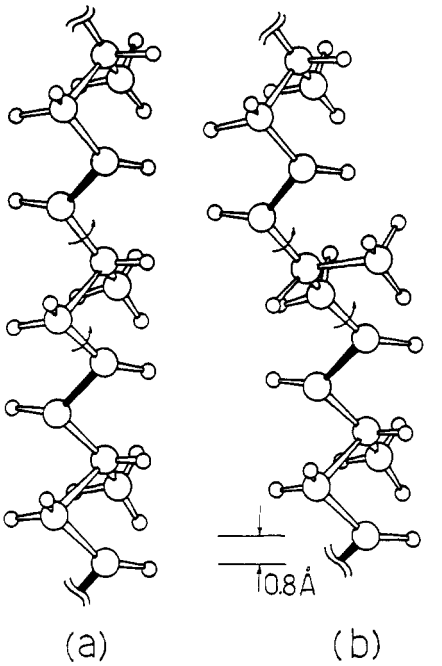


Figure 7. Possible model for conformational changes occurring within the PHTP channels. A pure skew sequence (a) is compared with a sequence where one side methyl group has switched to a cis arrangement relative to the nearest double bond (b). The arrows indicate chain bonds undergoing the conformational transition. A shortening of ca. 0.8 Å along the chain axis together with a displacement of ca. 2.2 Å between the two chain axes results from this conformational change.

powder sample. This is proved by the Pake-like contribution to the spectrum that still survives at high temperature. The most important conclusion to be drawn from these facts is that IPDP is surely nonrigid in the whole temperature range considered. This considerably attenuates the validity of any model based on a high specificity of polymer–PHTP contacts, as expected in view only of the stereoregularity obtained in the included polymerization; on the other hand, the primary role played by nonspecific steric interactions of the polymer with the rigid host structure is supported by the modest effect of the temperature on the chain mobility. A rough picture of the whole system is therefore that of a polymer chain that experiences both contraining and relatively free environments.

A more detailed inspection on Figure 6 where the results of T_1 measurements are summarized shows, however, that the description of the system in terms of a rigid and a mobile fraction of C–D bonds is actually an oversimplification of a situation that, at least at intermediate temperature (300 K), is surely more complex. We can see in fact not only that T_1 relaxations are nonexponential but also that they cannot be satisfactorily described by a combination of only two different exponentials. The slope of the relaxation curves is changing continuously, so that a combination of more than two exponentials is required to explain this behavior. A more complete model requires therefore the polymer chain to experience a variety of different local environments, quite free motions and high rigidity being only the extreme consequences of a differentiated ensemble of steric interactions with the host structure. A first reason for this can be found in the slightly different periodicities of the polymer chain (4.87 Å) and of PHTP (4.78 Å).[21,22] This mismatch is likely to produce "beats" of more or less close contacts of side methyl groups with the channel walls that periodically influence the chain mobility.

An additional source of disorder can be described with reference to Figure 7. In this figure we show a possible model for a conformational jump occurring within the PHTP channel, it is thus possible to compare a sequence where all side methyl groups are skew with respect to adjacent double bonds (skew conformation) and a sequence where one methyl group has switched to a cis arrangement relative to the double bond (cis conformation). These are the two most stable conformations available to the polymer chain[8,9] and it has been already been pointed out that a pure skew sequence and a pure cis sequence exhibit the same repeat period along the chain axis (4.87 Å).[8,9] From inspection of Figure 7 it is, however, clear that when a single cis conformer is intercalated within a skew sequence this produces a shortening of the repeat period of about 0.8 Å and a displacement of the chain axis of about 2.2 Å. The displacement of the chain axis might be compensated by a small reorientation of the chain in the vicinity of the conformational transition while the shortening of the repeat period persists as an additional source of disorder along the PHTP channel.

A last remark concerns the alternative possibilities of interpreting the mobile contribution to observed ^{2}H NMR spectra. A first hypothesis concerns the presence of chain fragments leaning out of PHTP channels. To rule out this possibility we must consider that the polymer is surely generated within the PHTP matrix. Leaning out of fragments could therefore occur only as a successive process where longer and longer sequences leave the host channels as temperature is increased. This behavior, however, is in contradiction with the thermodynamic stability of the IC as is displayed by its high melting point (170–180 °C) as compared with those of the pure components (PHTP melts at 126 °C and the polymer melts in the 85–100 °C range). Additional sources of dynamic disorder for the polymer chain could be represented either by chain-end effects or by crystalline imperfections disrupting the channels. The considerable amount of the mobile fraction, which has not been quantitatively analyzed but is surely higher than 20% at room temperature, cannot be accounted for only by chain end effects if we consider that the average degree of polymerization, evaluated from GPC and viscosity measurements, is on the order of 800. On the other hand crystal irregularities leading to such a high disorder should be detectable on X-ray diffraction photographs and should also affect the DSC melting peak. In both experiments, however, the observed features are typical of a substantially regular crystal lattice.[18] Moreover we should also mention that the observed spectra are completely reversible, in the sense that we always obtain the same spectrum, at a given temperature, irrespective of the thermal treatment previously exerted on the sample. This is further evidence that the totality of the polymer chains are included within PHTP, and therefore the mobility we observe is a characteristic of the polymer–crystal matrix adduct.

Figure 7 shows also that in a conformational transition skew–cis on the polymer chain both C–H bonds on the methylene group change their direction by the same angle (109.5°). Since in a two-site jump process it is the change in the direction of a C–D bond that is monitored in the ^{2}H NMR spectrum, we can conclude that the erythro/threo uncertainty in the configuration on carbon 4 does not affect the observed profile.

An interesting conclusion of this study is that the high stereospecificity on carbon 4 observed in inclusion polymerization of pentadiene is not related to a highly constrained situation for the resulting polymer chain. Of course this conclusion cannot be directly extended to the system at the moment of the addition of a new monomer to the growing chain due to the different encumbrances involved in the two cases.

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Registry No. PHTP, 15074-91-6; IPDP, 96095-08-8.

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