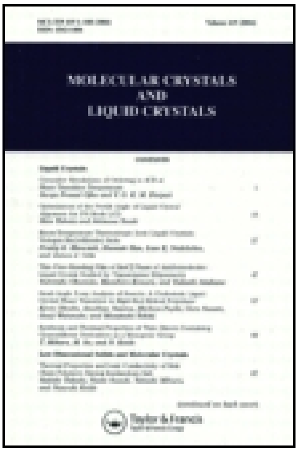

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Dynamics of Linear Alkanes of Different Chain-Length in Nanotubes

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DYNAMICS OF LINEAR ALKANES OF DIFFERENT CHAIN-LENGTH IN NANOTUBES

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Abstract A solid state characterization of inclusion compounds containing isolated molecules of linear alkanes and polyethylene was performed by Nuclear Magnetic Resonance. The chemical shifts in the ^{13}C high resolution experiments, the quadrupolar ^{2}H powder spectra and the relaxation experiments provided us a detailed description of the conformation and mobility of linear polymethylene chains of different length, once isolated in a crystalline hydrocarbon environment. The chain-length dependence of the internal methylene chemical shifts was observed for the first time, giving an evidence of the departure of the internal conformations from the *trans*-planar arrangement. Since the high relaxation rates are associated to fast reorientations of the C-H or C-D vectors, as referred to the nanotube walls, the departure from the *trans*-planar arrangement was interpreted according to a dynamic model. The longer is the chain the less frequent are those defects or smaller is the amplitude of the oscillations, indicating that the defects are associated to the presence of the chain-ends at a distance of several bonds. This is a suggestion for a concerted mechanism of motion, associated to a long correlation length, instead of a local dynamic process due to thermal excitations.

INTRODUCTION

The solid state behavior of polyethylene and normal alkanes is still addressed by the research in spite of the molecular simplicity[1] The conformational flexibility and the smooth average cross section make it possible the dislocation of the polymethylene chains into polymorphs; some of which contain a relevant amount of disorder and are considered as mesophases. The amount of dynamic disorder can be *increased* as compared to the bulk in nanotubes created by crystalline inclusion compounds - not *reduced,* as could be erroneously deduced by considering the presence of the matrix as a severe constriction to the chains. We exploited the use of the versatile matrix of perhydrotryphenylene (PHTP)[2,3], a saturated cyclic hydrocarbon without polar groups. A good opportunity is thus offered to select just the steric phenomena.

Our research has been previously focused to the NMR characterization of polyethylene confined as a single chain to a matrix; this being a part of a project about polymer chains isolated within a crystalline lattice[4,5,6,7]. Several questions have been answered in the course of this study, indicating the conformation adopted by the polymer chains in the unusual environment is such as the best filling up of the available space is obtained. Much freedom is gained by polyethylene chain, leading to motions not even frozen at a very low temperature. Theoretical RIS models by Tonelli and dynamic simulations by Mattice supported the existence of large *librations* about the *trans*-planar arrangement[8,9,10].

The experimental results and the model description might thus seem conclusive. But it was still unclear if any chain length dependence of the motion could occur and if librations are locally generated by thermal excitations, or motion can propagate into the inner chain from the chain-ends. This was made possible by observing the conformation at the chain ends and at the inner bonds along polymethylene chains of different molecular weights. Dynamic behavior of polyethylene in the crystalline lamellae of equivalent height is comparable as adequately scaled for temperature.

EXPERIMENTAL PART

Materials

PHTP (the fully *anti-trans* isomer) was synthesized in the racemic form by hydrogenation of dodecahydrotriphenylene, as described elsewhere[2], 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 analysis and was found to be >99% pure. The synthesis of linear high-density polyethylene was obtained by diazomethane; the polymer shows a melting point of 137°C[11]. GPC molecular weights were 1.75×10^4 and 7.49×10^4 M_n and M_w, respectively. PE-d4 was purchased by Merck & Co. and used as received. Inclusion compounds were formed by melting together the matrix and the polymer at 190°C in vials sealed under vacuum, and then slowly cooling to room temperature. Normal alkanes were obtained by Fluka and the inclusion compounds were formed as described elsewhere[2]. The formation of the adducts was monitored by DSC analysis.

Solid State NMR

NMR high resolution ^{13}C MAS NMR spectra were run at 75.5 and 100.7 MHz on a CXP300 Bruker instrument and a Varian XL400, respectively. A MAS Bruker probe was used with 7 mm ZrO_2 rotors spinning at a standard speed of 5 kHz. For cross polarization CP MAS spectra, the best contact time was found at 1 ms for ^{13}C. A high-power proton decoupling (DD) field of 15 G was applied, the delay between pulses was 5 s for CP MAS; for each spectrum about 5000-10000 transients were collected. For MAS without cross-polarization, a 90° pulse for carbon of 4 μs was used; a fully relaxed MAS (for the guest molecules) experiment was performed by applying a delay time of 50s; for a better contrast against the matrix shorter (typically 5s) recycle times were applied. Relaxation measurements of ^{13}C T_1 were performed by the Torchia method.[12] The spectra were elaborated using *WIN-NMR* purchased by Bruker. The values of T_1 were determined using a non-linear least squares fit. The resolution for carbon was checked on glycine (width at half-height = 26 Hz). Crystalline polyethylene (PE) was taken as an external reference at 33.63 ppm from tetramethylsilane (TMS).

The solid-state deuterium NMR spectra were recorded on a Varian Unity-400 spectrometer operating at a frequency of 61.4 MHz. The 90 degree pulse for the echo sequence was as long as 2.8 μs and the delay between pulses was typically 20 μs. The recycle delay between 2-10 s provides fully relaxed conditions. 1000 accumulations were normally collected. In order to compare absolute intensity signals at different temperatures corrections were made by comparison to the spectra of malonic acid, a rigid crystalline materials which undergoes no significant change in molecular dynamics with temperature.

RESULTS AND DISCUSSION

Polyethylene Into Channels

^{13}C chemical shift at 33.63 ppm, as measured by VanderHart [13], is believed to belong to a polymethylene chain in the *trans*-planar conformation. However, the chemical shift is not very sensitive to a moderate departure from the *trans* conformation. If chain motions are to be taken into account relaxation times constituted a valuable method. Lamellar-thickness dependence of longitudinal relaxation times were observed[14]. Being the ^{13}C T_1 relaxation times mainly due to a motional mechanism they must be related to increasing order of the annealed lamellae.

Polyethylene in PHTP shows at room temperature a ^{13}C chemical shift corresponding to the *trans* conformation; but a short T_1 value (6 s) indicates the high frequency motion of the chain[7]. ^{2}H NMR powder pattern provide a similar dynamic information and in fact larger amplitude motions are observed in the deuterium spectrum of PE as included than in the bulk. The deuterium NMR spectrum of the PE-d_4 chains in the channel of the IC shows below -140°C a peak separation of 125 kHz and a completely static powder Pake spectrum, indicating no significant reorientation of the C-D bonds occurs at that temperature on the time scale of the inverse line width, i.e. a few microseconds. In other terms this is only consistent with small amplitude and slow motion. Above +20°C the line shape remains that of a Pake doublet but with a peak separation of only 50 kHz (Figure 1).

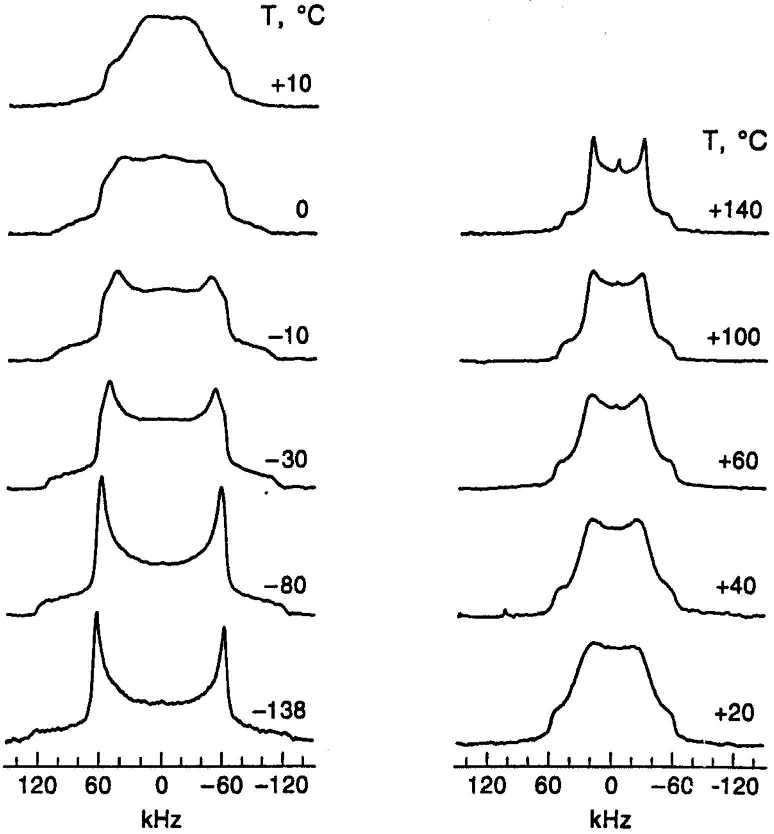

FIGURE 1. Fully relaxed solid-state ^{2}H NMR spectrum at 61.4 MHz for PE-d4/PHTP-IC at the indicated temperatures.

The narrowing of the spectral pattern is due to molecular motion. The intermediate spectra show much limited degree of motion[15].

In addition to the already published results about spin-spin relaxation times, deuterium inversion-recovery experiments for measuring the spin-lattice relaxation times at several temperatures were examined. The inversion-recovery experiments evaluated at the Pake double singularities and the center of the powder pattern indicates an average relaxation of 2.4 s (±0.2) at -100 °C s and 1.2 s (±0.2) at +100 °C, crossing a minimum of 0.27 s (±0.02) at +5 °C. The value presented at +5 °C by the edges of the pattern could be estimated from the null position due to the weak intensity of this signals (~0.15 s).

In Figure 2-5 portions of the inversion-recovery sequence are shown at different temperatures.

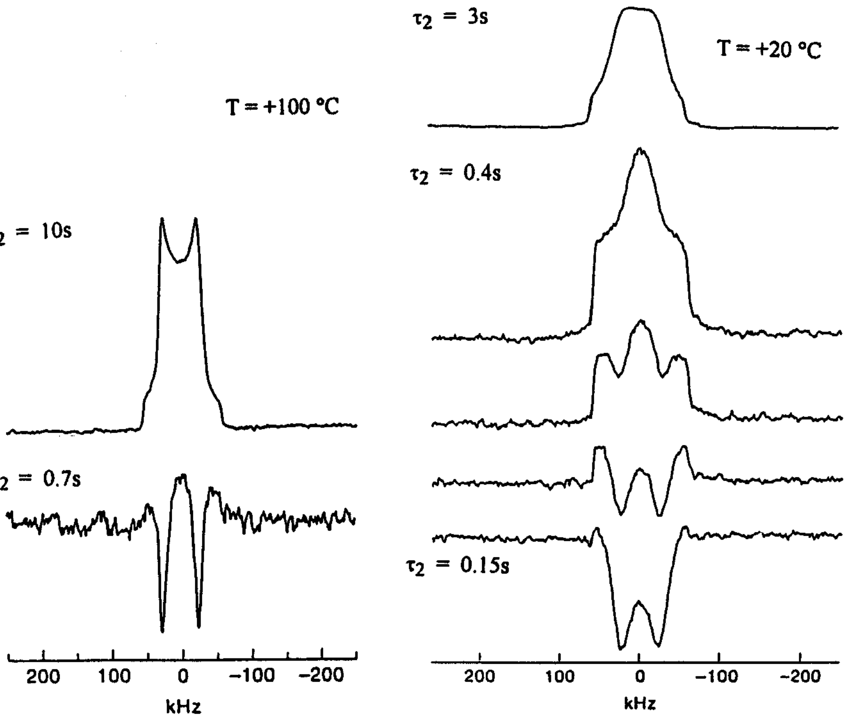

FIGURE 2-3. 61.4 MHz ^{2}H NMR inversion-recovery solid echo spectra for PE-d_4/PHTP-IC at +100°C and + 20°C, respectively.

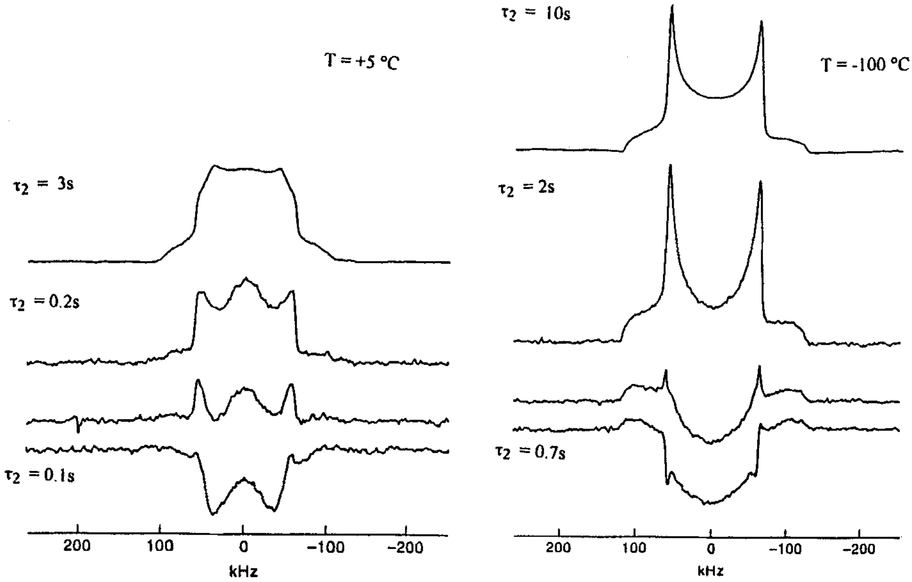

FIGURE 4-5. 61.4 MHz 2H NMR inversion-recovery solid echo spectra for PE-d4/PHTP-IC at +5°C and -100°C, respectively.

At each temperature an undistorted inverted spectrum (not shown) was obtained at very short values of τ_2. An analysis of inversion-recovery data near the null point would suggest anisotropy of the relaxations occurring at all temperatures. In figure 2 the spectrum near the null point in the inversion-recovery sequence recorded at +100°C (τ_2 = 0.7 s) is compared to the fully relaxed spectrum (τ_2 = 10 s). The positive intensities at the zero frequency position and at the edges of the pattern demonstrate a faster relaxation of the nuclei at these frequencies compared to the nuclei at the singularities of the pattern where the intensities are negative. At all temperatures studied (Figure 3-5) the null spectra suggest that the fastest relaxation occurs for nuclei represented at the edges of the pattern .

Distorted powder patterns reflect both anisotropic T_2 and T_1. Although distortions may occur in the lineshape due to the wide range of frequencies and the lack of homogeneous refocusing (the values are to be taken with some criticism as neat T_1 values) we believe the observed dependence of the pattern on the applied delays is significant, as separately discussed[16].

Both the deuterium lineshape and the relaxation data are consistent with a continuous free-diffusion motional model. Rapid rotation of the PE chain about the channel axis reduces the line shape significantly. Although this motion is associated with a high activation energy in the bulk crystal, in the isolation of the channels of the IC it is easily feasible. If such motion were the sole source of reorientation of the C-D bonds it would reduce the Pake doublet peak splitting to 62.5 kHz, one-half its rigid-lattice value. This is because the C-D bonds are perpendicular to the chain axis when the chain is in the all-*trans* state. The fact that the peak separation is reduced to 40% of the rigid-lattice value indicates an additional kind of internal motion and the deviation of the internal bonds from the *trans*-planar conformation has to be taken into account. Since the polymer chain is constrained in a nanotube of at most 5.5 A, conformational isomerization seems unlikely and the only internal motion possible is a torsion of the carbon backbone. Small-angle torsion oscillations about the *trans* position within the low energy well are enough for reorienting the C-D bonds and reducing the deuterium spectral line width[15].

The comparison of the deuterium NMR spectra shown in Figure 1 for the PE-d_4/PHTP-IC at below -30°C to spectra of bulk crystalline PE-d_4 samples at above room temperature (not shown) demonstrates the existence of the same kind of reorientation of the C-D bonds in the bulk as well. This is deduced by the presence in the spectra of some bulk samples of a splitting between singularities which is slightly smaller than 125 Mhz, and outer shoulders close to the singularities. Not much attention was generally paid to such detail in the spectrum of the bulk material, although it was already observed[17]. The shoulders are not always present, and in other cases a fully static spectrum is obtained: actually, thermal history is quite critical for detecting those shoulders in PE-d_4 spectrum at room temperature. Less restricted motions are observed in the inclusion compound and thus the shoulders become very apparent in between -30°C and -10°C.

Several modeling works describing chain oscillation in both polyethylene and linear alkanes have nevertheless been presented[1,18,19]. The following results will deal with the chain-length dependence of such motions in order to understand if the oscillations of C-H bonds are affected by some long range coherence.

Linear Alkyl Chains

The linear alkyl molecules used in this study range from 16 to 60 carbon atoms.

The inclusion compounds were obtained by melting PHTP together with the hydrocarbons at 230°C and slow cooling; or by co-crystallization by methylethylketone. Calorimetric measurements show a main endotherm at 160°-180°C and at 128°C due to excess PHTP. In those molecules the influence of the chain-ends is progressively increased lowering the molecular weight (Figure 6).

1 2 3 4

$(\mathbf{CH_3CH_2CH_2CH_2}\ CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_2$ C40

1 2 3 4

$(\mathbf{CH_3CH_2CH_2CH_2}\ CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\ CH_2)_2$ C32

1 2 3 4

$(\mathbf{CH_3CH_2CH_2CH_2}\ CH_2CH_2CH_2CH_2CH_2CH_2CH_2\ CH_2)_2$ C24

1 2 3 4

$(\mathbf{CH_3CH_2CH_2CH_2}\ CH_2CH_2CH_2CH_2)_2$ C16

FIGURE 6 Polymethylenes of different length included in the tubule. Terminal carbon numbers are indicated.

We have also the opportunity to observe in the intermediate elements of the series (from C_{32} to C_{40}) a growing core of methylenes (called in the following *internal* methylenes) which should be not directly affected by the chain-ends.

Exploiting the different properties as regards T_1 and T_2 of the rigid crystalline matrix and of the flexible chains, the two phases can be characterized separately by several ^{13}C MAS experiments. An example is presented in Figure 7.

The Chemical Shift (CS) values (Table 1; see numbering in figure 6) were measured a few times by repeated runs performed at random on the different samples. This procedure was necessary for establishing CS differences of the order of 0.2 ppm.

Low molecular weight polymethylenes show *gauche* conformations on the chain ends; the chemical shifts can be compared to the pure bulk alkanes[20]. The presence of *gauche* conformations is reasonable if one consider that the last few bonds require less lateral space for gaining motion, some constraints being removed. This is also consistent with the shortening of the longitudinal period of about 1 Å per chain described by X-ray diffraction in linear-alkane inclusion compounds with PHTP[21].

However, the most relevant observation is that the chemical shift of the internal bonds is asymptotically shifted from an upfield position and moves towards the value of polyethylene in inclusion state (33.8), as the chain length increases (Table 1). This indicates again that deviations of the internal bonds from the *trans* conformation occur: deviations are larger as chain-lengths are shorter. Conformations closer to *gauche* arrangements than in polyethylene must be present on some internal bonds in order to explain the chemical shifts. Although at a distance from the chain-ends, as in a molecule as long as 60 carbon atoms, the influence of the chain-ends is still present on conformations.

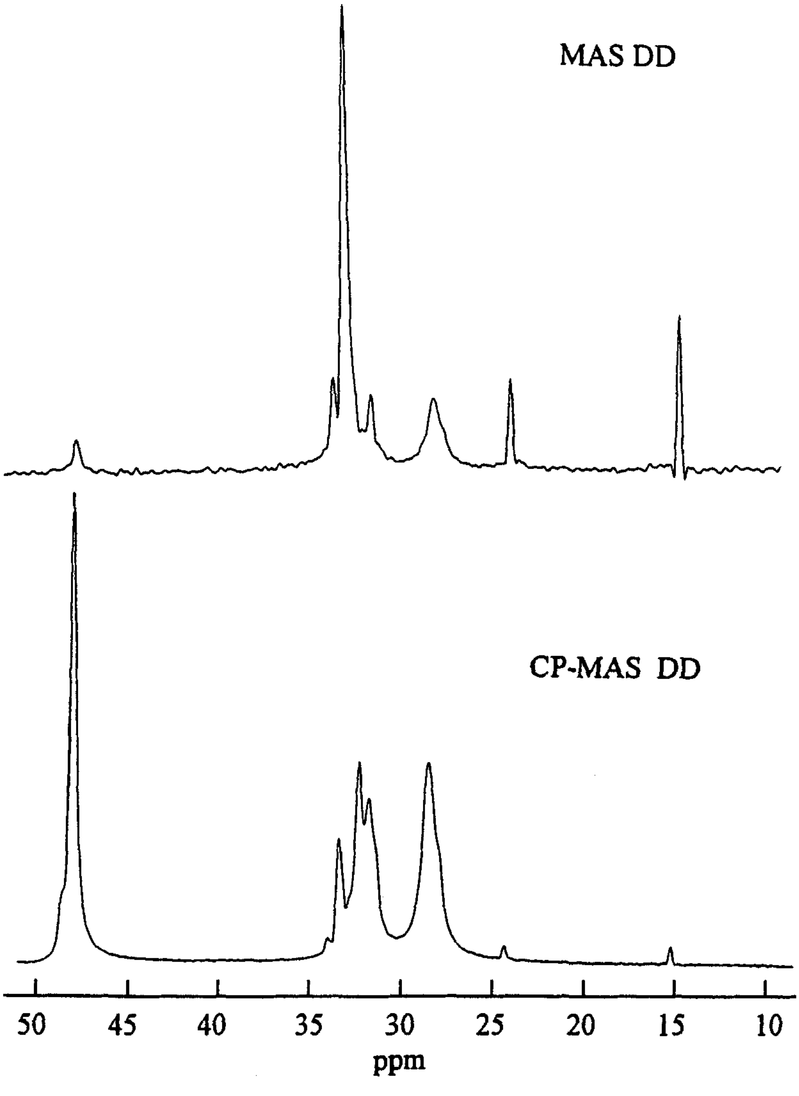

FIGURE 7. CP MAS DD and MAS DD carbon spectra of C32/PHTP-IC at room temperature and 75.5 MHz.

The motions generated on the chain-ends, endowed with a larger conformational freedom, propagate towards the inner chain with less tendency to form *gauche* conformations as longer the chain is. Since local librations have by definition limited coherence and identical frequency and amplitude in short and long molecules, some kind of waves must be conceived carrying the conformational defects. The waves must be though as chaotically generated. In our opinion those last evidences support the already proposed hypothesis of the existence along confined polymer chains of *traveling defects* or, if chain torsion is involved, of so called *twistons*[7,15].

TABLE 1 Chemical shifts (ppm) of polymethylenes in PHTP.

Chain length	Carbon: 3	Internal	4	2	1
C16	34.37	33.21	32.29	24.59	15.08
C16	34.34	33.21	32.26	24.59	15.08
C16	34.34	33.19	32.26	24.56	15.08
C32	34.15	33.45	31.99	24.37	15.15
C32	34.15	33.51	31.99	24.40	15.15
C32	34.10	33.48	31.98		
C40	34.20	33.60	32.04	24.41	15.15
C40	34.17	33.58	32.04	24.39	15.15
C40	34.19	33.58	32.01	24.42	15.15
C60	------	33.75	------	------	15.15
C60	------	33.73	------	------	15.15
C60	------	33.75	------	------	15.18
PE		33.80			

Measurements were repeated three times for each sample

The Matrix Point of View

How linear long molecules can affect with their substantial motions the crystal structure of the adduct? Are the observed librations of polymethylene bonds propagating to the surrounding matrix in the form of lattice vibrations? Is any difference on the multiplicity of signals produced by the chain-length and thus by the concentration of the chain-ends? The answers are provided by the spin-lattice relaxation times and by the chemical shifts of the matrix. The relaxation times are basically dependent on the amount of vibrations in the system and the chemical shift pattern describes the spatial relationships among carbon atoms.

A novel run of the CP MAS spectra provided higher resolution of the matrix spectrum than previously attained[7]. The spectra of racemic PHTP and of one of the inclusion compounds are presented in Figure 8. No difference is apparent in any of the inclusion compounds regardless of the chain-length. Minor signals corresponding to pure PHTP may appear, if the stoichiometry is not correctly balanced and an excess of PHTP is present.

PHTP CP-MAS spectrum shows, for carbon nr. 1 four definite signals of the same intensity but one. The multiplicity is consistent with six carbons of the molecule different one from another, except for two of the carbons. Less resolution is achieved on the remaining carbon atoms. The crystal structure of PHTP would not explain such a multiplicity without taking into account the presence of two enantiomers being substituted at the same site. A parallel study of optically active PHTP molecules in the pure and inclusion-compound form has been carried out[16]. Multiplicity of signals decreases in the inclusion compounds, due to a different crystal packing. In particular, carbon nr. 1, which is far enough from the walls to be not affected by the guest molecules, is a sharp singlet and is sensitive to the purity of the inclusion compound.

Apparently, due to the dynamic averaging of the guest molecules the carbons on the walls of the nanotube (carbon nr. 3) feel substantially indistinct objects as guests. In addition, no differences appear among the inclusion compounds from the point of view of the matrix chemical shifts. The chain-ends, the inner carbons and the interchain spacing are not distinguished by the wall carbons, suggesting that the guest molecules can fast translate along the nanotube.

The carbon longitudinal relaxation times of the pure PHTP are of the order of 300 s, suggesting a rigid crystal structure. A sharp decrease of the relaxation times of the matrix signals in the inclusion compounds, as compared to the pure PHTP, is instead noticed[6,7]. No substantial differences were detected in the series of inclusion-compounds for carbons nr. 1 and nr. 2, being not exposed to the guest motions. Particularly, methyne groups nr. 1 are essentially in a close relationship with other methyne groups on the next neighboring matrix molecule. Carbon nr. 3, being instead exposed to the guest molecules in the nanotubes, show shorter relaxation times and contains sometimes two components: the shorter relaxation is prevailing when shorter alkanes are included, indicating that the mobile guest acts as a magnetization sink for the carbons from the nanotube walls.

A similar behavior was already observed in polyisoprene/PHTP inclusion compound, where methyl carbons of polyisoprene can enhance the relaxation rates of a part of the tube-wall carbons of the matrix[6], and in a series of emiflorinated alkanes, where the hydrogen-containing part of the chain is associated to a faster relaxation compared to the fluorinated part[22].

FIGURE 8. CP MAS DD carbon spectra of pure PHTP (below) and a PHTP inclusion compound (above) at room temperature and 75.5 MHz.

CONCLUSIONS

Solid state nuclear magnetic resonance experiments performed on ^{13}C and ^{2}H nuclei, respectively in the high resolution and wide-line modes, provided us a detailed description of the conformation and the dynamics of linear polymethylene chains of different length, once isolated in a crystalline tubule. The existence of motions and the anisotropy of motion was proved by the longitudinal relaxation times and by the powder pattern of static deuterium spectrum. On the other hand, high resolution carbon spectra provided the average chemical shifts associated to the dynamics of the single conformations.

Gauche conformations were observed on the chain ends and a large departure of the internal conformations from the *trans*-planar arrangement was pointed out, especially in the short-chain elements of the series. Similarly to our observations, n-alkanes in the urea inclusion compounds as long as C_{20}, show the chemical shifts due to the terminal carbon atoms as independent of the chain length; on the other hand only the chemical shift of the gamma carbon is progressively shifted down field with increasing chain length[23]. In that series of short alkanes the behavior of the inner carbon atoms was not yet clearly highlighted. By following molecular mechanics calculations and estimating dipolar interactions, the existence of other conformations besides the all-*trans* was later deduced, against what it was generally believed[24]. Oscillations of the inner methylenes produced by chain twists have been already proposed in order to explain the deuterium NMR profile of included n-alkanes in urea[25]. However, a puzzling increasing of the dipolar scaling factor, with the chain length observed for the internal methylenes in ref. 24, forced the authors to state that the dipolar coupling constant is expected to *decrease* with the increasing size and torsion flexibility of the molecule and, in any case, *vibrational motions can not cause the scaling factor to increase with the carbon number*[24].

Actually the dependence of the internal methylene chemical shifts by the chain-length, shown here as our new contribution on a series of larger molecules, supports the description of the defects as containing conformations largely departed from the planar form, provided they can produce at least a slight γ interaction[26]. In our view this description can also include dynamically explored *gauche* conformations, although less and less probable, as the observation is moved towards the very core of the long molecule. Molecular mechanics calculations indicated the feasibility of *gauche* conformations even in the smaller tubes of urea at several bonds from the chain ends[24].

In addition, the present results can be considered as a strong suggestion for a concerted mechanism of motion, given the widely discussed chain-length dependence of the chemical shifts, because the defects propagate at a long distance from the chain-ends. Provided the dynamic nature of the phenomenon, as clearly demonstrated, thermally activated defects must be generated at the chain-ends, where they can more easily dwell and then travel like waves to the opposite end. The longer the chain, the lower the probability to find a defect. this model is reasonable considering that any mechanical system of sufficient length obeying to elastic laws, such as can be considered a long chain molecule, is subjected to wave propagation.

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