Isolated Linear Alkanes in Aromatic Nanochannels

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Novel channel-like inclusion compounds were formed by tris(*o*-phenylenedioxy)spirocyclotriphosphazene (TPP) with linear hydrocarbons. The molecular characterization was performed by ^{13}C and ^{31}P solid-state NMR under magic angle spinning conditions. The hexagonal symmetry of the host was verified in the ^{31}P and ^{13}C MAS spectra and by X-ray powder diffraction patterns. The new inclusion compounds present congruent meltings, and the temperatures increase with chain length. These compounds provide the opportunity to observe hydrocarbons confined as isolated chains in the solid state at temperatures 200 K above their melting points. Furthermore, the aliphatic chains are in the unusual state of being surrounded by aromatic rings displaced parallel to the channel. This geometry was proved by a through-space 1.4 ppm upfield shift on the ^{13}C resonances of the guests, due to the aromatic ring current. The mobility at the chain ends and the propagation of the conformational defects within the guest molecules is discussed and a comparison made with alkanes in different inclusion compounds and bulk alkanes in the high-temperature modification. The formation of the inclusion compounds was also highlighted by through-space transferring of magnetization from the hydrogens of the host matrix to the chain carbons of a deuterated guest under Hartmann−Hahn conditions.

Introduction

Molecular confinement is receiving marked interest by the scientific community.[1] The properties of the confined molecules can be set according to the space available and the properties of the matrix. Some years ago[2,3] we proposed the NMR characterization of macromolecules confined to restricted spaces, and several supramolecular adducts were prepared and described. Unusual properties were discovered for single polymer chains when surrounded by cylindrical nanochannels, light being also shed on the motional phenomena of the same polymers in the bulk. A little later the dynamics of single chains of included polyethylene (PE) and long-chain hydrocarbons, as well as the packing of the matrix, was addressed.[4,5] The inclusion compounds are formed by the saturated hydrocarbon host of perhydrotriphenylene (PHTP). In this case, the host−guest interaction is soft being based on van der Waals forces. Nonconventional mesophases are produced, and the guest molecules are mobile even at very low temperatures. The dynamic behavior of the included molecules is, from several aspects, similar to the high-temperature modification of crystalline polyethylene and the hydrocarbon rotator phases in the bulk.

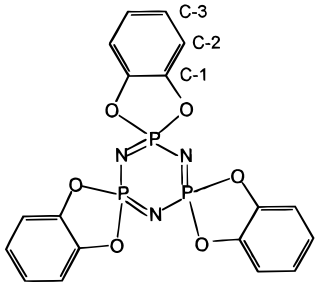

Figure 1. Representation of tris(*o*-phenylenedioxy)cyclotriphosphazene (TPP) molecule.

Our present interest lies in matrices (both organic and inorganic) with different spaces available and different guest molecules interactions; this work considers a nanochannel formed by aromatic rings facing the included polymethylene chains, a result that can be achieved by cyclic trimers of phosphazenes, particularly, tris(*o*-phenylenedioxy)spirocyclotriphosphazene (TPP) that presents channels of 4.5 Å width[6,7] in the crystal state (Figures 1 and 2). Aromatic rings are placed parallel to the channels, providing a special environment for the saturated hydrocarbon chains.

As recently shown, cyclo-[8] and polyphosphazenes[9,10] are also stimulating from the NMR point of view, due

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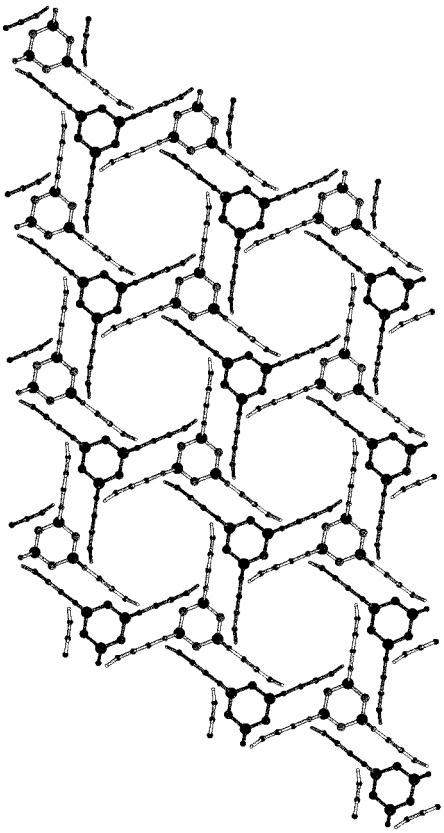

Figure 2. Hexagonal crystal packing of the TPP IC that forms channel-like structures with a 4.5 Å diameter, as reported by Allcock et al.[6]

to the presence of several nuclei suitable for magnetic resonance interaction experiments.

Molecular simulations of *n*-tetracontane in PHTP IC[11] and our NMR results of PHTP ICs with several *n*-alkanes[12] indicate a twisting of the chain, but the trans conformation is substantially retained. The chain must support diffusional motion along the axis, as shown by ^{13}C relaxation rates and deuterium NMR spectra.[5] A low activation energy of 1.1 Kcal per mole was measured in the PHTP/polyethylene system, consistent with the absence of trans/gauche conversion.[4] Also the chemical shift of polyethylene is coincident with the trans conformation. In any case, the mobility is large enough to obtain a fast relaxation process.

On the other hand, the chemical shift dependence of the inner-chain carbon atoms for a series of included normal alkanes from C_{16} to C_{60} studied in PHTP[12] suggested the presence of a few bonds in the gauche conformation, that are dynamically converted into the trans conformation and that propagate along the chains. Apparently the gauche conformations become less probable as chain length increases. Chemical shift dependence on the chain length was also observed by Terao in urea matrix.[13] Although the polarity is different, both matrices show an apolar environment toward the guest. A polymethylene chain completely embedded in an aromatic environment has never been studied by solid-state NMR; the main target of the present study was to understand chain-end conformations in nanochannels, how defects form and propagate within the polymethylene chains and, finally, how frequently the defects occur. This may depend on the polarizability of the aromatic rings in the matrix and the constraints of the unusual environment.

Experimental Section

Synthesis. The synthesis of TPP was carried out by the original method proposed by Allcock.[14] Under N_2 atmosphere, a solution of 10.8 g of cathecol in 27.5 mL of triethylamine and 90 mL of anhydrous tetrahydrofurane (THF) distilled from metal sodium solution was added dropwise under stirring to sublimed hexachlorophosphazene (11.53 g) dissolved in 175 mL of THF. The triethylamine had first been dried over calcium hydride for 1 h and then filtered. Stirring and refluxing was continued for 40 h at 60 °C. The white precipitate was filtered off, washed with THF, and then distilled water (3 L). The product was dried under vacuum (10^{-2} Torr) until reaching constant weight. A prolonged extraction with benzene in a Kumagawa apparatus and then crystallization in benzene yielded the TPP/benzene inclusion compound. Mass spectrometry identified the residue from the apparatus as triethylammonium tris(*o*-phenylenedioxy) phosphate.[15]

The TPP/*n*-alkanes ICs were obtained by crystallization from a benzene solution of TPP/benzene IC and *n*-alkanes (TPP/*n*-alkanes ratio of approximately 10:1.5 w/w). The *n*-alkanes were purchased from Fluka. The polyethylene used in the preparation of the polymer inclusion compound was synthesized from diazomethane. The molecular weights of the linear high-density polyethylene, M_n and M_w, are 1.75×10^4 and 7.49×10^4, respectively. The TPP/PE IC was prepared by intimately mixing together the two components (with excess of TPP: TPP/PE ratio of approximately 10:0.7 w/w) in the powder form, melting them together at 270 °C under an inert atmosphere for four 10-min intervals. The synthesis was monitored by DSC analysis. The TPP/PE IC could not be obtained from benzene solution due to the low solubility of the high molecular weight polymer. The linear PE-d_4 was obtained from Merck & Co. and used as received. The TPP/PE-d_4 IC was formed by heating a mixture of TPP and PE-d_4 at 120 °C for 10 min and then at 270 °C for 1 h under N_2 atmosphere (TPP/PE-d_4 ratio of approximately 10:0.7 w/w). The purity of the TPP inclusion compounds was checked by ^{31}P MAS NMR.

For the synthesis of PHTP molecules and the *n*-alkanes and PE ICs the reader is referred to ref 12.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) traces were performed on a Mettler Toledo Star thermal analysis system equipped with a N_2 cooling apparatus. The experiments were run under N_2 atmosphere from −100 to 400 °C. The sample weight for DSC measurements is 9 ± 1 mg.

X-ray Diffraction. XRD profiles of the powders were obtained with a Siemens D500 Diffractometer, using Cu Kα radiation and a diffracted-beam monochromator. The experiments were run at room temperature. The structures are confirmed by refinement with LeBail method.[16]

Solid-State NMR. NMR high-resolution ^{13}C and ^{31}P MAS NMR spectra were run at 75.5 and 121.5 MHz, respectively, on a Bruker MSL300 instrument operating at a static field of 7.4 T. A MAS Bruker probe head was used with 7 mm ZrO_2 rotors spinning at a standard speed of 4−6 kHz. All the experiments were made using a high-power proton decoupling (DD) field: 90° pulse for carbon was 4 μs, 90° pulse for

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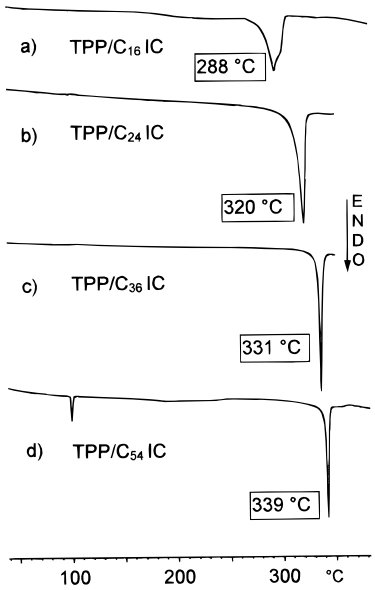

Figure 3. Differential scanning calorimetry traces from 25 to 350 °C: (a) TPP/C_{16} IC; (b) TPP/C_{24} IC; (c) TPP/C_{36} IC and TPP/C_{54} IC. The heating rate is 10 deg/min.

phosphorus was 5 μs, and 90° pulse for proton was 4 μs. Single pulse excitation (SPE) experiments were run using a recycle delay of 100 s for TPP ICs and 5 s for PHTP ICs. Cross Polarization (CP) MAS experiments were performed by applying a delay time of 6 s and a contact time ranging from 1 to 18 ms. All the experiments were performed at room temperature.

The resolution for carbon was checked on glycine (width at half-height = 23 Hz). Crystalline polyethylene (PE) was taken as an external reference at 33.63 ppm from tetramethylsilane (TMS).[17] The resolution for phosphorus was checked on a $NH_4(H_2PO_4)$ sample. It was used as the second standard, assigning the ^{31}P chemical shift of $NH_4(H_2PO_4)$ to +1 ppm with respect to 85% H_3PO_4.[18] ^{13}C T_1 values were obtained using the method developed by Torchia.[19] Spectra were acquired at 9−14 τ values.

Results and Discussion

DSC Characterization of the Inclusion Compounds. The adducts of TPP with linear saturated hydrocarbons of increasing molecular weight were obtained by cocrystallization in benzene. After drying, the crystalline TPP ICs melt at a far higher temperature (290−340 °C) than the pure hydrocarbons (the highest melting point is 129 °C for PE) and the pure matrix (245 °C), indicating a higher stability in the adducts than the components. Figure 3 reports the calorimetric scans of some TPP/*n*-alkane ICs; the TPP/C_{54} ICs DSC trace presents an endothermic peak associated with the pure *n*-alkane that has not been completely included in the channel.

The formation of the TPP/PE inclusion compound was not obtained by crystallization from a solution but by melting the PE and TPP mixture at 270 °C, the temperature at which both the components are melted and the crystallization of the adduct occurs. The first heating of the mixture (Figure 4) presents the endotherm peaks at 129 and 245 °C that, respectively,

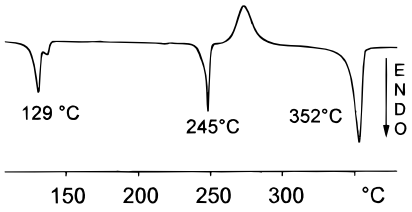

Figure 4. First differential scanning calorimetry run from 100 to 400 °C of a TPP and PE mixture. The weight fraction of PE corresponds to 7%. The heating rate is 10 deg/min.

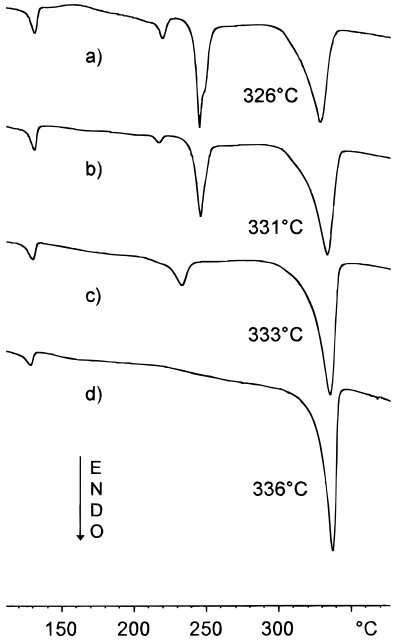

Figure 5. DSC runs of the TPP and PE (7% fraction weight) products after thermal treatment at 270 °C for (a) 10 min; (b) 20 min; (c) 30 min; and (d) 40 min. Before each thermal treatment at 270 °C the products were subjected to mixing and grinding. The heating rate is 10 deg/min.

correspond to the melting points of PE and pure TPP, the exotherm peak at 270 °C, related to the formation of the adduct and subsequently the melting of the TPP IC at 352 °C. In other DSC runs of the mixture the exotherm transition was not observed due to the overlapping at the melting transition of the pure TPP. After the melting of the adduct, decomposition partially took place.

A few hundreds of milligrams of the product were obtained by several cycles of grinding and thermal treatments. Each thermal treatment was carried out in an oven at 270 °C for 10 min. A DSC run was performed after each cycle (Figure 5). The DSC trace of the sample subjected to the first 10 min thermal treatment (Figure 5a) shows the unreacted PE and TPP peaks. The peak at 225 °C corresponds to the solid−solid transition of the monoclinic TPP crystalline cell, as previously described.[20] Only after the fourth thermal treatment the melting peak of free TPP at 245 °C is absent (Figure 5d). A small residue of free crystalline polymer (mp 129 °C) is still present, as revealed by solid-state NMR (see next section). After each thermal treatment the melting points of the adducts rise, but never reach 352 °C

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Table 1. Melting Points of TPP ICs (°C)[a]

C_{12}	C_{16}	C_{19}	C_{24}	C_{36}	C_{54}	PE
268	288	312	320	331	339	352

[a] The precision of the melting points is ± 1 °C.

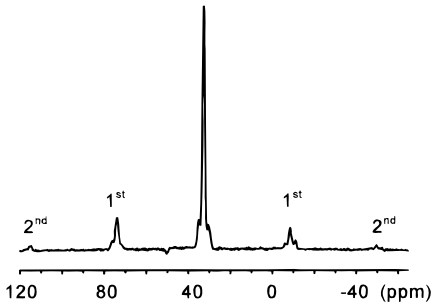

Figure 6. ^{31}P SPE MAS spectrum of TPP/C_{16} IC, spinning speed of 5000 Hz. A recycle delay of 60 s is applied.

(Figure 4) due the presence of free PE that disturbs the crystal formation of the adduct.

Table 1 shows the melting temperatures of the polymethylene chains in TPP ICs. They rise smoothly as the chain length increases and reach asymptotically the value of 352 °C. The melting entalpy (ΔH_m) values measured for TPP/*n*-alkanes ICs are about 140 J/g for guests containing more than 17 methylene units. The enthalpy value of C_{12} and C_{16} (105 J/g) may be affected by the volatility of the guests. The melting entropy is about 0.2 J/(g K).

The above results were compared with a series of inclusion compounds of *n*-alkanes in PHTP channel-like structures. The ΔH_m values of TPP/*n*-alkane ICs (per mole of TPP matrix) are about three times bigger than those of PHTP/*n*-alkane ICs (per mole of PHTP matrix), due to looser interactions in the saturated matrix. The melting entropy is about the same.

In both cases the melting temperatures are higher than the melting points of both pure guests (<130 °C) and hosts (PHTP 125 °C and TPP 245 °C). Thus the melting is congruent in both cases. A different melting behavior is shown for urea/*n*-alkane ICs.[21] A direct comparison of the PHTP and urea ICs with the same guest (C_{16}) was recently published.[22] In that report the factors influencing congruent/incongruent melting in binary compounds are summarized. In the case of TPP/*n*-alkane ICs, the congruent melting at high temperature is explained by the high ΔH of formation. In addition, the host and guest state of motion, later determined by NMR, gives a contribution to the increased entropy in the solid, decreasing the ΔS of melting.

NMR Characterization of the TPP ICs. The ^{31}P MAS spectrum of TPP/C_{16} IC shows an asymmetric triplet with the main peak at 32.7 ppm (Figure 6). The chemical shift value identifies the product as the cyclophosphazene ring; the absence of peaks at −83 and −7 ppm[20] in the ^{31}P spectrum, due to triethylammonium tris(*o*-phenylenedioxy) phosphate and (*o*-phenylenedioxy) phosphate, ensures its purity. The asymmetric triplet, more evident in the spinning sidebands, derives from the dipolar ^{31}P and ^{14}N coupling that is not completely suppressed by magic angle spinning[23−26] and is complicated by the dipolar coupling to two ^{14}N atoms. The ^{31}P MAS spectra of all the TPP ICs reproduce the same pattern. The presence of one main signal agrees with the high symmetry of the hexagonal cell where all the phosphorus atoms are equivalent. X-ray powder diffraction of TPP ICs confirms the formation of the hexagonal packing (space group $P6_3/m$). The unit cell dimensions are close to those reported by Allcock[6] for TPP/PE IC but there is a 5% deviation depending on the different chain lengths of the guests.

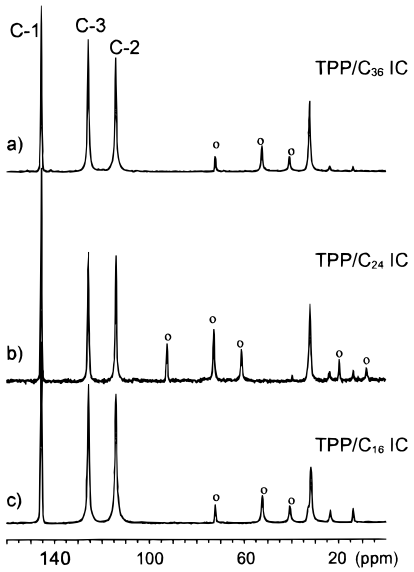

Figure 7. ^{13}C CP MAS spectra: (a) TPP/C_{36} IC sample, spinning speed of 5540 Hz; (b) TPP/C_{24} IC sample, spinning speed of 4000 Hz; (c) TPP/C_{16} IC sample, spinning speed of 5540 Hz. A contact time of 3 ms is applied. The circles indicate the spinning speed sidebands.

^{13}C CP MAS NMR spectra of the TPP/*n*-alkane ICs show three peaks for the TPP matrix at 145.5, 114.1, and 125.7 ppm associated with C-1, C-2, and C-3 carbon atoms, respectively (Figure 7). The NMR result is in agreement with a D_{3h} symmetry of the TPP molecule in the hexagonal crystal cell. The hexagonal crystal cell ensures that all the carbon atoms belonging to the same species (p.e. C-3) are equivalent. No deviation of the side aromatic paddle of the TPP molecule is observed in the ^{13}C NMR spectrum; in fact, any such deviation would generate a multiplicity of signals for each carbon species, as was detected in the monoclinic crystal cell of the TPP matrix.[20] All the TPP/*n*-alkane ICs present hexagonal crystal packing. Figure 7 shows the ^{13}C CP MAS of some selected TPP IC samples: in the aliphatic region, the signals of the *n*-alkanes included in the TPP nanochannels are detected. The intensities are weaker than those of the aromatic peak due to their higher mobility and less efficient cross polarization.

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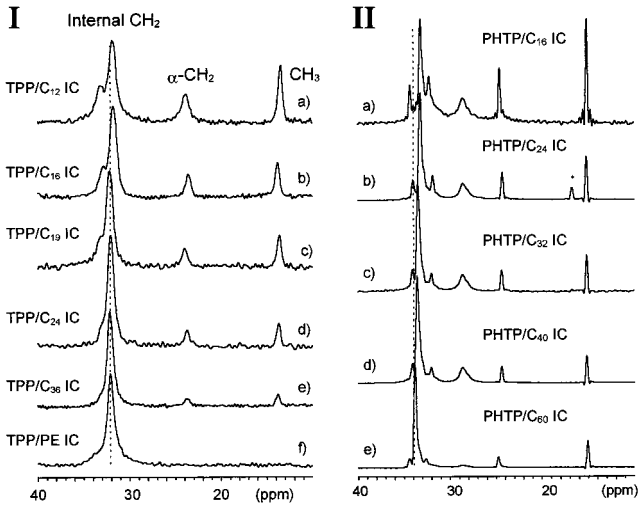

Figure 8. (I) ^{13}C SPE MAS spectra: (a) TPP/C_{12} IC; (b) TPP/C_{16} IC; (c) TPP/C_{19} IC; (d) TPP/C_{24} IC; (e) TPP/C_{36} IC; (f) TPP/PE IC; a recycle delay of 100 s is applied and spinning speed of 5000 Hz was used. (II) ^{13}C SPE MAS spectra: (a) PHTP/C_{16} IC; (b) PHTP/C_{24} IC; (c) PHTP/C_{32} IC; (d) PHTP/C_{40} IC; (e) PHTP/C_{60} IC; a recycle delay of 5 s is applied. The peak indicated with an asterisk (*) is associated to an impurity.

Table 2. ^{13}C δ (ppm) of TPP ICs Measured from ^{13}C MAS NMR Spectra (Recycle Delay = 100 s)[a]

^{13}C δ (ppm) TPP ICs	TPP/C_{12}	TPP/C_{16}	TPP/C_{19}	TPP/C_{24}	TPP/C_{36}	TPP/PE
C-1	145.50	145.54	145.56	145.55	145.58	145.61
C-3	125.68	125.70	125.72	125.72	125.74	125.76
C-2	113.98	114.07	114.07	114.08	114.17	114.21
CH_3-	13.46	13.84	13.57	13.70	13.76	–
C_α $-CH_2-$	23.81	23.70	23.87	23.82	23.77	–
C_β $-CH_2-$	33.18	33.02	33.19	–	–	–
int. $-CH_2-$	31.81	31.86	32.06	32.08	32.15	32.13

[a] The values were measured by repeated experiments. Values given have uncertainties of ± 0.05 ppm.

The aliphatic region of the guest molecules is highlighted in the ^{13}C SPE MAS spectra (Figure 8, part I). The signals of the methyl groups at 13.7 ppm the α-methylenes at 23.8 ppm and the β-methylenes at 33.1 ppm are detected separately from the inner carbons at 32.1 ppm. As the chain length increases, the chain end carbon signals appear weaker; the β-methylene peak in the TPP/C_{36} IC already disappears as it is overlapped by the signal of the inner carbon atoms that show the most intense peak at 32.1 ppm (Table 2). The intensity ratio of end/inner carbons shows good agreement with the theoretical ratio, the spectra being recorded with a long recycle delay (100 s) that ensures the quantitative response of the aliphatic region.

The chemical shifts of the aromatic TPP matrix do not change in the series, the crystal cell being hexagonal in all the ICs; therefore the TPP molecule chemical shift can be exploited as the internal reference to accurately measure the chemical shift of the inner carbon atoms. As the chain lengths increase, a careful analysis of the chemical shifts identifies a progressive downfield shift of the inner carbon signals (from 31.8 ppm in the TPP/C_{12} IC to 32.1 ppm in the TPP/PE IC) (Table 2). This is only slight considering the 0.05 ppm measurement error and the overlapping of C_γ atom signals in short-chain hydrocarbons.

Table 3. ^{13}C δ (ppm) of PHTP ICs[a]

^{13}C δ (ppm) PHTP ICs	PHTP/C_{16}	PHTP/C_{32}	PHTP/C_{40}	PHTP/C_{60}	PHTP/PE
CH_3-	15.08	15.15	15.15	15.15	–
C_α $-CH_2-$	24.59	24.37	24.41	–	–
C_β $-CH_2-$	32.29	31.99	32.04	–	–
C_γ $-CH_2-$	34.34	34.15	34.20	–	–
int. $-CH_2-$	33.21	33.48	33.58	33.75	33.8

[a] The values were measured by repeated experiments. Values given have uncertainties of ± 0.5 ppm.

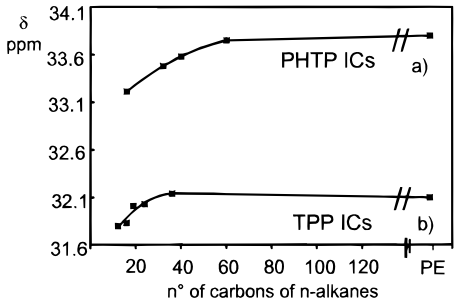

Figure 9. Comparison of the inner methylene ^{13}C chemical shifts vs number of carbon atoms of *n*-alkanes and PE: (a) in PHTP and (b) in TPP ICs.

The chemical shift values of *n*-alkanes in TPP ICs are compared to those detected for *n*-alkanes in PHTP ICs (Table 3) that were previously studied. The PHTP molecule forms a channel-like structure with a 5.7 Å diameter and provides a full aliphatic environment. The upfield drift of the inner carbon atoms for decreasing *n*-alkane length (from C_{60} to C_{16}) included in PHTP was previously demonstrated in repeated measurements (Figure 8, part II). The chemical shift, that is averaged by the conformations, suggests the presence of a small number of bonds exploring gauche conformation dynamically interconverted into trans conformations. The shorter is the chain length the more frequent are the gauche defects penetrating in the inner part of the chain. Complex gauche defect arrangements must propagate rapidly from one end to the other within the chains (see also next paragraph).

The above conclusions are derived from ^{13}C chemical shift dependence on γ-gauche interaction in linear alkanes, producing an upfield shift of about 5 ppm for a gauche arrangement.[27] Therefore the downfield chemical shift of PE in TPP IC compared to those of *n*-alkanes indicates the highest content of trans conformation. Considering the drift of inner methylene chemical shift from *n*-alkanes to PE in PHTP it can be observed that C_{60} and PE resonate at the downfield limit (all-trans conformation). On the contrary, in TPP the limiting value is already reached by short hydrocarbons ($<C_{20}$), owing to less space being provided by the TPP matrix, compared with the PHTP (Figure 9). Moreover, the smaller chemical shift difference between the signals of the inner carbons of C_{16} and PE in TPP highlights the larger and smoother chemical shift increase observed in PHTP (Figure 9). These results suggest that a smaller quantity of gauche defects is present in the

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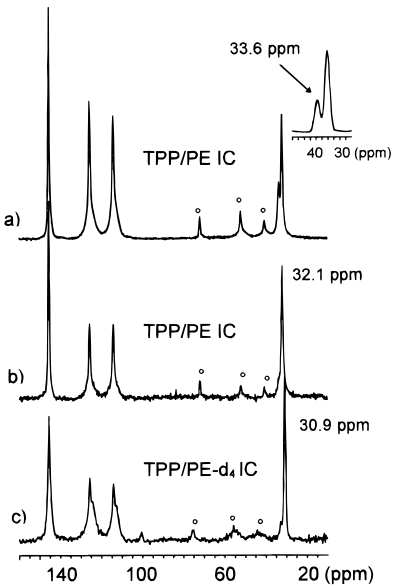

Figure 10. (a) ^{13}C CP MAS spectrum of TPP/PE IC, spinning speed of 5550 Hz, contact time of 3 ms. ^{13}C SPE MAS spectra: (b) TPP/PE IC sample, spinning speed 5550 Hz; (c) TPP/PE-d_4 sample, spinning speed of 5440 Hz. A recycle delay of 100 s is applied. The circles indicate the spinning speed sidebands.

hydrocarbon chains when confined in the TPP nanochannels. This result is due to the smaller free space experienced by the chains in the TPP channel. The average cross-section estimation for the channel by X-ray diffraction is 5.7 Å in PHTP hydrocarbon ICs and 4.5 Å in TPP ICs, showing a hexagonal crystal cell.

From Figure 9, it can be seen that the chemical shifts of the *n*-alkanes in TPP are also affected by the aromatic environment. The chemical shift resonates 1.4 ppm upfield compared to that of *n*-alkanes in PHTP. In fact, PHTP has a completely saturated environment that has little influence on the chemical shift, while TPP forms channels surrounded by aromatic rings facing the guests. The upfield chemical shift of polymethylenes in TPP ICs derives from the magnetic susceptibility contributions generated by the aromatic hosts.[28] The ring current shielding markedly influences the polymethylene chemical shift because of the specific adduct geometry, methylene units being directly above the aromatic rings. The chemical shift difference between PE surrounded by the aromatic environment and the orthorombic PE phase in the trans conformation is directly observed by ^{13}C CP MAS in the sample containing an excess of PE (Figure 10a). The orthorombic crystalline phase of PE gives rise to the signal at 33.6 ppm compared to the 32.1 ppm value of PE in TPP IC (Figure 10a). In the CP spectrum of Figure 10a, the pure PE phase can cross-polarize better than PE included in TPP nanochannels, the former being a more rigid system (Figure 10b).[29]

^{13}C signals of pure *n*-alkanes in the high-temperature modification, which experience a fully saturated environment, resonate 1.5 ppm downfield with respect to the same hydrocarbons in the unusual aromatic environment, in agreement with the above discussion. For

Table 4. ^{13}C Chemical Shift δ (ppm) Comparison of *n*-C_{36} Hydrocarbon in the "Rotator" Phase, *n*-C_{36} Hydrocarbon in TPP IC and C_{40} Hydrocarbon in PHTP IC[a]

^{13}C δ (ppm)	*n*-C_{36} hydr.	PHTP/C_{40} IC	TPP/C_{36} IC	*TPP/C$_{36}$ IC*(*)
CH_3-	15.2	15.2	13.8	15.2*
$C_\alpha -CH_2-$	24.8	24.4	23.8	25.1*
int. $-CH_2-$	33.6	33.6	32.1	33.5*

[a] The chemical shift values marked with an asterisk are shifted 1.4 ppm downfield to compensate the ring current contribution.

a comparison of *n*-alkane conformations in TPP hosts and in bulk in the high-temperature modification (rotator phase),[30] we report the chemical shift values of C_{36} in TPP IC shifted 1.4 ppm downfield to compensate for the ring current contribution (Table 4). The value of 1.4 ppm leads to the alignment of the inner methylene chemical shifts of C_{36} in TPP with those of the bulk phase at high temperature (within experimental error). In pure *n*-alkanes in the high-temperature phase, the chemical shift of 15.2 ppm for methyls and 24.8 ppm for α-methylenes are due to a considerable gauche content of the chain ends. The chemical shifts (marked with an asterisk in Table 4) of the chain ends in TPP IC are close to those of the high-temperature C_{36} phase, indicating that the same conformations are experienced by the chain-ends in both systems.

Dynamics of Host and Guest Molecules. The dynamic behavior of the TPP ICs can be studied by the measurement of the ^{13}C T_1 relaxation times and the application of specific pulse sequences. In the absence of other relaxation mechanisms ^{13}C T_1 values are mainly dependent on the correlation times of the observed atoms. The function describing the phenomenon shows a T_1 minimum value. This singularity corresponds to the most efficient relaxation mechanism obtained when the frequency of the observed nucleus matches the reciprocal of the correlation times. In our case the correlation times are in slow motion regime (except for the methyl groups), thus longer relaxation times describe rigid environments. The ^{13}C SPE MAS experiment, performed with short recycle delays which prevent the full relaxation of the system, highlights the carbon atoms endowed with high mobility, more specifically the guest molecules (Figure 8).

The relaxation rates of the C_{36} alkanes included in the TPP IC are fast: the ^{13}C T_1 of α-methylenes and the inner methylenes present relaxation times of 8 and 20 s respectively, instead the ^{13}C T_1 of the methyls are very short (3 s) and close the above-described minimum due to very high mobility of this group. At room temperature, the short ^{13}C T_1 values suggest that fast molecular motions exist in the ICs. Also the PE relaxation times included in TPP nanochannels are fast, in fact, we measured ^{13}C T_1 of 12 s. A selective detection of the PE guest signal can be made using SPE MAS with a recycle delay of 100 s (Figure 10b). The small quantity of orthorombic PE phase present in the sample, generates no signal at 33.6 ppm, the ^{13}C relaxation times being too long and in the order of hundreds of seconds.[31]

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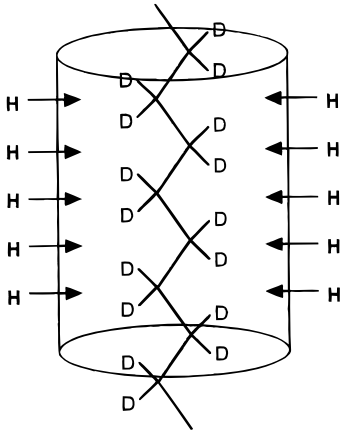

Figure 11. Schematic representation of the channel-like structure of TPP/PE-d_4 IC.

The relaxation times of guest molecules are also short compared to those of the TPP host molecules where values of 140, 90, and 100 s are respectively measured for C-1, C-2, and C-3 in the TPP/C_{36} IC. The values of aromatic side chains are compared to those of the TPP/benzene IC and TPP hexagonal phase obtained after the removal of benzene from the IC at 10^{-1} Torr at 75 °C. The inclusion compound with benzene shows ^{13}C T_1 relaxation times of 384, 304, and 195 s for C-1, C-2, and C-3, respectively. ^{13}C T_1 of 1000 s for the C-1 and 200 s for C-2 and C-3 atoms were measured for the latter sample. The relaxation mechanism can occur through motion of the guests and librations of the host molecules. The shortened relaxation time of the host matrix in the presence of *n*-alkane indicates that the aromatic carbons in the IC are also affected by a relaxation mechanism that occurs through a fast guest driven dynamic process.

Despite the mobility of the guest molecules, the cross polarization pulse sequence efficiently reveals the carbon nuclei of the methylene units even for a short contact time of 3 ms (Figures 7 and 10a), indicating the presence of spectral density components of a few thousand hertz motion regime. The cross polarization process allows the rare nuclei (^{13}C) to come into thermal contact with the neighboring system of abundant spins (protons) by means of a radio frequency pulse sequence. When the Hartmann−Hahn condition is fulfilled, the inverse of the cross polarization time $(T_{CH})^{-1}$ is proportional to the second moment of the dipolar coupling between the ^{13}C and ^{1}H nuclei, and considering that the second moment of the heteronuclear dipolar coupling varies, at a first approximation, as the inverse sixth power of the proton carbon distance, the cross polarization time (T_{CH}) is proportional to the sixth power of the proton carbon distance. To demonstrate the formation of the adducts we exploited the cross polarization phenomenon by applying $^{1}H-^{13}C$ CP pulse sequence at varying contact times on an appropriate supramolecular structure containing deuterons in the guest molecules (Figure 11), in a way similar to that already reported.[32] In particular, we formed the inclusion compound of perdeuterated PE (PE-d_4) and TPP molecules that contain protons only in aromatic rings. The CP experiments were also carried out on TPP/PE IC at varying contact times, for comparison. The ^{13}C signal intensities of the inner methylene for both the samples are reported in Figure 12. The signal intensity ratio of PE builds up faster than those of PE-d_4 because, in the former case, the carbon nuclei receive the magnetization directly from the ^{1}H covalently bonded to the methylene units. In the case of PE-d_4, the build-up of the ^{13}C magnetization derives from the TPP matrix hydrogens that are far from the methylene units.[32] The difference in behavior represents the magnetization transferred from the TPP protons to the methylene units of PE-d_4. Since this phenomenon is efficient for carbon nuclei surrounded by hydrogens within a few angstroms, the ^{13}C magnetization build-up of PE-d_4 demonstrates the through-space magnetization transfer from the matrix hydrogens at nanometric distances and thus the formation of the adduct. Extended phases of pure PE-d_4 do not give rise to any CP signal at 32.4 ppm (the ^{13}C δ of 32.4 ppm for pure PE-d_4 was measured by us with SPE pulse sequence). The ^{13}C signal of PE-d_4 included in TPP nanochannels is also recovered in the ^{13}C SPE MAS spectrum (Figure 10c) by applying a recycle delay shorter than expected for the bulk crystalline phase due to the higher mobility of the included molecules. The upfield shift (more than 1 ppm) of deuterated methylene units (30.9 ppm) derives from the isotope effect, as previously observed in deuterated polybutadiene.[2] Magnetic susceptibility contributions are added to the isotope effect, leading to a chemical shift 3 ppm upfield with respect to hydrogenated polymethylenes in the bulk.

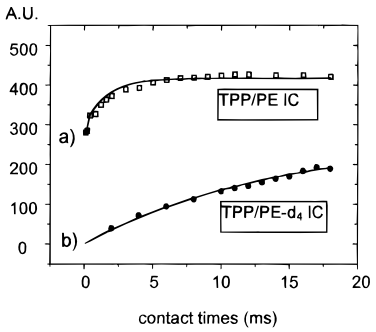

Figure 12. Intensities of the polymethylene ^{13}C chemical shifts vs contact times of (a) TPP/PE and (b) TPP/PE-d_4 ICs.

Conclusions

The melting points of the new adducts of TPP/*n*-alkane ICs are exceptionally high, providing a means of observing polymethylene chains in the solid state even at temperatures higher than the melting points of the bulk crystals. In particular, the TPP matrix (mp 245 °C) containing 15% of polyethylene (mp 129 °C) melts at 352 °C, showing an example of a stable molecular architecture, or in other words some kind of nanocomposite structure.

TPP provides an unusual environment for linear *n*-alkanes and polymethylene chains. TPP molecules packed in the hexagonal phase build up a tunnel for the single chain rich in π electrons. The through-space upfield shift due to the magnetic susceptibility of the aromatic environment is 1.4 ppm. The upfield shift

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demonstrates the interaction of the guest with the host and makes *n*-alkanes included in TPP IC easily distinguishable from the crystalline bulk state.

The *n*-alkane chains show motional disorder especially localized on the chain ends, where a high percentage of gauche bonds are present. This phenomenon was previously observed in the high-temperature crystalline modification of bulk alkanes,[30] in urea,[33] and in PHTP inclusion compounds.[12] Regardless of the space provided in the nanochannels, motion is always evident at the chain-ends because of their degree of freedom. A more general question is whether the gauche/trans disorder can penetrate the inner part of the chain and just how small the nanochannel diameter must be to prevent the occurrence of conformational defects. Once the diameter of the channel is reduced to a certain limit, the motion is realized by large librations around the trans conformation that can even twist the entire chains,[4,5] in a similar way as described by the dynamic simulations of Mattice et al.[11]

From a comparison of an extended range of molecular masses of alkanes included in TPP and PHTP matrices, we have come to the following conclusions:

(a) the concentration of gauche bonds in the inner chains decreases with increasing chain length; (b) TPP diameter channels are narrow enough to squeeze the alkyl chains very close to all-trans conformations in the inner bonds; (c) a slightly narrower nanochannel similar to that of TPP matrix (1 Å smaller than that of PHTP) does not prevent some dynamically averaged gauche bonds from forming along the chains; (d) when the gauche bonds are prevented, as in long alkyl chains, large librations are still present, as demonstrated by the short ^{13}C relaxation times of polyethylene in both the matrices (in PHTP, 6 s; in TPP, 12 s). From the deuterium NMR of deuterated polyethylene in PHTP mobility is still present even at low temperatures. The deuterium NMR of PE-d_4 in TPP is in progress to understand better the mechanism of motions.

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