Conformations and Motions of Polypropylenes Confined to Channels

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ABSTRACT: It is possible to study the solid-state conformations and motions of individual polymer chains, well-separated from neighboring chains, by observing their behavior in the narrow channels formed in their inclusion compounds with host clathrate molecules. The host clathrate channels provide a well-defined, constraining geometry for each included guest polymer chain. As a consequence, the experimental observations of the conformations and motions of constrained and isolated polymer chains are much easier to interpret than those of a bulk polymer sample where cooperative interchain interactions often predominate. In this paper we model the conformations and motions of polypropylene (PP) chains isolated in the narrow channels (D = 5.5 Å) of their inclusion compounds with perhydrotriphenylene (PHTP). We explicitly treat PP's with various stereosequences and find the following behavior: (i) neither stereoregular PP [isotatic (i) or syndiotactic (s)] can adopt its crystalline conformation in the PHTP channels; (ii) interconversion between channel conformers is not possible; and (iii) the channel conformers of s-PP are much more probable (have a much lower intramolecular energy) than the channel conformers of i-PP. These results are compared to the observations of PP–PHTP inclusion compounds reported by Sozzani et al.

Introduction

It has often been observed[1–3] that inclusion compounds may be formed between small-molecule host clathrates and high molecular weight guest polymers. These inclusion compounds have been formed by mixing the molten host and guest molecules or by precipitation from a common solution. In many instances a host clathrate–guest polymer complex may be produced by direct polymerization of monomer in the channels of the precurser host clathrate–guest monomer complex.

Independent of the method of preparation, the included guest polymer chains in these clathrate complexes reside in narrow cylindrical channels well separated from neighboring polymer chains by the walls of the host clathrate matrix. Examples of these polymer–clathrate complexes are presented in Figure 1, where the inclusion compounds[4,5] formed between urea and *n*-hexadecane and between *trans*-1,4-polybutadiene (TPBD) and perhydrotriphenylene (PHTP) are illustrated. Note the cylindrical shapes of the polymer-constraining channels and the separation of neighboring guest polymer chains by the walls of the host clathrate matrix.

Our primary interest in these polymer–clathrate inclusion compounds is the well-defined geometrical constraints placed on the included guest polymer by the walls of the host clathrate. We believe that observation of the conformations and mobilities of the included polymer chains can lead to a molecular level description of these polymer characteristics, which are free from the complications that arise in bulk, solid samples where neighboring polymer chains are closely packed and often move in a cooperative manner.

In previous papers[6–8] we have described our efforts to model the conformations and motions of polymers confined to the channels of their inclusion compounds with host clathrate matrices such as urea and PHTP. The inclusion compounds formed by *trans*-1,4-polydienes,[6] such as TPBD, with PHTP, polyethylene and poly(oxyethylene)[7] with PHTP and urea, and aliphatic polyamides and polyesters[8] with urea and PHTP were treated. Those conformations that fit in a cylinder whose diameter, D, is comparable to the channels in urea and PHTP (D = 5.25–5.5 Å) were derived for each polymer. A test was next performed to determine the possibility of interconverting between the various channel-bound conformers without any portion of the included polymer chain leaving the channel. In this manner it was possible to explain several aspects of the conformations and motions of these polymers when observed in their urea and/or PHTP inclusion compounds.

Here we report a similar treatment of polypropylene (PP) chains included in the channels of their clathrate compounds with PHTP. Sozzani et al.[9] have formed PHTP complexes with stereoregular isotatic (i) and syndiotactic (s) PP's. In addition, they[10] have succeeded in polymerizing propylene in the channels of its inclusion compound with PHTP, thereby producing the first free radical initiated PP in the form of its PHTP inclusion complex. After dissolution of the PHTP matrix, they were able to isolate the channel-polymerized PP and characterize its stereosequence via ^{13}C NMR spectroscopy and found the PP to be predominantly syndiotactic.

We will compare the results of our modeling PP chains confined to cylindrical channels with the observations reported for PP–PHTP complexes by Sozzani et al.[9,10] To provide the most realistic comparison, we have considered all possible PP tetrad stereosequences in our modeling.

PP in Clathrate Channels

Channel Conformers. To model PP chains confined to PHTP clathrate channels (see Figure 1), we simply considered only those PP conformations that fit into a cylinder with a diameter comparable to these clathrate channels (D = 5.5 Å). The portion of PP considered in our modeling is illustrated in Figure 2 and contains a tetrad stereosequence. Though only the *mmm* tetrad is drawn in Figure 2, we have considered the *rrr*, *mrm*, *rmr*, *rrm*, and *mmr* tetrads as well. Below the drawing are the statistical weight matrices, U, corresponding to the constituent bonds of PP. These matrices embody the rotational isomeric state (RIS) description of PP as established by Suter and Flory.[11]

In addition to the usual staggered rotational states t, g, and $\bar{g}$, Suter and Flory[11] found that the nearly eclipsed t^* and g^* bond conformations must also be considered in the configurational statistical treatment of PP. These rota-

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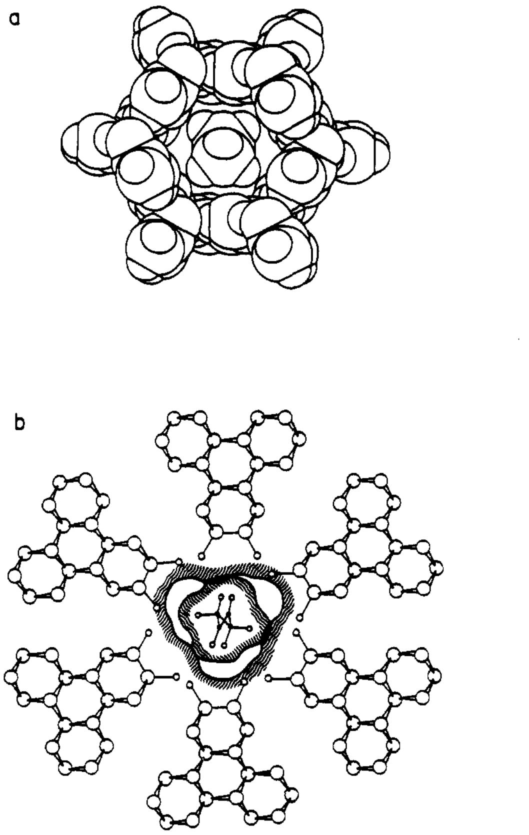
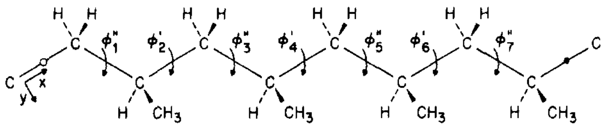


Figure 1. (a) Space-filling drawing of a channel in the urea–*n*-hexadecane clathrate.[4] (b) Schematic drawing of a *trans*-1,4-polybutadiene chain in the channel of its inclusion compound with PHTP.[5]



$$U' = \begin{array}{c} \\ t \\ t^* \\ g^* \\ g \\ \bar{g} \end{array}\begin{array}{c} \begin{array}{ccccc} t & t^* & g^* & g & \bar{g} \end{array} \\ \left[\begin{array}{ccccc} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 1 \\ 1 & 1 & 1 & 1 & 0 \end{array}\right] \end{array} \qquad U_m'' = \begin{bmatrix} 0 & \eta\omega^* & 0 & \eta & 0 \\ \eta\omega^* & 0 & 0 & 0 & \tau\omega^* \\ 0 & 0 & 0 & \omega^* & \tau\omega^* \\ \eta & 0 & \omega^* & 0 & 0 \\ 0 & \tau\omega^* & \tau\omega^* & 0 & 0 \end{bmatrix}$$

$$U_r'' = \begin{bmatrix} \eta^2 & 0 & \eta\omega^* & 0 & 0 \\ 0 & 0 & 0 & \omega^* & \tau\omega^* \\ \eta\omega^* & 0 & 0 & 0 & \tau\omega^* \\ 0 & \omega^* & 0 & 1 & 0 \\ 0 & \tau\omega^* & \tau\omega^* & 0 & 0 \end{bmatrix} \qquad U_1'' = \begin{bmatrix} \eta & \eta^* & \eta^* & 1 & \tau \end{bmatrix}$$

$$\eta = 1.0\ \exp(-60/RT) = 0.904$$
$$\tau = 0.4\ \exp(-500/RT) = 0.172$$
$$\omega^* = 0.9\ \exp(-1600/RT) = 0.061$$
$$\eta^* = 0.9\ \exp(-100/RT) = 0.760$$

Figure 2. PP tetrad fragment used to derive the conformations and motions of its channel-bound chains. The isotactic, or *mmm*, tetrad is drawn. Below the tetrad are presented the statistical weight matrices which embody the RIS model for PP derived by Suter and Flory.[11] Matrix elements have been evaluated for T = 25 °C.

tional states are defined in Figure 3, where $\phi_t = 15°$, $\phi_{t^*} = 50°$, $\phi_{g^*} = 70°$, $\phi_g = 105°$, and $\phi_{\bar{g}} = 245°$. The statistical weight matrix for the first CH$_2$–CH(CH$_3$) bond of the PP fragment in Figure 2 (ϕ_1'') is simply the row $[\eta\eta^*\eta^*1\tau]$ and corresponds to $\phi_1'' = t, t^*, g^*, g, \bar{g}$ as illustrated in Figure 3.

Bond lengths of 1.53 and 1.1 Å were adopted[11] for the C–C and C–H bonds, respectively, and valence angles ⟨C–C–C = 112° and ⟨H–C–H = ⟨C–C–H = 110° were also assumed.[11]

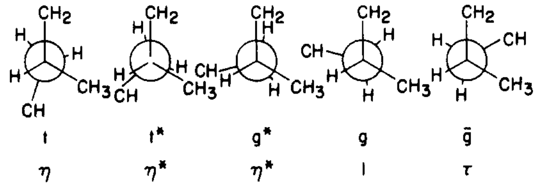


Figure 3. Newman projections along the CH(CH$_3$)–CH$_2$ bonds in PP illustrating the t, t^*, g^*, g, and $\bar{g}$ rotational states and their associated statistical weights η, η, η^*, 1, and τ, respectively.

A Cartesian coordinate system was affixed to the middle of the first C–C bond (see Figure 2) and was used as a reference frame for expressing the x, y, z coordinates of each of the atoms in the PP fragment (tetrad) considered. Of course, these atomic coordinates depend on the set of seven rotation angles resulting in $(5)^7$ = 78 125 total conformations. However, because not all neighboring bond pair conformations are energetically permitted (see U', U_m'', U_r'' in Figure 2), this number is reduced to between 2494 and 2622 depending on the stereosequence of the PP tetrad. For each of these conformations the x, y, z coordinates of all atoms were calculated and transformed to the Cartesian coordinate system x', y', z' whose z' axis connects the mid-points (○, ●) of the terminal bonds. The radius, r, of the corresponding cylindrical coordinate system with coincident z' axis is $r = (x'^2 + y'^2)^{1/2}$.

In selecting channel conformations we simply determined if $r = (x'^2 + y'^2)^{1/2} < r_c$, where r_c is the radius of the cylindrical channel. If each atom in the PP tetrad fragment passed this test, then the conformation was considered a channel conformer. The methyl protons were not explicitly considered in the search for channel conformers. Instead, each methyl group was approximated by a bare carbon atom, thereby ensuring that all conformers with $r \sim r_c$ would be identified as channel conformers.

Average Properties of Channel Conformers. Matrix multiplication techniques[12] were used to calculate various properties of the PP tetrad fragments, averaged over all conformations and averaged over just those sets of channel conformers found. This averaging was made possible by the RIS model developed for PP by Suter and Flory.[11] Average probabilities, or populations, of channel conformers and bond conformations averaged over all conformations and just those sets of channel conformations were obtained in this manner for channels (cylinders) of various radii.

Statistical weight matrices U', U_m'', U_r'', and U_1'' [for ϕ_1'' rotation about the first CH$_2$–CH(CH$_3$) bond] (see Figure 2) were used to obtain the PP tetrad partition functions $z(abc)$. For example, the sum of elements in the matrix product $U_1''U'U_m''U'U_m''U'U_m''$ yields $z(mmm)$, the partition function of the *mmm* (isotatic) PP tetrad. Let us suppose that the *mmm* tetrad adopts the *gtgtgtg* conformation. Its probability of occurrence was obtained from $[U_1''(4)U'(4,1)U_m''(1,4)U'(4,1)U_m''(1,4)U'(4,1)U_m''(1,4)]/z(mmm)$. To determine the probability of finding the second CH(CH$_3$)–CH$_2$ bond (ϕ_4) of the *mmm*-PP tetrad in the g rotational state, or conformation, we simply divided the matrix product $U_1''U'U_m''U'(g)U_m''U'U_m''$ by $z(mmm)$, where $U'(g)$ is the statistical weight matrix U' with first, second, third, and fifth columns, which correspond to the t, t^*, g^*, and $\bar{g}$ conformers, replaced by zeros.

Mobility of Channel Conformers. To obtain some measure of the mobility of PP's confined by the channels of their inclusion compounds with PHTP, we attempted to determine the possibility of interconverting between channel conformers without any part of the chain leaving the channel during any step of the interconversion process.

Table I
PP Tetrad Conformers

	no. of conformers			$\leftarrow$ $P(\phi_i = t, g, \bar{g})$ $\rightarrow$			
				bond 4[a]		bond 5[a]	
PP tetrad	D = 5.5 Å channel	free chain	probability of D = 5.5 Å channel conformers	D = 5.5 Å channel	free chain	D = 5.5 Å channel	free chain
mmm	36	2622	3.4×10^{-5}	0.030	0.530	0.559	0.415
				0.515	0.370	0	0.485
				0.030	0.016	0.353	0.015
rrr	19	2494	7.2×10^{-2}	0.994	0.680	0.999	0.685
				0	0.247	0	0.241
				0	0.012	0	0.013
rmr	19	2562	4.9×10^{-4}	0.386	0.421	0.004	0.522
				0	0.488	0	0.387
				0.249	0.013	0.359	0.015
mrm	28	2562	6.6×10^{-4}	0.843	0.742	0.955	0.736
				0.044	0.187	0.033	0.194
				0	0.014	0	0.012
rrm	22	2494	1.1×10^{-2}	0.977	0.666	1.0	0.669
				0	0.260	0	0.256
				0	0.012	0	0.013
rmm	18	2562	1.6×10^{-4}	0	0.438	0.643	0.504
				0.446	0.472	0	0.406
				0.013	0.013	0.344	0.014

[a] See Figure 2.

As each rotation angle was incremented ($\Delta\phi$ = 15°), the x', y', z' coordinates of each atom in the PP tetrad chain fragment (see Figure 2) were calculated and checked to see that all atoms remained inside the cylinder of the starting channel conformer. This procedure was repeated until one or more atoms passed through the cylinder wall or another channel conformer was reached. If the former occurred, then another channel conformer was selected as the starting conformer and the interconversion process was repeated.

After another channel conformer was reached, all rotation angles were reinitialized to the values of the new starting channel conformer and the interconversion process was restarted. The test for interconversion between channel conformers was complete after each cylinder conformer had been used as the starting conformation.

To reduce the size of the calculations for testing interconversion between channel conformers, the Suter–Flory[11] RIS model was modified from ϕ = 15(t), 50(t^*), 70(g^*), 105(g), and 245° ($\bar{g}$) to a four-state model with ϕ = 15(t), 60(t^*–g^*), 105(g), and 240° ($\bar{g}$). Compression of the nearly eclipsed t^* and g^* bond conformers into a single eclipsed conformer (t^*–g^*) resulted in a significant savings in computer time, but retained the nonstaggered aspect of the bond conformations in PP.

Results and Discussion

The channel conformers found for the tetrads of PP are partially characterized in Tables I and II, where their numbers, probabilities, and bond rotational state populations are compared for the PP–PHTP channel (D = 5.5 Å) and free chain conformations. Because in the search for channel conformers each atom was considered a volumeless point, a channel conformer found to fit in a cylinder of diameter $D' = 2r_c$ would actually fill a cylinder with a diameter $D = D' + 1$ Å if van der Waals spheres of radius 0.5 Å are assigned to each proton. Consequently, in the search for D = 5.5 Å conformers, as an example, the x', y', z' atomic coordinates were tested against r_c = 2.25 Å.

Two features of the results presented in Table I are very interesting. First, the probabilities of finding PP tetrad conformers that fit into D = 5.5 Å cylinders vary over 3 orders of magnitude depending on the tetrad stereosequence. The *rrr* conformers found to fit in a D = 5.5 Å cylinder are 1000 times more likely, or 3–4 kcal/mol lower in energy, than the *mmm*-PP tetrad conformers that fit in the same D = 5.5 Å channel, even though their number (36) is nearly twice that (19) found for the *rrr* tetrad. The probabilities of the remaining PP tetrad conformers that fit into the D = 5.5 Å cylinder lie between those of the *mmm* and *rrr* tetrads.

The reason for the disparity between the probabilities of the D = 5.5 Å conformers found for the isotactic *mmm*- and syndiotactic *rrr*-PP tetrads is revealed by the statistical weight matrices for the *m*- and *r*-PP diads shown in Figure 2. For a *m* diad the *tg* and *gt* conformations are most likely, with statistical weight η = 0.904 at T = 25 °C. As is well-known,[13,14] i-PP crystallizes in this low-energy, 3_1-helical, ...*tgtgtg*... conformation. However, the isotactic 3_1 helix does not fit into a cylinder with D < 6.5 Å, consistent with the interhelical separation between neighboring chains observed in its crystal structure.[13,14] Thus, in cylindrical channels of D = 5.5 Å, appropriate to the PP–PHTP inclusion complex, only conformations that are narrower and higher in energy than the ...*tgtgtg*..., 3_1 helix are permitted.

On the other hand, for a *r*-PP diad both the *tt* and *gg* conformations are likely (see U_r'' in Figure 2). In fact s-PP crystallizes[15–17] in the 2_1-helical, ...*ttggttgg*... conformation, with alternation of the two lowest energy *r* diad conformers *tt* and *gg*. Note from U' that neighboring *r* diads are not both permitted to adopt the *gg* conformation simultaneously, so that the all-*g*, ...*gggggggg*..., conformation is not possible for s-PP. At the same time, the all-trans, ...*tttttttt*..., conformation is permitted for s-PP. However, of the two low-energy s-PP conformations ...*ttggttgg*... and ...*tttttttt*..., only the narrower all-trans conformer will fit into the D = 5.5 Å channels found in PP–PHTP inclusion complexes.

Table II
Tetrad Frequencies

PP tetrad	Z (tetrad) channel $D = 5.5$ Å	Z (tetrad) free chain	PP tetrad frequency channel $D = 5.5$ Å	PP tetrad frequency free chain	tetrad frequency observed by DiSilvestro et al.[10] for PP polymerized in PHTP
mmm	3.83×10^{-4}	11.279	0	0.105	0.100
rrr	1.03	14.322	0.749	0.133	0.379
rmr	6.34×10^{-3}	12.945	0.005	0.124	0.030
mrm	8.87×10^{-3}	13.396	0.006	0.120	0.015
rrm + *mrr*	2 (0.162)	2 (14.594)	0.236	0.270	0.228
rmm + *mmr*	2 (2.10×10^{-3})	2 (13.351)	0.003	0.248	0.248
total	1.374	107.832	1.0	1.0	1.0

Table III
Comparison of *mmm*- and *rrr*-PP Tetrad Channel Conformers

					← $P(\phi_i = t, g, \bar{g})$ →			
	no. of channel conformers		probability of channel conformers		bond 4		bond 5	
D, Å	*mmm*	*rrr*	*mmm*	*rrr*	*mmm*	*rrr*	*mmm*	*rrr*
4.0	0	0	0	0				
4.5	0	0	0	0				
5.0	3	2	2.0×10^{-7}	3.7×10^{-2}	0	1.0	0	1.0
					0	0	0	0
					0.914	0	0.086	0
5.25	11	9	1.1×10^{-5}	4.0×10^{-2}	0	0.997	0.091	0.999
					0	0	0	0
					0	0	0.909	0
5.5	36	19	3.4×10^{-5}	7.2×10^{-2}	0.030	0.994	0.559	0.999
					0.515	0	0	0
					0.030	0	0.353	0
6.0	122	91	7.2×10^{-4}	0.135	0.229	0.959	0.051	0.992
					0.043	0.001	0	0
					0.294	0	0.425	0
7.0	598	417	0.014	0.386	0.247	0.931	0.033	0.960
					0.008	0.004	0.227	0.004
					0.443	0	0.277	0
8.0	1209	983	0.401	0.711	0.635	0.822	0.317	0.829
					0.315	0.121	0.633	0.105
					0.028	0.001	0.020	0
10.0	2280	2194	0.885	0.992	0.569	0.685	0.386	0.690
					0.371	0.246	0.524	0.240
					0.018	0.010	0.017	0.010
free chain	2622	2494	1.0	1.0	0.530	0.680	0.415	0.685
					0.370	0.247	0.485	0.241
					0.016	0.012	0.015	0.013

The tetrad partition functions, $z(abc)$, evaluated only for those conformations that are permitted in the $D = 5.5$ Å channel, may be used to obtain the relative frequency of finding each tetrad in the channel. These results are seen in Table II, where comparison is made to the tetrad frequencies calculated for unconstrained PP and those observed by DiSilvestro et al.[10] for a PP sample obtained by the free-radical polymerization of propylene in its inclusion compound with PHTP. For the $D = 5.5$ Å channel it is calculated that the *rrr* and *rrm*(*mrr*) tetrads account for over 98% of all PP tetrads, while for the free chain these same tetrads amount to only 38% of the total tetrad population. DiSilvestro et al.[10] find that the PP polymerized in the channels of the PHTP clathrate contains 61% of the *rrr* and *rrm*(*mrr*) stereosequence tetrads.

It appears likely that the propensity of PP polymerized in PHTP channels to contain consecutive *r* diads is a result of the lower energy (higher probability) of the channel conformers belonging to the syndiotactic, *rrr* stereosequence relative to the channel conformers of other stereosequences, such as the all-*m*, isotactic stereosequence *mmm*.

The second striking feature of the channel conformations found for PP is the major differences in the populations of the bond rotational states between the different tetrad stereosequences and between the channel and free chain conformers belonging to the same tetrad (see Table I). The constraints placed on each PP tetrad by its confining channel severely skew the distribution of conformers away from the free chain population. As mentioned before, the conformational characteristics of bonds such as 4 and 5 are contained in the statistical weight matrices $U_{m,r}''$ (see Figure 2). For a *m* diad in an unconstrained PP chain the *tg* and *gt* conformers are equally likely and most probable (see U_m''), and this is reflected in the rotational populations for bonds 4 and 5 in the *mmm* tetrad where $p(\phi_{4,5} = t) = 0.530, 0.415$ and $p(\phi_{4,5} = g) = 0.371, 0.485$. In the $D = 5.5$ Å channel, $p(\phi_4 = t)$ is nearly zero (0.03) and $p(\phi_5 = g) = 0.0$, while $p(\phi_4 = g) = 0.515$ and $p(\phi_5 = t) = 0.559$, because the *gt* conformation of bonds 4 and 5 is permitted while the *tg* conformation is not. However, consecutive *gt* pairs, as found in the 3_1-helical, ...*gtgtgt*... conformer, do not fit in the $D = 5.5$ Å cylinder.

Remembering from U_r'' that bonds of type 4 and 5 in the *rrr* tetrad may assume either *tt* or *gg* conformations with high probability, though consecutive *gg* pairs are forbidden (see U_r'' in Figure 2), it is not surprising that for PP chains in a $D = 5.5$ Å cylinder the *rrr* tetrad has $p(\phi_{4,5} = t) = 0.994, 0.999$.

The dependence of the channel conformers of the *mmm*- and *rrr*-PP tetrads on the channel size is described in Table III. Even though for any channel diameter the number of *mmm* tetrad conformers is larger than found for the *rrr* tetrad, the probabilities of the *rrr* tetrad channel conformers are much larger until the channel diameter exceeds 7.0 Å. For narrow channels, $5.0 < D < 7.0$ Å, the *mmm* tetrad conformers are characterized by significant amounts of the high-energy, nearly eclipsed t^* and g^* bond conformations and the sterically hindered, high-energy, staggered $\bar{g}$ bond conformation (see Figure 3). While for any channel size, the *rrr* tetrad conformers contain relatively little of these high-energy bond conformations.

It appears that at $D > 7.0$ Å both the i-PP and s-PP crystalline conformations, i.e., the 3_1-helical, ...*tgtgtgtg*..., and 2_1-helical, ...*ttggttgg*..., conformations, begin to fit and contribute to the population of channel conformers for the *mmm* and *rrr* tetrads, respectively [see $p(\phi_{4,5})$ in Table III]. For these larger channels now both PP tetrads adopt low-energy channel conformers, while for the small channels only the *rrr* tetrad can adopt low-energy conformers that fit, namely the all-trans bond conformer.

It was not possible to interconvert between the $D = 5.5$ Å channel conformers found for any of the PP tetrads until the channel was expaneded well beyond 6.0 Å. The only exceptions were the facile interconversions between the t^* and g^* bond rotational states which are accompanied by the minor conformational changes produced by ±20° rotations. In the narrow channels ($D = 5.5$ Å) of the PP–PHTP inclusion compounds the PP chains do not appear to have sufficient space to interconvert between the t, t^* and g^*, g, and $\bar{g}$ bond conformers.

In a preliminary study Sozzani et al.[9] recorded the solid-state ^{13}C CPMAS/DD NMR spectrum of the inclusion compound of i-PP with PHTP. They found both the chemical shifts and the spin–lattice relaxation times for the carbons of the included i-PP to be similar to those observed[18] in bulk, crystalline i-PP. Because we found the crystalline, 3_1-helical, ...*tgtgtg*... conformer for i-PP unable to fit in the narrow channels of its PHTP complex and because we were unable to interconvert between those $D = 5.5$ Å conformers which do fit in the PHTP channels, we are led to suggest that in its complex with PHTP i-PP adopts a relatively rigid conformation where each carbon atom experiences a magnetic shielding similar to that experienced by the carbons in the ...*tgtgtg*..., 3_1-helical i-PP chain in its bulk crystal.[18]

The only $D = 5.5$ Å conformers found here which meet this criterion are of the type ...(t^* or g^*) $\bar{g}$ (t^* or g^*) $\bar{g}$... with alternating (t^* or g^*) and $\bar{g}$ bond rotations. As can be seen from Figure 3, in both the bulk crystalline, ...*tgtgtg*..., 3_1-helical conformer and the ...(t^* or g^*) $\bar{g}$ (t^* or g^*) $\bar{g}$... conformer suggested here for the i-PP–PHTP inclusion compound the methyl and methylene carbons are gauche to one of their γ-substituent methine carbons separated by three intervening bonds. On the basis of the conformationally sensitive γ-gauche effect[19] on ^{13}C chemical shifts, we would expect both rigid i-PP conformers to evidence similar ^{13}C CPMAS/DD NMR spectra, as observed by Sozzani et al.[9]

By contrast, bulk, crystalline s-PP adopts the 2_1-helical, .*ttggttgg*., conformation, whose cross section is too broad for the narrow PP–PHTP channels. Instead, the relatively stable all-trans, planar zigzag, ...*tttttt*... conformer seems most likely for the s-PP chains in their complex with PHTP. In both s-PP conformers the methine carbons are gauche to two γ substituents: CH_2 and CH_3 for the 2_1 helix and two CH_3's for the all-trans conformer (see Figure 3). The methyl carbons in the 2_1 helix are gauche to a single γ-CH, while in the all-trans conformer both γ-CH carbons are gauche to the methyl carbon. We would therefore expect to see the methyl resonance in s-PP-PHTP to come 1 γ-gauche effect,[19] or ca. 5 ppm, upfield from the methyl resonance observed[20] in bulk, crystalline s-PP. Half the methylene carbons in the ...*ttggttgg*... conformer are gauche to both of their γ-CH substituents, while the other half are trans to their γ-CH's, as are all methylene carbons in the all-trans conformer proposed here for s-PP-PHTP.

Though Sozzani et al.[9] have not as yet reported the NMR spectrum of the PHTP inclusion compound with s-PP, when it is obtained[21] we would expect both the methyl and methylene resonances observed in its CPMAS/DD ^{13}C NMR spectrum to deviate significantly from those reported by Bunn et al.[20] for bulk, crystalline s-PP.

References and Notes

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(21) Sozzani has told me privately that the preliminary ^{13}C NMR spectra of bulk s-PP and s-PP–PHTP are substantially different.