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Conformations and Motions of Polyethylene and Poly(oxyethylene) Chains Confined to Channels

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ABSTRACT: Inclusion compounds formed by linear polymers and host clathrates, such as urea and perhydrotriphenylene (PHTP), provide a unique environment for the included polymer chains. We have investigated the conformations and mobilities of isolated polyethylene (PE) and poly(oxyethylene) (POE) chains when confined to the channels of their inclusion compounds. This was achieved by a two-step procedure: (i) from all possible conformations available to the free polymer chain, those conformations which fit into the channels of their inclusion compounds were defined; (ii) a test was performed to determine whether or not it was possible to interconvert between these channel conformations while the polymer chains remained inside their channels. Though several PE and POE conformers with diameters appropriate to the channels in their urea and PHTP inclusion compounds (D = 5.25–5.50 Å) were found, it was not possible to interconvert between them without some portion of each polymer chain leaving the channel. This is in marked contrast to the behavior of *trans*-1,4-polybutadiene and isotactic *trans*-1,4-poly(penta-1,3-diene), which were previously found capable of conformational interconversions in their inclusion compounds with the same host clathrates. On the basis of a comparison of the channel conformers derived for PE and POE with X-ray diffraction studies of their urea and PHTP inclusion compounds, we conclude the following: PE, as it does in its pure crystalline phase, assumes the all-trans, planar zigzag conformation in both clathrates. (ii) POE in the PHTP clathrate adopts several extended conformations, some with a few gauche bonds, in addition to the all-trans conformer. (iii) In its inclusion compound with urea, only more compact conformations with significant gauche bond contents are permitted. (iv) The POE chains in both clathrates adopt conformations that are more extended than the ...$g^{\pm}tt$... conformer found in POE crystals, which does not fit in either clathrate channel.

Introduction

Formation of inclusion compounds between small-molecule, host matrices and polymeric guest molecules permits the study of the conformations and motions of polymer chains confined to the channels of their inclusion compounds, where each chain is well-separated from neighboring chains by the host matrix. Two such host matrices are formed by the crystals of urea and perhydrotriphenylene (PHTP). In Figure 1, the inclusion compounds of urea with *n*-hexadecane[1] (a) and PHTP with *trans*-1,4-polybutadiene[2] (b) are illustrated as viewed down the channels of both complexes. Though the channel interiors are polar for the urea complex and nonpolar for the PHTP complex, each is nearly cylindrical in shape with diameters in the range 5.25–5.50 Å.

Though some polymers may be prepared directly in the channels of their inclusion compounds by irradiation of the inclusion compounds formed by their monomers,[3] the inclusion compounds of polyethylene (PE) and poly(oxyethylene) (POE) with both urea and PHTP are obtained[4-6] from solutions or melts of host matrix and guest polymer mixtures. X-ray diffraction studies[5,6] of the PE–urea and PE–PHTP clathrates reveal an extended, all-trans planar zigzag chain conformation was found in pure crystalline PE. In the POE clathrates with urea and PHTP, however, X-ray diffraction measurements[5,7] indicate unique chain conformations, both of which are different and more extended than the ...$g^{\pm}ttg^{\pm}tt$... chain conformation observed[8] for pure crystalline POE.

As an extension of our previous investigation, the preceding paper in this issue,[9] of the conformations and mobilities of *trans*-1,4-polydienes confined to the channels of their inclusion compounds with PHTP, we report here a similar modeling study for PE and POE chains in the channels of their urea and PHTP clathrates.

PE and POE in Clathrate Channels. Channel Conformers. To model PE and POE chains confined to the urea and PHTP clathrate channels illustrated in Figure 1, we simply consider only those PE and POE conformations which fit into a cylinder with a diameter comparable to these clathrate channels (5.25–5.50 Å). The portions of PE and POE considered in our model are drawn in Figure 2 and contain four and three repeat units, respectively. Below each drawing are the statistical weight matrices (U)[10] corresponding to the constituent bonds of PE and POE. These matrices embody the rotational isomeric state (RIS) descriptions of the conformations of PE[11] and POE[12] chains, and their elements are appropriate to room temperature.

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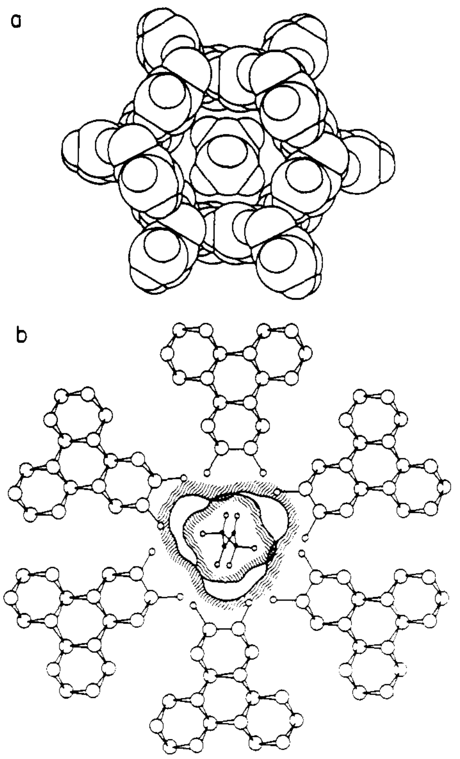


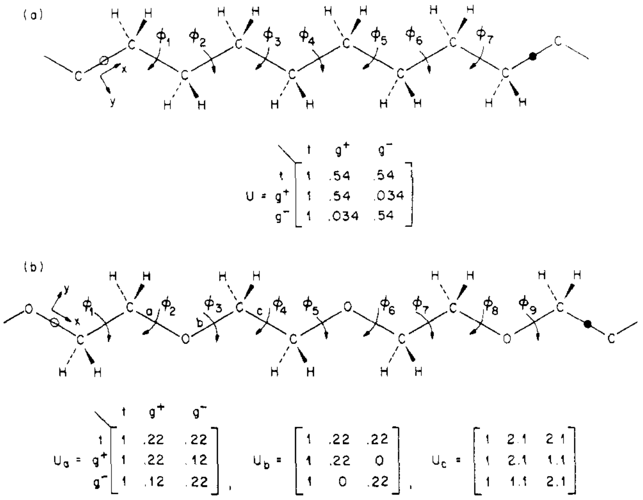
Figure 1. (a) Space-filling drawing of a channel in the urea–*n*-hexadecane clathrate.[1] (b) Schematic drawing of a *trans*-1,4-polybutadiene chain in the channel of its inclusion compound with PHTP.[2]

Each bond in both polymers is assumed[11,12] to adopt only the trans (t, 0°) and gauche ($g^{\pm}$, ±120°) conformations. Bond lengths of 1.53, 1.43, and 1.1 Å are adopted[11,12] for the C–C, C–O, and C–H bonds, respectively, and $\angle$C–C–C = 112° (PE) and 110° (POE) and $\angle$H–C–H = 110° are also assumed.[11,12]

A Cartesian coordinate system is affixed to the middle of the first C–C (PE) or C–O (POE) bond (see Figure 2) and is used as a reference frame for expressing the x,y,z coordinates of each of the atoms in both chain fragments. Of course the atomic coordinates depend on the sets of 7(PE) and 9(POE) rotation angles resulting in $(3)^7 = 2187$ and $(3)^9 = 19\,683$ total conformations for the free PE and POE chain fragments considered here. Actually, because $g^{\pm}g^{\mp}$ conformations are prohibited for neighboring C–O bonds (see U_b in Figure 2), the total number of conformations possible for the POE fragment is reduced to 9261. For each of these conformations, the x,y,z coordinates of all atoms are calculated and then transformed to the Cartesian coordinate system x',y',z' whose z'-axis connects the midpoints (○ and ● in Figure 2) 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 determine 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 PE or POE fragment passes this test, then the conformation is considered a channel conformer.

Average Properties of Channel Conformers. Matrix multiplication techniques[10] are used to calculate various properties of the PE and POE chain fragments, averaged over all conformations and averaged over just the set of channel conformers found. The averaging is made possible by the RIS models developed[11,12] for PE and POE. Average probabilities, or populations, of channel conformers and bond conformations averaged over all conformations and just the set of channel conformers are obtained in this manner for channels (cylinders) of various radii.



$$U = \begin{array}{c|ccc} & t & g^+ & g^- \\ \hline t & 1 & .54 & .54 \\ g^+ & 1 & .54 & .034 \\ g^- & 1 & .034 & .54 \end{array}$$

$$U_a = \begin{array}{c|ccc} & t & g^+ & g^- \\ \hline t & 1 & .22 & .22 \\ g^+ & 1 & .22 & .12 \\ g^- & 1 & .12 & .22 \end{array}, \quad U_b = \begin{bmatrix} 1 & .22 & .22 \\ 1 & .22 & 0 \\ 1 & 0 & .22 \end{bmatrix}, \quad U_c = \begin{bmatrix} 1 & 2.1 & 2.1 \\ 1 & 2.1 & 1.1 \\ 1 & 1.1 & 2.1 \end{bmatrix}$$

Figure 2. (a) Four repeat unit fragment of PE used to derive the conformations and motions of its channel-bound chains. (b) Three repeat unit fragment of POE used to derive the conformations and motions of its channel-bound chains.

Statistical weight matrices $\mathbf{U}$, $\mathbf{U}_a$, $\mathbf{U}_b$, and $\mathbf{U}_c$ for the bonds in PE and POE (see Figure 2) are used to obtain the partition functions (z_{PE} and z_{POE}) of each fragment. Summation of the elements of the matrix products $(\mathbf{U})^7$ and $\mathbf{U}_c(\mathbf{U}_a\mathbf{U}_b\mathbf{U}_c)^2\mathbf{U}_a\mathbf{U}_b$ yield z_{PE} and z_{POE}, respectively. Let us suppose that our PE fragment adopts the ttg^+tg^-tt conformation. Its probability of occurrence is obtained from $[\mathbf{U}(1)\mathbf{U}(1,1)\mathbf{U}(1,2)\mathbf{U}(2,1)\mathbf{U}(1,3)\mathbf{U}(3,1)\mathbf{U}(1,1)]/z_{PE}$, where $\mathbf{U}(1)$ is the matrix $\mathbf{U}$ of Figure 2 with all elements in columns 2 and 3 replaced by zeros. To determine the probability of finding the fourth C–C bond in our PE fragment in the g^- rotational state, or conformation, we simply divide the matrix product $(\mathbf{U})^3\mathbf{U}(g^-)(\mathbf{U})^3$ by z_{PE}, where $\mathbf{U}(g^-)$ is the statistical weight matrix $\mathbf{U}$ with the first and second columns, which correspond to the t and g^+ conformers, replaced by zeros.

Mobility of Channel Conformers. As a measure of the mobilities of PE and POE chains confined by the channels of their inclusion compounds with urea and 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. One of the channel conformers was selected as the starting conformation. As each rotation angle was incremented ($\Delta\phi = 20°$), the x',y',z' coordinates of each atom in the PE and POE chain fragments were calculated and checked to see that all atoms remained inside of 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 channel conformer interconversion procedure was repeated. After reaching another channel conformer, all rotation angles were reinitialized to the value of the new starting channel conformer, and the interconversion process was restarted. The test for interconversion between channel conformers was complete after each channel conformer had been used as the starting conformation.

Results and Discussion

Channel Conformations. The channel conformers found for PE and POE are partially characterized in Tables

Table I
Polyethylene Channel Conformers

D, Å	channel conformers	probability of channel conformers	$P(\phi_n = \mathrm{t})$ for n =			
			1, 7	2, 6	3, 5	4
4.0	1	0.012	1.0	1.0	1.0	1.0
4.5	3	0.014	0.855	1.0	0.855	1.0
5.0	5	0.016	0.746	1.0	0.746	1.0
5.25	11	0.032	0.591	1.0	0.591	1.0
5.5	25	0.058	0.575	0.750	0.640	0.870
6.0	101	0.164	0.481	0.756	0.648	0.751
7.0	365	0.349	0.519	0.618	0.695	0.650
8.0	805	0.659	0.522	0.605	0.663	0.674
9.0	1597	0.865	0.525	0.608	0.617	0.641
11.0	2165	0.998	0.539	0.605	0.596	0.599
free chain	2187	1.0	0.540	0.605	0.596	0.598

I and II, where their numbers and bond rotational-state probabilities are presented for cylinders of various radii. 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 were assigned to each proton. All cylinder diameters given in Tables I and II reflect the steric requirements of 0.5-Å van der Waals spheres placed on each proton.

Notice that for channels with D = 5.25–5.50 Å, which are roughly the size of the channels in their urea and PHTP clathrates, PE chains are more likely to fit than are POE chains; i.e., compare the probabilities of PE and POE channel conformers (0.032–0.058 versus 0.0035–0.014). This is a result of the higher probability of the all-trans, planar zigzag conformation in PE compared to POE (compare the D = 4.0 Å rows of Tables I and II). For channels with $D \leq 5.5$ Å, the all-trans conformer of PE accounts for at least 20% of all channel conformers, while less than 10% of the population of POE conformers able to fit in cylinders with $D \leq 5.5$ Å is attributable to its all-trans conformer.

PE, like the *n*-alkanes, crystallizes in the all-trans conformation, while POE crystallizes in the more compact ...$g^{\pm}ttg^{\pm}tt$... structure. The POE crystalline conformation was not found to fit in cylinders smaller than 7.0 Å in diameter. As a result, POE chains must adopt less stable conformations when confined by the channels of their urea and PHTP clathrates.

Mobility of PE and POE Channel Conformers. For channels with $D \leq 5.5$ Å, we did not find interconversions between those PE and POE conformers which fit in these channels. Expansion of the channels from 5.5 to 6.5 Å for PE and from 5.25 to 6.0 Å for POE still did not permit interconversions between the D = 5.5 and 5.25 Å channel conformers of PE and POE, respectively. The inability of PE and POE conformers to interconvert in cylinders of a size comparable to the channels in their urea and PHTP clathrates stands in marked contrast to the behavior[9] of *trans*-1,4-polybutadiene chains confined by the channels of its inclusion compound with PHTP.

The solid-state ^{13}C and ^{2}H NMR measurements of Sozzani et al.[13,14] performed on the PHTP clathrate of *trans*-1,4-polybutadiene confirm the mobility of these polymer chains, including the facile interconversion between different channel conformers. Solid-state NMR studies,[15-22] including ^{1}H, ^{2}H, and ^{13}C NMR, performed on the urea clathrates of several higher *n*-alkanes and PE indicate overall rotation of the confined chains coupled with a local wobbling about the C–C bonds but do not suggest the occurrence of trans ↔ gauche conformational interconversions. These observations are consistent with our modeling of PE in the channels of its inclusion compounds with urea and PHTP.

We were unable to find any published studies concerning the mobility of POE chains in their clathrates with urea and PHTP.

Summary

Our attempt to model the conformations and motions of PE and POE chains confined to the channels of their inclusion compounds with urea and PHTP appears consistent with the X-ray diffraction observations[5-7] of their structures and the NMR measurements[15-22] of their mobility. PE in its clathrates exists in the energetically preferred, all-trans conformation[5,6] without any indication[15-22] of the presence of gauche bond conformations or rapid interconversions between trans and gauche rotational states.

X-ray diffraction observations[5,7] of the urea and PHTP clathrates with POE suggest conformations that are considerably more extended than the most stable ...$g^{\pm}ttg^{\pm}tt$... conformation adopted in the crystals of pure POE.[8] This is consistent with our observation that the crystalline POE conformation cannot be accommodated in urea and PHTP clathrate channels with D = 5.25–5.50 Å. However, Farina et al.[5] have suggested that in the PHTP clathrate the POE chains adopt a single conformation characterized by trans ($\phi = 0°$) C–C bonds and alternating, nonstaggered conformations ($\phi = \pm 40°$) about the C–O bonds. This conformation matches the observed chain repeat distance of 6.87 Å per two repeat, or monomer, units.

On the basis of our modeling of the conformations and motions of POE in clathrates, where the chains are confined to channels with D = 5.25–5.50 Å, we would like to suggest an alternative interpretation of the X-ray diffraction results.[5,7] If, for example, the 35 POE conformers found to fit in a 5.25-Å channel are all assumed to be present there in the same proportions as their probabil-

Table II
Poly(oxyethylene) Channel Conformers

D, Å	channel conformers	probability of channel conformers	$P(\phi_n = 1)$ for n =								
			1	2	3	4	5	6	7	8	9
4.0	1	0.0012	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
4.5	5	0.0014	0.919	1.0	0.900	1.0	0.900	1.0	0.919	1.0	0.900
5.0	10	0.0018	0.767	1.0	0.686	1.0	0.827	1.0	0.797	1.0	0.752
5.25	35	0.0035	0.579	0.976	0.674	0.976	0.677	0.976	0.610	0.976	0.404
5.5	94	0.0140	0.280	0.983	0.779	0.855	0.437	0.843	0.413	0.974	0.591
6.0	266	0.0380	0.211	0.929	0.747	0.734	0.605	0.765	0.454	0.939	0.620
7.0	1259	0.1210	0.189	0.690	0.693	0.551	0.702	0.738	0.397	0.850	0.592
8.0	3096	0.2590	0.167	0.679	0.742	0.491	0.744	0.734	0.323	0.737	0.654
9.0	5349	0.4350	0.196	0.690	0.760	0.398	0.765	0.718	0.319	0.709	0.704
11.0	8616	0.8820	0.198	0.733	0.776	0.239	0.784	0.750	0.230	0.750	0.705
13.0	9259	0.9999	0.206	0.762	0.761	0.216	0.762	0.761	0.216	0.766	0.724
free chain	9261	1.0	0.206	0.762	0.761	0.216	0.762	0.761	0.216	0.766	0.724

ities of occurrence would suggest, then we may calculate a chain repeat distance averaged over all 35 channel conformers. The result is 3.39 Å/repeat unit, which agrees closely with the 6.87 Å/2 = 3.43 Å/repeat unit found by X-ray diffraction[5] for the POE–PHTP inclusion compound.

Because we did not find it possible to interconvert between POE channel conformations, we suggest, instead of the single channel conformer with trans C–C bonds and nonstaggered C–O bonds proposed by Farina et al.,[5] that in their clathrates the POE chains are static but conformationally disordered. All 35 conformers found for D = 5.25 Å can be characterized by the following sequences of bond rotations: (i) all-trans, (ii) kinks of the type tttg$^{\pm}$tg$^{\mp}$ttt, and (iii) jogs of the form ttg$^{\pm}$tttg$^{\mp}$t. We suggest from both energetic and entropic considerations that conformationally disordered POE chains are more likely to exist in their PHTP clathrate than the single seemingly high-energy conformation (trans C–C and alternating, nonstaggered C–O bonds) proposed by Farina et al.[5]

A feasible means for distinguishing these proposals is a comparison of the high-resolution, solid-state ^{13}C NMR spectra of pure and PHTP clathrate POE. Because the C–O bonds are trans in crystalline POE and only 40° away from trans in the single PHTP–POE conformation suggested by Farina et al.,[5] their ^{13}C chemical shifts should be similar.[23] On the other hand, many of the D = 5.25 Å channel conformers found here have some g$^{\pm}$ C–O bonds, which produce a gauche arrangement between carbons separated by three bonds (γ to each other). A γ-gauche arrangement of carbon atoms is expected[23] to shield both nuclei by ca. 5 ppm compared to their trans arrangement, so we would expect to see two resonances in the ^{13}C NMR spectra of PHTP–POE if the chains are conformationally disordered. One resonance should coincide with and the other should be upfield ~ 5 ppm from the single resonance observed in crystalline, pure POE.[24]

The chain repeat distance observed[7] in the urea–POE clathrate (3.04 Å/repeat unit) is much reduced from the value observed in the PHTP–POE clathrate (3.43 Å/repeat unit) but is still considerably extended from the repeat distance (2.76 Å/repeat unit) found[8] in pure, crystalline POE. It is likely that the polar interactions between the urea matrix and the POE chains alter their conformation(s). Infrared spectra of tetragonal urea, urea–POE clathrate, and urea–*n*-alkane clathrate indicate[7] involvement of the urea carbonyl groups with the POE chains. On the basis of the behavior of the IR spectral bands of POE, Tadokoro et al.[7] suggest that the POE chains in the urea clathrate are not all-trans, planar zigzag but may be in a conformation similar to that found for crystalline, pure POE. Again we believe that high-resolution, solid-state ^{13}C NMR could test this suggestion and differentiate between this proposal and the conformationally disordered channel conformers (derived here), some of which have gauche C–O bonds.

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