Inclusion Adduct Formation between Tris(*o*-phenylenedioxy)cyclotriphosphazene and Poly(ethylene oxide) or Polyethylene

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Within the field of organic-based inclusion compounds (clathrates) only perhydrotriphenylene (PHTP)[1] and urea[2−4] are known to readily form crystalline inclusion adducts with preformed polymers. Such polymer−host adducts allow the study of polymer conformations and chain mobility with the macromolecules isolated from the influence of chain−chain or chain−solvent interactions. Thus, both PHTP and urea have proved useful for novel fundamental studies of trapped preformed polymers.[5−7]

We report here that polyethylene (PE) and poly(ethylene oxide) (PEO) can be trapped within the tunnels of a crystalline inorganic−organic host, tris(*o*-phenylenedioxy)−cyclotriphosphazene (**1**) (Figure 1). It is known that tris(*o*-phenylenedioxy)cyclotriphosphazene readily forms inclusion adducts with a variety of organic small molecules.[8−11] Adduct formation can be induced either through recrystallization from the liquid guest or through direct uptake of the guest by crystals of **1**. In the direct imbibition process, the guest, in gas or liquid form, may be directly absorbed, causing the crystal structure of **1** to change from a monoclinic to a hexagonal form. The small molecule guests reside in tunnel-like voids which are approximately 5 Å wide and are oriented along the crystallographic *c*-axis, perpendicular to the plane of the phosphazene rings (Figure 1). High-energy irradiation of various dienes,[12] acrylates,[13] and vinyl monomers[14] trapped within the adducts of **1** results in the formation of isolated stereoregular polymer chains. Although much has been accomplished to describe the structure and function of **1** and its guest species, this is the first report of direct polymer inclusion within the host structure.

The polyethylene adducts of **1** were formed through simple recrystallization of **1** from a solution of high molecular weight polyethylene in benzene. Poly(ethylene oxide) (mw = 300 000) was incorporated into an adduct when it was mixed with a suspension of **1** in water. This adduct formation occurred despite the fact that water neither dissolves this host nor forms an inclusion adduct with it. For both PE and PEO, excess polymer was removed from the inclusion adduct by washing with excess solvent.

The melting points of the PEO and PE adducts were estimated using differential scanning calorimetry (DSC). These melting transitions were found to be approximately 60−90 deg higher than that of pure **1** or its adducts with small molecules, which melt at 245−250 °C. Unclathrated PEO and PE melted at 70 and 129 °C, respectively. An increase in the overall melting point of **1** containing trapped polymer molecules is thought to be due to favorable van der Waals forces between **1** and the polymer. Such an increase in lattice stability following polymer inclusion has been reported for host solids urea[2,3] and PHTP.[1] Therefore, the increase in the melting point of **1** provided tentative evidence that an inclusion adduct had been formed.

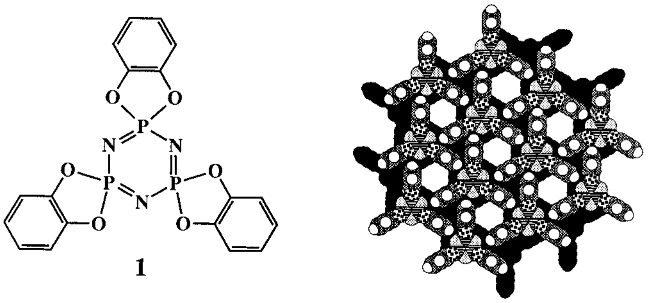

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Figure 1. Representation of the molecular and crystal structures of **1**. The spirocyclic side groups are oriented at right angles to the plane of the phosphazene ring. The right hand structure shows the hexagonal crystal arrangement of **1** in which the 5 Å diameter tunnel is visible. Guest molecules are accommodated within the tunnels.

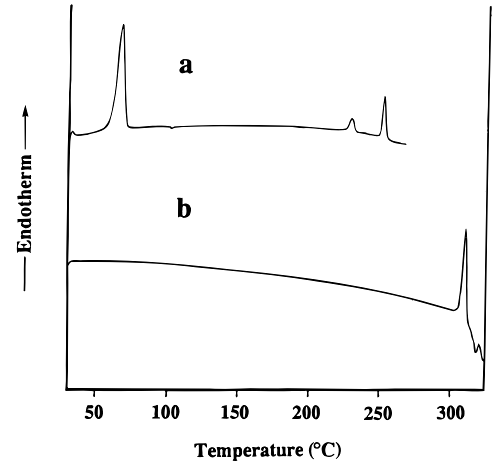

Figure 2. DSC thermograms (20 °C/min) of (a) a heterogeneous mixture of PEO and **1** and (b) the PEO−**1** adduct.

DSC analysis of a physical mixture of solid PEO powder with microcrystals of **1** showed endothermic peaks at 67 and 250 °C which correspond to the individual melting transitions for pure (unclathrated) poly(ethylene oxide) and unclathrated **1** (Figure 2a). The small peak appearing at 230 °C was attributed to a known phase transition in **1** from a pure monoclinic (guest free) phase to a mixed monoclinic/hexagonal type structure.[8] This peak was also detected in the heating of pure **1** in the absence of a potential guest.

In Figure 2b, a DSC thermogram of the PEO adduct of **1** is shown which contains a sharp melting transition at 310 °C. This is 58 deg higher than the melting point of pure **1**, and 240 deg higher than the melting point of poly(ethylene oxide). The response of the polyethylene adduct of **1** to heating was very similar and revealed a single endothermic melting transition at 330 °C.

The DSC thermograms of the PE and PEO adducts of **1** displayed no residual endotherms that might correspond to either the unclathrated host or the pure polymer. This suggests that 100% complexation of **1** had occurred and that unclathrated polymer was removed with the solvent wash. ^{1}H, ^{13}C, and ^{31}P NMR spectra of these solids indicated that no decomposition of the host or the polymer had taken place during adduct formation. Only a minimal amount of residual water was detected in the ^{1}H NMR spectra of the PEO adduct with **1** after extensive drying. This suggests that water

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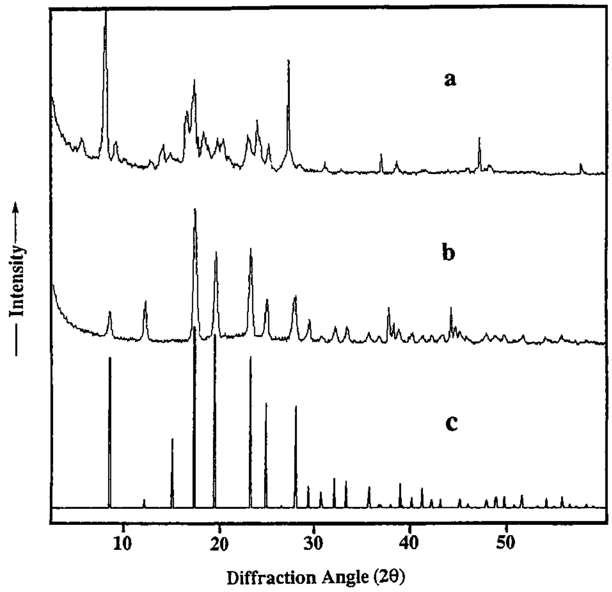

Figure 3. X-ray diffractograms of (a) pure **1** and (b) the PEO−**1** adduct.

is not co-included with PEO as a guest within **1** to any significant extent.

X-ray powder diffraction was used to confirm the hexagonal packing of **1** for both the PE and PEO adducts. The powder pattern of pure **1** is shown in Figure 3a and is similar to the simulated powder pattern generated for **1** from its single crystal monoclinic form. The X-ray diffraction pattern for the adduct formed between **1** and PEO is shown in Figure 3b. This pattern agrees quite well with the simulated powder pattern generated from the structural data for **1** in the hexagonal phase (Figure 3c). The apparent absence of the experimentally detected peak at 15° 2*θ*, together with relative differences in overall peak intensities, is possibly due to the influence of the guest electron density which is unaccounted for. Similar phenomena have been noted for zeolites which contain guest species.[15]

As stated earlier, water itself does not induce a monoclinic to hexagonal phase transition in **1**. Therefore, the presence of poly(ethylene oxide) must play a crucial role in the phase transition of the host solid. This phase change, along with the thermal analysis data, strongly suggests that **1** forms a hexagonal phase which is stabilized by the inclusion of PEO within its tunnel-like structure.

The single crystal X-ray structure of an adduct formed by combination of **1** with low molecular weight polyethylene (mw = 1000) was investigated.[16] The refinement of the atomic coordinates and the temperature factors converged to an agreement index, *R*, of 0.041. In Figure 4, an oblique view of the crystal structure shows the presence of individual extended polyethylene chains in each of the tunnel-like voids. There was no significant difference between the unit cell dimensions for this adduct and those formed previously through combination of **1** with small molecules. Each unit cell contains eight polyethylene carbon atoms arrayed along the tunnel cavities in the crystal. It is probable that lack of crystallographic order among chains in neighboring tunnels limits the direct assessment of chain conformation. However, the regular spacing of the carbon atoms along the *c*-axis of the tunnel suggests that the polymer assumes an all-trans planar conformation with a chain repeat length of 2.52 Å. X-ray diffraction studies[1,3] of PE−urea and PE−PHTP inclusion adducts reveal a similar PE zigzag planar conformation. It is important to note that the polyethylene used in forming the single crystal adduct has an average chain length of only 35 repeat units. However, the melting point of the solid remained near 340 °C. This is the same value found for the adduct that contained high molecular weight polyethylene.

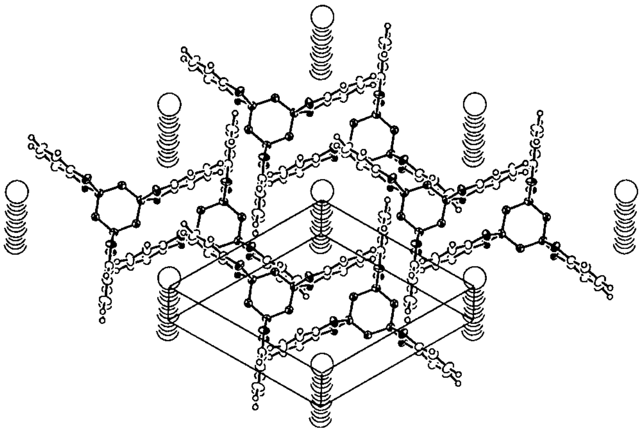

Figure 4. Hexagonal host lattice and low molecular weight polyethylene guests as seen in a projection oblique to the *c*-axis.

The single crystal X-ray structure of the adduct formed between **1** and PEO is isomorphous with that of the PE adduct and with the PEO chain disordered with large thermal motions.

In summary, it has been shown that the simple process of exposing microcrystals of **1** to an aqueous solution of PEO, or to an organic solvent based solution of PE, results in inclusion of the polymer molecules into the tunnels of the host crystal structure. The mechanism of adduct formation is still under investigation. It appears possible that molecules of PEO can initiate tunnel formation, driven perhaps by the opportunities for favorable van der Waals interactions with the tunnel walls. The preferential adduct formation by **1** with polyethylene, rather than with the benzene solvent, suggests that especially favorable interactions exist between **1** and linear polymeric guests. We have also found that poly(tetrahydrofuran), *trans*-poly(isoprene), and *cis*-poly(butadiene) form adducts with **1** in suitable solvents, and these adducts are currently under investigation.

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(16) Crystallographic data: $C_{18}H_{12}O_6N_3P_3{\cdot}4C$, fw = 527.07, crystallizes in the hexagonal space group $P6_3/m$ with unit cell dimensions $a = b = 11.5192(8)$ Å, $c = 10.068(1)$ Å, $V = 1156.9(1)$ Å^3, $D_{cal} = 1.456$ g cm^{-3}, $Z = 2$, and $\mu = 3.01$ cm^{-1} for Mo Kα ($\lambda = 0.710\ 69$ Å). The structure was solved by direct methods and refined by full-matrix least-squares calculations allowing non-hydrogen atoms of **1** to refine with anisotropic temperature factors, and the polyethylene carbon atoms with isotropic thermal parameters. H atoms were included at geometrically idealized positions. The refinement converged with $R = 0.041$ and $R_w = 0.036$ for 539 observed data with $I > 3.0\sigma(I)$ collected on a Rigaku AFC-6S diffractometer at 200(1) K.

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