Separation of Polymers and Small Molecules by Crystalline Host Systems

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ABSTRACT: Tris(*o*-phenylenedioxy)cyclotriphosphazene can entrap and separate various polymers and small molecules within its tunnels based on their microstructure, molecular weight, and end group functionality. Inclusion adducts with polyethylene, poly(tetramethylene oxide), poly(ethylene glycol), and 1,4-polybutadiene show a preferential inclusion for the type of polymer that will best stabilize the hexagonal structure of the host. Separations based on end groups show preferential inclusion of the species with the more hydrophobic end groups, possibly a response to the hydrophobic tunnels of the host. Exposure of the host to various small-molecule *n*-alkanes with different chain lengths revealed a preferential clathration of the longer chain species. Similarly, high polymers are preferentially included within the tunnels compared to analogues with lower molecular weights, presumably due to enhanced van der Waals interactions with the host. The polydispersity index was also improved by clathration, suggesting that the host can be used as a means to fractionate polymers on the basis of chain length.

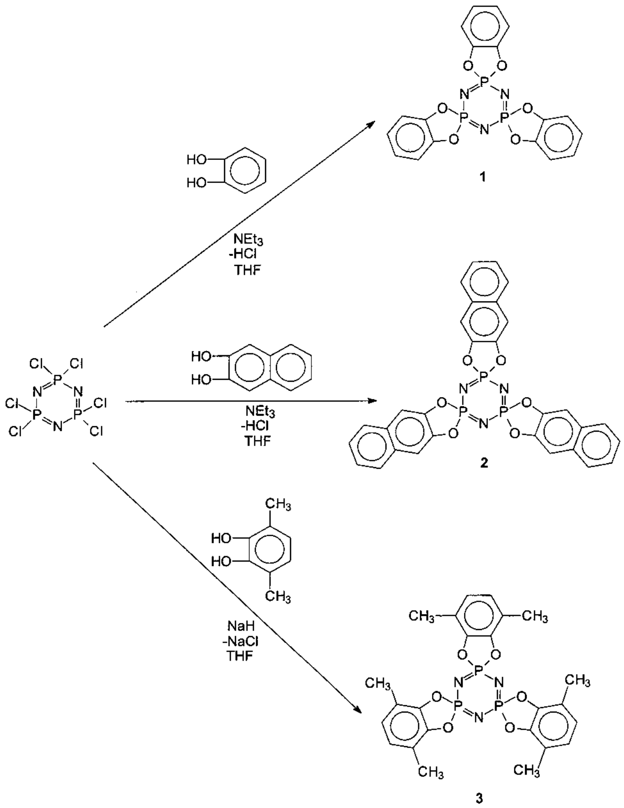
Introduction

Considerable interest exists in the creation and design of supramolecular assemblies for use in molecular entrapment. For example, Lehn[1] and Ward[2,3] have recently reported a series of charged host species that show promise for monomer polymerizations, electronic materials, and separations of fine chemicals. Giannelis has described the intercalation of polymer molecules in the galleries of layered silicates.[4,5] Inclusion adducts can also be formed from organic host compounds held together by noncovalent interactions, such as van der Waals forces and hydrogen bonding. Other host compounds that have been examined in the past include urea,[6] perhydrotriphenylene (PHTP),[7,8] and cyclic phosphazenes.[9] Many of these inclusion adducts have been studied for use in templating polymer growth in the free radical polymerization of included monomers, for nonlinear optical activity, and for separating molecules. A challenge is to design host compounds to allow precise control of the inclusion properties.

The separation of macromolecules based on specific characteristics such as molecular architecture and molecular weight is an important objective in modern chemistry. Achieving such separations would have many applications in industry and the biological sciences. Urea has shown some potential in the area of microscale separations of small molecules[10] and in the separation of linear from branched polymers. However, to our knowledge, there is has been no in-depth study of polymer separations with this host. We have recently discovered a phenomenon that could significantly improve the separation of macromolecules, which is the ability of certain cyclotriphosphazenes to absorb macromolecules into tunnels that penetrate the host structure.[11,12]

Cyclotriphosphazene clathrates are an unusual class of host−guest compounds. We discovered and reported previously the synthesis and clathration properties of several cyclotriphosphazenes including tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**),[13−16] tris(2,3-naphthalenedioxy)cyclotriphosphazene (**2**),[17,18] and tris(3,6-dimethylphenylenedioxy)cyclotriphosphazene (**3**).[19] The teams led by Kubono and Sozzani have also contributed to the field.[20,21] Crystal engineering of these spirocyclotriphosphazene hosts is facilitated by the ease with which the tunnel diameters can be tailored by systematic adjustments to the size and nature of the host side groups (Scheme 1). These rigid, paddle-wheel-shaped hosts form inclusion adducts with organic small molecules when recrystallized from organic solvents or simply exposed to the guest liquid or vapor.

Scheme 1. Synthesis of Cyclotriphosphazene Hosts



Host **1** is the most versatile of these three species, since it forms inclusion adducts with a wide range of

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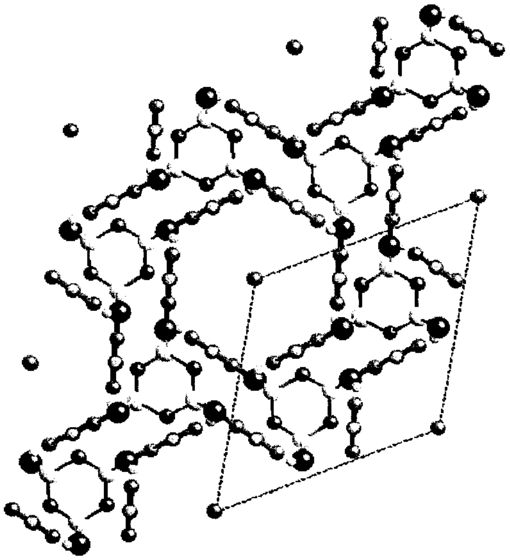

Figure 1. Crystal structure of host **1** in its hexagonal crystal form, with polyethylene included within the tunnels.

small molecules and polymers. A hexagonal host packing arrangement exists when guest molecules are accommodated within the 5 Å diameter tunnels that penetrate the crystal lattice (Figure 1). Inclusion of small molecules into **1** can be achieved either by recrystallization from a guest solvent or by direct imbibition into the solid host. Previous work has shown that selective absorption of guest molecules is possible on the basis of the relationship of the guest size to the tunnel diameter of the host.[13,22,23] For example, when **1** is exposed to an equimolar mixture of cyclohexane and heptane, heptane is preferentially absorbed with the almost total exclusion of cyclohexane.[13] Linear alkanes, oligoacrylates, and oligovinyl ethers form stable clathrates with host **1**, and these have been studied in some detail.[9,24−28]

The driving force for the formation of stable nanostructured host−guest adducts by spirocyclophosphazenes depends on the improved molecular packing efficiency that results from the presence of the guest molecules in the lattice. Host **1**, in its unclathrated form, exists in a monoclinic arrangement which requires a bending of sidearms presumably in an attempt to optimize the van der Waals interactions within the structure.[14] No tunnels exist in this structure. The presence of guest molecules allows the guest arms to be oriented radially and the structure to rearrange to generate tunnels. This process is driven by favorable van der Waals interactions between the host and the guest molecules in the tunnels. Removal of the guest molecules by heating under vacuum causes the host structure to revert to the monoclinic form. However, the hexagonal structure can persist if nearly all the guest molecules have been removed[14] or, under carefully controlled conditions, after all the guest molecules have left the structure.[29] Clearly, a delicate balance exists between the hexagonal and monoclinic structures which is tipped one way or the other by the presence or absence of the guests. It is this balance between the two polymorphs that provides opportunities for guest separations over and above the requirements imposed by guest shape fitting within the tunnels.

Recently, we reported the inclusion of various polymers such as polyethylene, poly(ethylene oxide), poly(tetramethylene oxide), and polybutadiene within the tunnels of crystalline **1**.[11,12] Polymer adducts were formed though recrystallization of **1** from a solution of the polymer. An increase in the melting point of **1** when it contains trapped polymer molecules suggested favorable van der Waals forces between **1** and the polymer. Furthermore, the host was found to separate 1,4- from 1,2-polybutadiene from solution, with the preferential inclusion of the 1,4-polymer within the tunnels of **1**. This phenomenon has the potential to bring about significant improvements in the separation of macromolecules.

The objective of this present work was to investigate the ability of tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**) to select, include, and separate a variety of small molecules and polymers on the basis of molecular weight, microstructure, and end group functionality and to understand the factors that affect such separations. The potential of this host for use in chromatographic separations is also reported.

Experimental Section

Reagents and Solvents. Hexachlorocyclotriphosphazene (**5**) (Ethyl Corp./Nippon Fine Chemical) was purified from two recrystallizations from heptane and a vacuum sublimation (60 °C, 0.050 mmHg). Tetrahydrofuran (OmniSolve) was distilled from sodium benzophenone. Triethylamine (Baker) was distilled from CaH_2. The linear alkane molecules, $CH_3(CH_2)_nCH_3$, where $n = 3-8$, benzene, 1,5-pentanediol, and 1,6-hexanediol (Aldrich) were used as received. Catechol (Aldrich) was sublimed before use. 1,4-Polybutadiene (average $M_n = 1800$ and 3000), *cis*-polybutadiene, polyethylene (average $M_n =$ 1700, 5500, and 7700), poly(ethylene glycol) (average $M_n = 650$, 1000, 1500, 2000, 6000, 8000, and 10 000), poly(ethylene glycol) dimethyl ether, poly(ethylene glycol) dibenzoate, poly(ethylene glycol) bis(carboxylmethyl)ether, poly(tetramethylene oxide) (average $M_n = 650$, 1000, and 2900), and poly(propylene glycol) were used as received from Aldrich.

Instruments. ^{31}P, ^{13}C, and ^{1}H spectra were recorded with a Bruker WM-360 NMR operated at 146, 90.27, and 360 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to an internal $CDCl_3$. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, American Polymer Standards AM gel 10 mm and AM gel 10 mm 104 Å column, with the system calibrated vs polystyrene standards (Polysciences). The samples were eluted with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv). Glass transition temperatures were determined by DSC using a Perkin-Elmer-7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. X-ray powder diffraction was obtained using a Philips analytical X-ray X'PERT MPD ($2\theta = 5-40°$, 1°/min).

Synthesis of 1. Tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**) was synthesized by literature procedures described previously.[16] Specifically, a mixture of catechol (3.0 equiv) and triethylamine (6.0 equiv) was added slowly to hexachlorocyclotriphosphazene (**5**) in the presence of tetrahydrofuran (THF). The resultant crystals were washed with THF and water, and **1** was subsequently recovered by Soxhlet extraction in benzene. After filtration, the solid was sublimed under vacuum (0.050 mmHg, 200 °C).

Preparation of Small-Molecule Inclusion Adducts. Separation of the small molecules based on molecular weight and end group termination was attempted by dissolving an equimolar amount of the two small molecules in an appropriate solvent (THF, CH_2Cl_2, or benzene) and subsequently adding host **1** to the solution. The mixture was stirred overnight and filtered, and excess solvent was removed under vacuum. Characterization of the preferentially included small molecule was achieved through GC/MS and solution ^{1}H NMR spectroscopy.

Preparation of Polymer Inclusion Adducts. The polyethylene−**1** inclusion adduct was prepared by refluxing an equal weight of host **1** and the polymer in benzene overnight to ensure complete recrystallization of **1**. After cooling, the mixture was filtered and excess polymer was washed away with hot hexane. The poly(ethylene glycol)−**1** inclusion adduct was formed by mixing poly(ethylene glycol) with an equal weight of **1** in an appropriate solvent such as water, methylene chloride, acetone, or THF at 25 °C and stirring the heterophase mixture at room temperature overnight. The poly(tetramethylene oxide)−**1** and the polybutadiene−**1** inclusion adducts were prepared by two methods: (1) interaction of the host and the polymer in refluxing benzene in order to recrystallize host **1** or (2) dissolution of the polymer in methylene chloride or THF and subsequently stirring the solution in the presence of **1** at room temperature. In all cases, the solids were collected after filtration and washed with an appropriate solvent to remove unclathrated polymer. The powdered material was then heated in a vacuum for 1 h at 100 °C to remove residual traces of small molecules.

Separation of a mixture of two polymers was attempted via two routes: (1) interaction of both polymers with host **1** in refluxing benzene in order to obtain recrystallization of the host or (2) dissolution of the two polymers in an appropriate solvent at room temperature and subsequent interaction with powdered solid **1**. This route avoids dissolution of the host, and separation will be based on direct imbibition of the polymers into the tunnels.

Results and Discussion

A. Selective Absorption of Small Molecules. Before any polymer inclusion and separations were attempted in host **1**, small molecules of the type $R(CH_2)_nR$ were used for trial separations based on microstructure, molecular weight, and end group type. Small-molecule separations based on microstructure have previously been demonstrated for cyclophosphazenes.[12−14] The driving force for such selectivity is believed to be the greater thermodynamic stability imparted to the host lattice by one guest over another. Similar results have been reported for various small molecule−urea adducts.[10,30]

(i) Separations Based on Molecular Weight. In this work, examination of the clathration behavior of a series of linear alkanes with different chain lengths indicated that the higher molecular weight alkanes are included preferentially within the tunnels of host **1**, with the almost total exclusion of the lower molecular weight analogues. Samples were prepared by stirring host **1** in an equimolar mixture of two hydrocarbons with different molecular weights, filtering off the host adduct, and subsequently drying the clathrate under vacuum for 30 min at 25 °C to remove excess solvent that may have been adsorbed on the surface of the host crystals. (Each hydrocarbon is retained within the tunnels of **1** under these conditions.) Characterization was achieved through GC/MS and solution ^1H NMR spectroscopy.

The results indicate that the host can discriminate between *n*-alkanes on the basis of a very small difference in chain length. Complete separation will occur if there is a difference of two or more carbon atoms in the chain. For example, the GC/MS spectrum of the clathrate formed by exposure of **1** to a mixture of decane and *octane* had a peak near 6.2 min (retention time) with a mass of 142, indicative of decane retention. The absence of a peak near 2.8 min indicated the exclusion of octane. Integration of the CH_3 and CH_2 peaks in the ^1H NMR spectrum of the resultant clathrate dissolved in $CDCl_3$ confirmed these results. However, the host did not absorb either type of molecule exclusively from a mixture of decane and *nonane*. In this case, there was a 2:1 decane:nonane co-inclusion. Co-inclusion also occurred from a mixture of decane and *undecane* or from decane and *dodecane*. However, the degree of co-inclusion of decane decreased as the molecular weight of the higher molecular weight component of the mixture increased. Complete separation occurred from a mixture of decane and *tridecane,* with favorable inclusion of the tridecane.

It appears that the hexagonal host structure is stabilized more by a higher molecular weight alkane than a lower molecular weight alkane. A direct consequence of this enhanced stabilization is an increase in the melting point of the clathrate as the molecular weight of the alkane increases. Crystal stability and melting point are affected in part by the internal motions of the guest molecules. The *n*-alkane chains show motional disorder near the chain ends where gauche bonds are present. However, the number of gauche bonds in the inner chains decreases with increasing chain length, as they are replaced by a trans conformation.[28] Similar chain dynamics have been reported for urea−alkane[30] and PHTP−alkane[31] adducts. Thus, longer chains may favor increased van der Waals interactions with the host assisted by this higher ratio of trans conformations.

Furthermore, longer alkane chains have a more effective surface area in contact with the host, thus providing better van der Waals stabilization than shorter chains. This is presumably due to the fact that there are fewer unoccupied regions between the guest molecules in the tunnel. A dramatic example of this stabilization requirement is found in urea inclusion compounds, where urea will form an inclusion compound only with guests that possess six or more carbon atoms, to gain the necessary stabilization to form an inclusion complex.[30]

(ii) Separations Based on End-Group Structure. Preferential inclusion based on end group type was also investigated. The tunnels of **1** are lined by hydrophobic units. Thus, alkanes with either hydrophobic or hydrophilic end groups were used in this study, specifically methyl-, phenyl-, and hydroxyl-terminated alkanes.

Heptane and 1,5-pentanediol were examined first, since they both contain the same number of CH_2 units. Host **1** was exposed to both molecules, either as liquids or in solvents such as acetone. Excess guest was washed from the surface of the host with an appropriate solvent, and the solid was dried under vacuum at 25 °C for 30 min. The ^1H NMR (in $CDCl_3$) spectrum (Figure 2) indicated a preferential retention of heptane, with only a small retention of the pentanediol. This was indicated by the small peak at 3.65 ppm from CH_2OH groups (Figure 2c). Similar results were obtained with mixtures of pentane and pentanediol or of hexane and 1,6-hexanediol in the presence of host **1**. The non-diol was included preferentially with the almost total exclusion of the diol, even though the latter has a slightly higher molecular weight. Competitive inclusion of 1,3-diphenylpropane and 1,5-pentanediol was also examined. The ^1H NMR spectra of the resultant inclusion adduct indicated the presence of the diphenylpropane only. Thus, a difference in hydrophobicity and hydrophilicity of the whole molecule, and not just the end group, will also control inclusion. This was confirmed by the fact that 1,3-diphenylpropane and pentane, both hydrophobic molecules, will co-include within the tunnels of host

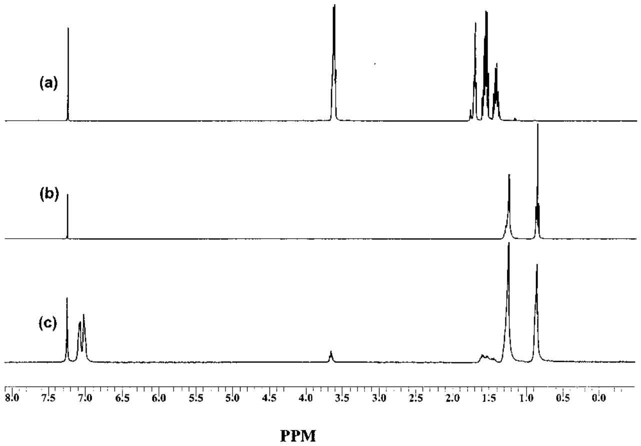

Figure 2. ^{1}H NMR spectra of (a) 1,5-pentanediol, (b) heptane, and (c) results of the imbibition of 1,5-pentanediol and heptane into host **1**.

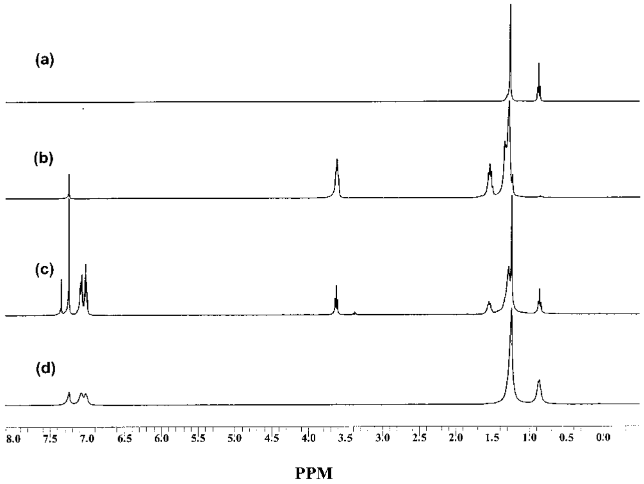

Figure 3. ^{1}H NMR spectra of (a) dodecane, (b) 1,10-dodecanediol, (c) results of refluxing (a) and (b) in the presence of host **1** in benzene, and (d) inclusion via the imbibition of (a) and (b) into host **1** from acetone.

1, as indicated by ^{1}H NMR, even though the phenyl group is bulkier than methyl groups.

Although the host preferentially separates these low molecular weight molecules, selective inclusion of the higher molecular weight dodecane and 1,10-decanediol molecules was dependent on whether the host was recrystallized from hot benzene or whether it imbibed the small molecules directly. Significant co-inclusion was detected when host **1** was exposed to the two molecules in refluxing benzene under conditions that allowed the host to dissolve and recrystallize on cooling (Figure 3c). Under these conditions, the crystallizing host presumably has very similar van der Waals interactions with both molecules due to the presence of the 10 hydrophobic methylene units in both guest molecules, and thus co-inclusion occurs. In contrast, when the two molecules are dissolved in solvents that do not dissolve the host, such as acetone or THF, only dodecane is absorbed by the host (Figure 3d). In this case, the end group type plays a greater role since the chain has to enter the tunnel starting from the chain terminus. Under these circumstances, the molecule with the more hydrophobic end group, such as dodecane, will be included preferentially, with little or no absorption of the molecule with the hydrophilic end group.

Table 1. Preferential Inclusion of Polymer Mixtures in Host 1 Based on Microstructure

polymer mixture[a]	melting point (°C)	inclusion results
PE(1700)	310[b]	PE
PB(1800)	290	
PE(1700)	310[b]	PE
PB(3000)	285	
PE(1700)	310[b]	PE
PEG(1500)	278	
PE(1700)	310[b]	PE
PTMO(2900)	285	
PTMO(2900)	285	PTMO
PB(3000)	285	
PTMO(1000)	283	PTMO
PEG(1000)	258	
PB(1800)	290	co-inclusion
PEG(2000)	260	

[a] Benzene was used as a refluxing solvent. [b] The melting point of 310 °C for these adducts is 40 °C below the value obtained by Sozzani et al.[28] for a similar complex produced by melting the host and the polymer together. This difference may reflect either the different preparative procedures or the lower molecular weight of the polyethylene used in this present work (1.7×10^3 vs 1.75×10^4).

The hydrogen-bonding effects of the end group can also play an important role in inclusion. For example, sebacic acid ($HO_2C(CH_2)_8CO_2H$) was not included in significant amounts by **1** when the solid host was exposed to a solution of the acid in THF (25 or 65 °C), or in water, perhaps because of the hydrogen-bonding effects generated by the two carboxylic acid groups. Hydrogen bonding of the $-$COOH group to the host is probably not a factor in this case, because alcohols are included within **1**. It is possible that the sebacic acid molecules are dimerized due to strong hydrogen bonding of the end groups, which results in a structure that is too bulky to fit into the tunnels of **1**. By contrast, dimethyl sebacate ($CH_3OC(CH_2)_8COCH_3$) is absorbed by **1**. Furthermore, molecules such as acetone and methyl ethyl ketone are absorbed. Decanoic acid ($CH_3(CH_2)_8CO_2H$), with one methyl end group, is also drawn into the tunnels of host **1**. In this latter case, it is reasonable to assume that inclusion occurs through the methyl-terminated end of the molecule, which can subsequently pull the whole molecule into the tunnel. In the next section, this end group effect will be shown to apply also to various polymer systems.

B. Selective Absorption of Polymers. In view of the separations demonstrated with small molecules, candidate polymers were chosen on the basis of microstructure, molecular weight, and end groups. These are discussed in the following sections.

(i) Separation of Polymers Based on Microstructure. Exposure of host **1** to oligomers or polymers of different types, such as polybutadiene and polyethylene of similar molecular weights in a refluxing benzene solution, resulted in a preferential incorporation of one polymer into the clathrate in preference to the other. In this case, polyethylene was preferentially absorbed into the adduct (Table 1). Polymer inclusion was monitored by solution ^{1}H NMR spectroscopy and powder X-ray diffraction. In each case, the absorbed polymer promoted a crystal phase change from monoclinic to hexagonal, as detected from the XRD pattern.

It appears that tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**) will preferentially include the polymer that imparts the greater thermodynamic stability to the overall clathrate system and the best packing arrangement. This becomes evident from the melting points of the adducts of **1** with various polymers. In most cases, exposure of host **1** to solutions containing the polymers listed in Table 1 leads to the preferentional incorporation of the polymer which also generates the highest melting point in the host–guest adduct. A polyethylene–**1** adduct has the highest melting point (310 °C), and this polymer is preferentially included from mixtures with poly(tetramethylene oxide), poly(ethylene glycol), or 1,4-polybutadiene.

Presumably, polyethylene has a high ability to stabilize the hexagonal crystal phase of **1** through strong van der Waals interactions with the tunnel lining compared to the other polymers. These enhanced interactions may be due to the conformation that the polyethylene chain adopts inside the tunnel. X-ray diffraction confirmed that polyethylene has a high content of trans conformation inside the host. The polyethylene repeat unit length in host **1** is 2.52 Å,[12] a value close to the repeat unit found in pure crystalline polyethylene in the trans-planar conformation. In addition, solid-state ^{13}C chemical shifts of the PE–**1** adduct indicate a downfield shift of the inner carbon signals compared to lower molecular weight alkanes, and this is indicative of a high degree of trans conformation.[28] Thus, the polyethylene chain adopts its preferred conformation inside the tunnels. This not only provides opportunities for favorable interactions with the tunnel walls, but it may also increase the occupancy of the tunnels. In other words, it may lead to less free volume within the tunnel space.

This is not the case for the poly(ethylene oxide)–**1** adduct. Pure crystalline poly(ethylene oxide) is known to assume a helical conformation in the crystalline state, with a repeat unit length of 2.76 Å.[32] However, when included inside the tunnels of host **1**, the repeat unit length increases to 3.02 Å, which is consistent with a near "trans" conformation. Similar observations have been reported for the inclusion adducts of polyethylene and poly(ethylene glycol) in perhydrotriphenylene (PHTP)[33] and in urea,[34] which also form tunnels of approximately 5 Å diameter. In the case of the PHTP adducts, included polyethylene was shown to retain a trans conformation with a repeat unit length of 2.54 Å, but included poly(ethylene glycol) had an increased repeat distance (3.43 Å) compared to the bulk crystalline state.[35] This conformational extension is probably not energetically favorable, as reflected in the melting point of the adduct. Poly(ethylene glycol)–PHTP melts at 144 °C, which is significantly lower than the polyethylene–PHTP melting point of 182 °C.[35] Similarly, the melting point of poly(ethylene glycol)–**1** (265 °C) is much lower than that of polyethylene–**1** (310 °C). The ease with which a polymer molecule can penetrate into a tunnel, or allow the host to crystallize around the macromolecule, will also be affected.

Host **1** will preferentially imbibe poly(tetramethylene oxide) from mixtures with poly(ethylene glycol) or polybutadiene. The poly(tetramethylene oxide)–**1** adduct also has a higher melting point than the poly(ethylene glycol)–**1** or polybutadiene–**1** adducts. It is speculated that the poly(tetramethylene oxide) chain adopts a more stable conformation in the tunnel compared to poly(ethylene glycol) and polybutadiene, and this is probably the defining factor in the preferential inclusion of this polymer and enhanced crystal melting point. Although no crystal data are available for the poly(tetramethylene oxide)–**1** adduct, studies of the chain conformation of poly(tetramethylene oxide) in urea have shown that the chains pack in a near trans conformation, with a small twist about each bond.[36] By contrast, this twist is not found in the polyethylene–urea complex,[37] and this affects the thermal stability of the clathrate as illustrated by the melting points. Poly(tetramethylene oxide)–urea melts at 139 °C, while polyethylene–urea melts at 148 °C.[32] In view of these observations, it is reasonable to assume that the chains in the poly(tetramethylene oxide)–**1** adduct are in a trans conformation, but with less favorable van der Waals interactions with the host than polyethylene, which may explain why the host will select polyethylene over poly(tetramethylene oxide). The role played by the hydrophilic etheric oxygen atoms is a matter for speculation.

The polymer conformation inside the host thus plays an important role in the overall stability of the clathrate. The host prefers to maximize van der Waals interactions with its guests, which means that polymers which readily adopt a conformation that leads to better interactions with the host, and possibly a smaller cross section, will be imbibed or retained in preference to polymers that generate poorer host–guest interactions. For example, previous work in our program has demonstrated that host **1** can separate 1,4- and 1,2-polybutadiene from solution, with preferential inclusion of the 1,4-polymer.[12] The 1,2-polybutadiene used for that specific study was not absorbed by the host, due to its high degree of 1,2-content (45%).

(ii) Separation of Polymers Based on Molecular Weight. The ability of tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**) to selectively include a polymer on the basis of its molecular weight was also investigated. Experiments were carried out using a method similar to the one described above. Molecular weights and polydispersities were determined by GPC methods.

Some surprising results were evident for the poly(tetramethylene oxide)–**1**, polybutadiene–**1,** and poly(ethylene glycol)–**1** adducts (Tables 2, 3, and 4, respectively). If host **1** was exposed to polydisperse polymers in the presence of a solvent (such as THF or CH_2Cl_2), the host preferentially absorbed the longer polymer chains. In doing so, the host effectively reduced the polydispersity of the included polymer (Figure 4) and the un-included material as well. Similar results have been described for poly(tetramethylene oxide)–urea[36] and aliphatic polyester–urea adducts,[38] where inclusion of the polymer leads to a lower polydispersity due to clathration of the longer polymer chains. This selective clathration has been attributed to the increased host–guest interactions between a higher molecular weight polymer chain and the host (a greater density of monomer units per tunnel volume). The poly(tetramethylene oxide)–**1** and polybutadiene–**1** inclusion adducts (Tables 2 and 3) clearly show a preference for inclusion of the higher molecular weight chains, with a resultant drop in polydispersity. However, the poly(ethylene glycol)–**1** inclusion adducts sometimes showed co-inclusion of both the higher and lower molecular weight species, as seen for $M_n = 2000$ and 8000 (Table 4). Overall, host **1** can be used as an effective means to fractionate molecular weights in order to obtain narrower polydispersities.

The next series of experiments involved the mixing of two polymers with different molecular weights with

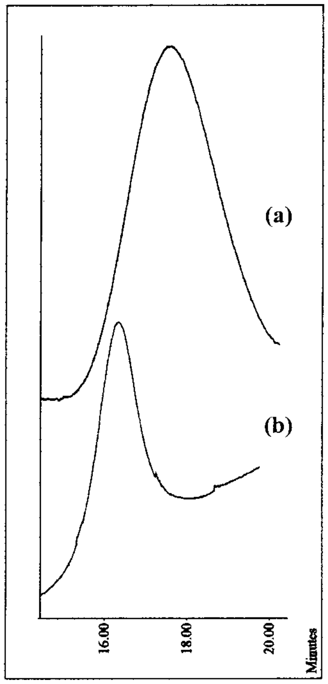

Figure 4. GPC spectra of (a) poly(tetramethylene oxide), M_n = 2900, and (b) poly(tetramethylene oxide) (M_n = 2900) included in host **1**.

Table 2. Molecular Weight Data for the Poly(tetramethylene oxide)−1 Adduct

polymer	bulk		clathrated with host **1**		mixture with MW = 2900	
MW[a]	M_n	PDI	M_n	PDI	M_n	PDI
650	972	1.389	3160	1.137	26 855	1.149
1000	1256	1.433	5238	1.154	27 352	1.152
2900	6372	1.868	26936	1.163		

[a] Molecular weight listed on bottle.

Table 3. Molecular Weight Data for the Polybutadiene−1 Adduct[a]

	bulk		clathrated with host **1**		mixture with MW = 3000	
polymer	M_n	PDI	M_n	PDI	M_n	PDI
1800[b]	3796	2.049	7491	1.475	8442	1.796
3000[b]	6547	2.730	8205	1.998		
5000[c]	11868	1.036	11873	1.040	11150	1.100

[a] Direct imbibition from CH_2Cl_2. [b] 1% 1,2-addition. [c] 20% 1,2-addition.

Table 4. Molecular Weight Data for the Poly(ethylene glycol)−1 Adduct[a]

	bulk		clathrated with host **1**		mixture with MW = 10 000	
polymer	M_n	PDI	M_n	PDI	M_n	PDI
1000	877	1.143	1331	1.080	17684	1.069
					1047	1.031
2000	10037[a]	1.021	9635	1.032	18651	1.059
	2201	1.089	2698	1.070	2320	1.057
4600	6342	1.055	8283	1.113	18522	1.052
					6117	1.027
8000	12961	1.058	28309	1.010	18528	1.103
			15790	1.031	sh[b]	
10000	15904	1.078	18701	1.057		

[a] Direct imbibition from water. [b] Shoulder.

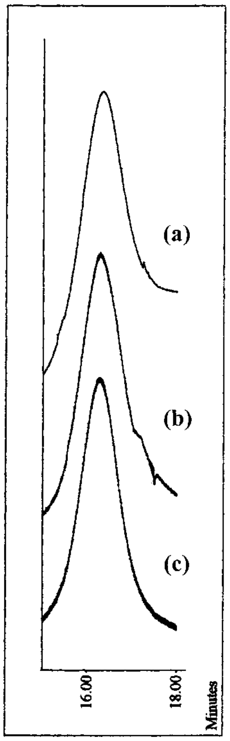

Figure 5. GPC spectra of (a) poly(tetramethylene oxide), M_n = 2900, (b) inclusion results from a mixture of poly(tetramethylene oxide) (M_n = 2900 and 1000) in the presence of host **1**, and (c) inclustion from mixture of poly(tetramethylene oxide) (M_n = 2900 and 650) in the presence of host **1**.

host **1** in appropriate solvents in order to allow direct competition for occupancy of the tunnels. The host was able to selectively clathrate the higher molecular weight polymer. For example, poly(tetramethylene oxide) (M_n = 650 or 1000) mixed with poly(tetramethylene oxide) (M_n = 2900) in the presence of **1** in THF, methylene chloride, or refluxing benzene consistently showed inclusion of the higher molecular weight poly(tetramethylene oxide) (M_n = 2900), with a resultant decrease in polydispersity (Table 2 and Figure 5). Similar behavior was detected for the polybutadiene−**1** adducts (Table 3). However, the poly(ethylene glycol)−**1** adducts consistently showed some co-inclusion with the lower molecular weight analogue from a mixture of high and low molecular weight species.

Table 3 also shows the separations obtained with a polybutadiene (M_n = 5000) that contained 20% 1,2-addition product, as opposed to the other two lower molecular weight polybutadienes which only contain 1% 1,2-addition species. Preferential inclusion of the higher molecular weight polybutadiene was detected, although the degree of 1,2-addition product in the included mixture was higher. As discussed, the higher molecular weight species probably results in enhanced van der Waals interactions with the host compared to the other two lower molecular weight polymers and to a more efficient utilization of the tunnel volume. A similar correlation exists with polymers that have different end groups, as discussed in the following section.

(iii) Separation of Polymers Based on End Group Functionality. Studies were undertaken to determine the effect of end groups at the termini of various functionalized poly(ethylene glycol)s. Four types of end-functionalized poly(ethylene glycol)s were used: hydroxyl-terminated poly(ethylene glycol), methyl-terminated poly(ethylene glycol) dimethyl ether, phenyl-

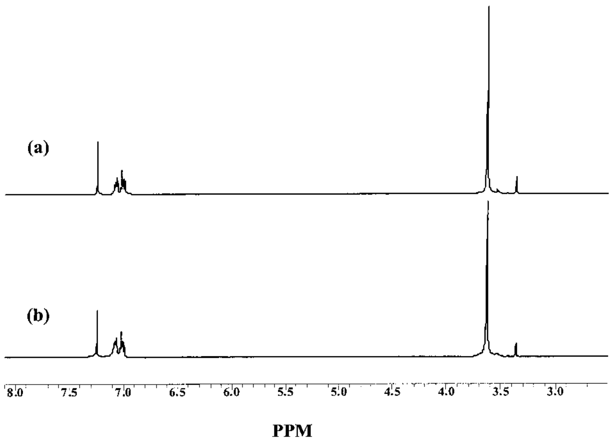

Figure 6. ^{1}H NMR spectra of (a) inclusion from a mixture of poly(ethylene glycol) dimethyl ether and poly(ethylene glycol) in the presence of host **1** and (b) inclusion of poly(ethylene glycol) dimethyl ether in host **1**. $M_\mathrm{n} = 1000$ for both polymers.

terminated poly(ethylene glycol) dibenzoate, and carboxyl-terminated poly(ethylene glycol) bis(carboxylmethyl) ether. Polybutadiene bis(carboxymethyl) ether was also investigated. All of these polymers are included into the host (either via direct absorption or by recrystallization of the host) except poly(ethylene glycol) bis(carboxylmethyl) ether. The analyses were by means of ^{1}H NMR spectroscopy and powder X-ray diffraction.

Preferential inclusion of the polymer with the more hydrophobic end group was found when the host was exposed to a mixture which contained one polymer with hydrophobic end groups and one polymer with hydrophilic end groups. For example, exposure of host **1** to an equimolar amount of poly(ethylene glycol) dimethyl ether ($M_\mathrm{n} = 250$) and poly(ethylene glycol) ($M_\mathrm{n} = 300$) resulted in the preferential inclusion of the more hydrophobic poly(ethylene glycol) dimethyl ether. Similar results were obtained when the host crystals were exposed to a mixture of higher molecular weight poly(ethylene glycol) dimethyl ether ($M_\mathrm{n} = 1000$) and poly(ethylene glycol) ($M_\mathrm{n} = 1000$) (Figure 6). Moreover, experiments with mixtures of poly(ethylene glycol) dibenzoate and poly(ethylene glycol) with similar molecular weights showed that the phenyl-terminated poly(ethylene glycol) was preferentially included within **1**.

The consequence of increasing the molecular weight of the more hydrophilic polymer was also investigated. Poly(ethylene glycol) dimethyl ether ($M_\mathrm{n} = 250$) (Figure 7a) was mixed with a series of poly(ethylene glycol)s having molecular weights $M_\mathrm{n} = 300$ (Figure 7b), $M_\mathrm{n} = 600$ (Figure 7c), $M_\mathrm{n} = 1000$ (Figure 7d), $M_\mathrm{n} = 4600$, and $M_\mathrm{n} = 10\,000$ in the presence of host **1** in acetone. ^{1}H NMR integration of the $-\mathrm{C}H_2\mathrm{OC}H_2-$ and $-\mathrm{OC}H_3$ peaks near 3.62 and 3.36 ppm, respectively, demonstrated that smaller amounts of poly(ethylene glycol) dimethyl ether were included as the molecular weight of the poly(ethylene glycol) increased. Poly(ethylene glycol) with a molecular weight of 1000 or higher was included by **1** with the almost total exclusion of the methyl-terminated poly(ethylene glycol) (Figure 7d). Again, it is presumed that this reflects enhanced van der Waals contacts between the host and the surface of the longer chains.

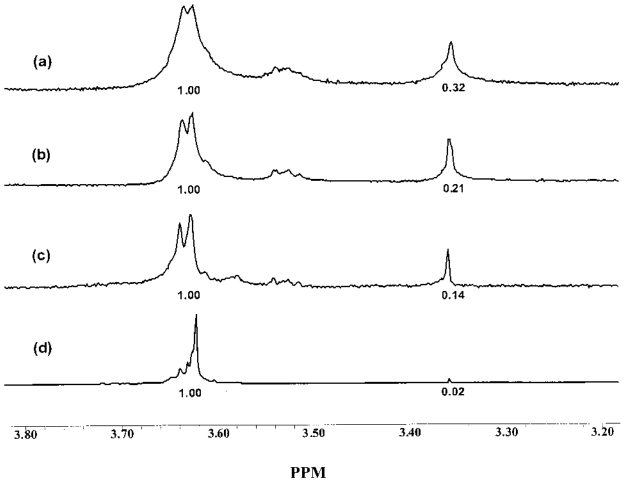

Figure 7. ^{1}H NMR spectra of (a) inclusion of poly(ethylene glycol) dimethyl ether ($M_\mathrm{n} = 250$) in host **1** and inclusion results from a mixture of poly(ethylene glycol) dimethyl ether ($M_\mathrm{n} = 250$) and poly(ethylene glycol) with (b) $M_\mathrm{n} = 300$, (c) $M_\mathrm{n} = 650$, and (d) $M_\mathrm{n} = 1000$.

The carboxyl-terminated poly(ethylene glycol) ($M_\mathrm{n} = 250$) was not incorporated into the crystal structure of tris(*o*-phenylenedioxy)cyclotriphosphazene when the polymer was dissolved in methylene chloride, acetone, or water. The proximity of the two carboxyl groups to each other and efficient hydrogen bonding with other polymer molecules could result in bulky species, which prevents inclusion. This effect for low molecular weight species was also detected for sebacic acid (MW = 202), which is not included by **1**. However, the higher molecular weight dicarboxyl-terminated polybutadiene ($M_\mathrm{n} = 4200$) was absorbed slightly within the tunnels of **1** from solution in CH_2Cl_2. Because there are fewer carboxyl end groups per macromolecule, the degree of polymer–polymer hydrogen bonding is presumably weaker. It is possible that one end of the longer chain can enter the tunnel and generate efficient host–guest interactions before the second carboxyl end group reaches the tunnel entrance. Inclusion of the dicarboxyl-terminated polybutadiene ($M_\mathrm{n} = 4200$) within the host was also achieved by the recrystallization route.

Conclusions

Tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**) is an effective host for the separation of different polymers and different small molecules based on microstructure, molecular weight, and end group functionality. In the case of linear alkanes, the evidence shows that the host can selectively absorb the higher molecular weight alkane. This applies also to the polymer separations. The selective inclusion is presumably due to enhanced van der Waals interactions between the longer molecular weight molecules and the host units that line the tunnels. The incorporation of high polymers presumably minimizes the free volume within each tunnel compared to the situation when many small molecules are present. A related factor may be the ability of the polyethylene chains to rotate within the tunnel, as has been demonstrated for the same polymer clathrated by perhydrotriphenylene.[39]

Selective inclusion of a polymer based on skeletal structure was also shown to occur, with polyethylene being included preferentially over polymers with double bonds or etheric units in the backbone. This is believed to reflect differences in the preferred conformations of the polymers or perhaps the hydrophilicity of etheric oxygen atoms.

Finally, separations based on end groups are also possible for both small molecules and polymers. Separation of molecules (with similar molecular weights) containing hydrophilic or hydrophobic end groups depends on whether the molecule is directly imbibed into the solid host or incorporated through a process of host recrystallization. When imbibed directly, molecules with hydrophobic end groups are preferentially included over those with hydrophilic end groups, probably due to the hydrophobic nature of the tunnels of the host. However, if the host is allowed to recrystallize around the guest molecule, co-inclusion of both guests occurs, as seen with the dodecane and 1,10-decanediol systems. This is probably due to similar van der Waals interactions generated by both molecules as the host crystallizes. For dicarboxyl-terminated molecules, only minimal inclusion of low molecular weight species (<300) takes place, due to the close proximity of the two end groups and the possibility of hydrogen bonding between each guest. However, inclusion occurs for higher molecular weight dicarboxylic acids, possibly because the two end groups are now separated by a chain that is long enough to reduce the probability of hydrogen-bonding effects, and thus provides more favorable interactions with the host.

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