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Polymerization in Clathrate Tunnel Systems: Stereocontrolled Polymerization of Unsaturated Monomers in Crystals of Tris(*o*-phenylenedioxy)cyclotriphosphazene

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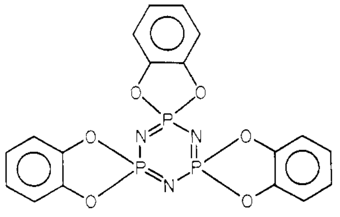
ABSTRACT: Acetylene, phenylacetylene, butadiene, isobutylene, divinylbenzene, styrene, and 4-bromostyrene have been trapped within the tunnel clathrate system of tris(*o*-phenylenedioxy)cyclotriphosphazene (I). For some of the adducts irradiation of the trapped monomers with ^{60}Co γ-radiation yielded short-chain polymer molecules within each tunnel. In specific cases (especially with butadiene) evidence was obtained that the polymerization products were stereoregular. Moreover, the polymer derived from divinylbenzene was un-cross-linked in contrast to the form of this polymer obtained by other methods. The clathrate between 4-bromostyrene and I was studied in detail by variable-temperature broad-line ^{1}H NMR techniques and by single-crystal X-ray analysis. The results enable a preliminary correlation to be made between the monomer packing arrangement and the mode of polymerization.

Introduction

A major challenge in polymer synthesis is the need for new techniques for the controlled polymerization of unsaturated monomers. Control may be needed to ensure stereospecific addition or, in some cases, to prevent side reactions such as cross-linking or branching. The classical approach to this problem has been to make use of organometallic initiators in which steric control is achieved through stereospecific association of the monomer within the coordination sphere of a metallic atom. However, in principle, other approaches are available to achieve similar results. The coordination of an unsaturated monomer to a solid metallic or organometallic surface is an alternative option. So, too, is the concatenation and orientation of monomer molecules under the influence of steric forces generated within a host crystallization lattice.[1]

In this paper we discuss the oligomerization or polymerization of a number of unsaturated organic monomers within tunnels that penetrate the crystalline lattice of an unusual host system derived from tris(*o*-phenylenedioxy)cyclotriphosphazene (I).



I

Spirocyclotriphosphazenes form molecular inclusion adducts (clathrates) with aliphatic hydrocarbons, benzene, toluene, xylene, tetralin, decalin, and a variety of other small molecules.[2-4] The clathrates are crystalline solids in which the guest molecules occupy tunnels that penetrate the host crystal system. The crystal and molecular structures of I with included benzene and xylene have been described previously.[2-5] In this paper we report the inclusion of acetylene, phenylacetylene, butadiene, isobutylene, divinylbenzene, styrene, and 4-bromostyrene into the tunnel system of I and the use of the crystal structure of I as a template for the controlled, γ-ray-induced polymerization of several of the monomers.

This work was initiated to answer the following questions: (1) Can olefins or acetylenes be polymerized within this clathrate system? (2) If so, does a difference exist between the included polymer and that formed in bulk without the influence of the host lattice?[6] (3) If a difference exists, what factors induce the difference—shape of the tunnel, mode of monomer packing, isolation of monomer "stacks" in separate tunnels, or other factors?

Special emphasis was placed on the use of 4-bromostyrene as a monomer. The 4-bromostyrene adduct of I was selected for detailed examination because of the following reasons: (1) It readily forms large single crystals which can be used for NMR analysis of molecular motion or for X-ray diffraction analysis. (2) 4-Bromostyrene has a low vapor pressure (the boiling point is higher than 145 °C) and molecules of this guest do not escape readily from the tunnels. (3) 4-Bromostyrene has a molecular size (about 6-Å diameter) and shape that should pack effectively into the tunnel system of I. (4) The bromine atoms of the guest molecules facilitated their location by X-ray diffraction techniques.

This clathrate system is unique because the diameter of the tunnels can be adjusted by variations in the size of the spiro side groups.[2] Hence, a wide range of subtle host–guest interactions can be explored. In this paper we examine the scope of this system for one of the available host frameworks. The broader ramifications will be considered in subsequent papers.

Overall Approach

Clathrate adducts of I were prepared (a) by the addition of the liquid monomer directly to the pure host, (b) by recrystallization of the host from the liquid guest, or (c) by passing the gaseous monomer over the pure host. The direct imbibition of guest by host (a) and (c) takes place with a change in host crystal structure in a manner that can be described as absorption by a "molecular sponge".[3] Method a was employed for phenylacetylene, styrene, 4-bromostyrene, divinylbenzene, butadiene, or isobutylene. Method c was appropriate for acetylene. Large single crystals of the 4-bromostyrene adduct were prepared by method b. In each case, formation of the adduct was monitored by changes in the melting point of the host[7] and by detection of the monomer in the mass spectrum of the products released from the clathrate.

Polymerization of the guests was induced by ^{60}Co γ-irradiation of the clathrate, often at low temperatures. Irradiation usually resulted in an elevation in and a broadening of the melting range of the clathrate. After irradiation, the resultant polymer was solvent extracted from

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the clathrate and was examined by infrared and ^{13}C NMR techniques. The degree of polymerization was estimated by gel permeation chromatography.

Infrared and ^{13}C NMR methods were particularly useful for detection of the polymers. The formation of infrared absorptions in the 3000–2800-cm^{-1} region was indicative of nonolefinic, aliphatic C–H bonds. Similarly, resonances with upfield shifts in the ^{13}C NMR spectra were present following irradiation, and these were considered to be good evidence for the presence of addition polymers or oligomers. The degree of polymerization was generally low.

Polymerization

Acetylene and Phenylacetylene. Irradiation of the acetylene adduct of I at −78 °C did not result in the formation of polyacetylene, as determined by ^{13}C NMR spectroscopy. Similarly, irradiation of the phenylacetylene adduct of I at −78 °C and +35 °C yielded no poly(phenylacetylene), as determined by ^{13}C NMR spectroscopy.

Butadiene. Polymerization of butadiene within the tunnel system of I yielded *trans*-1,4-polybutadiene. Infrared spectroscopic evidence for a small percentage of the 1,2-addition product was obtained, but no evidence for the formation of the cis-1,4-addition product was found. This result confirms an earlier observation by Finter and Wegner.[8] The trans-1,4 structure was indicated by a resonance at 33 ppm in the ^{13}C NMR spectrum (together with peaks at 128–130 ppm) and by the absence of a peak at 28 ppm (*cis*-1,4-polybutadiene). Furthermore, no resonances were detected at 113–115 ppm,[9,10] which would have been characteristic of the 1,2-addition product. The predominantly trans-1,4 structure was also confirmed by the infrared spectrum. The clathrate-synthesized polymer had a weak absorption at 910 cm^{-1} (1,2-addition product) and showed no absorption at 730 cm^{-1} (expected for the cis-1,4 product[11]). An intense absorption at 965 cm^{-1} (trans-1,4 product) was observed. The GPC average molecular weight was in the region of 5×10^3 (100 monomer units). These results are in contrast to those for the polymer formed by irradiation of the unclathrated bulk monomer: a mixture of all three addition products was obtained.

Isobutylene. No difference could be detected between the polyisobutylene prepared by irradiation of the clathrate and that produced by irradiation of the bulk monomer. The ^{13}C NMR resonances centered at 59.9, 38.5, and 31.5 ppm were assigned to methylene, quaternary carbon, and methyl carbon atoms, respectively.[12] The infrared spectrum was also consistent with the presence of aliphatic carbon–hydrogen stretching modes. The molecular weight range was from 3×10^3 (50 monomer units) to 5×10^2 (9 monomer units), with the center of the distribution at 1×10^3 (16 units).

Divinylbenzene. Irradiation of *p*-divinylbenzene trapped within the tunnels of I yielded a soluble, uncross-linked, linear polymer, with pendent styrene residues. By contrast, irradiation of the unclathrated monomer yielded an insoluble, cross-linked polymer. Thus, the clathrate-controlled polymerization provides one of the few methods available for the formation of linear poly(4-vinylstyrene).[13]

The ^{13}C NMR spectrum of the clathrate-polymerized polymer is summarized in Figure 1. An additional resonance at 26.0 ppm was attributed to the presence of a terminal methyl group.

The infrared spectrum of the polymer within the lattice of I showed absorptions at 2925 and 3000 cm^{-1} (backbone aliphatic C–H stretches). The gel permeation chromatography data showed a narrow molecular weight distribution, with a maximum chain length of approximately 30 monomer residues and an average of 10 residues. The low degree of polymerization observed for this monomer can be understood by analogy with the styrene and 4-bromostyrene systems discussed in the following sections.

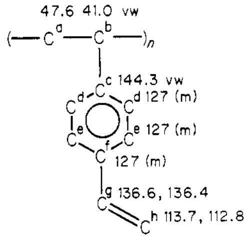


Figure 1. ^{13}C NMR shifts (ppm) for poly(4-vinylstyrene). Carbons d–f occur as a multiplet at 127 ppm.

Styrene. Irradiation of the styrene adduct of I at −78 and +35 °C did not result in the formation of polystyrene. Only the monomer was detected by ^{13}C NMR spectroscopy.

4-Bromostyrene. Polymers were formed when 4-bromostyrene was irradiated within the tunnels of I at −78 °C. Gel permeation chromatography was used to show that the molecular weight was in the region of 3×10^4, a value that is compatible with a chain length of approximately 200 repeating units. ^{13}C NMR spectra of the polymer showed the presence of two aliphatic carbon resonances in the ^1H-decoupled mode. A resonance at 40 ppm was assigned to the methine carbon of the backbone,[14] and a resonance at 47 ppm was attributed to the backbone methylene units.[14,15] Irradiation of the unclathrated bulk monomer yielded a polymer with a ^{13}C multiplet in the 42–45-ppm region. The downfield shift position of the methylene resonance for the clathrate-synthesized polymer may be a consequence of the short chain length[16] or, more likely, due to a stereoregular configuration. The two aliphatic carbon resonances could not be detected in the ^1H-coupled ^{13}C NMR spectrum, presumably because of extensive coupling. The aromatic region of the ^{13}C NMR spectrum was complicated. However, the characteristic quaternary aromatic resonance for the polymer at 144 ppm[17] was easily detected. The infrared spectrum of the polymerization product was compatible with that expected for poly(4-bromostyrene).

When the 4-bromostyrene adduct of I was irradiated at +35 °C, the molecular weight of the resultant polymer was centered at 1×10^5. The ^{13}C NMR spectrum was similar to that of polystyrene formed by a free-radical process. A resonance at 40 ppm due to the methine carbon atoms and a multiplet at 42–45 ppm, attributed to the methylene carbon atoms, were present in the spectrum.[14]

The relatively high molecular weight of the polymer formed at +35 °C may be a consequence of the freedom for translational motion of the monomer in the tunnel system at this temperature. No such motion occurs at −78 °C (see section on broad-line ^1H NMR). It is also possible that different mechanisms are operative at the two temperatures. At +35 °C, a free-radical polymerization process is likely. At −78 °C, an anionic mechanism may be operative, although this is unlikely (see section on other clathrate systems). This possibility might also explain the differences observed in the ^{13}C NMR spectra of the 4-bromostyrene polymers formed at the two temperatures.

The adduct of 4-bromostyrene with I was especially suited for X-ray diffraction studies. Hence, a crystal structure analysis was performed on this clathrate as an exploratory prototype for structural analyses of the other systems.

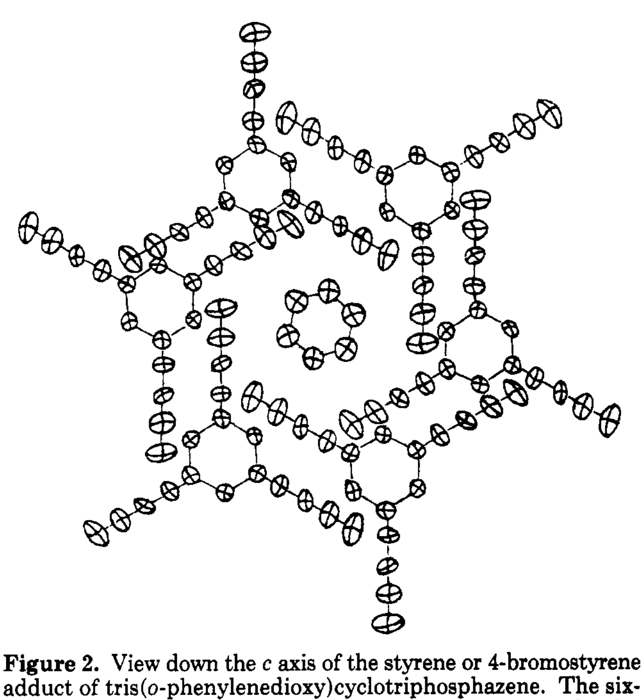


Figure 2. View down the *c* axis of the styrene or 4-bromostyrene adduct of tris(*o*-phenylenedioxy)cyclotriphosphazene. The six-membered ring in the center of the tunnel represents the dynamically disordered aryl ring of a monomer.

Structure Analysis

X-ray Diffraction of the 4-Bromostyrene Adducts of I. X-ray data sets were collected with the crystal at +20 and at −80 °C. Except where noted, the following remarks apply to the data set collected at 20 °C. The host crystal framework consists of alternating layers of cyclophosphazene molecules, with a distance of approximately 5 Å between the layers. Each phosphazene molecule has a symmetric "paddle wheel" shape, with the side groups oriented at right angles to the plane of the inorganic ring. The relative orientation of these molecules within the hexagonal unit cell generates tunnels that penetrate between the *o*-phenylenedioxy side groups. Crystallographically, the phosphazene rings are orthogonal to the *z* axis, at $z = {}^{1}/_{4}$ and $z = {}^{3}/_{4}$. Thus, the overall host structure resembles those found when other organic molecules such as benzene or xylene are present. Representations of the packing arrangement are shown in Figures 2 and 3.

The 4-bromostyrene molecules occupy discrete positions within the tunnels. The largest concentration of guest aryl rings is found in a set of planes parallel to the phosphazene ring planes but displaced above and below the level of each inorganic ring. Thus, most of the styryl rings were oriented orthogonal to the crystallographic *z* axis, at $z = 0$ and $z = {}^{1}/_{2}$, that is, at points in the tunnel between adjacent layers of phosphazene rings (Figure 3). The ring carbon atoms were moderately well resolved as were the 6-fold disordered bromine and α-carbon positions. Electron density attributed to the β-carbon atom was also located above and below each phenyl bromine/α-carbon site at the 6-fold disordered positions at $z = {}^{1}/_{8}$, ${}^{3}/_{8}$, etc. Thus, the aryl and vinyl groups are not coplanar. This lack of coplanarity may perhaps be attributed to the steric constraints on the system brought about by the presence of the bulky bromine atom. The guest monomers did not tumble in place at 20 °C, nor was completely free rotation detected about the *z* axis. However, the 6-fold disorder of the bromine atoms and the vinyl carbon atoms implied that rotational switching among the six possible orientations does occur at this temperature. This guest molecular motion was also detected from broad-line ^{1}H NMR experiments (see later).

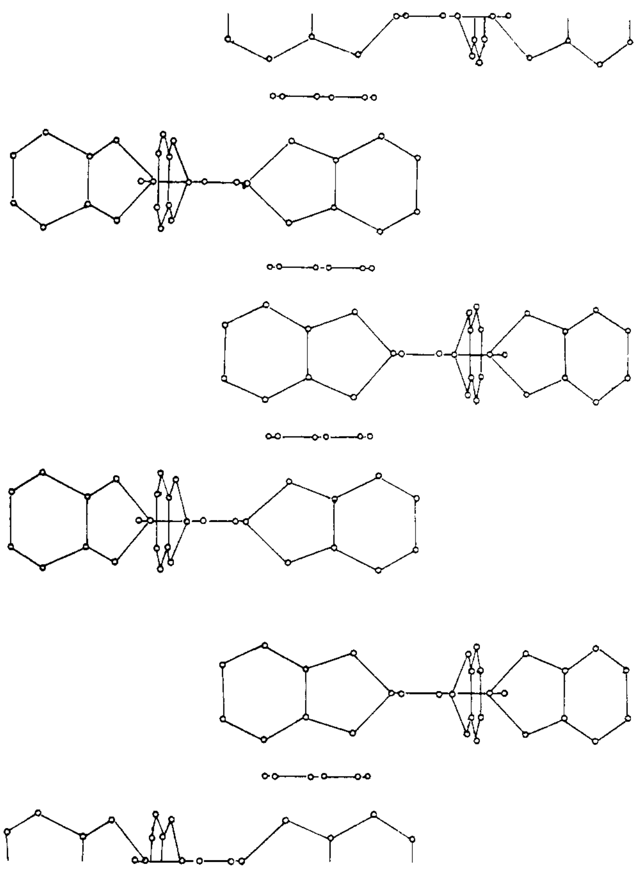


Figure 3. View into the *a*–*c* face of the 4-bromostyrene adduct of tris(*o*-phenylenedioxy)cyclotriphosphazene.

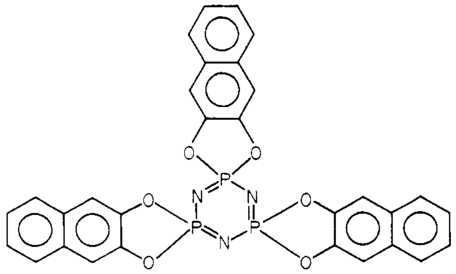
In addition to the bromostyrene rings at $z = 0$ and $z = {}^{1}/_{2}$, a second set of guest rings was located at $z = {}^{1}/_{4}$ and $z = {}^{3}/_{4}$, but with a lower occupancy factor than found for the first set. (The ratio of site occupation was ${}^{2}/_{3}$ to ${}^{1}/_{3}$.) The electron density, attributed to the β-carbon atom, appeared midway between two adjacent sets of styrene molecules and within a C–C bonding distance of both.

Overall, the monomer packing arrangement within the tunnel constitutes a parallel stacking of the aromatic rings, with the closest rings appearing to be only 2.5 Å apart. If this represents a genuine sandwich-type packing structure or a polymer that is generated by X-irradiation, it is one of the shortest distances ever reported for the approach of two aromatic rings.[18-20] However, it is important to note that these inferences are based on the solution of a partially disordered structure and one, moreover, in which many of the available monomer sites are unoccupied. Hence, the possibility exists that this apparent close approach is an artifact and that the electron density in the tunnel is a ramification of occupational disorder between two alternative sets of sites ($z = 0$ and ${}^{1}/_{2}$ and $z = {}^{1}/_{4}$ and ${}^{3}/_{4}$). Thus, both types of sites are occupied, but not in close proximity to each other. An alternative explanation is that the occupation of both sites represents poly(4-bromostyrene) molecules formed by the X-ray-induced polymerization of the monomer during data collection. (The X-ray dose during data collection was comparable to the γ-ray dose used for polymerization.) Hence, this alternative explanation cannot be ruled out completely and appears even more plausible in view of the results for the styrene adduct of I (see next section).

Disorder due to molecular motion can often be simplified by an X-ray analysis of a cooled crystal. However, a data set collected at −80 °C could not be used to resolve this problem. In fact, the X-ray diffraction characteristics changed as the crystal cooled. The width of the diffracted X-ray peaks *broadened* as the temperature of the crystal was lowered through the region −40 to −60 °C and narrowed again as the temperature was raised. Two explanations are plausible. First, the peak broadening could represent a host crystallographic phase change of the type reported for cyclohexane–thiourea inclusion adducts.[21] Alternatively, at low temperatures the 4-bromostyrene may occupy fixed, static disordered arrangements in a manner that superimposes new space group symmetry requirements on the system. We favor this latter explanation. So far, all attempts to resolve the residual electron density within the tunnels of the poly(4-bromostyrene) clathrate of I (produced by γ-irradiation) have been unsatisfactory.

X-ray Diffraction of the Styrene Adduct of I. A single-crystal X-ray study of the styrene adduct of I at 20 °C showed that the host molecules were organized in a hexagonal lattice (space group $P6_3/m$) in the manner shown in Figures 2 and 3. The planar styrene molecules were located from the residual electron density within the tunnels that penetrate the host lattice. The styrene molecules were positioned at right angles to the tunnel axis at positions $z = 0$ and $z = {}^1/_2$, with a separation of 5 Å between adjacent rings. No guest molecules were detected at positions $z = {}^1/_4$ and $z = {}^3/_4$, and this contrasts with the situation found for 4-bromostyrene. The phenyl carbon atoms of the styrene molecules were well resolved as were the α and β atoms in the same plane as the phenyl rings. However, electron density for these olefinic carbon atoms was located in a 6-fold disordered array around the peripheries of the phenyl rings. This would be compatible with either a static disordered arrangement or a 6-fold dynamic rotation of the styrene molecules around the z axis at 20 °C. The coplanarity of the phenyl and vinyl groups in each guest molecule is expected from electron-delocalization arguments. No evidence was seen for the existence of polystyrene within the tunnels. Apart from the planarity of the styrene molecules and the absence of guest molecules at positions $z = {}^1/_4$ and ${}^3/_4$, the crystal structure of the styrene adduct was very similar to that of the 4-bromostyrene clathrate. Hence, the details can be inferred from the description of the 4-bromostyrene system given in the previous section.

Tris(2,3-naphthalenedioxy)cyclotriphosphazene (II) as a Host. The 4-bromostyrene and styrene adducts of II were also examined. Tris(2,3-naphthalenedioxy)cyclotriphosphazene (II) has a tunnel diameter of 10 Å[22] (in contrast to 5.5 Å for I). Irradiation of trapped 4-bromostyrene in II at −78 °C yielded poly(4-bromostyrene). The ^{13}C NMR spectrum of this polymer was similar to that obtained for the irradiation product of the 4-bromostyrene adduct of I at +35 °C (comparable to the polymer formed in bulk by a free-radical process). It appears that the greater freedom of motion of 4-bromostyrene molecules in II at −78 °C is of the same type and magnitude as in I at +35 °C. In addition, irradiation of the styrene adduct of II at −78 °C resulted in the formation of polystyrene.



II

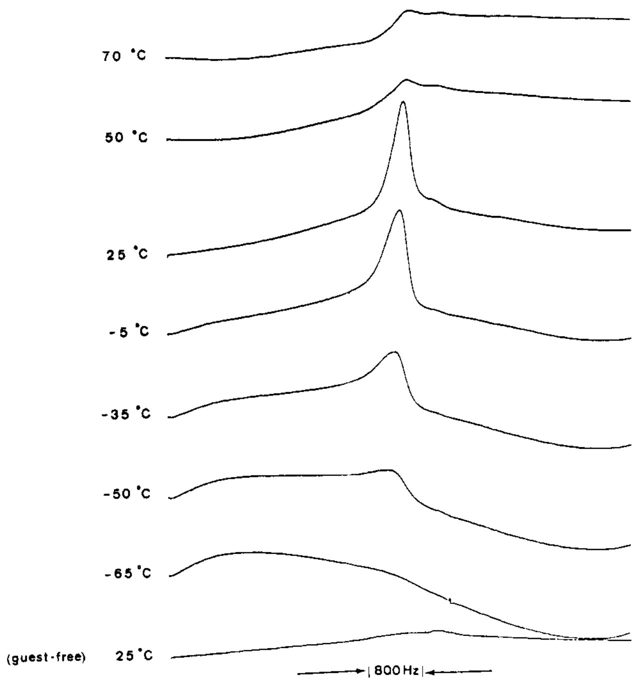


Figure 4. Series of broad-line ^{1}H NMR spectra obtained from the adduct of I with 4-bromostyrene at different temperatures. Increasing intensity of the signal indicated enhanced molecular motion of the 4-bromostyrene molecules.

Broad-Line ^{1}H NMR Studies for the 4-Bromostyrene Adduct of I. Variable-temperature broad-line ^{1}H NMR studies were carried out to determine if the monomer disorder within the tunnels of I was static or dynamic. Experimentally, care was taken to exclude water from the tunnels of I, since water molecules would be detected by the NMR technique. (This was accomplished by rigorous protection of the host and the clathrate from the atmosphere.)

The spectrum of the solid, guest-free I at 25 °C showed the usual very broad resonance that is typical of solid species. At −65 °C, the 4-bromostyrene adduct of I gave a similar spectrum. When the adduct was warmed to −50 °C, a second signal, 800-Hz wide, appeared and became more intense as the temperature was raised further (Figure 4). This relatively sharp peak is probably a consequence of dynamic rotational averaging of the 4-bromostyrene molecules. The line widths of this signal did not change as a function of temperature, which suggested that only one type of motion was associated with the guest molecules.[23] It is believed that free tumbling or translational motion of the guest molecules begins in the temperature range 40–50 °C.

Broad-line ^{1}H NMR was also used to show that the onset of molecular motion of the guest molecules for the styrene adduct of I and the 4-bromostyrene adduct of II begins at temperatures lower than that observed for the 4-bromostyrene adduct of I.

Conclusions

It seems clear that two independent conditions for polymerization exist in this system. These conditions can be deduced from comparisons of the behavior of 4-bromostyrene and styrene. The first condition requires that the functional group of the trapped monomer be oriented in a manner that favors interaction with neighboring guest molecules. This condition is met for the 4-bromostyrene adducts of I but is not met for the styrene adducts of I or the styrene and 4-bromostyrene adducts of II. The second condition requires that sufficient freedom of motion exists, i.e., tumbling, that intermolecular interactions between the guest molecules are possible. This condition is fulfilled for the styrene and 4-bromostyrene adducts of II and is not satisfied for the styrene adducts of I.

Short chain lengths found for poly(4-bromostyrene) can be attributed to the voids in each tunnel and to the fixed positions of the guest molecules at the polymerization temperature −78 °C. Improvements in the degree of polymerization result from the use of high temperatures which allow both rotational motion of each monomer and perhaps translation of monomer molecules along each tunnel. A higher monomer occupancy of each tunnel should have the same result. Investigations are under way to examine this possibility.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Ethyl Corp.) was purified by two sublimations [50 °C (0.5 mm)], followed by recrystallization from hexane. Catechol (Aldrich) and 2,3-dihydroxynaphthalene (Aldrich) were recrystallized from toluene. Anhydrous sodium carbonate (Fisher) was dried in a vacuum oven [80 °C (0.5 mm)]. Tetrahydrofuran (Fisher) was dried and distilled from sodium–benzophenone ketyl. Benzene (Baker, Photorex grade), xylene (Fisher), carbon tetrachloride (Fisher), chloroform-*d* (MSD Isotopes), 4-bromostyrene (Aldrich), divinylbenzene (Pfaltz and Bauer), isobutylene (Matheson), butadiene (Matheson), and acetylene (Matheson) were used as received. The purity of the 4-bromostyrene and divinylbenzene was confirmed by mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy. Styrene (Aldrich) and phenylacetylene (Aldrich) were purified by vacuum distillation.

Equipment. ^{13}C NMR spectra were obtained with a JEOL PFT100 Fourier transform NMR spectrometer operated at 25 MHz and linked to a Nicolet computer, a Varian CFT-20 Fourier transform NMR spectrometer operated at 20 MHz, or a Bruker 200-MHz Fourier transform NMR spectrometer operated at 50 MHz. The solvents used were $CDCl_3$ or C_6D_6 (polyisobutylene). Broad-line ^{1}H NMR spectra were obtained for solid samples in 5-mm NMR tubes with the Bruker spectrometer operated at 200 MHz. The sample temperature was varied over the range −65 to +70 °C. Positive ^{1}H and ^{13}C NMR chemical shift values were downfield relative to Me_4Si, with ^{13}C NMR chemical shifts internally referenced to $CDCl_3$, C_6D_6, or C_6D_{12}.

Gel permeation chromatography measurements were made with a Waters Associates ALC/GPC 501 instrument. Two separate sets of columns were used. One set of columns consisted of two columns packed with 100-Å μ-Styragel and one column with 500-Å μ-Styragel. The other set was made up of five columns, each individually packed with 10^6-, 10^5-, 10^4-, 10^3-, or 500-Å μ-Styragel. Tetrahydrofuran was employed as the solvent at a flow rate of 2.5 mL/min and a temperature of 25 °C. Both an ultraviolet detector and a refractive index detector were used. Approximate calibration of the columns was accomplished with polystyrene standards. Control experiments were used to ensure that neither I nor unpolymerized monomer was responsible for the observed peaks.

The infrared spectra of the polymers were obtained for films cast from either CCl_4 (polyisobutylene, poly(4-bromostyrene), or poly(4-vinylstyrene)), or $CDCl_3$ (polybutadiene) with the use of a Perkin-Elmer 580 spectrometer.

Synthesis of Tris(*o*-phenylenedioxy)cyclotriphosphazene (I). Compound I was synthesized by the method described previously. Specifically, catechol was allowed to react with hexachlorocyclotriphosphazene in the presence of sodium carbonate.[24] The compound was purified by recrystallization from hot xylene followed by triple sublimation at 175 °C (0.1 torr) to give a material with a melting point of 244 −245 °C.

Synthesis of Tris(2,3-naphthalenedioxy)cyclotriphosphazene (II). Compound II was prepared from hexachlorocyclotriphosphazene and 2,3-dihydroxynaphthalene by the method described previously.[25] The product was purified by recrystallization from hot xylene followed by sublimation at 300 °C (0.1 torr) to give a material with a melting point of 333–335 °C.

Collection and Reduction of X-ray Data. Crystals of the monomer adduct of I were grown by recrystallization techniques from 4-bromostyrene. The presence of the guest molecules was confirmed by the wide melting point range and by mass spectrometry. The crystals were hexagonal columns that were typically 0.2 mm × 0.2 mm × 0.7 mm. All crystals were mounted inside a capillary 0.3 mm wide to prevent loss of guest during data collection. A drop of liquid monomer was placed at one end of the capillary to maintain an atmosphere of 4-bromostyrene around the crystal during data collection. The capillary that contained the crystal was mounted on a goniometer head and was placed on an Enraf-Nonius CAD-4 diffractometer controlled by a PDP8/a computer. Twenty-five reflections were located and centered using the Enraf-Nonius program SEARCH with molybdenum X-radiation (λ(Mo Kα) = 0.7107 Å) from a graphite monochromator. Unit cell dimensions, as calculated from a least-squares refinement of the 2θ values for these 25 well-centered reflections for the 4-bromostyrene adduct, were a = 11.605 Å, b = 11.605 Å, and c = 10.112 Å; V = 1179.4 (5) Å^3, d_m = 1.537 g cm^{-3} (by flotation in aqueous potassium iodide solutions), Z = 2.38; a unit cell consists of 2.0 phosphazene molecules and 0.96 4-bromostyrene molecules. [The corresponding values for the styrene adduct were a = 11.680 Å, b = 11.680 Å, c = 10.093 Å; V = 1191.1 Å^3, d_m = 1.35 g cm^{-3} (by flotation in aqueous potassium iodide), Z = 2.10; a unit cell consists of 2.0 phosphazene molecules and 0.5 styrene molecules.] The linear absorption coefficient was calculated to be 21.07 cm^{-1} for molybdenum radiation. No absorption corrections were made.

Low-temperature X-ray diffraction data were collected with a Syntex Analytical Instruments LT-1 low-temperature unit that was modified to fit the CAD-4 diffractometer. The temperature in the cold nitrogen gas stream was monitored with a thermocouple at a distance of approximately 2.5 cm from the crystal. Monitored temperatures at the crystal were within ±5 °C of the temperature reported.

Intensity data were collected at 20 °C using a θ–2θ scan mode for all reflections for which $0.5° \leq 2\theta \leq 30°$. The observed systematic absences hkl, $l = 2n$, gave $P6_3/m$ as the space group.

Scan widths were determined with the formula SW = $A + B*\tan\theta$, where A was estimated from the mosaic character of the crystal and B accounts for the increase in width of the peak due to Kα_1 and Kα_2 splitting. The values determined for A and B were 0.50 and 0.35, respectively. A 25% increase in scan angle on each side of the reflection was employed for the measurement of background intensities. The net intensities, I, were calculated by using the formula I = CTS − 2(BGR + BGL), where CTS defines the total number of counts and BGR and BGL are the right and left background counts, respectively. Reflections for which the ratio $\theta(I)/I < 2$ were labeled weak and were automatically rejected by the computer. Three check reflections were measured every hour. No significant change in the intensities of these check reflections occurred throughout the entire collection process. All data were corrected for Lorentz and polarization effects. Of the total 739 reflections, 376 had an intensity greater than $1\sigma(I)$, 346 had an intensity greater than $2\sigma(I)$, and 323 had an intensity greater than $3\sigma(I)$. Only those reflections for which $I > 3\sigma(I)$ were used in the refinement.

Solution and Refinement in the Structure. The Enraf-Nonius structure determination package was employed, with the use of a PDP11/34 computer. The atomic scattering factors as tabulated by Cromer and Waber[26] were used for all atoms, and the anomalous dispersion factors $\Delta f'$ and $\Delta f''$ were those of Cromer.[27] The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma(F_o)^2$. The residuals R_1 and R_2 are expressed by $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

The structure of the host (I) was solved by using the atomic parameters from the previously solved molecular structure of the benzene adduct of I.[5] Three cycles of least-squares refinement resulted in the location of the entire host (I) within the unit cell. The phosphorus–nitrogen rings were found at $z = {}^1/_4$ and $z = {}^3/_4$ and were perpendicular to the z axis. The positions were of 3-fold symmetry. The weighted value was 14.44 and the unweighted R value was 25.00 at this point.

Table I
Effect of 4-Bromostyrene on the Refinement of the Adduct with I[a]

weighting scheme	ESD	R_1	R_2
unit weights without 4-bromostyrene	6.6187	14.44	25.00
unit weights with 4-bromostyrene	4.0451	12.81	16.76
$p = 0.02$	9.016	13.0	16.4
$p = 0.03$	7.299	12.8	16.4
$p = 0.04$	6.124	12.7	16.5
$p = 0.05$	5.292	12.6	16.7
$p = 0.06$	4.662	12.6	16.8
$p = 0.07$	4.172	12.6	17.0
$p = 0.035$ with 4-bromostyrene	6.5958	12.64	16.30
$p = 0.035$ without 4-bromostyrene	8.7988	14.64	21.99

[a] Both R_1 and R_2 are lower with the 4-bromostyrene than without.

Table II
Atomic Parameters for the 4-Bromostyrene Adduct of Tris(*o*-phenylenedioxy)cyclotriphosphazene (I)

atom	x	y	z
P	0.6408 (4)	0.4550 (4)	0.7500 (0)
N	0.517 (1)	0.306 (2)	0.7500 (0)
O	0.6196 (7)	0.5370 (7)	0.6332 (7)
C(1)	0.606 (1)	0.635 (1)	0.6844 (9)
C(2)	0.598 (1)	0.736 (1)	0.6060 (14)
C(3)	0.586 (2)	0.828 (1)	0.6825 (12)
H(2)	0.4102 (0)	0.2559 (0)	0.0000 (0)
H(3)	0.6152 (0)	0.4883 (0)	0.1211 (0)
C1S1	0.1200 (0)	0.0100 (0)	0.463 (5)
C1V1	−0.2621 (0)	−0.0525 (0)	−0.507 (0)
Br1	0.276 (4)	0.052 (4)	0.516 (4)
C2S2	0.8800 (0)	0.9800 (0)	0.750 (0)
C2V1	−0.3114 (0)	−0.1018 (0)	0.750 (0)
C-V2	0.2754 (0)	0.3398 (0)	0.630 (0)
Br2	0.300 (8)	0.093 (7)	0.750 (0)

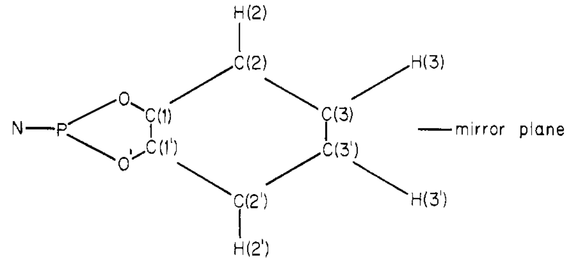
The structure of the guest within the host was solved by a series of difference Fourier syntheses. An initial difference Fourier, constructed with atoms of the host, revealed residual electron density at $z = 0$ and $z = {}^1/_2$ in the shape of two concentric rings in the x–y plane. These were included as a bromine and a carbon atom of the styrene plane. The ring was 6-fold disordered. Attempts at further refinement of bromostyrene x,y positions generated residual electron density at the center of each ring. This is a well-known observation when phenyl rings are present.[28]

The difference map at this stage revealed a second styryl ring system at $z = {}^1/_4$ and $z = {}^3/_4$. Inclusion of these positions and the first vinyl carbon atoms (which were set at negative respective bromine positions) yielded a difference map which indicated no density in the plane of the bromostyrene molecules that would account for the second vinyl carbon. Density was located midway between the two bromostyrene groups (again in 6-fold disorder), ostensibly at a C–C bonding distance.

The multiplicities of the bromostyrene positions were refined and indicated a ${}^2/_3$ to ${}^1/_3$ ratio in favor of the $(0, {}^1/_2 - z)$ location. Anisotropic refinement of the guest styrene temperature factors was deemed unfeasible because of the low concentrations, and temperatures were fixed at the largest anisotropic value [9.00 (0.34 Å) in comparison to 7 (0.30 Å) for the hydrogen atoms of the P–N ring system].

Tables I–III contain a summary of the refinement parameters with and without the guest, the atomic positional parameters, and bond angles and bond lengths. Table IV, a listing of observed and calculated structure factors, is available as supplementary material.

Table III
Bond Lengths (Å) and Bond Angles (Deg) for the 4-Bromostyrene Adduct of Tris(*o*-phenylenedioxy)cyclotriphosphazene (I)



P–N	1.59 (1)	C(2)–C(3)	1.38 (1)
P–O	1.61 (1)	C(3)–C(3′)	1.4 (1)
O–C(1)	1.33 (1)	C(2)–H(2)	1.1 (1)
C(1)–C(1′)	1.33 (1)	C(3)–H(3)	1.6 (1)
C(1)–C(2)	1.45 (1)		

P–N–P	119 (1)	C(1′)–C(1)–C(2)	123.1 (3)
N–P–N	121 (1)	C(1)–C(2)–C(3)	112.8 (5)
N–P–O	109 (1)	C(2)–C(3)–C(3′)	124.1 (4)
O–P–O′	94.3 (3)	C(1)–C(2)–H(2)	130.8 (6)
P–O–C(1)	109.8 (3)	C(3)–C(2)–H(2)	116.0 (6)
O–C(1)–C(1′)	112.9 (3)	C(2)–C(3)–H(3)	113.5 (6)
P–C(1)–C(2)	124.0 (4)	C(3′)–C(3)–H(3)	112.9 (2)

Tunnel Polymerization with ^{60}Co γ-Radiation. In a typical experiment, I (10 g) was placed in a thick-walled glass ampule (250 mL). 4-Bromostyrene (10 g) was added to I to form a slurry. The ampule was fitted to a vacuum line and two freeze–pump–thaw cycles were performed. The ampule was then sealed and irradiated with 2 Mrd (dose rate of 4×10^5 rd/h) of ^{60}Co γ-radiation at −78 °C. The irradiations were performed at the Breazeale Nuclear Reactor facility at The Pennsylvania State University.

After irradiation, the ampule was opened and the polymer adduct of I was washed in carbon tetrachloride (100 mL) for 48 h on a mechanical shaker to remove monomer and polymer adhering to the surface of the clathrate. The polymerized guest was then extracted from I by stirring the solid in refluxing benzene (300 mL) for 48 h. When cooled, the mixture was filtered to remove the solids, and the benzene was removed by means of a rotary evaporator to leave the polymer. The other monomers and polymers, excluding the polybutadiene adduct of I, were handled in a similar manner. In the case of butadiene, the host was base hydrolyzed with 3 equiv of KOH in a 20% aqueous dioxane solution (200 mL). The mixture was stirred at 25 °C for 48 h, after which the polymer was isolated by filtration.

Bulk Polymerization. Monomers in the solid state were sealed in glass ampules and irradiated in the manner described for monomer adducts of I.

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Supplementary Material Available: Table IV, a listing of observed and calculated structure factor amplitudes for the 4-bromostyrene adduct of I (4 pages). Ordering information is given on any current masthead page.

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Spontaneous 2:1 Sequence-Regulated Copolymerization of Cyclic Imino Ethers with Cyclic Carboxylic Anhydrides

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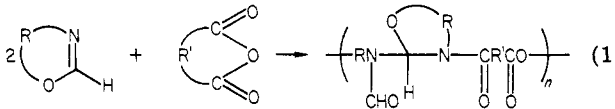
ABSTRACT: The present paper reports copolymerizations of two cyclic imino ethers, 2-oxazoline (OZO) and 5,6-dihydro-4*H*-1,3-oxazine (OZI), with two cyclic carboxylic anhydrides, succinic anhydride (SAn) and glutaric anhydride (GAn). The copolymerizations took place spontaneously around room temperature to 100 °C to produce 2:1 sequence-regulated copolymers (**1**). This result was explained by the concept of "no catalyst alternating copolymerization via zwitterion intermediate". Thus, OZO and OZI behaved as nucelophilic monomers (M_N) whereas SAn and GAn acted as electrophilic monomers (M_E). First, a 1:1 bicyclic adduct (such as **3**, **6**, and **7**) is formed by the reaction between M_N and M_E. Then the cyclic adduct behaved as M_E to react with another molecule of M_N, giving rise to a zwitterion like **5**, a key intermediate for the copolymerization, which has a 2:1 M_N/M_E composition. Subsequent reactions of these key intermediates led to the production of 2:1 sequence-regulated copolymers **1**.

In a series of studies on spontaneous copolymerization, cyclic imino ethers have served as reactive nucleophilic monomers (M_N) toward several electrophilic ones (M_E) such as β-propiolactone, acrylic acid, acrylamide, ethylenesulfonamide, and 3-hydroxy-1-propanesulfonic acid sultone.[1] This combination of M_N and M_E induced copolymerizations without added initiator to give in most cases 1:1 alternating copolymers via zwitterion intermediates. The present paper deals with spontaneous copolymerizations of two cyclic imino ethers (M_N), 2-oxazoline (OZO) and 5,6-dihydro-4*H*-1,3-oxazine (OZI), with two cyclic carboxylic anhydrides (M_E), succinic anhydride (SAn) and glutaric anhydride (GAn). These copolymerizations produced 2:1 sequence-regulated copolymers (**1**) in which one OZO or OZI unit is incorporated in a ring-opened form and the other unit is formed via reaction of the carbon–nitrogen double bond of OZO or OZI.



(1)

OZO, R = $-(\mathrm{CH_2})_2-$
OZI, R = $-(\mathrm{CH_2})_3-$
SAn, R′ = $-(\mathrm{CH_2})_2-$
GAn, R′ = $-(\mathrm{CH_2})_3-$
1a, R = R′ = $-(\mathrm{CH_2})_2-$
b, R = $-(\mathrm{CH_2})_2-$; R′ = $-(\mathrm{CH_2})_3-$
c, R = R′ = $-(\mathrm{CH_2})_3-$

Results and Discussion

Copolymerization of 2-Oxazoline (OZO) with Succinic Anhydride (SAn). The copolymerization of OZO with SAn took place around room temperature without added intiator to give a hygroscopic powdery material which was soluble in organic solvents such as chloroform, DMF, and acetonitrile and in water. The initial feed molar ratio of OZO/SAn was varied from 0.33 to 4.0. The copolymer structure, however, did not change and the OZO/SAn composition of the copolymers was 2:1 in all cases (no. 1–6 in Table I).

The copolymer structure was determined by ^{1}H NMR spectroscopy with the product copolymer itself and with the alkaline hydrolysis products of the copolymer, by IR spectroscopy, and by elemental analysis. Figure 1 (top) shows the ^{1}H NMR spectrum of the copolymer (sample no. 3) in D_2O. A large signal centered at δ 2.54 is assigned to $C(O)CH_2CH_2C(O)$ (4 H), signals in the region δ 3.1–4.4 are due to methylene protons of OCH_2 and NCH_2 (8 H), and sharp peaks at δ 6.26 and 8.25 are ascribed, respectively, to the characteristic methine proton of NCHN (1 H) and to the formyl proton of NCHO (1 H). The IR spectrum of the copolymer showed bands at 1735 and 1665 cm^{-1} due to $\nu_{C=O}$ of ester and of amide, respectively. These results strongly suggest structure **1a** for the copolymer.

The middle spectrum of Figure 1 is the ^{1}H NMR spectrum of the alkaline hydrolysis mixture of the copolymer in NaOH–D_2O. This spectrum was essentially the same as that of a mixture of authentic samples of ethanolamine, succinic acid, and formic acid in a ratio of 2:1:2 in NaOH–D_2O and indicates the production of these compounds in the same molar ratio. The hydrolysis experiment was further performed in D_2O without NaOH at 80 °C for 11 h. The ^{1}H NMR spectrum of the reaction system is shown in the bottom spectrum of Figure 1. Under these reaction conditions the cleavage took place selectively at the methine carbon moiety of the five-membered ring to produce a 1:1 mixture of formic acid and the amide–ester type product of succinic acid **2**. The signal assignments