7550 *Macromolecules* **1994,** *27,* 7550−7555

Inclusion Polymerization within a Tris(2,3-naphthylenedioxy)cyclotriphosphazene Clathrate

Harry R. Allcock,* Eric N. Silverberg, Gary K. Dudley, and Shawn R. Pucher

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received April 25, 1994; Revised Manuscript Received September 21, 1994[⊗]

ABSTRACT: The inclusion and ^{60}Co γ-ray initiated polymerization of olefinic and acrylic monomers within the 10 Å clathrate-tunnels formed by tris(2,3-naphthylenedioxy)cyclotriphosphazene is described. Methyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, isoprene, dimethylbutadiene, acrylonitrile, and methacrylonitrile monomers were included by direct contact imbibition. The resultant polymers were characterized by ^{1}H and ^{13}C NMR spectroscopy, and the molecular weights were estimated by gel permeation chromatography and solution viscometry. The results are explained in terms of the host/guest relationship and structure. Comparisons are made where appropriate to similar polymers synthesized previously within the 5 Å tunnel of tris(*o*-phenylenedioxy)cyclotriphosphazene.

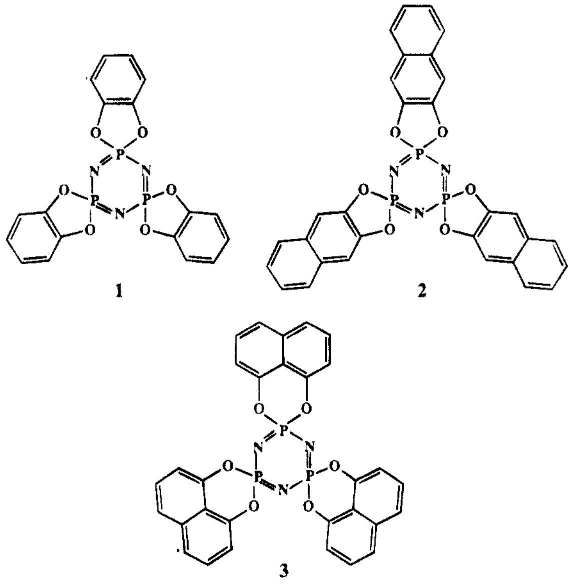
Introduction

The traditional methods used for the synthesis of polymers with well-defined structure and stereoregularity make use of Ziegler−Natta catalysts or other coordinating initiators, anionic, or group transfer polymerization methods.[1] The polymerization of unsaturated monomer guests within the cavities or tunnels of a host crystalline lattice, or clathrate, provides an important alternative to initiator-mediated polymerizations.[2] The earliest examples of polymerizations of this type were accomplished using urea and thiourea as hosts for the polymerization of 2,3-dimethylbutadiene.[3−5] Farina *et al.* further advanced the field of inclusion polymerization in a series of papers using the perhydrotriphenylene host system.[2,6,7] Several reviews on the subject are available.[8] The success of inclusion polymerization has led to a number of developments in the field. For example, solid state NMR has proved to be a valuable tool to study the motions of individual molecules and extended polymer chains trapped in the crystalline host.[9] In addition, the conformations and mobilities of these adducts have been modeled by computer-based techniques.[10]

Cyclophosphazenes form a broad class of inorganic heterocyclic systems with alternating phosphorus and nitrogen atoms in the ring. It was found by us in earlier work that certain trispirocyclotriphosphazenes form inclusion adducts with small molecule guests via a variety of routes.[11−14] For example, clathrates can be formed with tris(*o*-phenylenedioxy)cyclotriphosphazene, **1**, by recrystallization from or direct absorption of organic liquids or vapors. We have previously reported the inclusion of a series of unsaturated monomers within the tunnels of a clathrate system derived from tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**) and tris(2,3-naphthylenedioxy)cyclotriphosphazene (**2**) (Chart 1).[15−17] Finter and Wegner have also reported work in this area.[18]

In some cases, the macromolecules formed in this manner have been stereoregular. For example, butadiene polymerizes exclusively under γ-irradiation to give 1,4-trans polymers when included in host **1**, whereas the bulk polymerization of the monomer yields a polymer containing a mixture of 1,4-cis-, 1,4-trans-, and 1,2-addition. Polymerization takes place within the 5 Å diameter tunnels formed by **1** or 10 Å diameter tunnels of **2** under the influence of a quasiordered stacking of the guest molecules[19−21] (see Figure 1).

Chart 1



1

2

3

Clathrates derived from cyclophosphazenes are unusual in that the tunnel diameter can be varied by changes in the length of the side groups. The tunnel diameter of other clathrate systems can be somewhat flexible, but they do not offer the diversity or control over tunnel diameters that are available with cyclophosphazenes. For example, tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**) and tris(2,3-naphthylenedioxy)cyclotriphosphazene (**2**) have tunnel diameters of 5 and 10 Å, respectively. Tris(1,8-naphthylenedioxy)cyclotriphosphazene (**3**) has a cagelike structure, in which the free diameter of the channel varies from 5.2 to 7 Å. In this paper we describe the polymerization of methyl acrylate, butyl acrylate, hexyl acrylate, isoprene, dimethylbutadiene, acrylonitrile, and methacrylonitrile monomers within the 10 Å clathrate tunnels formed by **2**. In addition, octyl acrylate, a monomer that could not be incorporated into host **1**, was polymerized in this work. The effect of monomer shape and size was investigated

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.

0024-9297/94/2227-7550$04.50/0

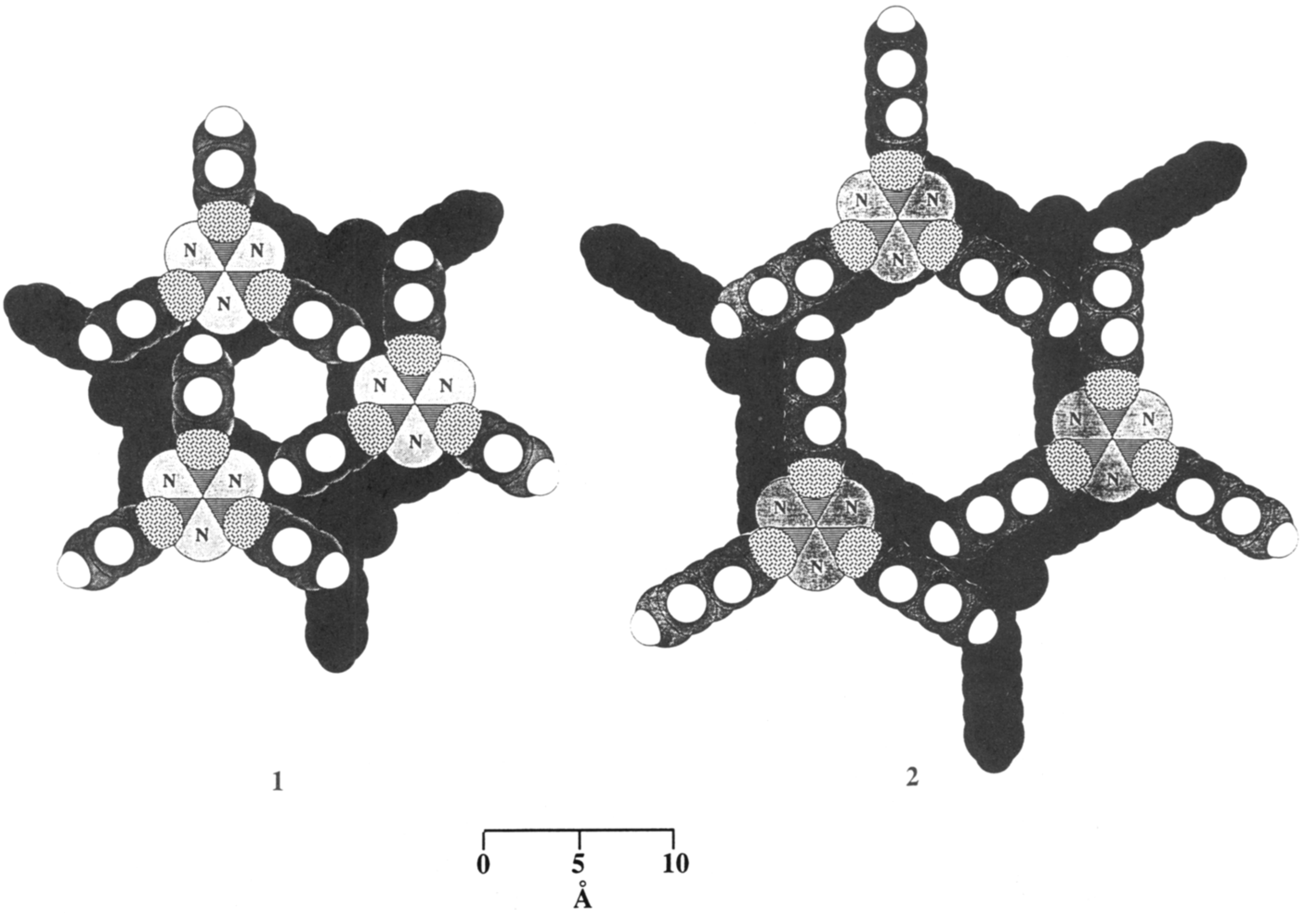
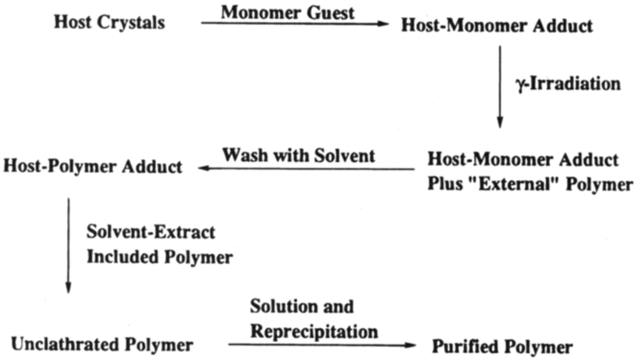


Figure 1. Space-filled idealized tunnel structure of tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**) and tris(2,3-naphthylenedioxy)cyclotriphosphazene (**2**).

Scheme 1



with respect to its influence on stereoregularity. Also, the degree of polymerization and the effect of the amount of monomer imbibed are discussed. In addition, comparisons are made to similar polymers synthesized with the use of host **1**. All the polymerizations discussed here make use of host system **2** as a solid-state template.

Adducts of tris(2,3-naphthylenedioxy)cyclotriphosphazenes were prepared by the addition of the liquid monomer directly to microcrystals of the pure host. Polymerization of the guests was induced by ^{60}Co γ-radiation.

Experimental Section

Clathrate Tunnel Polymerization. The experimental protocol followed in the present work is outlined in Scheme 1. In a typical experiment, tris(2,3-naphthylenedioxy)cyclotriphosphazene (**2**) was placed in a thick walled glass ampule under an inert atmosphere. The liquid monomer was added to **2** to form a slurry, and the mixture was stored for 12−24 h at room temperature. The slurry was then degassed (freeze−pump−thaw) three times and the excess monomer removed *in vacuo*. Each evacuated ampule was then sealed and irradiated with ^{60}Co γ-radiation at the specified temperature and dosage. All polymerizations involved the addition of sufficient monomer to saturate 5.0 g of compound **2**.

After irradiation, each ampule was opened and unreacted monomer was removed *in vacuo*. Any polymer that was formed on the outer surfaces of the crystals was removed by washing with an appropriate solvent. The included polymer was solvent-extracted from the host using a suitable solvent system and the solvent was then removed by rotary evaporation. The polymer was isolated by dissolution in a suitable solvent, followed by concentration and precipitation (see Table 1).

Reagents and Solvents. Hexachlorocyclotriphosphazene was obtained from a trimer−tetramer mixture (Ethyl Corp.) after two recrystallizations from heptane and a vacuum sublimation (60 °C, 0.1 Torr). Tetrahydrofuran (OmniSolve) was distilled from sodium benzophenone. Benzene (Aldrich) was used as received. 2,3-Dihydroxynaphthalene (Aldrich) was sublimed before use. Triethylamine (Baker) was distilled from CaH_2. Methyl acrylate, butyl acrylate, acrylonitrile, and methacrylonitrile (Aldrich) were dried and distilled to remove inhibitors. *n*-Octanol, *n*-hexanol, isoprene, dimethylbutadiene, and acryloyl chloride (Aldrich) were vacuum distilled before use. Hexyl acrylate and octyl acrylate were prepared from the corresponding alcohols and acryloyl chloride and purified by vacuum distillation.

Instruments. ^{31}P NMR spectra were recorded with the use of a Bruker WM-360 NMR spectrometer operating at 146 MHz. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 at 0 ppm with positive shift values downfield from the reference. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker WM-360

Table 1. Experimental Conditions for Clathrate-Mediated Polymerization and Isolation

monomer	polymerization temp (°C)	wash solvent[a]	extraction solvent[b]	dissolution solvent[c]	precipitation solvent	yield,[d] mg (%)
methyl acrylate	−78	MeOH	benzene	THF	hexane	375 (18)
butyl acrylate	−78	MeOH	benzene	THF	hexane	300 (53)
hexyl acrylate	−78	acetone	benzene	acetone	hexane	120 (36)
octyl acrylate	−78	chloroform	benzene	chloroform	hexane	100 (12)
dimethylbutadiene	25	THF	benzene	THF	hexane	100 (5)
isoprene	25	THF	benzene	THF	hexane	90 (16)
acrylonitrile	−78	DMSO	benzene	DMSO	hexane	110 (66)
methacrylonitrile	−78	acetone	benzene	CH_2Cl_2	hexane	100 (47)

[a] 200 mL, ambient temperature. [b] 48 h at reflux. [c] Minimum amount of solvent required to dissolve polymer. [d] Yields are based on the gravimetric determination of the host to guest molar ratio. Also, the assumption is made that the extraction of the clathrate mediated polymer is quantitative.

spectrometer operating at 360 and 90.5 MHz respectively. Chemical shifts are relative to tetramethylsilane at $\delta = 0$. Electron impact mass spectra were obtained with the use of a KRATOS MS9/50 spectrometer. Gel permeation chromatography data were obtained with the use of a Hewlett-Packard 1090 liquid chromatograph fitted with a refractive index detector. Polymer Laboratories PL gel columns were calibrated with narrow molecular weight polystyrene standards. The samples were eluted with a 0.1% by weight solution of $n\text{-}Bu_4N^+Br^-$ in THF.

Tris(2,3-naphthylenedioxy)cyclotriphosphazene (2). Compound **2** was synthesized by a modification of a previously described method.[22] A mixture of 2,3-dihydroxynaphthalene (3.0 equiv) and triethylamine (6.0 equiv) in tetrahydrofuran was added dropwise to a tetrahydrofuran solution of hexachlorocyclotriphosphazene. The mixture was stirred for 48 h at 40 °C. Crude **2** was filtered and washed with cold THF, dilute HCl, and distilled water. The product was vacuum dried to constant weight. ^{31}P NMR (benzene): δ 33.2 ppm (s). EI MS: *m/z* calcd 609, *m/z* found 609.

^{60}Co γ-Irradiations. Samples were degassed (freeze−pump−thaw method) and sealed under vacuum. The samples were placed in the ^{60}Co source (dose rate 1.6×10^5 rad/h or 8.0×10^4 rad/h) and irradiated for the specified time and temperature. The irradiations were carried out at the Breazeale Nuclear Reactor facility at the Pennsylvania State University.

Viscosity Data. Intrinsic viscosity measurements were obtained with use of a Cannon-Ubbelohde viscometer at 30 °C. Four different concentrations were used for each polymer, with three efflux times recorded at each concentration. A DMSO solution was used as the medium for poly(acrylonitrile), and a solution of acetone was used for poly(methacrylonitrile).

Bulk Polymerization. The monomers listed above were also vacuum sealed in thick walled glass ampules and were irradiated at temperatures and doses that corresponded to the clathrate-mediated polymerizations. Following irradiation, unreacted monomer was removed *in vacuo*, and the polymer was isolated by precipitation into the appropriate solvent.[23]

Results and Discussion

The monomers used in this study are shown in Chart 2.

Methyl Acrylate. Irradiation (2 Mrad γ-radiation) of the methyl acrylate adduct of **2** at −78 °C yielded poly(methyl acrylate) that was *soluble* in THF. The overall tacticity of the clathrate-mediated polymer proved to be heterotactic, and the relative stereochemistry was determined from the ^{13}C NMR spectrum. The spectrum consisted of resonances centered at 175.3 (CO), 51.8 (OCH_3), 41.9 (CH), and 35.5 (CH_2) ppm. The methylene resonances were resolved to the tetrad level, and the tacticity of the polymer was determined from the peak areas in the ^{13}C NMR spectrum.[24] The upfield methylene resonances (35.3 ppm) were more intense than the weaker downfield (36.6 ppm) portion of the spectrum. This suggests the presence of isotactic regions. The ratio of areas of isotactic to syndiotactic regions was found to be ca. 1.4:1.0. The corresponding ratio of the bulk polymer was ca. 1.2:1.0. This suggests that the clathrate host has some effect on the stereochemistry but only to a small extent. The results are significantly different from those obtained with the tris(*o*-phenylenedioxy)cyclotriphosphazene clathrate in which the polymer obtained after clathrate polymerization possessed an enhanced isotactic stereochemistry.[16] Gel permeation chromatography experiments indicated a GPC average molecular weight of 1.0×10^6 (1.4×10^4 repeat units). The average molecular weight found here is 3.4 times higher than poly(methyl acrylate) synthesized previously in the tunnels of **1**.[16] The higher molecular weight may be a result of the greater volume available for clathration in the tunnels of **2** versus **1** (see later). The guest to host mole ratio of methyl acrylate with **1** and **2** was determined by gravimetric analysis. The respective values of 0.45:1.0 and 1.04:1.0 clearly show the larger amount of monomer imbibed in the wider 10 Å tunnels.

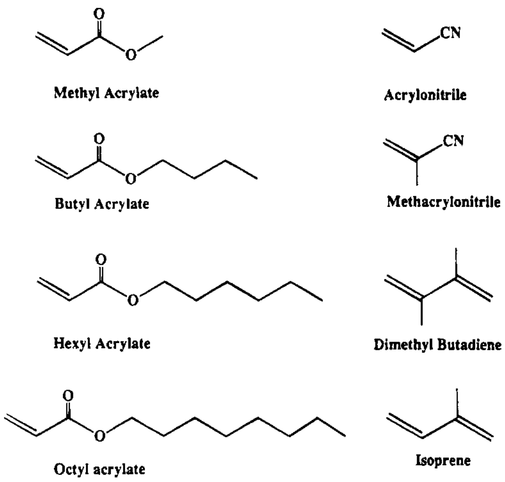
The radiation polymerization of methyl acrylate in the bulk state yielded mostly an insoluble, crosslinked matrix. However, a very small amount of soluble polymer was isolated. The GPC average molecular weight of this was estimated to be 6.1×10^5 (7.1×10^3 repeat units).

Butyl Acrylate. 2 Mrad irradiation of the butyl acrylate adduct of **2** at −78 °C yielded THF *soluble* poly(butyl acrylate). Initial ^{13}C NMR data confirmed the polymeric structure. The ^{13}C NMR spectrum consisted of resonances centered at 174.5 (CO), 64.4 (OCH_2), 41.4 (CH), and 35.3 (CH_2) ppm as well as resonances that corresponded to the alkyl chain. It is known that bulky alkyl acrylates produce syndiotactically enhanced polymers when polymerized by radical processes at low temperature.[25] The enhanced syndiotactic stereochemistry was revealed from the methylene and the methine resonances, with the tacticity being similar to that found in other acrylic esters. This is in contrast to the polymer prepared within host **1** which had more isotactic character. Again, this may be due to the greater volume available for the included monomer, which creates an environment more like that of the bulk liquid. The molecular weight was estimated by GPC to be 1.1×10^6 (9.8×10^3 repeat units). This value is almost 3 orders of magnitude higher than that of the corresponding polymer synthesized within the tunnels of **1**.[17a] This difference can be attributed to the larger tunnel diameter of **2** and the greater volume available for the monomers to occupy and interact (see later).

The radiation polymerization of butyl acrylate in the bulk state yielded an insoluble, crosslinked matrix.

Hexyl Acrylate. Polymerization of hexyl acrylate within the crystal lattice of **2**, using 2 Mrad of gamma

Chart 2



rays at −78 °C, yielded THF *soluble* poly(hexyl acrylate). The ^{13}C NMR spectrum of the polymer was very similar to that of the poly(methyl acrylate) and poly(butyl acrylate) clathrate-mediated polymers. An enhanced syndiotactic stereochemistry was detected from the methylene (35.4 ppm) and the methine (41.3 ppm) resonances, with the tacticity being virtually identical to that found for the butyl acrylate derivative. Gel permeation chromatography experiments suggested a GPC average molecular weight of 1.0×10^6 (7.1×10^3 repeat units). This value is almost 3 orders of magnitude higher than that of the corresponding polymer synthesized within the tunnels of **1**.[17a]

The polymerization of hexyl acrylate in the bulk state yielded an unsoluble, crosslinked matrix.

Octyl Acrylate. Polymerization of an octyl acrylate adduct of **2**, using a 2 Mrad radiation dose at −78 °C, yielded THF *soluble* poly(octyl acrylate). The ^{13}C NMR spectrum of the polymer was very similar to that of the poly(butyl acrylate) and poly(hexyl acrylate) clathrate-mediated polymers revealing the syndiotactic nature of the polymer. Previous attempts to include and polymerize this monomer within the tunnels of **1** were unsuccessful. The fact that octyl acrylate can be polymerized within the wider cyclophosphazene tunnels is an indication of the versatility of the system. The molecular weight was estimated by GPC to be 5.1×10^5 (3.0×10^3 repeat units).

The polymerization of octyl acrylate in the bulk yielded an insoluble crosslinked matrix.

Acrylonitrile. Polymerization of acrylonitrile (−78 °C) within the tunnels of the phosphazene clathrate **2** by γ-irradiation yielded atactic poly(acrylonitrile). The tacticity of the polymer was identified from the ^{13}C NMR resonances of the methine and cyano carbons of the polymer.[26] The methine carbon consisted of three peaks located at 27.9, 27.4, and 26.8 ppm, with the most intense of these peaks being at 27.4 ppm. This is indicative of a polymer that is predominately heterotactic in character. The cyano carbon showed three resonances that were located at 120.3, 120.0, and 119.7 ppm, with the 120.0 ppm peak being the most intense. The intensity of the 120.0 ppm peak is also indicative of an atactic polymer being formed in the clathrate. Using Bernoullian statistics, the P_m for the clathrate formed poly(acrylonitrile) was calculated to be $P_m = 0.59$, while the bulk polymer gave a $P_m = 0.64$. Comparison shows the polymers to be almost identical stereochemically and possessing a predominately heterotactic structure. The results are significantly different from those obtained with the tris(*o*-phenylenedioxy)cyclotriphosphazene clathrate in which the polymer obtained after polymerization possessed an enhanced isotactic stereochemistry.[16] The molecular weight was estimated by solution viscometry to be approximately 3.0×10^4 (560 repeat units). The bulk polymerizations was found previously to give an atactic polymer with a viscosity average molecular weight of 1.7×10^5 (3200 repeat units).[16] Figure 2 shows the similarities in the ^{13}C NMR spectra of the clathrate-mediated polymer and the polymer prepared in the bulk state. This is further evidence of the greater volume available in trimer **2** versus **1**.

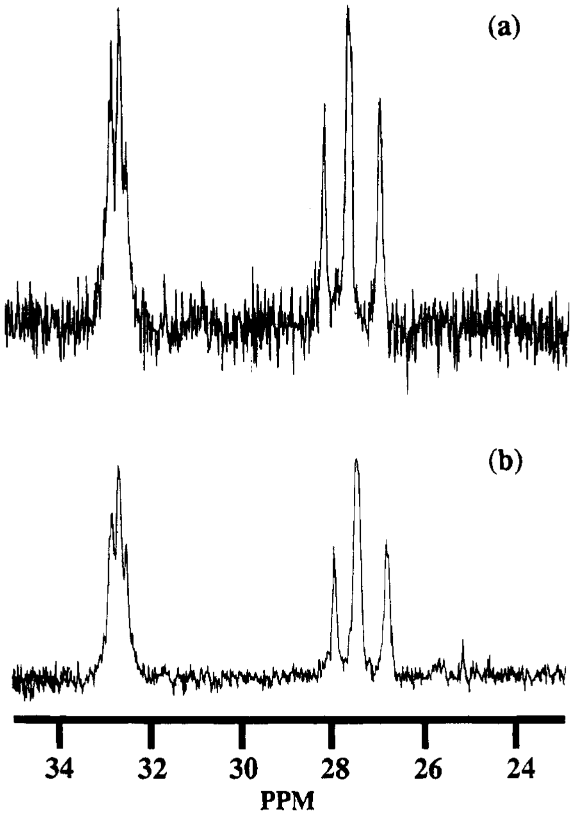


Figure 2. Expanded ^{13}C NMR spectra of poly(acrylonitrile) (a) synthesized from host **2** and (b) synthesized in the bulk.

Methacrylonitrile. Polymerization of methacrylonitrile (−78 °C) within the crystal lattice of host **2** yielded poly(methacrylonitrile). On the basis of ^{13}C NMR spectroscopy and relative peak intensities, the polymer possessed an enhanced isotactic–heterotactic structure.[27–29] The resonance pattern observed here was similar to that of poly(methacrylonitrile) synthesized in the bulk state. Bernoullian statistics for the clathrate formed polymer gave a calculated value of $P_m = 0.59$, while the bulk polymer was calculated to be $P_m = 0.57$. On the basis of Bernoullian statistics, the clathrate and bulk polymer possess a heterotactic structure and are similar to each other stereochemically. This similarity may again reflect the wide tunnel diameter of the clathrate **2**, which provides an environment of monomer molecules closer to that found in the bulk phase. The molecular weight of the clathrate-mediated polymer was estimated by viscometry to be 1.3×10^4 (190 repeat units).

Isoprene. The inclusion polymerization of isoprene in **2** (4 Mrad, 25 °C) yielded a polymer containing both 1,4-trans and 1,4-cis addition segments. The 1,4-trans and 1,4-cis configurations were assigned based on the ^{13}C NMR spectrum of the isolated polymer. The resonances for 1,4-trans addition consisted of seven peaks at 134.92 (C), 124.19 (CH), 39.77 and 38.52 (CH_2), 28.29 and 26.71 (CH_2), and 16.03 (CH_3) ppm. The two methylene carbon atoms yielded two peaks each at (39.77 and 38.52) and (28.29 and 26.71) ppm, which suggests their presence in different stereochemical environments.[30] The 1,4-cis addition assignment was based on the appearance of a resonance at 22.90 (CH_3) ppm, which is indicative of a 1,4-cis addition structure. The absence of any 3,4-addition was indicated by the absence of a peak at 42.1 ppm.[31]

Because the monomer occupancy level in the clathrate appeared to affect the stereochemistry and molecular weight of the polymers, an attempt was also made to determine if the degassing of the monomer/clathrate mixture had any effect on the structure of the polyisoprene synthesized within the clathrate. Two samples were prepared under identical conditions: one was subjected to the normal freeze–pump–thaw method to degass the ampule, and the second ampule was sealed without degassing. The two samples were then exposed to γ radiation (4 Mrad at 25 °C). Isolation and analysis of the polymers by ^{13}C NMR spectroscopy showed that the degassed samples and nondegassed samples possessed stereochemistries that were identical to each other as indicated by their chemical shifts discussed above. However, the molecular weights of the two polymers were affected by the procedure. The degassed monomer/clathrate mixture showed a 10-fold lower molecular weight (700 Da) compared to the nondegassed sample (8.4×10^3 Da).

The γ-ray induced polymerization of isoprene monomer in the bulk state yielded a polymer that contained both 1,4-cis and 1,4-trans addition sequences.

Dimethylbutadiene. γ-Ray induced polymerization of 2,3-dimethylbutadiene within the tunnels of **2** (4 Mrad at 25 °C) yielded a polymer that contained a mixture of both 1,4-cis and 1,4-trans addition segments. Again, the polymer microstructure was established by ^{13}C NMR spectroscopy. Three resonances centered at 18.16 (CH_3), 33.30 (CH_2), and 128.33 (C) ppm indicated the presence of 1,4-trans addition species, while resonances located at 18.60 ppm (CH_3) and 33.54 ppm (CH_2) were indicative of 1,4-cis addition to the polymer. The absence of any resonances in the unsaturated region of the ^{13}C NMR spectrum indicated the lack of any 1,2-addition for either the bulk or clathrated polymer.

The effect on polymer stereochemistry and molecular weight according to whether the monomer/clathrate mixture was degassed or not was also examined for the dimethylbutadiene monomer/clathrate mixture. The same experimental models were used as for the isoprene monomer, and with similar results. The ^{13}C NMR spectra of the two samples showed that the degassed and nondegassed systems yielded polymers with the same stereochemistries as indicated above. Thus, the monomer occupancy level had no effect on the stereochemistry of the polymers. However, the molecular weights were affected by degassing. The degassed samples showed a lower molecular weight (5.7×10^3 Da, 70 repeat units), than the nondegassed sample (estimated molecular weight of 1.0×10^4 Da, 122 repeat units).

The bulk polymerization of 2,3-dimethylbutadiene at 25 °C yielded a polymer that contained a mixture of both 1,4-cis and 1,4-trans addition sequences.

Thus, it was concluded that for isoprene or dimethylbutadiene clathrates, the degassing (freeze–pump–thaw) step of the monomer/clathrate mixture system is detrimental to achieving the highest molecular weights in this host system. Apart from the influence of monomer occupancy in the tunnels, it is also possible that the low temperatures maintained (77 K) during the repeated freeze–pump–thaw degassings may fracture the clathrates to give crystals of a smaller size, which would generate shorter tunnels and thus lower molecular weight polymers.

Comparison between Hosts 1 and 2. As mentioned earlier, the tunnel diameters in other clathrate systems can vary, but they do not offer the control over tunnel diameter found in cyclotriphosphazenes. Tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**) and tris(*o*-naphthylenedioxy)cyclotriphosphazene (**2**) have tunnel diameters of 5 and 10 Å, respectively. The differences in channel volume are illustrated by a crystal structure analysis of a benzene clathrate adduct formed from the two hosts. Fourier transform electron density maps indicated six "spheres" of tumbling benzene molecules per unit cell in host **2** whereas host **1** contained only one benzene molecule statistically occupying the volume within each unit cell.[12] The wide tunnel system affects two aspects of inclusion polymerization of monomers–molecular weight and stereochemistry.

As discussed, the polymers synthesized in the wider tunnels generally had higher molecular weights than those formed in host **1**. This is attributed to the larger tunnel volume available to the monomers in **2** verses **1** and the resultant larger numbers of monomer molecules per tunnel. Indirect support for this opinion comes from the guest to host mole ratio of methyl acrylate with **1** and **2**, as determined by gravimetric anaylsis. Respective values of 0.45:1.0 and 1.04:1.0 illustrate the larger amount of monomer imbibed in the wider 10 Å tunnels. Thus, an enhanced probability exists that monomer molecules will react with each other and this, in turn, means that the probability of forming higher molecular weight polymers is greater in host **2** than in **1**.[32]

The stereochemistry found for the polymers synthesized in the tunnels of **2** are more closely related to those of polymers prepared in the bulk phase. Again, this can be attributed to the larger tunnel dimensions. The large-volume tunnels allow an environment that more closely resembles that found in the bulk state, whereas in the host system **1** the monomer molecules are more constrained and are arranged in a more orderly manner. Finally, an added advantage of the larger tunnel dimensions and versatility of phosphazene clathrates is the successful inclusion and polymerization of octyl acrylate within the tunnels of the host **2**. This monomer was incapable of fitting into the tunnels of **1** due to its large size.

The propensity of vinyl monomers to yield crosslinked polymer matrix materials when irradiated in the bulk state depends on the number of aliphatic C–H bonds present in the system. These bonds are especially sensitive to homolytic cleavage and carbon radical cross-combination, and a synthesis procedure that reduces these side reactions is highly preferred. Thus, the entrappment of these monomers and polymers within the tunnel system of **2** provides an environment that reduces the opportunity for crosslinking. The encircling environment of *aromatic* C-H bonds, which are far less sensitive to gamma-radiation induced cleavage, serves as a stabilizing environment for the polymers. Hence, crosslinking of the included polymers is greatly reduced. Thus, from several points of view, the clathrate-mediated polymerization in host **2** provides additional opportunities for macromolecular structure control over and above those that exist for host **1**.

Acknowledgment. This work was supported by the National Science Foundation Polymers Program through grant no. DMR 9017366. We thank R. Sipos for help with the ^{60}Co γ-irradiations and C. Morrissey for assistance with Figure 1.

References and Notes

(1) (a) Amass, A. J. In *Comprehensive Polymer Science*; Eastman, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, 1989; Vol. 4, Part II, p 1. (b) Szwarc, M. Living Polymers and Mechanisms of Anionic Polymerization. *Advances in Polymer Science Series*; Springer-Verlag: New York, 1983. (c) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.

(2) Farina, M. In *Inclusion Compounds*; Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 3, p 297.

(3) Clasen, H. *Z. Elektrochem.* **1956**, *60*, 982.

(4) Brown, J. F.; White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5671.

(5) White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5678.

(6) Farina, M.; Natta, G.; Allegra, G.; Löffelholz, M. *J. Polym. Sci.* **1967**, *C16*, 2517.

(7) Farina, M.; Audisio, G.; Natta, G. *J. Am. Chem. Soc.* **1967**, *89*, 5071.

(8) (a) Farina, M.; Di Silvestro, G. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; J. Wiley and Sons: New York, 1988; Vol. 12, p 486. (b) Di Silvestro, G.; Sozzani, P. In *Comprehensive Polymer Science*; Eastman, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergaman Press: Oxford, 1989; Vol. 4, Chapter 18, p 303.

(9) (a) Sozzani, P.; Bovey, F. A.; Schilling, F. C. *Macromolecules* **1989**, *22*, 4225. (b) Sozzani, P.; Bovey, F. A.; Schilling, F. C. *Macromolecules* **1991**, *24*, 6764. (c) Schilling, F. C.; Sozzani, P.; Bovey, F. A. *Macromolecules* **1991**, *24*, 4369.

(10) (a) Tonelli, A. E. *Macromolecules* **1990**, *23*, 3129. (b) Tonelli, A. E. *Macromolecules* **1990**, *23*, 3134. (c) Tonelli, A. E. *Macromolecules* **1991**, *24*, 1275. (d) Tonelli, A. E. *Macromolecules* **1991**, *24*, 3069.

(11) Allcock, H. R. *Acc. Chem. Res.* **1978**, *11*, 81.

(12) Allcock, H. R.; Teeter-Stein, M. *J. Am. Chem. Soc.* **1974**, *96*, 49.

(13) Allcock, H. R.; Teeter-Stein, M.; Bissell, E. C. *J. Am. Chem. Soc.* **1974**, *96*, 4795.

(14) Allcock, H. R. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, p 351.

(15) Allcock, H. R.; Ferrar, W. T.; Levin, M. L. *Macromolecules* **1982**, *15*, 697.

(16) Allcock, H. R.; Levin, M. L. *Macromolecules* **1985**, *18*, 1324.

(17) (a) Allcock, H. R.; Silverberg, E.; Dudley, G. *Macromolecules* **1994**, *27*, 1033. (b) Allcock, H. R.; Dudley, G.; Silverberg, E. *Macromolecules* **1994**, *27*, 1039.

(18) Finter, J.; Wegner, G. *Makromol. Chem.* **1979**, *180*, 1093.

(19) Allcock, H. R.; Allen, R. W.; Bissell, E. C.; Smeltz, L. A.; Teeter, M. *J. Am. Chem. Soc.* **1976**, *98*, 5120.

(20) Siegel, L. A.; van den Hende, J. H. *J. Chem. Soc. A* **1967**, 817.

(21) Allcock, H. R.; Levin, M. L.; Whittle, R. R. *Inorg. Chem.* **1986**, *25*, 41.

(22) Allcock, H. R., Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1016.

(23) We recognize that on subsequent warming of the samples post-polymerization is possible; however, no attempts were made to avoid these effects in the bulk or clathrate-mediated systems.

(24) Matsuzaki, K.; Kanai, T.; Kawamura, T.; Matsumoto, S.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 961.

(25) Uryu, T.; Shiroki, H.; Okada, M.; Hosonuma, K.; Matsuzaki, K. *J. Polym. Sci.*; *A-1* **1971**, *9*, 2335.

(26) Inoue, Y.; Nishioka, A. *Polymer J.* **1972**, *3*, 149.

(27) Inoue, Y.; Koyama, K.; Chûjô, R.; Nishioka, A. *Makromol. Chem.* **1974**, *175*, 277.

(28) Inoue, Y.; Koyama, K.; Chûjô, R.; Nishioka, A. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 55.

(29) Báca, J. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 609.

(30) Sozzani, P.; Silvestro, G. D.; Grassi, M.; Farina, M. *Macromolecules* **1984**, *17*, 2532.

(31) Gronski, W.; Murayama, N.; Cantow, H. *Polymer* **1976**, *17*, 358.

(32) It could be argued that the tunnel length and volume beyond a critical minimum size do not control the molecular weight of the polymer and that the tunnel diameter is important only in the sense that it permits a higher degree of chain mobility that, in turn, leads to more rapid chain termination. This would be true if more than one polymer chain exists per tunnel. However, the 10 Å channel in the present system is too narrow for this to occur except with very small monomers.