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Stereocontrolled Polymerization within a Cyclophosphazene Clathrate Tunnel System

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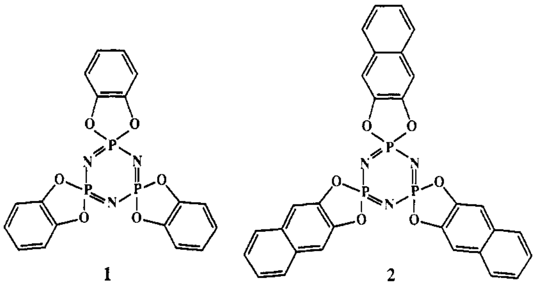
ABSTRACT: The inclusion and ^{60}Co γ-ray-initiated polymerization of vinylic and acrylic monomers within the clathrate tunnels formed by tris(*o*-phenylenedioxy)cyclotriphosphazene is described. Methacrylonitrile, methacrylic acid, ethyl acrylate, butyl acrylate, hexyl acrylate, allyl methacrylate, vinyl acetate, and vinylanisole monomers were included by direct contact imbibition. Varying degrees of stereoregularity were obtained from the inclusion polymerization of the monomers listed above. For example, poly(methacrylonitrile) synthesized within the host adduct showed an enhanced isotactic microstructure. Another aspect of clathrate-mediated polymerization is that no radiation cross-linked material was obtained for polymers derived from the acrylates and methacrylonitrile, in contrast to the corresponding radiation-induced bulk polymerizations. The copolymer poly(vinyl acetate-*co*-methyl acrylate) was also prepared using the inclusion polymerization method.

Introduction

The design and synthesis of polymers with precisely defined microstructure and stereocharacter are of great interest to polymer chemists. The current mainstream approach to these polymers is the use of Ziegler–Natta catalysts or other coordinating initiators, anionic, or group transfer polymerization methods.[1] We are exploring an alternative approach in which unsaturated monomers are included and polymerized within the cavities or tunnels of a host crystalline lattice. Clathrates are defined as crystalline lattice inclusion systems in which guest molecules occupy cavities, channels, or tunnels in the host lattice.[2] The polymerization of unsaturated monomer guests in clathrates provides an important alternative to initiator-mediated polymerizations.[3] The first examples of polymerizations of this type were accomplished using urea and thiourea as hosts for the polymerization of 2,3-dimethylbutadiene.[4-6] Further progress was accomplished with the use of the host system perhydrotriphenylene.[3,7,8] 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 motional behavior of individual extended polymer chains trapped in the crystalline host.[9] In addition, the conformations and mobilities of these polymer adducts have been computer modeled.[10]

Cyclophosphazenes form a broad class of inorganic heterocyclic systems with alternating phosphorus and nitrogen atoms in the ring. These rings are especially stable to high-energy radiation. 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. Furthermore, adducts can be formed when 1 is brought in contact with the vapor of organic compounds. The inclusion of a series of unsaturated monomers within the tunnels of a clathrate system derived from tris(*o*-phenylenedioxy)cyclotriphosphazene (1) and tris(*o*-naphthylenedioxy)cyclotriphosphazene (2) has been reported previously.[15-17] In some cases, the macromolecules formed in this manner have been stereoregular. For example, butadiene polymerizes exclusively under γ-radiation to give trans-1,4 polymers when included in host 1, whereas the bulk monomer yields a mixture of cis-, trans-, and 1,2-addition polymers. Polymerization takes place within the 5-Å-diameter tunnels formed by 1 under the influence of a quasi-ordered stacking of the guest molecules[18-20] (see Figure 1).

Chart 1



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In this paper we describe the polymerization or copolymerization of methacrylonitrile, methacrylic acid, ethyl acrylate, butyl acrylate, hexyl acrylate, allyl methacrylate, vinyl acetate, and vinylanisole monomers within the clathrate tunnels formed by 1. The effect of monomer shape and size was investigated with respect to its influence on stereoregularity. Also the degree of polymerization, temperature of polymerization, and the influence of the amount of monomer imbibed are discussed. All the polymerizations discussed here make use of host system 1 as a solid-state template.

Adducts of tris(*o*-phenylenedioxy)cyclotriphosphazene 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, sublimed tris(*o*-phenylenedioxy)cyclotriphosphazene (1) was placed in a thick-walled glass ampule under an inert atmosphere. The liquid monomer was added to 1 to form a slurry, and the mixture was stored for 12–24 h. The slurry was then degassed (freeze–pump–thaw) 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.

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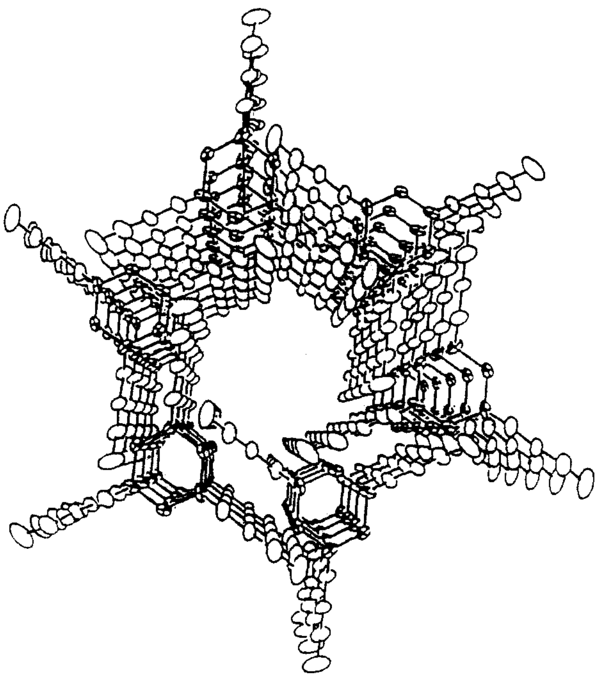
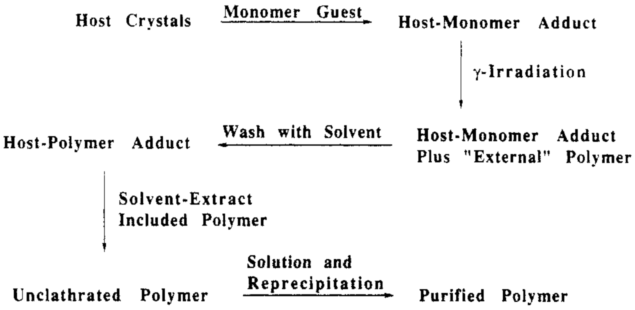


Figure 1. View of the hexagonal crystal lattice of tris(*o*-phenylenedioxy)cyclotriphosphazene (1).

Scheme 1



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. Finally, the included polymer was solvent extracted from the host using a suitable solvent system. The extraction solvent was removed by rotary evaporation, and the polymer was isolated by dissolution in a suitable solvent, 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). Catechol (Aldrich) was sublimed before use. Triethylamine (Baker) was distilled from CaH_2. Methacrylonitrile, methacrylic acid, ethyl acrylate, butyl acrylate, vinyl acetate, vinylanisole, and allyl methacrylate monomers (Aldrich) were dried and distilled free of inhibitors. 1-Octanol, 1-hexanol, 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. ^1H and ^{13}C NMR spectra were recorded with a Bruker WM-360 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. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Gel permeation chromatography data were obtained with the use of a Hewlett-Packard 1090 liquid chromatograph 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-$Bu_4N^+Br^-$ in THF.

Tris(*o*-phenylenedioxy)cyclotriphosphazene (1). Compound 1 was synthesized by a modification of a previously described method.[21] Hexachlorocyclotriphosphazene was allowed to react with catechol in the presence of triethylamine in tetrahydrofuran. Crude 1 was purified by washing with distilled water followed by vacuum sublimation (180 °C, 0.05 mmHg). ^{31}P NMR (benzene) δ 33.2 (s). EI MS m/z calcd 459, m/z found 459. Anal. Calcd: C, 47.06; H, 2.61; N, 9.15. Found: C, 46.92; H, 2.58; N, 9.18.

^{60}Co γ-Irradiations. Samples were degassed (freeze–pump–thaw method) and sealed under vacuum. The samples were placed in an aluminum-jacketed Dewar flask and were irradiated with 2 Mrad (dose rate 8.8×10^4 rad/h) of ^{60}Co γ-radiation at −78 °C. Vinylanisole was irradiated with 4 Mrad. The irradiations were carried out at the Breazeale Nuclear Reactor facility at The Pennsylvania State University.

Viscosity Data. Intrinsic viscosity measurements were obtained with the use of a Cannon Ubbelohde viscometer at 32 °C. Four different concentrations were used for each polymer, with at least three efflux times recorded at each concentration. A 2 M NaOH(aq) solution was used as the medium for poly(sodium methacrylate) to avoid extensive hydrogen bonding and the resultant viscosity anomalies.

Copolymerizations. A 50/50 (v/v) mixture of the two monomers was prepared and added to freshly sublimed 1 to form a slurry. After 12–24 h, the slurry was degassed (freeze–pump–thaw) and any monomer external to the host crystals was removed *in vacuo*. The adduct was sealed *in vacuo* in a thick-walled glass ampule and was irradiated at −78 °C. Following irradiation, unreacted monomer was removed *in vacuo*. The copolymer was extracted from the adduct with refluxing benzene followed by a precipitation from THF into hexane.

Bulk Polymerizations. The monomers listed above were vacuum sealed in thick-walled glass ampules and were irradiated at temperatures and doses that corresponded to the clathrate-mediated polymerizations. For the copolymerizations, 50/50 (v/v) mixtures of the monomers were prepared. Following irradiation, unreacted monomer was removed *in vacuo*, and the polymer was isolated by precipitation into the appropriate solvent. The bulk polymerization of crystalline monomers has been investigated previously.[22,23]

Results and Discussion

The monomers used in this study were chosen to investigate the effects of α-carbon substituents and

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

monomer	polymn temp (°C)	wash solvent[a]	extraction solvent[b]	dissolution solvent[c]	precipitation solvent	yield[f] (%)
methacrylonitrile	−78	CH_2Cl_2	*o*-xylene	CH_2Cl_2	hexane	81
methacrylic acid	−78	H_2O	*o*-xylene/H_2O	*d*	acetone	25
ethyl acrylate	−78, 25	MeOH	benzene	THF	hexane	16
butyl acrylate	−78	MeOH	benzene	THF	hexane	71
hexyl acrylate	−78	acetone	benzene	acetone	hexane	12
allyl methacrylate	−78	chloroform	benzene	chloroform	hexane	14
vinyl acetate	−78	MeOH	benzene	MeOH	hexane	46
vinylanisole	25	toluene	*o*-xylene	MEK[e]	hexane	32

[a] 200 mL, ambient temperature. [b] 48 h at reflux. [c] Minimum amount of solvent required to dissolve polymer. [d] Clathrate-mediated polymer was dissolved in water layer during extraction. [e] Methyl ethyl ketone. [f] 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.

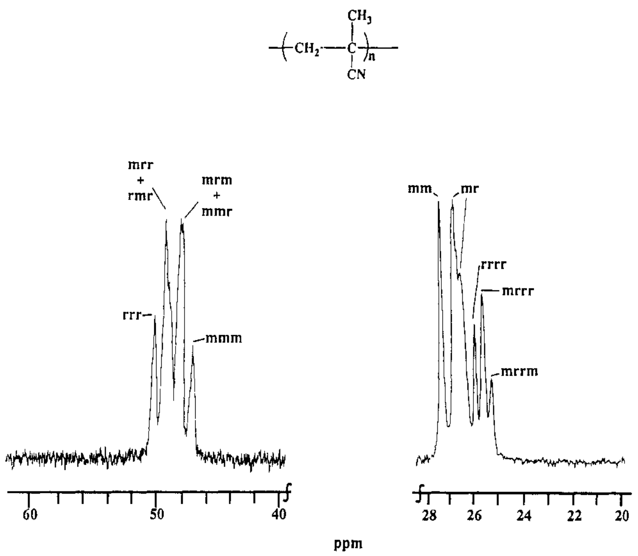
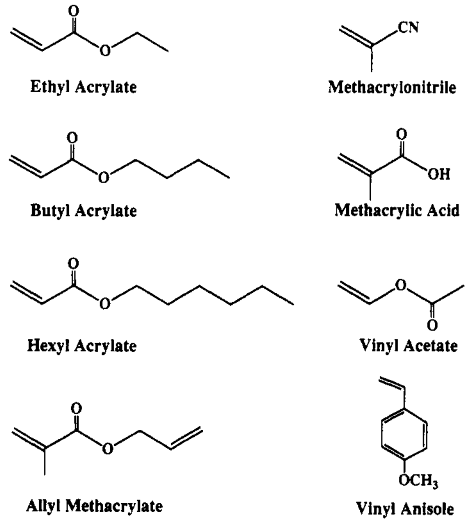


Figure 2. ^{13}C NMR spectrum of poly(methacrylonitrile). Expanded methylene and α-methyl region. Assignments are based on Bernoullian statistics of the peak intensities and cited literature.

Chart 2



different acrylic ester units on the clathrate polymerization behavior. Additionally, a styrene derivative was chosen to further explore the effects of a substituent in the para position. It was found previously that a para substituent was necessary for inclusion polymerization to occur[15] (see Chart 2).

Methacrylonitrile. Polymerization of the methacrylonitrile adduct of 1 yielded THF-*soluble* poly(methacrylonitrile). ^{13}C NMR spectroscopy resonances were centered at 123.8 (CN), 49.5 (CH_2), 33.3 (C), and 25.8 (CH_3) ppm. The stereoregularity of poly(methacrylonitrile) was clearly reflected in the ^{13}C NMR spectrum, particularly in the α-CH_3 resonance.[24-26] This region was analyzed for conformity to Bernoullian statistics using triad peak intensity data (^{1}H NMR) and was found to fit quite well (i.e., $P_{m/r} + P_{r/m} = 1$).[27] The downfield isotactic resonance was sensitive at the triad level, whereas the heterotactic and syndiotactic portions were resolved into pentad lines. The α-CH_3 portion of the spectrum (26.4 ppm) showed the most downfield resonance with the greatest intensity (see Figure 2). This indicates enhanced isotacticity (mm). The resonances of the methylene carbon (49.5 ppm) showed four distinct areas, probably resulting from overlap of the six possible tetrad peaks. The upfield portions (47.4 ppm) lend support to the isotactic nature of the polymer.

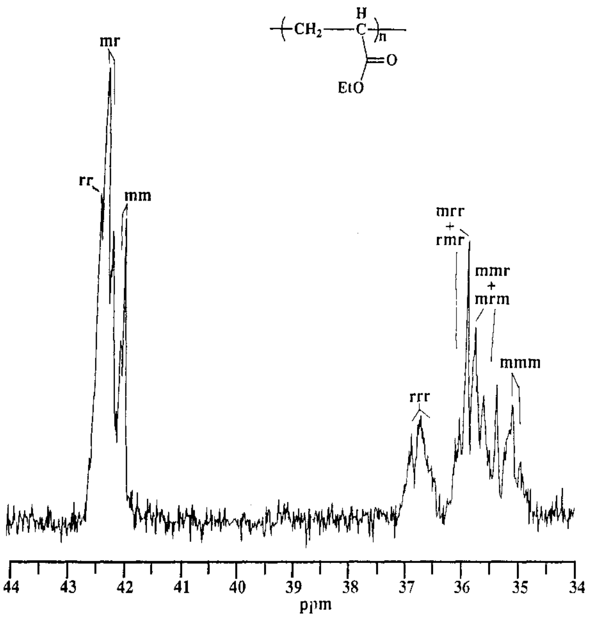


Figure 3. ^{13}C NMR spectrum of poly(ethyl acrylate). Expanded methylene and methine regions. Assignments are based on Bernoullian statistics of the peak intensities and cited literature.

The number-average molecular weight was estimated by GPC to be 7.0 × 10^3 (1.0 × 10^2 monomer repeat units).

Irradiation of methacrylonitrile in the bulk phase under identical conditions yielded an insoluble, cross-linked matrix.

Methacrylic Acid. Polymerization of methacrylic acid within the crystal lattice of 1 at −78 °C yielded syndiotactic poly(methacrylic acid). This is a similar result to that obtained from earlier work with acrylic acid.[16] The ^{13}C NMR spectrum of the poly(methacrylic acid) consisted of resonances centered at 187.6 (CO), 54.8(CH_2), 46.1(C), and 17.6 (CH_3) ppm. The distribution of peaks is consistent with a syndiotactic polymer structure.[28,29] For example, three distinct quaternary carbon resonances (46.97, 45.94, and 45.23 ppm) were detected, the most upfield having the strongest intensity. In addition, the α-CH_3 region of the spectrum revealed the most downfield resonance (17.3 ppm) to be the most intense. This suggests a syndiotactic microstructure. Solution viscosity measurements carried out with the sodium salt of internal poly(methacrylic acid) gave an intrinsic viscosity of 3.12 dL/g.

Polymerization of methacrylic acid in the bulk also yielded syndiotactic poly(methacrylic acid). The ^{13}C NMR spectroscopy resonances were nearly identical to those found in the clathrate-mediated polymer. The stereoregular structure found in bulk-polymerized methacrylic acid is probably influenced by strong hydrogen bonding matrix effects between the monomer molecules.[30] The sodium salt derivative of the bulk-synthesized polymer was found to have an intrinsic viscosity of 3.09 dL/g.

No significant difference in molecular weight could be detected between the bulk and clathrate-mediated polymers. This suggests that a high degree of hydrogen bonding exists within the clathrate tunnels.

Ethyl Acrylate. Irradiation of the ethyl acrylate adduct of 1 at −78 °C yielded THF-*soluble* poly(ethyl acrylate). The overall tacticity of the clathrate-mediated polymer proved to be heterotactic, with the isotactic and syndiotactic portions clearly resolved in the ^{13}C NMR spectrum. Using triad intensity data, Bernoullian statistics were found to apply. The spectrum consisted of resonances centered at 174.5 (CO), 60.4 (OCH_2), 41.4 (CH), 35.0 (CH_2), and 14.0 (CH_3) ppm (see Figure 3). Inspection of the spectrum revealed that the methylene resonances were resolved to the hexad level. In addition, eight of the ten possible pentad lines for the methine carbon were discernible. The tacticity of the polymer was determined from these two areas of the ^{13}C NMR spectrum.[31,32] The upfield methylene resonances (35.3 ppm) were more intense than the comparatively weaker downfield (36.6 ppm) portion of the spectrum. This suggests the presence of isotactic regions. Gel permeation chromatography experiments indicated a GPC-average molecular weight of 1.5×10^5 (1.5×10^3 repeat units). The average molecular weight found here is nearly the same as for poly(methyl acrylate) synthesized earlier by the clathration technique.[16] This similarity suggests that the one carbon atom difference between the two monomers has little or no effect on the degree of polymerization. This prompted us to examine the effect of bulkier monomers on the molecular weight of the resultant polymers (see later). Although the monomer size difference did not affect molecular weights, it did result in different microstructures. Poly(methyl acrylate)[16] synthesized in the earlier work via the clathrate tunnel technique was an isotactic-rich polymer. The polymer synthesized here is heterotactic.

Poly(ethyl acrylate) synthesized by irradiation of the adduct at the higher temperature of 25 °C also yielded a heterotactic polymer. However, the ^{13}C NMR spectrum revealed a larger amount of atactic regions when compared to the poly(ethyl acrylate) synthesized at −78 °C. This result probably reflects an increase in translational motion of the monomer within the tunnels. Translational motion of molecules within the clathrate formed by 1 has been investigated previously by variable-temperature NMR.[18]

The γ-ray-induced polymerization of ethyl acrylate in the bulk state yielded an insoluble, cross-linked matrix material. Thus, no solution-state NMR or GPC comparisons could be obtained.

Butyl Acrylate. Irradiation of the butyl acrylate adduct of 1 at −78 °C yielded THF-*soluble* poly(butyl acrylate). The ^{13}C NMR spectrum consisted of resonances centered at 174.5 (CO), 60.2 (OCH_2), 41.7 (CH), and 32.2 (CH_2) ppm as well as resonances that corresponded to the alkyl chain. The stereochemistry was revealed from the methylene and the methine resonances, with the tacticity being similar to that found previously for the ethyl ester. The molecular weight was estimated to be 2.1×10^3 (16 repeat units). The low molecular weight found here is probably related to the monomer size (see later). The possibility of a molecular weight dependence on tunnel length was investigated previously.[20] It was found that the average microcrystallite size was between 10^4 and 10^5 Å, dimensions that should not limit the degree of polymerization.

The radiation polymerization of butyl acrylate in the bulk yielded an insoluble, cross-linked matrix.

Hexyl Acrylate. Polymerization of hexyl acrylate within the crystal lattice of 1 at −78 °C yielded THF-*soluble* oligo(hexyl acrylate). The ^{13}C NMR spectrum of the oligomer was very similar to that of the poly(ethyl acrylate) and poly(butyl acrylate) clathrate-mediated polymers. The stereochemistry was determined from the methylene (35.2 ppm) and the methine (42.1 ppm) resonances, with the tacticity being virtually identical to that found for the ethyl and butyl derivatives. The molecular weight was estimated to be only 9.1×10^2 (6 repeat units). End group analysis was attempted to get a clearer picture of the termination step, i.e., combination, disproportionation, or hydrogen abstraction. The NMR data confirm a linear structure, but no head-to-head units were discernible although this is possible.

The polymerization of hexyl acrylate in the bulk yielded an insoluble, cross-linked matrix.

Allyl Methacrylate. The clathrate-mediated polymerization of allyl methacrylate in host 1 at −78 °C yielded syndiotactic poly(allyl methacrylate). The ^{13}C NMR spectrum consisted of resonances centered at 177.2, 176.88, 176.16 (CO), 131.6, 118.7 (allyl), 65.5 (OCH_2), 53.94, 51.9 (CH_2), 45.1, 44.8 (C), and 22.45, 18.67, 16.9 (α-CH_3) ppm. The syndiotactic nature of the polymer was revealed from the α-CH_3 portion of the spectrum.[33] The three shifts from downfield to upfield represent the isotactic, heterotactic, and syndiotactic microstructures, respectively. The ratio of syndiotactic to isotactic (rr/mm) regions was found to be over 20 to 1. The molecular weight was estimated to be 2.1×10^4 (1.6×10^2 repeat units).

Poly(allyl methacrylate) synthesized in the bulk was also syndiotactic. The spectrum was nearly identical to that of the clathrate-synthesized polymer, with the exception that a larger proportion of atactic regions was present in the bulk polymer. These results are consistent with the well-known fact that radical polymerization of methacrylates at low temperatures favors syndiotactic polymers and that the stereoregularity is dependent on the polymerization temperature.[34] The molecular weight was estimated to be 2.2×10^4 (1.7×10^2 repeat units).

Vinyl Acetate. Polymerization of vinyl acetate at −78 °C within the tunnels of 1 yielded poly(vinyl acetate) with an enhanced syndiotactic structure. The ^{13}C NMR spectrum consisted of resonances centered at 170.3 (CO), 67.2 (CH), 39.1 (CH_2), and 20.8 (CH_3) ppm. The syndiotactic composition of the polymer was revealed in the fine splitting found in the methine region of the spectrum.[35,36] The peak (67.2 ppm) was roughly split into three subpeaks, with the syndiotactic portion being furthest upfield. The number-average molecular weight was estimated by GPC to be 2.0×10^4 (2.3×10^2 repeat units).

Polymerization of vinyl acetate in the bulk yielded atactic poly(vinyl acetate). A set of ^{13}C NMR resonances similar to the data obtained for the clathrate-mediated polymer was detected. However, the distribution of resonances was consistent with an atactic structure. The number-average molecular weight as estimated by GPC was 3.7×10^4 (4.3×10^2 repeat units).

Vinylanisole. Irradiation of the vinylanisole adduct of 1 at 25 °C yielded poly(vinylanisole). The number-average molecular weight as estimated by GPC was 5.6×10^3 (42 repeat units). The ^{13}C NMR spectrum displayed resonances consistent with those expected for a derivative of polystyrene. The microstructure of the polymer was determined by examining the ipso (C1) aromatic carbon (138.2 ppm) and methine (40.5 ppm) resonances.[37] The C1 resonance was split into three main peaks (138.0, 138.4, and 138.8 ppm) with fine splitting in each. The upfield shift is indicative of a syndiotactic structure, while the downfield portion is derived from isotactic sequences. The ratio of syndiotactic to isotactic (rrr/mmm) was ca. 1.7/1.

Polymerization of vinylanisole in the bulk yielded a white, fibrous polymer. The ^{13}C NMR spectrum consisted of resonances similar to those found for the clathrate-mediated polymer. However, the syndiotactic to isotactic ratio had changed to 1.2/1. The lower ratio for the bulk polymer indicates a more random microstructure than for the inclusion-polymerized polymer. This difference can be attributed to host lattice effects on the monomer during the polymerization. The number-average molecular weight as estimated by GPC was 1.3×10^4 (97 repeat units).

Previously, single-crystal X-ray structures of host 1 with styrene-based monomers revealed that the monomer packing arrangement is critical for inclusion polymerization to occur.[15] For example, when styrene is subjected to inclusion irradiation, no polymerization occurs. However, 4-bromostyrene does polymerize. From these results it is inferred that the *p*-methoxy unit of the vinylanisole imparts a packing arrangement similar to that of 4-bromostyrene, thus allowing clathrate-mediated polymerization to occur.

Poly(vinyl acetate-*co*-methyl acrylate). A 50/50 (v/v) homogeneous mixture of vinyl acetate/methyl acrylate (49.4/50.6 molar ratio) was added to host 1 to form an adduct. Gas chromatography of the adduct revealed a preferential inclusion of vinyl acetate over methyl acrylate, giving an adduct molar ratio of ca. 70/30. Following radiation polymerization, ^1H NMR integration of the copolymer methyl groups indicated a final copolymer ratio closer to 76/24, $[(VAc)_{0.76}(MA)_{0.24}]_n$. The ^{13}C NMR spectrum consisted of resonances similar to those found for the respective homopolymers. The molecular weight as estimated by GPC was 6.3×10^4.

Effect of Monomer Shape and Size. As mentioned earlier, the effective tunnel diameter of 1 is ca. 5 Å. It was speculated that the packing behavior of monomers above a critical size would affect the stereoregularity and degree of polymerization.

Earlier work in our program revealed that, for acrylic acid and acrylonitrile, the molecular weights of the bulk-prepared and the clathrate-mediated polymers were similar. However, for the bulkier monomer, methyl methacrylate, the molecular weight of polymer produced in the bulk state was higher than that of the polymer formed in the clathrate.[16] Thus, it now appears that the degree of polymerization not only depends on the polymerization conditions but also depends on the host lattice/monomer size relationship. It was found previously that the dimensions of an organic guest species influences the ratio of host to guest when the adducts were prepared by spontaneous inclusion.[38] The longest molecular dimensions of ethyl acrylate, butyl acrylate, hexyl acrylate, and octyl acrylate are ca. 6.0, 8.5, 11.1, and 13.6 Å, respectively, when in an extended, linear form. Octyl acrylate proved to be too large to fit in the tunnels. Thus, this monomer was not considered further for polymerization studies.

Inclusion adducts were prepared with the remaining three acrylates by direct contact imbibition followed by careful vacuum drying. The molar ratio of guest to host was then determined by gravimetric analysis. Ratios of 0.39, 0.34, and 0.29 were calculated for ethyl acrylate, butyl acrylate, and hexyl acrylate, respectively. These data suggest that the smallest monomer was included to the largest extent within the tunnels of host 1. It seems possible that the larger monomers have difficulty filling all the available sites in each tunnel. The resultant voids in the tunnels cause a lower degree of polymerization than when the tunnels are fully occupied. The GPC data presented for the series of acrylates reinforce this view.

The propensity of vinyl monomers to yield cross-linked matrix materials when irradiated in the bulk state depends on the number of aliphatic C–H bonds in the polymer. These bonds are especially sensitive to homolytic cleavage and carbon radical cross-combination. Entrapment of the polymers within the tunnel system of 1 provides an encircling environment around each polymer chain. Hence, the cross-linking mechanism is inhibited.

In summary, the formation of stereoregular polymer sequences is due, in part, to the geometry of the monomer in relation to the tunnel. The precise geometry is not known at present, but it is clear that an ordered arrangement of monomers in the channel must exist. The overall size of a series of monomers was shown to be an important factor that controls the degree of polymerization. Large monomers may give rise to imperfectly filled tunnels, a concept that was supported by gravimetric and molecular weight data. Clathrate-mediated polymerization provides a useful method for the preparation of polymers with a defined structure and stereoregularity and for the synthesis of polymers that are difficult or impossible to prepare by standard solution-state or bulk polymerization.

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