(19) H. Kh. Mahabadi and G. Meyerhoff, *Eur. Polym. J.*, 15, 607 (1978).
(20) H. Kh. Mahabadi and K. F. O'Driscoll, *J. Polym. Sci., Chem. Ed.*, 15, 283 (1977).
(21) H. Kh. Mahabadi, "Effect of Chain Length Dependence of k_t on the Rate of Free Radical Polymerization", presented at the 22nd Canadian High Polymer Forum, Waterloo, Aug 1983.
(22) H. Kh. Mahabadi, to be submitted for publication.

Stereocontrolled Polymerization of Acrylic Monomers within a Tris(*o*-phenylenedioxy)cyclotriphosphazene Tunnel Clathrate

Harry R. Allcock* and Michael L. Levin

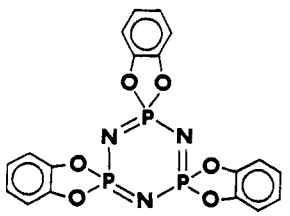
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received June 14, 1984*

ABSTRACT: The ^{60}Co γ-ray-initiated polymerization of acrylic monomers (acrylic acid, acrylic anhydride, acrylonitrile, methyl acrylate, methyl methacrylate, methyl vinyl ketone) within the tunnel-clathrate system formed by tris(*o*-phenylenedioxy)cyclotriphosphazene (I) provides a general route to the synthesis of enhanced stereoregular polymers. A feature of the clathrate-mediated polymerization is that no radiation cross-linking of multifunctional monomers occurs, in contrast to some of the bulk polymerizations. For example, the clathrate polymerization of acrylic anhydride yielded a new linear polymer, whereas the analogous bulk polymerization gave a cross-linked matrix. The molecular weights of the clathrate-synthesized polymers were similar to those of polymers prepared in the bulk phase. Copolymers were also prepared within host I, and these were found to have a random sequence distribution, in contrast to copolymers prepared in the bulk phase.

Introduction

The synthesis of polymers with precisely controlled structures is one of the main challenges confronting modern chemists. Ziegler–Natta, other coordination systems, anionic, or group-transfer methods are appropriate for the controlled synthesis of a few polymers, but a wide variety of unsaturated monomers have not yet been converted to polymers that have a precisely defined structure and stereo character. Acrylic and other polar monomers are often the most difficult to polymerize in a stereospecific manner.[1-9]. Di- or multifunctional unsaturated monomers present special problems because of the possibilities for cross-linking.

Our objective was to develop a method by which acrylic monomers could be polymerized in a stereoregular fashion. We have previously reported the inclusion of a variety of molecules within the tunnels of a clathrate system derived from tris(*o*-phenylenedioxy)cyclotriphosphazene (I).[10-17]

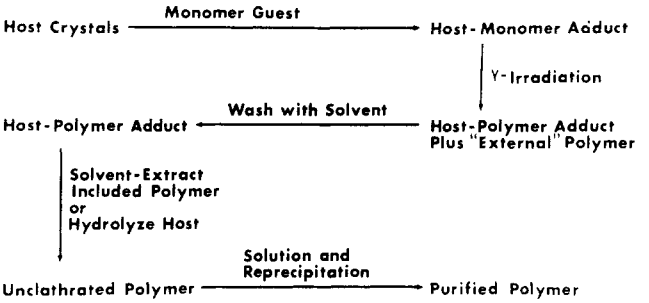


I

In this system the guest molecules are packed in 5 Å diameter tunnels that penetrate the host crystal structure (Figure 1). The constraints of the tunnel shape and dimensions allow a regular stacking of some guest molecules within the tunnels in a manner appropriate for ^{60}Co γ-radiation-induced polymerization.[16,18]

Spirocyclotriphosphazene clathrates have a distinct advantage over other inclusion systems in the sense that the tunnel diameter can be varied by alterations in the size of the spiro side groups.[10] This permits an unusually wide range of guest molecules to be incorporated into the clathrate. Other host systems, such as urea or thiourea, are much less versatile and are appropriate for the clathrate polymerization of fewer guests.[19] Perhydrotriphenylene clathrates a variety of acrylic monomers, but the tendency for stereoregular polymerization is low.[20]

Scheme I



In this paper we describe the stereospecific polymerization of acrylic acid, acrylic anhydride, acrylonitrile, methyl acrylate, methyl methacrylate, and methyl vinyl ketone, as well as some copolymerizations using combinations of those monomers. All these reactions make use of host system I as a solid-state template.

Experimental Section

Overall Experimental Approach. The methodology followed in the present work is summarized in Scheme I. First, the monomer molecules were absorbed by direct imbibition of the liquid guest into the crystal framework of the pure host. After saturation of the host tunnel system, excess monomer was removed in vacuo. Polymerization of the clathrated guest molecules was then induced by ^{60}Co γ-irradiation. Low temperatures were used when possible in order to favor stereoregular propagation. After irradiation, unreacted monomer was removed in vacuo, and any polymer present on the outer crystal surfaces was removed by washing. Finally, the included polymer was solvent extracted from the host in a one- or two-phase solvent system, or the host molecules were decomposed by hydrolysis. The resultant polymers were characterized by ^{13}C NMR spectroscopy. Elemental microanalysis data were also obtained for the copolymers. Molecular weights were estimated by solution viscometry. The exact yields for the clathrate-mediated polymerizations were difficult to estimate because the degree of occupancy of monomer within the host framework was variable from experiment to experiment. However, yields of 20–50% were typical.

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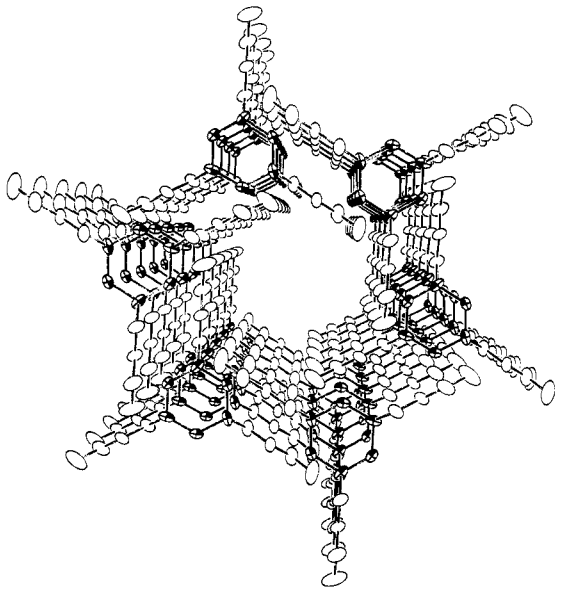


Figure 1. Representation of a perspective view down one of the tunnels that penetrate the hexagonal crystalline lattice of tris(*o*-phenylenedioxy)cyclotriphosphazene (I). The 5 Å diameter tunnels accommodate the organic monomer molecules. Note that some of the side-group atoms are omitted because of limitations in the number of atoms that can be accommodated by the program ORTEP 2.

Materials. Hexachlorocyclotriphosphazene (kindly provided by the Firestone Tire and Rubber Co.) was purified by two sublimations (50 °C (0.5 mmHg)), followed by recrystallization from hexane. Catechol (Aldrich) was recrystallized from toluene. Anhydrous sodium carbonate (Fisher) was dried in a vacuum oven (100 °C (0.5 mmHg)) before use. Tetrahydrofuran (Curtin Matheson) was dried and distilled from sodium benzophenone ketyl. Benzene (Fisher) was dried over and distilled from calcium hydride. Chloroform (Fisher), dimethyl sulfoxide (Aldrich), hexane (Fisher), toluene (Fisher), xylene (Fisher), and aqueous sodium hydroxide (VWR) were used as received. The monomers, acrylic acid (Aldrich), acrylic anhydride (ICN), acrylonitrile (Aldrich), methyl acrylate (Pfaltz and Bauer), methyl methacrylate (Aldrich), and methyl vinyl ketone (Pfaltz and Bauer), were dried over 3-Å molecular sieves, vacuum distilled, and degassed by three freeze–pump–thaw cycles.

Synthesis of Tris(*o*-phenylenedioxy)cyclotriphosphazene (I). Compound I was synthesized by the method described previously.[21] Specifically, catechol was allowed to react with hexachlorocyclotriphosphazene in the presence of sodium carbonate in boiling tetrahydrofuran. Sublimation (175 °C (0.1 mmHg)) of the crude product yielded I with a melting point of 244–245 °C.[22]

^{60}Co γ-Irradiations. Samples sealed under vacuum were placed in an aluminum-jacketed Dewar flask and were irradiated with 2 Mrd (dose rate of 2.7×10^5 rd/h) of ^{60}Co γ-radiation at −78 (2-propanol/CO_2), −45 (acetonitrile/N_2), or −29 (nitromethane/N_2) °C. The irradiations were carried out at the Breazeale Nuclear Reactor facility at the Pennsylvania State University.

^{13}C NMR Data. ^{13}C NMR spectra were obtained with a JEOL PFT-100 Fourier transform NMR spectrometer operated at 25 MHz and linked to a Nicolet computer, or with a Bruker 200-MHz Fourier transform NMR spectrometer operated at 50 MHz. Solvents used were Me_2SO-d_6 (MSD Isotopes) for poly(acrylic anhydride), poly(acrylonitrile), and acrylonitrile copolymers, C_6D_6 (MSD Isotopes) for poly(methyl acrylate) and poly(methyl methacrylate), D_2O (Stohler Isotopes) for poly(acrylic acid), and D_2O/NaOH (aq) for poly(sodium acrylate). Chemical shifts were referenced internally to the NMR solvent, to methanol when D_2O was used as the solvent, or to dioxane when D_2O/NaOH (aq) was used as the solvent.

Viscosity Data. Intrinsic viscosity ([η]) measurements were made with the use of a Cannon-Ubbelohde viscometer. A minimum of four different concentrations were used for each polymer, with at least three efflux times recorded at each concentration. Solvents and temperatures used were dimethyl sulfoxide for poly(acrylic anhydride) (20 °C), poly(acrylonitrile) (20 °C), and acrylonitrile/methyl methacrylate copolymers (20 °C), 2 M NaOH (aq) for poly(sodium acrylate) (25 °C) and sodium acrylate/acrylonitrile copolymers (25 °C), acetone for poly(methyl vinyl ketone) (20 °C) and poly(methyl methacrylate) (30 °C), and toluene for poly(methyl acrylate) (30 °C). It was necessary to convert the acrylic acid polymers and copolymers to the sodium salts to avoid extensive hydrogen bonding and the resultant viscosity anomalies.

Clathrate Polymerizations. Acrylic Acid. Freshly sublimed I (5 g) was placed in a thick-walled glass ampule in an atmosphere of dry N_2. Acrylic acid (~5 g) was added to I to form a slurry, which was maintained at 25 °C for 0.5 h. The mixture was then degassed by means of three freeze–pump–thaw cycles, after which excess monomer was removed in vacuo. The evacuated ampule was then sealed and irradiated with ^{60}Co γ-radiation at −78 °C.

Unreacted monomer was removed in vacuo, and any polymer external to the host crystals was removed by three washings with water (200 mL). The clathrated poly(acrylic acid) was then extracted from I by rapid stirring of the adduct in xylene/water (1 L, 65/35) at 100 °C for 16 h. The system was cooled to 25 °C, and the water layer was collected and then centrifuged to give a homogeneous solution of the polymer. The solution was concentrated with the use of a rotary evaporator and the polymer was isolated as a solution-cast film, yield 0.75 g.

Acrylic Anhydride. The acrylic anhydride adduct of I was prepared in a manner similar to that described for acrylic acid. The sample was irradiated at −78 °C. Following irradiation, unreacted monomer was removed in vacuo. The adduct was stirred in refluxing benzene (~200 mL) for 48 h to separate the internal polymer from I. The host was soluble in the hot benzene, whereas the polymer was not. The two solids were apparent when the system was cooled—a fine powder of I and large aggregates of a turquoise-colored polymer. The polymer was isolated and purified by soxhlet extraction with benzene, yield 2.7 g.

Acrylonitrile. The acrylonitrile adduct of I was prepared in a similar manner. The adduct was irradiated at −45 °C. Unreacted monomer was removed in vacuo, and polymer external to the clathrate was removed by three washings with dimethyl sulfoxide (200 mL). The washings also removed some internal polymer following the partial solution of I. The remainder of the clathrated poly(acrylonitrile) was separated from I by stirring of the adduct in refluxing benzene (500 mL) for 16 h. Benzene was removed by means of a rotary evaporator, and dimethyl sulfoxide (20 mL) was added to extract the polymer. The mixture was stirred for 2 h, after which time centrifugation yielded a homogeneous solution of the internal polymer. The solution was then concentrated and the polymer was isolated by precipitation into water, yield 0.9 g.

Methyl Acrylate. The methyl acrylate adduct of I was prepared in the same way as described above. The ^{60}Co γ-irradiation was carried out at −78 °C. Unreacted monomer was removed in vacuo, and polymer adhering to the surface of the crystals was dissolved by stirring of the adduct in benzene (200 mL) for 16 h. The solid adduct was then isolated by filtration and was stirred in boiling benzene (200 mL) for 5 days to separate the internal polymer from the host. The mixture was then allowed to cool to 25 °C, the solids were filtered off, and the filtrate was concentrated with the use of a rotary evaporator. The polymer was isolated by precipitation into methanol, yield 0.5 g.

Methyl Methacrylate. The methyl methacrylate adduct of I was prepared in the way described for the acrylic acid adduct. The clathrate was irradiated at −29 °C. Unreacted monomer was removed in vacuo and polymer external to the host crystals was extracted by stirring of the adduct in benzene (200 mL) for 16 h. The washed, crystalline adduct was recovered by filtration and was then stirred in boiling benzene (200 mL) for 48 h to separate the clathrate-synthesized polymer from the host. Benzene was then removed, and the polymer was extracted from the residue with the use of methylene chloride (~50 mL). This solution was then concentrated, and the polymer was isolated by precipitation into hexane, yield 1.25 g.

Methyl Vinyl Ketone. The methyl vinyl ketone adduct of I was prepared in the normal manner. The ^{60}Co γ-irradiation was

performed at −78 °C. Following irradiation, unreacted monomer was removed in vacuo, and the adduct was then stirred in chloroform (200 mL) for 4 h to remove any external polymer. The internal polymer was separated from I by stirring the adduct in refluxing benzene (~200 mL) for 24 h to give a homogeneous solution. When cooled, both I and the internal polymer precipitated from solution. The solids were collected by filtration, and the internal polymer was then extracted with chloroform (~50 mL). The chloroform solution was concentrated and the poly(methyl vinyl ketone) was isolated by precipitation into hexane, yield 0.4 g.

Acrylonitrile/Acrylic Acid. Freshly sublimed I (5 g) was placed in a thick-walled glass ampule in an atmosphere of dry N_2. A homogeneous 50/50 (v/v) solution of acrylonitrile (AN)/acrylic acid (AA) was prepared and added to I to form a slurry. After the mixture had been maintained at 25 °C for 0.5 h, excess monomer was removed in vacuo and the ampule was sealed. The sample was then irradiated at −45 °C. Following irradiation, unreacted monomer was removed in vacuo, and the internal copolymer was separated from I by treatment of the adduct with dimethyl sulfoxide (~200 mL) for 48 h. The Me_2SO solution was concentrated, and the copolymer was isolated by precipitation into water. Final purification, by Soxhlet extraction with benzene, resulted in the removal of I as indicated by elemental analysis for phosphorus, yield 0.5 g. Anal. Calcd for $[(AN)_{0.39}(AA)_{0.61}]_n$: C, 55.74; H, 5.59; N, 8.45. Found: C, 52.80; H, 5.67; N, 8.47.

Acrylonitrile/Methyl Methacrylate. A homogeneous 50/50 (v/v) mixture of acrylonitrile/methyl methacrylate (MMA) was used to form an adduct of I in a manner similar to that described for the acrylonitrile/acrylic acid system. The sample was irradiated at −29 °C. Following removal of unreacted monomer in vacuo, the clathrate-synthesized copolymer was separated from the host by stirring of the adduct in boiling benzene (200 mL) for 48 h. Benzene was then removed, and the copolymer was extracted from the residue with methylene chloride (~50 mL). The solution was then concentrated, and the copolymer was isolated by precipitation into hexane, yield 0.2 g. Anal. Calcd for $(AN)_{0.30}(MMA)_{0.70}]_n$: C, 61.47; H, 7.57; N, 4.89. Found: C, 63.73; H, 7.48; N, 4.84.

Bulk Polymerizations. Samples of the monomers were irradiated in bulk at temperatures that corresponded to those used in the clathrate-mediated polymerizations. For the comonomer systems, the same batch of comonomer was used for both the bulk and clathrate polymerizations. Following irradiation, unreacted monomer was removed in vacuo and the polymeric residue was then characterized by ^{13}C NMR spectroscopy and solution viscometry. Anal. Calcd for $[(AN)_{0.15}(AA)_{0.85}]_n$–PAA fraction (species B): C, 52.06; H, 5.57; N, 3.04. Found: C, 50.79; H, 5.46; N, 3.19. Anal. Calcd for $[(AN)_{0.40}(MMA)_{0.60}]_n$: C, 62.07; H, 7.39; N, 6.90. Found: C, 61.47; H, 7.50; N, 6.89.

Results and Discussion

Irradiation temperatures were chosen so that the control conversions from monomer to polymer for the *bulk* polymerizations were, in general, 50% or more. The polymerization results are summarized in Table I, and the characterization data are given in Table II.

Acrylic Acid. Polymerization of acrylic acid within the tunnels of I at −78 °C yielded syndiotactic poly(acrylic acid). The ^{13}C NMR resonances were centered at 178.9 (COOH), 41.8 (CH), and 34.5 (CH_2) ppm. Solution viscosity measurements on the derivative, poly(sodium acrylate), suggested a viscosity-average molecular weight of 4.4×10^5 (4.7×10^3 monomer repeat units) or 3.4×10^5 for the poly(acrylic acid) itself. This is the highest degree of polymerization yet detected for clathrates of I. ^{13}C NMR spectroscopy was used to estimate the efficiency of conversion to the sodium salt. A shift in the 178.9 ppm (COOH) resonance to 183.5 ppm (COONa) indicated quantitative conversion.

Polymerization of acrylic acid in bulk also yielded syndiotactic poly(acrylic acid). The NMR spectrum was nearly identical with that of the clathrate-synthesized polymer. The stereoregularity of the bulk polymer undoubtedly reflects a matrix orientation of monomer molecules as a consequence of strong hydrogen-bonding interactions.[4] Bulk-polymerized poly(acrylic acid) was converted to its sodium salt, which proved to have a viscosity molecular weight of 4.3×10^5 (4.6×10^3 monomer repeat units). This corresponds to a molecular weight of 3.3×10^5 for the original carboxylic acid polymer. Virtually no difference in molecular weight could be detected between the bulk- and clathrate-synthesized polymers. This suggests that the degree of polymerization depends more on the polymerization *conditions* than on the length of the clathrate tunnels. In addition, a small amount of cross-linking was detected for the bulk polymerization product, probably due to radical formation at the methine carbon atom during irradiation. No cross-linking was detected in the clathrate system.

Table I
Summary of Polymerization Results

monomer	temp, °C	clathrate-mediated polymerizn[a]	bulk polymerizn
acrylic acid	−78	syndiotactic	syndiotactic
acrylic anhydride	−78	un-cross-linked	cross-linked matrix
acrylonitrile	−45	isotactic	atactic
methyl acrylate	−78	isotactic	atactic
methyl methacrylate	−29	syndiotactic	syndiotactic
methyl vinyl ketone	−78	isotactic	atactic
acrylic acid/acrylonitrile	−45	very random	large blocks
methyl methacrylate/acrylonitrile	−29	very random	small blocks

[a] Clathrate refers to tris(*o*-phenylenedioxy)cyclotriphosphazene.

The similarities between the clathrate-mediated and bulk-polymerized poly(acrylic acid) are consistent with some degree of monomer hydrogen bonding in the clathrate. This would also explain why acrylic acid is clathrated in preference to acrylonitrile from mixtures of the two (see later). The concept of hydrogen bonding of small molecules within the tunnels of I has been demonstrated for water molecules trapped in I.[24]

Acrylic Anhydride. Irradiation of the acrylic anhydride adduct of I at −78 °C yielded an un-cross-linked polymer that was soluble in dimethyl sulfoxide. To the best of our knowledge, this is the first report of an un-cross-linked form of this polymer. The polymer was turquoise in color, apparently a consequence of extensive conjugation (the monomer is dark blue/purple). The ^{13}C NMR spectrum of the clathrate-synthesized polymer consisted of four groups of resonances at 175.9–172.0 (—CO—O—CO—), 131.0–128.5 (CH_2=CH—), 45.3 (CH), and 35.6–32.3 (CH_2) ppm. This is consistent with a polymer having pendent vinyl anhydride residues. One of the carbonyl resonances (175.9 ppm) (probably from the carbonyl group adjacent to the methine carbon atom) was considerably more intense than the others, and this may be evidence for stereoregularity. The intrinsic viscosity was 1.51 dL/g.

These results contrast with the polymerization of acrylic anhydride in the bulk phase under similar conditions. Such reactions yield an insoluble cross-linked matrix.

Acrylonitrile. Polymerization of acrylonitrile within the tunnel system of I at −45 °C yielded a poly(acrylonitrile) rich in isotactic character, with a relatively small

Table II
Summary of Characterization Data

	^{13}C NMR	[η], dL/g	$10^{-5}\bar{M}_v$[a]	10^{-3} (DP)
	Acrylic Acid			
clathrate	178.9, 41.8, 35.1–33.8	1.73 (Na salt)	3.4 4.4 (Na salt)	4.7
bulk[b]	178.7, 41.7, 34.9–34.1	1.70 (Na salt)[c]	3.3 4.3 (Na salt)	4.6
	Acrylic Anhydride			
clathrate	175.9–172.0, 131.0–128.5, 45.3, 33.7–33.5	1.51	*d*	
bulk		*e*	*e*	*e*
	Acrylonitrile			
clathrate	120.2, 119.9, 119.6, 32.5, 27.9, 27.3, 26.7	2.44	1.5	2.8
bulk[b]	120.3, 120.0, 119.7, 32.7, 27.9, 27.4, 26.8	2.67	1.7	3.2
	Methyl Acrylate			
clathrate	174.8, 51.5, 41.9, 36.4–34.9	0.51	3.0	3.5
bulk	174.8, 51.5, 41.8, 37.5–33.6	*e*	*e*	*e*
	Methyl Methacrylate			
clathrate	178.0, 177.7, 176.8, 55.0–53.4, 51.5, 45.4–45.1, 19.4, 17.5	0.68	4.3	4.3
bulk[b]	178.0, 177.7, 176.8, 55.0–53.5, 51.4, 45.4–45.1, 19.5, 17.5	0.91	6.5	6.5
	Methyl Vinyl Ketone			
clathrate	210.8, 210.6, 48.0, 33.7–32.0, 29.4	0.40	*d*	*d*
bulk	210.6, 48.0, 33.9–32.3, 29.5	*e*	*e*	*e*
	Acrylonitrile/Acrylic Acid			
clathrate	175.8–174.9, 121.7–120.0, 35.6–33.6, 32.9–32.2, 28.4–26.7	4.06 (Na salt)	*d*	*d*
bulk (PAN fraction)	120.9–120.0, 33.2–32.8, 27.9–26.2			
bulk (PAA fraction)	175.7, 121.5–120.1, 35.8–33.8, 33.2–32.1, 28.1–26.1	2.60 (Na salt)[c]	*d*	*d*
	Acrylonitrile/Methyl Methacrylate			
clathrate	177.1–175.7, 122.7–120.7, 54.6–53.2, 51.8, 44.5–43.6, 32.8–32.2, 27.5, 24.8–16.0	0.93	*d*	*d*
bulk	177.2–174.6, 122.8–120.3, 51.8, 44.5–43.7, 32.6–31.6, 25.5–16.8	0.56	*d*	*d*

[a] Mark–Houwink constants obtained from ref 23. [b] The viscosity molecular weight values for the bulk-synthesized polymers are for rough comparisons only since they are based on the assumption of polymer linearity. [c] Polymer was slightly cross-linked. [d] Mark–Houwink constants not available. [e] Data could not be obtained because of polymer cross-linking.

amount of atactic structure, as determined by ^{13}C NMR spectroscopy.[25] The ^{13}C NMR spectrum contained three groups of resonances centered at 119.9 ppm (CN) with the downfield group being the most intense. This indicates enhanced isotacticity. Also present were resonances at 32.5 ppm (CH_2) and three resonances centered at 27.3 ppm (CH), with the upfield resonance being the most intense. This also indicates enhanced isotacticity. These results are nearly identical with those obtained for acrylonitrile polymerized within the canals of a urea clathrate.[25] The solution viscosity-average molecular weight was 1.5×10^5 (2.8×10^3 monomer repeat units).

Polymerization of acrylonitrile in the bulk phase gave an atactic polymer. The ^{13}C NMR spectrum consisted of the same resonance observed for the clathrate-synthesized polymer, but with the relative intensities of the resonances centered at 119.9 and 27.3 ppm consistent with an atactic structure. The solution viscosity-average molecular weight was 1.7×10^5 (3.2×10^3 monomer repeat units). This was only slightly higher than that observed for the clathrate-synthesized polymer. Again, this suggests that the polymerization conditions rather than the tunnel length may be the limiting factor that governs the degree of polymerization.

The effect of the polymerization temperature on stereoregularity was probed by irradiation of the acrylonitrile adduct of I at +35 °C. The ^{13}C NMR spectrum of the resultant polymer was consistent with an enhanced isotactic structure similar to that of the clathrate-synthesized polymer prepared at −45 °C. However, slightly more atactic structure was detected. The relatively small difference in stereoregularity between these products suggests that little difference exists between the freedom of motion of the acrylonitrile guest molecules within the tunnels at the two different temperatures.

Methyl Acrylate. Irradiation of the methyl acrylate adduct of I at −78 °C yielded an enhanced isotactic poly(methyl acrylate). The ^{13}C NMR spectrum consisted of resonances centered at 174.8 (CO), 51.5 (OCH_3), 41.9 (CH), and 35.4 (CH_2) ppm. The methylene resonances were distributed in an envelope, with the central and upfield (35.4–34.9 ppm) resonances being the most intense, and with relatively weak downfield (36.4–35.4 ppm) resonances. This is consistent with an enhanced isotactic structure.[26] Solution viscosity measurements suggested a molecular weight of 3.0×10^5 (3.5×10^3 monomer repeat units).

Irradiation of methyl acrylate in the bulk phase under analogous conditions yielded an atactic polymer. A set of ^{13}C NMR resonances similar to that described for the clathrate-synthesized polymer was observed. However, the bell-shaped distribution of methylene resonances was consistent with an atactic structure. Solution viscosity data could not be obtained for the bulk-polymerized poly(methyl acrylate) because of considerable cross-linking. A much smaller amount of gelation was detected for the bulk-polymerized poly(acrylic acid). It is well-known that γ-radiation can cross-link polymers via radical formation, particularly when a carbonyl group is adjacent to a methine carbon atom.[27]

Methyl Methacrylate. Polymerization of methyl methacrylate within the tunnel of I at −29 °C gave a polymer with an enhanced syndiotactic structure, as determined by ^{13}C NMR spectroscopy.[28] The ^{13}C NMR spectrum consisted of groups of resonances at 178.0–176.8

(CO), 55.0–53.4 (CH_2), 51.5 (OCH_3), 45.4–45.1 (C), and 19.4–17.5 (CH_3) ppm. The relative intensities of the resonances within the carbonyl, quaternary carbon, and methyl carbon envelopes indicated a syndiotactic structure with a small amount of atactic character. The most intense carbonyl resonance occurred at 177.7 ppm. This corresponds to a syndiotactic pentad. No carbonyl resonance was present for an isotactic pentad. The most intense quaternary carbon resonance was at 45.1 ppm, which corresponded to a syndiotactic triad. A less intense resonance at 45.4 ppm indicated the presence of some atactic triad structure. No downfield resonance due to an isotactic triad was present. Similarly, only two methyl resonances were present, the most intense being at 17.5 ppm. This corresponded to a syndiotactic triad. A weaker resonance at 19.4 ppm indicated some atactic structure. No downfield methyl resonance was detected that might correspond to an isotactic triad. Viscosity measurements showed that the molecular weight was 4.3×10^5 (4.3×10^3 monomer repeat units).[29]

Radiation polymerization of methyl methacrylate in the bulk phase under the same conditions yielded a polymer similar in structure to that obtained from the clathrate system. The ^{13}C NMR spectrum was nearly identical with that described above, with only slight variations in relative intensities of the resonances. Viscosity measurements indicated that the molecular weight was 6.5×10^5 (6.5×10^3 monomer repeat units).

Irradiation of the methyl methacrylate adduct of I at +35 °C also yielded a polymer with an enhanced syndiotactic structure but with a greater amount of atactic character compared to the polymers synthesized at −29 °C. Poly(methyl methacrylate) prepared in the bulk phase at +35 °C had a structure virtually identical with that of the clathrate-synthesized polymer prepared at the same temperature. Temperature appears to have a greater influence on the stereoregularity than does the template effect of the clathrate framework.

Methyl Vinyl Ketone. Irradiation of methyl vinyl ketone within the tunnels of I at −78 °C yielded poly(methyl vinyl ketone) with an enhanced isotactic structure. The ^{13}C NMR spectrum consisted of resonances at 210.8–210.6 (CO), 48.0 (CH), 33.7–32.0 (CH_2), and 29.4 (CH_3) ppm. The relatively intense upfield peaks in both the carbonyl and methylene groups of resonances indicated enhanced isotacticity.[30] The intrinsic viscosity was 0.40 dL/g.

By contrast, irradiation of the bulk monomer under analogous conditions gave an atactic polymer. The same groups of resonances were observed in the ^{13}C NMR spectrum, but the distribution of the carbonyl and methylene resonances was consistent with a lack of stereoregularity. Solution viscosity data could not be obtained because the bulk-synthesized polymer was cross-linked. Again, this is presumably a consequence of radical formation at the methine carbon atom.

Acrylonitrile/Acrylic Acid. A 50/50 (v/v) homogeneous mixture of acrylonitrile/acrylic acid (corresponding to a 51/49 molar ratio of AN/AA) was used to form an adduct of I. Vapor-phase chromatography experiments demonstrated a preferential incorporation of acrylic acid into the clathrate. The copolymer formed by irradiation at −45 °C had a molar monomer composition of 39/61 (AN/AA) as determined by elemental analyses.

The ^{13}C NMR spectrum of the clathrate-synthesized copolymer consisted of resonances at 175.8–174.9 (CO(AA)), 121.7–120.0 (CN(AN)), 35.6–33.6 (CH_2(AA)), 32.9–32.2 (CH_2(AN)), and 28.4–26.7 (CH(AN)) ppm. The acrylic acid methine resonance was presumably buried beneath the Me_2SO solvent resonances. The spectrum resembled those observed for the two homopolymers, but with the following differences. Two relatively intense and several less intense carbonyl resonances were detected for the copolymer. Only a single carbonyl resonance was detected for the acrylic acid homopolymer. The two intense resonances are thought to be due to triad sequences in which an acrylic acid unit is flanked by an acrylonitrile unit and an acrylic acid unit, and where an acrylic acid unit is flanked by two acrylic acid units. The acrylonitrile methylene resonances for the copolymer consisted of several peaks. This contrasts with the situation in the acrylonitrile homopolymer, which showed only one methylene resonance. Again, this reflects the increased structural complexity of the copolymer and suggests a very random sequence distribution. Presumably, this distribution is a consequence of the random, competitive clathration of the monomer guest molecules by the host matrix. Finally, the added complexity of the copolymer caused the cyano resonances to appear over a broader range than was observed for the homopolymer. The intrinsic viscosity was 4.06 dL/g.

When the same 51/49 (AN/AA) molar mixture was irradiated in the bulk phase under identical conditions, two distinct polymers were obtained. The first fraction (species A) consisted entirely of poly(acrylonitrile), as determined by ^{13}C NMR spectroscopy. The second (species B) consisted predominantly of poly(acrylic acid) with a small amount of poly(acrylonitrile) as determined from the ^{13}C NMR spectrum. Elemental analysis indicated that the molar composition was 15/85 (AN/AA). The acrylic acid carbonyl resonance in the ^{13}C NMR spectrum was a single peak. This contrasts with the clathrate-synthesized copolymer and indicates that this polymer consists of either two homopolymers or of a copolymer with two very large block sequences. Apparently, the reactivity ratios of the two monomers are such that little, if any, interaction occurs between acrylonitrile and acrylic acid in the bulk phase. This is not the case within the tunnels of I.

The intrinsic viscosity of species B was 2.60 dL/g, significantly lower than that observed for the clathrate-synthesized copolymer. This discrepancy can be attributed to differences in the sequence distribution of the two copolymers. Block copolymers that consist of incompatible components (as reflected by differences in solubility behavior of the two respective homopolymers) are known to give rise to expanded coil configurations in solution.[31] This is especially significant when the medium is a good solvent for one component and a poor solvent for the other. The repulsive interactions between components cause the intrinsic viscosity of the block copolymer to be higher than that of either homopolymer. To our knowledge, no systematic study of the effect of sequence distribution on intrinsic viscosity has been performed. It is logical that the repulsive interactions (and, hence, the intrinsic viscosity) would be maximized by a random sequence distribution with all other factors (molecular weight and composition) being equal. The unfavorable interactions between acrylonitrile and sodium acrylate (the measurements were carried out in aqueous sodium hydroxide) units are apparently more pronounced for the random copolymer synthesized within the tunnel clathrate.

Acrylonitrile/Methyl Methacrylate. A 50/50 (v/v) homogeneous mixture of acrylonitrile/methyl methacrylate (corresponding to a 62/38 molar ratio of AN/MMA) was used to form an adduct of I. Gas chromatography of the comonomer adduct showed that a preferential clathration

of methyl methacrylate had occurred. Irradiation of the clathrate at −29 °C yielded a copolymer with a molar composition of 30/70 (AN/MMA), as determined by elemental analyses.

The ^{13}C NMR spectrum consisted of resonances at 177.1–175.7 (CO(MMA)), 122.7–120.7 (CN(AN)), 54.6–53.2 (CH_2(MMA)), 51.8 (OCH_3(MMA)), 44.5–43.6 (C(MMA)), 32.8–32.2 (CH_2(AN)), 27.5 (CH(AN)), and 24.8–16.0 (CH_3(MMA)) ppm. These resonances were similar to those found for the respective homopolymers but with differences in the methyl methacrylate quaternary carbon and methyl resonances. The quaternary carbon resonances in the copolymer consisted of two peaks. Only one resonance was detected for the homopolymer. The methyl resonances for the copolymer were distributed in two broad envelopes at 24.8–20.0 and 19.0–16.0 ppm. Only the upfield group of resonances was detected for the poly(methyl methacrylate) homopolymer. Also, the cyano resonances in the copolymer appeared over a broader range than was observed for the acrylonitrile homopolymer. The additional resonances for the copolymer are due to the increased structural complexity of triad and higher level sequences relative to the homopolymers. For example, the presence of a neighboring electron-withdrawing acrylonitrile unit has the effect of shifting the methyl resonance downfield. This explains the set of resonances at 24.8–20.0 ppm. Moreover, the extensive fine structure found in the spectrum, attributed to the presence of many monomer unit environments, is consistent with a very disordered sequence distribution. This in turn can be explained by the random clathration of monomer guest molecules. Clearly, the different monomer reactivity ratios have little influence on the sequence distribution. The intrinsic viscosity was 0.93 dL/g.

Irradiation of the same (62/38) (AN/MMA) molar mixture in the bulk phase under the same experimental conditions yielded a copolymer with a molar ratio of 40/60 (AN/MMA), as determined by elemental analyses. Unlike the clathrate-synthesized copolymer, the composition of the bulk copolymer is affected by the monomer reactivity ratios.

The ^{13}C NMR spectrum of the copolymer prepared in the bulk phase was similar to that of the clathrate-synthesized copolymer. However, the methyl methacrylate methylene and acrylonitrile methine resonances were very weak. In addition, the spectrum in general, and particularly the methyl resonances at 25.5–16.8 ppm, did not show the fine structure seen for the clathrate-synthesized product. This may be a consequence of a more ordered sequence distribution in the polymer prepared in bulk. It is possible that short blocks of methyl methacrylate units are separated by acrylonitrile units. The intrinsic viscosity was 0.56 dL/g. Once again, the clathrate-synthesized copolymer had a significantly higher intrinsic viscosity than the bulk copolymer. This is consistent with ^{13}C NMR data, which indicated that the internal copolymer had a more random sequence distribution.

Overall Utility of the Method. The tunnel polymerization of acrylic monomers with the use of host I as a template provides a useful method for the preparation of enhanced stereoregular polymers.

The method allows access to polymers with chain lengths similar to those obtained by bulk, radiation-induced polymerization. Thus, the polymerization conditions rather than the tunnel length probably limit the degree of polymerization. Based on the degrees of polymerization found in this work, the tunnels must be at least 10^4 Å in length. Scanning electron microscopy has been used to show that the microcrystallite size for adducts of I is generally 3–10 times this value.[24] This, too, is consistent with the idea that the polymer chain length is not limited by crystallite size or tunnel length.

The degree of stereoregularity generated by this method depends not only on the presence of the tunnel system, but also on the polymerization temperature. The stereoregularity of the clathrate-synthesized poly(methyl methacrylate) and poly(acrylonitrile) was in each case slightly lower when the polymerization was carried out at +35 °C than at −45 or −29 °C. This is probably due to the increased thermal motion of the monomer molecules at +35 °C.

Polymerization of multifunctional monomer molecules within the crystal matrix of I can yield hitherto unobtainable linear polymers. Previously, divinylbenzene[16] and now acrylic anhydride have been clathrate polymerized to give un-cross-linked products. By contrast, the bulk-synthesized homopolymers and copolymers derived from acrylic acid, methyl acrylate, and methyl vinyl ketone were cross-linked. Carbonyl groups adjacent to a methine carbon atom favor radiation-induced radical formation at the methine carbon and hydrogen atoms. This can lead to cross-linking in the bulk phase. However, radical recombination, rather than cross-linking, is more likely when individual polymer chains are separated within the protective environment of the clathrate tunnels.

Finally, this clathration system provides a method for the preparation of specialized copolymers, especially those with a random monomer distribution, itself induced by the random occupancy of the available tunnel sites by two different monomers. In fact, this is one of the few methods available for the preparation of homogeneous copolymers by a high-conversion batch process. An added novelty of this copolymerization method is the opportunity it provides for a control of the monomer ratios within a polymer as a consequence of the different propensities of various monomers to enter and remain in the tunnel system. It is interesting that, in the copolymeriation systems studied, no tendency was detected for long sequences of one monomer to occupy a tunnel with total exclusion of the second monomer. Hence, the sequencing of two different but similarly sized monomer molecules along a tunnel may depend on the probability with which incoming monomer molecules encounter the tunnel openings and the ease with which they can penetrate deep into the crystal structure.

Acknowledgment. This work was supported by the National Science Foundation Polymers Program through grant no. DMR 81-19934 #2. We thank J. Bonner for help with the ^{60}Co γ-irradiations, and J. L. Desorcie and K. D. Lavin for the NMR spectra. Figure 1 was prepared in collaboration with R. R. Whittle.

References and Notes

(1) Inoue, S.; Tsuruta, T.; Furukawa, J. *Makromol. Chem.* **1961**, *49*, 13.
(2) Acrylic acid can be polymerized in the bulk[3] and solution[4] states to yield a syndiotactic polymer, a reaction that is mediated by hydrogen-bonding effects. Acrylic[5,6] and methacrylic esters[7,8] can be polymerized stereospecifically, but such polymerizations are not common.
(3) Chapiro, A.; Sommerlatte, T. *Eur. Polym. J.* **1969**, *5*, 707, 725.
(4) Chapiro, A.; Dulieu, J. *Eur. Polym. J.* **1977**, *13*, 563.
(5) Miller, M. L.; Rauhut, C. E. *J. Am. Chem. Soc.* **1958**, *80*, 4115.
(6) Garrett, B. S.; Goode, W. E.; Gratch, S.; Kincaid, J. J.; Levesque, C. L.; Spell, A.; Stroupe, J. D.; Watanabe, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 1007.
(7) Fox, T. G.; Garrett, B. S.; Goode, W. E.; Gratch, S.; Kincaid, J. F.; Spell, A.; Stroupe, J. D. *J. Am. Chem. Soc.* **1958**, *80*, 1768.
(8) Tsuruta, T.; Makimoto, T.; Kanai, H. *J. Macromol. Chem.* **1966**, *1*, 31.

(9) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(10) Allcock, H. R. *Acc. Chem. Res.* **1978**, *11*, 81.
(11) Allcock, H. R.; Siegel, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 5140.
(12) Siegel, L. A.; van den Hende, J. H. *J. Chem. Soc. A* **1967**, 817.
(13) Allcock, H. R.; Teeter-Stein, M. *J. Am. Chem. Soc.* **1974**, *96*, 49.
(14) Allcock, H. R.; Teeter-Stein, M.; Bissell, E. C. *J. Am. Chem. Soc.* **1974**, *96*, 4795.
(15) Allcock, H. R.; Allen, R. W.; Bissell, E. C.; Smeltz, L. A.; Teeter, M. *J. Am. Chem. Soc.* **1976**, *98*, 5120.
(16) Allcock, H. R.; Ferrar, W. T.; Levin, M. L. *Macromolecules* **1982**, *15*, 697.
(17) Allcock, H. R. In "Inclusion Compounds"; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds. Academic Press: New York, 1984; Vol. 1.
(18) Finter, J.; Wegner, G. *Makromol. Chem.* **1979**, *180*, 1093.
(19) Takemoto, K.; Miyata, M. *Macromol. Sci.-Rev.-Macromol. Chem.* **1980**, *C18*, 83.
(20) Farina, M.; Natta, G.; Allegra, G.; Loffelholz, M. *J. Polym. Sci., Part C* **1967**, *16*, 2517.
(21) Allcock, H. R.; Walsh, E. J. *Inorg. Chem.* **1971**, *10*, 1643.
(22) The melting points of the host–guest adducts were as follows, with the monomer adduct given first and the polymer adduct in parentheses: acrylic acid, 205–222 °C (208–249 °C); acrylic anhydride, 213–223 °C (221–233 °C); acrylonitrile, 235–244 °C (235–246 °C); methyl acrylate, 232–245 °C (231–248 °C); methyl methacrylate, 237–243 °C (239–245 °C); methyl vinyl ketone, 192–231 °C (187–246 °C); acrylonitrile/acrylic acid, 208–229 °C (217–235 °C); acrylonitrile/methyl methacrylate, 231–239 °C (231–248 °C). All the host–guest adducts melted with apparent decomposition.
(23) Brandrup, J., Immergut, E. H. Eds. "Polymer Handbook", 2nd ed.; Wiley-Interscience: New York, 1975.
(24) Allcock, H. R.; Levin, M. L.; Whittle, R. R., submitted for publication in *Inorg. Chem.*
(25) Inoue, Y.; Nishioka, A. *Polym. J.* **1972**, *3*, 149.
(26) Matsuzaki, K.; Kanai, T.; Kawamura, T.; Matsumoto, S.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 961.
(27) Chapiro, A. "Radiation Chemistry of Polymeric Systems"; Interscience: New York, 1962; p 355.
(28) Peat, I. R.; Reynolds, W. F. *Tetrahedron Lett.* **1972**, *14*, 1359.
(29) Gel permeation chromatography suggested that both the bulk- and clathrate-synthesized poly(methyl methacrylate) had a broad molecular weight distribution with roughly the same dispersity (M_w/M_n = 6.6 and 7.4, respectively). The measurements were carried out with the use of a Waters Associates ALC/GPC 501 chromatograph equipped with one 10^3-Å and two 10^6-Å Polymer Laboratories PL gel columns. Tetrahydrofuran was used as the eluent at a flow rate of 0.5 mL/min and a temperature of 30 °C. Polystyrene standards were used to calibrate the instrument.
(30) Merle-Aubrey, L.; Merle, Y. *Eur. Polym. J.* **1980**, *16*, 227.
(31) Davies, W. G.; Jones, D. P. In "Colloidal and Morphological Behavior of Block and Graft Copolymers"; Molau, G. E., Ed.; Plenum Press: New York, 1971; p 63.

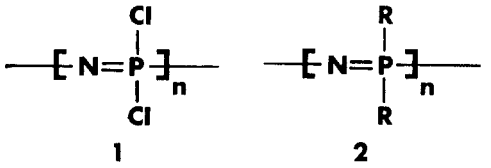
Polymerization and Halogen Scrambling Behavior of Phenyl-Substituted Cyclotriphosphazenes[1]

Harry R. Allcock* and Mark S. Connolly

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received June 14, 1984*

ABSTRACT: A new series of poly(organophosphazenes) with phenyl groups bonded to the skeleton has been prepared by the polymerization of phenylhalogenocyclotriphosphazenes. In addition, evidence about the mechanism of chlorophosphazene polymerization has been obtained by halogen scrambling studies. 1-Phenyl-1,3,3,5,5-pentachlorocyclotriphosphazene, $N_3P_3Cl_5Ph$ (**5a**), undergoes a ring-opening thermal polymerization at 250 °C. The resultant high polymer reacts with sodium trifluoroethoxide, sodium phenoxide, or piperidine to yield poly(organophosphazenes) that are free from P–Cl bonds. 1-Phenyl-1-bromo-3,3,5,5-tetrachlorocyclotriphosphazene, $N_3P_3Cl_4BrPh$ (**5b**), also polymerizes at 250 °C but with scrambling of the bromine atoms between different phosphorus sites. The trimer, **5b**, itself undergoes halogen scrambling at temperatures as low as 178 °C. The cyclophosphazenes, **5a** and **5b**, copolymerize at 250 °C with $(NPCl_2)_3$. The copolymerization of **5a** and $N_3P_3Cl_5Me$ provides a method for the synthesis of phosphazene polymers that bear both alkyl and aryl substituent groups. The trimers, **5b** and $N_3P_3Cl_4BrMe$, are accelerators for the polymerization of $(NPCl_2)_3$ at 250 °C, while **5a** and $N_3P_3Cl_5Me$ are weak inhibitors. However, polymers prepared in the presence of these inhibitors had molecular weights similar to those prepared from pure $(NPCl_2)_3$ or in the presence of the accelerators. The mechanistic implications of these results are discussed.

High molecular weight poly(organophosphazenes) of formula $[NP(OR)_2]_n$, $[NP(NHR)_2]_n$, and $[NP(NR_2)_2]_n$ are well-known.[2-9] These polymers are prepared by the interaction of poly(dichlorophosphazene) (**1**) with alkoxides,



1 **2**

aryl oxides, or amines. However, because these molecules possess organic side units bonded to phosphorus through oxygen or nitrogen, reaction pathways exist that permit decomposition or depolymerization at temperatures above 250 °C.

An approach to enhancing the thermal stability of polyphosphazenes and modifying their physical properties involves the synthesis of derivatives **2** that possess alkyl or aryl groups bonded directly to the skeletal phosphorus atoms. Such macromolecules would be analogues of alkyl- or arylpolysiloxanes. Earlier attempts to prepare such polyphosphazenes by the interaction of **1** with organometallic reagents[10-12] revealed some serious difficulties, since metal–halogen exchange reactions and skeletal cleavage accompanied substitution.[12] However, Neilson and Wisian-Neilson have recently reported a promising condensation–polymerization route that yields poly(alkyl- or alkylarylphosphazenes) of type **2**.[13]

An alternative approach being examined in our laboratory involves the synthesis of cyclotriphosphazenes that bear alkyl or aryl side groups bonded to the ring, and the polymerization of these species to linear polyphosphazenes.[14-18] Recently, we reported the first syntheses of 1-phenyl-1-halotetrachlorocyclotriphosphazenes, $N_3P_3Cl_4X(Ph)$ (**5**), and 1-phenyl-1-al-

0024-9297/85/2218-1330$01.50/0