perature, and the mixture was transferred to a methanol bath kept at −15 or −40 °C to initiate polymerization. For the HI/I$_2$-initiated reactions, hydrogen iodide and iodine solutions were added successively in this order to a monomer solution. The living polymerizations were terminated by adding prechilled ammoniacal methanol or the solution of sodiomalonic ester. In the latter case, the precipitating sodium iodide was subsequently removed by filtration.

The quenched reaction solution was sequentially washed with 10% aqueous sodium thiosulfate solution and with water, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers.

Hydrolysis and Decarboxylation. Malonate-capped poly(IBVE) (**4a**, **7a**, or **9a**) (0.1 g) was dissolved in ethanol (10 mL), and 5 N sodium hydroxide (5 equiv to the COOEt units in the polymer) was added. The mixture was magnetically stirred for 3 h, water (10 mL) was added, and stirring was continued for an additional 2–3 days. The resulting sodium salt was converted into the malonic acid form by treatment with 6 N hydrochloric acid (5 equiv to the COONa units in the sample). The polymer was isolated by evaporation under reduced pressure, dissolved in dioxane (20 mL), and kept at 90 °C for 1 h for decarboxylation. The product (**5a**, **8a**, or **10a**) was isolated by evaporation, dissolved in CH$_2$Cl$_2$ (50 mL), washed with water to remove the resulting sodium chloride, and then isolated by evaporation followed by vacuum-drying.

Malonate-capped poly(MVE)s **4b**, **7b**, and **9b** were treated in a similar manner, except that the decarboxylation was carried out in water at 50 °C for 24 h and the final products were dissolved in chloroform and washed with warm water at ca. 50 °C.

Polymer Characterization. The MWD of the polymers was determined by size-exclusion chromatography (SEC) in chloroform on a Jasco Trirotar-II chromatograph equipped with three polystyrene columns that were calibrated against at least 10 standard polystyrene samples in the molecular weight range 2×10^2 to 2×10^5.[3] The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values were obtained from SEC eluograms. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ or D$_2$O at room temperature on a Jeol FX-90Q instrument.

Conductometric titration was carried out in a glass cell with two platinum-plate electrodes connected to a Wayne Kerr B224 universal bridge. In a typical run, a stirred solution of a polymer sample (20–50 mg) in deionized water (60 mL) was pretreated with 0.2 N hydrochloric acid (5 mL) and then titrated with an 0.2 N sodium hydroxide standard solution.

Registry No. 2, 7553-56-2; I$_2$, 10034-85-2; HI, 10034-85-2; (EtO$_2$C)$_2$CHNa, 996-82-7.

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(7) We have recently found[8] that the HI/I$_2$-initiated living polymerizations of vinyl ethers proceed in not only nonpolar[3] but polar solvents such as CH$_2$Cl$_2$ as well. In the latter, the polymerization is much faster and requires less iodine (relative to hydrogen iodide), but is otherwise the same as those in *n*-hexane and other nonpolar media.

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Polymerization of New Metallocenylphosphazenes

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ABSTRACT: The polymerization behavior has been examined of four cyclophosphazenes that are bridged by transannular metallocenyl groups. It was found that two ferrocenyl units, one transannular and one pendent, do not block the polymerization process of a fluorocyclotriphosphazene, even though the trimer with only one pendent ferrocenyl group cannot be polymerized. Release of phosphazene ring strain induced by the transannular component appears to be responsible for the difference. A 1,5-transannular ferrocenyl or ruthenocenyl group has a lesser influence on the polymerizability of a phosphazene cyclic tetrameric ring. No evidence was found for a redistribution of monomer units in the conversion of the cyclic oligomers to polymers.

In recent publications,[1-4] we reported the first examples of metallocenylphosphazene high polymers. These were prepared by the ring-opening polymerization of cyclotriphosphazenes to which was linked one ferrocenyl or ruthenocenyl side group, in either a pendent or a transannular configuration. We also reported that the transannular bridging units enhanced the polymerization tendency of phosphazene trimers compared to their counterparts with one pendent metallocenyl side group.[5]

A number of questions arose from that work, including the following: (1) What effect on the polymerization process comes about if both transannular *and* pendent metallocenyl units are attached to the same cyclic trimeric phosphazene ring? (2) Does a polymerization difference result if the pendent component is geminal or nongeminal to the sites of attachment of the transannular linkage? (3) Do phosphazene cyclic *tetramers* that bear a transannular metallocenyl unit polymerize, and if so, what is the structure of the resultant polymers? For example, is there any evidence that repeating units are positionally redistributed as the tetramer is converted to high polymer?

With these questions in mind, we have synthesized the four cyclophosphazenes shown in **1**–**3** and have examined their polymerization behavior.

Results and Discussion

Polymerizations. Compound **1** polymerizes to a soluble macromolecule of type **4** when heated in the molten

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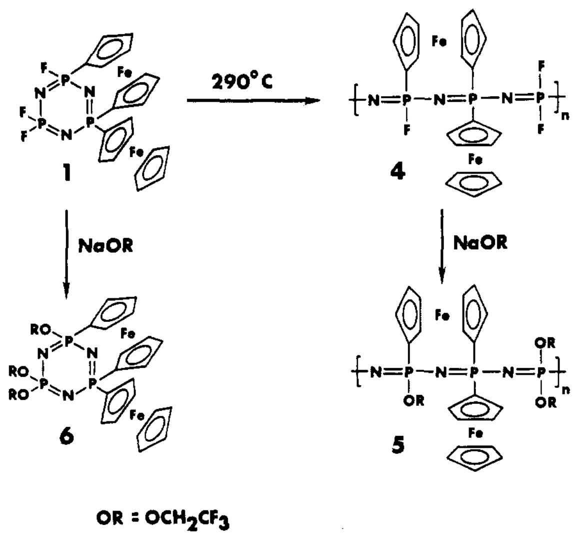
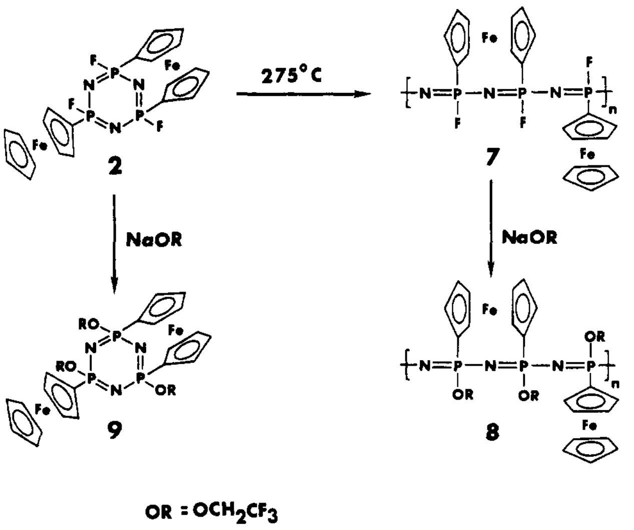
Scheme I



Scheme II

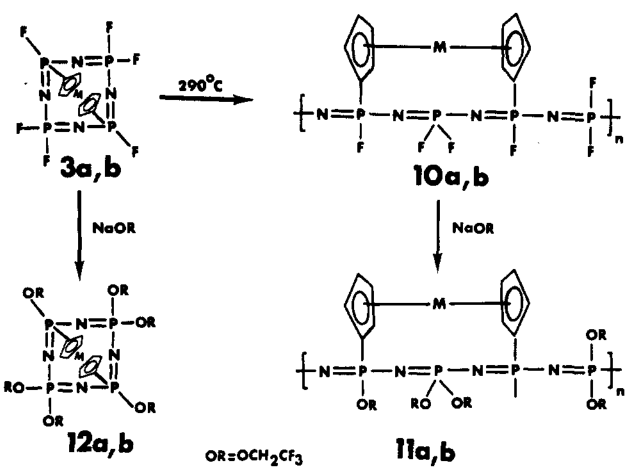


state at 290 °C (Scheme I). Because phosphorus–fluorine bonds are sensitive to hydrolysis in the atmosphere, the fluorine atoms were replaced by treatment with sodium trifluoroethoxide to yield polymer **5**. Similar substitution was performed on trimer **1** to yield trimer **6**, which served as a structural small-molecule model for **5**. Polymer **5** was hydrolytically stable and was soluble in organic solvents such as tetrahydrofuran (THF) or acetone. This property, together with the spectroscopic data (see later), is compatible with an open-chain or macrocyclic phosphazene polymer structure as depicted in **5**. The molecular weight of **5** (by gel permeation chromatography (GPC) analysis) was 2 × 10^4.

A deliberately mixed equimolar mixture of *cis*- and *trans*-**2**[6] polymerized readily when heated in the molten state at 275 °C to give polymer **7**. The product was soluble in organic media. As before, the fluorine atoms were replaced by treatment with sodium trifluoroethoxide to yield polymer **8**. This polymer was also soluble in THF or acetone and was, therefore, not cross-linked. It had a GPC molecular weight average near 2 × 10^4. Trimer **2**, as a model system, was also subjected to the same substitution reactions to yield **9**. These transformations are illustrated in Scheme II. The characterization data for **8** and **9** are reported in the Experimental Section.

The phosphazene cyclic tetramers **3a** and **3b** polymerized when heated in the molten state at 290 °C. Treatment

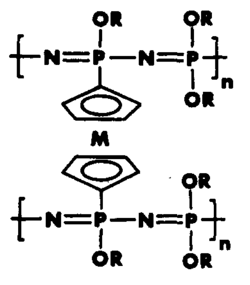
Scheme III



a, M = Fe
b, M = Ru

of the resultant polymers, **10**, with sodium trifluoroethoxide yielded the hydrolytically stable, derivative polymers **11a** and **11b** (Scheme III). Similar reaction of the cyclic tetramers, **3a** and **3b**, with trifluoroethoxide gave the model tetramers **12a** and **12b**. A fraction of polymers **10** and **11** formed a highly swollen gel in THF, but at least 80% of the polymer was soluble and, therefore un-cross-linked.

Cross-linked structures are perhaps more likely for polymers derived from a 1,5-transannular tetramer, such as **3**, if the tetramer can undergo skeletal cleavage at more than one site. This double cleavage could generate structures such as **13**. However, the low cross-link density found suggests that this pathway has a very low probability.



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Structure Determination. The structures of **4**–**12** were determined by a combination of ^1H, ^{31}P, and ^{19}F NMR and infrared spectroscopy and by microanalysis. In addition, mass spectrometric analysis was employed for the small-molecule models. The structures of the initial trimers and tetramers were confirmed earlier[4] by these same methods. The structure of **2** has been determined by single-crystal X-ray diffraction methods,[4] and the ruthenium analogue of **3** was studied by the same technique.[1]

The ^{31}P NMR spectrum of **5** consisted of two broad resonances at 3.0 and −12.8 ppm in a 2:1 integrated intensity ratio, respectively. The resonance at −12.8 ppm was assigned to the $P(OCH_2CF_3)_2$ units by comparison with the similar value (−7.0 ppm) found in the homopolymer $[NP(OCH_2CF_3)_2]_n$ and in a related metallocenylpolyphosphazene prepared previously.[5] The resonance at 3.0 ppm was assigned to an overlap between the $P(Cp)(OCH_2CF_3)$ and $P(Cp)_2$ units. The ^1H NMR spectrum of **5** consisted of a broad multiplet from overlapping resonances of the cyclopentadienyl and methylene protons.

The elemental analysis data for **5** were compatible with the presence of one bridging and one pendent metallocene unit for every three polymer repeating units. Thus, the ratio of repeating units in the cyclic trimer is retained in the polymer. This is an important result from the viewpoint of the reaction mechanism (see later). A gel permeation chromatography analysis showed a narrow molecular weight distribution with a peak maximum at 2×10^4.

For comparison with polymer **5**, it was found that trimer **6** gave a ^{31}P NMR spectrum that consisted of three doublets of doublets assigned to (a) the phosphorus atoms bearing the bridging metallocene unit and the pendent ferrocene unit, (b) the phosphorus atom that bears a cyclopentadienyl and a trifluoroethoxy unit, and (c) the $P(OCH_2CF_3)_2$ unit, in a 1:1:1 integrated ratio. The 200-MHz ^1H NMR spectrum consisted of nine multiplets from the twelve protons of both the bridging and pendent metallocene groups, a multiplet from the methylene protons of the trifluoroethoxy group, and a singlet from the protons of the terminal cyclopentadienyl ring.

Polymer **8** yielded a ^{31}P NMR spectrum that consisted of two broad resonances at 11.0 and 4.0 ppm, with an integrated intensity ratio of 2:1, assigned to the two phosphorus atoms bearing the bridging metallocene unit and the one phosphorus atom bearing the pendent metallocene unit. The ^1H NMR spectrum contained a broad resonance from an overlap of the cyclopentadienyl and methylene protons. The elemental analysis data were compatible with the structure shown for **8**. The molecular weight distribution was broad and extended from 2×10^5 to 5×10^3 with a peak maximum of 2×10^4.

Model trimer **9** gave a ^{31}P NMR spectrum that consisted of two AX_2 spin patterns, each arising from a different geometric isomer. The triplets were assigned to the phosphorus that bears the pendent metallocene, and the doublet was assigned to the phosphorus atoms linked to the transannular metallocene.

Polymer **11a** (M = Fe) yielded a ^1H-decoupled ^{31}P NMR spectrum that consisted of four broad resonances at 14.4, 10.2, −5.7, and −7.8 ppm. Those at 14.4 and 10.2 ppm were assigned to the $P(Cp)(OCH_2CF_3)$ units, while the resonances at −5.7 and −7.8 ppm were attributed to the $P(OCH_2CF_3)_2$ units, as described previously.[2] The peak areas were in a ratio of 1:1 for the $P(OR)_2$:$P(Cp)(OR)$ (OR = OCH_2CF_3). The ^1H NMR spectrum of **11a** consisted of a broad resonance centered at 4.5 ppm assigned to an overlapping resonance from the cyclopentadienyl and trifluoroethoxy protons. The elemental analysis data (Experimental Section) were consistent with a polymer with the same repeating structure as the cyclic tetramer, i.e., with one bridging metallocene per four P═N units. The gel permeation chromatography analysis of the soluble portion of **11a** showed a broad molecular weight distribution with a peak maximum at 2×10^6.

The ruthenocene analogue (**11b**) gave a ^{31}P NMR spectrum similar in appearance to that of **11a**, with resonances centered at 9.3, −1.8, and −8.2 ppm. The resonance at 9.3 ppm was assigned to the metallocenyl–P–OCH_2CF_3 groups, and the resonances at −1.8 and −8.2 ppm were assigned to the $P(OCH_2CF_3)_2$ groups. The peak areas were in a ratio of 1:1 for the $P(OR)_2$=$P(Cp)(OR)$ groups. The 200-MHz ^1H NMR spectrum of **11b** consisted of a broad multiplet at 4.5 ppm assigned to an overlapping resonance between the cyclopentadienyl and trifluoroethoxy protons. The elemental analysis data were again compatible with one bridging metallocene unit for every four P═N units. The soluble portion of **11b** showed a bimodal GPC and molecular weight distribution with peak maxima at 8×10^4 and 3×10^4.

The ^1H-decoupled ^{31}P NMR spectrum of model compound **12a** consisted of two multiplets at 14.58 and −2.33 ppm attributed to the $P(Cp)(OR)$ and $P(OR)_2$ groups in a 1:1 integrated intensity ratio, respectively. The 200-MHz spectra of **12a** and **12b** consisted of three multiplets centered at 4.54 (4 H), 4.35 (4 H), and 4.14 (12 H) for **12a** and at 4.90 (4 H), 4.29 (4 H), and 4.24 (12 H) ppm for **12b**. The resonances at 4.54, 4.35, 4.90, and 4.29 ppm were assigned to the protons of the bridging metallocene units. The resonances at 4.14 and 4.24 ppm were from the trifluoroethoxy protons. Electron impact mass spectra of **12a** and **12b** contained peaks for the expected molecular ions at *m/e* 958 and 1004, respectively.

Influence of Metallocenyl Groups on Polymerization. First, it is clear that the presence of a pendent ferrocenyl group on a cyclic trimeric phosphazene ring, in addition to a transannular ferrocenyl group, does not block the polymerization process. It is not possible to polymerize the compound $N_3P_3F_5C_5H_4FeC_5H_5$, which bears a pendent ferrocenyl unit.[5,7] However, the molecular weights of the polymers derived from **1** and **2** were somewhat lower (2×10^4) than the weights of those derived from $N_3P_3F_4(C_5H_4)_2Fe$ ($>2 \times 10^6$). It is known from earlier work from our laboratory that the polymerization of a phosphazene trimer becomes more difficult and the molecular weights of the polymers decline as increasing numbers of organic groups replace halogen atoms around the ring. The polymerization behavior of **1** and **2** may simply constitute another example of this effect, exacerbated by the steric size of a pendent metallocenyl unit. In this respect, it appeared from the experimental results that the trimer with a geminal pendent group (**1**) required more forcing conditions for polymerization than its counterpart (**2**) with the same group at the nongeminal site.

Second, the cyclic tetrameric fluorophosphazenes (**3a** and **3b**) appear not to undergo a sensitization toward polymerization when a transannular metallocene unit bridges the ring. Cyclic tetrameric phosphazenes are inherently capable of greater angular flexibility than the trimers and are unlikely to incur such serious ring strain penalties as bridged trimers.

Finally, the microanalytical and NMR evidence is compatible with the view that the repeating units present in the cyclic oligomers enter the polymer essentially intact, that certain repeating units are not "extruded" from the system as it polymerizes, and that, by inference, free "monomer" molecules do not play a significant role in the polymerization mechanism.

Experimental Section

Materials. $(NPF_2)_3$, $(NPF_2)_4$, and ruthenocene were prepared by literature procedures.[8,9] Ferrocene (Aldrich), $RuCl_3(III)\cdot 3H_2O$ (Strem), zinc dust (Aldrich), and *n*-butyllithium (Aldrich) (1.55 M solution in hexane) were used as received. Tetrahydrofuran (THF) (VWR) (MCB Reagents) and diethyl ether (Fisher) were dried and distilled over sodium benzophenone ketyl. Tetramethylethylenediamine (TMEDA) was dried over CaH_2 and then over BaO and was finally purified by fractional distillation. Fractions boiling at 120–122 °C were used. Column chromatography was performed with silica gel (230–400 mesh) (VWR) as packing material. All reactions were performed under an atmosphere of dry nitrogen by using standard airlessware (Kontes). The metallocene compounds, *gem*-$N_3P_3F_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}$ (**1**), *non-gem*-$N_3P_3F_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}$ (**2**), and 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2M$ (**3a,b**), were prepared as described previously.[1,4] The metallocene monomers were purified by two recrystallizations (dichloromethane/hexane solutions), followed by four high-vacuum sublimations at 50 °C and 1×10^{-4} Torr before polymerization.

Instrumentation. ^1H, ^{31}P, and ^{19}F NMR spectra were recorded on Varian EM-360 and CFT-20 NMR, JEOL PS-100 and FX 90Q FT NMR, and Bruker WP-200 FT NMR spectrometers. The ^{31}P NMR shifts are relative to aqueous 85% H_3PO_4, with positive shifts downfield from this reference. The ^1H NMR shifts were referenced to internal $CHCl_3$ or acetone. The ^{19}F NMR shifts were referenced to external C_6H_5F in a chloroform or acetone solution. Infrared (KBr disk or NaCl plate) spectra were recorded on a Perkin-Elmer 283B grating spectrometer. Electron impact mass spectral results were obtained by using an AEI MS 950 spectrometer and were tabulated by a linked computer. Approximate molecular weights (M_{GPC}) were determined with the use of a Waters ALC 201 GPC instrument with THF as a solvent and with the use of the Polymer Laboratories Columns (1 cm × 300 cm) (10^6, 10^6, and 10^3 Å) at an elution rate of 1.0 mL/min.

Purification of Trimers and Tetramers. The purity of cyclophosphazenes has a profound influence on their polymerization behavior. Hence, great care was taken to achieve the maximum possible purity and to protect these compounds from contact with atmospheric moisture by the use of Schlenk line and drybox techniques. Compound **1** was purified by two recrystallizations from dichloromethane–hexane mixtures, followed by four high-vacuum sublimations at 80 °C and 1×10^{-4} Torr. Compounds **3a** and **3b** were purified by two recrystallizations from dichloromethane–hexane mixtures, followed by four high-vacuum sublimations at 50 °C and 1×10^{-4} Torr.

Polymerization of 1. A pure sample of **1** (2.0 g, 3.57 mmol) was heated in an evacuated Pyrex glass tube in a thermoregulated oven at 290 °C for 14 h. After 10 h, a gradual increase in viscosity was noted. The contents of the tube, which contained a mixture of **1** and polymer **4**, were dissolved in THF (150 mL). A solution of sodium trifluoroethoxide, prepared from sodium (3.0 g, 130.4 mmol) and trifluoroethanol (20 g, 200 mmol) in THF (100 mL), was added, and the mixture was heated to reflux for 72 h. The polymer was isolated by the addition of a stoichiometric amount of concentrated hydrochloric acid (36.5%, 4.4 g, 120 mmol) to the reaction mixture to neutralize any excess base. The reaction mixture was then poured immediately into distilled water (2 L). The resultant oily precipitate was dissolved in THF (35 mL) and was poured slowly into hexane (2 L). A yellow polymeric material, $[N_3P_3(OCH_2CF_3)_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}]_n$ (**5**) (1.4 g, 50.0%) precipitated. The polymer was purified by further reprecipitations from THF into water (once) and hexane (twice). The hexane solutions were combined, filtered through a layer of silica gel, dried over $MgSO_4$, and finally concentrated to give orange crystals of *gem*-$N_3P_3(OCH_2CF_3)_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}$ (**6**) (0.6 g, 21.4%, mp 55–56 °C).

For **5**: IR 3100 (w, CH), 1220 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.58 (m); ^{31}P NMR 3.0 (m), −12.8 (m) ppm; molecular weight (THF) (M_{GPC}) 2×10^4. Anal. Calcd: C, 38.98; H, 2.89; N, 5.25. Found: C, 36.50; H, 2.69; N, 5.37.

For **6**: IR 2950 (w, CH), 1170 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.93 (m, 1 H), 4.83 (m, 2 H), 4.59 (m, 2 H), 4.55 (m, 2 H), 4.51 (m, 1 H, 4.41 (m, 2 H), 4.35 (m, 1 H), 4.34 (m, 1 H), 4.30 (m, 1 H), 4.17 (m, 6 H), 4.14 (s, 5 H); ^{31}P NMR 39.9 (dd, J_{PNP} = 17.49 Hz), 33.5 (dd, J_{PNP} = 17.35 Hz), 18.2 (dd, J_{PNP} = 35.49 Hz) ppm; ^{19}F NMR 38.9 (s) ppm. MS Calcd for $C_{26}H_{23}N_3F_9Fe_2O_3P_3$: 800.9506. Found: 800.9493 (deviation 1.7 ppm). Anal. Calcd: C, 38.98; H, 2.89; N, 5.25. Found: C, 39.17; H, 3.10; N, 5.29.

Polymerization of 2. A 1:1 mixture of *trans*- and *cis*-**2** (2.0 g, 3.6 mmol) was heated in a Pyrex glass tube in a thermoregulated oven at 275 °C for 3 h. A gradual increase in viscosity was noted after 2 h. The contents of the tube, which contained a mixture of the cyclic trimer and the polymer, were dissolved in THF (150 mL). A solution of sodium trifluoroethoxide, prepared from sodium (3.4 g, 147.8 mmol) and trifluoroethanol (20 g, 200 mmol) in THF (100 mL), was added, and the mixture was heated to reflux for 72 h. The polymer was isolated by the addition of a stoichiometric amount of concentrated hydrochloric acid (36.5%, 14.6 g, 148.0 mmol) to the reaction mixture to neutralize excess base. The reaction mixture was then poured immediately into distilled water (2 L). The resultant oily precipitate was dissolved in THF (35 mL) and poured slowly into hexane (2 L). A yellow polymeric material (**8**) (1.2 g, 41.4%) precipitated. The polymer was purified by further precipitations from THF into water (once) and hexane (twice). The hexane solutions were combined, filtered through a layer of silica gel, dried over $MgSO_4$, and finally concentrated to give an orange oil of *non-gem*-$N_3P_3(OCH_2CF_3)_3\{(\eta\text{-}C_5H_4)_2Fe\}\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}$ (**9**) (1.0 g, 34.5%).

For **8**: IR 2940 (w, CH), 1160 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.6 (m, br); ^{31}P NMR 11.0 (m), 4.0 (m) ppm; molecular weight (M_{GPC}) 2×10^4. Anal. Calcd: C, 38.98; H, 2.89; N, 5.25. Found: C, 38.76; H, 2.55; N, 5.29.

For **9**: IR 3180 (w, CH), 1200 (vs, br, PN) cm^{-1}; ^{31}P NMR 59.0 (t), 40.4 (d, J_{PNP} = 12 Hz), 29.9 (t), 39.1 (d, J_{PNP} = 11 Hz) ppm; ^{19}F NMR 38.2 (s) ppm. MS Calcd for $C_{26}H_{23}N_3F_9Fe_2O_3P_3$: 800.9506. Found: 800.9510 (deviation 0.4 ppm).

Polymerization of 3a. A pure sample of 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$ (**3a**) (2.0 g, 4.18 mmol) polymerized during a 48-h period at 290 °C. The polymerization products consisted of the cyclic tetramer (**3a**) and the polymer (**10a**). The contents of the tube were added to THF (150 mL) and stirred for 24 h. Most (80%) of the material dissolved in THF, but the remainder of the polymer swelled considerably. A solution of sodium trifluoroethoxide, prepared from sodium (2.8 g, 121.7 mmol) and trifluoroethanol (30 g, 300 mmol) in THF (100 mL), was added to the polymer solution, and the mixture was heated to reflux for 72 h. The polymer was isolated by the addition of a stoichiometric amount of concentrated hydrochloric acid (36.5%, 4.8 g, 131.5 mmol) to the reaction mixture to neutralize excess base. The solution was then poured immediately into distilled water (2 L). The resultant oily precipitate was dissolved in THF and added slowly to hexane (2 L). A yellow polymeric material, [1,5-$N_4P_4(OCH_2CF_3)_6(\eta\text{-}C_5H_4)_2Fe]_n$ (**11a**) (1.6 g, 40.0%), was isolated. The polymer was purified by reprecipitations from THF into water (once) and hexane (twice). The hexane solutions were combined, filtered through a layer of silica gel, dried over $MgSO_4$, filtered, and finally concentrated to yield orange crystals of 1,5-$N_4P_4(OCH_2CF_3)_6(\eta\text{-}C_5H_4)_2Fe$ (**12a**) (1.2 g, 30.0%, mp 105–106 °C).

For **11a**: IR 2950 (w, CH), 1170 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.5 (br, m); ^{31}P NMR 14.4 (m), 10.2 (m), −5.7 (m), −7.8 (m) ppm; molecular weight (THF) (M_{GPC}) 2×10^6. Anal. Calcd: C, 27.58; H, 2.10; N, 5.85. Found: C, 27.28; H, 2.25; N, 6.02.

For **12a**: IR 2950 (w, CH), 1170 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.35 (m, 4H), 4.34 (m, 4 H), 4.14 (m, 12 H); ^{31}P NMR 14.58 (m), −2.33 (m) ppm; ^{19}F NMR 38.5 (s) ppm. MS Calcd for $C_{22}H_{20}N_4F_{18}FeO_6P_4$: 958. Found: 958. Anal. Calcd: C, 27.58; H, 2.10; N, 5.85. Found: C, 27.73; H, 2.14; N, 6.11.

Polymerization of 3b. This polymerization was carried out in a manner identical with that described above except that a 17-h polymerization time was employed. The polymerization products, which consisted of a mixture of the unchanged cyclic tetramer and polymer **10b**, were added to THF (150 mL) and stirred for 24 h. Only a portion (80%) of the material was soluble in THF, but the remainder of this material swelled considerably in THF. This mixture was allowed to react as before with a solution of sodium trifluoroethoxide, prepared from sodium (2.7 g, 117.4 mmol) and trifluoroethanol (30 g, 300 mmol) in THF (150 mL). The trifluoroethoxy-substituted phosphazenes **11a** and **12a** were isolated as described above after neutralization with concentrated hydrochloric acid (36.5%, 11.5 g, 315.2 mmol). The polymer, [1,5-$N_4P_4(OCH_2CF_3)_6(\eta\text{-}C_5H_4)_2Ru]_n$ (**11b**) (1.2 g, 31.6%), and pale yellow crystals of 1,5-$N_4P_4(OCH_2CF_3)_6(\eta\text{-}C_5H_4)_2Ru$ (**12b**) (0.8 g, 21.1%, mp 108–109 °C) were obtained.

For **11b**: IR 2960 (w, CH), 1170 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.5 (m, br); ^{31}P NMR 9.3 (m), −1.8 (m), −8.2 (m) ppm; ^{19}F NMR: 38.71 (s) ppm; molecular weight (THF) (M_{GPC}) 2×10^4. Anal. Calcd: C, 26.34; H, 2.01; N, 5.58. Found: C, 24.91; H, 1.98; N, 5.74.

For **12b**: IR 2960 (w, CH), 1170 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.90 (m, 4 H), 4.29 (m, 4 H), 4.24 (m, 12 H); ^{19}F NMR 38.5 (s) ppm. MS calcd for $C_{22}H_{20}N_4F_{18}RuO_6P_4$: 1004. Found: 1004. Anal. Calcd: C, 26.34; H, 2.01; N, 5.58. Found: C, 26.57; H, 2.10; N, 5.70.

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Polymerization of 1-(Trimethylstannyl)alkyl Methacrylates: A New Class of Organotin Polymers and a Novel Case of Degradative Chain Transfer to Polymer

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ABSTRACT: The synthesis of poly[1-(trimethylstannyl)alkyl methacrylates], a new class of organotin polymers, is reported. The trimethyltin group is substituted on C-1 of the ester side chain, differing from conventional stannyl methacrylates where the tin is bonded directly to oxygen. The monomer synthesis was carried out by condensation of lithium trimethylstannate with a carbonyl compound, followed by esterification with methacryloyl chloride. Both homopolymers and MMA copolymers were prepared by radical polymerization. A reactivity ratio study showed copolymerization was perfectly random. A novel degradative chain transfer to polymer process was observed in the polymerization of monomers containing a secondary or benzylic hydrogen α to the trimethyltin group. The proposed mechanism involves a 5-membered cyclic transition state. The effect was most dramatic with tin substituted on a benzyl side chain, and the deuterium isotope effect for the polymerization of this monomer was determined to be 2.4. The effect of the trimethyltin group on the glass transition temperatures and the thermal stability of these materials is reported.

Introduction

Organotin polymers have been shown to be useful imaging materials for microlithography. For example, poly[(trimethylstannyl)styrene] is sensitive to electron beam radiation and also resistant to both oxygen- and fluorocarbon-based plasma degradation.[1,2] This combination of lithographic properties is not found in typical organic resist materials and is a consequence of the tin incorporated in the polymer.

Our recent work has focused on the synthesis of new organotin polymers for study as lithographic materials. We felt the area was ripe for the discovery of interesting new polymers, since research on organotin polymers has not kept pace with the use of organotin compounds as synthetic reagents.[3,4] Although several papers concerning organotin polymers have been published recently, they describe studies of well-known classes of organotin polymers and copolymers, including poly(stannylstyrenes)[5] and poly(stannyl methacrylates).[6] Utilization of current tin chemistry can potentially afford new organotin polymers with structural features that should impart both interesting polymer properties and the desired radiation sensitivity.

We chose to pursue organotin polymers that should degrade on irradiation, rather than cross-link, potentially functioning as positive tone resist materials. One approach to the design of an organotin polymer displaying this radiation chemistry is to incorporate tin pendent to a methacrylate polymer, since methacrylate-based polymers are well-known to undergo backbone scission upon irradiation and function as positive resist materials.[7] The materials we chose to prepare were homopolymers and copolymers of 1-(trimethylstannyl)alkyl methacrylates (1). This is a new class of methacrylate polymers where a trimethyltin group is substituted on the 1-position of the ester side chain, in contrast to conventional organotin methacrylates where tin is bonded directly to oxygen.[8] This paper will discuss the synthesis and characterization of these materials, as well as a unique degradative chain transfer to polymer process that occurs in the polymerization. The lithographic properties of homopolymers and methyl methacrylate copolymers of 1 have been published elsewhere.[2]

Experimental Section

Tetrahydrofuran (THF) and toluene were freshly distilled under nitrogen from sodium–benzophenone prior to use. Chloroform was purified by passage through basic alumina. Synthetic reactions were carried out under an argon atmosphere. Methyl methacrylate (MMA) was distilled from CaH_2 and stored at −10 °C. The petroleum ether utilized had a boiling point range of 35–60 °C. The α-deuteriobenzaldehyde was commercially available from Merck, Sharp, and Dohme, Isotope Division. Preparative HPLC was carried out on a Waters Prep 500 with silica gel columns.

(Trimethylstannyl)methyl Methacrylate (1a). Lithium trimethylstannate was prepared from 15 g (0.075 mol) of trimethyltin chloride and 2.5 g (0.36 mol) of lithium wire in 80 mL of THF.[9] The lithium trimethylstannate solution was cannula transferred to a 250-mL round-bottom flask and treated with 2.75 g (0.092 mol) of paraformaldehyde. The reaction was stirred 2.5 h at room temperature, quenched with 30 mL of half-saturated aqueous ammonium chloride, and then partitioned between petroleum ether and water. The organic layer was separated, washed with brine, and then dried (Na_2SO_4). Removal of the drying agent and solvents afforded 11 g of crude (hydroxymethyl)trimethylstannane as a colorless cloudy liquid. A solution of 8.4 mL (9.0 g, 0.086 mol) of methacryloyl chloride in 15 mL of chloroform was slowly added to a solution of the (hydroxymethyl)trimethylstannane, 3.7 g (0.030 mol) of (dimethylamino)pyridine (DMAP), and 30 mL of diisopropylethylamine in 40 mL of chloroform at room temperature. After stirring an hour, the reaction mixture was partitioned between petroleum ether and 0.5 N HCl and separated, and the organic layer was washed successively with 0.5 N HCl, water, aqueous sodium bicarbonate, and brine and

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