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Polymer Morphology of Poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$

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ABSTRACT: Poly[bis(trifluoroethoxy)phosphazene] (III) was prepared from poly(dichlorophosphazene) (II) and sodium trifluoroethoxide. The polymer morphology was varied as a function of the reaction time. The changes in the polymer morphology were studied with differential scanning calorimetry (DSC) and optical microscopy. Morphology differences were obtained on films cast from tetrahydrofuran (THF) solution. Depending on the reaction time, the level of crystallinity and the transition temperatures differed, including glass transition temperature (T_g), endothermic transition ($T(1)$), and melting temperature (T_m). The spherulitic films were elastomeric, but changed to brittle rodlike crystallites after heating through the melting temperature and cooling. Longer reaction times reduced the level of crystallinity more than could be achieved through rapid cooling. The changes were the result of attack by excess nucleophile on the fully substituted polymer chain. Thus, amorphous materials and materials with low levels of crystallinity could be prepared by adding sodium trifluoroethoxide to the highly crystalline form of III. This secondary reaction was modeled by using the cyclic trimer molecule hexakis(trifluoroethoxy)phosphazene (IV), where cleavage of the side group by excess alkoxide was observed.

Introduction

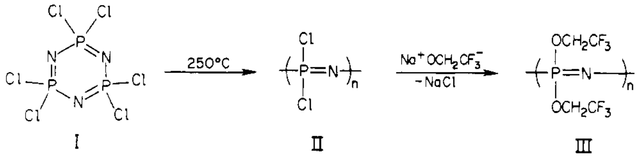
The synthesis of high-molecular-weight organophosphazenes that are technologically useful was developed by Allcock et al.[1,2] This synthesis is summarized in Scheme I.

The method makes use of the observation that soluble poly(dichlorophosphazene) (II) can be fully derivatized with sodium trifluoroethoxide. The macromolecule poly[bis(trifluoroethoxy)phosphazene] (III) has a low glass transition temperature (T_g) and remains flexible from this temperature up to its melting point at 240 °C. Solutions of III can be used to cast colorless, opalescent films that are highly water repellent, due to the fluorinated side groups.[2]

The tendency of III to undergo a crystalline transformation from spherulitic to rodlike crystalline domains has been well documented.[3-8] The changes were observed when a solvent-cast (spherulitic) sample was heated through its melting point and allowed to cool to form rodlike domains. The thermal history of the polymer is important in controlling these transformations, which have been studied by a number of techniques, including DSC, X-ray diffraction (XRD), and optical microscopy.

In this paper, we report that changes in the reaction conditions during the synthesis of III resulted in materials with different polymer morphologies.[9] Specifically, the thermal properties were found to be highly dependent on the length of the reaction time between the phosphazene polymer and the trifluoroethoxy nucleophile if excess nucleophile was employed in the synthesis. The substitution of chlorine atoms on II with sodium trifluoroethoxide was rapid and efficient. We show in this work that excess nucleophile will attack the trifluoroethoxy moieties and result in the introduction of altered side groups. The greater the introduction of the altered substituent (a copolymer is formed), the more the properties of the polymer varied from those reported in the literature.[1,2] The changes in properties were measured with differential scanning calorimetry (DSC) and optical microscopy and included differences in the melting points and the amount of crystallinity of the polymer. On the other hand, chemical differences in III from one preparation to another were hard to detect spectroscopically or with chemical analysis. Thus, the attack of the excess nucleophile on the substituted polymer III must be slow.

Scheme I



The cyclic trimer hexakis(trifluoroethoxy)cyclotriphosphazene (IV) was used as a small-molecule model compound to study the reaction of sodium trifluoroethoxide on the high polymer III. The cyclic IV was synthesized from the chlorocyclic, as outlined in Scheme II.

The products of the reaction of trifluoroethoxide with both III and IV were observed spectroscopically by ^{31}P nuclear magnetic resonance (NMR). A spectrum was obtained that is consistent with a monohydroxycyclic phosphazene (V) as a result of side-group cleavage from IV. A similar mechanism is thought to be operating in the polymer reactions resulting in the observed changes in the physical properties of III.

Experimental Section

A sample of III was received from Dr. R. E. Singler at the Army Materials and Mechanics Research Center (AMMRC) in Watertown, MA. Hexachlorocyclotriphosphazene (I) (>99% purity) was obtained from Tracon Industries Corp., Melville, NY, and purified as described below. Trifluoroethanol (Kodak Laboratory Chemicals, Rochester, NY, and Halocarbon Products, Hackensack, NJ) was refluxed over calcium oxide and distilled. Sodium spheres (MC/B Reagents, Gibbstown, NJ), sodium hydride (50% in oil) (J. T. Baker Chemical Co., Phillipsburg, NJ), and triphenylsilanol (Aldrich Chemical Co., Milwaukee, WI) were used as received. All other chemicals were obtained from Kodak Laboratory Chemicals. Tetrahydrofuran (THF) was refluxed over sodium benzophenone and distilled. Toluene was refluxed over calcium hydride and distilled. All manipulations were made with the sample under an argon atmosphere using standard airless techniques. The ^{31}P NMR spectra were obtained either at 80 MHz on a Nicolet NT 200 wide-bore multinuclear spectrometer in 12-mm-o.d. tubes or on a Varian XL-300 multinuclear spec-

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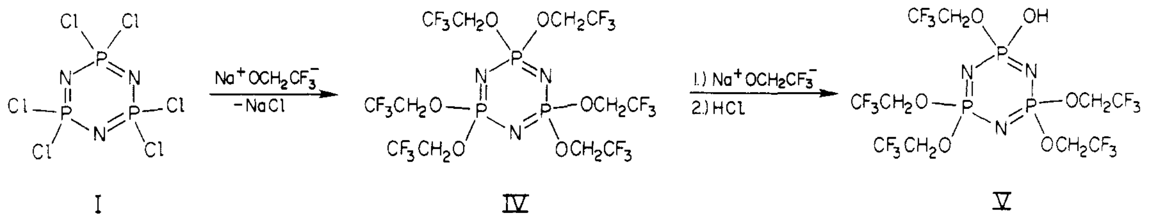
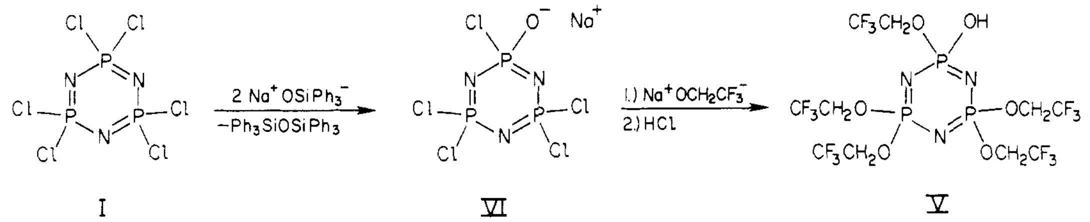
Scheme II



Scheme III



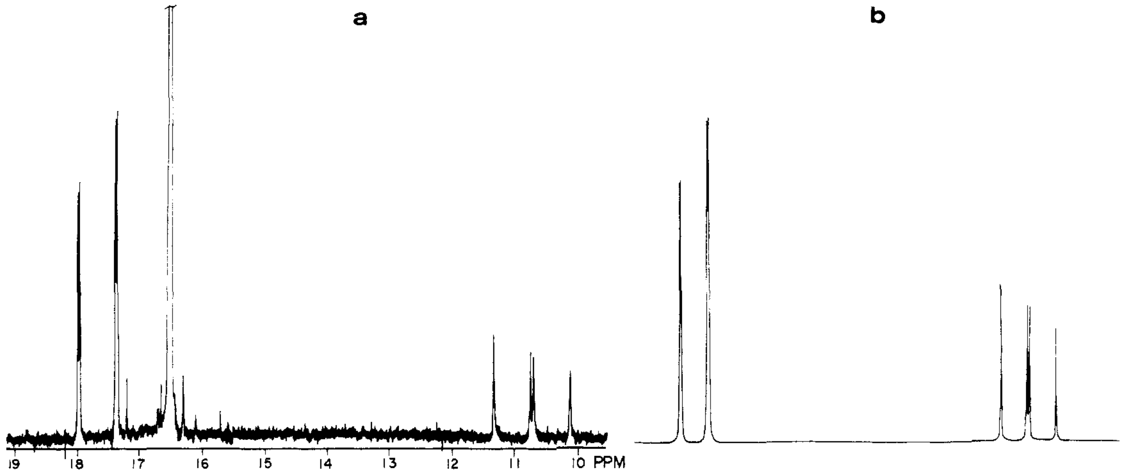


Figure 1. (a) ^{31}P NMR (^1H decoupled) in $CDCl_3$ of the reaction products from IV with sodium trifluoroethoxide. The AB_2 spin pattern was assigned to V and the singlet at 16.5 ppm was assigned to the starting material IV. (b) Computer simulation of the AB_2 spin system obtained by setting ν_A = 10.7 ppm, ν_B = 17.7 ppm, and J_{AB} = 70.6 Hz.

trometer at 121 MHz in 5-mm-o.d. tubes. All chemical shifts were referenced to 80% H_3PO_4 at 0 ppm. Following the IUPAC convention, downfield shifts are reported as positive. Spectrum simulation was carried out with the noniterative NMCSIM software on the Nicolet 1280 computer. Field desorption mass spectrometry was performed on a Varian-MAT 731 mass spectrometer.

Hexakis(trifluoroethoxy)cyclotriphosphazene, $[NP(OCH_2CF_3)_2]_3$ (IV). This compound was prepared as described previously[10,11] from hexachlorocyclotriphosphazene (80 g, 0.23 mol) dissolved in THF (500 mL) and sodium trifluoroethoxide. The alkoxide solution was prepared from sodium (45 g, 2.0 mol) and trifluoroethanol (180 mL, 2.3 mol) in THF (1 L). Final purification was accomplished by vacuum sublimation at 100 °C (0.4 Torr) to yield a white, crystalline solid, mp 49–51 °C; isolated yield 81%.

Reaction of $NaOCH_2CF_3$ with $[NP(OCH_2CF_3)_2]_3$ (IV). A solution of IV (5.0 g, 6.9 mmol) in THF (50 mL) was added rapidly to a stirred solution of sodium trifluoroethoxide, prepared from sodium (2.0 g, 0.087 mol) and trifluoroethanol (21 g, 0.21 mol) in THF (200 mL). The reaction mixture was stirred at room temperature for 72 h and then refluxed for 48 h. The reaction mixture was neutralized with 5% HCl followed by treatment with $NaHCO_3$. The resulting mixture separated into two layers, and the top layer was removed and dried under vacuum to yield a low-melting solid. A proton-decoupled ^{31}P NMR spectrum at 121.421 MHz showed an AB_2 spin pattern in addition to the major peak for the starting trimer IV (Figure 1). This pattern accounted for ~1% of the peak area, as compared to the singlet. The ^{31}P NMR spectrum was successfully simulated with the AB_2 parameters: ν_A = 10.7 ppm; ν_B = 17.7 ppm; J_{AB} = 70.6 Hz. The pattern was assigned to the monohydroxycyclic phosphazene $[N_3P_3(OCH_2CF_3)_5OH]$, which is V. ^{19}F NMR spectra of the reaction mixture showed no evidence of olefinic side groups, in contrast to the *n*-butyllithium reactions.[12]

Alternative Preparation of Compound V Using $NaOSi(C_6H_5)_3$ (Scheme III). This procedure is a modification of the synthesis by Allcock and Fuller.[13] A solution of triphenylsiloxide, prepared from triphenylsilanol (7.9 g, 28 mmol) and sodium hydride (2.7 g, 56 mmol), was filtered through a glass frit and added slowly to a solution of hexachlorocyclotriphosphazene (5.06 g, 14.4 mmol). A precipitate formed and was allowed to settle overnight. The soluble reaction products were transferred to another flask and cooled to 0 °C, and sodium trifluoroethoxide was added to the reaction. This alkoxide solution was prepared from sodium hydride (4.05 g, 86.1 mmol) and trifluoroethanol (18 mL) and was filtered through a glass frit. The reaction mixture was stirred for 1 h, and the solvent was removed on a rotary evaporator. A proton-decoupled ^{31}P NMR spectrum in THF of the crude reaction mixture showed an AB_2 spin pattern identical with the pattern obtained from the reaction of IV with trifluoroethoxide. Acidification of the sodium salt to form V resulted in the same AB_2 spin pattern as was observed with the proton-decoupled ^{31}P NMR of V shown in Figure 1. Thus the addition of HCl to form the hydroxy compound had little effect on the ^{31}P NMR spectrum. Further evidence for the formation of V was obtained by field desorption mass spectrometry, which gave a molecular ion at 647 amu.

Polymerization of $(NPCl_2)_3$ (I).[1] The starting material $(NPCl_2)_3$ was purified by recrystallization from hexane and sublimation at 50 °C. Polymerization of $(NPCl_2)_3$ was carried out in sealed Pyrex glass tubes 23 × 3.5 cm (200-g scale). The tubes were evacuated on a vacuum line for 30 min before they were sealed. The sealed tubes were rotated 360° in a Precision

Table I
Chemical Analysis of III (%)

	N	C	H	P	F	Cl
IIIAA	5.7	20.0	1.7	13.0	45.0	<0.3
IIIA	5.8	19.8	1.7	13.1	45.0	<0.3
IIIB	5.7	19.6	1.7	12.6	45.7	<0.3
IIIC	5.7	20.1	1.7	12.9	43.2	<0.3
IIID	5.8	19.8	1.6	13.3	46.7	<0.3
IIIE	6.0	19.7	1.7	12.4	43.7	<0.3
calcd	5.8	19.8	1.7	12.7	46.9	0

Scientific oven at 250 °C until the contents became viscous, ~24 h. After the tubes had cooled to room temperature, they were placed in a glovebag filled with argon and opened, and the contents were placed in a sublimator. The bulk of the starting trimer was removed from the polymer during the sublimation (50 °C, 16 h). The remaining polymer was a highly elastomeric white material that formed clear, viscous solutions in THF and toluene. In general, the ^{31}P NMR of II dissolved in THF showed a large singlet at −17 ppm, assigned to the polymer, and often a small singlet at +19 ppm, assigned to residual cyclic trimer. (In all cases, the cyclics were removed during the isolation of III by precipitation from acetone into toluene as evidenced by ^{31}P NMR spectroscopy.)

Polymer Synthesis. The sample of III provided by Dr. R. E. Singler was labeled AMMRC and used as a standard for comparison with the polymers synthesized in this laboratory. The polymers of III (described below) were prepared following the procedure described by Allcock et al.[1] Each preparation differed by the amount of time the sodium trifluoroethoxide was allowed to react with the poly(dichlorophosphazene) (II). This period of time is referred to as the "reaction time". An excess in the nucleophile concentration (often 50%) was used to ensure complete chlorine substitution on the polymer backbone. Other variables included separate polymerization of hexachlorocyclotriphosphazene (I) for most reactions, different concentrations of the reactants and products, different reaction temperatures (IIIA was cooled in an ice bath, and IIIE was refluxed in THF/toluene mixture), and differences in the reaction solvents. These differences were minimized in IIIB and IIIC where the reaction was divided in half. Chemical analysis data of IIIAA–IIIE are given in Table I.

Polymer IIIAA. A solution of poly(dichlorophosphazene) (II) (12.5 g, 0.11 mol) in THF (250 mL) was added over 30 min to a stirred solution of sodium trifluoroethoxide cooled in an ice bath. The alkoxide solution was prepared from sodium hydride (14.5 g, 0.30 mol) and trifluoroethanol (50 mL, 0.5 mol) in THF (200 mL) and was filtered through a glass frit. The reaction mixture was stirred for 30 min and precipitated into large volumes of water (6 × 3 L). The crude material was dissolved in acetone, precipitated into water (2×) to remove additional salts, and precipitated into toluene (2×) to remove oligomers.

Polymer IIIA. A solution of poly(dichlorophosphazene) (II) (30.6 g, 0.26 mol) in THF (600 mL) was added over 30 min to a stirred solution of sodium trifluoroethoxide cooled in an ice bath. The alkoxide solution was prepared from sodium (18.0 g, 0.78 mol) and trifluoroethanol (120 g, 1.2 mol) in THF (600 mL). The reaction mixture was stirred for 2.5 h and precipitated into large volumes of water (8 × 4 L). The crude material was dissolved in acetone, precipitated into water (2×) to remove additional salts, and precipitated into toluene (2×) to remove oligomers.

Reaction of $NaOCH_2CF_3$ with $[NP(OCH_2CF_3)_2]_n$ (IIIA). A solution of sodium trifluoroethoxide was added over 30 min to a stirred solution of polymer IIIA (5.0 g, 0.021 mol) in THF (300 mL). The alkoxide was prepared from sodium (2.0 g, 0.087 mol) and trifluoroethanol (14 g, 0.14 mol) in THF (200 mL). The reaction was stirred at room temperature for 119 h and precipitated into large volumes of water (2 × 4 L). No qualitative change in the material was observed.

Polymer IIIB. This procedure differed from that for IIIA in that any remaining cyclic trimer (I) not removed by sublimation was solvent extracted from the poly(dichlorophosphazene) (II). (This additional step was performed because the large quantity of II used in this reaction made sublimation to remove I less efficient. This reaction was carried out on a larger scale to facilitate dividing the reaction in half to form IIIC.) THF (50 mL) was added to II (70.7 g, 0.61 mol) and decanted off. The solvent was evaporated to yield 8.1 g of a crystalline product (mp 112 °C). II was dissolved in THF (800 mL) and added over a 2-h period to a stirred solution of sodium trifluoroethoxide. The alkoxide solution was prepared from sodium (42 g, 1.8 mol) and trifluoroethanol (260 g, 2.6 mol) in THF (600 mL). The reaction was stirred at room temperature for 8 h, after which half of the reaction mixture was precipitated into water as described in IIIA.

Polymer IIIC. The remainder of the reaction mixture from IIIB was allowed to stir at room temperature for an additional 11 h before it was precipitated into water. Additional precipitations were carried out as for IIIA.

Polymer IIID. A solution of poly(dichlorophosphazene) (II) (54.6 g, 0.47 mol) in THF (600 mL) was added over a 30-min period to a stirred solution of sodium trifluoroethoxide. The alkoxide solution was prepared from sodium (43 g, 1.9 mol) and trifluoroethanol (210 g, 2.1 mol) in THF (600 mL). Additional THF (600 mL) was added and the reaction mixture was stirred for 120 h. The polymer was precipitated into water, followed by additional precipitations as described in IIIA.

Polymer IIIE. A solution of poly(dichlorophosphazene) (II) (55 g, 0.47 mol) in toluene (600 mL) was added over 2 h to a stirred solution of sodium trifluoroethoxide, prepared from sodium (33 g, 1.4 mol) and trifluoroethanol (150 g, 1.5 mol) in THF (600 mL). The polymer precipitated from solution during the addition. The reaction mixture was stirred at reflux for 72 h and then at room temperature for 7 days. An additional 600 mL of THF was added to the reaction mixture to dissolve the polymer. Additional sodium trifluoroethoxide, prepared from sodium (3 g, 0.13 mol) and trifluoroethanol (35 mL, 0.35 mol) in THF (600 mL), was added to ensure complete chlorine replacement by the alkoxide on the polymer backbone. The reaction mixture was heated at reflux for an additional 48 h, cooled to room temperature, and precipitated into large volumes of water (6 × 4 L). Additional salts were removed by dissolving the crude material in acetone to give a viscous solution, and the polymer was precipitated for a second time into water. The white solid (55 g) was collected, dissolved in THF, precipitated into toluene to remove oligomers, dissolved again in THF, centrifuged at 2100 rpm for 6 h, and precipitated for the final time into toluene.

Polymer Characterization. The thermal properties of III were analyzed on a Du Pont 990 thermal analyzer equipped with a 910 differential scanning calorimeter cell. Three cooling cycles were carried out on each sample with the sample under a nitrogen atmosphere. In the first cycle, liquid nitrogen was poured onto the sample pan to cool the sample (~10 mg) to −100 °C, after which the sample was heated at 10 °C/min up to 260 °C. In the second cycle, the sample was quick-cooled (quenched) from above the melting point to −100 °C by pouring liquid nitrogen onto the sample pan followed by heating a second time through the melting temperature. Finally, the sample was allowed to cool slowly (overnight) to room temperature in the DSC cell before it was cooled to −100 °C. The heating scan was then carried out for a third time. In addiiton to these three cycles, annealing experiments were carried out on some of the samples. These experiments involved maintaining the sample temperature at 100 °C for 1 h before the sample was cooled to −100 °C and heated again. The annealing cycles were repeated several times for some samples.

Optical micrographs were obtained on an Olympus Vanox polarizing microscope equipped with a Mettler FP52 variable-temperature sample holder and a Mettler FP5 controller. Films for microscopy were prepared from solutions of III (200 mg/5.0 mL of THF), dropped onto glass microscope slides with a pipet, and allowed to evaporate slowly. Gel permeation chromatography (GPC) measurements were made with a Waters Associates instrument. THF was employed as a solvent at a flow rate of 1.0 mL/min with sample injected at a concentration of 0.3 wt vol %. A refractive index detector was used. Appropriate calibration of the columns was accomplished by means of narrow-molecular-weight polystyrene standards obtained from Pressure Chemical Co. Infrared spectra were obtained on a Nicolet 7000 Fourier transform infrared spectrometer with the samples cast as film onto salt plates.

Results and Discussion

The polymers of III were all similar in appearance. They were white, semicrystalline solids that were soluble in THF

Table II
Thermal Properties of III from DSC

	spherulites				rods (quick-cooled)				rods (slow-cooled)				
sample	T_g, °C	$T(1)$, °C	ΔH, cal/g	T_m, °C	$T(1)$, °C	ΔH, cal/g	T_m, °C	ΔH, cal/g	$T(1)$, °C	ΔH, cal/g	T_m, °C	ΔH, cal/g	reaction time, h
AMMRC		77	3.4	246	94	9.3	247	0.9					
IIIAA	−57	71	3.5	247	87	7.6	247	0.7	90	7.1	250	0.6	0.5
IIIA	−57	71	~3		87	6.1	244	0.5	88	6.7	246	0.5	2.5
IIIB	−56	70	~3		74	3.6	222	0.4	77	4.4	223	0.4	9
IIIC	−55	65	~3		64	2.8	197	0.3	68	3.9	197	0.3	21
IIID	−52	66	~3		59	2.3	180		64	3.4	179		120
IIIE	−51	59	~3		47	0.5	149		53, 58	1.8	150		336

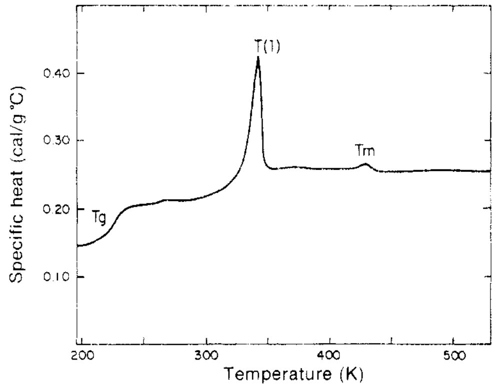


Figure 2. DSC thermogram of IIIE. This is representative of the thermograms of III.

and acetone. They formed tough, flexible films when cast from these solvents. Elemental analyses of these samples were consistent with the calculated values (Table I). However, large differences in the levels of crystallinity were observed with DSC and optical microscopy. ^{31}P NMR spectroscopy also revealed minor differences in the samples. Initial polymer solution characterization was complicated by shear dependence of dilute solution viscosities and the ultrahigh molecular weight of the samples. An anomalous solution viscosity has also been observed by other workers.[14] Because of differences in the characterization data of samples prepared in this laboratory with the data in the literature, a sample of III was obtained from AMMRC for use as a reference for comparison with polymers IIIAA–IIIE. The AMMRC sample has been well characterized and is believed to have high viscosity ($[\eta] \geq 1$ dL/g in THF), high molecular weight with $M_w > 6 \times 10^5$, and a very broad molecular-weight distribution of >10.[15]

Molecular-weight data obtained by GPC showed all of the samples prepared in this laboratory to be $>1 \times 10^6$. These data, along with viscosity, light scattering, and vibrational spectroscopy, will be the subject of a later manuscript.

Thermal Properties. The thermal properties of III have been studied previously.[1-8] Three distinct features were reported in the DSC thermogram of III: a glass transition temperature (T_g) at −66 °C, a melting temperature (T_m) at 240 °C, and a much larger endothermic transition ($T(1)$) that falls between 60 and 90 °C. $T(1)$ has been identified as a transition from a crystalline to a mesomorphic state, and T_m is the true melting point (transition to isotropic liquid) of the polymer.[4] These features were all observed in the DSC thermogram of the AMMRC sample.

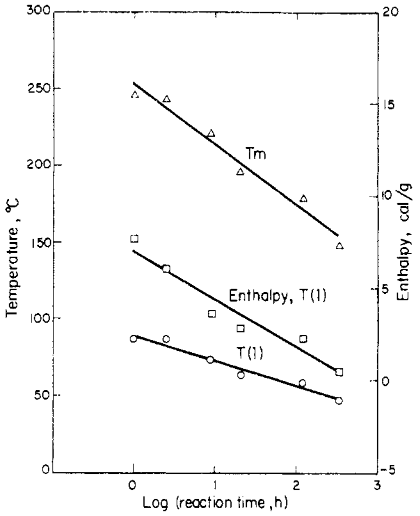


Figure 3. Plots of log (reaction time) vs. temperature and enthalpy. Data were obtained on the quick-cooled, rodlike samples.

The DSC thermogram obtained for sample IIIE (Figure 2) is representative of all of the thermograms of III. The thermal properties of polymers IIIAA–IIIE prepared in this laboratory varied from those of the AMMRC sample to different degrees. Although the same features were observed, $T(1)$ and T_m varied from sample to sample in both the size of the endotherms and the temperatures at which they were observed (Table II). We found the values for $T(1)$ and T_m were dependent not only on the thermal history of the polymer but also on the reaction time of the chloro polymer II for synthesis of the fluorinated polymers of III (see Experimental Section). Thus, IIIAA was exposed to the trifluoroethoxy base for 0.5 h, while each of the other samples were allowed to react for longer times.

The results of the prolonged reaction time on the polymer physical properties are shown graphically in Figure 3. Several trends resulting from increased reaction time were evident from the data in Table II. For the series of polymers from IIIAA to IIIE, T_m was lowered by 100 °C, $T(1)$ was lowered by 45 °C, and the magnitude (ΔH) of both T_m and $T(1)$ decreased. In addition, the percent crystallinity of the polymers decreased as is evident by the increased size of the T_g transition (ΔC_p). Each of these trends is discussed below.

T_m. The T_m's of polymers IIIAA–IIIE are given in Table II, along with the T_m value obtained from the AMMRC sample, which was used as a standard for comparison. The reaction time in hours is also given in Table II. The T_m's of IIIAA and the AMMRC sample are the same (247 °C). The T_m's for the other samples of III decreased significantly with increasing reaction time. A linear correlation was obtained when T_m was plotted against the logarithm of the reaction time (Figure 3). Thus, the polymer T_m decreased from 247 to 149 °C as the reaction time was increased from 0.5 to 336 h. Other variables such as differences in the temperature of the reaction mixture and the reaction solvent polarity did not appear to play as important a role as the reaction time.

Because there are many variables that could not be controlled from one synthesis to the next, materials IIIB and IIIC were isolated from the same reaction pot. This procedure eliminated variables such as differences in the polymeric intermediate II, changes in reaction temperature due to the exotherm of the substitution reaction, and differences in the concentrations of the reactants. Table II shows a decrease in T_m of >25 °C, which resulted from an increase in the reaction time from 9 to 21 h.

The DSC data also showed that the T_m endotherm was progressively less well-defined and the transition occurred over a broader temperature range as the T_m decreased. A consequence of this observation is that the T_m's of IIIAA and the AMMRC sample have similar values (ΔH = 0.7 and 0.9, cal/g, respectively), but the values decreased until, in IIIE, the transition was too broad to measure. Thus, the T_m's of the latter materials were lower and the transition was less well-defined than reported in the literature.[1-8]

***T*(1).** The $T(1)$ has been attributed to a transition from a crystalline to a mesomorphic state.[4] The temperature and size of the transition for IIIAA–IIIE were dependent on both the length of the reaction time and the thermal history of the sample. The $T(1)$ values for IIIAA and the AMMRC sample were not significantly different, while the value of IIIE was 47 °C lower for the quick-cooled samples (Table II). All of the DSC thermograms were obtained in the same manner in order to eliminate the effect of the thermal history on the $T(1)$ value. As with T_m, a linear correlation was obtained when $T(1)$ was plotted against the logarithm of the reaction time (Figure 3).

The magnitude of the endothermic transition at $T(1)$ was obtained from the value $\Delta H(T(1))$, the heat of fusion. The heat of fusion decreased as a function of the reaction time (Figure 3). This relationship indicated that longer reaction times increased the amorphous content of the polymers (i.e., the materials became progressively less crystalline). The amount of crystallinity in the material was also a function of whether the sample was quick-cooled (quenched) or slow-cooled. As anticipated, the slow-cool process allowed the crystallites more time to form.

Using the technique described above, it was possible to remove most of the crystallinity from fluorophosphazene IIIE. The long reaction time used in the preparation of IIIE resulted in a material with a low degree of crystallinity (ΔH = 1.8 cal/g after slow cool). It was found that almost all of the crystallinity could be removed from the material by quick-cooling from 180 °C, which was 30 °C above the T_m. However, the crystalline domains of the polymers were re-formed by allowing the material to slow-cool from 180 °C. In contrast, IIIAA–IIID could not be quick-cooled into an amorphous conformation.

T_g. The T_g's of all the samples of III were between −50 and −60 °C. The magnitude of the specific heat change at T_g was dependent on both the substitution time and the sample history. In general, ΔC_p is a measure of the amorphous content of the material. Although this quantity was not measured directly, it was implied from a comparison reaction time. This was consistent with the explanation that the increased reaction time resulted in a more amorphous polymer.

Optical Micrographs. Crystallinity in a polymer film can often be observed under polarizing light. It is known that films of III cast from solution form spherulites, and heating above 250 °C causes the spherulites to melt into an amorphous liquid, which form crystalline rods upon cooling.[4,8] These structures were present in all of the samples discussed above. Films of IIIAA, IIIa, and the AMMRC samples appeared identical under the microscope, the spherulites measuring ~40 μm in diameter. The spherulites of IIIC were smaller, measuring 25 μm. The structure of IIIE was the least well-defined and measured only 20 μm across the spherulite.

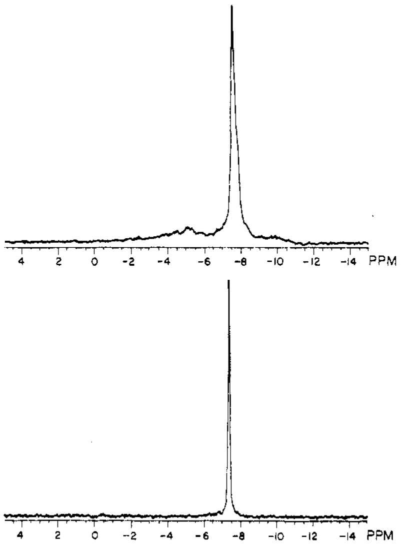


Figure 4. ^{31}P NMR (^1H decoupled) of IIIA (bottom) and IIIA after treatment with additional sodium trifluoroethoxide (top).

The transition from spherulite to rodlike crystals was observed at decreasing temperatures for IIIAA–IIIE. This depression of the transition temperature corresponded to the decreasing melting point of each material, as discussed above. Thus, while the spherulites of IIIAA remained unperturbed at 220 °C, IIIC formed an isotropic melt in which no structure was observed. Rodlike crystals formed upon cooling. The conversion of a film of IIIE from the spherulite to the rodlike structure was observed at even lower temperatures.

Reaction of (Trifluoroethoxy)phosphazenes with Sodium Trifluoroethoxide. An excess of sodium trifluoroethoxy nucleophile was used in the preparation of IIIAA–IIIE. This ensured complete chlorine substitution on the polymer backbone. The changes observed in the polymers prepared in this laboratory were observed because the excess ethoxide underwent a secondary reaction on fully substituted III. This was demonstrated by using the crystalline trifluoroethoxy-substituted phosphazene IIIA and the cyclic model compound hexakis(trifluoroethoxy)cyclotriphosphazene (IV) as substrates for reaction with the nucleophile. Previous workers used nearly stoichiometric amounts of nucleophile in the preparation of III.[1,4]

Reaction of IIIA with sodium trifluoroethoxide resulted in transformation of the crystalline polymer to an amorphous one. This was evident in the DSC thermograms, optical micrographs, and ^{31}P NMR spectra. The only evidence of crystallinity in the product by DSC was a small transition (≪0.1 cal/g) at 85 °C. Films of the polymer cast on microscope slides appeared completely amorphous under a polarizing microscope. Neither spherulites nor rods were observed, and repeated heating and cooling of the sample failed to produce birefringence.

The proton-decoupled ^{31}P NMR spectrum of IIIA before and after treatment with the alkoxide is shown in Figure 4. The crystalline polymer appeared as a sharp singlet at −7.5 ppm, 7 Hz wide a half-peak height. The product, isolated after reaction with the base, showed a major peak also centered at −7.5 ppm, but broadened to 21 Hz wide at half-peak height. In addition, the base line of this latter spectrum exhibited a broad cluster of additional resonances from −2 to −11 ppm, suggesting that not all the phosphorus atoms were in the same environment.

The reaction of fluorinated phosphazenes with *n*-butyllithium at −78 °C has been reported to cause dehydrohalogenation of the trifluoroethoxy side group, and an olefinic product has been isolated.[12] We have studied the attack of the alkoxy nucleophile on the fluorinated phosphazene III, using the small molecule IV.[16] The reaction studied is outlined in Scheme II. This cyclic trimer can be purified and characterized more rigorously than the high polymer, making the small-molecule system an easier one for product identification. The ^{1}H-decoupled ^{31}P NMR spectra of starting material IV and products from the reaction with trifluoroethoxide plus IV are shown in Figure 1. The spectrum shows a singlet for the starting material and an AB_2 spin pattern for the product (see Experimental Section). This product was assigned structure V.

The structure of V was deduced by comparison of its ^{31}P NMR spectrum with that of hydroxypenta(imidazolyl)cyclotriphosphazene, reported by Allcock and Fuller.[13] With the exception of the chemical shifts of the AB_2 spin pattern, the spectra appear much the same. The coupling constant reported for the imidazole hydrolysis product is 53 Hz and that for V is 70.6 Hz. Thus, excess trifluoroethoxy nucleophile appears to cleave the carbon–oxygen bond of the fluoroalkoxy side group to form the sodium salt. In the case of the cyclic trimer, the salt appears to form the hydroxy compound V upon workup with water. It is not known if this same process is followed in the high polymer III, although it would account for the observed differences in physical properties. It is possible that the hydrogen bonding between the hydroxy groups or with trifluoroethoxy side groups is responsible for the change in physical properties of IIIAA–IIIE. Although the variation in physical properties could also be attributed to branching, hydrogen bonding was the preferred explanation because (1) branched polymers would be much less soluble and (2) the work on small molecules suggested the formation of a hydroxy compound (V) and not a phosphazene dimer. The formation of P–OH moieties from the hydrolysis of residual P–Cl bonds in III has been studied.[17]

Further support for the assignment of V was obtained by preparing the compound via an alternative pathway (Scheme III). Following the synthetic scheme reported by Allcock and Fuller, the intermediate VI was prepared.[13] The compound was not isolated, but reacted with sodium trifluoroethoxide to form compound V. The product of this reaction displayed the expected AB_2 spin pattern in the ^{31}P NMR spectrum and gave the corresponding molecular ion in the mass spectrum.

The ^{31}P NMR spectrum of V prepared by this method (Scheme III) was identical with the spectrum obtained with IV as the starting material (Scheme II).

Conclusions

This paper reports our initial observations on the various polymer morphologies of (fluoroalkoxy)phosphazene polymer III. We found that excess nucleophile in the reaction mixture attacks the fully substituted polymer III. This attack resulted in changes in the polymer morphology that was detectable by thermal analysis, optical microscopy, and ^{31}P NMR spectroscopy. We used this reaction to prepare samples of III that were completely amorphous. The changes in polymer morphology were the result of attack by excess trifluoroethoxide on the fully substituted polymer chain. This reaction was modeled by using the cyclic trimer molecule IV, where cleavage of the side group by excess alkoxide was observed. The structure of the compound $[N_3P_3(OCH_2CF_3)_5OH]$ (V) was assigned based on the ^{31}P NMR spectrum and detection of the molecular ion in the mass spectrum. Isolation and further characterization of the compound are in progress.

The substitution of chlorine atoms on II with sodium trifluoroethoxide is rapid and efficient. We have shown that excess nucleophile will attack the side-group moiety on the substituted polymer III. This side-group modification is neither rapid nor efficient and thus is hard to detect spectroscopically. However, large changes in the polymer morphology were observed. For example, the melting point of homopolymer IIIAA was suppressed from 247 to 149 °C for IIIE (a copolymer) even though the chemical analyses of these materials did not detect a difference in the materials. Future work will be carried out to identify the factors that explain the changes in polymer morphology. Solution characterization of these polymers, including viscosity, GPC, and light scattering, is in progress. Through these measurements, we will attempt to relate the molecular structure to the changes in the polymer crystallinity and to the physical and mechanical properties of both the spherulite and rodlike crystalline domains.

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