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An Unusual Polymer Architecture for the Generation of Elastomeric Properties in Fluorinated Polyphosphazenes

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Supporting Information

ABSTRACT: We report the synthesis and characterization of a new linear polyphosphazene architecture in which rigid, bulky side units provide the possibility of interdigitation with their counterparts on neighboring chains to generate noncovalent cross-links and distinct elastomeric properties. The bulky side groups are cyclotriphosphazene rings substituted with trifluoroethoxy groups connected to the main chain via aryloxy spacers. These bulky units are distributed along the polymer backbone and separated from each other by trifluoroethoxy units linked directly to the main chain. Compared to the well-known poly[(bis-2,2,2-trifluoroethoxy)phosphazene], [NP(OCH₂CF₃)₂],, which is a microcrystal-line film- and fiber-forming polymer, several of the new materials are elastomers



with properties that arise partly from interactions of the protruding cyclotriphosphazene side units with those on nearby polymer chains. Specific elastomers are capable of regaining up to 89% of their original shape when elongated to high strain (up to 1000%) over four elongation cycles and show even longer elongations at break (>1600%). The overall physical properties depend on the ratios of the cyclic trimeric side units to main chain linked trifluoroethoxy side groups. The polymers were characterized using ¹H, ³¹P NMR, DSC, TGA, X-ray diffraction, GPC, and stress–strain techniques.

■ INTRODUCTION

Elastomers comprise one of the most important categories of polymeric materials, with applications that range from impactabsorbing, aerospace, automotive, and biomedical devices to membranes, seals, O-rings, and surface coatings.¹⁻³ Most of the known elastomers are lightly cross-linked flexible organic polymers or poly(organosiloxanes), many of which have properties that are compromised by solvents, oils, fire, or high-temperature oxidation. One class of elastomers, based on the polyphosphazene platform, has properties that are a distinct improvement over many of the classical counterparts. These are macromolecules with a backbone of alternating phosphorus and nitrogen atoms, with two fluorinated alkoxy groups attached to each phosphorus. If only one type of fluorinated side group is present, the polymers are microcrystalline thermoplastics (Chart 1, structure 1), but the presence of two different fluoroalkoxy groups in roughly equal amounts lowers the symmetry, eliminates the crystallinity, and allows low- T_{g} elastomeric properties to emerge. The best-known example of this class is "PN-F" or "Eypel-F" (Chart 1, structure 2), an elastomer developed originally for use in challenging automotive and aerospace environments but also studied for

Chart 1. Structures of Poly(bis-2,2,2trifluoroethoxy)phosphazene (1) and PNF (2)



cardiovascular applications and commercialized as a dental material. $^{\rm 4-6}$

The cross-linking of classical organic elastomers is accomplished by the formation of covalent bonds or by the phase separation of block or graft copolymers in which the rigid domains serve as meltable connection sites. The covalent crosslinking method is a permanent change so that the elastomer is no longer soluble and cannot be recycled by solution or thermal techniques. Like many traditional polymers, PN-F elastomers are cross-linked covalently by free radical coupling via allyl groups on aryloxy minor cosubstituents.⁷

In this paper we report a new method for the generation of elastomeric properties in fluoroalkoxyphosphazene polymers. It is based on the idea that rigid, bulky cosubstituents reduce crystallinity and may interdigitate with their counterparts on neighboring chains in such a way that adjacent chains become physically locked to reduce chain slippage when tensile stress is applied. This principle is illustrated in Figure 1. The concept can be likened to the interaction between the oars of rowed boats (think of rowing eights, Viking long ships, or Venetian galleys) when adjacent vessels move so close that their oars interlock and prevent independent motion of individual units.

Thus, the polymers described here consist of a polyphosphazene backbone with a majority of the side groups composed of trifluoroethoxy units, but with up to 20 mol % of the cosubstituent groups being *p*-aryloxy units terminated by cyclic

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Figure 1. Schematic representation of the proposed interdigitation of cyclic trimeric side groups linked to the polyphosphazene backbone.

trimeric phosphazene rings, which also bear trifluoroethoxy side groups (Chart 2, structure 3). The rubbery elastomeric

Chart 2. Structure of Cyclotriphosphazene Containing Polyphosphazene Elastomers



character of several of the new polymers, with striking tensile behavior, is in sharp contrast to the rigidity of organic backbone polymers with cyclophosphazene side groups.^{8,9}

RESULTS AND DISCUSSION

Synthesis of Cyclotriphosphazene Side Groups. The design of the functionalized cyclic trimer units was based on two main criteria. First, each bulky side group requires the presence of a single hydroxyl-terminated functional unit to allow for its eventual attachment to poly-(dichlorophosphazene). This requirement was imposed to avoid covalent cross-linking, which may occur through the use of multifunctional side units during macromolecular substitution reactions.¹⁰ Second, the reactive linking species was chosen to be a hydroxyl-terminated aryloxy species to provide rigidity and maintain chemical stability.^{10,11}

To fulfill these requirements, the phosphazene cyclic trimeric group was synthesized via a three-step procedure (Scheme 1a), which generated the final monohydroxy-functionalized side group. Specifically, hexachlorocyclotriphosphazene (4) was treated with the sodium salt of 4-methoxyphenol to generate the protected monosubstituted intermediate **5**. This reaction was monitored using ³¹P NMR spectroscopy by following the disappearance of the hexachlorocyclotriphosphazene phosphorus peak at δ = 20.0 ppm and the appearance of new signals at δ = 22.8 (d, 2P) and 13.4 (t, 1P) ppm, which represented

phosphorus atoms bearing either two chlorine atoms or one chlorine and one 4-methoxyphenol group, respectively. Next, the five remaining chlorine atoms on the ring were replaced using the sodium salt of 2,2,2-trifluoroethanol to generate the fully substituted cyclic trimer. The progress of this reaction was also monitored by ³¹P NMR spectroscopy, with the composition of the side group precursor confirmed by both ¹H NMR and mass spectrometry. Finally, the compound was treated with BBr₃ to remove the methoxy group to generate **6** and afford the required hydroxyl moiety. Characterization of the product indicated complete removal of the methoxy group with no detectable degradation of the structure, as indicated by ³¹P and ¹H NMR spectroscopy.

Synthesis of Polymers 8–15. The synthesis of polymers 8-15 followed a similar synthetic protocol (Scheme 1b). Specifically, poly(dichlorophosphazene) (7) was first prepared via the thermal ring-opening polymerization of hexachlorocyclotriphosphazene (4). The chlorine atoms in this polymer were then replaced in a two-step procedure to generate the final poly(organophosphazenes) (polymers 8-15). The reactions were monitored using ³¹P NMR spectroscopy. The bulky cyclotrimeric side groups were linked to the backbone first, followed by the trifluoroethoxy cosubstituents. For polymers with a trimer content of less than 10 mol % (8-13), the introduction of the trimer units onto the polymer backbone was accomplished at room temperature. However, for polymers 14 and 15, which contain 14.1 and 20.8 mol % of the cyclic trimer species, the reaction mixture required heating to reflux to ensure the complete linkage of the trimer. This need to reflux the reaction mixture probably stems from the large steric bulk of the side group, which can partially shield the chlorine atoms attached to adjacent phosphorus atoms. Thus, a roughly 20 mol % loading of the bulky side groups was the maximum attainable under the available reaction conditions. Moreover, the reaction sequence in which the bulkiest side groups were introduced first favors structures in which the cyclic trimeric units are well separated along the polymer backbone. Figure 2 illustrates the ability of the cyclic trimer group to shield the surrounding chlorine atoms after its linkage to the polymer backbone and hence to limit the total number of cyclic trimeric units that can be attached to the polymer. A total of eight polymers with different ratios of the two groups were synthesized, with their physical properties controlled by the ratio of the two side groups. Characterization data are provided in Table 1.

Synthesis of Polymer 1. Polymer 1, used for comparison purposes, was synthesized by the complete replacement of all the chlorine atoms in poly(dichlorophosphazene) (7) by the sodium salt of trifluoroethanol at room temperature in tetrahydrofuran (THF). This macromolecular substitution reaction was also monitored using ³¹P NMR spectroscopy. Once the reaction was complete, the product was purified by precipitation from THF into water and hexanes. The resulting material is a tough and opalescent microcrystalline polymer, with a high molecular weight and a low glass transition temperature (T_g) (Table 1). This is consistent with previously published results for this polymer.¹²

Characterization of the Polymers. Characterization data for polymers 1 and 8–15 are shown in Table 1.

Molecular Weights and Distributions. The gel permeation chromatography derived molecular weights of the polymers (Table 1) are in the range of 1.5–5 million, which is typical of fluoroalkoxyphosphazenes obtained from poly(dichlorophosphazene) that has been prepared via the ring-opening

Scheme 1. (a) Assembly of the Cyclic Trimeric Phosphazene Side Groups; (b) Linkage of the Side Groups to the Polyphosphazene Chain



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Figure 2. Ball-and-stick (left) and space-filling (right) models of the polyphosphazenes after the introduction of the cyclotriphosphazene side groups, but before replacement of the remaining skeletal chlorine atoms by trifluoroethoxy groups. The space-filling model illustrates the extensive steric bulk of the trifluoroethoxy-substituted cyclotriphosphazene side group and its shielding effect on the surrounding chlorine atoms.

polymerization route. In the case of the present polymers, this represents degrees of polymerization in the range of 3000–20 000 repeat units, depending on the side group trimer content. Thus, the synthesis protocol leads to minimal chain cleavage, and this is undoubtedly a factor favoring elastomeric behavior.

Glass and Mesophase Transition Temperatures. Figure 3 shows differential scanning calorimetry (DSC) traces for the synthesized polymers. The data reveal a near linear increase in the glass transition temperature (T_g) with an increase in the side chain trimer content. Specifically, the T_g increases from $-64.4 \,^{\circ}C$ for poly[(bis-2,2,2-trifluoroethoxy)phosphazene] (1) to $-26.6 \,^{\circ}C$ for the polymer with 21 mol % of the cyclotriphosphazene side group (15). This increase is consistent with the influence of the bulky cyclotriphosphazene rings, which restrict the polymer backbone motion by steric interactions. Similar trends have been noted for simpler polyphosphazene systems: for example, replacement of trifluoroethoxy groups in polymer 1 by aryloxy units results in an increase in the T_g^{13} .

Table 1. Characterization Data for Polymers 1 and 8-15

15. x = 0.420, y

= 1.580

0.047, y = 1.953

11. x = 0.080, v = 1.920

olymer	composition	$T_{\rm g}(^{\circ}{\rm C})$	T_1 (°C)	${M_{ m W} \over (10^6~{ m Da})}$	PDI	yield (%)
1	100% TFE	-62.0	79.7	1.945	1.60	82.3
8	0.6% trimer 99.4% TFE	-66.5	62.8	5.082	2.33	72.0
9	1.2% trimer 98.8% TFE	-60.8	62.8	2.324	1.86	52.2
10	2.3% trimer 97.7% TFE	-59.2	57.8	4.721	1.99	37.9
11	4.0% trimer 96.0% TFE	-50.9	49.2	4.239	1.86	51.0
12	5.8% trimer 94.2% TFE	-49.2	40.4	3.922	1.64	66.4
13	9.3% trimer 90.7% TFE	-40.6	NA ^a	4.687	1.77	81.7
14	14.1% trimer 85.9% TFE ²	-38.0	NA ^a	1.439	1.32	66.6
15	20.8% trimer 79.2% TFE	-26.4	NA ^a	4.759	1.56	63.3

^{*a*}A T_1 transition was not detected for these systems. TFE = 2,2,2-trifluoroethoxy; trimer = pentatrifluoroethoxycyclotriphosphazene.

The T_1 transition that is strongly evident in [NP-(OCH₂CF₃)₂]_n (1) shifts from 79.7 to 40.4 °C and decreases in intensity when only 5.9 mol % of the cyclic trimeric side groups are present. Previous X-ray diffraction studies on fluoroalkoxyphosphazene polymers showed that this transition arises from a crystalline-to-mesophase transformation, which corresponds to a significant, but not complete, loss of modulus in samples heated above this temperature.^{14–17} These decreases in the intensity of the T_1 transition signal in the new polymers supports the idea that the crystallinity is decreased as the cyclic trimer side group content increases. Once the trimer content is higher than 5.9 mol %, the mesophase transition peak



Figure 3. DSC traces of all polymers (left) and trend line for T_{e} as a function of the trimer side group content (right).

disappears, which probably is close to the critical trimer concentration above which the trifluoroethoxy units between the cyclic trimer side groups can no longer pack sufficiently well to allow efficient crystallization. This is a critical characteristic for the onset of elasticity. However, the physical properties of 13 suggest that small domains of crystallinity may persist up to a trimer loading of ~10 mol % or higher even though it is not detectable by DSC.

Polymer Crystallinity by X-ray Analysis. X-ray diffraction patterns obtained for the new polymers (Figure 4) reinforce the



Figure 4. Powder XRD traces of trimer side group containing polyphosphazenes.

conclusion that the crystallinity is decreased as the content of the cyclic trimeric side group is increased. All the polymers show the very strong reflection at $2\theta = 21^{\circ}$, which has been reported previously for $[NP(OCH_2CF_3)_2]_n$ (1).¹⁵⁻¹⁷ This signal is strong and sharp for the polymers that contain 0, 0.6, 1.2, and 2.3 mol % cyclic trimer side units (1 and 8-10), but it decreases in intensity and broadens extensively for the polymers with a trimer content at or above $5.9 \mod \% (12-15)$. However, polymer 11, which has 4.0 mol % of the trimeric side group, shows an intermediate, slightly broadened, but still easily discernible signal at $2\theta = 21^\circ$, showing that the sample still maintains a small degree of crystallinity. This information is consistent with the DSC data and shows that the crystallinity of the polymers decreases but is not completely eliminated until the trimer content is at or above 5.9 mol %. As mentioned above, some crystalline domains may persist in the presence of up to ~10 mol % trimeric side groups. The decrease in the crystallinity with increasing trimer concentration is readily understood, but the balance between crystallinity and elastomeric behavior may be a consequence of the two different interactions, which are discussed in a later section.

Thermal Stability and Resistance to Combustion. Polymer 1 is known to undergo depolymerization-type thermal breakdown to trifluoroethoxy-substituted phosphazene cyclic oligomers when heated above ~300 °C.^{18,19} TGA plots show that polymers 8–15 behave in a similar way (see Supporting Information). However, the presence of the side group cyclic trimer units appears to raise the depolymerization onset temperature and increases the temperature for T_{10} weight loss by as much as 100 °C. It is possible that the bulky cyclic trimeric side units inhibit backbiting, which is often a prerequisite for depolymerization.

polymer	film thickness (mm)	tensile strength (MPa)	break strength (MPa)	break elongation (%)	yield strength (MPa)	yield elongation (%)	Young's modulus (MPa)
1	0.489 ± 0.077	9.49 ± 1.13	9.49 ± 1.13	439.2 ± 40.1	3.22 ± 0.53	8.6 ± 1.4	53.1 ± 6.83
8	0.216 ± 0.029	7.86 ± 1.70	6.66 ± 2.73	433.6 ± 89.8	4.45 ± 0.46	20.1 ± 3.4	60.5 ± 10.1
9	0.283 ± 0.053	8.65 ± 1.32	8.45 ± 1.27	497.8 ± 50.4	4.90 ± 0.47	15.5 ± 2.6	114.4 ± 9.2
10	0.225 ± 0.044	8.99 ± 0.98	8.99 ± 0.98	555.1 ± 41.0	4.23 ± 0.68	16.9 ± 2.9	82.0 ± 13.0
11	0.246 ± 0.031	4.06 ± 0.87	4.06 ± 0.87	968.2 ± 82.0	0.16 ± 0.02	50.4 ± 4.3	0.35 ± 0.06
12	0.417 ± 0.031	1.68 ± 0.14	1.68 ± 0.14	1,683.0 ± 69.5	0.0459 ± 0.0087	45.5 ± 5.8	0.131 ± 0.022
13	0.793 ± 0.095	1.17 ± 0.22	1.17 ± 0.22	$1,598.5 \pm 77.2$	0.0236 ± 0.0032	50.2 ± 1.5	0.056 ± 0.009
14	0.759 ± 0.052	1.32 ± 0.16	1.32 ± 0.16	$1,460.8 \pm 56.3$	0.0200 ± 0.0020	48.5 ± 1.7	0.046 ± 0.004
15	0.520 ± 0.040	0.62 ± 0.25	0.62 ± 0.25	$1,853.9 \pm 430.2$	0.0184 ± 0.0022	28.3 ± 2.6	0.12 ± 0.03

Table 2. Mechanical Properties of Polymers 1 and 8-15

Previous work has shown that polymer 1 is resistant to combustion in air, although its utility in this regard is compromised by melting at the flame front.²⁰ However, polymers 8-16 are self-extinguishing in air and retain their physical structure during the initial pyrolysis.

Mechanical Properties. As the ratios between the two types of side groups are changed, the mechanical properties also change, with the result shown in Table 2. Representative stress-strain curves are shown in Figure 5.



Figure 5. Representative stress vs strain curves of the microcrystalline (polymer 9), midrange (polymer 11), and noncrystalline (polymer 13) polymers.

The mechanical testing revealed that increases in the content of the cyclic trimeric side groups moved the properties though three distinct phases. First, the microcrystalline polymers 1 and 8-10, with the smallest amounts of cyclophosphazene side groups (0-2.3 mol %), are relatively tough materials which orient and crystallize readily under tension and break at comparatively low strains (400-500%). Polymers 1 and 8-10 also show the weakest ability to retract after being elongated. For example, polymer 8 retracted only 30% of its stretched length after being elongated to 250% of its original gauge length. Figure 6 shows a representative hysteresis curve of polymer 8. In this sense, 8-10 have properties that are minor variations of 1. However, even low concentrations of the cyclic trimeric side groups brings about an increase in both the Young's modulus (60.5–114.4 MPa) and yield strength (4.23– 4.90 MPa), and this suggests a strong influence on these properties by even these small amounts of the bulky side units.

Second, polymers 11 and 12 with 4 and 5.9 mol % cyclic trimeric side units are unusual elastomers. Even though they are not covalently cross-linked, they display properties that would be typical of a lightly cross-linked organic elastomer. The tensile strengths (1.68-4.06 MPa) are one-fifth to one-half those observed for their microcrystalline counterparts (1 and 8-10), and the Young's modulus (0.131-0.35 MPa) is also decreased by 2-3 orders of magnitude. Moreover, these polymers can undergo significant elongations (≥1600%) before rupturing, and they possess a remarkable capacity to retract after extensive elongation. For instance, these samples are capable of retracting between 66 and 85% of their stretched length after being elongated to 600-1000% of their original gauge length over four elongation cycles. Figure 6 shows the hysteresis data for polymer 11. It is speculated that this may reflect a ratcheting behavior that involves the cyclotriphosphazene rings on adjacent chains slipping past each other during polymer elongation before encountering consecutive trimer units. This allows the ring-ring interchain interactions to be broken and re-formed continuously, which maintains the strength and some memory by the system as it is elongated.

However, polymers 13-15, with 9.3-20.8 mol % cyclic trimeric side units, are relatively soft, self-adhesive materials, with a diminished ability to retract after stretch elongation. Interestingly, they show a similar elongation to polymers 11 and 12 before rupturing. Polymer 13 (9.3 mol % trimer) has properties that are intermediate between those of 11 and 12 and the completely amorphous 14 and 15. The hysteresis curve is shown in Figure 6. The three stress/strain and hysteresis curves in Figures 5 and 6 illustrate the change in behavior as the bulky side group concentration is increased. Species 13-15 have relatively high trimer content but no evidence of crystallinity. Thus, it is concluded that the *combination* of microcrystallinity and bulky cosubstituents is responsible for the unusual behavior of polymers 11 and 12.

Conclusions Regarding the Elastomeric Properties. The system described here is an unusual example of elastomer structure/property tuning without the use of covalent crosslinking. Interchain packing in 1 leads to high levels of microcrystallinity, especially after orientation by tension. By comparison, the elasticity of 2 reflects the disruption of microcrystallinity following the introduction of the longer (but still flexible) fluoroalkoxy cosubstituent groups, although covalent cross-linking is still needed to generate good elastomeric strength under tension.

A different mechanism appears to be operative in the new polymers described here. Two forms of interchain interactions could influence the physical properties. First, the physical crosslinking provided by microcrystallites decreases as bulky



Figure 6. Hysteresis curves for polymers 8, 11, and 13.

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cosubstituents are introduced due to disruption of order by the bulkier side groups, until detectable crystallinity is lost when roughly 10 mol % of the larger side groups are present. In a classical polymer this would probably lead to the conversion of a microcrystalline solid to a marginally elastic extensible gum. This does not happen with polymers 11-15 where significant retraction after stretching is evident. We attribute this to the opportunities that exist for intermolecular interactions that involve the bulky cyclic trimeric side groups, perhaps by interdigitation. For polymers 14 and 15, which have the longest extensions tolerated before rupture and show a slight decrease in their ability to retract when the samples are allowed to relax after elongation, it is possible that interdigitation is the main mechanism that retards chain slippage, while the combination of interdigitation and residual microcrystallinity is responsible for the high elastic recovery of 11-13. A possible model for the side group-side group interactions is suggested in Figure 7.



Figure 7. 3D representation of polymer chains interacting, showing the trimer—trimer spacing along both chains and the pocket which would accept trimer units from adjacent chains to facilitate the trimer trimer interactions. These interactions are also favored by the ability of the trifluoroethoxy groups on the trimeric side groups to interact with the trifluoroethoxide groups attached to both adjacent trimer units and the polymer backbone.

MATERIALS AND METHODS

Reagents and Equipment for Polymer Synthesis. Unless otherwise stated, all syntheses were performed using standard Schlenkline techniques under a dry argon atmosphere. Glassware was dried for 24 h in an oven at 140 °C before use. Tetrahydrofuran (THF) was dried using solvent purification columns. 2,2,2-Trifluoroethanol (Halocarbon) was distilled over sodium and stored over molecular sieves (type 4A, EMD). Dichloromethane (EMD), hexanes (EMD), acetone (EMD), magnesium sulfate (anhydrous, Alfa Aesar), sodium hydride (60% w/w in mineral oil, Aldrich), and tetra-n-butylammonium nitrate (Alfa Aesar) were used as received. Dialysis of polymers was performed using Spectra/Por molecular porous cellulose dialysis membranes with molecular weight cutoffs of 12 000-14 000 Da. Hexachlorocyclotriphosphazene (Fushimi Chemical Company, Japan) was purified by recrystallization from hexanes followed by sublimation. Poly(dichlorophosphazene) was synthesized by the uncatalyzed thermal ring-opening polymerization of the purified hexachlorocyclotriphosphazene in evacuated Pyrex tubes at 250 °C. Unreacted cyclic trimer was removed by vacuum sublimation, leaving the polymer as a colorless elastomeric material.

Equipment for Polymer Characterization. Glass transition temperatures were measured using a TA Instruments Q10 DSC unit operated at a heating rate of 10 $^{\circ}$ C/min and a samples size of 10–15 mg, with analysis performed by means of TA Instruments Universal Analysis 2000 software. ¹H and ³¹P NMR analyses made use of a

Bruker AV-360 instrument operated at 360 and 145 MHz, respectively. ³¹P NMR shifts are reported in ppm relative to 85% H_3PO_4 at 0 ppm. Gel permeation chromatographs were obtained using a Hewlett-Packard 1047A refractive index detector and two Phenomenex Phenogel linear 10 columns, eluted at a rate of 1.0 mL/min using a 10 mM solution of tetra-*n*-butylammonium nitrate in THF. The elution times were calibrated with polystyrene standards. Mechanical measurements were obtained with use of an Instron 5866 tensile testing instrument at a fixed cross-head speed of 100 mm/min at ambient temperature using a 100 N load cell. Polymer films were cut into dog-bone-shaped samples according to ASTM D-1708 using a PioneerDietecs die. A minimum of six samples were tested for each polymer.

Synthesis of N₃P₃(Cl)₅(OC₆H₄OCH₃) (5). To a suspension of sodium hydride (11.5 g, 0.288 mol) in THF (100 mL) was slowly added a solution of 4-methoxyphenol (35.8 g, 0.288 mol) in THF (150 mL). After the sodium hydride was consumed, the solution was added dropwise to a solution of hexachlorocyclotriphosphazene (4) (100 g, 0.288 mol) in THF (1 L) at 0 °C. The resultant mixture was allowed to warm slowly to room temperature overnight while monitored by ³¹P NMR spectroscopy. After replacement of one chlorine atom per ring was complete, the solvent was removed under reduced pressure. The resulting sample was purified by vacuum distillation at a pressure of 4.5×10^{-1} Torr to afford 5 in 36.7% yield. ³¹P NMR (145 MHz, CDCl₃) δ (ppm): 22.9 (d, 2P), 13.4 (t, 1P).

Synthesis of 6. To a suspension of NaH (24.0 g, 0.601 mol) in THF (200 mL) at 0 °C was slowly added 2,2,2-trifluoroethanol (43.9 mL, 0.601 mol). Once the NaH was consumed, the sample was added slowly to a solution of 5 (50.0 g, 0.116 mol) in THF (200 mL) at 0 °C, and the mixture was stirred under continuous cooling for 8 h before removal of the solvent under reduced pressure. The resulting oil was dissolved in dichloromethane and washed with water, before removal of the solvent under reduced pressure and drying further under high vacuum. The sample was then deprotected by redissolution in dry DCM (300 mL), to which was added BBr₃ (14.2 mL, 0.147 mol), and the mixture was stirred for 18 h at room temperature. The sample was then added to water (200 mL) at 0 °C and stirred vigorously for 30 min. The organic layer was isolated and washed with sodium carbonate (1 N) and brine before drying over magnesium sulfate. The solvent was then removed under reduced pressure to afford 6 in 85% yield and 90% purity w/w (with 10% hexa(2,2,2trifluoroethoxy)cyclotriphosphazene impurity) as an oil. ³¹P NMR (145 MHz, CDCl₃) δ (ppm): 16.6 (dd, 2P), 13.4 (t, 1P). ¹H NMR (360 MHz, CDCl₃) δ (ppm): 7.10 (d, 2H), 6.83 (d, 2H), 5.51 (s, 1H), 4.44 (m, 2H), 4.29 (m, 4H), 3.95 (m, 4H). MS (ESI⁺, DCM): 740 m/ $z (M + H^{+}).$

Poly[bis(trifluoroethoxy)phosphazene] (1). This polymer was synthesized by methods reported earlier¹² and was purified by precipitation from THF into water three times and hexanes once to afford the title polymer as an opaque leathery material. Confirmatory characterization data are provided in Table 1.

Synthesis of Polymers 8-15. All syntheses followed a similar procedure, with an example provided for 13. To a suspension of NaH (0.692 g, 17.3 mmol) in THF (200 mL) was added 6 (14.2 g, 17.3 mmol), and the mixture was stirred. Once the NaH had been consumed, the sodium salt was added slowly to a solution of poly(dichlorophosphazene) (7) (10.0 g, 86.3 mmol) in THF (1 L) and stirred at 25 °C for 24 h and monitored by ³¹P NMR. In a separate vessel, 2,2,2-trifluoroethanol (11.9 mL, 163.9 mmol) was added slowly to a suspension of NaH (6.56 g, 163.9 mmol) in THF (300 mL), and the reaction mixture was stirred until the NaH was consumed. After the cyclic trimeric side group had been linked to the polymer backbone (as indicated by $^{31}\mathrm{P}$ NMR), the sodium salt of trifluoroethanol in THF was added to the polymer solution, and the mixture was stirred at room temperature for 8 h. Once complete, the reaction mixture was precipitated into water, and the sample was dried under high vacuum. The resulting material was then dissolved in acetone and dialyzed against 15% v/v methanol in acetone, before removal of the solvent under reduced pressure to afford the final polymer as a translucent elastomeric material. Characterization data

for all polymers are presented in Table 1. (For polymers 14 and 15, the solution was heated at reflux for 24 h after addition of the cyclic trimer 6, followed by replacement of the remaining chlorine atoms using 2,2,2-trifluoroethoxide at room temperature.)

Elasticity Comparison for Polymers 1 and 8–15. The polymers were solvent cast with use of the following protocol. Specifically, ~18 g samples of each polymer were dissolved in acetone (250-350 mL), before being poured into a 6 cm \times 25 cm Bytaccoated dish. The solvent was allowed to evaporate at room temperature in an acetone-saturated atmosphere until the polymer formed a coherent film. Each film was then dried further under high vacuum at room temperature for an additional 48 h. The final films were smooth with a uniform thickness across the entire sample. After cutting into dog-bone-shaped samples using a prefabricated die, the samples were stored under vacuum before testing. The polymers were evaluated using an Instron 5866 tensile testing instrument at a fixed cross-head speed of 100 mm/min at ambient conditions.

3D Structure Rendering. 3-Dimensional structures of the cyclotriphosphazene containing polymers (Figures 2 and 7) were obtained using ChemBio3D Ultra 11.0, utilizing the standard MM2 minimization function to generate the lowest energy structures.

ASSOCIATED CONTENT

Supporting Information

Thermal gravimetric analysis (TGA) plots of polymers 1 and 8-15. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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