# Macromolecules

# Elastomeric Polyphosphazenes with Phenoxy–Cyclotriphosphazene Side Groups

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**S** Supporting Information

**ABSTRACT:** New polymers with a phosphazene backbone and both 2,2,2-trifluoroethoxy- and phenoxy-functionalized cyclotriphosphazene substituents exist in three phases depending on the side group ratios. At low concentrations of the bulky substituents (up to ~7 mol %), the polymers are semicrystalline thermoplastics, with properties that are minor variations of poly[bis(2,2,2-trifluoroethoxy)phosphazene]. However, after the incorporation of between ~7 mol % and ~20 mol % of the bulky cyclic trimeric side groups, the polymers lose their semicrystalline properties and become amorphous elastomers. At still higher trimer loadings (>20 mol %) the materials develop gum-like behavior. The elastomeric phase appears to be generated by interdigitation or agglomeration of the bulky aryloxy-cyclotriphosphazene side groups, which act as quasi-physical cross-links between the polymer chains. The presence of these interactions allows the materials to experience high strain values before rupture (up to 1000%), and elastic recovery of more than 85% of the original dimensions when stressed up to 60% of the break elongation over four cycles. In addition, the chemical



and physical nature of the substituents on the cyclic trimeric side groups alters the physical characteristics of the polymer in a way that provides a facile method to tune the properties.

# INTRODUCTION

The utility of a large part of polyphosphazene chemistry rests on the ease of linkage of a wide variety of organic side groups to the inorganic backbone.<sup>1–11</sup> This has allowed the development of a substantial number of polymers with properties that vary from semicrystalline<sup>10,11</sup> or amorphous thermoplastics, to low  $T_g$  elastomers, hydrophobic films and fibers, polymer dyes, water-soluble polymers, and biomedically useful materials. Thus, the ease of chemical manipulation is one of the most important features of this field. Particularly interesting is the influence of bulky side groups on the physical properties of the polymers

In a recent publication, <sup>12</sup> we described the first members of a novel class of polymers based on a polyphosphazene backbone with 2,2,2-trifluoroethoxy side groups and a small percentage (0.5-20 mol %) of bulky cyclotriphosphazene units which themselves bear trifluoroethoxide units (structure 1). The bulky cyclic trimeric side units in that system act as anchoring points or interdigitation sites, and function as physical "cross-links" to impart elastomeric properties to polymers that would normally be either microcrystalline thermoplastics or noncrystalline, nonelastomeric gums. Several questions arose from that study, including the possible effects of linking even bulkier cosubstituent groups to the polyphosphazene backbone and the influence that larger side groups might have on the elastomeric properties.

Thus, in this paper we report the synthesis of a new series of phosphazene polymers (structure 2) that bear a majority of 2,2,2-trifluoroethoxy side groups plus small to medium ratios



(0.7–22 mol %) of cyclotriphosphazene units each decorated with phenoxy substituents. In principle, the aryloxy-functionalized cyclophosphazene cosubstituents could increase the interchain interactions in three ways. First, the increased steric bulk and rigidity of the aryloxy units, compared to the trifluoroethoxy counterparts, could generate stronger inter- and intramolecular steric interactions. Second, the phenoxy groups might undergo  $\pi$ - $\pi$  interactions, which could further increase the strength of the interchain forces. Third, the presence of both aryloxy and trifluoroethoxy substituents may cause them to phase separate, with the aryloxy units occupying clusters or

Received: August 30, 2015 Revised: October 5, 2015 Scheme 1. Synthesis of the Aryloxy-Functionalized Cyclotriphosphazene Side Group 5/5a<sup>a</sup>



<sup>a</sup>5a is the deprotonated unit after coupling to the polymer skeleton.

#### Scheme 2. Synthesis of Polymers 6–10

$$\begin{array}{c} \begin{array}{c} CI \\ N=P \\ -CI \\ CI \\ n \end{array} + HO \\ CF_{3} + 5 \\ \hline THF \\ \hline THF \\ 6. x = 0.056, y = 1.944 \\ 7. x = 0.126, y = 1.874 \\ 8. x = 0.218, y = 1.782 \end{array}$$

agglomerates that resemble the more traditional physical crosslinks in block copolymers.

Analysis of the newly synthesized macromolecules revealed that the aryloxy-functionalized cyclotriphosphazene groups do indeed have a significant influence on the mechanical properties of the polymers. Specifically, the new polymers have a higher Young's modulus and tensile strength than series 1 polymers at similar loadings. This change is evidence of increased interactions between the bulky side units as well as a decrease in overall polymer chain flexibility. Thus, in the following sections the emphasis is on the similarities and differences between polymers of types 1 and 2.

#### RESULTS AND DISCUSSION

**Synthesis of Aryloxy Functionalized Cyclotriphosphazene Side Group, 5.** Compound 5 was synthesized using a three step procedure (Scheme 1), which resembles the protocol employed for the trifluoroethoxy-substituted counterpart.<sup>12</sup> First, hexachlorocyclotriphosphazene was treated with the sodium salt of 4-methoxyphenol to replace one of the six chlorine atoms to generate intermediate **3.** The progress of this reaction and subsequent steps were monitored by <sup>31</sup>P NMR spectroscopy. Once the substitution was complete, the product was purified extensively to eliminate any impurity with more than one arylmethoxy group attached to the cyclotriphosphazene ring. Any multifunctional impurities would ultimately be a source of covalent cross-linking during subsequent synthesis steps.

After the monosubstituted intermediate **3** had been isolated and purified, it was treated with an excess of sodium phenoxide to replace the remaining five chlorine atoms on the cyclotriphosphazene ring to give **4**. Treatment with BBr<sub>3</sub> removed the methyl ether unit and generated the required monohydroxyl-functionalized **5**. The structure of **5** was confirmed by both  ${}^{1}$ H and  ${}^{31}$ P NMR spectroscopy.

**9.** x = 0.340, y = 1.660 **10.** x = 0.446, y = 1.554

Synthesis of Polymers 6-10. These polymers are variations of structure 2 with five different side group ratios. The synthesis of these species followed three-step procedures, with the preparation of polymer 6 following a slightly different procedure than the one used for polymers 7-10.

First, for polymers 7-10, which were designed to have 5-20mol % of 5a, respectively, 95-80 mol % of the chlorine atoms along the polymer backbone were replaced by the sodium salt of trifluoroethanol to generate a partially substituted intermediate. To favor a random distribution of the remaining chlorine atoms, the sodium salt solution was added dropwise to a vigorously stirred polymer solution at room temperature. This procedure allowed the required number of chlorine atoms to be left unreacted. Thus, their subsequent replacement by the sodium salt of 5 would control the loading of the cyclic trimeric groups along their backbone. The progress of these and future steps were monitored using <sup>31</sup>P NMR spectroscopy. The reaction mixture was then treated with a 4-fold excess of the sodium salt of 5 to replace the remaining chlorine atoms. This large excess allowed a near-complete replacement of the remaining chlorine atoms by 5. Finally, any remaining P-Cl bonds, below the detection limit of <sup>31</sup>P NMR signals, were replaced by a second treatment of the polymer with the sodium trifluoroethoxide. This protocol ensured the formation of chlorine-free, un-cross-linked polymer.

The synthesis of polymer **6** followed a slight variation of the above procedure due to the extremely low loading of **5**. In the first step only 90 mol % of the chlorine atoms were replaced using sodium trifluoroethoxide. This was necessary due to the

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Ta	ble	1.	Characterization	Data	for	Polymers	6-10"
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			composition (mol %)		$M_w$		yield
polymer	<sup>1</sup> H NMR (ppm)	<sup>31</sup> P NMR (ppm)	CTP	$T_{\rm g}/T_1~(^{\circ}{\rm C})$	(kDa)	PDI	<b>(</b> %)
BTFP	4.43 (s)	-7.05 (s)	0	-62.0/79.7			
6	4.42 (s, 283.7 H), 6.54–7.33 (m, 29.00 H)	8.73 (3.00 P), -7.52 (70.1 P)	0.7	$-61.0 \pm 1.1$ /60.9 $\pm 1.6$	4400	1.95	51
7	4.57 (s, 28.64 H), 6.57–7.41 (m, 29.00 H)	9.05 (3.00 P), -7.65 (8.40 P)	6.3	$-21.4 \pm 0.9$ /56.5 ± 4.3	2100	2.35	18
8	4.39 (s, 16.32 H), 6.69–7.33 (m, 29.00 H)	8.68 (3.00 P), -8.06 (3.11 P), -12.40 (0.99 P)	10.9	$-19.2 \pm 0.9$	2000	2.13	67
9	4.44 (s, 13.22 H), 6.50–7.32 (29.00 H)	8.68 (3.00 P), -8.66 (1.82 P), -12.42 (1.00 P)	17.0	$-3.2 \pm 0.4$	1600	1.79	41
10	4.48 (s, 6.67 H), 6.59–7.39 (29.00 H)	8.77 (3.00 P), -8.97 (1.37 P), -12.53 (1.04 P)	22.3	$4.8 \pm 0.1$	1100	1.87	19
<sup>a</sup> CTP: Cyclotriphosphazene (5a). BTFP: poly(bis-2,2,2-trifluoroethoxy)phosphazene.							

difficulty of preparing an intermediate with only 0.5 mol % of the chlorine atoms remaining. By leaving 10 mol % unreacted chlorine atoms, it was then possible to incorporate the precise amount of 5a in the second step, and to then replace the remaining chlorine atoms by trifluoroethoxy units to generate compound 6.

These synthetic procedures yielded fully substituted polymers in moderate to good yields (15–67%) and with high molecular weights ( $\geq$ 1000 kDa). The total concentration of the cyclotriphosphazene side group was determined for each polymer using both <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy. Representative examples of the <sup>31</sup>P and <sup>1</sup>H NMR spectra for polymer 7 are provided in the Supporting Information. Characterization data are provided in Table 1

**Solubility and Surface Character.** All the polymers described here are soluble in tetrahydrofuran, acetone, methyl ethyl ketone, and a number of other traditional organic solvents, and showed little deviation from the solubility profile of the parent  $[NP(OCH_2CF_3)_2]_n$ . The water contact angles for all polymers are in the range of 82–97 deg, with no discernible influence based on the concentration of 5a. This too reflects the properties of the parent  $[NP(OCH_2CF_3)_2]_n$ . Thus, the bulky phenoxy-functionalized cyclotriphosphazene groups have no appreciable influence on the surface properties of these polymers.

Thermal Transitions. Table 1 shows characterization data for these polymers, with the DSC traces provided in the Supporting Information. The  $T_g/T_1$  data are from DSC experiments. The important trends are (1) the glass transition temperatures rise as increasing numbers of the bulky side groups are present along the chains, and (2) the  $T_1$  transition, which is a well-known feature of the parent polymer  $[NP(OCH_2CF_3)_2]_m^{10,11}$  is detected in samples with a loading of the bulky groups of less than  $\sim 6-7$  mol %. Above this loading the  $T_1$  transition is no longer observed. As discussed in our previous publications<sup>12,13</sup> the observed decrease in the intensity of the  $T_1$  transition, and its eventual disappearance, with an increase in the concentration of the bulky cyclotriphosphazene side groups is due to disruption of chain packing due to the cyclotrimeric side group's steric bulk. Thus, the presence or absence of the  $T_1$  transition can be used to determine if the sample is microcrystalline or completely amorphous, respectively. A further indication of the loss of the  $T_1$  transition, and its correlation with the transition of the polymers from semi crystalline to amorphous, is evident from the X-ray scattering data (see later). The increase of the  $T_g$  is almost certainly a consequence of steric restrictions to backbone torsional motions caused by intra- and intermolecular

interactions, which reduces torsional freedom and yields a stiffer polymer.<sup>8</sup> Apart from purely steric interactions the possibility also exists that the aromatic nature of the substituents on **2** may further limit polymer flexibility though  $\pi - \pi$  interactions.

This is a similar trend to that found for polymers of type 1.<sup>12</sup> Figure 1 shows a comparison of the  $T_g$  values as a function of



**Figure 1.** Glass transition temperatures of polyphosphazene elastomers bearing phenoxy- and trifluoroethoxy<sup>12</sup>-functionalized cyclotriphosphazene cosubstituents.

side group concentration for the polymers of types 1 and 2. The  $T_{\rm g}$  values measured for the polymers of type 2 are on average 20–30 °C higher than those of their counterparts of type 1 at comparable concentrations. Figure 2 shows a 3D comparison of the size of the two bulky side groups, together with the 2,2,2-trifluoroethoxy unit for comparison.

Although the  $T_g$  values of the polymers are influenced by the bulk of the cyclotriphosphazene groups, the  $T_1$  transition appears to be relatively insensitive to the size of the larger substituents. Earlier reports have suggested that this transition represents a conversion of the microcrystallites found in the parent [NP(OCH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sub>n</sub> to a secondary mesophase.<sup>10,13,14</sup> Thus, because the larger side groups are associated with the noncrystalline sections of the chains it is understandable that changes in the size of the bulky side groups have a minimal effect on the behavior of the crystallites.<sup>12</sup> Thus, the presence or absence of this transition is a simple indicator of whether the polymer retains crystallinity or is amorphous. Only polymers 6



Figure 2. 3D rendering of the 2,2,2-trifluoroethoxy- (left), 2,2,2-trifluoroethoxycclotriphosphazene (middle), and phenoxycclotriphosphazene (right) side groups. These groups extend from the polyphosphazene backbone by ~4.8, 14.8, and 16.5 Å, respectively.

and 7 show evidence of this transition, while polymers **8–10** do not. This suggests that the *loading* of bulky groups required to eliminate crystallinity (between 6 and 10 mol %) is fairly constant regardless of the size or character of the bulky groups, at least within this polymer system.

WAXS Data and Crystallinity. Additional evidence of the change from semicrystalline to amorphous was provided by wide-angle X-ray scattering (WAXS) analysis. Figure 3 shows



Figure 3. WAXS patterns for poly(bis-trifluoroethoxy)phosphazene (TFE) and polymers 6-10 (Note: the patterns for polymers 8 and 9 show very minor, sharp signals from traces of sodium chloride impurity that are present even after extensive purification.)

the patterns collected for polymers **6–10** together with the profile for the parent poly(bis-2,2,2-trifluoroethoxy)-phosphazene. All the patterns reveal the presence of two signals centered at  $2\theta \approx 9$  and 21 deg. The same signals are also found for the previously studied polymers of series  $1^{12}$  as well as the more recently studied oligo-*p*-phenylene containing polyphosphazenes.<sup>13</sup> On the basis of the earlier work, these diffraction peaks represent the interchain spacing and the near-cis-trans planar repeat unit lengths, respectively.<sup>14–18</sup>

The data suggest two main conclusions. First, the WAXS patterns obtained for polymers 6, 7, and poly(bis-2,2,2-trifluoroethoxy)phosphazene contain sharper signals than

those of polymers 8–10. This provides additional confirmation that polymers 6 and 7 are semicrystalline, while 8–10 are most likely amorphous. These observations are further supported by the DSC data which show the presence or absence of the semicrystalline nature of these polymers though the presence or absence of the  $T_1$  transition, respectively. All of these observations reinforce the conclusion that the loading of the bulky cosubstituents required to transform a semicrystalline polymer, like [NP(OCH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sub>n</sub> to an amorphous material (5–10 mol %), is more a function of its concentration than its size.

Second, although the steric bulk of the cosubstituent group appears not to alter the loading at which the transition from semicrystalline to amorphous occurs, it does influence the degree to which the polymer chain packing is disrupted at higher cosubstituent loadings. Specifically, the WAXS trace of polymer **10**, which contains 22.3 mol % of **5a**, shows a nearly complete elimination of the two main signals at  $2\theta = 9$  and 21 deg. This is in contrast to its counterparts  $\mathbf{1}^{12}$  and the oligo-*p*-phenylene containing polyphosphazenes<sup>13</sup> which retains stronger crystalline signals at a similar bulky cosubstituent loading. Thus, the larger size of **5** appears to have a greater disruptive effect on chain packing than does its counterpart of series **1** and the oligo-*p*-phenylene containing polyphosphazenes.

The properties may be analogous to those observed for more traditional poly(dimethylsiloxane) (PDMS), poly-(diethylsiloxane) (PDES) and poly(dipropylsiloxane) (PDPS).<sup>19-21</sup> Of these polymers, PDES and PDPS, show the presence of a liquid-crystalline phase when heated above their  $T_{o}$ , but below their  $T_{m}$ , while PDMS does not show this transition. In these polymers, the ability of the longer side groups in PDES and PDPS to become oriented may allow the materials to show the presence of the liquid-crystalline phase, while in the case of PDMS the side chains are too short to allow these interactions to occur. A similar phenomenon may be occurring in this phosphazene system, in which the bulky cyclotriphosphazene side groups may interact with each other, and allow a similar liquid-crystalline like phase to exist. This could account for the retention of some of the order in the samples as indicated by the decrease, but not complete elimination, of the two main signals in the WAXS traces of the polymers that contained higher cyclotriphosphazene loadings.

**Mechanical Properties.** The mechanical properties of polymers 6-10 were examined using an Instron tensile testing instrument. The data are summarized in Table 2, with representative stress-strain curves shown in Figure 4.

polymer	tensile strength (MPa)	yield strength (MPa)	break elongation (%)	Young's modulus (MPa)
6	$5.6 \pm 0.5$	$1.8 \pm 0.1$	$440 \pm 40$	$19.5 \pm 2.3$
7	$3.9 \pm 0.3$	$1.0 \pm 0.1$	$720 \pm 80$	$12.2 \pm 2.7$
8	$2.2 \pm 0.3$	$0.05 \pm 0.01$	$1,400 \pm 120$	$0.24 \pm 0.05$
9	$2.1 \pm 0.1$	$0.04 \pm 0.01$	$2,200 \pm 70$	$0.48 \pm 0.15$
10	$0.47 \pm 0.04$	$0.03 \pm 0.01$	$3,100 \pm 300$	$0.42\pm0.15$



**Figure 4.** Representative stress-strain curves for polymers **6**–**10** and poly(bis-2,2,2-trifluoroethoxy)phosphazene (TFE).

The mechanical properties of the polymers follow the trends seen in the DSC and X-ray results and fall into three main groups at room temperatures: (a) semicrystalline (6 and 7), (b) amorphous elastomers (8 and 9) and (c) low  $T_g$  gum (10). These are similar results to those obtained for our previously published systems, and may represent a general trend for other polymers of this type.<sup>12,13</sup>

The semicrystalline polymers 6 and 7, which contain 0.7 and 6.3 mol % of 5a, respectively, are relatively tough materials. This is a consequence of their microcrystallinity, which is responsible for the highest tensile strength (3.9 to 5.6 MPa) and Young's modulus (12.2 to 19.5 MPa) and the shortest elongation at break (440 to 720%). For polymer 6, these properties are a minor variation of those found for its counterpart of type 1, and indeed of the single-substituent  $[NP(OCH_2CF_3)_2]_n$ . Thus, within this range, the major contributing factor to the mechanical behavior is the semicrystalline structure, with a minimal influence by the small amounts of the bulky cosubstituents. However, for polymer 7 the mechanical properties are changed significantly compared to those for series 1. Specifically, the tensile strength and Young's modulus are increased by a factor of 2 and 100, respectively, and the elongation at break is only half of the value measured for its counterpart in series 1. This change almost certainly originates from the onset of interactions between the aryloxy-cyclotriphosphazene side groups. These interactions could involve phase separation between aryloxy and fluorinated

domains,  $\pi - \pi$  stacking of the aryl groups, or interdigitation of the cyclotriphosphazene units. All three influences could generate properties that would normally be ascribed to covalent or physical cross-links.

Once the microcrystallinity is eliminated by the incorporation of more than  $\sim 10$  mol % of side group 5a (polymers 8) and 9), the mechanical properties undergo a major change which becomes manifest in the appearance of elastomeric behavior. Thus, amorphous polymers 8 and 9 show a good retention of tensile strength (2.2 and 2.1 MPa, respectively), while their Young's modulus decreases (0.24 and 0.48 MPa, respectively). In addition, the elongation at break (1400 and 2200%, respectively) is two to three times larger than that found for the semicrystalline 6 and 7. These changes are attributable to the elimination of crystallinity, which is confirmed by both WAXS and DSC analyses. In addition, the tensile strength and Young's modulus are two- and 10-fold larger (respectively) than in the polymer 1 series for an equivalent loading of the cyclo-trimeric side group. This increased tensile strength and Young's modulus probably originate from the ability of the bulky side groups to coassociate and form stronger interchain interactions than in series 1.

However, once the content of 5a reaches 22.6 mol % (polymer 10), the polymers take on the morphology of selfadhesive, low  $T_g$  gums, with a drastic loss of tensile strength (0.47 MPa) and a further increase in the break elongation (3,100%). These results are similar to those reported for the polymers based on structure 1.<sup>12</sup> The change in physical behavior is accompanied by an almost complete elimination of chain packing order, as detected in the WAXS data. This could be a result of steric crowding of 5a units along the polymer backbone, and the elimination of free volume needed to permit interdigitation. Thus, to summarize, it appears that the incorporation of ~20 mol %, or more of bulky cosubstituent groups causes polyphosphazenes to lose their elastomeric properties and to behave like uncross-linked gums. Elasticity can then be retained only by the presence of covalent crosslinks introduced, for example, by cross-coupling through unsaturated cosubstituents.

However, the main point is that the increase in both the tensile strength and Young's modulus of the elastomeric polymers 8 and 9, compared to their counterparts of type 1, illustrates that the mechanical properties can be controlled by the size and structure of the bulky substituents, and that this offers opportunities for the fine-tuning of useful properties.

**Elastomeric Recovery.** The elastomeric recovery of the polymers was examined by elongation of dog-bone shaped samples up to 60% of their break elongation, before retraction back to their original length. This cycling was performed four times, and the elastic recovery was calculated using the degree of nonrecoverable permanent deformation remaining after the fourth cycle. The data are summarized in Table 3. The degree

Table 3. Elastic Recovery of Polymers 5–9 after Four Elongation Cycles up to 60% of their Break Elongation

polymer	elastic recovery (%)
6	27
7	43
8	88
9	87
10	NA

to which the samples were capable of retracting to their original shape correlates well with the concentration of the cyclotriphosphazene side group **5a**. The elastomeric recovery information confirms the conclusions described above.

Thus, the semicrystalline polymers 6 and 7 had the lowest ability to retract after being elongated (27% and 43%, respectively). This low elastic recovery is similar to that measured for  $[NP(OCH_2CF_3)_2]_n$  (~25%), and is almost certainly a result of the semicrystalline character of the samples. However, once the concentration of 5a is increased to above  $\sim$ 7 mol %, the polymers become amorphous, and they show a drastic increase in their degree of elastic recovery (>85%), which resembles the behavior of polymers of series 1 at similar cyclic trimeric side group loading. The ability of these materials to retract back to almost their original shape exemplifies the cross-link-like interactions caused by the cyclotriphosphazene side groups 5a. However, once the concentration of 5a is higher than  $\sim 20$  mol %, the polymers become self-adhesive gum-like materials with a minimal ability to undergo elastic recovery. This appears to be a result of the nearly complete loss of chain orientation as indicated in the WAXS study described earlier, and the probable decreased ability of the cyclotriphosphazene side groups to interdigitate, thus leading to a decrease in "crosslink" efficiency.

## EXPERIMENTAL SECTION

Reagents and Equipment for Polymer Synthesis. The syntheses were carried out using standard Schlenk-line techniques under a dry argon atmosphere, unless specified otherwise. All glassware was dried in an oven at 140 °C overnight 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). Phenol (TCI) was sublimed under reduced pressure  $(10^{-2} \text{ mbar})$  and stored under dry argon before use. Dichloromethane (EMD), hexanes (EMD), sodium carbonate (Alfa Aesar), sodium hydride (60% w/w in mineral oil, Aldrich), acetone (EMD), methanol (EMD), and terta-n-butylammonium nitrate (Alfa Aesar) were used as delivered. Dialysis was accomplished 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 vacuum sublimation (10<sup>-2</sup> mbar) at 50 °C. Poly(dichlorophosphazene) was synthesized by the uncatalyzed thermal ring-opening polymerization of the purified hexachlorocyclotriphosphazene at 250 °C in an evacuated and sealed Pyrex tube. The unreacted trimer was removed by vacuum sublimation  $(10^{-2} \text{ mbar})$  at 50 °C, to leave the polymer as a colorless elastomeric material.

<sup>1</sup>H and <sup>31</sup>P NMR spectroscopy made use of a Bruker AV-360 instrument operated at 360 and 145 MHz, respectively. <sup>31</sup>P NMR shifts are reported in ppm relative to 85% H<sub>3</sub>PO<sub>4</sub> at 0 ppm. Thermal transitions were measured using a TA Instruments Q10 DSC unit operated at a heating rate of 10 °C/min, under a nitrogen stream with a sample size of 10–15 mg. Data analysis was carried out with use of a TA Instruments Universal Analysis 2000 Software. Polymer molecular weights were obtained using gel permeation chromatography using a Hewlett-Packard 1047A refractive index detector and two Phenomenex Phenogel linear 10 columns, eluted at a rate of 1 mL/min using a 10 mM solution of tetra-*n*-butylammonium nitrate in tetrahydrofuran. The elution times were calibrated using polystyrene standards.

Synthesis of Cyclotriphosphazene Intermediate 3. To a suspension of sodium hydride (60% w/w in mineral oil) (34.5 g, 0.863 mol) in tetrahydrofuran (0.25 L) at 0 °C was slowly added a solution of 4-methoxyphenol (107 g, 0.863 mol) in tetrahydrofuran (0.25 L). Once the addition was complete, the reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. After the sodium hydride was consumed, the mixture was added dropwise to a

vigorously stirred solution of hexachlorocyclotriphosphazene (300 g, 0.863 mol) in tetrahydrofuran (1.5 L), and the resulting reaction mixture was stirred for 48 h at room temperature. Once the substitution was complete, the solvent was removed under reduced pressure and the resulting oil was purified by vacuum distillation at 170 °C and  $10^{-2}$  mbar. The collected material contained **3** in 37% yield with no multifunctional groups detected by <sup>31</sup>P NMR. <sup>31</sup>P NMR (145 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 22.9 (d, 2P), 13.4 (t, 1P).

Synthesis of Cyclotriphosphazene Side Group 5. To a suspension of NaH (60% w/w in mineral oil) (16.6 g, 0.416 mol) in tetrahydrofuran (0.5 L) at 0 °C, was slowly added phenol (39.1 g, 0.416 mol). After the NaH was consumed, intermediate 3 (30.0 g, 0.070 mol) was added to the main reaction solution which was stirred at reflux for 24 h The progress of the reaction was monitored using <sup>31</sup>P NMR spectroscopy. After this reaction was complete, the solvent was removed under reduced pressure and the resulting oil was redissolved in dichloromethane (0.5 L) and was washed with water  $(2 \times)$  and brine  $(2\times)$ , before drying the organic phase over anhydrous magnesium sulfate and removal of the solvent under reduced pressure. The resulting product was centrifuged, and the mineral oil was removed from the surface of 4, which was a viscous oil. The product was dried further under high vacuum to remove any remaining moisture. Once dry, 4 was redissolved in DCM (0.15 L), to which was added BBr<sub>3</sub> (10.0 mL, 0.11 mol), and the solution was stirred at room temperature overnight. The solution was then poured into water (0.2 L,  $0^{\circ}C$ ) and the mixture was stirred vigorously for 30 min. The organic phase was isolated, washed with 0.1 M sodium carbonate (2X), and brine (2X), before removal of the solvent to afford 5 as an oil in 89.5% yield. <sup>31</sup>P NMR (145 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 9.39 (m). <sup>1</sup>H NMR (360 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 7.26–7.10 (m, 15 H), 6.95 (d, 10 H), 6.76 (d, 2H), 6.64 (d, 2H), 5.66 (s, 1H).

Synthesis of Polymer 6. To a suspension of sodium hydride (60% w/w in mineral oil) (2.97 g, 77.58 mmol) in tetrahydrofuran (200 mL) was slowly added 2,2,2-trifluoroethanol (5.65 mL, 77.58 mmol). The resultant solution of sodium trifluoroethoxide was added dropwise to a vigorously stirred solution of poly-(dichlorophosphazene) (5.00 g, 43.1 mmol) in tetrahydrofuran (750 mL). The mixture was then stirred at room temperature for 24 h. The progress of the substitution was monitored using <sup>31</sup>P NMR spectroscopy. In a separate vessel, which contained a suspension of sodium hydride (60% w/w in mineral oil) (0.02 g, 0.43 mmol) in tetrahydrofuran (100 mL), was added 5 (0.30 g, 0.43 mmol). After the NaH was consumed, this solution was added to the polymer solution and the reaction mixture was stirred at room temperature for 48 h. In a separate vessel, 2,2,2-trifluoroethanol (0.62 mL, 8.63 mmol) was added to a suspension of sodium hydride (60% w/w in mineral oil) (0.33 g, 8.63 mmol) in tetrahydrofuran (100 mL). Again, after the NaH was consumed, the mixture was added to the polymer solution. This suspension was stirred at room temperature for 2 h, after which time the product was concentrated under reduced pressure and was precipitated into water. The solid polymer was redissolved in acetone and dialyzed against 20% v/v methanol in acetone for 4 days. The solution was then concentrated under reduced pressure and was precipitated into water before being dried under high vacuum to afford the final material in 51% yield. Characterization data for all polymers are provided in Table 1.

**Synthesis of Polymers 7–10.** Polymers 7–10 were synthesized by followed a slightly different procedure, with a representative example provided for species **8**. To a suspension of sodium hydride (60% w/w in mineral oil) (1.18 g, 31.0 mmol) in tetrahydrofuran (100 mL) was added 2,2,2-trifluoroethanol (2.26 mL, 31.0 mmol). After the NaH was consumed, the solution was added dropwise to a vigorously stirred solution of poly(dichlorophosphazene) (2.00 g, 17.2 mmol) in tetrahydrofuran (300 mL). The resultant mixture was stirred at room temperature for 24 h while the progress of the reaction was monitored using <sup>31</sup>P NMR spectroscopy. In a separate vessel, which contained a suspension of sodium hydride (60% w/w in mineral oil) (0.53 g, 13.8 mmol) in tetrahydrofuran (200 mL) was added compound **5** (9.77 g, 13.8 mmol). After hydrogen evolution had ceased, this mixture was added to the polymer solution and the reaction mixture was stirred for 48 h at room temperature. In a separate vessel, 2,2,2-trifluoroethanol (0.24 mL, 3.45 mmol) was added to a suspension of sodium hydride (60% w/w in mineral oil) (0.13 g, 3.45 mmol) in tetrahydrofuran (100 mL). Once the NaH had been consumed, the sodium trifluoroethoxide solution was added to the polymer solution and the reaction mixture was stirred for an additional 2 h at room temperature. This ensured the total replacement of the remaining chlorine. The product was then concentrated under reduced pressure and precipitated into water. The solid was redissolved in acetone and dialyzed against 20% v/v methanol in acetone for 4 days. The resultant solution was concentrated under reduced pressure, precipitated into water, and the precipitate was dried under high vacuum to afford the final material in 67% yield. Characterization data for all the polymers are provided in Table 1

**Evaluation of the Mechanical Properties of Polymers 6–10.** The polymers were solvent cast from acetone (1.5 g in 50 mL) in Bytac coated dishes ( $6 \times 6$  cm). The solvent was allowed to evaporate slowly in an acetone-saturated atmosphere. Once solid, the films were dried under high vacuum for an additional 48 h. The resultant films were cut into dog-bone shaped samples according to ASTM D-1708 using a PioneerDietics die. The samples were kept under vacuum before testing.

**Tensile Tests.** Evaluation of mechanical properties was carried out with the dog-bone shaped films described above. The samples were pulled at a fixed cross-head speed of 100 mm/min until failure, using an Instron 5866 Tensile Testing System at ambient temperature using a 100 N load cell. The results are summarized in Table 2.

**Comparison of Elasticity.** The samples were cast and cut in a similar manner as described above. They were pulled at a fixed cross-head speed of 100 mm/min up to 60% of their previously determined break elongation, and retracted back to their original length. This cycling was performed 4 times per sample, and the percent recovery after the fourth cycle is reported in Table 3.

**Wide Angle X-ray Scattering.** Wide angle X-ray scattering (WAXS) patterns were obtained using a PANalytical X-Pert PRO MPD Theta-Theta goniometer with Cu K $\alpha$  radiation, and fixed slit incidence (0.25 deg divergence, 0.50 deg antiscatter, specimen length 10 mm) and diffracted (0.25 deg antiscatter, 0.02 mm nickel filter) optics. Sample films were cast using a method described in a previous section. The film samples were placed in a zero background holder for testing, and the data were collected at 45 kV and 40 mA from 5–50 deg in  $2\theta$  using a PIXcel detector in scanning mode with a PSD length of 3.35 degrees  $2\theta$  and 255 channels for a duration of ~20 min. The resulting patterns were analyzed using Jade+10 software. The WAXS patterns for polymers **5–9** are provided in Figure 3.

**3D Structure Rendering.** 3-Dimensional structures of 2,2,2-trifluoroethoxy-, phenoxy-, and 2,2,2-trifluoroethoxy-functionalized cyclotriphosphazene side groups (Figure 2) were generated using ChemBio3D Ultra 11.0, utilizing the MM2 minimization function to generate the lowest energy structure.

# CONCLUSIONS

New phosphazene polymers were synthesized with phenoxyfunctionalized cyclotriphosphazene side groups at various concentrations (0.7-22 mol %), with the remaining sites along the polymer backbone occupied by 2,2,2-trifluoroethoxy groups. The incorporation of ~10-22 mol % of the cyclotrimeric species disrupts the crystallinity characteristic of the parent poly[bis(2,2,2-trifluoroethoxy)phosphazene] polymer, and leads to the appearance of elastomeric properties. Because of the aromatic nature of the substituent groups present on the trimer units, and their incompatibility with the trifluoroethoxy units along the polymer backbone, the new polymers are tougher materials in terms of their tensile strength and Young's modulus compared to their counterparts with trifluoroethoxyfunctionalized cyclic trimeric units at comparable concentrations. This strengthening is attributed to the rigid aromatic nature of the cyclotriphosphazene side groups, which allows

them to interact though phase separation or interdigitation, possibly augmented by  $\pi - \pi$  interactions. However, larger amounts of the bulky groups eliminate the elastic properties and generate gums. Thus, the shape and size of the cyclotriphosphazene cosubstituent groups are the main factors that control the mechanical properties of the polymers. A very wide range of organic groups can be linked to phosphazene rings.<sup>2,16–19</sup> As a result, the opportunities for property tuning are almost unprecedented and provide a broad portfolio of options for the further development of this field.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.5b01892.

<sup>1</sup>H and <sup>31</sup>P NMR spectra for polymer 7 and Differential scanning calorimetry data for polymers **6–10** (PDF)

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#### Notes

The authors declare no competing financial interest.

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