Hybrid Polyphosphazene–Organosilicon Polymers as Useful Elastomers

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Supporting Information

ABSTRACT: Six high molecular weight, soluble, and stable elastomers were prepared derived from $-O(CH_2)_3Si(CH_3)_3/$ -OCH₂CF₃ cosubstituted polyphosphazenes with 1–92 mol % of the organosilicon component. The surface and morphological properties are appropriate for biomaterials, soft contact printing, or other elastomeric applications. Full substitution by either side group yields thermoplastics. The syntheses were facilitated by small molecule model reactions to establish appropriate reaction conditions.



KEYWORDS: polyphosphazene, organosilicon, hybrid, polymers, elastomers

INTRODUCTION

Poly(organophosphazenes) and poly(organosiloxanes) are hybrid inorganic-organic macromolecular systems that have several features in common.^{1,2} Both have highly flexible inorganic backbones to which are linked organic side groups, and both have been examined extensively for biomedical as well as engineering applications. The main difference is the wider variety of different side groups that can be linked to a polyphosphazene backbone via macromolecular substitution, and this opens access to a broader range of different structures and properties. Thus, hybrid macromolecules based on the two systems could allow the development of inert biomaterials, elastomers, hydrophobic coatings, and materials with other hard-to-find characteristics. A number of prior attempts have been made to achieve combinations of polyphosphazenes with organosiloxanes.³⁻¹⁴ These include the preparation of polymer blends and IPNs,⁵ phosphazene-substituted organosilicon polymers, ring-opening polymerization of small-molecule cyclophosphazenes with organosilicon side groups,⁹ polymers prepared by metalation of alkylphosphazene polymers followed by reaction with organosilicon halides,¹⁰ or alkylphosphazene halide polymers with the metalation of organosilicon side groups followed by further reaction with nucleophiles.¹¹ Polymers prepared from poly(organophosphazenes) with unsaturated side groups followed by hydrosilylation reactions¹² and reactions of chlorophosphazene high molecular weight polymers (high polymers) with organosilicon nucleophiles such as aminosiloxane reagents¹³ or POSS groups¹⁴ have also been explored. However, few of these earlier attempts established a reliable, scalable synthesis route to elastomeric linear high polymeric derivatives. Here, we describe a technique that provides access to a broad range of stable polymers with characteristics that range from elastomers to thermoplastics and with tunable variations in surface properties. The route described here has the advantage of synthetic simplicity, absence of side reactions, scalability, and ease of varying side group ratios to give different property combinations.

RESULTS AND DISCUSSION

Small Molecule Model Compound Studies. Macromolecular substitution reactions are inherently more challeng-

Scheme 1. Synthetic Route to Hexa-3-(trimethylsilyl)-1propanoxy-cyclotriphospha-zene $N_3P_3(O(CH_2)_3Si(CH_3)_3)_6$ (1)



ing than their small molecule counterparts. Therefore, we first explored the reaction of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, with the sodium salt of $(CH_3)_3Si(CH_2)_3OH$ in boiling THF and then transferred the optimized synthesis

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29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 1 Chemical shift (ppm)

Figure 1. ³¹P NMR spectra obtained at different reaction times during the formation of trimer 1, N₃P₃(O(CH₂)₃Si(CH₃)₃)₆, in THF solvent: (A) 0 min, (B) 10 min, (C) 1 h, (D) 2 h, and (E) 24 h.



Figure 2. ¹H NMR spectrum of cyclic trimer 1 N₃P₃(O(CH₂)₃Si- $(CH_3)_3)_6$ using CDCl₃ solvent.

Scheme 2. Synthetic Route to Polymers 3-9.



conditions to the corresponding high polymer reactions. A key question was whether the steric size of the organosilicon nucleophile would inhibit replacement of all the chlorine atoms in the cyclophosphazene. The model reaction is illustrated in Scheme 1.

The model reaction was monitored by ³¹P NMR spectroscopy (Figure 1), which showed that, with increasing reaction time, the singlet peak at 20.38 ppm from hexachlorocyclotriphosphazene (Figure 1A) disappeared quickly and other intermediate peaks appeared (Figures 1B-D). Finally, the multiplets converged to a singlet at 18.27 ppm (Figure 1E). These spectra confirmed that the chlorine atoms in the cyclic



Figure 3. ³¹P NMR spectra at different reaction times during the formation of polymer 5 {[NP(O(CH₂)₃Si- $(CH_3)_3)_{0.40}(OCH_2CF_3)_{1.60}]_n$: (A) 0 min, (B) 12 h later after NaOCH₂CF₃ was added, (C) 4 h later after NaO(CH₂)₃Si(CH₃)₃ was added, and (D) 17 h later after NaO(CH₂)₃Si(CH₃)₃ was added.



Figure 4. ¹H NMR spectrum of polymer 5 { $[NP(O(CH_2)_3Si (CH_3)_3)_{0.40}$ $(OCH_2CF_3)_{1.60}]_n$ using $(CD_3)_2CO$ as a solvent.

trimer were replaced progressively by $O(CH_2)_3Si(CH_3)_3$ groups until only one product was formed: the fully substituted derivative $N_3P_3(O(CH_2)_3Si(CH_3)_3)_6$ (1). The ratio of the integration intensities in the ¹H NMR spectrum confirmed the structure of trimer 1 (Figure 2). Moreover, the stable, hexasubstituted trimer peak at 18.27 ppm appeared rapidly after only 1 h of reaction at room temperature (Figure 1C) and persisted for at least an additional 3 days of exposure to the reaction mixture. This is important because it offered the prospect of extended reaction times at the level of the high polymers coupled with scale-up of the synthesis.

The mass spectra from trimer 1 showed the expected parent ion peaks at m/z = 922.39 (theoretical value is 922.47) and other isotope peaks at 923.41, 924.41, 925.43, and 926.44 (corresponding theoretical values are 923.48, 924.47, 925.47, and 926.47), which are consistent with the proposed structure.

The most important result was the demonstration that all six chlorine atoms in $(NPCl_2)_3$ can readily be replaced by the bulky organosilicon groups. Once the small molecule reaction was understood, the synthesis technique was transposed to the macromolecular level. Although substitution reactions carried out on a high polymer have obvious differences and constraints from those with a small molecule model system, the ease of

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Figure 5. ${}^{1}H$ (A) and ${}^{31}P$ NMR (B) spectra of polymer 9 in the solvent of CDCl₃.

100% substitution with the trimer provided encouragement that the same process could be repeated with the high polymer.

Synthesis of Polymers 2–9. Examples exist where difficulties are encountered in the linkage of bulky side groups to a high polymeric polyphosphazene chain. However, no such impediments were encountered with this system. Thus, 100% replacement of the chlorine in the high polymer by 3-(trimethylsilyl)-1-propanoxy groups occurred with minimal forcing conditions. We attribute this facility to the three methylene units in the spacer unit between the oxygen and trimethylsilyl unit, which separates the bulky trimethylsilyl group from the reaction site.

Moreover, a series of mixed-substituent polymers was produced by treatment of poly(dichlorophosphazene) first with sodium trifluoroethoxide followed by replacement of the remaining chlorine atoms by sodium 3-(trimethylsilyl)-1propanoxide. This sequence was chosen because sodium trifluoroethoxide is a more aggressive nucleophile than $NaO(CH_2)_3Si(CH_3)_3$, and the chosen sequence avoids the possibility that organosilicon units already linked to the inorganic chain might be displaced during the course of the reaction (Scheme 2). Moreover, complete halogen replacement by the organosilicon reagent was ensured by allowing the reaction to continue for additional hours after the appearance of complete substitution by ³¹P NMR analysis.

The progress of all the reactions was monitored using ${}^{31}P$ NMR spectroscopy. Figure 3 illustrates the NMR changes during the synthesis of a polymer. Thus, after the sodium trifluoroethoxide was added to the [NPCl₂]_n solution, the peak

polymer	O(CH ₂) ₃ Si(CH ₃) ₃	(10 mg/mL)	(10 mg/mL)	(10 mg/mL)	character (THF)	T_{g} (°C)	$T_1(^{\circ}C)$	(0°C)	(%)	(KDa) ⁹	units	IDI	(deg)	(deg)
7	0	insoluble	soluble	insoluble	leathery film	-62.0	58.2	375	1.85	937	3856	2.1	104.0	53.4
3	1	insoluble	soluble	insoluble	elastomer	-53.4	NA ^a	327	7.21	237	972	1.7	71.7	34.3
4	4	insoluble	soluble	insoluble	less adhesive elastomer	-55.4	NA ^a	319	8.69	257	1046	1.7	95.8	37.6
s	20	soluble	soluble	insoluble	adhesive elastomer	-53.5	NAª	315	9.05	585	2285	2.0	111.7	67.4
6	40	soluble	insoluble	soluble	more adhesive elastomer	-56.8	NA ^a	304	11.20	703	2615	2.2	101.1	75.7
~	20	soluble	insoluble	soluble	high adhesive polymer	-57.5	NA ^a	291	15.63	383	1329	1.8	112.1	57.2
×	92	soluble	insoluble	soluble	soluble adhesive wax	-62.4	NA ^a	317	18.51	284	939	1.9	106.2	52.3
6	100	soluble	insoluble	soluble	plastic film	-62.3	-17.4	334	18.39	684	2605	1.8	101.6	37.5
^{<i>a</i>} T ₁ trant deionized	vition was not detected l water. ^d Contact ang	l by DSC. ^b The polyn de to <i>n</i> -hexadecane.	ner synthesis used a dii	fferent batch of poly	(dichlorophosphazene)), which n	nay make	the $M_{ m w}$ a	nd repeati	ing units h	ave large	ranges.	^c Contact	angle to

HCA^d

WCA^c

repeat

Mw

char_{850°C}

solubility in hexane solubility in acetone solubility in chloroform film-forming



Table 1. Characterization Data for Polymers 2-9

nol



Figure 6. DSC traces of polymers 2-9.





at -18.00 ppm in [NPCl₂]_n (Figure 3A) changed to two different peaks at -10.04 ppm that corresponded to skeletal phosphorus atoms with both chlorine and $-OCH_2CF_3$ groups. The peak at -17.58 ppm corresponds to phosphorus atoms with two chlorine atoms (Figure 3B). After the sodium 3-(trimethylsilyl)-1-propanoxide was added, the remaining chlorine atoms were replaced by $-O(CH_2)_3Si(CH_3)_3$ groups, and the spectrum changed to two separate peaks at -8.56 ppm that corresponded to phosphorus atoms connected to $-O(CH_2)_3Si(CH_3)_3$ and $-OCH_2CF_3$ groups and at -7.49 ppm, which corresponds to phosphorus atoms connected to two $-OCH_2CF_3$ groups (Figure 3C). Finally, there was no change between the two ratios of the integration intensities for the peaks at -6.74 and -8.22 ppm (Figure 3D).

The NMR spectrum of polymer **5** after polymer purification is illustrated in Figure 4. The existence of both the $-OCH_2CF_3$ and $-O(CH_2)_3Si(CH_3)_3$ groups was evident from the signals in the ¹H NMR spectrum.

It is worth noting that polymer 9 with $100\% - O(CH_2)_3Si-(CH_3)_3$ side groups yielded the ¹H and ³¹P NMR spectra shown in Figure 5. From the very sharp peak in the ³¹P NMR spectrum (Figure 5B), it was concluded that all the chlorine atoms in [NPCl₂]_n had been replaced by $-O(CH_2)_3Si(CH_3)_3$ groups. For further confirmation, elemental analyses of



Figure 8. Comparison of Young's modulus (A) and tensile strength (B) as a function of 3-(trimethylsilyl)-1-propanoxy concentration for polymers 2-6 and 9.

polymer 9 were obtained for sodium and chlorine content. The analysis indicated 1.19% of nonhydrolytically sensitive chlorine, which could represent traces of hydrogen chloride coordinated to the polymer backbone or could indicate the presence of traces of sodium chloride. This latter possibility was supported by the detection of 1.80% sodium in the sample.

Characterization and Physical Properties of the Polymers. The physical properties of most polyphosphazenes are highly dependent on the nature of the substituents linked to the polymer backbone. The effect of incorporating $-O(CH_2)_3Si(CH_3)_3$ side groups into the phosphazene structure on the solubility, glass transition temperatures, thermal stability, mechanical properties, and surface properties was thus of considerable interest.

Solubility Properties. The $-O(CH_2)_3Si(CH_3)_3$ side groups altered the solubility dramatically (Table 1). Increasing amounts of $-O(CH_2)_3Si(CH_3)_3$ groups in polymers **6–9** (40–100 mol %) caused insolubility in acetone and solubility in chloroform, while polymers **2–5** (0–20 mol %) are soluble in acetone but insoluble in chloroform. Moreover, polymers **5–9** (20–100 mol %) dissolve in aliphatic hydrocarbons such as hexane, while polymers **2–4** (0–4 mol %) are insoluble in hexane. Polymer **5** dissolves in acetone and hexane. All of the polymers are soluble in THF.

Glass and Mesophase Transition Temperatures. Figure 6 shows the differential scanning calorimetry (DSC) curves of polymers 2-9 with the T_g and other transitions listed in Table 1. Compared with poly[bis(trifluoroethoxy)-phosphazene] (polymer 2), which is a semicrystalline solid, species 3-8 with two types of side groups are flexible,



Figure 9. Representative images of contact angle to water images of (A) polymer 3 (71.7°) and (B) polymer 5 (111.7°) and contact angle to *n*-hexadecane of (C) polymer 3 (34.30°) and (D) polymer 6 (75.65°).

noncrystalline materials. Introduction of $-O(CH_2)_3Si(CH_3)_3$ units eliminates microcrystallinity (polymer 2) and gives rise to elastomeric character even with just 1 mol % of the organosilicon substituents present (polymer 3).

Polymer 9, a microcrystalline polymer with 100% $-O_{(CH_2)_3}Si(CH_3)_3$ side groups, yielded the ¹H and ³¹P NMR spectra shown in Figure 5. The profile in Figure 6 indicates a clear T_1 transition at -17.4 °C, which is at a lower temperature than that in polymer 2 (58.2 °C). Moreover, another endothermic peak (probably a cold crystallization temperature) due to the T_m of polymer 9 appeared at -39.6 °C. These two peaks are probably a consequence of packing by $-O(CH_2)_3Si(CH_3)_3$ groups, and they demonstrate the high degree of crystallinity in polymer 9. However, the microcrystallization character of polymer 9 is less than that of polymer 2. A likely reason for this is the larger dimensions of the $-O(CH_2)_3Si(CH_3)_3$ group compared to that of $-OCH_2CF_3$, which makes microcrystallization difficult.

Moreover, the T_g values of all the polymers, which ranged from -62.4 to -53.4 °C, illustrate the influence of the flexible -O(CH₂)₃Si(CH₃)₃ side groups on the polymer properties.

Thermal and Mechanical Behavior. The thermal weight loss curves evaluated by TGA in nitrogen are shown in Figure S1 and in Table 1. All of the polymers except 2 show an abrupt weight loss in the temperature range of 300-350 °C. This matches the behavior of $[NP(OCH_2CF_3)_2]_n$ and is attributed to depolymerization to small-molecule cyclic phosphazenes. The presence of the organosilicon side groups in polymers 3– 9 alters the thermal profile slightly to raise the decomposition/ volatilization onset temperature and increase the amount of ceramic residue.

The mechanical properties of the polymers changed significantly as the ratios of the two types of side groups were changed, as illustrated in Figures 7 and 8. Increases in the proportion of $-O(CH_2)_3Si(CH_3)_3$ groups moved the properties through four distinct stages. First, the microcrystalline polymer **2** is a tough and leathery material which orients and

crystallizes readily under tension and breaks at very low strain (9%) and with a high Young's modulus (126.6 MPa) and tensile strength (6.25 MPa).

Second, polymer **3** with 1 mol % of $-O(CH_2)_3Si(CH_3)_3$ side units is a typical elastomer. Even though not covalently cross-linked, it displays properties that would be typical of a lightly cross-linked organic elastomer. The tensile strength (4.25 MPa) is nearly one-half the observed value for the microcrystalline counterpart (polymer **2**), and the Young's modulus (2.9 MPa) is decreased by almost 2 orders of magnitude. Moreover, this polymer can undergo significant elongations (1340%) before rupturing.

Third, polymers **4–6** with 4–40 mol % $-O(CH_2)_3Si(CH_3)_3$ side units are relatively soft, self-adhesive materials with a remarkably decreased Young's modulus (0.39–0.68 MPa) and tensile strength (0.35–2.64 MPa). Interestingly, they show a similar elongation (1090–1350%) to polymer **3** (1340%) before rupturing. Polymers 7 and **8** with 70–92 mol % $-O(CH_2)_3Si(CH_3)_3$ side units are a highly self-adhesive material and a soluble adhesive wax, respectively, and could not be fabricated into films.

Fourth, polymer 9 with 100 mol % –O(CH₂)₃Si(CH₃)₃ side units is a typical thermoplastic polymer with a yield point shown in Figure 7. However, its Young's modulus (20.4 MPa) and tensile strength (0.30 MPa) are much lower than the values for polymer 2.

These trends can be attributed to two influences. First, as the percentage of the $-O(CH_2)_3Si(CH_3)_3$ side units increases, the microcrystallinity of the samples is reduced. Even 1 mol % of $-O(CH_2)_3Si(CH_3)_3$ (polymer 3) is sufficient to bring about this transformation. This loss of microcrystallinity weakens the intermolecular interactions of the polymers and extends their break elongation. Second, when the percentage of $-O(CH_2)_3Si(CH_3)_3$ side units is 100 mol %, the solid state packing results in the reintroduction of microcrystallinity, as shown in the DSC analysis. However, these intermolecular

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interactions are weaker than those in 2, and this lowers the Young's modulus and tensile strength.

Surface Analysis. The uses of polymers in biomedical implant materials or as lithographic image transfer materials often depend on a combination of morphological and surface characteristics. Measurements of contact angles to water provide an initial indicator of surface structure and possible utility.¹⁵ Both $-OC_2CF_3$ and $-O(CH_2)_3Si(CH_3)_3$ groups are intrinsically hydrophobic, and it was of interest to trace the results of changes in the side group ratios. Surface contact angles for these polymers are listed in Table 1. For polymers 3-5, the contact angles to water increased with the $-O(CH_2)_3Si(CH_3)_3$ content from 71.7° (polymer 3) to 111.7° (polymer 5), as illustrated in Figure 9. For polymer 6, the contact angle decreased to 101.1°, then increased to 112.1° for polymer 7, and then decreased to 101.6° for polymer 9. Furthermore, the oleophilic values for the contact angles to *n*-hexadecane show a similar trend with the increasing $-O(CH_2)_3Si(CH_3)_3$ content from 34.30° (polymer 3) to 75.65° (polymer 6) (Figure 9) and then decreasing to 37.47° (polymer 9). It is significant that polymers 5 and 6 show contact angles to *n*-hexadecane over 67° , which is higher than for all the previously reported phosphazene fluoropolymers or indeed for Teflon.¹

These results can be understood if the $-O(CH_2)_3Si(CH_3)_3$ side group is considered to be an amphiphile in which the oxygen atom is hydrophilic and the trimethysilyl group is hydrophobic. Thus, a hydrophilic enhancement would result if the O atom units were oriented toward the surface, whereas hydrophobic enhancement would result if the trimethyl groups were concentrated at the surface. Yasuda and Sharma¹⁵ make the conclusion that the surface properties of a polymer are more a function of surface *orientation* and side group *mobility* rather than the nature of the bulk hydrophilic/hydrophobic side groups. The present results support this interpretation.

CONCLUSIONS

In this work, the first high molecular weight, soluble, and stable trifluoroethoxy/organosilicon cosubstituted polyphosphazenes with (0-100 mol %) of $-O(CH_2)_3Si(CH_3)_3$ side groups were prepared. Several of these hybrid polymers have useful combinations of surface and morphological properties of the type that may be appropriate for biomaterials, soft contact printing, and other elastomeric material applications. Moreover, the ease of synthesis points the way to a wide variety of related macromolecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsapm.9b00381.

Synthesis and characterization details of small molecules and polymers (PDF)

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Notes

The authors declare no competing financial interest.

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