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Synthesis and Characterization of Water-Soluble Cationic and Anionic Polythionylphosphazene Polyelectrolytes

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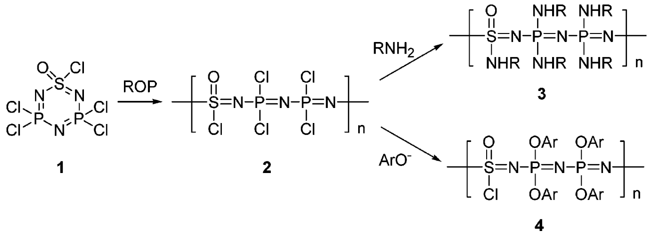
ABSTRACT: Convenient synthesis of a range of water-soluble polythionylphosphazene polyelectrolytes is reported. Facile reaction of 3-(dimethylamino)propylamines with the substitutionally labile poly(chlorothionylphosphazene) **2**, which is generated via thermal ring-opening polymerization of the cyclic thionylphosphazene **1**, afforded the water-soluble polymer **5**. The cationic polymer **6** was obtained upon quaternization of the dimethylamino groups in polymer **5** in the presence of dimethyl sulfate. The luminescent cationic polymer **7** was prepared through the covalent attachment of 30 mol % loading of an amino-functionalized ruthenium phenanthroline complex in the polythionylphosphazene side chains. The anionic polymeric precursor **14** was synthesized via substitution reactions of poly(chlorothionylphosphazene) **2** with amine **12**. Upon removal of the protective silyl groups, the anionic polythionylphosphazene **15** was obtained. All three polyelectrolytes **6**, **7**, and **15** were readily soluble in water, making them potentially useful materials for a range of applications.

Introduction

Polyelectrolytes are a class of water-soluble macromolecules which possess cationic or anionic charges along the polymer chains and are of considerable importance for many industrial and technological applications.[1] These materials have attracted intense recent attention as building blocks for the construction of nanometer-scale ultrathin films in layer-by-layer processes where oppositely charged polyelectrolyte monolayers are sequentially assembled through electrostatic interactions.[2] Despite significant efforts in this area, most of the polyelectrolytes reported in the literature are organic macromolecules. To date, few studies have been reported for inorganic polyelectrolytes based on main group elements which would be expected to possess unique properties and potential applications.[3−6]

Polythionylphosphazenes **3** and **4** are members of an interesting class of high molecular weight inorganic polymers which possess main group elements sulfur−phosphorus−nitrogen in the polymer backbone.[7−11] These polymers are readily accessible via substitution reactions of alkylamines or aryloxides with the hydrolytically sensitive poly(chlorothionylphosphazene) **2**, which in turn can be derived through thermal or Lewis acid-catalyzed ring-opening polymerizations (ROP) of the cyclic thionylphosphazene **1** (Scheme 1).[7,12−16] It should be noted that the properties of the resulting polymers **3** and **4** can be readily tuned by using various alkylamines or aryloxides as side chains.[12−14,16] These materials can display different and in some cases advantageous properties over polyphosphazene analogues such as lower T_g values and amorphous rather than crystalline morphologies.[8]

Scheme 1



Polythionylphosphazenes have been used in the construction of oxygen-sensing devices as polymer supports for luminescent transition metal complexes which are sensitive to oxygen quenching.[17,18] These oxygen sensors have attracted attention for biomedical and barometric applications to monitor breathing or to provide pressure profiles over aircraft models in wind tunnel experiments.[8,19−21] For example, we have previously reported that poly(*n*-butylaminothionylphosphazene) **3a** (Chart 1) exhibits good oxygen permeability and can be used as polymer matrices for luminescent dyes such as platinum octaethylporphyrin or ruthenium trisphenanthroline.[17,22] The resulting two-component oxygen sensors have demonstrated good oxygen sensitivities.[17,18,22,23] Furthermore, a ruthenium phenanthroline complex has been successfully attached, through covalent bonding, to poly(*n*-butylaminothionylphosphazene) **3b**, and the resulting one-component material exhibits much improved oxygen-sensing behavior in comparison to the two-component materials as a result of reduced dye aggregation.[24] Our recent efforts and those of our collaborators have been directed toward the construction of ultrathin luminescent electrostatic superlattices through layer-by-layer assembly of polythionylphosphazenes containing ruthenium phenanthroline complexes. These thin films have potential applications in the fast detection of sub-microsecond oxygen pressure changes. To this end, we have synthesized a range of polythionylphosphazene polyelectrolytes that can be used in the electrostatic assembly of nanometer-scale luminescent films. Thus, we report in this paper the synthesis and characterization of cationic and anionic polythionylphosphazene polyelectrolytes as well as a luminescent water-soluble cationic polythionylphosphazene, all of which are derived from substitution reactions of poly(chlorothionylphosphazene) **2** with various alkylamine nucleophiles.

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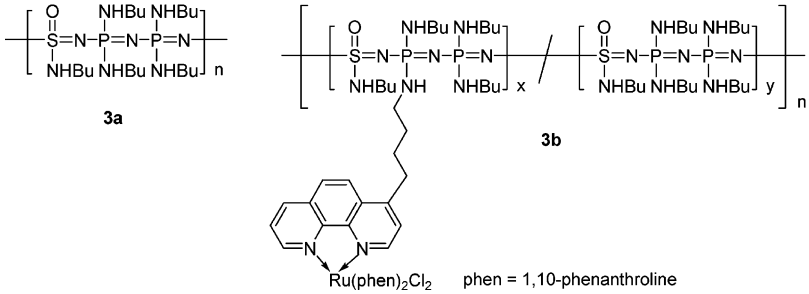
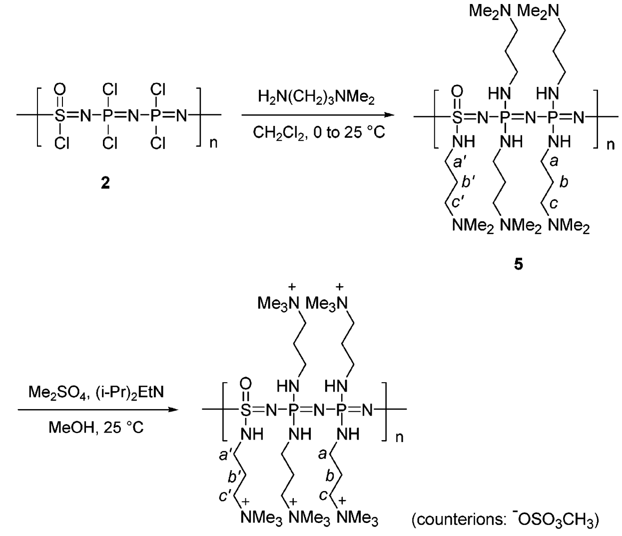
Chart 1



Scheme 2



Results and Discussion

Synthesis and Characterization of Water-Soluble Polythionylphosphazene 5 and Cationic Water-Soluble Polythionylphosphazene 6. Both polymers **5** and **6** can be derived readily from the hydrolytically sensitive poly(chlorothionylphosphazene) **2**, which is generated from the cyclic thionylphosphazene **1** via thermal ring-opening polymerizations (Scheme 2).[7] Reaction of polymer **2** with an excess amount of 3-(dimethylamino)propylamine gave the amino polythionylphosphazene **5** as a colorless gummy material. Quaternization of the dimethylamino groups in polymer **5** in the presence of dimethyl sulfate and diisopropylethylamine in methanol afforded the cationic polymer **6** as a white fibrous solid.

Polymer **5** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR analysis, all of which were consistent with the assigned structure. The ^{1}H NMR spectrum of **5** in D$_2$O showed broad peaks at 3.64 and 5.27 ppm, corresponding to the resonances of the amino protons adjacent to the phosphorus and sulfur atoms in the backbone, respectively. The resonances of the methylene protons at *a*, *a′*, *c*, and *c′* positions in the side chains were observed as a broad peak at 3.28 ppm, while the resonances of the methylene protons at *b* and *b′* positions were detected at 2.02 ppm. In the ^{13}C NMR spectrum of **5**, which was recorded in D$_2$O at 25 °C, the resonances of the carbons adjacent to phosphorus and sulfur at *a* and *a′* positions were detected at 38.3 and 40.0 ppm, respectively, and those of the carbons at *b* and *b′* positions were observed at 26.3 and 24.3 ppm, respectively. The carbons at *c* and *c′* positions, which were further removed from the phosphorus and sulfur atoms in the main chain, were detected as one peak at 55.5 ppm. The ^{31}P NMR spectrum recorded in D$_2$O showed one broad peak at −1.4 ppm, which was shifted significantly downfield from the phosphorus signal at −10.0 ppm in poly(chlorothionylphosphazene) **2** and in accordance with the structures of amine-substituted polythionylphosphazenes.[7,13]

The amino polymer **5** was obtained as a colorless gummy material which was readily soluble in water and methanol but insoluble in acetone and THF. Therefore, its molecular weight was determined indirectly from the analogous poly(*n*-butylaminothionylphosphazene) **3a** which was generated in a parallel reaction from the same starting chlorinated polymer **2** with an excess amount of *n*-butylamine.[13] The molecular weight thus obtained for polymer **3a** was $M_w = 3.9 \times 10^5$ with a polydispersity index (PDI) of 2.1.

The amino polythionylphosphazene **5** was unstable under ambient conditions, and ^{31}P NMR studies indicated that it started to degrade after ca. a week upon preparation.[16] Therefore, further functionalization of the amino groups was conducted immediately after the preparation of polymer **5**. The cationic ammonium-functionalized polythionylphosphazene **6** was obtained upon quaternization of the dimethylamino groups in polymer **5** and characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy as well as elemental analysis (Figure 1).

Notable chemical shifts observed in the ^{1}H spectrum recorded in D$_2$O were trimethylammonium protons at 3.16 ppm which were shifted downfield from the dimethylamino protons in polymer **5** at 2.92 ppm. The same downfield shift was also observed for the methylene protons adjacent to the ammonium moiety, which were shifted from 3.28 ppm in the amino polymer **5** to 3.44 ppm in the ammonium polyelectrolyte **6**. In the meantime, a singlet was detected at 3.74 ppm corresponding to the protons in the methyl sulfate counterions of the cationic polyelectrolyte **6**. The integration of the ^{1}H NMR signals was also in accordance with the quaternized structure. The ^{13}C NMR spectrum of the ammonium polythionylphosphazene **6** recorded in D$_2$O at 20 °C exhibited chemical shifts of the trimethylammonium carbons at 53.0 ppm and the methylene carbon adjacent to the ammonium moiety at 63.9 ppm, which were shifted significantly downfield from the corresponding carbons in the amino polymer **5** at 42.9 and 55.5 ppm, respectively. The absence of any dimethylamino carbon signal at 42.9 ppm in the spectrum of the ammonium polyelectrolyte **6** indicated that the quaternization reaction went to completion. As expected, the ^{31}P NMR spectrum recorded in D$_2$O exhibited a broad peak at −2.0 ppm, which is in accordance with the assigned structure of **6**.[13] The ammonium polythionylphosphazene **6** was obtained as

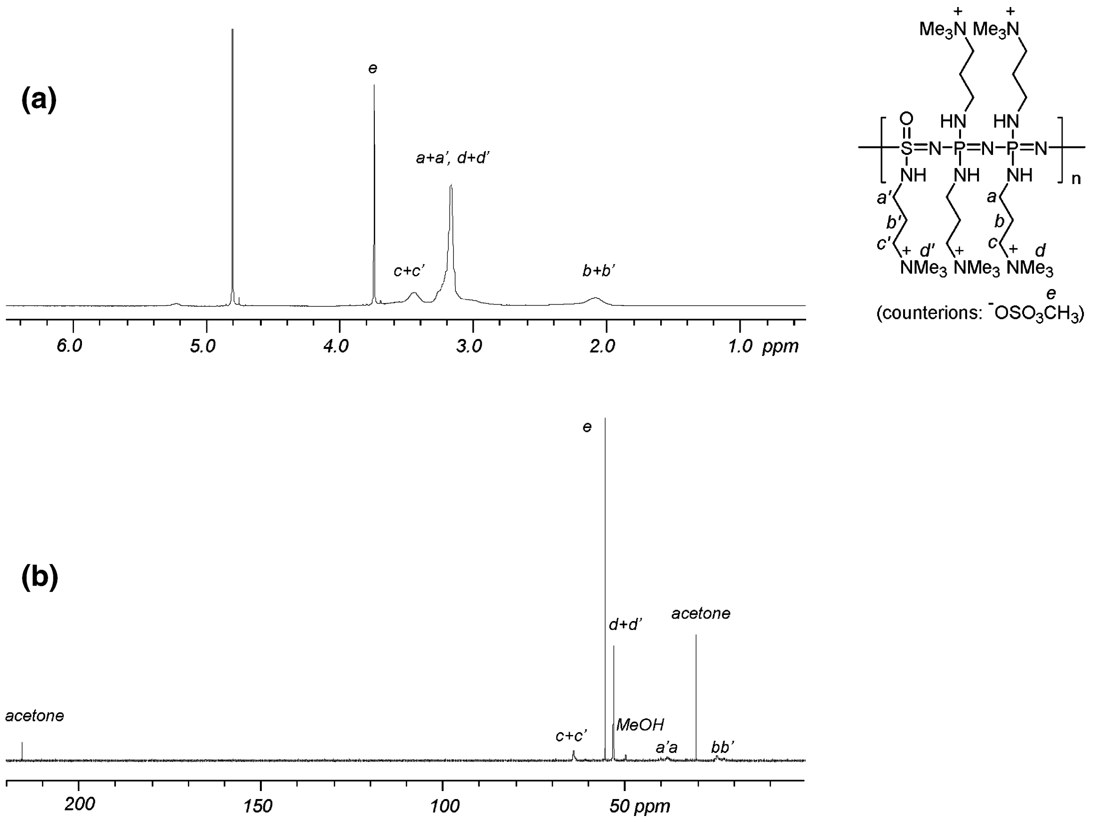


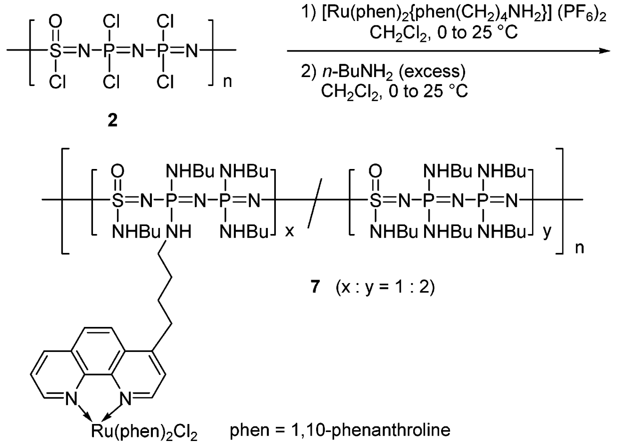
Figure 1. (a) ^{1}H (400 MHz) and (b) ^{13}C (100 MHz) NMR spectra of polymer **6** in D_2O.

a white fibrous solid. It was stable under ambient conditions and was readily soluble in water and methanol but insoluble in dichloromethane, acetone, and THF.

Covalent Attachment of a Ru(II) Phenanthroline Complex to a Polythionylphosphazene; Synthesis and Characterization of the Water-Soluble Cationic Luminescent Polymer 7. We have previously reported the synthesis of a luminescent polymer in which a ruthenium tris(1,10-phenanthroline) complex has been covalently attached to a polythionylphosphazene.[24] This procedure can be conveniently adapted to the synthesis of water-soluble luminescent polythionylphosphazenes through attachment of a large amount of the ruthenium complex to the polymer and thereby ensuring the water solubility of the resulting material. Alternatively, luminescent polyelectrolytes can be obtained through covalent attachment of a small amount of the ruthenium complex to polymer **2** followed by substitution of the remaining chlorine atoms in the polymer with the cationic ammonium moieties as illustrated in the synthesis of the ammonium polythionylphosphazene **6**. Here we report the preparation of a cationic dye-attached polymer via the former route.

The synthesis of the water-soluble luminescent polymer **7** was accomplished through reaction of poly(chlorothionylphosphazene) **2** with [Ru(phen)$_2${phen(CH$_2$)$_4$NH$_2$}](PF$_6$)$_2$[24] followed by substitution of the remaining chlorine atoms in the polymer with *n*-butylamine (Scheme 3). Counterion exchange of the hexafluorophosphate anion in the ruthenium complex to chloride was achieved by precipitating the crude product into acetone containing tetrabutylammonium chloride. This afforded a crude product which was purified by dialysis in water using molecularporous membrane bags (MWCO: 12 000−14 000) to give polymer **7** as a dark red solid.

Scheme 3



Polymer **7** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. In the ^{1}H NMR spectrum recorded in CD_3OD, the high loading of the transition metal complex in the polymer gave rise to signals in the aromatic region at 7.6−8.8 ppm which were attributed to the phenanthroline ligands (Figure 2). Integration of peaks indicated that the content of the transition metal complex in the polymer was approximately one [Ru(phen)$_2$-{phen(CH$_2$)$_4$NH}]Cl$_2$ in every three repeat units. The ^{13}C NMR spectrum clearly exhibited the phenanthroline carbon resonances in the region of 125−155 ppm and was consistent with the data obtained for the amine-functionalized ruthenium phenanthroline complex [Ru(phen)$_2${phen(CH$_2$)$_4$NH$_2$}]Cl$_2$.[24] The ^{31}P NMR data for polymer **7** were also in accordance with the assigned structure. The presence of two ^{31}P signals at 2.45 and 2.58 ppm is typical of the *r* and *m* dyads of atactic poly(aminothionylphosphazenes), where the S=O groups

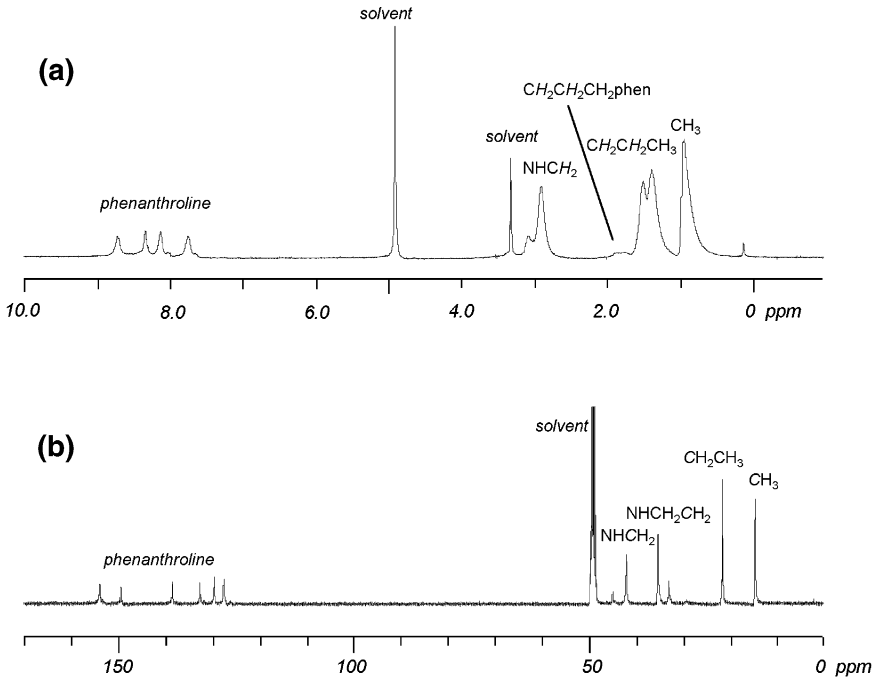
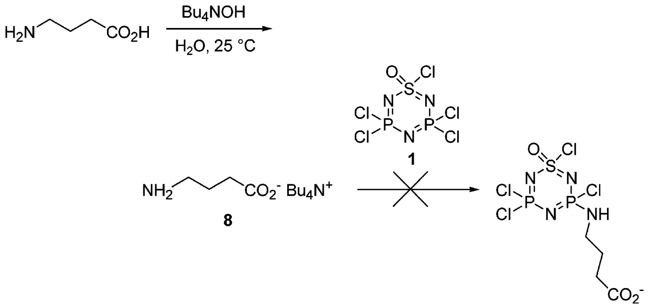


Figure 2. (a) ^1H (400 MHz) and (b) ^{13}C (100 MHz) NMR spectra of polymer **7** in CD_3OD.

Scheme 4



have random *cis*- or *trans*-orientations relative to one another along the polymer main chain.[13] As a result of the high loading of the transition metal complex, polymer **7** dissolves in water and methanol. However, in comparison to the cationic polyelectrolyte **6** which possesses five cationic ammonium moieties in every repeat unit, polymer **7** dissolves much slower in water as it contains only one cationic moiety in every three repeat units. It usually takes several hours for the luminescent polymer to dissolve in water to give a clear red solution. Polymer **7** is insoluble in aprotic solvents such as THF and acetone.

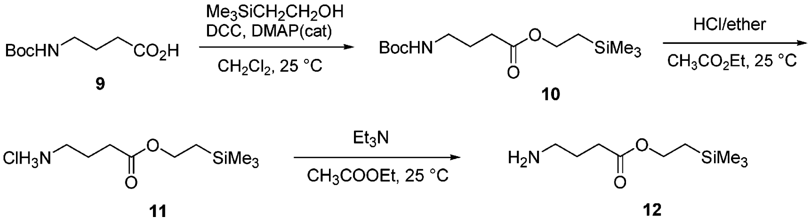
Synthesis and Characterization of the Protected Cyclic Thionylphosphazene 13. As the cyclic thionylphosphazene **1** provides an excellent structure to study nucleophilic substitutions by amines and aryloxides,[25] our initial work was directed at developing a synthetic pathway to anionic polythionylphosphazenes by using the cyclic monomer as a model compound. Thus, reaction of 4-aminobutyric acid with tetrabutylammonium hydroxide in water at room temperature afforded the carboxylic acid salt **8**, which was subsequently used in the substitution reaction with the cyclic thionylphosphazene **1** (Scheme 4). However, ^{31}P NMR analysis of the crude products from the reaction indicated that the carboxylate anion competed with the amino group in the substitution reaction, giving a mixture of amine-substituted and carboxylate-substituted cyclic thionylphosphazenes.

Our effort was therefore directed at the synthesis of amine **12** in which the carboxylic acid group was protected with a trimethylsilylethyl group which can be removed subsequently under mild conditions. To this end, reaction of acid **9**[26] with 2-(trimethylsilyl)ethanol in the presence of 1,3-dicyclohexylcarbodiimide and catalytic amount of 4-(dimethylamino)pyridine afforded ester **10** (Scheme 5). The Boc group was removed in the subsequent reaction with HCl in dry ethyl acetate to give ammonium salt **11**. Deprotonation of the ammonium moiety in **11** with triethylamine afforded amine **12**. Under ambient conditions, ammonium salt **11** is stable, but amine **12** is unstable and decomposes within a week after the preparation. Therefore, the latter should be prepared freshly from **11** prior to the substitution reaction with the cyclic chlorothionylphosphazene **1**.

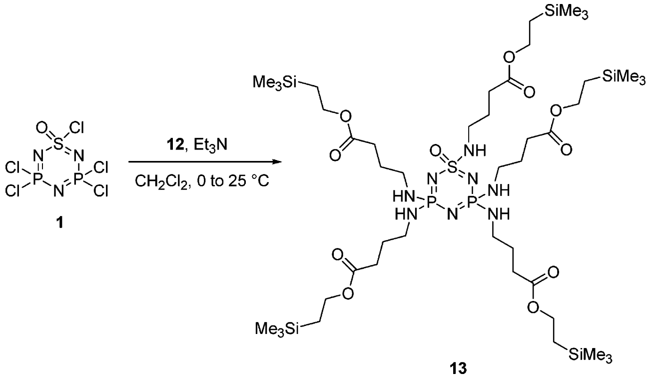
The substitution reaction of **12** and the cyclic chlorothionylphosphazene **1** proceeded smoothly at room temperature to afford the substituted cyclic thionylphosphazene **13** which can be isolated by column chromatography (Scheme 6). The substituted cyclic thionylphosphazene **13** was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and the data were in accordance with the assigned structure.

Synthesis and Characterization of the Protected Polythionylphosphazene 14. With the successful model reaction of cyclic chlorothionylphosphazene **1** and amine **12**, we anticipated that the same procedure could be applied to the preparation of macromolecule **14**, which could serve as a precursor to the anionic polyelectrolyte **15**. The substitution reaction of poly(chlorothionylphosphazene) **2** and amine **12** proceeded smoothly in the presence of triethylamine at room temperature to give the desired polymer (Scheme 7). Precipitation of the crude product into water afford the protected polythionylphosphazene **14** as a pale yellow gummy material with a molecular weight of $M_w = 1.43 \times 10^5$

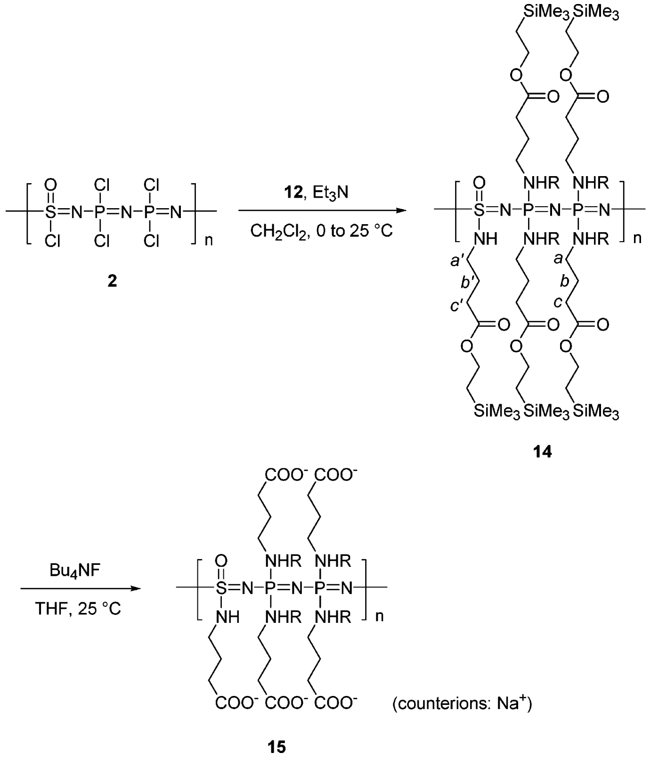
Scheme 5



Scheme 6



Scheme 7



and a PDI of 2.79. Complete substitution of the chloride groups in poly(chlorothionylphosphazene) **2** was indicated by NMR analysis within the error of the measurement (5%).

Polymer **14** was fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The resonances in both the ^{1}H and ^{13}C NMR spectra were in accordance with the assigned structure for the protected polythionylphosphazene **14**. Notably, in the ^{1}H NMR spectrum recorded in $CDCl_3$, the methylene protons at the *a* and *a′* positions exhibited chemical shifts at 2.89 and 3.06 ppm, respectively. These proton signals were shifted downfield in comparison to the corresponding proton signals in the free amine **12** ($\delta = 2.77$ ppm). These data were consistent with the results previously obtained from the successful substitution reactions of poly(chlorothionylphosphazene) **2** and alkylamines.[13] In the ^{13}C NMR spectrum of **14**, which was recorded in $CDCl_3$, the resonances of the carbons at *a* and *a′* positions were detected at 40.3 and 43.1 ppm, respectively, while those of the carbons at *b* and *b′* positions were observed at 26.8 and 24.8 ppm, respectively. These results were also consistent with the carbon chemical shifts in the previously reported amine-substituted polythionylphosphazenes.[13] The ^{31}P NMR spectrum of **14** in $CDCl_3$ exhibited two resonances at 0.74 and 1.09 ppm, which corresponded to the phosphorus signals in the *r* and *m* dyads of atactic poly(aminothionylphosphazenes).[13] All these results confirmed the successful substitution of the chlorine atoms in poly(chlorothionylphosphazene) **2** by amine **12**.

Synthesis and Characterization of the Anionic Polythionylphosphazene Polyelectrolyte 15. The trimethylsilylethyl protective groups in polymer **14** can be removed under mild conditions. Thus, reaction of polymer **14** and tetrabutylammonium fluoride at room temperature gave the desired anionic polyelectrolyte (Scheme 7). Counterion exchange from triethylammonium to sodium cations was accomplished by precipitation of the crude polymer into an acetone solution containing sodium tetraphenylborate or sodium hexafluorophosphate. Further purification of the precipitated polymer through dialysis in water using molecular-porous membrane bags (MWCO: 12 000−14 000) gave the anionic polyelectrolyte **15** as a colorless glassy material which was readily soluble in water but insoluble in THF, dichloromethane, and acetone.

The anionic polymer **15** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR in D_2O at 20 °C. The ^{1}H and ^{13}C NMR spectra are shown in Figure 3. The resonances for all expected proton and carbon environments were clearly detected, which indicated that the polymer was well-solvated in water. In the ^{1}H NMR spectrum, resonances for the trimethylsilylethyl protective groups were observed, and integration of the proton signals indicated that >96% of the protective groups had been successfully removed. The ^{13}C and ^{31}P NMR of the polymer were also consistent with the assigned structure. Importantly, no signals were detected in the ^{19}F NMR of the anionic polymer **15**, indicating that tetrabutylammonium fluoride did not react with the phosphorus and sulfur atoms in the polymer backbone.

As with the case of the cationic polythionylphosphazenes **6**, a direct estimate of the molecular weight of the anionic polyelectrolyte **15** was not made. However, the anionic polymer forms viscous solutions in water which is consistent with the behavior of a high molecular weight material.

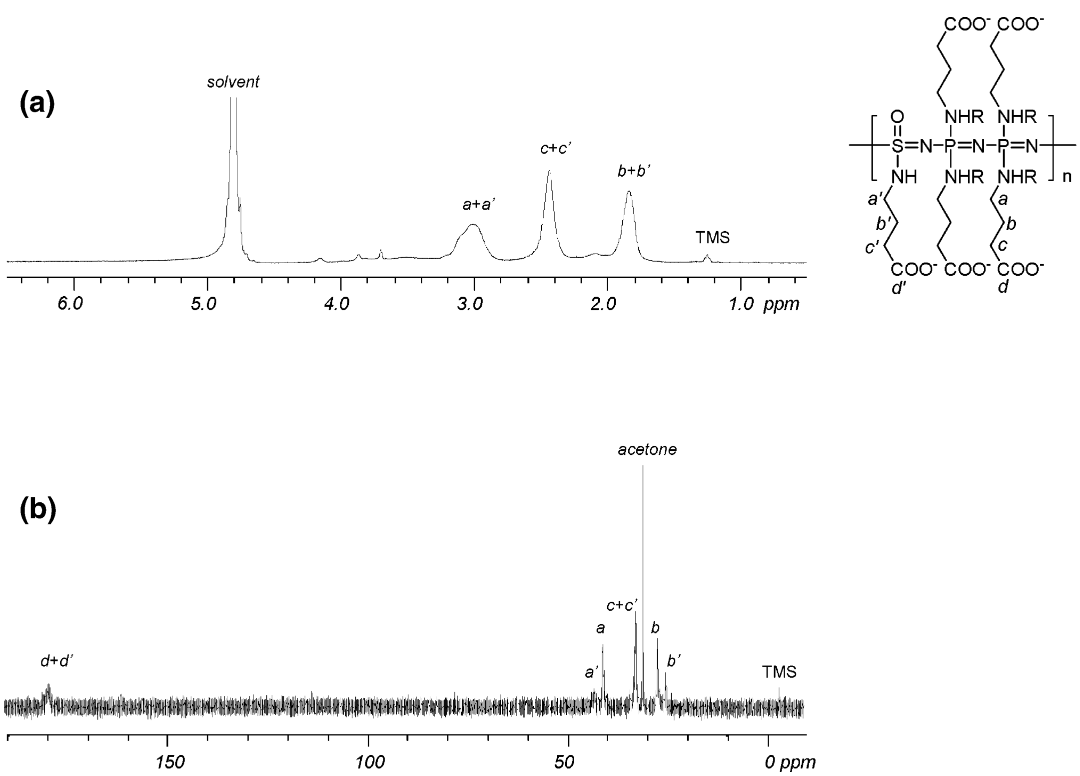


Figure 3. (a) ^{1}H (400 MHz) and (b) ^{13}C (100 MHz) NMR spectra of polymer **15** in D_2O.

Summary

Facile syntheses of water-soluble cationic and anionic polythionylphosphazene polyelectrolytes **6**, **7**, and **15** have been achieved. These materials were readily soluble in water, and their aqueous solutions remained stable after a period of several months. The polythionylphosphazenes were accessible from polymer **2** through substitution of the chlorine atoms by functionalized alkylamines. Further studies of the applications of the polythionylphosphazene polyelectrolyte materials in layer-by-layer assembly processes and luminescence studies of these materials will be reported in the future.

Experimental Section

Materials. All chemicals were purchased from Aldrich and used as received unless otherwise specified. Compounds $NSOCl(NPCl_2)_2$ (**1**),[27] $BocNH(CH_2)_3CO_2H$ (**9**),[26] $[Ru(phen)_2\{phen(CH_2)_4NH_2\}](PF_6)_2$,[24] and polymer $[NSOCl(NPCl_2)_2]_n$ (**2**)[7] were synthesized according to literature procedures. Solvents were dried according to standard methods.

Equipment. All manipulations of air-sensitive materials were performed under a nitrogen atmosphere either in an Innovative Technology glovebox or by standard Schlenk line techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian spectrometers (Unity 500, Unity 400, Gemini 300, Mercury 300 or Gemini 200) and referenced to residual protonated solvent (^{1}H), deuterated solvent (^{13}C), or externally to 85% H_3PO_4 (^{31}P) unless otherwise specified. Elemental analyses were performed at the University of Toronto using a Perkin-Elmer 2400 series CHN analyzer. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates 2690 separation module equipped with a column heater, in-line degasser, a high performance liquid chromatography (HPLC) pump, and an autosampler. The separation module was equipped with a Waters 410 differential refractometer as the concentration detector and, connected in parallel, a Viscotek T60A dual detector consisting of a right-angle laser light scattering detector with a laser source of 670 nm and a four-capillary differential viscometer. Software from Viscotek was used to analyze the data. Columns from Polymer Laboratories with pore sizes of 5×10^2, 1×10^4, and 1×10^5 Å were used with a solution of 0.1% tetra-*n*-butylammonium bromide THF as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards purchased from Aldrich and Viscotek were used for calibration.

Synthesis of $[NSO\{HN(CH_2)_3N(CH_3)_2\}\{NP[HN(CH_2)_3N(CH_3)_2]_2\}_2]_n$ (5). To a solution of 3-(dimethylamino)propylamine (6.64 mL, 52.8 mmol) in 30 mL of dichloromethane at 0 °C was added dropwise quickly a solution of poly(chlorothionylphosphazene) **2** (1.45 g, 4.40 mmol) in 60 mL of dichloromethane. The reaction mixture was stirred for 30 min at 0 °C before it was warmed to 25 °C and stirred overnight. The clear colorless solution was concentrated on a rotavap and precipitated into acetone. The precipitate was dissolved in methanol and precipitated again into acetone. Decantation of the supernatant followed by drying the residue under high vacuum overnight afforded **5** as a colorless gummy material. (2.42 g, 3.68 mmol, 84%). ^{1}H NMR (D_2O, 400 MHz): $\delta = 2.02$ (br, 2H, $NHCH_2CH_2$), 2.92 (br, 6H, $N(CH_3)_2$), 3.28 (br, 4H, $NHCH_2CH_2CH_2N$), 3.64 (br, PN*H*), 5.27 (br, SN*H*). ^{13}C NMR (D_2O, 100 MHz, $\delta_{ref(acetone)} = 30.2$): $\delta = 24.3$ ($SNHCH_2CH_2$), 26.3 ($PNHCH_2CH_2$), 38.3 ($PNHCH_2$), 40.0 ($SNHCH_2$), 42.9 ($N(CH_3)_2$), 55.5 (CH_2NMe_2). ^{31}P NMR (D_2O, 121 MHz): $\delta = -1.4$ (br).

Synthesis of $[NSO\{HN(CH_2)_3N(CH_3)_3(OSO_3CH_3)\}\{NP[HN(CH_2)_3N(CH_3)_3\ (OSO_3CH_3)]_2\}_2]_n$ (6). To a solution of polymer **5** (2.30 g, 3.50 mmol) in methanol (50 mL) was added dimethyl sulfate (3.8 mL, 40.1 mmol) and diisopropylethylamine (7.0 mL, 40.2 mL), and the reaction mixture was stirred at 25 °C for 3 days. Solvent removal followed by dissolution of the residue in methanol and precipitation into acetone gave a fibrous material. The precipitation process was repeated two more times to afford polymer **6** as a white fibrous solid (2.45 g, 1.90 mmol, 54%). ^{1}H NMR (D_2O, 400 MHz): $\delta = 2.09$ (br, 2H, $NHCH_2CH_2$), 3.16 (br, $N(CH_3)_3$ and $NHCH_2$), 3.44 (br, 2H, CH_2NMe_3), 3.59 (br, PN*H*), 3.74 (s, 3H, OSO_3CH_3), 5.23 (br, SN*H*). ^{13}C NMR (D_2O, 100 MHz, $\delta_{ref(acetone)} = 30.2$): $\delta = 22.7$ ($SNHCH_2CH_2$), 24.7 ($PNHCH_2CH_2$), 38.1 ($PNHCH_2$), 39.9 ($SNHCH_2$), 53.0 ($N(CH_3)_3$), 55.3 (OSO_3CH_3), 63.9 (CH_2NMe_3). ^{31}P NMR (D_2O, 121 MHz): $\delta = -2.0$ (br). Anal. Calcd for $(C_{35}H_{95}O_{21}N_{13}S_6P_2)_n$ (1288.58)$_n$: C, 32.62; H, 7.43; N, 14.13. Found: C, 30.14; H, 6.65; N, 14.62.

Synthesis and Characterization of Luminescent Polythionylphosphazene 7. The polymer was obtained by using a modified literature procedure.[24] To a solution of polymer **2** (315 mg, 0.957 mmol) in dichloromethane (7.0 mL) at 25 °C under nitrogen was added a solution of $[Ru(phen)_2\{phen(CH_2)_4NH_2\}](PF_6)_2$[24] (365 mg, 0.364 mmol) in 1.0 mL of dry acetonitrile. The dark red solution was cooled to 0 °C, and *n*-butylamine (1.13 mL, 11.5 mmol) was added dropwise slowly during a 2 h period. The reaction mixture was warmed to 25 °C and stirred overnight before it was concentrated on a rotavap and precipitated into water containing 1.0 g of $NaPF_6$. The solid was collected by suction filtration, dried under high vacuum overnight, redissolved in acetone, and precipitated into acetone containing 1.0 g of tetrabutylammonium chloride. Drying of the precipitate followed by dialysis in water using molecular membrane bags (MWCO: 12 000−14 000) afforded polymer **7** as a dark red solid (yield less than 10%). ^1H NMR (CD_3OD, 300 MHz): $\delta = 0.93$ (br, CH_3), 1.37, 1.49 (br, $CH_2CH_2CH_3$), 1.74 (br), 1.86 (br) ($phenCH_2CH_2CH_2$), 2.90 (br, $PNHCH_2$), 3.06 (br, $SNHCH_2$), 3.32 (br, $phenCH_2$), 7.64 (br), 7.75 (br), 8.02 (br), 8.12 (br), 8.33 (br), 8.41 (br), 8.71 (br) (phen). ^{13}C NMR (CD_3OD, 100 MHz): $\delta = 14.7$ (CH_3), 21.6, 21.9 (CH_2CH_3), 29.6 ($phenCH_2$), 33.1 ($SNHCH_2CH_2$), 35.3 ($PNHCH_2CH_2$), 42.1 ($PNHCH_2$), 45.0 ($SNHCH_2$), 126.2, 127.5, 129.6, 131,7, 132.3, 132.6, 138.4, 149.4, 149.6, 153.7, 153.9 (phen). ^{31}P NMR (CD_3OD, 121 MHz): $\delta = 2.45$, 2.58.

Synthesis of $BocNH(CH_2)_3CO_2(CH_2)_2Si(CH_3)_3$ (10). To a solution of acid **9**[26] (25.0 g, 0.123 mol) in 350 mL of dichloromethane at 0 °C under nitrogen was added 2-(trimethylsilyl)ethanol (14.54 g, 0.123 mol), 1,3-dicyclohexylcarbodiimide (27.85 g, 0.135 mol), and 4-(dimethylamino)-pyridine (1.50 g, 0.012 mol). The reaction mixture was warmed to 25 °C and stirred overnight. The precipitate was filtered, and the solid was washed with dichloromethane. The combined organic solutions were concentrated on the rotavap, and the crude product was purified by column chromatography to give **10** as colorless oil (24.33 g, 0.080 mol, 65%). ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 0.037$ (s, 9H, $Si(CH_3)_3$), 0.98 (m, 2H, OCH_2CH_2Si), 1.44 (s, 9H, $C(CH_3)_3$), 1.80 (quintet, $J = 7.2$ Hz, 2H, $NHCH_2CH_2$), 2.33 (t, $J = 7.2$ Hz, 2H, CH_2CO), 3.15 (m, 2H, $NHCH_2$), 4.16 (m, 2H, OCH_2CH_2Si). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -1.7$ ($Si(CH_3)_3$), 17.1 (OCH_2CH_2Si), 25.1 ($NHCH_2CH_2$), 28.2 ($C(CH_3)_3$), 31.5 (CH_2CO), 39.8 ($NHCH_2$), 62.4 (OCH_2CH_2Si), 78.8 ($C(CH_3)_3$), 155.8 ($OC(O)N$), 173.2 (CH_2CO).

Synthesis of $ClH_3N(CH_2)_3CO_2(CH_2)_2Si(CH_3)_3$ (11). To a solution of **10** (18.70 g, 0.0616 mol) in 150 mL of dry ethyl acetate at 25 °C under nitrogen was added HCl (154 mL of a 2.0 M solution in ether, 0.308 mol). The reaction mixture was stirred for 18 h before the solvent was removed on the rotavap. The crude product was dried under high vacuum overnight to afford the ammonium chloride **11** as a pale yellow oily solid (14.36 g, 0.0599 mol, 97%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.030$ (s, 9H, $Si(CH_3)_3$), 0.97 (t, $J = 8.4$ Hz, 2H, OCH_2CH_2Si), 2.12 (br, 2H, $NHCH_2CH_2$), 2.47 (br, 2H, CH_2CO), 3.13 (br, 2H, NCH_2), 4.15 (t, $J = 8.4$ Hz, 2H, OCH_2CH_2Si), 8.27 (br, NH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -1.5$ ($Si(CH_3)_3$), 17.3 (OCH_2CH_2Si), 22.7 ($NHCH_2CH_2$), 31.4 (CH_2CO), 39.5 ($NHCH_2$), 63.0 (OCH_2CH_2Si), 172.8 (CH_2CO).

Synthesis of $H_2N(CH_2)_3CO_2(CH_2)_2Si(CH_3)_3$ (12). To a solution of the ammonium chloride **11** (3.57 g, 14.9 mmol) in 20 mL of dry ethyl acetate at 25 °C was added triethylamine (2.08 mL, 14.9 mmol). The reaction mixture was stirred for 5 min before the precipitates were filtered. The filtered solid was further rinsed with ethyl acetate (4 × 2 mL), and the combined organic solutions were concentrated on a rotavap to give amine **12** as colorless oil which was brought to the next step without further purification. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 0.030$ (s, 9H, $Si(CH_3)_3$), 0.98 (m, 2H, OCH_2CH_2Si), 1.79 (quintet, 2H, $NHCH_2CH_2$), 2.10 (br, NH_2), 2.35 (t, 2H, CH_2CO), 2.77 (br, 2H, NCH_2), 4.16 (m, 2H, OCH_2CH_2Si).

Synthesis of $NSO\{HN(CH_2)_3CO_2(CH_2)_2Si(CH_3)_3\}\{NP[HN(CH_2)_3CO_2(CH_2)_2\ Si(CH_3)_3]_2\}_2$ (13). To a solution of the ammonium chloride **11** (700 mg, 2.92 mmol) in 5 mL of dichloromethane at 25 °C was added triethylamine (0.78 mL, 5.61 mmol). After 20 min of stirring, the white precipitate was filtered, and the filtrate was added to a solution of the cyclic chlorothionylphosphazene **1** (148 mg, 0.449 mmol) in 5 mL of dichloromethane at 25 °C under nitrogen. The reaction mixture was stirred for 3 days before it was diluted with 10 mL of dichloromethane, washed with saturated aqueous ammonium chloride, water, and brine, and subsequently dried over sodium sulfate. Solvent removal followed by column chromatography afforded the cyclic thionylphosphazene **13** as pale yellow oil (310 mg, 0.266 mmol, 59%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.03$ (s, 9H, $Si(CH_3)_3$), 0.97 (t, $J = 8.4$ Hz, 2H, OCH_2CH_2Si), 1.80 (m, br, 2H, $NHCH_2CH_2$), 2.34 (m, br, 2H, CH_2CO), 2.95 (m, br, $PNHCH_2$), 3.02 (m, br, $SNHCH_2$), 4.14 (m, 2H, OCH_2CH_2Si). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -1.5$ ($Si(CH_3)_3$), 17.4 (OCH_2CH_2Si), 24.7 ($SNHCH_2CH_2$), 26.80, 26.84, 26.88, 26.92, 26.96 ($PNHCH_2CH_2$), 29.7 ($SNHCH_2CH_2CH_2$), 31.6, 31.7 ($PNHCH_2CH_2CH_2$), 40.3, 40.4 ($PNHCH_2$), 42.7 ($SNHCH_2$), 62.62, 62.65, 62.69, 62.75 (OCH_2CH_2Si), 173.42, 173.49, 173.51 (CH_2CO). ^{31}P NMR ($CDCl_3$, 121 MHz): $\delta = 15.4$.

Synthesis of $[NSO\{HN(CH_2)_3CO_2(CH_2)_2Si(CH_3)_3\}\{NP[HN(CH_2)_3CO_2(CH_2)_2\ Si(CH_3)_3]_2\}_2]_n$ (14). To a solution of polymer **2** (0.70 g, 2.13 mmol) in 10 mL of dichloromethane at 0 °C under nitrogen was added dropwise a solution of amine **12** (3.0 g, 14.9 mmol) in 10 mL of dichloromethane. The reaction mixture was warmed to 25 °C and stirred for 10 min before it was cooled to 0 °C. Triethylamine (2.08 mL, 14.9 mmol) was added, and the reaction mixture was stirred overnight at 25 °C. It was then quenched with saturated aqueous ammonium chloride, and the separated organic layer was washed with saturated aqueous ammonium chloride (15 mL), saturated aqueous sodium bicarbonate (15 mL), and brine (15 mL), and dried over sodium sulfate. The solvent was removed on the rotavap, and the residue was dissolved in acetone (2 mL), precipitated in water, and dried under high vacuum overnight to afford polymer **14** as a pale yellow gummy material (1.62 g, 1.39 mmol, 65%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.016$ (s, 9H, $Si(CH_3)_3$), 0.95 (t, $J = 8.4$ Hz, 2H, OCH_2CH_2Si), 1.77 (br, 2H, $NHCH_2CH_2$), 2.33 (br, 2H, CH_2CO), 2.89 (br, $PNHCH_2$), 3.06 (br, $SNHCH_2$), 4.10 (t, $J = 8.4$ Hz, 2H, OCH_2CH_2Si). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -1.5$ ($Si(CH_3)_3$), 17.3 (OCH_2CH_2Si), 24.8 ($SNHCH_2CH_2$), 26.8 ($PNHCH_2CH_2$), 31.8 (CH_2CO), 40.3 ($PNHCH_2$), 43.1 ($SNHCH_2$), 62.2 (OCH_2CH_2Si), 173.3 (CH_2CO). ^{31}P NMR ($CDCl_3$, 121 MHz): $\delta = 0.74$, 1.09. GPC: $M_w = 1.43 \times 10^5$, PDI = 2.79.

Synthesis of $[NSO\{HN(CH_2)_3CO_2Na\}\{NP[HN(CH_2)_3CO_2Na]_2\}_2]_n$ (15). Procedure A: To a solution of polymer **14** (247 mg, 0.212 mmol) in 5 mL of THF at 25 °C under nitrogen was added tetrabutylammonium fluoride (4.2 mL of a 1.0 M solution in THF, 4.24 mmol). The reaction mixture was stirred for 4 days before it was concentrated and precipitated into acetone containing sodium tetraphenylborate (725 mg, 2.12 mmol). The precipitate was dissolved in water and precipitated again into acetone. Polymer **15** was isolated as a colorless glassy solid after dialysis in water using molecularporous membrane bags (MWCO: 12 000−14 000) and drying under high vacuum (30 mg, 0.039 mmol, 18%). Procedure B: To a solution of polymer **14** (82 mg, 0.070 mmol) in 0.5 mL of THF at 25 °C was added tetrabutylammonium fluoride (1.41 mL of a 1.0 M solution in THF, 1.41 mmol), and the reaction mixture was stirred for 1 week. A solution of 200 mg of poly(dimethylsiloxane) (monovinyl terminated, viscosity: 10 000) in 1.5 mL of THF was added, and the clear reaction mixture was stirred overnight to quench the excess tetrabutylammonium fluoride. Precipitation of the reaction mixture in hexanes afforded a white solid which was dissolved in acetone and precipitated in a solution of sodium hexafluorophosphate (237 mg, 1.41 mmol) in 5 mL of acetone. The white solid was isolated by suction filtration, dissolved in ca. 1 mL of water, filtered, and precipitated in acetone. The precipitation process was repeated two more times, and the product was dried overnight under high vacuum to afford polymer **15** as a white solid (55 mg, 0.071 mmol, quantitative yield). ^1H NMR (D_2O, 400 MHz): $\delta = 1.84$ (br, 2H, $NHCH_2CH_2$), 2.44 (br, 2H, CH_2CO), 3.02 (br, $NHCH_2$). ^{13}C NMR (D_2O, 100 MHz, $\delta_{ref(acetone)} = 30.2$): $\delta = 24.7$ ($SNHCH_2CH_2$), 26.8 ($PNHCH_2CH_2$), 32.3 (CH_2CO), 40.5 ($PNHCH_2$), 42.6 ($SNHCH_2$), 179.4 (CH_2CO). ^{31}P NMR (D_2O, 121 MHz): $\delta = 2.5$ (br). Anal. Calcd for $(C_{20}H_{35}O_{11}N_8SP_2Na_5)_n$ $(772.52)_n$: C, 31.10; H, 4.57; N, 14.50. Found: C, 28.75; H, 5.24; N, 16.30.

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