Improved Method for the Isolation and Purification of Water-Soluble Polyphosphazenes

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ABSTRACT: We report in this article an improved procedure to isolate and purify representative water-soluble polyphosphazenes that dramatically reduces the time and equipment involved, while maintaining or exceeding the yields and purity reported in the literature for these polymers obtained using dialysis methods. This technique takes advantage of the phase transition behavior exhibited by some hydrophilic polymers, namely that associated with the lower critical solubility temperature (LCST). The polymers used in this study were poly[*bis*-(2-(2-methoxyethoxy)ethoxy)phosphazene], MEEP (**1**), and two new water-soluble polymers. These polymers are similar to MEEP, yet they contain a small percentage of a crosslinkable pendant group; either 2-hydroxyethyl allyl ether (**2**), or *o*-allyl phenol (**3**). The observed behavior was quite different for these two polymers than that found for MEEP, and is a direct consequence of the pendant group substitution patterns. Although the homopolymer MEEP yielded a single sharp LCST point, the two heteropolymers exhibited this phase transition over a broader temperature range. Further, fractionation of polymer **3**, based on pendant group speciation, was possible due to the more hydrophobic nature of the phenol. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1092–1099, 2000

Key words: polymers; phosphazenes; hydrophilic; purification; solubility

INTRODUCTION

Polyphosphazenes are hybrid organic and inorganic polymers that have been widely studied as gas separation[1] and liquid pervaporation[2] membranes. These materials are composed of alternating phosphorus and nitrogen atoms in the backbone with alternating double and single bonds. These polymers generally are synthesized in a two-step process. First, the linear polymer, poly(dichlorophosphazene) is formed from hexachlorocyclotriphosphazene, followed by substitution of the chlorine atoms on the backbone with an appropriate nucleophile (see Fig. 1). Typical nucleophiles that are attached to the phosphorus atoms are organic pendant groups, such as phenols or aliphatic and aromatic amines.[3] Although pendant groups like these are well known, they impart a hydrophobic character to the polymer. Common purification procedures for these materials involve repeated precipitation from solvents such as THF into hexanes to remove low polarity impurities, followed by precipitation into water to remove ionic salts and high polarity impurities. In this manner, a highly pure material is produced—yet this method is only applicable to polymers that are insoluble in water.

Water-soluble polyphosphazenes have been increasingly utilized in recent years for a variety of applications including biomedical,[4] hydrogels,[5] and as solid polymer electrolytes.[6] These linear polymers are also synthesized from the parent polymer, polydichlorophosphazene, via nucleo-

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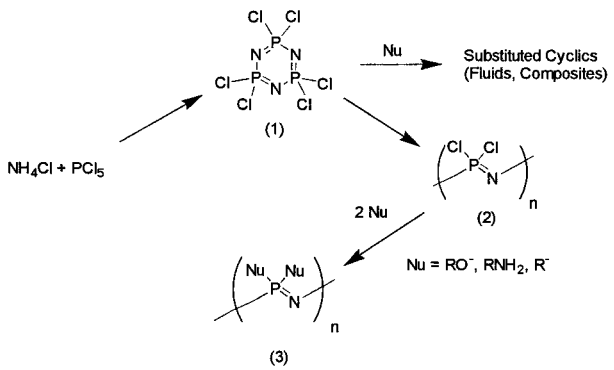

Figure 1 General synthetic route to cyclic trimer and linear phosphazene materials.

philic substitution reactions[7] in polar aprotic organic solvents, similar to water-insoluble polyphosphazenes. The substantial difference involved is in the isolation and purification procedures. The methodology recounted in the literature[8–10] for water-soluble phosphazenes involves a time-consuming dialysis against water and light alcohols to produce the final purified product. We report in this article an improved procedure to isolate and purify representative water-soluble polyphosphazenes that dramatically reduces the time and equipment involved, while maintaining or exceeding the yields and purity reported for polymers obtained using dialysis methods.

It is known that certain water-soluble polymers exhibit an unusual behavior known as a lower critical solubility temperature (LCST).[11] This phenomenon is a phase transition that occurs as an aqueous polymer solution is warmed. Below the LCST, the polymer is completely soluble; but above the LCST, the polymer abruptly begins to precipitate from solution. This transition is due to a shift in the balance between hydrophilic and hydrophobic interactions between the polymer and the solvent. The polymer poly-[*bis*-(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP, **1**) was chosen for this study because it is known to exhibit LCST behavior, and also due to the wealth of literature data available on the properties of this polymer. Two closely related derivatives, 95% 2-(2-methoxyethoxy)ethanol, 5% 2-hydroxyethyl allyl ether (**2**) and 95% 2-(2-methoxyethoxy)ethanol, 5% *o*-allyl phenol, (**3**) were also studied to reveal additional insight into the breadth of applicability of this method for the purification of mixed-substituent polyphosphazenes (see Fig. 2).

EXPERIMENTAL

General

Hexachlorocyclotriphosphazene was purchased from Strem Chemicals, Inc., and was purified by sublimation prior to use. The 2-(2-methoxyethoxy)ethanol (DEG) (Aldrich) was vacuum distilled immediately prior to use. THF (anhydrous, Aldrich), toluene (anhydrous, Aldrich), *o*-allyl phenol (Aldrich), and 2-hydroxyethyl ether (Aldrich) were used as received. Thermal analyses were performed using a TA Instruments Model 2910 Differential Scanning Calorimeter. NMR analyses were performed on a Bruker AC-300P spectrometer operating at a magnetic field strength of 7.04T (300 MHz, proton). Proton and ^{13}C-NMR (75.4 MHz) spectra were referenced to TMS. ^{31}P spectra (121 MHz) were referenced to 85% H_3PO_4; (internal, coaxial), with positive shifts recorded downfield of the reference. Elemental analysis was performed using a Carlo-Erba Instruments EA1108 CHNS-O elemental analyzer. Dilute solution techniques were used to characterize the macromolecular structures of the polymers. THF, filtered through a 0.02-μm filter, was used as the solvent and all experiments were performed at 22°C. Solution refractive index increment, *dn*/*dc*, values were obtained using a Rainin Dynamax RI-1 differential refractive index detector. The instrument constant was determined via calibration using known concentrations of polystyrene standards whose *dn*/*dc* values are known. Laser light-scattering (LLS) measurements were made using a Wyatt Technologies,

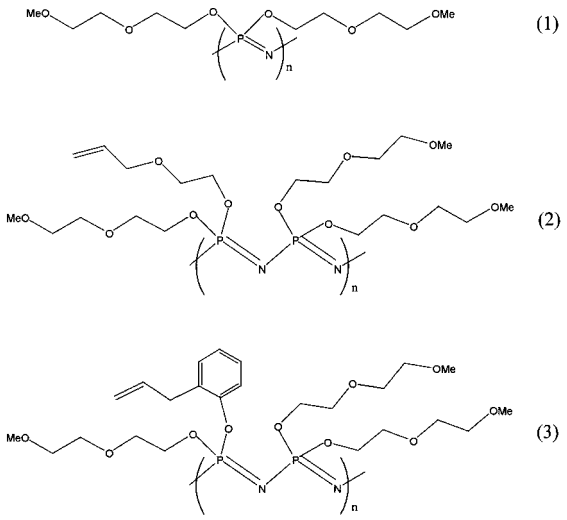

Figure 2 Representative structures of polymers **1–3**.

Dawn-DSP system that uses polarized light having a wavelength of 633 nm and measures scattered light intensities at 18 angles ranging from 22.5° to 147°. The instrument was calibrated with toluene that was filtered through a 0.02-μm filter. Dilute solutions in the 10^{-4} to 10^{-5} g/mL range were prepared for scanning on the LLS instrument. Debye plots were prepared to obtain weight-average molecular weights M_w, z-average square radii (mean square radii), and second virial coefficients.

Synthesis of Polydichlorophosphazene (4)

Hexachlorocyclotriphosphazene was sublimed immediately prior to use. Thick-walled glass tubes were washed with water, then acetone and dried in an oven at 130°C overnight. They were then cooled to room temperature, packed with hexachlorocyclotriphosphazene under flowing dry nitrogen, and rigorously degassed. The tubes were flame sealed while at reduced pressure (~ 0.03 Torr N_2) and placed into an oven at 250°C for 24 h. After the tubes were cooled to room temperature, they were scored, and the crude polymer removed and quickly transferred to an oven-dried flask flushed with Ar. Anhydrous toluene (250 mL) was added, and the flask was sealed with a septum stopper. After the mass was completely dissolved, the solution was poured into 1 L of hexanes, and the polymer was collected and washed twice with 50 mL portions of hexanes. The polymer was then quickly transferred to a vacuum/argon atmosphere oven and dried for 1.5–2.0 h (70 Torr Ar, 40°C).

Synthesis of Poly[*bis*-(2-(2-methoxyethoxy)ethoxy)phosphazene] (1)

A 2-L three-neck flask that was flame dried was charged with 360 mL of anhydrous THF under dry lightly flowing argon. To this was added freshly distilled 2-(2-methoxyethoxy)ethanol (44.2 g, 0.368 mol). Freshly cut metallic sodium (7.02 g, 0.306 mol) was added to the flask and the mix stirred at reflux until all of the sodium was consumed. A solution of poly(dichlorophosphazene) (12.0 g, 0.102 mol) in 250 mL of dry THF was slowly added via a cannula, and the reaction mixture stirred for 5.0 h at reflux under argon. Reaction progress was monitored by ^{31}P-NMR spectroscopy. After the reaction was complete, the flask was cooled to room temperature and the crude polymer was recovered by precipitation into 500 mL of hexanes. The resulting cream colored solid was then dissolved in 200 mL of nanopure water, resulting in a solution of approximately pH 12. The solution was neutralized with 4 M H_3PO_4 to a final pH of 6.5, and abruptly warmed on a hotplate (already very hot) above the LCST point to induce precipitation of the polymer. The polymer was collected by careful decantation of the supernatant while still warm. The polymer was then redissolved in nanopure water at room temperature (~ 200 mL) and the process repeated. After four sequential precipitations, the recovered material was dried in a vacuum oven (45°C, 70 Torr Ar) for 2 days to yield a clear gum (19 g, 66%): NMR ($CDCl_3$) ^{1}H δ (ppm) 3.3 (3H), 3.5 (2H), 3.7 (4H), 4.1 (2H); ^{31}P δ (ppm) −7.7; ^{13}C δ (ppm) 71.6, 70.3, 70.1, 65.8, 58.6. Anal. Calcd.: C, 42.4; H, 7.8; N, 4.9. Found: C, 42.5; H, 7.5; N, 4.8. LLS data: (M_w) = (3.33 ± 0.08) × 10^6, RMS Radius = 94.1 ± 2.6 nm, 2nd Virial Coefficient = (3.43 ± 0.1) × 10^{-5}. DSC: T_g −83°C.

Synthesis of [PN(2-(2-methoxyethoxy)ethoxy)$_{1.9}$(2-hydroxy allyl ether)$_{0.1}$]$_n$ (2)

This polymer was synthesized in a step-wise procedure identical to that for **3**. The polymer was a clear gum (yield 16.1 g, 56%): NMR ($CDCl_3$) ^{1}H δ (ppm) 3.3(s), 3.5(s), 3.7(s), 4.1(s), 5.1(d, br), 6.8 (s, br); ^{31}P δ (ppm) −7.7. (M_w) = (5.0(0.1) × 10^6, RMS Radius = 43.4 ± 2.3 nm, 2nd Virial Coefficient = (3.7 ± 0.3) × 10^{-6}. DSC T_g −81°C.

Synthesis of [PN(2-(2-methoxyethoxy)ethoxy)$_{1.9}$(*o*-allylphenoxy)$_{0.1}$]$_n$ (3)

This polymer was synthesized by use of a stepwise nucleophile addition methodology. In a 2-L three-neck flask that was flame dried, *o*-allylphenol (0.70 g, 5.2 mmol) was converted to the alkoxide with metallic sodium (0.12 g, 5.1 mmol) in 100 mL of anhydrous THF under dry argon. A solution of poly[*bis*-(dichloro)phosphazene] (12.0 g, 0.102 mol) in 250 mL of dry THF was slowly added via cannula, followed by reflux for 5 h to allow time for the phenoxide to be completely consumed. A previously prepared solution of the sodium alkoxide of 2-(2-methoxyethoxy)ethanol (43.4 g, 0.306 mol) in 320 mL of anhydrous THF was added to the flask and the reaction mixture was stirred for an additional 5 h at reflux. Reaction progress was monitored by ^{31}P-NMR. After the reaction was complete, the flask was cooled to room temperature and the crude polymer was

recovered by precipitation into 500 mL of hexanes. The resulting cream colored solid was then dissolved in 200 mL of nanopure water and purified by four sequential LCST precipitations in the manner described above. The polymer was a light tan gum (yield 15.2 g, 53%): NMR (D_2O) ^1H δ (ppm) 3.3 (s), 3.5 (s), 3.7 (s), 4.1 (s), 6.5 (br), 6.8 (br), 7.8 (d,br), 8.0 (d,br) ; ^{31}P δ (ppm) −7.7, −13.3. (M_w) = (4.8 ± 0.8) × 10^6, RMS Radius = 150.0 ± 15.3 nm, 2nd Virial Coefficient = (1.1 ± 0.9) × 10^{-6}.

DISCUSSION

Synthesis of MEEP (1)

When MEEP (**1**) was initially synthesized, the reaction progress was monitored by ^{31}P-NMR spectroscopy, and it was surprising to find that the spectrum displayed only one peak (at −7.7 ppm) after 4 h, in contrast to literature procedures,[9] which call for 24 h of reflux to complete the reaction. The reaction was continued for the stated 24 h, with periodic monitoring by ^{31}P-NMR spectroscopy. After the allotted time, the crude polymer was recovered from the mother liquor by precipitation into hexanes. This sticky mass was rapidly dissolved into water, and the excess base (produced by quenching the unreacted alkoxides) was neutralized. When the aqueous polymer solution was warmed above the LCST point, a viscous, oily precipitate was formed. This polymer mass was nearly intractable, and recovery from the warm solution was difficult, resulting in very low yields.

Analysis of the NMR spectra collected during the substitution reaction revealed a broad peak near zero ppm that appeared after 5–6 h and increased dramatically as the reaction proceeded. As shown in Figure 3, the peak assigned to the parent dichloropolymer [Fig. 3(A)] at −19 ppm was no longer observable soon after the substitution reaction was started. After 24 h of reaction time, the peak attributable to polymer **1** (−7.7 ppm) was evident, but so was a broad featureless peak near zero ppm [Fig. 3(B)]. It was postulated that this broad peak arose from degraded polymer, as it is well known that polyphosphazenes are susceptible to degradation in strong base, such as the excess alkoxides present in the reaction solution. This conclusion was further supported by molecular weight analyses, which determined that this polymer was of low molecular weight (M_w ~ 200,000) with wide scatter in the data, suggesting a high polydispersity index. After three iterations of the LCST purification described below, the broad feature in the NMR spectrum was less prominent though still observable [Fig. 3(C)], and the polymer mass became more tractable and much less flowable. These data suggest that lower molecular weight polymers are less suited to this technique than higher molecular weight polymers.

When the synthesis of polymer **1** was repeated, the reaction was terminated after 5 h at reflux and the crude polymer recovered as before. This time, however, the polymer exhibited only a single peak in the ^{31}P-NMR spectrum at −7.7 ppm, with no broad feature near zero [see Fig. 3(D)]. Purification of this polymer via the LCST procedure described below was performed, resulting in an easy workup, with extremely good yields of a tractable, highly pure material. Molecular weight determinations were again performed, and this time the molecular weight was much higher (M_w ~ 3,400,000), with substantially less scatter in the data, suggesting an undegraded polymer. This conclusion is further supported by additional GPC experiments[12] performed on representative batches of the unsubstituted parent dichloropolymer that revealed a molecular weight and polydispersity index consistent with **1** synthesized utilizing the shorter reaction time.

Purification of MEEP (1)

When the aqueous solution of the crude MEEP polymer, synthesized without excessive polymer degradation, was gently warmed with mechanical stirring on a hotplate above the LCST point, an intractable emulsion resulted. Upon cooling below the critical (LCST) point, the polymer quickly redissolved. In a second experiment, rapid heating, beginning with an already hot surface, created a temperature gradient (bottom to top) in the solution, and the polymer was forced out of solution, without mechanical agitation, with the polymer flocculating into a single mass in the hot zone. The temperature at which this behavior occurred was 52°C, a temperature lower than that reported for the onset of LCST behavior for the pure MEEP polymer.[10] This lower LCST temperature was expected due to the high ionic strength of the solution that contained the residual neutral salts from the synthesis. By maintaining the temperature just slightly above the observed LCST point for several minutes, the entire

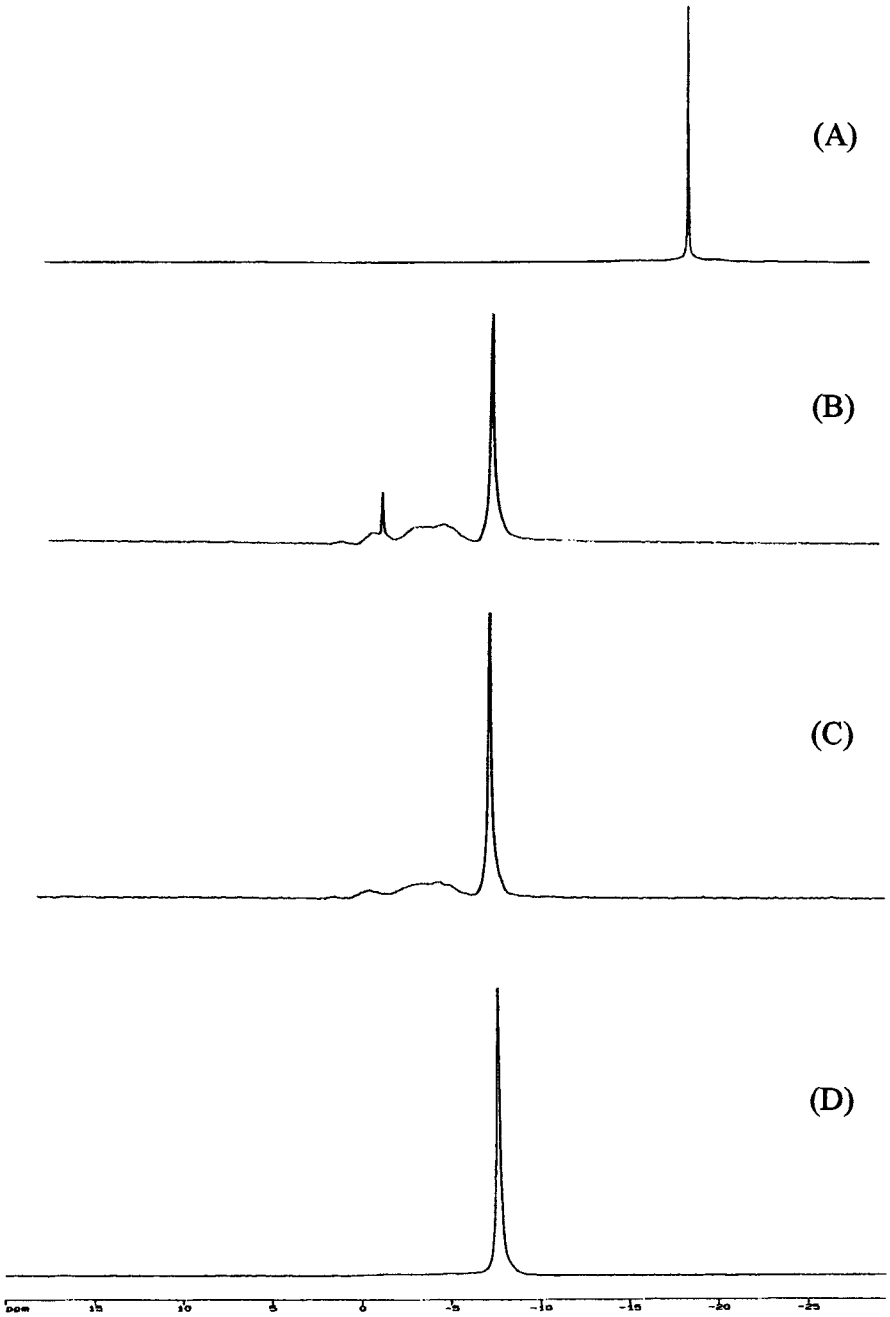

Figure 3 ^{31}P-NMR spectra from syntheses of polymer **1**. (A) Parent polymer $(NPCl_2)_n$. (B) Polymer **1** after 24 h at reflux. (C) LCST purified polymer **1** after 24 h at reflux. (D) LCST purified polymer **1** after 5 h at reflux.

polymer was collected into a single sticky mass. The supernatant was then quickly and carefully decanted away while still hot, with minimal loss of the solid polymer. Subsequent additional heating of the recovered polymer mass on the hotplate at a temperature significantly above the LCST point (~ 80°C) forced more of the salt/water solution from the polymer, and this was poured off in increments as it was exuded until no more could be decanted away. The polymer was then allowed to cool to room temperature and ~ 200 mL of nanopure water at room temperature was added to redissolve the polymer forming a solution that was 10–15% polymer.

Table I Properties of MEEP from LCST-Based Isolation and Purification Procedure

Analytical Method	Value for This Work	Literature Value[a]
NMR analysis		
^{31}P (1 peak)	−7.7 ppm	−7.7 ppm
^{1}H (4 peaks)	4.1	4.1
	3.7	3.7
	3.5	3.5
	3.3	3.3
^{13}C (5 peaks)	71.6	72.0
	70.3	70.4
	70.1	70.3
	65.8	65.2
	58.6	58.8
Thermal properties		
T_g	−83°C	−84°C
Elemental analysis		
% Carbon[b]	41.4%	42.4%
% Nitrogen[b]	4.57	4.95
% Hydrogen[b]	7.62	7.77
% yield[c]	66	26–86[d]
Cl^- contamination	None[e]	<2%
Purification time	3–4 h	2–3 weeks

[a] Values taken from ref. 9.
[b] Literature value reported are theoretical values calculated for a pure product.
[c] Based on starting amounts of $(NPCl_2)_n$.
[d] A wide range of yields is reported in the literature depending upon the source.
[e] As detectable by in-house SIMS methods. This method has been successfully applied to polyphosphazene analysis previously. See ref. 13.

This entire cycle was then repeated three more times. It was interesting to note that the observed LCST point rose with each of the first three cycles, as the ionic strength of the polymer solution fell. On the second cycle, the observed LCST point was 59°C, and on the third and fourth cycles it reached a final value of 65°C. The fact that the third and fourth cycles both exhibited the same LCST point was used as the primary indicator that all of the salts and excess 2-(2-methoxyethoxy)ethanol had been removed. After this treatment, the recovered material was dried in a vacuum oven (40°C, 70 Torr Ar) for 2 days to yield a clear gum. This product was then fully characterized and the data compared to literature values (see Table I).

Three additional tests were employed to assay for impurities. First, elemental analysis was performed of the purified polymer. The C, H, and N analyses were consistent with the theoretical values calculated for the pure polymer, and there was no detectable residual chloride in the polymer. The second analytical test that was performed for residual salt impurities was a simple silver nitrate test. A 15% aqueous polymer solution was prepared, and mixed with an equal volume of aqueous $AgNO_3$ (2.5 *M*), as a qualitative test for residual chloride. No cloudiness or turbidity was noted in the silver/polymer mixture. When this test was repeated with fractions of the decantate from the LCST purification cycles, insoluble silver salts were immediately produced. Third, secondary ion mass spectrometry (SIMS) was performed. This technique is extremely sensitive, and has been successfully applied to the analysis of phosphazene polymers.[13] The spectra that were produced were consistent with that expected for the MEEP polymer, with absolutely no peaks detected at either mass 35 or mass 37. This confirmed that there was no residual chloride in the purified polymer.

Purification of Polymer 2

As MEEP is a homopolymer, the LCST points were characterized by very sharp phase transitions, even in the presence of the residual salts. When this purification methodology was applied to heteropolymer **2,** a similar behaviour was observed. The principal difference in the behavior of this polymer was that instead of a sharp LCST point, the phase transition occurred over a narrow range of temperatures, typically 4–6 degrees. In a purification procedure identical to that described above for polymer **1**, this polymer exhibited critical point ranges of 42–48, 46–52, 52–57, and 56–61°C over the first four iterations. Subsequent iterations all exhibited a critical point range at 58–62°C, and the material was tested for purity by all three methods described above revealing a highly pure material. It was observed that this LCST procedure worked well for this heteropolymer as in the case of **1**, although the broader phase transition range made polymer recovery less efficient and did effect slightly lower yields.

Purification of Polymer 3

As polymer **3** is also a heteropolymer, behavior similar to that observed for polymer **2** was expected. However, the heteropolymer **3** exhibited quite different behavior, as the minor component, *o*-allyl phenol, was hydrophobic, not hydrophilic,

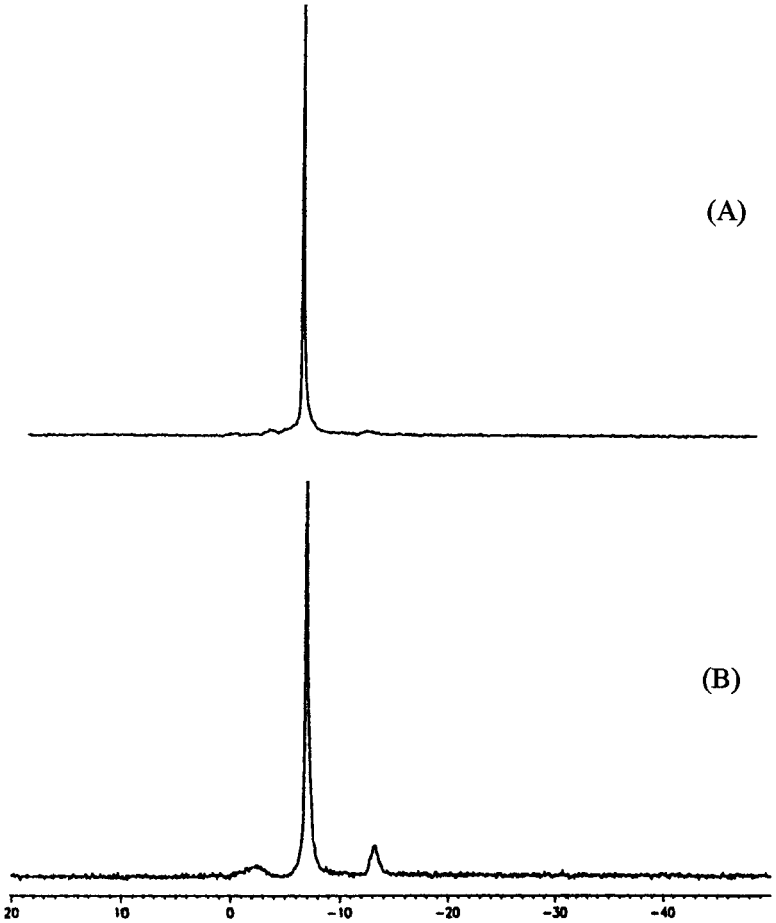

Figure 4 ^{31}P-NMR spectra of polymer **3**. (A) High-temperature LCST fraction. (B) Low-temperature LCST fraction.

as was the case for polymer **2**. Upon dissolution into water, a small fraction[14] of this polymer would not dissolve until the water was chilled to a few degrees below room temperature (15–18°C). As the polymer solution was warmed, a turbid milky precipitate was noted at all temperatures, with the amount of precipitated polymer increasing as the temperature rose. By selecting a temperature 5–10 degrees above the approximated LCST point of 65°C, all of the polymer was precipitated out of solution and collected in a similar procedure as that used to collect the MEEP polymer. In this manner, the entire heteropolymer could be isolated and purified in a single fraction.

By limiting the precipitation temperature to a selected lower value, fractionation of the polymer was possible. Polymer fractions that contained higher amounts of the *o*-allyl phenol exhibited a lower LCST temperature due to the additional hydrophobicity imparted by this ligand. Even after multiple cycles of purification, this fractionated polymer exhibited phase transition over a wider temperature range than that for the homopolymer, yet by keeping the desired LCST temperature a constant in each of the purification cycles, it was possible to obtain a purified fraction of the polymer.

As shown in Figure 4, each of these fractions was of a substantially different ligand group composition. In the bottom spectrum, collected from the fraction of polymer **3** with a maximum LCST point of 30°C, the peak at −13.3 ppm corresponds to those phosphorus that possess one DEG and one *o*-allyl phenol pendant group, while the peak at −7.7 ppm corresponds to a bis-DEG substitution. It is clear that this polymer fraction contains a much higher *o*-allyl phenol content than the 5% that the bulk, unfractionated polymer possesses. In contrast, the top spectrum, the fraction collected at 65°C, appears to be composed solely of DEG, behaves much like polymer **1**, in that it has the same LCST point and exhibits a sharper

phase transition range than for other fractions of polymer **3**.

These data give direct evidence that each individual polymer strand in the bulk material is substituted with slight variations of the component pendant groups. Although the bulk polymer possessed an average of 5% *o*-allyl phenol, some polymer strands must contain a slightly higher percentage, and consequently, others possess slightly less. Those with a higher percentage of the *o*-allyl phenol have a correspondingly lower LCST point, while those with less *o*-allyl phenol have a higher LCST point. The upper boundary, in which there is no detectable phenol incorporation, is a fraction that possesses the same LCST point as the MEEP polymer. Attempts to fashion a more quantitative scale that correlates the percentage of *o*-allyl phenol incorporation to LCST temperature were difficult as the low phenol concentrations made reliable integration of ^{1}H-NMR spectra signature peaks impossible. However, these experiments do show that fractionation of a water-soluble heteropolymer is possible using this method.

CONCLUSION

We have demonstrated that the isolation and purification of water-soluble polyphosphazenes exhibiting LCST behavior is possible through exploitation of this phase-transition phenomenon. This translates into significant savings in time, eliminates previously necessary dialysis equipment, and has been shown to be effective for both homopolymers and heteropolymers. It has also been demonstrated that selective fractionation, based upon pendant group composition, for some heteropolymers is possible. Further, this work yields direct evidence for the variation of composition of individual phosphazene polymer strands synthesized via standard nucleophilic substitution reactions. It must also be noted that this isolation procedure is more effective as the polymer increases in molecular weight, as low molecular weight polymers tend to form less tractable colloidal suspensions above the critical temperature.

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