# Poly(organophosphazenes) with Poly(alkyl ether) Side Groups: A Study of Their Water Solubility and the Swelling Characteristics of Their Hydrogels

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ABSTRACT: Five different poly[(alkyl ether)phosphazenes] were synthesized for studies of their water solubility as well as the swellabilities of their corresponding hydrogels in aqueous media. They are poly[bis(methoxyethoxy)phosphazene], poly[bis[(aminoethoxy)ethoxy]phosphazene], poly[bis[(methoxyethoxy)ethoxy]phosphazene], poly[bis[(ethoxyethoxy)ethoxy]phosphazene], and poly[bis[(butoxyethoxy)ethoxy]phosphazene]. Lower critical solution temperatures (LCST) were detected for four of the polymers. This phenomenon was independent of polymer concentration. However, poly[bis[(aminoethoxy)ethoxy]phosphazene] possessed no LCST in aqueous media and remained fully soluble at all polymer concentrations. Hydrogels of these polymers were prepared by subjecting them to $\gamma$ radiation (1, 5, and 10 Mrad). The cross-linked polyphosphazenes behaved in a manner similar to that of their soluble counterparts. As the temperature of the aqueous media was increased, the hydrogels became opaque and released water. During these experiments, the percentage of water lost by the hydrogels was independent of both the pH of the aqueous media and the radiation dose received by the gels. No detectable decomposition of the soluble polymers was found nor was any loss of integrity of the hydrogels detected through several heating and cooling cycles. This solubility phenomenon was characteristic only of the interaction with water and was not detected in organic solvents. The potential biomedical applications of these materials are discussed.

## Introduction

Poly[bis[(methoxyethoxy)ethoxy]phosphazene] (MEEP) has proved to be a useful and highly versatile polymer.[1-4] It is soluble in water, and the solid polymer can be cross-linked by $\gamma$ radiation to materials that absorb water to form hydrogels.[3] The cross-linking behavior is of interest for membrane research[3] as well as in studies of solid-state ionic conductivity.[1,2,4] Recently, we found that, in aqueous solutions at temperatures above 80 °C, MEEP becomes insoluble and precipitates from solution. This phenomenon, known as a lower critical solution temperature, is well-known for other polymers and has been discussed theoretically.[5] Even more significant was the observation that hydrogels formed from this polymer behave in a similar manner. As the temperature of the aqueous medium was increased above 60 °C, the cross-linked hydrogel matrix became cloudy and released water. The most significant water loss occurred between 70 and 80 °C, a temperature close to the LCST of the un-cross-linked polymer. When the aqueous medium was cooled to room temperature, the un-cross-linked polymer redissolved and the corresponding cross-linked gel again absorbed water. These heating and cooling cycles were carried out several times without decomposition of the un-cross-linked polymer or loss of the integrity of the hydrogel.

Several organic polymers, such as poly(ethylene glycol),[6] poly(propylene glycol),[6] poly(*N*-isopropylacrylamide),[7] and partially saponified poly(vinyl acetate),[8] also show this same solubility behavior. Hydrogels derived from these polymers have been used in drug delivery systems. In such systems, the gels are allowed to imbibe aqueous drug solutions at room temperature. Immersion of the polymers in hot aqueous media (50–60 °C) brings about a shrinkage, loss of the imbibed water, and entrapment of the drug molecule for later delivery.[9] Recently, Tanigami and co-workers have prepared a low molecular weight polyphosphazene with hydroxyl side groups which shows low-temperature water solubility.[10] However, the $^{31}P$ NMR spectrum of this polymer was extremely broad; therefore, its structure was difficult to determine.

Starting from our initial experiments with MEEP, we have carried out a broader investigation to include other poly[(alkyl ether)phosphazenes]. Two variations of the side-group structure were studied: (1) changes in the number of ether linkages in the alkyl ether chains and (2) variations of the end groups of the alkyl ether chains. The polymers shown in Chart I were synthesized to investigate these two variables: the polymers were poly[bis(methoxyethoxy)phosphazene] (**2**),[11] poly[bis[(methoxyethoxy)ethoxy]phosphazene] (**3**),[2] poly[bis[(aminoethoxy)ethoxy]phosphazene] (**4**),[12] poly[bis[(butoxyethoxy)ethoxy]phosphazene] (**5**),[13] and poly[bis[(ethoxyethoxy)ethoxy]phosphazene] (**6**).[13]

In this study, the dependence of the LCST on both the polymer concentration and the pH of the aqueous media was examined. Polymers **2–6** were then cross-linked by exposure to $\gamma$ radiation, and the thermal behavior of their hydrogels was studied. The questions of interest were as follows: (1) Do other poly[(alkyl ether)phosphazenes] show the same variation in water-solubility behavior as does MEEP? (2) Does the water solubility and water swellability depend on the length of the alkyl ether chain or on the nature of the side unit end group? (3) Is the solubility in aqueous media dependent on polymer concentration? (4) Does this phenomenon also control the behavior of the corresponding hydrogels?

## Results and Discussion

**Synthesis of Polymers 2–6.** Poly(dichlorophosphazene) (**1**) was allowed to react with a large excess of the sodium salt of the appropriate alcohol to yield polymers **2**, **3**, **5**, and **6**. The polymers were then isolated by precipitation into hexane. They were purified by dialysis against deionized water and methanol. For the preparation of polymer **4**, the amino group of (aminoethoxy)ethanol was initially protected with di-*tert*-butoxy dicarbonate to

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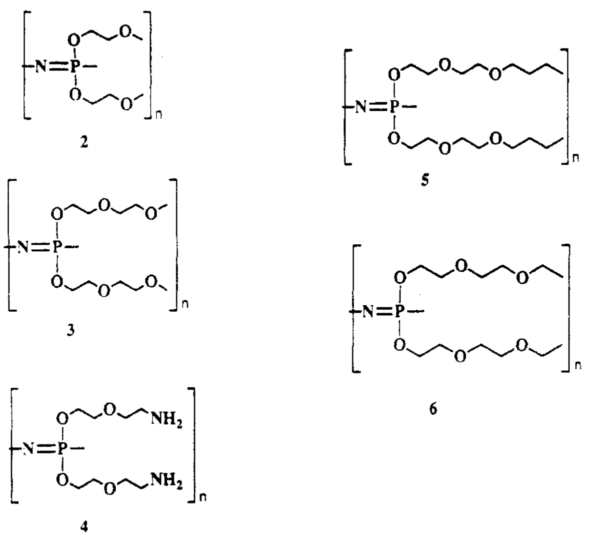
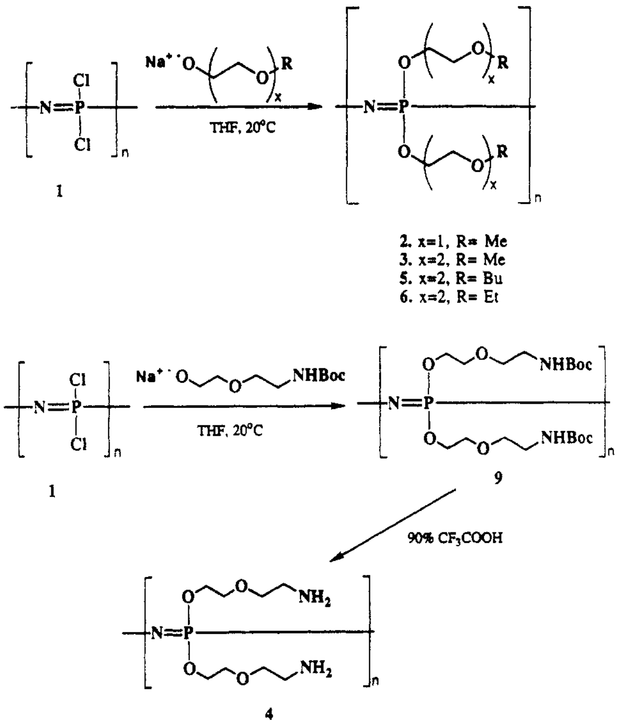
Chart I



Scheme I



avoid side reactions or cross-linking. The protected alcohol in the form of its sodium alkoxide salt was allowed to react with polymer 1. Isolation of the intermediate polymer, 9, followed by deprotection with trifluoroacetic acid gave the water-soluble polymer 4, which was purified by dialysis against water and methanol. The syntheses of these polymers are depicted in Scheme I. Characterization data for each polymer are shown in Table I.

**Preparation of Hydrogels from Polymers 2–6.** Samples of each polymer were exposed to three different doses of $^{60}$Co $\gamma$ radiation (1, 5, and 10 Mrad). The proposed cross-linking mechanism involves a free-radical recombination reaction as discussed in an earlier paper.[3] The cross-linked polymers were then allowed to swell in deionized water for 48 h before further experimentation.

**Water Solubility of the Un-Cross-Linked Poly[(alkyl ether)phosphazenes] 2–6.** Solutions of each polymer at six concentrations (400, 300, 200, 100, 10, 1 mg/mL) were prepared. The polymer solutions were placed in vials, which were then immersed in a water bath to control the polymer solution temperature. The water bath was heated slowly to 100 °C, and the temperature at which each of the polyphosphazenes precipitated from solution was recorded. Each solution was then cooled to room temperature. These heating and cooling cycles were repeated several times to ensure reproducible results. The lower critical solution temperatures found from these experiments were as follows: poly[bis(methoxyethoxy)phosphazene] (2), 30 °C; poly[bis[(methoxyethoxy)ethoxy]phosphazene] (3), 80 °C; poly[bis[(butoxyethoxy)ethoxy]phosphazene] (5), 51 °C; poly[bis[(ethoxyethoxy)ethoxy]phosphazene] (6), 38 °C Polymer 4, poly[bis[(aminoethoxy)ethoxy]phosphazene], did not show a lower critical solution temperature. In addition, it was found that the LCSTs of polymers 2, 3, 5, and 6 were independent of polyphosphazene concentration. The molecular weights of each polymer and their $^{31}$P NMR spectrum were monitored. After several heating and cooling cycles, no significant decline occurred in the molecular weight as estimated by gel permeation chromatography (GPC) nor was any decomposition detected by $^{31}$P NMR spectroscopy.

**Swellability of Cross-Linked Poly[(alkyl ether)phosphazenes] in Aqueous Media at Elevated Temperatures.** After water absorption in deionized water for 48 h, the hydrogels of the poly[(alkyl ether)phosphazenes] were placed in vials of buffer solutions and were then immersed in a water bath. The polymers previously exposed to 1 and 10 Mrad of $\gamma$ radiation were immersed in pH 7 buffer, while the polymers subjected to 5 Mrad were in buffer solutions of pH 4, 7, and 10. The objective was to monitor differences in water loss from each hydrogel following variations in radiation exposure or pH. The initial swollen gel weights of the hydrogels were determined at 20 °C. The swollen gels in aqueous buffers were heated incrementally to 100 °C. At every 10 °C interval, the wet weight of the hydrogel was recorded. The heating and cooling cycle was repeated several times to ensure reproducible results. The hydrogels retained their integrity during these processes, and this indicated that no hydrolysis of the polymer backbone or cleavage of the cross-links between the polymer chains occurred.

The data obtained in these experiments were plotted as the ratio of wet gel weight at temperature $T$ to the wet gel weight at room temperature (20 °C) multiplied by 100, as a function of temperature. Figure 1 illustrates the behavior of the polyphosphazenes after exposure to 5 Mrad of $\gamma$ radiation and swelling in pH 7 buffer.

**Influence of Environmental Changes on Hydrogel Swellability.** As stated previously, the LCSTs of these polymers were independent of their concentrations in aqueous media because of their relatively high polydispersities ($4 < M_w/M_n < 10$) as shown by GPC analyses[14] (see Table I).

Increasing the number of alkyl ether linkages appears to raise the LCST (30 °C for 2 as compared to 80 °C for MEEP). However, the size of the terminal alkyl group did not alter the LCST in a manner that could be correlated with the alkyl group structure. Nevertheless, the nature of the end group is clearly important for the hydrogen-bonding amino group (polymer 4), where no LCST behavior was detected.

The hydrogels from polymers 2–6 behaved in a manner similar to that of their soluble, un-cross-linked counterparts. The temperature at which the most significant water loss occurred from the hydrogels coincided with the temperature of precipitation of the soluble polyphosphazenes in aqueous media. The hydrogel from polymer

**Table I**
**Characterization Data for Poly[(alkyl ether)phosphazenes] 2–6**

| polymer | $^{31}$P NMR (ppm) | $^{1}$H NMR$^{a}$ (ppm) | $T_g$ (°C) | $M_w$ ($M_w/M_n$) | | elemental analysis | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | %C | %H | %N | %Cl |
| 2 | −7.4 | 3.5 (b s, 3 H) | −75 | $1.2 \times 10^6$ (4.2) | calcd | 36.92 | 7.18 | 7.18 | |
| | | 3.9 (b s, 4 H) | | | found | 36.79 | 7.21 | 7.12 | 0.31 |
| 3 | −7.6 | 3.5 (b s, 3 H) | −84 | $2.4 \times 10^6$ (6.0) | calcd | 42.40 | 7.77 | 4.95 | |
| | | 3.6 (b s, 2 H) | | | found | 42.21 | 7.81 | 4.87 | 0.07 |
| | | 3.7 (b s, 4 H) | | | | | | | |
| | | 4.1 (b s, 2 H) | | | | | | | |
| 4 | −8.0 | 2.7 (b s, 2 H) | −18 | $7.8 \times 10^6$ (9.5) | calcd | 37.94 | 7.91 | 16.60 | |
| | | 3.6 (b s, 4 H) | | | found | 38.07 | 7.96 | 16.40 | 0.03 |
| | | 4.0 (b s, 2 H) | | | | | | | |
| 5 | −8.1 | 1.1 (b s, 3 H) | −84 | $1.2 \times 10^6$ (7.2) | calcd | 52.32 | 9.26 | 3.81 | |
| | | 2.3 (b s, 4 H) | | | found | 52.48 | 9.37 | 3.64 | 0.19 |
| | | 3.5 (b s, 2 H) | | | | | | | |
| | | 3.6 (b s, 2 H) | | | | | | | |
| | | 3.8 (b s, 4 H) | | | | | | | |
| | | 4.2 (b s, 2 H) | | | | | | | |
| 6 | −7.9 | 1.3 (b s, 3 H) | −76 | $1.4 \times 10^6$ (8.3) | calcd | 46.30 | 8.36 | 4.50 | |
| | | 3.3 (b s, 2 H) | | | found | 46.21 | 8.42 | 4.38 | 0.26 |
| | | 3.4 (b s, 2 H) | | | | | | | |
| | | 3.6 (b s, 4 H) | | | | | | | |
| | | 3.8 (b s, 2 H) | | | | | | | |

[a] b s denotes that the resonance was a broad singlet without resolution.

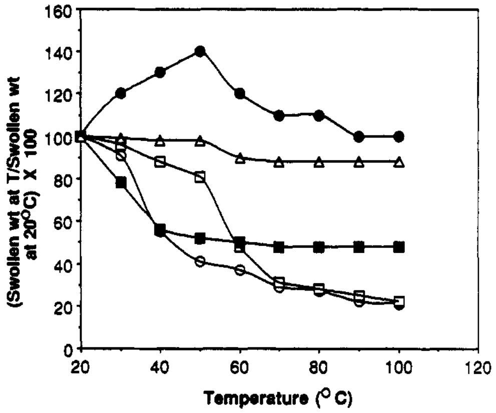


Figure 1. Percent weight retention of the hydrogels irradiated with 5 Mrad of $\gamma$ radiation in pH 7 buffer as a function of temperature: (○) poly[bis(methoxyethoxy)phosphazene] (2), (□) poly[bis[(methoxyethoxy)ethoxy]phosphazene] (3), (●) poly[bis[(aminoethoxy)ethoxy]phosphazene] (4), (△) poly[bis[(butoxyethoxy)ethoxy]phosphazene] (5), (■) poly[bis[(ethoxyethoxy)ethoxy]phosphazene] (6).

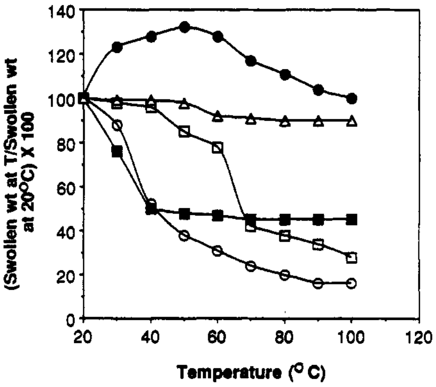


Figure 2. Percent weight retention of the hydrogels irradiated with 1 Mrad of $\gamma$ radiation in pH 7 buffer as a function of temperature: (○) poly[bis(methoxyethoxy)phosphazene] (2), (□) poly[bis[(methoxyethoxy)ethoxy]phosphazene] (3), (●) poly[bis[(aminoethoxy)ethoxy]phosphazene] (4), (△) poly[bis[(butoxyethoxy)ethoxy]phosphazene] (5), (■) poly[bis[(ethoxyethoxy)ethoxy]phosphazene] (6).

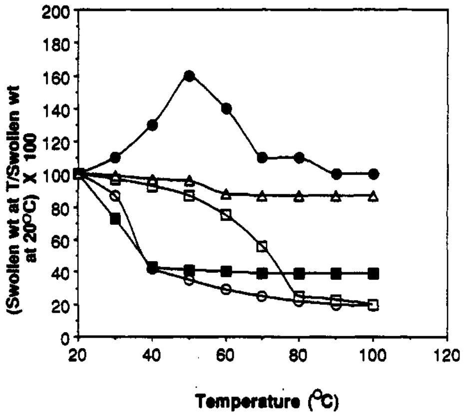


Figure 3. Percent weight retention of the hydrogels irradiated with 10 Mrad of $\gamma$ radiation in pH 7 buffer as function of temperature: (○) poly[bis(methoxyethoxy)phosphazene] (2), (□) poly[bis[(methoxyethoxy)ethoxy]phosphazene] (3), (●) poly[bis[(aminoethoxy)ethoxy]phosphazene] (4), (△) poly[bis[(butoxyethoxy)ethoxy]phosphazene] (5), (■) poly[bis[(ethoxyethoxy)ethoxy]phosphazene] (6).

4 showed no LCST behavior, and this is consistent with the behavior of its soluble counterpart. In fact, this gel gained weight up to 60 °C, after which the weight declined. Within the limits of these experiments, the degree of cross-linking had no effect on the weight/temperature profile of the hydrogels. This conclusion is supported by the data in Figures 2 and 3. These graphs are similar to Figure 1, and they show the loss/gain of water weight by the hydrogels from 20 to 100 °C.

It should be noted that, as the radiation dosage was increased, the ability of the resultant gels to imbibe water decreased (the system became more resistant to swelling). Poly[bis[(butoxyethoxy)ethoxy]phosphazene] (6) underwent a greater degree of cross-linking for a given radiation dose due to the high concentration of C–H bonds in the terminal butoxy group. However, each gel released approximately the same *ratio* of water regardless of the radiation dose (see Figures 1–3). As shown in Figures 1–3, the greatest water loss from each gel occurred at the LCST of the corresponding soluble polymer. The water loss from the gels showed no dependence on the pH of the aqueous media. The LCST of a polymer is usually dependent on the ionic strength of a solution and not necessarily on the pH of that solution. In our experiments, the ionic strengths of the buffer solutions were approximately the same. However, it was considered important

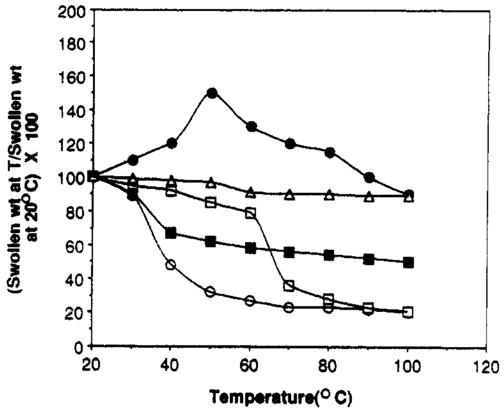


**Figure 4.** Percent weight retention of the hydrogels irradiated with 5 Mrad of $\gamma$ radiation in pH 4 buffer as a function of temperature: (○) poly[bis(methoxyethoxy)phosphazene] (2), (□) poly[bis[(methoxyethoxy)ethoxy]phosphazene] (3), (●) poly[bis[(aminoethoxy)ethoxy]phosphazene] (4), (△) poly[bis[(butoxyethoxy)ethoxy]phosphazene] (5), (■) poly[bis[(ethoxyethoxy)ethoxy]phosphazene] (6).

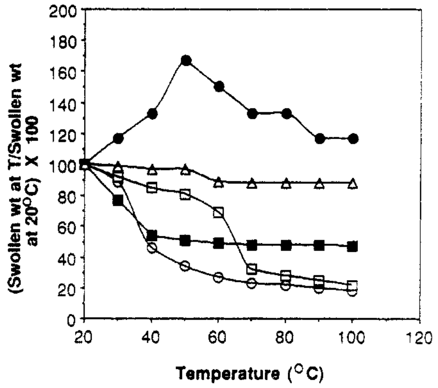


**Figure 5.** Percent weight retention of the hydrogels irradiated with 5 Mrad of $\gamma$ radiation in pH 10 buffer as a function of temperature: (○) poly[bis(methoxyethoxy)phosphazene] (2), (□) poly[bis[(methoxyethoxy)ethoxy]phosphazene] (3), (●) poly[bis[(aminoethoxy)ethoxy]phosphazene] (4), (△) poly[bis[(butoxyethoxy)ethoxy]phosphazene] (5), (■) poly[bis[(ethoxyethoxy)ethoxy]phosphazene] (6).

to examine the behavior within different pH ranges due to the potential biomedical applications of these hydrogels. This information is presented in Figures 4 and 5.

Because of their relatively low LCSTs, hydrogels derived from these polyphosphazenes appear to have the properties needed for use as drug delivery systems, by analogy with the use of cross-linked poly(*N*-isopropylacrylamide).[9] Hydrogels from both poly[bis(methoxyethoxy)phosphazene] (2) and poly[bis[(ethoxyethoxy)ethoxy]phosphazene] (5) appear to be particularly interesting since their lower critical solution temperatures are close to the temperature of the human body.

## Experimental Section

**Reagents and Equipment.** All polymer synthesis reactions were carried out under an atmosphere of dry nitrogen (Matheson) using standard Schlenk line techniques. Tetrahydrofuran (THF; Omnisolv) was distilled from sodium benzophenone ketal under a dry nitrogen atmosphere. 2-(2-Methoxyethoxy)ethanol, 2-methoxyethanol, 2-(2-aminoethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, and 2-(2-butoxyethoxy)ethanol (Aldrich) were distilled from barium oxide and stored over 4-Å molecular sieves. Di-*tert*-butoxy dicarbonate, sodium, and sodium hydride (60% mineral oil dispersion) (Aldrich) were used as received. Hexachlorocyclotriphosphazene (Ethyl Corp.) was obtained from a trimer/tetramer mixture via two fractional sublimations [30 °C (0.1 mmHg)]. Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C in a sealed evacuated Pyrex tube.[15] $^{31}P$ NMR spectra were obtained with use of a JEOL FX-90Q (36.23-MHz) spectrometer and a Bruker 360 WM (145-MHz) spectrometer. $^1H$ NMR spectra were obtained with the use of a Bruker 360 WM operated at 360 MHz. Glass transition temperatures were determined by using a Perkin-Elmer DSC Model 7 interfaced with TAS-7 software. Molecular weights of the polymers were estimated by gel permeation chromatography using a Hewlett Packard LC 1090 unit with a polystyrene stationary phase. Polystyrene standards were used to calibrate the columns. Sample concentrations were approximately 1.5% w/v in THF. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

**Synthesis of Polymers 2, 3, 5, and 6.** These polymers were synthesized via the same general procedure. The synthesis of polymer 3 was as follows. Poly(dichlorophosphazene) (1; 3.0 g, 0.026 mol) was dissolved in dry THF (250 mL). Sodium (2.38 g, 0.103 mol) was allowed to react with 2-(2-methoxyethoxy)ethanol (18.62 g, 0.155 mol) in dry THF (150 mL). The alkoxide was then added to the polymer solution. The reaction was then allowed to proceed for 72 h at room temperature. The reaction solution was concentrated, and the polymer was precipitated into hexane. It was then dissolved in deionized water, placed in cellulose dialysis tubing (12 000–14 000 molecular weight cutoff) for 72 h, and then dialyzed against methanol for 48 h. The polymer solution was then concentrated using a rotary evaporator, poured onto a Teflon sheet, and then dried under vacuum to give pure polymer 3.

**Synthesis of Polymer 4.** Poly(dichlorophosphazene) (1; 3.0 g, 0.026 mol) was dissolved in dry THF (250 mL). Sodium hydride (4.16 g, 0.104 mol, 60% dispersion in mineral oil) was allowed to react with Boc-protected 2-(2-aminoethoxy)ethanol (31.98 g, 0.156 mol) in dry THF (300 mL). The alkoxide solution was added to the polymer solution via a fritted addition funnel. The reaction was then allowed to proceed for 72 h at room temperature. The solution was concentrated, and the polymer was precipitated into hexane. The polymer was further purified by precipitation into hexane (3×) and deionized water (3×). The protected polymer (2.5 g, 0.006 mol) was then dissolved in 90% (v/v) trifluoroacetic acid (25 mL). The deprotection continued for 15 h. The reaction mixture was then neutralized with 5 M NaOH to pH 7. The polymer remained soluble during neutralization, and was placed in cellulose dialysis tubing (12 000–14 000 molecular weight cutoff) and dialyzed against water (72 h) and methanol (48 h). The dialysate was concentrated, poured onto a Teflon sheet, and dried in vacuo to give pure polymer 4.

**Preparation of Poly[(alkyl ether)phosphazene] Hydrogels.** Three 2.0-g samples of each polymer were placed in freeze dryers, which were evacuated for 48 h. These were then irradiated at the Brezeale Nuclear Reactor at The Pennsylvania State University with 1, 5, or 10 MRad of $^{60}Co$ $\gamma$ radiation. The samples were then weighed and allowed to swell in deionized water for 48 h before use.

**Solubility Studies of Un-Cross-Linked Poly[(alkyl ether)phosphazenes] in Aqueous Media.** Each polymer was dissolved in deionized water at six different concentrations (400, 300, 200, 100, 10, and 1 mg/mL). Approximately 5-mL samples of each solution were placed in vials, and the vials were heated in a water bath. The temperature of the water bath was raised from 20 to 100 °C over 3.5 h. The temperature at which the polyphosphazene precipitated from solution was taken as the LCST of that system. The water bath was then cooled to 20 °C, and the polymers were redissolved. The heating and cooling cycles were repeated three times in order to obtain reproducible results.

**Temperature Effects on the Swellability of Poly[(alkyl ether)phosphazene] Hydrogels in Aqueous Media.** Hydrogels exposed to 1 and 10 Mrad of $\gamma$ radiation were first swelled in deionized water and then placed in pH 7 buffer. Hydrogels exposed to 5 Mrad of radiation were immersed in buffers of pH 4, 7, and 10. After 48 h in the buffer solution, each gel was weighed at 20 °C. The gels had swelled to 3–8 times their dry weight. The vials containing the gels were then placed in a water bath and were heated to 100 °C over a 5-h period. The hydrogels were weighed after every 10 °C temperature increment. The heating and cooling cycles were carried out three times to ensure accurate results.

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## References and Notes

(1) Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.
(2) Allcock, H. R.; Austin, P. E.; Neenan, T. X.; Sisko, J. T.; Blonsky, P. M.; Shriver, D. F. *Macromolecules* **1986**, *19*, 1508.
(3) Allcock, H. R.; Kwon, S.; Riding, G. H.; Fitzpatrick, R. J.; Bennett, J. L. *Biomaterials* **1988**, *19*, 509.
(4) Bennett, J. L.; Dembek, A.; Allcock, H. R.; Heyen, B. J.; Shriver, D. F. *Chem. Mater.* **1989**, *1*, 14.
(5) Eagland, D.; Crowther, N. J. *Eur. Polym. J.* **1991**, *27*, 299.
(6) Malcolm, G. N.; Rowlinson, J. S. *Trans. Faraday Soc.* **1957**, *53*, 921.
(7) Heskins, M.; Guillet, J. E. *J. Macromol. Sci., Chem.* **1968**, *A2*, 1441.
(8) Kinieda, H.; Shinoda, K. In *Colloidal Dispersions and Micellular Behavior*; Mittal, K., Ed.; ACS Symposium Series 9; American Chemical Society: Washington, DC, 1975; p 278.
(9) Dong, L. C.; Hoffman, L. C. In *Reversible Polymeric Gels and Related Systems*; Russo, P., Ed.; ACS Symposium Series 350; American Chemical Society: Washington, DC, 1987; p 236.
(10) Tanigami, T.; Ono, T.; Suda, N.; Sakamaki, Y.; Yamaura, K.; Matsuzawa, S. *Macromolecules* **1989**, *22*, 1397.
(11) Allcock, H. R.; Gebura, M.; Kwon, S.; Neenan, T. X. *Biomaterials* **1988**, *19*, 500.
(12) Allcock, H. R.; Chang, J. Y. *Macromolecules* **1991**, *24*, 993.
(13) Allcock, H. R.; Connolly, M. S.; Suszko, J. T.; Al-Shali, S. *Macromolecules* **1988**, *21*, 1.
(14) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(15) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.