

Electron Beam Crosslinking of Fluoroalkoxy, Methoxyethoxyethoxy, and Substituted Phenoxy Polyphosphazenes: Physical and Chemical Characterization and Comparison to a Thermally Induced Free Radical Process and Ionic Complexation

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Received 11 March 1999; accepted 7 August 1999

ABSTRACT: Electron beam, thermal free radical, and cationic complexation mechanisms have been employed to investigate crosslinking in selected polyphosphazenes. In polyphosphazenes functionalized with *o*-allylphenol to facilitate free radical crosslinking, maximum crosslink density was achieved after 10 min at 130°C utilizing benzoyl peroxide as an initiator. Electron beam radiation was found to give an increased crosslink density with increased dose. The dose–crosslink density relationship observed for a aryloxyphosphazene terpolymer PPXP also was seen in poly[bis(2,2'-(methoxyethoxy)ethoxy)phosphazene] (MEEP). However, with two lots of a fluoroalkoxyphosphazene an initial crosslink density was achieved at a lower electron beam exposure with no additional crosslink density observed with increasing dose. These measurements are observations of net crosslinking, which is the result of crosslinking processes balanced by chain scission processes. DSC revealed that neither thermal- nor electron beam-initiated crosslinking cause any significant change in the T_g of the polymer. Metal ion complexation with MEEP consistently gave T_g values that were higher than MEEP. The T_g values measured for both MEEP and the lithium-complexed MEEP were unaffected by electron beam irradiation. These data suggest the location of lithium complexation may be at the nitrogen lone electron pair on the backbone, representing a new mechanism of lithium complexation in phosphazenes. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 55–66, 2000

Key words: polyphosphazenes; crosslinking; electron beam processing; lithium complexation; polymer swelling; free radical crosslinking

INTRODUCTION

Crosslinking technology is widely used commercially to improve the performance and durability

of numerous rubber, plastics, and fiber-reinforced composites as well as to improve the properties of thin-film membranes.¹ As part of our desire to develop polymers for membrane separations, we have investigated various crosslinking processes for polyphosphazene membranes, including thermal, free radical, and high energy electron beam (EB) processes.

Crosslinking processes are well understood for organic polymers. Crosslinking phenomena in inorganic polymers, on the other hand, have been

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Contract grant sponsor: United States department of Energy; contract grant number: DE-AC07-94ID13223.

Journal of Applied Polymer Science, Vol. 76, 55–66 (2000)
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explored to a lesser degree. Inorganic polymers, specifically polyphosphazenes offer several advantages over organic polymers for a variety of applications where harsh conditions exist. Polyphosphazenes are stable in acidic environments, enjoy thermal stabilities as high as 400°C,² and can be synthetically tailored to achieve a selected chemical affinity.³ Glass transition temperatures for this class of polymers have been reported⁴ to span from -100 to +100°C, testifying to the fact of their chemical and physical variability.

Chemical and physical variability in polyphosphazenes is due the inorganic backbone consisting of phosphorus and nitrogen atoms with alternating double and single bonds. This leaves phosphorus with two available sites for pendant groups. Most commonly, pendant groups consist of nucleophilic groups such as alkoxides,⁵ phenoxides,² amines,⁶ alkyls,⁷ aryls,⁸ and organometallics.⁹ The nature of the pendant groups has a dominant effect on the final properties of the polymer. Hydrophilic ligands, such as 2-(2-methoxyethoxy)ethanol,¹⁰ impart this character onto the polymer where hydrophobic ligands such as phenols and perfluorinated alcohols, and conversely, make the polymer insoluble with water.¹¹

Crosslinking of polyphosphazenes¹² has been reported using free radical methodology,¹³ gamma irradiation,^{14,15} ultraviolet radiation,¹⁶ and lithium ion inclusion.¹⁷ Free radical crosslinking can be done thermally using a free-radical initiator such as benzoyl peroxide. This method has been observed in our laboratories to cause some unwanted thermally induced decomposition of thin film membranes. Room temperature crosslinking has been performed through exposure of the polymer to ultraviolet radiation¹⁸ using benzophenone as a free radical initiator. Depth of penetration by UV into the polymer film is the primary problem that is encountered using this method. Achieving a homogeneous crosslink density throughout an entire polymer substrate, such as a membrane, is extremely difficult due to the high optical density in the UV region of the aromatic substituent pendant groups commonly used in phosphazene polymers. Additionally, residues from the initiator that remain in the polymer after crosslinking can lead to contamination concerns.

Radiation crosslinking has been reported^{16,19} for a variety of phosphazene polymers including poly[bis(2,2'-(methoxyethoxy)ethoxy)phosphazene] (MEEP), MEEP containing blends, poly[bis(phenoxy)phosphazene] (PPOP), and poly[bis(trifluoroethoxy)phosphazene] (PTFEP). PTFEP and

PPOP required heavy doses of radiation to yield crosslinked materials that were no longer soluble and formed swollen gels upon exposure to solvent. MEEP and MEEP blends were observed to crosslink at much lower radiation doses, indicating greater relative sensitivity of the etherial pendant group protons to radiation-induced crosslinking. Mechanistically, crosslinking in MEEP has been proposed²⁰ to occur through carbon-carbon bond formation between polyethers of adjacent polymer strands with concurrent loss of hydrogen. This has the potential to give long "bridges" between adjacent backbones, containing up to 16 atoms. Variability in dose requirements for polyphosphazenes with differing pendant groups suggests that the lability of hydrogens on the pendant groups is the dominant factor in the crosslinking mechanism, and that direct backbone crosslinking processes play a relatively minor role.

During either room or elevated temperature crosslinking processing, there are two possible results: (1) molecular weight increase due to bond formation between polymer chains, and (2) molecular weight decrease due to chain scission.²¹ These competing processes will effect polymer morphology and bulk properties. Simple inter-chain crosslinking gives dramatic increases in molecular weight. Competing crosslinking and chain scission processes can give either higher or lower molecular weight materials, depending on the relative rates, and dominant chain scission processes lead to polymer degradation. An understanding of the effects of crosslinking processes is critical to the further development of polyphosphazene-based materials.

In this article, we report on the characterization of several phosphazene polymers that were crosslinked using electron beam radiation. The efficacy of electron beam irradiation is assessed and compared to an alternate method, thermally initiated free radical crosslinking. Polymers chosen for these studies include polyfluoroalkoxy-phosphazene elastomers PFAP-1 and PFAP-2,²² MEEP, and PPXP, a mixed phenoxide substituent terpolymer. Additionally, a lithium-MEEP complex was prepared to examine the reported crosslinking effect of metal ions to gain insight into the nature of the crosslink.

EXPERIMENTAL

Methods

Thermal analyses were performed using a TA Instruments Model 2910 Differential Scanning

Calorimeter (DSC). NMR analyses were performed on a Bruker AC-300P spectrometer operating at 300 MHz (hydrogen). Proton spectra referencing was provided by either the residual protons in deuterated chloroform solvent (Cambridge Isotopes Laboratories) or by 99.5% D trimethylsilyl-2,2,3,3,-d₄-propionic acid, sodium salt. ³¹P spectra were referenced to 85% H₃PO₄ (internal, coaxial), with positive shifts recorded downfield of the reference. Elemental analysis was performed on Carlo Erba model EA1108 elemental analyzer.

Materials

The polymers used for this study were: (1) PFAP-1, a linear fluoroalkoxyphosphazene elastomer with substituents consisting of a mixture of approximately 35% CF₃CH₂O— and 65% CF₂H(CF₂)_xCH₂O— where x = 1, 3, 5, 7 with a small amount (~1%) of a reactive pendant group to facilitate crosslinking, molecular weight (M_w) = $(9.731 \pm 0.3) \times 10^8$ g/mol, RMS radius = 111.4 ± 0.8 nm, polydispersity (M_w/M_n) = 1.258 ± 0.062 ; (2) PFAP-2, a linear fluoroalkoxyphosphazene elastomer (similar to PFAP-1), molecular weight (M_w) = $(2.284 \pm 0.02) \times 10^7$ g/mol, RMS radius = 105.4 ± 12.6 nm, polydispersity (M_w/M_n) = 1.951 ± 0.028 ; (3) ORGAFLEX AMF 100 supplied by ELF ATOCHEM, S.A. (PPXP). PPXP is a terpolymer with the following pendant group composition: 55% *p*-methoxyphenol, 36% *p*-sec-butylphenol, and 9% *o*-allylphenol, molecular weight (M_w) = $(2.442 \pm 0.01) \times 10^6$ g/mol, RMS radius = 87.1 ± 0.7 nm, polydispersity (M_w/M_n) = 1.043 ± 0.008 ; (4) poly[bis(2,2'-methoxyethoxyethoxy)phosphazene] (MEEP) made at the INEEL by the procedure described in the next section. PFAP-1, PFAP-2, and PPXP were used without further purification.

Synthesis of Poly[bis(2,2'-(methoxyethoxy)ethoxy)phosphazene] (MEEP)

This polymer was synthesized according to literature procedures,¹⁰ but was isolated and purified via a novel route exploiting the lower critical solubility temperature (LCST) behavior of this material in aqueous solution.²³ 2-(2-Methoxyethoxy)ethanol (44.2 g, 0.368 mol) was added to 360 mL of anhydrous THF under dry lightly flowing argon. 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 by cannula, and the reaction mixture stirred for 15 h at reflux under argon and allowed to cool to room temperature. The crude polymer was recovered by precipitation into 500 mL of hexanes, and the resulting cream colored solid was then dissolved in 200 mL of deionized water, resulting in a solution of pH 12. The solution was neutralized with 4 M H₃PO₄ (final pH of 6.5) and gently warmed above the LCST point to induce precipitation of the polymer. The polymer was collected while still warm, and immediately placed in a separate container of deionized water at room temperature to dissolve the polymer. After four sequential cycles of this treatment, the recovered material was dried in a vacuum oven (50°C, 70 Torr Ar) for 2 days to yield a clear gum (19 g, 66%): ¹H-NMR (D₂O) δ (ppm) 3.3 (3H), 3.5 (2H), 3.7 (4H), 4.1 (2H); ³¹P-NMR δ (ppm) -6.6. Anal. Calcd.: C, 42.4; H, 7.8; N, 4.9. Found: C, 42.5; H, 7.5; N, 4.8; (M_w) = $(2.730 \pm 0.6) \times 10^7$ g/mol, RMS radius = 79.5 ± 0.4 nm; polydispersity (M_w/M_n) = 1.416 ± 0.465 . All solvents (Aldrich) were anhydrous grade and used as received. The 2-(2-methoxyethoxy)ethanol (Aldrich) was vacuum distilled prior to use. (BP 62–64°C at 0.7 Torr) Hexachlorocyclotriphosphazene (Strem) was purified by vacuum sublimation. (60°C at 50 mTorr) Poly(dichlorophosphazene) was prepared according to established procedures²⁴ by ring-opening bulk polymerization under vacuum in a sealed tube at 250°C.

Electron Beam Polymer Irradiation

Polymer irradiation experiments were conducted at Science Research Laboratory, Somerville, MA, on a high-energy electron beam (HEEB) linear induction accelerator. The operating parameters for the HEEB accelerator were 1.2 MeV/500 A/50 ns/25 Hz. The total irradiation dose as a function of time was determined using standard dosimetry calibration procedures. The polymers were attached to an aluminum target and irradiated for increasing amounts of time (3–12 min), which correspond to total irradiation doses between 5 and 20 Mrad, respectively. The MEEP polymers were also irradiated at shorter times for total doses between 1 to 4 Mrad to determine the lower limit of crosslinking.

Dilute Solution Characterization

Dilute solution techniques were used to characterize the macromolecular structures of the electron beam-irradiated polymers. Tetrahydrofuran

(THF), filtered through a 0.02- μm filter, was used as the solvent, and all measurements were made at 22°C. A refractive index increment, dn/dc , value was determined for the nonirradiated starting material using a Rainin Dynamax RI-1 differential refractive index detector. The instrument constant was determined using known concentrations of polystyrene standards whose dn/dc values are well known. Laser light-scattering (LLS) measurements were made using a Wyatt Technologies Dawn-DSP system, which used polarized light having a wavelength of 633 nm, and measures scattered light intensities at 18 angles ranging from 22.5 to 147°. The system was calibrated with 0.02- μm filtered toluene. Dilute solutions in the 10–100 $\mu\text{g}/\text{mL}$ range were prepared in scintillation vials for scanning on the LLS instrument.

MEEP Solubility Experiments

MEEP solutions were prepared by dissolution in filtered THF. Samples displaying insoluble material after 4 h with occasional mixing at 22°C were placed in a warm water bath for an additional 0.5 h to attain maximum solubility. These solutions were allowed to stand for approximately 15 h to allow the swelled insoluble portion of the sample to settle to the bottom of the sample vial. Aliquots of the supernatant liquid were then removed for solubility determination and LLS measurements. Solubility determinations were made by evaporating aliquots of the supernatant liquid to dryness, and then to constant weight under a stream of dry nitrogen. Solution concentrations for LLS measurements were corrected for the observed solubility.

Preparation of Thermally Crosslinked PPXP

Preparation of PPXP samples for thermal crosslinking involved dissolving the polymer in THF followed by centrifugation to ensure solution clarity. Benzoyl peroxide (Aldrich), 1% by polymer weight, was added and stirred for 10 min at room temperature. THF was allowed to evaporate from this solution under ambient laboratory conditions. To ensure total THF removal, the nearly dry rubber was placed under vacuum for at least 24 h. THF removal and benzoyl peroxide activity were verified by DSC. An exotherm was noted at 106°C, corresponding to the onset of the decomposition of benzoyl peroxide. No other exotherms were noted. The polymer rubber was crosslinked by heating in an oven for predetermined amounts of time.

Table I Acetone Solubility, Swelling, and T_g Data for Electron Beam Crosslinked PPXP

Electron Beam Dose (Mrad)	Solubility (%)	Swelling (%)	T_g (°C)
0	100	—	2
5	78.3	2333 ^a	3
10	16.0	432	3
15	7.6	366	5
20	6.1	317	4

^a This value is an estimate due to the highly swollen nature of the polymer.

Swelling and Solubility Determinations for Thermally Crosslinked PPXP

Swelling and solubility determinations on PPXP were performed by immersing weighed portions of the differing polymers in solvent, either acetone or THF, at room temperature. After 6 days, the polymer samples were removed from solution, reweighed to gain the swollen weight, dried under vacuum for 24 h, and weighed to gain the dry weight of insoluble material that was used to calculate the percent of solvent swelling. The solubilities were calculated from the initial and final dry polymer masses.

RESULTS AND DISCUSSION

PPXP

PPXP is a phosphazene terpolymer that contains *o*-allylphenol groups that facilitate free radical crosslinking processes. We have previously shown solvent inclusion in this polymer by liquid and solid-state NMR techniques.¹³ Samples of this polymer were crosslinked using an electron beam at 5-, 10-, 15-, and 20-Mrad dose levels. Crosslinking was verified through changes in solvent solubility and swelling measurements where the materials form insoluble gels with some attenuated degree of solubility at all radiation doses. Consistent with previous reports,¹⁶ both the degree of solvent inclusion in the polymer matrix and the soluble polymer fraction decrease with increasing radiation dose. Thermal analysis of the materials showed no increase in T_g (Table I) with increasing dose, which suggests that no significant constraint was placed on backbone motion with increasing radiation dose. DSC revealed no other thermal features, which indicates the amorphous nature of the polymer is maintained.

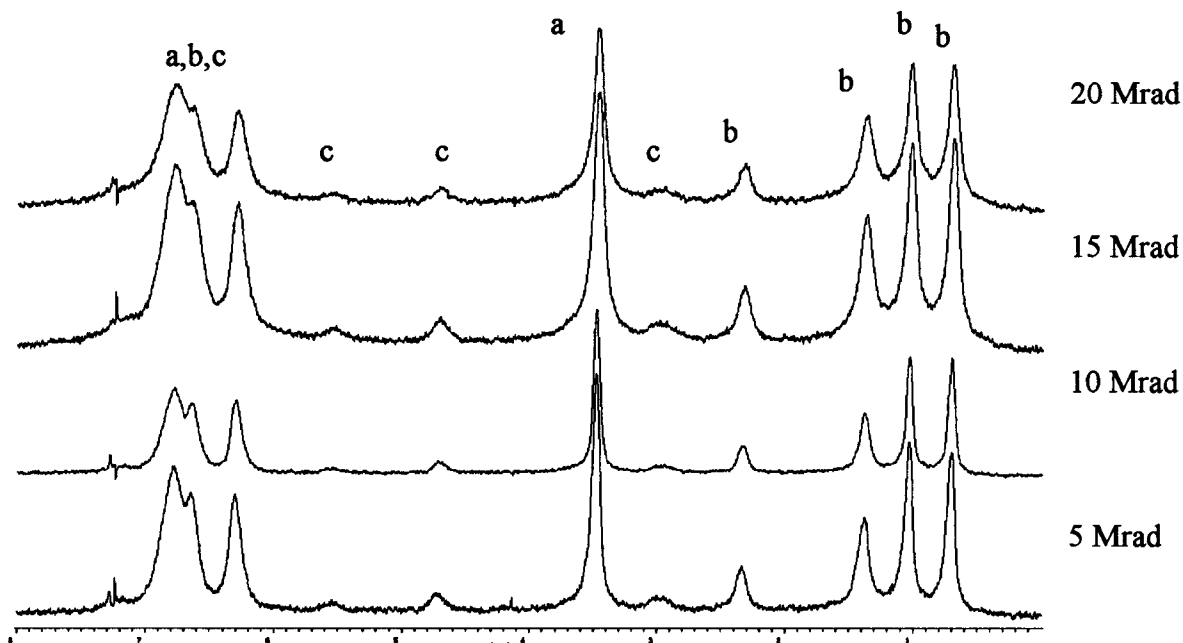


Figure 1 $^1\text{H-NMR}$ spectra of CDCl_3 swollen PPXP gels crosslinked with electron beam radiation: (a) *p*-methoxyphenol; (b) *p*-*sec*-butylphenol; (c) *o*-allylphenol.

Potential crosslinking sites on PPXP include the allylic, *sec*-butyl, and methoxy substituents on the aromatic pendant groups. Free radical crosslinking through these substituents involves either addition to the double bond or hydrogen abstraction followed by carbon-carbon bond formation with loss of hydrogen. Allylic and benzylic hydrogens have lower bond dissociation energies than methoxyl hydrogens,²⁵ and thus, are postulated to be major constituents in the crosslinking process. Joining of *o*-allyl phenolic or benzylic substituents together during crosslinking would be expected to form a short "carbon bridge" between the aromatic rings of neighboring phosphazene chains. The steric encumbrance created by two proximate rigid aromatic ring containing structures, would be expected to limit the degrees of motional freedom available in the crosslink. This effect, in turn, would be translated onto the backbone segments associated with the crosslink resulting in more restricted backbone motion. However, due to the inherent flexibility of the phosphazene backbone, the T_g does not rise significantly in this polymer after crosslinking.

Proton NMR analysis was performed on materials crosslinked at the four dose levels, and were compared to one another by curve-fitting integration. Samples of swollen polymer ranging from uncrosslinked (dissolved) to 20-Mrad crosslinked swollen gel give good NMR proton data in a liquid

state probe (see Fig. 1). No clear changes in relative intensities of the signals were detected by integration of the spectra, suggesting that the substitution on the polymer remains constant during electron beam exposure.

To contrast the electron beam crosslinking method, PPXP was thermally crosslinked at four differing temperatures using benzoyl peroxide as a free radical initiator. The four temperatures employed, 130, 150, 170, and 190°C, are all higher than the decomposition temperature of benzoyl peroxide (106°C), and would lead to the spontaneous and rapid generation of free radicals. Variable temperatures allow for the assessment of the free radical propagation in a thermal crosslinking process at a given temperature. All temperatures studied formed crosslinked materials within 10 min. Additional curing time beyond 10 min does not appear to increase crosslink density. In fact, the opposite trend is observed. At 130°C, PPXP does not form acetone insoluble materials until it has been heated for 10 min, and it was found to swell 395% in acetone (Table II). Increasing the curing time up to a maximum of 90 min gave materials with similar levels of acetone swelling. However, the soluble fraction increased modestly with increasing curing times. At higher temperatures (Table III) increases in solubility with increasing curing time becomes more pronounced, which suggests that there are two competing

Table II Acetone Solubility, Swelling, and T_g Data for PPXP Crosslinked Thermally (130°C Initiated with Benzoyl Peroxide)

Heating Time (min)	Solubility (%)	Swelling (%)	T_g (°C)
0	100	—	0.2
5	100	—	-13
10	13.6	395	-5
15	14.1	440	1
20	16.4	412	4
40	20.1	469	4
60	21.6	451	5
90	22.6	458	6

processes occurring—namely, radical induced crosslinking, and chain scission caused by thermal decomposition. At early stages of crosslinking, before the radical initiator is exhausted, the rate of crosslinking exceeds that of thermally induced chain scission, which results in an increase in crosslink density. At prolonged curing times, the rate of crosslinking dramatically decreases due to free radical termination. This results in a decrease in crosslink density, as the rate of thermal decomposition remains relatively constant. Material properties that are observed are a result of the “net” crosslink density. At higher temperatures, the rate of thermal decomposition is faster, thus less “net” crosslink density is achieved as observed in the large soluble fractions obtained, see Table III.

In Table II, the seven samples were crosslinked using 1 wt % initiator and 130°C for differing amounts of time from 0–90 min. Consistent with the electron beam experiments, thermal crosslinking does not cause the T_g to increase significantly with increased curing time. Initially, the T_g is approximately 0°C, and increases to approximately 5°C where it coincides with the data obtained from the electron beam crosslinked

PPXP. The two exceptions are the T_g s measured at -13 and -5°C for 5 and 10 min of heating time, respectively. A possible explanation could be thermally induced plasticization of the polymer by nondecomposed benzoyl peroxide or initiator residues. At this temperature and curing times, the polymer and the flat glass plate substrate may not have reached 106°C, where the spontaneous and totally decomposed peroxide would have initiated the crosslinking process. The net result of this is proposed to be an annealing of the polymer-initiator matrix resulting in a slightly lower T_g .

An estimation of crosslink density in these materials was performed using the Flory²⁶ swelling equation, which relates the molecular weight of polymer chains between crosslinks, $(M_n)_c$, to the volume fraction of polymer in a swollen gel, ν_s .

$$1/(M_n)_c = 2/(M_n)_o - \frac{(\nu/V_1[\ln(1 - \nu_s) + \nu_s + \chi\nu_s])}{\nu_s^{1/3} - \nu_s/2} \quad (1)$$

Determination of the volume fraction of the polymer in a swollen gel was accomplished by full immersion of the polymer with solvent until equilibrium was reached, measuring the mass of the swollen gel, and then desorbing the solvent under vacuum followed by measurement of the residual polymer mass. This method allows for an estimation of the amount of crosslinked polymer without including the soluble fractions in the calculation. Additionally, the solubility of the polymer after a crosslinking process was assessed. $(M_n)_o$ is the number-average molecular weight of the polymer prior to crosslinking. V_1 is the molar volume of the swelling solvent and, in the case of acetone, a value of 74.61 mL/mol was used. In addition, π_s and π_p are the densities of the solvent and the polymer, respectively. The polymer-solvent interaction parameter, χ , was reasonably assumed to be 0.5, the upper limit for small molecule

Table III T_g , Swelling, and Solubility Data for Thermally Crosslinked PPXP at 150°C, 170°C, and 190°C

Time (min)	T_g (°C)	Temperature 150°C			Temperature 170°C			Temperature 190°C	
		Solubility (%)	Swelling	T_g (°C)	Solubility (%)	Swelling	T_g (°C)	Solubility (%)	Swelling
10	3	14.7	401	4	18.2	474	4	19.6	467
20	4	21.7	489	5	22.6	547	4	33.2	635
30	6	18.4	433	5	27.1	567	6	42.2	726

Table IV Calculated $(M_n)_c$ Values, Mer/Crosslink Values, and Crosslink Densities (Γ) for Electron Beam Crosslinked PPXP

Electron Beam Dose (Mrad)	$(M_n)_c$ (g/mol)	Mers/Crosslink ^a	Crosslink Density (Γ)
5	1.7×10^3	5.2	1.5×10^3
10	1.1×10^3	3.4	2.3×10^3
15	9.7×10^2	3.0	2.5×10^3
20	8.7×10^2	2.7	2.8×10^3

^a Molecular weight of one mer = 321.4 g/mol, calculated from the percentages of each pendant group on the polymer.

plasticizer–macromolecule interactions, which describes a high level of penetration of a small molecule into the polymer matrix.²⁷ This assumption was made due to the fact that without crosslinking, the polymers are soluble in the solvent employed for these studies, namely acetone. The specific volume of the polymer, v , was calculated from the density of the polymer and was calculated to be $0.80 \text{ cm}^3/\text{g}$ for PPXP. The volume fraction of polymer in the swollen gel was calculated from eqs. (2) and (3):

$$\nu_s = \frac{1}{1 + Q} \quad (2)$$

$$Q = \frac{(W_w - W_d)(\rho_p)}{W_w(\rho_s)} \quad (3)$$

where W_w and W_d are the masses of the swollen gel and desorbed polymer, respectively.

Direct estimation of the crosslink density and determination of the average polymer chain length between crosslinks can be made from

$(M_n)_c$. Data calculated for these parameters (Table IV) show a clear trend where PPXP crosslinks to a higher degree with increasing dosage of electron beam radiation without significant competition from chain scission processes, consistent with previous reports.²⁸ Furthermore, this trend was not noted for thermal free radical crosslinking (Table V), where a maximum level of crosslinking was achieved after a relatively short amount of time. Higher curing temperatures did not further increase the crosslink density (see Table VI). Consistent with published reports,^{29,30} this higher temperature treatment leads to accelerated chain scission and a loss of crosslink density due to thermal degradative processes; thus, the “net” crosslink density decreases with increasing time and temperature.

PFAP-1 and PFAP-2

Polyfluoroalkoxyphosphazene elastomers, PFAP-1 and PFAP-2, were subjected to electron beam crosslinking using doses varying from 5–20 Mrad. The structure of these polymers is shown in Fig-

Table V Calculated $(M_n)_c$ Values, Mer/Crosslink Values, and Crosslink Densities (Γ) for Thermally Induced Free Radical Crosslinked PPXP at 130°C

Heating Time (min)	$(M_n)_c$ (g/mol)	Mers/Crosslink ^a	Crosslink Density (Γ)
5	Dissolved	Dissolved	Dissolved
10	1.0×10^3	3.2	2.4×10^3
15	1.1×10^3	3.4	2.2×10^3
20	1.1×10^3	3.3	2.3×10^3
40	1.1×10^3	3.5	2.2×10^3
60	1.1×10^3	3.5	2.2×10^3
90	1.1×10^3	3.5	2.2×10^3

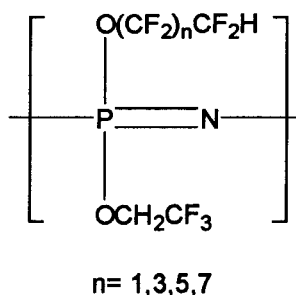
^a Molecular weight of one mer = 321.4 g/mol, calculated from the percentages of each pendant group on the polymer.

Table VI Calculated $(M_n)_c$ Values, Mer/Crosslink Values, and Crosslink Densities (Γ) for Thermally Induced Free Radical Crosslinked PPXP at 150°C, 170°C, and 190°C

Time (min)	Temperature 150°C			Temperature 170°C			Temperature 190°C		
	$(M_n)_c$ (g/mol)	Mers/Crosslink ^a	Crosslink Density (Γ)	$(M_n)_c$ (g/mol)	Mers/Crosslink ^a	Crosslink Density (Γ)	$(M_n)_c$ (g/mol)	Mers/Crosslink ^a	Crosslink Density (Γ)
10	1.0×10^3	3.2	2.4×10^3	1.1×10^3	3.5	2.1×10^3	1.1×10^3	3.5	2.2×10^3
20	1.2×10^3	3.9	2.0×10^3	1.2×10^3	3.8	2.0×10^3	1.3×10^3	4.0	1.9×10^3
30	1.1×10^3	3.4	2.3×10^3	1.2×10^3	3.8	2.0×10^3	1.4×10^3	4.2	1.8×10^3

^a Molecular weight of one mer = 321.4 g/mol, calculated from the percentages of each pendant group on the polymer.

ure 2. Verification of the crosslinked nature of these materials as well as the dependence of crosslink density on dose level was verified by solvent swelling measurements in acetone (Table VII). Consistent with previous reports, the estimated crosslink density increased at 5 and 10 Mrad; however with higher dose levels, no additional crosslinking was observed (Table VIII). This polymer system contains a small amount of *o*-allylphenol, and the lack of further crosslinking above 10 Mrad is postulated to be due to the exhaustion of active allylic moiety and may also be a demonstration of “net crosslinking” where the rate of crosslink formation is not significantly greater than the amount of chain scission. Additionally, this result provides insight into the relative lability of carbon–hydrogen bonds where little crosslinking is attributable to the fluoroalkoxy groups. Consistent with published bond activation energies, fluorine-containing hydrocarbons are less labile than either allylic or benzylic hydrocarbons. A slight increase in solubility was noted for both polymers at higher radiation doses, suggesting possible chain scission processes that were not observed for the PPXP polymer at this dose level.

**Figure 2** Representative structure of PFAP-1 and PFAP-2.

DSC analysis of the samples showed only a glass transition with no other prominent thermal features. Similar to PPXP, T_g values for these two polymers remain consistent upon irradiation, which again implies that the crosslinking process does not hinder backbone motion. Crosslinking of pendant groups in this polymer, as occurs through the longer chain fluoroalkoxide, would be performed through the terminal hydrogen. A crosslink with two of these types of groups has the capability of providing a “carbon bridge” of up to 18 atoms. The degrees of freedom inherent in alkyl chains would allow for crosslinks that would be expected to have little effect on the T_g value.

Thermal crosslinking, as described above, was applied to PFAP-2 without success. Materials generated using 1% (polymer weight percent) benzoyl peroxide as an initiator and 130°C heating resulted only in soluble materials. These data suggest that, under these conditions, the terminal hydrogens of the fluoroalkoxide pendant groups are not activated and do not yield crosslinks, and the concentration of free radicals generated was insufficient to significantly raise the crosslink density through the *o*-allylphenol pendant groups.

MEEP

Electron beam crosslinking of MEEP was observed to give materials that were no longer soluble in water or organic solvents. Additionally, the electron beam crosslinked materials were no longer flowable but were true elastomers. Incremental doses gave materials whose solubility in THF declined as the dose level was increased (Table IX). At the lower radiation dosages, polymer samples were found to have some solubility in THF with molecular weights (M_w) on the order of 10^7 . Solubilities were determined for the sam-

Table VII Glass Transition Temperature and Percent Acetone Uptake in Electron-Beam Crosslinked PFAP-1 and PFAP-2 Polymers

Electron Beam Dose (Mrad)	PFAP-1			PFAP-2		
	T_g (°C)	Solubility (%)	Swelling (%)	T_g (°C)	Solubility (%)	Swelling (%)
0	-60	100	—	-60	100	—
5	-58	22.8	496	-57	27.6	488
10	-57	12.3	364	-58	14.1	329
15	-58	18.0	412	-59	13.9	329
20	-58	25.3	402	-58	20.2	341

ples crosslinked at 5, 10, 15, and 20 Mrad, and the general trend observed was that solubility and dose are inversely proportional to each other, more crosslinking gives a lower amount of soluble polymer chains. Additionally, molecular weights and RMS radii remained constant, suggesting that the morphologies of the soluble fractions are similar at all doses.

It has been reported¹⁷ that MEEP can be doped with small metal ions such as Li^+ to form ionic crosslinks between etherial oxygens of adjacent polymer chains. The result is metal ion–MEEP complexes that give materials with higher T_g values.³¹ Using this behavior as a crosslinking method, a lithium-doped material was prepared at a level of loading of one lithium ion per four MEEP repeat units using lithium triflate for a total of one lithium ion per 24 oxygen atoms. The resulting material remained a flowable polymer that had poor mechanical integrity. DSC gave the T_g to be -59°C . This value is higher than nonlithiated MEEP by 15°C , suggesting that the presence of lithium ion lowers the mobility of the phosphazene backbone.

Coordination of lithium ion with MEEP can possibly occur at two points on the polymer—the lone electron pairs on either the etherial oxygens, or on the backbone nitrogens. Samples of lithium-loaded MEEP also were subjected to the same incremental doses of electron beam irradiation as the pure MEEP (see Table X). The measured values for T_g showed the same trend as the other phosphazenes discussed in this article, and no increases in T_g with irradiation. As previously discussed, the crosslinks induced by electron beam radiation occur through the organic pendant groups. It is highly unlikely that if these ligand-based covalently bonded crosslinks do not significantly increase T_g that ligand-based metal ion crosslinks would be able to do so. An argument could be made that states that lithium ion crosslinks more heavily, thus yielding higher T_g values, where radiation crosslinked materials are more lightly crosslinked and do not show increased T_g values. However, this argument is counterintuitive due to the physical observations of the materials. MEEP–lithium complexes retain much of the flowability of uncomplexed MEEP,

Table VIII Calculated $(M_n)_c$ Values and Crosslink Densities (Γ) for Electron-Beam Crosslinked PFAP-1 and PFAP-2

Electron Beam Dose (Mrad)	PFAP-1			PFAP-2		
	$(M_n)_c$ (g/mol)	Mers/Crosslink ^a	Crosslink Density (Γ)	$(M_n)_c$ (g/mol)	Mers/Crosslink ^a	Crosslink Density (Γ)
5	2.4×10^3	5.0	3.3×10^5	3.5×10^3	7.3	1.5×10^3
10	2.0×10^3	4.2	3.8×10^5	2.6×10^3	5.5	2.0×10^3
15	1.5×10^3	3.1	5.2×10^5	2.6×10^3	5.5	2.0×10^3
20	2.2×10^3	4.6	3.6×10^5	2.7×10^3	5.7	1.9×10^3

^a Molecular weight of one mer = 477 g/mol, calculated from the percentages of each pendant group on the polymer.

Table IX Solubility Percentage in Tetrahydrofuran and Light-Scattering Data for Electron-Beam Crosslinking of MEEP

Electron Beam Dose (Mrad)	Solubility (%)	Molecular Weight (M_w) (g/mol)	RMS Radius (nm)
0	100	$(1.3 \pm 0.7) \times 10^7$	163.3 ± 14.7
1	100	$(4.0 \pm 0.4) \times 10^7$	154.9 ± 10.8
2	100	$(4.5 \pm 0.5) \times 10^7$	152.7 ± 7.9
3	78.5	$(1.7 \pm 0.2) \times 10^7$	150.0 ± 8.6
4	68.9	$(4.8 \pm 0.5) \times 10^6$	124.5 ± 7.4
5	38.5	$(1.2 \pm 0.2) \times 10^7$	155.6 ± 10.5
10	29.6	$(1.7 \pm 0.2) \times 10^7$	160.3 ± 9.8
15	17.4	$(1.4 \pm 0.2) \times 10^7$	157.8 ± 9.1
20	14.7	$(3.4 \pm 0.8) \times 10^6$	148.2 ± 28.8

while electron beam crosslinked MEEP is a true elastomer.

A comparison of the loading of lithium ions, and thus the total possible amount of crosslinks (maximum of one crosslink per 2 mers, but considering the number of available oxygens, a lower level of crosslinking is more likely), it appears as if this amount is directly comparable to the radiation data presented above for several differing phosphazene polymers. This conclusion is supported further by considering the transient nature of the metal ion crosslinks as opposed to the “hard” covalently bonded crosslinks. Therefore, we propose that there is some degree of association of the lithium ions with the backbone nitrogens that, due to steric considerations, would not form interstrand crosslinks. Lithium coordination to the backbone nitrogen would serve to increase the barrier to rotation about the phosphorus–nitrogen bond in a single strand and could possibly explain increases in measured T_g values. Further studies to clarify this issue are underway and we anticipate a report soon.

Table X T_g Values for MEEP and MEEP–Lithium Intercalate Crosslinked by Electron Beam Exposure

Electron Beam Dose (Mrad)	MEEP ($^{\circ}\text{C}$)	MEEP–Lithium ($^{\circ}\text{C}$)
0	–76	–59
5	–75	–62
10	–74	–59
15	–74	–61
20	–75	–58

CONCLUSION

Glass transitions in phosphazene polymers are generally indicative of backbone motion with more restricted motion giving more glass-like materials and higher observed glass transition temperatures. Additionally, T_g can be effected by the size of the polymer side chain and intramolecular attractive forces. A lack of significant changes in the observed glass transition temperatures upon crosslinking implies that the backbone of the phosphazene has little role in the actual site of crosslinking. Crosslinking through pendant groups could be expected to hinder backbone motions as well as decrease the degrees of freedom for the pendant groups. However, crosslinking polymer chains through side chains introduces a “bridge” between adjacent individual polymer strands, and these bridges can be several carbons in length. The longer the bridge, the larger the numbers of the degrees of freedom, and thus the lower the amount of influence the crosslinks would be expected to have on the T_g value. Another feature of the DSC data collected for all of the polymers in this study was the lack of any first-order thermal transitions, which suggests that all of the polymers, both before and after crosslinking, are amorphous.

Swelling measurements performed on PPXP, PFAP-1, and PFAP-2 show remarkably consistent data, with most materials absorbing between 300 and 500% solvent when the solvent is acetone. Thermal processing appears to give crosslinks instantaneously, as dictated by the chemistry of the initiator, while electron beam crosslinks the polymer during the exposure duration, and that crosslink density may be prescribed and controlled through dose. The only significant deviations were observed for the thermal process where

elevated temperatures were employed. In these cases, the polymers were observed to swell more compared to lower temperature processing conditions, and this behavior is attributed to thermally induced backbone scission. Additional evidence to support this conclusion was seen through the solubility determinations. Higher processing temperatures not only gave polymers with higher degrees of swelling, but also gave materials that had a higher solubility in the swelling solvent. It is significant to note that backbone scission was not observed for any of the polymers cured with electron beam irradiation. Swelling and solubility were not observed to increase with higher radiation doses.

Electron beam irradiation of polyphosphazenes has been shown in this study to be an effective method for effecting crosslinking. This method compares favorably to the thermal processes that require initiation through free radical generation that cannot be controlled through either curing time or temperature. This leaves the amount of initiator as the only significant controlling factor, which can be problematic for obtaining highly crosslinked materials due to the level of initiator that must be doped into the polymer. Ionic crosslinking in phosphazenes, to the extent that it occurs, does not seem to be applicable to the generation of crosslinked materials. From empirical observations, MEEP does not crosslink ionically to the degree that it can be crosslinked using electron beam irradiation. MEEP is a viscous fluid polymer that will flow substantially even with the addition of lithium ion. However, application of electron beam irradiation in doses as low as 5 Mrad yields nonflowing elastomers. As a general method of crosslinking in polyphosphazenes, addition of an ionic species is also limited by the ability of the salt to dissolve in the polymer matrix. Much of the solubility of a phosphazene polymer is dictated by the pendant groups. The polarity of MEEP is much greater than PPXP, PFAP-1, and PFAP-2; thus, metal salts are far more soluble in MEEP. Chemistry between the less polar polymers and metal salts does not occur due to the high lattice energy of the salts.

A comparison of crosslinking moieties can be made from these data. Allylic and benzylic positions appear to be more labile than fluorinated alkyl chains, and are crosslinked under milder conditions. Likewise, electron beam radiation will activate less labile hydrogens; thus, it will crosslink all of the polymers discussed in this work. An additional comparison of crosslinking mechanisms reveals the limited lifetime of free radicals within a polymeric matrix; complete termination of all free

radical processes is rapid in the thermally induced crosslinking process studied.

Inclusion of metal ions within the polymeric matrix does yield complexes when the metal is lithium. In light of the data presented in this article, a new and potentially significant mechanism of lithium coordination has been proposed that has a portion of the ionic content within the polymer on the backbone nitrogens resulting in observed increases in T_g without yielding crosslinks. A comparison of crosslink densities resulting from radiation, as evidenced by PPXP, PFAP-1, and PFAP-2, and by the lithium ion loading appear to be of similar magnitude, suggesting that the T_g increases are not due to crosslinking, but can be explained through complexation to the nucleophilic backbone nitrogen atoms.

The work described in this article was supported by the United States Department of Energy through Contract DE-AC07-94ID13223. Additionally, the authors would like to thank Dr. Daniel Goodman and Dr. Catherine Byrne of Science Research Laboratory, Somerville, MA, for their assistance and advice with this work.

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