New Polyphosphazenes with Unsaturated Side Groups: Use as Reaction Intermediates, Cross-Linkable Polymers, and Components of Interpenetrating Polymer Networks

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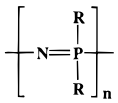
Received February 6, 1995; Revised Manuscript Received January 5, 1996[⊗]

ABSTRACT: A number of new poly(organophosphazenes) have been synthesized which bear 2-butenoxy or (4-(allyloxy)phenyl)phenoxy side groups. Cosubstituent groups included trifluoroethoxy, phenoxy, or (benzyloxy)phenoxy groups. Species with (4-(allyloxy)phenyl)phenoxy units underwent Si−H coupling with linear silanes or siloxanes to extend the side groups and form hybrid phosphazene/organosilicon polymers. A number of these polymers are rubbery elastomers which are readily cross-linked by heat or light. Seven of the mixed-substituent, cross-linked polymers were incorporated into interpenetrating polymer networks (IPN's) with polystyrene, poly(methyl methacrylate), polyacrylonitrile, poly(acrylic acid), and poly(dimethylsiloxane). The phase compatibility characteristics of the IPN's were assessed by DSC, TEM, FT-IR spectroscopy, and ^{1}H and ^{31}P NMR spectroscopy data.

Introduction

Phosphazene high polymers have the general structure shown in **1**, in which the side groups, R, can be organic, organometallic, or inorganic units, and the degree of polymerization, *n*, may be 15 000 or higher. Thus, the molecular weights can range as high as 2×10^6 to 6×10^6. Most polymers of this type are prepared via a ring-opening polymerization of an inorganic monomer (**2**) to give a reactive polymeric intermediate (**3**), followed by macromolecular substitution reactions as shown in Scheme 1.



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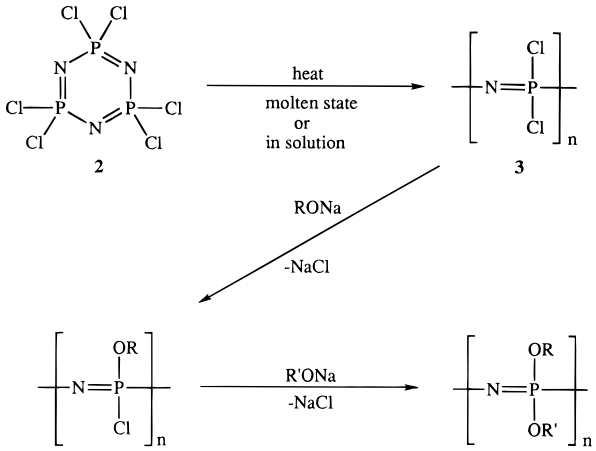
Scheme 1

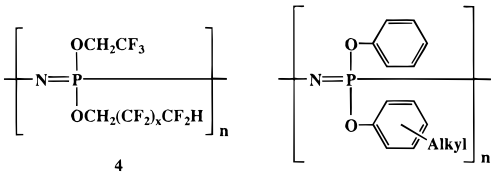


2 **3**

The properties of the resultant poly(organophosphazenes) depend on the types of side groups linked to the polymer chain. In general, if the side groups are small or highly flexible organic units, the polymers will have low glass transition temperatures (−100 to −30 °C). Bulkier side groups, especially those that contain aromatic residues, raise the T_g markedly as a result of their intramolecular steric restrictions and interchain interactions. Superimposed on these primary structure−property relationships is the condition that some polymers that bear only one type of side group are microcrystalline, whereas polymer molecules that bear two or more side groups tend to be amorphous, presumably because of the resultant lack of molecular symmetry.

Polyphosphazenes that have elastomeric properties have been developed technologically to a higher level than any of the other materials based on a phosphorus−nitrogen backbone.[1,2] Rubber-elasticity in polyphosphazenes becomes manifest in (a) single-substituent polymers that have low glass transition temperatures and side groups that are sufficiently flexible to resist crystallization (OCH_3, OC_2H_5, $OCH_2CH_2OCH_2CH_2OCH_3$, etc.) or (b) mixed-substituent polymers with low T_g's and, again, an amorphous morphology.

The two main classes of commercial phosphazene elastomers utilize this last principle and have the general structures shown in **4** and **5**.[3,4] We have recently described an additional class of elastomers based on the structure shown in **6**.[5] Note that structures **4**−**6** represent a few of many possible side group arrangements, including species with geminal structures.



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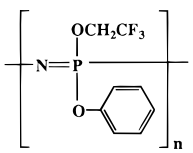

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Species **4** and **5** are converted to useful elastomers by cross-linking reactions that involve the incorporation of a few percent of unsaturated (usually allyl) cosub-

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

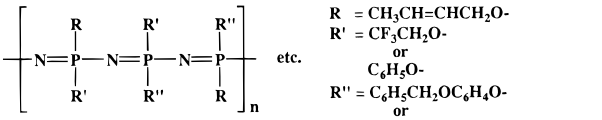
0024-9297/96/2229-2721$12.00/0

stituent units specifically introduced at the macromolecular substitution stage. The development of these and other methods of cross-linking underlies the conversion of a whole range of different polyphosphazenes into useful materials.[6]

In the present work, we have designed and synthesized a series of new polymers that bear either 2-butenoxy or (4-(allyloxy)phenyl)phenoxy groups. We have examined the use of the (4-(allyloxy)phenyl)-phenoxy units as sites for the linkage of organosilicon extension groups and have employed the two types of unsaturated side groups as cross-link sites *en route* to the preparation of interpenetrating polymer networks (IPN's) with more conventional organic polymers. The development of an ultraviolet photo-cross-linking system was of particular interest.

Results and Discussion

General Approach. The new polymers contain from one to three of the following different types of side groups—trifluoroethoxy, 2-butenoxy, (benzyloxy)phenoxy, phenoxy, or (4-(allyloxy)phenyl)phenoxy. Structure **7** illustrates the general composition of these



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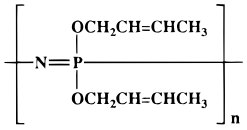
polymers, although the disposition of the various side groups along the chain may differ from that shown. The 2-butenoxy and (4-(allyloxy)phenyl)phenoxy groups were chosen both as cross-link sites and as functional units for secondary reactions. Trifluoroethoxy side groups were included because of their hydrophobicity and their known ability to generate polymer chain flexibility and low glass transition temperatures. The *p*-(benzyloxy)-phenoxy side units were employed as rigid, hydrophobic units that would be appropriate for subsequent reactions.[7]

The polymers were synthesized by the treatment of solutions of poly(dichlorophosphazene), $[NPCl_2]_n$ (**3**), in tetrahydrofuran (THF) with solutions or suspensions of the nucleophiles, $CH_3CH{=}CHCH_2ONa$, CF_3CH_2ONa, C_6H_5ONa, $C_6H_5CH_2OC_6H_4ONa$ or $CH_2{=}CHCH_2OC_6H_4$-OC_6H_4ONa in the same solvent. Hence, these reactions involved simultaneous competition by the nucleophiles for the reactive sites along the polymer backbone. Because the nucleophiles had different reactivities, the ratios of the side groups incorporated into each polymer did not directly reflect the ratios of the nucleophiles in the reaction mixtures. For example, the incorporation of the aryloxy side groups was less facile than that of the aliphatic nucleophiles, presumably for reasons of steric hindrance.

Poly[bis(2-butenoxy)phosphazene] (8): A New Elastomer. Polymer **8** was synthesized by the reaction of $CH_3CH{=}CHCH_2ONa$ with $[NPCl_2]_n$ (**3**). This poly-



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mer cross-links spontaneously in the dry state when exposed to the atmosphere to give a soft, rubber-elastic material with a T_g of −87.5 °C and a broad T_1 at approximately −22 °C. The elongation at break of this polymer is more than 900%, and the polymer retracts immediately to its original dimensions even after repeated stretching. This retraction could be due to the high mobility of the polymer (as evidenced by its low T_g) and the cross-linking within the material. Cross-linking can be retarded by storage of the polymer in solution in hexane or as a solvent-swollen organogel. The degree of cross-linking increased markedly when polymer **8** was exposed to UV light at 254 nm. Exposure times of 5 and 15 min introduced cross-links that limited the solvent imbibition volume to 1.7 and 0.9 and markedly reduced the flexibility and elasticity. Hence, the polymer is quite sensitive to photolytic cross-linking.

This is an extraordinary elastomer from a fundamental research viewpoint, but it is clearly of limited practical utility because of its high sensitivity to undergo cross-linking in the atmosphere and when exposed to light in the solid state. However, it suggested ways in which more controllable systems might be designed and prepared—specifically species in which the unsaturated units are diluted by other side groups which themselves confer additional properties on the system.

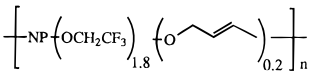
Polymers with 2-Butenoxy and Other Cosubstituent Groups. These polymers are shown as species **9**−**12** in Chart 1. ^1H and ^{31}P NMR and DSC (T_g) characterization data for polymers **9**−**12** are shown in Table 1. Some selected properties of these polymers are as follows: Polymer **9** is an opaque, white, amorphous, film-forming elastomer with a glass transition temperature of −68 °C. DSC measurements indicate that it is amorphous. It is soluble in organic solvents such as THF. The polymer cross-links when exposed to UV radiation at room temperature.

Polymer **10** is also an opaque, flexible, film-forming elastomeric, amorphous material with a glass transition temperature of −15 °C. This polymer is soluble in THF. The polymer cross-links following exposure to UV radiation at room temperature, especially in the presence of 2 mol % benzoyl peroxide initiator. Polymer **11** is a transparent, colorless, brittle, film-forming material with a glass transition temperature of +27 °C. DSC measurements indicated that the material is amorphous. Polymer **11** is soluble in both THF and dioxane. This polymer also cross-links when exposed to UV radiation at room temperature. Polymer **12** is a beige-colored, elastomeric, amorphous, very flexible transparent material with a T_g at −18 °C. Polymer **12** is soluble in THF and other common organic solvents and cross-links when exposed to UV radiation at room temperature.

Polymers Based on the (4-(Allyloxy)phenyl)-phenoxy Group. These polymers are shown as species **13**−**15** in Chart 1. Characterization data for polymers **13**−**15** are shown in Table 1. All three were prepared as described in the Experimental Section. Polymer **13** is a transparent, slightly brittle, amorphous, film-forming material with a T_g at +48 °C. This polymer could be isolated and stored in the solid state without cross-linking. However, the material cross-links when exposed to UV radiation at room temperature. Species **13** was soluble in THF. This polymer was examined from two points of view—first, as the cross-linked initial component for IPN preparation (see later) and, second, as a reaction intermediate for the linkage of organosilicon side chains.

Hybrid organophosphazene/organosilicon polymers have been prepared by several routes in the past.[8−10]

Chart 1



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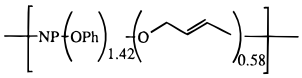

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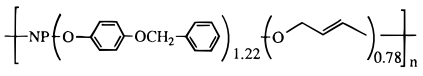

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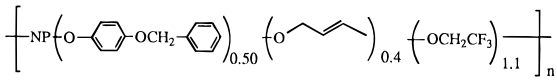

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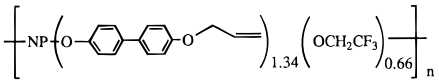

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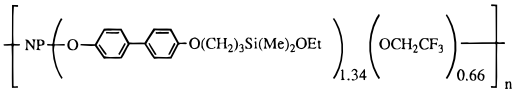

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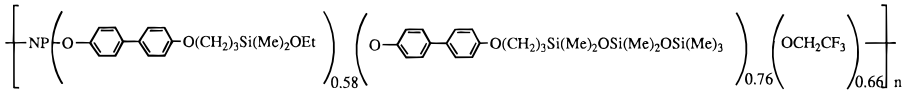

15

Table 1. Poly(organophosphazene) Characterization Data

polymer	^{1}H NMR (ppm)	^{31}P NMR (ppm)	DSC T_g (°C)
9	4.38 (br) (OCH_2CH) 5.74 (OCH$_2$CH=CH) 5.55 (CH=CHCH$_3$) 1.68 (CH=CHCH_3) 1.80 (OCH_2CF$_3$)	−5 (br sh)/−6.98 (br)	−68
10	7.00 (C$_6$H$_5$) 4.25 (OCH_2CH) 5.50 (OCH$_2$CH=CH) 5.35 (CH=CHCH$_3$) 1.60 (CH=CHCH_3)	−13.84/−16.18/−19.18	−15
11	6.83, 6.46 (C$_6$H$_4$) 4.53 (bzOCH_2bz) 7.12 (C$_6$H$_5$) 4.19 (OCH_2CH) 5.67 (OCH$_2$CH=CH) 5.52 (CH=CHCH$_3$) 1.65 (CH=CHCH_3)	−14.88/−16.25/−17.36	27
12	7.04, 6.81 (C$_6$H$_4$) 4.91 (bzOCH_2bz) 7.34 (C$_6$H$_5$) 4.19 (OCH_2CH) 5.67 (OCH$_2$CH=CH) 5.52 (CH=CHCH$_3$) 1.65 (CH=CHCH_3) 1.65 (OCH_2CF$_3$)	−9.29 (br)/−12.72 (br)[a]	−18
13	7.11, 6.80 (bz rings) 4.55 (bzOCH_2CH) 6.07 (CH=CH$_2$) 5.45, 5.32 (CH=CH_2) 1.45 (OCH_2CF$_3$)	−9.50/−12.55/−15.37	48
14	7.04, 6.68 (bz rings) 3.81 (bzOCH_2) 1.18 (bzOCH$_2$CH_2) 0.14 (CH_2Si, SiCH_3) 3.67 (SiOCH_2) 0.70 (SiOCH$_2$CH_3) 1.80 (OCH_2CF$_3$)	−13.49/−15 (shoulder)	42
15	7.05, 6.72 (bz rings) 3.84 (bzOCH_2) 1.20 (bzOCH$_2$CH_2) 0.11 (CH_2Si, SiCH_3) 3.70 (SiOCH_2) 0.68 (SiOCH$_2$CH_3) 1.82 (OCH_2CF$_3$)	−13.43/−15 (shoulder)	66

[a] Although three ^{31}P peaks were expected, the broadness of the detected peaks suggested that a third peak may have been masked.

The method described here involves the addition of dimethylethoxysilane (to form **14**) or heptamethyltrisiloxane followed by dimethylethoxysilane (to yield **15**) to the allyl double bond of **13**, both reactions being carried out in the presence of platinum divinyltetramethyldisiloxane complex as a coupling agent. Polymer **14** is a transparent, beige, amorphous material with a T_g of +42 °C. It was soluble in THF. The polymer was sensitive to cross-linking when exposed to air and was cross-linked further when exposed to UV radiation.

Polymer **15** also was a transparent, amorphous, slightly brittle material with a T_g of +66 °C. This material was soluble in THF. This polymer too was prone to cross-linking when exposed to air. It cross-linked further when exposed to UV radiation.

Interpenetrating Polymer Networks. In general terms, IPN's are prepared by the polymerization of a monomer within the cross-linked matrix of another polymer. This procedure results in an intimate mixing of the macromolecular components and provides greater opportunities for intermolecular interactions between the two polymers than may be found in conventional polymer blends.[11,12] The intimate mixing of the components in IPN's also generates a much finer and more integrated domain structure than would be possible in most other multicomponent polymer systems. In earlier work, we described IPN's prepared from radiation cross-linked polyphosphazenes and organic polymers.[13,14] Seven phosphazene polymers served as the initial cross-linked polymer matrices for the present work: [NP(OCH$_2$CH=CHCH$_3$)$_{0.2}$(OCH$_2$CF$_3$)$_{1.8}$] (**9**); [NP(OCH$_2$CH=CHCH$_3$)$_{0.58}$(OC$_6$H$_5$)$_{1.42}$] (**10**); [NP(OC$_6$H$_4$OCH$_2$C$_6$H$_5$)$_{1.22}$(OCH$_2$CH=CHCH$_3$)$_{0.78}$] (**11**); [NP(OC$_6$H$_4$OCH$_2$C$_6$H$_5$)$_{0.50}$(OCH$_2$CH=CHCH$_3$)$_{0.4}$(OCH$_2$CF$_3$)$_{1.1}$] (**12**); [NP(OC$_6$H$_4$C$_6$H$_4$OCH$_2$CH=CHCH$_3$)$_{1.34}$(OCH$_2$CF$_3$)$_{0.66}$] (**13**); [NP(OC$_6$H$_4$C$_6$H$_4$O(CH$_2$)$_3$Si(CH$_3$)$_2$(OCH$_2$CH$_3$)$_{1.34}$(OCH$_2$CF$_3$)$_{0.66}$] (**14**); [NP(OC$_6$H$_4$C$_6$H$_4$O(CH$_2$)$_3$Si(CH$_3$)$_2$(OCH$_2$CH$_3$)$_{0.58}$(OC$_6$H$_4$C$_6$H$_4$O(CH$_2$)$_3$Si(CH$_3$)$_2$OSi(CH$_3$)$_2$OSi(CH$_3$)$_3$)$_{0.76}$(OCH$_2$CF$_3$)$_{0.66}$] (**15**) (Chart 1). Exposure of the polymers to light or heat induced cross-linking and yielded materials which would no longer dissolve in but would swell in organic solvents or organic/inorganic monomers to form organogels. Poly(organophosphazenes) **14** and **15** were cross-linked thermally, while polyphosphazenes **9**, **11**, **12**, and **13** were cross-linked by exposure to UV radiation. Benzoyl peroxide was added to poly(organophosphazene) **10** to aid in the UV cross-linking of the polymer. Phosphazene polymers **14** and **15** were cross-linked by dehydrosilation (loss of HSi(CH$_3$)$_2$OEt) to generate cross-linkable alkene function-

Chart 2

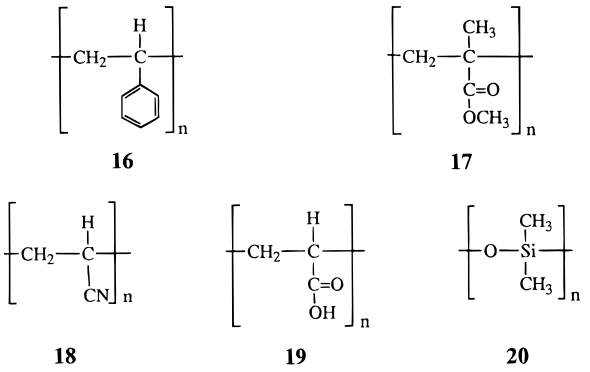

Table 2. Component Polymer Ratios for Semimiscible IPNs

IPN component polymers	ratio[a]	IPN component polymers	ratio[a]
9/16	1:1	**13/16**	1:2
9/17	1:1	**13/17**	1:1
10/16	1:2	**13/19**	4:1
11/16	1:3	**13/20**	1:35
11/17	1:8	**14/16**	3:1
11/18	1:4	**14/17**	1:1
11/19	26:1	**15/16**	1:2
12/16	1:2	**15/17**	1:1
12/17	1:1		

[a] Ratios determined by ^{1}H NMR spectroscopy.

alities. The monomers used for the formation of the second polymer in each IPN included styrene (**16**), methyl methacrylate (**17**), acrylonitrile (**18**), acrylic acid (**19**), and octamethylcyclotetrasiloxane (**20**). The nonphosphazene monomers used in this study were polymerized and cross-linked either thermally (styrene, methyl methacrylate, and octamethyltetrasiloxane) or by exposure to ^{60}Co γ-radiation. Potassium hydroxide was used as the polymerization initiator for octamethylcyclotetrasiloxane, and cross-linking was subsequently accomplished by exposure of the system to ^{60}Co γ-radiation. No solvents were employed for the swelling of the organic monomer systems, but THF was used to aid in the swelling by the cyclosiloxane. These monomers yielded the polymers depicted in Chart 2.

The synthesis of a polyphosphazene IPN is described in the Experimental Section. For example, a sample of cross-linked phosphazene polymer **14** was allowed to imbibe a solution of styrene monomer, azobis(isobutyronitrile) (AIBN) initiator, and ethylene glycol dimethacrylate cross-linking agent. After a period of 72 h at 25 °C, the resultant organogel had swollen to more than 10 times its original volume. The styrene component was then polymerized thermally, and the unpolymerized styrene and oligomers were removed by solvent extraction. In general, the final ratios of polyphosphazene to organic polymer were in the range of 26:1 to 1:7.5.

The IPN's were characterized by FT-IR, ^{1}H and ^{31}P NMR spectroscopy, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). FT-IR and NMR spectroscopy were used mainly to confirm the presence of the component materials in the IPN, while NMR was used to provide a rough estimate of the component ratios in the IPN. The final IPN ratios, determined by ^{1}H NMR spectroscopy, are depicted in Table 2.

DSC characterization is based on the following precepts. In a miscible IPN, only one glass transition temperature (T_g) is detected in the DSC spectrum, located between the values of the component polymer T_g values. In a semimiscible IPN, either two T_g's are detected displaced toward the center of the spectrum from the values of the parent polymers or three transitions are found, two displaced toward the center of the spectrum and one located between the values of the component polymers. This third transition indicates that significant intermolecular interactions exist between the component materials. In a totally immiscible system, two T_g's may be found at the T_g values of the component polymers.

Table 3. DSC Data for Semimiscible IPNs

IPN component polymers[a]	T_g (°C)	IPN component polymers[a]	T_g (°C)
9/16	66	**13/16**	74
9/17	79	**13/17**	54/62
10/16	81	**13/19**	70/102
11/16	66	**13/20**	−89/51
11/17	79/111	**14/16**	74
11/18	26/49	**14/17**	68
11/19	25/42	**15/16**	74/109
12/16	45	**15/17**	73
12/17	61		

[a] Component polymer T_g's: **9** = −67 °C, **10** = −15 °C, **11** = 23 °C, **12** = −18 °C, **13** = 48 °C, **14** = 42 °C, **15** = 66 °C, **16** = 100 °C, **17** = 105 °C, **18** = 85 °C, **19** = 105 °C, **20** = 124 °C.

TEM allowed the phase domain structure of each IPN to be determined. Electron microscopy is probably the most sensitive way to assess the miscibility or homogeneity of an IPN system. Even if an IPN appears to be totally miscible by DSC, a definite domain structure may still be detected by TEM analysis. Only samples with high structural rigidity can be examined using transmission electron microscopy due to the limitations of the methods of sample preparation. Thus, DSC was used as a primary means for the detection of miscibility, but TEM was needed to determine the extent of phase separation within the semimiscible material.

Several combinations of poly(organophosphazenes) **9**−**15** formed semimiscible IPN's with the organic or inorganic−organic monomers **16**−**20**. These semimiscible combinations and their T_g values are listed in Table 3. A number of the semimiscible combinations of phosphazene polymers **9**−**15** and organic polymers **16**−**20** were characterized by transmission electron microscopy. The properties and TEM micrographs of these mixtures are described in Table 4 and the TEM micrographs are depicted in Figures 2−13. One illustrative example is described below.

The TEM micrograph of polymer **13** is depicted in Figure 1. Polymer **13** forms semimiscible IPN's with polystyrene (**16**), poly(methyl methacrylate) (**17**), poly(acrylic acid) (**19**), and poly(dimethylsiloxane) (**20**). The semimiscible IPN formed from polymers **13** and **16** is a hard, opaque, white material which shows a single T_g in the DSC thermogram at 74 °C. This value is intermediate between the T_g's of the individual polymers, which occur at 48 (**13**) and 100 °C (**16**). The TEM micrograph of this material differs from that of pure **13** (Figure 1) and shows a distinct phase separation into regions of darker phosphazene polymer and lighter colored organic polymer (Figure 2). This mode of visualization is possible because regions that contain heavier elements appear darker in a TEM micrograph. This example illustrates the necessity for confirming miscibility, or semimiscibility, using TEM microscopy. In this example, semimiscibility may be due to inter-

Table 4. IPN Characterization

figure	IPN components	IPN T_g's (°C)	component T_g's (°C)	IPN appearance	TEM comments
2	**13/16**	74	48/100	white, opaque, hard	well-dispersed phases in the range of 0.1−0.85 μm
3	**13/17**	54/62	48/105	colorless, transparent, hard	well-dispersed phases in the range of 0.1−0.2 μm
4	**13/19**	70/102	48/105	beige, opaque, brittle	well-dispersed phases in the range of 0.05−0.35 μm
5	**14/17**	68	42/105	colorless, transparent, hard	well-dispersed domains in the range of 0.1-0.90 μm
6	**15/17**	73	66/105	colorless, transparent, hard	very finely dispersed phases in the range of 0.05−0.25 μm
7	**12/16**	45	−18/100	white, opaque, hard	well-dispersed phases in the range of 0.1−0.85 μm
8	**12/17**	61	−18/105	colorless, transparent, hard	well-dispersed phases in the range of 0.05−1.38 μm
9	**11/17**	79/111	23/105	white, opaque, hard	well-dispersed phases in the range of 0.05−0.25 μm
10	**11/18**	26/49	23/85	beige, opaque, brittle	well-dispersed phases in the range of 0.05−0.15 μm
11	**11/19**	25/42	23/105	beige, transparent, brittle	isolated organic polymer within phosphazene area; domains were in the range of 0.05−0.25 μm
12	**9/17**	79	−69/105	colorless, transparent brittle	isolated phosphazene within organic areas; domains were in the range of 0.05−0.45 μm
13	**10/16**	81	−15/100	colorless, transparent, brittle	streaks of organic within phosphazene regions; domains were in the range of 0.05−0.17 μm

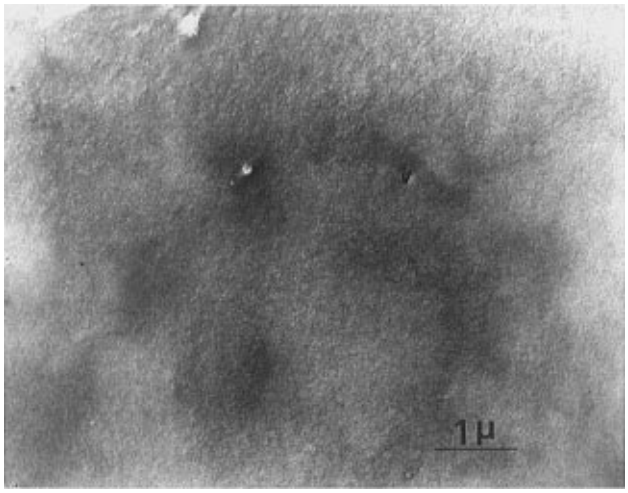

Figure 1. Transmission electron micrograph of polymer **13** before incorporation of organic polymer into an IPN system.

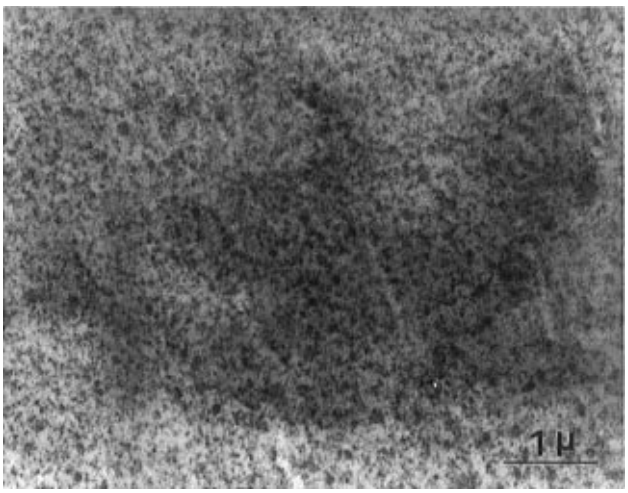

Figure 3. Transmission electron micrograph of an IPN composed of polymers **13** and **17**.

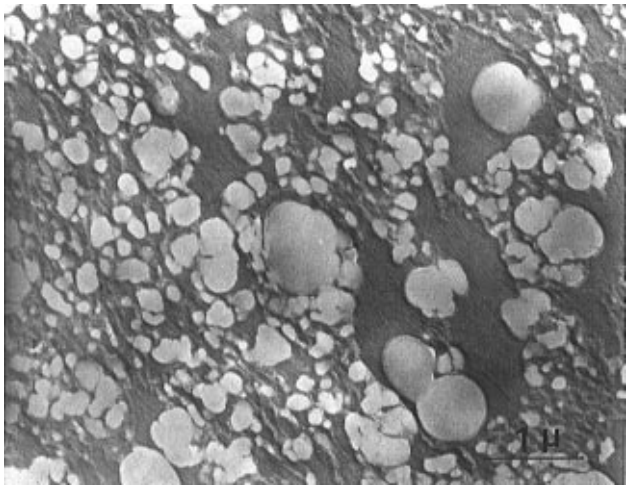

Figure 2. Transmission electron micrograph of an IPN composed of polymers **13** and **16**.

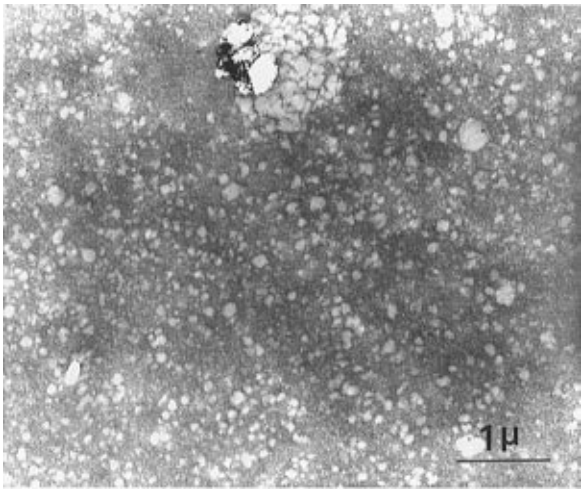

Figure 4. Transmission electron micrograph of an IPN composed of polymers **13** and **19**.

molecular interactions such as van der Waals forces or side group stacking between the component materials.

Conclusions

In the present work, we have designed and synthesized several new mixed-substituent phosphazene elastomer systems that can be cross-linked either thermally or by exposure to ultraviolet light. Interpenetrating polymer networks derived from cross-linked polyphosphazenes allow the materials' properties to be varied over a broad range depending on the nature and ratios of their component polymers. The work illustrates that the poly(organophosphazenes) described here are an excellent choice for incorporation into IPN's because of the ease with which the properties can be changed by varying the side groups. In general, IPN's that contain poly(organophosphazenes) are expected to be more flame resistant than their totally organic counterparts. Moreover, incorporation of these polymers into IPN's provides a way to utilize the unique properties of these macromolecules in combination with the advantages of

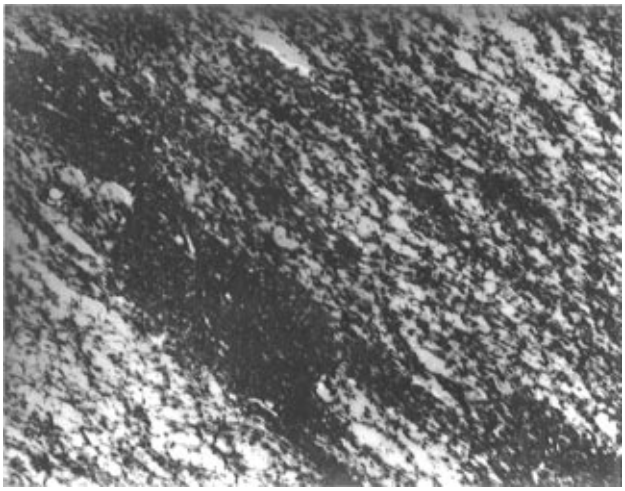

Figure 5. Transmission electron micrograph of an IPN composed of polymers **14** and **17**.

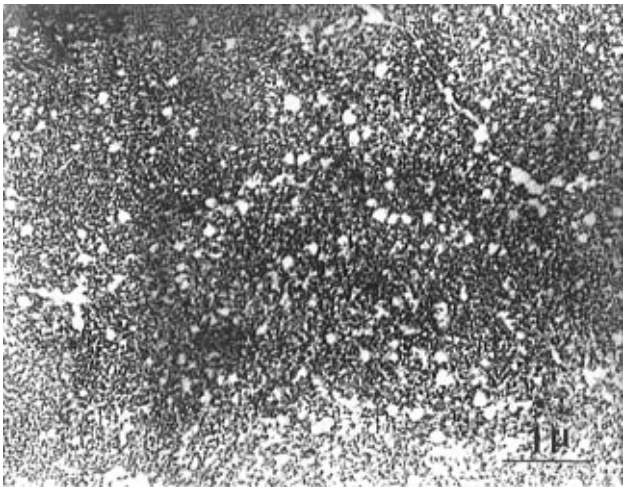

Figure 6. Transmission electron micrograph of an IPN composed of polymers **15** and **17**.

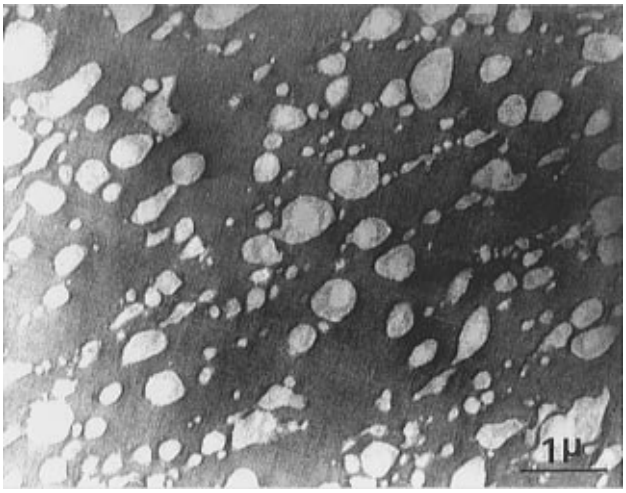

Figure 7. Transmission electron micrograph of an IPN composed of polymers **12** and **16**.

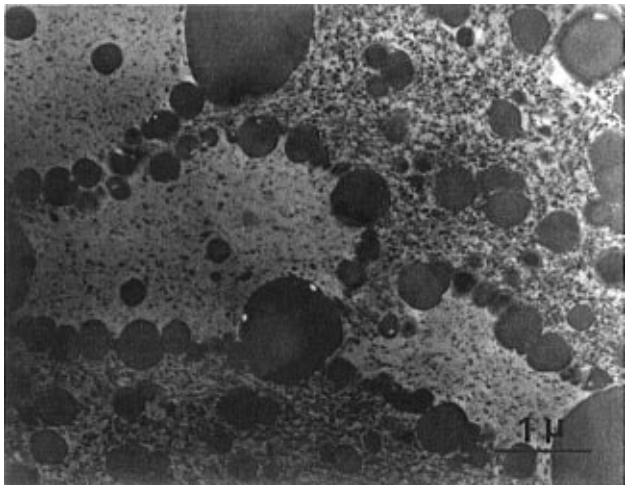

Figure 8. Transmission electron micrograph of an IPN composed of polymers **12** and **17**.

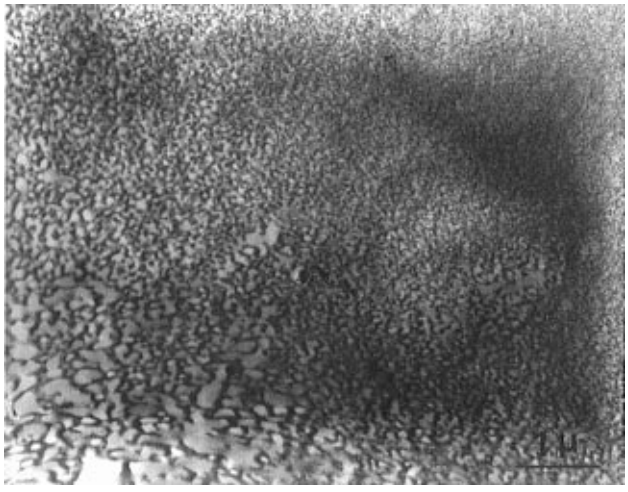

Figure 9. Transmission electron micrograph of an IPN composed of polymers **11** and **17**.

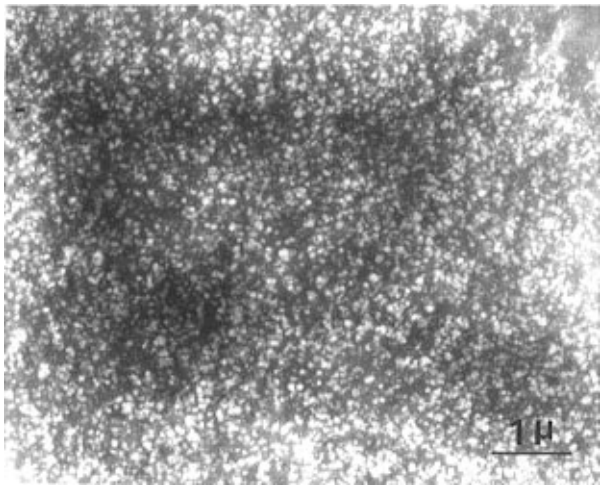

Figure 10. Transmission electron micrograph of an IPN composed of polymers **11** and **18**.

conventional polymers in membranes and biomedical materials.

Experimental Section

Materials. 2,2,2-Trifluoroethanol (Aldrich) was treated with sodium carbonate and was then distilled and stored over molecular sieves. 2-Butenol (Aldrich) was distilled under vacuum. 4-(Benzyloxy)phenol (Aldrich), 4,4′-biphenol (Aldrich), potassium hydroxide (Aldrich), sodium hydride (60% dispersion in mineral oil) (Aldrich), allyl bromide, benzoyl peroxide (Aldrich), sodium stick (Aldrich), dimethylethoxysilane (Huls America), heptamethyltrisiloxane (Huls America), absolute ethanol (Aldrich), platinum divinyltetramethyldisiloxane (Huls America), octachlorocyclotetrasiloxane (Huls America), and azobis(isobutyronitrile) (AIBN) (Polysciences Inc.) were used as received. Ethylene glycol dimethycrylate (Aldrich) was distilled under vacuum and stored over 3 Å

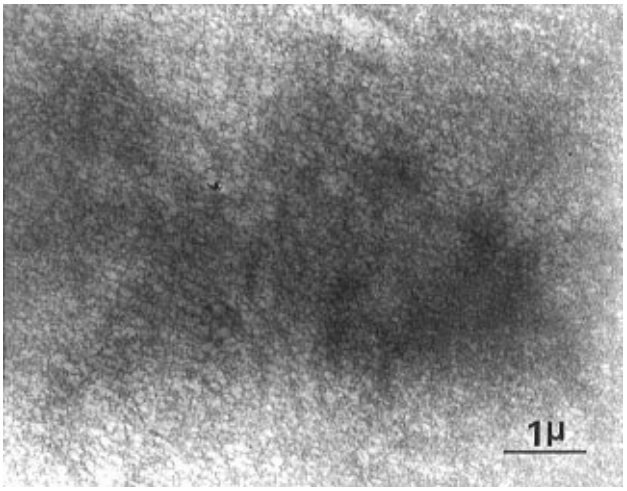

Figure 11. Transmission electron micrograph of an IPN composed of polymers **11** and **19**.

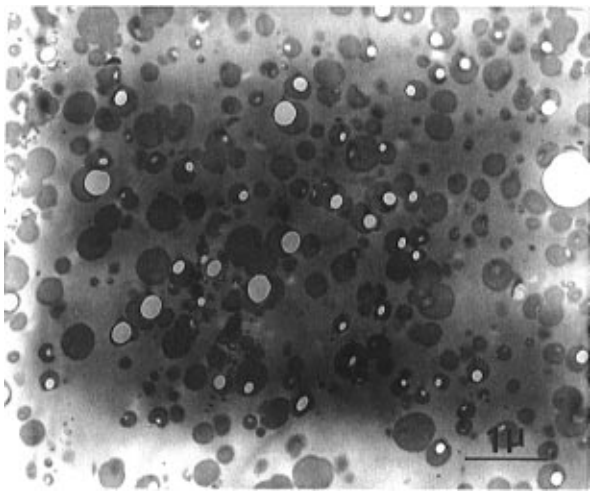

Figure 12. Transmission electron micrograph of an IPN composed of polymers **9** and **17**.

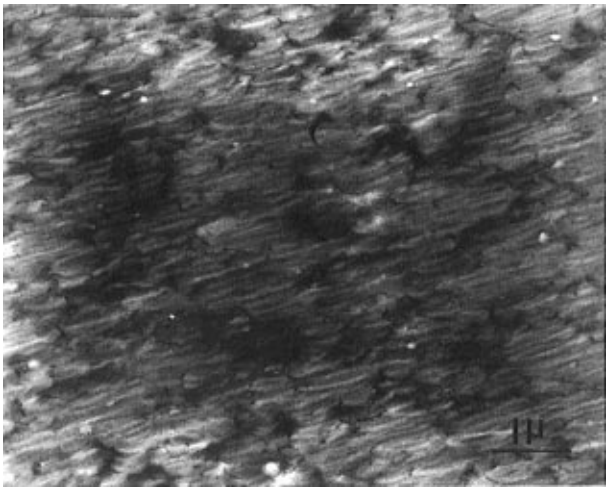

Figure 13. Transmission electron micrograph of an IPN composed of polymers **10** and **16**.

molecular sieves. Styrene (Aldrich), methyl methacrylate (Aldrich), acrylonitrile (Aldrich), and acrylic acid (Aldrich) were passed through alumina columns to remove inhibitors and were then stored over 3 Å molecular sieves. Tetrahydrofuran (THF) and dioxane were distilled under an atmosphere of dry argon from a sodium benzophenone ketyl drying agent.

All phosphazene syntheses were carried out under an atmosphere of dry nitrogen. Hexachlorocyclotriphosphazene (supplied by Ethyl Corp.) was purified by vacuum sublimation, recrystallization (from hexane), and a final sublimation. Poly(dichlorophosphazene) was obtained by the molten-phase thermal polymerization (250 °C) of hexachlorocyclotriphosphazene in an evacuated sealed glass tube.

Analytical Equipment and Techniques. ^{1}H and ^{31}P NMR spectra were recorded with the use of a Bruker WM-360 spectrometer operated at 360 and 145.8 MHz, respectively. For ^{31}P NMR spectra, positive chemical shifts are downfield from that of external phosphoric acid. For ^{1}H NMR spectroscopy, chemical shifts were recorded relative to tetramethylsilane at 0 ppm. NMR samples of the IPN's were prepared by swelling the purified IPN's with a deuterated solvent in a glass NMR tube. Infrared spectra were estimated with use of a Perkin-Elmer 1710 infrared Fourier transform spectrometer. The samples were prepared by pressing swollen IPN gels between salt plates. Glass transition temperatures (T_g) were recorded with the use of a Perkin-Elmer DSC-7 unit equipped with a PE 7500 computer. The samples (10−30 mg) were analyzed in crimped aluminum pans: a heating rate of 40 °C/min and a helium flow of 10 mL/min were used. The instrument was calibrated with a cyclohexane standard, with thermal transitions at −87.06 and 6.54 °C. Polymers **18**−**20** were cross-linked by exposure to ^{60}Co γ-radiation at the Breazeale Nuclear Reactor at The Pennsylvania State University. UV cross-linking was accomplished using a Rayonet photochemical reactor (The Southern N. E. Ultraviolet Co.) equipped with 16 Rayonet ultraviolet lamps (254 nm). The temperature of the sample was maintained near 25 °C by a cooling fan. Transmission electron micrographs (TEMs) were obtained using a JEOL 1200 EXII TEM with a power setting of 80 kV and an exposure time of 1 s. The magnification for all TEM photographs was 12076×. TEM samples were prepared using a LKB Ultratome III microtome.

Preparation of 4-(4′-(Allyloxy)phenyl)phenol. 4,4′-Biphenol (40 g, 215 mmol) and potassium hydroxide (24 g, 428 mmol) were dissolved in 600 mL of absolute ethanol in a 1 L, three-necked, round bottom flask. The solution was warmed and allyl bromide (26 g, 215 mmol) was added. The reaction mixture was heated to reflux overnight, after which additional allyl bromide (13 g, 107 mmol) was added. The reaction mixture was refluxed for an additional 24 h. The reaction mixture was cooled to room temperature and the solids were filtered off. The filtrate was poured into distilled water (4 L) and then acidified with concentrated aqueous HCl. The solid product was filtered off, washed with a large amount of water, and then dried. The product was purified by repeated recrystallization from ethanol. Product characterization data included the following: mp 168−170 °C; ^{1}H NMR (200 MHz, $CDCl_3$) 7.05 (m, 4H), 6.8 (m, 4H), 6.1 (m, 1H), 4.4 (m, 2H).

Preparation of $[NP(OCH_2CH{=}CHCH_3)_{0.2}(OCH_2CF_3)_{1.8}]_n$ (9). To a solution containing poly(dichlorophosphazene) (**3**) (2 g, 17.7 mmol) in THF (200 mL) was added a solution containing sodium trifluoroethoxide in THF (30 mL) (prepared from trifluoroethanol (3.1 g, 31 mmol) and sodium (1 g, 43.5 mmol)). The reaction mixture was stirred at room temperature overnight. To the reaction mixture was added a solution $CH_3CH{=}CHCH_2O^-\ Na^+$ in THF (100 mL) (from 2-butenol (1.3 g, 18 mmol) and sodium hydride (60% dispersion in mineral oil) (0.7 g, 17.5 mmol)). The reaction mixture was stirred for 24 h, and the polymer was isolated and purified by repeated precipitations into water(3×) and hexanes(1×). A ^{1}H NMR spectrum was consistent with a polymer that contained 90% of trifluoroethoxy and 10% of 2-butenoxy side groups.

Preparation of $[NP(OCH_2CH{=}CHCH_3)_{0.58}(OC_6H_5)_{1.42}]_n$ (10). To a solution of poly(dichlorophosphazene) (**3**) (6 g, 51.7 mmol) in THF (400 mL) was added a solution of sodium phenoxide (from phenol (7.1 g, 75.5 mmol) and sodium (1.8 g, 78.3 mmol)) in THF (100 mL). The reaction mixture was heated at 45 °C for 36 h and was then cooled to room temperature. To this reaction mixture was added a solution of $CH_3CH{=}CHCH_2O^-Na^+$ (prepared from 2-butenol (4 g, 55.6 mmol) and sodium hydride (2.0 g, 50 mmol)) in THF (100 mL). The reaction mixture was stirred at 25 °C for 24 h, and the polymeric product was purified by repeated precipitations into water (3×) and hexanes (1×). A ^{31}P NMR spectrum suggested

that this polymer contained 71% of phenoxy and 29% of 2-butenoxy groups.

Preparation of $[NP(OC_6H_4OCH_2C_6H_5)_{1.22}(OCH_2CH{=}CH\text{-}CH_3)_{0.78}]_n$ (11). To a solution of poly(dichlorophosphazene) (**3**) (2 g, 17.4 mmol) in dioxane (400 mL) was added by syringe a solution containing 100 mL of dioxane, sodium 4-(benzyloxy)-phenoxide (from 4-(benzyloxy)phenol (6.2 g, 31 mmol) and sodium hydride (1.3 g, 32.5 mmol)). The reaction mixture was heated to reflux for 48 h and then cooled to 25 °C. A solution containing sodium 2-butenoxide (prepared from 2-butenol (1.9 g, 26.3 mmol) and sodium hydride (1.1 g, 27.5 mmol)) in THF (50 mL) was added to the mixture. The resulting mixture was stirred at 25 °C for 24 h, and the polymer was isolated and purified by repeated precipitations into water (3×) and hexane (1×). A ^{31}P NMR spectrum suggested that the polymer contained 62% of 4-(benzyloxy)phenoxy and 38% of 2-butenoxy groups.

Preparation of $[NP(OC_6H_4OCH_2C_6H_5)_{0.50}(OCH_2CH{=}CH\text{-}CH_3)_{0.4}(OCH_2CF_3)_{1.1}]_n$ (12). Poly(dichlorophosphazene) (**3**) (3 g, 26.1 mmol) was treated with a mixture of the sodium salts of 4-(benzyloxy)phenol, 2,2,2-trifluoroethanol, and 2-butenol. The sodium salt of 4-(benzyloxy)phenol was prepared by the treatment of 4-(benzyloxy)phenol (3.8 g, 19 mmol) with sodium hydride (0.88 g, 20 mmol) in THF (50 mL), The sodium salt of 2,2,2-trifluoroethanol was prepared by the treatment of 2,2,2-trifluoroethanol (2.2 g, 22 mmol) with sodium (0.88 g, 34 mmol) in THF (30 mL). The sodium salt of 2-butenol was prepared by the treatment of 2-butenol (1.6 g, 22.2 mmol) with sodium hydride (0.9 g, 22.5 mmol) in THF (30 mL). The salts prepared separately were combined and then added to the poly(dichlorophosphazene) solution. The reaction mixture was stirred for 48 h and then concentrated. The polymeric product was then isolated and purified by repeated precipitation into water (3×) and hexanes (1×). The ^1H NMR spectrum showed that the resultant polymer contained 55% of 2,2,2-trifluoroethoxy, 20% of 2-butenoxy, and 25% of 4-benzyloxy groups.

Preparation of $[NP(OC_6H_4C_6H_4OCH_2CH{=}CH_2)_{1.34}(OCH_2\text{-}CF_3)_{0.66}]_n$ (13). Polymer **13** was synthesized by the sequential treatment of $(NPCl_2)_n$ (2 g, 17.4 mmol) in THF (200 mL) with $CH_2{=}CHCH_2OC_6H_4C_6H_4O^-Na^+$ and sodium trifluoroethoxide. $CH_2{=}CHCH_2OC_6H_4C_6H_4O^-Na^+$ was prepared by the treatment of $CH_2{=}CHCH_2OC_6H_4C_6H_4OH$ (5.5 g, 24.3 mmol) with sodium hydride (0.95 g, 23.8 mmol) in THF (200 mL). Sodium trifluoroethoxide was prepared from trifluroethanol (1.7 g, 17 mmol) and sodium (0.6 g, 26.1 mmol) in THF (50 mL). The reaction between $(NPCl_2)_n$ and $CH_2{=}CHCH_2OC_6H_4C_6H_4O^-Na^+$ was completed in 48 h at 40 °C. Sodium trifluoroethoxide was added at room temperature and the reaction mixture was stirred at room temperature for an additional 24 h. The solution was then concentrated and the polymer was isolated by precipitation into water. The polymer was further purified by repeated precipitation from a THF solution into water (3×) and hexanes (1×). The polymer contained 67% of ((allyloxy)-phenyl)phenoxy and 33% of trifluoroethoxy groups as determined by ^1H NMR spectroscopy.

Preparation of $[NP(OC_6H_4C_6H_4O(CH_2)_3Si(CH_3)_2OCH_2\text{-}CH_3)_{1.34}(OCH_2CF_3)_{0.66}]_n$ (14). Polymer **13** (1 g, 2.43 mmol) was dissolved in chloroform (50 mL). Three drops of platinum divinyltetramethyldisiloxane complex were added to the dissolved polymer solution. After 20 min, dimethylethoxysilane (1 g, 9.6 mmol) was added and the reaction mixture was stirred overnight at room temperature. The resultant polymer was purified by repeated precipitation from chloroform into ethanol to obtain polymer **14**.

Preparation of $[NP(OC_6H_4C_6H_4O(CH_2)_3Si(CH_3)_2OCH_2\text{-}CH_3)_{0.58}(OC_6H_4C_6H_4O(CH_2)_3Si(CH_3)_2OSi(CH_3)_2OSi(CH_3))_{0.76}\text{-}(OCH_2CF_3)_{0.66}]_n$ (15). Polymer **13** (1 g, 2.43 mmol) was dissolved in chloroform (50 mL). Three drops of platinum divinyltetramethyldisiloxane complex were added to the dissolved polymer solution. After 20 min, heptamethyltrisiloxane (0.15 g, 0.67 mmol) was added and the reaction mixture was stirred at room temperature overnight. Dimethylethoxysilane (1 g, 9.6 mmol) was then added to the reaction mixture. The reaction mixture was stirred for 24 h and the polymer was precipitated from chloroform into ethanol three times. A ^1H NMR spectrum showed that the polymer **15** contained 33%, 38%, and 29% of trifluoroethoxide, heptamethyltrisiloxane, and dimethylethoxysilane derivatized groups, respectively.

Cross-Linking of Polymers. The polymer films were prepared by solvent casting and were cross-linked by either UV irradiation or heating at 120 °C. The progress of the cross-linking process was followed by swelling the cross-linked polymers in THF. Polymers **14** and **15** cross-linked without further treatment when films were stored in the atmosphere overnight. These polymers were further cross-linked by warming at 80 °C for 1 h. Polymers **9**, **11**, **12**, and **13** were cross-linked by UV radiation. Thin films were prepared by solvent casting, and photolysis was carried out for 40 min with a Rayonet photochemical reactor. The temperature of the samples was maintained near 25 °C by a cooling fan. Thermal cross-linking of these polymers was attempted by heating the samples in a nitrogen atmosphere at 120 °C. Samples heated longer than 5 min appeared to decompose. Therefore, thermal cross-linking of these polymers was not pursued.

Polymer **10** was irradiated for 1 h under the same conditions described above, but the product was found to contain a significant amount of soluble polymer. To increase the cross-linking, 2 mol % of benzoyl peroxide was added to the polymer solution before the films were cast. The films containing benzoyl peroxide gave insoluble cross-linked polymer after being irradiated for 40 min.

Preparation of Interpenetrating Polymer Networks. All the IPN's in this work were prepared by the method illustrated in the following example. Polymer **14** (0.2 g), which had been cross-linked by exposure to UV radiation, was placed in a solution containing 10 mL of styrene , 0.05 g AIBN initiator, and 0.2 mL of ethylene glycol dimethacrylate cross-linker. Polymer **14**, the styrene, the initiator, and cross-linker were combined at room temperature and maintained in the absence of light for 48 h or until the volume of the swollen polyphosphazene had increased 10 times. At this point, the reaction mixture was heated to 80 °C for 12 h. After cooling, the IPN was removed from the reaction mixture and was repeatedly extracted with THF and/or water to remove unpolymerized monomer and un-cross-linked organic polymer. Following purification, the IPN was dried rigorously under vacuum and was characterized using ^1H , ^{31}P NMR, and FT-IR spectroscopy and DSC and TEM techniques.

Acknowledgment. We thank the U.S. Army Research Office for support of this work. The electron microscopy was carried out with the cooperation of Rosemary A. Walsh and Wayne S. Kaboord.

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MA9501398