

Polyphosphazene Membranes. II. Solid-State Photocrosslinking of Poly[(alkylphenoxy)(phenoxy)phosphazene] Films

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ABSTRACT: The solid-state UV photocrosslinking mechanism and the properties of dense crosslinked films composed of poly[(methylphenoxy)(phenoxy)phosphazene], poly[(ethylphenoxy)(phenoxy) phosphazene], and poly[(isopropylphenoxy)(phenoxy)-phosphazene] were investigated, where the alkyl substituent was in either the *meta*- or *para*-position. Solution-cast films containing dissolved benzophenone photoinitiator (at a concentration of 1–25 mol %) were crosslinked at either 25 or 70°C. The ordering of benzophenone disappearance during polymer irradiation was methylphenoxy > ethylphenoxy > isopropylphenoxy, indicating that the rate controlling step for photoinitiator disappearance was the consumption of benzophenone, either by benzopinacole formation (with the creation of a polymer crosslink) or by reaction of a benzophenone-derived ketyl radical with a polymer macro-radical. The presence of such a ketyl adduct in crosslinked ethylphenoxy/phenoxy and isopropylphenoxy/phenoxy phosphazene films was verified by solid-state NMR. The ordering of crosslinked polymer swelling (for a given initial benzophenone concentration) when films were equilibrated in dimethylacetamide (DMAc) was isopropylphenoxy/phenoxy > ethylphenoxy/phenoxy > methylphenoxy/phenoxy, indicating that steric effects of the alkyl group were playing a role during crosslink formation. The methylphenoxy/phenoxy phosphazenes were the best materials for crosslinking; the glass transition temperature increased by approximately 25°C (from –15 to 10°C) and the film swelling (in DMAc) decreased from infinity (complete solubilization) to 35% as the benzophenone concentration was increased from 0 to 25 mol %. © 1998 John Wiley & Sons, Inc.* J Appl Polym Sci 68: 827–836, 1998

Key words: UV photocrosslinking; polymer swelling; glass transition temperature; benzophenone; ketyl adduct formation; FTIR; NMR

INTRODUCTION

Phosphazene polymers have shown promise as base materials for a variety of different mem-

branes, including uncharged pervaporation membranes for organic/water separations, carboxylated ion-exchange membranes for the low-pressure reverse-osmosis separation of tritiated water from light water, and sulfonated cation-exchange membranes for possible electro dialysis and battery/fuel cell applications.^{1–3} Interest in these polymers stems from their reported chemical, thermal, and radiological stabilities and the ease of chemically altering the polymer by adding various sidechains onto the —P=N— backbone.⁴ Regardless of the method by which solute/solvent separation is achieved (e.g., electrostatic interac-

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tions or organophilic/hydrophilic affinities), polymer swelling usually results in a degradation in membrane performance. For the case of polyphosphazene-based ion-exchange membranes, solvent swelling lowers the local concentration of fixed charge sites, which in turn restricts possible separations applications due to low coion rejection and high water transport rates. It has been shown, for example, that an uncharged, water-insoluble poly[(methylphenoxy)(phenoxy)phosphazene] membrane became hydrophilic after the addition of a small number of SO_3^- groups to the polymer.⁵ The extent of water swelling increased as the membrane ion-exchange capacity was increased from 0.5 to 1.3 mmol/g, with the eventual creation of a completely water-soluble polymer when the sulfonate fixed-charge concentration was above 1.5 mmol/g. Similarly, organophilic interactions that promote the selective membrane absorption and transport of nonpolar organics from dilute organic-in-water feed solutions play an important role during pervaporation separations. If the membrane were to swell excessively by the absorbed organic, then such polymer/solute interactions could be overwhelmed by solute/water interactions, resulting in more water uptake and lower organic/water separation selectivities. Crosslinking of both neutral and charged phosphazene polymer membranes is obviously of critical importance for optimum membrane performance and is the subject matter of this article.

Although there are numerous literature references on phosphazene polymers, only a few articles dealt with photocrosslinking and these studies focused primarily on the photochemistry of polyphosphazene solutions, with applications to photolithography, photocurable coatings, and nonlinear optics (see ref. 5 for a review of this prior work). We have reported recently on the solid-state photocrosslinking of uncharged poly[(4-ethylphenoxy)(phenoxy)phosphazene] membranes with benzophenone as the photoinitiator. When dense films of polymer containing dissolved benzophenone were irradiated with UV light, benzophenone-derived diradicals abstracted hydrogen from the benzylic carbons of the ethylphenoxy side groups, creating polymer macroradicals and ketyl radicals. Crosslinks were formed by the recombination of macroradicals, while the ketyl radicals combined to form benzopinacole. It is also known that ketyl radicals can react with the polymer macro-radicals to produce a ketyl adduct.⁶ The photocrosslinking mechanism and the for-

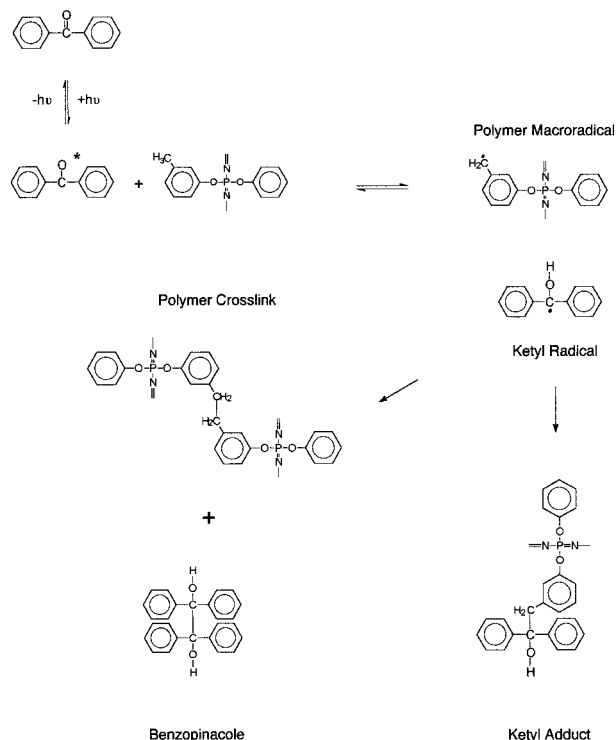


Figure 1 Reaction sequences for alkylphenoxy/phenoxy phosphazene crosslinking and ketyl adduct formation.

mation of the ketyl adduct are shown in Figure 1. Observed increases in the polymer's glass transition temperature and decreases in equilibrium membrane swelling in dimethylacetamide (a solvent that completely solubilized the uncrosslinked polymer) with increasing concentration of benzophenone provided evidence of crosslink formation.

In the present article, we have expanded upon our initial crosslinking work and report on new results dealing with the solid-state UV photocrosslinking of films composed of the following alkylphenoxy/phenoxy-substituted polyphosphazenes: poly[(methylphenoxy)(phenoxy)phosphazene], poly[(ethylphenoxy)(phenoxy)phosphazene], and poly[(isopropylphenoxy)(phenoxy)phosphazene], where the alkyl chain was located at either the *meta*- or *para*-position on the phenoxy rings. The purpose of this study was to assess the relative ease of hydrogen abstraction from the alkylphenoxy side groups, which should be in the order isopropyl > ethyl > methyl (i.e., 3° carbon > 2° carbon > 1° carbon), vs. the ease of crosslink formation, which was expected to follow the opposite order due to steric effects.⁷

Table I Initial Properties of the Alkylphenoxy/Phenoxy Phosphazene Polymers

Polymer	Average Molecular Weight (Daltons)	Glass Transition Temperature (°C)	Polymer Morphology
poly[3-methylphenoxy)(phenoxy)phosphazene] (hereafter denoted as 3-MEPOP)	3.0×10^6	-15	semicrystalline
poly[(4-methylphenoxy)(phenoxy)phosphazene] (4-MEPOP)	2.5×10^6	-20	semicrystalline
poly[(3-ethylphenoxy)(phenoxy)phosphazene] (3-ETPOP)	2.0×10^6	-25	amorphous
poly[(4-ethylphenoxy)(phenoxy)phosphazene] (4-ETPOP)	2.5×10^6	-30	amorphous
poly[(3-isopropylphenoxy)(phenoxy)phosphazene] (3-ISOPPOP)	2.3×10^6	-35	amorphous
poly[(4-isopropylphenoxy)(phenoxy)phosphazene] (4-ISOPPOP)	2.5×10^6	-35	amorphous

EXPERIMENTAL

The six phosphazene polymers examined in this study were purchased from, *technically*, Inc. (a company specializing in custom organic synthesis, located in Andover, MA) and are listed in Table I. The alkylphenoxy/phenoxy side-group ratio on the $-P=N-$ backbone, as determined by NMR spectroscopy, was 1.0 for all polymers. Each polymer was evaluated for its average molecular weight by gel permeation chromatography (Beckman HPLC with a Waters Styragel HT 6E column and a Waters refractive index detector), glass transition temperature by differential scanning calorimetry (TA Instruments Model 8000 DSC), and degree of crystallinity by wide-angle X-ray diffraction (Scintag XDS 2000 diffractometer). As shown in Table I, the two methylphenoxy/phenoxy polymers were semicrystalline, whereas the ethylphenoxy- and isopropylphenoxy-substituted polyphosphazenes were amorphous. The glass transition temperature of the amorphous phase was $< 0^\circ\text{C}$ for all of the polymers. The average molecular weight of the polyphosphazenes was in the range of $2.3\text{--}3.0 \times 10^6$ daltons.

Photocrosslinking/FTIR Experiments

Polyphosphazene films were prepared from a 5 wt % solution of polymer in THF (HPLC grade, inhibitor-free from Aldrich Chemical Co.) containing a known amount of benzophenone photoinitiator, where the benzophenone/phosphazene molar ratio was varied from 0.01 to 0.25. Samples were cast on sodium chloride plates and allowed to air dry for 12 h in darkness. After dry-

ing, the samples ($60 \mu\text{m}$ in thickness) and plates were stored in a vacuum desiccator. For the crosslinking experiments, a second NaCl plate was placed on top of each film and the two plates were sealed along the edge. FTIR (Mattson Instruments, Galaxy Series) spectra of the films were used to monitor the time rate of disappearance of the carbonyl stretching band of benzophenone (at 1660 cm^{-1}) and the appearance of the OH stretching band of benzopinacol (at 3560 cm^{-1}). The films were placed in the UV irradiation chamber (Fig. 2), flushed with argon for 20 min, and irradiated under Ar with a UV lamp (Cole-Parmer, 365 nm wavelength, 2.8 mW/cm^2 intensity) for 300 min. Periodically during the irradiation period, the samples were removed from the UV light source and additional FTIR spectra were recorded. The half-life of benzophenone was then calculated as the time required for the initial intensity of the carbonyl band to decrease by one-half. Crosslinking experiments with each polymer and with the same range of benzophenone concen-

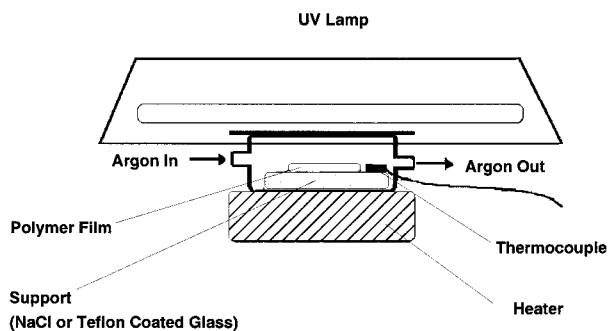


Figure 2 Schematic diagram of the reaction chamber for UV photocrosslinking.

trations were carried out at 25 and 70°C (the melting point of benzophenone is 50°C). For the high-temperature experiments, the irradiation chamber was placed on a hot plate and the NaCl plates were maintained at a temperature of 70°C (the temperature was monitored by a thermocouple fixed to the NaCl plate adjacent to the film). A control experiment was conducted to determine the effect of heating on the decay of the benzophenone carbonyl peak, where the polymer films were heated to 70°C for 120 min without UV radiation. FTIR analysis of these samples showed no change in the intensity of the carbonyl peak.

Photocrosslinking/Swelling Experiments

Membranes were cast on Teflon-coated plates from a 5 wt % polyphosphazene/THF solution containing a known weight of benzophenone. Dry film thicknesses, after solvent evaporation in darkness for 12 h, were found to be 100 ± 10 μm . The films were then deaerated for 30 min in a vacuum desiccator. Following deaeration, the films were placed in the UV irradiation chamber, flushed with argon for 20 min, and then irradiated under an argon atmosphere at either 25 or 70°C. Samples were irradiated at 25°C for 300 min, then inverted, and irradiated for an additional 300 min. For the 70°C crosslinking experiments, a film was first heated to the reaction temperature (this required ca. 20 min) and then irradiated for 300 min. In all experiments the FTIR carbonyl band of benzophenone had disappeared by the end of the irradiation period. After exposure to UV light all of the films were placed in a vacuum desiccator for 18 h to insure complete reaction of any residual radicals. The samples were then removed from the desiccator, weighed, and placed in *N,N*-dimethylacetamide (DMAc) at 25°C for 24 h. DMAc was found to completely dissolve all of the polymer films prior to crosslinking; thus, variations in polyphosphazene swelling in this solvent provided a measure of the extent of crosslinking. After equilibration in DMAc, the swollen samples were removed from the solvent, wiped with filter paper to remove any DMAc on the film surface, and weighed. The samples were then dried under vacuum and reweighed to obtain the dry weight of each film. The percentage swelling of the films was obtained using the following equation:

$$\% \text{ Swelling} = \left[\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \right] \times 100 \quad (1)$$

where W_{wet} and W_{dry} are the swollen and dry film weights, respectively.

DSC Measurements

DSC measurements were made on the same cross-linked membrane samples that were used in the swelling experiments. Circular polymer samples of approximately 20 mg in weight were encapsulated in aluminum pans after thorough drying in vacuum. Thermograms were recorded using a TA Instruments Model 8000 differential scanning calorimeter equipped with LN₂ cooling. The scanned temperature range was -70 to 120°C at a heating rate of $20^\circ\text{C}/\text{min}$. To avoid oxidation reactions and vapor condensation, dry gaseous N₂ was passed through the sample compartment.

¹³C NMR Measurements

Solid-state NMR analyses of the polymers were performed on the crosslinked polymer films to determine the presence of ketyl radical adducts. Samples of irradiated films were finely divided and packed in a 4 cm³ ZrO₂ rotor. The ¹³C spectra were recorded on a Bruker ASX 400 MHz spectrometer. A sample spinning rate of 5000 Hz and proton decoupling at a level of 45 Hz were employed under magic angle spinning (MAS) conditions using dipolar decoupling with crosspolarization (CP). Tetramethylsilane (TMS) was used as a reference and ¹³C-NMR spectra were obtained in the range of 0 to 200 ppm.

RESULTS AND DISCUSSION

Photocrosslinking Experiments

The purpose of this study was to determine which of the alkyl substituents on the phenoxy side chains of the phosphazene polymers produced the highest degree of crosslinking. It was presumed that the extent of polyphosphazene photocrosslinking with benzophenone would be influenced by two factors: (1) the ease of abstracting a benzylic hydrogen from the alkylphenoxy side group, and (2) steric hindrance to crosslinking imposed by the alkyl substituent. We sought to determine if one of these factors was rate controlling by examining the time rate of decay of the carbonyl band of benzophenone during film exposure to UV light and equilibrium swelling data of crosslinked films.

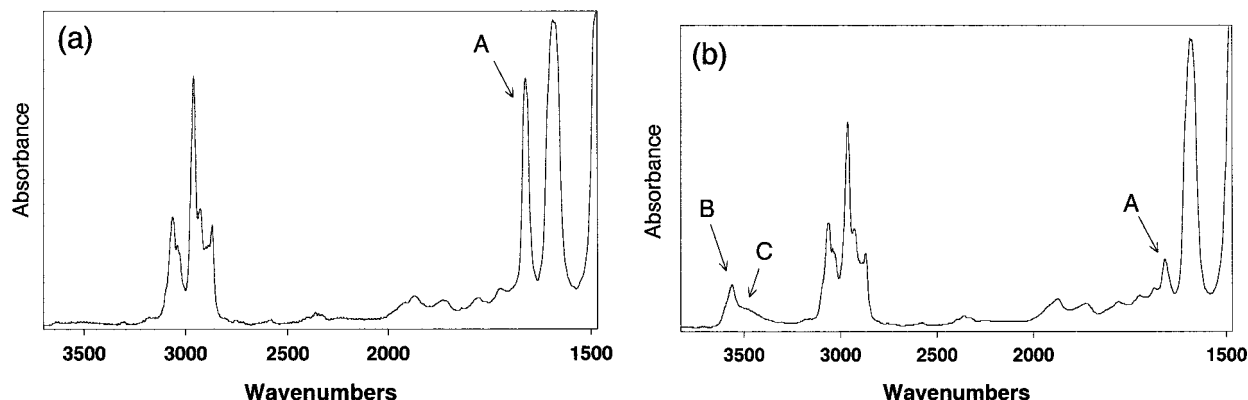


Figure 3 FTIR spectra of a poly[(3-methylphenoxy)(phenoxy)phosphazene] film containing 25 mol % benzophenone prior to [Fig. 3(a)] and after [Fig. 3(b)] exposure to UV light. The carbonyl stretching band is labeled (A) and two OH bands are labeled (B) and (C).

FTIR spectra of poly[(3-methylphenoxy)(phenoxy)phosphazene] and poly[(3-isopropylphenoxy)(phenoxy)phosphazene] films containing 25 mol % benzophenone prior to and after UV light exposure (for 300 min at 25°C under an argon atmosphere) are shown in Figures 3(a) and (b) and 4(a) and (b). A comparison of the two spectra for each polymer lead us to the following conclusions: (1) the carbonyl stretching band at 1661 cm^{-1} disappeared after irradiation, indicating essentially complete conversion of benzophenone; (2) a sharp absorption peak at 3560 cm^{-1} appeared during irradiation, indicative of a hydroxyl group originating from benzopinacole (the absorption spectrum of benzopinacole in a phosphazene polymer matrix was identified from FTIR spectra of polyphosphazene films containing reagent grade

benzopinacole); (3) there was a decrease in the aliphatic CH stretching bands at $2870\text{--}2960\text{ cm}^{-1}$, indicating hydrogen abstraction from the polymer's ethylphenoxy side group; and (4) a broad OH absorption band between $3350\text{--}3620\text{ cm}^{-1}$ (not associated with benzopinacole) was present in the spectra from the ethylphenoxy/phenoxy and isopropylphenoxy/phenoxy.

The stretching band at $3350\text{--}3620\text{ cm}^{-1}$ was suspected of being associated with another hydroxyl group in the film, either from ketyl adducts formed by the attachment of benzophenone photoradicals to the polymer (see Fig. 1) or some other polymer degradation product. Galerica et al. reported on a similar broad OH stretching band when poly[bis(benzylphenoxy)phosphazene] films (with benzophenone) were exposed to UV radia-

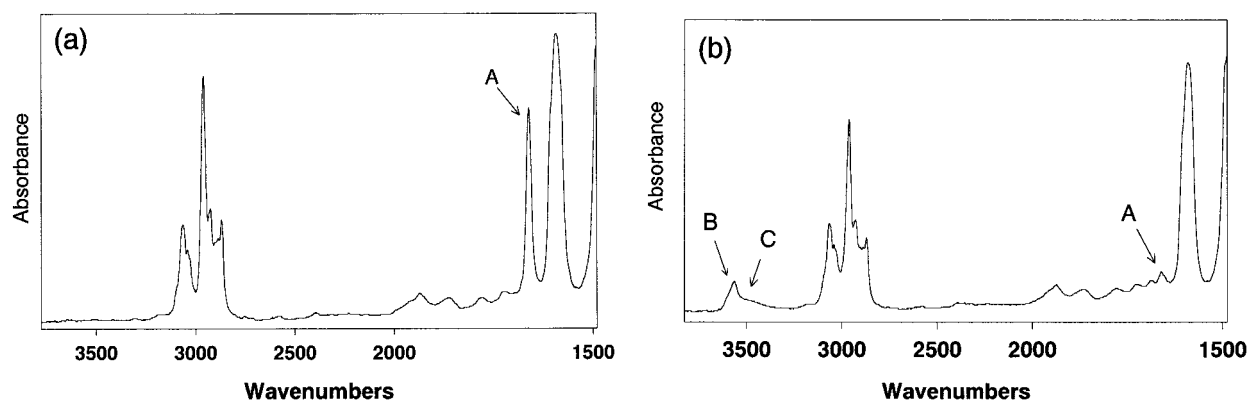


Figure 4 FTIR spectra of a poly[(3-isopropylphenoxy)(phenoxy)phosphazene] film containing 25 mol % benzophenone prior to [Fig. 4(a)] and after [Fig. 4(b)] exposure to UV light. The carbonyl stretching band is labeled (A) and two OH bands are labeled (B) and (C).

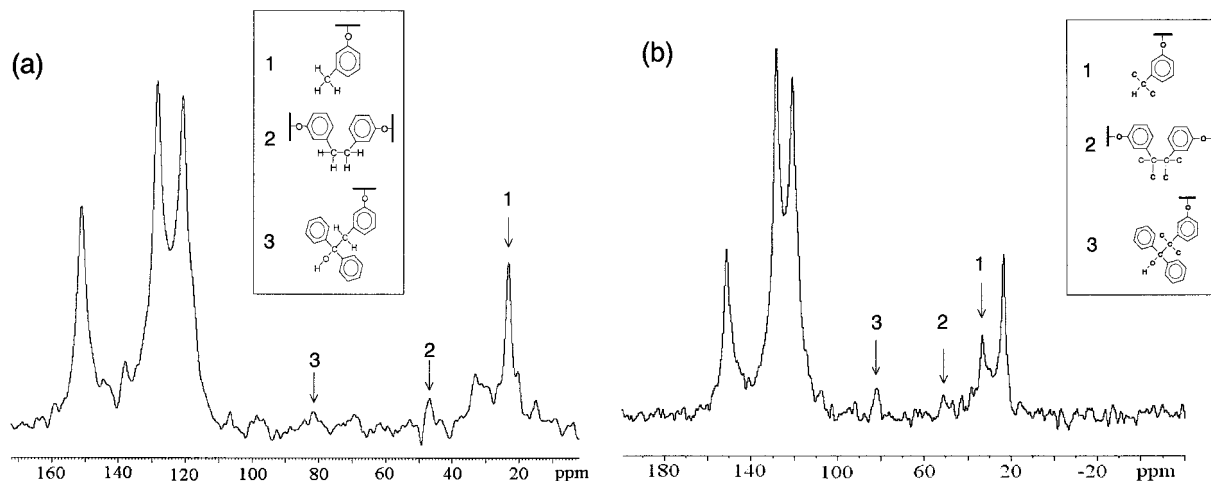


Figure 5 Solid-state NMR spectra of crosslinked polyphosphazenes. (a) Poly[(3-methylphenoxy)(phenoxy)phosphazene], and (b) poly[(3-isopropylphenoxy)(phenoxy)phosphazene]. The peaks are labeled as follows—peak 1: methyl groups; peak 2: benzylic carbons that crosslink; peak 3: benzylic carbons that form the ketyl adduct.

tion in an air atmosphere.⁸ The IR peak, which Galeria ascribed to the formation of alcoholic and hydroperoxidic polymer degradation groups, decreased significantly in size when the polyphosphazene films were bathed in argon during irradiation. Because our crosslinking experiments were carried out in an argon atmosphere, and because there was no obvious indication of polymer degradation (e.g., polymer discoloration after irradiation⁹), we associated the 3350–3620 cm^{-1} stretching band primarily to the formation of ketyl adduct (although we could not rule out the possibility of some polymer degradation). To verify the presence of this side-reaction product, irradiated poly[(3-methylphenoxy)(phenoxy)phosphazene] and poly[(3-isopropylphenoxy)(phenoxy)phosphazene] were analyzed by solid-state NMR. The ^{13}C -NMR spectra of these two polymers (each initially containing 25 mol % benzophenone) are shown in Figure 5(a) and (b). One group of peaks common to both spectra between 120 and 160 ppm was associated with aromatic carbons, either in the polymer, benzopinacol, or ketyl adduct.¹⁰ The various alkyl carbons in the polymers produced a second grouping of peaks between 20 and 50 ppm. The peaks at 23 ppm and 33 ppm in Figure 5(a) were ascribed to the two types of alkyl carbons of the isopropyl substituents, whereas the peak at 26 ppm in Figure 5(b) was attributed to methyl groups on the polymer's phenoxy side chains. A downfield shift of approximately 20 ppm would be expected if the primary or tertiary carbons in the alkylphenoxy side groups formed a crosslink and

such a peak at either 47 ppm [Fig. 5(a)] or 51 ppm [Fig. 5(b)] was observed. For the crosslinked isopropylphenoxy polymer, an additional peak was observed at 82 ppm, which was consistent with the chemical shift expected for the benzylic carbon of the isopropylphenoxy side group if it were attached to the ketyl adduct. Such a peak was not present in the NMR spectra of crosslinked methylphenoxy/phenoxy phosphazene polymers.

To obtain some insights into the crosslinking mechanism, the decay in the carbonyl stretching band in FTIR spectra was monitored as a function of UV radiation time, polymer type, benzophenone concentration, and temperature. Figures 6–8

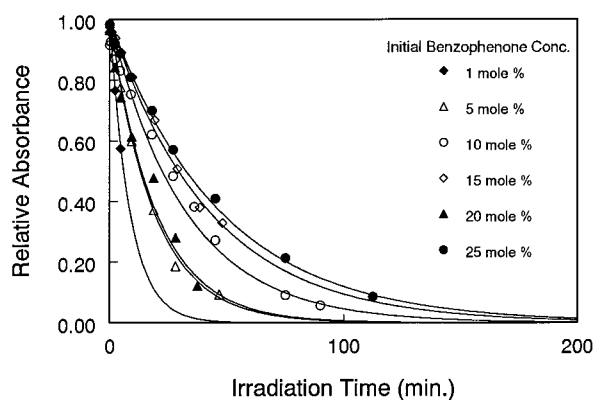


Figure 6 Rate of decay of the IR carbonyl absorption band in poly[(3-methylphenoxy)(phenoxy)phosphazene]/benzophenone films for different benzophenone concentrations. Film thickness = 60 μm ; irradiation temperature = 25°C.

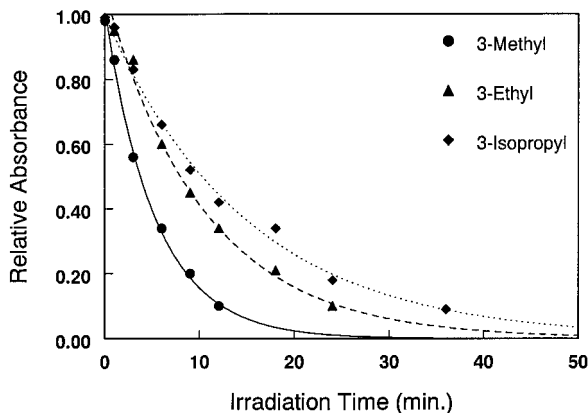


Figure 7 Rate of decay of the IR carbonyl absorption band in the three poly[(3-alkylphenoxy)(phenoxy)phosphazene]/benzophenone films for a benzophenone concentration of 25 mol %. Film thickness = 60 μm ; irradiation temperature = 25°C.

show representative decay curves during UV light exposure of 60- μm thick polyphosphazene films. Figure 6 is a plot of relative absorbance of the carbonyl peak vs irradiation time for poly[(3-methylphenoxy)(phenoxy)phosphazene] at 25°C with different initial concentrations of benzophenone. The decay data display a strong dependence on the benzophenone concentration with the photoinitiator half-life increasing by more than a factor of five as the benzophenone concentration increased from 1 to 25 mol %. This decrease in the disappearance rate was attributed to shielding of the interior polymer regions by benzophenone at the film surface. In Figures 7 and 8, benzophenone

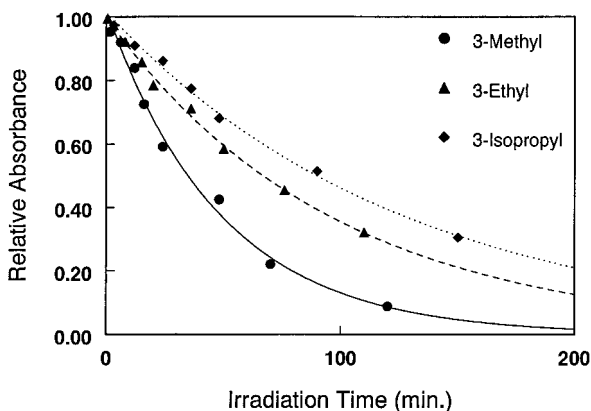


Figure 8 Rate of decay of the IR carbonyl absorption band in the three poly[(3-alkylphenoxy)(phenoxy)phosphazene]/benzophenone films for a benzophenone concentration of 25 mol %. Film thickness = 60 μm ; irradiation temperature = 70°C.

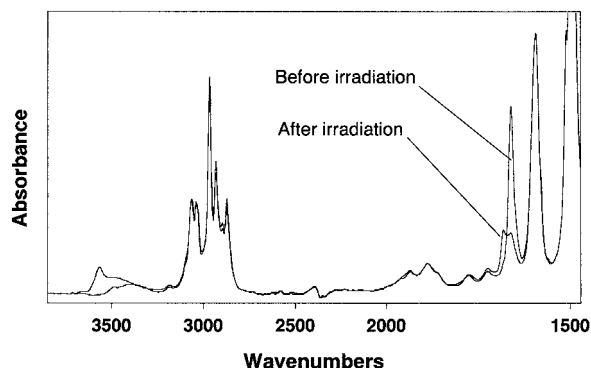


Figure 9 FTIR spectra of poly[(4-ethylphenoxy)(phenoxy)phosphazene]/benzophenone films before and after UV irradiation showing a new carbonyl stretching band at 1700 cm^{-1} and a broadening of the OH stretching band at 3450 cm^{-1} . Benzophenone concentration = 25 mol %; Film thickness = 60 μm ; irradiation temperature = 70°C.

decay curves are compared for poly[(3-methylphenoxy)(phenoxy)phosphazene], poly[(3-ethylphenoxy)(phenoxy)phosphazene], and poly[(4-isopropylphenoxy)(phenoxy)phosphazene] at either 25 or 70°C, with an initial benzophenone concentration of 25 mol %. The ordering of the decay curves was the same at the two temperatures, i.e., methylphenoxy > ethylphenoxy > isopropylphenoxy, indicating that: (1) the initial photoactivation steps (light-induced excitation of a benzophenone molecule and hydrogen abstraction from a benzylic carbon) were all reversible and rapid (i.e., in equilibrium), as has been observed by other investigators;¹¹ and (2) ketyl radical consumption (by either pinacole and polymer crosslink formation or ketyl adduct formation) was controlling the rate of benzophenone disappearance. As would be expected, the benzophenone decay rates were significantly faster at the elevated temperature, where the benzophenone half-life decreased typically by a factor of 6–8 when the temperature was increased from 25 to 70°C.

There was essentially no difference in the benzophenone decay rate for *meta*- and *para*-substituted polymers, and we concluded that the nature and not the position of the alkyl group on the aromatic side groups of the polymer influenced ketyl radical consumption. During crosslinking of *para*-substituted ethylphenoxy/phenoxy and isopropylphenoxy/phenoxy polymers, however, a new FTIR carbonyl stretching band at approximately 1700 cm^{-1} was observed, as shown in Figure 9. No such peak was found with the methylphenoxy-substituted

polymers nor for the *meta*-substituted ethylphenoxy and isopropylphenoxy films. Minto et al. reported on a similar IR peak when poly[bis(benzylphenoxy)phosphazene] was crosslinked in solution with benzophenone and attributed its presence to a photo-induced polymer degradation (oxidation) reaction.⁹

The faster rate of benzophenone disappearance for the methylphenoxy-substituted polymer, compared to the ethylphenoxy and isopropylphenoxy polymers, is consistent with a crosslinking mechanism where the consumption of ketyl radical, either by benzopinacol formation with macro-radical combination or the production of ketyl adduct, is rate controlling and where steric effects associated with the alkylphenoxy side groups play an important role. Both the primary macro-radical crosslinking reaction and the ketyl adduct byproduct reaction should be affected by steric interference imposed by the alkyl substituent on the polymer's alkylphenoxy side groups; hence, the benzophenone decay data alone did not tell us which alkyl moiety was best for polymer crosslinking.

Swelling Experiments

Figure 10(a)–(c) show representative results from the DMAc swelling test, where the % polymer swelling is plotted against the initial mol % benzophenone for the 3-alkylphenoxy/phenoxy polymers, irradiated at 25 and 70°C, and the 4-alkylphenoxy/phenoxy polymers, irradiated at 70°C. Although the benzophenone photoinitiator in all of the films was completely consumed during UV light exposure, the degree of crosslinking, as quantified by polymer swelling in DMAc, varied significantly with the type of alkylphenoxy side group. The ordering in film swelling was always isopropyl > ethyl > methyl, which is consistent with a crosslinking mechanism where steric effects control macro-radical combination. Also, film swelling decreased as the initial benzophenone concentration increased. Within experimental accuracy ($\pm 4\%$), swelling of the methylphenoxy polymers was independent of both irradiation temperature (25 vs. 70°C) and the position of the methyl group on the phenoxy ring (*meta* vs. *para*). The crosslinked 4-ethylphenoxy and 4-isopropylphenoxy polymers swelled more at a given initial benzophenone concentration than films with the same alkyl group in the *meta* position, presumably because the *para*-substituted polymers underwent some degradation during UV light exposure (as discussed above in reference to

Fig. 9). Also, the 4-ethylphenoxy and 4-isopropylphenoxy polymers swelled more at a given benzophenone concentration when they were irradiated at 70 as compared to 25°C, suggesting that the polymer degradation reaction is temperature dependent.

We can conclude from the swelling data (in combination with the FTIR and NMR results) that fewer crosslinks were produced in the isopropylphenoxy and ethylphenoxy polymers, compared to the methylphenoxy-substituted phosphazenes, for the same initial concentration of benzophenone, because some of the polymer macro-radicals were consumed by ketyl adduct formation. For all of the polymers, steric interference by the alkyl moieties played a critical role during the formation of both ketyl adducts and crosslinks, as evidenced by the ordering of the benzophenone decay data. The low swelling of the methylphenoxy-substituted polyphosphazene, meant that the ratio of the macro-radical recombination rate to the ketyl adduct formation rate was large (i.e., the number of crosslinks per ketyl adduct was large), compared to the ratio of rates in the ethylphenoxy and isopropylphenoxy polymers.

Additional evidence of crosslink formation was provided by glass transition temperature (T_g) measurements. Typical data are shown in Figure 11, where the glass transition temperatures of the 3-alkylphenoxy/phenoxy phosphazene polymers are plotted as a function of the initial concentration of benzophenone for films irradiated at 25°C. Qualitatively similar results were obtained for the 4-alkylphenoxy-substituted polyphosphazenes irradiated at 25°C and for all polymers crosslinked at 70°C. A direct comparison of the glass transition temperatures of the different crosslinked polymers could not be made because the base (uncrosslinked) polyphosphazenes differed in their semicrystalline/amorphous nature, degree of crosslinking, and extent of ketyl adduct byproduct formation. We interpreted the variation in glass transition temperature with benzophenone concentration for each individual polymer and found, as expected, that T_g increased with increasing benzophenone concentration. According to theoretical predictions, the dependence of the glass transition temperature on the crosslinking degree should be convex upward,¹² as was the case for the methylphenoxy/phenoxy phosphazene. The ethylphenoxy and isopropylphenoxy curves, on the other hand, were concave downward (a similar trend has been reported previously for poly[(3-

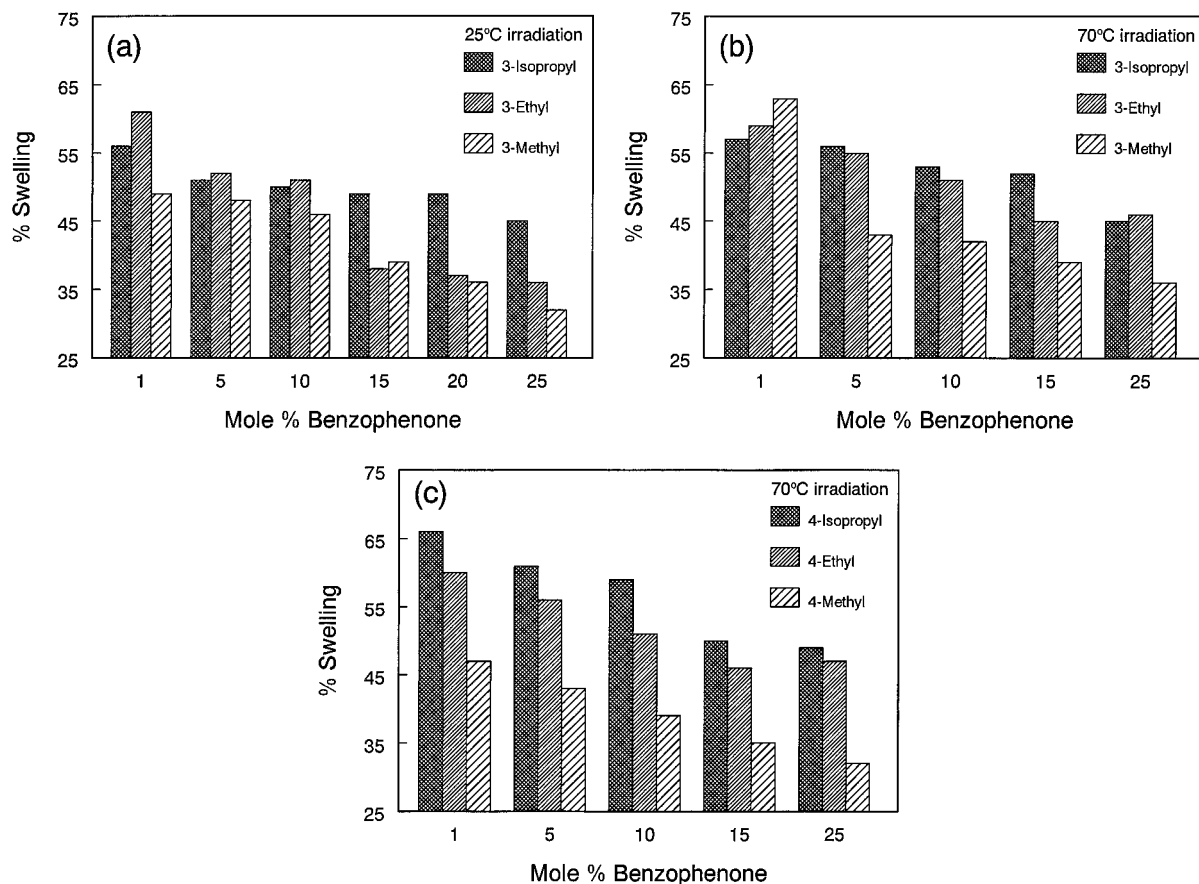


Figure 10 Effect of initial benzophenone concentration on the equilibrium swelling of crosslinked poly[(alkylphenoxy)(phenoxy)phosphazene] films in dimethylacetamide (DMAC) at 25°C. (a) 3-Alkylphenoxy/phenoxo polymers, irradiated at 25°C; (b) 3-alkylphenoxy/phenoxo polymers, irradiated at 70°C; (c) 4-alkylphenoxy/phenoxo polymers, irradiated at 70°C.

ethylphenoxy)(phenoxy)phosphazene]⁵). One possible explanation for this result, which is consistent with other data collected and reported in this study, is that the amount of photoinitiator as expressed by the mol % benzophenone does not reflect the true crosslinking degree because some polymer macro-radicals recombined with ketyl radicals and, thus, did not contribute to the formation of crosslinks.

CONCLUSIONS

Analyses of the solid-state UV photocrosslinking mechanism and the properties of dense crosslinked films composed of poly[(methylphenoxy)(phenoxy)phosphazene], poly[(ethylphenoxy)(phenoxy)phosphazene], and poly[(isopropylphenoxy)(phenoxy)phosphazene] were carried

out, where the alkyl substituent was in either the *meta*- or *para*-position. Solution-cast films containing dissolved benzophenone photoinitiator were used in the crosslinking experiments, where the benzophenone concentration was varied from 1 to 25 mol %.

The ordering of benzophenone disappearance during exposure of dry polymer films to UV light was methylphenoxy > ethylphenoxy > isopropylphenoxy, indicating that the rate controlling step for benzophenone disappearance was the consumption of the ketyl radical, either by benzopinacol formation (with the creation of a polymer crosslink) or the reaction of the ketyl radical with the polymer macro-radical to form a ketyl adduct. The presence of the ketyl adduct in ethylphenoxy/phenoxo and isopropylphenoxy/phenoxo phosphazene films was verified by solid-state NMR. The adduct was not observed in NMR spectra

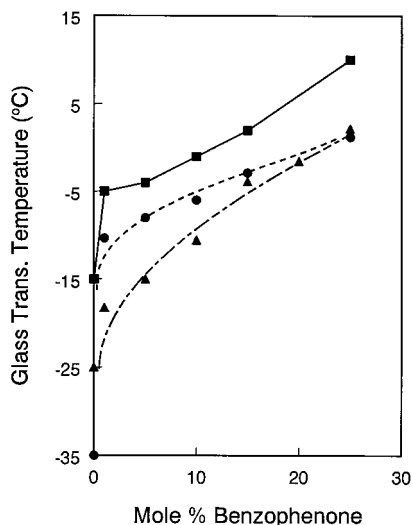


Figure 11 The dependence of the glass transition temperature on the benzophenone content in irradiated poly[(3-alkylphenoxy)(phenoxy)phosphazene] films (irradiation temperature = 25°C). ■ poly[(3-methylphenoxy)(phenoxy)phosphazene]; ● poly[(3-isopropylphenoxy)(phenoxy)phosphazene]; ▲ poly[(3-ethylphenoxy)(phenoxy)phosphazene].

of crosslinked methylphenoxy-substituted polymers.

The ordering of polymer swelling (for a given initial benzophenone concentration) when crosslinked polyphosphazene films were equilibrated in DMAc was isopropylphenoxy/phenoxy > ethylphenoxy/phenoxy > methylphenoxy/phenoxy. Within experimental accuracy, swelling of the methylphenoxy polymers was independent of both the irradiation temperature (25 or 70°C), and the position of the methyl substituent on the phenoxy ring (*meta* vs. *para*). Polymers containing 4-ethylphenoxy or 4-isopropylphenoxy side chains underwent some degradation during exposure to UV light and swelled more in DMAc than the corresponding polyphosphazenes with the alkyl group in the *meta*-position. Additional evidence of crosslink formation was provided by DSC measurements, where the glass transition temperature of all crosslinked phosphazene polymers increased with increasing benzophenone concentration.

From the sum total of all data collected in this study, we have concluded that the 3-methylphenoxy/phenoxy or 4-methylphenoxy/phenoxy phosphazenes were the best polymers for UV photo-

crosslinking with benzophenone. The smaller and less sterically hindered methyl substituent was superior to the bulkier ethyl and isopropyl moieties on the polymer's phenoxy side chains, in terms of facilitating the carbon-carbon macro-radical crosslinking reaction, with minimal ketyl adduct formation. Although an increase in temperature during UV irradiation was advantageous from the standpoint of increasing the reactivity of the photoinitiator and polymer radicals, it did not appear to produce a higher degree of crosslinking nor increase the amount of ketyl adduct in the methylphenoxy-substituted phosphazenes.

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