Polyphosphazene Membranes. I. Solid-State Photocrosslinking of Poly[(4-ethylphenoxy)-(phenoxy)phosphazene]

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SYNOPSIS

Dense films of poly[(4-ethylphenoxy)(phenoxy)phosphazene] (PEPP), a potentially attractive ion-exchange membrane material, were crosslinked to varying degrees using UV light and a photoinitiator. This polymer contained two kinds of substituents: phenoxy groups to be used for possible functionalization (e.g., sulfonation) and ethylphenoxy sidechains for photocrosslinking, where hydrogens at the benzylic carbons could be abstracted by a photoinitiator-leaving macroradicals that after recombination formed covalent bonds. The polyphosphazene polymer was synthesized, mixed with a photoinitiator, shaped into a thin film by solvent casting, and irradiated with UV light for a specified period of time. Benzophenone (BP), was selected as the photoinitiator because it was miscible with polyphosphazene, had the highest rate of hydrogen abstraction, and absorbed UV light of 365 nm wavelength. The half-life of benzophenone in 50 μm-thick irradiated films was determined to be 20 min. When the BP–PEPP molar ratio was increased from 0 to 0.5, the glass transition temperature increased after irradiation from -8.8 to $53.5°C$. At the same time, the equilibrium swelling in dimethylacetamide, at $25°C$, decreased from infinity to 0.31. Tensile strength tests of the crosslinked films revealed a nonlinear dependence on BP–PEPP molar ratio. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

To be regarded as a potential candidate for industrial applications, a polymeric membrane must meet a number of requirements. The most important is selectivity, which requires, for example, a high concentration of ionic groups in the case of ion-exchange membranes or an optimized lypophilicity/hydrophilicity balance for pervaporation applications. Low swelling is required in both instances. Next, the resistance to degradation must be high, which means that the polymer should be chemically and thermally inert. Additionally, the mechanical strength of the membrane should be sufficient so as to ensure some level of dimensional stability.

Until now, many different polymers have been tailored for a variety of membrane applications.[1]

However, there are still unexplored polymeric materials that offer new opportunities. This is especially true with polyphosphazenes. Polyphosphazenes are probably the most highly developed of all inorganic-backbone polymers.[2,3] With appropriate functionalization of the basic poly(dichlorophosphazene), an unlimited number of specialty polymers can be obtained (Fig. 1).

In general, there are two ways to prepare dense membranes. The first is to synthesize a polymer with given functionalities and then shape it into a film. To prevent excessive swelling or dissolution by the feed components, the polymer should be crosslinked. If the polymer is semicrystalline, the crystallites can act as crosslinks; otherwise, chemical crosslinking is required. The second preparation method is to crosslink the unfunctionalized polymer first and then introduce the required functional groups by a chemical posttreatment step.

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$$\begin{array}{c} \text{Cl} \\ | \\ +\text{N=P}+_n \\ | \\ \text{Cl} \end{array} \quad + \quad \begin{array}{c} \text{NaOR} \\ \\ \text{NaOR}' \end{array} \quad \rightarrow \quad \begin{array}{c} \text{OR} \\ | \\ +\text{N=P}+_n \\ | \\ \text{OR}' \end{array} \quad + \quad 2\text{NaCl}$$
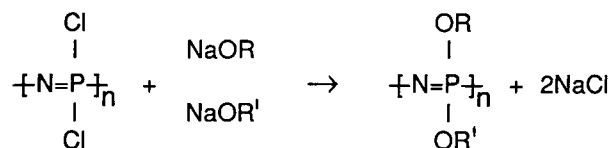
Figure 1 General scheme for the substitution of poly(dichlorophosphazene) with alkoxides and/or aryloxides.

In the present work the following scheme was adopted: (1) synthesis of a polyphosphazene with two kinds of substituents: the first one to be used for possible functionalization and the second one for photocrosslinking; (2) mixing the polyphosphazene with a photoinitiator and shaping into a thin film by a casting technique; and (3) irradiation of the film with UV light to photocrosslink the polyphosphazene.

Poly[(4-ethylphenoxy)(phenoxy)phosphazene] (PEPP), was selected as the starting material in this study. The ethylphenoxy groups were used for crosslinking because hydrogens at the benzylic carbons could be subtracted by a photoinitiator and the macroradicals thus generated could recombine to form crosslinks. The membranes could be used, as is, for possible pervaporation separations[4] or an ion-exchange membrane could be made by a suitable chemical treatment, e.g., sulfonation of the phenoxy substituents.

Although there are numerous literature references on polyphosphazenes, only a few articles deal with photocrosslinking, and focus mainly on the photochemistry of polyphosphazene solutions. In a series of articles Gleria et al.[5–8] discussed the photochemical behavior of various substituted polyphosphazenes both in solution and in films. They reported that the photocrosslinking of poly[bis(4-isopropylphenoxy)phosphazene] (PIPP), sensitized by either benzophenone (BP), hexakis(4-benzoylphenoxy)-cyclophosphazene (HBC), or poly[bis(4-benzoylphenoxy)phosphazene] (PBP), occurred readily in solution, and in swollen films irradiated with light of wavelength greater than 330 nm.[6,7] An intermolecular hydrogen abstraction from 4-isopropylphenoxy groups by the electronically excited BP was the primary act of the reaction. However, no photoreaction was observed in dry films of the HBC/PIPP and PBP/PIPP mixtures. This fact was explained in terms of a complete phase separation between HBC (or PBP) and PIPP in the solid state that prevented the contact of these materials and, hence, the bimolecular interaction between the excited carbonyl group and the tertiary hydrogen of

PIPP. To overcome this problem the authors synthesized a phosphazene copolymer with both BP and 4-isopropylphenoxy moieties attached to the same backbone, i.e., the material contained the hydrogen abstracting agent and the hydrogen supplying substrate on the same polymeric backbone.[8] In this case, a high efficiency of photocrosslinking was observed in the solid state. The crosslinking degree reached 90% after the polyphosphazene film absorbed 6 mJ/cm^2.

Minto et al.[9] presented results on the photolysis of poly[bis(4-benzylphenoxy)phosphazene] (PBBP), in solution and film form, both in the presence and absence of molecular oxygen. Light irradiation of the polymer in oxygen-saturated methylene chloride solutions resulted in a remarkable degradation of the polyphosphazene, while in argon-purged solutions no appreciable variations in the polymer structure could be detected. The photolysis of PBBP in films induced the crosslinking of the polymer regardless of the presence or absence of molecular oxygen. The main process observed during the photochemistry both in solution and in the solid state polymer was the oxidation of the 4-benzylphenoxy group on the polyphosphazene, without involvement of the inorganic backbone.

Nelson et al.[10] reported on the studies of BP initiated photocrosslinking of poly[bis(2-methoxyethoxyethoxy)phosphazene]. The process was meant to increase the dimensional stability of the polyphosphazene for solid polymer electrolyte applications. The effect of crosslinking was evidenced in the ^{1}H- and ^{13}C-NMR spectra. The polymer also swelled and did not dissolve in THF and water.

Scoponi et al.[11] studied thermo- and photo-oxidation of PBBP. They revealed that BP groups formed at the early stages of the oxidation were responsible for the high yields of photocrosslinking.

Allcock and Cameron[12,13] synthesized and characterized polyphosphazenes bearing cinnamate and chalcone groups. The polymers underwent a photochemically induced 2+2 cycloaddition reaction to form crosslinked matrices. A chalcone group was particularly useful because of the higher overall photosensitivity of the chalcone unit compared to that of the classical cinnamate system. This resulted from the close match between the absorption spectrum of the chalcone side group and the emission spectrum of the mercury arc UV light source. Other advantages over the cinnamate system were the ease of preparation, due to fewer synthetic steps and the higher glass transition temperature of the chalcone polymer.
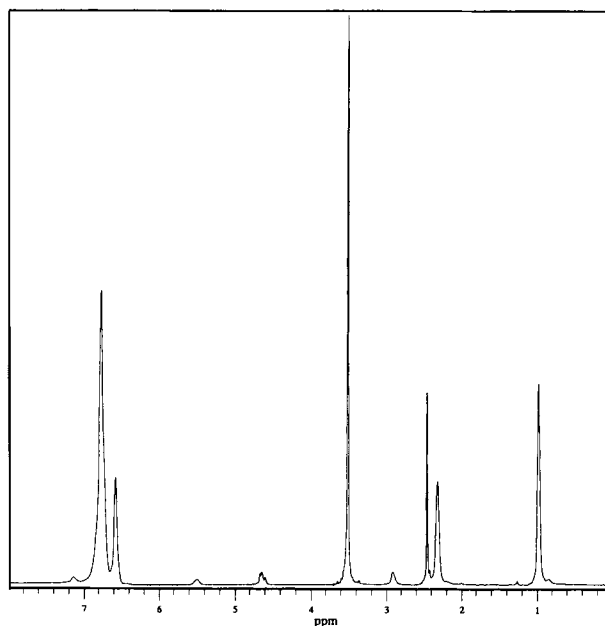
Figure 2 ¹H-NMR spectrum of the synthesized PEPP. The two signals at 2.46 and 3.51 ppm originated from the solvent. Based on the intensity of signals for methylene protons at 0.98 ppm and total aromatic protons at 6.58 and 6.77 ppm, the relative amount of phenoxy to 4-ethylphenoxy substituents was estimated to be 0.93.

Most of the research on the photocrosslinking of polyphosphazenes described above was directed toward uses in photolitography, photocurable coatings, and the stabilization of nonlinear optical properties.[14]

In the present article, results on the photocrosslinking of PEPP polymer films are reported. The use of crosslinked films in organic/water pervaporation and the sulfonation of the crosslinked polymer into an ion-exchange membrane will be the subject of future publications.

EXPERIMENTAL

Polymer Synthesis

Poly(dichlorophosphazene) (6.13 g; 0.053 mol), obtained by the thermal polymerization of hexachlorocyclotriphosphazene (Aldrich) at 250°C, was dissolved in 100 mL tetrahydrofuran (THF, Aldrich), and added slowly (over 1 h) to a solution of sodium 4-ethylphenoxide prepared from 4-ethylphenol (6.5 g; 0.055 mol, Aldrich) and sodium (1.2 g; 0.055 mol, Aldrich) in 200 mL THF and 0.1 g *tetra-n*-butylammonium bromide (Aldrich). The ratio of reactants was designed to bring about replacement of 50% of the chlorine atoms by 4-ethylphenoxy groups. The reaction mixture was stirred at reflux for 48 h, then

added slowly (over 1 h) to a solution of sodium phenoxide prepared from phenol (9.4 g; 0.10 mol, Aldrich) and sodium (2.3 g; 0.10 mol) in 50 mL THF. The reaction mixture was stirred for another 48 h, then cooled to room temperature and added dropwise into water to precipitate the polymer. The dissolution and precipitation were repeated again and the product was dried under reduced pressure overnight. Next, residual impurities were extracted with methanol in a Soxhlet apparatus for 4 days to yield 10 g of PEPP. The overall material yield was 80%.[14] In the final purification step the polymer was dissolved in THF to a concentration of 10 wt %. The solution was then centrifuged at 5000 rpm for 20 min. It was filtered through a 2 μm Millipore syringe filter and precipitated into water. The polymer was then dried under reduced pressure at 50°C for 1 week.

¹H-NMR spectrum (Genaral Electric, 500 MHz, PGS) of the polyphosphazene dissolved in deuterated dioxane is shown in Figure 2. Based on this spectrum, the ratio of phenoxy to 4-ethylphenoxy was determined to be 0.93. The average molecular weight of the polymer (as determined by gel permeation chromatography) was 1.3×10^6.

Kinetics of Photocrosslinking—UV Spectroscopy

A 15 wt % solution of PEPP in THF (Aldrich, HPLC grade, inhibitor-free) was prepared. To this mixture

BP (Aldrich, 99+%) was added to obtain a 0.5 molar ratio, i.e., 2 mol of PEPP mers per 1 mol of BP. The solution was cast on a quartz plate and the solvent was slowly evaporated in darkness to obtain a thin film of the PEPP–BP mixture. Next, the film was irradiated under nitrogen atmosphere with a UV lamp (Cole–Parmer, 365 nm, intensity 2.8 mW/cm^2) for a total time of 0 to 600 min. After each irradiation period, a spectrum was recorded with a spectrophotometer (Shimadzu UV-160) in the 300–420 nm range. The results of these experiments were used to determine the maximum absorbance at the 340 nm carbonyl band. The half-life of BP was then calculated as the time required for the initial intensity of the carbonyl band to decrease by one-half. This same procedure was repeated for films of different thickness ranging from 10 to 200 μm.

Kinetics of Photocrosslinking—FTIR Spectroscopy

A 15 wt % solution of PEPP in THF (Aldrich, HPLC grade, inhibitor-free) was prepared. To this mixture either BP (Aldrich, 99+%), 9-fluorenone (FN, Aldrich, 98%) or benzil (BZ, Aldrich, 98%) was added to obtain a 0.5 molar ratio, i.e., 2 mol of PEPP mers per 1 mol of BP (FN or BZ). The solution was cast on an NaCl plate and the solvent was slowly evaporated in darkness to obtain a film of the PEPP–BP (PEPP–FN or PEPP–BZ) mixture. The thickness of the film was kept within the 10–200 μm range. Next, the film was irradiated under nitrogen atmosphere with a UV lamp (Cole–Parmer, 365 nm, intensity 2.8 mW/cm^2) for a total time of 0 to 600 min. After each irradiation period, a spectrum was recorded with a FTIR spectrophotometer (Galaxy Series, Mattson Instruments) in the range 600–4000 cm^{-1}. The decay rate of the carbonyl stretching band (1661, 1717, and 1668 cm^{-1}, respectively for BP, FN, and BZ) was used to calculate the half-life of the photoinitiator in the irradiated film.

Photocrosslinking

A 15% solution of PEPP in THF was prepared. To this solution BP was added to obtain a given PEPP–BP molar ratio. The solution was cast on a glass plate and the solvent was slowly evaporated in darkness, at room temperature. Next, the film was irradiated under nitrogen or air with a UV lamp of wavelength 365 nm and intensity 2.8 mW/cm^2 for 300 min. A transparent film was produced in the N$_2$ atmosphere, whereas a slightly yellow film was obtained when the irradiation was carried out

in air. For all cases the film thickness was between 50 and 100 μm.

DSC Measurements

Circular polymer samples of 15 mg were encapsulated in aluminum pans and the thermograms were recorded in a differential scanning calorimeter (DSC, Perkin–Elmer 7 Series Thermal Analysis System) equipped with an LN$_2$ cooling module, in the temperature range −60–100°C. The heating rate was 20°C/min. To avoid water vapor condensation, gaseous N$_2$ was passed through the sample compartment. The glass transition temperature was determined with Perkin–Elmer's standard software package.

Equilibrium Swelling Measurements

Equilibrium swelling of the crosslinked films was measured gravimetrically and expressed as a weight increase per unit dry weight of the film after immersing the film for 24 h in N,N-dimethylacetamide (DMAc) at 25°C.

Mechanical Properties

Tests were performed on a tensile apparatus (Instron, Model 4201) at ambient conditions. Dumbbell-shaped samples were extended at a rate of 5 mm/min. The stress–time data were transformed into stress–strain records, and the ultimate strength and ultimate strain were then determined as the stress and strain at failure.

X-Ray Diffraction

Wide angle x-ray scattering (WAXS) patterns were obtained using a Scintag XDS 2000 diffractometer operated at 45 kV and 40 mA, with a Cu anode. The scan range was 3–60°, and scan rate was 2.00°/min. Polymer samples were deposited on zero background quartz plates from THF solutions.

RESULTS AND DISCUSSION

Photoinitiator

The choice of the proper photoinitiator was one of the most important tasks of this study. The photoinitiator was to meet the following requirements: (1) a high rate constant for hydrogen abstraction, (2) the wavelength of the exciting radiation must
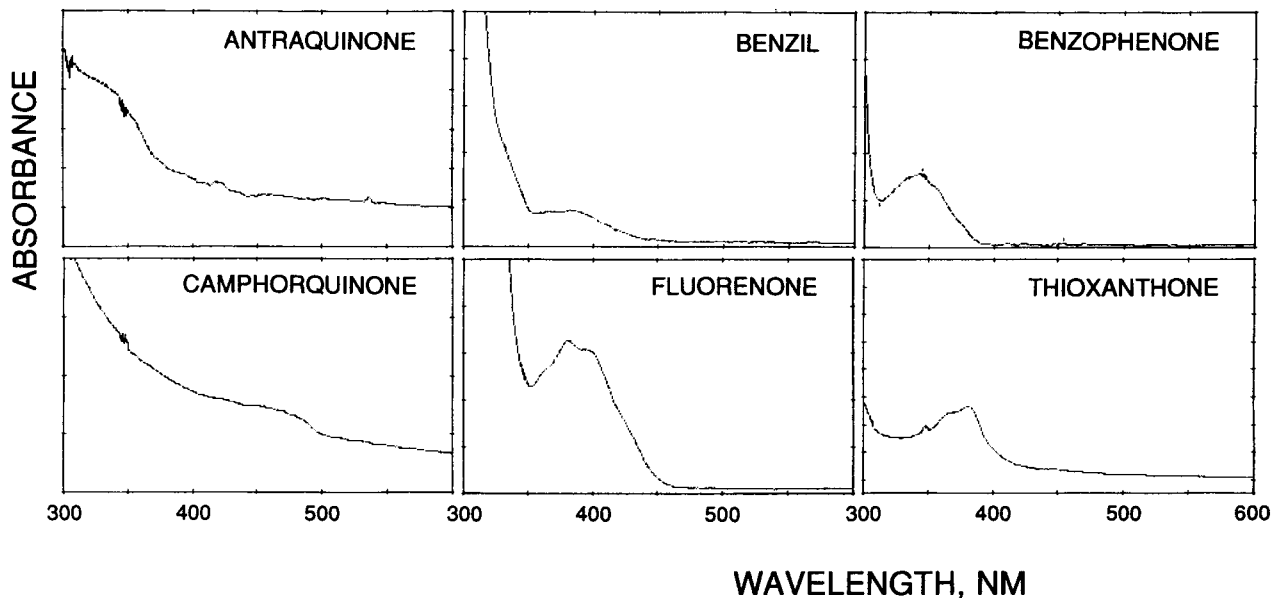
ABSORBANCE

| ANTRAQUINONE | BENZIL | BENZOPHENONE |
| CAMPHORQUINONE | FLUORENONE | THIOXANTHONE |

300   400   500   300   400   500   300   400   500   600

WAVELENGTH, NM

Figure 3   UV–VIS absorption spectra of dense films of PEPP with various photoinitiators. The photoinitiator/PEPP molar ratio was 0.5. The films were deposited on quartz slides.

not match the absorption spectrum of the poly-phosphazene, and (3) it must be nonvolatile and miscible with the polyphosphazene.

In the present work, six carbonyl compounds reported in the literature to be hydrogen ab-stractors[16,17] were considered initially. Their absorption spectra were recorded in the range of 300–600 nm and are shown in Figure 3. It can be seen that all the compounds absorbed UV radiation of 365 nm wavelength. However, only BP, benzil (BZ), and fluorenone (FN) were miscible with the polyphosphazene, as evidenced by visual observation, and by the lack of strong background scattering (Fig. 3). Of these three photoinitiators, the rate of hydrogen abstraction, as reflected by the rate of decay of the characteristic IR carbonyl band, was the highest in the case of BP (Fig. 4). Moreover, swelling measurements in DMAc of samples crosslinked with the three photoinitiators indicated that BP was the most effective photoinitiator. When the photoini-tiator/PEPP molar ratio was 0.5 and the UV irradiation time was 5 h, the equilibrium swelling in DMAc was 0.31, 0.57, and 0.68, for BP, BZ, and FN, respectively. The differences in photoreduction rate might be due to the difference in the energy of the excited triplet state (69.3, 53, and 53 kcal/mol, respectively, for the BP, BZ, and FN triplet state).[16] For the case of FN, the different nature of the triplet state [T(π,π^*) instead of T(n,π^*)] also might contribute to its weak photoreduction ability. Based on the above data, BP was chosen as the photoinitiator for further studies.

The photochemistry of benzophenone is relatively well understood.[18] When BP is irradiated with UV light of wavelength 340 nm it is excited to a singlet state S(n,π^*), which by intersystem crossing reverts to a reactive triplet state T(n,π^*). This state can be considered as a 1,2-diradical, which can abstract a
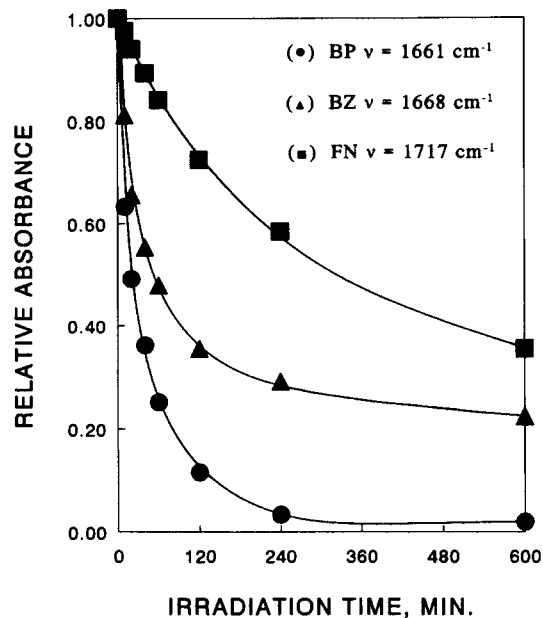
1.00
0.80
0.60
0.40
0.20
0.00

($\bullet$) BP v = 1661 cm^{-1}
($\blacktriangle$) BZ v = 1668 cm^{-1}
($\blacksquare$) FN v = 1717 cm^{-1}

RELATIVE ABSORBANCE

0   120   240   360   480   600

IRRADIATION TIME, MIN.

Figure 4   Rate of decay of IR carbonyl absorption band in the PEPP/BP ($\bullet$), PEPP/BZ ($\blacktriangle$), and PEPP/FN ($\blacksquare$) films of thickness 50 μm irradiated under Ar. From this data, the half-life was determined to be 20, 50, and 340 min, respectively, for BP, BZ, and FN.

hydrogen from a benzylic carbon of PEPP and create a macroradical and a ketyl radical. Recombination of the macroradicals leads to crosslinking while the ketyl radicals recombine to give pinacol. The crosslinking mechanism is presented schematically in Figure 5. This scheme is very simplified; possible complications will be discussed below.

Kinetics of Photocrosslinking

The progress of hydrogen abstraction from PEPP was followed using UV and IR spectroscopy. First, the results of the UV spectroscopy study will be discussed. Figure 6 shows four spectra recorded at crosslinking times 0, 10, 60, and 300 min. The BP molar ratio was 0.5 (the maximum BP/PEPP ratio studied in the present work). The decrease in intensity of the absorption band at 340 nm (carbonyl n-π^* transition) with increasing time of irradiation is evident. The rate of disappearance of the carbonyl band was then correlated with time and from this data the half-life of BP during photocrosslinking was determined to be 32 min. However, the accuracy
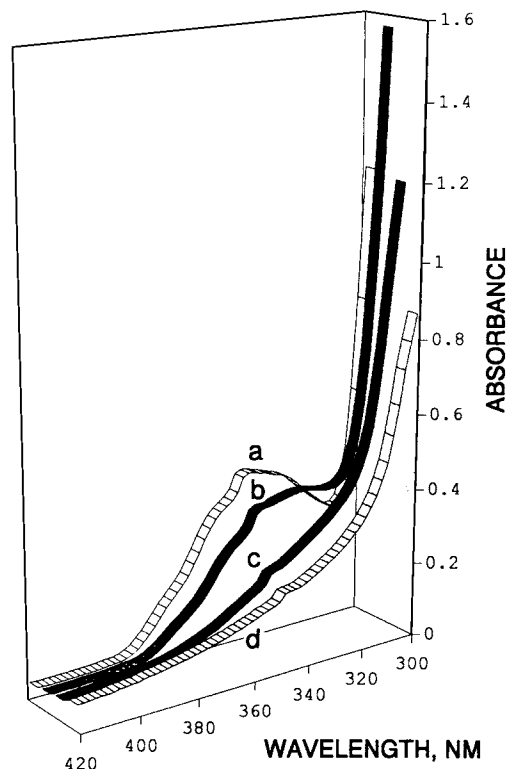

Figure 6 Disapearance of the UV carbonyl absorption band in PEPP/BP films irradiated under argon atmosphere. The irradiation time was (a) 0, (b) 10, (c) 60, and (d) 300 min.

of this determination was not good because the analytical band chosen for examination was localized at the edge of a very strong absorption band originating from the carbonyl π-π^* transition.

More precise measurements of the photocrosslinking kinetics were performed by use of FTIR spectroscopy. In these experiments the disappearance of the carbonyl stretching band at 1661 cm^{-1} was followed. The dependence of the absorbance at 1661 cm^{-1} on the time of irradiation is shown in Figure 4. A very steep decrease in absorbance during the initial period is apparent. The half-life of BP, as determined from the data in Figure 4 was 20 min, which was somewhat smaller than the value obtained from the UV measurements.

It should be noted that during the course of photocrosslinking the flexibility of the polyphosphazene chains decrease, which lowered the diffusion coefficient of BP in the polymer. This is especially true for high BP concentrations, where diffusion control was the main limitation for the rate of crosslinking. Additionally, when the concentration of the BP was very high, the BP at the surface acted as a filter for photoinitiator in the underlying polymer,[19] and the photocrosslinking rate decreased dramatically.

Figure 5 The photocrosslinking mechnism of PEPP by BP: (a) generation of a macroradical and a ketyl radical, (b) recombination of the macroradicals.

When the thickness of the irradiated film was greater than 100 μm, the intensity of the UV light source used was insufficient, and exposures longer that 5 h were required for the total conversion of BP when the BP/PEPP molar ratio was equal to 0.5. For this reason samples of thicknesses of 50–100 μm were used in the studies.

FTIR Spectra Analysis

Infrared spectra provided not only data on the disappearance of BP, but were also used to extract information on the possible mechanism of photocrosslinking. In Figure 7 there are two FTIR spectra, recorded before irradiation and after 300 min of irradiation under nitrogen. A comparison of the two spectra leads to the following conclusions: (1) the carbonyl stretching band at 1661 cm^{-1} vanishes nearly completely, which indicates almost total conversion of BP; (2) the intensity of C—H stretching bands at 2870–2960 cm^{-1} decreases, which supports the postulate that hydrogen subtraction takes place; (3) a very intense band with a maximum wavelength around 3600 cm^{-1} is indicative of the transformation of the benzophenone CO groups into COH; and (4) the bands at 1210–1240 and 940 cm^{-1} assigned to P=N and P—O—Ph stretching, respectively, decrease slightly after irradiation, which may indicate some degradation of the polyphosphazene (it was not possible to characterize the extent of this degradation process in a quantitative way).

When irradiation was carried out in air, some oxidation of the samples was observed. This process was evidenced by a very broad absorption band between 3200–3600 cm^{-1} and by the formation of a new carbonyl band at 1680 cm^{-1}, as shown in Figure 8. The carbonyl band was probably the result of decomposition of hydroperoxides formed at the surface of the film irradiated in the air. From Figure 8 it can be seen that the intensity of the carbonyl band increases as the irradiation continues. At the same time, the BP carbonyl band at 1661 cm^{-1} vanishes.

The presence of O$_2$ could, in principle, interfere with the crosslinking reaction by quenching the excited triplet state of BP and/or scavenging PEPP macroradicals.[20] During our experiments, however, only polymer oxidation was observed, as discussed above. We attribute this finding to the low solubility of O$_2$ gas in the polymer.

WAXS Measurements

Wide-angle x-ray scattering was used to investigate the crystallinity of the parent polyphosphazene and
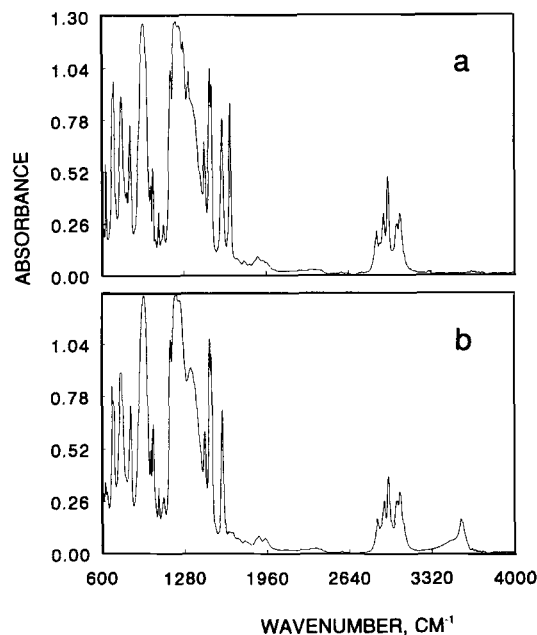

Figure 7 FTIR spectra of the PEPP/BP films. (a) Before irradiation and (b) after 300 min irradiation under argon atmosphere. The initial BP–polyphosphazene molar ratio was 0.5.

the resultant photocrosslinked films. Futamura et al.[21] studied the crystallinity of a series of phenoxy/p-ethylphenoxy–substituted polyphosphazenes. They showed that the crystallinity or order along the polymer chains (longitudinal order) was destroyed when approximately one-half of the phenoxy groups were substituted with p-ethylphenoxy. At this composition, however, lateral order was retained. Based on Futamura's report little crystallinity was expected to be present in the studied PEPP.

In Figure 9 there are shown WAXS diffractograms of some representative samples. It can be seen that the polyphosphazene is an amorphous polymer with some mesomorphic order that is destroyed after mixing with BP. In fact, the intensity of the peek at 2θ = 8° decreases from ca. 30,000 to 1500 counts after mixing with BP. The photocrosslinked films were also found to be amorphous.

Analyses of the diffractograms also lead to the conclusion that BP and PEPP were miscible over the investigated BP molar ratio range because there were no observable crystalline peaks characteristic of BP seen in the diffractogram of the polymer prior to UV irradiation.

DSC Measurements

Crosslinking of the polyphosphazene should lead to a reduction of segmental mobility of the polymer
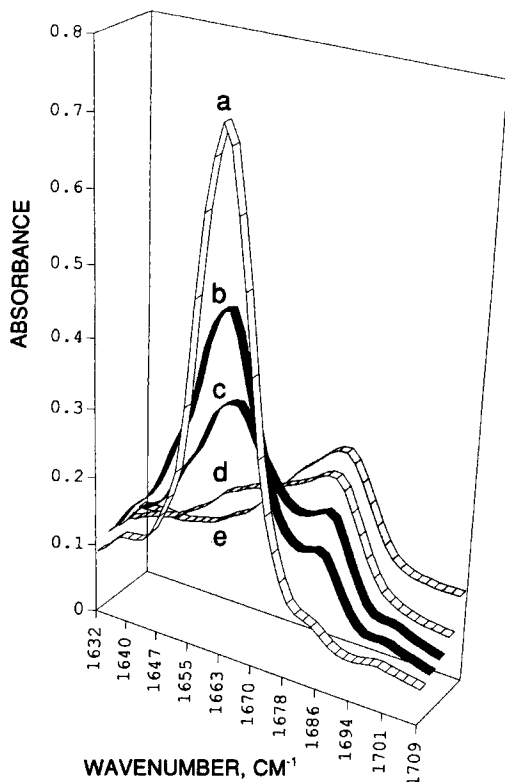
Figure 8 Oxidation of PEPP during irradiation of PEPP/BP films in air. Films thickness was 50 μm. The irradiation time was (a) 0, (b) 10, (c) 30, (d) 60, and (e) 300 min.

chains, which in turn should be reflected as an increase in the glass transition temperature. Differential scanning calorimetry was used to follow the changes in the glass transition temperature as a function of the BP concentration in the PEPP polymer prior to exposure to UV light. The results are shown in Figure 10. A clear upward shift of the glass transition temperature is apparent. It can be seen that when the BP/PEPP molar ratio was increased from 0 to 0.5, the glass transition temperature increased after UV irradiation from −8.8 to 53.5°C.

According to theoretical predictions, the dependence of the glass transition temperature on the crosslinking degree should be convex,[22] whereas the curve in Figure 10 is concave. There can be two factors accounting for this discrepancy. The first is that the amount of BP as expressed by the BP molar ratio does not reflect the true crosslinking degree because not all of the BP molecules generated crosslinks. It is possible, especially at a high BP content, that some of the macroradicals recombined with ketyl radicals and, thus, did not contribute to the formation of crosslinks. The second factor that may have influenced the curvature of the glass transition

temperature dependence is the diluent effect.[22] It should be recalled that there were two products of the photocrosslinking reaction (Fig. 5): a crosslink, i.e., a covalent bond between polymer chains, and a pinacol molecule, which acted as a low molecular weight diluent in the crosslinked polyphosphazene. The presence of this diluent should cause the glass transition temperature to decrease.

It should be concluded that crosslinking with benzophenone was very efficient, as evidenced by the fact that in the extreme case of BP/PEPP molar ratio (0.5) the glass transition temperature increased by approximately 60°C with respect to that of the uncrosslinked polyphosphazene.

Swelling in DMAc

The purpose of crosslinking PEPP was to make the polymer insoluble in organic solvents and to improve its mechanical properties. It was also important to be able to control the extent of crosslinking and, thus, the degree of membrane swelling in solvents.
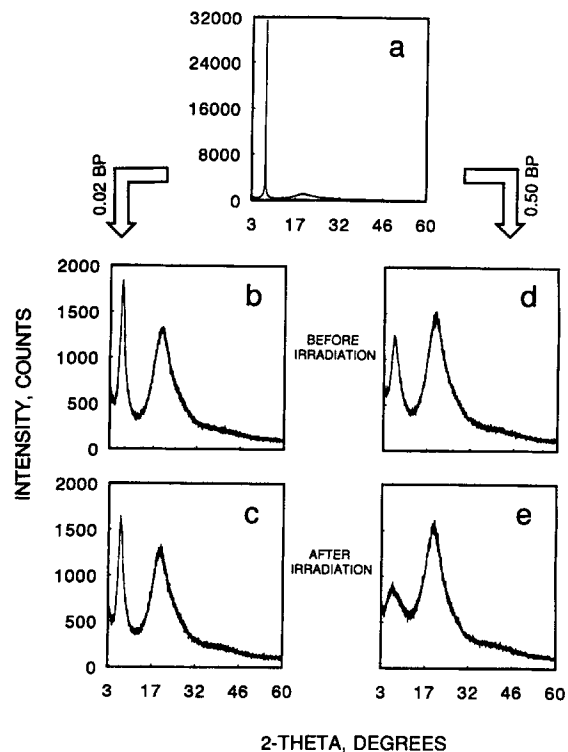

2-THETA, DEGREES

Figure 9 WAXS diffractograms of 100 μm thick PEPP films. (a) Base polymer, (b) BP/PEPP molar ratio of 0.02 before irradiation, (c) BP/PEPP molar ratio of 0.02 after irradiation for 5 h, (d) BP/PEPP molar ratio of 0.5 before irradiation, (e) BP/PEPP molar ratio 0.5 after irradiation for 5 h.
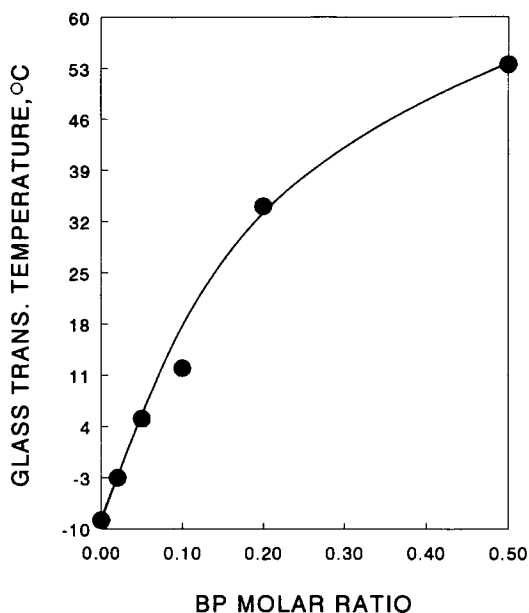
Figure 10 The dependence of the glass transition temperature on the BP/PEPP molar ratio in films irradiated for 300 min under argon atmosphere.

Figure 11 The dependence of equilibrium swelling of the photocrosslinked films in DMAc at 25°C on BP/PEPP molar ratio. Irradiation time was 300 min.

In the present study equilibrium swelling measurements were performed to determine indirectly the extent of crosslinking. The use of THF (the solvent used in the film casting procedure) was impractical for this purpose because of its high volatility. DMAc, which is also a good solvent for polyphosphazene, was used in place of THF. The results of the swelling experiments (Fig. 11) show that the equilibrium swelling decreased from infinity to 0.31 when the BP/PEPP molar ratio was increased from 0 to 0.5.

In Figure 12, the swelling properties of films irradiated for different times in nitrogen and air atmospheres are compared. In both cases, the rate and degree of crosslinking was the same. Thus, the inhibiting effect of O_2 on photocrosslinking and oxidation processes that degrade the polymer, as mentioned previously, must have been nonexistent or limited to the film surface and did not influence the bulk film properties.

Mechanical Properties

The starting, uncrosslinked polyphosphazene at room temperature was a soft and weak material with $T_g = -8.8°C$. Its tensile strength was small and the polymer flowed upon stretching. Crosslinking was expected to convert the polymer into a hard and tough rubber or a hard and brittle glass. In fact, high-performance elastomers are one of the possible
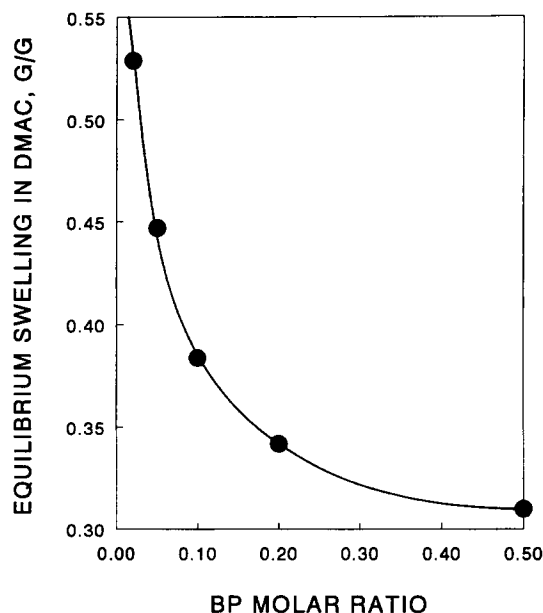
applications of the phosphazene polymers.[14] For the present study, the effect of crosslinking on the mechanical properties of PEPP was quantified. In Figure 13, the ultimate strain is plotted as a function of the BP/PEPP molar ratio prior to irradiation. It
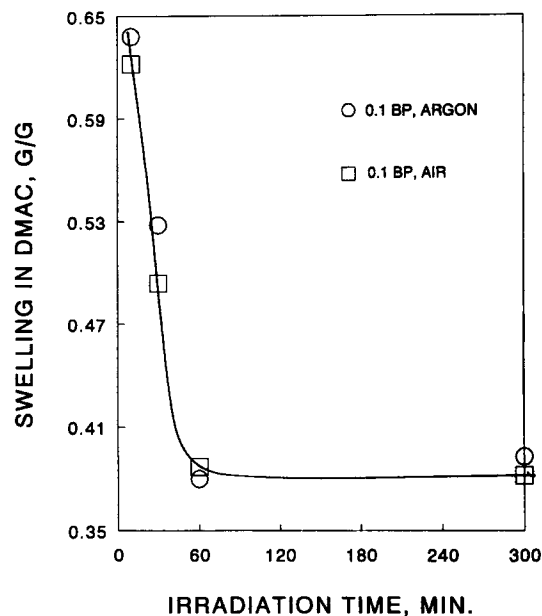

Figure 12 Comparison of the equilibrium swelling of crosslinked PEPP films irradiated for different times under argon and air atmosphere. The BP/PEPP molar ratio was equal 0.1.

can be seen that when the BP/PEPP molar ratio approached 0.15, the polymer became brittle. This is in close agreement with the T_g dependence on BP content (Fig. 10), which shows that T_g reached room temperature at a BP molar ratio of 0.15. As a result of the T_g increase, the polymer became brittle and its ultimate strain decreased dramatically. When the BP/PEPP molar ratio was greater than 0.15, only a very small residual strain of about 0.04 was observed.

The dependence of the ultimate membrane strength on the BP/PEPP molar ratio (Fig. 14) shows a maximum at a BP molar ratio of approximately 0.3. One possible explanation of this surprising finding is based on arguments analogous to that used above when analyzing the glass transition dependence on the BP molar ratio. The generation of pinacol, which acted as a low molecular weight filler (diluent) for the crosslinked polyphosphazene caused the tensile strength of the mixture to decrease. When the BP content in the polymer was low before crosslinking, the final concentration of pinacol after irradiation could not be high, and the crosslinking effect predominated over that of the filler with the net result being an increase in tensile strength. For polymer films with high BP contents prior to exposure to UV light, more pinacol was present after UV irradiation and the associated loss of strength overwhelmed the toughening effect of crosslinking.
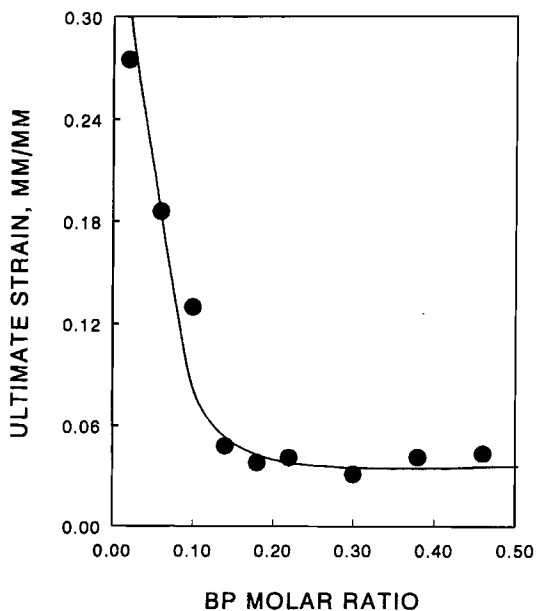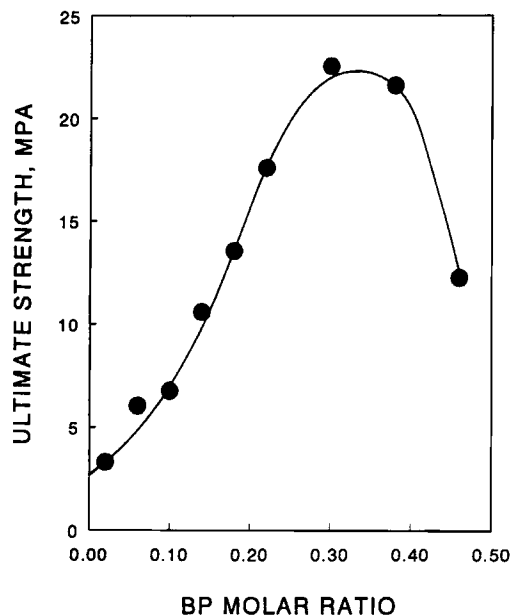

Figure 14 Ultimate strength of the photocrosslinked films as a function of the BP/PEPP molar ratio. Films thickness was 100 μm, and irradiation time was 300 min.

CONCLUSIONS

Dense films containing PEPP, with an ethylphenoxy/phenoxy molar ratio of 0.93, and a photoinitiator were crosslinked using UV light. Of six photoinitiators examined, BP worked best because it was miscible with the polyphosphazene, had the highest rate of hydrogen abstraction, and absorbed UV light of 365 nm wavelength. Its half-life during photocrosslinking was 20 min for films 50 μm in thickness.

Irradiation carried out in air atmosphere led to some surface oxidation of the samples. This oxidation, however, did not influence the photocrosslinking rate, which was the same as in the case of irradiation under an argon atmosphere.

When the BP-polyphosphazene molar ratio was increased form 0 to 0.5, the glass transition temperature of the polymer after photocrosslinking increased from -8.8 to $+53.5°C$, and the equilibrium swelling in dimethylacetamide decreased from infinity to 0.31.

Figure 13 Ultimate strain of the photocrosslinked films as a function of the BP/PEPP molar ratio. Films thickness was 100 μm, and irradiation time was 300 min.

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