Synthesis of Photo-Cross-Linkable Chalcone-Bearing Polyphosphazenes

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ABSTRACT: Cyclic and high-polymeric phosphazenes that bear 4-(1-oxo-1-phenyl-2-propen-3-yl)phenoxy (4-oxychalcone) side groups have been prepared to study their photochemical behavior. Small-molecule cyclic trimers of the general formula $N_3P_3R_5R'$, where R = phenoxy, 2,2,2-trifluoroethoxy, chloro, and 4-oxychalcone and R′ = 4-oxychalcone, were synthesized to model the cross-linking reactions at the high-polymer level. Single-substituent and cosubstituent polymeric phosphazenes $[NPRR']_n$, where R = phenoxy, 2,2,2-trifluoroethoxy, or 4-oxychalcone and R′ = 4-oxychalcone were also prepared. Their photolytic cross-linking was monitored by ultraviolet spectroscopy. The high-polymeric system is of interest for uses in photolithography, photocurable coatings, and the stabilization of nonlinear optical properties.

Introduction

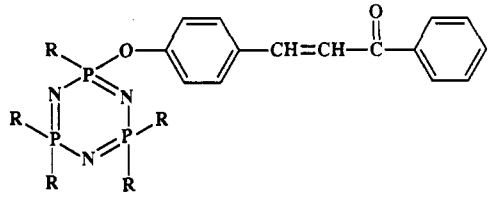
The field of photo-cross-linkable polymers has been widely studied and is of broad current interest. Such polymers are used in the preparation of photoresists for use in macro- and microlithography,[1] in the preparation of chemically-resistant coatings, and in the field of nonlinear optical (NLO) materials.[2,3]

A classical photosensitive moiety is the cinnamate group. This system is well-studied and widely used in photo-cross-linkable polymers[1] because of the high sensitivity to UV radiation and the chemical resistance of the resultant polymers. However, another photosensitive unit, the chalcone group, is particularly useful for these purposes because of the higher overall photosensitivity of the chalcone unit compared with that of the classical cinnamate system. This is a result of the closer match between the absorption spectrum of the chalcone side group and the emission spectrum of a mercury arc UV light source. This improved spectral match allows for increased photo-cross-linking efficiency without the use of an added sensitizer.

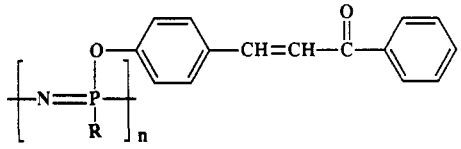
Polymeric materials that contain chalcone-type groups have existed since 1959.[4] These species include macromolecules with chalcone-type groups in the side chain,[4–14] in the main chain,[15–19] and in epoxy resins.[20–23] Due to the solubility difficulties arising from the rigid-rod nature of main-chain-containing chalcone polymers, a recent emphasis has been on polymers with side-chain chalcone units. Although the photo-cross-linking of polymers that bear side-chain chalcone units has been reported both in the open literature and in patents, use of the polyphosphazene inorganic backbone as a platform for chalcone-bearing side units is unexplored. The work described here involves the synthesis and characterization of both small-molecule model cyclic trimers and high-polymeric phosphazenes that bear chalcone side groups (see Chart 1).

The use of the phosphazene system has several advantages in the field of photoreactive materials. (1) The small-molecule cyclic trimers allow a detailed study to be made of the ultraviolet (UV)-induced 2 + 2 cycloaddition of chalcone side units as a model for the photo-cross-linking of the related high polymer. Photoreactivity studies with small molecules are facilitated by the ease of solution characterization using ^1H, ^{13}C, and ^{31}P NMR spectroscopy, UV spectroscopy, and mass spectrometry. (2) The presence of two photo-cross-linkable groups per repeat unit in polyphosphazenes should result in a high cross-link density following UV irradiation compared to classical organic-backbone polymers. (3) The method of side-group incorporation in polyphosphazenes allows the properties of the photoreactive polymers to be controlled over a broad range by the choice of cosubstituents. (4) The phosphazene backbone is transparent from the near- and mid-UV to the near-infrared region, and this minimizes degradation of the skeleton both under the high-intensity UV irradiation required for the photo-cross-linking reaction and during subsequent exposure to light.

Chart 1



2: R = Cl
3: R = OPh
4: R = OCH_2CF_3
5: R = $OC_6H_4CH{=}CHC(O)C_6H_5$



6: R = $OC_6H_4CH{=}CHC(O)C_6H_5$
7: R = OCH_2CF_3
8: R = OPh

Results and Discussion

Synthesis and Characterization of Cyclic Phosphazene Model Compounds. The synthetic route to cyclic trimeric phosphazenes used as reaction models for the high polymers is shown in Scheme 1. The primary model system was simplified by use of monofunctional cyclotriphosphazenes. In addition, a hexachalcone-substituted cyclic trimer was prepared to model a polymer in which every phosphorus atom would bear two photosensitive side groups. Cyclotriphosphazenes 2–4 were synthesized in

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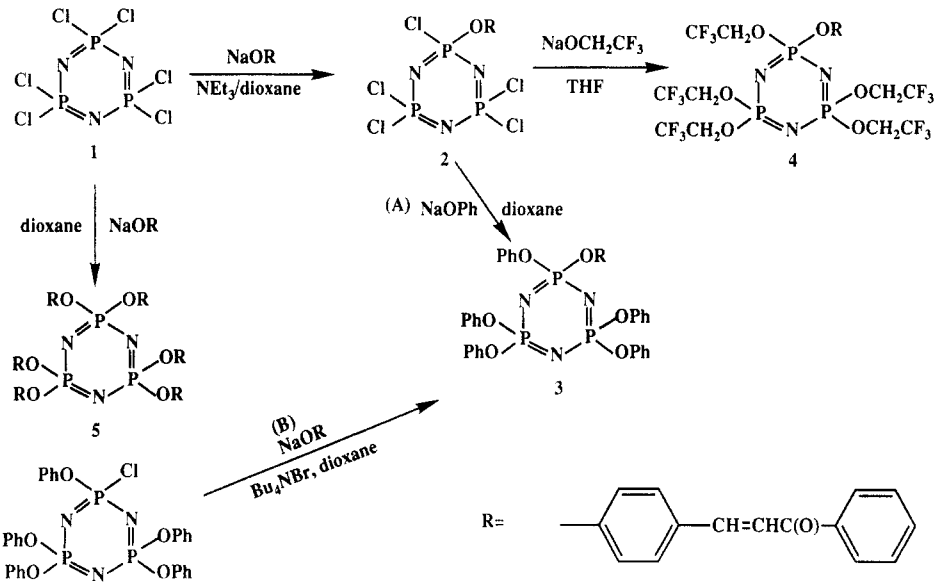
Scheme 1



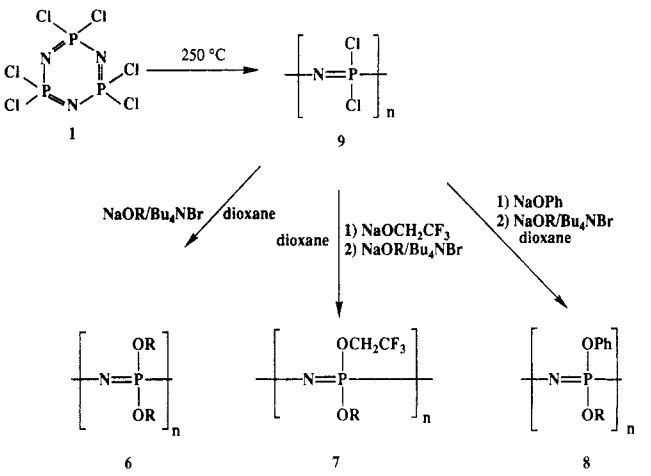
the following way: The pentachloromonochalcone derivative, $N_3P_3Cl_5\{OC_6H_4CH{=}CHC(O)C_6H_5\}$ (**2**), was obtained in 35% yield by the interaction of hexachlorocyclotriphosphazene (**1**) with 4-hydroxychalcone in the presence of triethylamine (as a hydrochloride acceptor) in dioxane heated to reflux. This compound, which was isolated as beige plates after column chromatography, was characterized by ^{31}P, ^{13}C, and ^1H NMR, mass spectrometry, melting point, ultraviolet (UV) absorption spectroscopy, and elemental analysis (see Experimental Section).

The pentaphenoxymonochalcone derivative, $N_3P_3(OC_6H_5)_5\{OC_6H_4CH{=}CHC(O)C_6H_5\}$ (**3**), was synthesized via two routes. Route A involved the addition of 5.2 equiv of sodium phenoxide to trimer **2** at 12 °C, followed by warming to 45 °C for 12 h. Route B involved the treatment of $N_3P_3(OPh)_5Cl$ with 3 equiv of $NaOC_6H_4CH{=}CHC(O)C_6H_5$ in the presence of Bu_4NBr in dioxane heated to reflux. Both routes gave nearly quantitative yields of trimer **3**. However, route A is preferred due to the shorter reaction time and less drastic reaction conditions required. Trimer **3** was characterized by ^{31}P, ^{13}C, and ^1H NMR, +FAB-MS, UV spectroscopy, and elemental analysis (see Experimental Section).

The pentakis(trifluoroethoxy)monochalcone derivative, $N_3P_3(OCH_2CF_3)_5\{OC_6H_4CH{=}CHC(O)C_6H_5\}$ (**4**), was synthesized by the addition of 5.2 equiv of $NaOCH_2CF_3$ to a THF solution of trimer **2** cooled to −80 °C. After purification, trimer **4** was characterized by ^{31}P, ^{13}C, and ^1H NMR spectroscopy, mass spectrometry (MS), and elemental analysis. The structure of trimer **4** was further elucidated by nuclear Overhauser effect (NOE) difference spectroscopy. In the ^1H NMR spectrum, the trifluoroethoxy group geminal to the aryloxy group and the four other trifluoroethoxy groups nongeminal to the aryloxy group were found to be nonequivalent. However, nonequivalency was detected in the four nongeminally substituted trifluoroethoxy groups. A slight NOE was detected in the aryloxy protons when the signal at 3.97 ppm was irradiated, thus allowing the assignment of this signal as that of those trifluoroethoxy groups *cis* to the aryloxy group.

Lastly, the hexachalcone-substituted cyclotriphosphazene, $[NP\{OC_6H_4CH{=}CHC(O)C_6H_5\}_2]_3$ (**5**), was synthesized in 30% yield from **1** and $NaOC_6H_4CH{=}CHC(O)C_6H_5$ in dioxane heated to reflux. Trimer **5** was characterized by ^{31}P, ^{13}C, and ^1H NMR, +FAB-MS, UV spectroscopy, and elemental analysis.

Scheme 2

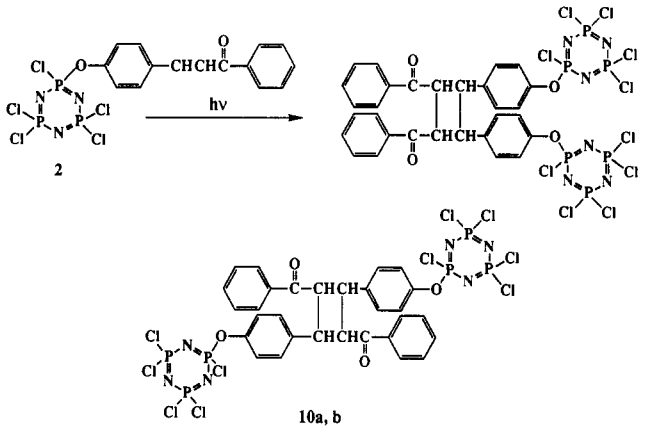


Synthesis and Characterization of High-Polymeric Phosphazenes. The synthetic pathway to polymers **6**, **7**, and **8** is illustrated in Scheme 2. Poly(dichlorophosphazene) (**9**) was prepared by the thermal ring-opening polymerization of **1**.[24-26] The synthesis of polymer **6** was accomplished by allowing an excess of the sodium salt of 4-hydroxychalcone to react with **9** in dioxane heated to reflux. The polymer was isolated by precipitation of concentrated THF solutions into water (4×), 2-propanol (3×), and hexane (2×). Polymer **6** was characterized by ^{31}P, ^{13}C, and ^1H NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), UV spectroscopy, and elemental analysis.

The synthesis of polymer **7** was carried out in the following manner. Compound **9** was treated with 1 equiv of sodium 2,2,2-trifluoroethoxide in dioxane followed by an excess of the sodium salt of 4-hydroxychalcone in the presence of Bu_4NBr. The mixture was heated to reflux for 10 days. Polymer **7** was characterized by ^{31}P, ^{13}C, and ^1H NMR spectroscopy, GPC, DSC, UV spectroscopy, and elemental analysis.

The phenoxy cosubstituent polymer **8** was obtained first by treatment of polymer **9** with 1 equiv of sodium phenoxide. This partially substituted polymer was then treated with an excess of $NaOC_6H_4CH{=}CHC(O)C_6H_5$ in the presence of Bu_4NBr in dioxane heated to reflux for 9 days. The polymeric product was isolated by precipitation from THF into water (4×), 2-propanol (2×), and hexane (1×) and characterized by ^{31}P, ^{13}C, and ^1H NMR, UV

Scheme 3



spectroscopy, DSC, and elemental analysis.

Glass Transition Studies of High Polymers. The thermal behavior of polymers **6–8** was investigated with the aid of differential scanning calorimetry. The chalcone homopolymer **6** possesses a T_g at 62 °C, which indicates a moderate degree of backbone stiffness induced by the sterically demanding side groups. The incorporation of the less hindered trifluoroethoxy and phenoxy cosubstituents lower the T_g's of polymers **7** and **8** respectively to 44 and 37 °C.

Ultraviolet Absorption Studies of Cyclic Trimers. The UV-induced 2 + 2 cycloaddition reaction of cyclic trimers that bear the chalcone side group was investigated by the irradiation of trimer **2** with a medium-pressure Hg lamp (see Scheme 3). Trimer **2** had an absorption at 305 nm (THF solvent). Species **2** was irradiated in the solid state for 7 h, during which time a decrease occurred in the absorbance in the region of 305 nm, with concurrent formation of a mixture of dimers **10a** and **10b**. The mixture was isolated by preparative thin-layer chromatography and was characterized in its impure form by ^{31}P and ^{1}H NMR spectroscopy and mass spectrometry. Positive FAB mass spectrometry detected the molecular ion MH^+ at 1071 mass units, which matches the masses of the expected cyclobutane-type dimers. The mass spectrum of the mixture showed no evidence of open-chain (non-cyclobutane) saturated species (M^+ = 1073). The ^{1}H NMR spectrum of the mixture, which showed several symmetrical multiplets in the region of 3.9–5.0 ppm, is consistent with the formation of isomers **10a** and **10b**.

The UV spectra of trimers **3**, **4**, and **5** were also studied. UV absorption experiments indicated a λ_{max} in the region of 315, 309, and 312 nm for trimers **3**, **4**, and **5**, respectively. The hypsochromic shift of the λ_{max} of trimers **2** and **4** is attributed to the withdrawal of electrons by the chloro and the trifluoroethoxy ligands in **2** and **4**, respectively.

Ultraviolet Absorption of High Polymers. The 2 + 2 cycloaddition reactions of polymers **6–8** were also investigated. Thin films of the polymers were cast onto a quartz plate from inhibitor-free THF followed by complete removal of the casting solvent in vacuo. The λ_{max} due to the chalcone chromophore was found to be 320 nm and was independent of the cosubstituent. This suggests minimal electronic interaction between side groups through the phosphazene backbone.

Photolytic Cross-Linking Studies of High Polymers. The photolytic cross-linking of polymers **6–8** was followed by UV spectroscopy (see Figures 1–3). Thin films were cast from THF and were irradiated with a filtered sunlamp (λ = 260–380 nm) UV source. Figure 1 also gives some insight into the effect of UV radiation on polymer **6**. Immediately apparent is the decrease of the absorbance at 320 nm, attributed to a UV-induced 2 + 2 cycloaddition reaction. Also evident is a small increase in the absorbance at 244 nm due to the *cis* form of the chalcone group arising from *cis–trans* isomerization. However, the predominant reaction is cross-linking as shown by the greater change in the 320-nm absorption and the insolubility of polymers **6–8** in common organic solvents.

Photochemical cross-linking was monitored by measuring the relative intensity of the 320-nm absorption. It

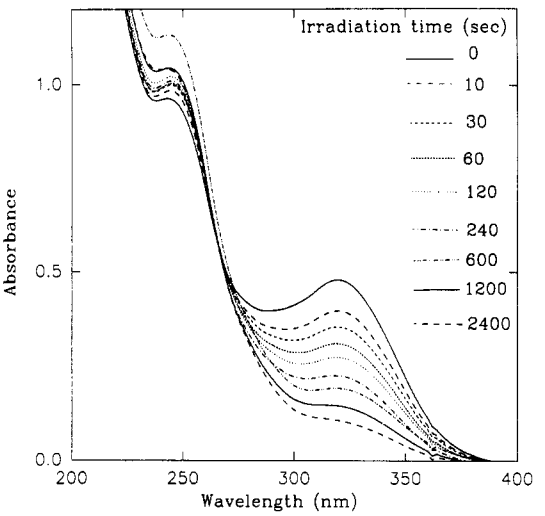


Figure 1. Effect of UV irradiation time on the UV spectrum of polymer **6**.

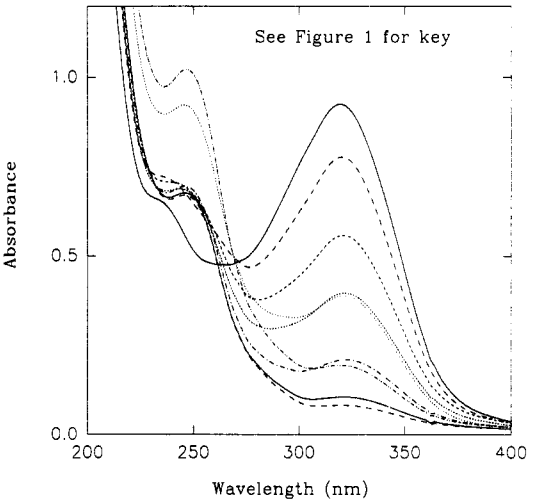


Figure 2. Effect of UV irradiation time on the UV spectrum of polymer **8**.

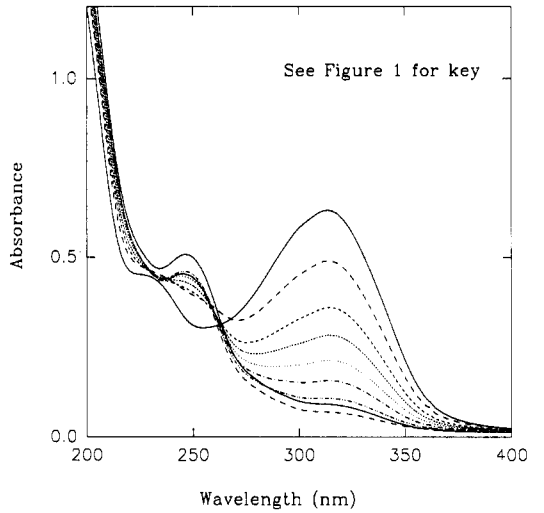


Figure 3. Effect of UV irradiation time on the UV spectrum of polymer **7**.

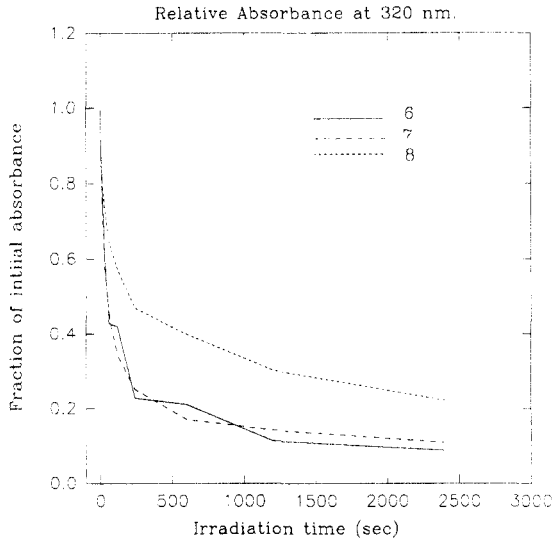


Figure 4. Relative absorbances at 320 nm of polymers 6–8 during irradiation.

was found that, after a total of 10-min exposure to UV light, the absorption corresponding to the carbon–carbon double bond α to the carbonyl at 320 nm had decreased in intensity to approximately 10–30% of the initial value.

Also, the relative sensitivities of the polymers $[NP\{OC_6H_4CH{=}CHC(O)C_6H_5\}_2]_n$ (**6**), $[NP\{OCH_2CF_3\}_{0.93}\{OC_6H_4CH{=}CHC(O)C_6H_5\}_{1.07}]_n$ (**7**), and $[NP\{OC_6H_5\}_1\{OC_6H_4CH{=}CHC(O)C_6H_5\}_1]_n$ (**8**) were studied by comparing the UV absorbances at 320 nm *versus* irradiation time (see Figure 4). Minimal differences were found between **7** and **8**, but polymer **6** was found, perhaps surprisingly, to be the least sensitive to UV irradiation, with the absorbance reaching a plateau at 30% of the initial absorption.

Attempts to sensitize polymer **6** with 4-nitrophenol and 4-nitroanisole yielded only a modest increase in the rate of photo-cross-linking.

Conclusions

The thermal analysis of chalcone-substituted polymers **6–8** indicated that all possessed T_g's above room temperature, with polymer **6** having the highest T_g at 62 °C. These T_g's provide a better starting point for microlithographic, nonlinear optical, or surface coating applications than those generated by the cinnamate systems (T_g's of −25 to +59 °C) discussed in the preceding paper.

The photo-cross-linking reaction of chalcone polymers **6–8** can be understood in terms of intermolecular 2 + 2 cycloaddition reactions. These reactions were modeled by the irradiation of a small-molecule chalconechlorophosphazene species, **2**, and its cyclodimerization to form species **8**.

The chalcone polymer system has several advantages over the cinnamate system, in addition to the higher T_g's. The absorption maximum of the chalcone group at 320 nm closely matches the emission spectrum of a medium-pressure mercury arc lamp.[1] This improved spectral match should provide greater photosensitivity than in the cinnamate system, and without the use of a photosensitizer. Lastly, the chalcone-derivatized polyphosphazenes are easier to prepare than the cinnamate counterparts due to the smaller number of synthetic steps.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was provided by Ethyl Corp. It was recrystallized from hexane and sublimed (40 °C, 0.05 mmHg) before use. Tetrahydrofuran and dioxane were distilled from sodium benzophenone under dry argon before use. Triethylamine was distilled from calcium hydride in an atmosphere of argon before use. 2,2,2-Trifluoroethanol (Halocarbon) was distilled from anhydrous barium oxide and was stored over 4-Å molecular sieves. 4-Hydroxychalcone was obtained from Lancaster Synthesis (Windham, NH) and was used as received. Phenol (Aldrich) was dried azeotropically with benzene before use and was stored under argon. All other reagents and solvents were used as received. The reactions were performed under an atmosphere of dry argon using standard Schlenk line techniques. Column chromatography was carried out with the use of silica as a stationary phase with the eluents as indicated in the text. Poly(dichlorophosphazene) was prepared by the standard literature procedure.[24–26]

Equipment. High-field ^{31}P (146 MHz), ^{13}C (90 MHz), and ^1H (360 MHz) NMR spectra were obtained with a Bruker WM360 spectrometer. ^{13}C (50 MHz) and ^1H (200 MHz) NMR spectra were also obtained with a Bruker WP200 spectrometer or a Bruker ACE200 spectrometer. Nuclear Overhauser effect (NOE) difference spectra were obtained with a Bruker AM300 spectrometer. Both ^{13}C and ^{31}P NMR spectra were proton decoupled unless otherwise specified. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 with positive shifts recorded downfield of the reference. ^1H and ^{13}C NMR spectra were referenced to external tetramethylsilane. Elemental analyses were by Galbraith Laboratories (Knoxville, TN). Irradiations were accomplished with a "Blak-Ray" ultraviolet lamp (Ultra-Violet Products, Inc., San Gabriel, CA) or a Canrad-Hanovia medium-pressure quartz mercury vapor lamp equipped with a water-cooled quartz immersion well. Electron-impact mass spectra (EI/MS) were obtained with a Kratos MS 9/50 spectrometer. Chemical ionization (CI) mass spectra were obtained with a Kratos MS-25 spectrometer. Fast atom bombardment (FAB) mass spectra were obtained with a Kratos MS-50 spectrometer. Molecular weights were determined with a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a HP-1037A refractive index detector and a Polymer Laboratories PL gel 10-μm column. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF. The GPC column was calibrated with polystyrene standards (Waters) and with fractionated samples of poly[bis(trifluoroethoxy)phosphazene] provided by Drs. R. Singler and G. Hagnauer of the U.S. Army Materials Research Laboratories, Watertown, MA. UV–visible spectra of all compounds as solutions in spectroscopic grade THF or methanol were obtained with a Hewlett-Packard Model HP8450A UV–visible spectrometer. The spectra were recorded in quartz cells (1-cm path length) or on quartz plates for solid polymeric samples. Glass transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer 7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. Heating rates of 10–40 °C/min under a nitrogen atmosphere were used. Sample sizes were between 10 and 30 mg.

Synthesis of $N_3P_3Cl_5\{OC_6H_4CH{=}CHC(O)C_6H_5\}$ (2). To a solution of **1** (4.0 g, 11.50 mmol) in dioxane (250 mL) and triethylamine (15 mL) was added 4-hydroxychalcone (2.58 g, 11.52 mmol). The solution was heated to reflux overnight and filtered. The solvent was removed under reduced pressure, and the oil was chromatographed on silica using THF/hexane as the eluent. ^{31}P NMR (146 MHz, $CDCl_3$) AM_2, ν_A = 12.7 ppm, ν_B = 23.1 ppm, J_{PNP} = 61 Hz. ^1H NMR (200 MHz, $CDCl_3$) δ 8.06–8.00 (d, 2 H), 7.84–7.47 (m, 7 H), 7.37–7.31 (m, 2 H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 190.2, 150.7 (d, J = 10.4 Hz), 143.0, 138.1, 133.7 (d, J = 2.2 Hz), 133.0, 130.05, 128.8, 128.6, 123.0, 122.0 (d, J = 5.5 Hz). MS, m/z calcd 535, m/z found 536 (MH^+). λ_{max}(THF) = 315 nm. mp = 112–115 °C. Anal. Calcd for $C_{15}H_{11}Cl_5N_3O_2P_3$: C, 33.65; H, 2.07; N, 7.85; P, 17.35; Cl, 33.10. Found: C, 33.49; H, 2.19; N, 8.10; P, 17.89; Cl, 32.70.

Synthesis of $N_3P_3(OC_6H_5)_5\{OC_6H_4CH{=}CHC(O)C_6H_5\}$ (3). Sodium phenoxide was prepared from phenol (1.05 g, 11.2 mmol) and sodium metal (0.26 g, 10.8 mmol) in dioxane (250 mL). To the sodium salt solution at 10 °C was added **2** (1.0 g, 2.87 mmol) in dioxane (40 mL) over 1 h with stirring. The solution was allowed to warm slowly to room temperature and was stirred overnight at 40 °C. The solvent was removed under reduced pressure, and the residue was chromatographed on silica using THF/hexane as the eluents to obtain a pale yellow oil. ^{31}P NMR (146 MHz, $CDCl_3$) δ 9.36–9.11 (m). ^1H NMR δ 8.06–8.01 (m, 2

H), 7.81–7.73 (d, 2 H, J = 16 Hz), 7.62–7.40 (m, 5 H), 7.3–6.91 (m, 28 H). MS, m/z calcd 823, m/z found 824 (+FAB). UV λ_{max}(THF) = 315 nm. Anal. Calcd for $C_{45}H_{36}N_3O_7P_3$: C, 65.62; H, 4.41; N, 5.10; P, 11.28. Found: C, 65.43; H, 4.51; N, 5.18; P, 11.40.

Synthesis of $N_3P_3\{OCH_2CF_3\}_5\{OCH{=}CHC(O)C_6H_5\}$ (4). To a suspension of sodium metal (0.22 g, 9.17 mmol) in THF (50 mL) was added 2,2,2-trifluoroethanol (0.97 g, 9.7 mmol). This solution was stirred overnight and was then added over 2 h to a solution of **2** (1.0 g, 1.86 mmol) in THF (50 mL) cooled to −80 °C. The mixture was stirred for 1 h after the addition of $NaOCH_2CF_3$ was complete and was then allowed to warm slowly to room temperature. After the mixture had been stirred overnight at room temperature, the solvent was removed by rotary evaporation, and the residue was dissolved in diethyl ether (200 mL) and washed with water (3 × 100 mL). The organic layer was dried ($MgSO_4$), the solvent was removed, and the oil was dissolved in 8 mL of 40% THF/hexane. The oil was chromatographed on silica using increasing amounts of THF in hexane (0 → 50%, 5% increments, 500-mL fractions) to yield a pale yellow oil. ^{31}P NMR ($CDCl_3$, 146 MHz) AM_2, ν_A = 17.4 ppm, ν_B = 13.7 ppm, J_{PNP} = 92 Hz. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.06–8.00 (m, 2 H), 7.76 (d, 1 H, J = 15 Hz), 7.67–7.43 (m, 6 H), 7.37–7.23 (m, 2 H), 4.49–4.37 (m, 2 H (OCH_2CF_3 *gem* to OAr)), 4.35–4.18 (m, 4 H (OCH_2CF_3 *trans* to OAr)), 4.08–3.80 (m, 4 H (OCH_2CF_3 *cis* to OAr)). MS, m/z calcd 853, m/z found 853.5 (+FAB). λ_{max}(THF) = 308 nm. Anal. Calcd for $C_{25}H_{21}F_{15}N_3O_7P_3$: C, 35.19; H, 2.48; N, 4.92; P, 10.89; F, 33.39. Found: C, 34.96; H, 2.48; N, 4.93; P, 10.03; F, 32.01.

Synthesis of $[NP\{OC_6H_4CH{=}CHC(O)C_6H_5\}_2]_3$ (5). To a suspension of NaH (0.62 g, 26.0 mmol) in dioxane (250 mL) was added 4-hydroxychalcone (5.79 g, 25.8 mmol). The orange solution was heated gently overnight, after which was added solid **1** (1.0 g, 2.87 mmol). The solution was then heated to reflux for 4 days. The solvent was removed by rotary evaporation, and the yellow oil was chromatographed on silica using THF/hexane as the eluent. Yield: 1.29 g (30%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.00–7.94 (m, 2 H), 7.77 (d, 1 H, J = 16 Hz), 7.61–7.41 (m, 6 H), 7.06 (d, 2 H, J = 9 Hz). ^{13}C NMR ($CDCl_3$, 90 MHz) δ 189.9, 151.9, 143.1, 137.9, 132.9, 132.2, 129.7, 128.6, 128.4, 122.1, 121.4. MS, m/z calcd 1473, m/z found 1475 (MH^+) (+FAB). λ_{max}(THF) = 312 nm. Anal. Calcd for $C_{90}H_{66}N_3O_{12}P_3$: C, 73.31; H, 4.51; N, 2.85. Found: C, 72.59; H, 4.45; N, 2.70.

Synthesis of $[NP\{OC_6H_4CH{=}CHC(O)C_6H_5\}_2]_n$ (6). To a suspension of NaH (0.83 g, 34 mmol) and Bu_4NBr in dioxane (250 mL) was added 4-hydroxychalcone (7.72 g, 34.75 mmol). After this solution had been heated at 35 °C overnight, it was added dropwise to a solution of **9** (1.0 g, 8.6 mmol) in dioxane (500 mL). The solution was heated for 11 days at reflux. The solvent was removed under reduced pressure, and the polymeric product was isolated and purified by precipitation of viscous THF solutions into water (4×), 2-propanol (2×), and hexane (1×). ^{31}P NMR ($CDCl_3$, 146 MHz) δ −20.36 (s). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.70–6.68 br m. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 189.41, 152.36, 142.65, 137.59, 132.70, 131.39, 129.53, 128.47, 128.39, 121.43, 120.99. λ_{max}(THF) = 317 nm. M_w = 4.4 × 10^6; M_n = 6.1 × 10^6; M_w/M_n = 1.4. T_g = 62 °C. Anal. Calcd for $C_{30}H_{22}O_2NP$: C, 80.35; H, 4.91; N, 3.12; P, 6.75; Cl, 0. Found: C, 71.87; H, 4.88; N, 2.54; P, 6.16; Cl, 0.026.

Synthesis of $[NP\{OCH_2CF_3\}_{0.93}\{OC_6H_4CH{=}CHC(O)C_6H_5\}_{1.07}]_n$ (7). A suspension of sodium metal (0.40 g, 16.7 mmol) in dioxane (150 mL) and 2,2,2-trifluoroethanol (1.73 g, 17.3 mmol) was stirred overnight. This was added dropwise to a solution of **9** (2.0 g, 17.2 mmol) in dioxane (1000 mL). After this solution had been stirred overnight at 35 °C, a solution of $NaOC_6H_4CH{=}CHC(O)C_6H_5$ (prepared from $HOC_6H_4CH{=}CHC(O)C_6H_5$ (11.59 g, 51.7 mmol) and NaH (1.24 g, 52 mmol) and Bu_4NBr (0.55 g, 1.72 mmol) in dioxane (250 mL)) was added, and the orange solution was heated to reflux for 10 days. The solvent was removed under reduced pressure to give a viscous solution which was poured slowly into water (4×), 2-propanol (1×), and hexane (1×) to precipitate the polymeric product. ^{31}P NMR ($CDCl_3$, 146 MHz) δ −9.75, −13.62, −17.89 (1:3:1). ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.0–6.6 (Ar, br), 4.1–3.7 (br, OCH_2CF_3). ^{13}C NMR ($CDCl_3$, 90 MHz) δ 189.8, 140.0 (q, J = 443 Hz), 132.9, 129.7, 128.7, 128.5, 127.8, 124.1, 121.9, 120.9, 62.9. M_w = 5.8 × 10^6; M_n = 4.4 × 10^6; M_w/M_n = 1.3. T_g = 44 °C. Anal. Calcd: C, 53.88; H, 3.45; N, 3.91; Cl, 0; F, 17.02. Found: C, 56.73; H, 3.98; N, 3.54; Cl, 0.52; F, 14.01.

Synthesis of $[NP\{OC_6H_5\}_1\{OC_6H_4CH{=}CHC(O)C_6H_5\}_1]_n$ (8). To a stirred suspension of NaH (0.62 g, 25.8 mmol) in dioxane (250 mL) was added phenol (2.43 g, 25.8 mmol). After the solution had been stirred overnight at room temperature, it was added dropwise to **9** (3.0 g, 25.8 mmol) in dioxane (1000 mL). This solution was heated to 45 °C overnight. $NaOC_6H_4CH{=}CHC(O)C_6H_5$ (prepared from 17.3 g (77.2 mmol) of $HOC_6H_4CH{=}CHC(O)C_6H_5$ in 300 mL of dioxane) and Bu_4NBr (0.83 g, 2.6 mmol) were added over 15 min, and the orange solution was stirred at a gentle reflux for 9 days. The polymeric product was isolated by precipitations into water (4×), 2-propanol (2×), and hexane (1×). ^{31}P NMR ($CDCl_3$, 146 MHz) δ −19.2. ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.8–6.8 (br). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 189.70, 152.82, 151.06, 143.39, 137.87, 132.67, 130.75, 129.33, 129.10, 128.44, 128.34, 124.24, 121.17, 120.70. M_w = 3.1 × 10^6; M_n = 1.5 × 10^6; M_w/M_n = 2.1. T_g = 37 °C. Anal. Calcd: C, 69.8; H, 4.4; N, 3.5; Cl, 0. Found: C, 68.05; H, 4.66; N, 3.71; Cl, 0.68.

Irradiation of 6, 7, and 8. Solutions of polymers **6–8** (approximately 0.1% w/v) were cast onto quartz plates. Following evaporation in air and vacuum drying, they were irradiated 23 cm from a Blak-Ray lamp equipped with a 260–380-nm bandpass filter for varying lengths of time. Sensitization experiments were accomplished with the above lamp in the absence of a filter on similar films with 1 wt % of photosensitizer (as indicated in the text) based on polymer.

Synthesis of 10. Trimer **2** (100 mg) was irradiated in the solid state from a distance of approximately 7 cm from an unfiltered 450-W Hanovia ultraviolet light source in air for approximately 7 h. Dimer **10** was isolated by preparative TLC (silica gel substrate, 10% EtOAc/hexane). ^{31}P NMR ($CDCl_3$, 146 MHz) AM_2, ν_A = 12.7 ppm, ν_B = 23.1 ppm. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8–7.0 (m, 18 H), 5.05–4.75 (m, 4 H). MS, m/z calcd 1071, m/z found 1072 (+FAB).

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References and Notes

(1) Reiser, A. *Photoreactive Polymers*; Wiley-Interscience: New York, 1988.
(2) Tripathy, S. K.; Mandal, B. K.; Jeng, R. J.; Kumar, J. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 607.
(3) Tripathy, S. K.; Mandal, B.; Jeng, R. J.; Lee, J. Y.; Kumar, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 94.
(4) Unruh, C. C. *J. Appl. Polym. Sci.* **1959**, *6*, 358.
(5) Akelah, A.; Selim, A.; El-Deen, N. S.; Kandil, S. H. *Polym. Int.* **1992**, *28*, 307.
(6) Unruh, C. C. *J. Polym. Sci., Part A-1* **1960**, *45*, 325.
(7) Watanabe, S.; Harashima, S.; Tsukada, N. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 1227.
(8) Watanabe, S.; Kato, M.; Kogakai, S. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2801.
(9) Kato, M.; Ichijo, K. I.; Hasegawa, M. *J. Polym. Sci., Part A-1* **1971**, *9*, 2109.
(10) Panda, S. P. *J. Appl. Polym. Sci.* **1974**, *18*, 2317.
(11) Hatanaka, H.; Sugiyama, K.; Nakaya, T.; Imoto, M. *Makromol. Chem.* **1975**, *176*, 3231.
(12) Panda, S. P.; Sadafule, P. S. *J. Appl. Polym. Sci.* **1979**, *24*, 511.
(13) Panda, S. P. *Indian J. Technol.* **1976**, *14*, 444.
(14) Panda, S. P. *J. Armament Stud.* **1975**, *11*, 30.
(15) Malm, B. *Makromol. Chem.* **1981**, *182*, 1307.
(16) Panda, S. P. *Inst. Armament Technol.* **1973**, *11*, 356.
(17) Davidson, R. S.; Lowe, C. *Eur. Polym. J.* **1989**, *25*, 159.
(18) Malm, B.; Lindberg, J. J. *Makromol. Chem.* **1981**, *182*, 2747.
(19) Rusu, G. I.; Oleinek, H.; Zugravescu, I. *Makromol. Chem.* **1974**, *175*, 1651; *Chem. Abstr.* **1974**, *82*, 17595p.
(20) Panda, S. P. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1757.
(21) Davidson, R. S.; Lowe, C. *Eur. Polym. J.* **1989**, *25*, 167.
(22) Davidson, R. S.; Lowe, C. *Eur. Polym. J.* **1989**, *25*, 159.
(23) Panda, S. P. *Indian J. Technol.* **1971**, *9*, 387.
(24) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(25) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(26) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.