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3-(4-oxyphenyl)-1-phenyl-2-propen-1-one (4-oxychalcone) side groups have been prepared in order 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 in order to model the crosslinking reactions at the high polymer level. Single-substituent and cosubstituent polymeric phosphazenes $[NPRR'_2]_n$, where R= phenoxy, 2,2,2-trifluoroethoxy or 4-oxychalcone, and R'= 4-oxychalcone were also prepared. Their photolytic crosslinking was followed by ultraviolet spectroscopy.

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The Synthesis of Photocrosslinkable Chalcone-Bearing Polyphosphazenes

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The Synthesis of Photocrosslinkable Chalcone-Bearing Polyphosphazenes

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A Contribution from the Department of Chemistry

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Abstract

Cyclic and high polymeric phosphazenes that bear 3-(4-oxyphenyl)-1-phenyl-2-propen-1-one (4-oxychalcone) side groups have been prepared in order 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 in order to model the crosslinking reactions at the high polymer level. Single-substituent and cosubstituent polymeric phosphazenes $[NPRR'_2]_n$, where R= phenoxy, 2,2,2-trifluoroethoxy or 4-oxychalcone, and R'= 4-oxychalcone were also prepared. Their photolytic crosslinking was followed by ultraviolet spectroscopy.

Introduction

The synthesis of photocrosslinkable polymers has been widely studied and is of broad current interest. Such polymers are used in the preparation of photoresists for use in

microlithography¹, chemically-resistant coatings, and in the field of non-linear optical (NLO) materials.^{2,3}

A classical photosensitive moiety is the cinnamate group. This system is well-studied and widely used in photocrosslinkable polymers¹ because of the need for high sensitivity photoresists and UV-cured chemically-resistant coatings. The chalcone side group is particularly well-suited for these uses because of: (1) the high overall photosensitivity of the chalcone group compared with the classical cinnamate system, and (2) the closer match between the absorption spectrum of the chalcone side group and the emission spectrum of a Hg arc UV light source. This improved spectral match allows for increased photocrosslinking 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 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 side chain chalcone polymers. Although the photocrosslinking of polymers that bear side-chain chalcone units has been disclosed both in the open literature and in patents, use of the phosphazene inorganic backbone as a platform for chalcone-bearing side-chain polymers 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).

Chart 1 Near Here

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 as a model for the photocrosslinking of the chalcone high polymer. Photoreactivity studies with small molecules are facilitated by the ease of solution characterization using ¹H, ¹³C and ³¹P NMR spectroscopy, UV spectroscopy and

mass spectrometry. (2) The presence of two photocrosslinkable groups per repeat unit in polyphosphazenes is expected to result in a high crosslink 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 backbone both under the high intensity UV radiation required for the photocrosslinking reaction and during subsequent exposure to light.

Results and Discussion

Synthesis and Characterization of Cyclic Phosphazene Model Compounds. The synthesis route to cyclic trimeric phosphazenes used as reaction models for the high polymers is shown in Scheme 1. The model system was simplified by use of monofunctional cyclotriphosphazenes. In addition, a hexa-chalcone-substituted cyclic trimer was used to model a polymer in which every phosphorous atom bears two photosensitive side groups. Cyclotriphosphazenes 2-4 were synthesized as follows: The pentachloro 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 pentaphenoxy 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 equivalents of sodium phenoxide to trimer 2 at 12 °C, followed by warming to 45 °C for twelve hours. Route B involved the treatment of $N_3P_3(OPh)_5Cl$ with three equivalents 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 (details will be found in the Experimental section).

The pentakis(trifluoroethoxy) derivative, $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5\{\text{OC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5\}$ (4), was synthesized by the addition of 5.2 equivalents of $\text{NaOCH}_2\text{CF}_3$ 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, 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 non-geminal to the aryloxy group, were found to be non-equivalent. However, non-equivalency was detected in the four non-geminally substituted trifluoroethoxy groups. A slight NOE effect was detected in the aryloxy protons when the signal at 3.97 ppm was irradiated, thus allowing the assignment of these trifluoroethoxy groups as those cis to the aryloxy group.

Lastly, the hexasubstituted cyclotriphosphazene $[\text{NP}(\text{OC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5)_2]_3$ (5), was synthesized in 30% yield from 1 and $\text{NaOC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5$ in dioxane heated to reflux. Trimer 5 was characterized by ^{31}P , ^{13}C and ^1H NMR, +FAB-MS, UV spectroscopy and elemental analysis.

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 (4X), isopropanol (3X), and hexane (2X). Polymer 6 was characterized by

^{31}P , ^{13}C and ^1H NMR, 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 one equivalent 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 and was heated to reflux for ten days. Polymer 7 was characterized by ^{31}P , ^{13}C and ^1H NMR, GPC, DSC, UV, and elemental analysis.

The phenoxy cosubstituent polymer 8 was obtained first by treatment of polymer 9 with one equivalent of sodium phenoxide. This partially-substituted polymer was then treated with an excess of $\text{NaOC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5$ with Bu_4NBr in dioxane heated to reflux for nine days. The polymeric product was isolated by precipitation from THF into water (4X), isopropanol (2X), hexane (1X) and characterized by ^{31}P , ^{13}C and ^1H NMR, UV, DSC and elemental analysis.

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. Trimer 2 had an absorption at 305 nm (THF solvent). Species 2 was irradiated in the solid state for a period of seven hours during which time a decrease occurred in the absorbance in the region of 305 nm, concurrent with the formation of dimer 8. Dimer 8 was characterized in its impure form by ^{31}P , ^{13}C and ^1H NMR, and mass spectrometry.

The UV spectra of trimers 3, 4 and 5 were also studied by UV spectroscopy. 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 reaction 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 Crosslinking Studies of High Polymers. The photolytic crosslinking of polymers 6-8 was examined and followed by UV spectroscopy (see Figures 1-3). Thin films were cast from THF and were irradiated with a filtered sunlamp UV source ($\lambda = 260\text{-}380$ nm.). 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 crosslinking as shown by the greater change in the 320 nm. absorption and the insolubility of polymers 6-8 in common organic solvents.

Photochemical crosslinking was monitored by measuring the relative intensity of the 320 nm absorption. It was found that, after a total of ten minutes 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 sensitivity of the polymers $[\text{NP}\{\text{OC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5\}_2]_n$ 6, $[\text{NP}\{\text{OCH}_2\text{CF}_3\}_{0.93}\{\text{OC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5\}_{1.07}]_n$ 7, and $[\text{NP}\{\text{OC}_6\text{H}_5\}_1\{\text{OC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5\}_1]_n$ 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.

Conclusions

The photochemical behavior of cyclic phosphazene trimers and linear high polymers has been investigated. The results indicate that the pentachloro derivative **2** undergoes a photochemically induced 2+2 cycloaddition reaction quite readily to form dimer **8** and that polymers **6**, **7** and **8** are crosslinked rapidly during UV irradiation with a total loss of the 320 nm. absorption.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was provided by Ethyl Corp. It was recrystallized from hexane and sublimed (40°C, 0.05 mm Hg) 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 stored over 4Å molecular sieves. 4-Hydroxychalcone was obtained from Lancaster (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. $[\text{NPCl}_2]_n$ 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 by the use of a Bruker WM360 spectrometer. ^{13}C (50 MHz) and ^1H (200 MHz) NMR spectra were also obtained by the use of a Bruker WP200 spectrometer or a Bruker ACE200 spectrometer. Nuclear Overhauser Effect (NOE) difference spectra were obtained with the use of a Bruker AM300 spectrometer. Both ^{13}C and ^{31}P 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 Laborato-

ries Knoxville, TN. Electron-impact mass spectra (EI/MS) were obtained with use of Kratos MS 9/50 equipment. Chemical ionization (CI) mass spectra were obtained with use of a Kratos MS-25 spectrometer. Fast Atom Bombardment (FAB) mass spectra were obtained with use of 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- μ m column. The samples were eluted with a 0.1% by weight solution of tetra-n-butyl ammonium 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 by means of 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 eluents. ^{31}P NMR (146 MHz) ($CDCl_3$) δ 12.7 ppm., δ 23.1 ppm; J_{PNP} =61 Hz. 1H (200 MHz $CDCl_3$) 8.06-8.00 (d, 2H), 7.84-7.47 (m, 7H), 7.37-7.31 (m, 2H). ^{13}C (90 MHz) ($CDCl_3$) 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). m/z calc.=535; found=536 (MH^+). UV λ_{max} (THF)=315 nm. Anal. Calc. for $C_{15}H_{11}Cl_5N_3O_2P_3$: 33.65 %C; 2.07 %H; 7.85 %N; 17.35 %P; 33.10 %Cl. Found: 33.49 % C; 2.19 % H; 8.10 % N; 17.89 % P; 32.70 % Cl.

Synthesis of $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\{\text{OC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5\}$ (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 one hour 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 (146 MHz CDCl_3) 9.36-9.11 ppm. (m). ^1H : 8.06-8.01 (m, 2H), 7.81-7.73 (d, 2H, $J=16$ Hz), 7.62-7.40 (m, 5H), 7.3-6.91 (m, 28H). m/z calc.=823; found=824 (+FAB). UV: λ_{max} (THF)=315 nm. Anal. Calc. for $\text{C}_{45}\text{H}_{36}\text{N}_3\text{O}_7\text{P}_3$: 65.62 %C; 4.41 %H; 5.10 %N; 11.28 %P. Found: 64.92 % C; 4.46 % H; 5.09 % N; 11.70 % P.

Synthesis of $\text{N}_3\text{P}_3\{\text{OCH}_2\text{CF}_3\}_5\{\text{OC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5\}$ (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 two hours to a solution of **2** (1.0 g, 1.86 mmol) in THF (50 mL) cooled to -80°C. The mixture was stirred for one hour after the addition of $\text{NaOCH}_2\text{CF}_3$ 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 (3x100 mL). The organic layer was dried (MgSO_4), the solvent removed, and the oil was dissolved in 8 mL 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. m/z calc.= 853; m/z found= 853.5 (+FAB). ^1H (CDCl_3 , 200 MHz) 8.06-8.00 (m, 2H), 7.76 (d, 1H, $J=15$ Hz), 7.67-7.43 (m, 6H), 7.37-7.23 (m, 2H), 4.49-4.37 (m, 2H (OCH_2CF_3 gem to OAr)) 4.35-4.18 (m, 4H, OCH_2CF_3 distal to OAr)) 4.08-3.80 (m, 4H (OCH_2CF_3 near to OAr). ^{31}P (CDCl_3 146 MHz): AM_2 $\nu_{\text{A}}=17.4$ ppm., $\nu_{\text{B}}=13.7$ ppm. ($J_{\text{PNP}}=92$ Hz). UV/Vis (THF) $\lambda_{\text{max}}=308$ nm. Anal. Calc. for $\text{C}_{25}\text{H}_{21}\text{F}_{15}\text{N}_3\text{O}_7\text{P}_3$: 35.19 %C; 2.48 %H; 4.92 %N; 10.89 %P; 33.39 %F. Found: 34.96 % C; 2.48 % H; 4.93 % N; 10.03 % P; 32.01 % F.

Synthesis of [NP{OC₆H₄CH=CHC(O)C₆H₅}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 heated to reflux for four days. The solvent was then removed by rotary evaporation and the yellow oil was chromatographed on silica using THF/hexane as the eluent. Yield: 1.29 g (30%). ¹H (CDCl₃, 200 MHz) 8.00-7.94 (m, 2H), 7.77 (d, 1H, J=16 Hz), 7.61-7.41 (m, 6H), 7.06 (d, 2H, J=9 Hz). ¹³C (CDCl₃) (90 MHz) 189.9, 151.9, 143.1, 137.9, 132.9, 132.2, 129.7, 128.6, 128.4, 122.1, 121.4, Anal. Calcd. for C₉₀H₆₆N₃O₁₂P₃: C, 73.31; H, 4.51; N, 2.85. Found: C, 72.59; H, 4.45; N, 2.70; m/z calc.=1473; found (+FAB)=1475 (MH⁺). UV, IR

Synthesis of [NP{OC₆H₄CH=CHC(O)C₆H₅}₂]_n (6): To a suspension of NaH (0.83 g, 34 mmol) and Bu₄NBr 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 (4X), isopropanol (2X) and hexane (1X). ¹H (CDCl₃) (200 MHz) 7.70-6.68 ppm br, m ¹³C (CDCl₃) (50 MHz) 189.41, 152.36, 142.65, 137.59, 132.70, 131.39, 129.53, 128.47, 128.39, 121.43, 120.99 ³¹P (CDCl₃) (146 MHz) -20.36 ppm. (s). λ_{max}=317 nm. (THF). GPC, IR. Anal.: Calc.: for C₃₀H₂₂O₂NP %C: 80.35; %H: 4.91; %N: 3.12; %P: 6.75; %Cl: 0 Exptl.: %C: 71.87; %H: 4.88; %N: 2.54; %P: 6.16; %Cl 0.026. T_g: 62 °C.

Synthesis of [NP{OCH₂CF₃}_{0.93}{OC₆H₄CH=CHC(O)C₆H₅}_{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 NaOC₆H₄CH=CHC(O)C₆H₅ (prepared from

$\text{HOC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5$ (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 (4X), isopropanol (1X) and hexane (1X) to precipitate the polymeric product. Anal. calc. %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 ^1H (CDCl_3) (360 MHz) 8.0-6.6 ppm (Ar) (br), 4.1-3.7 ppm br (OCH_2CF_3) ^{31}P (CDCl_3) (146 MHz) -9.75, -13.62, -17.89 ppm (1:3:1) ^{13}C (CDCl_3) (90 MHz) 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. T_g : 44 °C

Synthesis of $[\text{NP}\{\text{OC}_6\text{H}_5\}_1\{\text{OC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5\}_1]_n$ (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. $\text{NaOC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5$ (prepared from 17.3 g, 77.2 mmol $\text{HOC}_6\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{C}_6\text{H}_5$ in 300 mL dioxane) and Bu_4NBr (0.83 g, 2.6 mmol) was added over 15 minutes and the orange was solution stirred at a gentle reflux for 9 days. The polymeric product was isolated by precipitations into water (4X), isopropanol (2X) and hexane (1X). Anal. calc. %C: 69.8, %H: 4.4, %N: 3.5, %Cl: 0 found: %C: 68.05, %H: 4.66 %N: 3.71 %Cl: 0.68. ^1H (CDCl_3) (360 MHz) 7.8-6.8 ppm, br. ^{13}C (CDCl_3) (50 MHz) 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 ^{13}P (CDCl_3) (146 MHz) -19.2 ppm. T_g : 37 °C.

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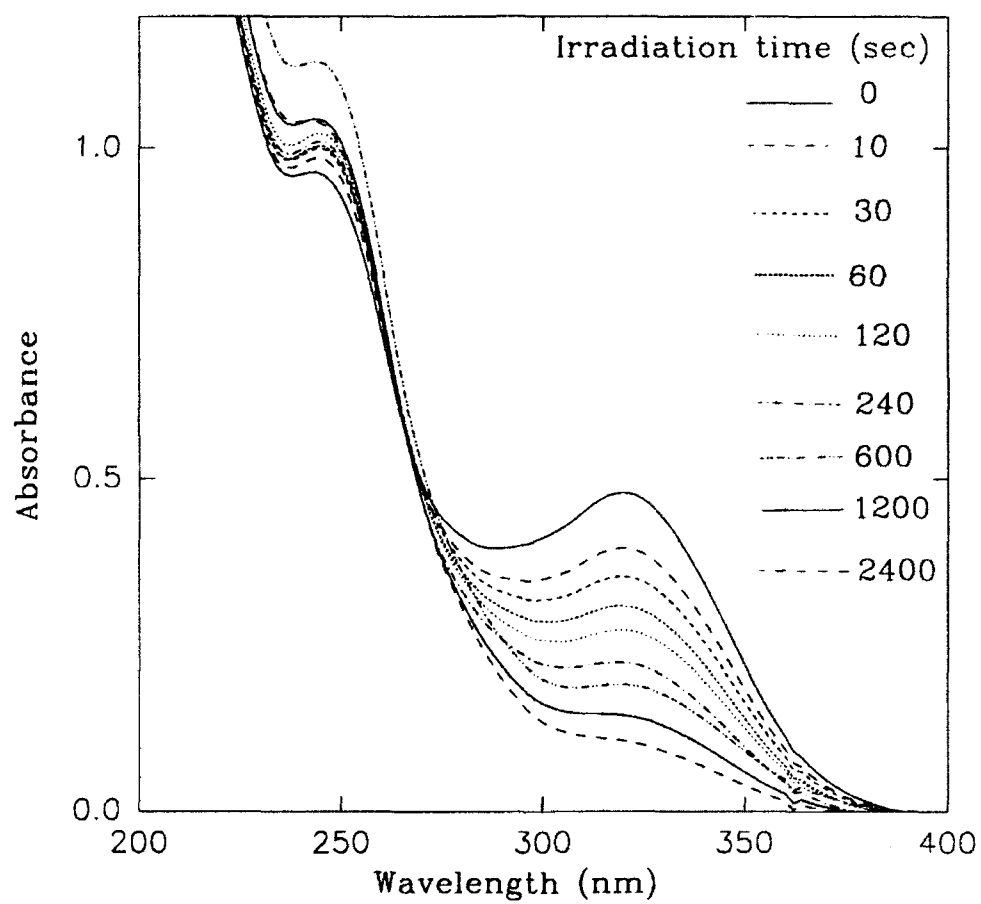


Figure 1: The effect of UV irradiation on polymer 6

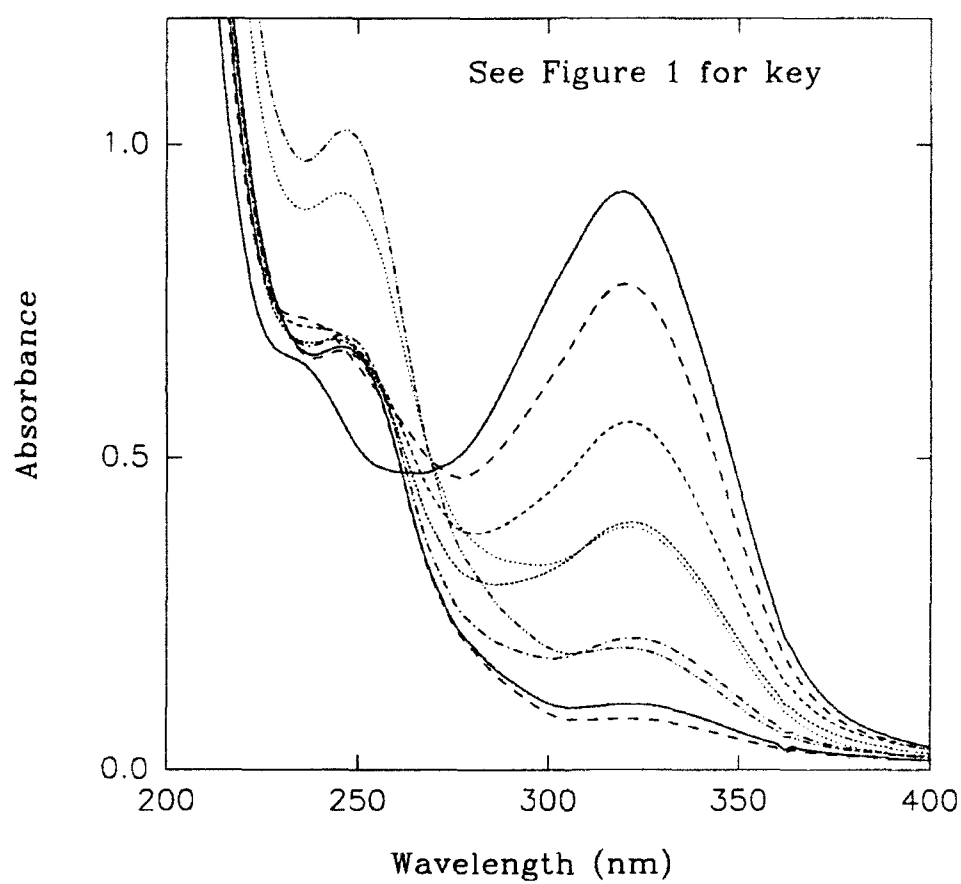


Figure 2: The effect of UV irradiation on polymer 8

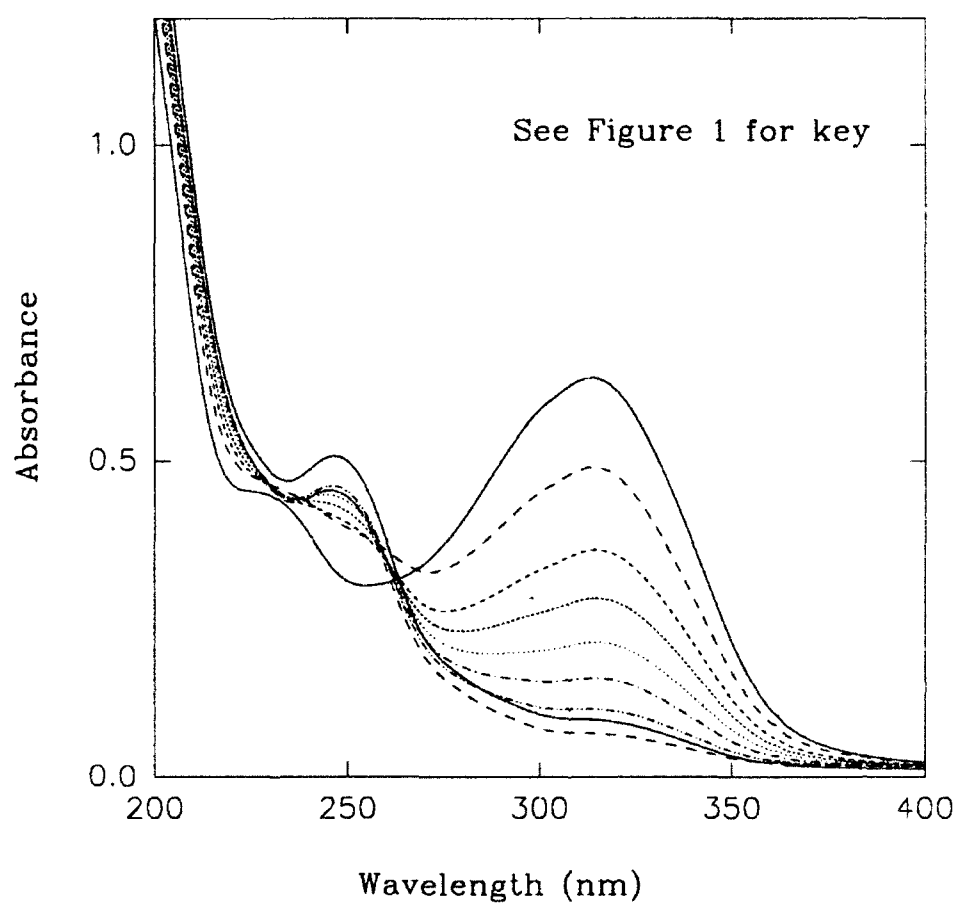


Figure 3: The effect of UV irradiation on polymer 7

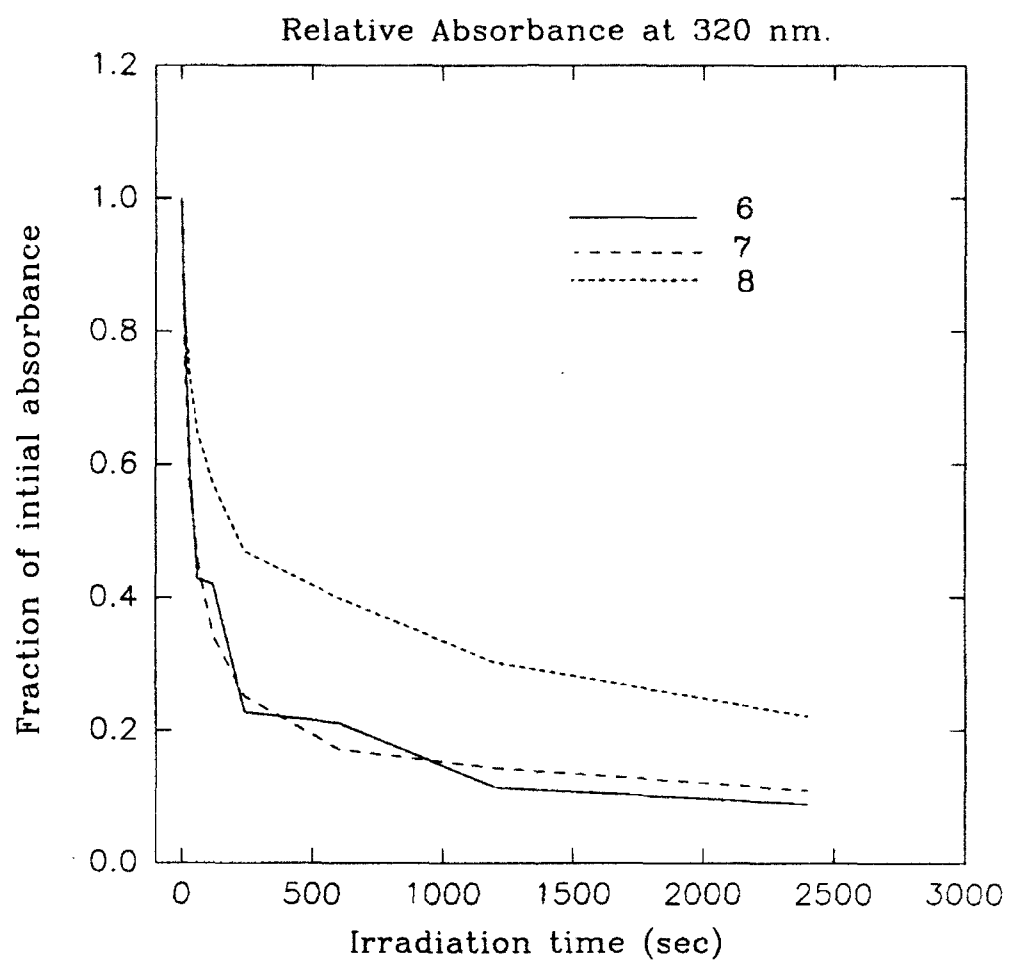
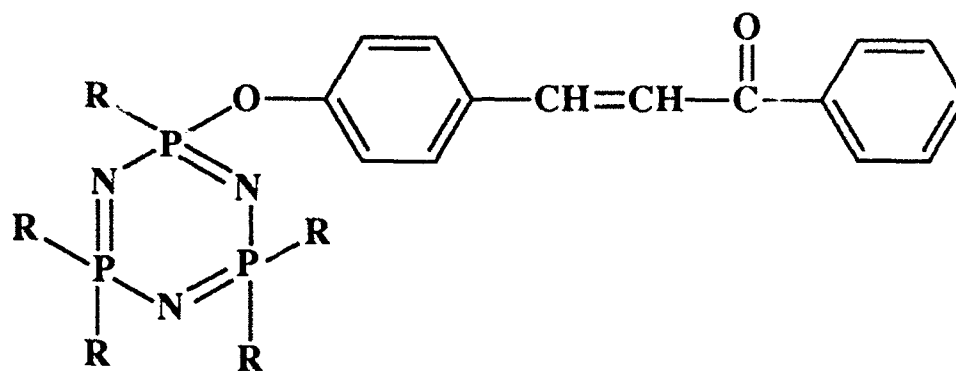
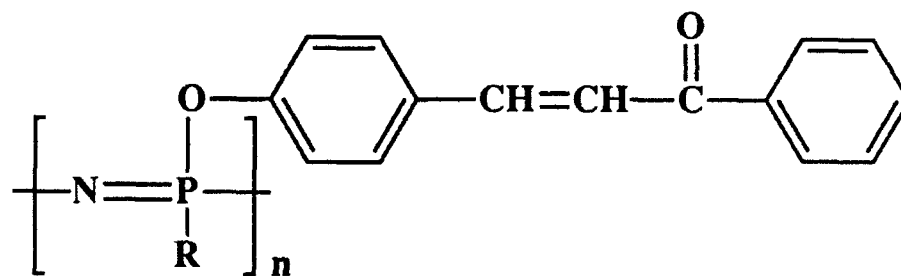


Figure 4: The relative absorbances at 320 nm. of polymers 6-8.

Chart 1

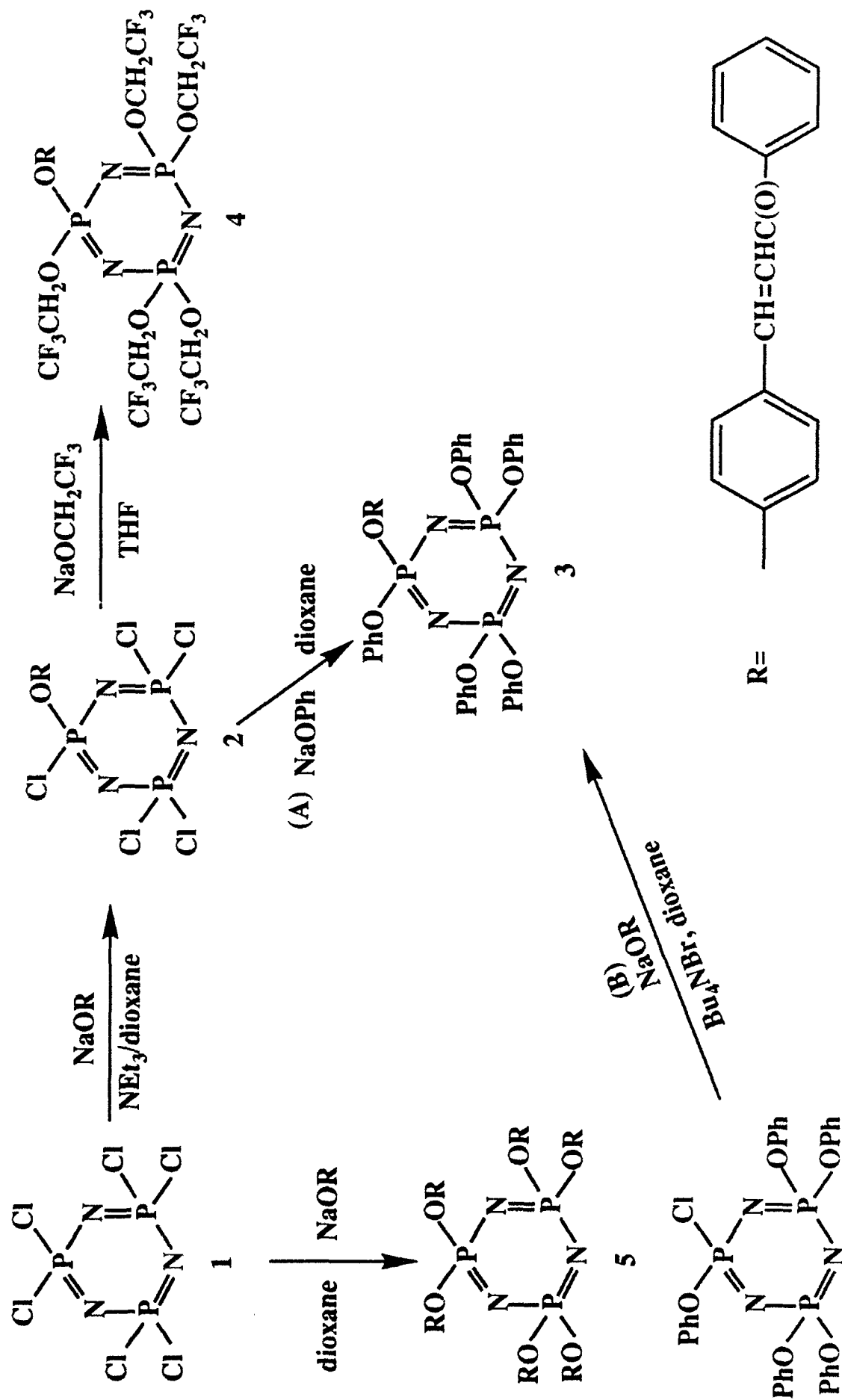


- 2: R = Cl
 3: R = OPh
 4: R = OCH₂CF₃
 5: R = OC₆H₄CH=CHC(O)C₆H₅

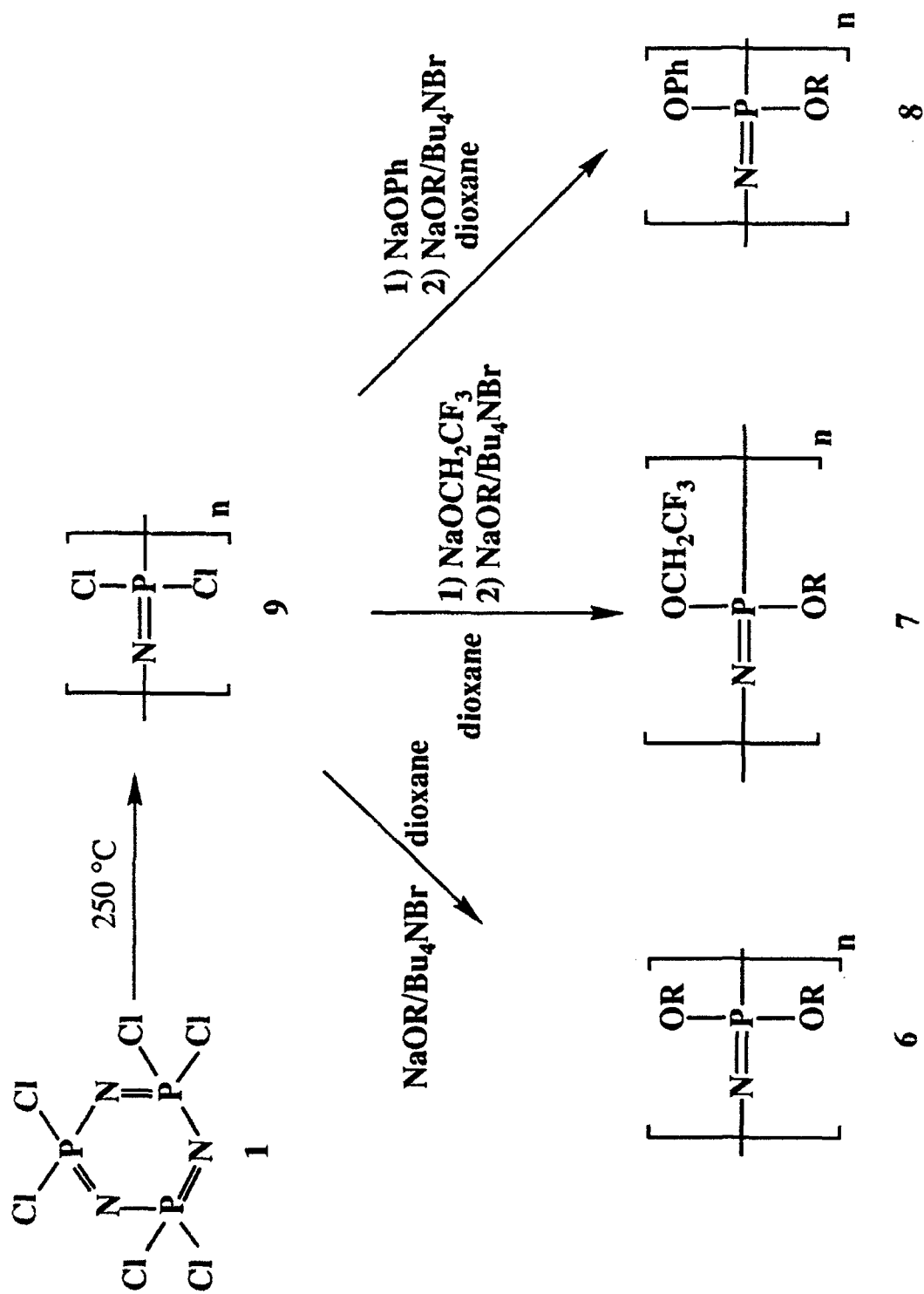


- 6: R = OC₆H₄CH=CHC(O)C₆H₅
 7: R = OCH₂CF₃
 8: R = OPh

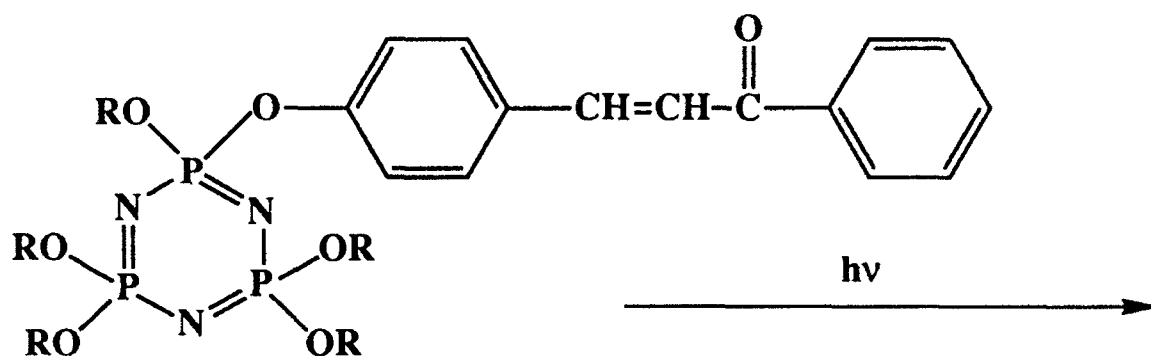
Scheme 1



Scheme 2

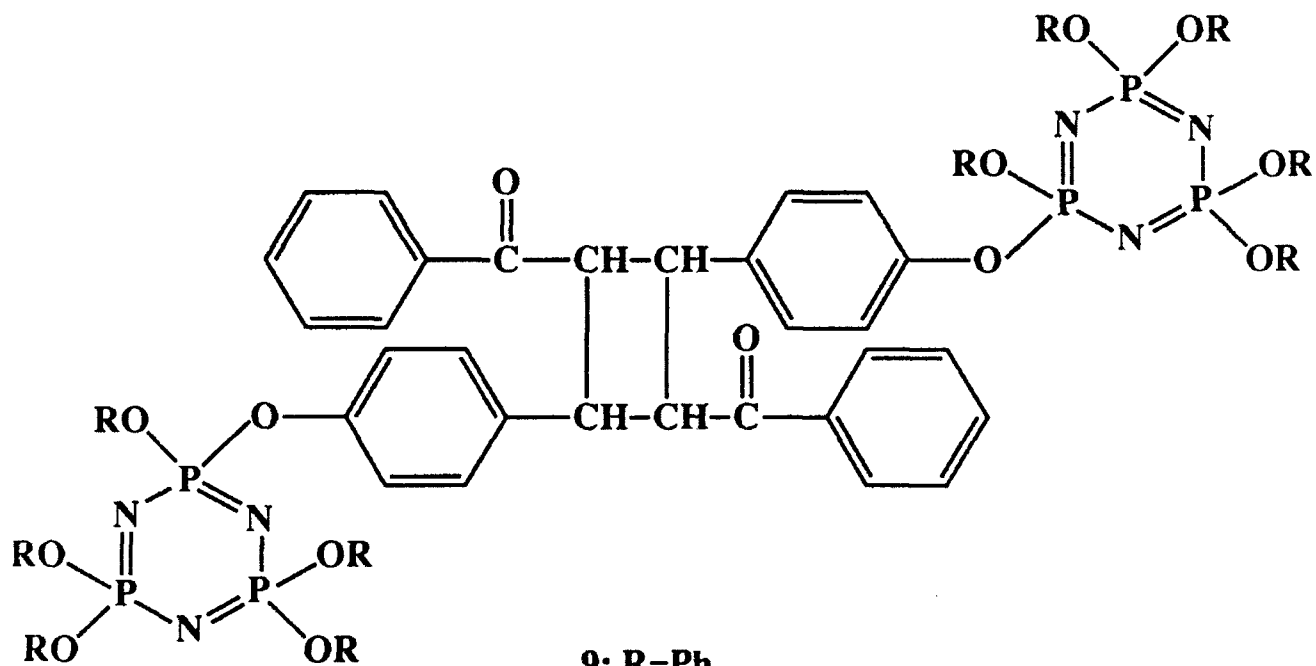


Scheme 3



3: R=Ph

4: R= CH_2CF_3



9: R=Ph

10: R= CH_2CF_3

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