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### Synthesis and Characterization of Photosensitive Phosphorus Based Polymers Containing $\alpha,\beta$ -Unsaturated Ketones in the Main Chain

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## Synthesis and Characterization of Photosensitive Phosphorus Based Polymers Containing $\alpha,\beta$ -Unsaturated Ketones in the Main Chain

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*1,3-Bis(4-hydroxyphenyl)propanone (BHPP) and 3-(4-hydroxy-3-methoxy phenyl)-1-(4-hydroxyphenyl)propanone (HMPHPP) were used as monomers for preparing photosensitive phosphorus containing polyesters. The photosensitive monomers BHPP and HMPHPP were prepared respectively by refluxing 4-hydroxybenzaldehyde and 3-methoxy-4-hydroxybenzaldehyde with 4-hydroxy acetophenone. The polyesters were synthesized by interfacial polycondensation of photosensitive diols with N-phenylphosphoramidic dichloride using hexadecyltrimethyl ammonium bromide (HDTMAB) as phase-transfer catalyst. Copolymers were also prepared by incorporating terephthaloyl chloride in the polymer backbone. The synthesized monomers and polymers were characterized by UV, FT-IR and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ -NMR spectroscopic techniques. The resulting polymers had inherent viscosities in the range of 0.15–0.51 dL/g and showed good solubility in polar organic solvents. The thermal properties of the polymers were studied by thermogravimetric analysis and differential scanning calorimetry under nitrogen atmosphere. The TGA data revealed that the 10% weight loss occurs at 275–320°C and all the synthesized polymers showed high char residues. DSC studies indicate that these polymers possess  $T_g$  in the range of 48 to 64°C. The photosensitive property of the polymers in film and solution state was investigated by ultraviolet spectroscopy. The effect of incorporation of terephthaloyl unit on photocrosslinking and thermal properties of the polymers was also studied.*

**Keywords** photosensitive polymers, phosphorus containing, photocrosslinking, polycondensation, interfacial polymerization

### Introduction

Photosensitive polymers have gained more attention of chemists in the recent past due to their vast applications in different fields such as microelectronics, integrated circuit boards, photocurable coatings, non-linear optics, energy exchange materials and optical memory devices (1–7). Polymers employed for these applications should possess photo-reactive groups like cinnamoyl, coumaroyl, cyclic carbonate and stilbene derivatives. Photocrosslinkable moieties present in the polymers, on irradiation with UV light can

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induce significant change in physical properties like solubility, film formation and optical transparency. Photosensitive polymers, which on exposure to UV light, undergo cross-linking to form a hardened coating and resistance to etching solutions constitute negative type photoresists (8–18). Photosensitive polymers with pendant cinnamoyl units have been reported by various researchers (19–22). The photosensitive property of these polymers is mainly due to the  $\pi$ -electron cloud of the photoreactive groups. Among many types of photosensitive materials, chalcone bearing polymers attracted much attention due to their high sensitivity to UV radiation (23–29). Solubility and thermal stability are vital properties of the polymers to be used as photoresists. The literature reveals that the polymers containing phosphorus in the main chain impart special properties like thermal stability, high char yield and solubility in common organic solvents (30–37). In continuation of our research in this domain, the present investigation deals with the synthesis and characterization of thus far unreported phosphorus based polyesters containing photosensitive  $\alpha,\beta$ -unsaturated ketones in the main chain and the study of the thermal stability and photocrosslinking properties.

## Experimental

### Materials

Aniline, phosphoryl chloride, ethanol, chloroform and other solvents were purified by the reported procedures (38, 39). 4-Hydroxybenzaldehyde (Merck), 4-hydroxy acetophenone (Ranbaxy), 3-methoxy-4-hydroxybenzaldehyde (Merck), borontrifluoride diethyl etherate (Merck) and hexadecyltrimethylammonium bromide (HDTMAB, Fluka) were used as received. Terephthaloyl chloride was prepared by reacting terephthalic acid with thionyl chloride (40).

### Synthesis of Monomers

*Synthesis of 1,3-bis(4-hydroxyphenyl)propenone (BHPP).* 4-Hydroxybenzaldehyde (0.1 mol) and 4-hydroxy acetophenone (0.1 mol) were charged into a 250 mL round bottom flask. The mixture was dissolved in 60 mL of methanol and 1 mL of borontrifluoride diethyl etherate was added as a catalyst. The reaction mixture was refluxed for 4 h with constant stirring in an oil bath and cooled to room temperature. The precipitated product was filtered, washed with distilled water and recrystallized from methanol. The recrystallized bright yellow needle-shaped product was dried in vacuum at 60°C. Yield: 85%, mp: 197.5°C (lit. 197°C) (41). FT-IR (KBr): 3299  $\text{cm}^{-1}$  ( $\nu_{\text{OH}}$ ), 1641  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1601  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ), 3069  $\text{cm}^{-1}$  (aromatic  $\nu_{\text{C-H}}$ ).  $^1\text{H-NMR}$  (DMSO- $d_6$ ): 7.5–8.3  $\delta$  (m, 8H, aromatic), 9.7  $\delta$  (s, 2H, –OH), 6.8–6.9  $\delta$  (dd, 2H, –CH=CH–). UV-Vis (C<sub>2</sub>H<sub>5</sub>OH)  $\lambda_{\text{max}}$ : 351 nm (–C=C–). Elemental analysis: Calcd. for C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>: C-75.00%, H-5.00%. Found: C-74.64%, H-5.07%.

*Synthesis of 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)propenone (HMPHPP).* The monomer HMPHPP was synthesized from 4-hydroxy-3-methoxy benzaldehyde and 4-hydroxyacetophenone using borontrifluoride diethyl etherate as a catalyst by following the procedure described above. Yield: 85%, mp: 181°C; FT-IR (KBr): 3400  $\text{cm}^{-1}$  ( $\nu_{\text{OH}}$ ); 1641  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ); 1591  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ ).  $^1\text{H-NMR}$  (DMSO- $d_6$ ): 7.1–8.0  $\delta$  (m, 7H, aromatic), 3.6  $\delta$  (s, 3H, –OCH<sub>3</sub>), 9.7  $\delta$  (s, 2H, –OH), 6.8–6.9  $\delta$  (dd, 2H,

–CH=CH–). UV-Vis (C<sub>2</sub>H<sub>5</sub>OH)  $\lambda_{\text{max}}$ : 353 nm (–C=C–). Elemental analysis: Calcd. for C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>: C-71.10%, H-5.18%. Found: C-70.88%, H-4.95%.

*Synthesis of N-phenylphosphoramidic dichloride.* N-Phenylphosphoramidic dichloride was synthesized by a reported procedure (42). Phosphoryl chloride (0.05 mol) was dissolved in 30 mL dry chloroform in a 250 mL round bottom flask. To this mixture, aniline (0.1 mol) in 30 mL chloroform was added in different portions over a period of 15 min with vigorous stirring at ambient temperature. Subsequently, the mixture was stirred for a further 30 min. The aniline hydrochloride separated was filtered. The filtrate was distilled under reduced pressure to yield a white solid mass of the product. Yield: 87%.

### Polymerization

All polymers were synthesized by interfacial polycondensation using HDTMAB as a phase transfer catalyst (43). The procedure adopted for the synthesis of homopolymer **1a** is as follows: BHPP (0.01 mol) was dissolved in 20 mL of 1 N NaOH solution containing a pinch of HDTMAB. To this mixture, 25 mL chloroform solution of N-phenylphosphoramidic dichloride (0.01 mol) was added with vigorous stirring at 20°C. After 30 min of stirring, the polymer formed between the organic and aqueous layer was separated and dried in vacuum. The polymer **1b** from HMPHPP and N-phenylphosphoramidic dichloride was also prepared in a similar fashion.

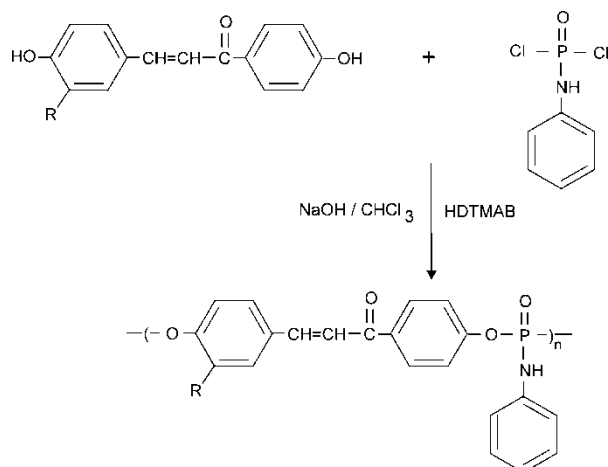
The copolymers **2a** and **2b** were prepared by adopting the following procedure. The appropriate diol monomer (0.02 mol) was dissolved in 40 mL of 1 N NaOH solution. A pinch of HDTMAB was added and stirred well to form a froth. Chloroform solutions of N-phenylphosphoramidic dichloride (0.01 mol) and terephthaloyl chloride (0.01 mol) were prepared separately and added to an alkaline solution of diol monomers simultaneously using addition funnels at 20°C with constant stirring. Stirring was continued for 30 min, then the polymer formed between the aqueous and organic layer was filtered and dried.

### Characterization

Solubility of the synthesized polymers was tested with various organic solvents. The inherent viscosity of the polymers was measured in DMF (0.5 g/dL) at 30°C using a suspended level Ubbelohde viscometer. The IR spectra of the polymers were recorded in KBr pellets on a Bruker IFS 66 V FTIR spectrometer. The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P-NMR spectra were recorded in DMSO-*d*<sub>6</sub>, on an AMX-400 NMR spectrometer. The UV spectra were recorded on a Systronics UV-119 spectrophotometer. The DSC traces were obtained with a Perkin-Elmer-Pyris 6 differential scanning calorimeter at a heating rate of 10°C min<sup>-1</sup> under nitrogen atmosphere. The glass transition temperature (T<sub>g</sub>) was obtained from the first run for all the polymer samples. Thermogravimetric studies were performed with a Perkin-Elmer thermal analyzer, in nitrogen atmosphere, at a heating rate of 20°C min<sup>-1</sup> with a sample weight of 3–5 mg.

### Photocrosslinking Studies

The photocrosslinking property of the polymers in film state and solution state was studied by a UV spectrophotometer. A thin film was cast on the outer surface of the quartz cuvette from acetone solution. The film was irradiated with a medium-pressure mercury vapor lamp (Heber Scientific Photoreactor-UV, 125W, 365 nm) kept at a distance of 10 cm



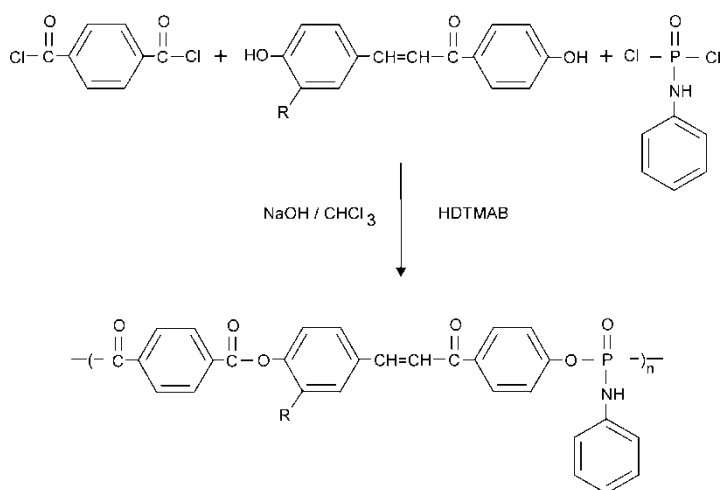
**Scheme 1.** Synthesis of homopolymers 1a ( $R = H$ ) and 1b ( $R = -OCH_3$ ).

from the sample for various intervals of time. Subsequently, the irradiated film was subjected to spectral analysis. The photoreactivity of the polymers in solution state was also studied by dissolving the sample in DMSO (20 mg/L) and irradiated with a UV lamp at a distance of 10 cm. The rate of disappearance of the double bond in the polymer main chain was monitored by a UV spectrophotometer.

## Results and Discussion

### Synthesis

The photosensitive diols namely 1,3-bis(4-hydroxyphenyl)propenone and 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)propenone were prepared by a Claisen-Schmidt



**Scheme 2.** Synthesis of copolymers 2a ( $R = H$ ) and 2b ( $R = -OCH_3$ ).

condensation of 4-hydroxyacetophenone with 4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde, respectively. The spectral and elemental analysis data confirmed the structure of the monomers. A series of photocrosslinkable polymers were prepared. The homopolymers (**1a** and **1b**) were synthesized by reacting the monomers BHPP and HMPHPP with N-phenylphosphoramidic dichloride, respectively using phase transfer catalyzed interfacial polycondensation method (Scheme 1). The copolymers (**2a** and **2b**) were also prepared using an interfacial polycondensation technique by reacting the aromatic diol monomers BHPP and HMPHPP with N-phenylphosphoramidic dichloride and the co-monomer terephthaloyl chloride (Scheme 2). All the polymers were obtained in good yields (75–85%).

### Polymer Characterization

The solubility of the photoreactive polymers is one of the most important requirements for practical applications of these polymers. The solubility of homo and copolymers was tested in various solvents. All the synthesized polymers were soluble in polar aprotic solvents like THF, DMSO and DMF and insoluble in methanol, chloroform, benzene, toluene, n-hexane and other hydrocarbon solvents. It was observed that the homopolymers have higher solubility than their copolymers. The good solubility in polar organic solvents may be due to the presence of phosphorus linkage in the main chain, which increases the polarity (44). The higher solubility of homopolymers may be attributed to the presence of more P–O–C and P–N–C linkages compared to the copolymers.

The inherent viscosity of the polymers was determined in DMF and were in the 0.15–0.51 dL/g range. Compared to copolymers, homopolymers have low viscosity.

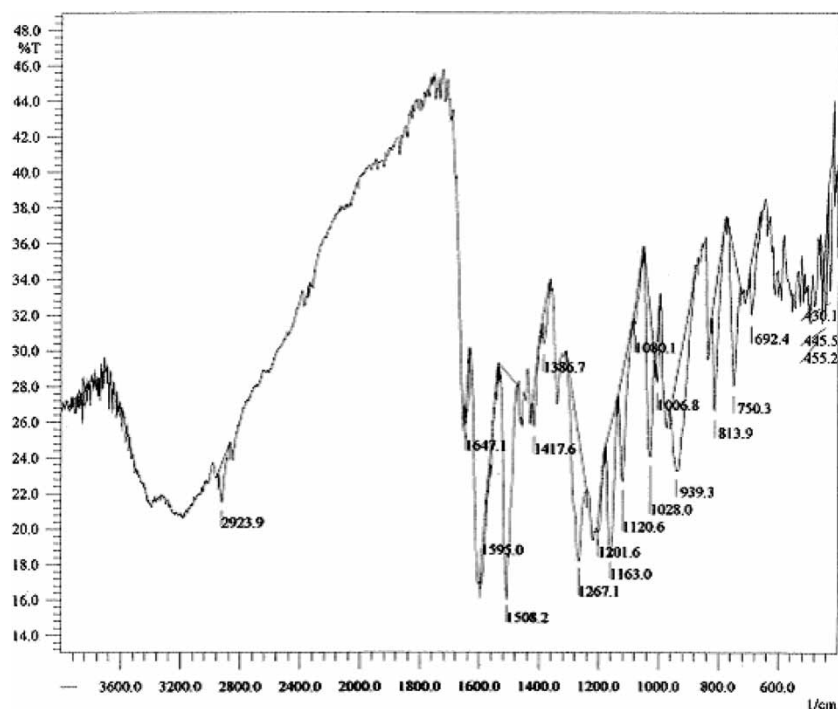


Figure 1. FT-IR spectrum of homopolymer **1b**.

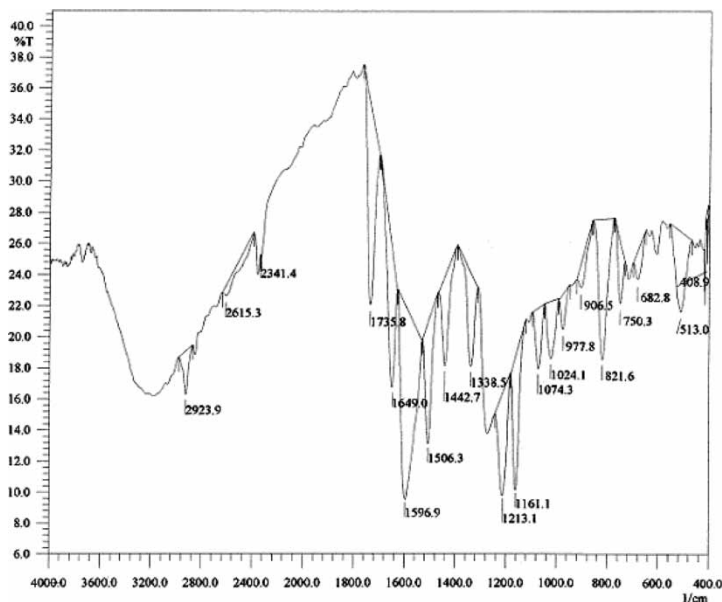


Figure 2. FT-IR spectrum of copolymer 2a.

This may be due to the high reactivity of N-phenylphosphoramidic dichloride, which may easily get hydrolyzed during interfacial polycondensation.

### Spectral Characterization

Chemical structures of the polymers were confirmed by UV, IR, and,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ -NMR spectroscopic techniques and the results are in good agreement with the

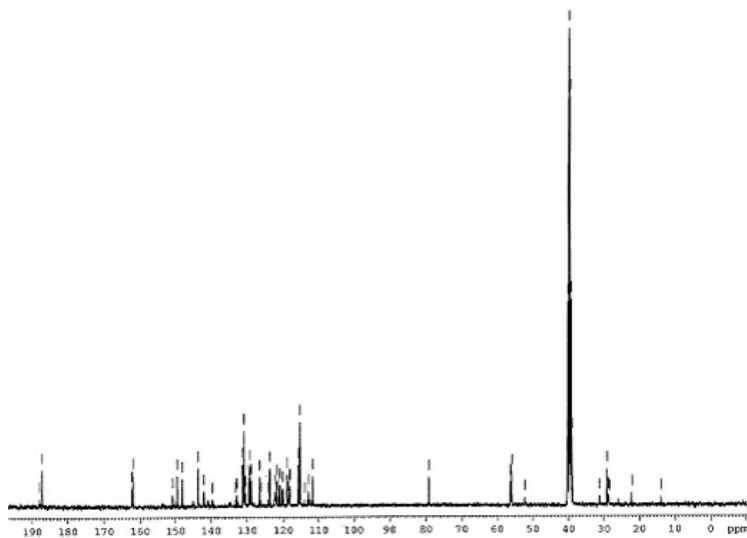


Figure 3.  $^{13}\text{C}$ -NMR spectrum of homopolymer 1b.

structure of the polymers. The infrared spectrum of homopolymer **1b** is shown in Figure 1. The absorption bands corresponding to P–N, P=O and C=O stretching appeared at around 939, 1267 and 1647  $\text{cm}^{-1}$ , respectively. Both the homopolymers and copolymers showed absorptions at 1330 and 1163  $\text{cm}^{-1}$  corresponding to P–N–C (aromatic) and P–O–C (aromatic) bond stretching, respectively (45). The olefinic  $>\text{C}=\text{C}<$  stretching was observed at around 1600  $\text{cm}^{-1}$ . In addition to these results, the disappearance of –OH stretching vibrations of diol monomers confirms the formation of polymers. The copolymers (**2a**, **2b**) showed an additional band at 1735  $\text{cm}^{-1}$ , and correspond to the ester carbonyl group. The representative infrared spectrum of copolymer **2a** is shown in Figure 2. The UV spectrum of all the polymers showed an absorption maximum at around 350 nm, which is due to the  $\pi \rightarrow \pi^*$  transition of the olefinic double bond in the polymer chain (46).

The structure of the synthesized polymers was also confirmed by  $^1\text{H}$ -NMR spectroscopy. The aromatic protons were observed as multiplet at 7.5–8.3  $\delta$ . All the polymers exhibit a singlet at 3.3  $\delta$  and double doublet at 6.8  $\delta$  due to methoxy and olefinic protons, respectively.  $^{13}\text{C}$ -NMR spectrum of the synthesized polymers fall into three main regions: 20–60  $\delta$  for the aliphatic carbons, 110–150  $\delta$  for the aromatic carbons, and 163  $\delta$  for the carbonyl carbons. The  $^{13}\text{C}$ -NMR spectrum of homopolymer **1b** is shown in Figure 3. The  $^{31}\text{P}$ -NMR spectrum of all the polymers showed two doublets in the region of 3 to –17  $\delta$ . This may be due to the spin–spin coupling of  $^{31}\text{P}$  resonance with proton present on nitrogen nucleus (47). The representative  $^{31}\text{P}$ -NMR spectrum of polymer **1a** is shown in Figure 4. These results support the formation of polymers.

### Thermal Characterization

The thermal properties such as decomposition temperature, glass transition temperature ( $T_g$ ) and crystalline melting temperature ( $T_m$ ) of the prepared polymers were studied by thermogravimetric analysis and differential scanning calorimetry in nitrogen atmosphere.

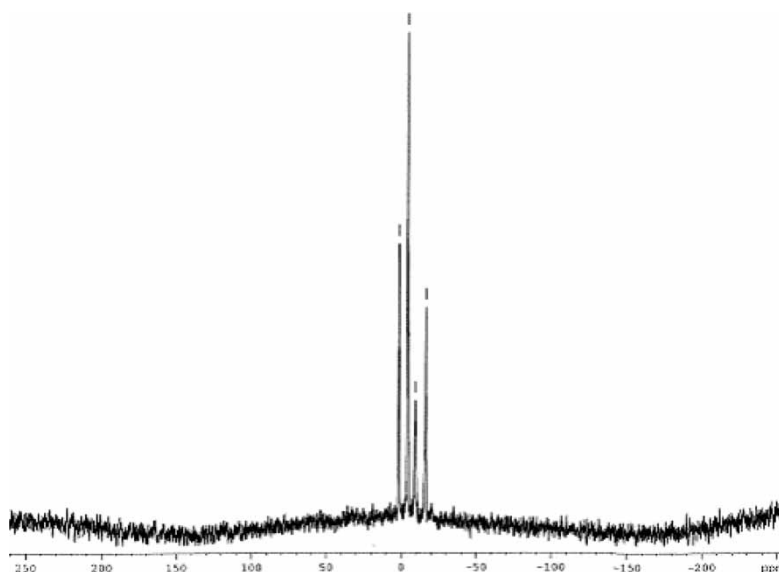
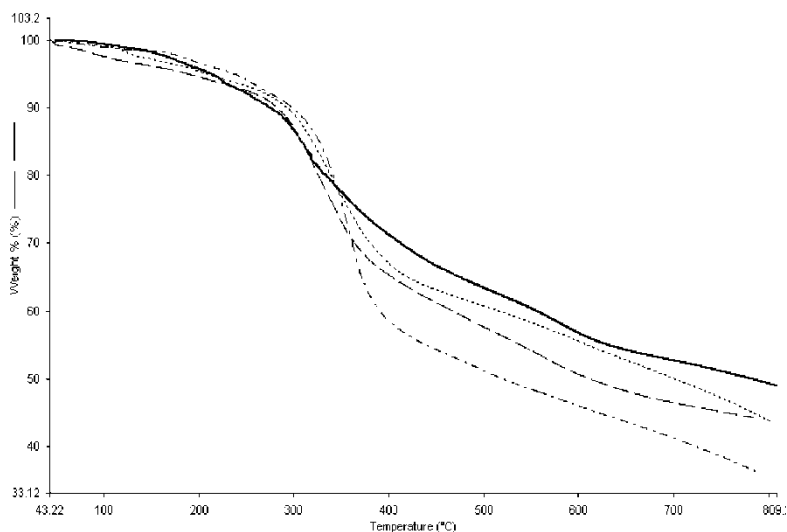


Figure 4.  $^{31}\text{P}$  NMR spectrum of homopolymer **1a**.





**Figure 5.** Thermogravimetric traces of homopolymers 1a (Solid), 1b (Dotted) and copolymers 2a (Dashed), 2b (DashDot).

The thermogravimetric traces of all the synthesized polymers are shown in Figure 5. The temperature corresponding to 10, 20, 30, 40 and 50% weight loss and char residue at 800°C are summarized in Table 1. Polymers containing unsubstituted aromatic diol moiety start to degrade relatively at lower temperatures compared to the polymers bearing methoxy substitution. Copolymers start degrading at higher temperatures compared to the corresponding homopolymers. This may be due to the incorporation of additional rigid aromatic segments in the main chain, which increase the thermal stability of polymers.

The  $T_g$  and  $T_m$  data observed in DSC are summarized in Table 2. The glass transition temperatures of the synthesized polymers were in the range of 48–64°C. The DSC traces of homo- and copolymers exhibit a broad exothermic peak at around 190–290°C and 340–380°C, respectively. This may be attributed to the thermal crosslinking of the polymer backbone (48, 49). Thermal crosslinking of copolymers takes place at a higher temperature than the corresponding homopolymers. This may be due to the incorporation

**Table 1**  
Thermogravimetric analysis data of polymers in nitrogen atmosphere

Polymer code	Temperature (°C) corresponding to weight loss					Char residue at 800°C (%)
	10%	20%	30%	40%	50%	
<b>1a</b>	271	334	411	561	786	49
<b>1b</b>	297	340	386	537	728	54
<b>2a</b>	285	327	365	470	615	54
<b>2b</b>	300	342	361	392	521	56

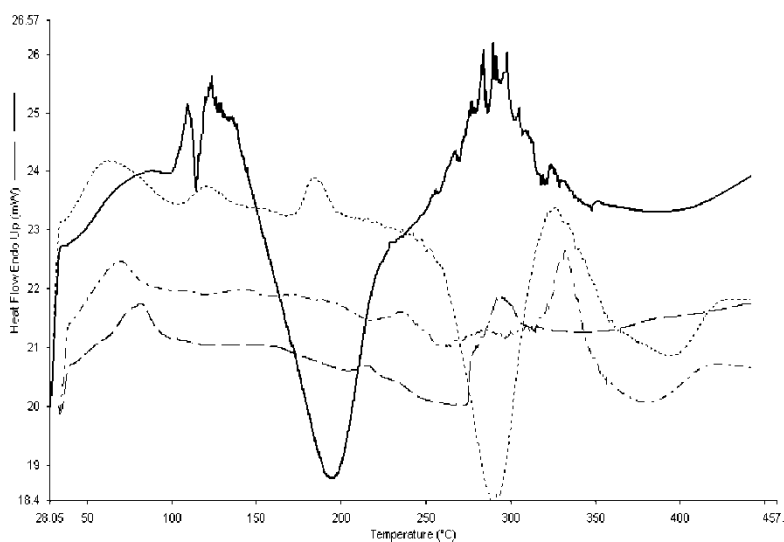
**Table 2**  
Differential scanning calorimetry data analysis of  
polymers under nitrogen atmosphere

Polymer	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	Exothermic peak (°C)
<b>1a</b>	57	—	194
<b>1b</b>	48	—	288
<b>2a</b>	64	283	340
<b>2b</b>	53	327	379

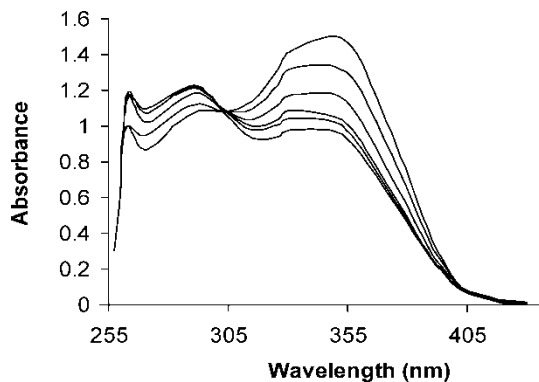
of terephthaloyl unit in the copolymer, which reduces the chances of orientation of olefinic double bonds for thermal crosslinking. The copolymers showed crystallization peaks followed by a melting peak at around 280–340°C, while homopolymers do not show any melting peaks. This may be attributed to the incorporation of ester linkages in the copolymer, which facilitate crystallization. These results indicate that the co-monomer play an important role in thermal stability of the prepared polymers. The DSC traces of homo and copolymers are shown in Figure 6.

### Photocrosslinking Properties

The photocrosslinking property of the polymers in solution and film state was studied by a UV spectrophotometer. The rate of conversion of >C=C< to –C–C– was calculated using the expression,  $[(A_0 - A_t) \times 100]/(A_0 - A)$ . Where, A<sub>0</sub>, A<sub>t</sub> and A are the absorption intensities of >C=C< at irradiation times 0, t and a time after which there is no further significant change in the absorption, respectively. All the polymers showed an



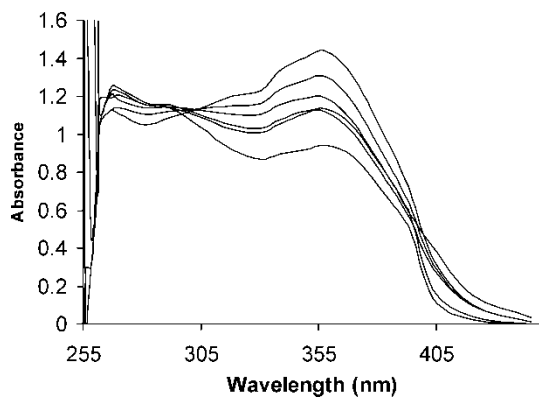
**Figure 6.** DSC traces of homopolymers **1a** (Solid), **1b** (Dotted) and copolymers **2a** (Dashed), **2b** (DashDot).



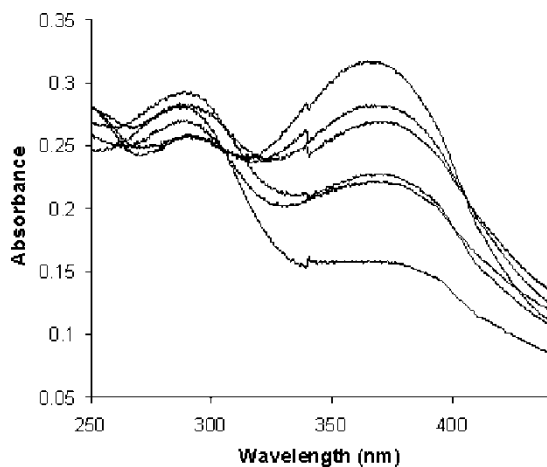
**Figure 7.** Change of UV-Vis absorption spectrum of homopolymer **1a** in DMSO solution during UV irradiation, top to bottom, after irradiation time  $t = 0, 2, 4, 7, 10$  and 30 min.

absorption maximum at around 350 nm due to  $\pi \rightarrow \pi^*$  transition of the olefinic double bond present in the polymer chain. The photocrosslinking behavior of the homopolymer **1a** and copolymer **2b** in solution phase is shown in Figures 7 and 8, respectively. A decrease in the intensity of absorbance was observed in all polymers during the successive irradiation with regular time intervals. This may be attributed to the formation of cyclobutane ring by the  $2\pi + 2\pi$  cycloaddition of the olefinic double bond (50, 51). These polymers also showed an isobestic point at around 290–305 nm due to the *cis-trans* isomerization of olefinic double bond present in the polymer chain. Figure 9 indicates the change of UV-Vis absorption spectrum of polymer **1a** in film state.

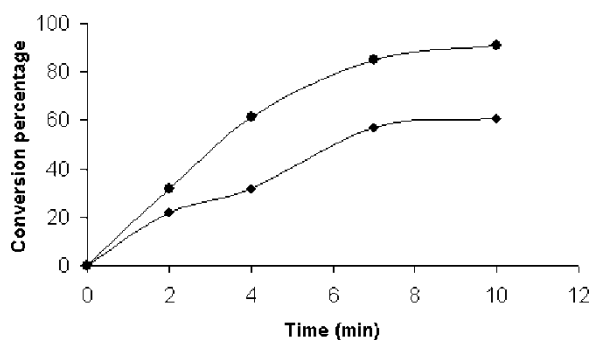
These UV spectral studies indicate that all the synthesized polymers are photosensitive in both solution and film state. After 10 min of irradiation time, photoconversions of about 91% and 61% were observed for solution and film state, respectively for the homopolymer **1a**. The results reveal that the rate of photocrosslinking of polymer **1a** in solution state was faster than that in film state. Figure 10 represents the comparison of relative rate of photocrosslinking of polymer **1a** in film and solution state. Homopolymers show a higher rate of crosslinking than their copolymers. This may be due to the possible



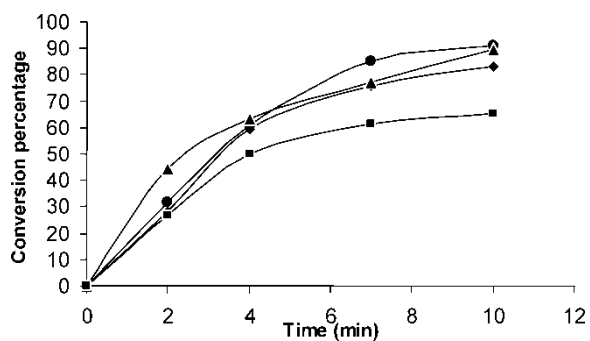
**Figure 8.** Change of UV-Vis absorption spectrum of copolymer **2b** in DMSO solution during UV irradiation, top to bottom, after irradiation time  $t = 0, 2, 4, 7, 10$  and 30 min.



**Figure 9.** Change of UV-Vis absorption spectrum of polymer **1a** in film state during UV irradiation, top to bottom, after irradiation time  $t = 0, 2, 4, 7, 10$  and  $30$  min.



**Figure 10.** The comparison of relative rate of photocrosslinking of polymer **1a** in film (◆) and solution (●) state.



**Figure 11.** Rate of disappearance of  $>C=C<$  of photoreactive groups of homopolymers **1a** (●), **1b** (◆) and copolymers **2a** (▲), **2b** (■) in solution state.

symmetrical arrangement of photoreactive moieties in the adjacent homopolymer chain which leads to the formation of maximum number of cyclobutane rings. Figure 11 shows the relative rate of conversion of olefinic double bond to C–C single bond for various polymers in solution state. The solubility of the irradiated polymer films was examined and found to be insoluble in common organic solvents. This observation further confirms the photocrosslinking behaviour of the polymers.

## Conclusions

Four new phosphorus containing homo and co-polyesters with photosensitive moieties in the main chain were synthesized from 1,3-Bis(4-hydroxyphenyl)propanone and 3-(4-hydroxy-3-methoxy phenyl)-1-(4-hydroxyphenyl)propanone by interfacial polycondensation technique using HDTMAB as phase transfer catalyst. The structures of synthesized polymers were confirmed through UV, FTIR and  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and  $^{31}\text{P-NMR}$  spectroscopic techniques. The presence of flexible P–O–C linkages provides good solubility in common organic solvents like DMF, DMSO and THF. Thermogravimetric results indicate that the synthesized polymers are stable up to  $250^\circ\text{C}$  and possess high char residue at  $800^\circ\text{C}$ . DSC analysis reveals that the copolymers are more crystalline and undergo thermal crosslinking at higher temperature than the corresponding homopolymers. The photocrosslinking property of the polymers was monitored by ultraviolet spectroscopy and was found to be highly sensitive in both solution and film states. The rate of photocrosslinking of homopolymers is higher than that of copolymers. These results indicate that these polymers can be used as negative photoresists.

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