Photocrosslinkable Phosphorus Containing Homo- and Copolyesters: Synthesis, Characterization, and Photosensitive Properties

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ABSTRACT: A new series of homo- and copolyphosphoramide esters containing pendant chlorine group was synthesized from dihydroxy chalcones, *N*-(4-chlorophenyl)phosphoramidic dichloride, and terephthaloyl chloride by interfacial polycondensation technique. The diol monomers were prepared by condensing 4-hydroxy benzaldehyde and 3-methoxy-4-hydroxybenzaldehyde with 4-hydroxy acetophenone. The synthesized monomers and polymers were characterized by UV, IR and ^{1}H, ^{13}C, and ^{31}PNMR spectroscopic techniques. Molecular weight of the polymers was determined by gel permeation chromatography. The thermal properties of the polymers were studied by thermogravimetric analysis and differential scanning calorimetry under nitrogen atmosphere. The photo-crosslinking ability of the polymers in various solvents was observed with UV spectrophotometer. The photocrosslinking proceeds via $2\pi + 2\pi$ cycloaddition reaction of α, β-unsaturated carbonyl group. The comparison study on the rate of photocrosslinking of homo and copolymers was also carried out. The chemical and physical properties of these polyesters are compared with those of the unsubstituted polyesters and the results are discussed herein. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1606–1614, 2009

Key words: photocrosslinkable; phosphorus containing; poly(phosphoramide ester)s; chalcone containing

INTRODUCTION

Photosensitive polyesters are a special class of processable materials that have found use in a variety of commercial applications. Photosensitive polymers are widely used in energy exchange materials, photocurable coatings, microelectronics, integrated circuits, printing plates, photo recorders, optical recording devices, and photo sensitizers for organic synthesis.[1–5] The feasibility of processing of polymers may depend upon the solubility, flexibility, and softening or melting temperatures of the polymers. Most of the polymers are insoluble in organic solvents and due to their high melting and softening temperatures they may not be employed for practical applications. Polymers employed for photosensitive applications should possess good solubility, photosensitivity, and thermal stability.

Chalcone containing polymers are attracting great attention as photosensitive and thermally stable polymers owing to their film forming tendency, resistance towards solvents after crosslinking, and higher thermal stability.[6,7] UV irradiation causes significant changes in physical and chemical properties of the polymers having photosensitive moieties such as cinnamoyl, stilbene, triazene, azobenzene, coumarine, and acetylene. Polymers with photoresponsive polybenzoxazole precursor for microelectronic applications,[8] methacrylate polymers containing pendant chalcone moieties for photoresist applications,[9] photosensitive microspheres for photoresists,[10] and maleimide based photopolymers for photo aligning of liquid crystalline molecules[11] have been reported. Among various photosensitive materials, no much reports have been observed with polymers containing α, β-unsaturated carbonyl moiety in the main chain.

In continuation of our research in this domain,[12] the present investigation deals with the synthesis, spectral and thermal characterization, and photocrosslinking studies of hitherto unreported phosphorus containing photosensitive homo- and copolyesters with pendant chlorine moiety.

EXPERIMENTAL

Materials

p-Chloroaniline, phosphorus oxychloride, and other solvents were purified by reported procedures.[13,14] 4-Hydroxy benzaldehyde (Merck), 4-hydroxy acetophenone (Ranbaxy), 4-hydroxy-3-methoxy benzaldehyde
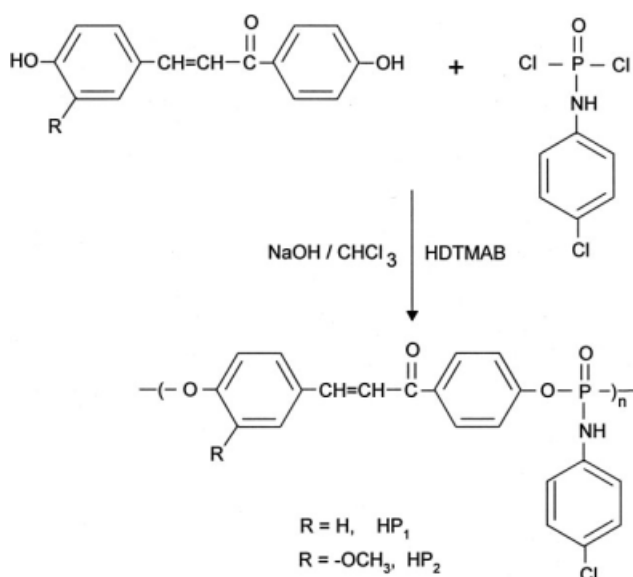
Scheme 1 Synthesis of homopolymers.

Monomer synthesis

Synthesis of 1,3-bis(4-hydroxyphenyl) propenone

4-Hydroxy benzaldehyde (0.1 mol) and 4-hydroxy acetophenone (0.1 mol) were taken in a 250-mL-round bottom flask. The mixture was dissolved in 60 mL of methanol, and two drops of borontrifluoride diethyl etherate was added as a catalyst. The reaction mixture was stirred and refluxed for 4 h at 55°C in an oil bath and cooled to room temperature. The precipitated product was filtered 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).[16] FT-IR (KBr): 3299 cm^{-1}(v_{OH}), 1641 cm^{-1}($v_{C=O}$), 1601 cm^{-1}($v_{C=C}$), 3069 cm^{-1}(aromatic v_{C-H}). ^{1}HNMR (DMSO-d_6): 7.5–8.3 δ (m, 8H, aromatic), 9.7 δ (s, 2H, OH), 6.9 δ(d, 2H, —CH=CH—). UV-VIS λ_{max}(C$_2$H$_5$OH) = 351 nm (—C=C—).

(Merck), borontrifluoride diethyl etherate (Merck), and hexadecyl trimethyl ammonium bromide (HDTMAB, Fluka) were used as received. Terephthaloyl chloride was prepared by reacting terephthalic acid with thionyl chloride.[15]
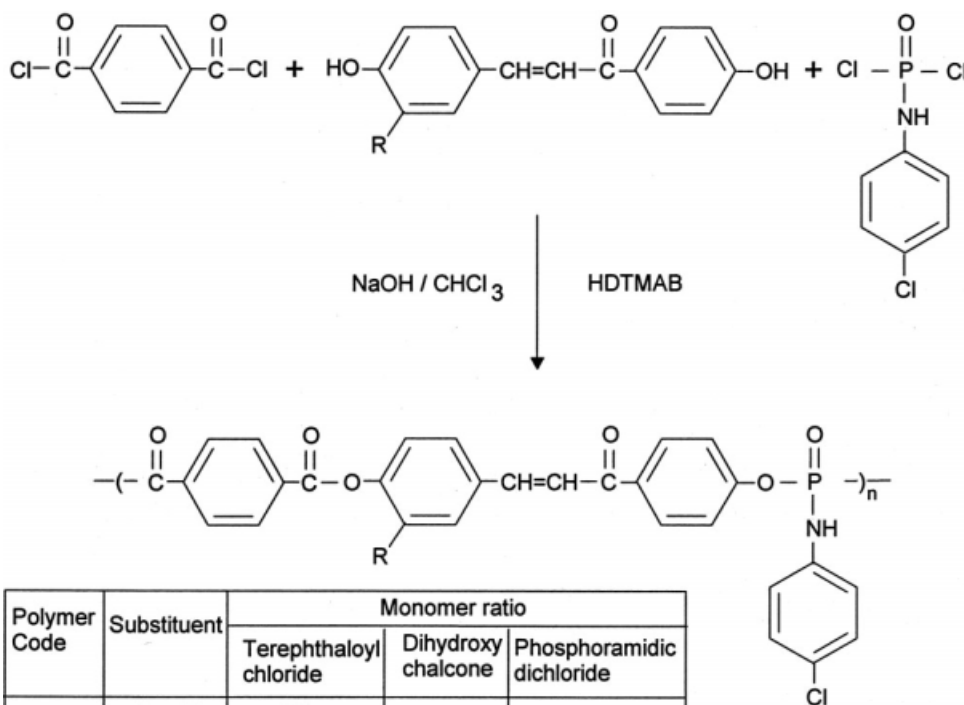
Synthesis of 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)propenone

The monomer 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl) propenone (Hmhp) was prepared from 4-hydroxy-3-methoxy benzaldehyde and 4-

Polymer Code	Substituent	Monomer ratio		
		Terephthaloyl chloride	Dihydroxy chalcone	Phosphoramidic dichloride
CP$_1$	R = -H	0.5	1.0	0.5
CP$_2$	R = -OCH$_3$	0.5	1.0	0.5
CP$_3$	R = -OCH$_3$	0.75	1.0	0.25
CP$_4$	R = -OCH$_3$	0.25	1.0	0.75

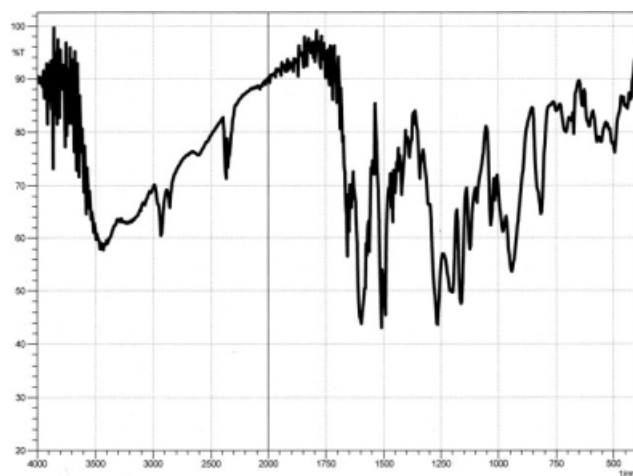**Scheme 2** Synthesis of copolymers.

Figure 1 FT-IR spectrum of homopolymer HP_2.

hydroxy acetophenone using borontrifluoride diethyl etherate as a catalyst, by following the procedure described above. Yield: 85%, mp 181°C; FT-IR (KBr): 3400 cm^{-1}(v_{OH}), 1641 cm^{-1} ($v_{C=O}$), 1591 cm^{-1}($v_{C=C}$). ^{1}HNMR (DMSO d_6, TMS): 7.1–8.0 δ (m, 7H, aromatic), 3.6 δ (s, 3H, —OCH$_3$), 9.7 δ (s, 2H, —OH), 6.9 δ (d, 2H, —CH=CH—). UV-VIS λ_{max} (C$_2$H$_5$OH) = 353 nm (—C=C—).

Synthesis of *N*-(4-chlorophenyl)phosphoramidic dichloride

This monomer, *N*-(4-chlorophenyl)phosphoramidic dichloride (CPD), was prepared by condensing phosphorus oxychloride with *p*-chloroaniline.[17] Phosphorus oxychloride (0.05 mol) was dissolved in 30 mL dry chloroform in a 250-mL-round bottom flask. *p*-Chloroaniline (0.1 mol) in 30 mL chloroform was added over a period of 15 min with vigorous stirring at ambient temperature. Subsequently, the mixture was stirred for further 30 min. The separated *p*-chloroaniline hydrochloride was filtered, and the filtrate was dis-
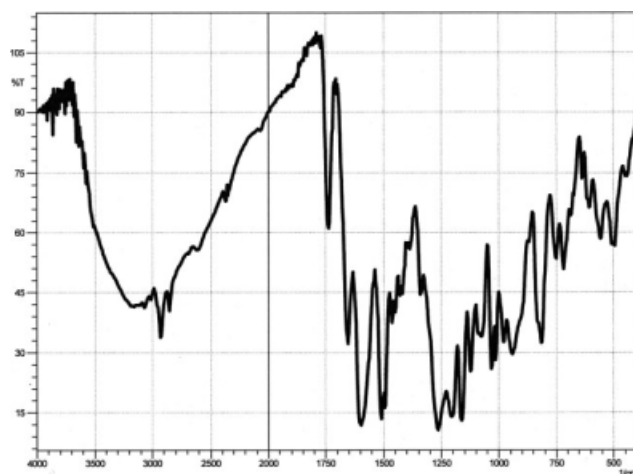
tilled under reduced pressure to yield a white solid mass of the product. Yield : 87%, mp 128°C; FT-IR (KBr): 3200 cm^{-1}($v_{N—H}$), 1340 cm^{-1}($v_{P—N—C}$, aromatic), 1280 cm^{-1}($v_{P=O}$), 1595 and 1500 cm^{-1} ($v_{C—C}$, aromatic), 1095 cm^{-1}($v_{P—Cl}$). ^{1}HNMR (DMSO d_6, TMS): 9.25 δ (s, 1H, —NH), 7.4 δ (d, 1H, aromatic), 7.2 δ (d, 1H, aromatic). ^{31}PNMR (DMSO d_6): −0.5 δ (s).

Polymerization

All the polymers were prepared by interfacial polycondensation method using HDTMAB, as phase transfer catalyst.[18] A typical procedure for the synthesis of polymer HP_1 is as follows: 1,3-bis(4-hydroxyphenyl)propenone (0.01 mol) was dissolved in 20 mL of NaOH (1N) solution, containing a pinch of HDTMAB. Twenty-five milliliter of chloroform solution of CPD (0.01 mol) was added to this mixture with vigorous stirring at 20°C. After 30 min the precipitated polymer was filtered off. It was then dried to constant weight in vacuum at 50°C; the yield was 82%. The other homo polymer (HP_2) was also prepared in a similar manner.

The copolymers (CP_1-CP_4) were prepared by adopting the following procedure. The appropriate dihydroxy chalcone (0.02 mol) was dissolved in 40 mL of 1N NaOH solution. A pinch of HDTMAB was added and stirred well to form froth. Chloroform solutions of CPD (0.01 mol) and terephthaloyl chloride (0.01 mol) were added to NaOH solution of dihydroxy chalone simultaneously, using funnels at 20°C with continuous stirring. Stirring was continued upto 30 min, then the polymer precipitated was filtered, washed with water and methanol, and dried to constant weight in vacuum at 50°C.

Characterization

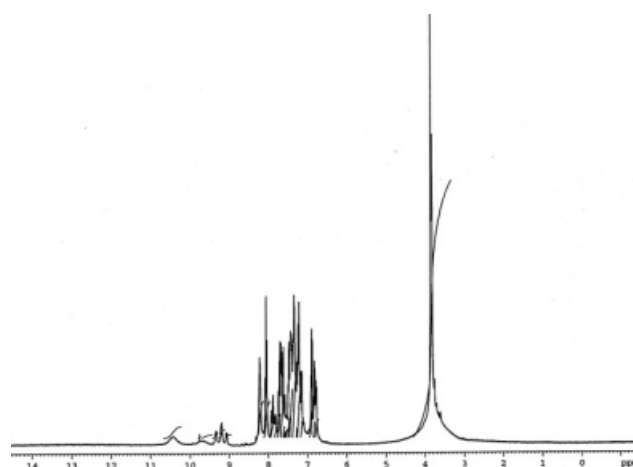The solubility of the synthesized polymers was tested with various organic solvents. The inherent

Figure 2 FT-IR spectrum of copolymer CP_2.
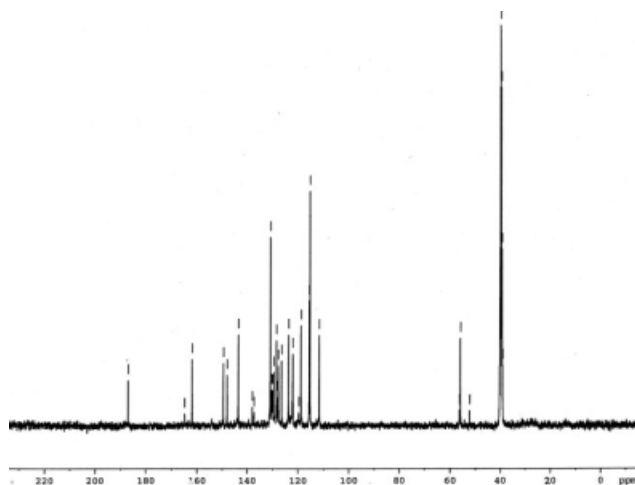
Figure 3 ^{1}HNMR spectrum of polymer HP_2.

Figure 4 ^{13}CNMR spectrum of copolymer CP$_3$.

Figure 5 ^{31}PNMR spectrum of polymer CP$_3$.

viscosity of the polymers was measured in DMSO (0.5 g/dL) at 27°C, using a suspended level Ubbelhode viscometer. The IR spectra were recorded with a Bruker IFS 66V Fourier transform infrared spectrophotometer using KBr pellets. The ^{1}H, ^{13}C, and ^{31}PNMR spectra were recorded on an AMX-400 NMR spectrometer using DMSO-d_6 as the solvent. The molecular weight of the polymers were determined on a SHIMADZU GPC analyzer with a TSK-GEL H-type column (styrene gel column) in tetrahydrofuran, using polystyrene as the standard. The UV spectra were recorded on a Systronics UV-119 spectrophotometer. The DSC traces were obtained on a Perkin-Elmer-Pyris six instrument with a heating rate of 10°C min^{-1} in nitrogen atmosphere. Thermogravimetric studies were performed on a Perkin-

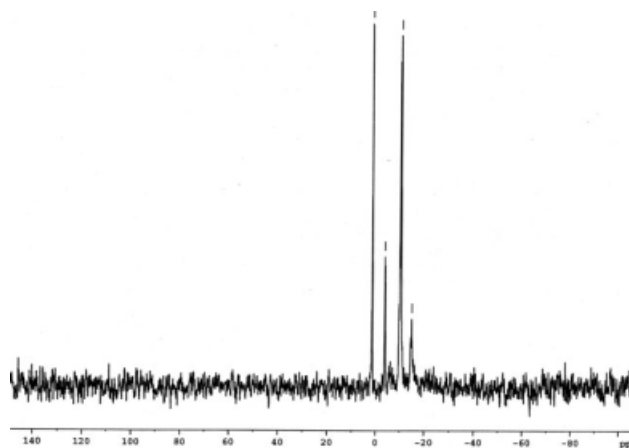Elmer thermal analyzer in nitrogen atmosphere at a heating rate of 20°C min^{-1}.

Photocrosslinking studies

The photosensitive properties of homo- and copolymers were studied by UV spectrophotometer in both film and solution state. A thin film of the polymer was cast on the outer surface of the quartz cuvette from the acetone solution and irradiated with 125W medium pressure mercury vapor lamp, which is kept at a distance of 10 cm from the sample for various intervals of time. The UV spectrum of the polymer film was recorded immediately after every exposure in a UV spectrophotometer. The rate of disappearance of >C=C< double bond was followed using the expression,

$$\text{Rate of conversion (\%)} = [(A_0 - A_t) \times 100]/[A_0 - A]$$

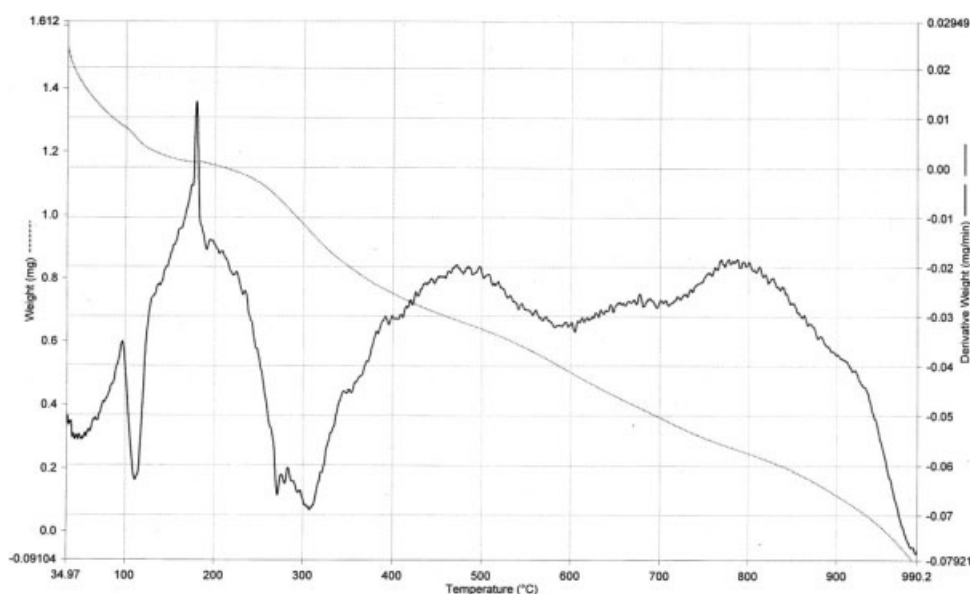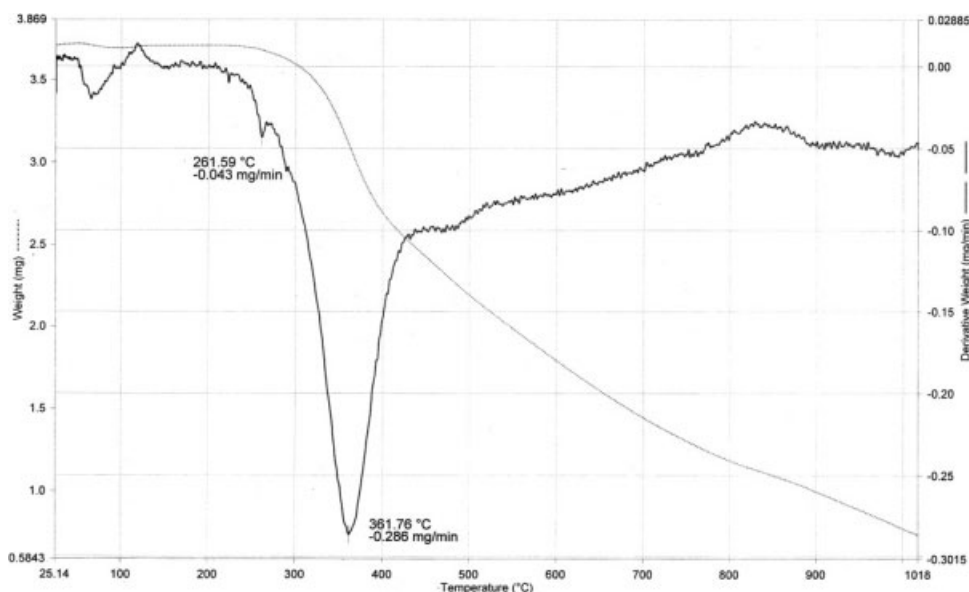**Figure 6** The TGA and DTG curves of homopolymer HP$_2$.

Figure 7 The TGA and DTG curves of copolymer CP_3.

Where, A_0, A_t, 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.

RESULTS AND DISCUSSION

The homo- and copolyphosphoramide esters were synthesized by an interfacial polycondensation method using HDTMAB as a phase transfer catalyst at 20°C with more than 75% yield (Schemes 1 and 2). The solubility of the prepared polymers were checked in different solvents. The homopolymers were soluble in DMF, THF, DMSO, dioxane, and acetone, and insoluble in chloroform, benzene, toluene, and other hydrocarbons. This good solubility in polar organic solvents may be attributed to the introduction of phosphorus linkage in the main chain, increasing the polarity.[19] The copolymers show poor solubility when compared with homopolymers, which may be due to the introduction of rigid aromatic groups in the main chain. The inherent viscosity of the resulting polymers was determined in

DMSO solution and they were in the range of 0.32–0.54 dL/g. The homo polymers possess comparatively lower viscosity than copolymers. The average molecular weight of homopolymers are in the range of 8300–8500, whereas that of copolymers are in the range of 9200–9500. This may be due to the high reactivity of phosphoramidic dichloride leading to side reactions like hydrolysis.[20]

Spectral Characterization

The Chemical structures of the prepared polymers were confirmed with UV, IR, and ^{1}H, ^{13}C, and ^{31}PNMR spectroscopic techniques. The infrared spectrum of the representative homopolymer (HP_2) and copolymer (CP_3) are given in Figures 1 and 2, respectively. The IR spectrum of the homopolymer showed absorption bands at around 1490, 1450 cm^{-1} due to aromatic $>C=C<$ skeletal stretching vibrations; bands at 1650 cm^{-1} due to Ar-C=O and at 1597 cm^{-1} due to olefinic $>C=C<$ of the chalcone moiety. The absorption peaks of P—N and P=O bonds appeared at around 940 and 1265 cm^{-1},

TABLE I
Thermogravimetric Analysis Data and of Polymers

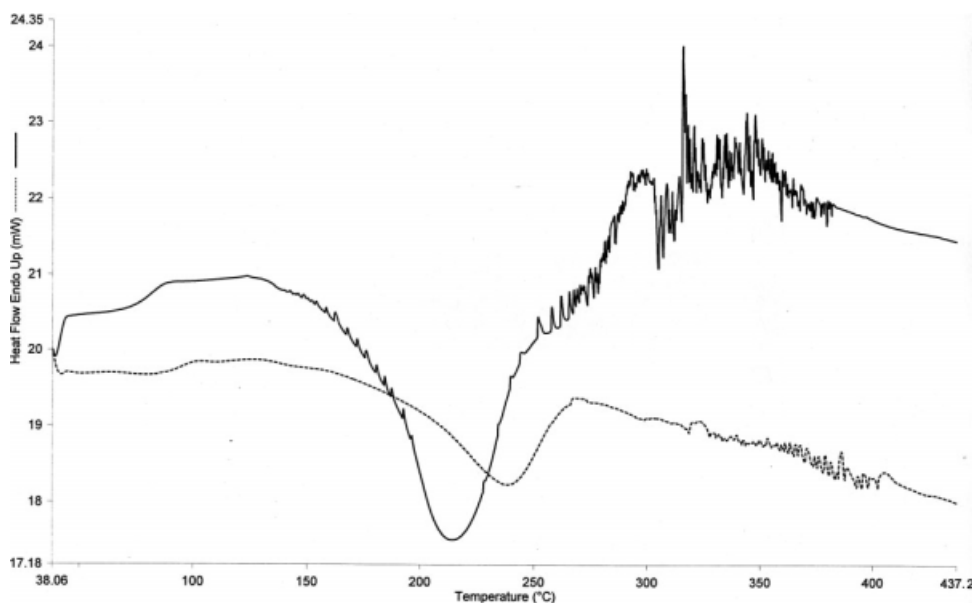| Polymer code	Temperature (°C) corresponding to weight loss							Char at 800°C (%)
	10%	20%	30%	40%	50%	60%	80%	
HP_1	61	101	181	300	365	476	700	15
HP_2	63	113	263	315	386	515	741	17
CP_1	63	196	339	400	473	538	692	12
CP_2	127	265	346	392	477	589	958	29
CP_3	342	373	416	494	585	692	1000	32
CP_4	59	135	300	362	408	481	635	10

Figure 8 DSC traces of homopolymers HP_1 (Solid) and HP_2 (Dashed).

respectively. Both the homopolymers and copolymers showed absorptions at 1340 and 1162 cm^{-1} corresponding to P—N—C(aromatic) and P—O—C (aromatic) bonds respectively.[21] The copolymers showed an additional band at 1735 cm^{-1}, corresponding to ester carbonyl group. The UV spectrum of all the polymers showed an absorption maximum at around 350 nm which may be due to the $\pi \rightarrow \pi^*$ transition of olefinic double bond present in the polymer main chain.[22]

Figure 3 shows the ^{1}HNMR spectrum of polymer HP_2. The aromatic protons resonate in the range of 6.7–7.3 δ. The olefinic and methoxy protons were appeared at 6.8 and 3.3 δ, respectively. The resonance signal at 9.3 δ may be due to end group hydroxyl protons. The N—H proton resonates as a singlet at 10.5 δ. The ^{13}CNMR spectrum exhibited the expected absorption peaks for every carbon atoms of homo- and copolymers. The α, β-unsaturation in the carbonyl compound makes the carbonyl carbon to resonate in the upfield at around 185–187 δ. The signal appearing in the range of 163–170 δ corresponds to ester carbonyl carbon. The methoxy carbons of polymers HP_2, CP_2-CP_4 appear at around 55–57 δ. The olefinic carbons, α, and β, show two resonating signals at around 129–132 δ and 144–148
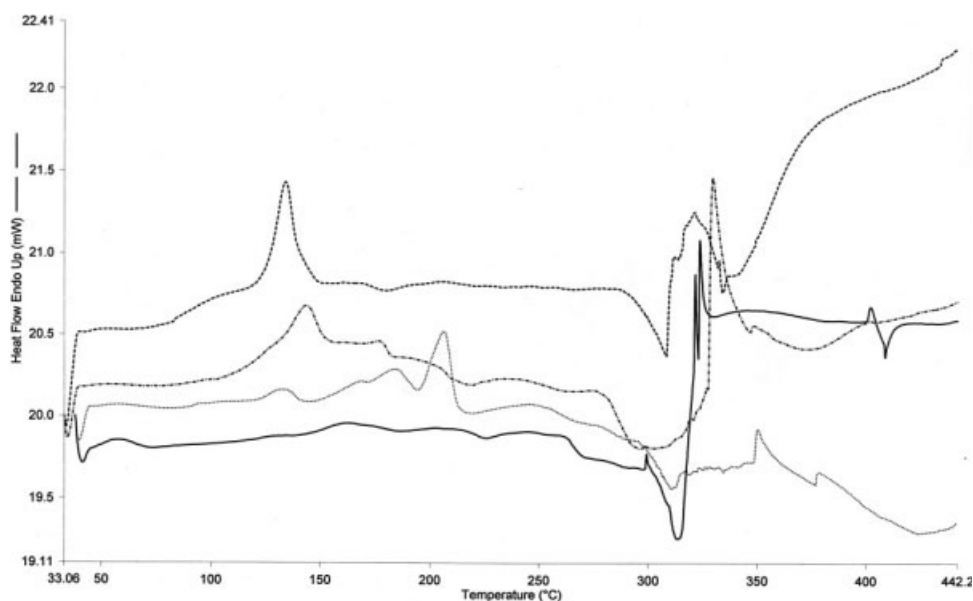

Figure 9 DSC traces of copolymers CP_1 (Solid), CP_2 (Dashed), CP_3 (Dotted) and CP_4 (DashDot).
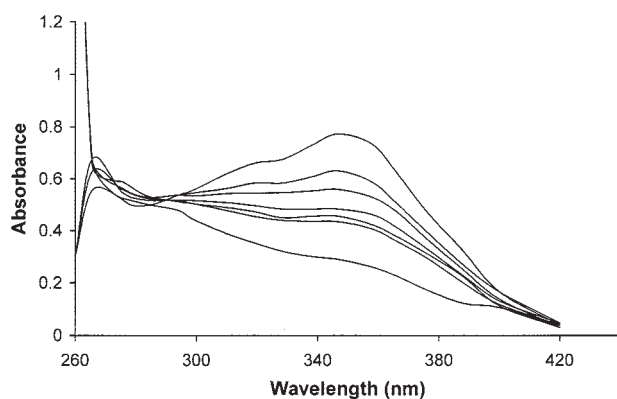
TABLE II
DSC Data Analysis of Polymers

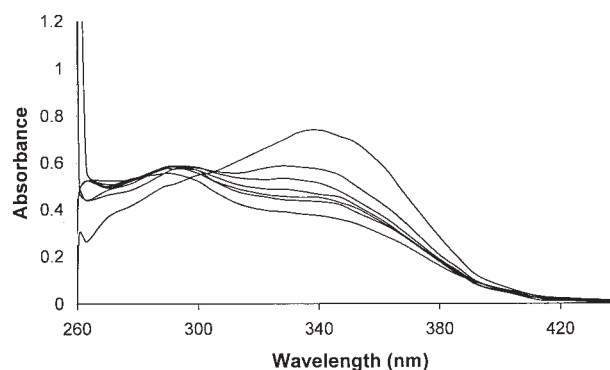| Polymer	T_g (°C)	T_m (°C)	Exothermic peak (°C)
HP$_1$	80	–	213
HP$_2$	94	–	237
CP$_1$	113	162	313
CP$_2$	90	134	308
CP$_3$	92	206	310
CP$_4$	90	143	302

δ, respectively. The aromatic carbons resonate at around 110–155 δ. The representative ^{13}CNMR spectrum of copolymer CP$_3$ is shown in Figure 4. The ^{31}PNMR spectrum of all the polymers showed four signals. The four signals are attributed to the presence of three inequivalent phosphorus atoms in the main chain and one phosphorus atom at the chain end.[23] The three inequivalent phosphorus nuclei arise due to the formation of three types of repeating units by the head to head, head to tail, and tail to tail addition of unsymmetrical bisphenol monomer to *N*-phenyl phosphoramidic dichloride. The representative ^{31}PNMR spectrum of polymer CP$_3$ is shown in Figure 5. The phosphorus atoms surrounded by aryloxy is more shielded and appeared upfield ($\sim$ −17.0, −10.0, and −4.5 δ) than the phosphorus at the chain end ($\sim$ 2.0 δ). These spectral data confirmed the formation of homo- and copolymers.

Thermal characterization

The thermal properties of the synthesized polymers were studied by thermogravimetry and differential scanning calorimetry in nitrogen atmosphere. The TGA and DTG curves for homopolymer HP$_2$ and copolymer CP$_2$ are shown in Figures 6 and 7, respectively. The temperatures corresponding to 10, 20, 30,
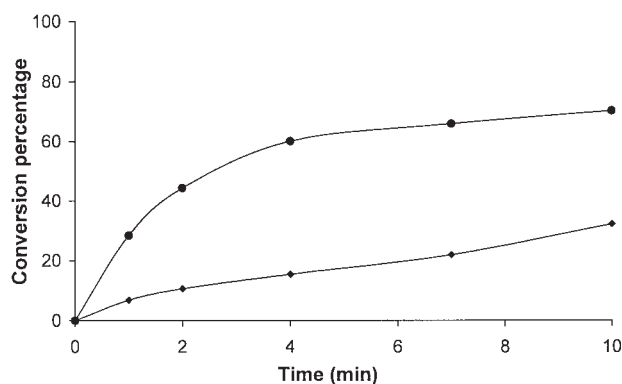
Figure 11 Change of UV-Vis absorption spectrum of copolymer CP$_1$ in DMSO solution during UV irradiation, top to bottom, after irradiation time $t = 0$, 1, 2, 4, 7, 10, and 30 min.

40, 50, 60, and 80% weight loss and char residue at 800°C are given in Table I. The initial weight loss in homopolymers may be due to the loss of water molecules and appreciable weight loss takes place at around 240°C, whereas the copolymers are stable upto 320°C and starts degrading thereafter. The homopolyesters show two stage degradation compared with that of copolyesters. This may be attributed to the higher percentage of phosphorus content in the homopolymers. The first stage corresponding to the formation of small fragments which may subsequently carbonize in the second step.[24] It was observed that the methoxy substituted polymers are more stable than the respective unsubstituted polymers. The copolymers with higher percentage of terephthaloyl units show higher thermal stability which may be due to the increasing rigidity of main chains.

Figures 8 and 9 show the DSC traces of the homo- and copolymers, respectively. The T_g and T_m data are summarized in Table II. The glass transition temperatures of the synthesized polymers are in the range of 80–115°C. The DSC traces of homo- and copolymers exhibit a broad exothermic peak in the

Figure 10 Change of UV-Vis absorption spectrum of homopolymer HP$_2$ in DMSO solution during UV irradiation, top to bottom, after irradiation time $t = 0$, 1, 2, 4, 7, 10, and 30 min.

Figure 12 The relative rate of crosslinking of homopolymer HP$_2$ in solution (•) and film (◆) states.
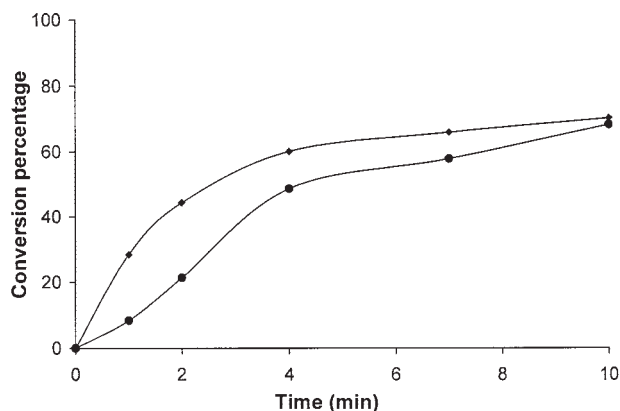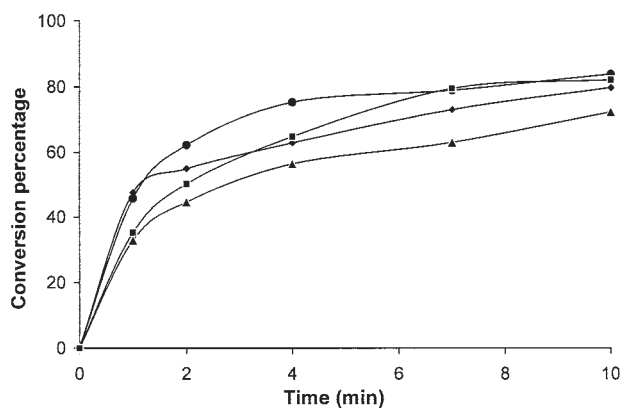
Figure 13 The rate of photocrosslinking of homopolymers HP$_1$ (●) and HP$_2$ (◆).
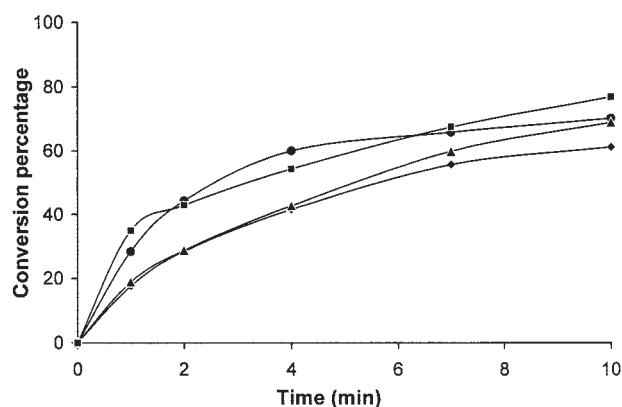
range of 210–240°C and 300–315°C, respectively. This may be attributed to the thermal crosslinking of the polymer backbone.[25] Thermal crosslinking of copolymers takes place at a higher temperature than the corresponding homopolymers. The copolymers showed melting peak at around 280–340°C which are not observed in homopolymers. The incorporation of ester linkages in the copolymer enhances the crystallinity of the polymers. This may be the reason for high melting and thermal crosslinking temperatures observed in copolymers.

Photocrosslinking studies

The photocrosslinking ability of the prepared polymers was studied in solution and film state by UV spectrophotometry. Figures 10 and 11 show the changes in the UV spectral pattern during the photolysis of polymers HP$_2$ and CP$_1$, respectively, at different time intervals. The absorption band at around 350 nm corresponds to $\pi \rightarrow \pi^*$ transition of the olefinic double bond. A decrease in the intensity of the absorption was observed during the successive irradiation. This may be due to $2\pi + 2\pi$ cycloaddition of
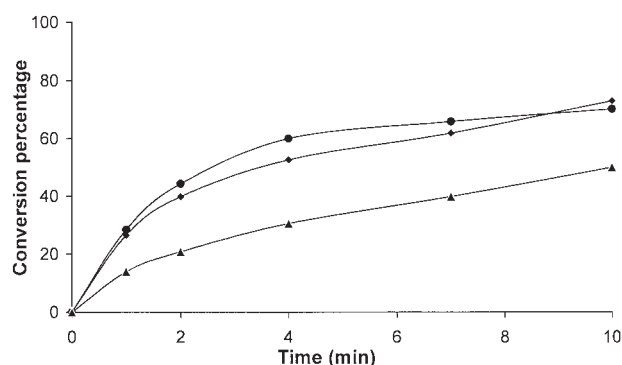

Figure 15 The rate of photocrosslinking of homopolymer HP$_2$ at different solvents DMSO (●), 1,4-Dioxan (◆), THF (▲) and DMF (■).

olefinic double bond lead to the formation of cyclobutane ring.[26,27] It was observed that maximum crosslinking occur within 10 min of irradiation. No appreciable crosslinking was observed after 30 min of irradiation. Figure 12 shows the relative rate of crosslinking of homopolymer HP$_2$ in solution and film states. The rate of photocrosslinking of polymers in solution state was faster than that in thin film state. This may be due to the ease of orientation of chromophoric olefinic groups in solution phase for photocrosslinking.

The rate of crosslinking of homo- and copolymers are shown in Figures 13 and 14. Copolymers showed higher rate of crosslinking than that of the homopolymers. This may be attributed to the presence of more pendant phenyl group in the homo polymers which hinder the orientation of olefinic group for photocrosslinking. The effect of various solvents such as DMSO, DMF, THF, and dioxane on the rate of photocrosslinking of polymer HP$_2$ was also studied, and the results are shown in Figure 15. The rate of photocrosslinking of homopolymer with different solvents is in the order: DMF > DMSO > THF > dioxane. This indicates that the polarity of the solvents

Figure 14 The rate of photocrosslinking of copolymers CP$_1$ (●), CP$_2$ (▲), CP$_3$ (◆) and CP$_4$ (■).

Figure 16 The rate of photocrosslinking of homopolymer HP$_2$ (●) with benzophenone (◆) and michlers ketone (▲).

influences the photocrosslinking rate. The photocrosslinking ability of polymers in the presence of photosensitizers was also evaluated. Figure 16 shows the effect of photosensitizer on photocrosslinking. It was observed that the triplet photosensitizers such as benzophenone and Michler's ketone have no effect on photosensitivity. This shows that the photocrosslinking occurs through one-step $2\pi + 2\pi$ cycloaddition and not via triplet (T) state.[28]

CONCLUSIONS

A new series of homo- and copolyphosphoramide esters containing photosensitive moieties in the main chain were synthesized from dihydroxy chalcones, CPD, and terephthaloyl chloride by interfacial polycondensation technique, using HDTMAB as phase transfer catalyst. The structures of synthesized homo- and copolymers were confirmed through UV, FT-IR and ^{1}HNMR, ^{13}CNMR, and ^{31}PNMR spectroscopic techniques. The presence of polar phosphoryl group (P=O) provides good solubility in many organic solvents like DMF, DMSO, and THF. The thermogravimetric analysis result clearly shows that the copolymer with higher percentage of terephthaloyl units shows good thermal stability. DSC results indicate that the copolymers possess high crystallinity than the homopolymers due to the presence of ester linkages in the main chain. The photo-crosslinking property of the polymers was monitored by ultraviolet spectroscopy and was found to be sensitive in both solution and film states. The results indicate that maximum photocrosslinking takes place within 10 min. The rate of photocrosslinking of polymers in solution state was higher than that in thin film state. The copolyphosphoramide esters showed higher rate of photocrosslinking than the corresponding homopolymers. The results obtained in this investigation suggest that these polymers can be used as negative photoresists and photocurable coatings.

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