

Synthesis and Spectral, Thermal, and Photocrosslinking Studies of Poly(benzylidene phosphoramidate ester)s

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ABSTRACT: A new class of poly(benzylidene phosphoramidate ester)s containing a photoreactive benzylidene chromophore in the main chain were synthesized from bis(4-hydroxy-3-methoxy benzylidene)acetone with various substituted *N*-aryl phosphoramidic dichlorides by an interfacial polycondensation technique. The synthesized polymers were characterized by inherent viscosity, IR, and ^1H -, ^{13}C -, and ^{31}P -NMR spectroscopy. The molecular weights of these polymers were determined by gel permeation chromatography. These polymers were studied for their thermal stability and photochemical properties. Thermal properties were evaluated by thermogravimetric analysis and differential scanning calorimetry. It was found that halogen-containing polymers show a higher thermal stability than that of nonhalogenated polymers. The photocrosslinking property of these polymers was studied by ultraviolet spectroscopy. The photoreactive benzylidene chromophore in the main chain dimerizes via $2\pi + 2\pi$ cycloaddition reaction to form a cyclobutane derivative and leads to crosslinking. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2151–2157, 1997

Key words: poly(benzylidene phosphoramidate ester)s; spectral studies; photolyses; thermal stability

INTRODUCTION

Polymers with photofunctional groups have gained considerable interest in recent years. These polymers possess wide applications such as in photoresists to make integrated circuits, printing plates, photocurable coatings, photorecorders, photoconductors, energy-exchange materials, and photosensitizers for organic synthesis.^{1–5} Polymers containing pendant cinnamic ester have been used as photopolymers.^{6,7} Photoresists in combination with multiple imaging devices have enabled engineers to produce microcircuits and thereby reduce considerably the size of the digital computers.⁸ Polymers bearing a photodimerizable stilbazolium group are potential candidates for

the immobilization of enzymes.^{9,10} Photocrosslinkable liquid crystalline polymers find applications in anisotropic network systems like LC elastomers and LC thermosets,¹¹ information-storage devices,¹² and thin films with a controlled orientation of functional groups, which are of interest in microelectronics and optoelectronics.^{13–15} Photosensitivity, solubility, and thermal stability are the prime requirements for the use of these polymers. Incorporation of a flexible organophosphorus functionality in the polymer backbone imparts thermal stability and flame retardancy and helps to overcome the problems of processibility due to limited solubility in common solvents with high glass transition or melt temperature.^{16–23} The present work deals with the synthesis and characterization of a new class of polyphosphoramidate esters containing a photoreactive benzylidene chromophore in the main chain and studies their thermal and photocrosslinking properties.

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EXPERIMENTAL

Materials

Vanillin (Merck) and hexadecyltrimethylammonium bromide and phosphorus oxychloride (Fluka) were used as received. Acetone, aniline, *p*-anisidine, *p*-toluidine, *p*-chloroaniline, *p*-bromoaniline, and solvents were purified by the reported procedure.²⁴

Bis(4-hydroxy-3-methoxy benzylidene)acetone (HMBA)

To a mixture of 0.1 mol of vanillin and 6.183 g of boric acid in a 250 mL round-bottom flask, 50 mL of concentrated hydrochloric acid was added. The flask was cooled to 0°C. To this mixture, 0.05 mol of acetone was added dropwise with vigorous stirring and continued for 24 h. Then, the mixture was poured into 1 L of cold water. The precipitated product was filtered, washed with distilled water, and dried. Recrystallization from methanol gave light orange crystals with more than 83% yield of the title compound; mp 161°C (literature,²⁵ 159.5–160.5°C). IR (KBr): 3393 cm⁻¹ (ν_{OH}), 1636 cm⁻¹ ($\nu_{\text{C=O}}$), 1585 cm⁻¹ ($\nu_{\text{C=C}}$). ¹H-NMR (DMSO-*d*₆, TMS): 6.7 δ (m, 6H, aromatic), 3.7 δ (s, 6H, —OCH₃), 9.6 δ (s, 2H—OH), 7.2–7.7 δ (d, 4H, —CH=CH—).

N-Aryl Phosphoramidic Dichlorides (APD)

The *N*-phenylphosphoramidic dichloride was prepared from POCl₃ and aniline by adopting the similar reported procedure.²⁶ The other substituted APD were obtained following a similar procedure.

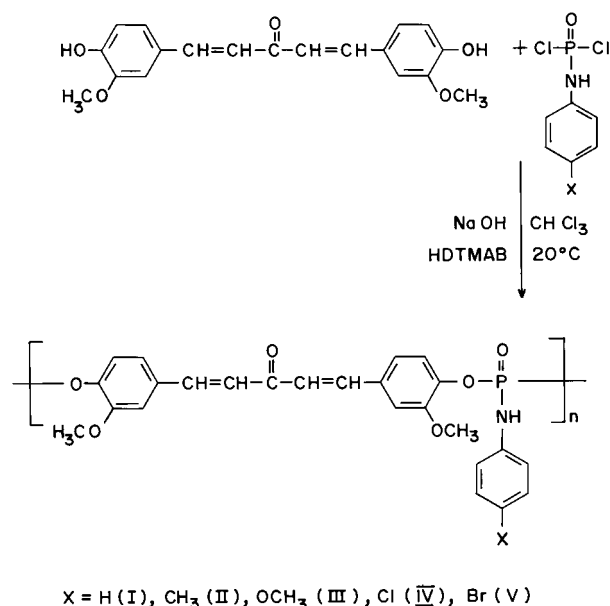
Polymerization

All the polymers were synthesized by interfacial polycondensation using hexadecyltrimethylammonium bromide (HDTMAB) as a phase-transfer catalyst.²⁷ A typical procedure for the synthesis of polymer I is as follows: 1 mmol of HMBA was dissolved in 20 mL of aqueous sodium hydroxide (1*N*) solution containing HDTMAB (2 wt % of the diol). To this aqueous solution, 1 mmol of APD in 20 mL of chloroform was added with vigorous stirring at 20°C. After 30 min, the organic layer was separated, washed with water, and poured over *n*-hexane. The precipitated polymer was filtered and washed with water. Further purification

was done by repeated precipitation from the chloroform solution using *n*-hexane as a nonsolvent. It was then dried to a constant weight *in vacuo* at 50°C; the yield was 78%. The other polymers (II–V) were also prepared in a similar manner.

Characterization

The inherent viscosity of the polymers was measured using a suspended level Ubbelohde viscometer in DMF (0.5 g dL⁻¹) at 30°C. The molecular weights (\bar{M}_w and \bar{M}_n) of polymers were determined by gel permeation chromatography (Waters 501) calibrated with polystyrene standards. The IR spectra were recorded on a Bruker IFS 66V FTIR spectrophotometer using KBr pellets. The ¹H- and ¹³C-NMR spectra were recorded in DMSO-*d*₆ using TMS as the internal standard on an EM-3990-90 MHz and a JEOL GSX 400 NMR spectrometer, respectively. The ³¹P-NMR spectra were recorded on Varian FT 80 A (32.2 MHz) spectrometer in DMSO-*d*₆ under broad-band ¹H decoupling conditions. D₂O and phosphoric acid (85%) were used as the external lock and external standard, respectively. The UV absorbance spectra were recorded on a Hitachi U2000 spectrophotometer. Thermogravimetric studies were performed on a Mettler TA 3000 thermal analyzer in a nitrogen atmosphere, at a heating rate of 20°C/



Scheme I Synthesis of poly(benzylidene phosphoramidate ester)s.

Table I Yield, Viscosity, and Molecular Weight of the Polymers I-V

Polymer No.	Yield (%)	η_{inh}^a (dL/g)	Molecular Weight ^b		
			\overline{M}_n	\overline{M}_w	$\overline{M}_w/\overline{M}_n$
I	78	0.48	4900	5200	1.06
II	76	0.40	4500	4900	1.08
III	78	0.45	4700	5000	1.06
IV	82	0.50	5100	5400	1.05
V	80	0.48	5000	5200	1.04

^a $C = 0.5$ g/dL in DMF at 30°C.

^b Determined by GPC.

min with a sample weight of 3–5 mg. The DSC traces were measured on a Perkin-Elmer differential scanning calorimeter at a heating rate of 20°C/min under a nitrogen atmosphere.

Photosensitivity Measurements

Photocrosslinking of the polymers was done in the form of films in a UV spectrophotometer. A thin film was cast on the outer surface of the quartz cuvette from the chloroform solution. The film was irradiated with a UV lamp kept at a distance of 10 cm from the sample for various time intervals. Subsequently, the irradiated film was subjected to spectral analysis.

RESULTS AND DISCUSSION

A series of photosensitive poly(benzylidene phosphoramidate ester)s were synthesized by interfacial

polycondensation using HDTMAB as a phase-transfer catalyst at 20°C with more than 76% yield (Scheme 1). All the polymers were soluble in chloroform, methylene chloride, tetrahydrofuran, DMF, dimethyl acetamide, and dimethyl sulfoxide and insoluble in benzene, toluene, and other hydrocarbons. This good solubility in polar organic solvents may be attributed to the introduction of flexible phosphorus linkage in the main chain.^{22,23} The inherent viscosity of the polymers determined in DMF at 30°C and the molecular weights obtained from GPC analysis are summarized in Table I. The low molecular weights of these polymers may be attributed to the low reactivity of phosphoramidic dichlorides leading to side reactions such as hydrolysis.²⁸

The infrared spectrum of polymer I is shown in Figure 1. The absorptions around 3170, 1642, and 1600 cm^{-1} correspond to γ_{NH} , $\gamma_{\text{C=O}}$, and $\gamma_{\text{C=C}}$, respectively. All the polymers showed strong ab-

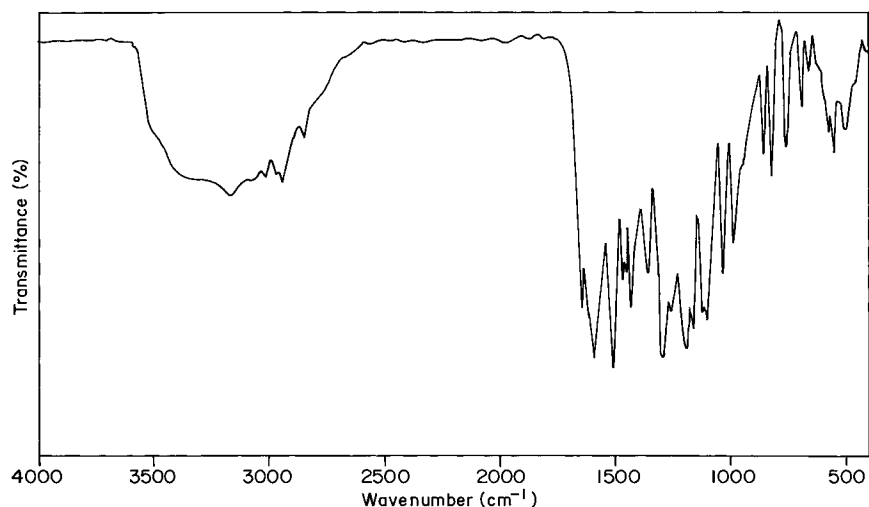


Figure 1 FTIR spectrum of polymer I.

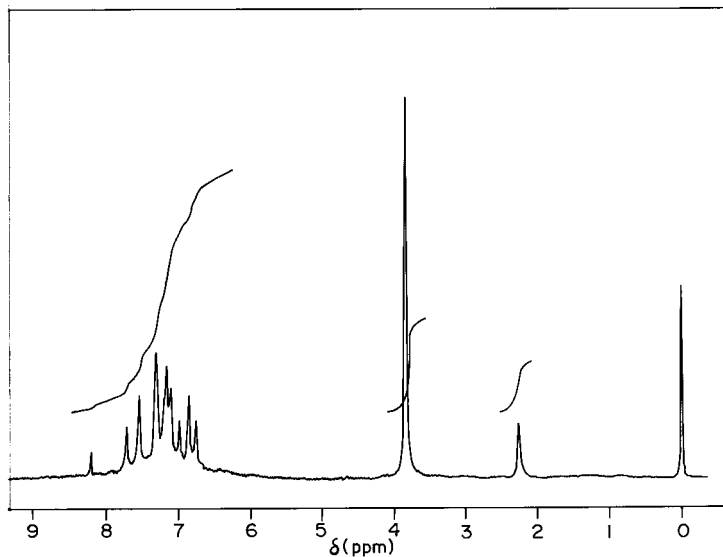


Figure 2 $^1\text{H-NMR}$ spectrum of polymer II.

sorptions of $\gamma_{\text{P-N-C(aromatic)}}$ at 1325, $\gamma_{\text{P=O}}$ at 1300, and $\gamma_{\text{P-O-C(aromatic)}}$ at 1182 and 960 cm^{-1} and support the formation of the polymers.^{29,30}

The representative $^1\text{H-NMR}$ spectrum of polymer II is shown in Figure 2. The N—H proton resonates as a singlet at 8.2 δ . The aromatic pro-

tons of the main chain, pendant phenyl ring, and the olefinic protons appeared as a broad multiple at 6.7–7.8 δ . The methoxy and methyl protons appeared as a singlets at 3.8 δ and 2.3 δ , respectively.

A typical proton decoupled $^{13}\text{C-NMR}$ spectrum of polymer II is shown in Figure 3. The resonance

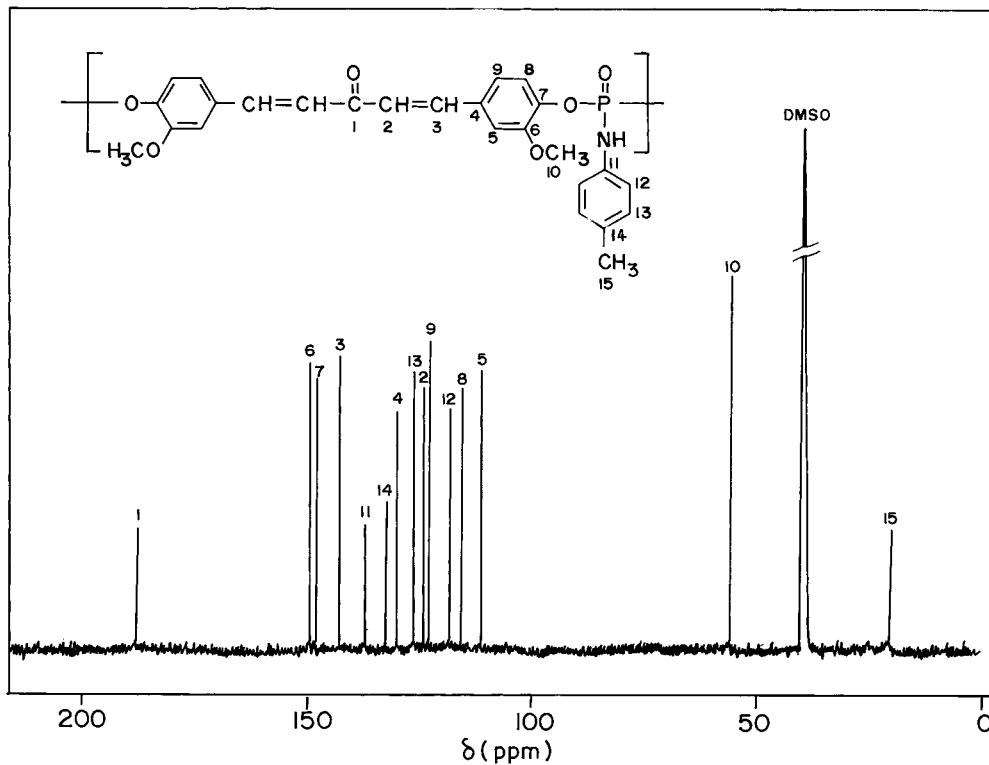


Figure 3 $^{13}\text{C-NMR}$ spectrum of polymer II.

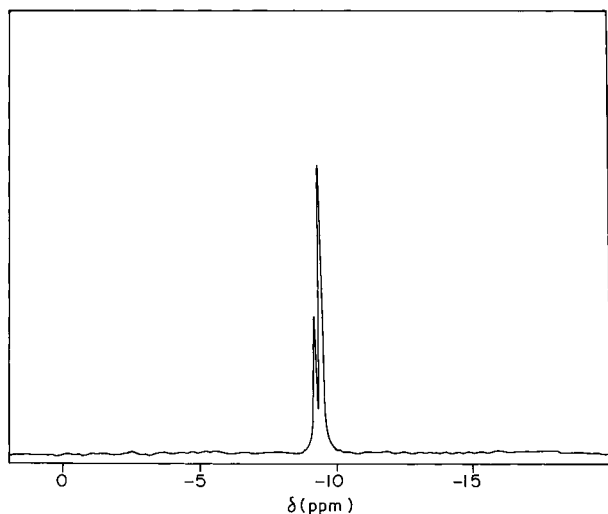


Figure 4 ^{31}P -NMR spectrum of polymer III.

lines in the spectrum falls into three main regions: 20–55 δ for the methoxy and methyl carbons, 110–150 δ for aromatic carbons of the main and pendant phenyl group, and 188 δ for the carbonyl carbon.³¹

The representative ^{31}P -NMR spectrum of polymer III is shown in Figure 4. All the polymers show a doublet around -9.8δ . This may be attributed to the spin–spin coupling of the ^{31}P resonance with hydrogen on nitrogen.³² The substituents on the pendant phenyl ring does not change the δ values.³³ These results support the formation of polymers.

The thermal properties of the polymers were studied by thermogravimetry and differential scanning calorimetry. Figure 5 shows thermograms of polymers I–V. The temperature corresponding to 10 and 50% weight loss and the char yield remaining at 800°C are given in Table II. All the polymers are stable up to 275°C and start degrading thereafter. The degradation occurs in

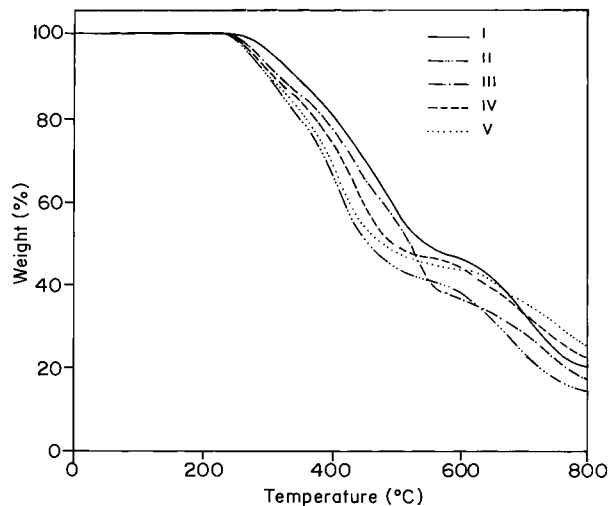


Figure 5 Thermogravimetric traces of polymers I–V.

a two-step process, the first step corresponding to the formation of various small fragments which subsequently carbonize in the second step. The char yield at 800°C shows some variation. This may be attributed to the substituent effect on the pendant phenyl ring. The halogen-containing polymers exhibited a higher char yield than that of the nonhalogenated polymers. Figure 6 shows the DSC trace of polymer I and the T_g and T_m values are given in Table II. The glass transition temperatures of these polymers are in the range of 85–90°C and the melting temperatures are in the range of 181–195°C. All the polymers show a broad exothermic peak around 400°C. This may be due to the thermal crosslinking of the polymer backbone.^{34,35}

The photosensitive property of these polymers was studied by a UV spectrophotometer. The change in the UV spectral pattern during the photolysis of polymer I at various intervals of time is shown in Figure 7. The absorbance band at 395

Table II Thermal Behavior of Polymers I–V

Polymer No.	DSC		Temperature (°C) Corresponds to		
	T_g (°C)	T_m (°C)	10% Wt Loss	50% Wt Loss	Char Yield at 800°C
I	86	185	340	545	20
II	—	180	290	465	15
III	85	181	310	520	18
IV	90	195	300	500	23
V	88	192	290	480	26

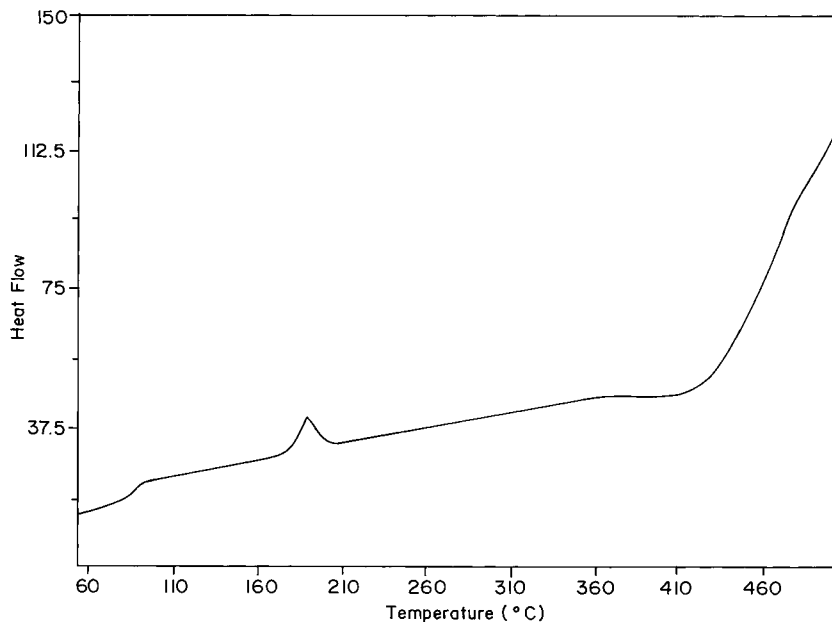


Figure 6 DSC trace of polymer I.

nm corresponds to a $\pi \rightarrow \pi^*$ transition of the olefinic double bond. A decrease in the intensity of the absorbance was observed during the successive irradiation. This may be ascribed to the photocrosslinking of the polymer chain which involves a $2\pi + 2\pi$ cycloaddition reaction of the olefinic double bond, leading to the formation of the

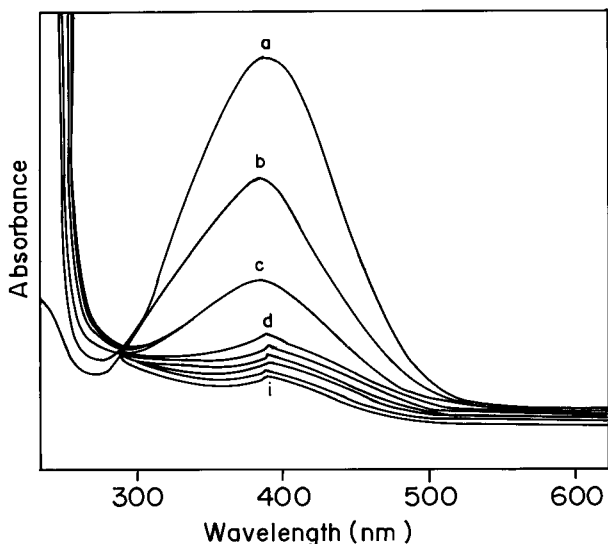


Figure 7 Changes in UV spectral characteristics during the photolysis of polymer I at various intervals of time.

cyclobutane ring.^{36,37} Figure 8 shows the rate of photocrosslinking of polymer I. The relative reactivity $A_0 - A_t/A_0$ is plotted against the time of irradiation, where A_0 is the absorption before irradiation, and A_t , after irradiation at time "t." It was noticed that the substitution on the pendant phenyl group does not influence the rate of crosslinking.

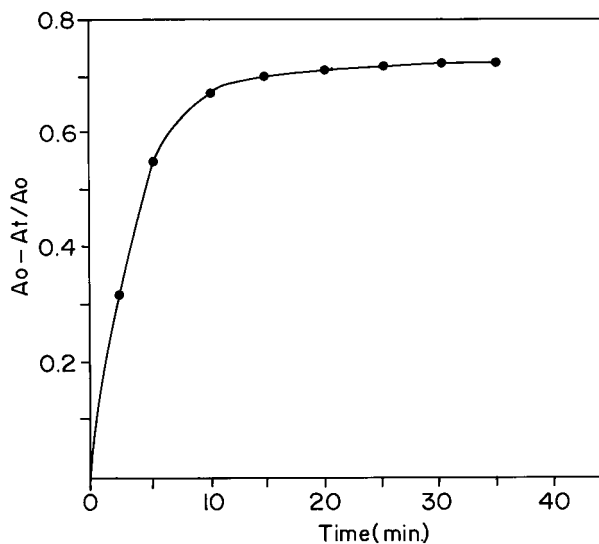


Figure 8 Dependence of photocrosslinking rate on irradiation time of polymer I.

CONCLUSION

A series of photoreactive benzylidene-containing poly(phosphoramidate ester)s were synthesized by interfacial polycondensation in the presence of an HDTMAB catalyst. The structures of the polymers were confirmed spectroscopically. All the polymers possess good solubility in polar solvents due to incorporation of flexible organophosphorus segments in the polymer backbone. The inherent viscosity and GPC data reveal that these polymers are of low molecular weights. The photochemical studies reveal that these polymers undergo crosslinking under the influence of UV irradiation. Furthermore, the substituents on the pendant phenyl ring does not affect the rate of crosslinking. Thermal studies revealed that the thermal stability depends on the structure of the polymers. The halogen-containing polymers are more stable than are the nonhalogenated polymers. The glass transition temperatures observed together with the solubility studies suggest that these polymers may be used both as melt and solution processable photosensitive materials.

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