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Synthesis and characterization of photo-crosslinkable poly(benzylidene phosphoramide ester)s

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Polyphosphoramide esters containing a photo-sensitive bisbenzylidene group in the main chain were synthesized from 2,7-bis(4-hydroxy-3-methoxybenzylidene) cycloheptanone with various N-arylphosphoramidic dichlorides by interfacial polycondensation using a phase transfer catalyst. The structure of the polymers was confirmed by infra-red and ^{1}H, ^{13}C and ^{31}P nuclear magnetic resonance spectroscopy. The molecular weights were determined by gel permeation chromatography, and the thermal stabilities were evaluated by thermogravimetric analysis and differential scanning calorimetry. The photo-crosslinking property of these polymers was studied by ultraviolet spectroscopy. The crosslinking proceeds via $2\pi + 2\pi$ cycloaddition reaction of the benzylidene group. The substitution on the pendant phenyl group has no significant effect on the rate of crosslinking. © 1997 Elsevier Science Ltd.

(Keywords: polyphosphoramide ester; thermal stability; photo-crosslinking ability)

INTRODUCTION

In recent years, polymers containing photo-sensitive segments in the main or side chain have become attractive due to the photo-crosslinking properties conferred by the presence of such units. Polymers with pendant cinnamic ester groups were used as photo-sensitive polymers[1,2]. These polymers are being used as photoresists to make integrated circuits, printing plates, photocurable coatings, photo recorders and energy exchange materials[3-7]. Photoresists in combination with multiple-imaging devices have enabled engineers to produce microcircuits and thereby reduce the size of digital computers[8]. Polymers bearing photo-dimerizable stilbazolium groups find applications in immobilization of enzymes[9,10]. Poly(di-tert-butyl fumarate) based polymers were useful in the preparation of deep ultraviolet photoresists[11]. Polyarylates containing photo-sensitive groups are used as photoresist and non-linear optic materials[12]. Photo-crosslinkable liquid crystalline (LC) polymers are potential candidates for applications in anisotropic network systems such as LC elastomers and LC thermosets, non-linear optics and information storage devices[13,14]. Photo-crosslinkable main chain LC polymers containing bisbenzylidene cycloalkanone groups possess useful properties in the poling of non-linear optical materials[15]. The solubility of these polymers is an essential requirement for their applications. Incorporation of a phosphorus segment into the polymer backbone increases the solubility behaviour and imparts good thermal stability and flame retardancy[16-21]. In continuation of our research in this domain, the present investigation deals with the synthesis and

characterization of hitherto unreported polyphosphoramide esters containing a photo-sensitive bisbenzylidene moiety in the main chain, and the study of the thermal stability and photo-crosslinking properties.

EXPERIMENTAL

Materials

Cycloheptanone (Merck), vanillin (Merck), hexadecyltrimethylammonium bromide and phosphorus oxychloride (Fluka) were used without further purification. Aniline, p-anisidine, p-toluidine, p-chloroaniline, p-bromoaniline and various solvents were purified by reported procedures[22].

Synthesis of monomers

2,7-Bis(4-hydroxy-3-methoxybenzylidene)cycloheptanone (HMBCH). The monomer was synthesized, based on a reported procedure[14]. To a mixture of cycloheptanone (0.01 mol) and vanillin (0.02 mol), 3 ml of dry piperidine was added dropwise. After the addition, the mixture was stirred at 80°C for 6 h. Subsequently, it was diluted with 15 ml of pyridine and poured into 250 ml of cold water. Acidification of the solution with HCl yielded a yellow precipitate. It was then filtered and recrystallized from ethanol, yield 74%; m.p. 153°C. Infra-red (i.r.) (KBr): 3358 cm^{-1} (γ_{OH}), 1640 cm^{-1} ($\gamma_{C=O}$), 1580 cm^{-1} ($\gamma_{C=C}$).

Proton nuclear magnetic resonance (^{1}H n.m.r.) [DMSO-d$_6$, tetramethylsilane (TMS)]: 1.8 δ (s, 4H, γ to the keto group of cycloheptanone), 2.9 δ (s, 4H, β to the keto group of cycloheptanone)[14], 3.8 δ (s, 6H, -OCH$_3$), 6.7–7.1 δ (m, 6H, aromatic), 7.3 δ (s, 2H, -CH=), 9.8 δ (s, 2H, -OH).

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N-Arylphosphoramidic dichlorides. The *N*-phenyl-phosphoramidic dichloride was prepared from $POCl_3$ with aniline by a reported procedure[23]. The other substituted arylphosphoramidic dichlorides were obtained following a similar procedure.

Polymerization

All the polymers were prepared by interfacial polycondensation method using hexadecyltrimethylam-moniumbromide (HDTMAB) as phase transfer catalyst[24]. A typical procedure for the synthesis of polymer I is as follows: in a solution of HMBCH (1 mmol) in 20 ml of aqueous NaOH (1 N), HDTMAB (2 wt% of the diol) was dissolved, then 20 ml chloroform solution of *N*-phenylphosphoramidic dichloride (1 mmol), was added to this mixture with vigorous stirring at 20°C. After 10 min the organic layer was separated, washed with water and poured over n-hexane. The precipitated polymer was filtered off and washed with water. Further purification was carried out by repeated precipitation from chloroform solution using n-hexane as a non-solvent. It was then dried to constant weight *in vacuo* at 50°C; the yield was 80%. The other polymers (II–V) were prepared in a similar manner. All the polymers were light-yellow powders.

Characterization

The inherent viscosity of the polymers was measured, using a suspended level Ubbelohde viscometer, in dimethylformamide (DMF) $(0.5 g dl^{-1})$ at 30°C. The molecular weights of the polymers were determined by gel permeation chromatography (g.p.c.) (Waters 501) calibrated with polystyrene standards. The i.r. spectra of the polymers were recorded in KBr pellets on a Brucker IFS 66V Fourier transform i.r. spectrophotometer. The ^1H and ^{13}C n.m.r. spectra were recorded in DMSO-d_6 using TMS as the internal standard, on a EM3900 (−90 MHz) and Jeol GSX 400 n.m.r. spectrometer, respectively. The ^{31}P n.m.r. spectra were recorded on a Varian FT 80A (32.3 MHz) spectrometer in DMSO-d_6 under broad band ^1H decoupling conditions. D_2O and phosphoric acid (85%) were used as the external lock and external standard, respectively. The ultraviolet (u.v.) absorbance spectra were recorded on a Hitachi U2000 spectrophotometer. Thermogravimetric studies were performed on a Mettler TA3000 thermal analyser, in nitrogen atmosphere, at a heating rate of 20°C min^{-1} with a sample weight of 3–5 mg. The differential scanning calorimetry (d.s.c.) traces were measured on a Perkin Elmer differential scanning calorimeter at a heating rate of 20°C min^{-1} under nitrogen atmosphere.

Photo-crosslinking studies

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

RESULTS AND DISCUSSION

A new series of polyphosphoramide esters were synthesized by an interfacial polycondensation

X = H (I), CH₃ (II), OCH₃ (III), Cl (IV), Br (V)
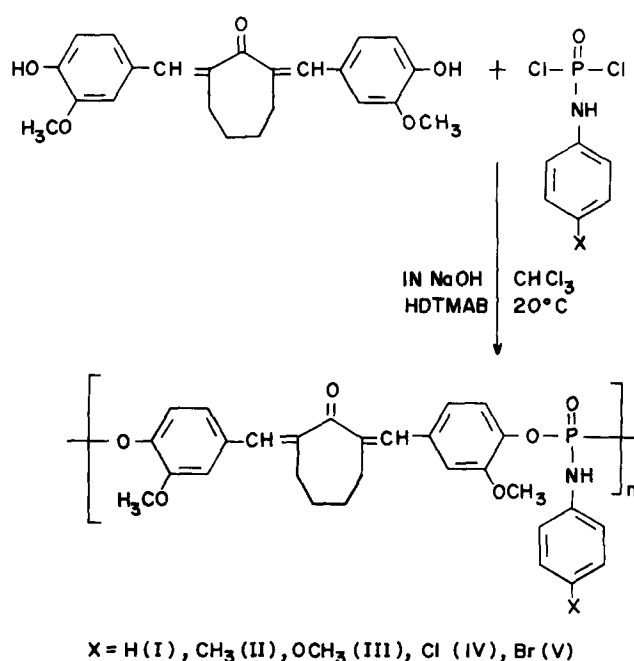
Scheme 1 Synthesis of polymers I–V

method using a phase transfer catalyst at 20°C with more than 73% (*Scheme 1*). All the polymers were yellow in colour and powdery. These polymers were soluble in chloroform, methylene chloride, tetrahydrofuran, DMF, dimethylacetamide 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 phosphorus linkage in the main chain increasing the polarity[15]. The inherent viscosity of the polymers determined in DMF at 30°C and the molecular weights obtained from g.p.c. analysis are shown in *Table 1*. The results reveal that these polymers are of low molecular weight. This may be due to the low reactivity of phosphoramidic dichlorides leading to side reactions such as hydrolysis[25].

The i.r. spectrum of these polymers show absorption bands around 3100, 1640 and 1605 cm^{-1} corresponding to N–H stretchings, C=O of cycloheptanone and exocyclic double bond stretchings, respectively. All the
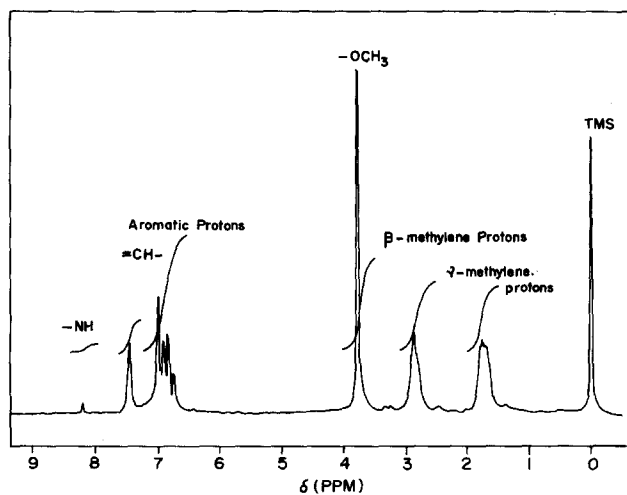
Figure 1 ^1H n.m.r. spectrum of polymer I

Table 1 Yield, viscosity and molecular weight of polymers I–V

Polymer No.	Yield (%)	η_{inh}[a]	Molecular weight[b]		
			$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
I	80	0.45	4900	5200	1.06
II	73	0.40	4500	4800	1.06
III	75	0.41	4600	4800	1.04
IV	83	0.52	5200	5500	1.05
V	80	0.48	5100	5300	1.03

[a] $C = 0.5\,g\,dl^{-1}$ in DMF at 30°C
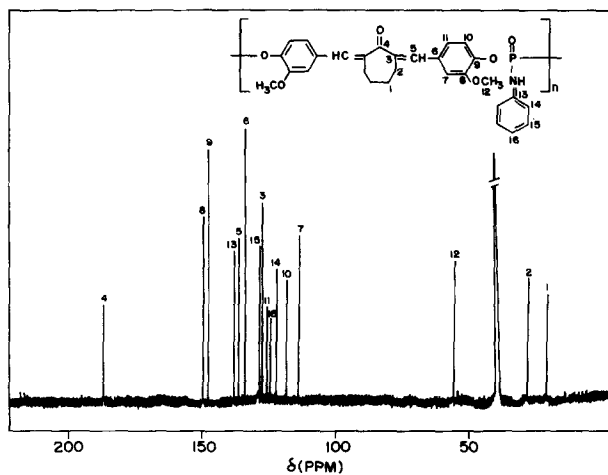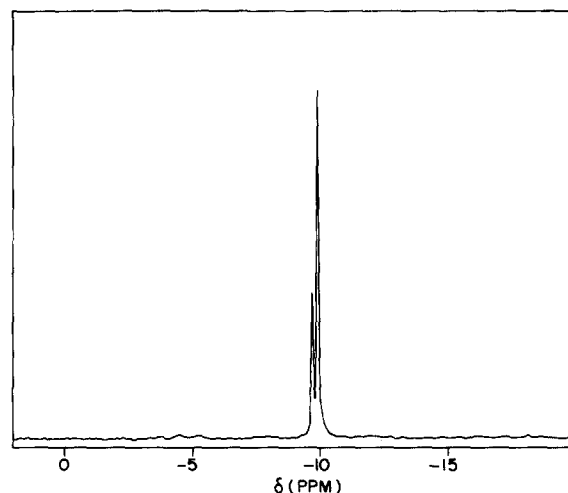[b] Determined by g.p.c.

polymers showed absorption band around 1325, 1300, 1180 and 960 cm^{-1} owing to the P–N–C (aromatic), P=O and P–O–C (aromatic) stretchings of phosphoramide esters[26,27].

The ^{1}H n.m.r. spectrum of polymer I is shown in *Figure 1*. The aromatic protons of the main chain and pendant phenyl ring appear as a broad multiplet in the region of 6.7–7.2δ. The N–H proton resonates as a singlet at 8.3δ. The olefinic protons and methoxy protons resonate at 7.5 and 3.8δ, respectively. The methylene protons of the cycloheptanone appear at 1.7 and 2.9 δ.

The proton decoupled ^{13}C n.m.r. spectrum of polymer I is shown in *Figure 2*. The aromatic carbons of the main and pendant phenyl group are centred around 115–149 δ. The signal at 186 δ corresponds to the carbonyl carbon of the cycloheptanone. The resonance peaks at 130, 28 and 22 δ may be assigned to α, β and γ carbons of the cycloheptanone. The signal corresponding to methoxy carbon emerges at 56 δ and the other characteristic carbon resonances are indicated in the spectrum[28].

The representative ^{31}P n.m.r. spectrum of polymer I is shown in *Figure 3*. All the polymers show a doublet at -10 δ[29]. The substitutents on the phenyl ring do not change in δ values[30]. These results support the formation of polymers.

The thermogravimetric traces of the various polymers are shown in *Figure 4*. The temperatures corresponding to 10 and 50% weight loss and the char remaining at 800°C are given in *Table 2*. All the polymers are stable up to 200°C and start degrading thereafter in nitrogen. The degradation occurs in a two-step manner, the first step corresponding to formation of various small fragments which subsequently carbonize in the second step. The

Figure 3 ^{31}P n.m.r. spectrum of polymer I
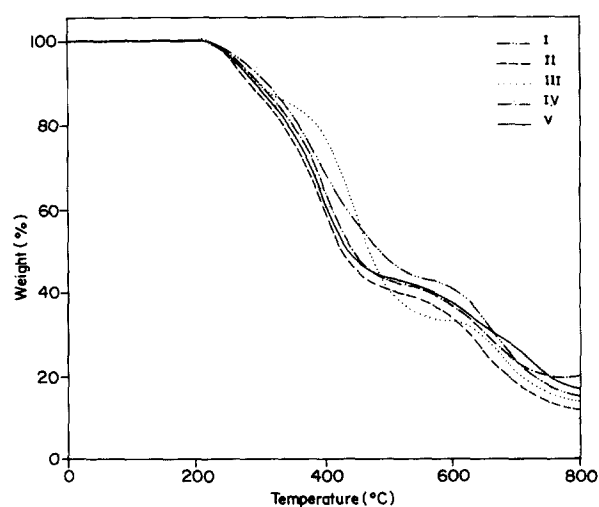
Figure 4 Thermogravimetric traces of polymers I–V

char yield at 800°C shows some variations owing to the different substituents. The halogen containing polymers exhibited higher char yield than the non-halogenated polymers. This may be ascribed to phosphorus–halogen synergism, which prevails in the char formation mechanism. Polymer II is found to be the least thermally stable. The d.s.c. trace of polymer I is shown in *Figure 5*. The T_gs of these polymers are in the range 72–87°C, and the T_ms are in the range 161–173°C. In addition to the glass transition and melting temperatures, the d.s.c traces of these polymers exhibit a broad exothermic peak around 410°C. This may be attributed to the thermal crosslinking of the polymer backbone[31,32].

Table 2 Thermal behaviour of polymers I–V

Polymer no.	D.s.c.		Temperature (°C) corresponds to		
	T_g (°C)	T_m (°C)	10% wt loss	50% wt loss	Char yield at 800°C
I	—	168	300	480	15
II	72	161	275	415	12
III	—	165	290	465	13
IV	80	173	290	450	17
V	77	172	280	440	20

Figure 2 Proton decoupled ^{13}C n.m.r. spectrum polymer I
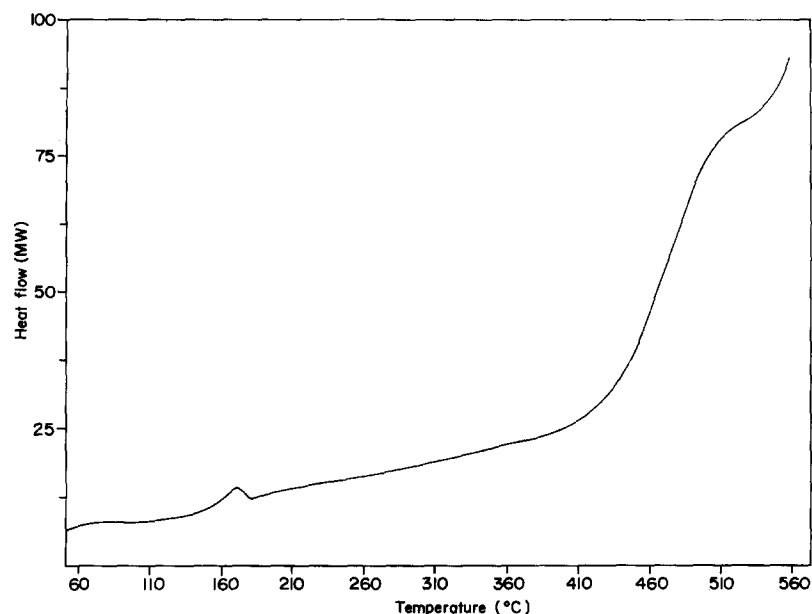
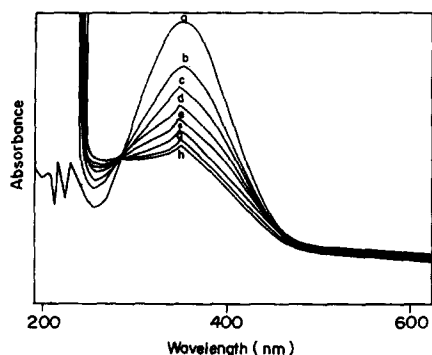**Figure 5** D.s.c. trace of polymer I

Figure 6 Change in u.v. spectral characteristics during the photolysis of polymer I for different time intervals
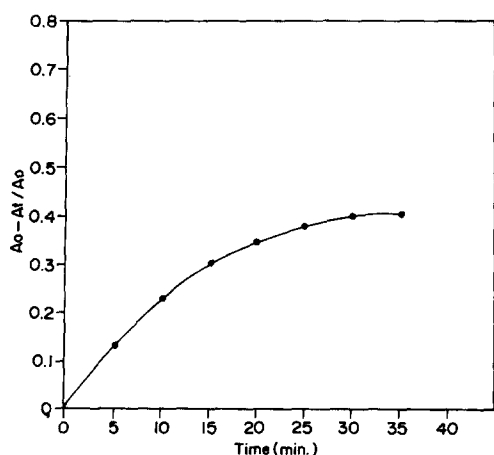

Figure 7 Dependence of photo-crosslinking rate on irradiation time of polymer I

The photo-crosslinking property of these polymers was studied by u.v. spectrophotometry. *Figure 6* shows the changes in the u.v. spectral pattern during the photolysis of polymer I at various intervals of time. The absorbance band at 358 nm corresponds to the $\pi \rightarrow \pi^*$ transition of the exocyclic double bond. During the

successive irradiation, a decrease in the intensity of the absorbance was observed. This may be attributed to the photo-crosslinking of the polymer chain, which involves the $2\pi + 2\pi$ cycloaddition reaction leading to the formation of the cyclobutane ring[14,33]. *Figure 7* shows the relative rate of photo-crosslinking of polymer I. The relative reactivity $(A_0 - A_t)/A_0$ is plotted against the time of irradiation, where A_0 is the absorbance before irradiation, and A_t after irradiation for time t. The substitution on the pendant phenyl ring does not have a significant effect on the rate of photolysis.

CONCLUSION

A series of polyphosphoramide esters containing a photo-sensitive benzylidene group have been synthesized and their structures confirmed by spectroscopy. The inherent viscosity and g.p.c. data reveal that these polymers are low molecular weight materials. The thermal stability of the polymers was found to vary, depending on the substitution on the pendant phenyl ring, the halogen substituted polymers being more stable than the non-halogenated polymers. Photochemical studies indicate that these polymers undergo crosslinking under the influence of u.v. irradiation. The u.v. absorbance studies show that substitution on the pendant phenyl group does not cause significant change in the rate of photo-crosslinking.

ACKNOWLEDGEMENT

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