

Novel photo-crosslinkable flame retardant polyvanillylidene arylphosphate esters

P. Kannan*, Gangadhara and K. Kishore†

Department of Inorganic and Physical Chemistry, Indian Institute of Science,
 Bangalore-560 012, India

(Received 28 March 1996; revised 23 September 1996)

A new class of photo-crosslinkable flame retardant arylphosphate ester polymers based on diarylidene-cycloalkanone groups has been synthesized by polymerizing 2,5-divanillylidene cyclopentanone and 2,6-divanillylidene cyclohexanone with various arylphosphorodichloridates by interfacial polycondensation using a phase transfer catalyst. The resulting polymers were characterized by inherent viscosity, g.p.c., i.r., ^1H , ^{13}C , ^{31}P n.m.r. spectroscopy. These polymers were studied for their photochemical and flame retardant properties. The divanillylidene cycloalkanone group in the chain function as photoactive centres while arylphosphate ester groups impart flame retardancy. The photo-crosslinking proceeds via $2\pi + 2\pi$ cycloaddition reaction of the divanillylidene cycloalkanone moieties. The crosslinking rate, thermal stability and flammability characteristics of the polymers increase with decrease in the size of the cycloalkanone ring.

© 1997 Elsevier Science Ltd.

(Keywords: polyarylyphosphate esters; photo-crosslinkable; flame retardant)

INTRODUCTION

In recent years, photo-crosslinkable polymers have attracted considerable attention for application in surface coatings, printing inks, printing plates, photoresists due to their faster curing, higher thermal stability and superior chemical resistance^{1–5}. However, for these photo-crosslinkable polymers their inherent inflammability is one of the serious drawbacks. Simple halogenated or phosphorus containing compounds are commonly used to repress flammability. But these flame retardant additives are susceptible for migration leading to inhomogeneity of their distribution besides getting exuded out of the system. Incorporation of halogen and phosphorus moieties into the backbone of these photo-crosslinkable polymers may be sought as a promising approach to overcome these problems. Such novel photo-crosslinkable flame retardant polymers are hitherto unknown. Studies on polyphosphate esters as well as photo-crosslinkable liquid crystalline polymers from this laboratory, has led us to undertake a renewed look into this class of polymers^{6–14}.

In this paper, we present a new class of bifunctional polymers containing divanillylidene cycloalkanone and arylphosphate esters in their backbone. The former provides photo-crosslinking ability and the latter imparts flame retardant properties. The present study deals with the synthesis and characterization of new photo-crosslinkable flame retardant polyphosphate esters derived from 2,5-divanillylidene cyclopentanone and 2,6-divanillylidene cyclohexanone with various arylphosphorodichloridates via interfacial polycondensation

using a phase transfer catalyst. Besides synthesis and structural characterization, studies on photo-crosslinking, thermal stability and flammability behaviour are the main focus of the present work.

EXPERIMENTAL

Materials

Vanillin (Merck-Schachart) and hexadecyltrimethylammonium bromide were used as supplied. Cyclohexanone, substituted phenols, α -naphthol and solvents were purified by a procedure reported elsewhere¹⁵. Cyclopentanone was prepared from adipic acid using barium hydroxide as a catalyst¹⁶.

Divanillylidene cyclopentanone (DVCP)

A mixture of cyclopentanone (0.05 mmol) and 4-hydroxy-3-methoxy benzaldehyde (vanillin, 0.1 mmol) was dissolved in 25 ml of absolute ethanol and the solution refluxed for 4 h with three drops of boron trifluoride ethyl etherate. The reaction mixture was then cooled to 0°C and the crystallized product filtered and washed with cold ethanol. Recrystallization from methanol gave 90% yield of fine yellow crystals (m.p. 215°C¹⁷) of the title monomer.

Divanillylidene cyclohexanone (DVCH)

This monomer was also prepared according to the similar procedure used for divanillylidene cyclopentanone. Recrystallization from 3/1 mixture of methanol and water gave 85% yield with fine yellowish green crystals (m.p. 179°C¹⁷) of DVCH.

Arylphosphorodichloridates

The arylphosphorodichloridates were prepared from

* Present address: Department of Chemistry, Anna University, Madras 600 025, India

† To whom correspondence should be addressed

POCl_3 with corresponding phenols/naphthol as a reported procedure^{18,19}.

Polymerization

The polymers were prepared by interfacial polycondensation using hexadecyltrimethylammonium bromide (HDTMAB) as a phase transfer catalyst. A typical procedure for the synthesis of copolymer I is as follows: in a solution of DVCP (1 mmol) in 20 ml of aqueous sodium hydroxide (1 N), HDTMAB (2 wt% of the DVCP) was dissolved. Subsequently, 20 ml of methylene chloride solution of phenylphosphorodichloridate (1.1 mmol) was added to the mixture with vigorous stirring at 20°C. The stirring was continued until the yellow solution formed (10 min), then the organic layer was separated and poured over methanol–water (90/10 v/v). The precipitated polymer was filtered and dried to a constant weight *in vacuo* at 30°C (yield, 95%). Other polymers (II–X) were also prepared in a similar manner. These polymers are soluble in methylene chloride, acetone, DMSO, DMF, pyridine, NMP and insoluble in benzene and pentane.

Characterization

The inherent viscosities of the polymers in methylene chloride solution (0.1 g dl^{-1}) were measured using an Ubbelohde viscometer at 30°C. The molecular weights (\bar{M}_n) of the polymers were determined on a Waters 501 gel permeation chromatograph, using THF as solvent, equipped with an RI detector and calibrated with polystyrene standards. The i.r. spectra of the polymer films were recorded on a BioRad, FT 7 model spectrophotometer. ^1H and ^{13}C n.m.r. spectra were recorded on a Bruker 200 MHz and Bruker 270 MHz FT n.m.r. spectrometer using $\text{DMSO}-d_6$. The chemical shifts were calibrated using tetramethylsilane (TMS) as the standard. U.v. absorption spectra were recorded on a Hitachi U-3400 spectrophotometer.

Photochemical studies

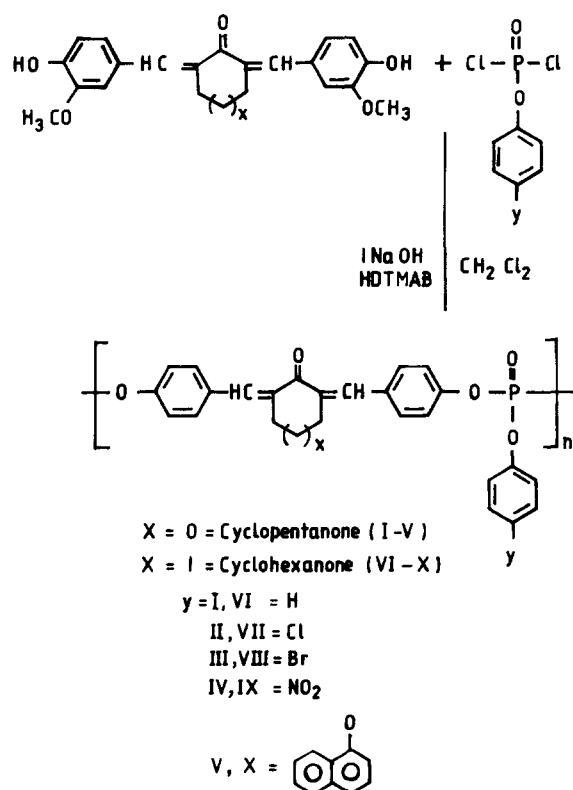
The photolyses studies of the polymers were done in the form of films. For u.v. spectral studies, films were cast on the outer surface of a 1 cm quartz cuvette from chloroform solution. For comparative study the film thickness was kept constant by adjusting the optical density of the film between 1.0 and 1.5. The photochemical studies were carried out in a discontinuous mode, i.e. the samples were exposed to u.v. radiation from a 125 W medium-pressure mercury lamp, kept at a distance of 10 cm from the sample, for varying intervals of time. The irradiated films were subsequently subjected to spectral analyses.

Thermal and flammability studies

The TG studies were carried out on a Dupont thermal analyser, in nitrogen, at a heating rate of $20^\circ\text{C min}^{-1}$ with a sample of 3–5 mg. The limiting oxygen index (LOI) data were obtained on an apparatus fabricated in accordance with the ASTM-D 2863-70 standard and measurements were made using a modified procedure²⁰.

RESULTS AND DISCUSSION

In the present study the polymers have been prepared by an interfacial polycondensation method using a phase transfer catalyst. This method has several advantages



Scheme 1 Synthesis of polymers I–X

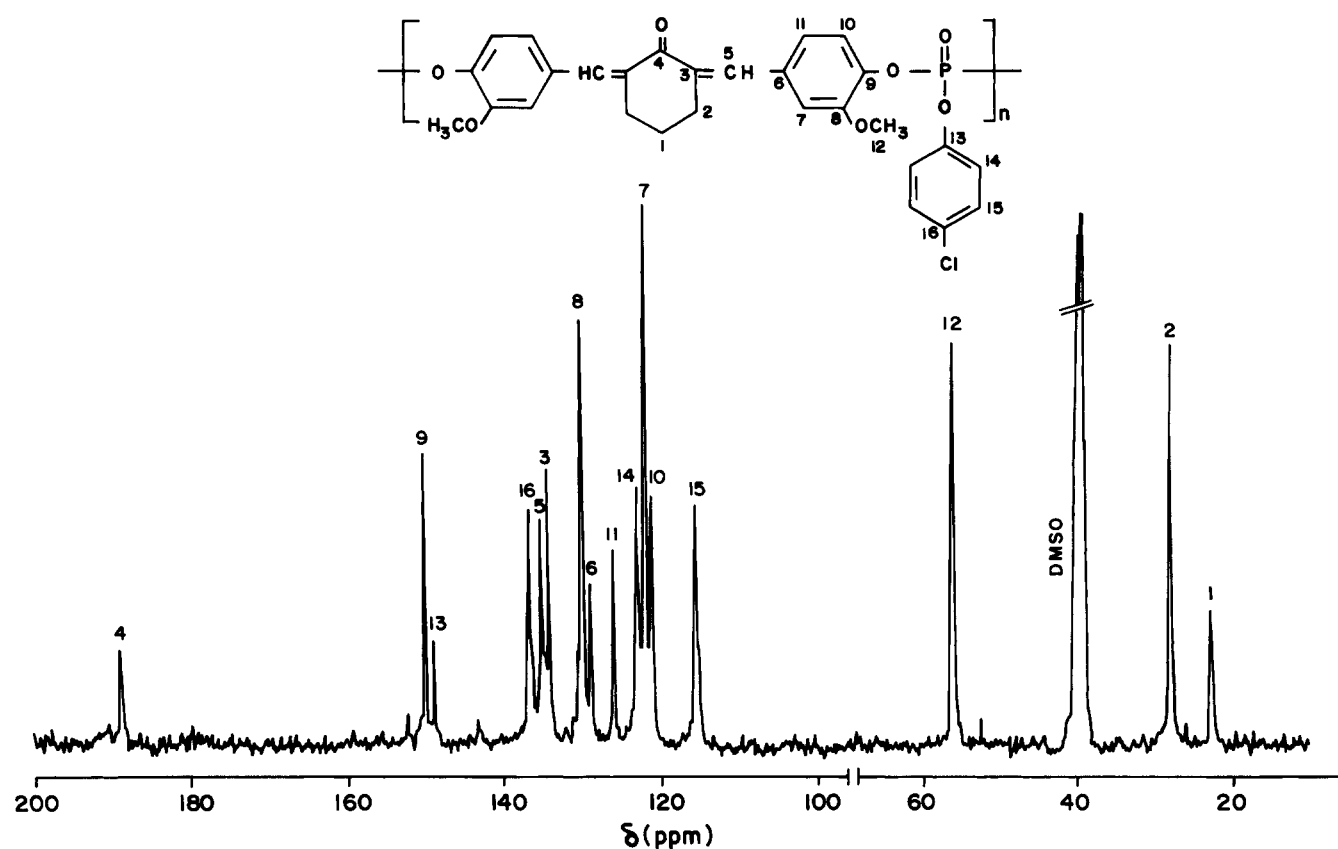
over solution polycondensation, for example elimination of thermally induced side reactions and faster rate as well as high degree of polymerization. Thus, the polymerization was carried out in a dichloromethane–water mixture in the presence of hexadecyltrimethylammonium bromide at 20°C, as shown in Scheme 1. In all the polymers, the diol to dichloride ratio was kept at 1/1.1 to incorporate the P–OH end groups in the resultant polymers. The inherent viscosities of the polymers were determined in methylene chloride at 30°C, and \bar{M}_n was obtained from g.p.c. The results are summarized in Table 1. The inherent viscosity and \bar{M}_n values were found to be fairly high compared to our previous report on flame retardant polyphosphate prepared by solution polycondensation ($\bar{M}_n = 1810\text{--}3600$)⁶. This may be due to interfacial polycondensation. The i.r. spectra of the polymers show the characteristic absorption bands at 1380 cm^{-1} for P–Ph, 1180 and 980 cm^{-1} for P–O–C(Ar), around 1300 cm^{-1} for P=O stretching of the phosphate ester groups, around 1670 cm^{-1} for C=O of the cycloalkanone group and at 1600 cm^{-1} for the C=C exocyclic vanillylidene stretching, respectively^{17,21,22}.

^1H n.m.r. spectra show the aromatic protons of the main chain and the pendent phenyl which appear as broad multiplets in the region 6.2–8 δ . The cycloalkanone groups appear in the region 1.7 and 2.9 δ . The OCH_3 protons resonate around 3.9 δ . The broad band ^1H decoupled ^{13}C spectrum of polymer VII is shown in Figure 1. The ^{13}C resonances of aromatic carbons are centered in the region 116–136 δ and they are indicated in the spectrum²³ (Figure 1).

The ^{31}P n.m.r. spectra of all the polymers show one intense and one weak signal. They respectively correspond to the phosphorophenyl of the repeat unit and to the P–OH end group. The shielded P in the repeat unit, connected to three aryloxy groups, appear at -11.6δ

Table 1 Inherent viscosity, molecular weight, thermal and flammability data of polymers I–X

Polymer	η_{inh} (g dl ⁻¹)	\bar{M}_n	\bar{DP}_n	Temperature (°C) corresponding to		Char at 700°C (%)	LOI ^a
				1% wt loss	50% wt. loss		
I	0.51	4560	11	258	440	38	26
II	0.42	4150	9	261	452	39	25
III	0.45	4210	8	272	510	41	31
IV	0.43	4125	9	268	512	40	28
V	0.38	4040	8	275	542	42	32
VI	0.51	4600	10	236	420	26	24
VII	0.63	4150	9	242	432	28	23
VIII	0.43	4220	8	253	578	32	25
IX	0.47	4380	9	263	484	35	26
X	0.65	4475	9	258	520	41	29

^a Estimated \pm 1%**Figure 1** Broad band proton decoupled ¹³C n.m.r. spectrum of polymer VII

whereas the end group P appears at -16.8δ . The substitution on the phenyl ring does not cause any significant change in the δ values²⁴.

The diarylidene cycloalkanone groups contain the photosensitive α,β -unsaturated ketone functionality and can undergo photodimerization. When these groups are present in the polymer, the photolysis leads to crosslinking. The photo-crosslinking ability of the polymers were compared to the u.v. spectra recorded in the form of a thin film. *Figure 2* shows the changes in the u.v. spectral pattern during the photolysis of polymer I and VI films, the absorption band corresponds to the $\pi-\pi^*$ transition. The changes in the intensity of the bands is due to the involvement of the C=C in the photo-reactions. After 30 min irradiation the films become

completely insoluble indicating that crosslinking has taken place.

Comparing the rate of decrease of the u.v. absorption band with the photolysis time, the cyclopentanone containing polymers undergo photo-crosslinking faster than the cyclohexanone polymers. In our earlier studies⁸⁻¹⁰ we have shown that the photoreactions involve a $2\pi + 2\pi$ cycloaddition of the bisbenzylidene double bonds. It is interesting to compare the relative rates of photoreactions with a non-phosphorus polymer namely poly(bisbenzylidene) ester derived from bis(4-hydroxybenzylidene) cyclohexanone with tetragolic acid dichloride¹² (*Figure 3*). The rate of photo-crosslinking was determined by comparing the relative decrease in the intensity of u.v. absorption bands at

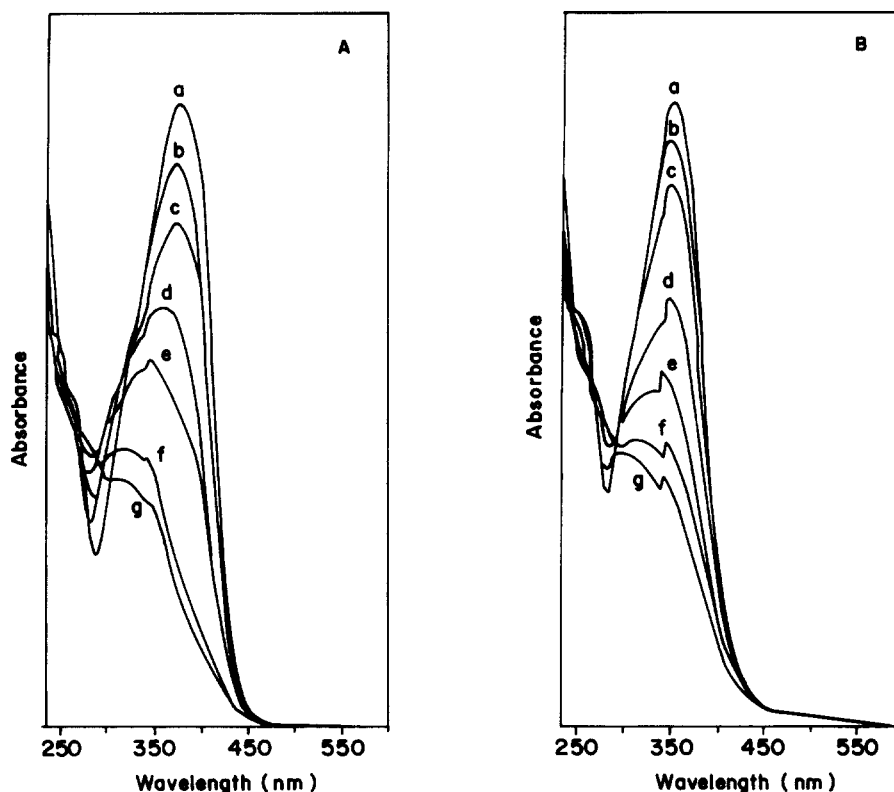


Figure 2 Change in u.v. spectral characteristics during the photolysis of polymer I (A) and VI (B) films for different time intervals: A (a) 0, (b) 0.5, (c) 2, (d) 7, (e) 15, (f) 30 min. B (a) 0, (b) 7, (c) 15, (d) 30, (e) 50 min, (f) 60 min. (g) After the irradiated film was washed with chloroform

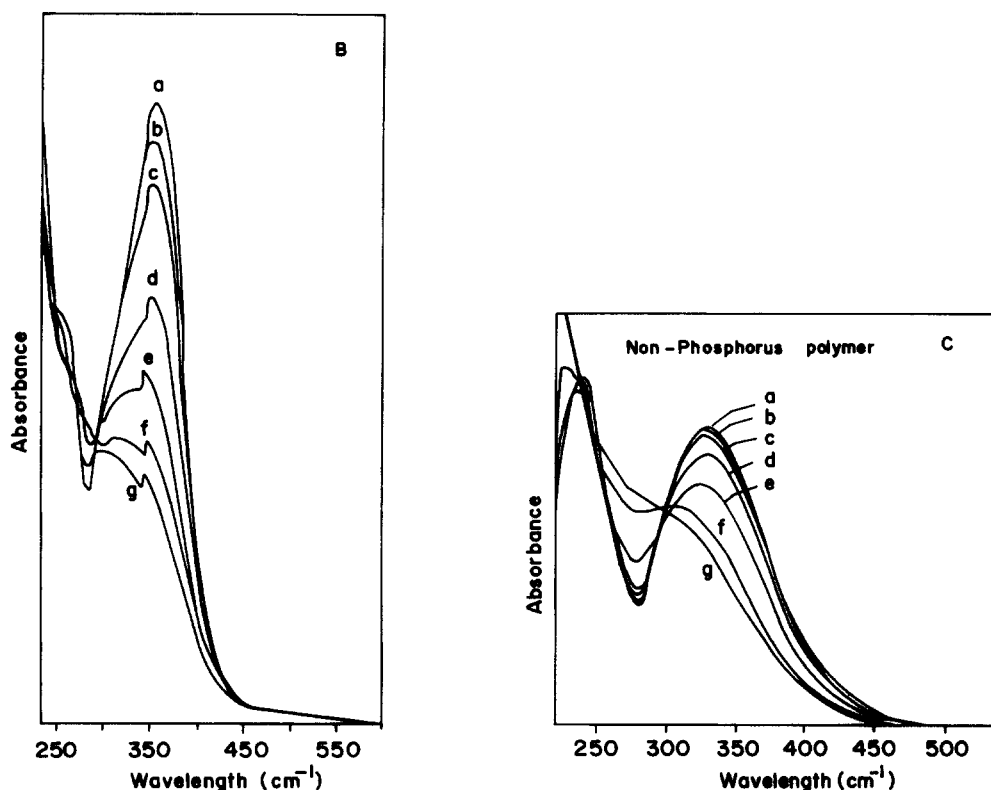


Figure 3 Change in u.v. spectral characteristics, during the photolysis of B (a) 0, (b) 7, (c) 15, (d) 30, (e) 50, (f) 60 min. C (a) 0, (b) 0.5, (c) 1, (d) 10, (e) 40, (f) 160 min. (g) After the irradiated film was washed with chloroform

340 nm. The values are given in *Table 2* and plotted in *Figure 4*. The data reveals that the phosphorous containing polymer possesses crosslinking ability three times faster than that of a non-phosphorous polymer. After 30 min of irradiation, phosphorus containing

polymer showed 55% crosslinking while the non-phosphorus system attained only 18% crosslinking. *Figure 5* shows the *FTi.r.* spectra of the polymer VI. During the photolysis the decrease of the C=C stretching band intensity at 1600 cm^{-1} confirms that α, β -unsaturated

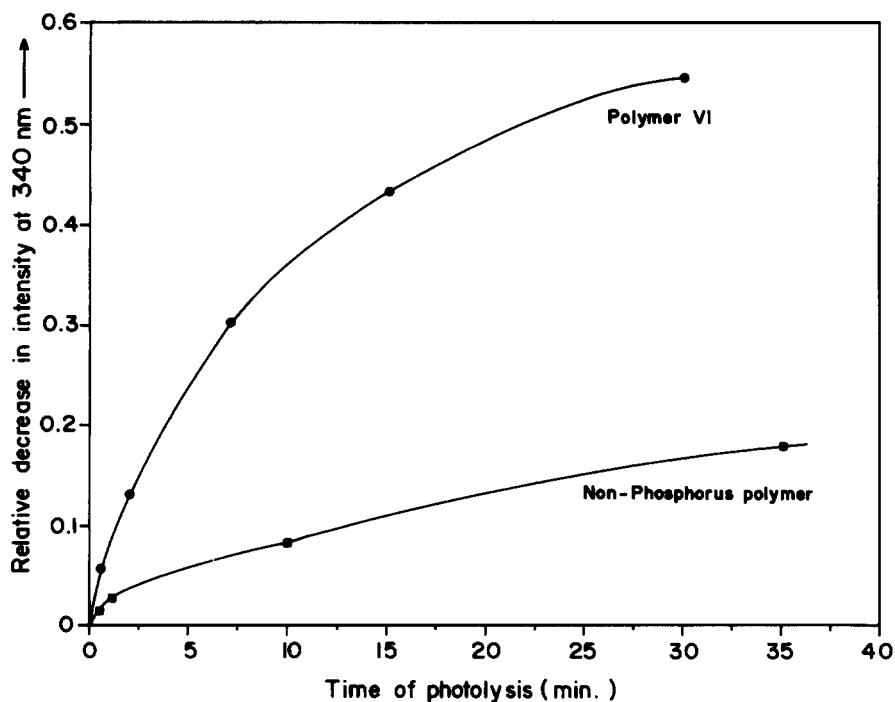


Figure 4 Extent of crosslinking based on the relative decrease in u.v. spectral intensity with irradiation time

Table 2 Comparison of phosphorus and non-phosphorus polymers on relative rates of photoreaction

Phosphorus polymer (VI)		Non-phosphorus polymer ¹²	
Photolysis time (min)	Decrease in intensity at 340 nm	Photolysis time (min)	Decrease in intensity at 340 nm
0.0	0.0000	0.0	0.0000
0.5	0.0569	0.5	0.0166
2.0	0.1301	1.0	0.0330
7.0	0.3090	10.0	0.0830
15.0	0.4509	40.0	0.1830
30.0	0.5447	160.0	0.3300

ketone functionality is the site of the photoreaction. A small shift towards the higher value in the C=O stretching band, around 1660 cm^{-1} , is due to the breaking of the double bond during the $2\pi + 2\pi$ cycloaddition reactions.

The thermogravimetric studies were performed for all the polymers. The temperature corresponding to 1% and 50% weight loss, together with the char at 700°C , are given in Table 1. Representative thermograms are shown in Figure 6. All the polymers show good thermal stability up to 250°C and start degrading thereafter. Polymers

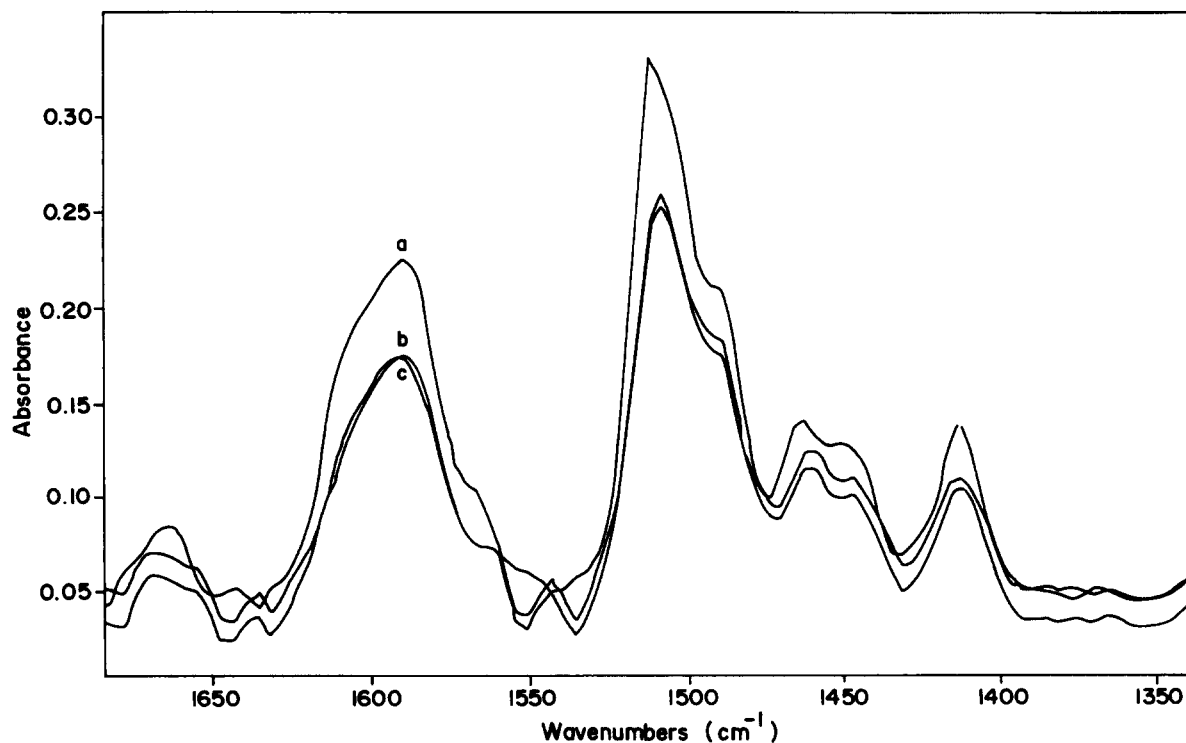


Figure 5 Change in i.r. spectral characteristics of polymer VI film on irradiation (a) 0, (b) 60 min, (c) after the irradiated film was washed with chloroform

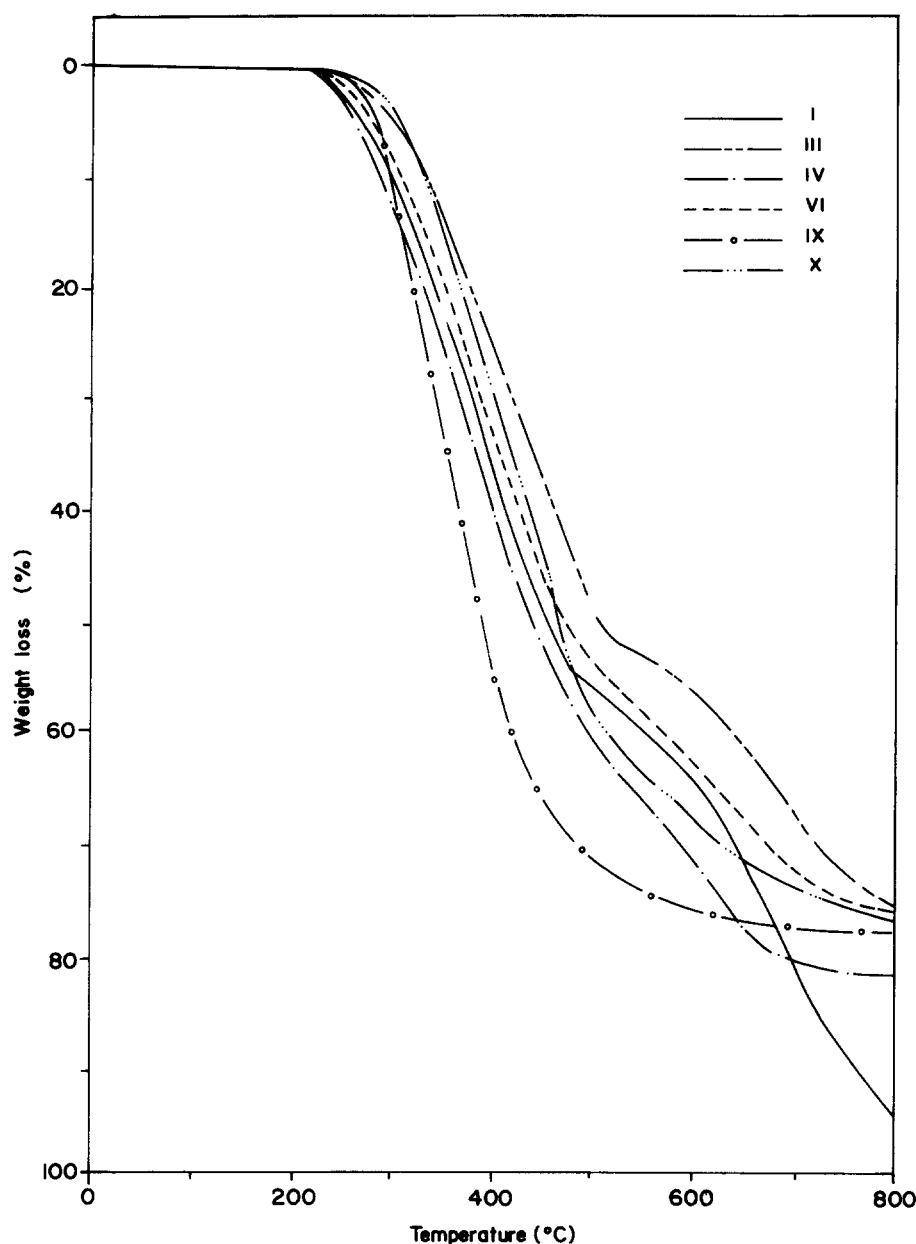


Figure 6 T.g. traces of polymers

containing cyclopentanone group (I–V) exhibit better thermal stability than the cyclohexane polymers. This may be attributed to the rigid cycloalkyl ring of the cyclopentanone moiety than the flexible cyclohexanone moiety²⁵. In both series, the substituents in the pendant phenyl group affect the stability of the polymers in the following sequence: Br > NO₂ > Cl > H. The pendant naphthyl polymers show good thermal stability owing to the high aromaticity of the polymer backbone.

The LOI values of the polymers are given in *Table 1*. These polymers show considerably higher LOI values than our earlier report for polyphosphoramidate sulfides (LOI = 21.27)²⁶ and hence exhibit superior flame retardancy. Cyclopentanone polymers show significantly higher LOI values than cyclohexanone polymers.

CONCLUSION

Two series of polyvanillylidene arylphosphate esters have been synthesized and characterized spectroscopically. The inherent viscosity data reveal that these polymers are of

moderately higher molecular weight. The photochemical studies reveal that these polymers undergo efficient crosslinking under the influence of u.v. radiation. The thermal stability and flammability show that these polymers have good thermal, as well as flame retardance, characteristics. Finally, it may be concluded that these polymers can be suitably exploited for developing photoresist, printing plate and surface coating applications, where thermal stability, flame retardancy and photo-crosslinking properties are collectively required.

ACKNOWLEDGEMENT

The authors are grateful to the Department of Science and Technology, New Delhi, for financial support.

REFERENCES

1. Vandeweyer, P. H. and Smits, G. J., *J. Polym. Sci., Part A: Polym. Chem.*, 1987, **8**, 2361.

2. Kamogawa, H., *J. Polym. Sci., A-1*, 1971, **9**, 335.
3. Hayashi, Y., Kuoda, M. and Inami, A., *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1660.
4. Gipstain, G., Hewett, W. A. and Need, O. V., *J. Polym. Sci., A-1*, 1970, **8**, 3285.
5. Shigehara, Nishimura, M. and Tsuchida, E., *Bull. Chem. Soc. Jpn.*, 1977, **50**, 3397.
6. Annakutty, K. S. and Kishore, K., *Polymer*, 1988, **29**, 7563.
7. Kishore, K. and Kannan, P., *J. Polym. Sci., Part A: Polym. Chem.*, 1990, **28**, 3481.
8. Kanna, P., Gangadhara and Kishore, K., *Polymer*, 1991, **32**, 1909.
9. Kannan, P. and Kishore, K., *Polymer*, 1992, **33**, 418.
10. Kishore, K., Kannan, P. and Iyanar, K., *J. Polym. Sci., Part A: Polym. Chem.*, 1991, **29**, 1039.
11. Kanna, P. and Kishore, K., *Die Angew. Makromol. Chemie*, 1993, **206**, 63.
12. Gangadhara and Kishore, K., *Macromolecules*, 1993, **26**, 2995.
13. Gangadhara and Kishore, K., *Macromolecules*, 1995, **28**, 806.
14. Gangadhara and Kishore, K., *Polymer*. In press.
15. Perrin, D. D. and Armario, W. L. F., *Purification of Laboratory Chemicals*. Pergamon Press, New York, 1988.
16. Adams, R. and Noller, C. R., *Organic Syntheses Collect*, Vol. I. Wiley, New York, 1941, p. 192.
17. Borden, D. G., *J. Appl. Polym. Sci.*, 1978, **22**, 239.
18. Kosolapoff, G. M. and Maier, L., *Organic Phosphorus Compounds*, Vol. 6. Wiley, New York, 1973, p. 299.
19. Francis, X. M. and Calvin, J. W., US Patent No. 3153081, 1964.
20. Annakutty, K. S. and Kishore, K., *Polymer*, 1988, **29**, 1273.
21. Thomas, L. C., *Interpretation of the Infrared Spectra of Organophosphorus Compound*. Heyden, London, 1974.
22. Bellamy, L. J., *The Infrared Spectra of Complex Molecules*, Vol. 2. Chapman and Hall, London, 1980.
23. Johnson, L. F. and Jankowski, W. C., *Carbon-13 NMR Spectra*. Wiley, New York, 1972.
24. Gorenstein, D. G., *Phosphorus-31 NMR Principles and Applications*. Academic Press, Orlando, FL, 1984.
25. Mohamed, M. Abd-Alla, Maher, F. El. Zohry, Kamal, I. Aly and Mohamed M. M. Abd-El-Wahab, *J. Appl. Polym. Sci.*, 1993, **47**, 323.
26. Kannan, P. and Kishore, K., *Indian J. Natl. Rub. Res.*, 1993, **6**, 75.