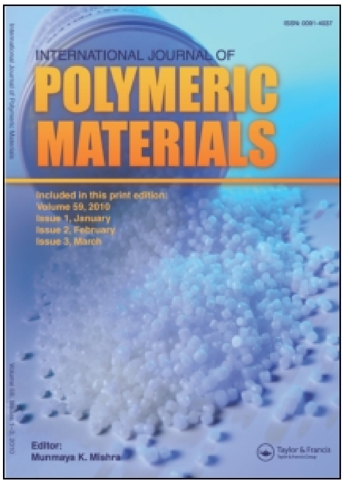

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Sabitabrata Roy[a]; Sukumar Maiti[a]
[a] Materials Science Centre, Indian Institute of Technology, Kharagpur, India

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Synthesis and Characterization of Polyphosphonates having Azomethine Linkages

SABITABRATA ROY and SUKUMAR MAITI*

Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

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Two bishydroxy azomethine monomers were synthesized and reacted with dichlorophenyl phosphine oxide by the interfacial polycondensation method using a phase transfer catalyst at 0°C. The polymers were characterized by IR, ^{1}H-NMR, ^{31}P-NMR, elemental analyses and X-ray diffraction study. These polymers are soluble in chlorinated aliphatic hydrocarbon solvents, such as CH_2Cl_2, $CHCl_3$ as well as polar aprotic solvents such as DMF, DMAC, NMP, DMSO. Thermal and flammability studies were carried out by TGA, DTA and limiting oxygen index (LOI) measurements. The polymers are self-extinguishing and begin to lose weight at around 290°C in air.

Keywords: Polyphosphonate; azomethine; interfacial polymerization; flammability; thermal behavior

INTRODUCTION

Thermal stability of polymers is known to be determined by the energy of interatomic bonds, the possibility of the formation of intermolecular bonds, resonance stabilization and other structural parameters such as double strand or multi strand or network structures [1]. All of these factors depend on the polymer chain structure. The high thermal stability of aromatic polyazomethines is due to their extended conjugation, resonance stabilization and possibility of crosslinking on

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[*] Corresponding author.

heating. Because of their thermal stability they can be selected as an important candidate for flame retardant polymers. But these polymers are virtually insoluble in common organic polar solvents. The effort to increase the solubility of these polymers had been done by incorporating phosphorus in the main chain previously from our laboratory [2]. These phosphorus containing azomethine polymers were soluble only in highly polar solvents such as DMF, DMAC, NMP, DMSO and HMPA, but they are not soluble in chlorinated hydrocarbon solvents. This may be due to the higher stiffness of the polymer chains which is offered not only by the azomethine linkage but also by the higher aromatic content. The solubility can be further improved with little change of thermal stability by lowering the aromatic content of the polymers so that these polymers will be soluble not only in higher polar solvents but also in chlorinated hydrocarbon solvents such as CH_2Cl_2, $CHCl_3$ and similar other chlorinated solvents. The improved solubility of these polymers will help use these polyphosphonates as flame retardant additives for a wide variety of polymers. This paper deals with the preparation and characterization of two bishydroxyazomethine monomers and polyphosphonates from these monomers, which have exhibited improved solubility, good thermal stability and flame retardancy.

EXPERIMENTAL

4-Hydroxybenzaldehyde (Lancaster) was purified by recrystallization from water and decolorized by characolization, m.p. 115°C. *p*-Phenylene diamine (Fluka) was purified by vacuum sublimation, m.p. 136°C. Hydrazine hydrate (BDH) was used as received. Dichlorophenyl phosphine oxide (Fluka) was vacuum distilled before use. Cetyltrimethylammonium chloride (Fluka) was used as received. Dichloromethane, ethanol, benzene, *n*-butyl alcohol were dried and purified by following the usual procedures [3].

Monomer Synthesis

4-[4-(4-Hydroxybenzylidene Amino) Phenyliminomethyl] Phenol

4-Hydroxybenzaldehyde (0.1 mol, 12.2 g) and 1,4-phenylene diamine (0.05 mol, 5.45 g) in 250 mL of benzene were refluxed in a 500 mL flask fitted with a Dean-Stark trap until the calculated amount of water was collected. The content was cooled and the crude product was filtered, dried and recrystallized from *n*-butyl alcohol, m.p. 264°C.

4,4′-Dihydroxybenzalazine

It was prepared by refluxing a dry ethanol solution of hydrazine hydrate with 4-hydroxybenzaldehyde (mole ratio 0.45:1) and a catalytic amount of concentrated HCl for 6–8 h. The azine separated out upon cooling the solution overnight. It was then filtered off and recrystallized from aqueous ethanol, m.p. 266°C.

Polymer Synthesis

In a reaction flask fitted with a stirrer 5 m mol of the bisphenol monomer were mixed with 20 mL of aqueous KOH (10 mmol). To the mixture 0.320 g (1 m mol) CTMAC was added. The solution was stirred and cooled to 0°C. Next, a solution of 0.975 g (5 m mol) dichlorophenylphosphine oxide in 10 mL dichloromethane was added dropwise with vigorous stirring. The mixture was stirred at this temperature for another 1.5 h. The supernatent aqueous layer was decanted and the residue was washed repeatedly with water. The solution was diluted by 10 mL dichloromethane and the polymer was precipitated by pouring the solution into excess hexane. The product was collected and dried at 55°C under vacuum.

Characterization

The elemental analysis was performed on a Heraeus C, H and N analyzer. The phosphorus content was measured by the Schöniger combustion method [4]. The IR spectra were recorded with a Shimazdu 470 spectrophotometer with a KBr disc. The ^{1}H-NMR spectrum was recorded with a Bruker 200 MHz NMR spectrometer in DMSO-d_6 and $CDCl_3$ solvents for monomers and polymers respectively using TMS as internal standard. The ^{31}P-NMR spectrum was recorded with the same spectrometer using $CDCl_3$ as solvent and H_3PO_4 as internal standard. TGA and DTA of the polymers were carried out with a

Shimazdu DT 40 instrument in air at a heating rate of 10°C/min. LOI of the polymers were measured using a modified method [5]. X-ray diffraction of the polymers was recorded with a Philips, Model PW 1729 X-ray diffractometer using Ni-filtered CuKα radiation.

RESULTS AND DISCUSSION

Monomer Synthesis and Characterization

The reaction for monomer preparations can be represented as shown in Figure 1. Table I summarizes the physical characteristics of the monomers. The chemical structure of these monomers was established by elemental analysis, IR spectroscopy and NMR analysis (Tab. I). The elemental compositions of the monomers agree well with the theoretical values obtained from the structures shown in Figure 1. The presence of the hydroxy and azomethine linkages in the monomers was confirmed by the characteristic stretching absorption at about 3300 cm^{-1} and 1596 cm^{-1} [6] respectively in the IR spectra (Fig. 2).. The ^{1}H-NMR spectra (Fig. 3) were also used to confirm the monomers. A singlet in the ^{1}H-NMR spectrum at 10.1 and that at 8.5 ppm

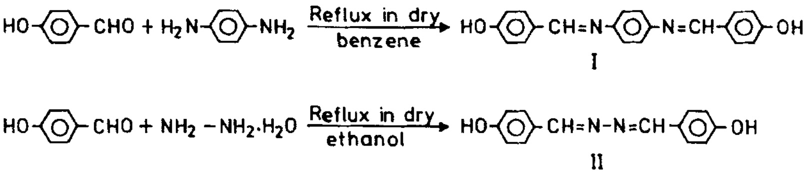

FIGURE 1 Synthesis of monomers.

TABLE I Physical characteristics and analysis of monomers

Monomer code	*Yield %*	*Color*	*IR (cm^{-1})* $\tilde{\gamma}_{OH}$	$\tilde{\gamma}_{CH=N}$	*^{1}H-NMR (ppm)* *OH CH=N*	*Elemental analysis Found (Calc.)* *C*	*N*	*H*
I	83	Brown	3300	1596	10.1 8.49	75.85 (75.95)	8.72 (8.86)	5.12 (5.07)
II	88	Orange	3300	1598	10.1 8.50	69.18 (70.00)	11.58 (11.66)	4.98 (5.00)

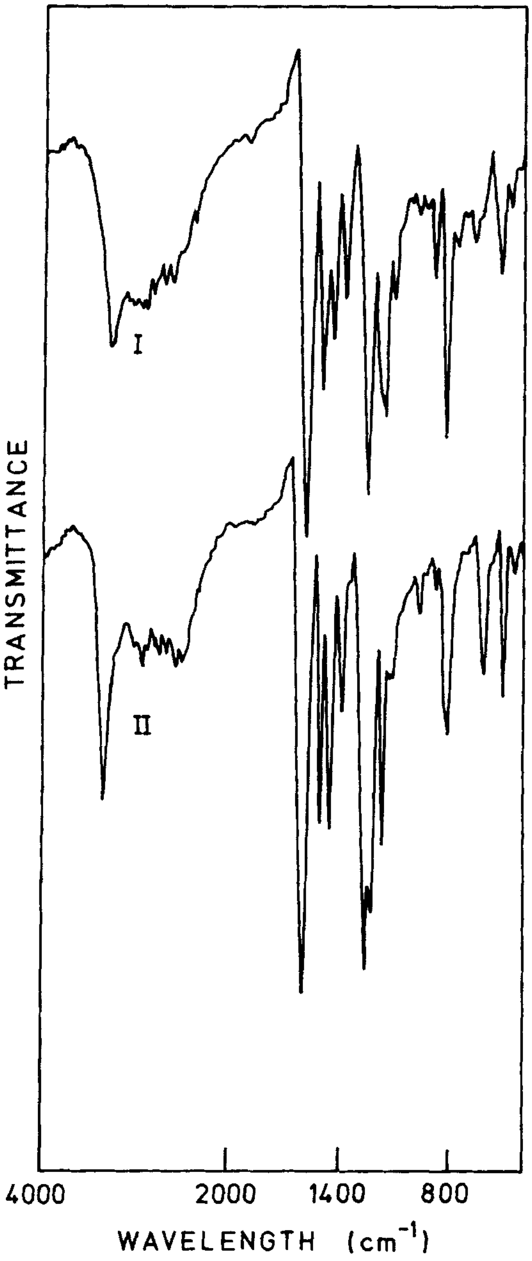

FIGURE 2 IR Spectra of monomers.

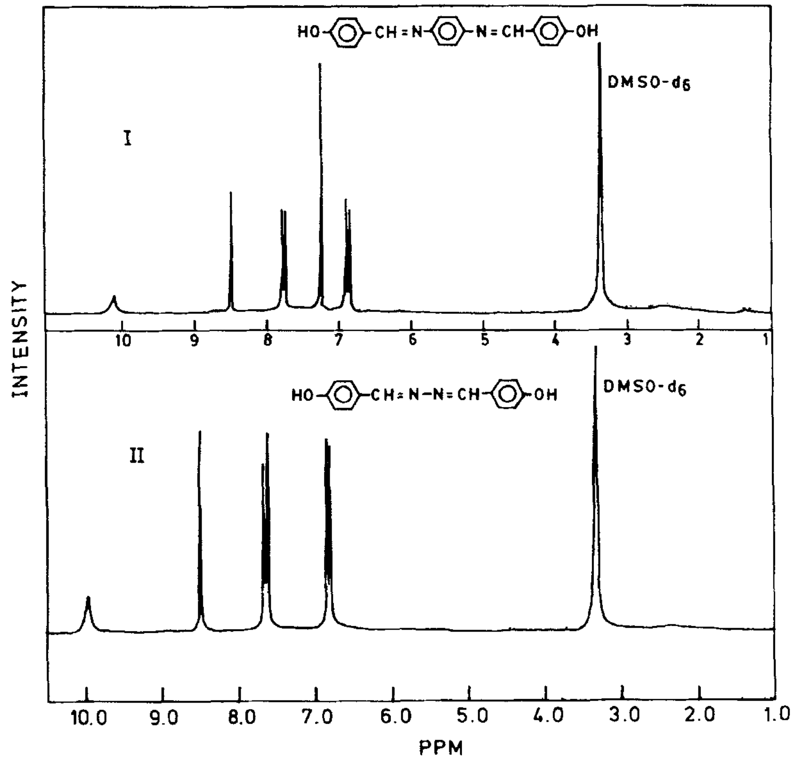

FIGURE 3 ^{1}H-NMR spectra of monomers.

are due to the protons of the —OH group and the —CH=N group [7], respectively. The aromatic protons appear as doublets at 7.7 ppm (*m*-proton) and 6.9 ppm (*o*-proton) and a singlet at 7.13 ppm for monomer I and doublets at 7.6 ppm (*m*-proton) and 6.8 ppm (*o*-proton) for monomer II.

Polymer Synthesis and Characterization

Polyphosphonates were synthesized by the reaction of bisphenols I and II with dichlorophenylphosphine oxide. The reaction is represented by the following scheme (Fig. 4). Imai *et al.* [8] reported that interfacial polycondensation with phase transfer catalysts is very useful for the preparation of high molecular weight polyphosphonates.

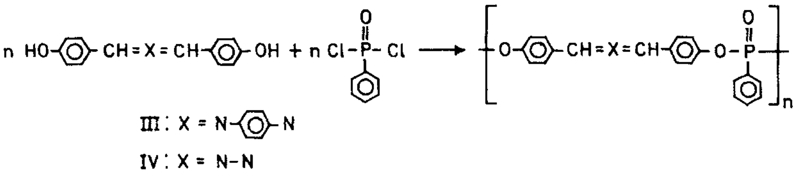

FIGURE 4 Synthesis of polymers.

It was found that chlorinated hydrocarbon solvents are more effective in producing high molecular weight polymers than the aromatic solvents. In this study dichloromethane was used as the organic phase solvent. Results of the synthesis and physical characteristics of the polymers are summarized in Table II. The low inherent viscosities of the polymers are due to hydrolysis of the chlorophenyl end groups of the growing oligomers [9]. The qualitative solubility behavior of the polyphosphonates show all the polymers are soluble in DMAC, DMF, THF and chloroform, dichloromethane but are insoluble in acetone, methanol and hexane.

The chemical structures of polymers III and IV were authenticated on the basis of elemental analysis, IR, ^{1}H-NMR and ^{31}P-NMR analysis (Tab. III). Elemental analyses of the polymers agree well with the theoretical values based on the chemical structures shown in Figure 4.

TABLE II Yield and physical characteristics of polymers

Polymer code	*Color*	*Yield* (%)	η_{inh}[a] (*DL/G*)
III	Brown	78	0.20
IV	Orange	84	0.22

[a] Measured in DMF solution (0.5 g/dL) at 30°C.

TABLE III Characterization of polymers

Polymer code	*Elemental analysis Found (Calculated)* C	H	N	P	*IR(cm^{-1})* $\tilde{\gamma}_{CH=N}$	$\tilde{\gamma}_{P-O-C}$	$\tilde{\gamma}_{P=O}$	$\tilde{\gamma}_{P-Ph}$	*^{1}H-NMR(ppm)* CH=N	*aromatic proton*
III	69.85 (71.23)	4.02 (4.30)	6.01 (6.39)	6.86 (7.07)	1595	1194	1270	1447	8.5	6.3-8.04
IV	65.84 (66.24)	3.98 (4.14)	7.19 (7.73)	8.42 (8.56)	1596	1199	1222	1443	8.5	6.2-8.03

The IR spectra of polymers III and IV are presented in Figure 5. The IR spectra exhibit characteristic absorption peaks around 1600 (CH=N) [6], 1440 (P—Ph), 1270 (P=O) and 1190 cm^{-1} (P—O—C) [10, 11]. The spectra show small plateau around 3300 cm^{-1} due to the —OH group of the bisphenol monomer as the end group.

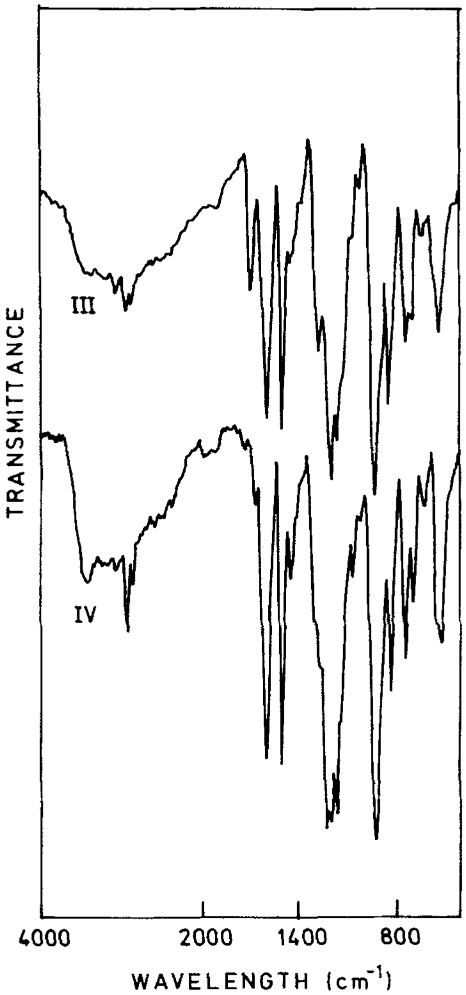

FIGURE 5 IR spectra of polymers.

NMR Analysis

The ^{1}H-NMR spectra of polymers III and IV are presented in Figure 6. The spectra show a singlet at 8.5 ppm which corresponds to the proton of the azomethine linkage [7]. The spectra do not show any peak due to the —OH proton present in the monomer. This confirms the formation of polyphosphonates. The aromatic protons appear as a broad multiplet in the region 6.4–8.04 ppm.

The presence of phosphorus was confirmed not only by elemental analysis but also by the ^{31}P-NMR [12] spectrum. It shows a sharp peak at 11.9 ppm (Fig. 7). However, the ^{31}P-NMR spectrum of dichlorophenyl phosphine oxide [$PhPOCl_2$] shows a peak at 33.7–34.5 ppm [13]. This shift to lower field is due to shielding on the phosphorus atom caused by the substitution of electronegative chlorine atoms

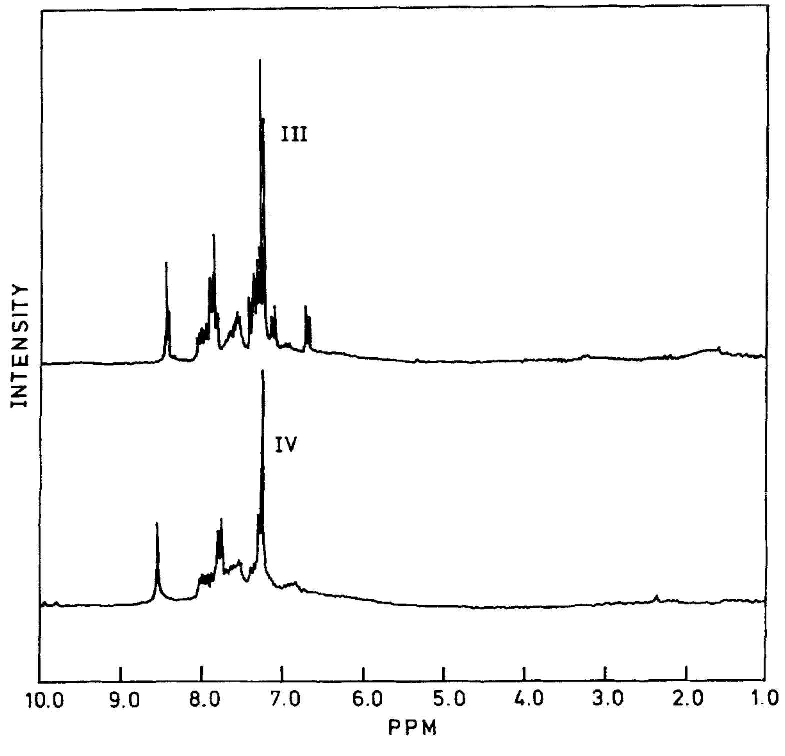

FIGURE 6 ^{1}H-NMR spectra of polymers.

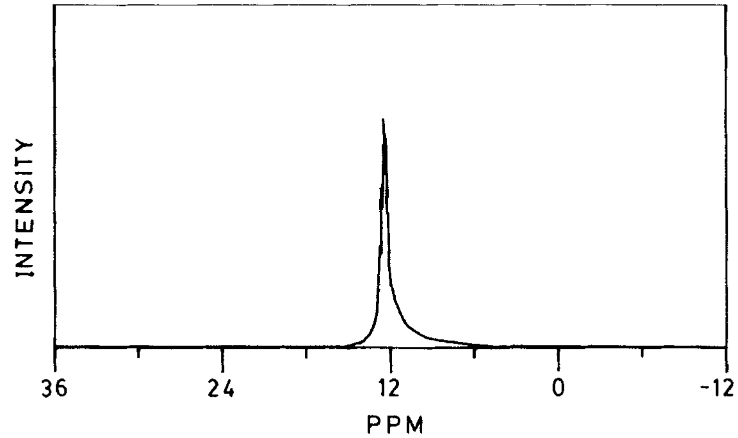

FIGURE 7 ^{31}P-NMR spectra of polymer III.

by —OPh groups in polymers. This shielding is comparable with [PhP(O)(OPh)$_2$] in which the chemical shift in the ^{31}P-NMR spectrum appears at 11.8 ppm.

X-Ray Diffraction Study

The X-ray diffraction of polymers III and IV is shown in Figure 8. The diffraction pattern of polymer III shows scattered intense peaks whereas polymer IV does not show any intense peak. Thus polymer III is somewhat crystalline whereas polymer IV is completely amorphous. The crystallinity of polymer III is due to the presence of phenyl ring in the backbone chain, which offers extra rigidity besides the azomethine linkage.

Thermal Study

Thermal properties of polymers III and IV were investigated by TGA and DTA in air (Fig. 9). Thermal data obtained from TGA and DTA are given in Table IV. Both polymers begin to lose weight at 290°C. The 10% and 50% weight losses of polymer occur at around 340°C and 600°C respectively. DTA study shows that both polymers exhibit an exotherm at around 270°C. This might be attributed to the thermally induced crosslinking *via* the azomethine double bond [14].

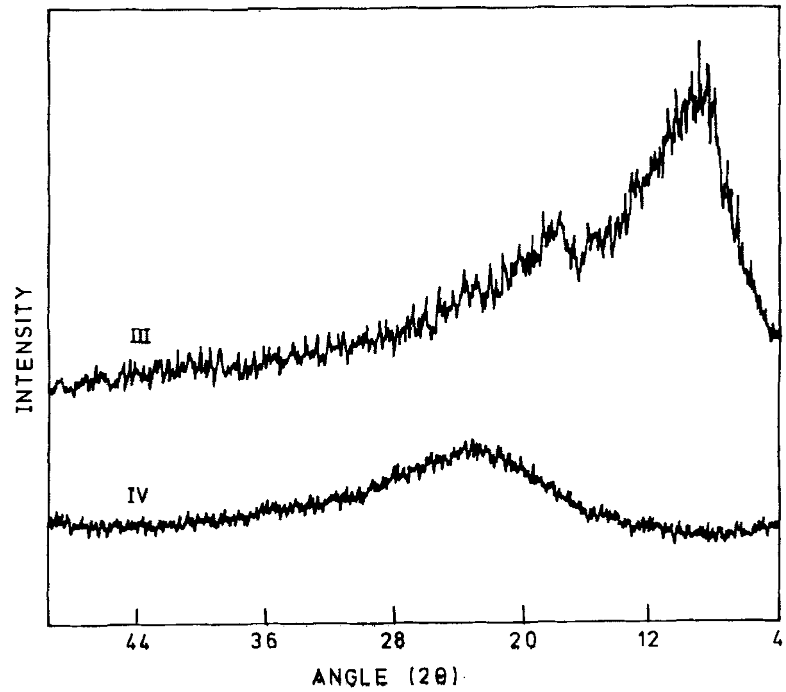

FIGURE 8 X-ray diffraction pattern of polymers.

The polymers, on heating at about 280°C, become insoluble in the solvents. This insolubility and the absence of the peak for the —CH=N group at near 1600 cm^{-1} in the IR spectra of the heated polymers also confirmed the onset of crosslinking at this temperature. DTA study in the N_2 atmosphere also shows a peak at around 270°C. Had there not been any such crosslinking no exotherm at this temperature region was observed under N_2 atmosphere. During crosslinking *via* opening up of double bonds no weight loss occurs. The absence of any weight loss in the TGA curve at around 270°C also supports crosslinking. Further, absence of this exotherm in the DTA curve of the polymer samples heated at about 300°C prior to the DTA study leads additional support.

The large exotherm observed at around 510°C is due to the thermo-oxidative degradation of the polymers. The char yield of the polymer at 600°C in air is about 40%. The higher char yield of the polymers

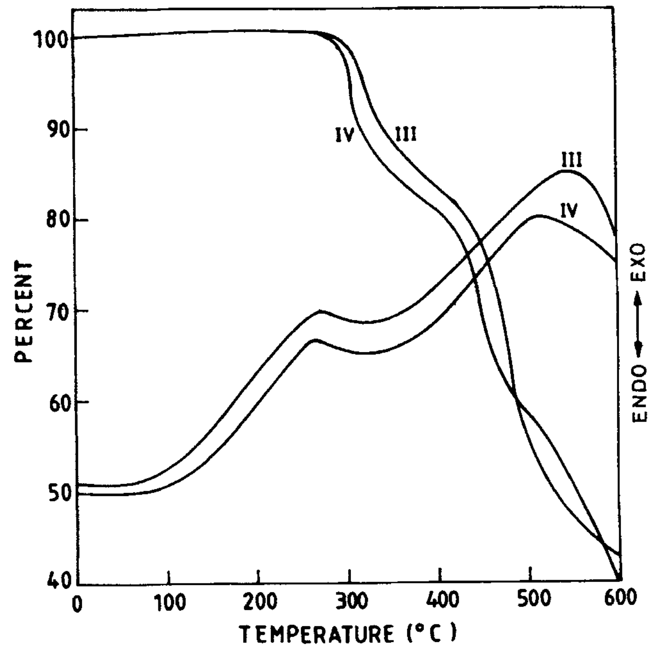

FIGURE 9 TGA and DTA curves of polymers.

TABLE IV Thermal analysis of the polymers

Polymer code	*Char residue (%) in air at 600°C*	*Temp. °C for*[a]		*Peak temp. of exotherm (°C)*[b]
		10% *wt. loss*	50% *wt. loss*	
				1st. 2nd.
				272 540
III	42.8	352	555	270 510
IV	40.0	325	525	

[a] Measured from TGA.
[b] Measured from DTA.

may be due to higher phosphorus content. Similar higher char yields were reported for phosphorus containing polymers from this laboratory as well as by others earlier [2, 5, 15]. This is due to the crosslinking of the azomethine linkage at higher temperature (≥270°C) which also facilitates the formation of char. Between polymers III and IV, the former yields higher char residue and shows somewhat better thermal stability than the latter (Tab. IV). This is due to the presence of higher aromatic ring content in the polymer structure and higher percentage of phosphorus present in polymer III (Tab. III).

Flame Retardant Behavior

Both the polyphosphonates III and IV are well characterized by their selfextinguishing behavior similar to other polyphosphonates [16]. The limiting oxygen [$(OI)_m$] values are measured by a modified method [5]. Polymers III and IV have [$(OI)_m$] values of 37.0 and 39.5 respectively. These values are comparable to the other polyphosphonates reported earlier [2].

It is reported that nitrogen and phosphorus shows the synergistic effect in flame retardancy [17]. The literature contains only scattered examples of the nitrogen-phosphorus synergism in polymer flammability other than cellulose. However, the mechanism of such action has not been investigated in detail. Willard and Wondra's [18] reported that there is no specific N/P ratio at which the synergistic effect is at a maximum. Instead of depending on the concentration of phosphorus and the structure of the nitrogen compound, synergism may be observed but it is believed that the mechanism involved takes place chiefly through the condensed phase, as in the case when phosphorus compounds are used alone [17, 18]. The higher LOI values of the polymers may be due to the synergistic effect of phosphorus and nitrogen present in the macrochain. Between polymers III and IV, IV has the higher LOI value than III possibly due to its higher phosphorus content. These polyphosphonates can be used as fire retardant additives for other polymers.

The elemental analysis of the char of polymer IV at 600°C was done. The percentage of elements are as follows: C: 33.72%; H: 3.07%; N: 4.78%. The amount of phosphorus, if any present in the char obtained cannot be determined by the analytical method available with us. The percentage of C, H and N of polymer IV is given in Table III. Comparison of these two data indicates that the percentage of carbon in char is reduced almost by half of the initial percentage, the nitrogen percentage is reduced but to a lower extent. On the basis of this limited information it is not possible to ilucidate the mechanism of char formation. However, the percentage of nitrogen in the char possibly indicate the synergism of N and P operating through the condensed phase mechanism.

CONCLUSION

Two polyphosphonates having azomethine linkages were synthesized and they were fully characterized spectroscopically as well as elemental analyses. Such polyphosphonates can be used as possible flame retardant additives where both thermal stability and flame retardancy are important.

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