Flame retardant polyphosphate esters: 1. Condensation polymers of bisphenols with aryl phosphorodichloridates: synthesis, characterization and thermal studies

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Polyphosphate esters were synthesized by the solution polycondensation of bisphenols with aryl phosphorodichloridates. The polymers were characterized by i.r. and ^{1}H, ^{13}C and ^{31}P n.m.r. spectroscopy. The molecular weights were determined by end group analysis using ^{1}H and ^{31}P n.m.r. spectral data. The thermal stability of the polymers was analysed by thermogravimetry.

(Keywords: flame retardancy; polyphosphate esters; bisphenols; aryl phosphorodichloridates; infra-red and nuclear magnetic resonance spectroscopy; thermogravimetry)

INTRODUCTION

Polyphosphate esters are an important class of organophosphorus polymers in that, in addition to their flame retardant characteristics as in the case of other organophosphorus polymers, they possess attractive plasticizing properties too. Much attention has been drawn in recent years towards polyphosphates, mainly as polymeric additives to other polymers[1-23]. The polymeric additives are preferred to conventional non-polymeric ones due to their better resistance to extraction, migration, volatile-loss etc. and thus making the flame retardancy available permanently[24-26]. The literature on polyphosphates, notwithstanding a large number of patents, does not provide any systematic study on the synthesis and properties of these polymers; the spectral characterizations of these polymers are unavailable. Thermal stability too has been studied only in a few cases[21]. In the present communication, a number of low molecular weight polymers with different structures (*Scheme 1*) have been synthesized, a few of them being reported for the first time. The polymers were characterized by i.r. and ^{1}H, ^{13}C and ^{31}P n.m.r. spectroscopy. The molecular weights of these polymers were determined by end group analysis using ^{1}H and ^{31}P n.m.r. spectral data; low molecular weight polymers were prepared keeping in view their applications as flame retardant plasticizers. The thermal stability of these polymers were also evaluated by thermogravimetry (t.g.).

EXPERIMENTAL

The various bisphenols used in the present study were obtained commercially and recrystallized before use. The aryl phosphorodichloridates were prepared from $POCl_3$ and the corresponding phenols according to the reported procedure[27,28].

A typical procedure for the synthesis of polymer I is as follows: bisphenol A (50 mmol) was taken in dry toluene (30 ml) and refluxed with phenyl phosphorodichloridate (55 mmol) under dry conditions for 48 h with constant stirring. The polymer was separated and purified by successive reprecipitation from $CHCl_3$ solution by pentane; the yield was about 85%. The polymer, dissolved in chloroform, was then refluxed with methanol (10 ml) for another 3 h; the higher molecular weight fraction was precipitated by adding excess of methanol. The polymers II–V were also prepared in a similar manner.

For the polymers VI–VIII the polymerization procedure was the same as mentioned above, except that the solvent was xylene. Polymer IX was prepared by treating tetrabromobisphenol A (12.5 mmol) with an aqueous solution of NaOH (25 mmol); water was completely removed azeotropically. The resulting sodium derivative was refluxed with the phosphorodichloridate in xylene for 48 h. The polymer was purified as before. In the case of polymer VI–IX, the yield was 60–70%.

Polymers I and II were gummy liquids whereas the others were powdery. All the polymers were soluble in $CHCl_3$, acetone, dioxane, *N,N*-dimethyl formamide and dimethyl sulphoxide.

The i.r. spectra were recorded on a Perkin–Elmer model 715 spectrophotometer as thin films between KBr windows. The ^{1}H n.m.r. spectra were recorded on a Varian T-60 spectrometer and the ^{13}C n.m.r. spectra on a Bruker FT 270 spectrometer (67.89 MHz) in $CDCl_3$ using TMS as the internal standard. The ^{31}P n.m.r. spectra were recorded on a Varian FT-80 A (32.2 MHz) spectrometer in $CHCl_3$ under broad band ^{1}H decoupling conditions. D_2O was used as the external lock and phosphoric acid (85%) as the external standard.

The thermogravimetric studies were carried out on a Sinku-Riko TGD 500 thermogravimetric analyser in

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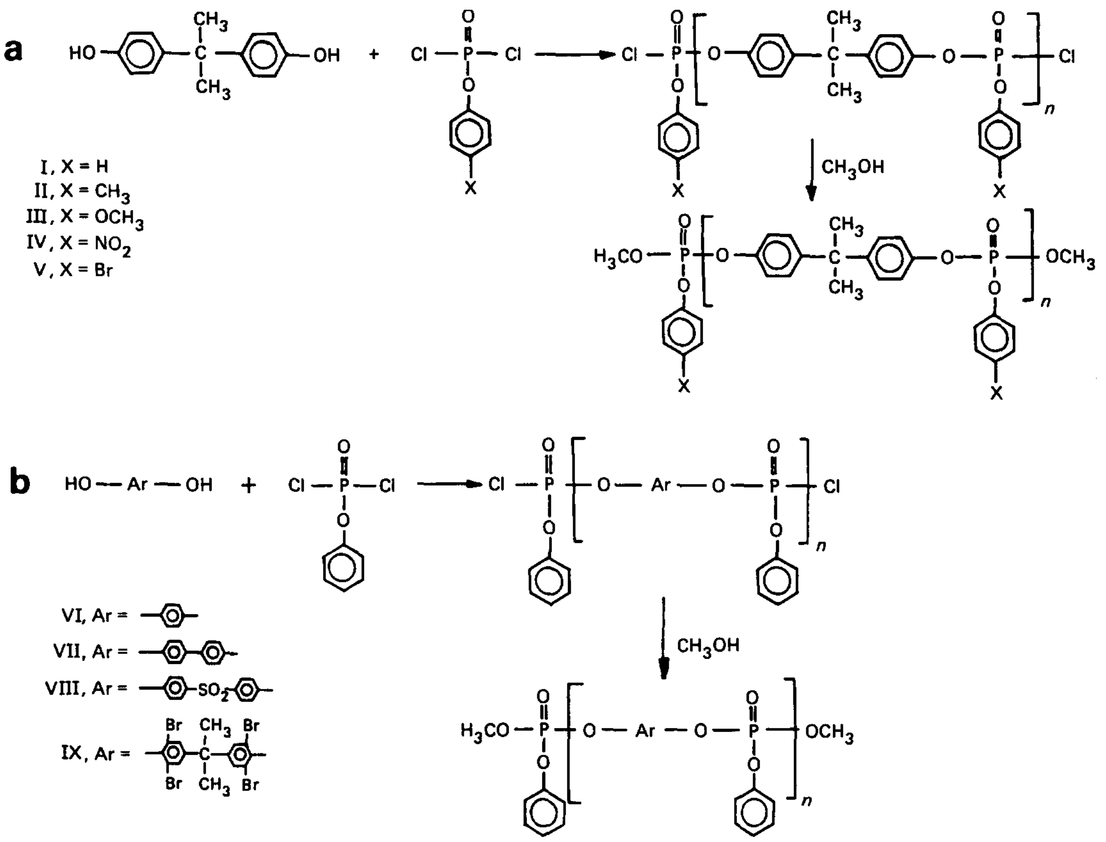

Scheme 1 Synthesis of polyphosphates I–IX

argon atmosphere at a heating rate of 20°C min^{-1} with a sample weight of 3–5 mg.

RESULTS AND DISCUSSION

The various phosphate polymers synthesized are shown in *Scheme 1*; polymers II–V are new. In the present study, solution polycondensation was carried out in the absence of any acid acceptor since low molecular weights were preferred. The bisphenol to phosphorodichloridate ratio was kept at 1:1.1 in all the cases so that the polymers may have phosphate end groups.

The i.r. spectra of the polymers were similar and a typical spectrum is shown in *Figure 1*. The strong absorption around 1300 cm^{-1} corresponds to $\nu_{P=O}$ which is characteristic of phosphate ester compounds[29,30]. Also, all the polymers showed strong absorptions around 1180 and 960 cm^{-1} corresponding to P–O–C(aromatic) stretching; the P–O–C(aliphatic) stretching absorption is weak since this group is present only at the chain ends. The spectra of polymers I and II showed small percentages of bisphenol end groups whereas in others it was completely absent. The other absorptions were characteristic of the aromatic, aliphatic or functional groups present in the polymer depending on the various bisphenols and phosphorodichloridates used and support the polyphosphate structure.

The ^{1}H n.m.r. spectral data of all the polymers are summarized in *Table 1*; two representative spectra are shown in *Figure 2*. The polymers I–V show a singlet at 1.6δ for the isopropylidene protons and a doublet at 3.9δ for the P–O–CH_3 group ($^3J_{PH} = 12$ Hz)[31]. The aromatic protons of the main chain give rise to a singlet around 7.0δ due to the two electron donating substituents at 1 and 4 positions. The resonances corresponding to the pendent phenyl group vary in both the position and splitting pattern depending on the substituents. In polymer I, the pendent phenyl protons give rise to a singlet at 7.2δ whereas in II, they merge with a peak at 7.0δ. In III–V, they are observed as multiplets; in III they appear upfield compared with the main chain phenyl protons due to the methoxy substituent and in IV and V they appear downfield due to the Br and NO_2 substituents.

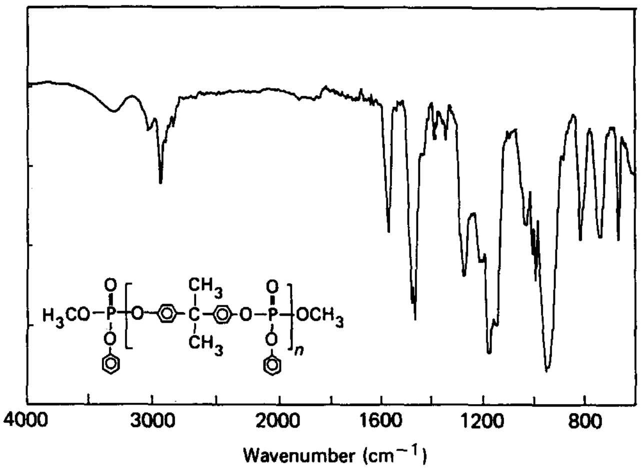

Figure 1 I.r. spectrum of polymer I

In the case of polymers VI–IX, since the pendent group was the same, a singlet at 7.2δ was observed in all these cases in addition to the doublet at 3.9δ for the P–O–CH_3 end groups. The main chain aromatic protons varied depending on the substitution. Thus in VI, they give rise

Table 1 ^1H n.m.r. spectral data of the polymers

Polymer	Chemical shift values in ppm					Ratio of integration[a]	Molecular weight
	$C(CH_3)_2$	$P–O–CH_3$	Main chain phenyl	Side chain phenyl	Others		
I	1.6(s)	3.9(d)	7.0(s)	7.2(s)	6.6–7.0(m) (bisphenol end group)	1:5	2030
II	1.6(s)	3.9(d)	7.0(s)	7.0(s)	6.6–7.0(m) (bisphenol end group); 2.2(s)(CH_3)	1:4.2	1810
III	1.6(s)	3.9(d)	7.1(s)	6.8–7.4(m)	3.7(s)(OCH_3)	1:6.8	2920
IV	1.6(s)	3.9(d)	7.1(s)	7.7(q)	–	1:4.3	2010
V	1.6(s)	3.9(d)	7.1(s)	7.0–7.6(m)	–	1:7	3400
VI	–	3.9(d)	7.2(s)	7.2(s)	–	1:9	2430
VII	–	3.9(d)	7.0–7.6(m)	7.3(s)	–	1:7.5	2600
VIII	–	3.9(d)	7.7(q)	7.2(s)	–	1:8.8	3620
IX	1.6(s)	4.0(d)	7.4(s)	7.2(s)	–	1:4.1	3000

[a] For I–V the ratio is $P–O–CH_3$ protons to isopropyl protons, and for VI–IX $P–O–CH_3$ to aromatic protons

Abbreviations: s = singlet, d = doublet, m = multiplet and q = quartet

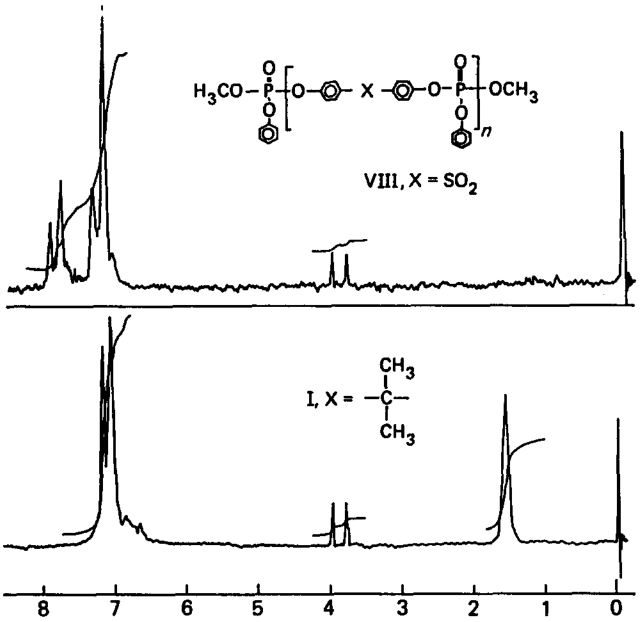

Figure 2 ^1H n.m.r. spectrum of polymers I and VIII

to a singlet at 7.2. which merges with the side chain protons, in VII and VIII they appear as multiplets around 7.4 and 7.6δ, respectively, and in IX they appear as a singlet around 7.4δ.

Both broad band and off-resonance ^1H decoupled ^{13}C n.m.r. spectra of the polymers were recorded; a typical spectrum is shown in *Figure 3* and the chemical shift values of all the polymers are given in *Table 2*. The assignments were carried out using the normal additivity parameters of the substituents[32,33] in the benzene ring and the considerations of the off-resonance spectra in conjunction with the difference in intensities among the quaternary, methine, methylene and methyl carbons. The phosphate group causes the *ortho* and *para* carbons to shift to higher field and the carbon of attachment to lower field, while the *meta* position is not much different from benzene[33,34]. The signal for the $P–O–CH_3$ group was observed but was very low in intensity. No peaks corresponding to the phenolic end groups have been observed suggesting that they are in very low concentration.

The ^{31}P n.m.r. spectra of all these polymers show two signals; one corresponds to the P in the repeat unit and the other one to the P at the chain end (*Figure 4*, *Table 3*). For example, the P in the repeat unit is attached to three aryloxy groups whereas that at the end is attached to two aryloxy and one alkoxy group. Since the phenoxy group exerts more shielding on P compared with alkoxy group[35,36], the P in the repeat unit appears upfield (~ −12 ppm) compared with that in the end group (~ −18 ppm). The substituents on the phenyl ring do not cause much change in the δ values, probably due to the fact that the substituents are more than five bonds away from the P atom[36].

Since the end group protons of phosphorus could be distinguished from those of the repeat unit by n.m.r. their integration could be used to calculate the number average molecular weight of these polymers. As seen by i.r. and ^1H n.m.r. the polymers contain phosphate groups at both ends; I and II contain some phenolic groups but they are in negligible amounts. Thus in the ^1H n.m.r. of polymer I, the ratio of the integration of the $P–O–CH_3$ protons to that of the isopropyl protons is 1:5. Since the number of protons in both cases are equal (6H), the repeat units are five times that of the end groups, i.e. the degree of polymerization is 5 and the molecular weight is ~2000. The molecular weights of all the other polymers were also calculated in a similar manner (*Table 1*). In the case of polymer I, the ratio of the integration of the P at the chain end to that at the repeat unit is found to be 1:2, i.e. the number of repeat units is 5. The molecular weights obtained from ^{31}P spectral data are found to be concordant (within ±3%) with those obtained by ^1H n.m.r. (*Tables 1* and *3*).

The t.g. thermograms of the various polymers are shown in *Figures 5* and *6* and the temperatures corresponding to 1% weight loss, 50% weight loss, inception of fast degradation and the char remaining at 700°C are given in *Table 4*. All the polymers except II are stable up to 250°C and start degrading between 250°C and 300°C; the degradation occurs in a two-step process. Pyrolysis gas chromatographic studies on polymer I showed that the first step (300–450°C) corresponds to the formation of various phenols and phosphates with some amount of char remaining which subsequently carbonizes

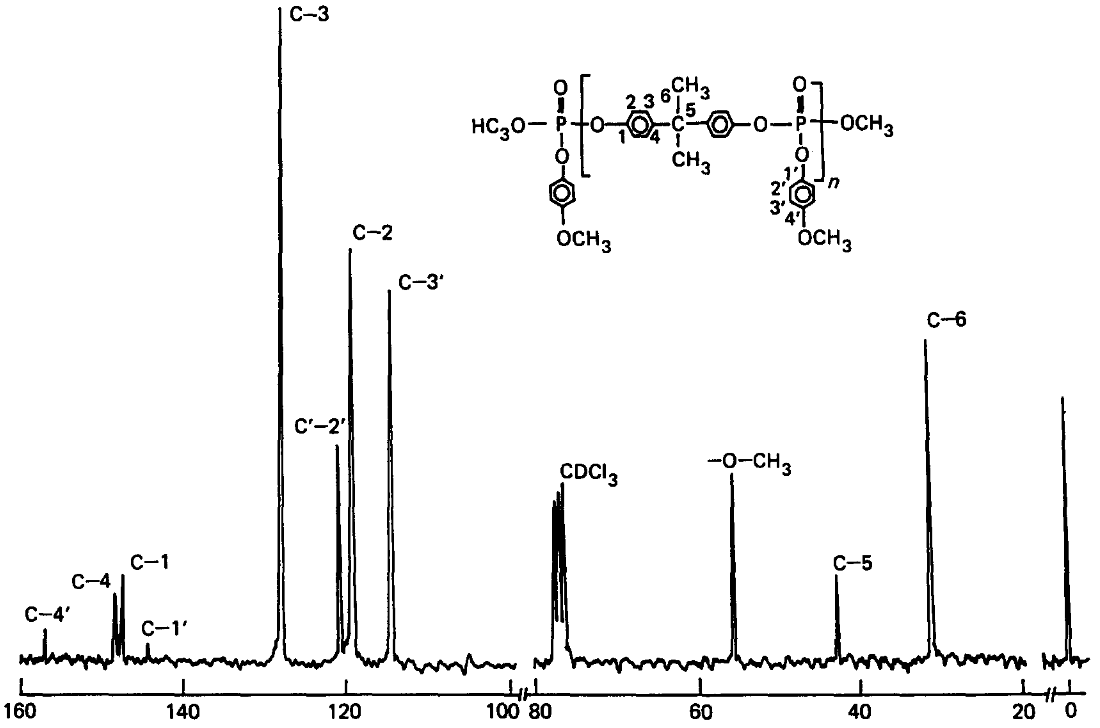

Figure 3 Broad band decoupled ^{13}C n.m.r. spectrum of polymer III

Table 2 ^{13}C n.m.r. chemical shift values (ppm) of the polymers

Polymer	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-X
I	148.5	119.7	128.2	147.8	42.4	30.9	150.6	120.2	129.9	125.6	–
II	148.7	120.0	128.3	148.6	42.4	31.1	47.8	119.8	130.4	134.8	20.9
III	148.7	119.7	128.2	147.7	42.4	30.9	144.0	121.1	114.9	157.2	55.7
IV	148.0	120.0	128.3	148.0	42.4	30.7	154.7	120.8	125.7	114.9	–
V	148.5	119.7	128.3	147.9	42.1	30.9	149.7	122.1	133.0	118.7	–
VI	147.7	121.5	–	–	–	–	150.3	120.0	130.0	125.9	–
VII	150.2	120.6	128.5	137.8	–	–	150.7	120.2	130.0	125.8	–
VIII	154.2	120.6	130.6	139.5	–	–	150.7	120.2	130.0	125.8	–
IX	154.9	116.0	129.7	151.0	30.5	42.5	150.9	120.1	130.0	125.5	–

Table 3 ^{31}P n.m.r. spectral data of the polymers

Polymer	Chemical shift values (ppm) P at the chain end	P in the repeat unit	Ratio of the integration (P end/P repeat)	Molecular weight
I	−11.5	−18.2	1:2	2030
II	−11.2	−18.2	2:3	1740
III	−11.3	−18.0	1:3	3000
IV	−12.2	−18.8	2:3	1890
V	−11.8	−18.4	1:3	3400
VI	−11.5	−18.3	1:4	2430
VII	−11.9	−18.6	1:3	2470
VIII	−12.9	−20.4	1:4	3690
IX	−13.1	−22.6	2:3	2930

in the second step (450–1000°C). In the case of polymers I–V having different substituents in the side chain phenyl ring, only the NO_2 group is found to have much effect on the thermal degradation. In this case, the first step ends at a much lower temperature and the rate of the second step is faster compared with other polymers. The NO_2 group

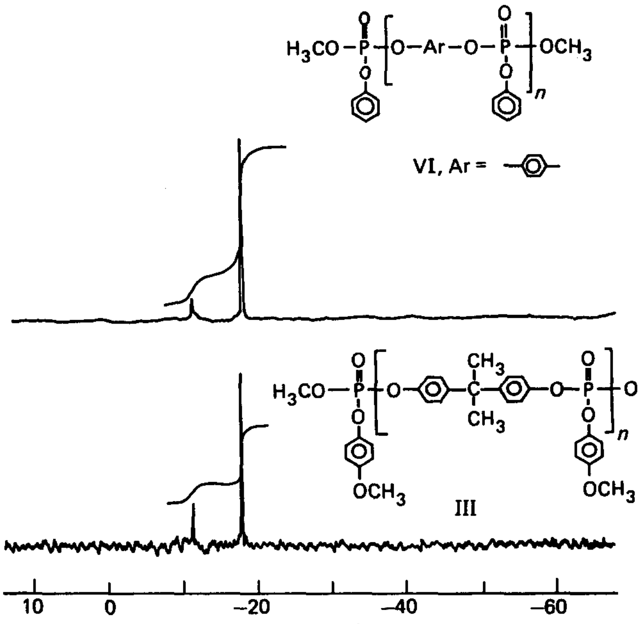

Figure 4 ^{31}P n.m.r. spectra of polymers III and VI

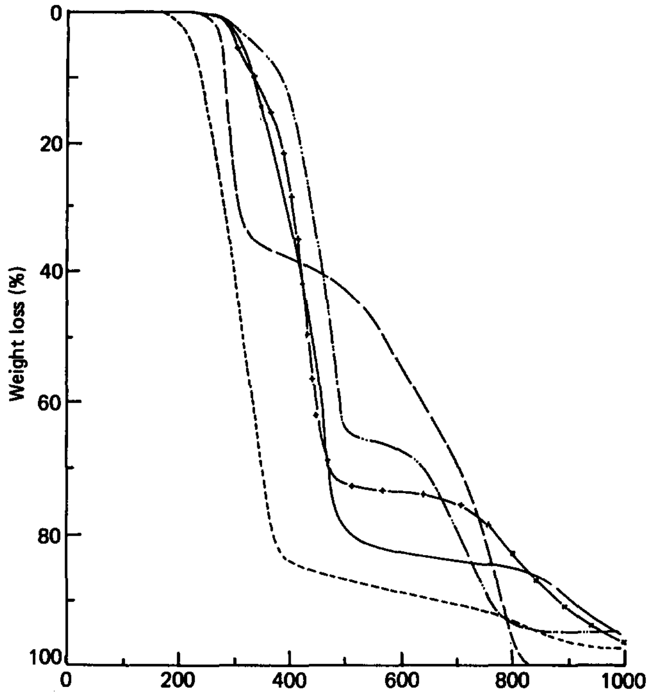

Figure 5 Thermogravimetric traces of polymers I–V in argon: I, ——; II, -----; III, -··—; IV, ---; V, —+—

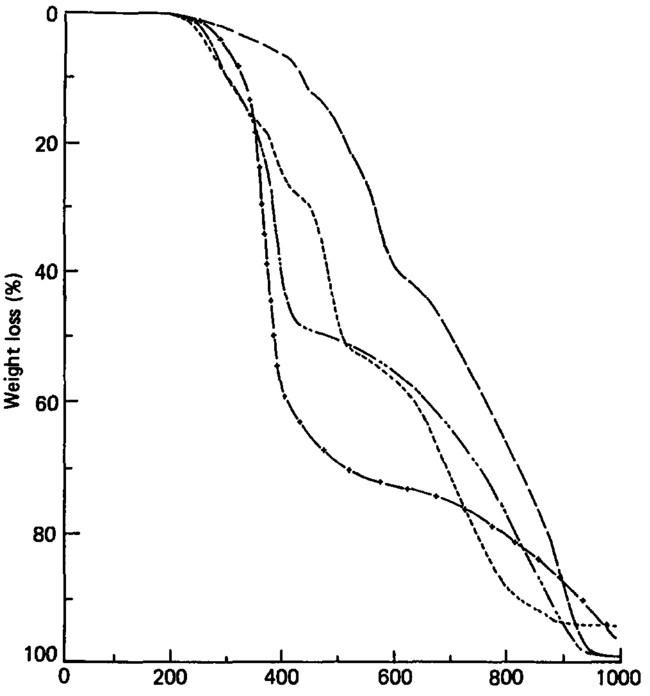

Figure 6 Thermogravimetric traces of polymers VI–IX in argon: VI, -----; VII, ——; VIII, -··-; IX, -+-

Table 4 Thermogravimetric data of the polymers

	Temperature (°C) corresponding to			
Polymer	1% weight loss	inception of fast degradation	50% weight loss	Char percentage at 700°C
I	250	300	450	19
II	200	220	330	11
III	290	390	470	23
IV	270	270	530	28
V	260	360	400	25
VI	250	270	510	32
VII	270	450	720	50
VIII	260	280	510	40
IX	270	340	490	25

is found to cause similar effects in other polymer systems as well[37]. Though the effect on the thermal stability of substituents other than nitro is not marked, some influence was found to exist. Polymer II is found to be the least thermally stable and III the most stable. The char yield at 700°C also shows some variation owing to the different substituents.

The polymers having different backbone structures (VI–IX) were found to show a large difference in their thermal stability and char yield compared with those having different side chains (I–V). Thus the temperature corresponding to 50% weight loss varied from 450 to 720°C in the former case whereas only from 330 to 530°C in the latter. The char yield also varied from 20 to 50% for polymers with different backbone structures, and from 10 to 30% for those with different side chains.

CONCLUSIONS

The structures of the polyphosphates were confirmed spectroscopically. Thermal stability of the polymers was found to vary depending on the structure. Changing the structure of the backbone was found to have more effect on the thermal stability compared with a change in the side chain structure.

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