Flame retardant polyphosphate esters: 2. Condensation polymers of bisphenol A with alkyl phosphorodichloridates: synthesis, characterization and thermal studies

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Polyphosphate esters based on bisphenol A and alkyl phosphorodichloridates have been synthesized and characterized by i.r. and n.m.r. spectroscopy. The molecular weights were calculated from ^{31}P n.m.r. The thermal stability of the polymers were analysed by thermogravimetry.

(Keywords: flame retardancy; polyphosphate esters; bisphenol A; alkyl phosphorodichloridates; i.r. and n.m.r. spectroscopy; thermogravimetry)

INTRODUCTION

The synthesis and characterization of polyphosphates from various bisphenols and aryl phosphorodichloridates have already been reported in a previous paper[1]. The polyphosphates derived from alkyl phosphorodichloridates have received much less attention compared with those derived from aryl phosphorodichloridates[2-12]. A systematic study on the synthesis and properties of these polymers will reveal their potential as flame retardants. In the present communication, condensation polymers of bisphenol A with different alkyl phosphorodichloridates have been synthesized (scheme 1) and characterized by i.r. and n.m.r. spectroscopy. The molecular weights of these polymers were determined by ^{31}P n.m.r. spectroscopy and thermal stability by thermogravimetry.

EXPERIMENTAL

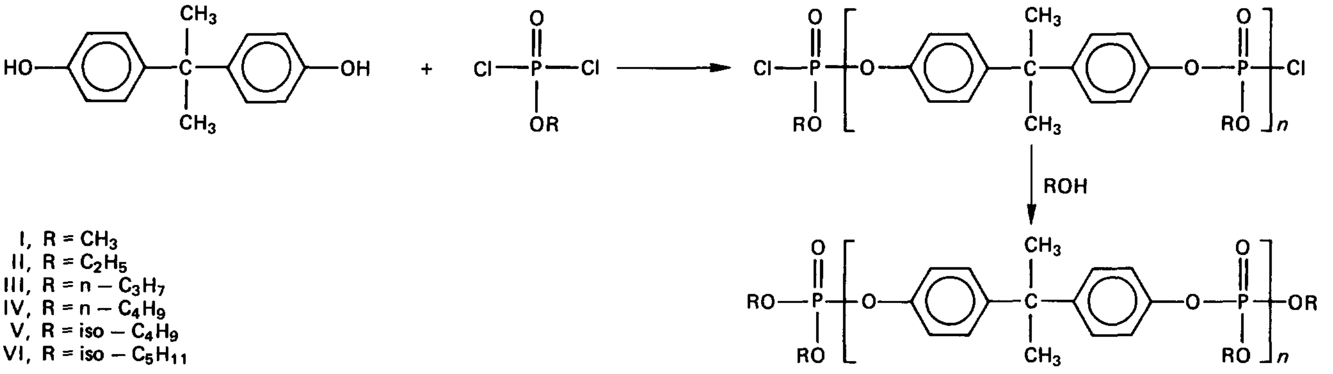
The bisphenol A was obtained commercially and used after recrystallization from toluene. The alkyl phosphorodichloridates were prepared from the alcohols and $POCl_3$ according to the procedure reported[13,14].

A typical procedure for the synthesis of polymer I is as follows: bisphenol A (50 mmol) was taken in dry benzene (30 ml) and refluxed with methyl phosphorodichloridate (55 mmol) in the absence of moisture for about 48 h with constant stirring. The polymer was separated and purified by repeated reprecipitation of $CHCl_3$ solution by pentane; the yield was around 80%. The polymer, dissolved in $CHCl_3$ solution, was then refluxed with methanol (10 ml) for another 3 h; the polymer was separated by adding excess of pentane. The other polymers (II–VI) were also prepared according to the same procedure except that they were refluxed with the corresponding alcohols instead of methanol (scheme 1).

The details of the techniques used were the same as previously described[1].

RESULTS AND DISCUSSION

The various polymers synthesized are shown in scheme 1; polymers III–VI being new. The polycondensation was carried out in solution in the absence of any acid acceptor. The ratio of bisphenol to phosphorodichloridate was kept at 1:1.1 as in the previous cases[1].



Scheme 1

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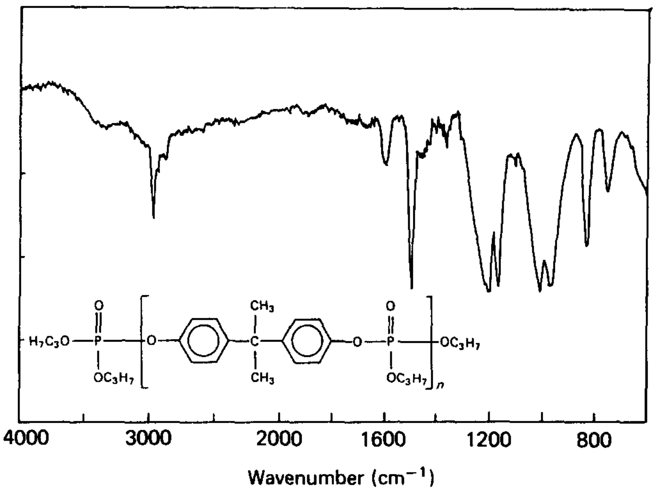

Figure 1 I.r. spectrum of polymer III

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

	Chemical shift values (ppm)			
Polymer	Isopropylidene	Aromatic	P–O–R	Bisphenol end group
1	1.6 (s)	7.0 (s)	3.7 (d)	6.6–7.0 (m)
II	1.6 (s)	7.0 (s)	4.1 (m), 1.3 (t)	6.6–7.0 (m)
III	1.6 (s)	7.0 (s)	3.9 (m),1–2 (m)	6.6–7.0 (m)
IV	1.6 (s)	7.0 (s)	3.9 (m), 0.6–2.0 (m)	6.6–7.0 (m)
V	1.6 (s)	7.0 (s)	4.0 (m), 1.7–2.1 (m) 0.9 (d)	–
VI	1.6 (s)	7.0 (s)	4.0 (m), 1.2–2.1 (m) 0.9 (d)	–

The i.r. spectra of the polymers were similar except in the case of the absorptions of the alkyl group, and a typical spectra is shown in *Figure 1*. The spectra show strong absorptions of $\nu_{P=O}$ at 1300 cm^{-1}, $\nu_{P\text{–}O\text{–}C\,(\text{aromatic})}$ at 1180 and 960 cm^{-1} and $\nu_{P\text{–}O\text{–}C\,(\text{aliphatic})}$ at 1000 cm^{-1}, and support the polyphosphate structure[15]. Polymers I–IV showed the presence of some bisphenol end groups.

The ^1H n.m.r. spectral data of all the polymers are summarized in *Table 1*; representative spectra are shown in *Figure 2*. The spectrum of I shows a singlet at 1.6δ for the isopropylidene protons, a double at 3.9δ for the P–O–CH_3 protons ($^3J_{PH} = 12$ Hz) and a singlet at 7.0δ for the aromatic protons. The spectrum of the other polymers differ from I only in the splitting pattern of the aliphatic group. In all cases, the P–O–R groups of the repeat units have merged with that of the chain ends.

The ^{13}C spectra of the polymers show the resonances corresponding to all the carbons of the given polyphosphate structure (*Figure 3*, *Table 2*). The P–O–R groups of the chain end could not be distinguished from those of the repeat unit. The ^{31}P n.m.r. spectra show two signals at −5.0 and −11.0δ; (*Figure 4*, *Table 3*) the one at −5.0δ corresponds to P at the chain ends which is attached to two alkoxy and one aryloxy groups and the one around −11.0δ corresponds to P in the repeat units which is attached to two aryloxy and one alkoxy groups[16].

The molecular weights of these polymers were determined from ^{31}P n.m.r. spectral data. Since the polymers contain P–O–R groups in both repeat unit and chain ends, the ^1H n.m.r. was not used for molecular weight calculation. For polymer I, the integration of P in the repeat unit to that at the chain end is found to be 1:1 (*Figure 4*) and the molecular weight is ~1000. The molecular weights obtained for the other polymers are given in *Table 3*.

The thermograms of the various polymers are shown in *Figure 5* and the data are summarized in *Table 4*. All the polymers start degrading between 180°C and 230°C and show a two-step degradation. Pyrolysis gas chromatographic studies on polymer I showed that the first step corresponds to the formation of various phenols and phosphates with some amount of char remaining which subsequently carbonizes in the second step. The different alkyl substituents were found to cause little change to the thermal stability and char yield of the polymers.

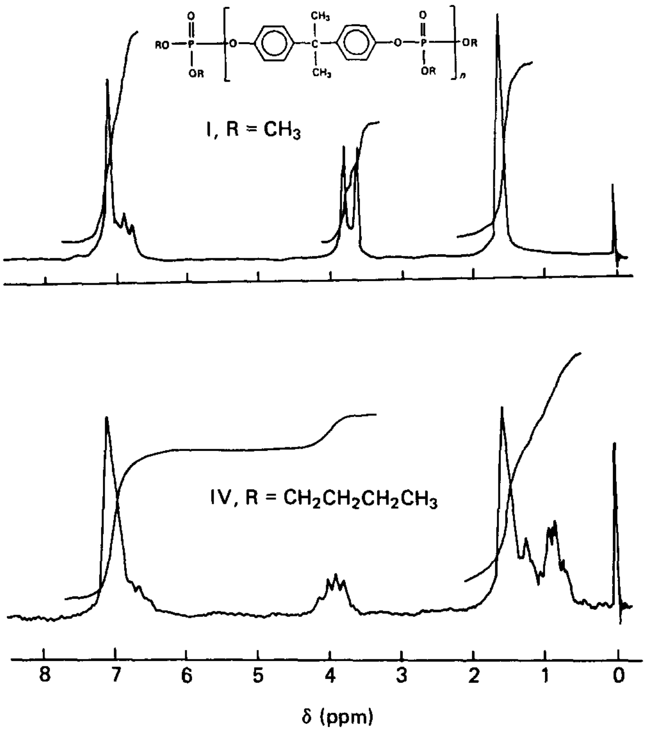

Figure 2 ^1H n.m.r. spectrum of polymers I and IV

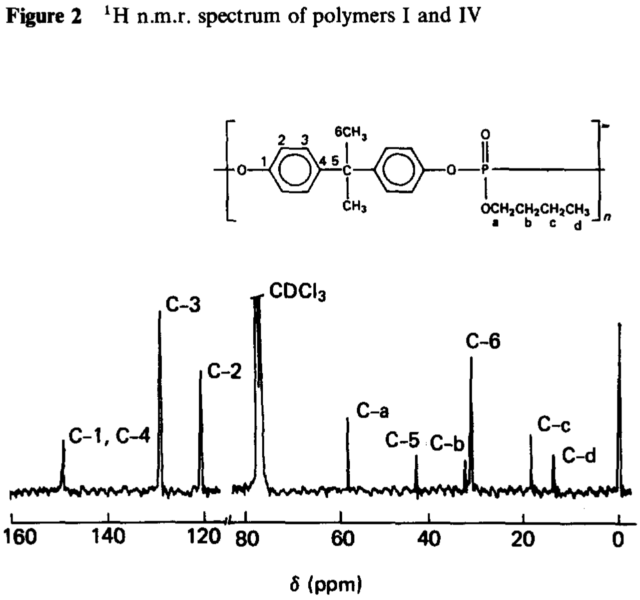

Figure 3 Broad band decoupled ^{13}C n.m.r. spectrum of polymer IV

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-a	C-b	C-c	C-d
I	150.8	119.6	129.7	148.7	42.3	30.9	49.0	–	–	–
II	154.0	119.6	128.2	148.6	42.4	31.1	58.5	16.0	–	–
III	154.0	119.6	128.2	148.7	42.0	31.0	58.5	23.6	–	–
IV	153.9	119.6	128.0	148.6	42.2	31.0	58.5	32.2	18.5	13.5
V	150.7	119.6	128.0	148.5	42.5	30.2	66.7	31.4	18.6	–
VI	150.9	119.7	128.1	148.0	42.3	30.9	59.6	40.8	24.5	22.3

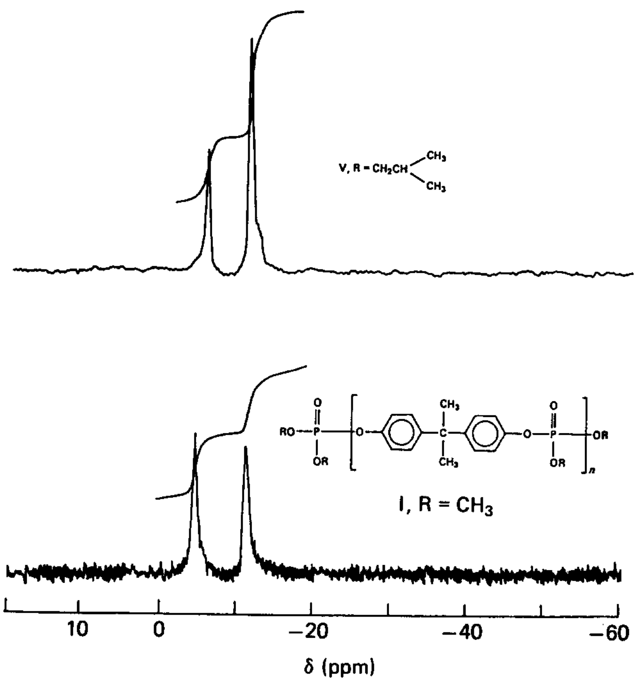

Figure 4 ^{31}P n.m.r. spectra of polymers I and V

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

Polymer	Chemical shift values (ppm) P at the chain end	Chemical shift values (ppm) P in the repeat unit	Ratio of integration (P_{end}/P_{repeat})	Molecular weight
I	−5.0	−11.6	1:1	1050
II	−5.0	−10.5	1:1	1120
III	−6.0	−11.6	1:1	1200
IV	−5.9	−11.4	1:2	1970
V	−6.5	−12.0	1:2	1970
VI	−5.1	−11.0	2:3	1730

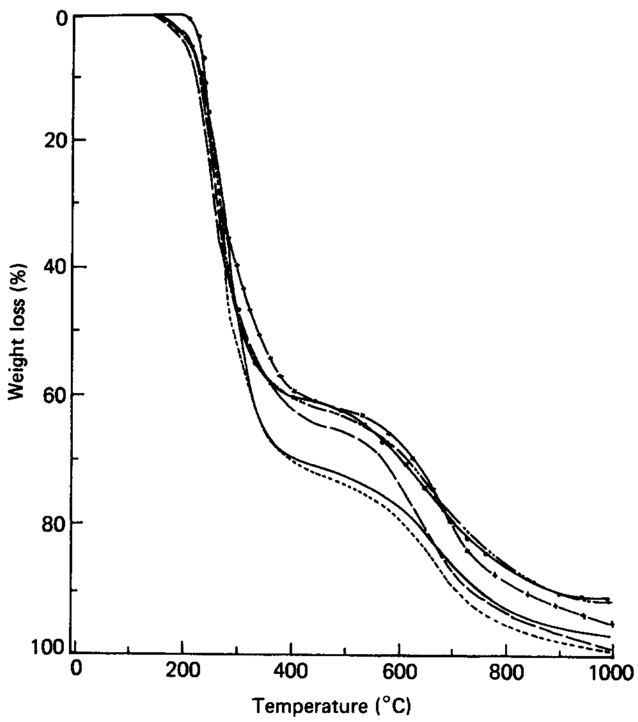

Figure 5 Thermogravimetric traces of polymers I–VI in argon. I, ———; II, - - - - -; III, —··—; IV, —●—; V, – – –; VI, —×—

Table 4 Thermogravimetric data of the polymers

Polymer	Temperature (°C) corresponding to 1% weight loss	Temperature (°C) corresponding to Inception of fast degradation	Temperature (°C) corresponding to 50% weight loss	Char percentage at 700°C
I	180	230	310	14
II	180	230	300	12
III	190	230	320	20
IV	210	220	310	21
V	180	210	300	13
VI	170	220	330	20

CONCLUSIONS

The structure of the polyphosphate esters, based on bisphenol A and alkyl phosphorodichloridates, were confirmed spectroscopically. The thermal stability of the polymers were found not to be affected much by the change in the alkyl pendent group.

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