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Synthesis of novel flame retardant polyamidophosphate esters from aromatic diols and *N*-arylphosphoramidic dichlorides

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Summary

Several new polyamidophosphate esters were synthesized by the solution polycondensation of aromatic diols with N-aryl phosphoramidic dichlorides.The polymers were characterized by the IR and ^1H, ^{13}C and ^{31}P NMR spectroscopy.From their thermal stability and flammability data, these polymers reveal their capacity as potential flame-retardants. Structural dependancy on flammability seems to be discernible in these polymers.

Introduction

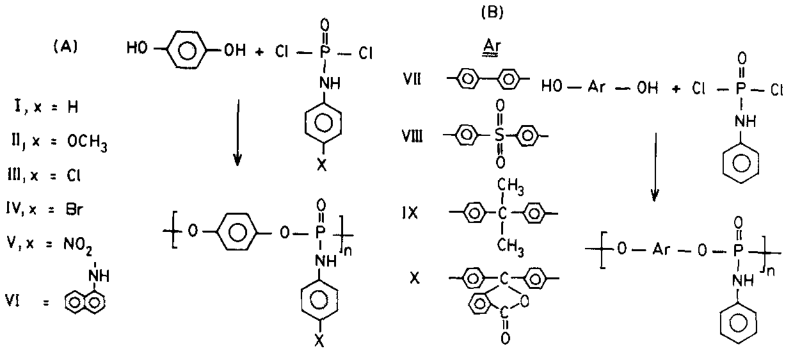
Several hundred tons of fire-retardant compounds are annually used world over to abate the fire-risk and enlarge the usage of commercial polymers-inherently flammable as they are. We have recently demonstrated that polyphosphate esters exhibit excellant-flame retardant properties(1,2) in their ownself and as fire-proof additives in PVC. Furthermore, we observed that thermally stable aryl polyphosphate esters possess superior flame-retardant properties than their alkyl counterparts. We report here the step-growth synthesis of hitherto new aromatic polyamidophosphate esters from aromatic diols and N-aryl phosphoramidic dichlorides of different structures.

Experimental

Materials: Analar grade hydroquinone,biphenol,Sulfonyl diphenol, bisphenol-A and phenolphthalein were used as such. 1,1,2,2, tetrachloroethane was dried and vacuum distilled over P_2O_5. Anilines, $POCl_3$, benzene and methanol were purified by usual procedures.

N-Arylphosphoramidic dichloride: The N-phenyl phosphoramidic dichloride was prepared from $POCl_3$ and aniline as reported earlier(3). Other monomers were also prepared in a similar manner. p-NO_2 phenyl phosphoramidic dichloride was prepared using dry diethyl ether solvent.

Polymerization : The polymers (I - X) were prepared by solution polycondensation as follows. Hydroquinone (5 mmol) was taken



Scheme 1 Synthesis of polyamidophosphate esters

in dry tetrachloroethane (30 ml) and refluxed with N-phenylphosphoramidic dichloride (5.5 mmol) under dry conditions for 12 hrs. The precipitated polymers were filtered and washed with hot methanol and acetone followed by vacuum drying at 80°C for 4 hrs. All polymers were coloured and rigid in texture.

Characterization : The IR spectra were recorded on a Perkin-Elmer Model 715 spectrophotometer using KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded on a Brucker FT 270 spectrometer (67.89 MHz) in DMSO-d_6 using TMS as the internal standard. ^{31}P NMR spectra were recorded on a Varian FT 80A (32.2 MHz) spectrometer in DMSO-d_6 under broad band ^{1}H decoupling conditions. D_2O and phosphoric acid (85%) were used as the external lock and external standard respectively.

The thermogravimetric studies were carried out using Sinko-Riko TGD 5000 thermal analyser in air at a heating rate of 20°C min^{-1} with a sample of 3-5 mg. The LOI data were obtained on a home made assembly(2).

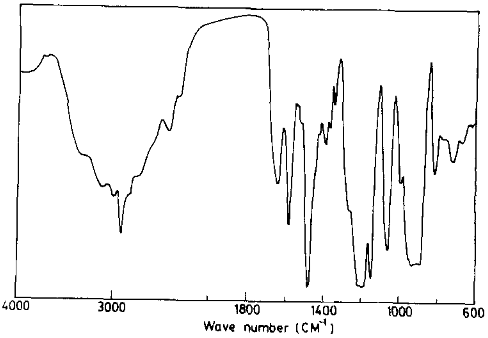


Figure 1. I.R. Spectrum of polymer IX

Results and discussion

Several polyamidophosphate esters were prepared by solution polymerization method (Scheme 1)with a yield over 60%. Except for the polymer VIII, which is soluble at room temperature, other polymers were sparingly soluble in dipolar aportic solvents such as DMSO, DMAc, DMF and NMP under hot conditions. The polymers were insoluable in common organic solvents such as acetone and chloroform.

Typical IR spectrum of polymer VII is shown in Figure 1. The absorption bands around 3470-3300 cm^{-1} and 1650-1620 cm^{-1} are for the -NH-stretching and deformation respectively, and those at 1603 and 1515 cm^{-1} are due to the aromatic ring breathing bands (4,5). Characteristic absorptions at 1300, 1320, 960 cm^{-1} correspond to P=O, P-N-C(Ar) and P-O-C(Ar) stretchings respectively(6). Typical ^{1}H NMR spectra of polymers II and VII are shown in Figure 2. The aromatic protons of the main chain and pendent phenyl are centred at 6.88 to 7.58 , the splitting pattern varies depending on the substituents. The mobile -NH proton appeared at 5.28 and 9.98 in the polymers II and VI.

Typical broad band ^{1}H decoupled ^{13}C NMR spectrum of polymer IX is shown in Figure 3. The chemical shifts, indicated in the spectrum, correspond to the literature values of the monomers(7,8). The phosphoramido group in polymers causes the pendent phenyl ortho and para carbons to shift to higher field, the meta carbons are however unaltered. The splitting of several signals into two or three peaks may be ascribed to the scaler coupling with the ^{31}P nucleus(9).

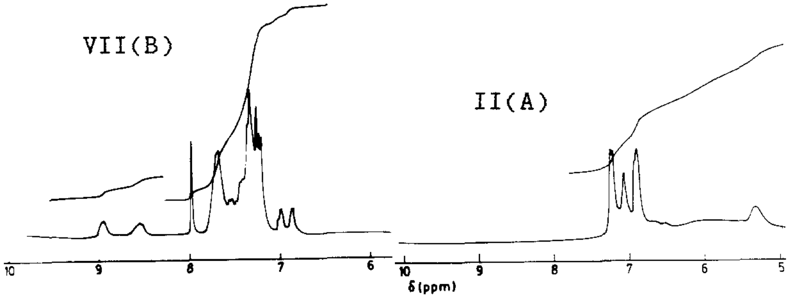


Figure 2. ^{1}H n.m.r spectra of polymers II(A) and VII(B)

Typical ^{31}P n.m.r spectrum of polymer IX is shown in Figure 4, we get four signals due to the splitting of each P nucleus of the main chain and the P at the chain end. The observation of these spin-spin splittings show minimal electrical quadrapolar interactions arising from the nitrogen nucleus(10). Accordingly, the more shielded main chain P shows two signals at -13.4 and - 18.71 but the deshielded end group P appeared at -2.7 and - 7.56 .

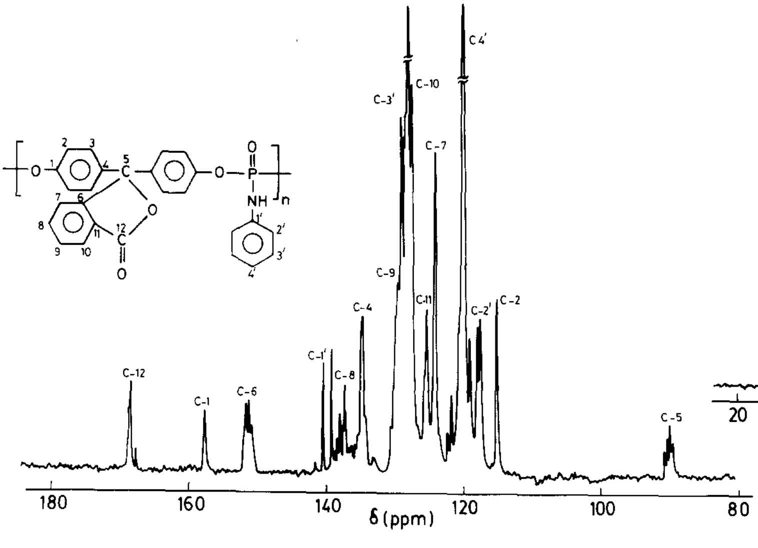


Figure 3. Broad band decoupled ^{13}Cn.m.r.spectrum of polymer X

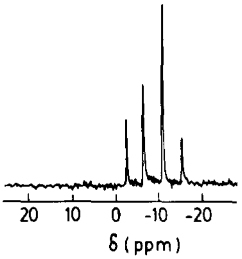


Figure 4. ^{31}P n.m.r. spectrum of polymer IX

The phosphorous content and thermal stability data viz., 1% and 50% weight loss and the char percantage at 700°C, in a specified fashion, are shown in Table 1. This has emanated from our previous experience(2) while establishing structure-flammability relationship in polyphosphate esters. Thermograms of the various polymers are shown in Figure 5. The degradation pattern is similar to our previous polymers (1,2). The weight (1%) loss data shows that these polymers are stable upto 250-310°C and commences degrading, in air, thereafter. It is apparent that the polymer derived from bisphenol-A (VIII) is the least stable than the others. However, the incorporation of -NH-group enhances the thermal stability considerably set against polyphosphate esters(1,2).

The LOI and phosphorus content of the polymers are given in Table 1. The polymers display LOI values ranging from 42% to 52% depending upon their structures. The LOI of these polymers (I-VI) decreases in the sequence : NO_2 > Naphthyl > Br > OCH_3 > Cl > H. Phenolphthalein polymer proved to be the least flammable.

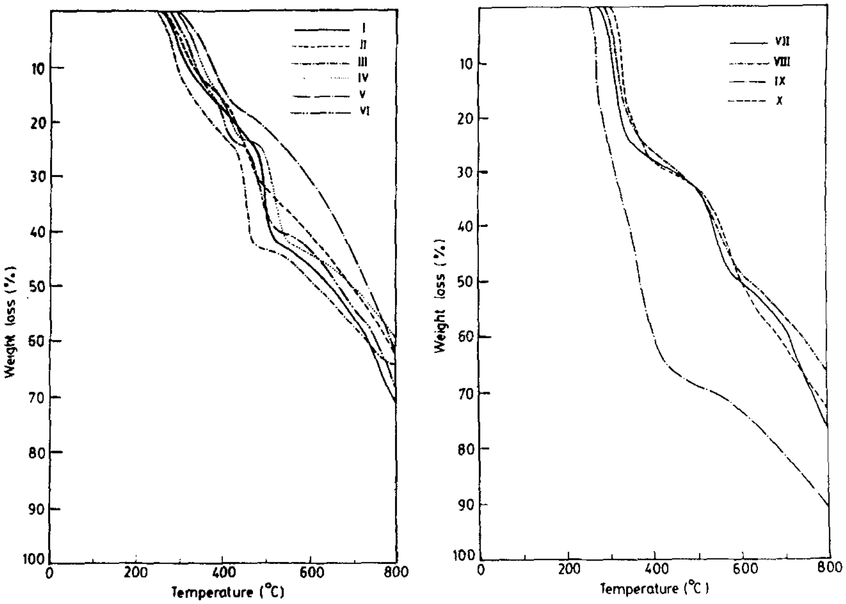


Figure 5. Thermogravimetric traces of polymers

Table 1 Thermogravimetric and LOI data of polymers

Sl. No.	Colour of Polymer	Temperature (°C) corrosponding to		Char % at 700°C [a]	Phosphorus content %	LOI [b]
		1% weight loss	50% weight loss			
I	Dark-Violet	270	650	49	12.5	47
II	Dark-Violet	275	710	51	11.2	48
III	Blue	250	610	43	11.0	48
IV	Dark-Blue	300	700	50	9.5	50
V	Dark-Blue	310	730	55	10.6	52
VI	Violet	280	670	47	10.4	49
VII	Brown	280	600	42	9.6	42
VIII	Brown	290	610	45	8.7	43
IX	Dark-Brown	260	380	19	8.5	35
X	Brown	310	620	39	6.8	51

[a,b] The error = ± 1%

Conclusions

Two series of new polyamidophosphate esters have been prepared from N-aryl phosphoramidic dichloride and characterized spectroscopically. The thermal stability and flammability exhibit strong structural dependence.

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