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SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF SOME POLYARENE-PHOSPHOROCHLORIDATES

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ABSTRACT

Aromatic polyarene-phosphochloridates were prepared by condensation of various bisphenols (4,4′-isopropylidenediphenol,4,4′-dihydroxydiphenyl sulphone, and 4,4′-dihydroxybiphenyl) with phosphorus oxychloride in pyridine medium. These polymers were characterized by IR spectrophotometry. The isothermal decomposition of these polymers and their 2% mixtures with PVC were studied.

INTRODUCTION

Polyarene phosphates were prepared by condensation of a mixture of monohydric and dihydric phenols with phosphorus oxychloride [1–6]. More recently poly(4,4′-isopropylidenediphenylene phosphorochloridate) has been prepared by condensation of bisphenol(A) (4,4′-isopropylidenediphenol) with phosphorus oxychloride [7]. In the present work we have synthesized some polymeric phosphate esters. The effect of these polymers on the thermal behaviour of PVC has been reported since the organic phosphite compounds have been used to stabilize PVC and other polymers [8,9].

EXPERIMENTAL

Materials

4,4′-Isopropylidenediphenol (**I**) and 4,4′-dihydroxydiphenyl sulphone (**II**) were obtained from Fluka and purified by recrystallization in toluene (m.p. 160°C) and in a methanol–water mixture (m.p. 249°C), respectively. 4,4′-Dihydroxybiphenyl (**III**) and phosphorus oxychloride were purchased from Riedel company and used as received. Pyridine was BDH quality. PVC powder was obtained from Fluka with a *K* value of 55.57.

Measurements

The IR spectra were recorded on a Pye-Unicam SP 1000 spectrophotometer using KBr discs. Thermogravimetric analyses were carried out using a MOM (Hungary) Derivatograph in air at a heating rate of 5°C min^{-1} for the following samples:

(1) Pure PVC and pure polyarene-phosphorochloridate samples from zero to 500°C.

(2) PVC mixed with 2% of the polyarene-phosphorochloridate samples at constant temperature for 200 min.

Isothermal TG

Samples (500 mg) of PVC and PVC mixed with polyarene-phosphorochloridate were used in isothermal TG studies. The samples were heated in a constant-temperature furnace at various temperatures in ceramic crucibles. The mass losses were recorded as a fucntion of time.

Polymerizations

The polymers were synthesized by reacting equimolar mixtures of phosphorus oxychloride with various bisphenols in pyridine medium.

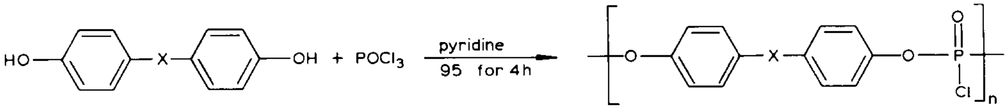
Recrystallized bisphenol (**I**) (0.01 mol) and phosphorus oxychloride (0.01 mol) were weighed and transferred carefully into a (100 ml) 3-necked round-bottom flask fitted with a nitrogen inlet, a condenser, a thermometer, and a mechanical stirrer.

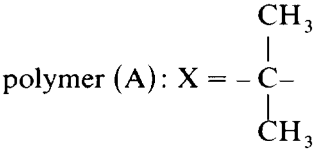
The reaction mixture was heated under nitrogen at 95°C for 4 h. Finally the temperature was raised to 240–250°C for 6 h. A hard solid material was obtained. This solid was washed three times with acidified water, water and finally with ether. The product was dried overnight at 80°C in a vacuum oven.

Reaction of bisphenols (**II**) and (**III**) with phosphorus oxychloride in a similar manner as above gave polymers (B) and (C), respectively.

RESULTS AND DISCUSSION

The polyarene-phosphorochloridates (A, B and C) were obtained according to the following reaction:





$$\text{polymer (A)}: X = -\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-$$

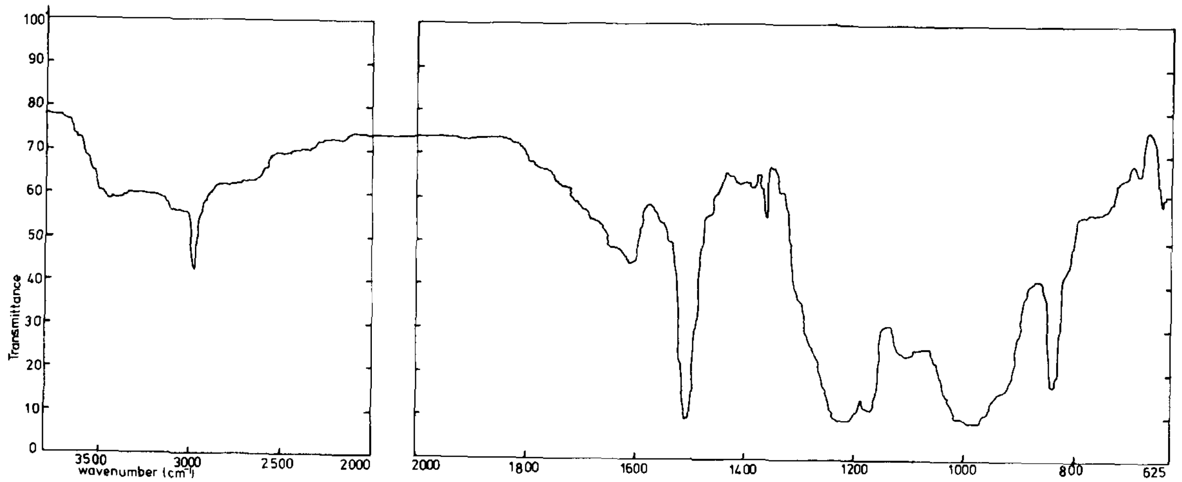


Fig. 1. Infrared spectrum of polymer (A).

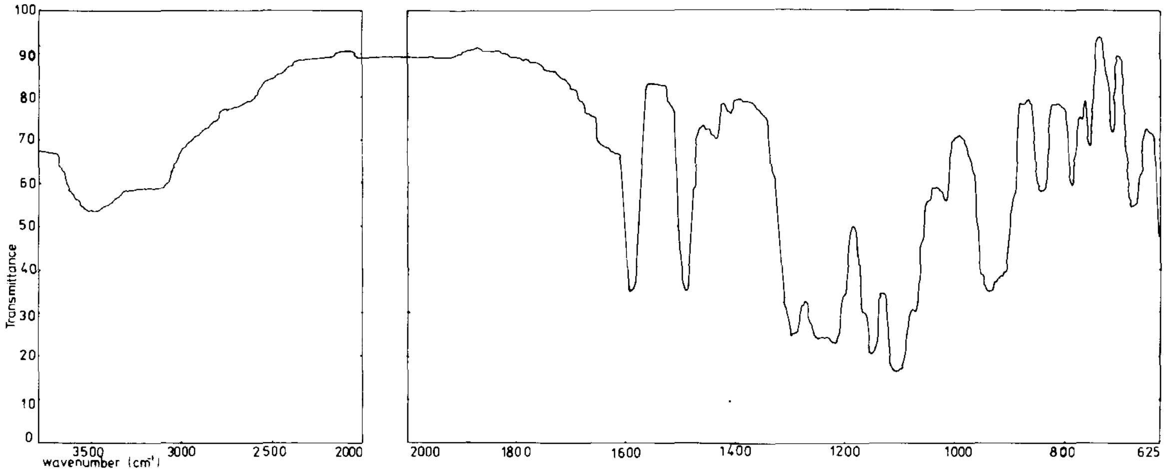


Fig. 2. Infrared spectrum of polymer (B).

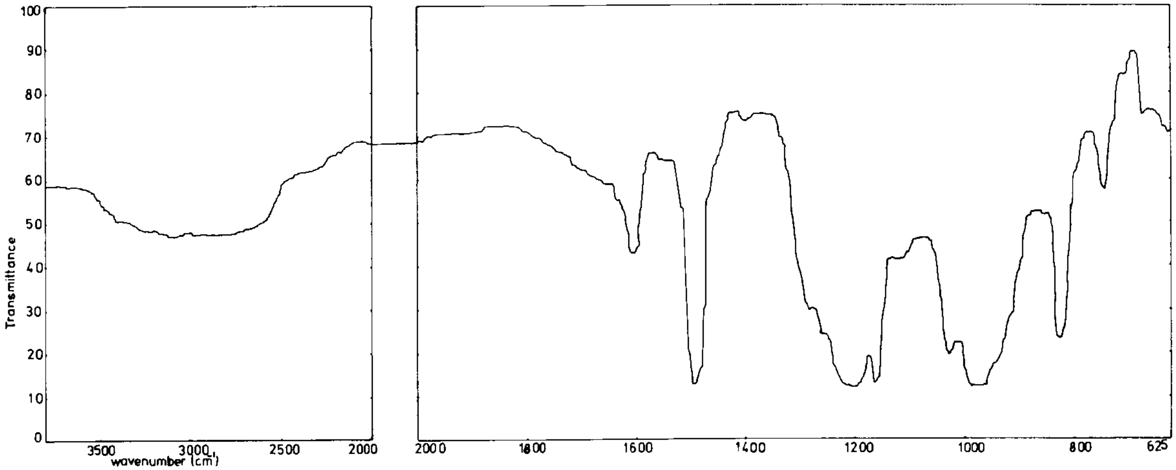


Fig. 3. Infrared spectrum of polymer (C).

polymer (B): $X = SO_2$

polymer (C): X = chemical bond

IR studies

The IR spectra (Figs. 1, 2 and 3) are consistent with the polymers of structures (A), (B) and (C). The characteristic peaks in the IR spectra of these polyarene-phosphorochloridates are assigned as given in Table 1 [16].

Thermal behaviour of polymers (A, B and C)

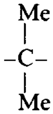
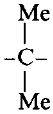
TG curves of the pure polymer samples at various temperatures from zero to 500°C are shown in Fig. 4. All samples undergo thermal decomposition according to the following scheme:

B > C > A from 0 to 240°C

B > A > C from 240 to 500°C

TABLE 1

Assignment of characteristic frequencies in IR spectra

Polymer	Wavenumber (cm^{-1})	Intensity	Assignment
A	1385	w, sh	 $-C(Me)_2-$
	1365	w, sh	 $-C(Me)_2-$
	1290	s, b	P=O
	1260	s, b	P=O
	980	s, b	P–O–aryl
	940	s, b	P–O–aryl
	2990	m, sh	C–H aliphatic
B	1335	m, b	SO_2
	1150	s, sh	SO_2
	1290	s, b	P=O
	1250	s, b	P=O
	935	s, b	P–O–aryl
C	1285	s, sh	P=O
	1260	s, b	P=O
	980	s, b	P–O–aryl
	940	s, b	P–O–aryl

sh = sharp, b = broad, s = strong, w = weak, m = medium.

Thermal behaviour of the mixtures of 2% polymer (A, B and C) with PVC

TG curves of pure PVC and the PVC mixed with 2 wt.% of different polymers (A, B and C) at various constant temperatures (200, 220, 240 °C) were recorded in air. The results of these degradations are shown in Figs. 5, 6 and 7. The rate of thermal degradation was initially found to be rapid with each polymer added and finally became constant in weight loss. The

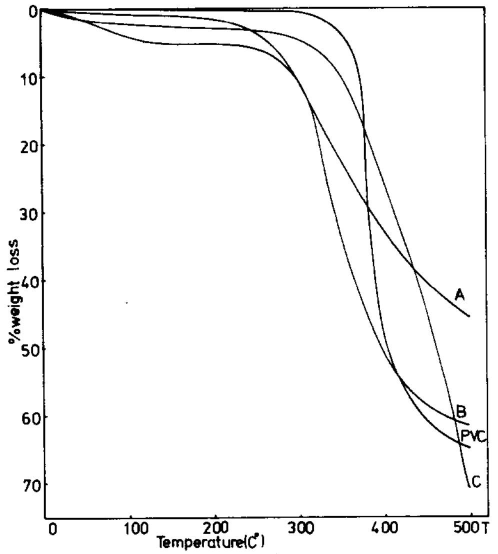


Fig. 4. Thermogravimetric analysis of pure PVC and polymer samples (A, B, C).

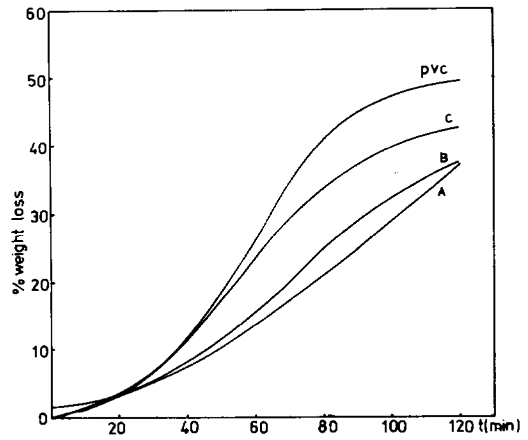


Fig. 5. Thermogravimetric analysis of pure PVC and PVC mixed with 2 wt.% of polymer samples (A, B, C) at a constant temperature of 200 °C.

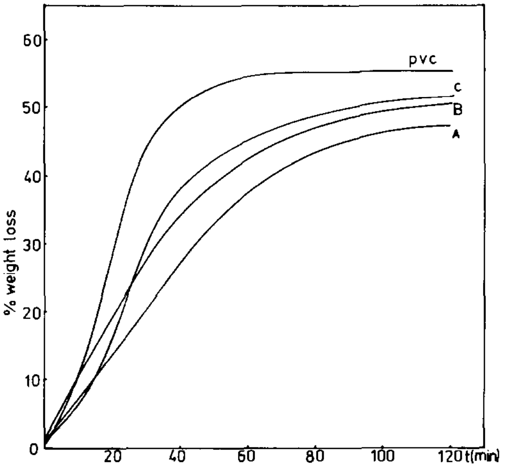


Fig. 6. Thermogravimetric analysis of pure PVC and PVC mixed with 2 wt.% of polymer samples (A, B, C) at a constant temperature of 220 °C.

Avrami–Erofeev equation [10,11] of kinetic processes was applied to study the rate of thermal degradation of pure PVC and PVC mixed with different polymers (2%). This equation gave straight lines with average slopes and α values as shown in Table 2.

$$[-\ln(1-\alpha)]^{1/n} = kt$$

$$\frac{1}{n}\ln[-\ln(1-\alpha)] = \ln k + \ln t$$

where α = degree of decomposition $= (W_0 - W)/(W_0 - W_f)$; W_0 = initial

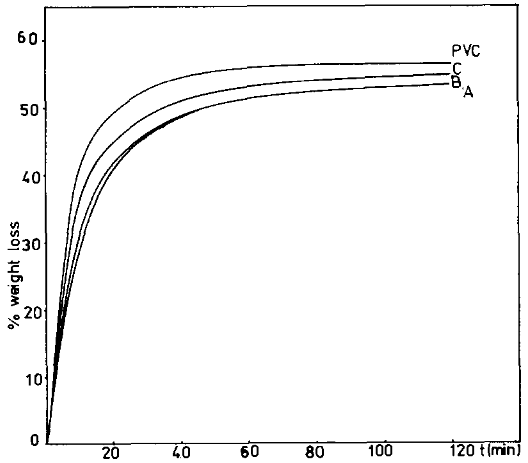


Fig. 7. Thermogravimetric analysis of pure PVC and PVC mixed with 2 wt.% of polymer samples (A, B, C) at a constant temperature of 240 °C.

TABLE 2

Kinetic parameters obtained for the decomposition of pure PVC and PVC with 2% polymer (A, B, C)

Treatment	Temp. (°C)	Activation energy (E) (kcal mol^{-1})	α-Value	Mean slope
Pure PVC	200			
	220	34.62	0.495–0.983	0.73
	240			
PVC with 2% polymer (A)	200	67.3	0.156–0.997	1.145
	220			
	240			
PVC with 2% polymer (B)	200	61.89	0.036–0.964	1.114
	220			
	240			
PVC with 2% polymer (C)	200	72.99	0.06–0.996	1.182
	220			
	240			

weight of polymer; W_f = final weight of polymer; W = weight remaining at a given time; n = order of reaction; k = rate constant.

Values of k were obtained from the intercept of the plot of $\ln[-\ln(1-\alpha)]$ versus $\ln t$ and $1/n$ was calculated from the slope of the line.

Activation energy (E) was calculated from the Arrhenius equation:

$$k = A\ e^{-E/RT}$$

$$\ln k = \ln A - \frac{E}{RT}$$

$\ln k$ was plotted versus $1/T$ to calculate the activation energy of thermal degradation. The resulting activation energies are shown to increase the thermal stability of PVC according to the following order: B < A < C. This is in agreement with the degradation order of the pure polymer samples: B > A > C (decreasing thermal degradation). This observation is probably due to the degraded phosphorus-containing species which may act in various roles to stabilize PVC; for example reactions with proton donors, in particular evolved [12,13] HCl, or reactions with free radicals, or any other reactions [14,15].

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