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Synthesis and characterization of thermally stable cardo polyphosphonates

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Two new thermally stable polyphosphonates were prepared from dichlorophenyl phosphine oxide and bisphenols with pendant heterocyclic ring by interfacial polycondensation using a phase transfer catalyst at 0°C. They were characterized by 1R, ^{1}H and [31]P n.m.r. spectroscopy. These polymers are amorphous in nature and readily soluble in chlorinated aliphatic hydrocarbons, such as CH_2Cl_2, $CHCl_3$ etc., as well as polar aprotic solvents such as DMF, DMAC, NMP etc. Thermal and flammability studies were carried out by t.g.a., DTA and limiting oxygen index determination, respectively. Polymers are self extinguishing and begin to lose weight at around 350°C. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyphosphonate; interfacial polymerization; flammability)

INTRODUCTION

Aromatic polyphosphonates have been of commercial interest because of their flame retardancy[1]. Polyphosphonates are generally prepared from organophosphorus compounds such as dichlorophenyl phosphine oxide and bisphenols[2]. Aromatic polyphosphonates as flame-retardant additives are superior to non-polymeric additives because of their lower volatility, lower leaching tendency and better compatibility with base polymers. Among several properties, thermal stability is one of the important properties of flame-retardant polymers. If the empolyed additive is thermally labile, the thermal stability of the polymer system will be reduced. In order to reduce the observed effects of flame-retardant additives on the thermal stability of polymeric mateials, higher thermally stable polymeric additives are of great interest. Imai *et al.*[3] prepared high thermally stable polyphosphonates having rigid ring structures. This paper deals with the preparation and characterization of two new polyphosphonates with pendant heterocyclic ring, the cardo group, which provides thermal stability to the polymer.

EXPERIMENTAL PROCEDURE

Materials

Dichlorophenyl phosphine oxide (Fluka) was purified by vacuum distillation before use. Cetyltrimethyl ammonium chloride (CTMAC) (Fluka) was used as received. Dichloromethane was dried following the usual method[4]. Phenolphthalein (S. D. Fine Chem.) was recrystallized from methanol–water; melting point, 261–263°C.

Monomer preparation

N-phenyl 3,3-*bis*(4-hydroxyphenyl)phthalimidine(bisphenol I) was synthesized from phenolphthalein in aniline hydrochloride, with refluxing in aniline for 5 h[5]. The product was recrystallized from ethanol; melting point, 290–293°C [6].

N-methyl 3,3-*bis*(4-hydroxyphenyl) phthalimidine (bisphenol II) was synthesized according to the reported procedure [7]. The product was recrystallized from methanol water; melting point, 271–273°C.

POLYMERIZATION

Polymerizations were carried out by interfacial procedure. The polymerization procedure for bisphenol II was as follows [3].

In a reaction flask fitted with a mechanical stirrer 5 mmol bisphenol II was dissolved in 30 mL of aqueous NaOH (10 mmol) solution. To the mixture 0.320 g (1 mmol) CTMAC was added. The solution was stirred and cooled to 0°C. Next, a solution of 0.975 g (5 mmol) dichlorophenyl phosphine oxide (DCPO) in 10 mL dichloromethane was added dropwise. The mixture was stirred at this temperature for another 1 h. The supernatant aqueous layer was decanted and the polymer solution was washed repeatedly with water to neutral pH. The polymer was precipitated by pouring the solution into excess hexane. The product was collected and dried at 50°C in vacuum.

For the polymerization of bisphenol I with DCPO, the same procedure as for bisphenol II along with slight modification as developed by Morgan[7] was employed. In the presence of alkali, bisphenol I is transformed into highly coloured quinomethine structure. As the DCPO in dichloromethane was added dropwise to the alkaline solution, there occured a rapid loss of deep red color. Alkali was added to bring back the color, stirring was continued, and a small portion of DCPO in solution was added. These steps were repeated twice to complete the polymerization.

CHARACTERIZATION

The elemental analysis was performed on a Heraeus C, H, N analyser. Phosphorus was estimated by the Schoniger

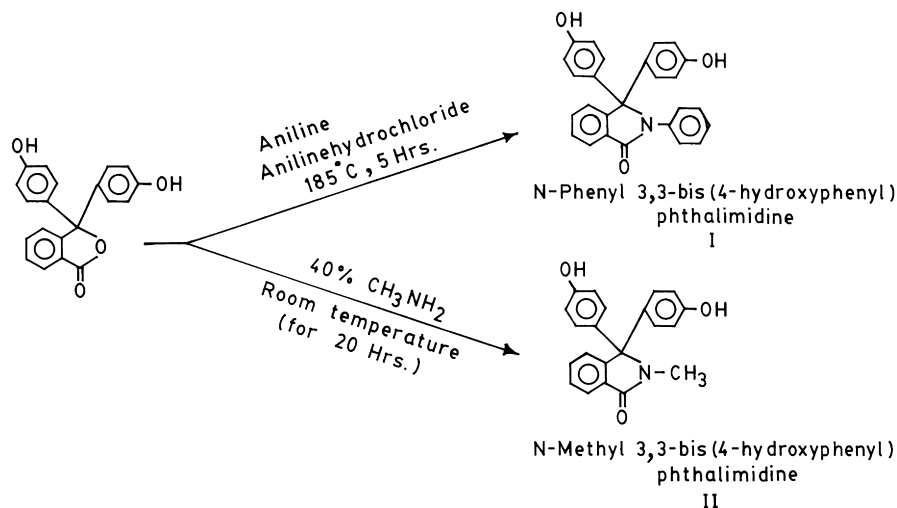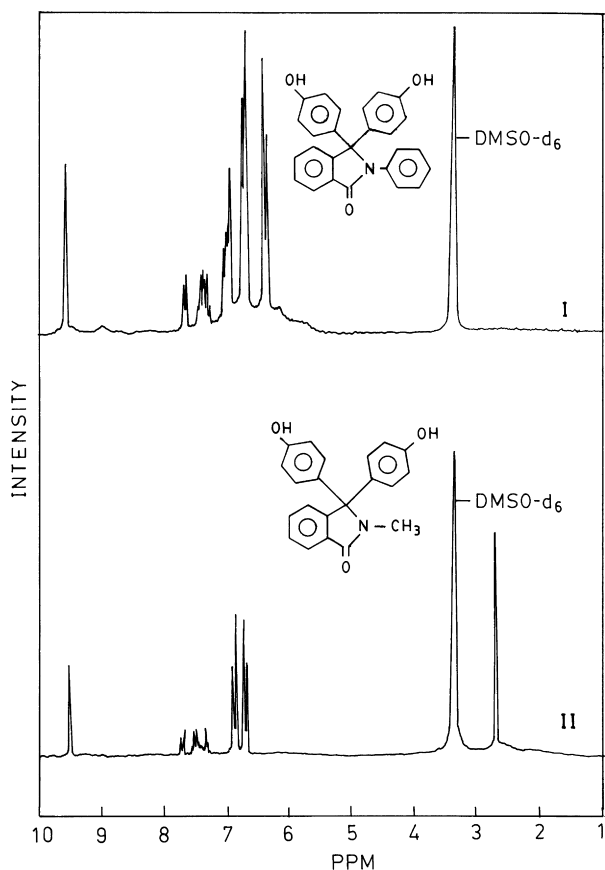* To whom correspondence should be addressed

Figure 1 Reactions scheme for synthesis of bisphenols

Table 1 Physical characteristics and analysis of monomers

Monomer	Yield	M_p (°C)	Colour	Solvent	Elemental analysis Found (calcd.) (%)		
					C	H	N
I	79%	290–293	White	DMF, DMSO	78.56	4.75	3.41
				DMAC, NMP, C$_2$H$_5$OH	(79.88)	(4.83)	(3.56)
II	98%	271–273	White	DMF, DMSO	75.40	5.05	4.20
				DMAC, NMP, C$_2$H$_5$OH	(76.11)	(5.17)	(4.23)

Figure 2 ^{1}H-n.m.r. spectra of bisphenols

combustion method[8]. The i.r. spectra were recorded with a Shimadzu 470 spectrophotometer with KBr pellets. The ^{1}H n.m.r. spectra were recorded with a varian EM 390 spectrometer in DMSO-d$_6$ and CDCl$_3$ using TMS as internal standard for monomers and polymers, respectively. The ^{31}P-n.m.r. spectrum was recorded with the same instrument using CDCl$_3$ as solvent and H$_3$PO$_4$ as internal standard. T.g.a. and DTA of the polymers were carried out with a Shimadzu DT 40 Thermal analyser in air at a heating rate of 10°C min^{-1}. The limiting oxygen index (LOI) values of the polymers were measured using a modified method[9].

RESULTS AND DISCUSSION

Monomer synthesis and characterization

The reactions for monomer synthesis can be represented as shown in *Figure 1*. *Table 1* summarizes the physical characteristics of the monomers. The chemical structure of these monomers was established on the basis of elemental analysis, i.r. spectroscopy and n.m.r. analysis (*Table 1*). The elements—carbon, hydrogen and nitrogen—present in the monomer were analysed. It has been observed that the experimental results of analysis agree well with the theoretical values obtained from the structure shown in *Figure 1*. The presence of hydroxy and lactam carbonyl linkages in the monomers was confirmed by the characteristic stretching absorption at about 3300 cm^{-1} and 1700 cm^{-1}, respectively, in the i.r. spectra (not shown).

The ^{1}H-n.m.r. spectra were also used to authenticate monomers I and II (*Figure 2*). The spectra show a singlet at 9.5 and 2.7 ppm which is due to the –OH group and the CH$_3$ group of monomer II, respectively. The aromatic protons of monomers I and II appear as the multiplet at 6.4–7.8 ppm and 6.7–7.7 ppm, respectively.
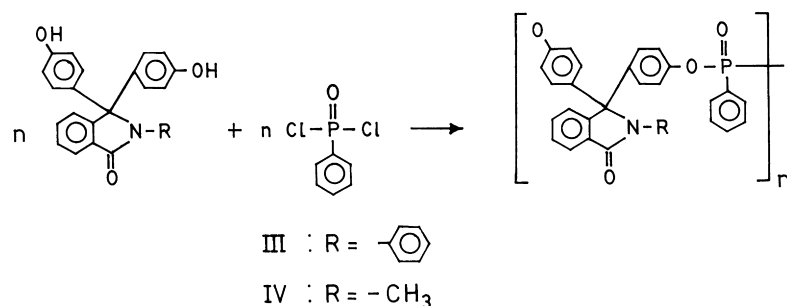
Figure 3 Synthesis of polyphosphonates

Table 2 Results of synthesis and physical characteristics of polymers

Polymer code	Yield (%)	η_{inh}^a (dL g^{-1})	Colour	Solvent
III	85	0.31	White	CHCl$_3$,CH$_2$Cl$_2$,
IV	94	0.29	White	DMF,DMSO etc.

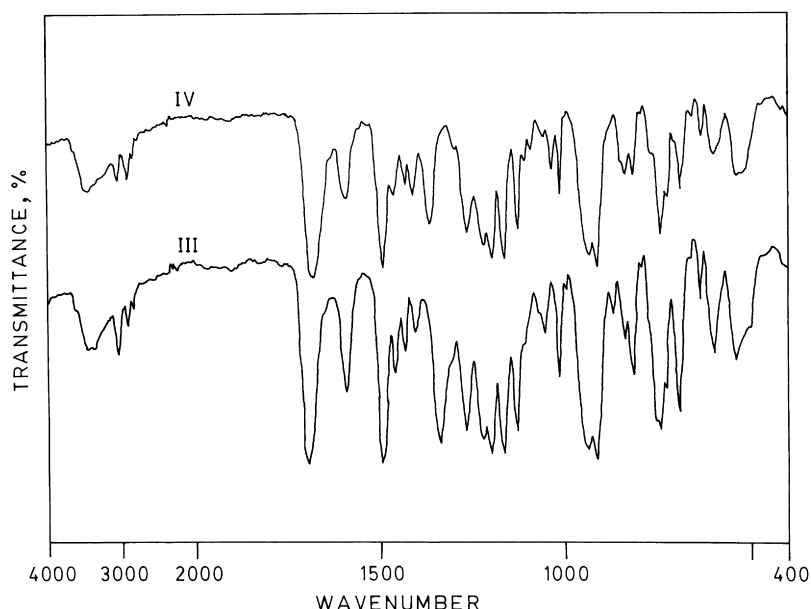^{a}Measured in CHCl$_3$ (0.5 g dL^{-1}) at 30°C

Figure 4 I.r. spectra of polyphosphonates

Polymer synthesis and characterization

Polyphosphonates were synthesized by the reaction of bisphenols I and II with dichlorophenylphosphine oxide. The reaction is represented in *Figure 3*.

The polymers were synthesized by the two-phase polycondensation technique with a phase transfer catalyst. The results of the synthesis and the physical characteristics of the polymers are summarized in *Table 2*. Pure monomer II is not transformed into a highly colored quinomethine species unlike bisphenol I. The straightforward polymerization of monomer I as II leads to the formation of a polymer with very low intrinsic vicosity. In order to enhance the intrinsic viscosity of the polymer formed the Morgan's procedure [7] was used for this case.

The chemical structure of polymers III and IV was determined on the basis of elemental analysis, i.r. and n.m.r. studies. Elemental analysis of the polymers agrees well with the calculated values of the elemental composition based on the chemical structures shown in *Figure 3*.

Infrared spectra

The i.r. spectra of polymers III and IV are presented in *Figure 4*. Results of elemental analysis and characteristic i.r. absorption peaks are presented in *Table 3*. The i.r. spectra of these two polymers are similar and exhibit characteristic absorption peaks around 1710 cm^{-1} ($>$ C=O), 1435 cm^{-1} (P–Ph), 1267 cm^{-1}(P=O), 1200 cm^{-1}(P–O–C) [10,11] and 3000–3200 cm^{-1} (phenyl stretching). The spectra of polymers show also a small plateau around 3350 cm^{-1} corresponding to bisphenol end groups.

Nuclear magnetic resonance analysis

The ^{1}H-n.m.r. spectra of the polymers are presented in *Figure 5*. The spectra show no peak due to the –OH protons present in the monomers which confirms the formation of polyphosphonates. The aromatic protons of polymers III and IV appear as a broad multiplet in the region 6.8 and 7.9 ppm, respectively. Polymer IV shows an additional
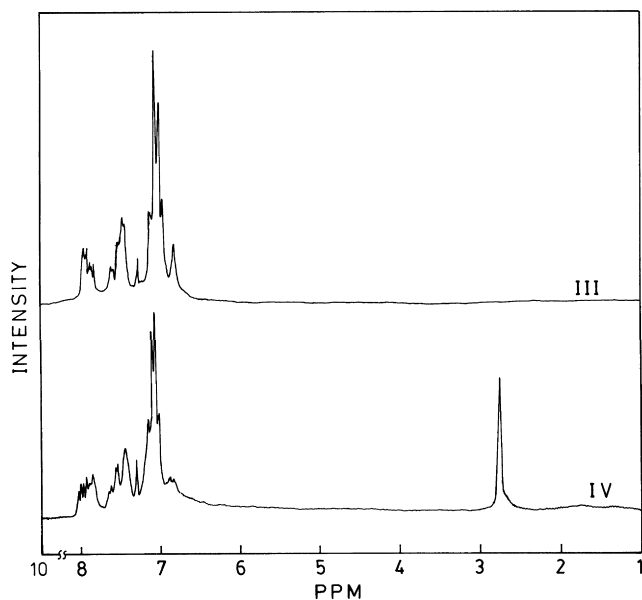
Table 3 Characterization of polyphosphonates

Polymer code	Elemental analysis found (calcd) (%)				IR(cm^{-1})			
	C	H	N	P	$\gamma_{C=O}$	$\gamma_{P=O}$	γ_{P-Ph}	γ_{P-O-C}
III	73.47	4.02	2.56	5.82	1710	1268	1435	1200
	(74.56)	(4.27)	(2.71)	(6.01)				
IV	69.95	4.36	3.01	6.59	1712	1267	1435	1202
	(71.52)	(4.41)	(3.09)	6.84				

Table 4 Thermal behavior of polyphosphonates

Polymer code	Temperature (°C) corresponding to		Peak temp.(°C) for decomposition[a]	Char residue[b] (%)
	10% wt.loss	50% wt. loss		
III	418	> 600	544	53
IV	408	600	528	50

[a] From DTA
[b] At 600°C in air

Figure 5 ^{1}H-n.m.r. spectra of polyphosphonates
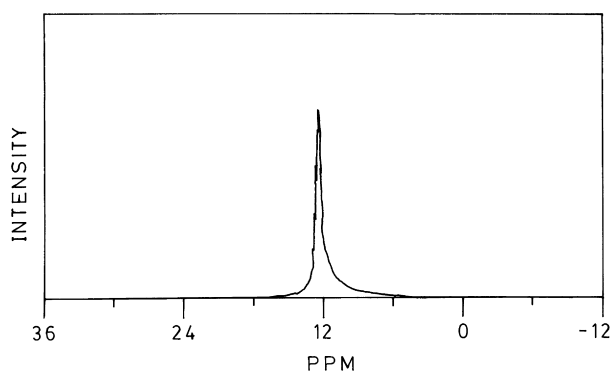
Figure 6 ^{31}P-n.m.r. spectrum of polymer III

sharp singlet at 2.7 ppm due to $-CH_3$ protons present in the polymer structure. Further, polymers III and IV were characterized by a peak at 12 ppm in the ^{31}P n.m.r. spectrum (*Figure 6*). The ^{31}P n.m.r. spectrum of dichlorophenyl-phosphine oxide [PhP(O)Cl$_2$] shows peaks at 33.7–34.5 ppm [12,13]. This shielding on the phosphorus atom is caused by the substitution of electronegative chlorine atoms by $-$OPh groups in the polymers. This shielding is comparable with [Ph P(O) (OPh)$_2$] in which the chemical shift in the ^{31}P n.m.r. spectrum appears at 11.8 ppm [13].

Thermal behavior of polyphosphonates

Thermal properties of the polymers were investigated by t.g.a. and DTA. The thermal and thermo-oxidative stabilities of polymers III–IV were evaluated by t.g.a. and DTA in air (*Figure 7*). The polymers start to loose weight above 350°C. The 10% and 50% weight loss temperatures are listed in *Table 4*. The char residues of these polymers in air at 600°C are about 50% (*Table 4*). Differential thermal analysis (DTA) curves exhibit discontinuous shift of the base line. Onset of the oxidative degradation of polymers III and IV begins at 377°C and 417°C, respectively, and sharp exotherms are observed at 544°C and 528°C, respectively. The values for weight loss and decomposition temperature are comparable to other reported polyphos-phanates[14]. The higher thermal stability of polymer III may be due to the presence of a phenyl ring as well as a lactum ring.

Flame-retardant behavior

Both polyphosphonates III and IV are well characterized by self-extinguishing behavior in a similar way to other phosphorus-containing polymers[15]. Polymers III and IV have LOI values of [(01)$_m$] 40 and 38, respectively. The lower value of polymer IV is due to the presence of aliphatic methyl group which readily converts into volatile products. The L0I values are comparable to those of other polyphos-sphonates[16,17]. These polyphosphonates can be directly used as fire-retardant polymers or as additive for other polymers, as reported earlier, used for diene rubbers[18].

Both these polymers have a high aromatic content and this leads to the formation of higher crosslinking during
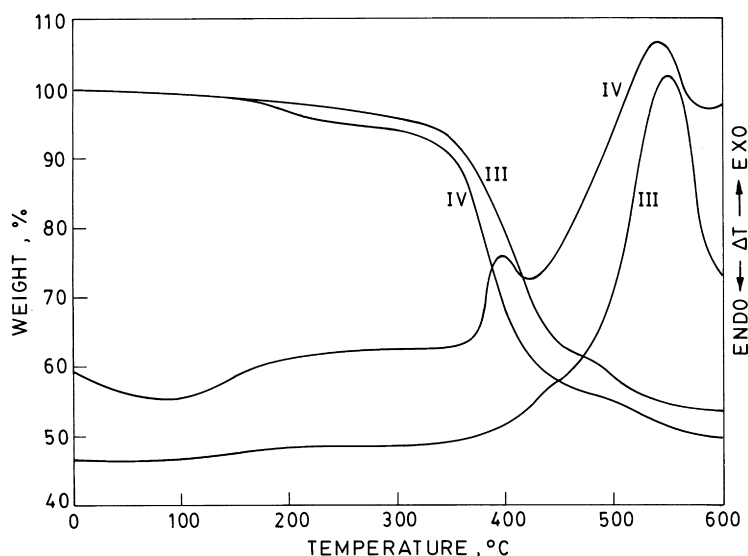
Figure 7 TGA and d.t.a. thermograms of polyphosphonates

pyrolysis. This factor and the presence of phosphorus lead to the formation of a higher char yield at 600°C.

CONCLUSION

Two cardo polyphosphonates were designed and synthesized by interfacial polycondensation in the presence of CTMAC as phase transfer catalyst. The structures of these polymers were confirmed by i.r. and n.m.r. spectroscopy as well as by elemental analyses. Both polymers are fairly soluble in chlorinated hydrocarbon and polar solvents. The high thermal stability and good flame retardancy of these polymers are expected to become candidate flame-retardant polymers.

ACKNOWLEDGEMENTS

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