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Phosphorus Containing Polymers.
Part 5. Polyazoxyphosphonate

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Abstract: A new polyazoxyphosphonate was synthesized by reaction of 4-4′-dihydroxyazoxybenzene and dichlorophenyl phospine oxide by interfacial polycondensation using a phase transfer catalyst. The polymer was characterized and the results obtained by various analytical techniques indicate that it is mostly amorphous, low molecular weight and soluble in organic solvents such as DMF, DMAC, NMP, etc. The high char residue (~ 40%) and limiting oxygen index indicate flame retardancy of the polymer which is due to phosphorus. Thermal stability of this polymer is moderate. The T_g appears to be at 152 °C.

Key words: Polyazoxyphosphonate – XPS – L01 – ^{31}P-NMR – Flame retardancy

Introduction

Polyphosphonates have been of commercial interest because of their flame retardant characteristics [1]. Polyphosphonates are mainly prepared by addition [2, 3] and condensation polymerization methods. The condensation polymerization involves mainly the reaction of dichlorophosphine oxides and diols by melt [4, 5], interfacial [6–10] and solution [11] polymerization techniques. It is observed that polyphosphonates from aliphatic dichlorophosphine oxides and aliphatic diols are low melting and hydrophillic [12]. Therefore, industrial interest has been concentrated on the aromatic polyphosphonates for their good thermal stability, high glass transition temperature and flame retardancy [10, 11].

We have reported on a few phosphorus containing polymers such as polyphosphonates and polyphosphoanhydrides [13–15]. In order to prepare polyphosphonates having the T_g and better thermal stability, we planned to incorporate the rigid azoxy linkages in the main chain of aromatic polyphosphonates.

This paper reports our investigation on the synthesis of a new polyazoxyphosphonate, its characterization and study of thermal and fire retardancy behavior.

Experimental

Materials

Cetyltrimethyl ammonium chloride (CTMAC) (Fluka) and benzyltriethylammonium chloride (BTEAC) (Aldrich) were used as received. Dichlorophenylphosphine oxide (Fluka) was purified by vacuum distillation prior to use. The other chemicals were purified by standard methods [16].

Synthesis of 4,4′-dihydroxyazoxybenzene

This was prepared by reducing *p*-nitrophenol with glucose in alkaline medium as follows [17]: To a stirred solution of 16.96 g (0.122 mol)

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p-nitrophenol in 150 ml methanol, 25 g (0.625 mol) NaOH in 40 ml water were added. The mixture was heated to 60–70 °C and 21.9 g (0.122 mol) of glucose were added in small portions as a paste (25 ml water) in 1 h. The solution was stirred for another 3 h and then the volume of the solution was reduced to half by distilling off the methanol. The hot solution was quickly filtered and, after cooling in an ice-bath, it was neutralized by conc. HCl to maintain pH at 7. A brownish yellow product was separated from the solution. It was filtered, washed with cold water, and purified by recrystallization from aqueous methanol. A reddish-yellow needle-shaped solid was obtained; yield: 60%, mp. 222 °C-dec (lit. [18] 224 °C-dec).

Synthesis of polyazoxyphosphonate

The polyazoxyphosphonate was synthesized by reacting dihydroxyazoxybenzene with dichlorophenyl phosphine oxide as follows:

In a flask fitted with a stirrer 1.15 g (5 mmol) dihydroxyazoxybenzene were mixed with 10.1 ml of 1 M aqueous potassium hydroxide. To the mixture 0.320 g (1 mmol) CTMAC was added. The solution was stirred and cooled to – 6 °C. Next, a solution of 0.975 g (5 mmol) dichlorophenyl phosphine oxide in 5 ml dichloromethane was added dropwise over 5 min period with vigorous stirring. The mixture was stirred at – 3 °C for 2 h. The supernatent aqueous layer was decanted and washed successively with water and acetone. The solution was diluted by 20 ml dichloromethane and the polymer was precipitated by pouring the solution into 250 ml hexane. The product was collected and dried at 50 °C in vacuum.

Measurements

Inherent viscosity of polymer solutions (0.5% w/v) in DMF was determined at 30 °C using a ubbelohde suspended level viscometer. Molecular weight was determined by end-group analysis of 5% polymer solution in HMPA using 0.02 N methanolic KOH as titrant in the presence of phenolphthalein indicator. Carbon, hydrogen and nitrogen of the polymer sample were analyzed by a Heraeus Carlo Erba 1108 elemental analyzer. Element phosphorus was analyzed by the Schöniger combustion flask method [19]. The IR spectrum was recorded with a Perkin Elmer model 837 spectrophotometer with a KBr disc. The ^{1}H-NMR spectrum was recorded with a variun EM 390 spectrometer in DMSO-d_6 using TMS as internal standard. The ^{31}P-NMR spectrum was recorded with Bruker 270 MHz FT-NMR spectrometer using $CDCl_3$ as solvent. Photoelectron spectra (XPS or ESCA) was recorded with ESCALAB MK II (V.G. Scientific), spectrometer using Al target at 12 KV–10 mA and pass energy of 40 eV. X-ray diffractogram was obtained with a Philips, PW 1729 diffractometer using Ni filtered CuK$_\alpha$ radiation.

TGA of the polymer was carried out with a Shimazdu DT 40 instrument in air and nitrogen at a heating rate of 10 °C/min. TMA of the polymer was made with a Shimazdu TMC-30 at a heating rate of 10°/min in air. LOI of the polymer was measured using a modified method [20].

Results and Discussion

Monomer synthesis and characterization

Dihydroxy azoxybenzene was synthesized by reducing *p*-nitrophenol with glucose in alkaline medium [2, 5]. The reaction may be represented as shown in Fig.1.

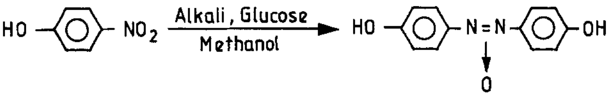
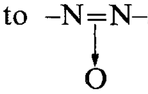


Fig. 1. Reaction scheme for synthesis of dihydroxyazooxybenzene

Dihydroxy azoxybenzene was characterized by IR, elemental analysis, and by melting point determination. The compound starts to decompose at 222 °C (literature value 222 °C-dec.) [18]. The IR spectrum (not shown) shows intense bands at 1600, 1230 cm^{-1} assigned to  $-\underset{\overset{\downarrow}{O}}{N{=}N}-$streching [4]. The result of elemental analysis is as follows: C, calcd. 62.60%, found 62.80%; N, calcd. 12.17% found 12.52%; H, calcd. 4.34%, found 4.15%.

Polymer synthesis and characterization

Polyazoxyphosphonate was synthesized according to the following scheme (Fig. 2):

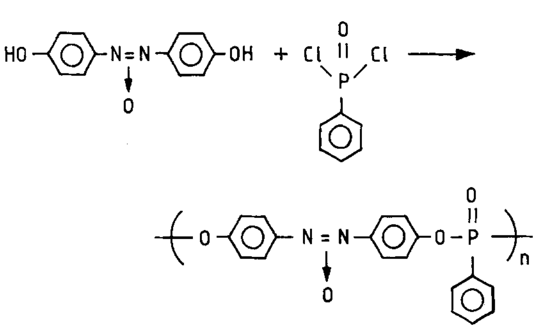


Fig. 2. Reaction scheme for synthesis of polyazoxyphosphonate

Imai et al. [21] have reported that the phase transfer catalyzed polycondensation is useful for preparation of high molecular weight aromatic polyphosphonates. Therefore, this method was applied to the polycondensation of dichlorophenylphosphine oxide with 4,4′-dihydroxyazoxybenzene to obtain a novel polyphosphonate. The polymer was synthesized with or without any PTC. It has been observed that the use of PTC increases the yield and inherent viscosity of the polymer solution; CTMAC is more effective as a PTC than BTEAC. The same phenomenon has also been reported by Imai et al. [10] in the synthesis of polyphosphonates. The results of polymer synthesis and characterization are summarized in Table 1. The polymer is soluble in polar organic solvents like DMF, DMSO, NMP, DMAC and halogenated solvents like dichloromethane, dichloroethane, chloroform, etc., but not soluble in chlorobenzene or other non-polar or less polar organic solvents.

Elemental analysis of the polymer was done by chemical analysis and also by the ESCA peak area calculation. The results of both the analysis agree well with the theoretical values. Elemental analysis agree well with the theoretical values. Elemental analysis from the XPS peak area calculation is a novel technique which also confirms the presence of carbon $(C \rightarrow I_{S_{1/2}})$; nitrogen $(N \rightarrow I_{S_{1/2}})$; phosphorus $(P \rightarrow 2_{P_{1/2}})$; and oxygen $(O \rightarrow I_{S_{1/2}})$; in the polymer by showing sharp peaks corresponding to their binding energies at 290, 405, 135 and 535 eV respectively [25].

The characteristic IR bands of the polymer at 1480 cm^{-1} assigned to $-\underset{\overset{\downarrow}{O}}{N}=N-$ [16, 22], intense band at 1280 cm^{-1} assigned to $P=O$ [23, 24], bands at 1425 cm^{-1} and 1020 cm^{-1} assigned to $P\text{–}C_6H_5$ [23, 24], and band at 1140 cm^{-1} attributed to P–O–C [23, 24] confirm the structure of the polymer. The presence of a multiplet in the region of 6.2–8.1 ppm may be assigned to the aromatic protons. No peak due to –OH protons is present in the NMR spectrum of the polymer.

The ^{31}P-NMR spectrum of the polymer is shown in Fig. 3. A number of peaks in the region of 4 to 15.5 ppm is observed.

Recently, Kim reported [11] the ^{31}P-NMR peaks of polyphosphonates as singlet at 12.3 and 12.7 ppm. The sharp singlet at 12.5 ppm may be due to the polyphosphonate. The x-ray diffractogram of the polymer (not shown) shows that the polymer is mostly amorphous, although

Table 1. Polymer synthesis and characterization

	Without PTC		BTEAC		CTMAC			Elemental anal.			IR (cm^{-1})			
Color	Yield (%)	η_{inh} [a]) (dl/g)	Yield (%)	η_{inh} [a]) (dl/g)	Yield (%)	η_{inh} [a]) (dl/g)	$\bar{M}_n$ [b])	Found	Calcd.	From XPS	$-\underset{\overset{\downarrow}{O}}{N}=N-$	$P=O$	P–Ph	P–O–C
Dark brown	86	0.07	88	0.19	94	0.29	5,280	C:61.89	61.36	61.36	1480	1270	1420	1140
								H: 3.21	3.69	–				
								N: 7.83	7.95	7.67				
								P: 9.02	8.80	9.20				
								O:18.05	18.18	19.17				

[a]) Measured in DMF solution (0.5g/dl) at 30° C

[b]) By end-group analysis

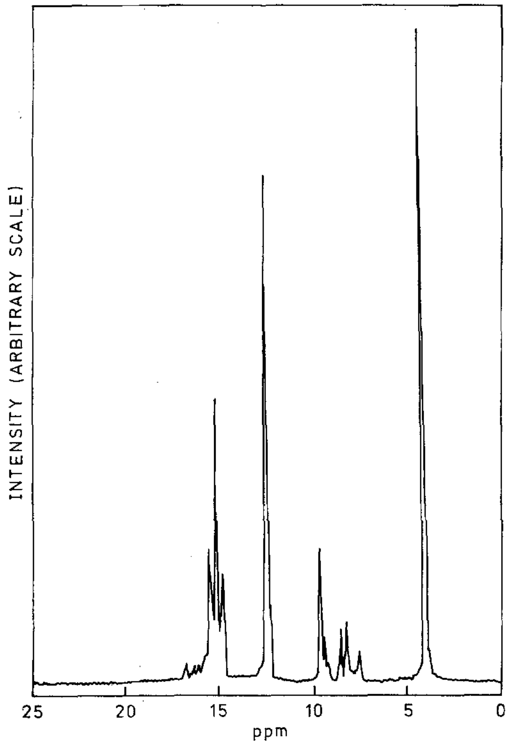


Fig. 3. ^{31}P-NMR spectrum of polyazoxyphosphonate

non-phosphorus polymers containing azoxybis (1,4-phenylene) unit are reported to be fairly crystalline [17].

Thermal and flame retardancy behavior

TGA thermogram of the polymer (Fig.4) shows that the polymer starts to lose weight around 250 °C in air and 275 °C in nitrogen, and char residues in nitrogen at 600°C and in air at 700 °C were 47% and 40%, respectively. The higher char residue of this polymer compared to that of previously reported polyphosphonates [10, 11] is probably due to the presence of nitrogen and phosphorus in the same macrochain. Nitrogen appears to have a somewhat synergistic effect on the fire retardancy of phosphorus.

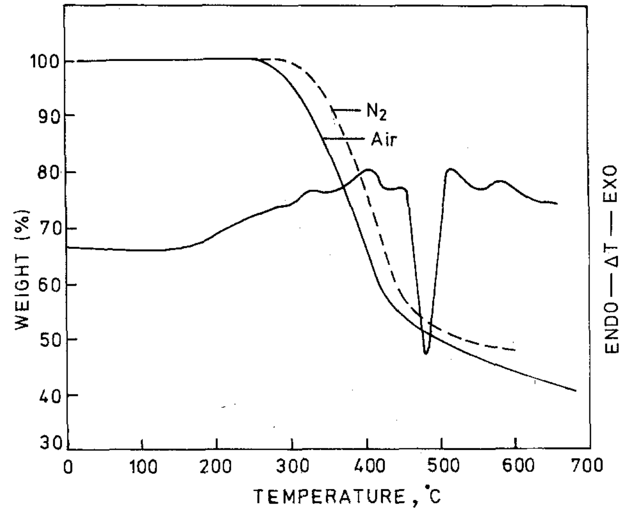


Fig. 4. TGA and DTA curves of polyazoxyphosphonate

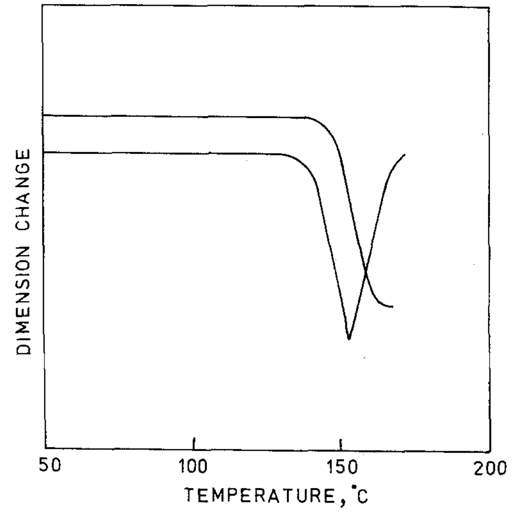


Fig. 5. TMA curve of polyazoxyphosphonate

TMA curve and derivative TMA curve (Fig.5) show a sharp peak at 152 °C which is due to the glass transition temperature of the polymer. The fire retardancy of the polymer was investigated by measuring the oxygen index of the polymer using a modified technique [20]. It has been observed that the polymer is self-extinguishing like other phosphorus containing polymers [14]. It shows modified oxygen index $(\mathrm{OI})_m$ value ~ 51. The high value of $(\mathrm{OI})_m$ is due to the high percentage of phosphorus (8.80%) in the polymer chain compared to other phosphorus polymers reported earlier [25–27-]. These low molecular weight polymers have been recently used as polymeric flame retardant additives to diene rubbers such as natural rubber, SBR, nitrile rubber and chloroprene rubber [28].

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