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Synthesis of fluorine-containing polyphosphonates: low temperature solution polycondensation of bisphenol AF and phenylphosphonic dichloride

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This paper describes the synthesis of polyphosphonates from the reaction of phenylphosphonic dichloride (PPD) with bisphenol AF (BPAF) and its derivatives in a chlorinated hydrocarbon solvent under low temperature conditions. The polyphosphonates obtained were characterized by i.r., inherent viscosity, differential scanning calorimetry, thermogravimetric analysis, X-ray diffraction and molar mass. The polyphosphonate obtained from BPAF has a larger inherent viscosity by 0.50 dl g^{-1} and a higher glass transition temperature than those derivatives which contain flexible oxyethylene units or bromine atoms. Polyphosphonate derived from BPAF begins to lose 10% of its mass at 415°C and the mass percentage remaining at 700°C is 20.3% under nitrogen. The X-ray diffraction patterns revealed that almost all the polymers were amorphous, except for one polymer which was semicrystalline. The PPD/BPAF and PPD/3,3′,5,5′-tetrabromo bisphenol AF polymers have good flame retardancy, as indicated by high limiting oxygen index values of 43 and 65, respectively. The contact angles of PPD/BPAF polymer formed by water, glycerine and ethylene glycol were larger than those of other polyphosphonates which contain flexible oxyethylene units or bromine atoms.

(Keywords: bisphenol AF; polyphosphonate; solution polycondensation)

INTRODUCTION

Polyphosphonates and polyphosphates are of commercial interest because of their flame-retarding characteristics[1] and potential as high-performance plastics[2]. Several researchers have published results on the synthesis of polyphosphonates by interfacial polycondensation[3-6], by melt[7,8], by high-temperature solution polymerization[9], or by the phase-transfer-catalysed method[10-12].

The low-temperature solution polycondensation process has been widely used to prepare polymers such as polyesters and polycarbonates[13]. However, published results for polyphosphonates using this technique are relatively scarce. Kim[14] studied the low-temperature polycondensation of phosphonic dichloride with 4,4′-thiodiphenol and 4,4′-sulfonyl diphenol (SDP). Natansohn[15] reported that an aryl polyphosphonate with an inherent viscosity of 0.08 dl g^{-1} was synthesized from the reaction of chloromethyl phosphonic dichloride with SDP.

In previous studies[16], we reported the synthesis of aromatic polyphosphate by low-temperature solution polycondensation of SDP with phenoxy dichlorophosphate. Methylene chloride and chloroform are the best polymerization solvents and triethylamine is the best acid acceptor. Considerable attention has been devoted to the preparation of fluorine-containing condensation polymers because of their unique properties and high performance[17]. This paper describes the low-temperature solution polycondensation of phenylphosphonic dichloride with bisphenol AF and its derivatives. The effects of a flexible ether linkage and bromine atom on the inherent viscosity, thermal behaviour and flame-retardant characteristics are discussed.

EXPERIMENTAL

Reagents

2,2-Bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF; supplied by Central Glass Co., Ltd) was recrystallized from benzene; m.p. 162–163°C (lit.[18] 163–165°C). Phenylphosphonic dichloride was obtained commercially and purified by vacuum distillation; b.p. 136°C/23 torr (lit.[11] 143°C/25 torr) (1 torr = 133.3 Pa). Ethylene carbonate and bromine were supplied by Janssen Chimica. The solvents were purified by standard methods.

Preparation of monomers

Bis[4-β-hydroxyethoxy phenyl] hexafluoropropane (HEPAF). The procedure for synthesis of HEPAF is

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*To whom correspondence should be addressed similar to that for bis[4-β-hydroxyethoxy)phenyl]sulfone, described previously[19,20]. A 500 ml round-bottomed flask, equipped with a reflux condenser, stirrer, thermometer and nitrogen inlet, was charged with bisphenol AF (33.6 g, 0.1 mol), ethylene carbonate (17.6 g, 0.2 mol), and sodium carbonate (0.1 g) was used as a catalyst. The mixture was heated to 175–180°C under nitrogen for 2 h. The crude product was washed with water several times to remove unreacted ethylene carbonate. A yellowish, viscous liquid was obtained. The yield was about 82%. The reaction takes place according to *Scheme 1*.

3,3′,5,5′-Tetrabromo bisphenol AF (TBPAF). A round-bottomed flask (1 l) equipped with a dropping funnel was charged with bisphenol AF (33.6 g, 0.1 mol) and distilled water (500 ml). While the suspension mixture was heated from 30 to 80°C, bromine (65 g, 0.41 mol) was added to the reaction flask through the dropping funnel over a period of 40 min. The flask was maintained at about 80°C for 4 h. After the reaction was completed, the crude product was washed with aqueous sodium sulfite solution and distilled water to remove residual hydrogen bromide.

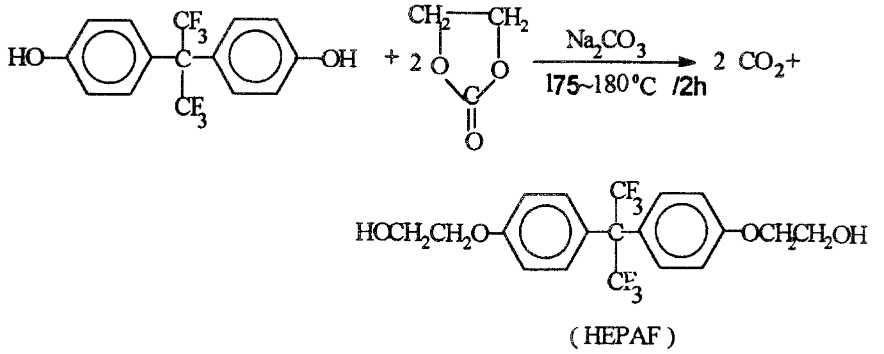
The final product was dried *in vacuo* at 60°C for 24 h. A white powder of m.p. 256°C was obtained. The yield was over 94%. The reaction takes place according to *Scheme 2*.

*Bishydroxyethyl ether of TBPAF (HEETBPAF).*The procedure for the synthesis of HEETBPAF is similar to that of HEPAF as described above. A round-bottomed flask was charged with TBPAF (65.2 g, 0.1 mol), ethylene carbonate (17.9 g, 0.2 mol), and sodium hydroxide (0.12 g) was used as a catalyst. The mixture was heated to 210–220°C under nitrogen for 4 h. Upon completion of the reaction, the brown product was washed with distilled water several times to remove unreacted ethylene carbonate, and recrystallized with methanol. The final product was dried *in vacuo* at 60°C for 24 h. A white powder of m.p. 117–119°C and a yield of 81% was obtained. The reaction occurs according to *Scheme 3*. In contrast to the above procedure, if bisphenol AF had been incorporated into the oxyethylene unit by addition of ethylene carbonate prior to bromination, the brominated HEPAF compound would have only approximately 2.5 bromine atoms added to the benzene rings, as deduced from calculation of elemental analysis. This fact could be explained by bromination being relatively difficult owing to steric effects of the oxyethylene unit at the *para*-position of the benzene ring.

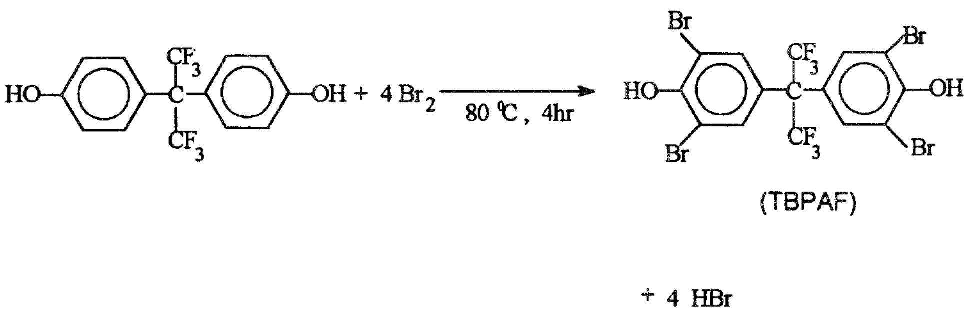
Polymerization

A typical polymerization procedure is as follows. A flask equipped with a paddle stirrer, addition funnel and reflux condenser was charged with bisphenol AF (BPAF) (6.72 g, 20 mmol), 60 ml of methylene chloride, and 4.44 g (44 mmol) of triethylamine, and subjected to vigorous stirring at 0°C. Then a solution of 3.9 g (20 mmol) of phenylphosphonic dichloride (PPD) and 10 ml of methylene chloride was slowly added to the flask (~1 h). During the addition, an exothermic reaction occurred. After the whole quantity was added, the reaction mixture was allowed to warm to room temperature and was subsequently refluxed for 4 h. *Scheme 4* illustrates the synthesis and corresponding reactions.

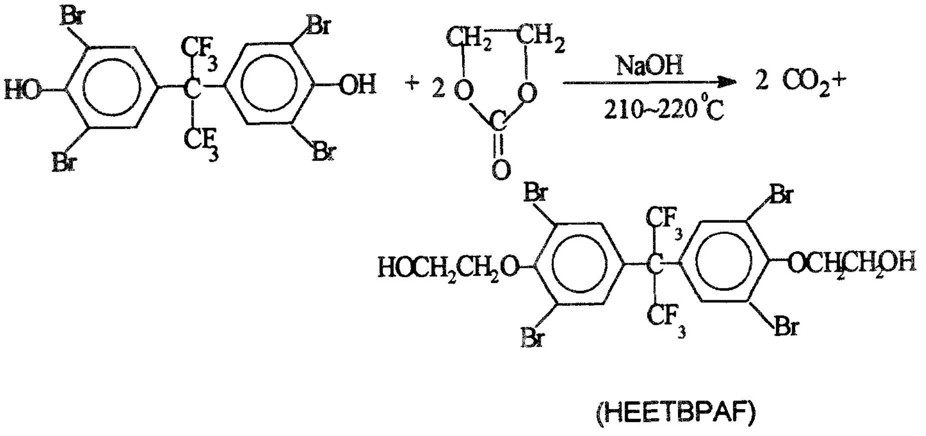
The polymer solution was washed with diluted HCl (1%) and distilled water until the aqueous phase was



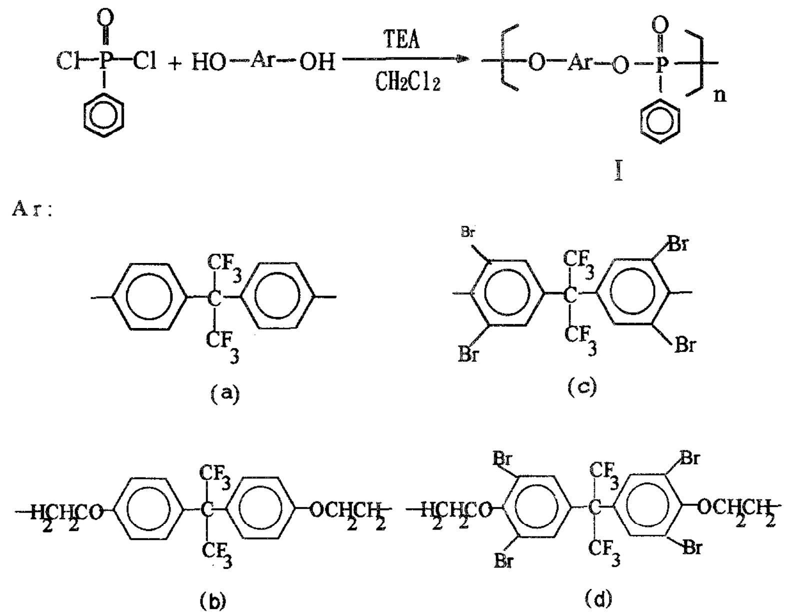
Scheme 1



Scheme 2



Scheme 3



Scheme 4 Synthesis of fluorine-containing polyphosphonates

neutral to litmus paper. The solution was filtered and the polymer precipitated with methanol. The white polymer was dried *in vacuo* at 60°C for 24 h. The yield was determined at 95% (8.70 g).

Elemental analysis of $[C_{21}H_{13}F_6O_3P]_n$. Calculated: C 55.02; H 2.84%. Found: C 54.64; H 3.03%.

Characterization

The inherent viscosity of polymer **Ia** at a concentration of $0.1\,g\,dl^{-1}$ in 1,2-dichloroethane was $0.50\,dl\,g^{-1}$ at 25°C. The glass transition temperature (T_g) was measured with a DuPont 9000 differential scanning calorimeter at a heating rate of $10°C\,min^{-1}$, under a nitrogen atmosphere. Number-average molar mass ($\bar{M}_n$) was determined by gel permeation chromatography (g.p.c.). Four Waters (Ultrastyragel) columns $300 \times 7.7\,mm$ ($10^2, 10^3, 10^4, 10^5$ Å in series) were used for g.p.c. analysis with tetrahydrofuran (THF) ($1\,ml\,min^{-1}$) as the mobile phase. The eluents were monitored with a Gilson model 116 using a 254 nm UV detector. Polystyrene was used as standard. The weight-average molar mass ($\bar{M}_w$) was determined by light scattering using an Otsuka DLS-7000 photometer. X-ray diffraction was recorded by the powder method (Philips X-ray diffractometer, model PW 1710). A standard procedure (JIS K-7201) was used to measure the limiting oxygen index (LOI). Contact angles of polymers **Ia**–**Id** were measured with a contact-angle meter (Kernco, GIII). Static contact angles were measured at 25°C and 65% relative humidity by the sessile drop of a volume of $2\,\mu l$. The contact angle was read 1 min after application of the droplet. Nine measurements at various positions on the surface were averaged. Deionized water, glycerine and ethylene glycol were used for the measurements. ^{31}P nuclear magnetic resonance (n.m.r.) spectra were taken on a Bruker AM-300 WB.

RESULTS AND DISCUSSION

The polymers obtained from condensation of PPD with BPAF derivatives were insoluble in aliphatic hydrocarbons and alcoholic solvents but soluble in

Table 1 Characterization of several polyphosphonates

Polymer	Yield (%)	η_{inh}[a] (dl g^{-1})	$\bar{M}_n \times 10^4$[b]	I.r. characteristic group (cm^{-1}) P=O	P–O–C	Ph	T_g[d] (°C)	T_m[d] (°C)
Ia	95	0.50[c]	1.39	1300	1171,963	3054,1601,1436,740	117	–
Ib	86	0.11	0.28	1297	1179,964	3060,1589,1496,750	40	205
Ic	95	0.14	0.30	1300	1180,965	3060,1543,1453,767	97	–
Id	85	0.10	0.26	1300	1178,965	3060,1591,1496,738	20	118

[a] Solution (0.1 g dl^{-1}) of 1,2-dichloroethane at 25°C
[b] Measured by g.p.c. in THF, polystyrene was used as standard
[c] The weight average molar mass ($\bar{M}_w$) was determined to be 58 000 by light scattering in $CHCl_3$
[d] Determined by d.s.c. at a heating rate of 10°C min^{-1}

Table 2 Effect of acid acceptor on the preparation of PPD/BPAF polymer

Acid acceptor	pK_b[a]	Yield (%)	η_{inh}[b] (dl g^{-1})	$\bar{M}_w$[c]
Triethylamine	3.1	95	0.50	58 000
Tri-n-butylamine	3.1	60	0.25	21 000
Pyridine	7.8	0	–	
Dimethyl aniline	8.0	0	–	

[a] Data from ref. 27
[b] Solution (0.1 g dl^{-1}) of 1,2-dichloroethane at 25°C
[c] Measured by light scattering in chloroform

chlorinated aliphatic hydrocarbons such as CH_2Cl_2 and $CHCl_3$, and aprotic solvents such as dimethylsulfoxide (DMSO) and dimethylformamide (DMF). In the previous paper[16], we reported that chlorinated aliphatic hydrocarbons, such as methylene chloride or chloroform, are the best polymerization solvents in low-temperature solution polycondensation of SDP with phenoxy dichlorophosphate. *Table 1* shows the i.r. spectral data, polymer yield, inherent viscosity and thermal properties of several polyphosphonates. The ^{1}H n.m.r. spectrum shows that there are two peaks at 7.99 and 7.19–7.29 ppm, which are attributed to the protons in the *ortho* and *meta* positions to the hexafluoropropane group resonance, respectively[15]. The resonance of the phenyl group falls in the range 7.53–7.64 ppm. The inherent viscosities of all polymers were in the range 0.50–0.10 dl g^{-1}. A diol such as BPAF (**a**) has a moderate inherent viscosity. Saegusa *et al.*[18] reported that the viscosity values of the copolycarbonates became markedly lower with increasing feed ratio of BPAF to bisphenol A. They explained that this result was probably due to the lower nucleophilicity of BPAF, induced by strongly electron-withdrawing trifluoromethyl groups at the *para* position, than of bisphenol A[18]. Diol **b** incorporated an aliphatic oxyethylene unit which forms an alcoholate anion with difficulty[21]. A diol such as **c** gave a less favourable result. This phenomenon may have resulted from the electron-withdrawing characteristic of the bromine atom, which may decrease the nucleophilicity of the phenols. Diol **d** had the electron-withdrawing characteristic of the bromine atom and also incorporated an aliphatic oxyethylene unit, causing the most unfavourable result for inherent viscosity.

The melting temperature (T_m) and glass transition temperature (T_g) measured by d.s.c. are also shown in *Table 1*. The fluorine-containing polyphosphonates had T_gs between 20 and 117°C, and T_ms between 118 and 205°C. Polymers **Ib** and **Id**, having flexible ether linkages, which increase free volume, had lower T_gs[16]. On the other hand, the decrease in T_g of polymers **Ic** and **Id** may be explained by an increase of free volume caused by bromine substitution[22]. Similar behaviour has been observed for other halogenated polyesters[23], polyamides[24] and polyarylcarboxylates[22].

Table 2 shows the effect of acid acceptor on the viscosity of PPD/BPAF polyphosphonate. It indicates that the condensation system requires a moderately strong base such as triethylamine or tri-n-butylamine as an acid acceptor. The PPD reaction did not proceed in the presence of weaker bases such as pyridine or *N,N*-dimethylaniline. This phenomenon has been reported previously by Kim[14] for the polycondensation of PPD with 4,4′-thiodiphenol, and by Liaw and Shen[16] for phenoxy dichlorophosphate with SDP. A ^{31}P n.m.r. spectrum of the polycondensation products also confirms the formation of phosphonate (a singlet at 12.7 ppm for the PPD/BPAF polymer in DMSO-d_6, reference H_3PO_4). Results from elemental analysis (see above) are in agreement with the proposed polyphosphonate structure.

Table 3 Data of t.g.a., LOI and surface properties of polyphosphonates

Polymer	$T_d^{10\%}$[a] (°C)	$T_d^{20\%}$[a] (°C)	$T_d^{50\%}$[a] (°C)	Mass remaining[a] at 700°C (%)	LOI[b]	P(%)	BR(%)	θ_w[c]	θ_g[d]	θ_e[e]
Ia	415	460	482	20.3	43	6.76	0	103	110	69
Ib	273	296	366	13.5	30	5.67	0	91	82	52
Ic	300	317	350	10.5	65	4.00	41.3	95	80	48
Id	227	256	306	11.2	44	3.59	37.1	87	68	37

[a] T.g.a. conducted at a heating rate 10°C min^{-1} in nitrogen
[b] Limiting oxygen index
[c] Contact angle by water was measured at 25°C in air
[d] Contact angle by glycerine was measured at 15°C in air
[e] Contact angle by ethylene glycol was measured at 25°C in air

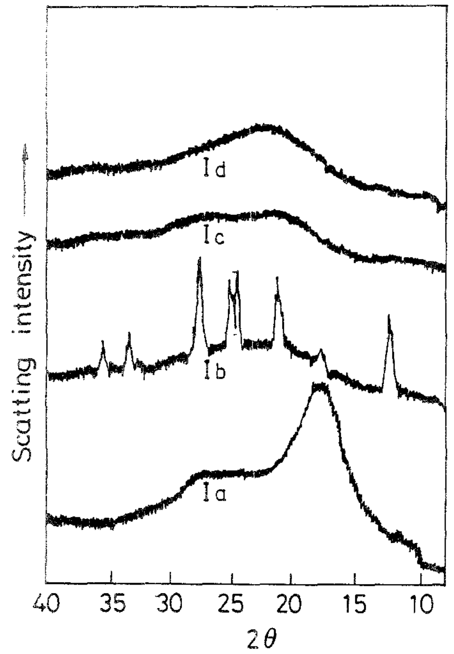


Figure 1 X-ray diffraction patterns of polyphosphonates **Ia**–**Id**

Thermogravimetric analysis (t.g.a.) data, LOI and surface properties of the polyphosphonates are shown in *Table 3*. The PPD/BPAF polymer (polymer **Ia**) begins to lose mass at about 320°C under nitrogen and a 10% mass loss was measured at approximately 415°C. The mass percentage remaining at 700°C is 20.3% under nitrogen. It is observed from *Table 3* that polymers **Ic** and **Id**, containing a bromine atom, had lower temperatures of thermal degradation. This may be explained by the fact that hydrogen bromide is easily evolved for the bromine-containing polymers during the thermal degradation process[25]. In addition, polymers **Ib** and **Id** had lower degradation temperatures. This may be attributed to the flexible ether linkage of the polymers.

The flame resistance of the polymers was measured by the LOI values. As shown in *Table 3*, the PPD/BPAF polymer containing 6.76% phosphorus has LOI = 43. Furthermore, PPD/TBPAF containing 41.3% bromine has the largest value (LOI = 65). It is not surprising that the LOI value of **Ia** is larger than that of **Ib** (and LOI of **Ic** > LOI of **Id**). This could be explained in terms of the higher contents of phosphorus in the former and bromines in the latter. The hydrophilic data of the polyphosphonate films by water, glycerine and ethylene glycol are also compiled in *Table 3*. The contact angles (θ_w, θ_g and θ_e) of PPD/BPAF polymer formed by water, glycerine and ethylene glycol were larger than those of other polyphosphonates which contain flexible oxyethylene units or bromine atoms.

X-ray diffraction patterns of various polyphosphonates are shown in *Figure 1* in terms of intensity *versus* 2θ where θ is the angle of diffraction (Bragg angle). It is observed that a polyphosphonate containing a flexible ether linkage (polymer **Ib**) has a relatively large degree of crystallinity (semicrystalline)[21]. However, polyphosphonates containing a bromine atom (polymers **Ic** and **Id**), which has a larger van der Waals radius to disturb the molecular arrangement, had an amorphous structure[18,26]. In general, the solubility decreased with increasing crystallinity[21].

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