

Preparation and Properties of Flame-Retardant Polyphosphate Esters: Low-Temperature Solution Polycondensation of 3,3',5,5'-Tetrabromobisphenol AF and Aryl Phosphorodichloridates

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ABSTRACT: This article describes the syntheses of aromatic polyphosphates from the reaction of various aryl phosphorodichloridates with 3,3',5,5'-tetrabromobisphenol AF (TBPAF) in a chlorinated hydrocarbon solvent under low-temperature conditions. The new polyphosphates obtained were characterized by infrared, ^{13}C and ^{31}P nuclear magnetic resonance spectra, elemental analysis, inherent viscosity, thermogravimetric analysis, differential scanning calorimetry, X-ray diffraction, limiting oxygen index, contact angle, and molar mass measurement. All of the polyphosphates obtained had high yields, and the inherent viscosities were in the range $0.12\text{--}0.15\text{ dL g}^{-1}$. All of the polymers start degrading between 210 and 267°C and had 14–26% residual mass at 700°C in nitrogen. Polymer E, having a methoxy group in the side chain phenyl ring, showed better thermal stability than the other polymers. The X-ray diffraction patterns revealed that all of the polyphosphates were amorphous. These polyphosphates had glass transition temperatures between 140 and 154°C. Polymers obtained from TBPAF had excellent flame retardancy, as indicated by high limiting oxygen index values in the range of 63–68. The water contact angles (θ_w) of all of the polyphosphates were in the range of 74–87°. The contact angles of polymers A and B were larger than those of other polyphosphates that contain more oxygen (polymers C and E) or bromine atoms (polymer D). © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 59–65, 1997

Key words: 3,3',5,5'-tetrabromobisphenol AF; LOI; thermal stability; flame retardancy; low-temperature solution polycondensation

INTRODUCTION

Polyphosphonates and polyphosphates are of commercial interest because of their flame-retarding characteristics¹ and their potential as high-performance plastics.² The usual method of preparation of polyphosphates and polyphosphonates is based on the esterification of diols with equimolar amounts of dichlorophosphates and phosphonyl dichlorides, respectively. For polyphosphates, with aliphatic diols, polycondensation proceeds

faster than with bisphenols, but some side reactions are difficult to eliminate and lead to low-molecular-weight product formation.^{3–5} Several researchers have published results on the synthesis of polyphosphonates by interfacial polycondensation,^{6–9} by melt,^{10,11} by high-temperature solution polymerization,¹² or by a phase-transfer-catalyzed method.^{13–15} For example, Massai et al.¹² investigated the high-temperature solution copolymerization of phenylphosphonic dichloride (PPD) with 4,4'-sulfonyldiphenol (SDP) in tetrachloroethane, using CaCl_2 as a catalyst. Kim¹⁶ studied the low-temperature polycondensation of PPD with 4,4'-thiodiphenol (TDP) and SDP. Na-

tansohn¹⁷ reported that an aryl polyphosphonate with an inherent viscosity of 0.08 dL g⁻¹ was synthesized from the reaction of chloromethylphosphonic dichloride with SDP.

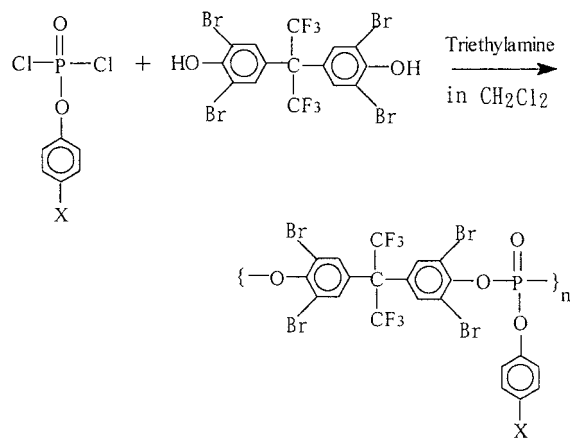
In previous studies, we reported the syntheses of aromatic polyphosphate¹⁸ and polyphosphonate^{19–21} by low-temperature solution polycondensation of phenoxy dichlorophosphate (PDCP) with SDP, PPD with 2,2'-bis(4-hydroxyphenyl)-hexafluoropropane (bisphenol AF, BPAF) and its derivatives, and various aryl phosphorodichlorides with BPAF. Methylene chloride and chloroform are the best polymerization solvents, and triethylamine is the best acid acceptor. Extending our previous research,^{18–21} we synthesized polyphosphates containing fluorine atoms, because fluorine atoms improve the solubility^{22–26} of polymers, enhance their high performance,²⁷ and increase their thermal stability.^{22–26} Organic bromides have long been recognized to be effective flame retardants for polymeric materials, and there are many data about them. Many patents describe the preparation of flame-proofed aromatic polyesters when introducing bromine into the polymer chain.^{28,29} A bisphenol of a popular type is 3,3',5,5'-tetrabromobisphenol A (TBBPA) and its homologues.^{24,30} In general, the incorporation of halogen substituents into the polymer chain leads to increased flame retardancy and decreased thermal stability.^{31,32} Thus, polymers containing bromine and fluorine atoms should be excellent candidates to improve flame retardancy while retaining good thermal stability.

This article describes the low-temperature solution polycondensation of various aryl phosphorodichloridates with 3,3',5,5'-tetrabromobisphenol AF (TBPAF). The effects of different substituents in the side chain phenyl ring of polymers on the surface properties, the degree of crystallinity, the thermal behavior, and the flame-retardant characteristics are discussed. The effects of bromine atoms of polymers on physical properties such as the contact angle, the glass transition temperature, and flame-retardant characteristics are also investigated.

EXPERIMENTAL

Reagents and Monomers

BPAF (supplied by Central Glass Co., Ltd.) was recrystallized from benzene (melting point, 162–163°C; lit.^{19,22} 163–165°C). The aryl phosphoro-



- A, X=H
 B, X=CH₃
 C, X=NO₂
 D, X=Br
 E, X=OCH₃

Scheme 1 Synthesis of fluorine-containing polyphosphates.

dichloridates were prepared by reacting POCl₃ with the corresponding phenols by the procedure reported earlier,^{18,20,33,34} while the TBPAF was prepared from BPAF and bromine using the method by Liaw et al.^{19,24} Bromine was supplied by Janssen Chimica. The solvents were purified by standard methods.

Polymerization

A typical polymerization procedure of polymer A is as follows. A flask equipped with a paddle stirrer, addition funnel, and reflux condenser was charged with TBPAF (13.04 g, 20 mmol), 60 mL of methylene chloride, and 4.44 g (44 mmol) of triethylamine and was subjected to vigorous stirring at 0°C. Then, a solution of 4.22 g (20 mmol) of PDCP 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 1 illustrates this synthesis and the corresponding reactions.

The polymer solution was washed with dilute HCl (1%) and distilled water until the aqueous phase was neutral to litmus paper. The white polymer was dried *in vacuo* at 150°C to constant weight. The yield was determined as 93% (14.62 g). The elemental analysis of [C₂₁H₉F₆O₄Br₄P]_n was as follows:

ANAL. Calcd: C, 31.89%; H, 1.14%. Found: C, 32.20%; H, 1.15%.

The other polymers (B–E) were prepared according to the same procedure (Scheme 1).

Characterization

Infrared spectra were measured in the range 4,000–400 cm^{-1} for the polymers in KBr disks (JASCO IR-700 Spectrometer). The inherent viscosities of the polymers were measured at a concentration of 0.1 g dL^{-1} in 1,2-dichloroethane at 30°C. Elemental analyses of the polymers were made (Perkin–Elmer 2400 instrument). Thermogravimetric analysis (TGA) was measured on an instrument (Du Pont 9900) at a heating rate of 10°C min^{-1} in nitrogen. The glass transition temperature (T_g) was measured with a Du Pont 9000 differential scanning calorimeter at a heating rate of 10°C min^{-1} , under a nitrogen atmosphere. The number average molar mass (\overline{M}_n) was determined by gel permeation chromatography (GPC). Four 300 \times 7.7 mm Waters (Ultrastayragel) columns (10^2 , 10^3 , 10^4 , and 10^5 Å in a series) were used for GPC analysis with tetrahydrofuran (1 mL min^{-1}) as the mobile phase. The eluents were monitored with an ultraviolet detector (Gilson model 116) at 254 nm. Polystyrene was used as the standard. The weight average molar mass (\overline{M}_w) was determined by light scattering with an Otsuka DLS-7000 photometer. An X-ray diffraction spectrum was recorded by the powder method (Philips X-ray diffractometer, model PW 1710). A standard procedure (ASTM D-2863-77) was used to measure the limiting oxygen index (LOI). Contact angles of polymers A–E 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 volume 2 μL . The contact angle was read 1 min after the

Table I Elemental Analysis of Polyphosphates

Polymer		C (%)	H (%)	N (%)
A	Calcd	31.89	1.14	—
	Found	32.20	1.15	—
B	Calcd	32.84	1.37	—
	Found	33.07	1.48	—
C	Calcd	30.18	0.96	1.68
	Found	30.41	1.08	1.70
D	Calcd	29.00	0.92	—
	Found	29.19	0.97	—
E	Calcd	32.20	1.34	—
	Found	32.75	1.38	—

application of the droplet. Nine measurements at various positions on the surface were averaged. Deionized water was used for the measurement. ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectra were taken on a Bruker AM-300WB.

RESULTS AND DISCUSSION

The polyphosphates obtained were characterized by elemental analysis, infrared (IR), ^{31}P and ^{13}C NMR spectra, inherent viscosity, differential scanning calorimetry (DSC), TGA, LOI, X-ray diffraction, contact angle measurement, and molar mass. The elemental analysis data of the polymers are summarized in Table I. The results of elemental analysis agreed well with theoretical values. The polymers A–E obtained from the condensation of various aryl phosphorodichloridates with TBPAP were soluble in chlorinated aliphatic hydrocarbons, such as CH_2Cl_2 and CHCl_3 , and aprotic solvents, such as dimethyl sulphoxide and dimethyl formamide, but insoluble in aliphatic hydrocarbons and alcoholic solvents.

The IR spectra of the polymers were similar,

Table II IR Spectral Data of Polyphosphates

Polymer ^a	—C(CF ₃) ₂ — (cm^{-1})	P=O (cm^{-1})	P—O—C (cm^{-1})	Ph (cm^{-1})	C—X (cm^{-1})
A	1,243	1,317	1,180; 965	3,066; 1,586; 1,485; 775	—
B	1,243	1,318	1,180; 967	3,094; 1,586; 1,500; 771	2,912; 2,858
C	1,242	1,320	1,178; 963	3,076; 1,588; 1,487; 774	1,523; 1,345
D	1,243	1,318	1,178; 965	3,090; 1,580; 1,479; 776	1,479; 722
E	1,245	1,319	1,179; 968	3,074; 1,587; 1,499; 771	2,942; 2,828

^a A, X=H; B, X=CH₃; C, X=NO₂; D, X=Br; E, X=OCH₃.

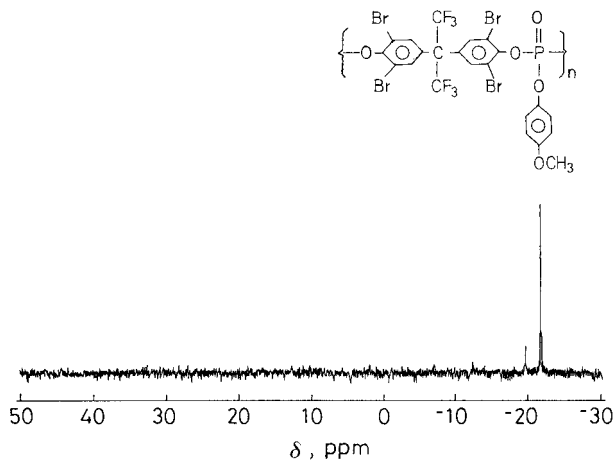


Figure 1 ^{31}P -NMR spectrum of polymer E.

and the data are shown in Table II. For instance, polymer E shows a strong absorption around $1,319\text{ cm}^{-1}$, corresponding to $\nu_{\text{P=O}}$, which is characteristic of phosphate ester compounds.^{35,36} Also, all of the polymers showed strong absorptions around $1,179$ and 968 cm^{-1} , corresponding to P—O—C (aromatic) stretching. The other absorptions are characteristic of the aromatic or functional groups present in the polymer depending on the various aryl phosphorodichloridates. The ^{31}P -NMR spectra of all of these polymers show two signals: one corresponds to the P in the repeat unit, and the other corresponds to the one at the chain end. A typical example for polymer E is shown in Figure 1.

For example, the P in the repeat unit is attached to three aryloxy groups, whereas that at the end is attached to two aryloxy groups and one chlorine group. Since the chlorine is an electron-withdrawing group, the P in the repeat unit appears upfield ($\sim -22\text{ ppm}$) with respect to that in the end group ($\sim -20\text{ ppm}$). The substituents on the phenyl ring do not cause much change in the δ values, probably because the substituents are more than five bonds away from the P atom.^{37,38}

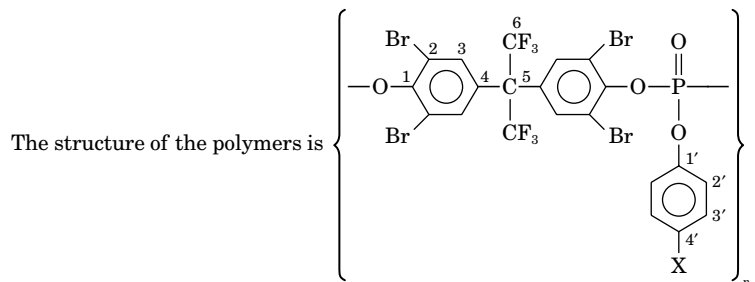
The ^{13}C -NMR spectra of the polymers show the resonances corresponding to all of the carbons of the given polyphosphate structure. The data are shown in Table III.

The assignments were carried out using the normal additivity parameters of the substituents^{39,40} in the benzene ring. The phosphate group causes the *ortho* and *para* carbons to shift to higher fields and the carbon to which it is attached to shift to a lower field, while the *meta* position is not much different from that of benzene.^{40,41}

As summarized in Table IV, these polymers obtained in high yields have inherent viscosities of $0.12\text{--}0.15\text{ dL g}^{-1}$. The weight average molar masses (\overline{M}_w) are in the range of $3.8 \times 10^3 \sim 6.0 \times 10^3$ with relatively narrow molar mass distribution ($\overline{M}_w/\overline{M}_n = 1.2\text{--}1.4$). The weight average molar masses of polyphosphates measured by GPC were almost in agreement with those measured by light scattering. The polyphosphates obtained from TBPAF showed lower viscosity values than

Table III ^{13}C -NMR Chemical Shift Values (ppm) of the Polymers

Polymer ^a	C-1	C-2	C-3	C-4	C-5	C-6	C-1'	C-2'	C-3'	C-4'	X
A	147.5	110.3	134.4	117.5	63.0	125.0	150.5	120.0	129.7	125.9	—
B	147.6	110.3	134.9	117.5	62.9	125.0	148.4	119.7	130.2	135.6	20.7
C	147.0	110.2	134.5	117.3	63.1	125.0	154.7	120.8	125.7	115.5	—
D	147.3	110.2	134.5	117.4	63.0	125.8	149.2	121.6	133.0	119.0	—
E	147.5	110.3	134.4	117.5	63.1	125.0	144.1	120.9	114.9	157.3	55.7



^a A, X=H; B, X=CH₃; C, X=NO₂; D, X=Br; E, X=OCH₃.

Table IV Result of the GPC and Light Scattering of Polyphosphates

Polymers	Yield ^a (%)	η_{inh}^b (dLg ⁻¹)	$\overline{M}_w \times 10^{-3}^c$	PDI ^c	$\overline{M}_w \times 10^{-3}^d$
A	93	0.13	3.9	1.2	4.1
B	94	0.13	4.2	1.2	4.7
C	98	0.14	3.8	1.2	4.6
D	96	0.12	4.3	1.2	4.0
E	97	0.15	6.0	1.4	6.7

^a The yield was calculated on the basis of the theoretical structure.

^b Measured at concentration of 0.1 g dL⁻¹ in 1,2-dichloroethane at 30°C.

^c Measured by GPC in THF; polystyrene was used as the standard.

^d Measured by light scattering in dichloromethane at 20°C.

those obtained from BPAF.²⁰ This phenomenon may have resulted from the electron-withdrawing characteristic of the bromine atom, which may decrease the nucleophilicity of the phenols.¹⁹

The thermal behavior of the polymers was evaluated by means of TGA and DSC. The TGA results of polyphosphates are summarized in Table V. All of the polymers start degrading between 210 and 267°C and exhibited residual masses of 14–26% at 700°C in nitrogen. Figure 2 shows an example of polyphosphates with a 10°C min⁻¹ heating rate in nitrogen. The degradation of all polymers occurs in a two-step process. This phenomenon was also found by Annakutty and Kishore.³⁷ They explained that the first step corresponds to the formation of various phenols and phosphates with some amount of char remaining, which subsequently carbonizes in the second step. Polymer E, having a methoxy group in the side chain phenyl ring, showed better thermal stability than the other polymers. Polymer D, having a higher bromine content, had a lower thermal degradation. This result may be explained by the fact that hydrogen bromide is easily evolved from bromine-

containing polymers during the thermal degradation process.^{19,29}

From Table V, the polyphosphates had glass transition temperatures between 140 and 154°C. These polyphosphates obtained from TBPAF showed higher glass transition temperatures than those obtained from BPAF ($T_g = 81$ – 108°C).²¹ This result may be accounted for by bromine substitution, which increases steric hindrance, thus decreasing chain flexibility. The same results have also been found by Marks⁴² and Liaw and Chang²⁵ for copolycarbonates based on TBBPA and TBPAF, respectively.

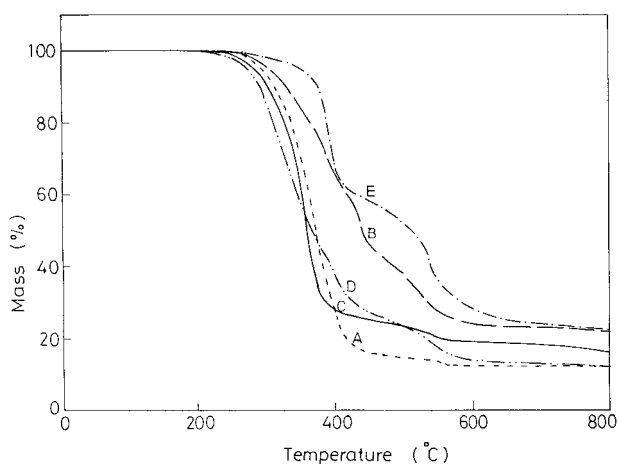
The LOI and surface properties of the polymers are shown in Table VI. The LOI values of the polyphosphates are between 63 and 68. These polymers show higher LOI values and better flame retardancy compared with the bisphenol A- and phenolphthalein-based polyphosphate ester^{43–45} (LOI = 26–44). These results indicate that the flame retardancy of the polyphosphates

Table V Thermal Properties of Fluorine-Containing Polyphosphates

Polymer	T_d^a (°C)	Residue at 700°C (%)	T_g^b (°C)
A	229	14	140
B	233	24	146
C	215	20	154
D	210	16	152
E	267	26	151

^a TGA conducted at a heating rate of 10°C min⁻¹ in nitrogen.

^b DSC analysis conducted at a heating rate of 10°C min⁻¹ in nitrogen.

**Figure 2** Thermogravimetric traces of polymers A–E in nitrogen.

is considerably increased by the introduction of bromine into the polyphosphate system.⁴⁶ Furthermore, Liaw et al.^{20,24,25} reported that trifluoromethyl groups in the polymer would bring about an unexpected improvement in flame resistance. Polymer A, which contains the most phosphorus and bromine, has the highest LOI values, as indicated by a high LOI of 68.

The hydrophilic data of the polyphosphate films by water are compiled in Table VI. The water contact angles (θ_w) are in the range of 74–87°. The contact angles of polymers A and B are larger than those of other polyphosphates, which have a higher oxygen content (polymers C and E) or contain more bromine atoms (polymer D). This may be explained by the fact that introducing oxygen and bromine atoms into the polymer would increase the overall hydrophilicity of the polymer and the contact angle would decrease.^{24,47,48}

The X-ray diffraction patterns of various polyphosphates are shown in Figure 3 in terms of intensity versus 2θ ; θ is the angle of diffraction (Bragg angle). The X-ray measurements indicated that all polyphosphates are amorphous. Nagata et al.³¹ reported that polyamides incorporating halogen substituents on the ring led to a decrease in crystallinity in terms of their larger van der Waals radius. The same results have also been found by Liaw and Chang²⁵ for copolycarbonates based on TBPAF.

CONCLUSIONS

New fluorine-containing polyphosphates incorporating bromine atoms were successfully synthesized by the low-temperature solution polycondensation of TBPAF with various aryl phosphoro-

Table VI Contact Angle and LOI of Polyphosphates

Polymer	LOI	θ_w^a (deg)	P ^b (%)	Br ^c (%)	O ^d (%)
A	68	83	3.92	40.5	8.1
B	67	87	3.85	39.8	8.5
C	63	74	3.71	38.3	11.5
D	65	78	3.57	46.0	7.4
E	65	78	3.78	39.0	9.8

^a Contact angle by water was measured at 25°C in air.

^b The mass percent of phosphorus atom.

^c The mass percent of bromine atom.

^d The mass percent of oxygen atom.

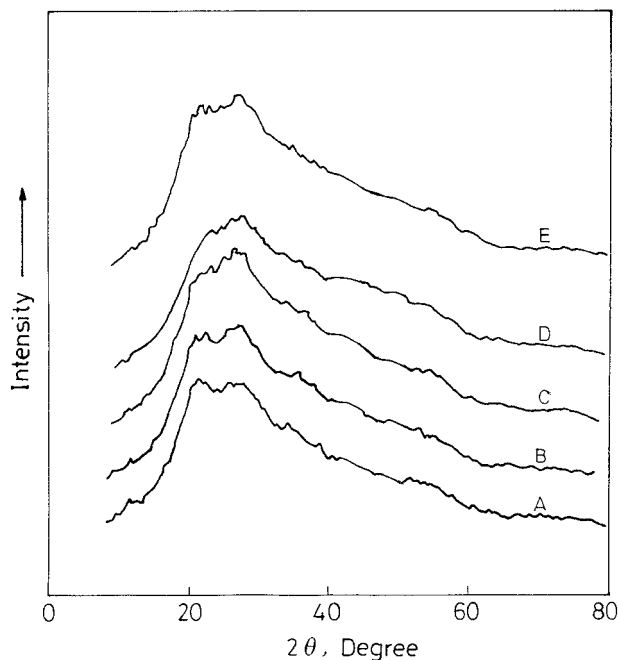


Figure 3 X-ray diffraction patterns of polymers A–E.

dichloridates, and the structures are confirmed spectroscopically. All of the polymers start degrading between 210 and 267°C. The incorporation of bromine atoms into the polymer chain leads to high glass transition temperature and increased flame retardancy. The LOI values of the polyphosphates are between 63 and 68. The contact angles of polymers A and B are larger than those of other polyphosphates, which contain more oxygen (polymers C and E) or bromine (polymer D) atoms. Polyphosphates incorporating bromine atoms on the ring led to decreased crystallinity in terms of their larger van der Waals radius.

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