

Phosphorus-Containing Polymers. II. Preparation and Properties of Copoly(carbonate-Phosphonate)s

INTRODUCTION

The bisphenol-A-based polycarbonate introduced in the late 1950's by Schnell¹ and Fox² is a high performance plastic. Although this polycarbonate is known to have relatively good flame retardancy, to meet the special industrial codes, enhanced flame retardancy is generally achieved by either copolymerizing with halogenated bisphenols such as 2,2',6,6'-tetrabromobisphenol-A (TBBPA)³ or by the incorporation of additives like sodium 2,4,5-trichlorobenzene sulfonate.⁴ The flame-retardant polycarbonate based on TBBPA has poor thermal stability, which results in turn in poor processability.⁵ Sodium 2,4,5-trichlorobenzene sulfonate is reported as a very effective flame-retardant additive to polycarbonate.⁴

The incorporation of phosphonate groups in the polycarbonate backbone has also been reported to improve flame retardancy.^{6,7} A series of copoly(carbonate-phosphonate)s has been prepared by reaction of organophosphonic dichlorides, such as methyl- and phenylphosphonic dichloride, phosgene with bisphenols, such as bisphenol-A, 2,2',6,6'-tetrachlorobisphenol-A (TCBPA) and 4,4'-sulfonyldiphenol (SDP), to determine the effect of the phosphonate group in the polycarbonate backbone chain on the physical and thermal properties of the polymers.

EXPERIMENTAL

Materials

Methylphosphonic dichloride [methyl phosphorus oxydichloride (MPOD)] was supplied by Mr. E. Uhing, Stauffer Chemical Co. All other chemicals were obtained commercially. Phenylphosphonic dichloride [benzene phosphorus oxydichloride (BPOD)] was distilled *in vacuo* before use. All bisphenols were dried at 100°C *in vacuo* to remove surface moisture. Methylene chloride was dried over 3A molecular sieves. The solvent contained <100 ppm water by Karl Fisher titration. Triethylamine was distilled and dried over potassium hydroxide.

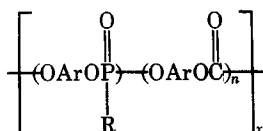
Polycondensation

A typical procedure for polymerization is as follows: A three-necked flask equipped with a paddle stirrer, addition funnel, reflux condenser, and gas inlet tube was charged with 27.2 g (0.074 mol) of TCBPA, 150 mL of methylene chloride, and 16 g (0.16 mol) of triethylamine. A solution of 3.92 g (0.020 mol) of BPOD in 50 mL of methylene chloride was slowly added to the flask with rapid stirring. Phosgene, 6.0 g (0.060 mol), was then added slowly to the reaction mixture through the gas inlet tube. Stirring was continued for 1 h following the addition. The viscous polymer solution was washed with dilute hydrochloric acid, followed by distilled water until the aqueous phase was neutral to litmus paper. The copolymer was precipitated by adding the methylene chloride solution to a Waring Blender containing methanol and the precipitate was collected by filtration. The white polymer in powder form was dried *in vacuo* at ~100°C overnight. Table I summarizes the polycondensation results.

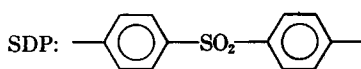
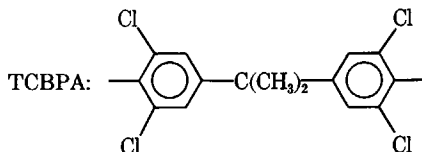
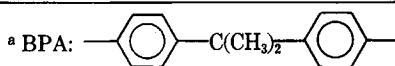
Characterization

Solution viscosities were measured at 25°C in about 0.5% 1,1,2,2-tetrachloroethane solution. Glass transition temperatures were measured with a Perkin-Elmer DSC-2 Differential Scanning Calorimeter. The midpoint in the baseline shift was taken as T_g . Thermogravimetric data were obtained on a DuPont 950 Thermogravimetric Analyzer with a heating rate of 10°C/min under a nitrogen atmosphere. ASTM D-2863 procedure was used to measure the limiting oxygen index (LOI). Hydrolytic stability was measured with melt-pressed films on a Carver laboratory press. The films with thickness of about 12 mils were immersed in 3M hydrochloric acid or 3M sodium hydroxide

TABLE I
Low-Temperature Polycondensation of Bisphenols with Phosgene and Organophosphonic Dichloride



Polymer no.	Monomers			Yield (%)	Polymers			PMT (°C)	T_g (°C)
	R—	—Ar— ^a	n'/m' ^b		P (%)		η_{inh}		
					Found	Calcd			
Ia	C ₆ H ₅	BPA	4.71/1	96	2.01	2.00	0.43	230	132
Ib	C ₆ H ₅	BPA	1.67/1	97	3.86	4.00	0.59	230	118
IIa	C ₆ H ₅	TCBPA	2.71/1	95	2.04	2.00	0.27	260	200
IIb	C ₆ H ₅	TCBPA	0.72/1	95	4.03	4.02	0.25	240	187
IIIa	C ₆ H ₅	SDP	1.42/1	93	4.29	4.05	0.41	250	178
IIIb	C ₆ H ₅	SDP	0.52/1	96	5.99	6.01	0.37	240	164
IVa	CH ₃	BPA	4.97/1	98	2.07	2.00	0.72	240	149
IVb	CH ₃	BPA	1.92/1	95	4.00	4.00	0.79	240	140
Va	CH ₃	TCBPA	2.86/1	93	1.93	2.00	0.24	260	202
VIa	O	BPA	1/0	96	0	0	0.59	230	151



at 60°C for 5 days and the solution viscosity changes of the polymers were recorded. Infrared spectra were recorded with a Perkin-Elmer Grating Infrared Spectrophotometer and ³¹P NMR spectra with a Bruker HFX-90 Spectrometer. Phosphorus elemental analyses were performed by Swartzkopf Microanalytical Laboratory, New York.

Mechanical Properties

The polymers in powder form were compression molded into 6 × 6 × 1/6 in. plaques at a temperature near their melt temperature. These were then cut to give test specimens for property measurements. The following ASTM procedures were used for measuring tensile strength: elongation (D-882), flexural modulus (D-790), tensile impact (D-1822-61-T), and heat distortion temperature under 264 psi (D-468).

RESULTS AND DISCUSSION

The previous study⁸ on polyphosphonates showed that a high molecular weight polymer can be readily prepared from water sensitive BPOD and bisphenols by a low-temperature solution polycondensation. Therefore, the solution polymerization technique has been extended to prepare copoly(carbonate-phosphonate) from various bisphenols, phosgene, and an organophosphonic dichloride. In these experiments, methylene chloride, a good solvent for both polycarbonate and polyphosphonate, was used as a polymerization solvent. Triethylamine was used as an acid acceptor because polymerization of BPOD with bisphenols requires strong base.⁸ The low-temperature polycondensation of phosgene and an organophosphonic dichloride with bisphenols produced high yields of copolymers having inherent viscosities of >0.2.

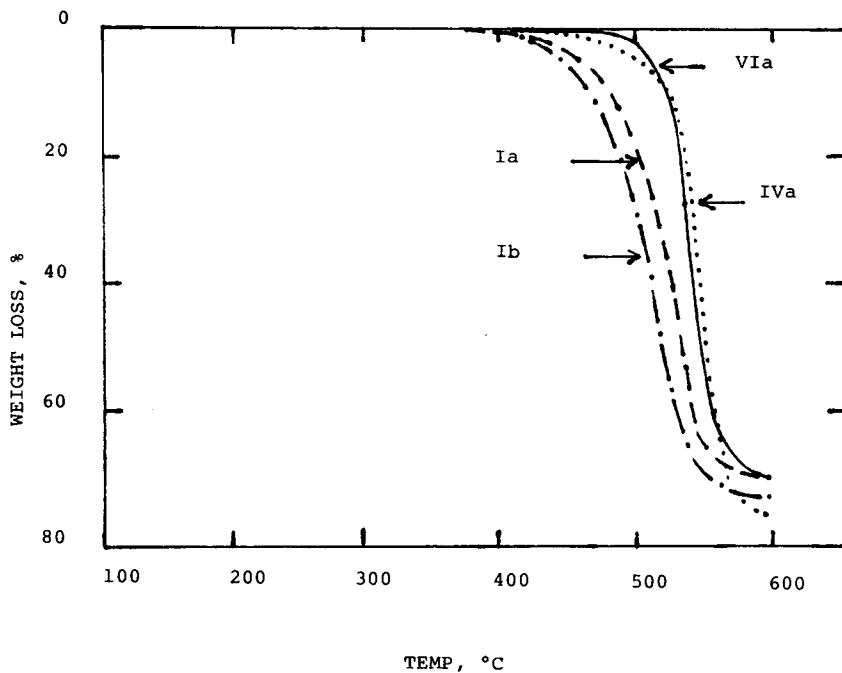
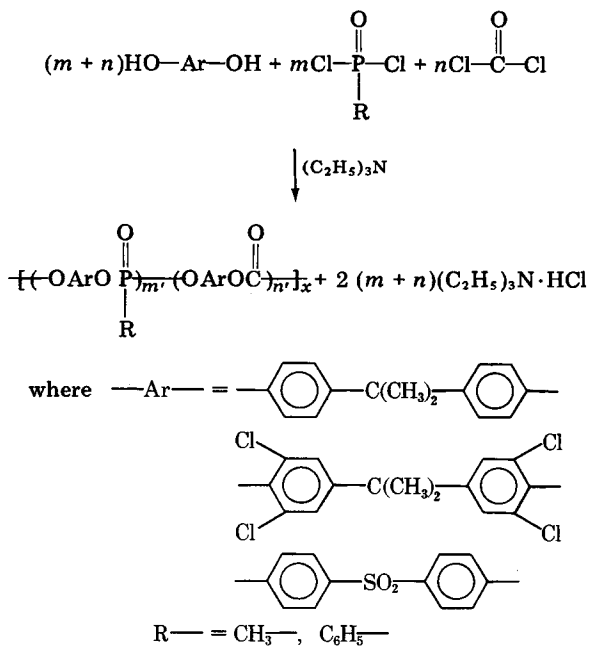


Fig. 1. Thermogravimetric analysis of copolymers. Heating rate $10^{\circ}\text{C}/\text{min}$ under nitrogen.

Table I shows data on the physical properties of these products. The following illustrates the reaction scheme for the copolymerization:



Infrared spectra of the typical copoly(carbonate-phosphonate)s I and IV showed the following absorption bands: 1770 cm^{-1} ($\text{C}=\text{O}$), 920 cm^{-1} ($\text{P}-\text{O}-\text{Ar}$), and 1440 cm^{-1} ($\text{P}-\text{Ar}$ for BPOD based copolymer I) or 1310 cm^{-1} ($\text{P}-\text{CH}_3$ for MPOD based polymer IV). The proton decoupled ^{31}P NMR

TABLE II
Initial Decomposition Temperatures of Copoly(carbonate-phosphonate)s

Polymers	Initial decomposition temp. ^a (°C)
Ia	380
Ib	370
IVa	400
VIa	400

^a Heating rate = 10°C/min under nitrogen.

TABLE III
Limiting Oxygen Index (LOI) of Copoly(carbonate-phosphonate)s

Polymers	P found (%)	LOI
Ia	2.01	30
Ib	3.86	35
IIIa	4.29	37
IIIb	5.99	40
VIa	0	26

TABLE IV
Effect of H₂O, NaOH, and HCl at 60°C on Copoly(carbonate-phosphonate)s

Polymers	Time (days)	Medium	Inherent viscosity	
			Original	Recovered
Ia	5	H ₂ O	0.43	0.43
Ia	5	3M HCl	0.43	0.41
Ia	5	3M NaOH	0.43	0.42
Ib	5	H ₂ O	0.59	0.59
Ib	5	3M HCl	0.59	0.58
Ib	5	3M NaOH	0.59	0.55
VIa	5	H ₂ O	0.59	0.59
VIa	5	3M HCl	0.59	0.59
VIa	5	3M NaOH	0.59	0.57

signal was a singlet at +12.0 ppm for copolymer I and +24.3 ppm for copolymer IV indicating the presence of phosphonate bonds. Elemental analyses compared favorably with the calculated values (Table I).

The solubilities of copoly(carbonate-phosphonate)s were tested qualitatively in a variety of solvents. All the copolymers are soluble in chlorinated aliphatic hydrocarbons such as methylene chloride and chloroform as well as in polar aprotic solvents such as *N,N*-dimethylacetamide and 1-methyl-2-pyrrolidinone. The copolymers are insoluble in alcohols and aliphatic hydrocarbons. The phosphorus-containing copolymers produced colorless transparent films from methylene chloride solution. All the films are tough except the copolymers III based on SDP.

The DSC data in Table I indicate that the increase in phosphorus content in the copolymers prepared from the same bisphenol caused a decrease in the T_g ; for example, VIa > Ia > Ib, IIa > IIb, IIIa > IIIb, VIa > IVa > IVb. The same trend was observed in the melt temperatures (Table I). The glass transition temperatures of the copolymers synthesized using MPOD as a phosphorus-containing monomer are higher than those of the polymers using BPOD at the same phosphorus level, e.g., IVa > Ia, IVb > Ib, Va > IIa. The bulky phenyl groups of BPOD may contribute to lowering the transition temperatures. This trend was found but further work related to exact distribution of phosphorus units is needed.

Higher melt temperatures and T_g of the copolymers II, made from TCBPA, and III, made from SDP, as compared to I, made from BPA, are probably due to the structural rigidity provided by the TCBPA and SDP monomers.

TABLE V
Mechanical Properties of Copoly(carbonate-phosphonate)s

Properties	Polymers		
	Ia	IVa	VIa
Tensile strength at break (psi)	6800	7800	8700
Elongation at break (%)	53	70	120
Tensile impact (ft-lb/in. ²)	110	25	220
Flexural modulus ($\times 10^5$ psi)	3.3	3.6	2.9
DTL, 264 psi ($^{\circ}$ C)	127	127	136

The thermogravimetric analytical data are shown in Figure 1. The copolymers generally possess good thermal stability below 370 $^{\circ}$ C in nitrogen atmosphere. However, it appears that the introduction of phosphonate groups into the polycarbonate backbone leads to increased ease of thermal degradation (Table II). Copolymers derived from MPOD exhibited higher thermal stability than the BPOD analogs.

The copoly(carbonate-phosphonate) showed a significant improvement in flame retardancy, as indicated by high LOI (Table III). Thus, bisphenol-A polycarbonate VIa containing no phosphorus has an LOI of 26, but copolymers I containing 2% and 4% phosphorus have LOI values of 30 and 35, respectively. Copolymer IIIb containing 6% phosphorus has an LOI of 40. This confirms that phosphorus contributes good flame retardancy to copoly(carbonate-phosphonate)s.^{6,7}

Polycarbonates are stable in acids but not in alkalis.⁹ The effect of dilute sodium hydroxide and hydrochloric acid on film samples of Ia and Ib was investigated at 60 $^{\circ}$ C. The results are shown in Table IV. The copolymers exhibited slightly less stability in acid and alkali than did the polycarbonate based on bisphenol-A.

Some of the significant mechanical properties of the compression molded copolymers Ia and IVa are listed in Table V. Polycarbonate VIa, derived from bisphenol-A, is included for comparison. Properties such as tensile strength and flexural modulus of the copolymers are quite the same as those of the nonphosphorus analog. The copolymers Ia and IVa have lower DTL, elongation, and tensile impact than the control polycarbonate.

References

1. H. Schnell, *Angew. Chem.*, **68**, 623 (1956).
2. D. W. Fox (assigned to General Electric Co.), Australian Pat. No. 221, 192 (1959).
3. J. K. S. Kim (assigned to General Electric Co.), U.S. Pat. 3,334,154 (1967).
4. V. Mark, *Am. Chem. Soc., Div. Org. Coat Plast. Chem.*, **43**, 71 (1980).
5. *Mater. Eng.*, p. 36 (1976).
6. Gevaert Photo-Production, N. V., Belg. Pat. 610,954 (1961).
7. K. S. Kim, A. J. Yu, and S. Altscher (assigned to Stauffer Chemical Co.), U.S. Pat. 4,223,104 (1980).
8. K. S. Kim, *J. Appl. Polym. Sci.*, **28**, 1119 (1983).
9. H. Schnell, *Ind. Eng. Chem.*, **51**, 157 (1959).

KI-SOO KIM

Eastern Research Center
Stauffer Chemical Company
Dobbs Ferry, New York 10522

Received November 19, 1982

Accepted January 14, 1983