

Phosphorus-Containing Polymers. I. Low Temperature Polycondensation of Phenylphosphonic Dichloride with Bisphenols

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Synopsis

This paper describes the synthesis of aryl polyphosphonates from the reactions of phenylphosphonic dichloride [benzene phosphorus oxydichloride (BPOD)] with 4,4'-thiodiphenol (TDP) and with 4,4'-sulfonyldiphenol (SDP) employing a dry chlorinated hydrocarbon polymerization solvent, an amine acid acceptor and under low temperature conditions. The glass transition temperatures of the polymers from BPOD/SDP and BPOD/TDP are 146°C and 83°C, respectively, and the polymers begin to lose weight at about 395°C in a nitrogen atmosphere. These polymers have good flame retardancy (FR), as indicated by high limiting oxygen indices (LOI) of 50–60. Thermoplastic polybutylene terephthalate containing 7% BPOD/SDP or BPOD/TDP polymer as an FR additive has LOI values of 29 and 30, respectively.

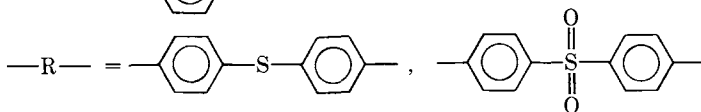
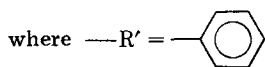
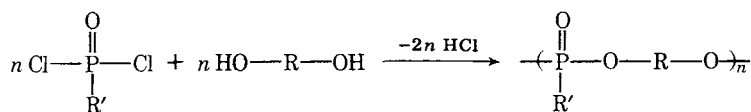
INTRODUCTION

Polyphosphonates have been of commercial interest because of their flame retardant characteristics.¹ Linear polymers with phosphorus in the backbone are produced from bifunctional organophosphorus compounds such as arylphosphonic dichlorides with bisphenols.

Millich and Carraher²⁻⁵ studied the interfacial polycondensation reaction of phenylphosphonic dichloride (BPOD) with hydroquinone, and they reported those factors influencing the polymer molecular weight and yield. The interfacial polymerization by employing barium hydroxide³ or phase-transfer catalysts⁶ yielded high polymers. Several patents describe the synthesis of polyphosphonates. For example, Toy⁷ carried out the polycondensation reaction of BPOD with hydroquinone as a melt. Coover and McCall⁸ prepared polyphosphonates by the melt reaction with catalytic amounts of alkaline earth halides. Masai et al.⁹ reported the high-temperature solution polymerization of BPOD with 4,4'-sulfonyldiphenol in tetrachloroethane, using a CaCl₂ catalyst.

Although the low-temperature solution polycondensation process has been widely used to prepare polymers such as polyesters¹⁰ and polycarbonates,¹⁰ there has not been a study of the synthesis of polyphosphonates using this technique. In this paper, the low temperature solution polycondensation of BPOD with 4,4'-thiodiphenol (TDP) and with 4,4'-sulfonyldiphenol¹¹ (SDP) is described

along with the physical properties and thermal and flame retardant characteristics. The following scheme illustrates the synthesis:



EXPERIMENTAL

Materials

Phenylphosphonic dichloride was distilled *in vacuo* before use. The 4,4'-sulfonyldiphenol and 4,4'-thiodiphenol were obtained from Crown Zellerbach Corp. and dried at 120°C *in vacuo* to remove surface moisture. Methylene chloride was dried over molecular sieves (Linde, Type 3A). The solvent generally contained <100 ppm water by Karl Fisher titration. All amines were distilled and dried over KOH.

Polymerization

A flask equipped with a paddle stirrer, addition funnel, and reflux condenser was charged with 25.0 g (0.10 mol) of 4,4'-sulfonyldiphenol, 300 mL of methylene chloride, and 22.2 g (0.22 mol) of triethylamine. A mixture of 19.5 g (0.10 mol) of BPOD and 50 mL of methylene chloride was slowly added to the flask while rapidly stirring. During the addition, an exothermic reaction ensues to produce sufficient heat to maintain a gentle reflux of methylene chloride. At the end of the addition, the reaction mixture was refluxed for 1 h. The polymer solution was cooled to room temperature, washed with dilute HCl, and distilled water until the aqueous phase was neutral to litmus paper. The polymer was precipitated by adding the reaction solution to a Waring Blender containing methanol. The precipitate was collected by filtration. The white polymer was dried *in vacuo* at ~100°C overnight. Table IV summarizes results of physical properties of the polymers.

TABLE I
Effect of Solvent on the Viscosity of BPOD/SDP Polymer

Solvents	Yield (%)	η_{inh} (dL/g)
CH ₂ Cl ₂	95	0.63
CHCl ₃	95	0.51
ClCH ₂ CH ₂ Cl	96	0.38
C ₆ H ₅ Cl	0 ^a	—

^a Yields insoluble amine/SDP complexes.

TABLE II
Effect of Acid Acceptor on the Viscosity of BPOD/TDP Polymers

Acid acceptors	pK _a ^a	Yield (%)	η_{inh} (dL/g)
Triethylamine	3.1	94	0.51
Tri- <i>n</i> -butylamine	3.1	95	0.31
Pyridine	7.8	0	None
<i>N,N</i> -dimethylaniline	8.0	0	None

^a Data from Hall.¹²

Characterization

Solution viscosities were measured at 25°C in a 1% solution of 1,1,2,2-tetrachloroethane. Glass transition temperatures (T_g) 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). ³¹P NMR spectra were taken on Bruker HFX-90 spectrometer.

RESULTS AND DISCUSSION

Morgan¹⁰ systematically reviewed the low-temperature polycondensation of diacid chlorides with bisphenols. The process consists of combining fast-reacting intermediates in an inert medium and removing the acidic byproducts using acid acceptors. This avoids the problem of acid chloride hydrolysis, normally encountered in an aqueous two-phase system. This method has been extended to the low-temperature polycondensation of water-sensitive BPOD with bisphenols, and a high molecular weight polyphosphonate was readily obtained in high yield (>94%). The low-temperature polycondensation of BPOD with either SDP or TDP in the presence of triethylamine as an acid acceptor is best carried out in methylene chloride solvent, as shown in Table I. However, chlorinated aliphatic hydrocarbons such as either chloroform or 1,2-dichloroethane are also suitable as polymerization solvents. The system requires at least a moderate base such as triethylamine (Table II). The BPOD reaction, unlike the condensation of phosgene or a dicarboxylic acid chloride with a bisphenol, will not proceed in the presence of weaker bases such as pyridine or *N,N*-dimethylaniline. Schlott et al.¹³ observed the same trend in the polycondensation of 4,4'-biphenyldisulfonyl chloride with bisphenol-A.

The hydrolysis of BPOD to give phenylphosphonic acid is well known.¹⁴ It

TABLE III
Effect of Monomer Hydrolysis on the Molecular Weight of BPOD/TDP Polymers

H ₂ O in CH ₂ Cl ₂ (ppm)	Yield (%)	η_{inh} (dL/g)
<100	94	0.51
110	95	0.46
220	94	0.25

TABLE IV
Physical Properties of Polyphosphonates

Properties	BPOD/SDP polymer	BPOD/TDP polymer
η_{inh}	0.63	0.51
PMT ^a (°C)	185	170
T_g (°C)	146	83
P (%) found	8.2	9.1
calcd	8.3	9.1
S (%) found	8.7	8.7
calcd	8.6	9.4
C (%) found	55.4	63.6
calcd	58.1	63.5
H (%) found	3.4	4.1
calcd	3.5	3.8

^a Polymer melt temperature.

is believed that hydrolysis of the monomer and hydrolysis of chlorophosphonyl end groups of the growing oligomers result in low molecular weight polymers.

Table III shows the effect of the addition of water on the molecular weight of the polymers. This indicates the importance of the exclusion of water to obtain a high molecular weight polymer in the solution polymerization.

³¹P NMR spectra of the polycondensation products support formation of phosphonates; a singlet at +12.3 ppm for the BPOD/TDP polymers and at +12.7 ppm for the BPOD/SDP polymers. Elemental analyses were in agreement with the assigned polyphosphonate structures (Table IV).

The solubilities of the resulting polyphosphonates were determined qualitatively in a variety of solvents. Both BPOD/TDP and BPOD/SDP polymers are

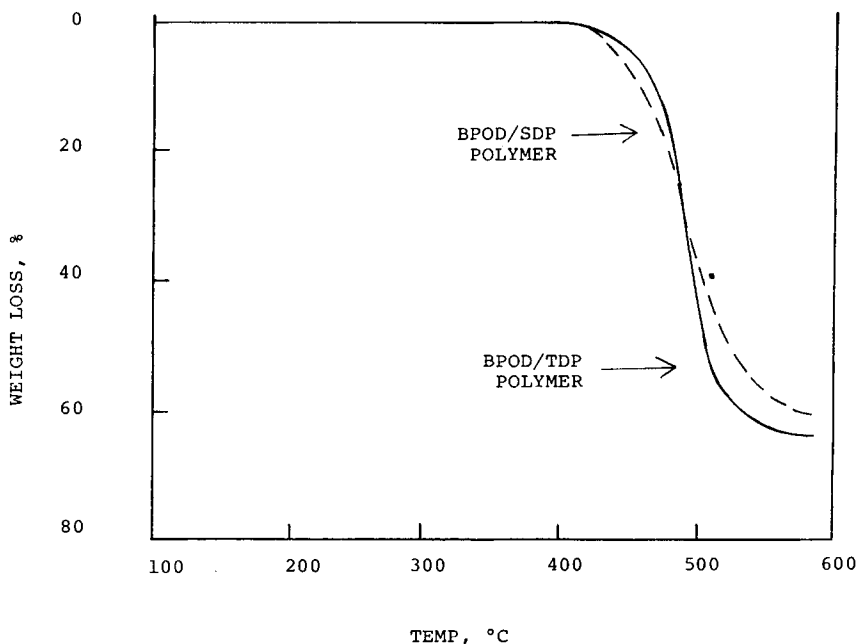


Fig. 1. Thermogravimetric analysis of polyphosphonates. Heating rate 10°C/min under nitrogen.

TABLE V
LOI of Polyphosphonates

Polymers	LOI
BPOD/SDP	50
BPOD/TDP	60
93 PBT/7 BPOD/SDP ^a	29
93 PBT/7 BPOD/TDP ^a	30
100 PBT	23

^a By weight.

soluble in chlorinated aliphatic hydrocarbons, such as methylene chloride, carbon tetrachloride, as well as polar aprotic solvents such as *N,N*-dimethylacetamide, 1-methyl-2-pyrrolidinone and dimethylsulfoxide. The polymers are insoluble in aliphatic hydrocarbons and alcohols.

The BPOD/TDP and BPOD/SDP polymers have melt temperatures of $\sim 170^{\circ}\text{C}$ and $\sim 185^{\circ}\text{C}$, respectively. The value for T_g of BPOD/TDP (83°C) is 60° lower than that of BPOD/SDP (146°C); this is attributed to the flexible sulfide linkages (Table IV). Thermogravimetric analytical data for the polyphosphonates are shown in Figure 1. Both polymers begin to lose weight at about 395°C in a nitrogen atmosphere, and a 10% weight loss is observed at about 465°C .

The polyphosphonates are distinguished by their high flame retardancy, as indicated by high limiting oxygen indices (LOI) (Table V). The BPOD/TDP polymer, containing 9.1% phosphorus, has an LOI of 60 and the BPOD/SDP polymer containing 8.2% phosphorus an LOI of 50. The higher phosphorus content of the BPOD/TDP polymer appears to contribute to a higher LOI. The BPOD/SDP and BPOD/TDP phosphonate polymers may be used as FR additives in polyesters. For example, blends of thermoplastic polybutylene terephthalate with 7% BPOD/SDP or BPOD/TDP polymer have LOI values of 29 and 30, respectively. The polyester without the additives has an LOI of 23.

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