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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Deits, W. and Vogl, O.(1981) 'Functional Polymers. VIII. Polyesters from Hindered Bisphenols', Journal of Macromolecular Science, Part A, 16: 6, 1145 – 1159

**To link to this Article:** DOI: 10.1080/00222338108063222

**URL:** <http://dx.doi.org/10.1080/00222338108063222>

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## Functional Polymers. VIII.\* Polyesters from Hindered Bisphenols

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### ABSTRACT

It was demonstrated that highly hindered bisphenols could be used to produce polyesters of moderate molecular weight. Bisphenols linked in the 4 and 4' or the 2 and 2' positions and substituted in positions ortho and para to the phenolic hydroxyl groups with methyl or tertiary butyl groups (these bisphenols are now used as very effective antioxidants) formed polymers, their reactivity depending more on the nature of the group linking the two phenyl rings than on the steric effects of the ortho substituents. Bisphenols linked in the 2 and 2' positions and containing bulky electron-withdrawing groups were found to be least effective as condensation monomers although successful polymerization to moderate molecular weight could be achieved using melt polycondensation techniques.

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\*For Part VII, see Y. Sumida and O. Vogl, *Polym. J.*, **13**(6), 521 (1981).

†Deceased, February 16, 1981.

## INTRODUCTION

A great number of reports exist describing the preparation, characterization, and properties of polyesters [1-3]. Aromatic polyesters and copolyesters have been the subject of numerous studies where reactive intermediates, such as diacids, diacid chlorides and diesters, and bisphenols and bisphenol diesters, are used as polymer intermediates [4-6]. Aromatic polyesters typically have high melting points, high glass transition temperatures, and high degrees of crystallinity which when combined with a lack of solvent makes the commercial preparation of high molecular weight polymers of this type a problem [3-6]. The use of diacids or bisphenols which impart less ordered structures into the polymer backbones is helpful and often results in more workable materials. A good example is the recent commercialization of the polymer prepared from isophthaloylchloride and 2,2'-(4-hydroxyphenyl)propane (bisphenol A) [7].

Very few studies concerning the preparation of aromatic polyesters from highly hindered bisphenols have been undertaken. Essentially all investigations involved bisphenols linked in the 4 and 4' positions where the four positions ortho to the phenolic hydroxyl groups were substituted with halogens or methyl groups [8-15]. Many of these preparations were aimed at the production of polyesters with good overall properties and low flammability, and the bisphenols used were selected for their halogen content and ease of incorporation into high molecular weight materials.

The properties of several polyesters synthesized from sterically hindered bisphenols illustrate some of the effects that can be expected when components of this type are incorporated into aromatic polyesters. Morgan [13], for example, synthesized a series of polyesters from substituted phenolphthaleins and isophthaloyl chloride by an interfacial process. The polymer melt temperature (PMT) of the polyester prepared from unsubstituted phenolphthalein was 355°C, that of the tetrachlorosubstituted (all substituents in the positions ortho to the phenolic hydroxyl groups) phenolphthalein decreased to 300°C, but the PMT of the polymer with bromine in place of chlorine increased to 326°C and that with iodine substitution to >400°C. It is clear from this data that substitution in the ortho positions disrupts the packing of the chains and causes a sharp decrease in the PMT. As the size of the substituents increases, the chain becomes stiffer but it is not until the bulkiness of the tetraiodo derivative is reached that the chain stiffness is sufficient to raise the PMT to the point where the ineffectiveness of chain packing present in the unsubstituted polymer is counterbalanced. It is nevertheless remarkable that polymers from even the tetraiodobisphenol can be made in high molecular weight.

Conix and Laridon [14, 15] studied the preparation of a number of aromatic polysulfonates based on methyl-substituted derivatives of bis(4-hydroxyphenyl) methane and 4,4'-biphenyldisulfonyl chloride. They found that the softening temperature of the polymers increased

from 111-118°C for the unsubstituted polymer to 114-120°C for the polymer substituted in the ortho position by one methyl group. The more hindered ortho-dimethyl substituted bisphenol gave a polymer whose softening temperature was increased to 140-170°C, while the softening temperature for the unsymmetrically substituted 2,5-dimethyl polymer was only to 100-105°C.

It was the objective of this work to establish the polymerizability of highly hindered bisphenols for the preparation of aromatic polyesters. Our study focused particularly on those bisphenols whose phenol rings were linked in the 2 and 2' positions. Bulky substituents such as electron-donating tertiary butyl groups and electron-withdrawing chlorine groups were selected. Similarly substituted bisphenols linked in the 4 and 4' positions were also studied for comparative purposes. The preparation of polyesters of reasonable molecular weight from such bisphenols is described here. Our work on the preparation of polycarbonates from hindered bisphenols will be discussed in a subsequent paper.

## EXPERIMENTAL PART

### Materials

#### Purification of Solvents and Reagents

The following solvents and reagents were distilled and stored over molecular sieves:\* Acetone (A), sulfolane (E), diethyl oxalate (A) and dimethyl sebacate (PB). Chloroform was washed with water and dried over calcium chloride. Benzene (F), toluene (F), 2,46 trimethylpyridine (E), pyridine (E), and quinoline (E) were distilled from metallic sodium or sodium/potassium (50/50 by wt) alloy. Dimethylformamide (DMF) (A), dimethylacetamide (DMAc) (A), dichloromethane (F), and dimethylsulfoxide (DMSO) (E) were distilled from calcium hydride, and acetonitrile (E) was distilled from phosphorus pentoxide.

The following reagents were recrystallized as indicated and dried at 0.4 mm for 1 to 2 d: Dimethylisophthalate (A) twice from water, isophthaloylchloride (A) and terephthaloylchloride (A) twice from n-hexane, bis-(4-hydroxyphenyl) methane (A) twice from dry n-hexane, 2,2'-(4-hydroxyphenyl) propane (A), 4,4'-methylene bis-(6-tert-butyl-o-cresol) (PB), 2,2'-methylene bis-(6-tert-butyl-p-cresol) (PB), 4,4'-thiobis-(6-tert-butyl-m-cresol) (PB), and 4,4'-thiobis-(6-tert-butyl-o-cresol) (PB) twice from toluene.

Bithionol [2,2'-thiobis-(4,6-dichlorophenol)] was prepared according to the method of Cooper and Godfrey [16] and recrystallized three times from toluene/ethanol.

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\*Sources: A = Aldrich Chemical Co., E = Eastman Organic Chemicals, F = Fisher Scientific Co., PB = Pfaltz and Bauer, Inc.

Distillations were carried out using a 30-cm Vigreux column equipped with a variable reflux ratio distillation head. Reduced pressure distillations were carried out with magnetic stirring and a Cartesian-type diver manostat.

All other solvents and reagents were used as received.

## Measurements

Infrared spectra were recorded on Perkin-Elmer Model 727 or Model 283 spectrophotometers. Solid samples were measured as KBr pellets and liquid samples were measured between NaCl plates. The infrared spectra of some of the polymer samples were measured as films cast directly onto a single NaCl plate from a dichloromethane solution. The peak assignments were made to the nearest  $5\text{ cm}^{-1}$ .

The  $^1\text{H}$  NMR spectra were recorded on a 60 MHz R-24 Hitachi Perkin-Elmer spectrometer. Solutions were generally 10 to 15% in deuterated chloroform, deuterated dimethylsulfoxide, deuterated acetone, or deuterated dimethylformamide.

The thermal properties of the polymers were examined on a Perkin-Elmer DSC-2 differential scanning calorimeter at a scanning rate of  $20^\circ\text{C}/\text{min}$ . The instrument was calibrated against an indium standard.

The melting points of low molecular weight compounds were measured on a MEL-TEMP capillary melting point apparatus and are uncorrected.

Microanalyses were done by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

## Preparations

### Preparation of Hindered Bisphenol Polyesters

A. Poly[4,4'-methylene bis-(6-tert-butyl-o-cresol)sebacate]. A 25-mL round-bottomed flask was charged with 1.70 g (5.0 mmol) of 4,4'-methylene bis-(6-tert-butyl-o-cresol), 1.86 g (10.0 mmol) of tri-n-butylamine and 5 mL of chloroform. To the clear solution was added 1.19 g (5.0 mmol) of sebacyl chloride in 5 mL of chloroform in one portion. The mixture was stirred for 8 h, then poured into 100 mL of methanol. The resulting yellow product was washed with methanol and dried for 48 h at 0.1 mm. A hard elastomer was obtained in a 77% yield (1.96 g), and its inherent viscosity was 0.24 dL/g (0.5% in  $\text{CHCl}_3$ ). The infrared spectrum showed absorptions at 2930 and 2850  $\text{cm}^{-1}$  (C-H stretching) and 1755  $\text{cm}^{-1}$  (C=O stretching). The  $^1\text{H}$  NMR spectrum showed absorptions at  $\delta$  1.3-1.8 (internal  $\text{CH}_2$  and  $(\text{CH}_3)_3$ , 39), 2.1 ( $\text{CH}_3$ , 6), 2.5-2.9 ( $\text{CH}_2\text{COO}$ , 4), 3.9 ( $\phi\text{-CH}_2\text{-}\phi$ , 2), and 6.9-7.2 (aromatic protons, 4).

Analysis: Calculated for  $C_{33}H_{46}O_4$ : C, 78.22%; H, 9.15%. Found: C, 76.61%; H, 9.80%.

**B. Poly[2,2'-methylene bis-(6-tert-butyl-p-cresol)sebacate].** 2,2'-Methylene bis(6-tert-butyl-p-cresol) (1.69 g, 5.0 mmol), tri-n-butylamine (1.86 g, 10.0 mmol), and sebacyl chloride (1.19 g, 5.0 mmol); yield of white elastomers was 1.67 g (67%); inherent viscosity: 0.23 dL/g (0.5% in  $CHCl_3$ ); infrared spectrum: 2930 and 2850  $cm^{-1}$  (C-H stretching) and 1755  $cm^{-1}$  (C=O stretching).  $^1H$  NMR spectrum:  $\delta$  1.2-2.0 (internal  $CH_2$  and  $(CH_3)_3$ , 31), 2.0-2.7 ( $CH_3$  and  $CH_2COO$ , 12), 3.4-3.8 ( $\phi-CH_2-\phi$ , 3), and 6.7-7.2 (aromatic protons, 4).

Analysis: Calculated for  $C_{33}H_{46}O_4$ : C, 78.22%; H, 9.15%. Found: C, 76.43%; H, 9.55%.

**C. Poly[4,4'-thiobis(6-tert-butyl-m-cresol)-sebacate].** 4,4'-Thiobis-(6-tert-butyl-m-cresol) (1.78 g, 5.0 mmol), tri-n-butylamine (1.86 g, 10.0 mmol), and sebacyl chloride (1.19 g, 5.0 mmol); yield of a colorless, leathery polymer: 2.42 g (93%); inherent viscosity: 0.59 dL/g (0.5% in  $CHCl_3$ ); infrared spectrum: 2930 and 2860  $cm^{-1}$  (C-H stretching) and 1755  $cm^{-1}$  (C=O stretching).  $^1H$  NMR spectrum:  $\delta$  1.1-2.0 (internal  $CH_2$  and  $(CH_3)_3$ , 41), 2.1-2.8 ( $CH_3$  and  $CH_2COO$ , 16), and 6.8-7.4 (aromatic protons, 4).

Analysis: Calculated for  $C_{32}H_{44}O_4S$ : C, 73.24%; H, 8.45%; S, 6.11%. Found: C, 72.67%; H, 9.17%; S, 5.85%.

**D. Poly[4,4'-thiobis-(6-tert-butyl-o-cresol)-sebacate].** 4,4'-Thiobis-(6-tert-butyl-o-cresol) (1.79 g, 5.0 mmol), tri-n-butylamine (1.86 g, 10.0 mmol), and sebacyl chloride (1.19 g, 5.0 mmol); yield of a light yellow, leathery polymer: 2.35 g (90%); inherent viscosity: 0.65 dL/g (0.5% in  $CHCl_3$ ); infrared spectrum: 2930 and 2850  $cm^{-1}$  (C-H stretching) and 1755  $cm^{-1}$  (C=O stretching).  $^1H$  NMR spectrum:  $\delta$  1.1-2.2 (internal  $CH_2$ ,  $(CH_3)_3$ , and  $CH_3$ , 51), 2.3-2.8 ( $CH_2COO$ , 6), and 7.0-7.4 (aromatic protons, 5).

Analysis: Calculated for  $C_{32}H_{44}O_4S$ : C, 73.24%; H, 8.45%; S, 6.11%. Found: C, 72.19%; H, 8.34%; S, 6.18%.

#### E. Bithionol Polyesters

**1. Poly(bithionol sebacate), Procedure I.** A 25-mL round-bottomed flask was charged with bithionol (1.83 g, 5.2 mmol), tri-n-butylamine (2.02 g, 10.9 mmol), and chloroform (10 mL) to give a clear yellow solution. Sebacyl chloride (1.23 g, 5.2 mmol) in chloroform (5 mL) was added in one portion. The reaction mixture became warm and a precipitate began forming. After 14 h the mixture was poured into 250 mL of methanol. The resulting fluffy white precipitate was filtered, washed with methanol, and dried at 20 mm. The yield of polymer was 2.29 g (85%) and the inherent viscosity was 0.18 dL/g (0.5% in DMAc). The infrared and  $^1H$  NMR spectra were identical to those described in Procedure II.

**Procedure II.** A 6-in test tube was charged with 3.56 g (10.0 mmol) of bithionol and 2.31 g (10.0 mmol) of dimethylsebacate. The tube was alternately evacuated and flushed with nitrogen a total of 4 times. Leaving nitrogen flowing slowly through the tube, the contents were

heated to 205°C over a period of 1.5 h where they were left for 4.5 h. The pressure was then lowered to 20 mm and left for 12 h. After 3 more hours at 3 mm, the viscous, slightly colored polymer was cooled and gave a hard glass which was dissolved in dichloromethane (40 mL), precipitated into 350 mL of methanol, and gave 4.9 g (94%) of a white powder with an inherent viscosity of 0.56 dL/g (0.5% in DMAc). The infrared spectrum showed absorptions at 2930 and 2850  $\text{cm}^{-1}$  (C-H stretching), and 1775  $\text{cm}^{-1}$  (C=O stretching). The  $^1\text{H}$  NMR spectrum showed peaks at  $\delta$  1.3 (internal  $\text{CH}_2$ , 8H), 1.7 ( $\text{CH}_2\text{CH}_2\text{COO}$ , 4H), 2.6 ( $\text{CH}_2\text{COO}$ , 4H), and 7.1-7.6 (aromatic protons, 4H).

Analysis: Calculated for  $\text{C}_{22}\text{H}_{20}\text{Cl}_4\text{O}_4\text{S}$ : Cl, 27.15%. Found: Cl, 27.41%.

**2. Poly(bithionol isophthalate), Procedure I.** Bithionol (3.57 g, 10.0 mmol), tri-*n*-butylamine (3.89 g, 21.0 mmol), and isophthaloylchloride (2.04 g, 10.0 mmol); yield: 4.70 g (97%) of a white polymer; inherent viscosity: 0.02 dL/g (0.5% in  $\text{CHCl}_3$ ). This procedure was repeated using DMAc in place of chloroform and gave 4.52 g (93%) of polymer; inherent viscosity: 0.06 dL/g (0.5% in  $\text{CHCl}_3$ ). The infrared and  $^1\text{H}$  NMR spectra were identical to those described in Procedure IV.

**Procedure II.** Bithionol (3.56 g, 10.0 mmol), tetra-*n*-butylammonium bromide (0.20 g, 0.6 mmol), and sulfolane (15 mL) were charged into a 50-mL round-bottom flask. The contents were heated to 185°C and gave a clear, light yellow solution. Isophthaloylchloride (2.03 g, 10.0 mmol) in sulfolane (10 mL) was then added during 30 min while nitrogen was continuously bubbled through the solution. After 24 h the viscous reaction mixture, containing a considerable amount of colored precipitate, was cooled and poured into 300 mL of methanol; 4.59 g (94%) of an insoluble beige polymer was obtained. The infrared  $^1\text{H}$  NMR spectra were identical to those described in Procedure IV.

**Procedure III.** A 1-quart Waring blender was charged with bithionol (3.56 g, 10.0 mmol), sodium hydroxide (0.81 g, 20.0 mmol), tetra-*n*-butylammonium bromide (0.66 g, 2.1 mmol), sodium dodecyl sulfate (1.00 g, 3.5 mmol), water (110 mL), and chloroform (10 mL). To the rapidly stirred solution was added 2.03 g (10.0 mmol) of isophthaloyl chloride in 20 mL of chloroform. After stirring for 20 min the emulsion was broken by adding methanol (200 mL). The resulting precipitate was filtered, washed with water and methanol, and dried at 20 mm. The yield of polymer was 4.87 g (100%) and the inherent viscosity was 0.07 dL/g (0.5% in DMAc). The infrared and  $^1\text{H}$  NMR spectra were identical to those described in Procedure IV.

**Procedure IV.** A 6-in. test tube was charged with 3.56 g (10.0 mmol) of bithionol and 1.94 g (10.0 mmol) of dimethylisophthalate. After alternately evacuating and flushing with nitrogen 4 times, the contents were heated to 205°C over a period of 1.5 h. While nitrogen was passed through the reaction melt the mixture was left at 205°C for 4.5 h, after which the pressure was lowered to 20 mm. After 12 h the pressure was lowered to 3 mm and left for an additional 3 h. The melt was cooled, resulting in a hard, glassy product which was

dissolved in DMAc (50 mL) and precipitated into 400 mL of methanol and gave 4.87 g (100%) of beige-colored polymer with an inherent viscosity of 0.38 dL/g (0.5% in DMAc). The infrared spectrum showed absorptions at 3070  $\text{cm}^{-1}$  (aromatic C-H stretching), 1760  $\text{cm}^{-1}$  (C=O stretching), and 1195  $\text{cm}^{-1}$  (C-O stretching). The  $^1\text{H}$  NMR showed broad absorptions at  $\delta$  7.0-8.3 (aromatic protons).

Analysis: Calculated for  $\text{C}_{30}\text{H}_8\text{Cl}_4\text{O}_4\text{S}$ : Cl, 29.17%. Found: 29.70%.

#### F. Bithionol Polymers Containing Phosphorus

1. Poly(bithionol phenylphosphate). A 6-in. test tube was charged with 7.95 g (22.3 mmol) of bithionol and 4.71 g (22.3 mmol) of phenyl-dichlorophosphate. After alternately evacuating and flushing the tube with nitrogen 5 times, the tube was lowered into an oil bath held at 205°C. When the contents had melted, nitrogen was passed through the melt to ensure mixing. The mixture gradually became more viscous. After 6 h the pressure was lowered to 20 mm where it was held for 12 h. The temperature was then raised to 235°C and the pressure lowered to 3 mm. After 6 h the tube was removed from the oil bath and cooled. The hard, glassy product was dissolved in 30 mL of dichloromethane, filtered and poured into 200 mL of 80% methanol, and gave 8.4 g (76%) of white powdery powder with an inherent viscosity of 0.19 dL/g (0.5% in DMAc). The infrared spectrum showed absorptions at 3070 (aromatic C-H stretching), 1435  $\text{cm}^{-1}$  (aromatic C-C stretching), 1305  $\text{cm}^{-1}$  (P=O stretching), and 1190  $\text{cm}^{-1}$  (P-O stretching). The  $^1\text{H}$  NMR showed absorptions at  $\delta$  7.2-7.7 (aromatic protons).

Analysis: Calculated for  $\text{C}_{18}\text{H}_9\text{Cl}_4\text{O}_4\text{PS}$ : Cl, 28.70%. Found: Cl, 28.51%.

2. Poly(bithionol phenylphosphonate). Bithionol (7.45 g, 20.9 mmol) and phenylphosphonic dichloride (4.07 g, 20.9 mmol) gave a beige polymer in 57% yield: 5.7 g; inherent viscosity: 0.08 dL/g (0.5% in DMAc); infrared spectrum: 3060  $\text{cm}^{-1}$  (aromatic C-H stretching), 1430  $\text{cm}^{-1}$  (aromatic C-C stretching), and 910  $\text{cm}^{-1}$  (P-O stretching).

Analysis: Calculated for  $\text{C}_{18}\text{H}_9\text{Cl}_4\text{O}_3\text{PS}$ : Cl, 29.66%. Found: Cl, 29.21%.

3. Poly(bithionol phenylphosphinate). Bithionol (7.64 g, 21.5 mmol), and dichlorophenylphosphine (3.84 g, 21.5 mmol) gave a yield of 1.9 g (19%) of a tacky, orange polymer; inherent viscosity: 0.16 dL/g (0.5% in DMAc); infrared spectrum: 3400 and 3340  $\text{cm}^{-1}$  (O-H stretching), 3070  $\text{cm}^{-1}$  (aromatic C-H stretching), 1455  $\text{cm}^{-1}$  (aromatic C-C stretching) and 1220  $\text{cm}^{-1}$  (P-O stretching).  $^1\text{H}$  NMR:  $\delta$  6.9 and 7.2 (bithionol aromatic protons, 19) and 7.4-8.0 (phosphinate aromatic protons, 26).

Analysis: Calculated for  $\text{C}_{18}\text{H}_9\text{Cl}_4\text{O}_2\text{PS}$ : Cl, 30.69%. Found: 34.10%.

## RESULTS AND DISCUSSION

During the course of this work it was found that reaction of diacid chlorides with hindered bisphenols resulted in the formation of



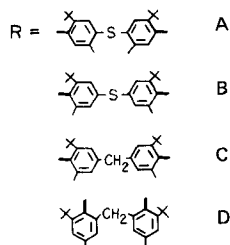
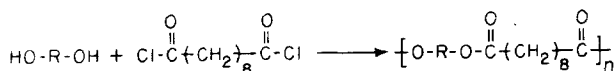


FIG. 1. Synthesis of polymers from hindered bisphenols.

TABLE 1. Preparation of Polyesters<sup>a</sup> from Hindered Bisphenols

Bisphenol <sup>c</sup>	Yield (%)	$\eta_{inh}^b$ (dL/g)
A	67	0.23
B	77	0.24
C	93	0.59
D	90	0.65

<sup>a</sup>Polysebacate prepared from bisphenol and sebacyl chloride.

<sup>b</sup>0.5% in  $\text{CHCl}_3$ .

<sup>c</sup>See Fig. 1.

polyesters of low to moderate molecular weight. A number of polymerization reactions were carried out using bisphenols which were substituted in the 2 and 2' or the 4 and 4' positions (Fig. 1). Two of the bisphenols had a thioether group linking the two phenolic moieties, and two had a methylene link. The bisphenols were sterically hindered, having methyl and/or tert-butyl substituents in positions ortho to the phenolic hydroxyl groups. All of the bisphenols used are currently utilized as antioxidants and their behavior as polymer intermediates were of interest.

The hindered bisphenols were condensed with sebacyl chloride in chloroform solution with tri-*n*-butylamine as the acid acceptor. The purity of the solvent, base, and acid chloride were checked by carrying out a test polymerization with 2,2-(4-hydroxyphenyl)propane

(bisphenol A) as the bisphenol. Polyesters with an inherent viscosity of 0.83-0.98 dL/g (0.5% in  $\text{CHCl}_3$ ) were readily obtained.

The results of the polymerizations with the hindered bisphenols are shown in Table 1. It is clear that the position of the linkage of the phenol groups had little effect on the polymerizability of either of the isomeric methylene bisphenols. Both polymerizations gave materials in similar yields and with about the same inherent viscosities. The nature of the group joining the two phenol rings, however, seemed to play a significant role in the polymerization reaction as the thiobisphenols produced polyesters in higher yields and with higher molecular weights than did the methylene bisphenols. It was thus demonstrated that bisphenols with a considerable amount of steric hindrance can still be polymerized to polyesters of reasonable molecular weight.

In light of these results and because 2,2-thiobis-(4,6-dichlorophenol) phenol (bithionol) was of particular interest to us, the introduction of this group into the backbone of a polyester of at least reasonable molecular weight was highly desirable. Although high molecular weight polymers were eventually prepared, a number of factors were seen as possibly having contributed to the difficulties which were encountered when the initial attempts were made to incorporate bithionol into polyesters. Bithionol has the phenolic hydroxyl groups ortho to the thioether linking group, whereas most bisphenols used for the commercial production of polyester and polycarbonate engineering plastics have the phenolic hydroxyl groups para to the linkage. The coupling of the two phenolic rings ortho to the hydroxyl groups in bithionol could clearly have an effect on its chemical behavior and reduce its polymerizability. Bithionol is additionally substituted in the remaining positions ortho to the phenolic hydroxyl groups. The steric hindrance was expected to substantially decrease the ease with which bithionol underwent polymerization. Bithionol's substituents include four electron-withdrawing chlorine atoms, which makes the bisphenol considerably more acidic. An increase in acidity usually results in a decrease in the reactivity of phenolic compounds. Finally, the two phenolic rings in bithionol are connected with a sulfur atom, and it was not clear what effect this might have on the polymerizability of the compound in light of the other structural features also present.

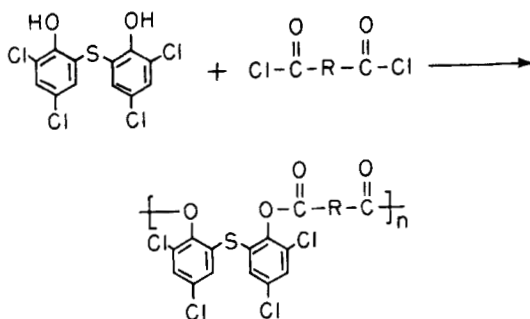
Our studies on the polymerization of bithionol as well as other bisphenol model compounds seemed to indicate that the inductive effect of the four electron-withdrawing chlorine groups and the consequent increase in acidity of the bisphenol bithionol was primarily responsible for the low molecular weights obtained in polymerizations involving bithionol. An examination of the literature reveals numerous examples of the polymerization of ortho halo-substituted bisphenols to high molecular weight polymers [5, 6]. There is no report in the literature, however, on the use of a tetrachlorosubstituted 2,2'-bisphenol in a condensation polymerization; all reports are concerned with 4,4'-bisphenols. In light of these results, it seemed that the

difficulty in producing high molecular weight polymers from some of the polymerization reactions carried out with bithionol may not have been exclusively due to any one of the factors mentioned, but may have actually been the result of a combination of all of them.

Bithionol was prepared according to the procedure of Cooper and Godfrey [16]. 2,4-Dichlorophenol and sulfur dichloride were condensed in carbon tetrachloride using an aluminum chloride catalyst to give a 43% yield of bithionol after purification by recrystallization. The infrared and  $^1\text{H}$  NMR spectra were identical to those presented in the literature [17, 18]. The ultraviolet spectrum was recorded in an aqueous buffer at pH 10.0; absorption maxima were observed at 318 and 226 nm with molar extinction coefficients of  $1.58 \times 10^4$  and  $6.75 \times 10^4$  L/mol cm, respectively. In methanol solution, bithionol has been shown [19] to have absorption maxima at 307 and 208.5 nm. The bathochromic shift of the absorption maxima in dilute base can be attributed to the additional pair of nonbonding electrons in the phenolate anion that are available for interaction with the  $\pi$ -electron system of the phenol rings.

In order to produce various polyesters of bithionol, the acid chlorides of oxalic, malonic, succinic, fumaric, adipic, sebacic, isophthalic, and terephthalic acids were individually mixed with equimolar portions of bithionol in chloroform with tri-*n*-butylamine as the acid acceptor (Fig. 2). All mixtures formed precipitates during the course of the polymerization reactions. The mixture containing oxalyl chloride formed a white precipitate within a few minutes, while the mixtures containing malonyl and succinyl chloride formed orange and dark blue-black precipitates, respectively, also within a few minutes. The presence of fumaryl chloride, however, caused an immediate thickening of the reaction mixture with the formation of a dark solid mass. Rapid reactions of that type are characteristic of highly reactive aliphatic acid chlorides. The immediate formation of a precipitate was an indication of the insolubility of even low molecular weight polymers. The formation of colored reaction mixtures was indicative of the occurrence of side reactions. When the more flexible and less reactive adipyl and sebacyl chlorides were used, however, precipitates formed much less readily, and the precipitates were swollen in the reaction media. Precipitates formed in the reactions of bithionol with isophthaloyl or terephthaloyl chloride formed slowly and were white in color. The yield and inherent viscosity of the product isolated from each of the reaction mixtures are listed in Table 2. As can be seen, low molecular weight materials were obtained in all cases with the exception of the product from the reaction of bithionol and sebacyl chloride, which had an inherent viscosity of 0.18 dL/g. This result was consistent with the increased solubility of the oligomeric reaction products and the lower reactivity of the acid chloride used in the polymerization reaction.

The technique used to prepare bithionol polyesters was also found to have a great influence on both the yield and molecular weight of the polymers. As can be seen from the data in Table 2, both solution



R = Oxalate

—CH<sub>2</sub>—

—CH<sub>2</sub>CH<sub>2</sub>—

/CH=CH/

—(CH<sub>2</sub>)<sub>4</sub>—

—(CH<sub>2</sub>)<sub>8</sub>—



FIG. 2. Synthesis of bithionol polyesters.

TABLE 2. Preparation of Bithionol Polyesters from Bithionol and Diacid Chlorides

Acid chloride	Yield (%)	$\eta_{inh}^a$ (dL/g)
Oxalyl	60	0.08
Malonyl	55	0.05
Succinyl	86	0.07
Fumaryl	78	0.03
Adipoyl	52	0.08
Sebacyl	85	0.18
Isophthaloyl	97	0.02
Terephthaloyl	92	Insoluble

<sup>a</sup>0.5% in DMAc.

TABLE 3. Preparation of Bithionol Polyesters: Effect of Various Polymerization Techniques on Molecular Weight<sup>a</sup>

Polyester	$\eta_{inh}^b$ (dL/g)	Polymerization technique
Adipate <sup>c</sup>	0.05	Solution
Adipate	0.18	Interfacial
Sebacate <sup>d</sup>	0.56	Melt
Isophthalate	0.06	Solution
Isophthalate	Insoluble	High temperature solution
Isophthalate	0.07	Interfacial
Isophthalate <sup>d</sup>	0.38	Melt

<sup>a</sup>Bithionol + diacid chloride (quantitative yield).

<sup>b</sup>0.5% in DMAc.

<sup>c</sup>65% yield.

<sup>d</sup>Bithionol + dimethyl ester.

and interfacial polymerization techniques gave low molecular weight polymers, although the yields of polymer were nearly quantitative.

It was found that higher molecular weight bithionol polyesters could be prepared by a melt polycondensation procedure (Table 3), however. This technique utilized the dimethyl esters of sebacic and isophthalic acids in place of the respective acid chlorides. The melt polycondensations were performed at 205°C. After 6 h at atmospheric pressure nearly all of the by-product methanol had distilled from the reaction mixtures, after which the pressure was lowered to 20 mm. After an additional 12 h the pressure was lowered to 3 mm to remove the last traces of methanol and complete the polycondensation. In this manner, poly(bithionol sebacate) and poly(bithionol isophthalate) with inherent viscosities of 0.56 and 0.38 dL/g were produced in yields of 94 and 100%, respectively.

The poly(bithionol polysebacate) displayed a weak absorption in the infrared spectrum at 3075  $\text{cm}^{-1}$  corresponding to aromatic C-H stretching and stronger absorptions at 2930 and 2850  $\text{cm}^{-1}$  corresponding to aliphatic C-H stretching; a carbonyl absorption at 1775  $\text{cm}^{-1}$ , typical of aliphatic/aromatic polyesters, was also observed. The <sup>1</sup>H NMR spectrum showed three multiplets assignable to methylene protons, one centered at  $\delta$  1.35 corresponding to internal methylene protons, one centered at  $\delta$  1.65 and partially superimposed on

O

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the first multiplet corresponding to  $\underline{\text{CH}}_2\text{CH}_2\text{C}-\text{O}$  protons, and one

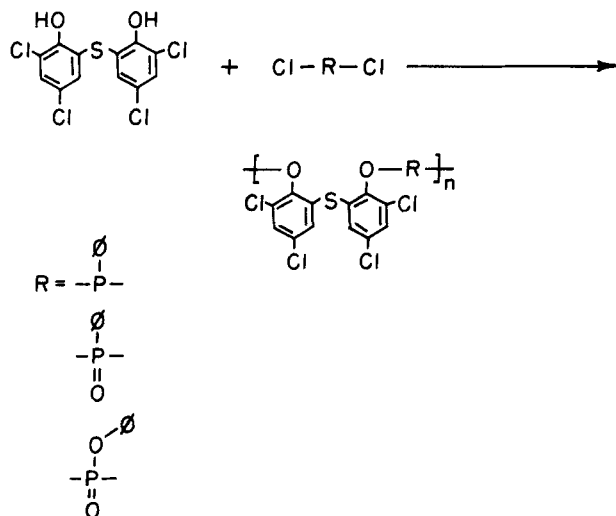


FIG. 3. Synthesis of bithionol polymers containing phosphorus.

centered at  $\delta$  2.6 due to  $\text{CH}_2\text{C}=\text{O}$  protons; a symmetrical multiplet due to the aromatic protons in the polymer was observed centered around  $\delta$  7.3. The ratio of integrated peak areas was consistent with the proposed structure.

The infrared spectrum of poly(bithionol isophthalate) displayed a weak absorption at  $3070 \text{ cm}^{-1}$ , characteristic of aromatic C-H stretching, a strong carbonyl stretching absorption at  $1760 \text{ cm}^{-1}$ , typical of aromatic/aromatic polyesters, and a strong absorption in the C-O stretching region at  $1195 \text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum showed an overlapping of multiplets due to aromatic protons from  $\delta$  7.0 to 8.3.

Three polymers containing both bithionol moieties and phosphorus, in the main chain, were synthesized as illustrated in Fig. 3. The preparations were carried out as melt polycondensations of bithionol with phenyldichlorophosphate, phenylphosphonic dichloride, and dichlorophenylphosphine. The synthetic procedures were relatively straightforward and all preparations were performed simultaneously and under identical conditions. The polymerizations were carried out in three test tubes, each tube containing equimolar portions of bithionol and one of the phosphorus dichloride compounds mentioned above. The tubes were heated under nitrogen at  $205^\circ\text{C}$  for 6 h, after which the pressure was lowered to 20 mm where it was held for an additional 12 h. The reactions were completed by raising the temperature to  $235^\circ\text{C}$  while lowering the pressure to 1 mm over a 1-h period. During the course of the reactions, some gas bubbles were observed

escaping from the increasingly viscous melts. When cooled, all of the polymers formed pale orange glasses which were dissolved in dichloromethane and precipitated into methanol. Poly(bithionol phenylphosphate) was obtained as a white powder in 76% yield with an inherent viscosity of 0.19 dL/g. The poly(bithionol phenylphosphate), on the other hand, was obtained as a beige powder in 57% yield and an inherent viscosity of only 0.08 dL/g. The poly(bithionol phenylphosphate) was a tacky orange polymer obtained in 19% yield and with an inherent viscosity of 0.16 dL/g. The identity of the polymers was confirmed by infrared and  $^1\text{H}$  NMR spectra as well as by microanalysis.

Poly(bithionol phenylphosphate) showed a weak absorption in the infrared at  $3070\text{ cm}^{-1}$  attributed to C-H stretching, as well as stronger absorptions corresponding to aromatic C-C stretching at  $1435\text{ cm}^{-1}$ , P=O stretching at  $1305\text{ cm}^{-1}$ , and P-O stretching at  $1190\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR showed multiplets due to aromatic protons at  $\delta$  7.2-7.7. The multiplets were superimposed on one another, however, making their respective integrations impossible.

The infrared spectrum of poly(bithionol phenylphosphonate) displayed a weak absorption in the aromatic C-H stretching region at  $3060\text{ cm}^{-1}$ , as well as stronger absorptions in the aromatic C-C and P-O stretching regions at  $1430$  and  $910\text{ cm}^{-1}$ , respectively. The  $^1\text{H}$  NMR spectrum was similar to that of poly(bithionol phenylphosphate) with differentiation of the aromatic proton multiplets impossible due to significant overlap.

The infrared spectrum of poly(bithionol phenylphosphinate) showed strong phenolic O-H stretching at  $3400$  and  $3340\text{ cm}^{-1}$ . A weak absorption at  $3070\text{ cm}^{-1}$  and a moderate absorption at  $1455\text{ cm}^{-1}$  were attributed to aromatic C-H and C-C stretching, respectively. The  $^1\text{H}$  NMR spectrum showed the expected aromatic proton multiplets centered at  $\delta$  7.1 and 7.5. The strong absorptions in the infrared spectrum at  $3400$  and  $3340\text{ cm}^{-1}$  indicated that the polymer was end-capped with bithionol phenolic groups. The polymer was also found to have a Cl content of 34.10%, an increase of 3.41% over the theoretical content of 30.69% Cl, further evidence of the presence of bithionol end groups in the polymer of relatively low molecular weight. A degree of polymerization of 8-10 was calculated from the microanalytical data.

#### ACKNOWLEDGMENTS

This work was supported by the National Science Foundation, in part under a grant of the Materials Research Laboratory. We would like to thank W. Harris for his assistance in preparing this manuscript.

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Accepted by editor July 31, 1980

Received for publication September 4, 1980