

# Synthesis and Characterization of Some Aromatic Polyphosphonates

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## Synopsis

Novel aromatic polyphosphonates are synthesized by polycondensation of chloromethyl (methyl, phenyl) phosphonic dichloride with bisphenols using three procedures: melt, solution, and phase transfer catalysis. The molecular weights and spectral characteristics are presented. Mixtures of the polyphosphonates with polyacrylonitrile and nylon 66 are compatible only when the chloromethyl group is present. Eight percent of polyphosphonate in the mixture confers flame resistance to the polymers.

## INTRODUCTION

Polycondensation of bisphenols with phosphonic acid dichlorides generates aromatic polyphosphonates. The polycondensation procedure is important for achieving high molecular weights. Known procedures include melt,<sup>1</sup> interfacial,<sup>2</sup> solution<sup>3</sup> and phase transfer catalyzed<sup>4,5</sup> polycondensations. Of the phosphonic acid dichlorides, phenyl phosphonic dichloride (PPD) is the most widely used, probably because it improves the thermal stability by bringing one more aromatic nucleus into the polymer structure. Chloromethylphosphonic dichloride (CMPD) was used to study the mechanism of melt polycondensation by NMR.<sup>1</sup>

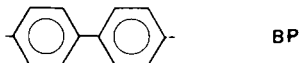
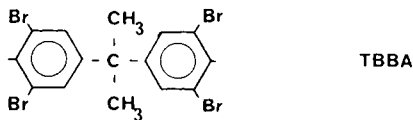
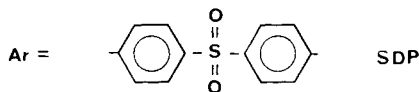
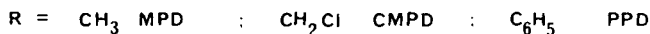
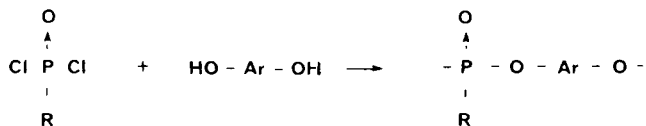
These polyphosphonates are noncombustible thermoplastic materials that are generally used as flame retardants.<sup>6</sup> Their possible use as high performance plastics was proposed recently.<sup>5</sup>

In the present study we use CMPD polycondensation with a series of bisphenols: 4,4'-sulfonyldiphenol (SDP); 2,2'-bis(3,5-dibromo-4-hydroxyphenyl)propane (tetrabromobisphenol A) (TBBA); 4,4'-biphenol (BP); and 2,7-dihydroxynaphthalene (2,7DHN). For comparison, polyphosphonates with PPD and methylphosphonic dichloride (MPD) are also synthesized and characterized.

The influence of the polycondensation procedure on the polyphosphonate molecular weight is presented together with the spectral characterization of the polymers obtained. The thermal stability in nitrogen and in air and the glass transition temperatures are presented elsewhere.<sup>7</sup> Mixtures of polyphosphonates and commercial polymers are being tested for their compatibility and flame resistance.

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The reaction proceeds according to the scheme



## EXPERIMENTAL

### Polycondensations

Three synthesis procedures were used: melt, solution, and phase transfer catalyzed polycondensations. Typical procedures are the following.

#### *Melt Polycondensation*

0.0376 mol phosphonic dichloride and 0.0376 mol aromatic diol were placed in a two-necked flask together with 0.075 g magnesium chloride as catalyst (0.2 g magnesium chloride to each 0.1 mol phosphonic dichloride). The mixture was kept under constant flow of argon for the whole reaction time. Reaction takes place even at room temperature at a very slow speed. A reasonable reaction rate is obtained by gradual heating (10–20°C/h) up to 180–200°C, depending on the diol used. The reaction is considered ended in ca. 11 h, and the reaction product is purified by dissolution in an appropriate solvent and reprecipitation with methanol.

### *Solution Polycondensation*

Among several solvents used for the polyphosphonate synthesis, the most suitable was tetrahydrofuran (THF). 0.0375 mol aromatic diol dissolved in ca. 60 mL THF were stirred together with 0.075 mol triethylamine in an ice-water bath. 0.0375 mol phosphonic dichloride diluted with ca. 20 mL THF were added dropwise under strong stirring. After the whole quantity was added, the reaction mixture was allowed to heat up to room temperature and subsequently heated at reflux for 3–4 h. When the polymer was soluble in THF, it was separated by filtration and precipitation with methanol. When the polymer was insoluble in THF, the precipitate was washed thoroughly with water, and then purified by reprecipitation.

### *Phase Transfer Catalyzed Polycondensation*

0.0375 mol aromatic diol were dissolved in approximately 20 mL 3*N* solution NaOH together with the phase transfer catalyst (PTC) tetrabutylammonium hydrogen sulphate (TBAH). The mixture was vigorously stirred in an ice–salt bath. Because of the increasing viscosity of the reaction medium during the reaction, addition of the organic solvent prior to addition of the phosphonic dichloride was sometimes necessary. The phosphonic dichloride (0.0375 mol) diluted with ca. 20 mL organic solvent (chloroform, toluene, *o*-dichlorobenzene) was added dropwise and the temperature was strictly maintained at –5–8°C in order to avoid basic hydrolysis of the phosphonic dichloride or of the polyphosphonate. In several cases, the appearance and disappearance of the phenolate anion (green) could be observed. If the polymer was soluble in the organic solvent, the reaction mixture was separated in a separatory funnel, the organic layer was washed with water to neutral pH, and the polymer was precipitated with methanol. If the polymer precipitated during synthesis, the precipitate was washed with water and then purified by reprecipitation.

### **Instrumental Methods**

FTIR spectra were registered on a Nicolet MX-1 spectrophotometer. Gel permeation chromatograms were obtained in THF on columns calibrated according to the polystyrene universal standard. Viscosities were measured on THF solutions (0.05g/dL) at 25°C. NMR spectra were recorded on Varian CFT-20 (proton) and Bruker WH-90 (phosphorus) spectrometers. DSC curves were obtained on a Mettler TA 3000 system. Flame resistance was determined according to the procedure described in Ref. 8, subjecting a polymer sample to a butane flame for 10 s and measuring the burning time and the ashes.

### **Materials**

CMPD, PPD, MPD, SDP (Aldrich), BP, TBAH (Sigma), TBBA (Makhteshim, Israel), 2,7DNH (BDH), commercial nylon 66 (N66) (Nilit, Israel), and poly(acrylonitrile) (PAN) (Acrylan, Israel) were used as received.

## RESULTS AND DISCUSSION

Bisphenols as SDP and 2,7DHN are supposed to confer increased thermal stability,<sup>1</sup> whereas TBBA could improve the fire retardant ability of the polyphosphonate, due to the presence of bromine. Aromatic<sup>9</sup>- and aliphatic<sup>10</sup>-brominated diols are used as components for polyphosphonate synthesis. BP, along with SDP and 2,7DHN, are supposed to increase the probability of generating a crystalline structure.

CMPD was selected in order to obtain polyphosphonates with a reactive group (chloromethyl). Of the polyphosphonates described in the present article, PPD-BD was already reported.<sup>5</sup> Melt synthesis of CMPD-TBBA<sup>11</sup> and CMPD-2,7DHN<sup>1</sup> was reported, but the polymers were not completely characterized. As part of the present project, the mechanism of melt polycondensation of SDP with CMPD and MPD<sup>12</sup> is to be published separately.

## Molecular Weight

Table I summarizes the average degree of polymerization of the polyphosphonates, the calculated polydispersity from the GPC curves, and the inherent viscosity. One can notice the general increase in the average degree of polymerization from melt to solution and to PTC. PTC indeed generates high molecular weight polymers. However, the molecular weight distribution is not improved from solution to PTC; sometimes it is even broader.

## Spectral Characterization

Figure 1 represents the <sup>1</sup>H-NMR spectra of the polyphosphonates that are soluble in chloroform. The methyl protons of MPD resonate at 1.83 ppm in MPD-BP [Fig. 1(a)]. The doublet is due to phosphorus coupling. Another doublet, arising from the methylene protons of CMPD, appears at 3.87 ppm in CMPD-BP [Fig. 1(b)] and CMPD-2,7DHN [Fig. 1(d)], and at 4.24 ppm in CMPD-TBBA [Fig. 1(e)]. The aromatic protons resonate at 7.32 ppm and the methyl group at 1.51 ppm in CMPD-TBBA [Fig. 1(e)]. Protons of BP give signals at 7.47 ppm (inner) and 7.27 ppm (outer) when enchainned to CMPD [Fig. 1(b)]. Protons 1 and 8 of the naphthalene nucleus of 2,7DHN give a signal at 7.65 ppm, protons 3 and 6 resonate at 7.36 ppm, and protons

TABLE I  
Average Degree of Polymerization ( $DP_n$ ), Polydispersity ( $M_w/M_n$ ), and Inherent Viscosity ( $\eta_{inh}$ )

Polymer	Synthesis procedure	Melt			Solution			PTC		
		$DP_n$	$M_w/M_n$	$\eta_{inh}$	$DP_n$	$M_w/M_n$	$\eta_{inh}$	$DP_n$	$M_w/M_n$	$\eta_{inh}$
CMPD-2,7DHN	—	—	—	14	1.9	0.33	15	1.5	0.39	
CMPD-TBBA	4	1.4	0.20	6	1.5	0.38	47	1.8	0.79	
CMPD-SDP	5	1.4	0.12	2	1.1	0.08	6	1.3	0.13	
MPD-SDP	—	—	—	—	—	—	10	1.2	0.25	
MPD-BP	—	—	—	—	—	—	12	1.2	0.23	
PPD-BP	—	—	—	9	1.3	0.22	24	2.2	0.56	
CMPD-BP	—	—	—	4	1.4	0.11	12	1.4	0.31	

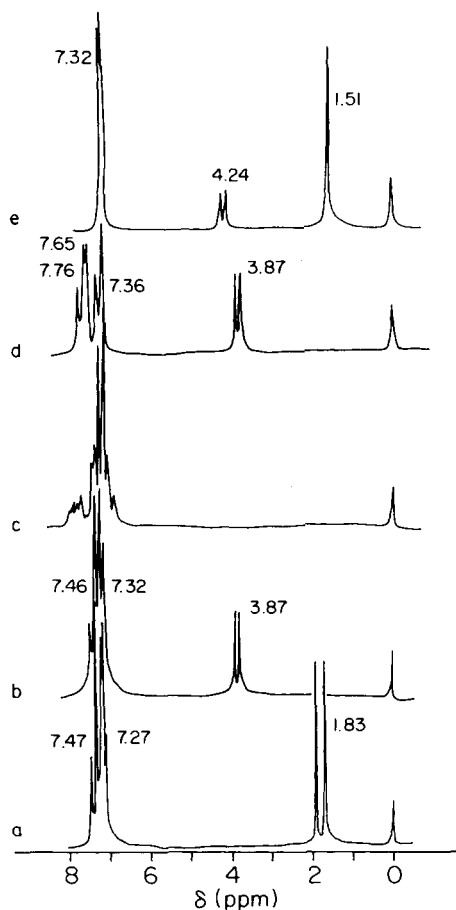


Fig. 1. Proton-NMR spectra in  $\text{CDCl}_3$  of: (a) MPD-BP; (b) CMPD-BP; (c) PPD-BP; (d) CMPD-2,7DHN; (e) CMPD-TBBA.

4 and 5 at 7.76 ppm [Fig. 1(d)]. In the spectrum of PPD-BP, [Fig. 1(c)] the only separation appears from the lowest field resonance, which is assignable to the ortho protons of the aromatic ring of the PPD.

Figure 2 represents the  $^1\text{H-NMR}$  spectra of the polyphosphonates soluble in DMSO. The methyl resonance appears at 1.97 ppm in MPD-SDP [Fig. 2(a)], whereas the methylene resonance can be seen at 4.54 ppm in CMPD-SDP [Fig. 2(b)]. There are differences in the SDP resonances also. Protons in ortho position to the sulfonyl group resonate at 7.99 ppm in MPD-SDP [Fig. 2(a)] and at 8.03 ppm in CMPD-SDP [Fig. 2(b)], whereas those in metha resonate at 7.39 ppm [Fig. 2(a)] and 7.48 ppm [Fig. 2(b)].

Phosphorus resonances are presented in Table II. The main chain signal is an intense singlet (protons are decoupled) in all the samples. Samples obtained by melt and solution polycondensation present an additional signal assignable to the phosphonic end groups. The degree of polymerization calculated from the ratio of end groups/main chain signals is approximately twice that determined by GPC (Table I). Consequently, it is reasonable to suppose that melt and solution polycondensation generate random chain ends, whereas PTC generates phenolic chain ends only.<sup>13</sup> The data in Table

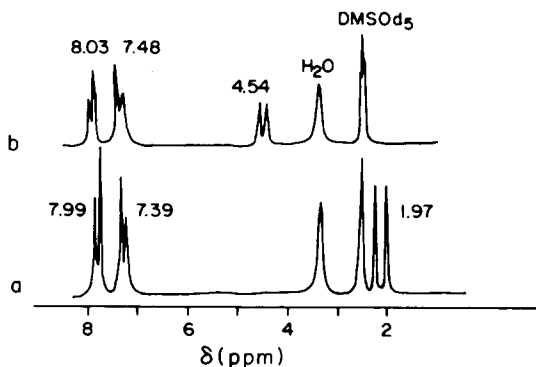


Fig. 2. Proton-NMR spectra in  $\text{DMSO}_d_6$  of: (a) MPD-SDP; (b) CMPD-SDP.

It also suggests that there are no essential differences between a chloromethyl and a phenyl group attached to the phosphorus, from the chemical shift point of view. A rather big difference arises from a methyl group. The presence of bromine in the bisphenol shifts the phosphorus signal toward lower fields by ca. 2 ppm. A lower field shift when bromine is present was noticed in the methylene proton resonance also [compare Fig. 1(e) with Figs. 1(b) and (d)].

Table III summarizes some FTIR characteristic bands for the newly synthesized polymers.

### Fireproofing of Commercial Polymers

Polyphosphonates can be used as additives for polyesters to confer flame resistance.<sup>3,8</sup> Mixing of polyphosphonates with polyesters at high temperatures, usually in melt, can produce transesterification reactions to some extent, generating a homogenous product. However, polyphosphonates confer flame resistance to acrylic and nylon polymers also.<sup>6</sup> Their use as fireproofing additives to acrylic and nylon type fibers requires the knowledge of their miscibility with the commercial polymer and the crystallinity of the resulting mixture.

An accepted criterion for polymer-polymer miscibility is the existence of a single  $T_g$  of the mixture.<sup>14</sup> Thus, 1:1 molar mixtures of polyphosphonate and N66 and PAN, respectively, were pressed into pellets which were subsequently heated to the melting temperature of N66 (PAN). The heating was performed usually in a DSC pan under nitrogen. The second DSC scan generated the glass transition temperatures which are shown in Table IV. The data in Table IV indicate that miscibility of the polyphosphonate with

TABLE II  
Phosphorus Chemical Shifts in Chloroform (Reference  $\text{H}_3\text{PO}_4$ )

Polymer	Main chain	Chain end
CMPD-2,7DHN	12.4	15.8
CMPD-TBBA	10.0	14.7
CMPD-BP	12.1	15.6
MPD-BP	24.6	27.8
PPD-BP	12.2	16.1

TABLE III  
 FTIR Characteristic Bands ( $\text{cm}^{-1}$ )

Polymer	P → O	P-O-C aromatic		Aromatic ring stretching		SO <sub>2</sub>	
CMPD-2,7DHN	1285	938	1199	1634	1509		
CMPD-TBBA	1278	933	1244	1548	1454 <sup>a</sup>		
CMPD-SDP	1290	934	1204	1588	1490	1154	573
MPD-SDP	1291	923	1206	1587	1490	1154	571
MPD-BP	1265	917	1193	1601	1490		
PPD-BP	1264	924	1195	1600	1491		
CMPD-BP	1281	935	1191	1601	1490		

<sup>a</sup> Band characteristic to halogenated benzene.

 TABLE IV  
 Glass Transition Temperatures of the Mixtures (°C)

Polymer	$T_g$	$T_g$ of the 1:1 molar mixture with	
		N66 ( $T_g = 87$ )	PAN ( $T_g = 102$ )
CMPD-2,7DHN	103	93	98
CMPD-TBBA	165	121	130
CMPD-SDP	156	117	125
MPD-SDP	92	a	a
MPD-BP	126	a	a
PPD-BP	111	a	a
CMPD-BP	100	90	97

<sup>a</sup> No single  $T_g$ .

N66 and with PAN is conferred by the chloromethyl group. Where this group is absent (MPD and PPD polymers), the mixture presents two  $T_g$ s, indicating nonmiscibility. Preliminary studies by FTIR seem to suggest an interaction between the nylon carbonyl bond and one of the methylene's hydrogens, somehow similar to the interaction between poly(vinyl chloride) and poly( $\epsilon$ -caprolactone).<sup>15</sup>

Two of the polyphosphonates (CMPD-TBBA and CMPD-BP) were mixed in different ratios with N66 and PAN, respectively, and tested for flame resistance. The results show that there is a higher minimum quantity of polyphosphonate necessary to confer flame resistance for N66 and PAN, as compared with poly(ethylene terephthalate).<sup>8</sup> This minimum quantity was found to be 8%, which corresponds to 0.8% phosphorus (CMPD-BP) or 0.4% phosphorus and 4% bromine (CMPD-TBBA).

Study of the influence of this kind of additive on the polymer crystallinity is in progress.

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