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# Polyphosphonates obtained by vapor-liquid interfacial polycondensation

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## Summary

A series of polyphosphonates were synthesized by base promoted liquid-vapor interfacial polycondensation of various alkyl (aryl) phosphonic dichlorides (methylphosphonic dichloride (MPD), cyclohexylphosphonic dichloride (CPD) and phenylphosphonic dichloride (PPD)) with different bisphenols (hydroquinone (HQ), bisphenol A (BA), 4,4′ - biphenol (BP), 1,5-naphtalenediol (ND) and 4,4′ - sulfonyldiphenol (SD)). The polyphosphonates were characterized by infrared (IR) and proton magnetic resonance ($^1$H-NMR) spectroscopy. Yields in the range of 20-80% and Mn of ~ 8500-35000 were obtained. DSC measurements show Tg in the range 95°-148°C. These polymers are soluble in solvents such as *N*,*N*-dimethylformamide, tetrahydrofuran and chloroform. Polyphosphonates were stable up 240°-300°C in air atmosphere.

## Introduction

Polyphosphonates are well known to be useful flame-retardant engineering plastics or additives of other polyesters. [1] Other interesting features of these polymers are adhesion to metals, metal ion-binding characteristics, plasticizing properties and increased polarity. [2] The alternative polycondensations in melt [3], solution [4] and liquid-liquid interfacial [5-7] gave poor results: low yields and low molecular weights ($<10^4$) were obtained. Better results were achieved in vapor-liquid (v-l) interfacial polycondensation. Sokolov [8,9] applied this system only for polyamides synthesis. Bubbling the vapor monomers through the aqueous solution of the other monomer readily performs the contact of the monomers in this system.

In a previous paper [10] we have reported the possibility of obtaining polyphosphonates by vapor-liquid interfacial polycondensation. For the reaction of cyclohexylphosphonic dichloride (CPD) with bisphenol A (BA) the optimal reaction conditions were established in order to prevent the possibility of secondary hydrolysis reactions.

Continuing our work on the application of vapor-liquid system to polyphosphonates synthesis, we present here the synthesis and characterization of other polyphosphonates by vapor-liquid interfacial polycondensation.

Despite the low vapor pressures of substituted phosphorus acid chlorides, the following alkyl (aryl) phosphonic dichlorides (PD) were employed: methylphosphonic dichloride (MPD), cyclohexylphosphonic dichloride (CPD), phenylphosphonic dichloride (PPD). In order to prepare polymers with higher $T_g$s, the bisphenols containing structures, such: hydroquinone (HQ), bisphenol A (BA), 4,4′ - biphenol (BP), 1,5 naphtalenediol (ND) and 4,4′ - sulfonyldiphenol (SD) were selected.

## Experimental

Alkyl and arylphosphonic dichlorides and bisphenols were supplied by Aldrich and were used without further purification.

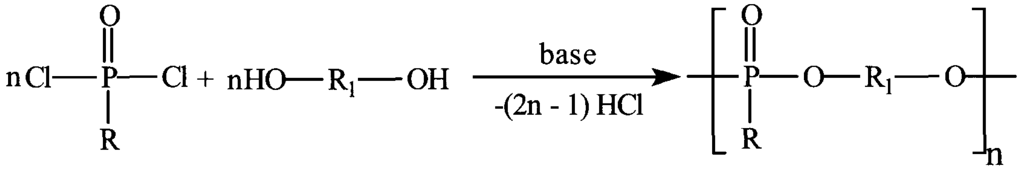
The general procedure of the vapor-liquid interfacial polycondensation of CPD with BA was presented previously. [10] Since phosphonic dichlorides are more volatile than bisphenols they are employed in the vapor phase mixed with nitrogen. The stream of nitrogen protects the system from oxygen, provides agitation, transports vapors of the phosphonic dichloride and controls the rate of reaction. The solvent for bisphenols is water. The formed polymer is separated by filtration, washed with water and dried.

### *Instruments*

The IR and $^1H$- NMR spectra were recorded on a SPECORD M80 spectrophotometer (film) and a JEOL-C-60 MHz spectrometer ($CDCl_3$), respectively. The inherent viscosities of polymers were determined for solutions of 0.5 g/100mL in tetrachloroethane, at 30ºC using an Ubbelohde suspended level viscosimeter. Molecular weight was determined by gel permeation chromatography, on an Evaporative Light Scattering Detector: PL-EMD 950. Glass-transition temperature (Tg) was determined by differential scanning calorimeter method (DSC), on a Seiko DSC 220 device. The thermogravimetrical analyses were carried out on a PAULIK-PAULIK-ERDEY THERMAL ANALYZER (MOM Budapest) by heating in air from initial temperature of 20ºC to 600ºC with a rate of 12º/min

## Results and discussion

In our previous paper [10] it was demonstrated that vapor-liquid interfacial polycondensation was useful for the preparation of polyphosphonates with molecular weights ~ $10^4$. Therefore, this method was applied to the vapor-liquid interfacial polycondensation of various phosphonic dichlorides (PD) with bisphenols (B) to give polyphosphonates (reaction 1).



$$n\,Cl-\underset{R}{\underset{|}{\overset{\overset{O}{\|}}{P}}}-Cl + n\,HO-R_1-OH \xrightarrow[-(2n-1)\,HCl]{base} \left[ -\underset{R}{\underset{|}{\overset{\overset{O}{\|}}{P}}}-O-R_1-O- \right]_n \qquad \textbf{(1)}$$

$R = CH_3; C_6H_{11}; C_6H_5$

$R_1 = C_6H_4; C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4; C_6H_4\text{-}C_6H_4; C_{10}H_8; C_6H_4\text{-}SO_2\text{-}C_6H_4$

Table 1 shows the yields and inherent viscosities for the obtained polyphosphonates. The most appropriate conditions for the synthesis of high-molecular weight polymers by this method are as follows [10]: reaction temperature 50° C (temperature of reaction mixture in flask 2, Figure 1, see [10]), molar ratio PD : B = 2.7 :1, 1M $NaOH_{aq}$.

Table1. Reaction conditions and results of vapor-liquid interfacial polycondensation of various phosphonic dichlorides with bisphenols[a]

| Polym. | PD | B | $T^b$ | Yield | $\eta_{inh}$ | %P | |
|---|---|---|---|---|---|---|---|
| | | | °C | % | dl/g | calc. | exp |
| $P_1$ | MPD | HQ | 65 | 22 | 0.15 | 10.84 | 6.80 |
| $P_2$ | MPD | BA | 65 | 28 | 0.18 | 10.76 | 7.50 |
| $P_3$ | MPD | BP | 65 | 32 | 0.45 | 12.60 | 7.60 |
| $P_4$ | MPD | ND | 65 | 44 | 0.48 | 14.09 | 8.35 |
| $P_5$ | MPD | SD | 65 | 24 | 0.16 | 10.00 | 6.90 |
| $P_6$ | CPD | HQ | 70 | 72 | 0.90 | 13.02 | 12.08 |
| $P_7$ | CPD | BA | 70 | 85 | 0.95 | 8.70 | 8.20 |
| $P_8$ | CPD | BP | 70 | 75 | 1.80 | 9.87 | 9.50 |
| $P_9$ | CPD | ND | 70 | 80 | 2.30 | 10.78 | 10.15 |
| $P_{10}$ | CPD | SD | 70 | 48 | 0.75 | 8.20 | 7.90 |
| $P_{11}$ | PPD | HQ | 80 | 65 | 0.98 | 13.36 | 13.05 |
| $P_{12}$ | PPD | BA | 80 | 70 | 1.10 | 8.85 | 8.50 |
| $P_{13}$ | PPD | BP | 80 | 62 | 1.93 | 9.01 | 8.90 |
| $P_{14}$ | PPD | ND | 80 | 73 | 2.50 | 10.99 | 10.80 |
| $P_{15}$ | PPD | SD | 80 | 54 | 1.02 | 8.33 | 7.80 |

[a] reaction conditions: 0.108 moles PD, 0.040 moles B, 0.220 moles NaOH 1M, 50-70 minutes, reaction temperature 50°C;

[b] Tb = temperature of phosphonic dichloride maintained by an oil bath (flask 1, Figure 1, see [10]);

[c] The inherent viscosities $\eta_{inh}$ were determined for solutions of 0.5 g/100mL in tetrachloroethane, at 30°C

Solvent is not required in this synthesis and for that reason the auxiliary procedures in v-l interfacial polycondensation are simplified considerably: only ionic impurities (i.e. NaCl) needs to be washed from the polymer. After a definite time of reaction (usually 50-70 minutes) the polymer is filtered from the liquid phase and washed. The polymers obtained by this technique contain strongly adsorbed water, which should be removed prior to further polymer characterization or processing. This can be achieved by drying under vacuum. Polyphosphonates with high inherent viscosities ($P_6$-$P_{15}$), as a film covering on a gas bubble passing through the liquid layer, or polyphosphonates with low inherent viscosities ($P_1$ –$P_5$), as a fine dispersed powder, will be formed depending on utilized reagents.

Yields in the range 20-80% were obtained. Inherent viscosity measurements showed that varied from 0.20 – 2.50 dl/g. The polyphosphonates ($P_1$-$P_5$) derived from MPD have the lowest values obtained, which suggests that PPD and CPD are less succeptible than MPD to saponification. This is consistent with the expected lower hydrophilicity of CPD and PPD in relation to MPD.

Table 2 presents the main characteristics of the corresponding polymers. The structure of the polyphosphonates synthesized was elucidated by IR and $^1$H-NMR spectroscopy.

Table 2. Various properties of polyphosphonates obtained by v-l interfacial polycondensation

| Nr | $M_n$ | $M_w$ | $T_g$, °C | IR, cm$^{-1}$ | $^1$H-NMR, ppm |
|---|---|---|---|---|---|
| $P_6$ | 9800 | 14400 | 125 | 930-945(P-O-$C_{phenyl}$);<br>1282(P=O, P-O-$C_{phenyl}$),<br>1294-1320(P-$C_{alkyl}$) | 6.2(s, 4H, phenyl),<br>1.1-2.4(m, 11H, cyclohexyl) |
| $P_7$ | 9300 | 13500 | 95 | 940,1377(P-O-$C_{phenyl}$);<br>1285(P=O); 1320- 1290 (P-$C_{alkyl}$) | 1.5-2.8(m,11H, cyclohexyl); 1.55(s, 6H, methyl); 7.06-7.12(m, 8H, phenyl) |
| $P_8$ | 19800 | 35800 | 127 | 1290(P=O), 1195, 920(P-O-$C_{phenyl}$); 1280-1265(P-$C_{alkyl}$) | 1.5-2(m,11H, cyclohexyl); 7-7.5(m, 8H, phenyl) |
| $P_9$ | 29300 | 56800 | 140 | 910-922((P-O-$C_{phenyl}$);<br>1240(P=O, P-O-$C_{phenyl}$);<br>1250-1280(P-$C_{alkyl}$) | 1-2(m, 11H, cyclohexyl); 7.1-8.2(m, 6H, phenyl) |
| $P_{10}$ | 8500 | 12100 | 132 | 1300-1320(P-$C_{alkyl}$);<br>1280($SO_2$, P=O); 1150-1185($SO_2$, P-O-$C_{phenyl}$);<br>920-940(P-O-$C_{phenyl}$) | 1.6-1.9(m, 11H, cyclohexyl); 6.9-7.1 and 7.4-7.8(m, 8H, phenyl) |
| $P_{11}$ | 9100 | 13800 | 138 | 1465, 10012, 720(P-$C_{phenyl}$); 1275(P=O); 920, 1250(P-O-$C_{phenyl}$) | 6.1-6.5(m, 4H, phenyl); 8.2(s, 5H, phenyl) |
| $P_{12}$ | 8800 | 13750 | 99 | 1440, 1005, 715 and 686 P-$C_{phenyl}$); 1275(P=O);<br>1250, 980(P-O-$C_{phenyl}$) | 7.20-8.15(m, 5H, phenyl); 7.01-7.24(m, 8H, phenyl); 1.68(s, 6H, methyl) |
| $P_{13}$ | 25300 | 41600 | 130 | 1454, 1002, 609 (P-$C_{phenyl}$);<br>1290(P=O); 1255, 910 (P-O-$C_{phenyl}$) | 7.8-8.0(m, 5H, phenyl); 7.1-7.3(m, 8H, phenyl) |
| $P_{14}$ | 35000 | 58900 | 148 | 1410, 1018, 702(P-$C_{phenyl}$),<br>1260-1275(P=O, P-O-$C_{phenyl}$); 920-940(P-O-$C_{phenyl}$) | 7.7-8.3(m, 5H, phenyl); 6.9-7.3(m, 6H, phenyl) |
| $P_{15}$ | 8650 | 11940 | 135 | 1475, 1018, 723(P-$C_{phenyl}$);<br>1280-1300($SO_2$,P=O);1140($SO_2$);<br>1260, 980(P-O-$C_{phenyl}$) | 8.1-8.3(m,5H, phenyl);<br>7.5-7.9(m, 8H, phenyl) |

The molecular weights $M_n$ values, listed in Table 2, fall into the range of 8500-35000.

The Tg values for the obtained polyphosphonates are also listed in Table 2. All polyphosphonates are, as expected from literature data, entirely amorphous materials, which do not crystallize despite prolonged annealing (24 h) above their glass-transition temperature (Tg). When linear bisphenols are used (HQ, BP) the ordering capacity is favored. The ordering capacity is influenced by the flexibility of the chain. For the polyphosphonates based on BP difficulties have been met in providing Tg by DSC measurements; rapid cooling (50°C/min) is necessary to obtain the corresponding signals. The low Tg found in most cases fit well the hypothesis of relatively flexible main chains. As expected, the flexible phosphonate groups enhance the segmental mobility of the polyphosphonate chains, and thus, reduce Tg.

Table 3 shows qualitative solubility behavior of polyphosphonates. All the polymers are soluble in N,N-dimethylformamide, pyridine, and tetrahydrofuran. Polyphosphonates based on ND and SD did not dissolve in chloroform. All these polyphosphonates are insoluble in acetone, methanol and hexane.

Table 3. Solubility of polyphosphonates

| Solvent | $P_6$ | $P_7$ | $P_8$ | $P_9$ | $P_{10}$ | $P_{11}$ | $P_{12}$ | $P_{13}$ | $P_{14}$ | $P_{15}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| N,N-dimethylformamide | + | + | + | + | + | + | + | + | + | + |
| Pyridine | + | + | + | + | + | + | + | + | + | + |
| Tetrahydrofuran | + | + | + | + | + | + | + | + | + | + |
| Chloroform | + | + | ± | - | - | + | + | ± | - | - |
| Benzene | + | + | + | ± | ± | + | + | + | ± | ± |
| Dimethylsulfoxide | + | + | - | - | ± | + | + | - | - | ± |

+: soluble at room temperature; ±: partially soluble or swelling; -: insoluble

Thermal characteristics, such as initial decomposition temperature IDT, T10, T25, and Tmax, i.e. temperatures at 10%, 25% and maximum decomposition, respectively, are incorporated in Table 4.

Table 4. Thermal characteristics of polyphosphonates

| Polymer | IDT,°C | T10, °C | T25, °C | Tmax, °C |
|---|---|---|---|---|
| $P_6$ | 240 | 320 | 340 | 380 |
| $P_7$ | 250 | 325 | 345 | 380 |
| $P_8$ | 275 | 330 | 350 | 385 |
| $P_9$ | 285 | 340 | 360 | 400 |
| $P_{10}$ | 230 | 300 | 350 | 375 |
| $P_{11}$ | 260 | 330 | 360 | 390 |
| $P_{12}$ | 260 | 330 | 360 | 390 |
| $P_{13}$ | 280 | 360 | 390 | 410 |
| $P_{14}$ | 300 | 380 | 400 | 440 |
| $P_{15}$ | 230 | 310 | 350 | 380 |

The thermostability of polyphosphonates was studied by thermogravimetry analyses (TGA) conducted at a heating rate of 12°C/min in air. It can see that the obtained polyphosphonates were stable to 240°-300°C. The TGA curves of all polyphosphonates were nearly identical. In all cases 10% loss of weight occurred in the temperature range of 300-380°C. The thermal stability is high enough for use of these polymers in fighting fire. [11, 12]

## Conclusions

This paper presents the synthesis of phosphorus-containing polymers of molecular weights $\approx 10^4$ by variation in chemical constitution of the phosphorylating and bisphenol agents, using the vapor-liquid interfacial polycondensation. Vapor-liquid interfacial polycondensation permits the use in reaction of readily hydrolyzing monomers, which is impossible in other aqueous systems. Solvent is not required in this technique and only ionic impurities needs to be washed from the polymer. A maximum molecular weight $M_n$ of 35000 was obtained, which is better compared to those reported by other techniques.

Results show that vapor-liquid interfacial polycondensation is a versatile method for preparing polyesters with phosphonyl groups in the main chain and is recommended for further studies.

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