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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** Kricheldorf, Hans R. and Koziel, Holger(1986) 'New Polymer Syntheses. 13. Synthesis of Aromatic Polyphosphates from Silylated Bisphenol A or Tetrachlorohydroquinone', *Journal of Macromolecular Science, Part A*, 23: 11, 1337 – 1347

**To link to this Article:** DOI: 10.1080/00222338608081126

**URL:** <http://dx.doi.org/10.1080/00222338608081126>

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## **New Polymer Syntheses. 13.\* Synthesis of Aromatic Polyphosphates from Silylated Bisphenol A or Tetrachlorohydroquinone**

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### ABSTRACT

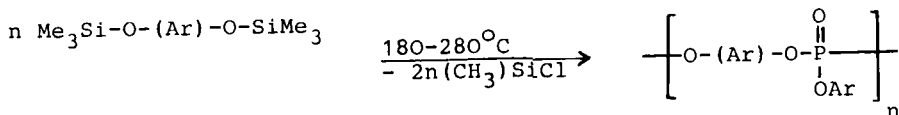
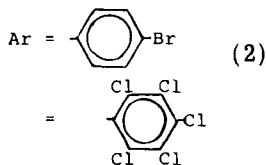
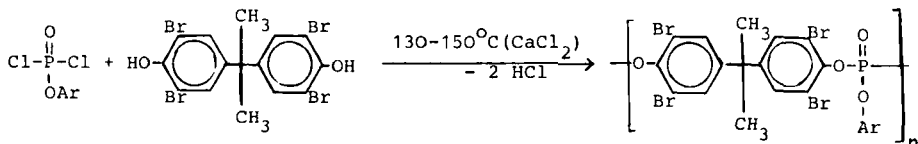
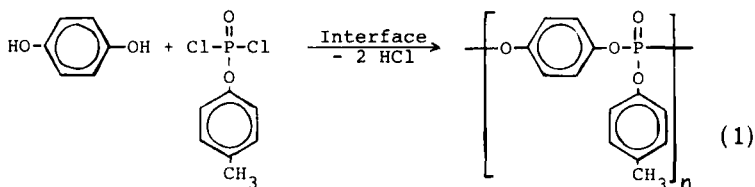
Bulk condensations of bissilylated Bisphenol A and tetrachlorohydroquinone with various aryl phosphorodichloridates (phosphoric acid aryloxy dichlorides) were conducted at temperatures between 180 and about 300°C. Only when the pentachlorophenylester of phosphoric dichloride was condensed was partial crosslinking observed. Yields in the range of 80-95%, and  $\bar{M}_n$  of ~12 000 were obtained. DSC measurements above 25°C show  $T_g$  in the range of 65-145°C, whereas melting endotherms were never found. Thermogravimetric analyses indicate that the thermal stability decreases with an increasing number of chlorines in the aryloxy group. Consequently, the fully chlorinated polyphosphate possesses the lowest thermal stability.

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\*For Part 12, see H. R. Kricheldorf and R. Pakull, J. Polym. Sci., Polym. Lett. Ed., **23**, 413 (1985).

## INTRODUCTION

Phosphorus-containing polymers have found great interest as flame-retardant engineering plastics or additives to other polymers. Most investigations on phosphorus-containing aromatic polyesters concentrate on polyphosphonates, whereas few papers deal with syntheses and properties of polyphosphates [1-3]. The lower interest in aromatic polyphosphates is mainly due to the risk of crosslinking in the course of polycondensation and during thermal processing. Two synthetic methods have been described so far, namely, the interfacial condensation of hydroquinone with aryesters of the phosphoric acid dichloride [1] (Eq. 1), and the thermal condensation of aryl dichlorophosphoridates with tetrabromobisphenol A [3] (Eq. 2). Because high molecular weight aromatic polyesters are easily prepared in good yield from silylated monomers [4-6], it was the aim of the present work to study the synthesis of aromatic polyphosphates from silylated phenols (Eq. 3).



## EXPERIMENTAL

Materials

Phenylphosphorodichloridate (IIIa) and p-chlorophenylphosphorodichloridate (IIIb), from Aldrich Chemical Co., were purified by vacuum distillation before use. Tetrachlorobenzoquinone (Aldrich Chemical Co.) and pentachlorophenol (Bayer AG) were used as received.

ProceduresBis(trimethylsilyl)bisphenol-A (I) [7]

Two moles of Bisphenol A was dissolved in 1 L of dry toluene. Under stirring, 1.1 mol of hexamethyldisilazane was added, and the reaction mixture was refluxed for 2 h. Evaporation of the solvent and distillation in vacuo (150-160°C) yielded 98% of silylated Bisphenol A ([7]: bp 173°C/2 mbar).

Analyses: Calculated for  $C_{21}H_{32}O_2Si_2$  (MW 372.6): C, 67.7; H, 8.7%. Found: C, 67.7; H, 8.6%.

Bis(trimethylsilyl)tetrachlorohydroquinone (II)

Tetrachlorobenzoquinone (1.2 mol) was suspended in 1.2 L of dry toluene, and 0.75 mol dry hydrazine was added dropwise under stirring. Afterwards 1.4 mol of hexamethyldisilazane was added, and the reaction mixture was refluxed for 2 h, when the evolution of ammonia nearly ceased. The resulting toluene solution was concentrated in vacuo and stored at 0°C for several hours. The crystallized product was isolated by filtration under a blanket of dry argon. Washing with a small amount of cold ligroin and drying in vacuo gave a yield of 61%; mp 71°C ([8]: mp 70-71°C).

Analyses: Calculated for  $C_{12}H_{18}Cl_4O_2Si_2$  (MW 392.3): C, 36.7; H, 4.6; Cl, 36.2%. Found: C, 36.7; H, 4.7; Cl, 36.0%.

(Dichlorophenyl)- and (Trichlorophenyl)phosphorodichloridate (IIIc, d)

These monomers were prepared according to the procedure given by Owen et al. [9].

Pentachlorophenylphosphorodichloridate (IIIe)

Silylation of Pentachlorophenol. Pentachlorophenol (0.5 mol) and hexamethyldisilazane (0.3 mol) were refluxed in 600 mL of dry toluene for 3 h; a clear solution was obtained. Finally, the mixture was concentrated in vacuo, and the product was isolated by distillation at 130-140°C/0.1 mbar. Yield: 93% of trimethylsilylpentachlorophenol; mp 43-44°C ([10]: mp 35-36°C).

Analysis: Calculated for  $C_9H_9Cl_5OSi$  (MW 338.5); C, 31.9; H, 2.7; Cl, 52.4%. Found: C, 31.4; H, 2.4; Cl, 52.3%.

**Phosphorylation.** Molten trimethylsilylpentachlorophenol (0.5 mol) was added dropwise under stirring to 1.5 mol phosphor-oxy chloride. The mixture was refluxed for 24 h and dried in vacuo. The product was purified by two distillations over a short distillation apparatus at 165-175°C/0.1 mbar. Yield: 89%; mp 98°C ([11]: 98°C).

Analysis: Calculated for  $C_6Cl_7O_2P$  (MW 383.2): C, 18.8; Cl, 64.8%. Found: C, 19.4; Cl, 64.2%.

### Polycondensations

Silylated Bisphenol A or tetrachlorohydroquinone (40 mmol), 40 mmol of an aryl phosphorodichloridate, and about 200 mg of benzyltriethylammonium chloride were weighed into a cylindrical reaction vessel with silanized glass walls (silanization was carried out by treating the vessel with dichlorodimethylsilane for 30 min). The reaction mixture was stirred and heated under a slow stream of dry nitrogen according to the temperatures and reaction times listed in Tables 1 and 2. During the last 30 min of the condensation reaction, vacuum was applied (0.1 mbar). After cooling, the resulting polyphosphate was dissolved either in pure methylene chloride or in a mixture of methylene chloride and trifluoroacetic acid 4:1 by volume. These solutions were filtered and precipitated into ~2 L of cold methanol. The polymers were isolated by filtration and dried at 60°C/12 mbar.

### Measurements

Glass-transition temperatures ( $T_g$ ) were determined on a differential scanning calorimeter (DSC 4; Perkin-Elmer) at a scanning rate of 20°C/min. Thermogravimetric analyses was performed with a Perkin-Elmer TGS-2 at Bayer AG, Leverkusen, at a heating rate of 10°C/min in air. Viscometry was conducted at 20°C in an Ubbelohde viscometer.

## RESULTS AND DISCUSSION

Two series of polyphosphates were synthesized. One series was based on silylated Bisphenol A (I), the second series on silylated tetrachlorohydroquinone (II). A new synthetic route was developed for the latter compound which permits the conversion of tetrachlorobenzoquinone to bis(trimethylsilyl)tetrachlorohydroquinone in an "one-pot procedure."

TABLE 1. Synthesis of Aromatic Polyphosphates from Silylated Bisphenol A and Various Arylphosphoro-dichloridates

No.	ArOP(O)Cl <sub>2</sub> : Ar =	Temperature, °C	Time, <sup>a</sup> h	Yield, <sup>b</sup> %	Empirical formula, MW	Elemental analysis		
						C	H	
1-1	Ph- (IIIa)	180/200/220	2.0/1.0/2.0	83	C <sub>21</sub> H <sub>19</sub> O <sub>4</sub> P (366.35)	Calc	68.85	5.23
		240/260	2.0/1.0			Found	68.81	5.26
1-2	Cl-Ph- (IIIb)	180/220/240	2.0/2.0/1.0	84	C <sub>21</sub> H <sub>18</sub> ClO <sub>4</sub> P (400.80)	Calc	62.93	4.53
		260/280/320	1.0/1.0/1.0			Found	62.63	4.55
1-3	Cl <sub>2</sub> Ph- (IIIc)	180/220/240	2.0/2.0/1.0	80	C <sub>21</sub> H <sub>17</sub> Cl <sub>2</sub> O <sub>4</sub> P (435.24)	Calc	57.95	3.94
		260/280/300	1.0/0.5/1.0			Found	57.57	3.90
1-4	Cl <sub>3</sub> Ph- (IIIc)	180/200/220	0.5/0.5/0.5	80	C <sub>21</sub> H <sub>16</sub> Cl <sub>3</sub> O <sub>4</sub> P (469.69)	Calc	53.70	3.43
		240/280	0.5/1.5			Found	53.39	3.41
1-5	Cl <sub>5</sub> Ph- (IIIe)	180/200/220	1.0/0.5/1.5	57 <sup>c</sup>	C <sub>21</sub> H <sub>14</sub> Cl <sub>5</sub> O <sub>4</sub> P (538.58)	Calc	46.83	2.62
		240/260	2.0/1.0			Found	46.61	2.47

<sup>a</sup>The temperature was raised stepwise.<sup>b</sup>After reprecipitation.<sup>c</sup>Partially crosslinked; yield of soluble fraction.

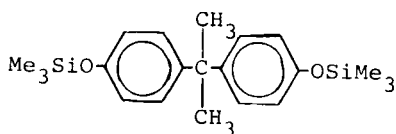
TABLE 2. Synthesis of Aromatic Polyphosphates from Silylated Tetrachlorohydroquinone and Various Aryl-phosphorodichloridates

No.	Ar	ArOP(O)Cl <sub>2</sub> <sup>a</sup>	Temperature, °C	Time, a h	Yield, b %	Empirical formula, MW	Elemental analysis		
							C	H	
2-1	Ph-	(IIIa)	180/200/220	2.0/2.0/1.0	96	C <sub>12</sub> H <sub>5</sub> Cl <sub>4</sub> O <sub>4</sub> P (385.96)	Calc	37.34	1.31
			240/260/280	1.5/2.0/1.0			Found	37.32	1.46
2-2	Cl-Ph-	(IIIb)	180/200/220	1.0/1.0/1.0	85	C <sub>12</sub> H <sub>4</sub> Cl <sub>5</sub> O <sub>4</sub> P (420.40)	Calc	34.28	0.96
			240/260/280	1.0/1.0/1.0			Found	34.29	0.87
2-3	Cl <sub>2</sub> Ph-	(IIIc)	180/200/220	1.0/0.5/2.0	94	C <sub>12</sub> H <sub>3</sub> Cl <sub>6</sub> O <sub>4</sub> P (454.84)	Calc	31.69	0.66
			240/280/300	0.5/0.5/1.0			Found	31.24	0.72
2-4	Cl <sub>3</sub> Ph-	(III d)	180/200/220	0.5/0.5/0.5	83	C <sub>12</sub> H <sub>2</sub> Cl <sub>7</sub> O <sub>4</sub> P (489.29)	Calc	29.46	0.41
			240/260/280	0.5/1.0/2.0			Found	30.51	0.66
2-5	Cl <sub>5</sub> Ph-	(IIIe)	180/220/240	0.5/0.5/0.5	40 <sup>c</sup>	C <sub>12</sub> Cl <sub>9</sub> O <sub>4</sub> P (558.18)	Calc	25.82	
			280/300	0.5/0.5			Found	26.42	

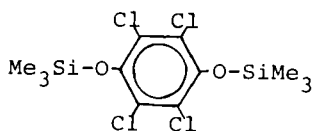
<sup>a</sup>The temperature was raised stepwise.

<sup>b</sup>After reprecipitation.

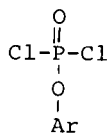
<sup>c</sup>Partially crosslinked; yield of soluble fraction.



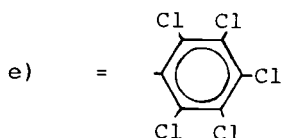
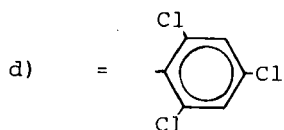
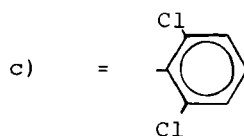
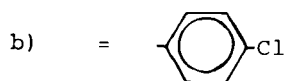
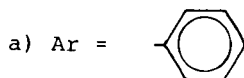
I



II



III



In the case of the phosphoric dichloride (IIIa-e), the phenylester group was varied such that there were one to five chlorine substituents. In this connection, a new procedure for the preparation of pentachlorophenylphosphorodichloridate (IIIe) was elaborated. The two series of polyphosphates derived from I and II allow a comparison of two extreme structures, namely, a chlorine-free polyphosphate obtained from I and IIIa and a hydrogen-free polyphosphate prepared from II and IIIe. All condensations were conducted in the melt, and chloride ions (in the form of benzyltriethylammonium chloride) were added as catalyst. Condensation started at 180°C in all experiments. The temperature was raised stepwise depending on the reaction rate. The final reaction temperature was chosen based on the thermal stability of the polymer.



Both series of polycondensations have in common that linear, completely soluble polyphosphates were obtained from phosphoric dichlorides IIIa-d (Tables 1 and 2). After precipitation, yields were in the 80-93% range. However, when the pentachlorophenylester (IIIe) was condensed, partially crosslinked materials were obtained regardless of whether silylated Bisphenol A or silylated tetrachlorohydroquinone was used. The uncrosslinked fraction of these polyphosphates was extracted and, after precipitation from methanol, subjected to characterization by elemental analysis, which gave satisfactory results (Tables 1 and 2, Nos. 1-5 and 2-5).

The viscosity measurements gave relatively low values except for polyphosphate 2-2 (Table 2). In no case was an inherent viscosity above 1.0 dL/g found. Viscosity and molecular weight data of aromatic polymethylphosphonates in recent patents of Bayer AG [12, 13] indicate that inherent viscosities below 0.5 dL/g may well correspond to  $\bar{M}_n$  about 10 000. In agreement with these literature data, vapor pressure osmometry conducted with the polyphosphate prepared from I and IIIa (No. 1-1) gave  $\bar{M}_n$  of 12 100 in chloroform. This molecular weight and the literature data [12, 13] in combination with low viscosities suggest that aromatic polyphosphates and polyphosphonates have rather flexible chains compared to other aromatic polymers. Obviously the P-O bonds possess low rotational barriers. For polyphosphates derived from I and IIIb, IIIc, IIId, or from II and IIIa, VPO measurements yielded  $\bar{M}_n$  in the range of 5 000-10 000 (Table 3). All these results indicate that the silyl method did not permit the preparation of polyphosphates of really high molecular weight under the given reaction conditions. As described in the succeeding part, better results were obtained when polyphosphonates were synthesized from phenylphosphonic acid dichloride.

In agreement with the results of other groups, all polyphosphates were found by DSC to be completely amorphous, and prolonged annealing 20°C above  $T_g$  for up to 48 h did not result in crystallization.

The low  $T_g$  (Table 3) found in most cases fit well the hypothesis of relatively flexible main chains. Thermogravimetric analysis in air gave an unexpected result. An increasing number of chlorine substituents in both components, bisphenol and aryloxy side chain, significantly reduces the thermostability. The two extremes (with the exception of No. 2-2 in Table 2) are displayed in Fig. 1. Thus, despite low sensitivity to oxidative degradation, highly chlorinated polyphosphates are rather useless as engineering plastics or flame-retardant additives. Since the thermal degradation of the hydrogen-free polyphosphate below 300°C is not likely to result from attack by oxygen, an ionic degradation mechanism is possibly involved. Since chlorinated phenoxides are good leaving groups and because the positive charge at the phosphorus is stabilized by delocalization, ionic cleav-

TABLE 3. Properties of Polyphosphates Prepared from Silylated Bisphenol A (Nos. 1-5, Table 1) or from Silylated Tetrachloroquinone (Nos. 1-5, Table 2)

Polymer no.	$\eta_{inh}$ , dL/g	$\bar{M}_n^d$ (VPO)	T <sub>g</sub> , °C	Weight loss at the listed temperature, %				
				5%	10%	20%	50%	
1-1	0.39 <sup>a</sup>	12 000	67	390	420	430	445	
1-2	0.16 <sup>a</sup>	7 000	71	405	430	455	475	
1-3	0.11 <sup>a</sup>	5 500	96	345	400	440	470	
1-4	0.19 <sup>a</sup>	7 500	94	290	320	355	435	
1-5	0.20 <sup>b,c</sup>	-	130	325	360	400	430	
2-1	0.26 <sup>a</sup>	8 000	79	285	300	320	355	
2-2	0.89 <sup>b</sup>	-	119	-	-	-	-	
2-3	0.25 <sup>b</sup>	-	144	-	-	-	-	
2-4	0.12 <sup>b</sup>	-	127	-	-	-	-	
2-5	0.18 <sup>b,c</sup>	-	133	250	285	320	375	

<sup>a</sup> Measured at  $c = 2$  g/L in  $\text{CH}_2\text{Cl}_2$  at 20°C.

<sup>b</sup> Measured in  $\text{CH}_2\text{Cl}_2$ /trifluoroacetic acid (4:1 by volume) with  $c = 2$  g/L at 20°C.

<sup>c</sup> Partially crosslinked, only the soluble fraction was measured.

<sup>d</sup> Determined in chloroform.

<sup>e</sup> Heating rate 10°C/min in air.

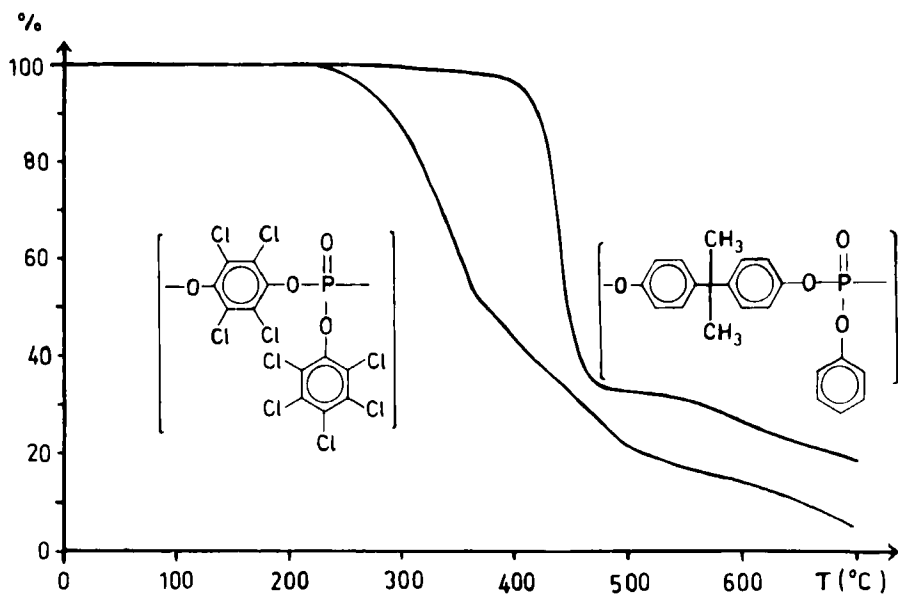
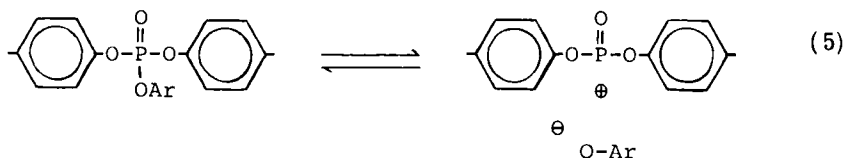
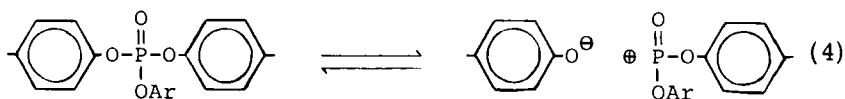


FIG. 1. Thermogravimetric analysis of the two polyphosphates prepared from II and IIIe or I and IIIa, measured in air at a heating rate of  $10^{\circ}\text{C}/\text{min}$ .

age of a P-O bond is likely to be the first step of the thermal degradation mechanism (Eq. 4 and 5). A more detailed study of the degradation mechanism by means of pyrolysis-mass spectroscopy is in progress.



## ACKNOWLEDGMENT

We thank Dr H. Biskup (Bayer AG, Leverkusen) for the TGA measurements.

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Received August 1, 1985

Revision received December 14, 1985