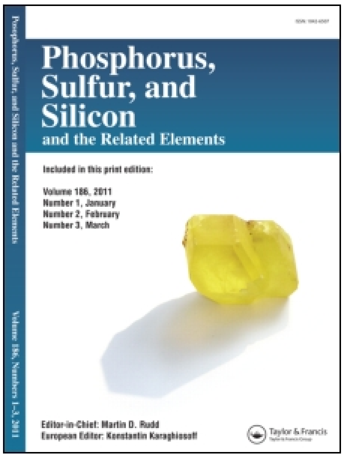

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REACTION RATE DETERMINATION DURING POLYCONDENSATION OF BISPHENOL A WITH BIS(2,3-DICHLOROPROPYL)PHOSPHOROCHLORIDITE

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Polycondensation of bisphenol A with bis(2,3-dichloropropyl)phosphorochloridite takes place by HCl and 2,3-dichloropropanol abstraction together with an Arbuzov rearrangement. From the ^{1}H-nmr spectra of samples taken during the reaction, the conversion and the total rate of polycondensation can be determined.

INTRODUCTION

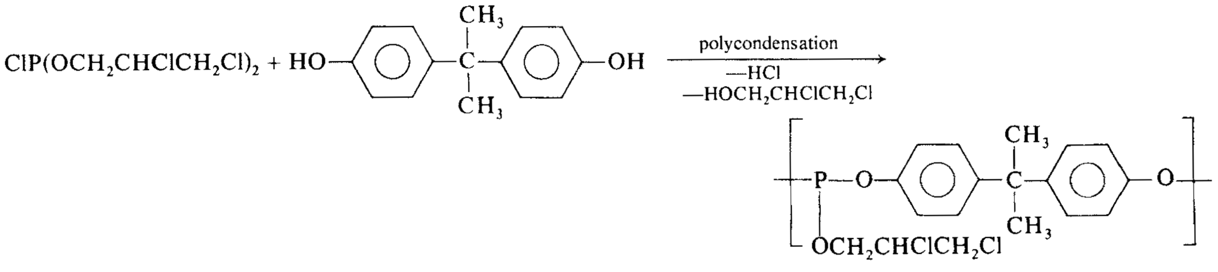
Flame-resistant polyphosphonates are obtained by reaction of phosphonic acid dihalides with diols,[1–3] phosphonic acid diamides with diols[4] and phosphonates transesterification with diols.[5,6] The ring-opening polymerization of cyclic phosphonates,[7] is also known, while the same reaction associated with an Arbuzov rearrangement can be applied to cyclic phosphites.[8]

This paper establishes the mechanism and rate of synthesis for a flame-retardant polyphosphonate obtained by melt polycondensation without catalysts.

POLYCONDENSATION MECHANISM

The two compounds subjected to polycondensation are bis(2,3-dichloropropyl)phosphorochloridite[9] and 2,2-bis(*p*-hydroxyphenyl)propane (bisphenol A).

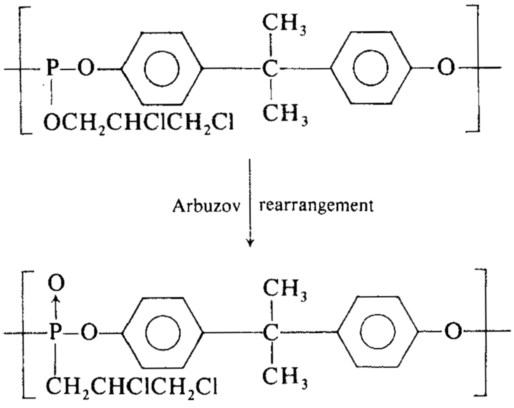
The reaction takes place by HCl and 2,3-dichloropropranol abstraction:



polyphosphite

The vigorous HCl evolution and in order to avoid phosphorus-containing monomer decomposition, requires a gradual rise of temperature.

The polycondensation is accompanied by an Arbuzov rearrangement from P^{III} to P^{V}, respectively, from polyphosphite to polyphosphonate:



polyphosphonate

TABLE I

The programme of temperatures for the polycondensation

Temperature (°C)	Time (min)
70	210
100	640
120	60
140	360
150	120
160	240
170	60
180	300

The polyphosphonate obtained by Arbuzov rearrangement is clearly superior to the initial polyphosphite by its thermal and hydrolytic stability.

EXPERIMENTAL

A 100 ml, three-necked round-bottomed flask equipped with thermometer, nitrogen inlet and reflux condenser having a fraction collector, is charged at room temperature with 22.8 g (0.1 moles) of bisphenol A and 32.2 g (0.1 moles) of bis(2,3-dichloropropyl)phosphorochloridite.

The temperature programme is given in Table I.

The ir spectra were recorded on a Perkin–Elmer 577 spectrometer on KBr pellets for the initial compounds, the final product, and the reaction mixture after 300 min.

During the reaction, samples were taken from time to time dissolved in $CDCl_3$ and their ^{1}H-nmr spectra were obtained on a JEOL (C-6OHL at 60 MHz) spectrometer using hexamethyldisiloxane as reference.

SPECTRAL ANALYSIS

Ir Spectroscopy

The ir spectra (Figures 1 and 2) of bis(2,3-dichloropropyl)phosphorochloridite (a), bisphenol A (b), the reaction mixture at 300 min (c) and the final product (d) give some information about the structure.

The OH group from bisphenol A decreases progressively showing that the polycondensation process continues during the Arbuzov rearrangement (3340 cm^{-1} (b), 3300 cm^{-1} (c) and 3280 cm^{-1} (d)). The presence of the OH groups in the final product indicates the existence of OH chain ends. The absorption band shift can be explained by the nature of OH groups (phenolic and acid from P–OH ends).

The 2400 cm^{-1} absorption band was assigned initially[10] to P^{III}–H vibration, then it was identified generally with trivalent phosphorus. From Figure 1 it is clear that the 2425 cm^{-1} absorption band loses its intensity and disappears in the final product, indicating the Arbuzov rearrangement.

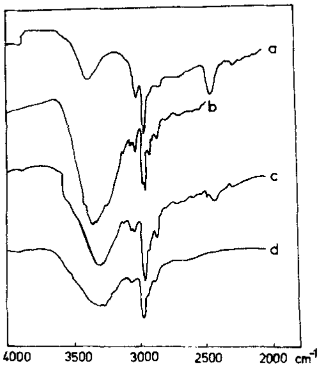


FIGURE 1 Ir spectra (2000–4000 cm^{-1} spectral domain) for: (a) bis(2,3-dichloropropyl)phosphorochloridite; (b) bisphenol A; (c) the reaction mixture at 300 min; (d) the final product.

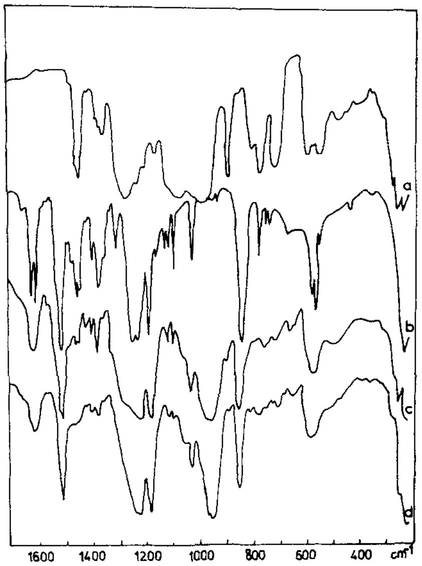


FIGURE 2 Ir spectra (300–1400 cm^{-1} spectral domain) for: (a) bis(2,3-dichloropropyl)phosphorochloridite; (b) bisphenol A; (c) the reaction mixture at 300 min; (d) the final product.

The characteristic absorption band for P^V → O bond is present in the final product (d) at 1220 cm^{-1} and cannot be confused with the 1230 cm^{-1} band from bisphenol A (b) Figure 3, because this does not appear in the polyphosphite spectrum (c).

^{1}H-nmr Spectroscopy

The ^{1}H-nmr spectra of the two initial compounds consist in an AB quartet ($\delta = 7.08$ ppm for *ortho* aromatic protons and $\delta = 6.82$ ppm for *meta*

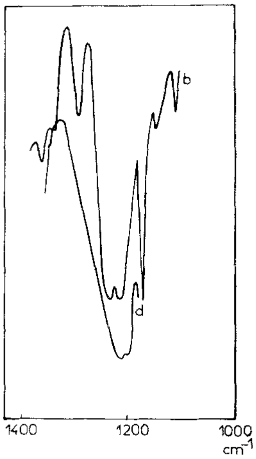


FIGURE 3 Extended ir spectra (1000–1400 cm^{-1} spectral domain) for: (b) bisphenol A; (d) the final product.

aromatic protons with $J_{ortho} = 9$ Hz) for bisphenol A and two groups of signals for bis(2,3-dichloropropyl)phosphorochloridite. This last spectrum has a complex aspect, due to different types of proton couplings and to $-OCH_2-$ and phosphorus atom coupling. The intense signal from the high field (3.78 ppm) can be assigned to CH_2 groups, and the weak one at 4.82 ppm to the CHCl group.

Aromatic Zone of the Spectrum

The spectra of this region, at three different reaction times, are represented in Figure 4. As expected, the AB quartet due to bisphenol A disappears during polycondensation, and a new larger signal due to all aromatic protons in bisphenol A, enchained in polymer, appears and grows at 7.16 ppm. The low field shift is explained in a precedent paper.[11] The OH proton signal disappears during polycondensation, but its intensity cannot be measured, its position being variable. In Figure 4, the OH proton signal is visible at 560 min, but at 140 min, for example, it has to be in the 7–7.5 ppm region. Because there is a direct correlation between the *meta* protons signals (4 protons) and those of OH protons (2 protons) from the unreacted bisphenol A, it is possible to calculate from the spectra the fraction of free bisphenol A in the reaction mixture. Figure 5 shows the rate of consumption for this component during polycondensation.

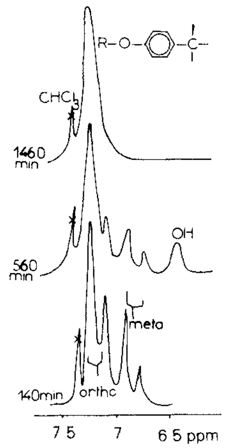


FIGURE 4 ^1H-nmr spectra (aromatic domain) at three different reaction times.

Saturated Zone of the Spectrum

The $-CH_3$ protons signal from bisphenol A (1.58 ppm) remains essentially unmodified during the reaction. It suffers only a slight broadening, as in the polycondensation with chloromethylphosphonic dichloride.[11]

Figure 6 shows the 2–5.5 ppm region with the phosphorus compound resonances. Three main groups of signals can be observed. They change their relative intensities in time and can be assigned by analogy with other phosphorus-compounds:[12] At 4.82 ppm the –CHCl– signal from the initial compound, polyphosphite and polyphosphonate; at 3.78 ppm the $-CH_2OP-$ and $-CH_2Cl$ groups from

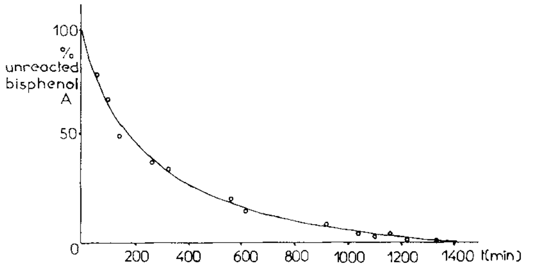


FIGURE 5 Bisphenol A concentration in the reaction mixture against time.

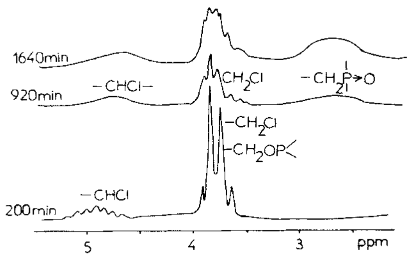


FIGURE 6 ^1H-nmr spectra (phosphorus-compound region) at three different reaction times.

the initial compound and polyphosphite and only the CH_2Cl group from polyphosphonate; at 2.71 ppm the CH_2P group from polyphosphonate, the broad signal being to phosphorus coupling.

The high-field shift of CH_2 group in polyphosphonate compared with polyphosphite is a proof for the Arbuzov rearrangement and can be a measure of the degree of rearrangement during polycondensation.

Component Concentration Changes with Time

Because the obtained spectra are not completely resolved, and therefore cannot be completely interpreted in terms of chemical shifts and coupling constants (the phosphorus compound), two indexes were introduced to characterize the total reaction rate.

I_1 represents the ratio of aromatic zone integral (including the phenolic OH) to the 3.78 ppm signal integral. Table II indicates the number of protons which resonate in these signals at the beginning and at the end of polycondensation. The I_1 changes during polycondensation are shown in Figure 7. This index is a measure of the total reaction rate, including the decrease of bisphenol A, the halogenated alcohol elimination and the Arbuzov rearrangement. As it is clear in the figure, the polycondensation develops linearly up to 1400 min, then the rate decreases. At 1880 min the reaction is finished.

The Arbuzov rearrangement can be studied separately, introducing the index I_2: the ratio of the 2.71 ppm signal integral to that of the 3.78 ppm signal integral. I_2 grows from zero to maximum one, as can be seen in Table II. The I_2 changes are represented in Figure 8. The Arbuzov rearrangement can be observed after approximately 300 min and takes place during polycondensation, as far as the polyphosphite chains are formed. It becomes the fundamental process after 1400 min.

TABLE II

Number of protons in some parts of the ^1H-nmr spectrum

Signal \ Time	Initial	Final
Aromatic	8 + 2	8
3.78 ppm	8	2
2.71 ppm	0	2
$I_1 = \frac{\text{aromatic area}}{\text{3.78 ppm area}}$	1.25	4
$I_2 = \frac{\text{2.71 ppm area}}{\text{3.78 ppm area}}$	0	1

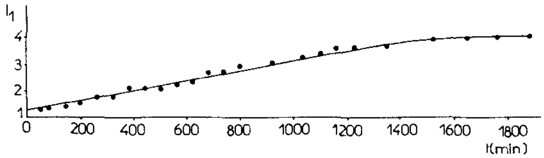


FIGURE 7 The I_1 change in time.

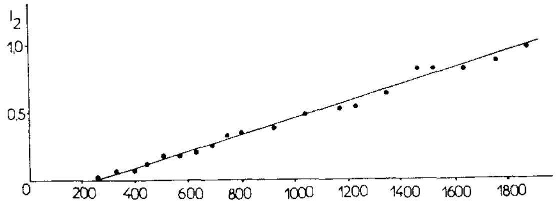


FIGURE 8 The I_2 change in time.

CONCLUSIONS

The studied polycondensation reaction has two steps: the first is a polyphosphite formation by HCl and halogenated alcohol abstraction, and the second is an Arbuzov rearrangement of the polyphosphite leading to polyphosphonate. The second step is observed after 300 min and develops parallel with the polyphosphite formation. After 1400 min the polycondensation is ended and up to 1880 min only the Arbuzov rearrangement takes place.

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