Kinetic data on the polycondensation of tetrachlorobisphenol A with bis(2,3-dichloropropyl) phosphorochloridite

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(Received 23 April 1979)

Tetrachlorobisphenol A and bis(2,3 dichloropropyl)phosphorochloridite form a polycondensate with the elimination of HCl and 2,3 dichloropropanol. The polyphosphite formed undergoes an Arbuzov transposition leading to a more stable polyphosphonate. I.r. and ^{1}H-n.m.r. spectroscopy give support for the described mechanism. From the ^{1}H-n.m.r. spectral integrals which were registered during the reaction, the separate processes and the rate of consumption of tetrachlorobisphenol A, may be quantitatively determined. The reaction temperature has to be kept below 200°C in order to avoid side reactions.

INTRODUCTION

Polycondensation of phosphonic acid dihalides with diols[1–3] is a known method for the synthesis of flame-retardant polyphosphonates. Bisphenol A and bis(2,3 dichloropropyl)phosphorochloridite polycondensation followed by the Arbuzov transposition of the polyphosphite obtained, gives a polyphosphonate with flame-retardant properties[4].

Taking into account the phosphorus–halogen synergism with respect to flame retardancy[5,6], this paper aims to study the mechanism and rate of synthesis of a polyphosphonate with higher chlorine content using bis(2,3dichloropropyl) phosphorochloridite and tetrachlorobisphenol A.

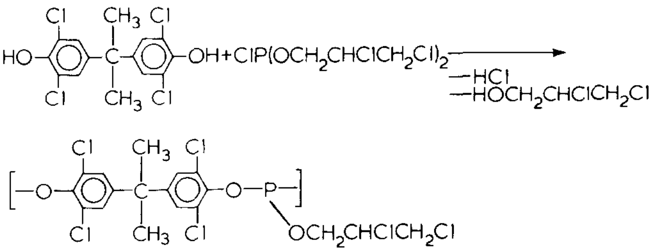
EXPERIMENTAL

Equivalent quantities of bis(2,3-dichloropropyl)phosphorochloridite[7] and tetrachlorobisphenol A[8] were heated in a three-necked flask equipped with thermometer, N_2 inlet and reflux condenser having a fraction collector. The temperature was raised according to the programme described in *Table 1*.

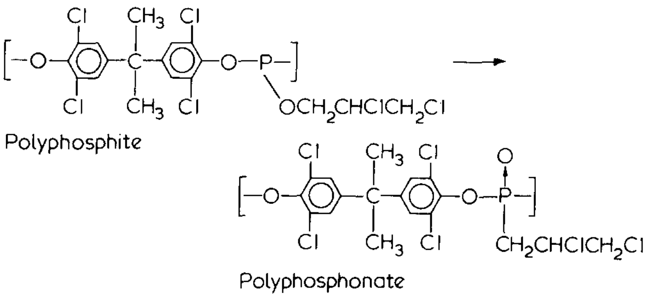
Each hour a sample is taken, dissolved in $CDCl_3$ and its ^{1}H-n.m.r. spectrum is registered on a Jeol C-60HL spectrometer, reference HMDS. The i.r. spectra are obtained in KBr pellets on a Perkin–Elmer 577 spectrophotometer.

REACTION MECHANISM

Polycondensation takes place by elimination of HCl and 2,3 dichloropropanol:



The gradual rise in temperature is demanded by the vigour of HCl evolution, and in order to avoid decomposition of the phosphorus-compound. The polyphosphite undergoes an Arbuzov rearrangement giving a polyphosphonate ($P^{(III)} \rightarrow P^{(V)}$):



The polyphosphonate is thermally and hydrolytically more stable. This mechanism is analogous to that of bisphenol A and bis(2,3-dichloropropyl)phosphorochloridite reaction[4].

SPECTRAL ANALYSIS

I.r. spectroscopy

Figure 1 presents the i.r. spectra for the initial compounds, the polyphosphite obtained after 37 h polycondensation at 80 90°C and the polyphosphonate.

Table 1 Temperature programme

Time (h)	Temperature (°C)
1	80
2	100
1	120
2	140
4	160
6	180
6	190
3	200

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The 2460 cm^{-1} band, assigned to P$^{(III)}$–Cl stretching[9,10] and characteristic of trivalent phosphorus[11], exists in the bis(2,3 dichloropropyl)phosphorochloridite spectrum, also in the polyphosphite spectrum, and disappears in the polyphosphonate spectrum, indicating that all phosphorus is pentavalent. The 1060 and 950 cm^{-1} bands are mixed bands indicating the presence of P–O–C bonds[12]. The P–Cl vibration (at 455 and 530 cm^{-1}), which exists in the phosphorus-compound spectrum, is not present in the polyphosphonate spectrum. Finally, in 1140–1350 cm^{-1} range the P$^{(V)}$–O band appears, its position depending on the electronegativity of the phosphorus-substituent. Because in this range, some mixed absorptions from the two initial compounds are also present, the P$^{(V)}$–O band from the polyphosphonate spectrum is located at 1275 or at 1255 cm^{-1}.

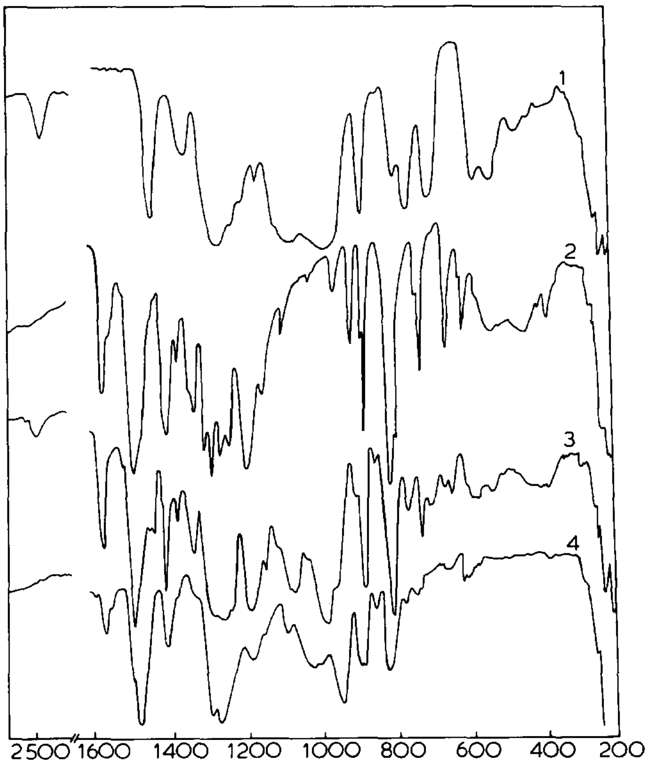
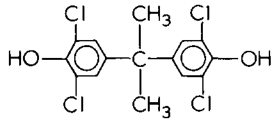


Figure 1 I.r. spectra of: (1) bis(2,3 dichloropropyl)phosphorochloridite; (2) tetrachlorobisphenol A; (3) polyphosphite; (4) polyphosphonate

^{1}*H-n.m.r. spectroscopy*

The ^{1}H-n.m.r. spectrum of tetrachlorobisphenol A consists of a singlet in the aromatic region (6.96 ppm) corresponding to the four aromatic equivalent protons:



a singlet with varying position for OH phenolic protons, and a singlet at 1.58 ppm assigned to the CH_3 groups[13].

The bis(2,3 dichloropropyl)phosphorochloridite spectrum is complex, due to H–H and H–P couplings and to steric hindrance by Cl atoms. The intense signal to high field (3.78 ppm) can be assigned to the CH_2Cl and CH_2O groups and the weak one at 4.82 ppm to the CHCl group[4]. The ^{1}H-n.m.r. spectra at four different reaction times are given in *Figure 2*.

Signal A, corresponding to the aromatic protons, consists of three singlets at 6.96 ppm (A_1), 7.02 ppm (A_2) and 7.08 ppm (A_3). A_1 (from tetrachlorobisphenol A) decreases with time; A_2 increases, reaches a maximum at 10–11 h, then decreases and disappears after 24.5 h of reaction; A_3 becomes visible at 4 h from the beginning, increases progressively and remains the only signal after 24.5 h. This evolution permits the assignment of A_3 signal to tetrachlorobisphenol A enchained in the polymer and of A_2 signal to tetrachlorobisphenol A chain-end[14]. The shift to lower field can be explained by phosphorus-compound binding.

Signal B is the resonance of OH proton. Its position is variable, due to the varying acidity of the medium. Its intensity progressively decreases, and the signal disappears after 24.5 h of reaction.

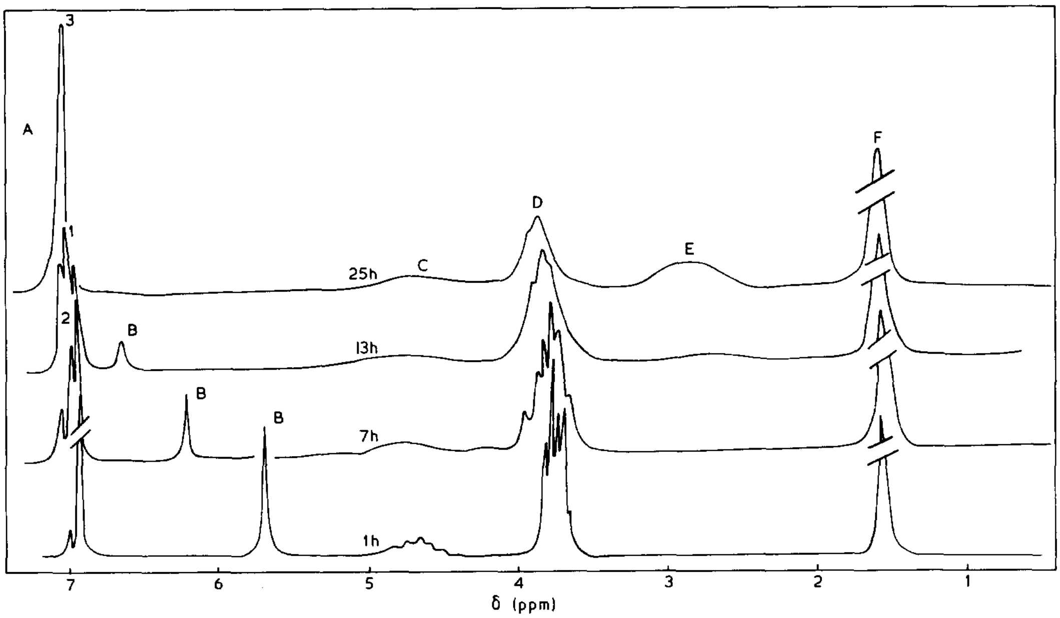


Figure 2 ^{1}H-n.m.r. spectra for four different reaction times

Table 2

	A	B	C	D	E	F	A/F	B/F	C/F	E/F
Initial mixture	4	2	2	8	0	6	0.67	0.33	0.33	0
Final polyphosphonate	4	0	1	2	2	6	0.67	0	0.17	0.33

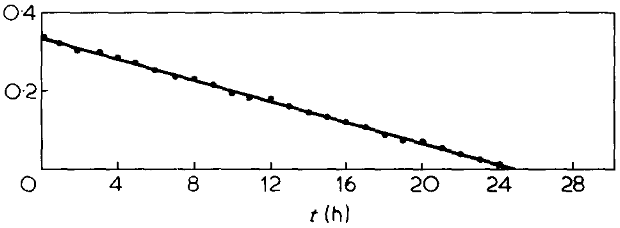


Figure 3 B/F ratio against time

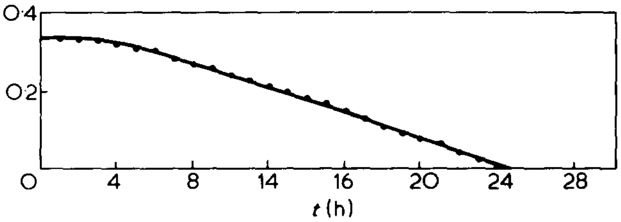


Figure 4 C/F ratio against time

Signal C was assigned to the CHCl group in the phosphorus compound. During the reaction, it slowly shifts to higher field, and that could be explained by the aromatic ring screening effect and/or direct binding of CHCl to CH_2P from polyphosphonate.

Signal D is given by the CH_2Cl and OCH_2 groups from the phosphorus-compound. During the polycondensation it is reduced to a half by the elimination of the 2,3-dichloropropanol, and by Arbuzov transposition it is again reduced to a half, because the OCH_2 group becomes CH_2P and resonates at a higher field.

Signal E, centred at approximately 2.71 ppm, is assigned to the CH_2P group from polyphosphonate[4]. This signal can be observed at 7 h of reaction, is broad and unresolved, because of CHCl and phosphorus couplings. Signal E increases progressively during the reaction.

Signal F is assigned to the CH_3 groups from tetrachlorobisphenol A. It does not modify during the reaction, with the exception of a small broadening given by the increasing molar mass.

The ^{1}H-n.m.r. spectrum of the reaction mixture at 25 h is identical with the purified polyphosphonate spectrum[15].

REACTION RATE

Because, according to the reaction scheme, the CH_3 groups remain unmodified during the synthesis, signal F was chosen as a reference for the determination of spectral changes. *Table 2* gives the proton number for each signal, according to the reaction scheme, and the values of ratios chosen for determination of reaction rate.

For all samples the ratios A/F, B/F, C/F and E/F were calculated from spectral integrals. The A/F ratio is an accuracy control for the spectrum integral which has to be constant for all samples taken during the reaction.

Total polycondensation rate

The B/F ratio is a measure of disappearance from system of the OH groups, which therefore indicates the total polycondensation rate, including HCl and 2,3-dichloropropanol elimination. *Figure 3* shows that the polycondensation process is linear and ends after 24.5 h of reaction.

Halogenated alcohol elimination

The C/F ratio best illustrates the 2,3-dichloropropanol elimination. Signal D was not used, because it also reflects the Arbuzov transposition. *Figure 4* demonstrates that 2,3-dichloropropanol elimination begins after 2–3 h of reaction, then increases linearly up to 24.5 h of reaction.

HCl elimination

Indirectly, by correlation of B/F and C/F ratios, an HCl index can be calculated to illustrate the evolution of HCl from the system. This index is defined as:

$$\text{HCl index} = [(B/F) - (C/F)]$$

and is represented in *Figure 5*, which shows that HCl eliminination is preferred at the beginning of the polycondensation, reaches a maximum at 8–9 h, then decreases progressively up to 23 h.

Arbuzov transposition

The E/F ratio, a measure for Arbuzov transposition, increases progressively, beginning with the 7th hour of reaction (*Figure 6*). The transposition takes also place linearly and ends at 25 h of reaction.

Tetrachlorobisphenol A consumption rate

The plot of A_1, A_2, A_3 components against reaction time is given in *Figure 7*. The overall aspect of curves resembles the successive reaction type[16]:

$$A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_2} A_3$$

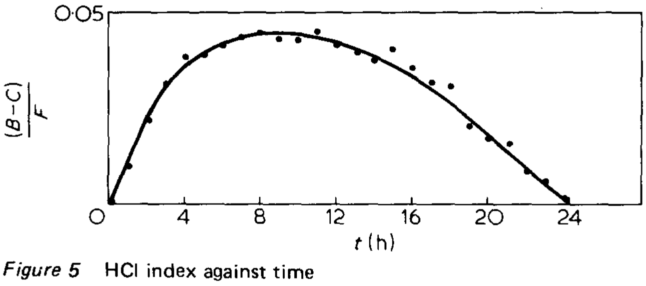


Figure 5 HCl index against time

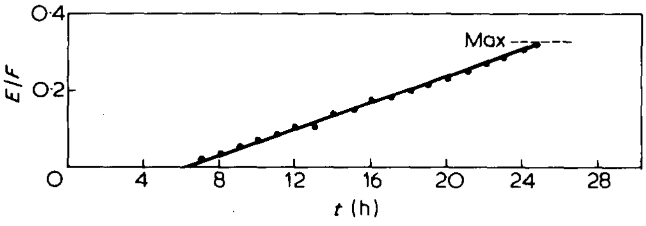


Figure 6 E/F ratio against time

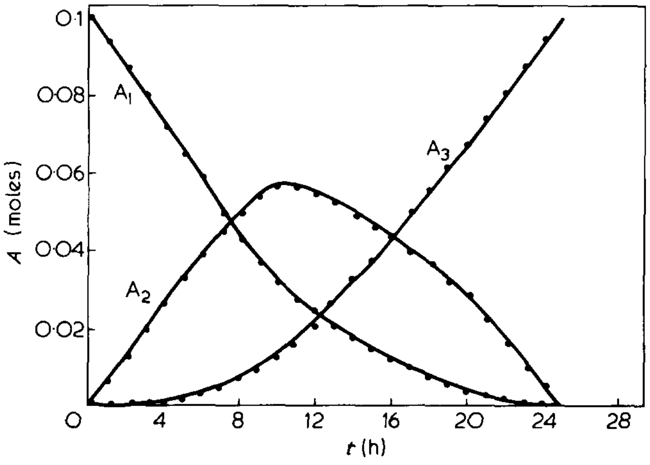


Figure 7 Tetrachlorobisphenol A components against time

The attempt to obtain k_1 and k_2 values by the nonlinear regression algorithm[17] failed, mainly because A_1 evolution is not really exponential. This can be explained because the elimination of HCl and 2,3-dichloropropanol from tetrachlorobisphenol A are two different kinds of reaction having different rates, as previously shown. On the other hand, the rate constants for the bisphenol A and chloromethylphosphonic dichloride polycondensation, could be determined because there was essentially only one process: HCl elimination[14].

SIDE REACTIONS

After 25 h and above 200°C, side reactions occur, such as dehydrochlorination and breaking of ester bonds to give free acids. These acids can also increase the degradative processes above 200°C. In the ^{1}H-n.m.r. spectra, these side reactions produce unidentified signals in the saturated region. These processes were not studied, but indicated that the reaction should be terminated at 25 h without raising the temperature above 200°C.

CONCLUSIONS

The reaction of bis(2,3 dichloropropyl)phosphorochloridite with tetrachlorobisphenol A is slower than with bisphenol A[4]. This is a consequence of the strong electron-attracting inductive effect of the chlorine atoms, which decreases the nucleophilic character of the diol and was also observed when chloromethylphosphonic dichloride was polycondensated with bisphenol A[14] and tetrachlorobisphenol A[13], respectively.

The chosen temperature programme permits a constant reaction rate. Initially, HCl elimination takes place preferentially; after approximately two hours the 2,3-dichloropropanol begins to evolve. These two processes take place concurrently, but with different rates up to the end of the polycondensation (24.5 h). The Arbuzov transposition is observed after 6 h of reaction and increases progressively as the polyphosphite chains are formed. It also continues for ½ h after the polycondensation is finished.

The synthesis must be stopped at 25 h and the temperature must be kept under 200°C in order to avoid side reactions.

REFERENCES

1 Coovery, H. W., Connell, R. L., McCall, M. A. *Ind. Eng. Chem.* 1960, **52**, 409
2 Conix, A. J., Belg. Pat. 610953 1965, Gevaert, N. V., Ger. Pat. 1199500 1965, *C. A.* 1965, **63**, 16502
3 Yvernault, T., Guilloton, O. *Comp. Rend.* 1963, **257**, 1923
4 Percec, S., Popescu, F., Natansohn, A. *Phosphorus and Sulphur* 1979, **7**, 149
5 Lyons, J. W. 'The chemistry and uses of fire retardants', J. Wiley, N. Y. 1970
6 Popescu, F., Percec, S., Rom. Pat 63975 1976
7 Boyer, N. E., Parkerburg, W. A. U. S. Pat 3758646, 1973
8 Goodrich Co., U. S. Pat. 2455652 1945, C. A. 1949, 2234
9 Arbuzov, A. E., Batisev, M. J., Vinogradova, V. S. *Dokl. Akad. Nauk. SSSR* 1946, **54**, 599
10 Bell, J. V., Herster, J., Tannenbaum, H., Goldenson, J. *J. Am. Chem. Soc.* 1954, **76**, 5185
11 Peppard, D. F., Ferraro, J. R., Mason, G. W. *J. Inorg. Nucl. Chem.* 1958, **7**, 251; 1959, **10**, 275; 1961, **16**, 246
12 Goncalves, H., Mathis, F., Wolf, R. *Bull. Soc. Chim. (France)* 1961, 1597
13 Percec, S., Natansohn, A., Dima, M. *Angew. Makromol. Chem.* 1979, **80**, 143
14 Percec, S., Natansohn, A., Galea, D., Dima, M. *Angew. Makromol. Chem.* 1978, **72**, 1
15 Percec, S., Natansohn, A., Popescu, F. *Brit. Polym. J.* submitted
16 Schneider, I. A. *Cinetica chimica (Ed. did. pedag.)* Bucharest 1974
17 Marquardt, D. W. *J. Soc. Ind. Appl. Math.* 1963, **11**, 431