Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis of Some Flame-Retardants Containing Phosphorus and Halogen

Oana Petreus[a]; Florin Popescu[a]; Virgil Barboiu[a]; Lidia Rosescu[a]
[a] "P. Poni" Institute of Macromolecular Chemistry, Jassy, Romania

To cite this Article Petreus, Oana , Popescu, Florin , Barboiu, Virgil and Rosescu, Lidia(1988) 'Synthesis of Some Flame-Retardants Containing Phosphorus and Halogen', Journal of Macromolecular Science, Part A, 25: 8, 1033 — 1038
To link to this Article: DOI: 10.1080/00222338808052139
URL: http://dx.doi.org/10.1080/00222338808052139

J. MACROMOL. SCI.–CHEM., A25(8), pp. 1033-1038 (1988)

NOTE

SYNTHESIS OF SOME FLAME-RETARDANTS CONTAINING PHOSPHORUS AND HALOGEN

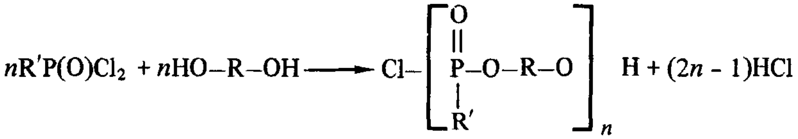
OANA PETREUS, FLORIN POPESCU, VIRGIL BARBOIU, and
LIDIA ROSESCU

"P. Poni" Institute of Macromolecular Chemistry
Aleea Gr. Ghica-Voda 41 A, Jassy 6600, Romania

INTRODUCTION

Polyphosphonates, one of the longest known classes of organophosphonic compounds, are of interest because they can confer low flammability, plasticity, thermal stability, and lubrication properties on polymers.

The most important method of synthesis is the esterification of diols with phosphonic acid dihalides:



$$n\mathrm{R'P(O)Cl_2} + n\mathrm{HO{-}R{-}OH} \longrightarrow \mathrm{Cl}{-}\left[\begin{array}{l}\mathrm{O}\\ \|\\ \mathrm{P{-}O{-}R{-}O}\\ |\\ \mathrm{R'}\end{array}\right]_n \mathrm{H} + (2n-1)\mathrm{HCl}$$

The condensation reaction of phosphonic acid dichlorides with aliphatic diols can be carried out either in solution in the presence of bases [1, 2] or under pressure [3]. However, only polyphosphonates of low molecular weight are formed under these conditions.

With aromatic diols the reaction takes place in the melt, either without catalyst or with catalytic quantities of $MgCl_2$, $CaCl_2$, or $AlCl_3$ [4, 5], or in solution with an acid acceptor [6].

The purpose of this paper is to determine the reaction mechanism and kinetic constants for the polycondensation of 2,2′-isopropylidene-bis(2,6-dichloro-*p*-phenyleneoxy)dialkanol (IBD) or tetrachlorobisphenol A (TBP) and cyclohexylphosphonic acid dichloride (CPAD) in the molten state in the absence of catalysts.

EXPERIMENTAL

A. Chemicals

1. IBD was obtained from the Polytechnic Institute of Timișoara, Romania, where it was synthesized by hydroxyethylation of TBP [7]. Mp: 102-103°C. OH index: calculated, 246.69 mg KOH/g; found, 240 mg KOH/g. Analysis: $C_{19}H_{20}Cl_4$: calculated, C, 50.24; H, 4.40; Cl, 31.24; found, C, 51.43; H, 4.72; Cl, 30.74.
2. TBP, commercial sample, purified by recrystallization from acetic acid solution. Mp: 131-132°C. Analysis: $C_{15}H_{12}Cl_4O_2$: calculated, C, 49.42; H, 3.28; Cl, 38.76; found, C, 50.15; H, 3.57; Cl, 38.65.
3. CPAD was synthesized by the method of Graff [8].

The structure of all these starting derivatives was confirmed by IR and ^1H NMR.

B. General Procedure for Polyphosphonate Synthesis

Equimolar quantities of CPAD and IBP or TBP were polycondensed at 60, 80, or 100°C. The synthesis flask was connected to a sealed system for HCl absorption. The amount of HCl evolved was determined at various times.

In another series of experiments the polycondensation reactions took place directly in NMR tubes, and the NMR spectra were recorded at the same temperatures and time intervals.

C. Test Methods

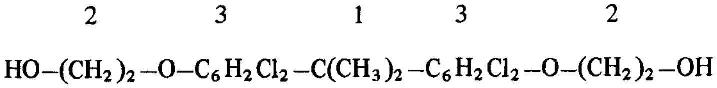
1. Chemical Methods

The amount of HCl evolved from the reaction was correlated with the number of functional groups reacted. The reaction rate constants were determined according to

$$1/(a - x) = kt, \tag{1}$$

where a represents the molar concentration of dichloride plus dialkanol, x is the concentration of reacted functional groups, t stands for the reaction time in minutes, and k represents the reaction rate constant.

TABLE 1. ^{1}H-NMR Spectra for Monomers and Polycondensate ($CDCl_3$, 50°C, 60 MHz)



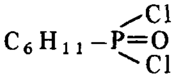
$$\overset{2}{HO{-}(CH_2)_2}{-}O{-}\overset{3}{C_6H_2Cl_2}{-}\overset{1}{C(CH_3)_2}{-}\overset{3}{C_6H_2Cl_2}{-}O{-}\overset{2}{(CH_2)_2}{-}OH$$

δ_1 = 1.65 ppm (singlet)

δ_2 = 3.5-4.3 ppm (multiplet)

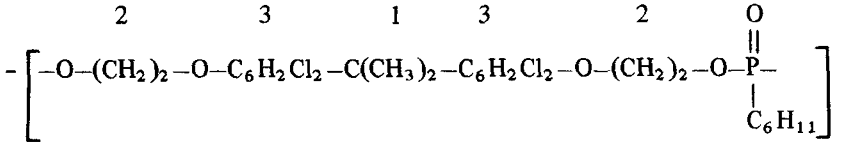
δ_3 = 7.1 ppm (singlet)

δ_{OH} = 2-3 ppm (singlet)



$C_6H_{11}{-}P({=}O)Cl_2$

C_6H_{11} = 1-2.5 ppm (complex multiplet)



$$-\left[-O{-}\overset{2}{(CH_2)_2}{-}O{-}\overset{3}{C_6H_2Cl_2}{-}\overset{1}{C(CH_3)_2}{-}\overset{3}{C_6H_2Cl_2}{-}O{-}\overset{2}{(CH_2)_2}{-}O{-}\underset{C_6H_{11}}{\overset{\overset{O}{\|}}{P}}{-}\right]$$

δ_1 = 1.65 ppm (singlet)

δ_2 = 4.3 ppm (quasisinglet)

δ_3 = 7.1 ppm (singlet)

$\delta_{C_6H_{11}}$ = 1-2 ppm (multiplet)

2. Spectral Methods

a. ^{1}H-NMR spectra were recorded on a JEOL-C-60 MHz Spectrometer. The characteristic NMR signals for monomer and polycondensate are presented in Table 1. The kinetics of polycondensation is best expressed by signals of methylenic protons observed at various times. The instantaneous component concentrations were determined from the integrals, and the conversion, g, was calculated by

$$g = (I_1 - I_2)/(I_1 + I_2), \tag{2}$$

where I_1 and I_2 are the integrals for 4.3 ppm protons of the ($-CH_2-CH_2-O-$) group in the dialkanol and polycondensation product, respectively.

b. IR spectra were recorded on a UNICAM-Sp-100 Spectrophotometer, using films deposited on KBr pellets. The conversion was evaluated from the ratio of the absorbances of OH groups (A_{3280}) and $-CH_2-$ groups (A_{2910}) according to

$$g = 1 - \frac{(A_{3280}/A_{2910})_t}{(A_{3280}/A_{2910})_0}, \tag{3}$$

where the subscripts t and 0 refer to the reaction times.

RESULTS AND DISCUSSION

The polycondensation between a phosphonic dichloride and a diol takes place by a nucleophilic attack of the hydroxylic oxygen atom on the positive phosphorus atom. The chlorine atoms in the diol structure have a strong inductive electron-withdrawing effect. The result is a decrease in the nucleophilic character of the diol and, consequently, of its reactivity toward phosphonic dichloride. The ethoxylic group positioned between the halogenated aromatic nucleus and the reactive OH group decreases the halogen effect mentioned above, leading to an increase of reactivity of the chlorinated dialkanols.

These considerations are supported by the different time courses of HCl evolution for IBP and TBP reactions (Fig. 1). Thus, at 60°C, 35% conversion is obtained in 3 h for IBP, while only 11% of TBP is converted. Similarly, the rate of HCl evolution is higher for IBP. As expected, higher temperature raises the reaction rate (Table 2).

Very good agreement was observed between the values of reaction constants obtained by chemical and spectral methods at 80 and 100°C (Fig. 2).

TABLE 2. Reaction Rate Constants for Polycondensation of IBP and CPAD

Temperature, °C	k, $L \cdot mol^{-1} \cdot min^{-1} \cdot 10^{-4}$
60	7.83
80	17.63
100	36.30

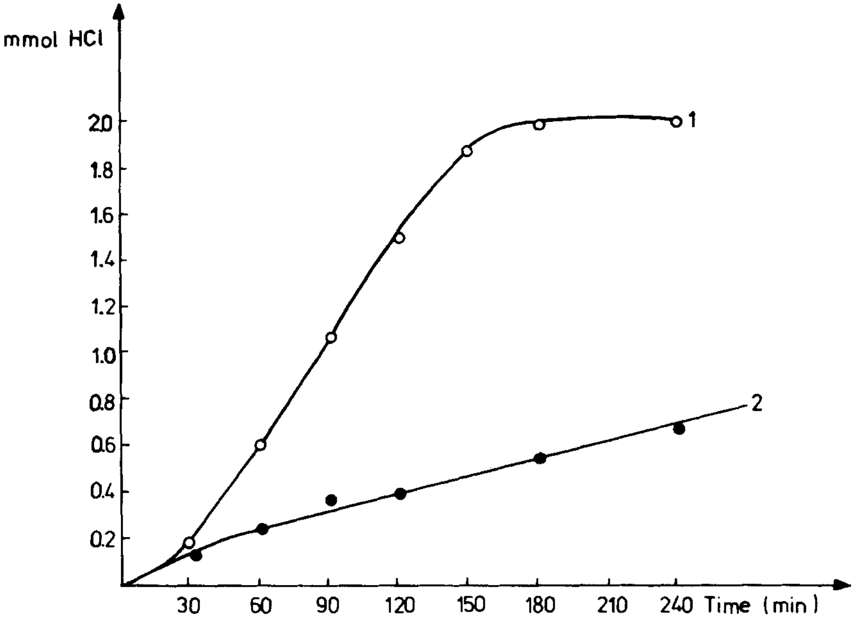


FIG. 1. HCl evolution from the polycondensation between CPAD and two diols. Temperature, 60°C. (1) IBD, (2) TBP.

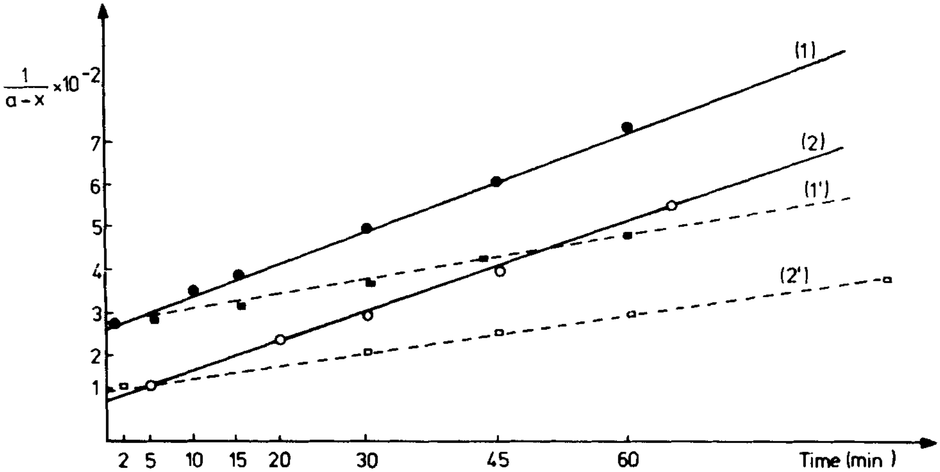


FIG. 2. Kinetic results for the polycondensation between IBD and CPAD. (1) and (1′) NMR data: (●) 100°C, (■) 80°C. (2) and (2′) data resulted from chemical methods: (○) 100°C, (□) 80°C.

REFERENCES

[1] L. A. Datskevich, V. D. Maiborodo, and I. P. Losey, *Vysokomol. Soedin.*, p. 73 (1964); *Chem. Abstr., 61,* 4500 (1964).

[2] L. A. Datskevich, V. D. Maiborodo, and I. P. Losey, *Vysokomol. Soedin.*, p. 243 (1964); *Chem. Abstr., 61,* 5779 (1964).

[3] W. Starck, A. Vilcsek, J. Winter, and F. Rochlitz, German Patent 1,164,093 (1964); *Chem. Abstr., 56,* 13102 (1962).

[4] H. W. Coover and M. A. McCall, U.S. Patent 2,716,100 (1955), to Eastman Kodak Co.; *Chem. Abstr., 50,* 1370 (1956).

[5] O. Petreus and Fl. Popescu, Romanian Patent 71,829 (1979).

[6] O. Petreus, Fl. Popescu, C. Deltin, and D. Cioloca, Romanian Patent 84,115 (1984).

[7] L. Mirci, Fl. Popescu, and O. Petreus, To Be Published.

[8] R. Graff, *Methoden der Organishen Chemie,* Georg Thieme Verlag, Stuttgart, 1963, p. 400.

Received May 15, 1987
Revision received November 19, 1987