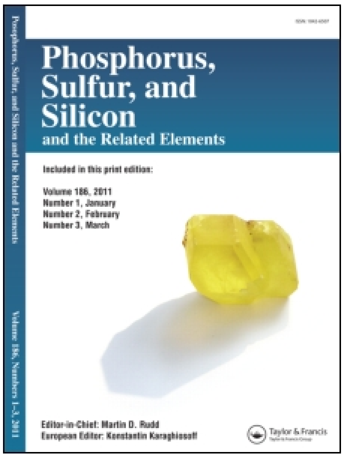

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Simona Percec[a]; Almeria Natansohn[a]; Dan Glea[a]; Mihai Dima[a]
[a] "P. Poni" Institute of Macromolecular Chemistry, Jassy, Romania

To cite this Article Percec, Simona , Natansohn, Almeria , Glea, Dan and Dima, Mihai(1980) 'CATALYST INFLUENCE ON THE BISPHENOL A AND CHLOROMETHYLPHOSPHONIC DICHLORIDE POLYCONDENSATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 8: 1, 109 — 113

To link to this Article: DOI: 10.1080/03086648008078171

URL: http://dx.doi.org/10.1080/03086648008078171

Phosphorus and Sulfur, 1980, Vol. 8, pp. 109–114
0309-664X/80/0801-0111$04.50/0

CATALYST INFLUENCE ON THE BISPHENOL A AND CHLOROMETHYLPHOSPHONIC DICHLORIDE POLYCONDENSATION

SIMONA PERCEC, ALMERIA NATANSOHN, DAN GÂLEA and MIHAI DIMA

"P. Poni" Institute of Macromolecular Chemistry, Jassy, Romania

(*Received April 19, 1979*)

The influence of some catalysts on the total polycondensation rate of bisphenol A and chloromethylphosphonic dichloride is studied. The reaction is followed by ^{1}H-NMR spectroscopy. By comparing the total reaction time, the maximum temperature and the reaction rate constants values, the most efficient catalyst is proved to be $MgCl_2$, followed by Mg and $CaCl_2$. The polycondensations in presence of $AlCl_3$, $CoCl_2$ and $ZnCl_2$ are accompanied by important side reactions.

INTRODUCTION

Acid dichlorides polycondensation with bisphenol A is catalysed by $MgCl_2$, $AlCl_3$, $SnCl_4$[1]. For phosphorus acids dichlorides and different aromatic diols, $MgCl_2$ and Mg were proved to be active, and Cu powder and P_2O_5 inefficient.[2]

In a precedent paper[3] the mechanism and kinetic constants for bisphenol A and chloromethylphosphonic dichloride polycondensation in melt, without catalyst, were determined. This paper is a study on the catalyst nature and concentration influence on this polycondensation. The catalysts are introduced in order to reduce the reaction time and the temperature for the polyphosphonate synthesis.

EXPERIMENTAL

In a 50 ml flask equipped with stirrer, N_2 inlet and reflux condenser, 0.1 moles (22.8 g) bisphenol A, 0.1 moles (16.75 g) + 2% excess chloromethylphosphonic dichloride and 0.1 g catalyst are heated according to the temperature programme in Table I. For the $MgCl_2$ catalyst, quantities of 0.1 g, 0.2 g and 0.3 g were used. The general temperature programme is the same as in the polycondensation without catalyst, and is stopped, when the reaction is finished. Used as catalysts: anhydrous $ZnCl_2$, anhydrous $AlCl_3$, anhydrous $CoCl_2$ sicc., $MgCl_2$ sicc. and metallic Mg.

Samples were taken from time to time, dissolved in $CDCl_3$ and their ^{1}H-NMR spectra were registered on a JEOL C-60 HL spectrometer operating at 60 MHz with HMDS as reference.

We did not perform polycondensation in the NMR spectrometer's sample tube, for two reasons:

a) the melted sample is very inhomogenous all the time, due to the much more vigorous HCl evolution from the system than in the uncatalysed reaction

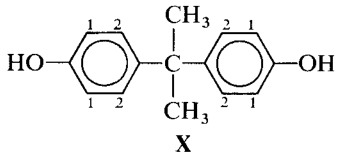
b) the reaction rate is higher at lower temperatures, consequently the sample viscosity becomes too high to permit a good spectral resolution

The first reason could be avoided by modifying the temperature programme, but we prefered to work at the same temperature in order to have the comparison with the uncatalysed reaction.

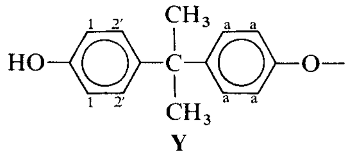
RESULTS AND DISCUSSION

1 *Bisphenol A*

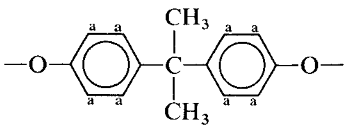
The ^{1}H-NMR spectrum of the melted reaction mixture permits the identification and measuring of structures:[3]



X



Y



Z

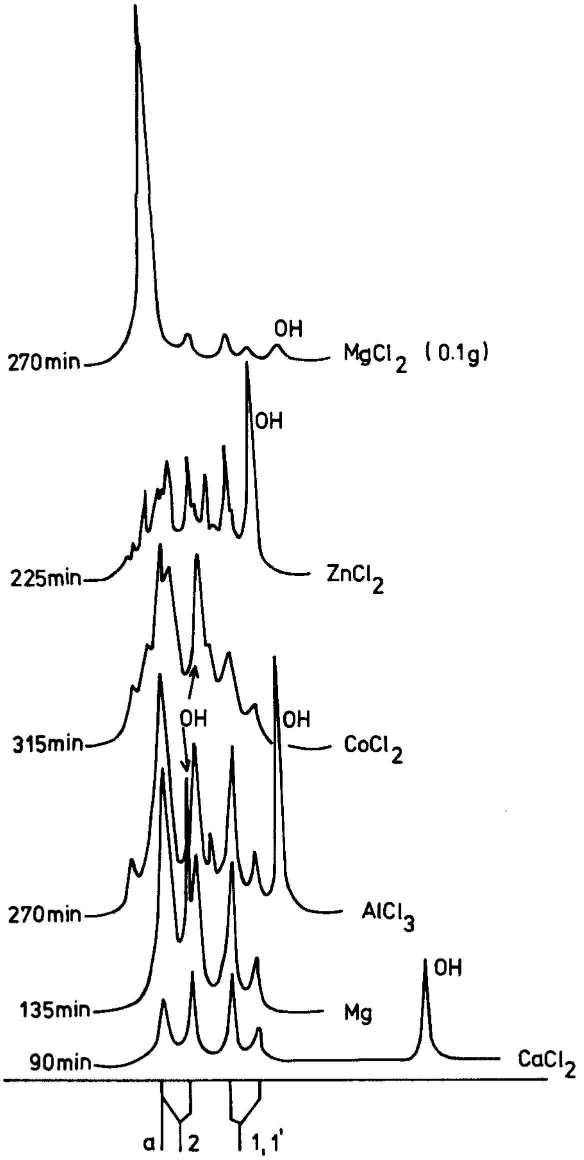


FIGURE 1 Aromatic region of the ^{1}H-NMR spectra for different catalysts and reaction times.

TABLE I

The temperature programme

Temperature (°C)	Time (min.)
60	60
80	120
100	120
120	120
140	240

The $CDCl_3$ solutions give less resolved spectra. Figure 1 presents some spectra (aromatic region) of different catalysed reactions at different times. Signals of OH phenolic protons, of 1 and 1′ protons from X and Y structures (not resolved in $CDCl_3$ solutions spectra), of the protons from X and Y structures and of protons (7.16 ppm) from Y and Z structures can be observed and measured. For the reactions in presence of $ZnCl_2$, $AlCl_3$ and $CoCl_2$ the aromatic region of the spectrum is more complex, consisting in many signals. These reaction mixtures give also in the saturated region of the ^{1}H-NMR spectrum unexpected and unidentified signals from the beginning of the process and increasing during the polycondensation. It is not the purpose of this paper to study the nature and the mechanism of these side reactions.

Because it is not possible to measure, from $CDCl_3$ solutions spectra, the ratio of X, Y and Z structures, the reactions rate constants according to the known scheme:

$$X \xrightarrow{k_3} Y \xrightarrow{k_4} Z$$

could not be determinated.

From the OH signal integral and the 1 and 1′ protons signal integral, the "free" bisphenol A in the reaction mixture (i.e. $X + \frac{1}{2}Y$) can be measured. The difference up to the total quantity of bisphenol A is the "enchained" bisphenol A ($Z + \frac{1}{2}Y$). The "free" and "enchained" names do not properly characterize the system state, because a half of bisphenol A—ended chains are considered to be "free" and the other half "enchained." Figure 2 gives the bisphenol A enchainment rate for the reactions catalysed by $CaCl_2$, Mg and $MgCl_2$ at three different concentrations. The enchainment rate increases as below:

$$CaCl_2 < Mg < 0.1\text{ g } MgCl_2 < 0.2\text{ g } MgCl_2 < 0.3\text{ g } MgCl_2$$

For $AlCl_3$, $ZnCl_2$ and $CoCl_2$, which give side reactions the "free" bisphenol A consumption rate is represented in Figure 3. The difference up to the total bisphenol A quantity is here a sum of "enchained" bisphenol A and bisphenol A participating in side reactions. The most important side reaction seems to be given by $AlCl_3$ (the slowest bisphenol A consumption) followed by $CoCl_2$ and $ZnCl_2$.

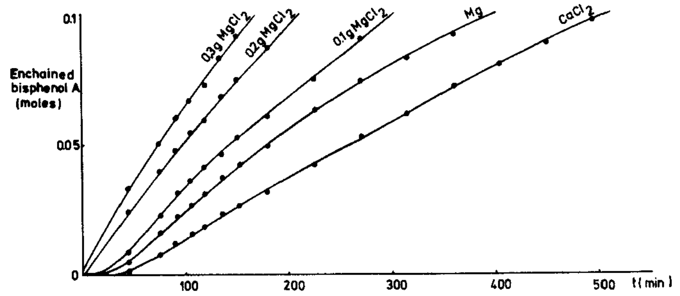
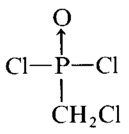


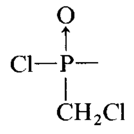
FIGURE 2 Bisphenol A enchainment rate for different catalysts.

2 *Chloromethylphosphonic Dichloride*

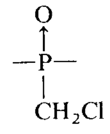
The ^{1}H-NMR spectrum of the reaction mixture dissolved in CDCl$_3$ permits identification and measuring of the three structures:


$$\mathrm{Cl{-}\overset{\overset{\displaystyle O}{\uparrow}}{P}{-}Cl},\ \mathrm{P{-}CH_2Cl}$$

A


$$\mathrm{Cl{-}\overset{\overset{\displaystyle O}{\uparrow}}{P}{-}},\ \mathrm{P{-}CH_2Cl}$$

B


$$\mathrm{{-}\overset{\overset{\displaystyle O}{\uparrow}}{P}{-}},\ \mathrm{P{-}CH_2Cl}$$

C

Figure 4 presents this spectral region for different reaction mixtures at different times. As it is clear in Figure 4, the side reactions do not affect the phosphorus-compound, which experiences only the known successive reactions scheme:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

In order to calculate k_1 and k_2 by the nonlinear regression algorithm,[4] the evolution of A, B and C structures are represented against reaction time for each experiment. For CaCl$_2$, Mg and MgCl$_2$ catalysed reactions, the plot is analogous to that obtained for the uncatalysed reaction.[3] Figure 5 gives this plot for CaCl$_2$ catalysed reaction. The other plots resemble very much this one, only the total reaction time is shorter, as it can also be seen in Figure 2.

For the reactions in presence of AlCl$_3$, ZnCl$_2$ and CoCl$_2$, the A, B and C plot against time is very different from the successive reactions type. Figure 6 presents this plot for AlCl$_3$ catalysed reaction, for ZnCl$_2$ and CoCl$_2$ similar plots are obtained. It is clear in Figure 6 that side reactions

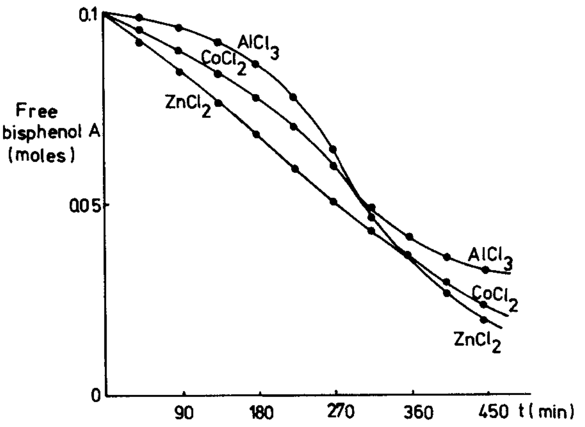


FIGURE 3 Bisphenol A consumption rate for AlCl$_3$, ZnCl$_2$ and CoCl$_2$ catalysed reactions.

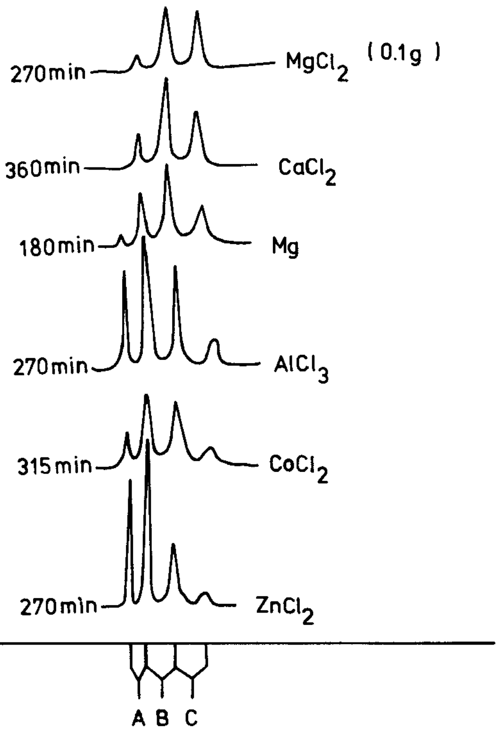


FIGURE 4 Chloromethylphosphonic dichloride resonance for different catalysts and reaction times.

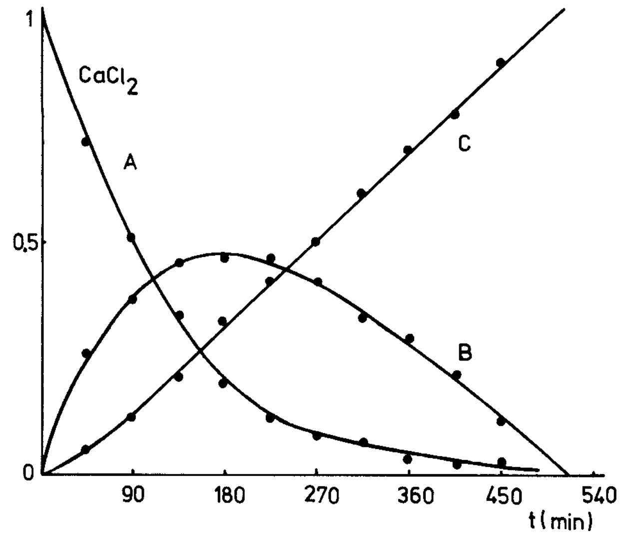


FIGURE 5 The **A**, **B** and **C** plot against time for the CaCl$_2$ catalysed reaction.

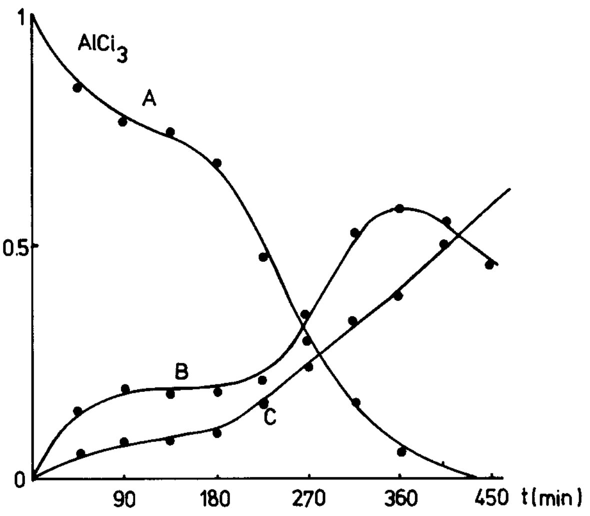


FIGURE 6 The **A**, **B** and **C** plot against time for the AlCl$_3$ catalysed reaction.

occur mainly at the beginning of the process, the polycondensation being visible only after 250 minutes. It is clear that such compounds could not be recommended as catalysts for polycondensation.

3 *Reaction Rate Constants k_1 and k_2 Determination*

Using the nonlinear regression algorithm[4] the reaction rate constants k_1 and k_2 could be determinated for the polycondensations without side reactions and with same approximations as in the uncatalysed reaction.[3] The results are given in Table II, in the inverse order of catalyst efficiency.

In order to compare the catalytic effect of the compounds used, the total polycondensation time (Figure 7) and k_1 and k_2 values (Figure 8) are represented against the MgCl$_2$ catalyst quantity added at 0.1 moles bisphenol A. Figure 8 indicates that k_1 and k_2 linearly grow with increasing the catalyst quantity. The total polycondensation time is significantly reduced only in the 0.05–0.15 g MgCl$_2$ range. In Figures 7 and 8 are represented also the points which correspond to 0.1 g CaCl$_2$ and 0.1 g Mg. It can be seen that 0.1 g CaCl$_2$ has the same effect as 0.035 g MgCl$_2$ and 0.1 g Mg the same effect as 0.06 g MgCl$_2$. Consequently, the catalytic efficiency of MgCl$_2$ is triple that of CaCl$_2$ and almost double than that of Mg.

From Figure 7 it is clear why Coover[2] recommended the use of 0.1–0.2 g catalyst for 0.1 moles diol. Above 0.2 g the shortening of reaction time can be neglected.

TABLE II

The total reaction time, the maximum temperature and the k_1 and k_2 values for some catalysts

Catalyst	Quantity (g. for 0.1 moles bisphenol A)	Total reaction time (min)	Maximum temperature (°C)	k_1 (min^{-1})	k_2 (min^{-1})
—[a]	—	675	190	6.4×10^{-3}	3.3×10^{-3}
CaCl$_2$	0.1	510	140	8.8×10^{-3}	5.5×10^{-3}
Mg	0.1	400	120	1.2×10^{-2}	7.5×10^{-3}
MgCl$_2$	0.1	300	100	1.7×10^{-2}	1.0×10^{-2}
MgCl$_2$	0.2	210	100	2.5×10^{-2}	1.9×10^{-2}
MgCl$_2$	0.3	165	80	3.5×10^{-2}	2.5×10^{-2}

[a] See Reference 3.

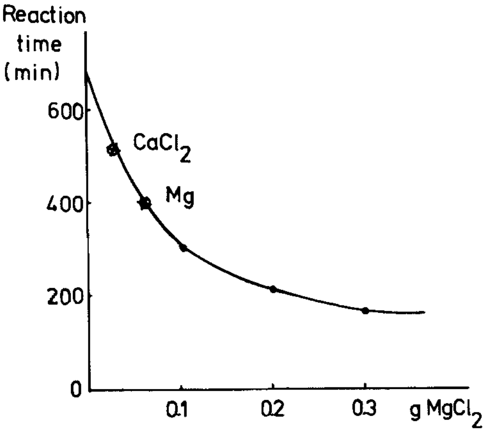


FIGURE 7 The total time of reaction represented against $MgCl_2$ quantity.

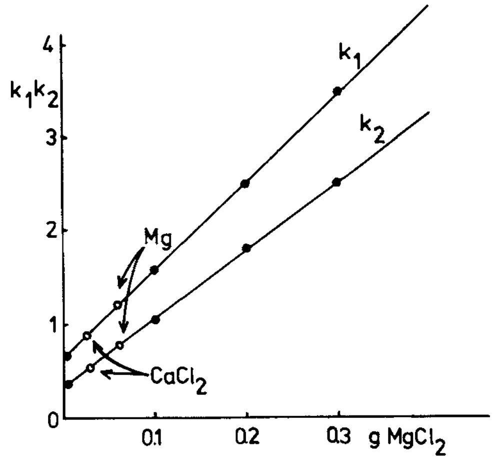


FIGURE 8 k_1 and k_2 dependence on the $MgCl_2$ quantity.

The catalyst function can be supposed to complex and polarize the chloromethylphosphonic dichloride, increasing its electrophilic activity:

$$ClCH_2P(O)Cl_2 + MeCl_x \longrightarrow ClCH_2P^+(O)ClMeCl^-_{x+1}$$

Me = Mg, Ca, Zn, Co, Al $\quad x = 2 - 3$

The formed anion reacts with the nucleophilic agent according to the classical scheme of intermediate complex.

The explanation of Mg catalytic activity can be the $MgCl_2$ formation in these reaction conditions. This was observed also[1] in polycarbonates synthesis from bisphenol A. For Al, Co and Zn chlorides, side reactions given from bisphenol A—catalyst interactions occur. The Friedel–Crafts type reactions at the aromatic nucleus could not be excluded, also.

CONCLUSIONS

From the catalysts studied here, the most active is $MgCl_2$ in the 0.1–0.2 g for 0.1 moles bisphenol A concentrations range. It permits an important decrease of the total polycondensation time and, consequently, of the reaction maximum temperature. For this process, Mg and $CaCl_2$ were proved active, also.

$AlCl_3$, $CoCl_2$ and $ZnCl_2$ generate mainly side reactions, therefore we do not recommend their use for this polycondensation.

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