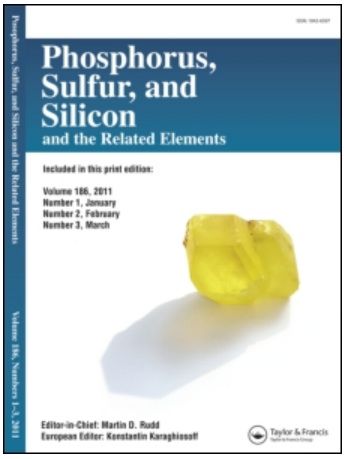

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THE VAPOR-LIQUID POLYCONDENSATION OF CYCLOHEXYLPHOSPHORIC DICHLORIDE WITH HYDROQUINONE

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The vapor-liquid polycondensation of cyclohexylphosphoric dichloride with hydroquinone was investigated. The influence of the temperature, reaction time, base concentration, and molar ratio of reagents on the yield, inherent viscosity, and molecular weight of the obtained polymer was studied. Second order, central, composite, rotatable experimental design was used in order to carry out this work and to mark limits of the experimental field for optimal yields and high inherent viscosities.

Keywords: Experimental design; polyphosphate; vapor-liquid polycondensation

Polyphosphates are used for preparation of flame retardant polymers,[1] ion-exchange resins, model for natural biopolymers such as nucleic acid[2,3] (components of bacterial cell walls) and polynucleotides.[4] The main methods for obtaining polyphosphates are solution,[5] mel,[6] and interfacial[7,8] polycondensations or ring opening polymerization of cyclic phosphates.[2,3,9,10] Moderate yields and low molecular weights ($<10^4$) were obtained. Better results were achieved in vapor-liquid (v-l) interfacial polycondensation. Sokolov[11,12] applied this system only for polyamides synthesis. Bubbling the vapor monomers through the aqueous solution of the other monomer readily performs the contact of the monomers in this system.

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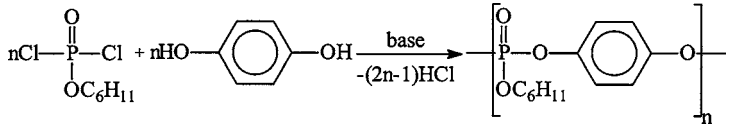
In previous articles[13,14] we have reported the possibility of obtaining polyphosphonates by vapor-liquid interfacial polycondensation. Continuing our work on the application of the vapor-liquid system to polyphosphates synthesis, we present here the synthesis and characterization of the polyphosphates by vapor-liquid polycondensation of cyclohexylphosphoric dichloride (CPPD) with hydroquinone (HQ) (Scheme 1).



SCHEME 1

These results are presented concerning the influence of various parameters (reaction temperature, reaction time, base concentration, and molar ratio CPPD:HQ) on reaction conditions (yield) and inherent viscosity.

For correlation the concomitant influence of these parameters on yield and inherent viscosity and for the determination of the best reaction conditions, an experimental design as described in the literature was used (adapted).[15,16]

EXPERIMENTAL

General Procedure

The experimental apparatus is presented in Figure 1. In the round-bottom flask 1, immersed in an oil bath, the appropriate phosphorus dichloride was heated and carried, by a stream of nitrogen, into the flask 2, containing aqueous NaOH and hydroquinone.

A stream of nitrogen was passed through the reaction apparatus to provide agitation, to protect the system from oxygen, to transport vapors of the phosphorus acid chlorides, and to control the rate of reaction. The entire quantity of phosphoric dichloride is transported with nitrogen from the round-bottom flask 1 to 2. For the separation of the formed polymer, the reaction mixture from flask 2 was filtered on G4 glass funnel, under vacuum.

In order to prevent the possibility of condensation of the reagent vapor on the apparatus walls, the vapor mixture is overheated so that the partial pressure of the vapor reagent in the gas mixture is lower than its saturation vapor pressure.

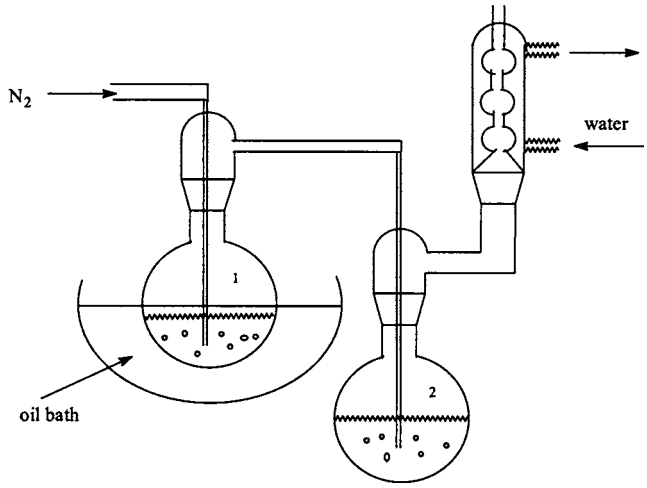


FIGURE 1 The experimental apparatus for vapor liquid.

The polymer separates from the solution as a tacky, coherent mass, adhering to the container surface. The solid polymer was washed with distilled water until free of chloride ion and dried at 50°C in the vacuum.

The yield of the polyphosphate was 75%. The inherent viscosity of the polymer in dichloroethane was 1.10 dl/g, measured at a concentration of 0.5 g/dl, at 30°C.

The infrared (IR) spectrum (film) exhibited absorptions at 930–940 cm^{-1}, 1320–1290 cm^{-1} (P(O)—O—C_{phenyl}); 1280 cm^{-1} (P=O); 1040 cm^{-1} (P—$OC_{cyclohexyl}$). The nuclear magnetic resonance (^{1}H-NMR) spectrum in $CDCl_3$ showed signals (δ) at 6.1 ppm (s, 4H, phenyl); 1.2–4.6 (m, 11H, cyclohexyl). The phosphorus content, which was determined by the Schöniger method, was 11.78%. The glass transition temperature was 108°C. The determined molecular weights were: Mn = 10500 and Mw = 15450.

Instruments

The IR and ^{1}H-NMR spectra were recorded on a SPECORD M80 spectrophotometer (film) and a JEOL-C-60 MHz spectrometer ($CDCl_3$) respectively. The polymer was characterized by viscosity, using an Ubbelohde viscosimeter, at 20°C. Molecular weight was determined by gel permeation chromatography, on an Evaporative Light Scattering Detector: PL-EMD 950. Glass-transition temperature (Tg) was determined by differential scanning colorimeter method (DSC) on a Seiko DSC 220 device.

Experimental Design

To carry out the work, the second order, central, composite, rotatable experimental design was used.[15,16] The advantages of this method are:

- the number of experiments is reduced
- the regression equation obtained by data processing is defined on the whole experimental field;
- the complexity of calculation of regression coefficients is reduced due the orthogonality of many independent variables vectors.

The experimental results were processed using a multiple regression method to obtain response surface **Y** (Eq. 1):

$$Y = a_0 + \sum a_i x_i + \sum a_{ij} x_i x_j \quad i \leq j \tag{1}$$

where a_i, a_{ij}, are the regression coefficients for the property **Y**.

Actual independent variables were transformed according to Eq. 2:

$$x_i = (\chi_i - \chi_{ic})/\Delta\chi_i \tag{2}$$

where: x_i = encoded variable, dimensionless, χ_i = actual variable, χ_{ic} = central value for "i" variable, $\Delta\chi_I$ = factorial interval for "i" variable.

To perform the calculus, standard subroutines which compute regression coefficients from Eq. 1 together with the statistics necessary to test their significance and the regression significance, were used. The obtained response surfaces were studied to give the influence of the reaction parameters (reaction temperature, reaction time, base concentration, and molar ratio) on the polycondensation of CPPD with HQ.

RESULTS AND DISCUSSION

In order to get data for preparing polyphosphates with high molecular weights, the influence of temperature, reaction time, base concentration, and molar ratio CPPD:HQ on the yield and inherent viscosity of the obtained polyphosphate was studied. Those reaction conditions must be chosen to obtain higher yields and inherent viscosities to prevent the degradation of polymer and terminating competing reactions.

The influence of reaction temperature (in round-bottom flask 2) on the yield, inherent viscosity and molecular weight is presented in Table I.

The best results ($\eta_{inh} = 1.10$ dl/g and $M_n = 9800$, $M_w = 14100$) were obtained at 60°C. At higher temperatures the yield, inherent viscosity,

TABLE I The Influence of the Reaction Temperature on the Yield, Inherent Viscosity, and Molecular Weight in the Vapor-Liquid Polycondensation of Cyclohexylphosphoric Dichloride with Hydroquinone[a]

T (°C)	Yield (%)	η^b_{inh} (dl/g)	$M_n \times 10^4$	$M_w \times 10^4$
35	22	0.30	0.28	0.65
40	38	0.50	0.55	0.72
45	64	0.83	0.90	1.20
55	70	0.90	0.95	1.28
60	75	1.10	0.98	1.41
80	32	0.38	0.48	0.62
90	20	0.28	0.40	0.55

[a]Reaction conditions: 0.625 moles CPPD, 0.025 moles HQ, 1 M $NaOH_{aq}$ (0,052 moles), at 100°C (in round-bottom flask 1), 50 min.

[b]Determined at a concentration of 0.5 g/dl, in tetrachloroethane, at 30°C.

and molecular weight decrease because of hydrolysis as secondary reactions.

The effect of the reaction time on the yield and inherent viscosity of the obtained polyphosphate is presented in Table II.

The reaction time may vary but should not be so great as to affect a considerable decrease in the monomer concentration of the liquid phase. The highest yields and inherent viscosities were obtained at 50–60 min.

In order to get data for preparing polyphosphates with high molecular weights, the effect of the alkaline medium on the yield and the inherent viscosity was studied. The reaction conditions must be carefully chosen in order to obtain high yields and inherent viscosities, to prevent the degradation of polymer (caused by the attack of base on CPPD on phosphoryl chloride end-groups of intermediary oligomers and on

TABLE II The Dependence of the Yield, Inherent Viscosity, and Molecular Weight of the Obtained Polyphosphate on the Reaction Time[a]

Reaction Time (min)	Yield (%)	η^b_{inh} (dl/g)	$M_n \times 10^4$	$M_w \times 10^4$
30	25	0.30	0.45	0.60
40	44	0.60	0.64	0.85
50	68	0.92	0.90	1.15
60	72	1.00	0.98	1.28
70	58	0.70	0.56	0.78
90	30	0.60	0.55	0.85

[a]Reaction conditions: CPPD : HQ : NaOH = 2.5 : 1 : 2; 60°C.

[b]Determined at a concentration of 0.5 g/dl, in tetrachloroethane, at 30°C.

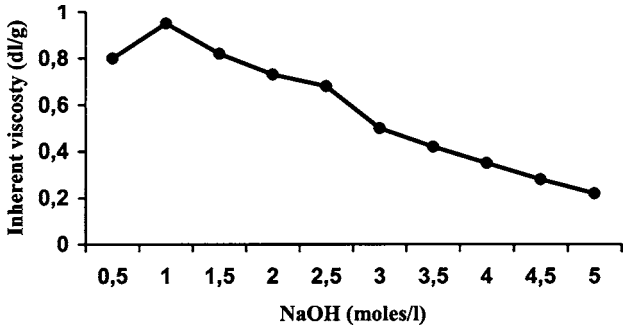


FIGURE 2 Influence of NaOH concentration on the inherent viscosity.

ester-phosphoric bonds of polymer), and terminating competing reactions. Different aqueous sodium hydroxide concentrations were used in the synthesis of the cyclohexylpolyphosphate. The best results were obtained with 1 M aqueous sodium hydroxide (Figure 2).

In order to follow the influence of the molar ratio between reagents on the yield, the inherent viscosity, and molecular weight (Table III), the quantities added in the two flasks were varied, maintaining an invariable stream of nitrogen (10 ml/s), the temperatures in the two flasks and the reaction time. Like in other polycondensations that take place by diffusion mechanism, the best results were obtained at nonequimolecular ratios, especially in excess of CPPD (CPPD:HQ = 2.5:1).

TABLE III The Influence of the Reagents Molar Ratio on the Yield, Inherent Viscosity, and Molecular Weight in the Base-Promoted Liquid-Vapor Polycondensation of CPPD with HQ[a]

CPPD:HQ	η^{b}_{inh} (dl/g)	$M_n \times 10^4$	$M_w \times 10^4$	Yield (%)
5.5:1.0	0.70	0.88	1.20	58
3.5:1.0	0.88	0.95	1.18	65
2.5:1.0	1.10	1.00	1.36	74
2.0:1.0	0.82	0.93	1.35	70
1.6:1.0	0.78	0.92	1.27	64
1.2:1.0	0.75	0.90	1.20	60
1.0:1.0	0.70	0.88	1.15	58
1.0:1.2	0.68	0.79	0.93	44
1.0:2.0	0.64	0.80	0.97	50
1.0:2.5	0.60	0.81	0.98	50

[a]Reaction conditions: (1 M NaOH), at 60°C (in round-bottom flask 2) and 100°C (in round-bottom flask 1).

[b]Determined at a concentration of 0.5 g/dl, in tetrachloroethane, at 30°C.

TABLE IV Transformation of Variables

Coded values→ Real values↓	−2	−1	0	1	2
Reaction time (min) X_1	30	40	50	60	70
Temperature (°C) X_2	35	45	55	60	80
NaOH concentration (moles/l) X_3	1	2	3	4	5
Molar ratio (CPPD/HQ) (moles) X_4	1	1.2	2	2.5	3.5

Using the "Experimental Design" the correlation of the concomitant influence of these parameters on the yield and inherent viscosity was determined.

Variable transformation and experimental conditions are listed in Tables IV and V.

To illustrate the influence of the studied parameters on the progress of the polycondensation process, Figure 3 represents the variation of the polyphosphate yield versus one parameter, all the others being taken at values corresponding to the center of the experimental field.

This graphic representation of the independent variables shows that, for the chosen experimental domain, the curves $Y_A = f(X_1)$ and $Y_A = f(X_4)$ have a maximum at the values of time and molar ratio situated in middle of the domain (i.e., $X_1 = 0.70$ and $X_4 = 0.70$, corresponding to the real values of 60 min and molar ratio CPPD : HQ ~ 2.5 : 1.0). For longer reaction time and higher molar ratio values the yield decreases slightly. If the reaction time exceeds the optimal value the secondary reactions are promoted (i.e., the saponification of the end-groups of the oligomers and of the ester-phosphoric groups).

From the curves $Y_A = f(X_2)$ and $Y_A = f(X_1)$, which illustrate the influence of the temperature and reaction time on the yield, it can be observed that for lower temperatures (<40°C) the influence is significant. For temperature and time values that overtake the middle of the experimental domain, the temperature has the highest influence.

The curve $Y_A = f(X_3)$ show that the NaOH concentration has the most significant influence. For 1 M NaOH concentration value ($X_3 = -2$), the highest yield is obtained (74%). Increasing NaOH concentration, the yields decrease because of the secondary reactions (i.e., saponification of the P—Cl groups). For higher NaOH concentration values that exceed the middle of chosen experimental domain, the influence on the yield is lower compared with the influence of other parameters.

TABLE V Experimental Design and Experimental Results

No.	X_1	X_2	X_3	X_4	Yield (%)	η_{inh} (dl/g)
0	1	2	3	4	5	6
1	−1	−1	−1	−1	15.4	0.8401
2	1	−1	−1	−1	18.3	0.8451
3	−1	1	−1	−1	38.2	0.9523
4	1	1	−1	−1	79.6	0.9700
5	−1	−1	1	−1	8.2	0.2004
6	1	−1	1	−1	10.1	0.1901
7	−1	1	1	−1	30.4	0.7510
8	1	1	1	−1	34.6	0.7780
9	−1	−1	−1	1	16.9	0.8620
10	1	−1	−1	1	23.0	0.8750
11	−1	1	−1	1	60.5	1.1100
12	1	1	−1	1	82.6	1.6590
13	−1	−1	1	1	9.8	0.2282
14	1	−1	1	1	11.5	0.2556
15	−1	1	1	1	32.6	0.2816
16	1	1	1	1	33.2	0.5218
17	−2	0	0	0	18.7	0.6012
18	2	0	0	0	39.2	0.6216
19	0	−2	0	0	0.45	0.0213
20	0	2	0	0	55.6	1.0255
21	0	0	−2	0	85.7	1.7830
22	0	0	2	0	24.9	0.2910
23	0	0	0	−2	17.6	0.6200
24	0	0	0	2	40.6	0.6280
25	0	0	0	0	36.2	0.5551
26	0	0	0	0	37.1	0.5900
27	0	0	0	0	38.5	0.6000
28	0	0	0	0	38.2	0.5850
29	0	0	0	0	37.3	0.5510
30	0	0	0	0	35.6	0.5112
31	0	0	0	0	38.8	0.5010

The most evident conclusion is that the influence of the base concentration on the yield is very important because high base concentrations lead to secondary hydrolysis reactions. Also, it was demonstrated that by the correlation of the NaOH concentration with the reaction temperature, very high yields were obtained (95%).

The individual influence of the same parameters on polyphosphate inherent viscosity [$Y_B = f(Xi)$] is presented in Figure 4.

The curves $Y_B = f(X_2)$ and $Y_B = f(X_1)$ (inherent viscosity as function on the temperature and the reaction time) show that at low temperatures <50°C, the influence of the reaction time is more important for obtaining high inherent viscosities. For higher values of these parameters,

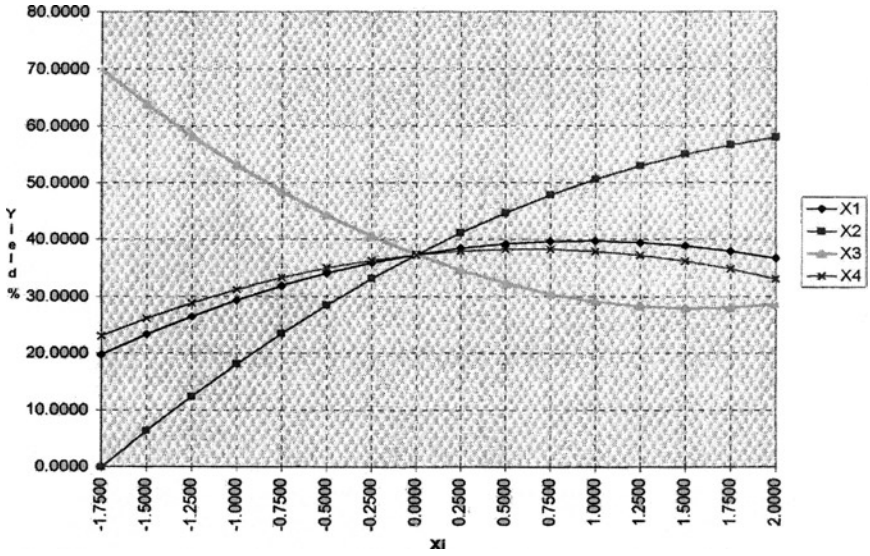


FIGURE 3 The influence of the independent variables on the yield.

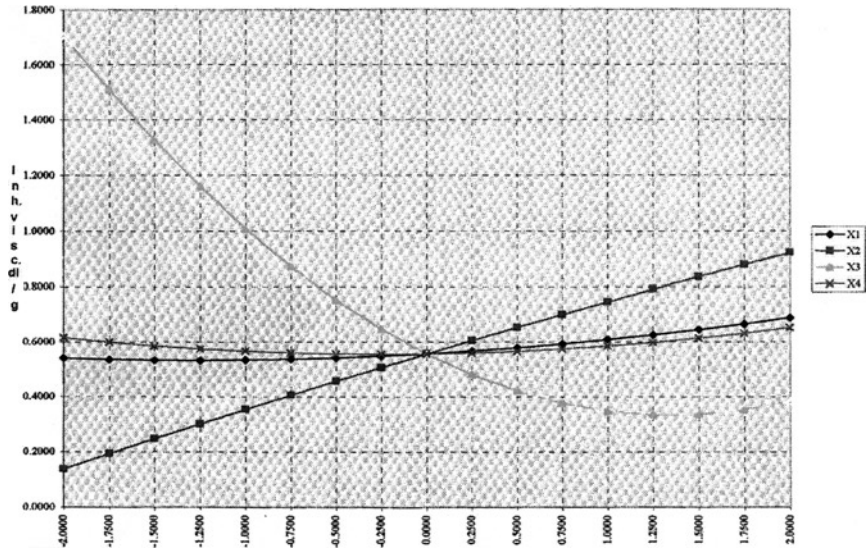


FIGURE 4 The influence of the independent variables on the inherent viscosity.

as shown in the center of the chosen experimental domain, the temperature influences more the polyphosphate viscosity than the reaction time. Also, for $X_2 = 2$, respectively 58°C, an inherent viscosity of 0.99 dl/g was obtained. It was observed that a high inherent viscosity ($\eta_{inh} = 1.1$ dl/g) was obtained with 1 M NaOH concentration. With 5 M NaOH concentration (X_3) = 2, the inherent viscosity decreases at 0.40 dl/g.

By individual influence of the four parameters on the inherent viscosity, presented in Figure 3, the following order of the independent variables can be established $X_2 > X_1 > X_4 > X_3$.

CONCLUSIONS

The vapor-liquid method is versatile in the synthesis of phosphorus compounds having a lot of advantages:

- this method permits the use in reaction of readily hydrolyzing compounds, which is impossible in other aqueous systems;
- only ionic impurities need to be washed from the polyphosphate;
- the solvent is usually water.

A second order, central, composite, rotatable experimental design was used to study the simultaneous influence of various parameters (reaction time, temperature, base concentration, and molar ratio CPPD:HQ) on the yield and inherent viscosity of the obtained polyphosphate. Interesting correlations were realized to establish optimal reaction conditions. The calculated results were in concordance with the experimental data, respectively: reaction time 50–60 min; temperature 60°C; 1 M NaOH concentration and molar ratio CPPD : HQ = 2.5 : 1. From the experimental and calculated data, it results that the most important factors are the NaOH concentration and the reaction temperature.

These investigations allowed marking better limits of the experimental domain in order to obtain good yields, high inherent viscosities, and molecular weights respectively.

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