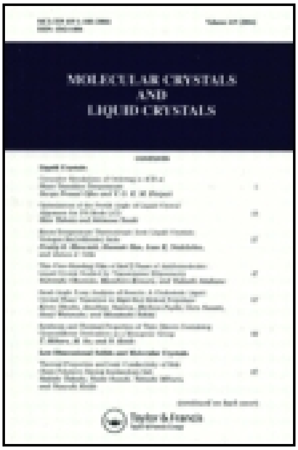

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Synthesis of Polyphosphates Related to Biopolymers

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SYNTHESIS OF POLYPHOSPHATES RELATED TO BIOPOLYMERS

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Polyphosphates were synthesized by base promoted liquid-vapor polycondensation of cyclohexylphosphoric dichloride with bisphenol A. The effects of temperature, reaction time, base concentration and molar ratio of reagents on yield, inherent viscosity and molecular weight of the obtained polymer were studied. A second order, central composite, rotatable experimental design was used to find domain experimental field for optimal yields and high inherent viscosities.

Keywords: bisphenol A; cyclohexylphosphoric dichloride; polyphosphate; rotatable experimental design

INTRODUCTION

Polymer chemistry has contributed in various ways to the present progress in biology, biochemistry and medicine, providing new methods for preparing and studying macromolecules as well as providing new, highly specified materials. One of these ways is the synthesis of new polymers, structurally related to the natural biopolymers with poly(alkylene phosphate) main chains [1,2].

The main methods of obtaining polyphosphates are solution, mass, interfacial polycondensations, ring opening polymerization of cyclic phosphates or polycondensation via transesterification. Low yields and low molecular weights ($<10^4$) were obtained [3–6].

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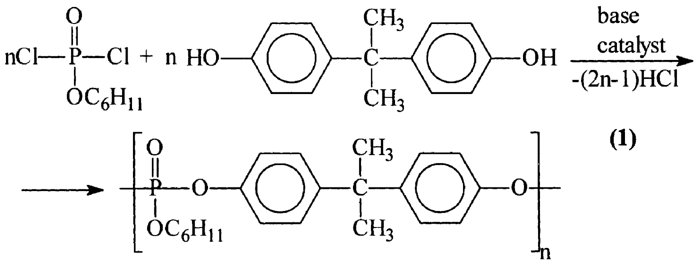
In this paper we summarize our recent and older works, mostly on the vapor-liquid interfacial polycondensation of polyphosphates with molecular weights $>10^4$.

In a previous paper [7] we have reported the possibility of obtaining polyphosphonates by vapor-liquid interfacial polycondensation.

For the reaction of cyclohexylphosphoric dichloride (CPPD) with bisphenol A (BA) (reaction 1) the optimal reaction conditions were established in order to prevent the possibility of secondary hydrolysis reactions. The influence of various parameters (temperature, base concentration, reaction time and molar ratio CPPD:BA) on yield and inherent viscosity is presented in this paper.



(1)

For correlation the concomitant influence of these parameters on yield and inherent viscosity and for determination the best reaction conditions, an experimental design soft was used (adapted) [8,9].

Experimental

The general procedure of the vapor-liquid interfacial polycondensation of CPPD with BA was presented previously [7].

The yield of polymer was 85%. Inherent viscosity of the polymer in dichloroethane was 0.95 dl/g, measured at a concentration of 0.5 g/dl, at 30°C.

The infrared (IR) spectrum (film) exhibited absorptions at 950 cm^{-1}, 1390 cm^{-1} (P(O)−O−C (phenyl)), 1285 cm^{-1} (P=O), 1320–1350 (P−O−C_{alkyl}). The nuclear magnetic resonance (^1H−NMR) spectrum in $CDCl_3$, showed signals (δ) at 1.5–4.2 (m, 11H, cyclohexyl); 1.58 (s, 6H, methyl); 7.10–7.12 (m, 8H, phenyl). The phosphorus content, determined by Schöniger method, was 8.0%. The glass transition temperature was 86°C. The determined molecular weights were: Mn = 8500 and Mw = 10500.

Measurements

The IR and ^1H NMR were recorded on a SPECORD M80 spectrophotometer and a JEOL C-60 HL spectrometer, respectively. The polymers were characterized by viscosity, on an Ubbelohde viscosimeter, at 20°C and by gel permeation chromatography, on an Evaporative Light Scattering Detector. Glass-transition temperature (Tg) was determined by differential scanning colorimeter method (DSC), on a Seiko DSC 220 device.

Experimental Design

It was used a second order, central composite, rotatable experimental design [8,9]. The experimental results were processed by using a multiple regression method to obtain response surface **Y**(Eq. (1)):

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

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

Actual independent variables were transformed according to the following equation (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 that 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 find the influence of reaction parameters (temperature, reaction time, NaOH concentration, molar ratio of CPPD: BA) upon the yield and the inherent viscosity.

RESULTS AND DISCUSSION

In order to chose successfully the optimal conditions of the synthesis of high-molecular-weight polymers, the influences of temperature, reaction time, base concentration and molar ratio CPPD:BA on yield and inherent viscosity of the obtained polyphosphate were studied and presented in Table 1.

The best results ($\eta_{inh} = 0.85$ dl/g and $M_n = 8000$, $M_w = 11500$) were obtained at 55°C. At higher temperatures the yield and inherent viscosity decrease because of hydrolysis secondary reactions. It was observed the highest yields and inherent viscosities were obtained at 60–70 minutes. In order to get data for preparing polyphosphates with high molecular weights, the effect of alkaline medium on yield and inherent viscosity was studied. The best results were obtained with 1 M aqueous sodium hydroxide. Experimental data exhibited in Table 1 show that the highest

TABLE 1 The Influence of Reaction Temperature, Reaction Time, NaOH Concentration and Molar Ratio (CPPD:BA) on Yield and Inherent Viscosity and Molecular Weight, in the Liquid-Vapor Polycondensation of Cyclophosphoric Dichloride (CPPPD) (0.020 moles) with Bisphenol A (BA) (0.020 moles), NaOH 1 M (0.042 moles), at 100°C in Round-Bottom Flask 1, 60 min (Catalyst Tetrabutylammonium Bromide)

	Temperature, °C					Reaction time, minute					NaOH conc., mol/l				Molar ratio, CPPD:BA			
Variable	35	40	55	60	80	30	50	60	70	90	0.5	1	1.5	4.5	3.5:1	2.5:1	2.0:1	1.6:1
Yield %	20	38	60	54	35	25	40	68	60	30	50	68	60	15	48	70	40	35
$\eta_{inh}{}^{a}$ dl/g	0.30	0.50	0.85	0.55	0.35	0.30	0.60	0.90	0.85	0.50	0.75	0.88	0.75	0.25	0.60	0.98	0.53	0.28
$M_n \times 10^4$	0.20	0.48	0.80	0.50	0.38	0.13	0.53	0.75	0.67	0.30	0.60	0.80	0.58	0.30	0.85	1.28	0.72	0.28
$M_w \times 10^4$	0.55	0.65	1.15	0.70	0.60	0.50	0.60	1.05	0.90	0.68	0.98	1.15	0.90	0.50	1.06	2.35	1.00	0.38

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

yields and inherent viscosities were obtained at non-equimolecular ratios, especially in excess of CPPD (CPPD:BA = 2.5:1).

Variable transformation and experimental conditions are listed in Tables 2 and 3.

In Figure 1 is illustrated the individual influence of the four independent variables (Xi) on yield (Y_A, dependent variable) [$Y_A = f(X_1)$] and the influence of a parameter on yield, all the others being taken at values corresponding to the center of the experimental field was presented. This graphic representation of the independent variables shows that, for 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 domain (i.e. $X_1 = 0.75$ and $X_4 = 0.75$, corresponding to the real values of 55 minutes and molar ratio CPPD:BA$\sim$2.5:1.0). 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 yield, it can observed that for lower temperatures (<40°C) influence is significant. For temperature and time values that overtake the middle of the experimental domain, 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 (79%). 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 yield is lower compared with the influence of other parameters.

The examination of concomitant influence of these variables upon yield can be analyzed by plotting the yield in the plane of two variables, keeping the others in the middle of the chosen experimental data. Figure 2 (yield in the plane of X_1X_2) show that the rising of temperature and reaction time leads to the increasing of yield.

Figure 3 indicates that high yield (75.80%) was obtained increasing reaction time and decreasing NaOH concentration.

The curves presented in Figure 4 show that by correlation of reaction time with molar ratio an optimal yield is obtained (for $X_1 = 0.8470$ and

TABLE 2 Transformation of Variables

Coded values→ Real values↓	– 2	– 1	0	1	2
Reaction time (minutes.), X_1	30	40	50	60	70
Temperature, (°C), X_2	30	40	50	60	70
NaOH concentration, (moles/l), X_3	1	2	3	4	5
Molar ratio (CPD/ BA), (moles), X_4	1	1.5	2	2.5	3.5

TABLE 3 Experimental Design and Experimental Results

Nr.	X_1	X_2	X_3	X_4	Yield %	η_{inh}, dl/g
1	– 1	– 1	– 1	– 1	15.8	0.8542
2	1	– 1	– 1	– 1	18.7	0.8566
3	– 1	1	– 1	– 1	38.5	0.9600
4	1	1	– 1	– 1	79.5	0.9780
5	– 1	– 1	1	– 1	8.0	0.2184
6	1	– 1	1	– 1	10.9	0.1900
7	– 1	1	1	– 1	30.5	0.7586
8	1	1	1	– 1	33.2	0.7780
9	– 1	– 1	– 1	1	15.8	0.8635
10	1	– 1	– 1	1	22.5	0.8732
11	– 1	1	– 1	1	60.0	1.1090
12	1	1	– 1	1	81.5	1.6527
13	– 1	– 1	1	1	9.0	0.2153
14	1	– 1	1	1	10.2	0.2481
15	– 1	1	1	1	31.0	0.2790
16	1	1	1	1	32.8	0.5210
17	– 2	0	0	0	17.8	0.6010
18	2	0	0	0	38.9	0.6200
19	0	– 2	0	0	0.58	0.0295
20	0	2	0	0	54.9	1.0242
21	0	0	– 2	0	84.5	1.7790
22	0	0	2	0	23.2	0.2885
23	0	0	0	– 2	16.7	0.6200
24	0	0	0	2	39.1	0.6300
25	0	0	0	0	35.0	0.5605
26	0	0	0	0	36.8	0.5900
27	0	0	0	0	37.8	0.6090
28	0	0	0	0	37.9	0.5750
29	0	0	0	0	36.5	0.5500
30	0	0	0	0	34.5	0.5100
31	0	0	0	0	37.4	0.4950

$X_4 = 0.4269$, respectively, 58 minutes and molar ratio CPPD:BA = 2.65:1, $\eta = 63.26\%$).

The correlation of temperature with NaOH concentration, presented in Figure 5, is very important. The highest yield (95.94%) was obtained by increase of temperature and decrease of NaOH concentration.

Yields increase by increasing of temperature and molar ratio CPPD:BA, too, but by correlation of these parameters does not obtain high yield (maximum 44.52%) (Fig. 6).

Data plotted in Figure 7 show that highest yield (80.68%) was obtained by decrease of NaOH concentration. The program calculates a minimum

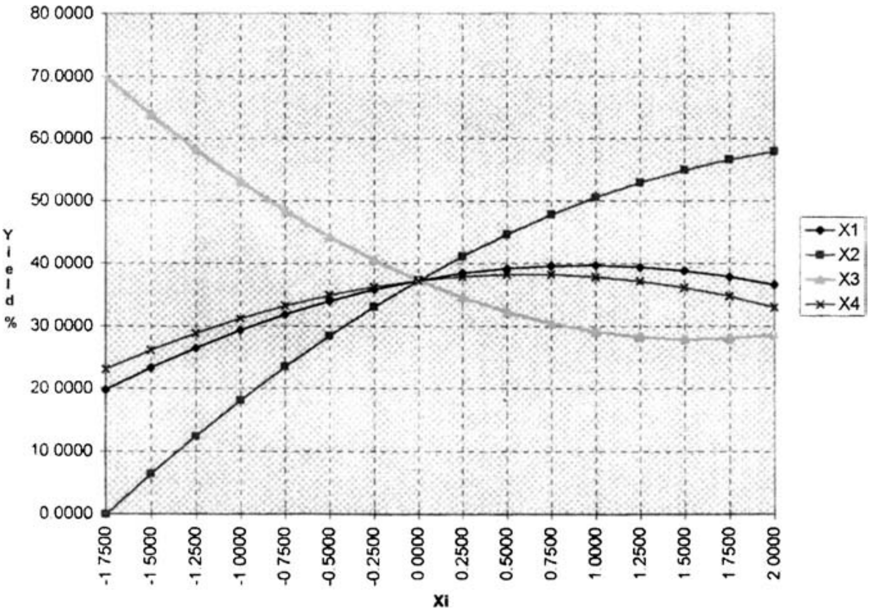


FIGURE 1 The influence of independent variables on the yield.

yield (30%), for $X_3 = 1.2920$ and $X_4 = 1.1008$, respectively at 4.5 M concentration and a molar ratio CPPD:BA = 3.25:1; that demonstrate the necessity to limit NaOH concentration.

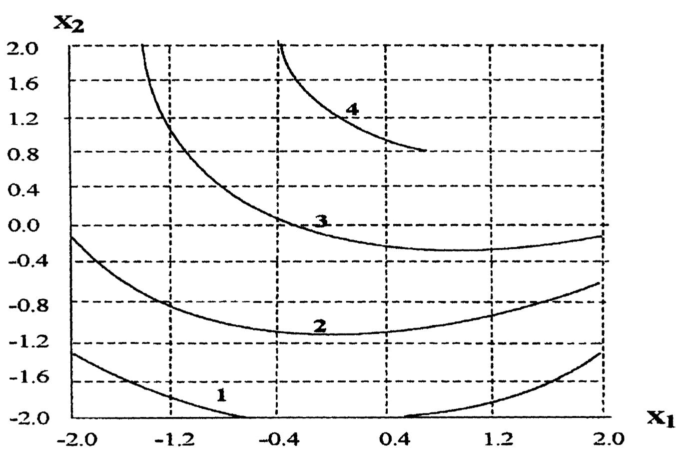


FIGURE 2 Yields curves in the plain of variables X_1X_2 for: $\eta = 2.95$ (curve 1); $\eta = 15.57\%$ (curve 2); $\eta = 34.09\%$ (curve 3); $\eta = 52.62\%$ (curve 4).

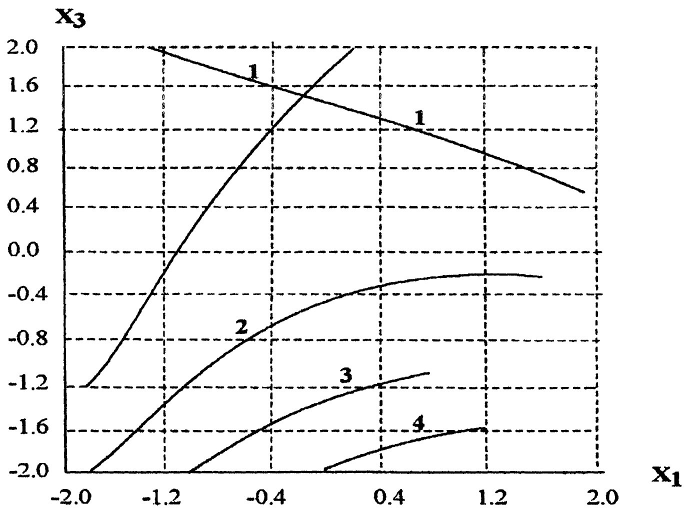


FIGURE 3 Yields curves in the plain of variables X_1X_3 for: $\eta = 27.95\%$ (curve 1); $\eta = 43.90\%$ (curve 2); $\eta = 59.85\%$ (curve 3); $\eta = 75.80\%$ (curve 4).

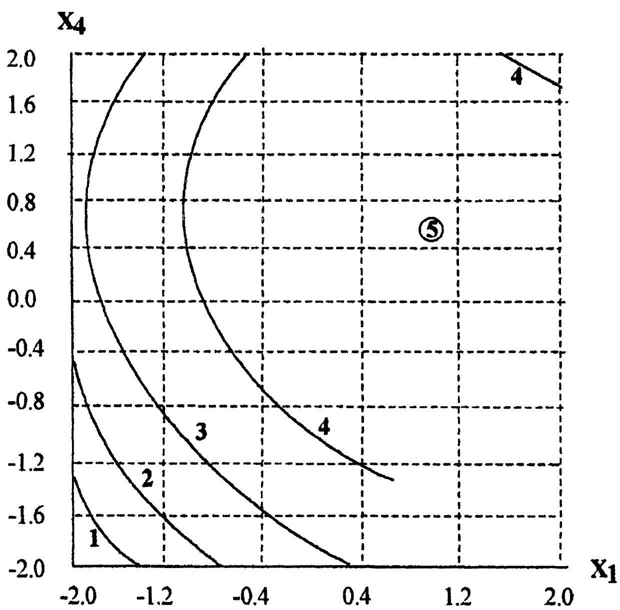


FIGURE 4 Yields curves in the plain of variables X_1X_4 for: $\eta = 2.85\%$ (curve 1); $\eta = 12.19\%$ (curve 2); $\eta = 21.53\%$ (curve 3); $\eta = 40.20\%$ (curve 4).

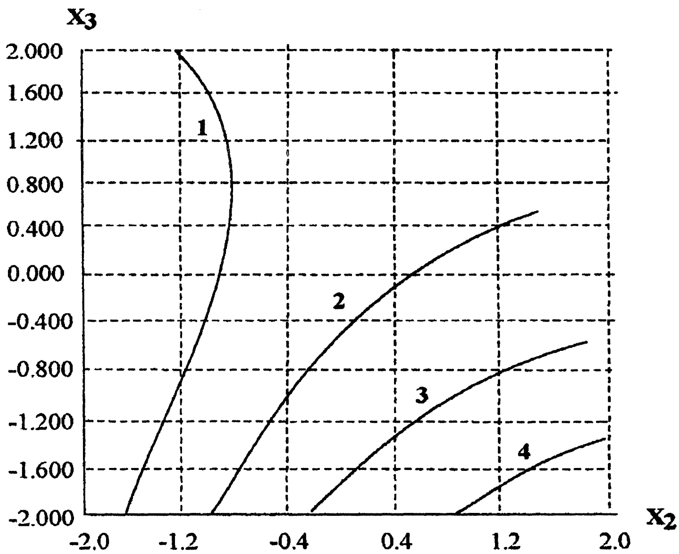


FIGURE 5 Yields curves in the plain of variables X_2X_3 for: $\eta = 18.80\%$ (curve 1); $\eta = 44.51\%$ (curve 2); $\eta = 70.23\%$ (curve 3); $\eta = 95.94\%$ (curve 4).

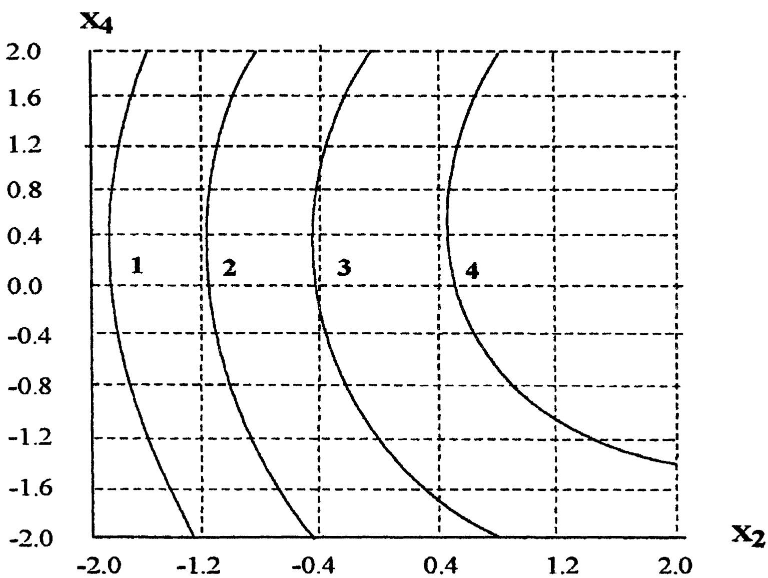


FIGURE 6 Yields curves in the plain of variables X_2X_4 for: $\eta = -4.00\%$ (curve 1); $\eta = 12.17\%$ (curve 2); $\eta = 28.34\%$ (curve 3); $\eta = 44.52\%$ (curve 4).

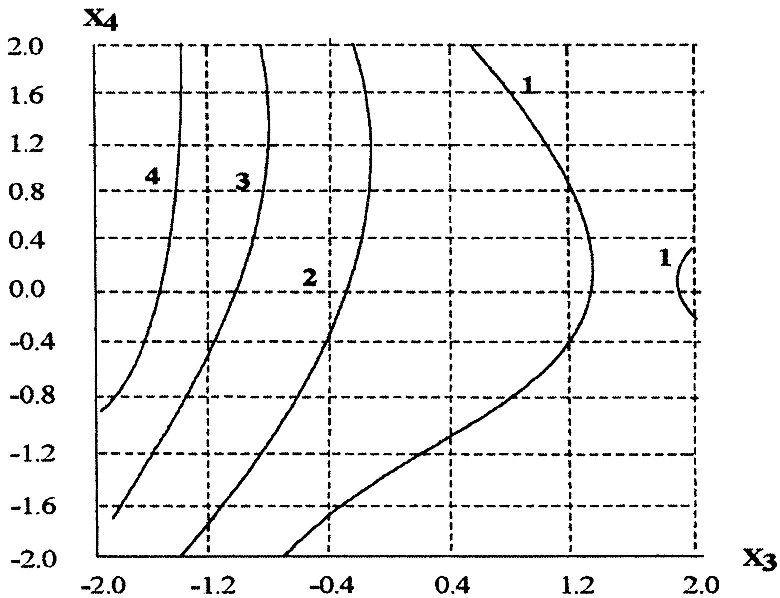


FIGURE 7 Yields curves in the plane of variables X_3X_4 for: $\eta = 28.08\%$ (curve 1); $\eta = 41.23\%$ (curve 2); $\eta = 54.38\%$ (curve 3); $\eta = 80.68\%$ (curve 4).

Even the examination of concomitant influence of these variables upon yield is not significant, correlation of some parameters is very important to determine the optimal reaction conditions. The most evident conclusion is that the influence of base concentration on yield is very important, because high base concentrations lead to secondary hydrolysis reactions. Also, it was demonstrate, that by correlation of NaOH concentration with reaction temperature, high yields were obtained (75%).

CONCLUSIONS

In this study it was verified the experimental results obtained by liquid-vapor polycondensation of CPPD and BA with the data obtained with a second order, central, composite, rotatable experimental design. The individual and simultaneous influences of various parameters (reaction time, temperature, base concentration and molar ratio CPPD:BA) on yield and inherent viscosity of the obtained polyphosphate were studied. Interesting correlations were realized to establish optimal reaction conditions. The calculated results were in concordance with the experimental data, respectively: reaction time 60–70 minutes; temperature 55°C; 1 M NaOH concentration and molar ratio CPPD:BA = 2.5:1. From the experimental and calculated data, it results that the most important factors are the base concentration and the reaction temperature.

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