

The study of the vapor-liquid interfacial polycondensation of the cyclohexylphosphonic dichloride with bisphenol A

The influence of temperature, reaction time, base concentration and molar ratio on yield, inherent viscosity and molecular weight

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Summary

Polyphosphonate esters of molecular weights $\sim 10^4$ were synthesized by base promoted liquid-vapor polycondensation of cyclohexylphosphonic dichloride with bisphenol A. The effect of temperature, reaction time, base concentration and molar ratio of reagents on yield, inherent viscosity and molecular weight of the obtained polymer was studied. A second order, central composite, rotatable experimental design was used to find domain experimental field for optimal yields and high inherent viscosities.

Introduction

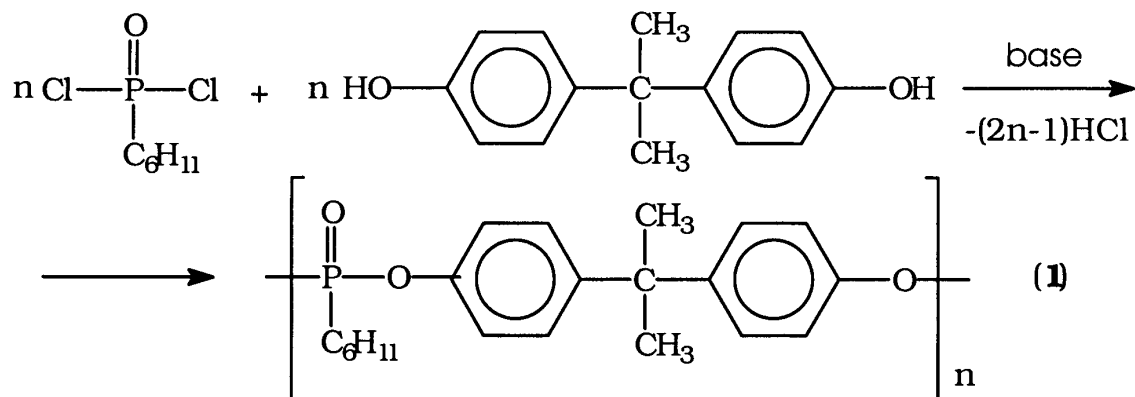
Fully aromatic polyesters have been found, in the past years, to have technical interest as engineering plastics. Between them, polyphosphonates have been studied because their excellent mechanical, electrical and flame resistance properties [1].

From main methods of obtaining phosphorus-containing polymers (2,3), i.e. solution, mass and interfacial polycondensation, polytransesterification, Arbuzov type reactions, liquid-liquid interfacial polycondensation, is frequently used in the macromolecular chemistry [4-8]. Another system is the liquid-vapor interfacial polycondensation, defined by Sokolov [9-12] in synthesis of polyamides. This system utilizes pairs of highly reactive reagents with one of the reagents in the vapor state and the other in solution.

In this study, liquid-vapor interfacial technique was modified for polyphosphonates, despite the low vapor pressures of phosphonyl chlorides.

Using this system, the polyphosphonate from cyclohexylphosphonic dichloride (CPD) and bisphenol A (BA) (reaction 1) was obtained. It was studied the influence of

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)[14,15].



Experimental

Materials

- cyclohexylphosphonic dichloride was obtained commercially and purified by vacuum distillation (b.p. 104-105°C/4 mmHg);
- bisphenol A obtained commercially, was recrystallised from benzene (m.p. 154-155°C)

General procedure

For the liquid-vapor interfacial polycondensation we have used the experimental apparatus 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, in the flask 2, containing aqueous NaOH and bisphenol A.

The nitrogen stream acts as carrier gas for the phosphorus dichlorides, as reaction mixture protector from the atmospheric oxygen and for agitation of the reaction mixtures. The reaction rate can be controlled by the nitrogen flow rate. The entire quantity of phosphonic 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 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.

Polymer separates from solution as 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 vacuum.

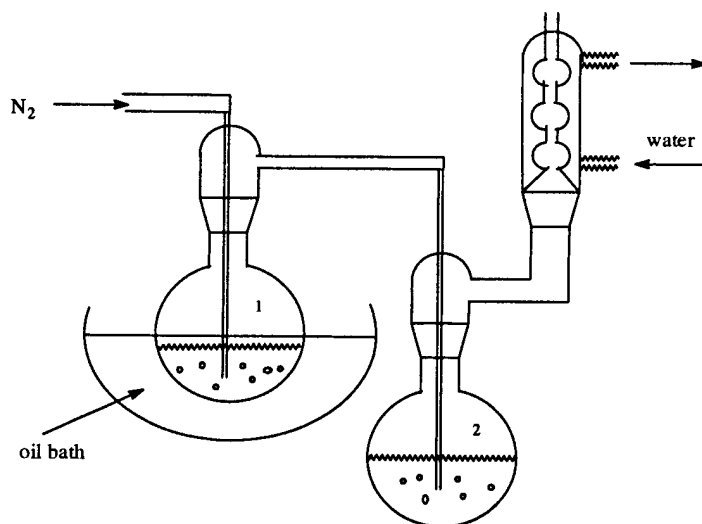


Figure 1

The yield in 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 930-940 cm^{-1} , 1377 cm^{-1} (P(O)-O-C (phenyl)); 1280 cm^{-1} (P=O); 1320-1290 cm^{-1} (P-C (cyclohexyl)). The nuclear magnetic resonance ($^1\text{H-NMR}$) spectrum in CDCl_3 , showed signals (δ) at 1.55 ppm (s, 6H, methyl); 7.06-7.12 ppm (m, 8H, phenyl); 1-2.8 (m, 11H, cyclohexyl). The phosphorus content, determined by Schöniger method, was 7.9%. (P % theoretical = 8.3%). The glass transition temperature was 95°C. The determined molecular weights were: $M_n=9300$ and $M_w=13500$.

Instruments

The IR and $^1\text{H-NMR}$ 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 (T_g) was determined by differential scanning calorimeter method (DSC, on a Seiko DSC 220 device).

Experimental Design.

It was used a second order, central composite, rotatable experimental design [4,5]. The experimental results were processed using a multiple regression method to obtain response surface Y (equation 1):

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

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

Actual independent variables were transformed according to the following equation (equation 2):

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

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 equation 1, together with the statistics necessary to test their significance and the regression significance, was used.

After experimental data processing results, the equations for yield (equation 3) and inherent viscosity were obtained (equation 4).

$$Y_A = 37.30001 + 5.18333X_1 + 16.20833X_2 - 11.95833X_3 + 3.34167X_4 - 2.76042X_1^2 + 3.47500X_1X_2 - 2.94792X_2^2 - 3.998750X_1X_3 - 6.13750X_2X_3 + 3.81458X_3^2 - 1.87500X_1X_4 + 1.08750X_2X_4 - 1.72500X_3X_4 - 2.73542X_4^2 \quad (3)$$

$$Y_B = 0.5580717 + 0.03683X_1 + 0.19570X_2 - 0.33025X_3 + 0.00937X_4 + 0.01419X_1^2 + 0.50820X_1X_2 - 0.00676X_2^2 - 0.01943X_1X_3 + 0.01432X_2X_3 + 0.12180X_3^2 + 0.04986X_1X_4 - 0.00309X_2X_4 - 0.09464X_3X_4 + 0.01916X_4^2 \quad (4)$$

The obtained response surfaces were studied to find the influence of reaction parameters (temperature, reaction time, NaOH concentration, molar ratio of CPD : BA) upon the yield and the inherent viscosity.

Results and discussion

In order to chose successfully optimal conditions of the high-molecular-weight polymers synthesis it was studied the influence of temperature, reaction time, base concentration and molar ratio CPD:BA on yield and inherent viscosity of the obtained polyphosphonate.

The effect of reaction temperature (in round-bottom flask 2) on yield, inherent viscosity and molecular weight is presented in Table 1.

The most distinguishing feature of liquid-vapor interfacial polycondensation is a dependence of inherent viscosity and molecular weight, respectively, on the temperature: in this system, inherent viscosity and molecular weight, respectively, increase with increase of the reaction temperature. In liquid-liquid interfacial polycondensation the molecular weight decreases with increase of the reaction temperature [13]. The best results ($\eta_{inh} = 0.95$ dl/g and $M_n = 9300$, $M_w = 13800$) were obtained at 55°C. At higher temperatures yield, inherent viscosity and molecular weight decrease because of hydrolysis secondary reactions.

Table 1. The influence of temperature reaction on yield, inherent viscosity and molecular weight, in the liquid-vapor polycondensation of cyclophosphonic dichloride (0.020 moles) with bisphenol A (0.020 moles), 1M NaOH_{aq} (0,042 moles), at 100° C (in round-bottom flask 1), 60 min.

T, [°C]	Yield, [%]	η_{inh}^a , [dl/g]	$M_n \times 10^4$	$M_w \times 10^4$
35	25	0.35	0.24	0.62
40	41	0.52	0.51	0.70
45	60	0.81	0.89	1.0
55	75	0.95	0.93	1.36
60	54	0.61	0.58	0.78
80	38	0.32	0.41	0.60
90	22	0.24	0.38	0.52

^a determined at a concentration of 0.5 g/dl, in tetrachloroethane, at 30° C

The effect of reaction time on yield and inherent viscosity of obtained polyphosphonate is presented in Table 2.

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

Table 2. The dependence of yield, inherent viscosity and molecular weight of the obtained polyphosphonate on reaction time

Reaction time, [minutes]	Yield, [%]	η_{inh}^a , [dl/g]	$M_n \times 10^4$	$M_w \times 10^4$
30	30	0.32	0.40	0.59
40	46	0.65	0.60	0.81
50	72	0.82	0.85	1.05
60	75	0.90	0.90	1.20
70	60	0.68	0.53	0.75
90	32	0.55	0.51	0.79

^a reaction conditions: CPD : BA : NaOH = 1 : 1 : 2, 55° C;

^b determined at a concentration of 0.5 g/dl, in tetrachloroethane, at 30° C

In order to get data for preparing polyphosphonates with high molecular weights, the effect of alkaline medium on yield and inherent viscosity was studied. Reaction conditions must be chosen that to obtain high yields and inherent viscosities, to prevent the degradation of polymer (caused by the attack of base on CPD, on phosphoryl chloride end-groups of intermediary oligomers and on ester-phosphonic bonds of polymer) and terminating competing reactions. In synthesis of

polyphosphonate it was used aqueous sodium hydroxide at different concentrations. The best results were obtained with 1M aqueous sodium hydroxide (Figure 2).

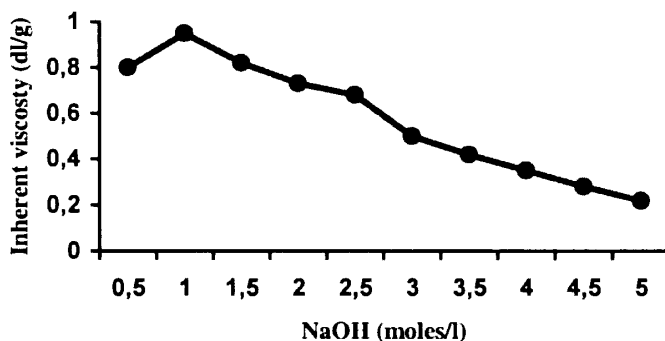


Figure 2. Influence of NaOH concentration on inherent viscosity

In order to follow the influence of molar ratio between reagents on yield, inherent viscosity and molecular weight (Table 3), quantities added in the two flasks were varied, maintaining invariable stream of nitrogen (10 ml/s), the temperatures in the two flasks and the reaction time. Like in other polycondensations that are taking place by diffusion mechanism, the best results being obtained at non-equimolar ratios, especially in excess of CPD (CPD:BA = 2.7:1).

Table 3. The influence of reagents molar ratio on yield, inherent viscosity and molecular weight, in the base-promoted liquid-vapor interfacial polycondensation of CPD with BA (1M NaOH), at 55⁰C (in round-bottom flask 2) and 100⁰C (in round - bottom flask 1).

CPD:BA	η_{inh}^a [dl/g]	M_n $\times 10^4$	M_w $\times 10^4$	Yield, [%]
3.5:1.0	0.78	0.84	1.08	70
3.2:1.0	0.85	0.90	1.18	75
2.7:1.0	0.98	0.98	1.38	85
2.0:1.0	0.85	0.95	1.35	78
1.6:1.0	0.78	0.92	1.27	75
1.2:1.0	0.75	0.90	1.20	70
1.0:1.0	0.70	0.88	1.15	65
1.0:1.2	0.72	0.79	0.93	68
1.0:2.0	0.74	0.80	0.97	70
1.0:2.7	0.76	0.81	0.98	70

^a determined at a concentration of 0.5 g/dl, in tetrachloroethane, at 30⁰C

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

Variable transformation and experimental conditions are listed in Table 4 and 5.

Table 4. Transformation of variables

	Coded values→	-2	-1	0	1	2
Real values↓						
Reaction time (minutes), X_1		30	40	50	60	70
Temperature, ($^{\circ}\text{C}$), X_2		35	45	55	60	80
NaOH concentration, (moles/l), X_3		1	2	3	4	5
Molar ratio (CPD/ BA), (moles), X_4		1	1.2	2	2.7	3.5

In Figure 3 is illustrated the individual influence of the four independent variables (X_i) on yield (Y_A , dependent variable) [$Y_A = f(X_i)$]. To understand the influence of the studied parameters of liquid-vapor polycondensation process, Figure 3 represents the influence of a parameter on yield, 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 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 CPD : BA ~ 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-Phosphonic groups).

From the curves $Y_A = f(X_2)$ and $Y_A = f(X_1)$ which illustrate the influence of temperature and reaction time on yield, it can be observed that for lower temperatures (<40 $^{\circ}\text{C}$) 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 1M 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 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

Table 5. Experimental design and experimental results

Nr.	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	15.2	0.8501
2	1	-1	-1	-1	18.0	0.8551
3	-1	1	-1	-1	38.1	0.9623
4	1	1	-1	-1	79.8	0.9800
5	-1	-1	1	-1	8.1	0.2105
6	1	-1	1	-1	10.2	0.1902
7	-1	1	1	-1	30.0	0.7520
8	1	1	1	-1	34.3	0.7810
9	-1	-1	-1	1	16.3	0.8720
10	1	-1	-1	1	23.0	0.8850
11	-1	1	-1	1	60.5	1.1000
12	1	1	-1	1	82.6	1.6500
13	-1	-1	1	1	9.5	0.2250
14	1	-1	1	1	11.5	0.2510
15	-1	1	1	1	32.1	0.2810
16	1	1	1	1	33.2	0.5215
17	-2	0	0	0	18.4	0.6012
18	2	0	0	0	39.2	0.6215
19	0	-2	0	0	0.5	0.0210
20	0	2	0	0	55.6	1.0251
21	0	0	-2	0	85.7	1.7831
22	0	0	2	0	24.5	0.2915
23	0	0	0	-2	17.6	0.6215
24	0	0	0	2	40.2	0.6320
25	0	0	0	0	36.2	0.5561
26	0	0	0	0	37.2	0.5902
27	0	0	0	0	38.5	0.6100
28	0	0	0	0	38.7	0.5860
29	0	0	0	0	37.0	0.5520
30	0	0	0	0	35.0	0.5122
31	0	0	0	0	38.5	0.5000

reaction temperature, very high yields were obtained (95 %).

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

The curves $Y_B = f(X_2)$ and $Y_B = f(X_i)$ (inherent viscosity as function on temperature and reaction time) show that at low temperatures < 50°C, the influence of reaction time is more important for obtaining high inherent viscosities. For higher values of these parameters, as exceed the center of the chosen experimental domain, temperature influences more the polyphosphonate viscosity than reaction time. Also, for $X_2 = 2$, respectively 55°C, an inherent viscosity of 0.99 dl/g was obtained. It was observed that high inherent viscosity ($\eta_{inh} = 1.1$ dl/g) was obtained with 1M NaOH concentration. With 5M NaOH concentration ($X_3 = 2$), inherent viscosity decreases at 0.40 dl/g.

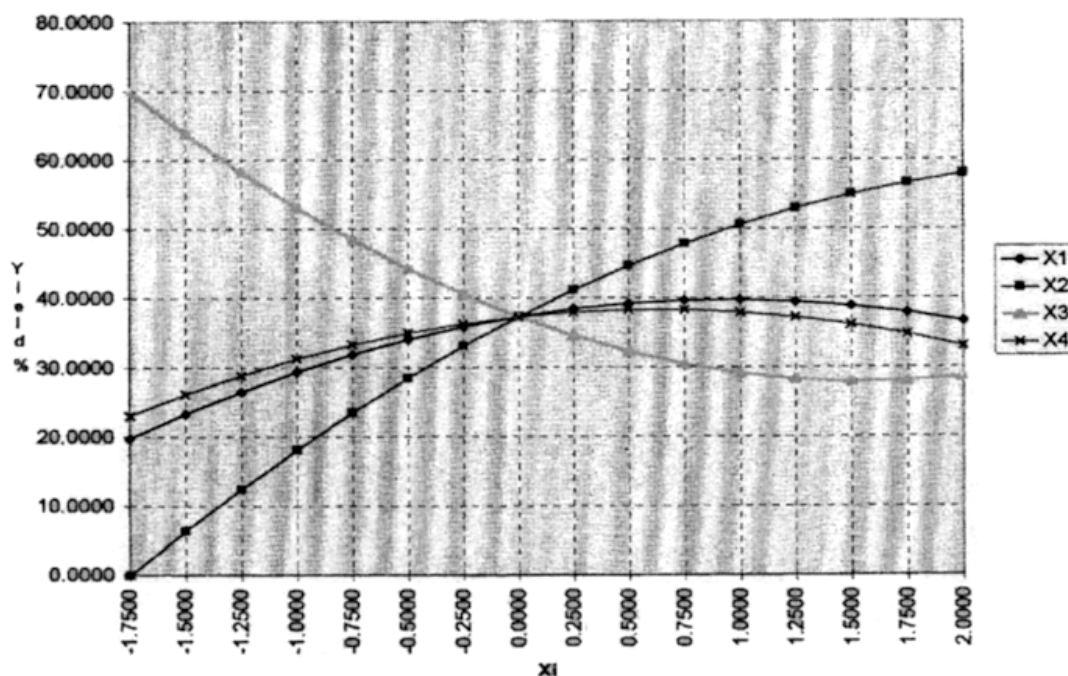


Figure 3. The influence of independent variables on the yield

By individual influence of the four parameters on inherent viscosity, presented in Figure 8, the following order can be established $X_2 > X_1 > X_4 > X_3$

Conclusions

The polyphosphonate with high molecular weight (10^4) can be obtained from cyclohexylphosphonic dichloride and bisphenol A using liquid-vapor interfacial polycondensation. In order to find optimal conditions for this reaction it was studied the influence of different parameters (temperature, reaction time, base concentration and molar ratio) on yield and inherent viscosity. The best results were obtained at 55°C , 50-60 minutes, $1\text{M NaOH}_{\text{aq}}$ and $\text{CPD:BA} = 2.7 : 1$. Given these encouraging results other model systems are being investigated.

Also it was verified the experimental results obtained by liquid-vapor polycondensation of CPD and BA with the data obtained with a second order, central, composite, rotatable experimental design. The simultaneous influences of various parameters (reaction time, temperature, base concentration and molar ratio CPD:BA) on yield and inherent viscosity of the obtained polyphosphonate was studied. Interesting correlations were realized to establish optimal reaction conditions. The calculated results were in concordance with the experimental data, respectively: reaction time 50-60 minutes; temperature 50°C ; 1M NaOH concentration and molar ratio $\text{CPD} : \text{BA} = 2.6 : 1$. 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.

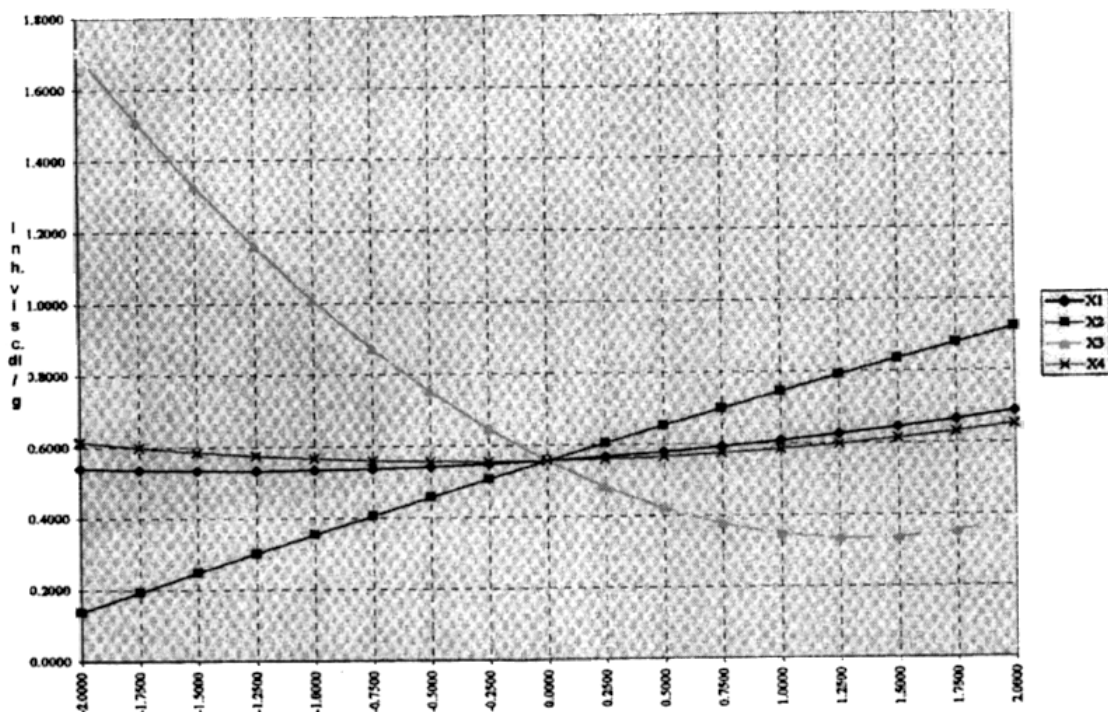


Figure 4. The influence of independent variables on inherent viscosity

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