Phase Transfer Catalysis in Polycondensation Processes. IX. Study on Polyetherification of 3,3-bis (chloromethyl) Oxetane and Bisphenol A

Bulacovschi V., Hurduc N., Camelia Mihailescu, Constanta Ibanescu and Simionescu C.I.

Department of Macromolecules, Polytechnical Institute of Jassy, Jassy, Romania

ABSTRACT

The polycondensation of 3,3-bis (chloromethyl) oxetane (BCMO) with bisphenol A (BPA) under the phase transfer conditions is investigated. Second order, central, composite, rotatable experimental design is used in order to carry out this work and to mark limits of the experimental field for better yields and stable mesophase on a large domain.

Key Words

INTRODUCTION

Phase transfer catalysis (PTC) has been widely used in synthesis of various polymers [1-5]. Good results were obtained in preparation of polymers with ordered structure which might display liquid - crystalline (LC) properties [1,3,4].

In a previous paper [3], we have reported the possibility of obtaining polyethers from 3,3-bis (chloromethyl) oxetane (BCMO) and bisphenol A (BPA) under phase transfer conditions and we found that these polymers have anisotropic properties in the molten state.

Here results are presented concerning the influence of various parameters, both on reaction conditions and on the most important LC

characteristics.

EXPERIMENTAL

Materials

BCMO was prepared according to the method presented in [2]. Commercial bisphenol A (CAROM S.A.) was twice recrystallised from benzene. The PT catalyst (triethyl benzyl ammonium chloride - TEBAC) was prepared in the laboratory from triethylamine and benzylchloride and purified by usual methods. Nitrobenzene (Merck) was used as purchased.

The polyethers were synthesised as in [3]. Transition temperatures (structural (T_s) and isotropisation (T_i) temperatures) were measured on a VEB analytic optical polarised microscope equipped with a hot stage.

Experimental Design

To carry out the work, the second order, central, composite, rotatable experimental design was used [7].

The advantages of this method are:

- the number of experiments is reduced, a fact which results in the reduction of the amount of material, energy and time spent;

- the regression equation obtained by data processing is defined on the whole experimental field;

- the complexity of calculation of regression coefficients is reduced due to the orthogonality of many independent variables vectors.

Actual independent variables were transformed according to the following formula:

$$x_i = (\chi_i - \chi_{ic})/\Delta\chi_i \tag{1}$$

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.

Variable transformation is given in Table 1, and experimental conditions are listed in Table 2.

Data Processing

The experimental results were processed by using a multiple regression method in order to obtain response surfaces in the form:

$$Y = a_o + \Sigma a_i x_i + \Sigma a_{ij} x_i x_j \qquad i \leqslant j \tag{2}$$

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

To perform the calculus standard subroutines which compute regression coefficients from equation (2), 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 reaction parameters (reaction temperature, concentration of TEBAC, concentration of NaOH and reaction time) on the polyetherification of BCMO with BPA.

RESULTS AND DISCUSSION

To understand the influence of the studied

Table 1. Transformation of variables.

Coded values / Real values	-2	-1	0	1	2
Polymerisation time (X_1)[h]	3	5	7	9	11
Reaction temperature (X_2)[°C]	60	68	76	84	92
Concentration of NaOH (X_3) [equivalent/L]	4	8	12	16	20
PT catalyst (X_4) [mmol]	0.8	1.6	2.4	3.2	4.0

Table 2. Experimental design and experimental results.

No.	X_1	X_2	X_3	X_4	Conv. (%)	T_t(°C)	T_f(°C)
1	-1	-1	-1	-1	5.0	223	228
2	+1	-1	-1	-1	8.9	222	229
3	-1	+1	-1	-1	34.4	218	223
4	+1	+1	-1	-1	77.6	237	247
5	-1	-1	+1	-1	3.7	224	226
6	+1	-1	+1	-1	7.7	220	227
7	-1	+1	+1	-1	37.8	210	219
8	+1	+1	+1	-1	72.3	240	245
9	-1	-1	-1	+1	6.3	224	230
10	+1	-1	-1	+1	31.8	205	212
11	-1	+1	-1	+1	40.1	215	225
12	+1	+1	-1	+1	86.7	243	251
13	-1	-1	+1	+1	8.7	226	230
14	+1	-1	+1	+1	9.1	220	226
15	-1	+1	+1	+1	84.8	243	259
16	+1	+1	+1	+1	85.3	236	250
17	-2	0	0	0	18.4	212	217
18	+2	0	0	0	36.8	208	215
19	0	-2	0	0	0.8	197	200
20	0	+2	0	0	96.0	248	255
21	0	0	-2	0	8.1	220	223
22	0	0	+2	0	24.7	210	217
23	0	0	0	-2	17.6	210	217
24	0	0	0	+2	81.8	237	250
25	0	0	0	0	26.5	210	217
26	0	0	0	0	28.9	210	218
27	0	0	0	0	29.2	209	215
28	0	0	0	0	29.4	209	217
29	0	0	0	0	28.9	210	217
30	0	0	0	0	27.8	210	218
31	0	0	0	0	32.5	211	217

parameters on the progress of the polyetheri - fication process, Figure 1 represents the variation of the polymer yield versus a parameter, all the others being taken at values corresponding to the center of the experimental field.

The shape of these curves assert a significant influence of reaction temperature (X_2) and concentration of the PT catalyst (X_4) for values which exceed 0.15 mmol/L. The improvement of the polymer yield at high concentrations of the catalyst is presumed to result from the increase of

BPA transferred in the organic phase. One should note also that for the selected experimental domain, the conversion curve retains a maximum, which corresponds to a concentration of NaOH of 13.5 N ($X_3 = 0.378378$). For higher concentrations, a slight decrease in the yield is observed and is justified by the transfer of HO^- ions in the organic phase. Here they compete with bisphenolate ions in modifying part of $-CH_2Cl$ groups into $-CH_2OH$ ones which are less active polyetherification:
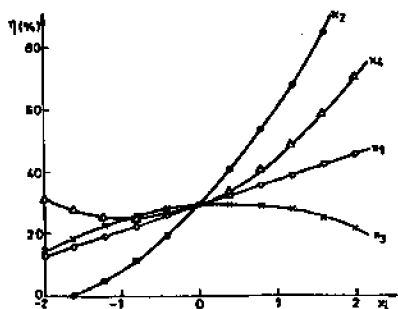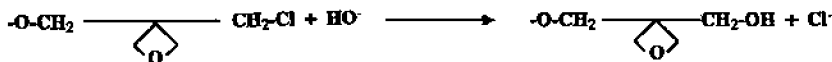
Such a phenomenon was notified also for

$$-O-CH_2 \xrightarrow{\quad\quad} \underset{O}{\triangle} \quad CH_2-Cl + HO^- \xrightarrow{\quad\quad} -O-CH_2 \xrightarrow{\quad\quad} \underset{O}{\triangle} CH_2-OH + Cl^-$$

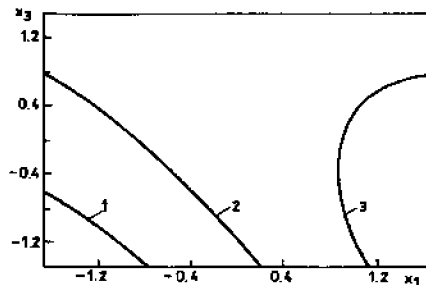**Fig.1. Influence of independent variables upon conversion.**

Fig.3. Conversion curves in the plane of variables X_1X_3 for: $\eta= 6.5\%$ (curve 1); $\eta= 21.2\%$ (curve 2); $\eta= 35.9\%$ (curve 3).

other PT assisted polyetherification reaction [8,9].

The shape of the curves representing the variation of conversion in the experimental field of X_1 and X_4, shows that at low temperatures, evolution of the polymer yield depends dominantly on reaction time. This subordination modifies when X_1 and X_4 overtake the middle of the experimental domain.

The examination of concomitant influence of these variables upon conversion is not significant (Figures 2,3 and 4). Moreover, drawings in the plane of two parameters assert that the yield evolution is mainly dependent on the reaction

temperature (Figures 2,5 and 6).

Figures 7 illustrates the influence of the four independent variables upon T_g. All the curves pass through a minimum which is placed somewhere on the left side of the experimental domain.

Taking into account the individual influences of the selected parameters upon T_i (a significant characteristic for LC structures), one obtains the representation in Figure 8. All drawings reveal a minimum located before the center of the experimental field. In this zone the polymer yield
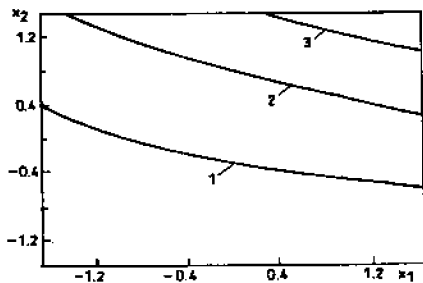

Fig.2. Conversion curves in the plane of variables X_1X_2 for: $\eta= 20.8\%$ (curve 1); $\eta= 50.9\%$ (curve 2); $\eta= 80.0\%$ (curve 3).
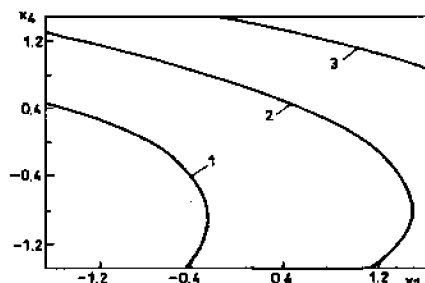

Fig.4. Conversion curves in the plane of variables X_1X_4 for: $\eta= 22.2\%$ (curve 1); $\eta= 37.5\%$ (curve 2); $\eta= 52.9\%$ (curve 3).
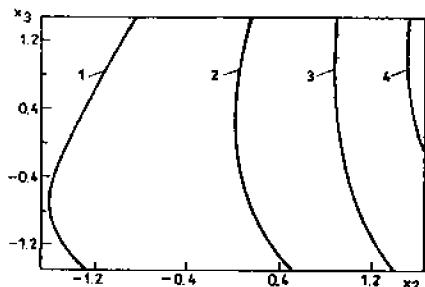
Fig.5. Conversion curves in the plane of variables X_2X_3 for: $\eta = 1.7\%$ (curve 1); $\eta = 29.1\%$ (curve 2); $\eta = 56.4\%$ (curve 3); $\eta = 83.7\%$ (curve 4).
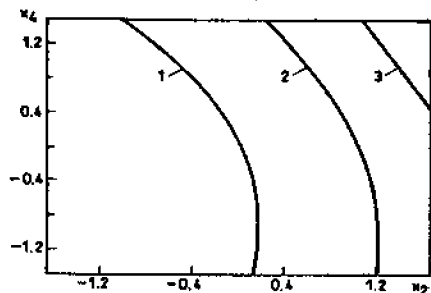

Fig.6. Conversion curves in the plane of variables X_2X_4 for: $\eta = 28.1\%$ (curve 1); $\eta = 59.7\%$ (curve 2); $\eta = 91.3\%$ (curve 3).
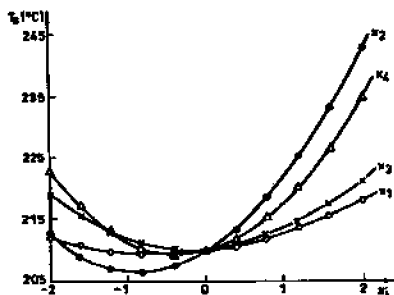

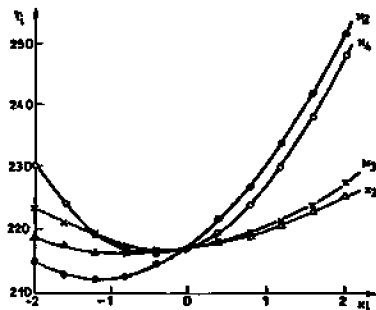Fig.7. The influence of independent variables upon T_i.

Fig.8. The influence of independent variables upon T_i.

does not exceed 30%.

It is worth mentioning that the most important evolution of the conversion occurs in the second part of the experimental domain, and that, among the four parameters, X_2 and X_4 have an ascendency over the X_1 and X_3.

The isotropisation temperature depends more on X_2 than on X_1, especially when real values of X_2 are higher than 80 °C (Figure 9).

No major influence is seen from reaction time (X_1) and concentration of NaOH (X_3) upon isotropisation temperature. It rises only by 16 °C for the entire domain of X_1 and X_3.

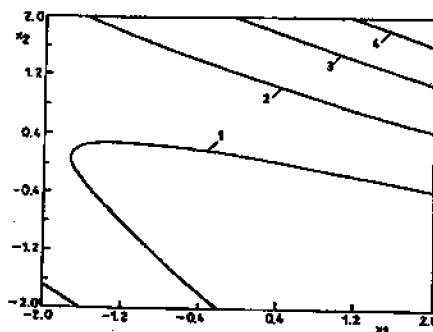By comparing representations in Figures 7 and 8, the following order of the independent

Fig.9. Variation of T_i as function of variables X_1X_2 for: $T_i = 217.6$ °C (curve 1); $T_i = 233.6$ °C (curve 2); $T_i = 249.7$ °C (curve 3); $T_i = 265.8$ °C (curve 4).

78

Iranian Journal of Polymer Science and Technology. Vol 2, No 2, June 1993

variables can be established as they influence the polyetherification process: $X_2 > X_4 > X_3 > X_1$.

CONCLUSIONS

A second order, central, composite, rotatable experimental design was used to study the influence of polyetherification period, temperature, PT catalyst and NaOH concentrations on the polycondensation of BCMO with BPA.

From the obtained data, it results that the most important factors are reaction temperature and concentration of the PT catalyst.

These investigations allowed us to mark better limits of the experimental field in order to obtain good yields and stable mesophases on a large domain.

REFERENCES

1 Percec, V., Nava, H., Jonsson, H., J.Polym.Sci.Polym. Chem.Ed., **Vol.25**, pp.1943 (1987).

2 Bulacovschi, V., Simionescu, C.I., Acta Polym., **Vol.36**, pp.191 (1984).

3 Hurduc, N., Bulacovschi, V., Simionescu, C.I., Eur. Polym.J., **Vol.28**, pp.791 (1992).

4 Hurduc, N., Bulacovschi, V., Bordeianu, A., Simionescu, C.I., Polym.Bull., **Vol.28**, pp.639 (1992).

5 Tagle, L.H., Diaz, F.R., Munoz, A.M., Polym.Bull., **Vol.11**, pp.493 (1984).

6 Simionescu, C.I., Bulacovschi, V., Hurduc, N., Revue Roumaine de Chimie - in press.

7 Coohran, W.G., Cox, G.M., "Experimental Design", N. Y., London, John Wiley and Sons (1968).

8 Shaffer, T.D., Jamaludin, M., Percec, V., J.Polym.Sci.: Polym.Chem.Ed., **Vol.23**, pp.2913 (1985).

9 Percec, V., Shaffer, T.D., Nava, H., J.Polym.Sci.: Polym.Lett.Ed.Polym.Lett.Ed., **Vol.22**, pp.637 (1984).