Application of a thermochemical method for studying a low-temperature polycondensation process

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A thermochemical method has been used for investigating the course of a polycondensation process. Measurements were performed in a Calvet-type calorimeter. The reactions of triethylamine complex formation with bisphenols and terephthaloyl chloride were investigated. Both hydroxyl groups in the bisphenols are found to be equally reactive with triethylamine. Stability constants, rate constants, and the ΔH^0, ΔG^0 and ΔS^0 values for the reaction of triethylamine with hydroxyl groups were determined. The acid chloride groups in the terephthaloyl chloride are found to exhibit different reactivities with triethylamine. Thermal effects on the reaction of these groups were determined. Results of the measurements are also presented in the form of thermokinetic curves. Such curves obtained for the polycondensation process were compared with those determined for reactions involving the formation of the complex of triethylamine with each of the monomers separately. A mechanism of the polycondensation process is proposed.

INTRODUCTION

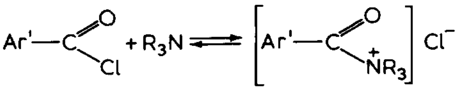
Low-temperature polycondensation is one of the methods of synthesizing polyarylates[1]. This process takes place in the presence of tertiary amines which act as catalysts and as acceptors of hydrogen chlorde. The mechanism has not yet been fully elucidated, although it is thought to proceed either according to a base-catalysis mechanism[1,2] or through a nucleophilic catalysis mechanism[3–5]. Tertiary amines are assumed to play different roles in both proposed reaction mechanisms. In the case of base catalysis the tertiary amine is thought to form a complex with the hydroxyl monomer which then reacts with the acid dichloride according to reactions (1), (2) and (3):

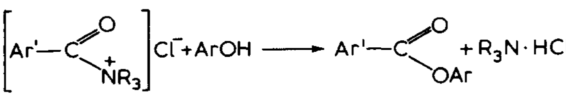
$$\text{Ar–OH} + \text{NR}_3 \rightleftarrows \text{Ar–OH} \ldots \text{NR}_3 \qquad (1)$$

$$\text{Ar–OH} \ldots \text{NR}_3 \rightleftarrows \text{ArO}^- \ldots \overset{+}{\text{H}}\text{NR}_3 \qquad (2)$$

$$\begin{array}{l} \text{Ar–OH} \ldots \text{NR}_3 \\ \qquad\quad + \\ \text{ArO}^- \ldots \overset{+}{\text{H}}\text{NR}_3 \end{array} + \text{Ar}'\text{COCL} \rightarrow \text{Ar}'\text{COOAr} + \text{R}_3\text{N}\cdot\text{HCl} \qquad (3)$$

On the other hand, in the nucleophilic catalysis process the tertiary amine is thought to form a complex with the acid dichloride which then reacts with the hydroxyl monomer as shown in reactions (4) and (5).


(4)


(5)

The aim of the present studies was to apply a thermochemical method for studying the mechanism of a low-temperature polycondensation process. Polycondensation of terephthaloyl chloride with different bisphenols was chosen for the investigations. Triethylamine was used as the catalyst and dichloroethane as the solvent. Triethylamine complex formation with monomers was investigated at the start of our research. Triethylamine complexes with bisphenols[6] and terephthaloyl chloride[7] have already been shown by spectrophotometric methods to exist in solution. However, there are no thermochemical and thermodynamic data available on the process of the formation of these complexes.

EXPERIMENTAL

Reagents

2,2-di(4-hydroxyphenyl)propane (Bisphenol A) was purified by double crystallization in chlorobenzene, m.p. 157°–158°C.

2,2-di(4-hydroxy-3-chlorophenyl) propane (Bisphenol B) was purified by double crystallization in hexane, m.p. 90.5°–91.5°C.

2,2-di(4-hydroxy-3-methylphenyl)propane (Bisphenol C) was synthesized and purified according to a method described by Linke[8], m.p. 137°–139°C.

Terephthaloyl chloride was synthesized from terephthalic acid and thionyl chloride and purified by successive crystallizations from n-hexane, m.p. 83.5°C.

Triethylamine was purified by reaction with benzoyl chloride and distillation over metallic sodium, b.p. 80–80.5°C.

Dichloroethane was purified by washing with a solution of potassium hydroxide and with water, dried, and distilled over phosphorus pentoxide, b.p. 83–83.5°C.

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Table 1 Heats of reaction of triethylamine and bisphenols

		First series of measurements	First series of measurements	
			Heat of reaction	
No	Bisphenol	Heat of reaction (kJ/mol Et_3N)	(kJ/mol of bisphenol)	(kJ/mol of hydroxyl groups)
1	2	3	4	5
1	A	25.3 ± 0.1	50.7 ± 0.4	25.3 ± 0.2
2	B	29.9 ± 0.3	59.2 ± 1.3	29.6 ± 0.6
3	C	23.3 ± 0.2	47.2 ± 1.3	23.6 ± 0.6

Apparatus and measuring technique employed

Measurements were made in a Calvet-type calorimeter[9]. The measuring cell contained a solution of the studied monomer in dichloroethane, a carefully weighed amount of triethylamine being placed in a sealed phial. Reaction started on breaking the phial, the heat evolved being recorded as a thermogram.

Thermokinetic curves were obtained by a graphical transformation of the recorded thermograms[9]. I.r. spectra were obtained in a UR-10 (Jena, Zeiss) i.r. spectrophotometer.

RESULTS AND DISCUSSION

Thermal effects of the reaction of triethylamine with monomers were studied in dichloroethane at 28°C at a pressure of 1 atm. In all experiments a known amount of triethylamine was introduced into solutions of the monomers. Consequently, besides the heat of the reaction of triethylamine with a particular monomer, the measured heat effect also comprised the heat of dissolution of triethylamine. This was determined in a preliminary experiment and found to be -19.2 ± 0.08 J g^{-1}.

Two series of measurements were performed to determine the heat of reaction of triethylamine with bisphenols. In the first series the molar ratio of bisphenol to triethylamine was at least 10:1 whereas in the second series the molar ratio was 1:10. The heat of reaction was calculated per mole of that component of which there was a deficiency in the reaction mixutre. In *Table 1* are listed average values of the heats of formation of the complexes of triethylamine with the bisphenols studied. It was assumed that in the case of measurements carried out in the presence of a large excess of the triethylamine there would be complete conversion of the bisphenol. The calculated heat effect per mole of the bisphenol would therefore refer to the formation of a complex in which both hydroxyl groups are bound. Experiments carried out in the presence of a large excess of a particular bisphenol would lead to the complete consumption of the triethylamine for the formation of a complex with the bisphenol. If our assumption was correct and the reactivity of the first hydroxyl group in an unsubstituted bisphenol (first group) is equal to that of the second group, the calculated heat effects per mole of hydroxyl groups should be the same for both series of measurements. The data listed in columns 3 and 5 of *Table 1* indicate that the measured heat effects were the same within the limits of experimental error. This in turn makes it possible to assume equal reactivity of both hydroxyl groups of studied bisphenols irrespective of any of these groups being bound.

Two analogous series of experiments concerned the heat of formation of the triethylamine complex with terephthaloyl chloride. In the first experimental series the value was $Q_I = 143.7 \pm 0.50$ kJ mol^{-1} of triethylamine; in the second a value of $Q = 304.7 \pm 1.8$ kJ mol^{-1} of terephthaloyl chloride was obtained. I.r. spectrophotometric analyses of the same solutions as those used in the calorimetric measurements were made. These i.r. spectra did not show an absorption maximum at 1770 cm^{-1} corresponding to the carbonyl group of the terephthaloyl chloride. This confirms the complete consumption of both terephthaloyl chloride groups in the reaction with triethylamine. Therefore the value of Q obtained constitutes the total thermal effect of the reaction involving the formation of the complex by both functional groups of terephthaloyl chloride. Since the terephthaloyl chloride was present in a large excess during the determination of Q_I it may be supposed that the first functional groups had reacted. The Q_I value may therefore be considered as an approximate value for the heat of formation of the complex by the first functional group of terephthaloyl chloride. The heat of formation of the complex by the second functional group of terephthaloyl chloride (Q_{II}) may be approximated by the following expression:

$$Q_{II} = Q - Q_I = 163.5 \pm 2.18 \text{ kJ mol}^{-1} \qquad (6)$$

The thermal effect resulting from the formation of the complex by the second functional group is greater than that found in the case of the first functional group of terephthaloyl chloride. However, it is not yet fully ascertained whether it is only the first functional group of terephthaloyl chloride which reacts when used in large excess so that its concentration is higher in the reacting system. The observed numerical values of the thermal effect corresponding to the formation of the complex by the first functional group are too high while those determined for the second functional group are too low. It is therefore to be emphasized that the observed values of the thermal effects do not provide an accurate quantitative characterization of the phenomena. However, these experimental results indicate different reactivities of the functional groups of terephthaloyl chloride with respect to triethylamine. In view of the fact that the heat of formation of the complex by the second functional group is greater than that found for the first group, the second functional group of terephthaloyl chloride may be considered to exhibit a higher reactivity than the first one.

It was interesting to determine whether the reactivity of a hydroxyl end-group of the macromolecule is equal to the reactivity of the hydroxyl group in the monomer. In order to solve the problem, additional experiments were carried out using a polymer containing exclusively hydroxyl end-groups. Such a polyester was obtained by a synthetic route involving non-equimolar proportions of starting monomers, i.e. of bisphenol A and terephthaloyl chloride. Spectrophotometry showed that only hydroxyl end-groups were present in the synthesized macromolecule. The average value for the heat of formation of the complex for the macromolecule end-groups was found to be -25.1 ± 0.3 kJ mol^{-1}. This is comparable with the Q value obtained for the bisphenol A, and thus equal reactivity for hydroxyl groups of the bisphenol and the macromolecule can be inferred.

Due to the equal reactivity of the both of the hydroxyl groups of the bisphenols it was possible to determine the stability constants of complexes with triethylamine. For this reason a third series of experiments was performed using

Table 2 Thermodynamic parameters of triethylamine complexes with the hydroxyl group of bisphenols

No.	Bisphenol	$-\Delta H^\circ$ (kJ/mol)	$-\Delta S^\circ$ (kJ/mol)	$-\Delta G^\circ$ (kJ/mol)	K (dm^3/mol)	k(dm^{3}mol^{-1} min^{-1})
1	2	3	4	5	6	7
1	A	25.3 ± 0.1	54.6	8.9	35.1 ± 1.0	14.0 ± 0.5
2	B	29.9 ± 0.3	71.8	8.3	27.4 ± 0.3	8.2 ± 0.4
3	C	23.3 ± 0.2	53.5	7.2	17.7 ± 0.9	3.7 ± 0.7

equimolar concentrations of functional groups. The assumption generally used in the spectroscopic and calorimetric studies of hydrogen bond complexes is that the reactivity coefficients are equal to unity[10–13]. Therefore the complex constant could be expressed by the equation[7]:

$$K = \frac{c_{\mathrm{OH...N}}}{c_{\mathrm{OH}} \cdot c_{\mathrm{Et_3N}}} \tag{7}$$

where $c_{\mathrm{OH...N}}$ = concentration of hydrogen bonds formed; c_{OH} = equilibrium concentration of hydroxyl groups; $c_{\mathrm{Et_3N}}$ = equilibrium concentration of triethylamine. The concentration of hydrogen bonds formed was determined from the expression (8):

$$c_{\mathrm{OH...N}} = \frac{Q}{\Delta H \cdot V} \ (\mathrm{mol\ dm^{-3}}) \tag{8}$$

where Q = measured heat of reaction; ΔH = heat of complex formation; V = the total volume of the solution (dm^3). The concentrations of hydroxyl groups and triethylamine were calculated from the following relations:

$$c_{\mathrm{OH}} = c^0_{\mathrm{OH}} - c_{\mathrm{OH...N}} \tag{9}$$

$$c_{\mathrm{Et_3N}} = c^0_{\mathrm{Et_3N}} - c_{\mathrm{OH...N}} \tag{10}$$

where: c^0_{OH} and $c^0_{\mathrm{Et_3N}}$ = the respective initial concentrations of hydroxyl groups and triethylamine. The observed average values of complex stability constants are listed in *Table 2*. To calculate the standard changes of thermodynamic potentials the following equation was used:

$$\Delta G^\circ = -RT\ln K \tag{11}$$

Owing to the fact that measurements of heats of dilution of the investigated complex did not yield measurable heat effects at infinite dilution, the calculated heats of complex formation can be assumed to be close to the values of the standard formation enthalpies ΔH°. The standard changes of entropy were calculated from equation (12):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

The results are also presented in *Table 2*.

Kinetic studies were also carried out in order to find the approximate values of rate constants for complex formation between the triethylamine and bisphenol hydroxyl groups, the formation of these complexes in the presence of a large excess of bisphenol was treated as a pseudo first-order reaction:

$$-\mathrm{OH} + \mathrm{N(C_2H_5)_3} \overset{k}{\longleftrightarrow} -\mathrm{OH}\ldots\mathrm{N(C_2H_5)_3} \tag{13}$$

The rate constant of reaction is given by the equation:

$$k't = 2.303 \log \frac{a}{a-x} \tag{14}$$

assuming that a is the initial concentration of triethylamine and is proportional to Q; $a - x$ = the actual concentration of triethylamine is proportional to $Q - Q_t$ and where Q is the heat of formation of the complex involving the complete consumption of the whole initial amount of triethylamine; and Q_t is the actual value of the heat of reaction. Reaction (14) can hence be expressed as follows:

$$k't = 2.303 \log \frac{Q}{Q - Q_t} \tag{15}$$

The reaction rate constants k' are equal to the gradient of the straight line given by the relationship (15) and were computed using the method of least squares; the complex formation rate constants k were calculated from equation (16):

$$k = \frac{k'}{c_0} \tag{16}$$

where c_0 is the initial concentration of hydroxyl groups (mol cm^{-3}). The average values of k obtained are listed in *Table 2*. In the same way, the rate of reaction of triethylamine with the first functional group of terephthaloyl chloride was found to be 0.78 ± 0.20 dm^3 mol^{-1} min^{-1}. Unfortunately the above value contains an additional error resulting from the different reactivity of both functional groups of terephthaloyl chloride.

It was the aim of the last part of our paper to apply research studies of complex formation of triethylamine with functional groups of both monomers in an investigation of the polycondensation mechanism. In order to compare the course of the reactions of the complex between triethylamine and the respective monomers with the reaction of their polycondensation, the results of relevant measurements were plotted in the form of thermokinetic curves. Typical curves obtained for the reaction involving the formation of 0.1 mol of a complex of triethylamine with one of the hydroxyl groups of the bisphenols are given in *Figure 1*. The curves obtained have essentially the same shape and can therefore be used for the approximate characterization of the process of complex formation. *Figure 2* illustrates thermokinetic curves of 0.1 mol triethylamine complex formation with a bisphenol hydroxyl group and with one functional group of terephthaloyl chloride. These curves can be seen to differ significantly from each other. The measured thermal effect in the case of terephthaloyl chloride is several times higher and the rate of the reaction considerably smaller. This result is in good agreement with the calculated numerical values of the heats and the rate constants for forming the corresponding complex.

In order to obtain information about the type of the complex in the polycondensation process, the thermal effects

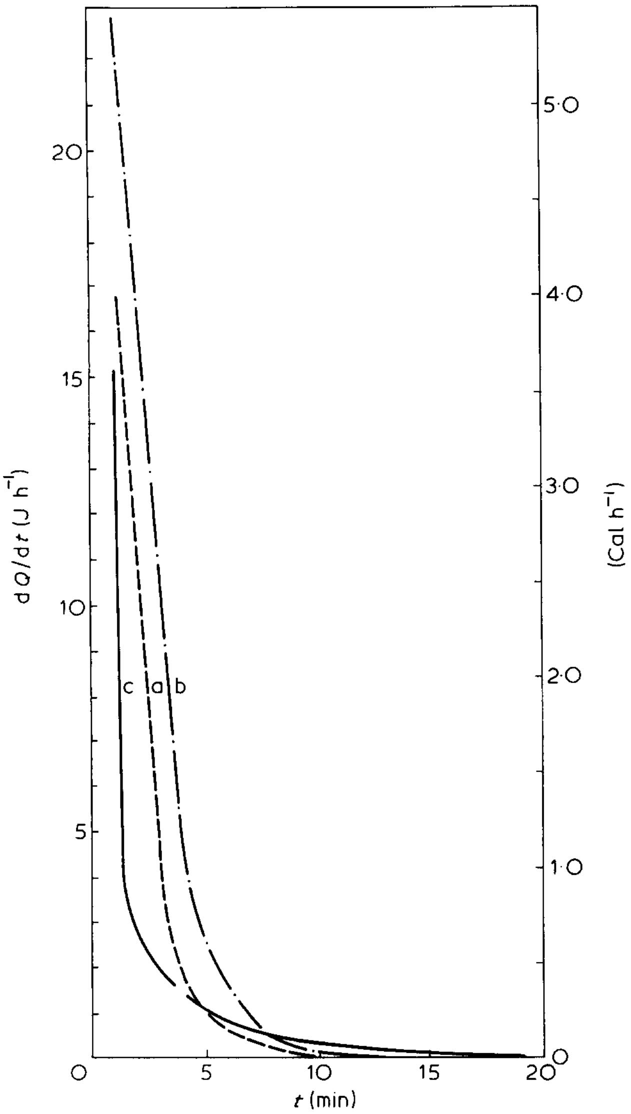

Figure 1 Thermokinetic curves of 0.1 mol triethylamine complex formation with hydroxyl group of bisphenols: (a) bisphenol A, (b) bisphenol B, (c) bisphenol C

accompanying this process were measured. The polycondensation reaction in which known amounts of triethylamine were introduced into a solution of a bisphenol and terephthaloyl chloride in dichloroethane was studied. The following initial molar ratio of reagents was used, bisphenol: terephthaloyl chloride: triethylamine = 1:1:2. Results of those measurements are presented in the form of thermokinetic curves (*Figure 3*). The curves were obtained for an initial triethylamine concentration of about 7 x 10^{-3} mol/dm^{-3}. Slight deviations from equimolarity are not significant, owing to the fact that we are interested in studying the character of the process and are not concerned with its quantitative interpretation. Triethylamine can be assumed to have reacted completely in view of the high degrees of polycondensation reported in the literature for the process considered[5,14]. This assumption is based on literature data[1–5] which suggest that the low temperature polycondensation process in solution must involve a complex formation reaction. Thus the extent of the reaction of end-groups depends on the number of complexes formed. The thermokinetic curves of the polycondensation reaction were therefore compared with those resulting from the formation of complexes by the whole initial amount of triethylamine with the corresponding bisphenols and terephthaloyl chloride. These curves are given in *Figure 4*.

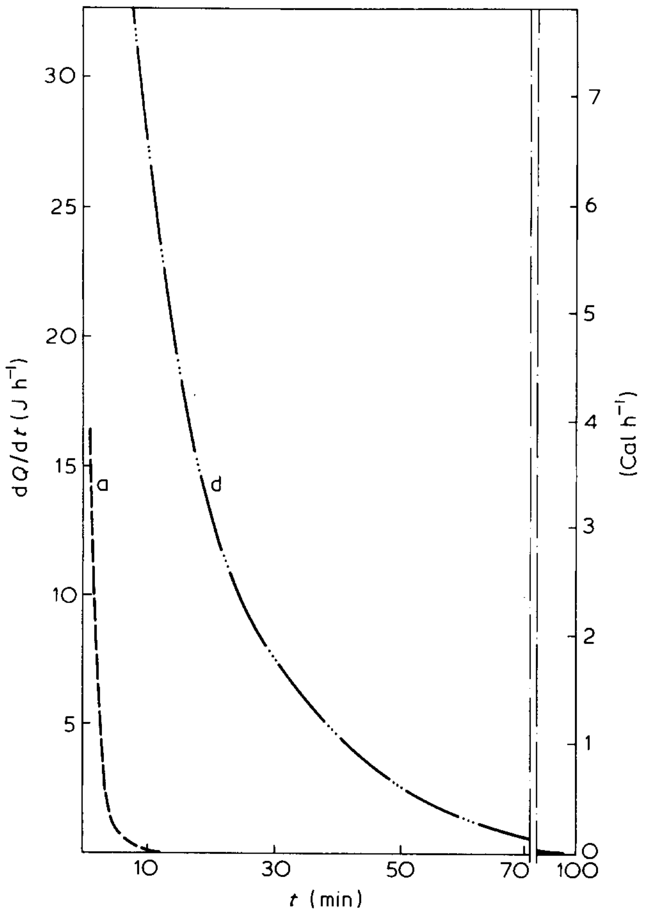

Figure 2 Thermokinetic curves of 0.1 mol triethylamine complex formation with a hydroxyl group of bisphenol A and functional group of terephthaloyl chloride: (a) bisphenol A; (d), terephthaloyl

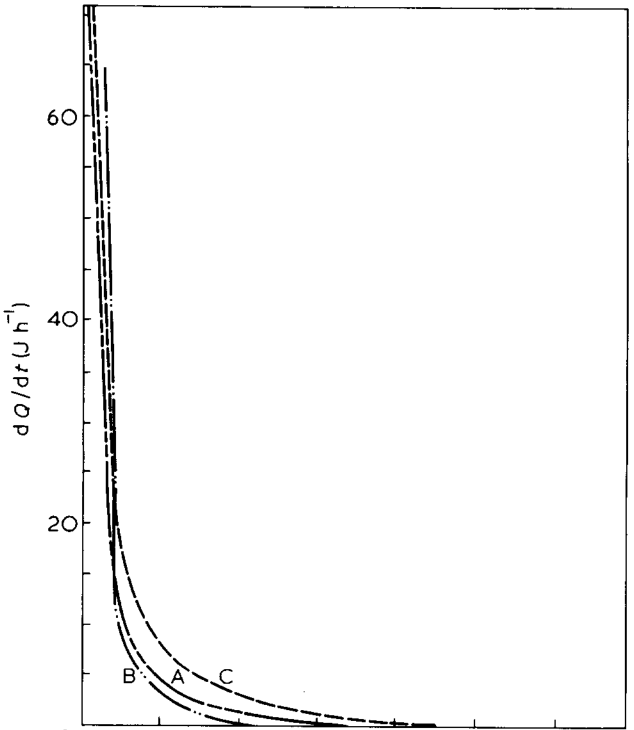

Figure 3 Thermokinetic curves of polycondensation process. A, bisphenol A; B, bisphenol B; C, bisphenol C

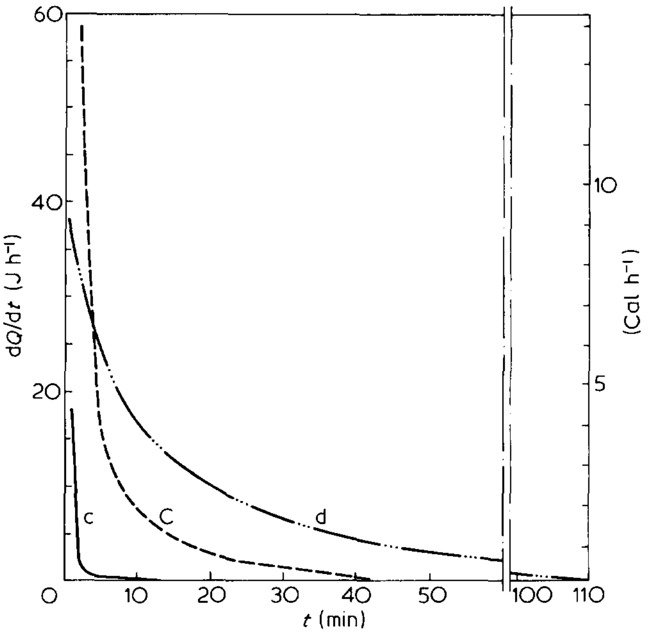

Figure 4 Comparison of the thermokinetic curves of the polycondensation reaction with bisphenol C with those corresponding to the triethylamine complex formation with the studied monomers; (c) bisphenol C, (d) terephthaloyl chloride, (C) the polycondensation process

Complexes are formed when triethylamine is introduced into an equimolar mixture of the monomers. The number of the triethylamine complexes with the hydroxyl groups containing monomers is initially considerably larger because the rate of this particular reaction is much higher than that of the reaction between triethylamine and terephthaloyl chloride. Consequently, it is not the complexes of triethylamine with terephthaloyl chloride which are chiefly taking part in the polycondensation process investigated. The concentration of the triethylamine complex with terephthaloyl chloride increases with time, which implies that the concentration is highest in the case of the longest lasting polycondensation process, i.e. the one involving bisphenol C (*Figure 3*). In this case, however, the polymer obtained has the lowest molecular weight. Alternatively, in the case of bisphenol B (fastest polycondensation process) the amount of triethylamine complex with terephthaloyl chloride is lowest and the resultant polymer has the highest molecular weight. This would suggest that the polycondensation process does not involve the formation of the complex of terephthaloyl chloride with triethylamine. The above assumption is further justified by the fact that the rate of formation is considerably lower than the overall rate of the polycondensation process, (see *Figure 4*). As already stated, the duration of the polycondensation is longest for bisphenol C and shortest for bisphenol B. This finding correlates fully with the values of the enthalpies of triethylamine complex formation with the investigated bisphenols.

CONCLUSIONS

Results of thermochemical investigations have shown both hydroxyl groups of the bisphenols studied to have the same reactivity in the reaction with triethylamine. But the two functional groups of terephthaloyl chloride were found to exhibit different reactivities, the second group being the more reactive.

Thermodynamic parameters ΔH^0, ΔG^0 and ΔS^0, rate constants and stability constants of triethylamine complexes with bisphenols hydroxyl groups were determined.

A preliminary analysis of the thermokinetic curves would suggest that the polycondensation process proceeds according to a base catalysis mechanism. Further investigations are being carried out to find if this polycondensation process follows the same kinetic scheme in other reaction conditions.

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