

# Oligocarbonate Diols from Ethylene Carbonate—Optimization of the Synthesis Process

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**ABSTRACT:** Oligocarbonate diols due to their resistance to oxidation and hydrolysis are particularly valuable components of polyurethanes for biomedical applications. It was shown that for their synthesis “green monomer,” ethylene carbonate can be used in the reaction with 1,6-hexanediol, instead of usually applied toxic and harmful phosgene. Depending on reaction conditions, besides ester exchange leading to the desired product, competitive etherification is often observed. To optimize the reaction conditions leading to oligocarbonates of high molecular weight without oxyethylene fragments, the method of an experimental design was applied. Such approach enabled the estimation of the influence of reaction temperature, ethylene carbonate to 1,6-hexanediol molar ratio and cata-

lyst (NaCl) concentration on the molar mass of oligocarbonate diol, content of ether bonds and reaction time. Application of central composite method as an experimental design allowed not only to choose the optimal set of conditions, but also the coefficients of the regression equation were interpreted in a chemical way. Oligocarbonate diols obtained under optimal conditions were used for synthesis poly(urethane-urea)s which exhibited very good mechanical properties (tensile strength 45–50 MPa and elongation at break up to 500%). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 683–691, 2011

**Key words:** polycarbonates; synthesis; oligomers; ethylene carbonate; oxyethylene units

## INTRODUCTION

Polyurethanes exhibit many favorable mechanical properties, as well as good biocompatibility, and can be used for manufacturing various types of implants. The basic components used in the production of polyurethanes are oligomerols and diisocyanates. As oligomerols usually oligoesters or oligoethers having molecules terminated with hydroxyl groups are used. Nowadays, for production of polyurethanes which can be used as biomedical materials oligocarbonate diols are preferred as oligomerols. These types of polyurethanes are resistant to oxidative and hydrolytical degradation.

Oligocarbonate diols can be obtained by environmentally friendly method using polymerization of six-membered cyclic carbonates such as trimethylene carbonate or polyesterification method using ethylene carbonate or dimethyl carbonate—“green monomers,” which are produced on industrial scale.

In contrast, five-membered alkylene carbonates, such as ethylene and propylene carbonate do not homopolymerize, due to thermodynamically stable structure.<sup>1</sup> Five-membered cyclic carbonates heated

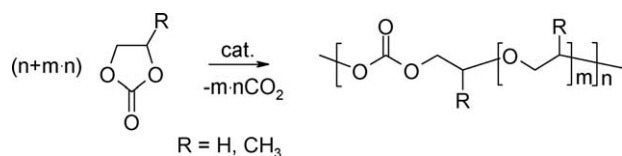
at temperatures above 170°C in the presence of metal (Sn, Zn, Zr) alkoxides or carboxylates lead to oligo(ether-carbonates), in which the number of ether units much exceed 50% (Scheme 1).<sup>2–4</sup> The reaction proceeds with decarboxylation.

Alkylene carbonates react with alcohols at elevated temperatures leading to 2-hydroxyethylethers.<sup>5</sup> In the late 80's of the last century, Harris et al.<sup>6,7</sup> applied ethylene carbonate for synthesis of oligo(ether-carbonate) diols. Low molecular 1,4-butanediol was used as a initiator-starter. The reaction proceeded with transesterification of 2-hydroxyethoxyethylcarbonate groups and formation of diethylene glycol as a volatile by-product (Scheme 2). The resultant oligomer contained a significant amount of ether bonds.<sup>8,9</sup>

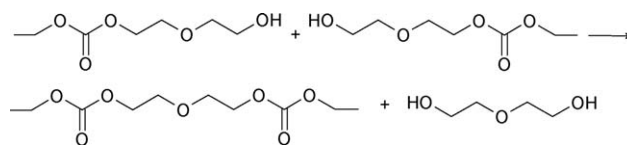
It was found by us that when the reaction of alkylene carbonate was carried out with diols containing more than five carbon atoms in a molecule in the presence of organotin catalyst (in the case of propylene carbonate)<sup>10,11</sup> or sodium chloride (bromide) (in the case of ethylene carbonate)<sup>12</sup> aliphatic oligocarbonates practically without ether linkages can be selectively obtained.

Alkylene carbonates, depending on reaction conditions, can react with diols or growing polymer chains terminated with OH groups according to two reaction mechanisms. In the first case the carbonyl carbon atom is attacked (Scheme 3, pathway 1) and linear oligocarbonate diol is formed. In the second case, the

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**Scheme 1** Synthesis of oligo(ether-carbonate)s from five-membered cyclic carbonates.



**Scheme 2** Transesterification of 2-hydroxyethoxyethylcarbonate groups.

alkyl carbon atom is subjected to nucleophilic attack, resulting in decarboxylation and irreversible formation of oligo(oxyethylene) fragments (Scheme 3, pathway 2). We have also found that the presence of oxy- gen atom in diol in the beta position to OH group promotes the further attack on the alkyl carbon atom in cyclic carbonate by another diol molecule.

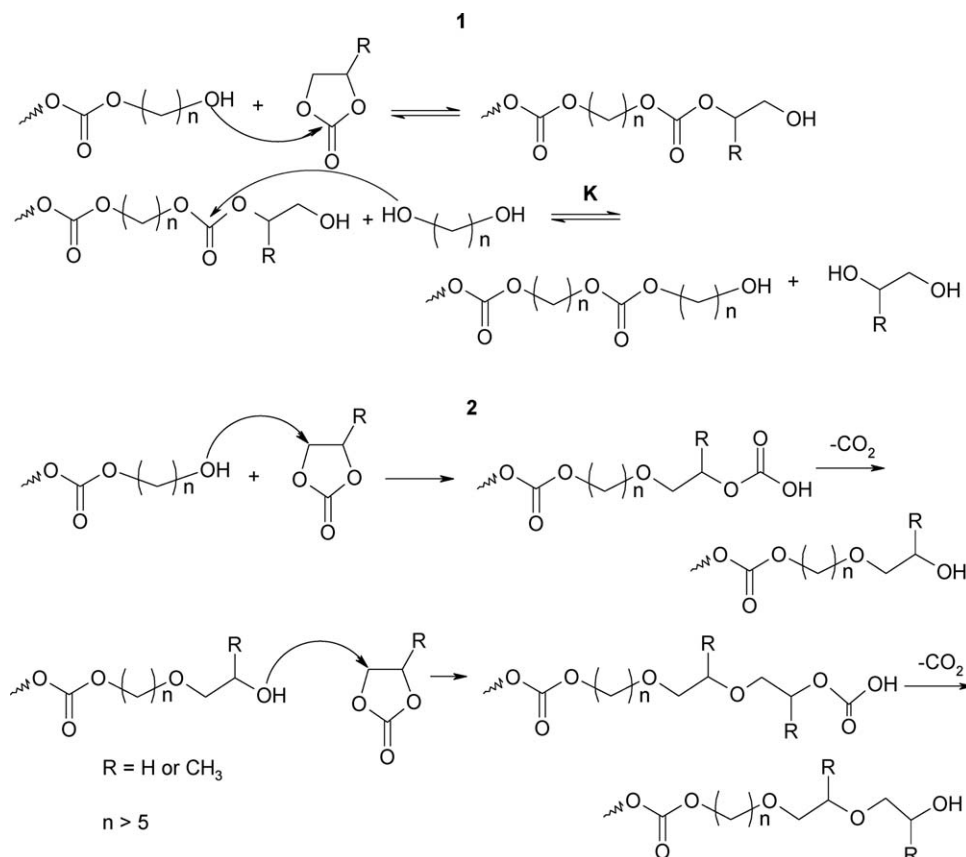
Because of the small value of the reaction equilibrium constant ( $K$ ) (Scheme 3, pathway 1) side product (ethylene glycol or 1,2-propylene glycol) of the polycondensation should be continually removed from the reaction system to obtain oligomers of required molar mass. For this purpose, we applied the solvent forming heteroazeotrop with glycol. Xylene was tested as an azeotropic solvent in the case of ethylene carbonate and heptane in the case of propylene carbonate.<sup>11</sup>

Thus, polycondensation of five-membered cyclic carbonates with  $\alpha,\omega$ -diols can provide oligocarbonate diols, in the structure of which the carbonate linkages

are separated by hydrocarbon fragments containing more than five carbon atoms depending on diol used (Scheme 3, pathway 1). The diols with shorter chains because of low boiling point can distill together with azeotropic solvent, resulting in lower molar mass and yield of the oligomerol. Moreover, the reaction of ethylene carbonate with diols containing less than five carbon atoms in a molecule leads to greater participation of oxyethylene units in the product.<sup>12</sup>

Taking into account the preliminary results, we surveyed optimization of the synthesis of oligocarbonate diols from ethylene carbonate and 1,6-hexanediol applying the method of an experimental design. The aim of the experiment was also to identify mathematical models.

Experimental designs are frequently performed in the study of empirical relationships between one or more measured responses and a number of variables. Having such relations, it can specify a combination of



**Scheme 3** Possible reaction pathways for the reaction of five-membered cyclic carbonates with diols.

variables that will achieve some practical benefit. In the chemical industry, experimental designs are particularly applied to the study of process variables and how they affect the product. The basic types of experimental design are factorial design, fractional factorial design, and central composite design which are a common type of statistical experiment especially applicable to optimization analysis.<sup>13</sup>

The aim of this work is to study the synthesis of oligocarbonate diol from ethylene carbonate and 1,6-hexanediol, and the effect of reaction temperature, ethylene carbonate to 1,6-hexanediol molar ratio and catalyst concentration on the molar mass of oligocarbonate diol, content of ether bonds and reaction time applying central composite method as a experimental design.

## EXPERIMENTAL

### Materials

Ethylene carbonate of purity 98%, 1,6-hexanediol of purity 97%, toluene of purity 98%, xylene (mixture of isomers) (Aldrich) and NaCl (POCH) were used without additional purification.

### Apparatus

Molecular weight of the oligomerols and ether bonds content in the oligomerols were estimated from <sup>1</sup>H-NMR spectra by means of a Varian VXR 400 MHz spectrometer using tetramethylsilane as an internal standard.<sup>14</sup>

The optimization was carried out using the system IKA® LR 2000, a modularly expandable laboratory reactor, designed and planned for reproducing and optimizing chemical reaction processes at laboratory scales. Our setup included 2 dm<sup>3</sup> double-walled jacketed glass reactor vessel with bottom discharge valve and an anchor stirrer, heating circulator bath, the torque measuring instrument VM 600 basic and temperature sensors. A special type of Dean-Stark distillation trap was applied. It allowed cooling of the distillate before its flowing back into the reactor to improve the separation of ethylene glycol from xylene (Fig. 1). The reactor was combined and controlled via PC using Labworldsoft® software.

### Experimental procedure

Into a 2 dm<sup>3</sup> reactor equipped with a mechanical stirrer, Dean-Stark distilling trap, thermometer and reflux condenser 354.0 g (3.0 mol) of 1,6-hexanediol, an appropriate amount of ethylene carbonate, sodium chloride, and xylene was placed. The reaction temperature was governed by xylene content in the reaction mixture. The polycondensation was carried out at boiling point of the reaction mixture while continuously removing ethylene glycol by distilla-



**Figure 1** The IKA® LR 2000 system; (A) reactor vessel, (B) heating circulator bath, (C) torque measuring instrument, (D) temperature sensors, (E) Dean-Stark distillation trap, (F) PC with Labworldsoft® software. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

tion together with xylene. After vapor condensation two phases are formed, ethylene glycol was separated and upper phase—xylene turned back to the reactor. The reaction was carried out additionally for 30 min from the moment when no ethylene glycol drops formation was observed. After cooling to 50°C additional 400 cm<sup>3</sup> of xylene was added and the oligomer solution was washed three times with demineralized water until the conductivity of the aqueous phase was lower than 50 μS. Organic solvent was evaporated under reduced pressure (below 100°C) and the product as soft wax was obtained.<sup>12,15</sup> Series of experiments were carried out while reaction temperature (amount of xylene), EC:diol molar ratio and catalyst concentration were changed.

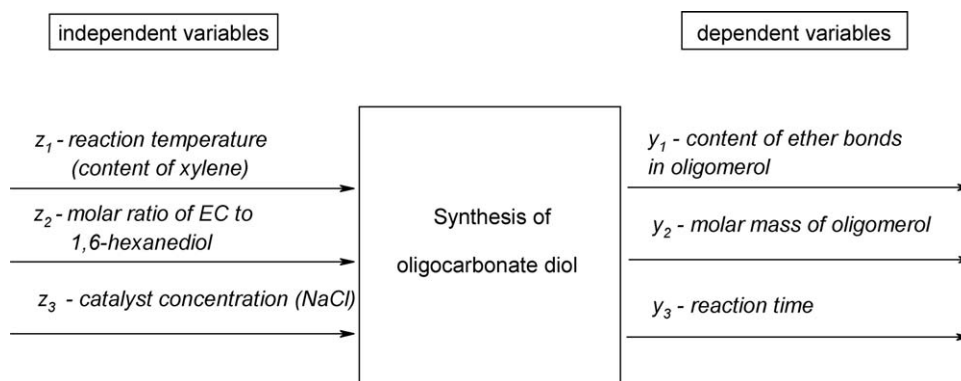
### Mathematical modeling

A second order polynomial mathematical model was used to represent the content of ether bonds (oxyethylene units) in the oligomerol— $y_1$ , molar mass of oligocarbonate diol— $y_2$ , and reaction time (until no ethylene glycol drops appear in the distillate)— $y_3$ , as functions of reaction temperature (solvent content)— $z_1$ , ethylene carbonate to 1,6-hexanediol molar ratio— $z_2$ , and catalyst (NaCl) concentration— $z_3$  (Scheme 4). Other variables were fixed. The general form of this model for three independent variables is represented by the following equation:

$$y_1 = a_0 + a_1z_1 + a_2z_2 + a_3z_3 + a_4z_1z_2 + a_5z_1z_3 + a_6z_2z_3 + a_7z_1^2 + a_8z_2^2 + a_9z_3^2$$

Similar equations can be employed for  $y_2$  and  $y_3$ .

An experimental design based on central composite circumscribed (CCC) method was used to organize the



**Scheme 4** Functional scheme of technological process of oligocarbonate diol synthesis.  $z_1, z_2, z_3$ —independent variables,  $y_1, y_2, y_3$ —dependent variables.

experiments. The experiment was designed to allow to estimate the interaction and even quadratic effects, and therefore give us an idea of the (local) shape of the response surface we are investigating. For three factors as response surface method a central composite design was selected. This design contains star points which represent new extreme values (low and high) for each factor in the design.<sup>16</sup>

The operating range of the variables was first specified and limits established.

Lower (llv) and upper limit values (ulv) are as follows:

$z_1$ , reaction temperature (°C):

llv—130°C, boiling point of xylene and minimal temperature at which the reaction proceeds with rational rate,

ulv—160°C, the maximal temperature at which less than 30 mol % of ether linkages are formed;

$z_2$ , molar ratio of ethylene carbonate to 1,6-hexanediol (dimensionless):

llv—1.0, for that molar ratio theoretically a maximal high molecular weight of the oligomerol can be obtained,

ulv—1.5, larger excess leads to suppression of the transesterification reactions;

$z_3$ , catalyst concentration (wt.% calculated in relation to 1,6-hexanediol):

llv—0 wt %, no catalyst,

ulv—1 wt %, resulting from the preliminary experiments.

The total number of experiments  $N$  was calculated according to the following equation:

$$N = 2^P + 2P + 2, \text{ then, } N = 2^3 + 2 \cdot 3 + 2 = 16$$

where:

$P$ —number of levels

#### The area of the experiment (range of variation)

Selected for testing the maximum and minimum levels of independent variables— $z_i$  and coded variables— $x_i$  are given in Table I.

The optimization criteria set by us are as follow: the minimization of the ether bonds content in the oligomerol— $y_1$ , the maximization of the oligomerol molar mass— $y_2$ , and the minimization of the polycondensation time— $y_3$ :

$$\min(y_1), z_1 - z_3$$

$$\max(y_2), z_1 - z_3$$

$$\min(y_3), z_1 - z_3$$

Table II illustrates the factor settings required for a CCC design (standard order), assuming three factors, each with low and high settings, respectively.

Number of runs required by central composite design equals 16. Treatments 1 to 8 in each case are the factorial points in the design, 9 to 10 are the system-recommended center points, and treatments 11 to 16 are the star points. In the CCC design the low and high values of each factor have been extended to create the star points.

## RESULTS AND DISCUSSION

The first task was to choose an azeotropic solvent. Taking into consideration the influence of the reaction temperature on the formation of oligo(oxyethylene) units in the oligomerol we have chosen solvents with boiling point, at which the reaction of ethylene carbonate with a diol proceeds with reasonable rate and the solubility of by-product—ethylene glycol is minimal. These criteria are met by two solvents: xylene and toluene (Table III). At the beginning xylene (bp 130°C) was used as azeotropic solvent. It was established that the reaction should be carried out below 150°C. At higher temperature the participation of etherification (formation of oligo(oxyethylene) units) significantly increased. It is worth mentioning that xylene acts also as a reaction temperature regulator. The boiling point of the reaction mixture depends on the amount of xylene in the

TABLE I  
Factor Settings for CCC Designs for Three Factors

Independent variables ( $z_i$ )	Lower limit value	Coded variables, $x_i$					Upper limit value
		(-1.682)	(-1)	(0)	(+1)	(+1.682)	
$z_1$	130°C	137°C	140°C	145°C	150°C	154°C	160°C
$z_2$	1.00	1.00	1.05	1.15	1.25	1.32	1.50
$z_3$	0 wt %	0.26 wt %	0.40 wt %	0.60 wt %	0.80 wt %	0.94 wt %	1.0 wt %

reaction system. However, to maintain the temperature of 140–145°C xylene content in the reaction mixture should be greater than 50%. It means that the yield of oligocarbonate diol from one manufactured unit is relatively small. Application of azeotropic solvent with a lower boiling point such as toluene (bp 110°C) enabled to reduce the solvent content in the system at the same reaction temperature. However, as a result higher degree of etherification was observed. It was surprising, that relatively high content of oligo(oxyethylene) units was present in the products despite decreasing of the reaction temperature down to 135°C (Table I). It means that not only reaction temperature has decisive influence on etherification but also monomers and oligomers concentration. Higher concentration promotes irreversible attack on an alkyl carbon atom in ethylene carbonate molecule.

Thus, for the optimization process xylene was used as an azeotropic solvent. On the basis of previous studies, we have chosen sodium chloride as a catalyst.<sup>12</sup> It should be underlined that NaCl is non-toxic and easy to remove from the product.

### Analysis of CCC design results

Table II shows the coded and real values of independent variables for the experiments to be con-

ducted according to CCC method, and the experimental response represented by ether bonds content in the product ( $y_1$ ), molar mass of oligocarbonate diol ( $y_2$ ), and reaction time ( $y_3$ ).

A nonlinear least-squares regression program based on Gauss-Newton method was used to fit to the coded data and experimental response given in Table II. This fitting gave the predicted values of  $y_1$ ,  $y_2$ , and  $y_3$ , the residual error " $e_i$ " and the coefficients " $a$ " of this equation.

### Effect of three independent variables on ether bonds content in the oligomerol

The fitted response surface of the model for ether bonds content in the product is as follows:

$$y_1 = 3049.55 - 44.96 z_1 + 237.56 z_2 - 56.17 z_3 - 2.63 z_1 z_2 + 0.06 z_1 z_3 + 3.12 z_2 z_3 + 0.17 z_1^2 + 54.14 z_2^2 + 37.84 z_3^2$$

The analysis of variance ( $F$ -test) was used for testing the significance of each effect in the model. An estimate of the variance  $S_a^2$  is obtained by dividing the experimental error variance  $S_r^2$  by the sum of square of each effect  $\sum \bar{z}_i^2$ , as follows,  $S_a^2 = S_r^2 / \sum \bar{z}_i^2$ ,

TABLE II  
Central Composite Circumscribed (CCC) Design for Three Factors and the Obtained Results

Runs	Coded variables			Real variables			Dependent variables (output)		
	$x_1$	$x_2$	$x_3$	$z_1$ (deg C)	$z_2$ (-)	$z_3$ (wt %)	$y_1$ (mol %)	$y_2$ (g/mol)	$y_3$ (h)
1	-1	-1	-1	140	1.05	0.4	2.5	1000	18
2	+1	-1	-1	150	1.05	0.4	19	1100	8
3	-1	+1	-1	140	1.25	0.4	1.5	1200	21
4	+1	+1	-1	150	1.25	0.4	13	800	7.5
5	-1	-1	+1	140	1.05	0.8	3	1050	17
6	+1	-1	+1	150	1.05	0.8	20	1050	8.5
7	-1	+1	+1	140	1.25	0.8	2.5	1250	20
8	+1	+1	+1	150	1.25	0.8	14	700	5.5
9	0	0	0	145	1.15	0.6	3	1300	11.5
10	0	0	0	145	1.15	0.6	3	1250	13.5
11 <sup>a</sup>	-1.682	0	0	136.6	1.15	0.6	3	1150	18
12 <sup>a</sup>	+1.682	0	0	153.4	1.15	0.6	26.5	800	4
13 <sup>a</sup>	0	-1.682	0	145	0.982	0.6	7	1000	14
14 <sup>a</sup>	0	+1.682	0	145	1.318	0.6	1.5	900	13
15 <sup>a</sup>	0	0	-1.682	145	1.15	0.264	6.5	1200	13
16 <sup>a</sup>	0	0	+1.682	145	1.15	0.936	7.5	1150	13.5

<sup>a</sup> Star points

**TABLE III**  
Effect of Azeotropic Solvent on the Participation of Ether Bonds in Oligomerol

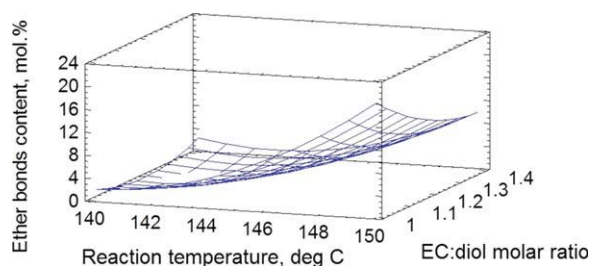
Azeotropic solvent	The content of ether bonds in oligomerol (mol %)	
	135°C	145°C
Xylene	<1	<2
Toluene	5	12

where,  $S_r^2 = \Sigma z^2 / \gamma$ , and  $\gamma = N - n$ . The significance of effects may be estimated by comparing the values of the ratio  $a^2/S_a^2$  with the critical value of the *F*-distribution at 95% confidence level ( $F_{0.95} = 6.61$ ). If the ratio  $a^2/S_a^2 > 6.61$  then the effect is significant. Thus, according to the results obtained it appears that interaction effects  $z_1 \cdot z_3$  and  $z_2 \cdot z_3$  are not significant. The best response function is then conveniently written as follows:

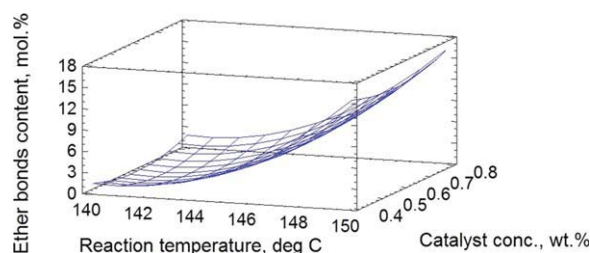
$$y_1 = 2778.59 - 42.27 z_1 + 363.97 z_2 - 38.57 z_3 - 2.63 z_1 z_2 + 0.16 z_1^2 + 32.14 z_3^2$$

This equation represents the best form of the mathematical model that relates the ether bonds content in the oligomerol to the three independent variables. These relations can be illustrated by the response plots in Figure 2.

As shown Figure 2, the smaller amount of ether bonds is observed when the polycondensation is carried out at lower temperature. At low reaction temperature, the etherification reaction and oligo(oxyethylene) units formation are significantly suppressed. It should be underlined that when azeotropic distillation is carried out at lower temperature it means that monomers and oligomers concentration is also lower. However, at low temperature the reaction rate is reduced and to finish polycondensation (no ethylene droplets are observed in xylene after vapors condensation) longer time is needed. The influence of catalyst concentration on ether bonds formation seems to be less important (Fig. 3).



**Figure 2** Influence of the reaction temperature and EC to 1,6-hexanediol molar ratio on the ether bonds formation. The polycondensation was carried out in the presence of 0.6 wt % of NaCl as a catalyst. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]



**Figure 3** Influence of the reaction temperature and catalyst concentration on the ether bonds formation. The polycondensation was carried out for 1.2 EC to 1,6-hexanediol molar ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

### Effect of three independent variables on oligomerol molar mass

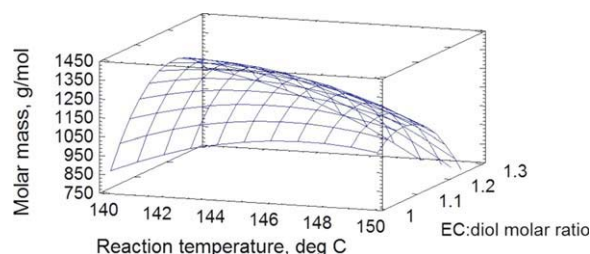
The fitted response surface of the model for molar mass of oligocarbonate diols is:

$$y_2 = 146693.0 + 1529.7 z_1 + 64367.8 z_2 + 5901.7 z_3 - 262.5 z_1 z_2 - 31.2 z_1 z_3 - 312.5 z_2 z_3 - 4.2 z_1^2 - 11488.7 z_2^2 - 883.4 z_3^2$$

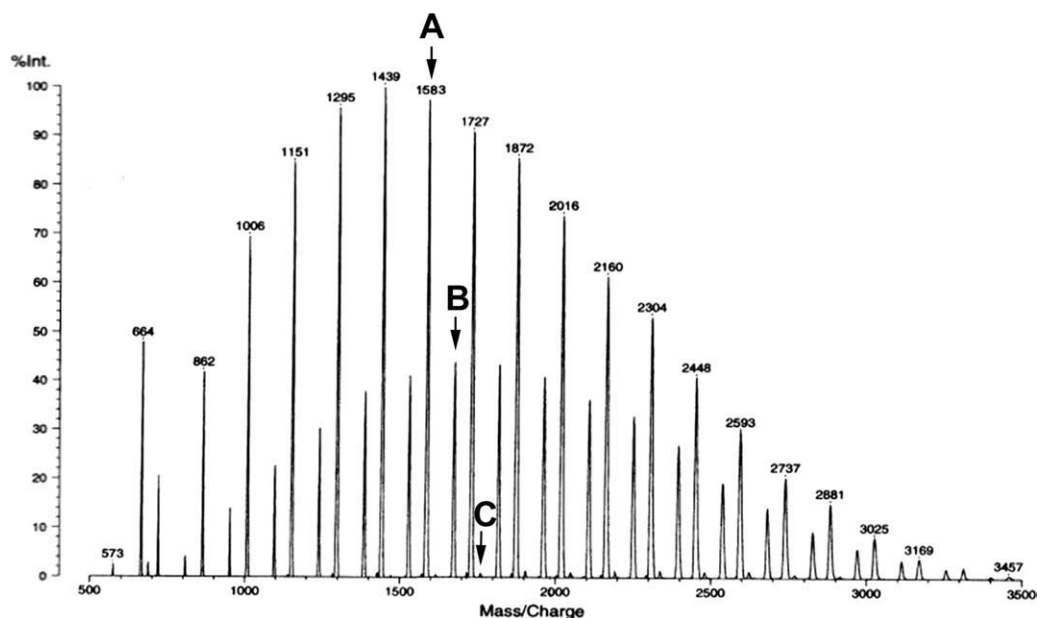
Taking into account the analysis of variance it appears that interaction effect  $z_2 \cdot z_3$  is not significant and the response function is as follows:

$$y_2 = 146507.0 + 1529.7 z_1 + 64180.3 z_2 + 5591.4 z_3 - 262.5 z_1 z_2 - 31.2 z_1 z_3 - 4.2 z_1^2 - 11488.7 z_2^2 - 883.4 z_3^2$$

As can be seen (Fig. 4) at above 150°C the resultant oligomerol molar mass is reduced. When the reaction proceeds at that temperature the formation of oligo(oxyethylene) units takes place and ethylene carbonate is consumed but the molar mass increases in a very small extent (by 44 in one reaction act) (Scheme 3, pathway 2). In contrast, in a transesterification reaction (Scheme 3, pathway 1) ethylene carbonate binds two growing chains by carbonate



**Figure 4** Influence of reaction temperature and EC to 1,6-hexanediol molar ratio on the molar mass of oligomerol. The polycondensation was carried out in the presence of 0.6 wt % of NaCl as a catalyst. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

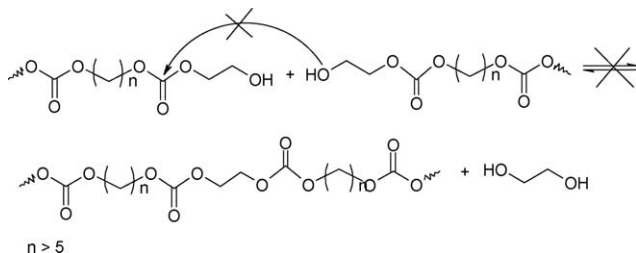


**Figure 5** MALDI-TOF mass spectrum of oligocarbonate diol obtained from ethylene carbonate and 1,6-hexanediol in the presence of NaCl as a catalyst at 143–145°C without postpolycondensation carried out under reduced pressure. A: molecules terminated with  $-\text{OC}(\text{O})\text{O}(\text{CH}_2)_6\text{OH}$  groups, (B) terminated both with  $-\text{OC}(\text{O})\text{O}(\text{CH}_2)_6\text{OH}$ , and  $-\text{OC}(\text{O})\text{O}(\text{CH}_2)_2\text{OH}$  groups, (C) terminated with  $-\text{OC}(\text{O})\text{O}(\text{CH}_2)_2\text{OH}$  groups.

linkage and as a result the molar mass of the oligomer increases more rapidly (Figs. 2–4).

It has also been established that the molar ratio of ethylene carbonate to 1,6-hexanediol is an important factor influencing the oligomer molar mass. Too high excess of ethylene carbonate causes that the growing chains are terminated mainly with 2-hydroxyethylcarbonate groups. MALDI-TOF mass spectrometry analysis confirmed that oligocarbonate diol could not contain more than two ethylene carbonate fragments in a molecule (Fig. 5). It means that no homofunctional polycondensation between two 2-hydroxyethylcarbonate groups takes place (Scheme 5). However, this type of polycondensation (homopolycondensation of 2-hydroxyethyl terephthalate groups) is applied in the production of poly(ethylene terephthalate).

It was found that oligomeric chains terminated with 2-hydroxyethylcarbonate groups cannot react with ethylene carbonate to form oligo(ethylene carbonate) units as well (Scheme 6).



**Scheme 5** Forbidden homofunctional polycondensation.

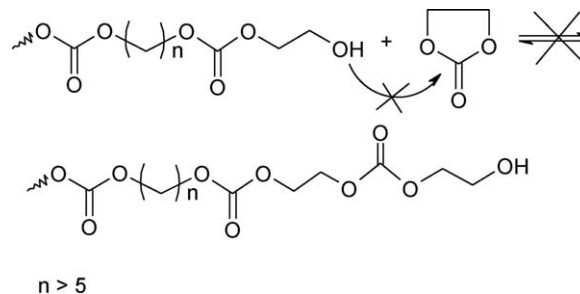
Thus, due to the thermodynamic reason 2-hydroxyethylcarbonate groups can react only with oligomers terminated with OH groups derived from 1,6-hexanediol (Scheme 3, pathway 1, R = H).

### Effect of three independent variables on polycondensation time

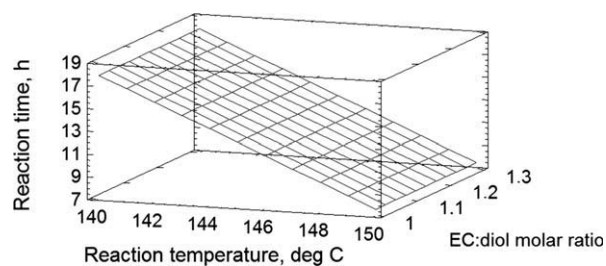
As far as the reaction time is concerned it was found, after the analysis of variance, that only reaction temperature has significant effect on this dependent variable (Fig. 6).

When the reaction is carried out at 150°C the polycondensation time is shortened to ~ 7 h but a high amount of oligo(oxyethylene) fragments is formed and molar mass of the product is reduced.

It is worth mentioning that the catalyst concentration has small influence on the time of polycondensation.



**Scheme 6** Forbidden reaction between ethylene carbonate and oligomeric chains terminated with 2-hydroxyethylcarbonate groups.



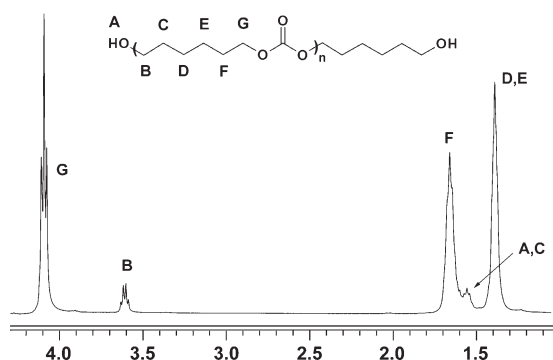
**Figure 6** Influence of reaction temperature and EC to 1,6-hexanediol molar ratio on the polycondensation time. The polycondensation was carried out in the presence of 0.6 wt % of NaCl as a catalyst.

It is due to limited solubility of sodium chloride in the reaction mixture.

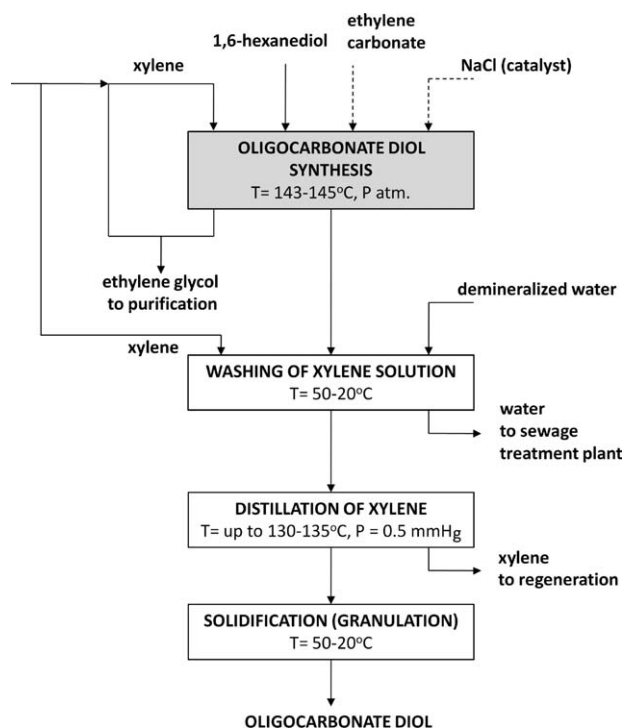
It was established that the reaction product isolated from the postreaction mixture by washing with water and solvent evaporation under reduced pressure consists of molecules terminated with 6-hydroxyhexyl-carbonate groups (1,6-hexanediol residues) as well as with 2-hydroxyethylcarbonate groups (derived from ethylene carbonate ring opening). In the MALDI-TOF spectrum of the product there are series of signals which can be assigned to "pure" oligo(hexamethylene carbonate) molecules (A) and oligo(hexamethylene carbonate) molecules with 2-hydroxyethylcarbonate terminal groups (B and C) (Fig. 5).

When the postreaction mixture was heated at 130°C under reduced pressure (up to 0.5 mmHg) to remove solvent and excess of ethylene carbonate the resultant product did not contain 2-hydroxyethylcarbonate groups (Fig. 7). Due to regular structure such oligomers easily crystallize. It should be mentioned that during ethylene carbonate removing also small amount of ethylene glycol was distilled off and the product exhibited higher molecular weight (up to 2500).

Thus, the optimum conditions are: reaction temperature 143°C, 10 mol % excess of ethylene carbon-



**Figure 7**  $^1\text{H-NMR}$  spectrum of oligocarbonate diol obtained from ethylene carbonate and 1,6-hexanediol in the presence of NaCl as a catalyst at 143°C after postpolycondensation proceeded at 130°C under reduced pressure for 3 h.



**Scheme 7** Schematic diagram of oligocarbonate production.

ate relating to 1,6-hexanediol and 0.6 wt % of the catalyst. Under these conditions, the optimum theoretical ether bonds content was less than 3 mol % and experimental 2.5 mol %, optimum molar mass of oligocarbonate diol was 1350 g/mol, whereas experimental one 1300 g/mol.

Oligocarbonate diols obtained according to the optimized procedure (Scheme 7) were used for synthesis of polyurethanes by prepolymer method using isophorone diisocyanate and water vapor as a chain extender. The synthesis was carried out according to Ref. 17. The resultant elastomer exhibited relatively high tensile strength (45–50 MPa) and elongation at break (up to 500–600%).

## CONCLUSIONS

The reaction conditions of oligocarbonate diol synthesis were studied using a second order mathematical model. The result calculated using this model was in a good agreement with the experimental data. Model and experiment result exhibited a significant effect due to reaction temperature and ethylene carbonate to 1,6-hexanediol molar ratio affecting the molar mass of oligomerol and ether bonds content. The highest molar mass (1300 g/mol) was observed when the reaction temperature was 143–145°C and cyclic carbonate to diol molar ratio was 1.10–1.15. The content of oligo(oxyethylene) fragments in the product was less than 3 mol %. Statistical



modeling leads to chemical insight: not only is it possible to identify the optimal set of conditions, but the coefficients of the equation can also be interpreted in a chemical way.

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