

Synthesis of Polyetherols from Melamine and Ethylene Carbonate

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ABSTRACT: Attempts to synthesize *s*-triazine ring containing polyetherols from melamine and ethylene carbonate are described. The conditions of synthesis providing optimal yields of the polyetherols were 165°C, melamine to ethylene carbonate molar ratio 1 : 9 to 1 : 18, and 4 g of potassium carbonate or diazabicyclo[2.2.2]octane catalyst per mole of melamine. The structure of the products was established by ¹H-NMR and IR spectroscopy. The kind and amount of side products [mostly poly(ethylene glycols)] was determined by GLC. The polyetherols have been found useful in the synthesis of polyurethanes of improved thermal stability. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1776–1784, 2001

Key words: melamine; ethylene carbonate; polyetherols; thermally stable polyurethanes

INTRODUCTION

Polyurethane foams with improved thermal stability have been sought for many years. The traditional products of this type have rather poor stability and start to decompose at 90–100°C.¹ A remedy might be the use of polyol components containing heterocyclic *s*-triazine rings, which are known to improve thermal stability of organic compounds.^{2–5} Melamine (MEL) contains such a ring.

MEL based polyetherols are usually obtained by reacting MEL itself,³ or some of its derivatives,^{4,6} with oxiranes, e.g., ethylene oxide, propylene oxide, or epichlorohydrin. The reactions are carried out at elevated temperatures (60–120°C) in DMSO or DMF solution in the presence of alkylammonium hydroxides or tertiary amines as catalysts. The disadvantage of this method is the use of toxic and flammable oxiranes, which

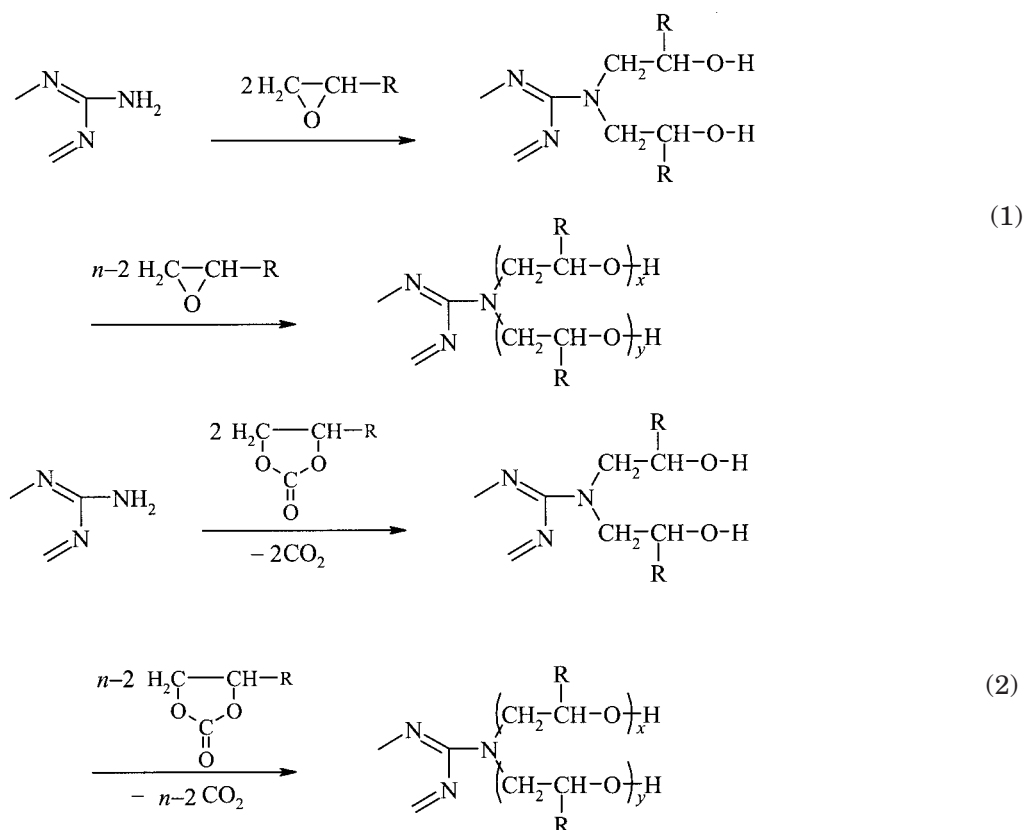
could explode when mixed with air. Also, oxiranes low boiling point requires autoclave reactors. Hence, new methods of synthesis of *s*-triazine ring containing polyetherols have been tested in order to avoid the use of oxiranes at elevated temperatures. The idea of reacting MEL with alkyl carbonates seems promising because the structure of the products would be the same as that of the products of the reaction of MEL with its respective oxiranes (Schemes 1 and 2).

Formally, the polyetherols obtained by this route are the compounds of MEL and ethylene oxide, or propylene oxide of respective molar ratios.

We have not found in the literature any information on reactions of MEL with alkylene carbonates, besides one US patent⁷ that very generally describes products of reaction of the carbonates with *s*-triazine compounds, including MEL. There is, however, information on several applications of ethylene carbonate (EC) in the chemical, pharmaceutical, and cosmetic industries. Thus, in compositions with polyamides, EC improves the impact strength of

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where $x + y = n$; R = —H, —CH₃

composites⁸ and acts as an antistatic agent,⁹ whereas when added to novolacs, it reduces considerably the time of hardening.⁸ EC has also been used as a plasticizer for rapidly hardening polyurethanes, including polyurethane adhesives.^{10,11} The compound has also been utilized as an ethoxylation agent in the modification of polysaccharides¹² and alcohols.¹³

In this article, we report on the laboratory scale studies of the reaction conditions as well as the selectivity of the synthesis of polyetherols based on MEL and alkylene carbonates. We have tested several catalysts of the reaction and determined the amount of side products formed during the synthesis.

EXPERIMENTAL

Syntheses

MEL (3.2 g, 0.025 mole) was placed along with predetermined amounts of EC (Note 1) and catalyst (Note 2) in a three-necked round-bottomed

flask equipped with mechanical stirrer, efficient reflux condenser, and thermometer. The content was heated to 175–180°C (Note 3) and kept at this temperature until no more release of carbon dioxide was observed, and then for yet another hour.

The reaction was considered completed when the weight of the products corresponded to that calculated from mass balance, i.e., with all EC reacted and all carbon dioxide removed from the system.

Notes:

1. The amount of EC was adjusted to have MEL : EC molar ratios 1 : 6, 1 : 7.2, 1 : 8, 1 : 12, and 1 : 18.
2. The following compounds were used as catalysts:
 - potassium carbonate in the amount 16, 8, 4, or 1 g/mole MEL
 - 1,4-diazabicyclo[2.2.2]octane in the amount 16 or 4 g/mole MEL
3. The reactions were also carried out at temperature ranges 170–175, 160–165, or 145–155°C.

Analyses

The extent of the reaction was followed by monitoring the total weight of the system, which decreased due to carbon dioxide liberation. The content of hydroxyl groups was determined using the standard acetic anhydride addition method.¹⁴ The density was measured pycnometrically,¹⁵ the viscosity was measured in a Hoppler viscometer, surface tension was measured by the ring detach method, and refractive index was measured in an Abbe refractometer.

¹H-NMR spectra of the products were recorded on an 80 MHz spectrometer BS-586A (Tesla, Czechoslovakia) in d₆-DMSO solutions, HMDS internal standard. IR spectra were recorded on an PARAGON 1000 FT-IR spectrometer (Perkin-Elmer).

GLC analyses were made on a Hewlett-Packard 5890 machine equipped with a flame-ionization detector using a capillary column HP-FFAP 10 m long, 53 mm diameter with 0.1 μm layer thickness; temperature profile: initial: 50°C (0 min), increasing: 20°/min, final: 220°C (6 min); injector and detector temperature: 220°C; carrier gas velocity: 18.3 cm³/min; sample volume 0.2 μL.

The concentration of side products was estimated using cyclohexanone as an internal standard, according to the equation:

$$\frac{S_{\text{sample}}}{S_{\text{CH}}} = a \left(\frac{m_{\text{sample}}}{m_{\text{CH}}} \right) + b \quad (1)$$

where S is the surface area under the signal and m is the weight of sample or cyclohexanone (CH). The parameters of the calibration lines are presented in Table I. The retention times were measured for the products of reaction of EC with water. The times were unaffected by the presence of the polyetherols.

RESULTS AND DISCUSSION

Synthesis of Polyetherols and Their Properties

The studies were started with the run where the molar ratio of MEL : EC was equal to 1 : 6. The temperature was 170–175°C and the catalyst was K₂CO₃ in the amount of 16 g/mole MEL. Under these conditions, some part of solid MEL remained unchanged. At the molar ratios 1 : 7.2 or 1 : 8, MEL dissolved completely. After the reac-

Table I Diols Used as Calibration Standards in GLC Analysis of Side Products Formed in the Reactions of MEL with EC

| Reaction | Formula | Name | Calibration Line Coefficients | | Correlation Coefficient | Retention Time, R_t (min) |
|-----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|-------------------------------|---------|-------------------------|-----------------------------|
| | | | a | b | | |
| EC + H ₂ O | $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$ | ethane-1,2-diol (ED) | 0.3343 | -0.0094 | 0.9976 | 3.32 |
| ED + EC | $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$ | 3-oxapentane-1,5-diol (OPD) | 0.3512 | 0.0722 | 0.9734 | 5.21 |
| OPD + EC | $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$ | 3,6-dioxaoctane-1,8-diol (DOOD) | 0.3482 | 0.0717 | 0.9849 | 6.88 |
| DOOD + EC | $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2 \\ \quad \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$ | 3,6,9-trioxaundecane-1,11-diol (TOUD) | 0.3198 | 0.4365 | 0.9833 | 8.48 |

Table II Conditions of Reaction of EC with MEL and Compositions of Postreaction Mixtures

| Number of Synthesis | Initial MEL : EC Molar Ratio | Catalyst (g/mol MEL) | Temperature (°C) | Reaction Time (h) | Initial Composition of Reacting Mixture (wt %) | | | Calculated Mass Fraction of Products (wt %) | Found Mass Fraction of Products (wt %) | Number of Moles of EC Per Mole of MEL That: | |
|---------------------|------------------------------|-----------------------------------|------------------|-------------------|------------------------------------------------|------|----------|---------------------------------------------|----------------------------------------|---------------------------------------------|-----------------------------|
| | | | | | MEL | WE | Catalyst | | | Reacted with MEL | Decomposed and Left Reactor |
| 1 | 1 : 18 | K ₂ CO ₃ 16 | 175-185 | 5.5 | 7.4 | 91.7 | 0.93 | 53.2 | 48.4 | 16 | 2 |
| 2 | 1 : 18 | 8 | 160-165 | 5 | 7.4 | 92.1 | 0.47 | 53.5 | 52.8 | 17.7 | 0.3 |
| 3 | 1 : 18 | 4 | 160-165 | 5.5 | 7.5 | 92.3 | 0.25 | 53.6 | 52.9 | 17.7 | 0.3 |
| 4 | 1 : 12 | 16 | 175-185 | 17 | 10.7 | 88.0 | 1.33 | 54.7 | 48.7 | 10.3 | 1.7 |
| 5 | 1 : 12 | 8 | 160-165 | 14 | 10.6 | 88.7 | 0.67 | 55.0 | 53.3 | 11.5 | 0.5 |
| 6 | 1 : 12 | 4 | 160-165 | 6 | 10.6 | 89.0 | 0.34 | 55.1 | 54.3 | 11.7 | 0.3 |
| 7 | 1 : 12 | 1 | 170-175 | 4 | 10.7 | 89.3 | 0.09 | 55.3 | 55.3 | 12 | — |
| 8 | 1 : 8 | 16 | 170-175 | 8 | 14.8 | 83.2 | 1.89 | 56.5 | 56.0 | 7.28 | 0.72 |
| 9 | 1 : 7.2 | 16 | 170-175 | 9 | 16.2 | 81.8 | 2.06 | 57.1 | 53.0 | 6.13 | 1.07 |
| 10 | 1 : 6 | 16 | 170-175 | 8 | 18.8 | 78.8 | 2.39 | 56.1 | 51.3 | 5.59 | 0.41 |
| 11 | 1 : 18 | DABCO ^a 16 | 145-150 | 25 | 7.41 | 91.7 | 0.92 | 53.2 | 52.8 | 17.8 | 0.2 |
| 12 | 1 : 18 | 16 | 165 | 6.5 | 7.41 | 91.7 | 0.92 | 53.2 | 53.0 | 17.9 | 0.1 |
| 13 | 1 : 12 | 4 | 145-150 | 4 | 10.6 | 89.0 | 0.34 | 53.1 | 56.3 | 12 | — |

^a diazobicyclo[2.2.2]octane

Table III Composition of the Products of Addition of EC to MEL as Determined from Mass Balance and by GLC

| Synthesis No. ^a | Moles of EC Per Mole of MEL | Moles of EC Per Mole of MEL That Decomposed and Left Reactor | Moles of EC Per Mole of MEL Converted into ^b : | | | | Moles of EC Per Mole of MEL That Reacted Directly with MEL |
|----------------------------|-----------------------------|--------------------------------------------------------------|-----------------------------------------------------------|------|------|------|------------------------------------------------------------|
| | | | ED | OPD | DOOD | TOUD | |
| 1 | 18 | 2 | 0.04 | 0.60 | 0.51 | 1.50 | 13.4 |
| 2 | 18 | 0.3 | 0.07 | 0.63 | 0.52 | 1.04 | 15.4 |
| 3 | 18 | 0.3 | 0.00 | 0.68 | 0.66 | 2.16 | 14.2 |
| 4 | 12 | 1.7 | 0.11 | 0.76 | 0.36 | 0.79 | 8.3 |
| 5 | 12 | 0.5 | 0.05 | 0.57 | 0.37 | 0.87 | 9.6 |
| 6 | 12 | 0.3 | 0.02 | 0.62 | 0.43 | 1.17 | 9.5 |
| 7 | 12 | — | 0.03 | 0.62 | 0.44 | 1.22 | 9.7 |
| 11 | 18 | 0.2 | 0.01 | 0.98 | 0.75 | 2.22 | 13.8 |
| 12 | 18 | 0.1 | 0.02 | 0.75 | 0.66 | 2.09 | 14.4 |
| 13 | 12 | — | 0.00 | 0.75 | 0.54 | 0.10 | 10.6 |

^a Conditions as in Table II.^b See Table I for abbreviations.

tion was completed, however, a solid precipitated from the product, which was a mixture of unreacted MEL and its hydroxyethyl derivatives. Composition of the precipitate was established by ¹H-NMR. The products obtained at the initial molar ratios of reagents 1 : 7.2 or 1 : 8 were semisolid slightly opaque resins of dark brown color. Clear liquid products were obtained only at the molar MEL : EC ratio 1 : 12 or at a higher proportion of carbonate.

MEL was found to dissolve well in EC when heated. The dissolution was in fact a chemical reaction that led to formation of a polyetherol. The synthesis was carried out in the presence of potassium carbonate or diazabicyclo[2.2.2]octane (DABCO) catalysts used in the amount ranging from 1 to 16 g/mole of MEL and at various temperatures (145–175°C).

The time of MEL dissolution in EC depended on the excess of the latter. At 12- or 18-fold excess of EC over MEL the dissolution time was 15–20 min. At a smaller EC excess it became somewhat longer (30–60 min).

The simplest method of following the extent of the reaction was to observe the mass decrease due to release of carbon dioxide from the reactor. The reaction was considered completed when the total weight of the products was equal to or smaller than that calculated, assuming all carbon dioxide left the system. The lack of unreacted EC was confirmed by IR and ¹H-NMR analysis. As follows

from Table II, however, the total weight of the products was smaller than that calculated from the mass balance. In the presence of catalyst, some amount of EC probably decomposed at the beginning of polymerization to volatile ethylene oxide.

Hence, in order to maintain the predetermined molar ratio of MEL to EC in the products, one has to use a slightly higher excess of EC than that following from stoichiometry. Furthermore, some amount of water was introduced to the system with the hygroscopic EC or with catalysts. Water reacts with EC to form ethane-1,2-diol. The latter further reacts with EC to form subsequent diols. The extent of these side reactions will be discussed later in this article.

The difference between the calculated and the real weight of the reaction product was used to assess the amount of EC that decomposed and left the reactor in the form of ethylene oxide. The results of calculations of both the amount of EC that left the system and that converted into glycols are presented in Table III.

Calculations of this kind are correct provided no unreacted EC remains in the system. This can easily be verified by ¹H-NMR analysis. The protons of methylene groups in EC are clearly seen in the spectra at 4.45 ppm.

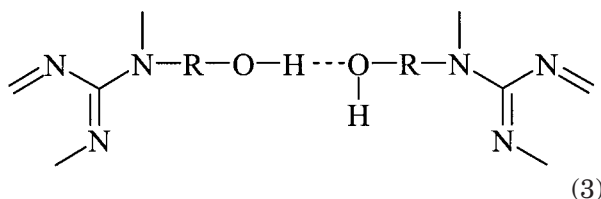
The basic physical properties of polyetherols were determined, including density, viscosity,

surface tension, and refractive index. The respective values and their dependence on temperature are presented in Table IV, along with the hydroxyl number of the polyetherols.

Spectral Analysis

In the $^1\text{H-NMR}$ spectrum of the reaction product of 1 mole of MEL with 6 moles of EC one finds signals at 3 to 3.5 ppm from methylene groups $-\text{CH}_2-\text{O}-\text{CH}_2-$ and, in the range 4.5–5.1 ppm, from the proton of the hydroxy group. This signal was pretty “fuzzy” due to strong intermolecular hydrogen bonding (Fig. 1). It vanished after some heavy water was added. The signals at 5.9 to 6.1 ppm came from protons in unreacted primary amino groups, and at 6.2 to 6.5 ppm from protons in secondary amino groups. As the excess of EC in the reaction system increased, the signal from protons of primary amino groups eventually disappeared completely, and that from secondary amino groups was substantially reduced (Fig. 1). This means that MEL was 5- to 6-functional in the reactions with EC. The IR spectrum of solid MEL contains characteristic bands at $3330\text{--}3470\text{ cm}^{-1}$ from stretching vibrations at amino nitrogen, 1632 cm^{-1} from deformational $>\text{N-H}$ vibrations, and at 1653 cm^{-1} from stretching $>\text{C=N}$ vibrations (Fig. 2). These bands disappeared from the spectra of the products resulting from the addition of EC to MEL. New bands appeared that are characteristic of polyetherols, namely: at 1060 cm^{-1} due to stretching vibration of C-O bonds, and at 1116 cm^{-1} due to antisymmetric stretching vibration of C-O-C bonds. The intensity of the latter increased with EC : MEL molar ratio.

The IR spectra also revealed the presence of strong hydrogen bonding (bands at $3328\text{--}3375\text{ cm}^{-1}$) that led to formation of aggregates of the form seen in Scheme 3.



Chromatographic Analysis

All products were analyzed chromatographically (GLC) in order to determine the amount of side products. Compounds that served as standards of the side products were obtained by

Table IV Some Physical Properties of Polyetherols Obtained from MEL and EC as Functions of Temperature in the Range 20–80°C

| Property Equation | Refractive Index, n_{20}^D $n_{20}^D = aT + b$ | | Density, ρ (g/cm^3) $\rho = aT + b$ | | Viscosity, η ($\text{Pa} \cdot \text{s}$) $\eta = a + b \exp(-T/c)$ | | Surface Tension, τ (N/m) $t = aT + b$ | | Hydroxyl Number ($\text{mg KOH}/\text{g}$) L_{OH} | | |
|----------------------------|-----------------------------------------------------|-------|---------------------------------------------------------------|-------|-------------------------------------------------------------------------------|-------------------|-----------------------------------------------------------------|--------|-----------------------------------------------------------------|--------|-------|
| | a | b | a | b | a | b | a | b | | r^a | r^a |
| Synthesis no. ^b | | | | | | | | | | | |
| 2 | $-3.2 \cdot 10^{-4}$ | 1.504 | 0.9924 | 1.245 | 0.9998 | $68.2 \cdot 10^3$ | 10.45 | -0.115 | 46.9 | 0.9745 | 395.7 |
| 5 | $-2.8 \cdot 10^{-4}$ | 1.517 | 0.9918 | 2.532 | 0.9999 | $25.2 \cdot 10^3$ | 10.63 | -0.189 | 52.4 | 0.9428 | 486.8 |

^a Correlation coefficient.

^b Conditions as in Table II.

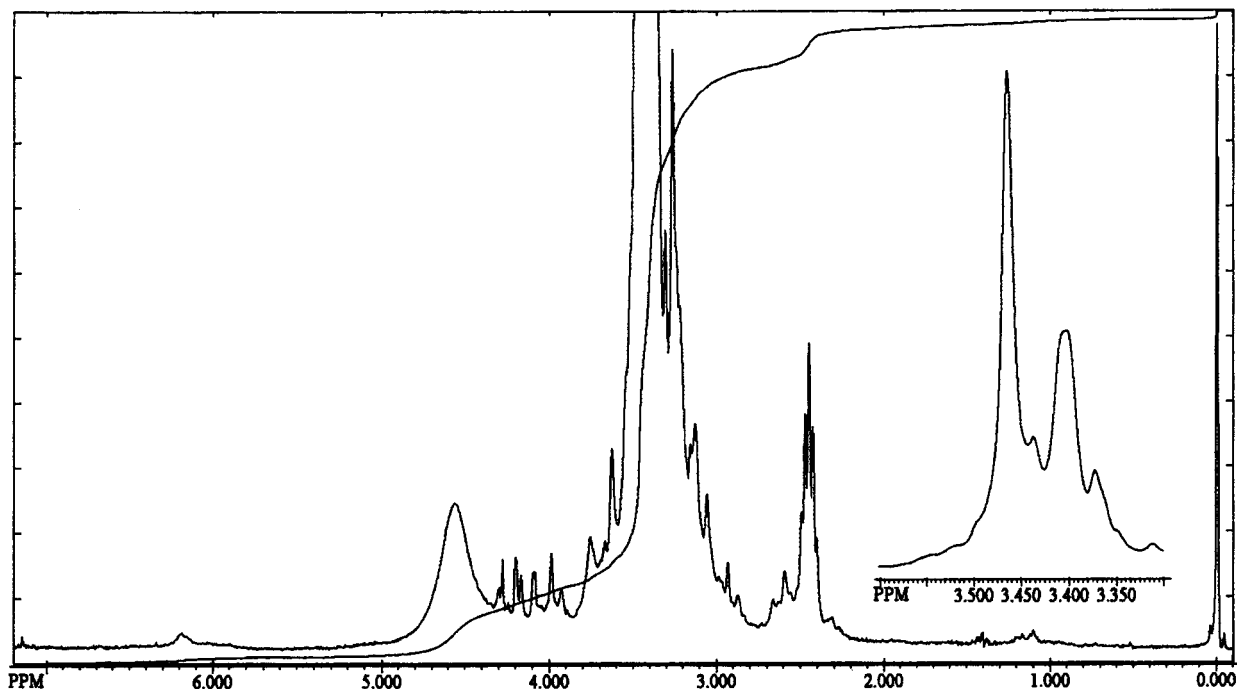


Figure 1 $^1\text{H-NMR}$ spectrum of the reaction product MEL : EC = 1 : 18, 4 g $\text{K}_2\text{CO}_3/\text{mol}$ MEL, temperature 160–165°C.

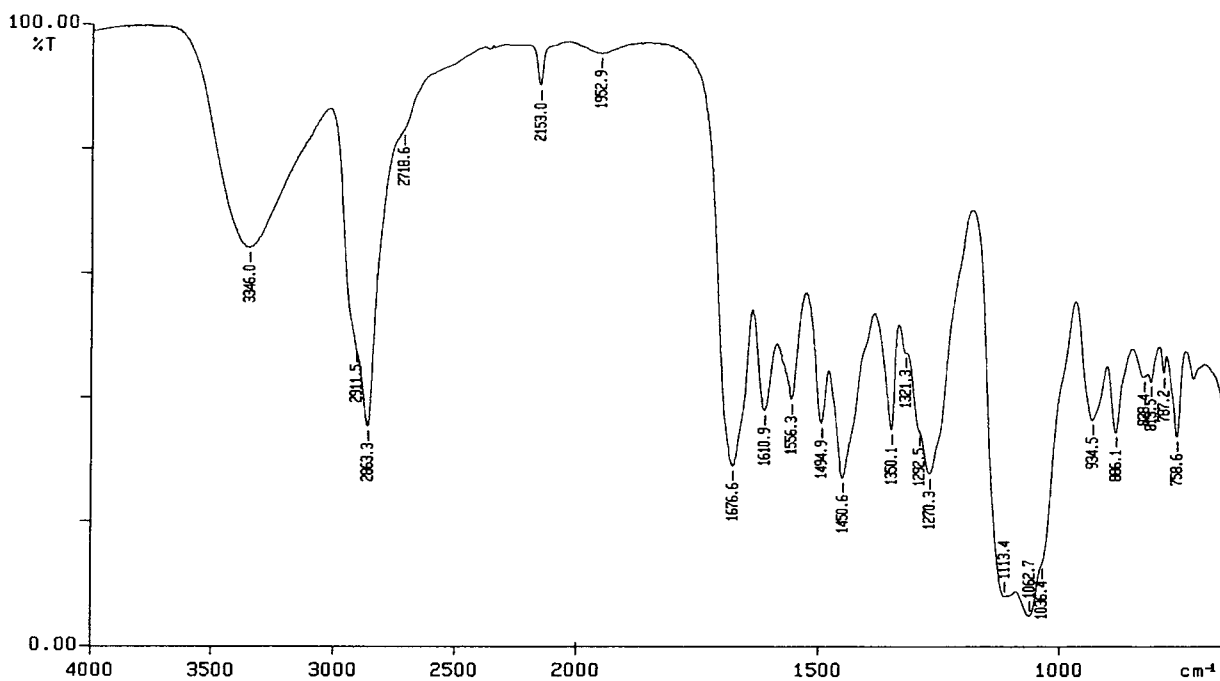
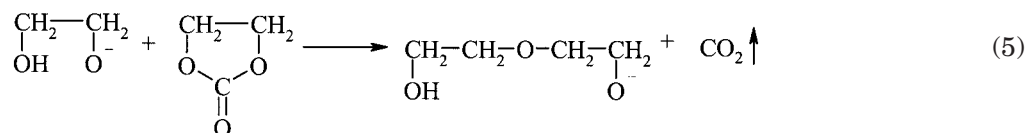
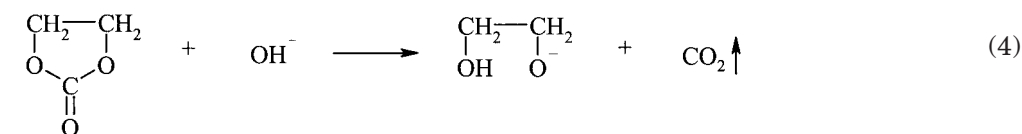


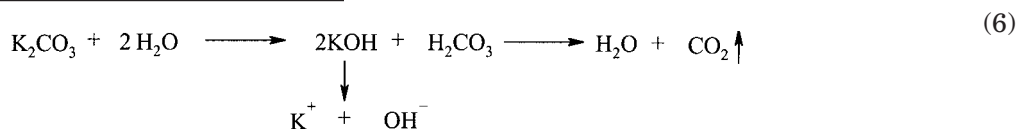
Figure 2 IR spectrum of the reaction product MEL : EC = 1 : 18, 4 g $\text{K}_2\text{CO}_3/\text{mol}$ MEL, temperature 160–165°C.

reacting EC with water at molar ratios 1 : 1 and 1 : 4. The results from the chromatograms of these compounds are presented in Table I. The result of chromatographic analysis of the products resulting from addition of EC to MEL are presented in Table III. As follows from the data in Table III, the amount of side products in the reaction was controlled by temperature and the concentration

of the catalyst. This amount became smaller as reaction temperature increased (Table III, runs 1 and 3). The reason for this is probably that at low catalyst concentration and low temperature, the alcoholate anions from ethane-1,2-diol were more reactive than the amino groups of MEL. Reactions (4) and (5) became favored over main reaction (2):

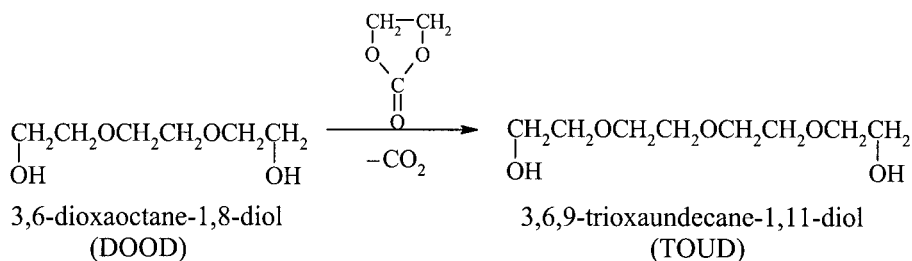
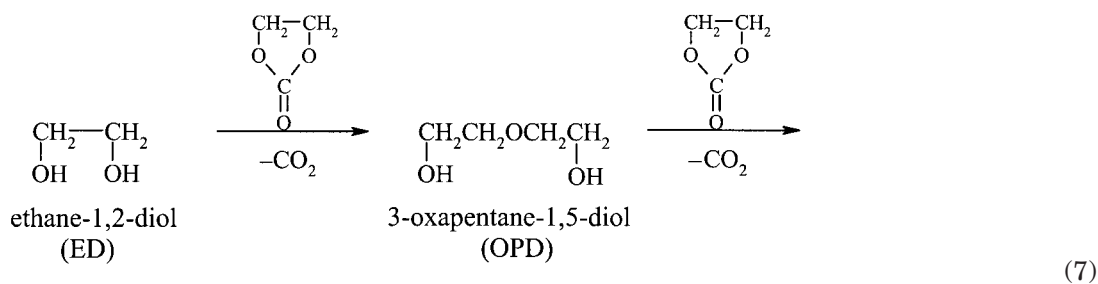


Hydroxy anions were formed from the potassium carbonate catalyst, as shown in Scheme 6.



Only a small peak due to ethane-1,2-diol was observed in chromatograms of the products of reaction of MEL with EC. This is because

this compound reacted readily with the excess of EC to form the products shown in Scheme 7.



A long reaction time also favors formation of polyglycols (Table III, runs 1 and 4). The type of catalyst did not affect the yield of polyglycols. The major factors were the temperature and time of reaction (Table III, runs 1 and 11).

Because we measured the amount of the glycols in the products by GLC, we could estimate the fraction of EC wasted on their formation. The relevant figures are shown in Table III.

These data may help in estimating an excess of EC over its calculated amount, which should be used to obtain a product of predetermined molar ratio of ethylene groups to MEL.

Concluding, it seems worth mentioning that polyetherols obtained at the initial MEL : EC molar ratio 1 : 12, yielded in reactions with MDI and water stiff foams, were of much improved thermal stability compared to traditional foams. The properties of polyurethane foams obtained from the polyetherols prepared in this work will be described in a separate article.

CONCLUSIONS

1. It is feasible to obtain polyetherols containing *s*-triazine rings by reacting MEL with excess of EC.
2. The polyetherols obtained as in point 1 have essentially the same structure as those prepared directly from MEL and ethylene oxide and can be used as raw materials for preparation of thermostable polyurethane foams.
3. The advantage of EC over ethylene oxide is that one avoids the danger of explosion,

poisoning, or fire, which always exists when using the latter, and one can carry on synthesis without an autoclave. One also avoids the need of using additional solvents of MEL.

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