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POLY(ETHER-CARBONATE)S FROM FIVE-MEMBERED CYCLIC CARBONATES AND OXIRANES

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ABSTRACT

Studies on the reactions of oxiranes with various carbonates (cyclic and linear, aliphatic and aromatic) in the presence of $BF_3{\cdot}Et_2O$ are presented. The reaction mechanism is proposed. It was found that poly(ether-carbonate) is formed not only as the product of polymerization of spiroorthocarbonate but mainly directly from oxirane and cyclic carbonate. Spiroorthocarbonate is one of the possible reaction products of trioxocarbenium ion - the product of its cyclization. It was shown that as a result of the copolymerization of epichlorohydrin with ethylene carbonate initiated by $BF_3{\cdot}Et_2O$ poly(ether-carbonate) containing of about 10 % of units originated from ethylene carbonate and 4-chloromethyl-1,3-dioxolan-2-one was obtained.

INTRODUCTION

Five-membered cyclic carbonates: 1,3-dioxolan-2-ones, due to the ease of obtaining are attractive materials for many applications. They are usually obtained by insertion of carbon dioxide into an oxirane ring. The latter method is already used in a technical scale [1]. The patent literature on the preparation and application of that kind of cyclic carbonates is very abundant [2]. Such non toxic monomers are used for the synthesis and modification of many polymers, e.g., epoxy resins [3].

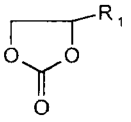
Unfortunately, 1,3-dioxolan-2-ones, in contrast to six-membered 1,3-dioxane-2-ones, do not homopolymerize under normal conditions according to both the cationic and anionic mechanisms [4]. As it was earlier indicated [5], they may polymerize above 170°C yielding poly(ether-carbonate)s. The loss of small molecules of CO_2 additionally compensates for a part of the entropy loss.

On the other hand five-membered cyclic carbonates react under mild conditions with oxiranes in the presence of Lewis acids giving spiroorthocarbonates (SOC) - bicyclic five-membered acetals. These monomers may be polymerized by cationic initiators yielding, similarly to the high temperature polymerization of 1,3-dioxolan-2-ones, poly(ether-carbonate)s enriched in ether units and a cyclic carbonate as a by-product [6]. Due to the presence of ether units, poly(ether-carbonate)s as less susceptible to cyclization in the back-biting reaction may be useful substrates for polyurethane elastomers.

Taking the above into consideration it seemed interesting to investigate the possibility of direct cationic copolymerization under mild conditions of reactive oxiranes with inert cyclic five-membered carbonates utilizing the enthalpy of the opening of the strained oxirane three-membered ring as the reaction driving force. In this paper kinetic measurements of the reaction of cyclic carbonates with oxiranes are reported and plausible mechanism as well as chemical structure of the resulting poly(ether-carbonate)s is discussed.

MATERIALS

Ethylene carbonate (**1a**), propylene carbonate (**1b**), diethyl and diphenyl carbonates ("Merck", Germany), $BF_3 \cdot OEt_2$ ("Fluka AG" Switzerland) were used without further purification. Propylene oxide (**2b**), epichlorohydrin (**2c**), phenyl glycidyl ether (**2d**) ("Koch Light Lab." U.K.) were purified by the usual methods [7].



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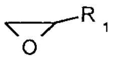

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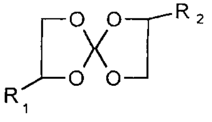


3

where:
for **1** and **2**: **a** $R_1 = H$, **b** $R_1 = CH_3$, **c** $R_1 = ClCH_2$, **d** $R_1 = PhOCH_2$
for **3ac** $R_1 = H$ and $R_2 = ClCH_2$

Methylene chloride was distilled after the removal of water and stored over molecular sieves (4A).

Synthesis of Cyclic Carbonates and Spiroorthocarbonates

Cyclic carbonates: 4-chloromethyl-1,3-dioxolan-2-one (**1c**) and 4-phenoxymethyl-1,3-dioxolan-2-one (**1d**) were prepared according to the method reported elsewhere [7]. 2-Chloromethyl-1,4,6,9-tetraoxaspiro[4,4]nonane (**3ac**) was prepared from **2c** and **1a**, respectively, according to the Endo method [8].

Synthesis of Poly(ether-carbonate) from Ethylene Carbonate and Epichlorohydrin

30 g (0.32 mole) of **2c** and 4.53 g (0.053 mole) of **1a** were dissolved in 33 cm^3 of CH_2Cl_2 and 0.05 cm^3 (0.4 mmol) of $BF_3 \cdot OEt_2$ was added. Reaction was carried out at 25°C and after 5 h 1 cm^3 of triethylamine was added to stop the reaction. The resulting reaction mixture was washed with 50 g of 10 % aq. NaOH and then with 100 cm^3 of water. The organic layer, after drying over anhydrous $MgSO_4$, was evaporated, and the residue was dissolved in 15 cm^3 of CH_2Cl_2 and prcipitated into 200 cm^3 of n-hexane. The precipitated polymer was collected as viscous material by decantation and dried under vacuum: yield 15 g (44 %), $M_n = 1470$.

MEASUREMENTS

IR spectra were recorded with Specord 71 spectrometer. ^1H NMR spectra were recorded on Varian 200 MHz spectrometer, using TMS as internal standard in $CDCl_3$ at 25°C. Molecular weight determinations were carried out by means of a Knauer vapor pressure osmometer in chloroform solutions.

Kinetic Measurements of Model Reactions

The reactions of carbonates (8.5 mmol) with oxiranes (54 mmol) dissolved in 33 cm^3 of CH_2Cl_2 were carried out in a thermostated flask under dry nitrogen. After cooling to a required temperature an appropriate amount of $BF_3 \cdot OEt_2$ was added. The samples of the reaction mixture of 0.5 cm^3 were diluted to 4 cm^3, 0.2 cm^3 of triethylamine was added and IR spectra (film of 0.123 mm width) were recorded. The molar ratio of five-membered cyclic or linear carbonates, and epoxide group was calculated from their characteristic IR absorptions at 1800 cm^{-1} (cyclic carbonate, $\nu_{C=O}$), or 1745 cm^{-1} (linear carbonate, $\nu_{C=O}$) and 910 cm^{-1} (epoxide, ν_{C-O-C}), respectively. The carbonate and epoxy groups concentrations were calculated from corresponding absorption bands using external reference curves.

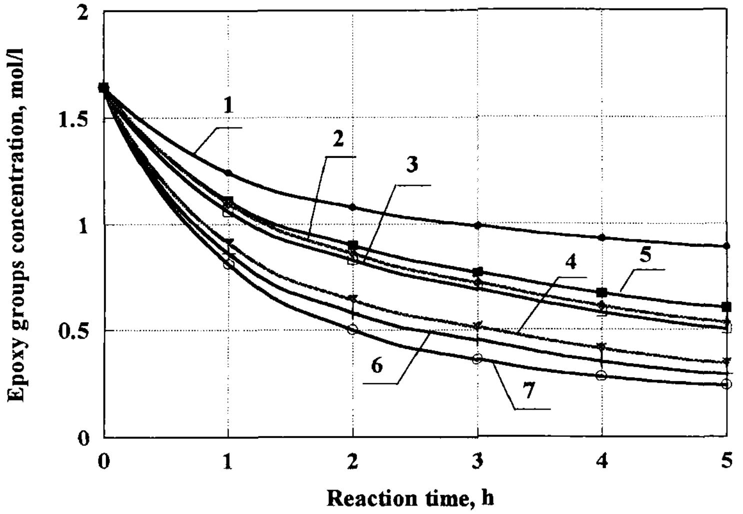


Figure 1. Dependence of the epoxy groups concentration on the reaction time for the reaction of **2c** (1-5) and **2b** (6,7) with various carbonates ($BF_3 \cdot OEt_2$ concentration: 0.01 mol·dm^{-3}; molar ratio of **2b** to carbonate: 1 : 0.16; solvent: CH_2Cl_2; temperature: 15°C)
1 - diethyl carbonate; 2 - **1b**; 3 - **1a**; 4 - diphenyl carbonate; 5 - **2b**; 6 - **1a**; 7 - **2b**.

RESULTS AND DISCUSSION

The epoxy groups conversion for the reaction of **2c** with different carbonates catalyzed by $BF_3 \cdot OEt_2$ is shown in Figure 1. It was found that for all carbonates, except diphenyl carbonate (curve 4), an evident decrease in the rate of the epoxy groups conversion takes place in comparison to that of the **2c** homopolymerization (curve 5).

For other oxiranes (**2b**) the drop in the reaction rate when the aliphatic carbonate (**1a**) was present in the reaction mixture was also significant (curves 6 and 7). That drop in the reaction rate of oxiranes indicates that aliphatic carbonates take part in the process of obtaining of both polyethers and poly(ether-carbonate)s.

The kinetic measurement results (Figure 2) indicate that in the reaction with cyclic carbonates (**1a** or **1b**), among investigated by us, mainly **2c** and **2e** are involved.

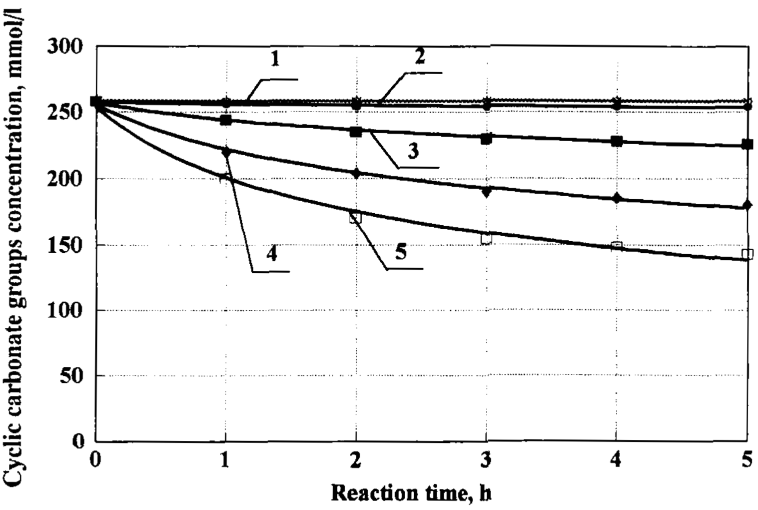
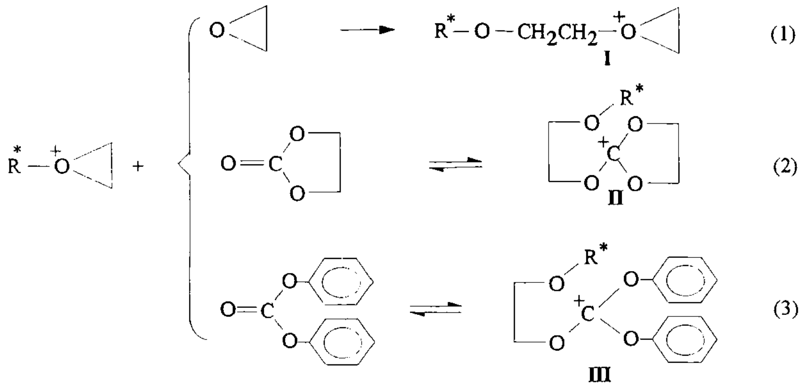


Figure 2. Dependence of the cyclic carbonate groups concentration on the reaction time for the reaction of **1b** with various oxiranes ($BF_3 \cdot OEt_2$ concentration: 0.01 mol·dm^{-3}; molar ratio of **1b** to oxirane: 0.16 : 1; solvent: CH_2Cl_2; temperature: 15°C) 1 - **2d**; 2 - **2b**; 3 - butyl glycidyl ether; 4 - **2d**; 5 - **2c**;

When **2b** was used there was no change in the carbonate concentration. Due to the electron donor effect of the methyl group, **2b** polymerizes according to eq. 1 and neither SOC nor poly(ether-carbonate) are formed. A similar effect of the electron donor substituent in the oxirane ring was observed in the case of the synthesis of SOCs from **2b** and **1a** when an excess of the carbonate reagent was used. The yield of the product, in contrast to that when **2c** is used as the oxirane reagent, was very low (1-2 %).

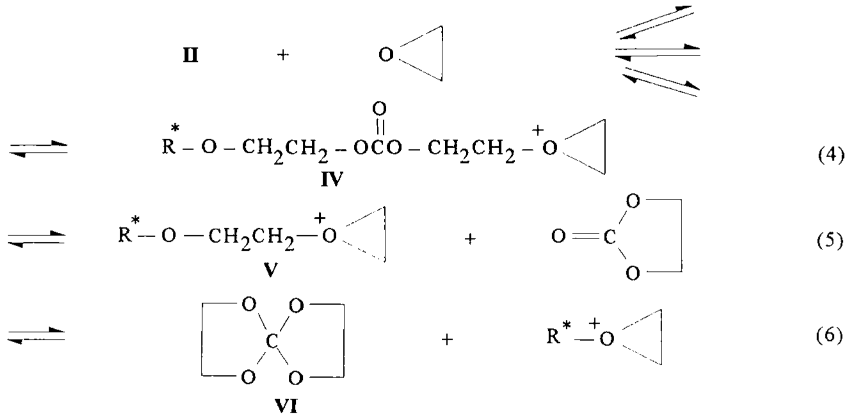
When aliphatic carbonates are present, the contribution of the classical mechanism of oxirane cationic polymerization, consisting of the nucleophilic (S_N2) attack of oxirane onto the oxonium ion (eq. 1) is small and mainly the aliphatic carbonate reacts with the oxonium ion yielding trioxocarbenium ion **II** (eq. 2).



The carbenium ion, as less strained than the oxonium one and stabilized by adjacent three oxygen atoms is thermodynamically favored.

Trioxocarbenium ion **II** may react according to three possible reaction pathways:

- exocyclic carbon atom of **II** is attacked by oxirane and the ether-carbonate part of the polymer chain is formed (**IV**) (eq. 4)
- endocyclic carbon atom of **II** is attacked by oxirane leading to the ether part of the polymer chain (**V**) and cyclic carbonate as a by-product (eq. 5)
- in intramolecular reaction carbocation is attacked by exocyclic oxygen atom of linear ether of **II** and SOC (**VI**) is formed (eq. 6).



Depending on the oxirane structure and reaction temperature the reaction with carbonates proceeds according to eqs 4 and 5 (**2c** and **2d**) or mainly according to eqs 1 and 5 (**2b**).

The yield of products containing linear carbonate groups formed in the polymerization of SOC in the presence of **2c** (Figure 3, curve 1) was much lower than that of those formed in the model reaction of **2c** with **1a** (curve 5), preserving the same molar ratio of the oxirane component to the cyclic carbonate one (6.4:1). In SOC the molar ratio of the oxirane component to carbonate one is as 1:1. The last two experiments indicate that poly(ether-carbonate)s are formed not only as the products of polymerization of SOC but may be obtained directly from oxiranes and cyclic carbonates.

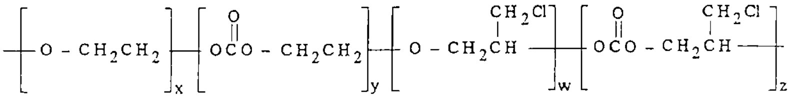
The ^1H NMR spectrum exhibits characteristic peaks at $\delta = 3.55$ and 3.65 ppm assigned to $-C\underline{H}_2-$ and $-C\underline{H}(C\underline{H}_2Cl)-$ protons neighboring to ether linkages, $\delta = 4.09$ and 4.22 ppm assigned to $-C\underline{H}_2CH_2-$ and $C\underline{H}_2CH(CH_2Cl)-$ protons neighboring to carbonate linkages respectively.

The results of elemental analysis, ^1H NMR and IR spectra of the products of the **2c** and **1a** copolymerization are shown in Table 1 and Figures 4 and 5, respectively.

The infrared spectrum displays strong absorption peaks at near 1745, 1255 and 1110 cm^{-1}, that are attributable to the carbonyl and carbonyl-oxygen stretching vibrations of the carbonate linkage, and the carbon-oxygen stretching vibrations of the ether linkage, respectively.

The elemental analysis (Table 1) confirmed that the polymer chain contains, units originated from ethylene oxide and **1c** besides **2c** and **1a**.

The preceding results indicate that the polymer may have a chemical structure as shown below:



$$\left[O-CH_2CH_2\right]_x\left[O\overset{\overset{O}{\|}}{C}O-CH_2CH_2\right]_y\left[O-CH_2\overset{\overset{CH_2Cl}{|}}{C}H\right]_w\left[O\overset{\overset{O}{\|}}{C}O-CH_2\overset{\overset{CH_2Cl}{|}}{C}H\right]_z$$

where: $x = 0 - 0.077$
$y = 0.084 - 0.161$
$w = 0.685 - 0.762$
$z = 0 - 0.077$

The molecular weight of those polymers did not exceeded 1500 g/mol.

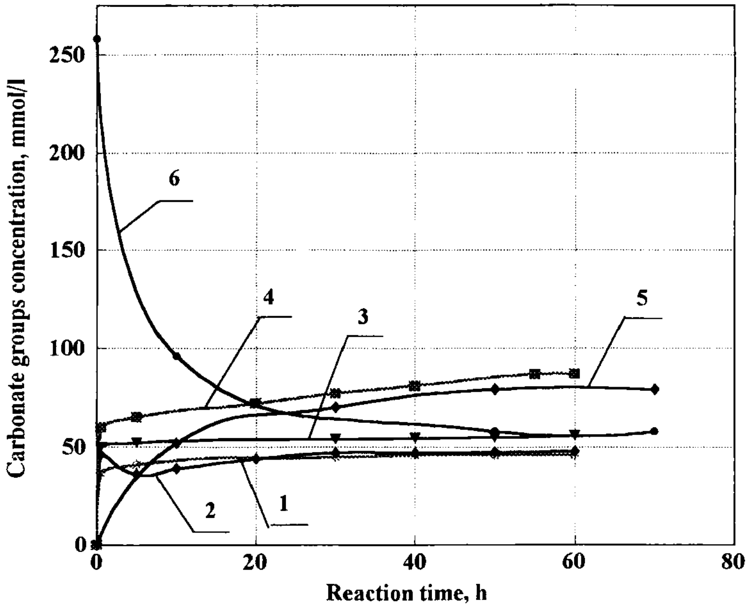


Figure 3. Dependence of the carbonate groups concentration on the reaction time for the polymerization of **3ac** alone (3, 4), in the presence of **2c** (1, 2) and for the reaction of **2c** with **1a** (5, 6) (molar ratio of **3ac** to **2c**: 1 : 5.4 and **1a** to **2c**: 1 : 6.4; $BF_3 \cdot OEt_2$ concentration: 0.012 mol·dm^{-3}; solvent: CH_2Cl_2; temperature: 15°C)
1, 3, 5 - linear carbonate, 2, 4, 6 - cyclic carbonate groups.

TABLE I. Elemental analysis of the product of the reaction of **1a** with **2c**.

Element contents (weight %)	C	H	Cl
Found	39.8	5.6	33.4
Calculated [a]	39.2	5.3	33.4
Calculated [b]	39.8	5.5	33.4

[a] calculated from the chlorine contents originated from **2c**, assuming that only **1a** was the other comonomer

[b] assuming that: 76.2 mol %. of the units were from **2c**, 16.1 mol % of units were from ethylene oxide and 7.7 mol % of carbon dioxide as incorporated.

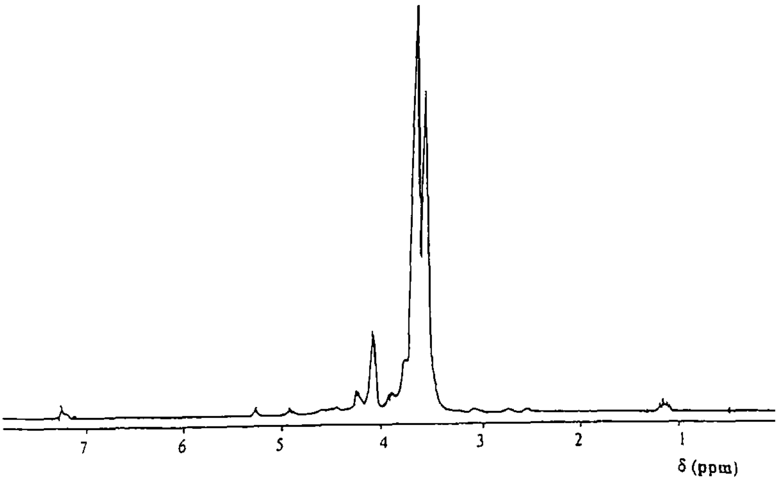


Figure 4. ^{1}H NMR spectrum of poly(ether-carbonate) obtained from **2c** and **1a**.

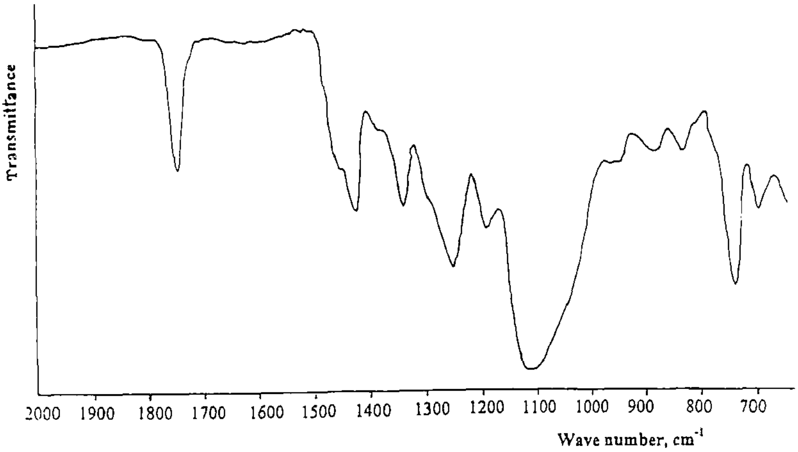


Figure 5. IR spectrum of poly(ether-carbonate) obtained from **2c** and **1a**.

Conclusions

- In the presence of aliphatic carbonates, both the cyclic and linear one, the conversion rate of oxiranes catalyzed by $BF_3 \cdot OEt_2$ is significantly suppressed.
- The substituents in the oxirane ring such as $-CH_2Cl$ and $-CH_2OPh$ favor the conversion of cyclic carbonates into spiroorthocarbonates and poly(ether-carbonate)s in their reaction with oxiranes.
- Poly(ether-carbonate)s are formed not only as the product of polymerization of spiroorthocarbonates but mainly directly from oxiranes and cyclic carbonates. Spiroorthocarbonate is one of the possible reaction products.

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