

EFFECT OF ETHYLENEGLYCOL ON THE COPOLYMERIZATION OF TETRAHYDROFURANE AND PROPYLENE OXIDE ON BORON TRIFLUORIDE TETRAHYDROFURANATE*

A. I. KUZAYEV, G. N. KOMRATOV, G. V. KOROVINA, G. A. MIRONTSEVA
and S. G. ENTELIS

Branch of the Institute of Chemical Physics, U.S.S.R. Academy of Sciences.

(Received 26 February 1968)

NUMEROUS papers have recently been published dealing with the copolymerization of tetrahydrofuran (THF) with three-membered cyclic esters [1-7]. Products of copolymerization of THF with ethylene oxide [1] and propylene oxide (PO) [2, 3], which have relatively low molecular weights and contain hydroxyl groups at both ends of the macromolecule are raw material for production of polyurethane rubbers.

Although studies of copolymerization of THF and PO [2-4] have been mainly devoted to the synthesis of polyesterdiols, considerable importance is attached to elucidating the role of glycols in the reaction, in order to control molecular weight in processes of initiation and chain rupture. This is also confirmed by another paper [5] on copolymerization kinetics of THF and PO in the presence of 1,2-propylene-, 1,3-propylene- and 1,4-butyleneglycols.

This paper deals with a study of the effect of ethylene glycol (EG) on the copolymerization kinetics of THF and PO in 1,2-dichloroethane (DCE) using $\text{BF}_3 \cdot \text{THF}$ as catalyst.

EXPERIMENTAL

Raw materials. Tetrahydrofuran was stored over KOH for 5 days and distilled in a column. A fraction of b.p. 65.5-66° was dried with sodium for two days and redistilled in a column (80 theoretical plates); the fraction of b.p. 66° was taken. The purity of THF was examined chromatographically; the moisture content (Fischer method) was less than 0.01 wt. %.

Propylene oxide was dried with calcium chloride and distilled. A fraction of b.p. 34-35° was dried with calcium hydride and fractionated in the column. The fraction of b.p. 34.5-35°, as determined chromatographically, was free from impurities; the moisture content by the Fischer method was less than 0.01 wt. %.

Commercial dichloroethane was dried with freshly calcined calcium chloride and distilled in a column. A fraction of b.p. 84° was again dried and redistilled; the moisture content (Fischer) was not more than 0.01 wt. %.

Boron fluoride tetrahydrofuranate was obtained by saturation of purified THF with BF_3 vapour. The complex obtained was distilled and a fraction of b.p. 69-71°/4 mm taken.

* Vysokomol. soyed. A11: No. 2, 443-452, 1969.

Ethylene glycol was distilled *in vacuo* and a fraction of b.p. 83–85°/4 mm taken; the moisture content (Fischer) was not more than 0.01 wt. %.

n-Butanol was purified by the Clark method [8]. The fraction of b.p. 117° had a moisture content according to Fischer of 0.012 wt. %.

The molecular weight (\bar{M}_n) of copolymers was determined from the content of terminal hydroxyl groups [9] and with a Ray ebulliometer allowing for the variation of the constant of the device over a certain range of molecular weights.

Measurement of the rate of polymerization. Copolymerization of THF and PO was carried out in excess DCE ([DCE] = 67 vol. %) at 10°. The concentration of $\text{BF}_3 \cdot \text{THF}$ was 0.02 mole/l., except for cases which will be noted.

To maintain isothermal conditions, the process was carried out in a metal reactor provided with a stirrer, thermostatic jacket, thermocouple to monitor temperature, sampling device, hopper for feeding raw materials and a system for circulating dry nitrogen. The copolymerization kinetics were investigated by two methods: by sampling followed by chromatographic separation of the reaction mixture and by sampling followed by isolation of the copolymer. The latter involved rinsing the sample with distilled water to eliminate BF_3 , separation of the polymer from the washing water and drying to constant weight *in vacuo* at 60°.

The reaction mixture was chromatographically analysed in a "Tsvet" chromatograph with a column 1 m in length. A katharometer was used as detector. Helium was the carrier gas. The temperature of the thermostat was 60°, of the evaporator 75°. The headpiece of the column consisted of solid (brick, kieselguhr) and liquid (SKG mixture, triethyleneglycol and tricresylphosphate) phases. Under certain conditions the ternary phase consisting of PO, THF and DCE was separated with the following retention times: PO—2.5 min, THF—9 min and DCE—14 minutes.

The device was calibrated using synthetic mixtures prepared in ampoules with self-sealing rubber stoppers, thus avoiding loss of the volatile component during sampling. The sample volume introduced in the chromatograph varied from $2\text{--}12 \times 10^{-6}$ litres. The amount of sample added had no effect on the ratio of the areas under the peaks of PO (S_{PO}) and THF (S_{THF}) to S_{DCE} . An analysis of the sample from the reactor (the reaction was stopped with pyridine) makes it possible to calculate residual concentrations of THF and PO in solution and thus observe the kinetic consumption of monomers and the accumulation kinetics of the polymer.

Kinetics curves of polymer accumulation plotted from chromatographic data and the gravimetric method coincide.

EXPERIMENTAL RESULTS

Effect of catalyst concentration on the rate of copolymerization. Figure 1 shows kinetic curves of polymer accumulation and the consumption of co-monomers according to catalyst concentration and indicates that in all cases the reaction was complete after the same consumption of PO, which corresponds to a 93% copolymer yield and is independent of catalyst concentration. The residual concentration of THF is 0.28 mole/l.

From the gradients of the initial parts of the kinetic curves of monomer consumption, the initial rates of THF (w_0^{THF}) and PO (w_0^{PO}) consumption were calculated. By summarizing w_0^{THF} and w_0^{PO} the initial rate of copolymerization (w_0^c) was found, w_0^{THF} and w_0^{PO} being linearly dependent on catalyst concentration. It should be noted that the values of w_0^{THF} and w_0^{PO} are similar. Re-

sults obtained are in agreement with data previously published on copolymerization of THF and PO [5] and confirm the order of the reaction according to the catalyst.

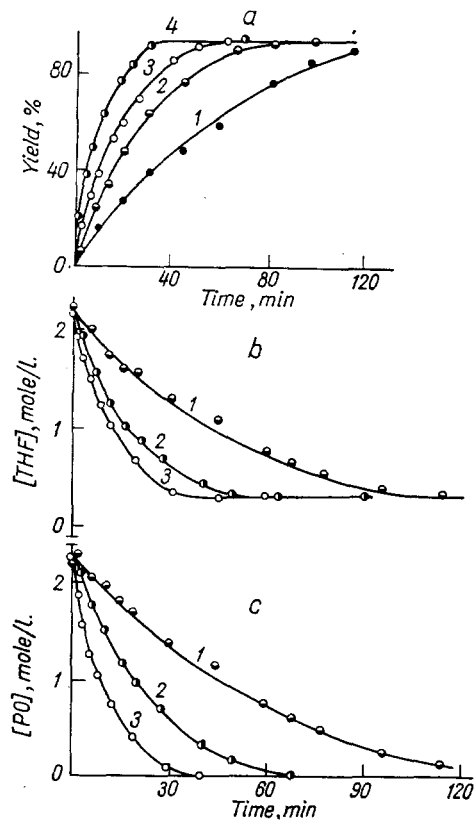


FIG. 1

FIG. 1. Kinetics of copolymer accumulation (a) and monomer consumption (b, c) at different catalyst concentrations. THF/PO=1:[BF₃·THF] (mole/l.): 1—0.02, 2—0.03 (a) and 0.05 (b, c), 3—0.05 (a) and 0.1 (b, c), 4—0.1.

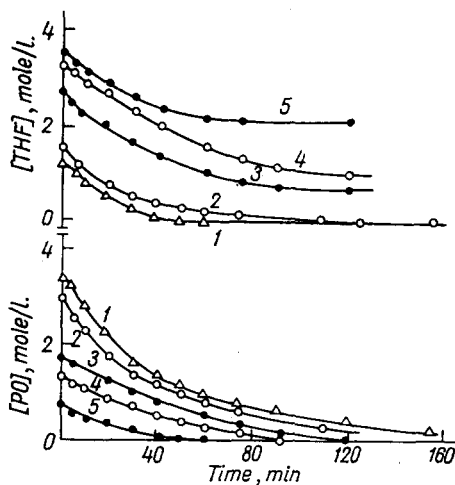


FIG. 2

FIG. 2. Kinetics of monomer consumption with different initial ratios. Molar ratio of PO : THF: 1—2.8, 2—2.0, 3—0.6, 4—0.4, 5—0.2.

Effect of initial composition on final copolymer yield. Figure 2 shows kinetic curves of THF and PO consumption at constant catalyst concentration and for different initial ratios of THF : PO. While PO is fully co-polymerized, THF is only used fully during copolymerization of initial mixtures enriched with PO. In this case the copolymer yield is 100% (Table 1). As the PO content decreases in the initial mixture the residual concentration of THF ($[THF]_{res}$) increases and the copolymer yield decreases. The maximum value of $[THF]_{res}$, which is 1.9–2.0 mole/l., characterizes the equilibrium polymerization of THF [10].

TABLE 1. EFFECT OF INITIAL COMPOSITION ON THE YIELD AND COMPOSITION OF COPOLYMER, INITIAL RATE AND TIME OF COMPLETION OF COPOLYMERIZATION

Molar fraction of PO in initial mixture	[THF·BF ₃], mole/l.	Time of completion of reaction, min	Copolymer yield, %	Molar fraction of PO in the copolymer	[THF] _{res} , mole/l.	w ₀ ^c , mole/l.·min
0.74	0.02	280	100	0.74	0	0.12
0.67	0.02	240	100	0.67	0	0.129
0.54	0.02	150	97	0.55	0.10	0.13
0.50	0.02	158	94	0.54	0.23	0.11
0.50	0.10	31	93	0.54	0.28	0.51
0.38	0.02	180	90	0.41	0.45	0.150
0.28	0.02	120	75	0.37	1.03	0.087
0.20*	0.10	48	70	0.28	1.80	0.84
0.17	0.02	180	52	0.35	2.10	0.064
0.16	0.10	60	67	0.24	1.96	0.29
0.12*	0.02	—	55	0.24	2.00	0.045
0.0	0.1	2 days	0	—	4.1	—

* DCE concentration 50 vol. %.

Dependence of rate of copolymerization on composition. Table 1 shows the initial rate of copolymerization of THF and PO for various initial compositions. It is well known [11] that without adding α -oxides homopolymerization of THF on boron fluoride etherates does not take place. For $[PO] \geq [BF_3 \cdot THF]$ the value of w_0^c becomes equal to the rate of homopolymerization of THF, but with small

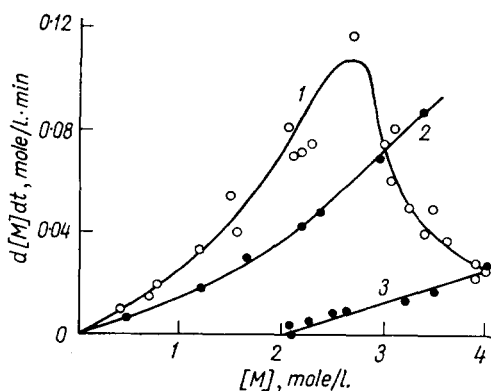


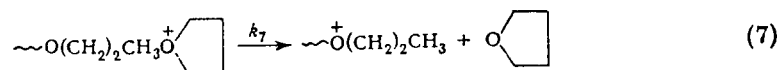
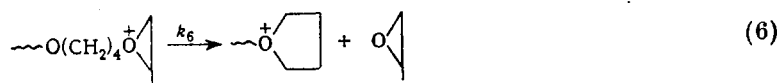
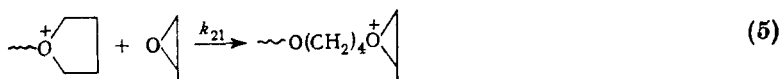
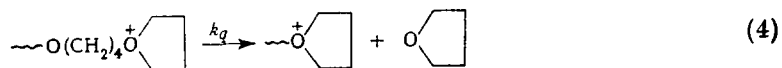
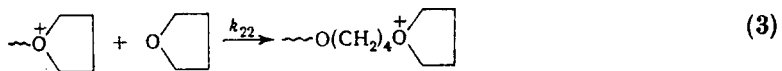
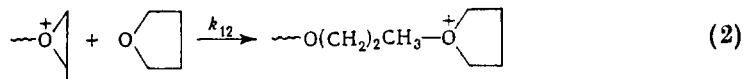
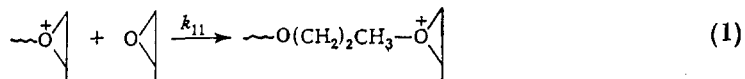
FIG. 3. Dependence on monomer concentration of the rate of THF (1) and PO (2) consumption during copolymerization and of the rate of THF (3) consumption during homopolymerization.

amounts of PO the initial rate increases. A further increase in the PO content in the initial monomer mixture leads to a maximum w_0^{PO} and the rate of copolymerization then decreases to the rate of homopolymerization of PO.

Figure 3 illustrates the dependence of the rate of THF and PO consumption on concentration during copolymerization, which shows that the rate of THF consumption in copolymerization is higher than during homopolymerization; this proves a higher activity of THF than of PO.

Rate constants of chain growth. From limited sections of kinetic curves for compositions enriched with THF or PO the rates of consumption of THF ($-d[\text{THF}]/dt$) and PO ($-d[\text{PO}]/dt$) were determined respectively. From the dependence of $-d[\text{THF}]/dt$ on $[\text{THF}] - [\text{THF}]_p$ ($[\text{THF}]_p$ at 10° is 2.0 mole/l.) the rate constant of homopolymerization of THF was found to be 1.03×10^{-2} l./mole·sec. The rate constant of homopolymerization of PO found from the dependence of $\log w^{\text{PO}}$ on $\log [\text{PO}]$ was 1.3×10^{-2} l./mole·sec at 10° .

Considering the equilibrium nature of the polymerization of THF the overall scheme of reactions taking place during copolymerization of THF and PO can be shown as



Calculations for this scheme were made in an electronic computer (EC). They showed that reactions (6) and (7) do not take place in the system, i.e. the tetrahydrofuran end of the macromolecule can only be depolymerized in cases preceding a similar unit: the oxypropylene end is not depolymerized in this case.

Reactions (1)–(5) fully describe copolymerization of THF and PO with the following rate constants (l./mole·sec): $k_{11}=1 \times 10^{-2}$, $k_{12}=2 \times 10^{-1}$, $k_{22}=1 \times 10^{-2}$, $k_{21}=2 \times 10^{-2}$, $k_{dep}=2 \times 10^{-2}$. Figure 4 shows agreement between the experimental kinetic curve of copolymerization (continuous line) and data obtained by calculation (points).

For other compositions the experimental results obtained are also satisfactorily described by the above constants. A comparison of the rate constants of polymerization of THF and depolymerization of polytetrahydrofuran obtained in this study with literature data [12, 13] shows satisfactory agreement.

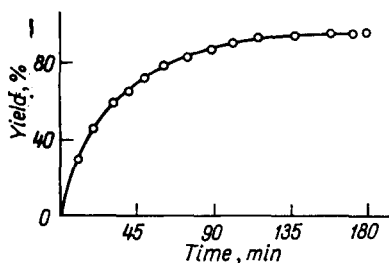


FIG. 4

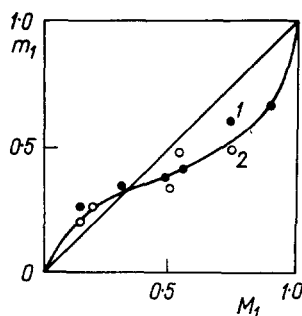


FIG. 5

FIG. 4. Kinetics of copolymer accumulation with a THF : PO ratio of 0.86. The continuous line is the experimental curve; the points were obtained by calculation.

FIG. 5. Curve of copolymer composition: M_1 is the molar proportion of PO in the initial mixture, m_1 in the copolymer: 1—refractometrically; 2—chromatographically.

The relative activities of monomers during copolymerization of THF and PO, which were obtained from the ratio of corresponding constants determined by calculation using a computer, give the values $r_{PO}=0.05-0.065$ and $r_{THF}=0.5-0.55$. These are in satisfactory agreement with values based on the dependence of the copolymer composition on the initial mixture composition (Fig. 5). The relative monomer activities [14] are: $r_{PO}=0.1 \pm 0.1$ and $r_{THF}=0.5 \pm 0.1$.

THF is more active during copolymerization with PO in the same way as during copolymerization with epichlorohydrin [6, 7] and ethylene oxide [1].

According to a previous study [5], $r_{PO}=1.5$ and $r_{THF}=0.6$, i.e. PO is more active than THF during copolymerization. This is because the authors investigated copolymerization of THF and PO with glycols which form complexes with BF promoting (as pointed out below) the consumption of PO, and enrich the copolymer with units of this monomer.

Effect of EG on the rate of copolymerization. The effect of EG on the rate

of copolymerization, yield, composition and molecular weight of copolymers was studied at 10° with a THF : PO initial ratio of 5 : 1. The DCE concentration was 50 wt.%, $[\text{BF}_3 \cdot \text{THF}] = 0.11$ mole/l.

Figure 6a indicates that with increase of EG concentration the final copolymer yield decreases and the reaction rate increases. At the same time since PO is fully used in all cases, the residual concentration of THF increases in proportion to the increase of $[\text{EG}]$; consequently the copolymer is enriched with propylene oxide (Table 2).

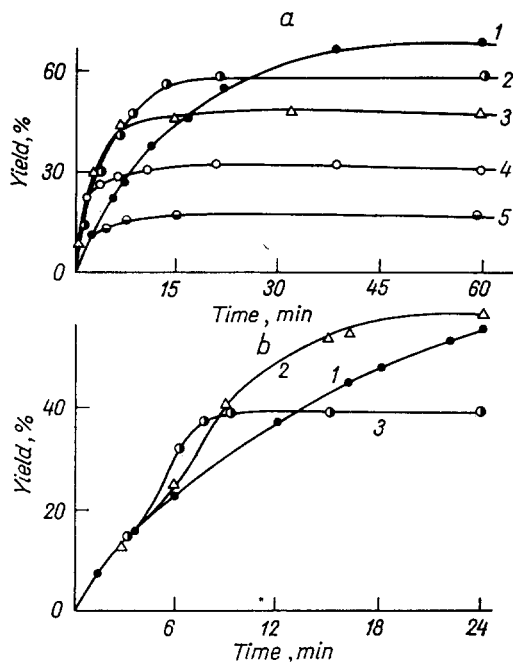


FIG. 6

FIG. 6. Kinetics of polymer accumulation for different EG concentrations (a) and EG additions during the process (b); $[\text{EG}]$, mole/l.: a-1-0.06, 2-0.12, 3-0.23, 4-0.34, 5-0.53; b-1-0, 2-0.124, 3-0.343.

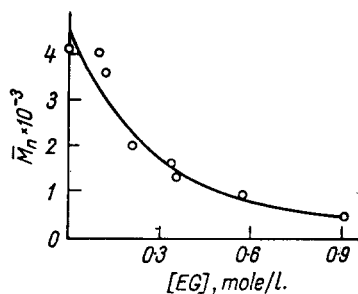


FIG. 7

FIG. 7. Effect of EG concentration on final copolymer yield.

Special experiments were carried out with addition of EG during the reaction at an earlier stage of the process (Fig. 6b). Without adding EG the rate of copolymerization decreases as the reaction goes on; the final copolymer yield reaches 70 wt.%. On adding EG, the rate of copolymerization markedly increases with a degree of conversion of 13% (3.3 min). Subsequently, the nature of curves showing polymer accumulation is similar to kinetic curves obtained with the initial addition of EG (Fig. 6).

Dependence of the yield and composition of copolymer on the amount of EG added. It has been pointed out that the final copolymer yield decreases on

increasing the EG concentration. On adding the same amount of ethylene glycol (0.34 mole/l.) at different stages of conversion the final copolymer yield decreases as the time of addition approaches the beginning of the reaction (see below).

It can be seen that with a reduction in copolymer yield the PO content increases.

Time of adding EG, calculated from the

beginning of the reaction, min	0	3.3	12	Without adding EG
Copolymer yield, %	31	39	51	70
Molar fraction of PO in the copolymer	0.48	0.42	0.31	0.24

The addition of PO to the system which is "limited" according to yield, again causes polymerization. Results of experiments with addition of PO, epichlorohydrin (ECH) and THF are shown in Table 3 (the limited system, after the addition was retained for 48 hr).

Table 3 indicates that addition of THF has no effect, whereas addition of PO and ECH increases the copolymer yield.

Figure 7 illustrates the relationship between the final copolymer yield and concentration of EG added before the reaction. It should be noted that extrapolation of this relation gives a yield value of zero when $[EG] \cong 1.2$ mole/g. When $EG=PO=1.1$ mole/l. no copolymer is formed, although the PO is fully used up. Low molecular weight glycols formed ($\bar{M}_n=200$) with a yield of less than 20% unfortunately could not be separated by vacuum distillation.

Molecular weight and nature of copolymer end groups. Figure 8 shows curve of molecular weight (\bar{M}_n) variation of THF and PO copolymers during the

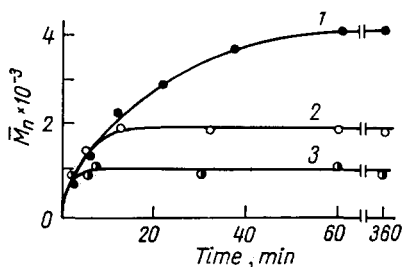


FIG. 8

FIG. 8. Variation of copolymer molecular weight during the reaction for different $[EG]$, mole/l.: 1—0.0, 2—0.23, 3—0.53.

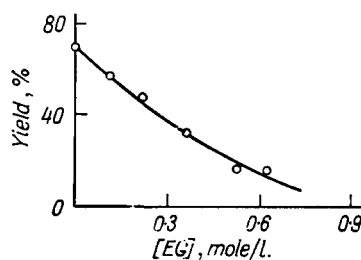


FIG. 9

FIG. 9. Effect of EG concentration on final molecular weight of copolymers.

reactions at different EG concentrations and constant $THF \cdot BF_3$ concentration. Figure 8 indicates that \bar{M}_n increases with polymerization, reaching a maximum at the end of the reaction: in proportion to the increase of $[EG]$ the final molecular weight of the copolymers decreases.

Figure 9 shows the variation of \bar{M}_n of terminal copolymer samples according to the concentration of EG introduced into the polymerization system. The data prove that EG effectively restricts chain growth.

It is well known that the nature of terminal groups is of considerable importance in the practical use of the copolymer, particularly further chemical conversion.

For urethane formation the copolymer macromolecules should first of all have hydroxyl groups at both ends, which is achieved by the addition of EG. However, as Table 2 indicates, a 3-4-fold EG excess is required in relation to $\text{BF}_3 \cdot \text{THF}$ for the complete elimination of double bond formation. During polymerization without EG approximately 40% of all terminal groups are represented by double bonds. The presence of double bonds was also confirmed by IR spectra.

TABLE 2. DEPENDENCE OF THE INITIAL RATE OF COPOLYMERIZATION (w_0^c), FINAL YIELD (α_∞), COMPOSITION AND \bar{M}_n OF THE COPOLYMER ON EG CONCENTRATION

[EG], mole/l.	w_0^c , mole/l. \times \times min	α_∞ , wt. %	Time of completion of the reaction, min*	Molar proportion of PO in the copolymer	[THF] _{res} , mole/l.	Molecular weight		Bromine number, g/100 g
						ebullio- scopic	by OH groups	
0.00	0.31	68.0	90	0.24	2.1	4110	—	51.60
0.12	0.55	57.0	25	0.29	3.1	—	4000	1.35
0.23	0.70	48.0	20	0.33	3.7	1840	1850	0.2
0.34	0.75†	33.3	16	0.48	4.65	1290	1310	0.0
0.53	0.75†	16.3	14	0.85	5.66	885	950	0.0

* After the above time α does not increase on keeping the reaction mixture for 24 hr at a given temperature.

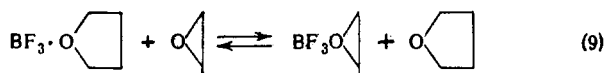
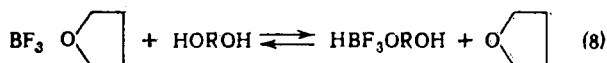
† The reaction was accompanied by considerable liberation of heat.

TABLE 3. EFFECT OF PO, THF AND ECH ADDITIVES ON COPOLYMER YIELD

Molar ratio of THF : PO in the initial mixture	EG, mole/l.	Additive (mole/mole of the initial mixture)	Copolymer yield, %	
			before addition	after addition
5	0.344	THF (1)	33.3	33.0
5	0.344	PO (0.5)	33.3	78.6
5	0.231	PO (0.25)	45.6	86.1
4	0.143	THF (0.8)	48.1	47.6
4	0.143	ECH (0.3)	48.1	93.3
2	0.15	ECH (0.08)	70.0	85.0

RESULTS

As has been noted, with increase in the concentration of EG added the initial rate of copolymerization increases. Considerable increase in reaction rate is also observed on adding EG during the process. The data can be explained by the fact that on adding EG, active centres (AC) of the type $H^+BF_3OCH_2CH_2OH$ (I) are apparently formed in the system. It is well known that BF_3 readily forms complexes with electron-donor compounds (ethers, water, alcohols) [15-17]. The BF_3 distribution in a system containing THF, PO and EG can, therefore, be presented as equilibrium reactions:



Reaction (9), as is well known [12], forms AC capable of polymerization both with PO and THF which are apparently zwitterions of the type $BF_3^- - O^+ \text{THF}$ (II).

TABLE 4. REACTION PRODUCTS OF PO AND n-BUTANOL IN DCE AT 10°. CONCENTRATION, MOLE/L. $[BF_3 \cdot THF] = 0.07$; $[PO] = 1.6$, $[n\text{-BUTANOL}] = 0.8$

Substance	Yield, %	B.p., °C	n_D^{20}	d_4^{20} , g/cm ³	MR	
					calcu- lated	found
n-Butanol	11.7	117	1.3993	0.8098	—	—
$CH_3CHCH_2OC_4H_9$ OH	3.3	41/5	1.4180	0.8810	37.684	37.800
$CH_3CHCH_2OCHCH_2OC_4H_9$ OH CH ₃	29.5	60/4	1.4270	0.9180	53.191	53.153
Propyleneglycol	8.5	126/5	1.4328	1.000	—	—
$CH_3CHCH_2[OCHCH_2]_2OC_4H_9$ OH CH ₃	38.5	—	1.4395	0.947	68.60	69.03
Losses	7.5	—	—	—	—	—

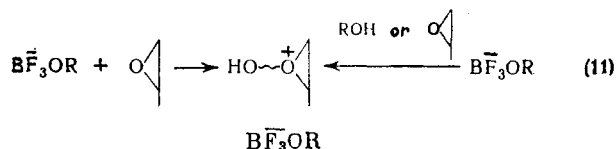
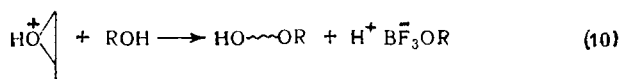
In proportion to the increase in concentration of EG reaction (8) becomes increasingly significant and results in the formation of AC of type (I). THF does not polymerize [5] on AC of this type as with boron fluoride hydrates [11].

As with other α -oxides, PO reacts with hydroxyl-containing compounds

even without catalysts [18]. This explains the fact that with increase of [EG], the proportion of unpolymerized THF increases and the reaction products are enriched with PO units.

It was of interest to examine the reaction products of PO and EG. Although the reaction products cannot be separated it was established that when [EG]=0.5 [PO], the EG is fully used. To identify products under similar conditions a study was made of the reaction between PO and n-butyl alcohol. Table 4 indicates that the alcohol is not wholly used up in the reaction, whilst the PO is fully used. In addition, the low propylene glycol butyl ester content in the reaction products can be noted.

According to the reaction mechanism of α -oxides and alcohols [19] the main reactions in the PO-ROH(HOROH) system can be represented as:



According to the basicity (nucleophilic nature) of the compounds containing hydroxyl groups the ratio between these reactions will vary. Thus for EG reaction (10), and for n-butanol reaction (11) is more marked. It should be noted that products of reaction (10) can themselves interact with AC, the process consequently becoming more complicated.

CONCLUSIONS

(1) A chromatographic study was made of the copolymerization kinetics of propylene oxide and tetrahydrofuran on $\text{BF}_3 \cdot \text{THF}$ in 1,2-dichloroethane at 10°.

(2) It was pointed out that for initial compositions enriched with tetrahydrofuran, as a consequence of the equilibrium nature of polymerization of tetrahydrofuran, the copolymer yield decreases as the concentration of this monomer increases in the initial mixture. For compositions enriched with propylene oxide the copolymer yield is 100%.

(3) Rate constants of chain growth were determined for tetrahydrofuran and propylene oxide and relative monomer activities found: $r_1 = 0.05 \pm 0.02$ (propylene oxide), $r_2 = 0.5 \pm 0.05$ (tetrahydrofuran).

(4) During copolymerization of tetrahydrofuran and propylene oxide in the presence of significant additions of ethylene glycol the reaction rate increases and the copolymer formed is enriched with propylene oxide.

(5) The addition of ethylene glycol not only reduces the molecular weight, but also ensures formation of hydroxyl groups at both ends of the macromolecules of the copolymer formed.

Translated by E. SEMERE

REFERENCES

1. **W. J. MURBACH** and **A. ADICOFF**, *Industr. and Engng Chem.* **52**: 772, 1960
2. **J. A. DICKINSON**, *J. Polymer Sci.* **58**: 857, 1962
3. **O. K. MANAGADZE**, **E. P. ZAKHAROV**, **D. B. IZYUMOV** and **T. A. USATOVA**, *Plast. massy*, No. 9, 9, 1967
4. **L. I. REITBURD**, **M. A. MARKEVICH** and **M. S. AKUTIN**, *Vysokomol. soyed.* **A9**: 1144, 1967 (Translated in *Polymer Sci. U.S.S.R.* **9**: 5, 1275, 1967)
5. **L. P. BLANCHARD**, **J. SINGH** and **M. D. BAIJAL**, *Canad. J. Chem.* **44**: 2679, 1966
6. **T. SAEGUSA**, **T. UESHIMA**, **H. IMAI** and **J. FURUKAWA**, *Makromolek. Chem.* **79**: 221, 1964
7. **B. A. ROZENBERG**, **E. B. LYUDVIG**, **N. B. DESYATOVA**, **A. R. GANTMAKHER** and **S. S. MEDVEDEV**, *Vysokomol. soyed.* **7**: 1010, 1965 (Translated in *Polymer Sci. U.S.S.R.* **7**: 6, 1116, 1965)
8. **A. VAISBERGER**, **E. PROSKAUER**, **T. RIDDIK** and **E. TUPS**, *Organicheskie rastvoriteli (Organic Solvents)*, p. 318, *Izd. inostr. lit.*, 1958
9. **C. L. OGG**, **W. L. PORTER** and **C. O. WILLITS**, *Industr. and Engng. Chem.* **17**: 394, 1945
10. **K. J. IVIN** and **J. LEONARD**, *Polymer* **6**: 621, 1965
11. **H. MEERWEIN**, **D. DELFS** and **H. MORSCHER**, *Angew Chem.* **72**: 927, 1960
12. **B. A. ROZENBERG**, *Dissertation*, 1964
13. **D. VOFSI** and **A. V. TOBOLSKY**, *J. Polymer Sci.* **A1**: 3261, 1965
14. **F. MAYO** and **F. LEWIS**, *J. Amer. Chem. Soc.* **66**: 2050, 1944
15. **H. C. BROWN** and **R. M. ADAMS**, *J. Amer. Chem. Soc.* **64**: 2557, 1942
16. **N. N. GREENWOOD** and **R. L. MARTIN**, *Quart. Rev.* **8**: 1, 1954
17. **J. M. CLOYTON** and **A. M. EASTHAM**, *J. Amer. Chem.* **79**: 5368, 1957
18. **M. C. MALINOVSKII**, *Okisi olefinov i ikh proizvodnye (Olefin Oxides and their Derivatives)*, *Goskhimizdat*, 1961
19. **N. N. LEBEDEV** and **V. F. SHVEN**, *Kinetika i kataliz* **6**: 782, 1965