COPOLYMERIZATION OF TETRAHYDROFURAN WITH 1,3-DIOXANE AND TELECHELIC OLIGOMERS

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ABSTRACT

Copolymers of tetrahydrofuran (**T**) with 1,3-dioxane (**D**) were prepared by cationic copolymerization initiated with benzoylium hexafluoroantimonate or triflic anhydride in order to prepare macromolecules having predominantly hydrolitically stable ether (interunit) bonds with some hydrolitically unstable acetal bonds. Structure of copolymers was determined by ^{1}H and ^{13}C NMR. The proportion of the acetal bonds in copolymers was additionally confirmed in studies of the products of hydrolysis (only the acetal bonds hydrolyze). **D** is unable to homopolymerize for the thermodynamic reasons and therefore, mostly copolymers with long blocks of **T** separated with one or a few units of **D**: $(-\mathbf{D}_x\mathbf{T}_y-)_z$ $x \ll y$, are formed. Nevertheless, the reshuffling reactions are responsible for the appearance of "wrong" units. These are: the separate oxymethylene (**M**) and oxy-1,3-propylene units (**P**), subunits of **D**, located between two **T** units. Only the acetal bonds are cleaved in the acidic hydrolysis with dilute HCl. This gives telechelic oligomers of mostly HO-$\mathbf{P}$-$\mathbf{T}_x$-OH structure.

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INTRODUCTION

In our recent paper, related to the copolymerization of 1,3-dioxane (**D**) with cyclic ethers, we explored possibilities of the synthesis of promesogenic telechelic oligomers [1]. These oligomers were prepared by copolymerization of **D** with a bicyclic ether 7-oxabicyclo[2.2.1]heptane (**B**) and subsequent acidic hydrolysis of copolymers (only acetal bonds are cleaved).

Attempts of copolymerization of cyclic ethers with cyclic acetals, undertaken in the past, were almost exclusively unsuccessful; mixtures of homopolymers were usually obtained [2, 3]. Mostly systems involving tetrahydrofuran (THF) and 1,3-dioxolane (DXL) were studied. There is only one paper available in which evidence of copolymer formation is sound, although no attempt was made to hydrolyze the final product in order to verify the NMR data [4]. Moreover, the segmental exchange between homopolymers - polyethers and polyacetals, may also lead to copolymer formation [5]. This may occur when one of the comonomers polymerizes first and the second follows only when the first one is already practically converted into homopolymer, what is the case of the THF/DXL pair.

We used in our studies 1,3-dioxane (**D**) as a comonomer. This six-membered cyclic acetal, known to be unable to homopolymerization, exhibits practically no ring strain [6, 7]. Therefore, longer sequences of polymer units derived from this monomer should not be expected.

Kinetic analysis, spectroscopic observations and results of the hydrolytic cleavage described in the present paper indicate that copolymers have been formed directly by copolymerization. Thus, it looks that this paper describes the first documented case of real copolymerization of tetrahydrofuran with a cyclic acetal and opens a way of preparing telechelic α,ω-dihydroxypolyethers by the cleavage of the acetal bonds in the resulted copolymers:

$$\tag{1}$$
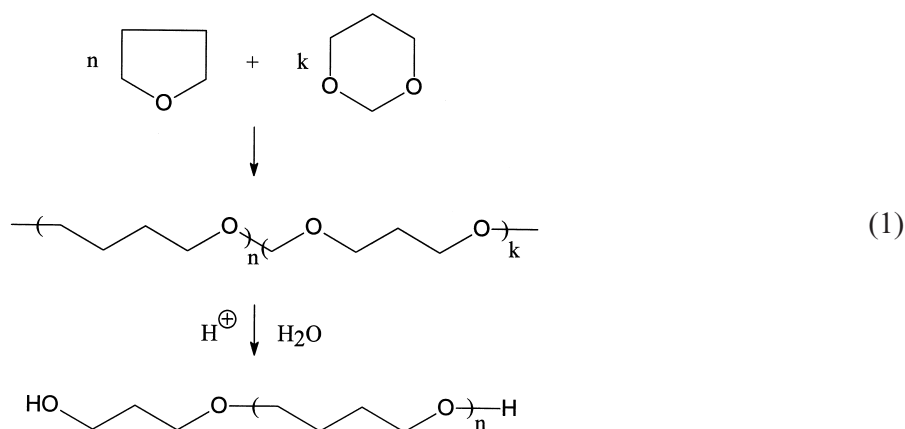
EXPERIMENTAL

Materials

Tetrahydrofuran (Aldrich) and 1,3 dioxane (Aldrich) were purified by distillation, then dried with and kept over Na/K alloy in vacuum ampoules. Solvent -CH_2Cl_2 (POCh, Poland) was purified conventionally, dried and kept over Na mirror in vacuum ampoules. Ethylene oxide (Plock, Poland) was purified by distillation and dried with calcium hydride.

Initiators

Benzoylium hexafluoroantimonate was prepared as described in Reference 13, triflic anhydride (Aldrich) was distilled, kept in vacuum ampoules. Vials with desired amounts of initiator were prepared using vacuum technique, avoiding contact with atmosphere.

Copolymerization

All copolymerizations were carried out at room temperature or at 0°C in vacuum ampoules, avoiding contact with air. No solvent was used (copolymerizations were carried out in the mixture of monomers). The vials with initiator (0.03-0.1 g) were broken at low (about -10°C) temperature, then the system temperature was raised to desired level (20 or 0°C). Reactions were terminated (after desired time) by adding an excess of NH_3, dissolved in a small amount of CH_3OH. Then, all the volatile substances (comonomers, CH_3OH, NH_3) were removed in vacuum. The crude product, after the preliminary analysis, was purified by precipitation in CH_3OH or in hexane from THF solution.

Control Experiment of the Reaction of Living Poly-T with D

After preliminary polymerization of T in a vacuum ampoule (with a Teflon stopcock), the calculated amounts of **D** and **T** (in order to get desired starting conditions) were added. Then after various time intervals, samples of reaction mixtures were being taken out (in dry nitrogen conditions) and terminated (and analyzed) as copolymerization samples.

Hydrolysis of Copolymers

All hydrolyses were performed heterogeneously by boiling small amounts of copolymer in 5% HCl for 5 to 8 hours. Then the reaction mixture
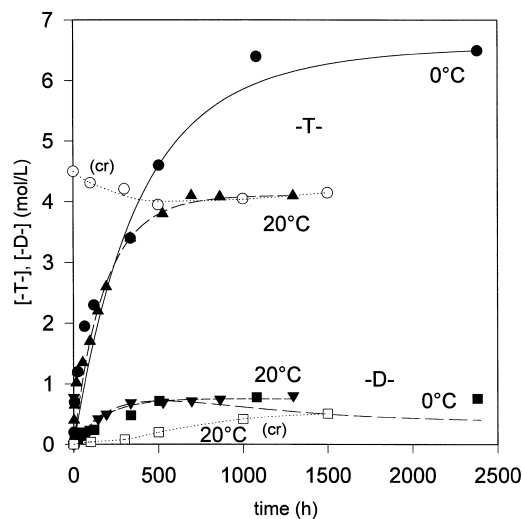
Figure 1. Kinetics of copolymerization of **D** with **T** initiated with triflic anhydride at 20° and 0°C and of control reaction (cr) of living poly-T with D at 20°. Initial conditions - copolymerization: 20° - $[D]0 = 4.2$ mol/L , $[T]0 = 7.8$ mol/L, $[I]0 = 4.4 \times 10\text{-}3$ mol/L; 0° - $[D]0 = 4.1$ mol/L, $[T]0 = 7.9$ mol/L, $[I]0 = 4.9 \cdot 10\text{-}3$ mol/L; control reaction: $[D]0 = 4.2$ mol/L, $[T]0 = 3.3$ mol/L, $[\text{-T-}]0 = 4.5$ mol/L, $[T^*]0 = 4.8 \cdot 10\text{-}3$ mol/L (initiated with triflic anhydride). Experimental points present the changes of concentration of copolymer units with time, while lines given for copolymerizations are the fitted simulated kinetic curves assuming modified dyad model of copolymerization (different propagation rate constants of active species differing by penultimate units). Rate constants obtained from fitting (20° and 0°, respectively; k_{XYZ} in L/(mol·s), k_{-XY} in s^{-1}): $k_{DDD} = 2.77 \cdot 10^4$, $9.38 \cdot 10^2$; $k_{-DD} = 5.35 \cdot 10^5$, $2.31 \cdot 10^4$; $k_{DDT} = 1.6 \cdot 10^5$, $5.1 \cdot 10^3$; $k_{-DT} = 5.5 \cdot 10^4$, 7.8A103; $kTTD = 7.7A10\text{-}1$, $4.0 \cdot 10^0$; $k_{-TD} = 2.4 \cdot 10^0$, $3.4 \cdot 10^0$; $k_{TTT} = 3.1 \cdot 10^0$, $2.6 \cdot 10^0$; $k_{-TT} = 1.4 \cdot 10^1$, $3.6 \cdot 10^0$; $k_{TDD}/k_{DDD} = k_{TDT}/kDDT = 0.11$; $k_{DTT}/k_{TTT} = k_{DTD}/k_{TTD} = 0.13$.

was cooled to 0°C. If the product was solid it was separated by filtration and washed with water until the negative reaction for Clθ ions (with AgNO$_3$). If the product was liquid it was extracted with a small volume of CH$_2$Cl$_2$, the solution washed with water until the negative reaction for Clθ ions (with AgNO$_3$), and then the solvent was removed in vacuum. The completeness of hydrolysis was checked by ^{1}H NMR (the absence of the acetal OCH$_2$O groups). A control experiment of treating of poly-T ($\overline{M}_n$ =2000) with 5% HCl in hydrolysis conditions for

10 hours has shown no significant change of $\overline{M}_n$ of this polymer, indicating that poly-T sequences practically do not hydrolyze in diluted HCl.

NMR Measurement

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 spectrometer operating at 200 MHz (^{1}H spectra). Standard acquisition conditions were applied.

Mass Spectrometry

Mass spectra were recorded on a Finnigan MAT 95 spectrometer using direct chemical ionization with isobutane as the reacting gas.

Determination of the Hydroxyl Groups in the Products of Hydrolysis

Products of hydrolysis were analyzed by ^{1}H NMR after reaction with trifluoroacetic anhydride (Aldrich) in CDCl$_3$ solution directly in the NMR tube. Ten-fold excess of anhydride was added.

RESULTS AND DISCUSSION

Copolymerization of Tetrahydrofuran (T) with 1,3-Dioxane (D)

Copolymerization was studied under conditions typical for cationic polymerization without solvent, using benzoylium hexafluoroantimonate, triflic anhydride, or triflic acid as initiators. When triflic acid was used a small amount of ethylene oxide was added in some experiments as coinitiator.

Some of the results of copolymerization of **T** with **D**, initiated with benzoylium hexafluoroantimonate, triflic anhydride, or triflic acid are presented in Table 1. Initial concentration of **T** [**T**]$_o$ was varied from 3.5 to 11.0 mol/L, whereas [**D**]$_o$ was varied from 8.4 to 0.11. The content of **D** in copolymer was always much lower than in the feed. Even at the highest [**D**]$_o$ the mole fraction of **D** in total copolymer did not exceed 40%. This result was expected, due to the known inability of **D** to homopolymerize. The number average molecular weights ($\overline{M}_n$) of copolymers, determined by size exclusion chromatography (SEC) were found to be lower than 1.5×10^4, always several times lower than

TABLE 1. Results of Copolymerization of **T** with **D** at 20°C (Experiments No. 13 and 15 at 0°C)

No.	$[I]_0$ [a,b,c] (mol/L)	$[T]_0$ (mol/L)	$[D]_0/[T]_0$	copolym. time (h)	$[-T-]/[T]_0$	$\overline{M_n}$ [e] obs./calc.	$\overline{M_w}/\overline{M_n}$	$[-OCH_2O-]/[-T-]$	PMP:(PMT+TMP):TMT [f]
1	1.5×10^{-2} [a]	6.6	0.85	160	0.78	$2.0 \times 10^3 / 3.1 \times 10^4$	1.97	0.236	0.04 : 1 : 0.41
2	2.4×10^{-2} [a]	8.6	0.40	20	0.91	$4.0 \times 10^3 / 2.5 \times 10^4$	1.98	0.075	0.11 : 1 : 1.10
3	8.3×10^{-3} [a]	8.6	0.41	67	0.74	$1.4 \times 10^3 / 6.1 \times 10^3$	1.97	0.115	0.14 : 1 : 1.31
4	1.5×10^{-2} [a]	9.6	0.26	13	0.82	$3.5 \times 10^3 / 4.0 \times 10^4$	2.04	0.056	0.09 : 1 : 1.38
5	1.1×10^{-2} [a]	10.5	0.16	15	0.96	$8.3 \times 10^3 / 6.9 \times 10^4$	2.21	0.042	0.09 : 1 : 1.46
6	1.2×10^{-2} [a]	11.0	0.10	16	0.96	$9.9 \times 10^3 / 6.5 \times 10^4$	2.09	0.018	0.11 : 1 : 1.71
7	5.7×10^{-3} [b]	3.5	2.4	94	0.21	$3.9 \times 10^3 / 7.8 \times 10^3$	2.43	0.37	0.21 : 1 : 0.49

8	1.5×10^{-2} [b]	4.5	1.64	20	0.21	$2.3\times10^3/5.0\times10^3$	1.58	0.11	0.12 : 1 : 0.53
9	7.9×10^{-3} [b]	4.6	1.63	350	0.36	$9.5\times10^2/1.7\times10^4$	5.72	0.18	0.04 : 1 : 1.62
10	9.7×10^{-3} [b]	4.6	1.64	1370	0.49	$9.4\times10^2/1.9\times10^4$	6.41	0.14	0.21 : 1 : 1.73
11	1.2×10^{-2} [b]	6.6	0.85	19	0.42	$4.0\times10^3/2.5\times10^4$	2.24	0.052	0.10 : 1 : 0.71
12	4.5×10^{-3} [b]	6.6	0.85	429	0.38	$1.3\times10^4/4.8\times10^4$	3.47	0.061	0.29 : 1 : 0.74
13	4.9×10^{-3} [b]	7.9	0.51	204	0.34	$1.1\times10^4/5.6\times10^4$	6.41	0.054	0.31 : 1 : 1.22
14	4.4×10^{-3} [b]	7.8	0.52	193	0.37	$1.4\times10^4/5.7\times10^4$	2.81	0.11	0.28 : 1 : 0.96
15	7.1×10^{-3} [b]	8.6	0.40	30	0.57	$1.6\times10^4/5.5\times10^4$	4.74	0.046	0.30 : 1 : 1.81
16	4.5×10^{-3} [b]	8.6	0.40	48	0.51	$5.2\times10^3/7.2\times10^4$	3.45	0.063	0.12 : 1 : 3.04
17	1.7×10^{-2} [b]	9.6	0.28	20	0.70	$1.2\times10^4/2.9\times10^4$	1.95	0.028	0.19 : 1 : 3.19

(continued)

Table 1. (Continued)

18[d]	5.0×10^{-3} [b]	7.6	0.52	44	0.48	$9.7 \times 10^3 / 6.2 \times 10^4$	15.3	0.091	nd
19	1.8×10^{-2} [c]	8.0	0.49	259	0.50	$6.2 \times 10^3 / 1.6 \times 10^4$	5.21	0.11	0.21 : 1 : 0.94
20[d]	1.6×10^{-2} [c]	7.9	0.50	19	0.47	$1.0 \times 10^3 / 1.9 \times 10^4$	18.5	0.12	nd

[a,c] initiator: benzoylium hexafluoroantimonate, trifluoromethanosulfonic anhydride, trifluoromethanosulfonic acid, respectively.

[d] ethylene oxide added: $[EO]_0 = 0.05$ mol/L.

[e] number average molecular weights: determined by SEC (observed) and expected (calculated) assuming no side reactions.

[f] proportion of acetal connectivities computed on the basis of ^{1}H NMR spectra (nd: not determined).

expected assuming complete initiation and no side reactions. The results were explained by the relatively effective cyclization reactions involving acetal bonds:

$$(2)$$
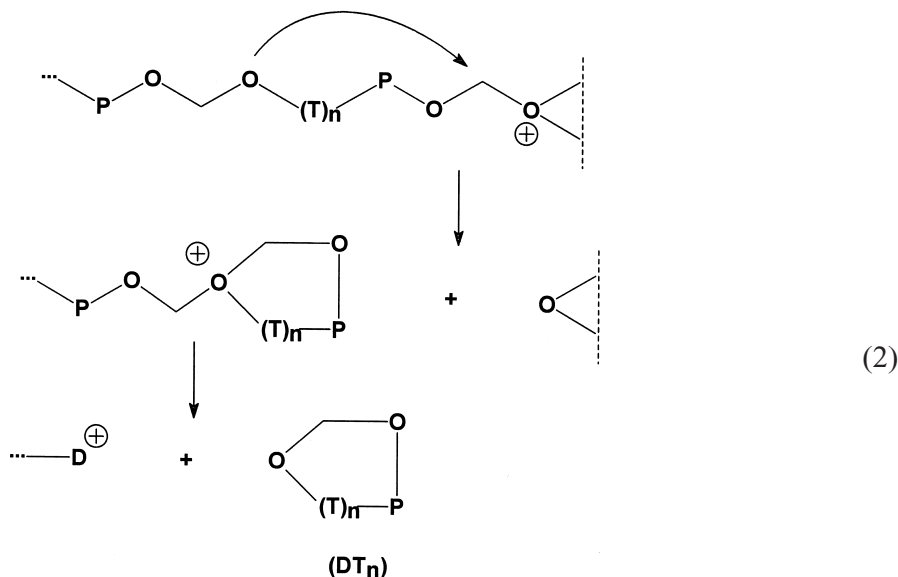
These fast reactions are intramolecular transacetalization reactions leading to a series of cyclic oligomers of general formula **DT**$_n$, detected by mass spectroscopy (cf. Figure. 2). No cyclic oligomers of different composition (but cyclic dimer of **T**) were observed. It can be explained by the fact that transacetalization (not transetherification) is the main route of formation of these compounds (hence the presence of **D** unit) and that the statistical factors (cyclization or longer chains is slower) are responsible for low (undetectable) content of cyclics with more than one unit of **D**. Formation of these oligomers is not, however, influencing the opportunity of synthesis of telechelics. Cyclic oligomers can be hydrolyzed in acidic medium together with linear copolymer giving also desired product: polytherodiols (however of lower $\overline{M}_n$, decreasing in that way the overall $\overline{M}_n$ of telechelics).

Initiation (and reinitiation) of copolymerization with triflic acid appeared to be a slow reaction. Consequently, copolymerization time needed to get satisfactory conversion is long (several days; cf. experiment 19 in Table 1) and as a main product cyclic oligomers are formed. Addition of a small amount of oxi-
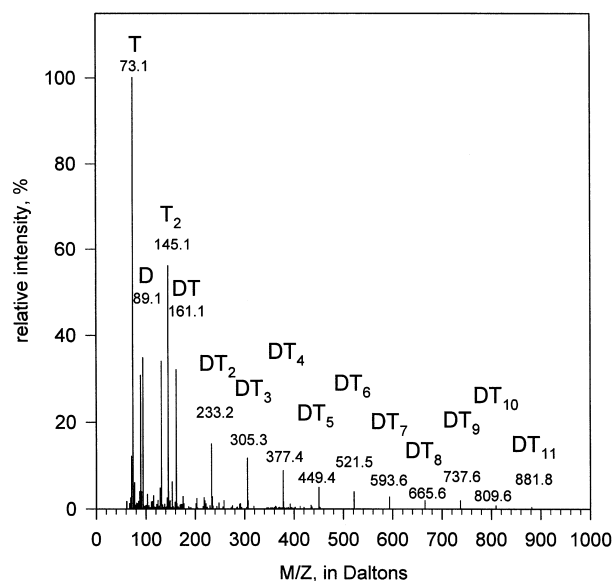
Figure 2.   Mass spectrum of oligomer fraction of D-T copolymer (no. 9 of Table 1).

rane (ethylene oxide EO) improves the process. The copolymerization time could be decreased to 19 hours (cf. experiment 20 in Table 1) This can be explained by increasing of the overall rate of copolymerization due to participation of oxirane in the initiation and reinitiation steps:

(3)
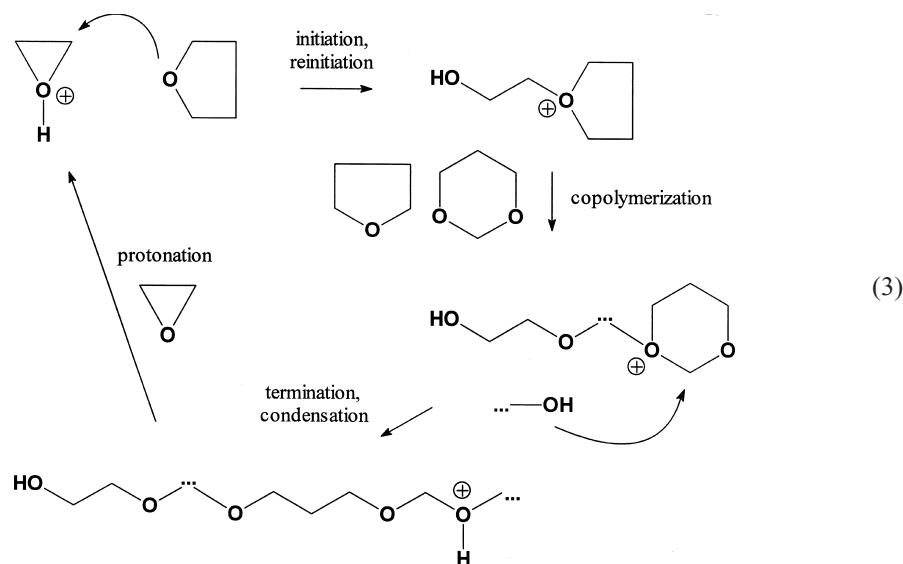
Consequently, copolymer obtained in such a process contains up to 2% of EO units. Hydrolysis of this copolymer gives telechelic polyetherodiols similarly as from binary copolymer.

Copolymer Structure

Copolymer structure was determined by ^{1}H and ^{13}C NMR spectroscopy. No end groups (but aromatic ones – using UV spectroscopy – when copolymerizations were initiated with benzoylium hexafluoroantimonate) were detected. It stems from a high ratio of concentrations of consumed comonomers and initiator. One can, however, expect the presence of methoxyl and/or NH_2- end groups formed during termination of copolymerization with diluted methanolate solution of NH_3.

Proton spectrum of copolymer formed in copolymerization carried out at relatively high concentration of **D** is presented in Figure 3. Three main groups of signals can be distinguished in the spectrum. Signals of acetal OCH_2O protons are located in the range 4.5-5.0 ppm, while signals of ether OCH_2 and of aliphatic CH_2 groups are placed in regions 3-4 and 1.3-2.0 ppm, respectively. In the aliphatic region signals of protons of units **T** and **D** are clearly separated what enables to determine copolymer composition. Independently, copolymer
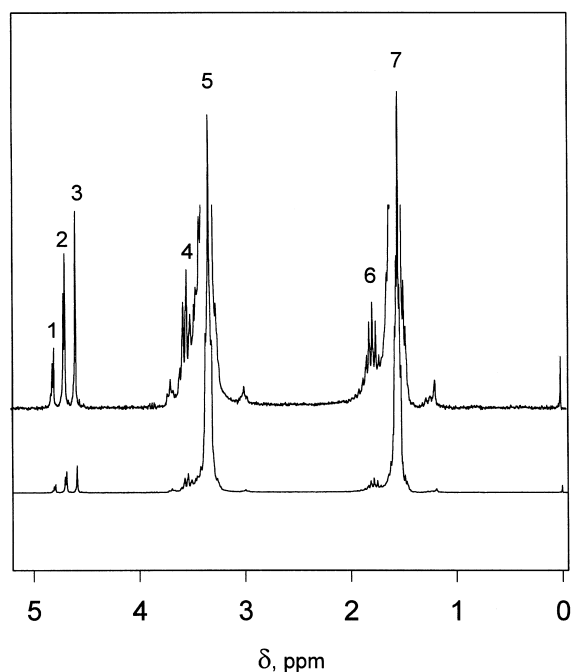
Figure 3. ^{1}H NMR spectrum of D-T copolymer (no. 14 of Table 1). Assignments of signals: 1, 2, 3: acetal OCH_2O groups in **PMP**, **PMT** (**TMP**), and **TMT** sequences, respectively; 4 and 5: OCH_2 groups in **P** and **T** units, respectively; 6 and 7: $CH_2C\underline{H}_2CH_2$ protons in **P** and **T** units, respectively.

composition can be determined by comparing integrals of acetal and ether groups. Different peaks in acetal range can be ascribed to different locations of acetal group in copolymer chain. The acetal CH$_2$ group (**M**) can be placed between two oxytrimethylene (**P**) groups (**PMP**), between one oxytrimethylene and one oxytetramethylene groups (**PMT**, **TMP**), and between two oxytetramethylene groups (**TMT**). The first two locations give two expected signals at about 4.8 and 4.7 ppm, respectively. If a simple mechanism of copolymerization operated without side reactions the third signal would be absent. Having experience with similar copolymerization of **D** with bicyclic monomer 7-oxabicyclo[2.2.1]heptane (B) we could however predict that the third signal (at about 4.6 ppm) would be present due to disproportionation reaction operating in the system.

$$2\,\textbf{PMT} \;\rightarrow\; \textbf{PMP} \;+\; \textbf{TMT} \tag{4}$$

This fast transacetalization reaction is a multi-step reaction with three-branch oxonium cation intermediates, mentioned previously in the kinetic section. In the first step of disproportionation the acetal active center **D*** reacts with acetal group in polymer chain (interchain reaction) leading to three-branch oxonium cation intermediate, which then disintegrates giving "incorrect" acetal active species of dioxepanium cation structure (**TM***):

(5)
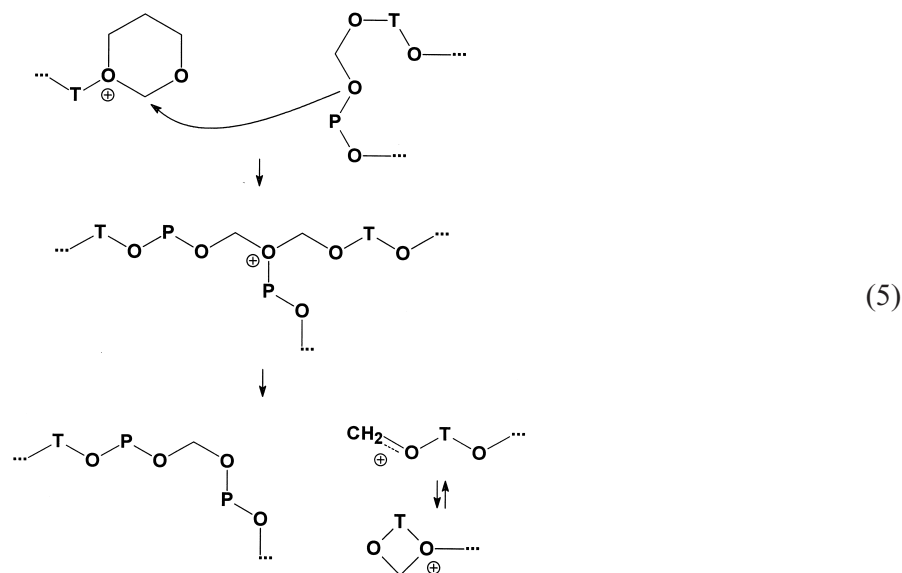
Dioxepane, which can then be formed in backbiting reaction has a low equilibrium concentration and therefore could not be detected. However, diox-

epanium active species can react with comonomers or with polymer segments. Both reactions can lead to **TMT** structures:

$$\mathbf{TM}^* + \mathbf{T} \rightarrow \mathbf{TMT}^* \tag{6}$$

$$(7)$$
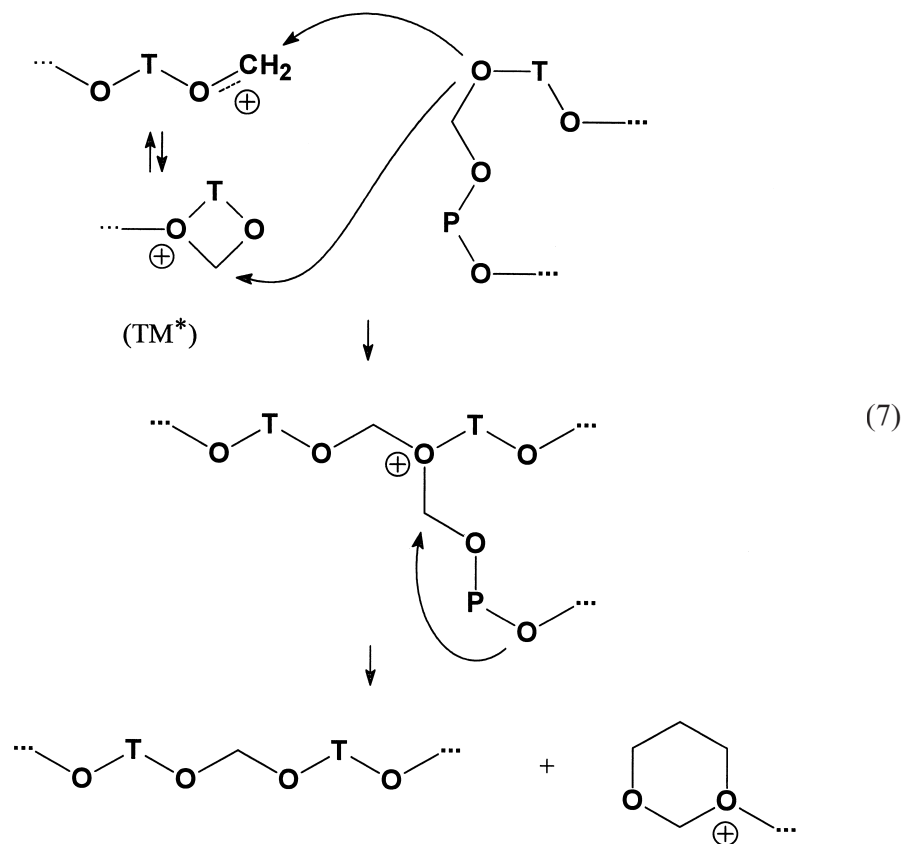
The second of the above reactions is the third step of disproportionation reaction involving acetal chain groups.

If only disproportionation and propagations were responsible for the formation of different acetal connectivities in copolymer chains then the fraction of **TMT** groups would be lower than the proportion of **PMP** groups. However, due to thermodynamic reasons the fraction of **PMP** units is low (the observed proportions of **PMP**:**TMP**:**TMT** groups in obtained copolymers are presented in Table 1). Depropagation of **D*** leads to that result. **D*** can be formed in reaction of other active species with **PMP** units:

(8)
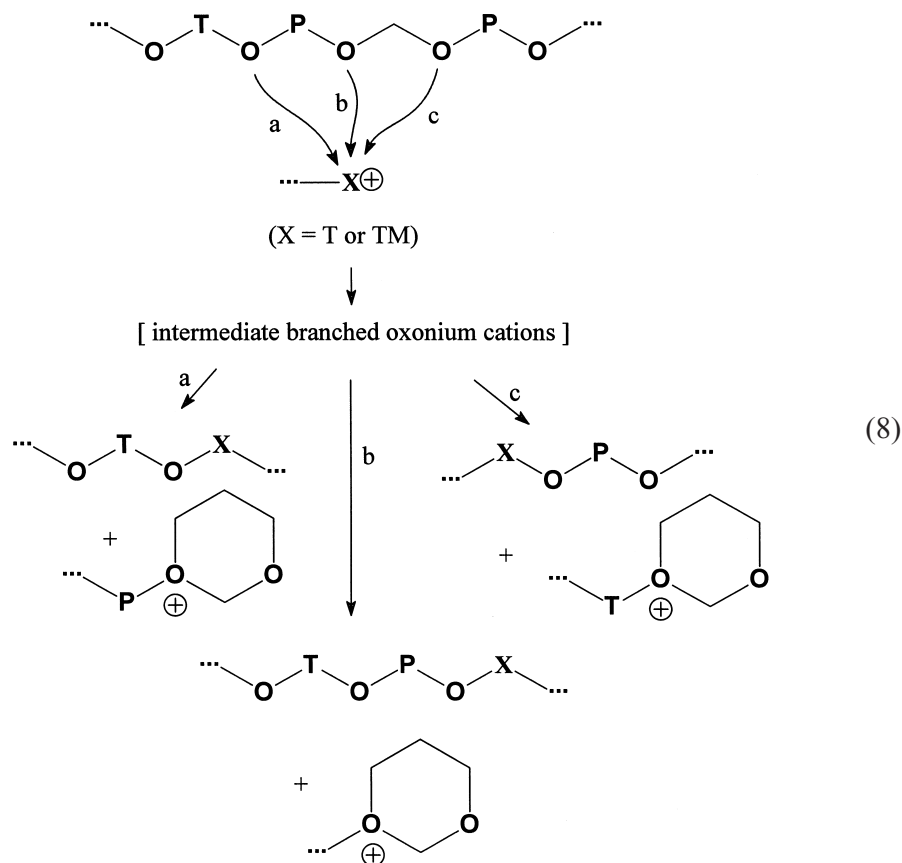
It is worth noting, that if the attacked cation is T^* then the "incorrect" structure **TPT** can be formed as well (cf. route b).

The "incorrect" structures are probably responsible for splitting of signals corresponding to **PMP**, **PMT**, and **TMT** due to slightly different magnetic environments of groups **M** in groups such as **MPMPT** and **TPMPT**, or **MPMT** and **TPMT**. However, the observed different signals ascribed to the given acetal bond can be explained as well by formation of cyclic oligomers with the considered acetal structures. Formation of cyclic oligomers beside the interchain segmental exchange reactions is responsible for a broad MWD of copolymers (cf. Table 1). ^{13}C NMR spectra (cf. Figure 4) confirm the conclusions drawn from ^{1}H NMR spectra.
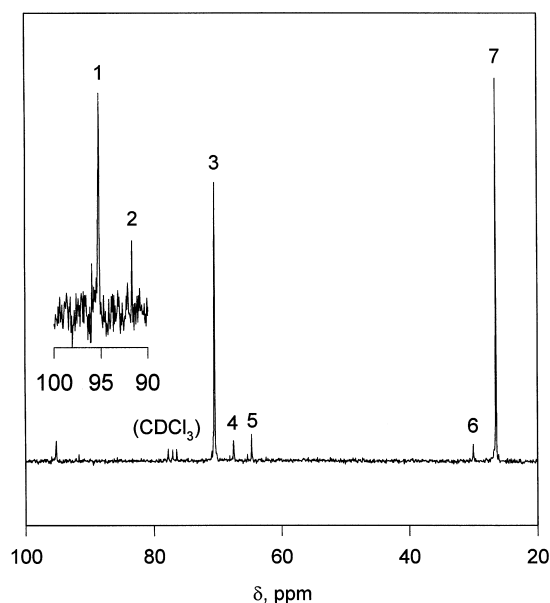
Figure 4. ^{13}C NMR spectrum of **D-T** copolymer (no. 8 of Table 1). Assignments of signals: 1, 2: acetal OCH_2O groups in **PMT** (**TMP**) and **TMT** sequences, respectively; 3: OCH_2 groups of **T** units; 4, 5: OCH_2 groups of **P** units in acetal and ether connectivities, respectively; 6, 7: aliphatic CH_2 groups of **P** and **T** units, respectively.

Kinetics of Copolymerization

In Figure 1, changes of the concentrations of copolymer units **D** and **T** during copolymerization, as well as during control experiment of reaction of living poly-**T** with **D**, are presented for 20ºC, and (only copolymerization kinetic changes) for 0ºC.

The control experiment has shown that incorporation of **D** units occurs mainly by normal copolymerization route and only a small proportion of these units can be introduced into copolymer chain by the interchain exchange reactions (of terminal –**D*** units with poly-**T** sequences). The observed relatively slow incorporation of **D** units in the control reaction can be attributed either to the interchain exchange reaction or (at least partly) to the normal copolymerization steps following partial (observed; cf. Figure 1) and dynamic (counter-balanced by propagation) depolymerization of living poly-**T**.

Time scales of copolymerizations seem to be almost independent of temperature. As activation enthalpy of homopolymerization of **T** is quite high (37-53 kJ/mol depending on polymerization conditions) [8] one would rather expect much slower copolymerization at lower temperature. However, several factors should be taken into account while predicting differences at different temperatures. First, the rate of reversible polymerization is proportional to the difference between the given and equilibrium monomer concentration. Lowering temperature one usually increases this difference, dependent on initial monomer concentration and thermodynamic parameters of polymerization. Enthalpy of homopolymerization of **T** is rather high (about -18 kJ/mol in bulk and about -15 kJ/mol in CH_2Cl_2) [9], what, by decreasing equilibrium monomer concentration, compensates to some extent the decrease of the rate constant of propagation.

Additionally, negative enthalpy of covalent species - ionic species equilibrium, shifting the system farther to the ionic species side at lower temperature, works in the same direction, as ionic species are about two orders of magnitude more reactive than covalent ones.

However, most important are equilibria between different types of ionic active species. Assuming dyad model of copolymerization four types of active species have to be taken into account: **TT***, **DT***, **TD***, **DD***. Reactivities of these active species concerning propagations and depropagations determine not only the equilibrium between these species but the overall rate of copolymerization as well.

The analyzed copolymerization system comprise two comonomers differing strongly in their polymerization abilities and active species reactivities. Tetrahydrofuran is capable of homopolymerization. Its equilibrium monomer concentration depends on temperature (enthalpy of polymerization was mentioned above), solvent, and initial monomer concentration. For instance, at 25°C, depending on initial monomer concentration, the equilibrium concentrations vary in CH_2Cl_2 and CCl_4 between about 5.7 and 4.3, respectively, at minimum monomer concentrations capable to give polymer in these solvents at this temperature, and equal to about 3.2 mol×L^{-1} in virtually pure THF [8]. Rate constant of propagation (corresponding to copolymerization propagation rate constant k_{TT}) on ionic active species is more than two orders of magnitude higher than on triflic covalent species (at 25°C in CH_2Cl_2 equal to 3×10^{-2} and 1.7×10^{-4}, respectively). The ratio of concentrations of ionic to covalent active species is equal at 25°C to 0.07 in CCl_4, 0.6 in CH_2Cl_2, and 40 in CH_3NO_2 [10].

On the other hand, **D** cannot homopolymerize due to thermodynamic reasons - its computed equilibrium monomer concentration is equal to 23.3 and 17.9 mol×L^{-1} at 21°C and 0°C, respectively, about twice higher than [**D**] in bulk (ceiling temperature is equal to about –70°C) [6]. Active species of propagation are, however, very reactive because of cyclic acetal structure of this monomer. One can expect that the order of magnitude of propagation rate constant (corresponding to copolymerization propagation rate constant k_{DD}) on ionic active species is 10^4 mol×L×s^{-1} at room temperature, close to the corresponding elementary reaction rate constants in polymerizations of 1,3-dioxolane and 1,3-dioxepane [11, 12]. This is, however, counterbalanced by depropagation, resulting in nonhomopolymerizability of **D**.

Taking into account these properties of both comonomers, together with a general mechanism of copolymerization of cyclic monomers, one can predict the orders of magnitude of rate constants of crosspropagations and crossdepropagations.

Thus, if only ionic species are considered, one can expect that crosspropagation rate constants are rather similar to the corresponding homopropagation rate constants: $k_{TD} \sim k_{TT}$, $k_{DT} \sim k_{DD}$, because reactivities of the labile active species do not strongly depend on the nature of monomer. On the other hand, the crossdepropagation rate constants are rather similar to the homodepropagation rate constants of the penultimate-unit type monomer: $k_{-DT} \sim k_{-DD}$, $k_{-TD} \sim k_{-TT}$, because depropagation reaction mostly depends on the ring strain of newly formed ring and entropy of this process, both quantities being similar for depropagations in systems with the same penultimate unit.

These estimations are rather crude, because of some additional factors. Thus, active species **DT*** are probably much less reactive in propagation reactions than **TT*** because of lower positive charge at corresponding endocyclic carbon atoms, due to charge delocalization on alkoxymethyl group:

$$(9)$$
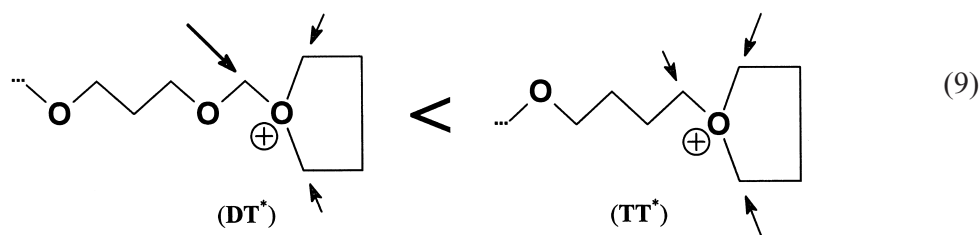
Besides, because of higher basicity of **T** in comparison to **D**, **DT*** is probably much less reactive in depropagation than **DD***.

Analogously, reactivity of **TD*** in propagation reactions is lower than of **DD*** because the first active species is an alkoxymethyl dialkyl oxonium cation, while the latter belongs to a class of more reactive di(alkoxymethyl) alkyl oxonium cations [11]. Depropagation of **TD*** is, however, probably significantly faster than of **TT*** because of lower basicity of **D**, resulting in a weaker bond connecting the penultimate **T** unit with the ultimate unit **D** (in comparison to the ultimate unit **T**).

Analysis of kinetics of copolymerization of the system under consideration is additionally difficult, because exocyclic carbon atom of active species **DT*** (alkoxymethyl group) is much more reactive than the endocyclic carbon atoms of **T** unit moiety (c.f. Scheme (9)). Moreover, some additional reactions, such as reactions of active species with polymer chains leading to branched oxonium cations, or formation of "incorrect" active species and copolymer structures, already mentioned in the previous sections, complicate additionally the kinetics of the analyzed process.

Due to the complexity of copolymerization of **T** with **D** discussed above, our simplified kinetic analysis led only to some average quantities concerning rate constants of homo- and cross- propagations and depropagations (cf. Capture to Figure 1). We achieved that by fitting the observed kinetic relationships to kinetic curves computed assuming a simple dyad model of copolymerization, modified by allowing different propagation rate constants of XY* and YY* active species (X, Y = **T** or **D**, X ≠ Y) and assuming additionally independence of conditional probabilities of following the given units by the other ones (p_{DD}, p_{DT}, p_{TD}, p_{TT}) in respect to unit position in copolymer chain. As it was shown by simulations (not presented here) the last assumption is only valid for constant ratio of comonomer concentrations or for very effective segmental interchain exchange (the second was assumed). Moreover, the coexistence of ionic and covalent species was neglected in the analysis, what gave us average reactivities of species of the given kind (**DD***, **DT***, **TD***, or **TT***, each type comprising ionic and ester species).

Acidic Hydrolysis of Copolymer of T with D

Figure 5 presents an example of the size exclusion chromatography (SEC) curve of polyetherodiols (obtained by hydrolysis of **T-D** copolymer in
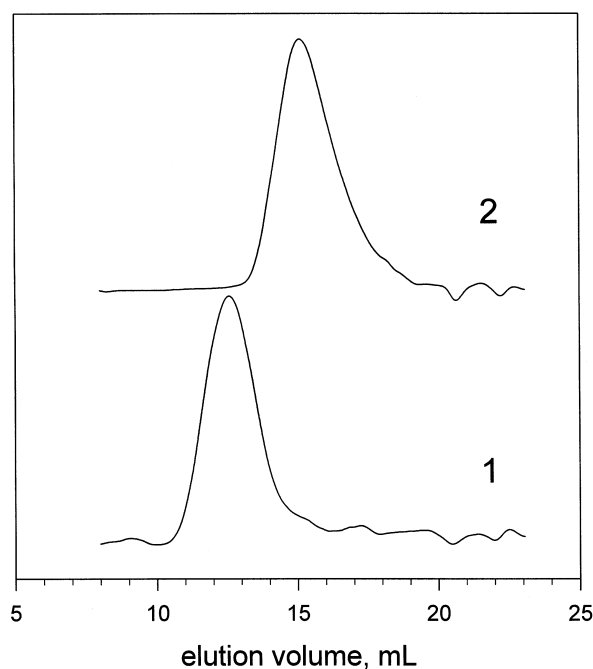
Figure 5. SEC chromatograms of **D-T** copolymer (1) (no. 12 of Table 1; $\bar{M}_n = 1.3 \times 10^4$) and of telechelic oligomers (2) (cf. Table 2; = 1.4×10^3) obtained by its acidic hydrolysis.

diluted HCl) in comparison to the SEC curve of initial copolymer. Results of hydrolysis are listed in Table 2.

In the Table, one can see beside initial copolymer data the results of the SEC analysis of resulted oligomers and of the analysis of ^{1}H NMR spectra of oligomers (reacted with trifluoroacetic anhydride). The total number of OH groups is twice higher than the number of oxytrimethylene groups (cf. Figure 6). This indicates that on the average one oxytrimethylene group is present in one diol molecule. On the other hand, the number of OH groups attached to **T** units is equal or not much higher than the number of OH groups attached to **P** (oxytrimethylene) units. This results proves that most of oligomer molecules have a structure given by the formula HO**PT**$_n$OH. Nevertheless, both present hydroxyl groups are primary ones presumably with identical chemical properties, what makes the oligomers suitable for polycondensation purposes. End groups coming from initiation of copolymerization can be neglected because besides their low

TABLE 2.   Results of Acidic Hydrolysis of **T-D** Copolymers

No.[a]	$[D]_0/[T]_0$ (copolymer)	$[-OCH_2O-]/[-T-]$ (copolymer)	$\overline{M}_n$ (copolymer) (SEC)	Yield[c]	$\overline{M}_n$ (oligomers) (SEC / NMR)	$\overline{M}_w / \overline{M}_n$ (oligomers) (SEC)	$[OH]/$ $[O(CH_2)_3O]$ (NMR)	$[HO(CH_2)_3O]/$ $[HO(CH_2)_4O]$ (NMR)
5	0.16	0.042	8.3×10^3	0.84	$1.6 \times 10^3 / 1.9 \times 10^3$	2.24	2.01	0.84
6	0.10	0.018	9.9×10^3	0.86	$3.4 \times 10^3 / 3.0 \times 10^3$	1.71	1.98	0.81
7	2.4	0.37	3.9×10^3	0.37	$6.0 \times 10^2 / 6.3 \times 10^2$	1.24	1.97	1.00
12	0.85	0.061	1.3×10^4	0.71	$1.4 \times 10^3 / 1.1 \times 10^3$	1.85	2.06	0.91
16	0.40	0.063	5.2×10^3	0.77	$1.8 \times 10^3 / 1.5 \times 10^3$	1.81	2.00	0.70
18[b]	0.52	0.091	9.7×10^3	0.73	$1.9 \times 10^3 / 1.5 \times 10^3$	1.62	1.94	nd
19	0.49	0.11	6.2×10^3	0.69	$1.6 \times 10^3 / 1.1 \times 10^3$	2.53	2.02	0.89
20[b]	0.50	0.12	1.0×10^3	0.64	$7.2 \times 10^2 / 6.8 \times 10^2$	3.41	2.01	nd

[a] Numbers correspond to rows in Table 1.

[b] Minute amounts of ethylene oxide units are present.

[c] Hydrolysis yields (the ratios of masses of isolated oligomers to masses of initial copolymers).

Figure 6. ^{1}H NMR spectrum of telechelic oligomers obtained by the acidic hydrolysis of **D-T** copolymer (no. 7 of Table 1) after reaction with trifluoroacetic anhydride. Assignments of signals: 1, 2: $CF_3C(O)OCH_2$ protons corresponding to HO**T** and HO**P** groups, respectively; 3: ether OCH_2 protons; 4, 5: aliphatic CH_2 groups of **P** units in terminal and inside-chain positions, respectively; 6: aliphatic CH_2 groups of **T** units.

proportion all or most of them (Ph-C(O)-O-..., CH_3O-CH_2-O-..., NH_2-O-CH_2-O-...) are converted to hydroxyl groups during copolymer hydrolysis.

Results of hydrolysis can be explained by much higher susceptibility of acetal bonds to acidic hydrolysis than of ether ones. In contrast to ether bonds, they can easily be hydrolyzed in diluted mineral acids. Copolymer of **T** with **D**, containing both types of bonds, while hydrolyzed in diluted HCl, gives telechelic polyetherodiols:

(10)

The cleavage only of acetal bonds during hydrolysis is evidenced by disappearance of acetal region signals in ^{1}H NMR spectra of the product of hydrolysis and by the agreement of the average molecular weight of the resulted oligomers with the prediction. The prediction could be done assuming that the number of polyether blocks (the number of oligomer molecules) was equal to the number of **PMT** and **TMT** bonds, while the cleavage of **PMP** bonds corresponded to formation of trimethylene diol, soluble in diluted acid and therefore separated from the insoluble product.

No other end groups were observed in ^{1}H NMR spectra. This indicates that the deprotonation reaction (expected in many cationic systems):

$$\tag{11}$$
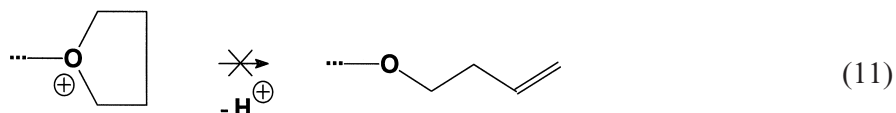
does not practically operate in copolymerization system or this reaction in copolymerization conditions is reversible and shifted strongly to the left side.

The molecular weights of obtained telechelic oligomers were in the range 600-3000, while the polydispersity indexes in the range 1.24-3.4. The longer copolymerization time the broader MWD what can be explained by interchain exchange reactions involving to some extent ether bonds besides acetal ones. Formation of cyclic oligomers leads as well to broadening of the MWD of final oligomers. It is so because smaller rings ($\mathbf{DT}_n$, n=1,2,..) are favored, what gives after hydrolysis the increase of the fraction of low molecular weight polyetherodiols.

CONCLUSION

It has been demonstrated that 1,3-dioxane (**D**), cyclic acetal unable to homopolymerize, copolymerizes cationically with cyclic ether tetrahydrofuran (**T**). The formation of copolymer directly in copolymerization process was confirmed by preliminary kinetic studies, by NMR analysis of the resulted products, and by acidic hydrolysis studies of the obtained copolymer.

It was shown that interchain exchange reactions, mainly transacetalization reactions, influence copolymerization resulting not only in broadening of the molecular weight distribution of copolymer but giving origin of some "incorrect" sequences in copolymer chains, such as

$-(CH_2)_4OCH_2O(CH_2)_4-$ (**TMT**) or $-(CH_2)_4O(CH_2)_3O(CH_2)_4-$ (**TPT**), as well. Transacetalization reactions while operating intramolecularly are cyclization reactions giving origin of a series of cyclic oligomers, mostly of the general formula **DT**$_n$. Consequently, the observed average degree of polymerization is much lower than expected assuming no side reactions.

The acidic hydrolysis of copolymers in diluted HCl gives telechelic polyetherodiols of the average composition HO**T**$_n$**P**OH and of the average molecular weights in the range 600-3400. The MWD of these oligomers is rather broad, with polydispersity ratios in the range 1.2-3.4.

The present work gives for the first time an evidence of a direct copolymerization of tetrahydrofuran with cyclic acetal in a purely cationic ring opening polymerization. It is the second example of a direct copolymerization of cyclic ether with cyclic acetal (previously we described copolymerization of **D** with bicyclic ether 7-oxabicyclo[2.2.1]heptane, much more strained and more nucleophilic monomer [1]).

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