Macromol. Symp. ***132****, 349-358 (1998)*

COPOLYETHERS WITH CONTROLLED STRUCTURE : MECHANISM OF FORMATION AND MICROSTRUCTURE

Melania Bednarek and Przemysław Kubisa*

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences
Sienkiewicza 112, 90-362 Łódź, Poland

Abstract: Cationic copolymerization of 3-membered cyclic ethers (oxiranes) with 5-membered cyclic ether (tetrahydrofuran) leads to linear copolyethers containing significant amount of cyclic fraction. When the copolymerization is conducted in the presence of diols, telechelic copolymers are formed by the process in which oxirane is incorporated into copolymer irreversibly by Activated Monomer mechanism, while tetrahydrofuran is incorporated reversibly by Active Chain End mechanism. Thus both kinetic and thermodynamic factors can be used to control the rate of the incorporation of comonomers. Studies of the kinetics of the competing reactions leading to formation of copolymer, studies of copolymer microstructure by ^{13}C-NMR and analysis of the composition of the cyclic fraction, led to the correlation between the copolymer microstructure and the amount of cyclic fraction formed. The dependence of the cyclic fraction content on the reaction conditions was therefore explained.

INTRODUCTION

Cationic polymerization of 5-membered cyclic ether: tetrahydrofuran (THF) is one of a few examples of industrially important processes proceeding by cationic mechanism. Telechelic polymers of THF terminated with hydroxyl groups are used for the synthesis of multiblock copolymers, mainly polyurethanes but also block copolyesters or copolyamides, providing so called "soft segments" (Ref. 1). Both the process and the product has some disadvantages. Large

CCC 1022-1360/98/$ 17.50

quantities of strong acid or acid anhydrides are required to form the polymer with molecular weight in the range 1000-2000, which leads to large amounts of waste material after or hydrolysis of originally formed ester groups and neutralization. The product has a melting point above room temperature, which causes storage and handling problems.

One of the possible approaches to overcome these disadvantages, is based on the copolymerization of THF with suitable monomer. Several systems has been studied, involving mostly 3-membered cyclic ethers (oxiranes), which are known to act as "promoters" of THF polymerization, increasing the rate of initiation. Surprisingly, majority of the papers deals with copolymerization of THF with substituted oxiranes, while copolymerization of THF with parent monomer of this group, namely ethylene oxide, received little attention. One of the possible reasons is the high tendency of ethylene oxide to undergo cyclization (by back-biting) at the conditions of cationic polymerization. Indeed, the extensive cyclization has been observed in the cationic copolymerization of THF with EO by DuPont researchers (Ref. 2).

In cationic homopolymerization, cyclization is extensive in the case of EO (Ref. 3), while, for the kinetic reasons, it is negligible in the case of THF (Ref. 4). Thus it is reasonable to assume, that in copolymerization, cyclization involves mainly EO units at the chain end or within the chain.

Several years ago, it was shown by our group, that cationic polymerization of three membered cyclic ethers (oxiranes) in the presence of hydroxyl group containing compounds (e.g. diols) proceeds by Activated Monomer mechanism (AM) (Refs. 5-7), according to the scheme below:

(I)

At the same conditions i.e. in the presence of hydroxyl groups containing compounds, five membered cyclic ether (tetrahydrofuran - THF) does not polymerize. Protonic acids may initiate the cationic polymerization of THF, although the rate of initiation is low (Ref. 4). Apparently, in the presence of hydroxyl groups, formation of hydrogen bonds decreases further the reactivity of protonated THF, reducing the rate of initiation to the very low value.

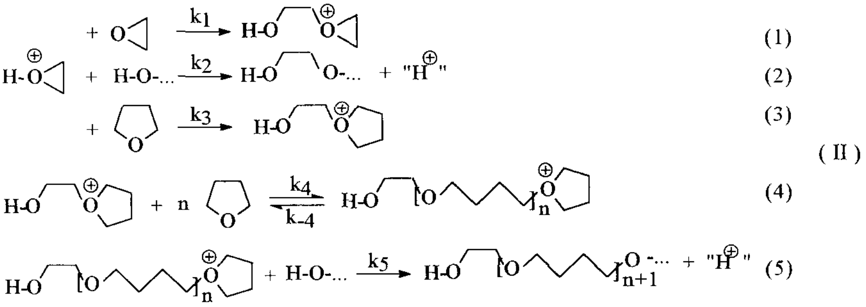
If, however, oxirane is introduced to the reaction mixture consisting of THF, low molecular weight diol and catalytic amounts of protonic acid, the polymerization starts and THF is incorporated into copolymer. Apparently, the reaction in such system is initiated by more reactive protonated oxirane, thus oxirane act as a "promoter".

In the polymerization of oxiranes proceeding by AM mechanism, cyclization is limited, because no tertiary oxonium ion active species are present at the growing chain end. The reaction pathway for back-biting, leading to cyclization is thus excluded. The possibility of cyclization is not, however, eliminated completely, because with increasing chain length, reaction of activated monomer with the ether groups within the chain, followed by chain scission leading to tertiary oxonium ion terminated chains, becomes increasingly important.

These reactions are of lesser importance for substituted oxiranes, because of the steric hindrance for the intramolecular reaction, but prohibit formation of longer poly-EO chains, free of cyclic fraction (Ref. 8).

The logical conclusion is, that in copolymerization, in order to avoid formation of cyclics according to discussed above reaction scheme, formation of longer EO sequences should be excluded.

The reaction scheme, leading to formation of THF-EO copolymer in the presence of diol, may be visualized as follows:



(II)

In order to prepare telechelic EO-THF copolymers not containing longer EO sequences i.e. containing minimum amount of EO required to achieve high THF conversion, reactions 1 and 2 should be avoided. If reaction scheme consisted only of reactions 3, 4 and 5, the copolymers with the structure $\{[EO]\text{-}[THF]_n\}_m$ should be formed. At such conditions, due to the absence of longer EO sequences, the cyclization should be limited.

In order to check this hypothesis, the kinetics of competing reactions has been studied, the conclusions coming from kinetic studies were verified by the investigation of copolymer microstructure and, finally, the influence of the reaction conditions on the content of cyclic fraction was determined.

RESULTS AND DISCUSSION

Kinetics of the copolymerization

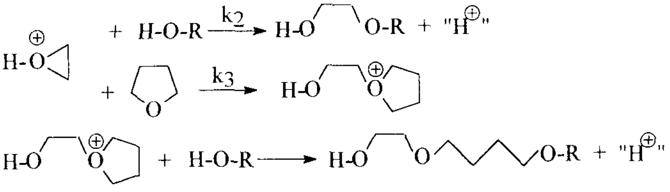
Reactions of protonated EO

When protonic acid is added to the reaction mixture consisting of THF, EO and low molecular weight diol (e.g. ethylene glycol - EG) (5-10%mol with respect to THF) , protonation of both cyclic ethers and diol occurs, leading to formation of corresponding secondary oxonium ions. Protonated THF is not able to initiate the polymerization in the presence of HO- groups (no polymerization was observed for the system: THF (bulk) - HO-R-OH (5 mol%) - $HBF_4 \cdot Et_2O$ (1 mol%) for several weeks at room temperature). Protonated diol serves only as the reservoir of protons. The only species, which may initiate the process is thus the protonated EO. Protonated EO may react with either nucleophile present in the system, i.e., THF, EO or HO- groups (reactions 1,2 and 3 in scheme II).

To exclude the possibility of formation of longer EO sequences, reactions 1 and 2 should be avoided. The conditions should therefore be created, at which rate of reaction 3 is much larger than the rates of reactions 1 and 2. Rate of chemical reaction depends on its rate constant and on the concentration of reactants. Reaction 1 may therefore easily be suppressed by carrying out the reaction at very low instantaneous concentration of EO ($[EO]_{inst.} < 0.05$ mol·L^{-1}), i.e., with continuous feeding of EO into the reaction mixture.

The ratio of the rates of two other reactions appearing in the scheme cannot be influenced by adjusting the concentration of the reactants, because the ratio of concentrations: [THF]/[HO-] is predetermined by the required DP_n of the product. Thus, to estimate the ratio of the rates of these two competing reactions, the knowledge of the ratio of rate constants is necessary.

This ratio was measured in the model system. At the conditions, when concentration of model alcohol ROH ($C_6H_5OCH_2CH_2OH$) was equal to 3-5 mol·L^{-1} and concentration of THF was much lower ([THF] = 1.6-2.5 mol·L^{-1}), reaction of EO in the presence of acid, led to formation of only two lowest oligomers, as shown in scheme below:



(III)

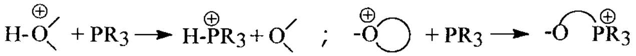
The oligomers were identified on the basis of glc-MS analysis. The reaction was performed at different [ROH]/[THF] ratios and relative concentrations of both products were determined from HPLC chromatograms. Due to the presence of aromatic moiety in both oligomers, the ratio of concentrations could easily be determined by measuring the peak areas in the chromatograms obtained with UV detection (it was assumed, that the extinction coefficient of the aromatic group was the same in both molecules). The composition of the reaction mixture was determined at still low THF conversion (<20%mol) and it was assumed, that at this stage of the reaction, the ratio of concentrations of both products is close to the ratio of the rates of their formation, i.e., that:
$[\text{HO-EO-OR}]/[\text{HO-EO-THF-OR}] = k_2\,[\text{H-EO}^+]\,[\text{HO-R}] / k_3\,[\text{H-EO}^+]\,[\text{THF}]$
The plot of $[\text{HO-EO-OR}]/[\text{HO-EO-THF-OR}]$ vs $[\text{HO-R}]/[\text{THF}]$ gave indeed the straight line with a slope equal to $k_2 / k_3 = 0.6$ (CH_2Cl_2, 25^0).

Reactions of alkylated THF

Protonated EO may react either with HO- group (this reaction corresponds to AM propagation of EO, liberating the proton, which may start the sequence of reactions described above) or it may react with THF, forming tertiary oxonium ion, i.e., alkylated THF. The latter species, similarly to secondary oxonium ion (protonated EO) may react with either of the nucleophiles present in the system.

Due to the low instantaneous concentration of EO in the system, reaction of tertiary oxonium ion with EO may be neglected. Thus, as in the case of protonated EO, two competing reactions, namely reaction with THF and with HO- groups, should be considered. Reaction of tertiary oxonium ion (alkylated THF) with THF corresponds to THF homopropagation (reaction 4 in scheme II). Although both kinetic and thermodynamic parameters of reversible THF propagation, known from the literature, correspond to propagation of active species attached to longer chains, the differences between these parameters determined for the first few additions are not large. The rate and equilibrium constants for THF homopropagation can therefore be used as an approximate values characterizing also the first few additions i.e. reaction 4 in scheme II .

To estimate the relative rates of both competing reactions, the rate constant of reaction 5, i.e., the reaction of tertiary oxonium ion (alkylated THF) with HO- groups, should be determined. In this reaction, tertiary oxonium ion is converted into secondary oxonium ion. To measure the rate of this process, the ion trapping method, developed earlier in this laboratory, has been applied (Refs. 9,10). The method is based on fast, quantitative and irreversible conversion of oxonium ions into phosphonium ion by reaction with tertiary phosphines. Secondary oxonium ions are converted into tertiary phosphonium ions while tertiary oxonium ions give quaternary phosphonium ions, as shown in the scheme below:



(IV)

The concentration of both kinds of phosphonium ions may be determined by ^{31}P NMR spectroscopy.

The rate of reaction of tertiary oxonium ions with HO- groups has been measured in both model system for triethyloxonium cation and in real polymerizing system for alkyltetrahydrofuranium cation (living poly-THF). In the model experiments, the alcohol was introduced to the solution of triethyloxonium tetrafluoroborate in methylene dichloride in an ampoule sealed in vacuum equipped with breakseals. In the real polymerizing system, THF (3.0 mol L^{-1}) was polymerized in methylene dichloride solution with $C_6H_5CO^+,SbF_6^-$ as initiator at -70^0 and alcohol was introduced to the solution of living poly-THF. The samples were withdrawn at different stages of reaction and two-fold excess of tributylphosphine was added under vacuum

Typical ^{31}P NMR spectrum, from which the concentrations of tertiary and secondary oxonium ions were determined, is shown in Fig.1. The kinetic data were analyzed in terms of second order kinetic equation; the corresponding semilogarythmic plots for the reactions proceeding at different temperatures , are shown in Fig.2

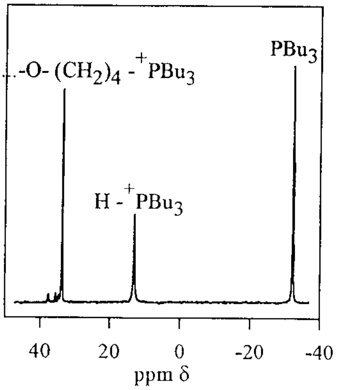


Fig. 1. ^{31}P NMR spectrum of reaction system : living poly-THF$^+$ + ROH terminated with PBu$_3$ (CH$_2$Cl$_2$, -78^0)

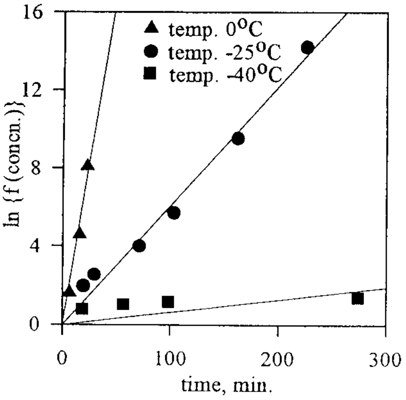


Fig. 2. Kinetic plots for the reaction: Et_3O^+,BF_4^- + ROH (CH$_2$Cl$_2$) (semilog. anamorphoses of II-order equation)

From the kinetic data, the rate constant of the reaction between tertiary oxonium ion (alkylated THF) and HO- groups, may be determined as equal to: $k_5 = 1.0 \cdot 10^{-3} mol^{-1} \cdot L \cdot s^{-1}$ (CH_2Cl_2, -25^0). This value is very close to the value of the rate constant of THF propagation (reaction of alkylated THF with THF), equal to k_p ($\approx k_4$) = $8.0 \cdot 10^{-4} mol^{-1} \cdot L \cdot s^{-1}$ (CH_2Cl_2, -25^0) (Ref. 11).

Summary of the kinetic results

The results presented in the preceding two paragraphs indicate, that there is rather small (if any, considering limited accuracy of the kinetic measurements and extrapolations) difference between rate constants of the reactions of both protonated EO and alkylated THF with THF and HO-groups. Thus, from two sets of competing reactions (reactions 2 vs 3 and 4 vs 5 in scheme II) neither one is kinetically preferred. To favor the reaction of protonated EO and alkylated THF with THF it is thus necessary to carry out the process at the conditions when [THF] >> [EO]. This requirement is fulfilled at the early stages of the reaction, because $[THF]_0$ is > 10 times higher than [HO-]. With increasing conversion of THF, however, the ratio [THF]/[EO] decreases. To determine the influence of [THF]/[EO] ratio on the course of reaction, the microstructure of copolymers formed at different stages of reaction, was studied by ^{13}C NMR.

Microstructure of copolymers by ^{13}C NMR

Fig. 3 shows the ^{13}C NMR spectra (only $-CH_2-O-$ groups absorption region) of copolymers isolated at different THF conversions. The signals were assigned to homo- and heterodiads on the basis of the analysis of the spectra of model copolymers, containing various fractions of comonomer units.. Up to~ 60% conversion of THF, the content of EO-EO diads is small, indicating, that indeed at [THF]>>[EO] the contribution of reactions leading to formation of EO-EO diads is low. At higher THF conversions, the contribution of these reactions is becoming significant and EO-EO diads are formed in increasing proportion, as indicated by the presence of the corresponding signal in ^{13}C NMR spectra.

Cyclic oligomers

GPC curves of the copolymerization products show the main peak in the medium molecular weight range and the series of small peaks in the low molecular weight region. The low molecular weight fraction was isolated by extraction with ethanol and analyzed by gas chromatography coupled with mass spectroscopy. Components of low molecular weight fraction has been identified as the cyclic oligomers of the following structure:

mixed cyclic tetramers: THF_3-EO (45 %), THF_2-EO_2 (30 %), THF-EO_3 (15 %)

mixed cyclic trimer: THF_2-EO (2.5 %)

cyclic dimers: THF-EO (4 %), EO_2 (1,4-dioxane) (2 %)

low quantities (about 2%) of cyclic pentamers

Numbers in parenthesis correspond to the relative intensities of signals in glc. It is evident, that the cyclic fraction is composed primarily of mixed cyclic tetramers containing 18, 16 and 14 atoms in the ring. Fragmentation pattern for THF_2-EO_2 cyclic oligomer indicates block rather than alternating structure, thus approximately 50% of cyclics contain EO-EO diads (THF_2-EO_2 and THF-EO_3 tetramers and EO_2 dimer (1,4-dioxane)). These results confirm, that for the formation of at least some cyclic oligomers, the presence of EO-EO diad is required. Indeed, analysis of the gpc curves for the copolymers obtained at 60% conversion of THF, i.e., at the conditions when there is very little of EO-EO diads and at 80% conversion, when the content of EO-EO diads is already significant indicate, that the content of cyclic fraction is considerably higher in the latter case. It should be noted, that the final M_n was the same in both cases, due to the proper adjusting of concentration of diol (initiator). The corresponding gpc curves are shown in Fig. 4.

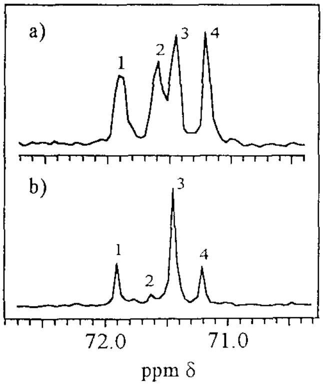


Fig.3. ^{13}C NMR spectra (OCH_2 groups) of copolymers with M_n= 1100 obtained at: a-60 % THF conv., b-80% THF conv.
1:THF-EO,2:EO-EO,3:THF-THF,4:THF-EO

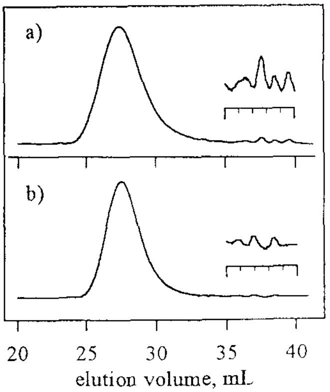


Fig. 4. GPC curves of copolymers with M_n= 1100 obtained at:
a-60 % THF conv., b-80% THF conv.

The considerably lower content of cyclic fraction at the conditions when [THF]>>[HO-]

confirms, that indeed by carrying out the process in such a way, that probability of formation of EO-EO diads is minimized, one can considerably reduce the content of cyclic fraction in the product. Formation of cyclic fraction cannot be, however, suppressed completely, because even at these conditions mixed cyclic tetramer THF_3-EO can still be formed, and, as shown by the analysis of cyclic fraction composition, this is the most abundant cyclic oligomer.

There is still one more factor influencing the probability of formation of cyclic fraction. The requirement: [THF]>>[HO-] should be formulated more precisely as: ([THF] - $[THF]_e$)>>[HO-] where $[THF]_e$ is an equilibrium concentration of THF (although in copolymerization it may be different than in homopolymerization). $[THF]_e$ decreases with decreasing temperature, thus effective concentration of THF (i.e. [THF] - $[THF]_e$) for the same [THF] is higher at lower temperature. Consequently, the content of cyclic fraction should decrease with decreasing the temperature in which copolymerization is conducted, at otherwise identical conditions. This is indeed the case, as shown by the data of Table 1.

Table 1. The dependence of the content of cyclic fraction in copolymerization of THF with EO in the presence of diols on temperature

Temperature, ^{0}C	-25	25	65
Content of cyclic fraction, % wt	3	3.5	4.5

Results indicate, that formation of cyclic oligomers in the cationic copolymerization of THF with EO cannot be avoided. The content of cyclic fraction may be, however, considerably reduced by rational design of the reaction conditions. Previously, formation of up to 10% of cyclic fraction was observed, in the copolymerization of THF with EO in the absence of diol. In the present work, by carrying out the copolymerization in the presence of diol, at low temperature and at the conditions when [THF]>>[EO] and [THF]>>[HO-], the content of cyclic fraction was reduced to ~ 3 %wt. Because cyclic fraction is composed predominantly of cyclic tetramers, which are still volatile, it may be relatively easily removed from linear product by heating in vacuum or by steam distillation. After such treatment, the content of cyclic fraction is below detection level by gpc method.

Some properties of linear telechelic THF-EO copolymers

The linear products are THF-EO copolymers with M_n close to the values calculated as $M_n = 72([THF]_0-[THF]_e)+44[EO]+62[EG]/[EG]$ (EG- ethylene glycol) and functionality: f = 2.

At room temperature, all the products are viscous liquids, with the viscosity ranging from 200 cP for M_n ~ 1000 to 2000 cP for M_n ~ 3000. Some thermal properties are given in Table 2.

Table 2. Dependence of the thermal properties of THF-EO copolymers on M_n and n ([THF]/[EO] units)

M_n, n	1600, 1.5	1600, 2.9	3100, 2.9	poly-EO	poly-THF
T_g, ^{0}C	-75	-83	-80	-65	-86
T_m, ^{0}C	-12	4	8	60	43
ΔH_m, J/g	50	48	42		

The significant depression of melting temperature and the crystallinity (relatively low values of ΔH_m) is observed for copolymers as compared with corresponding values for homopolymers.

Acknowledgment: This work constitutes a part of Ph. D. thesis of Mrs M. Bednarek and was supported by the grant from Polish State Committee for Scientific Research: KBN T09B 039 08.

REFERENCES

1. P. Dreyfuss, *"Polytetrahydrofuran"*, Gordon and Breach, New York, 1982
2. I. M. Robinson, G. Pruckmayr, *Macromolecules* **12**, 1043 (1979)
3. A. Eastham, *Adv. Polymer Sci.* **2**, 18 (1960)
4. G. Pruckmayr. T. K. Wu, *Macromolecules* **11**, 265 (1978)
5. K. Brzezinska, R. Szymanski, P. Kubisa, S. Penczek, *Makromol. Chem. Rapid Commun.* **7**, 1 (1986)
6. S. Penczek, P. Kubisa, R. Szymanski, *Makromol. Chem., Macromol. Symp.* **3.** 203 (1986)
7. S. Penczek, H. Sekiguchi, P. Kubisa, *"Activated Monomer Polymerization of Cyclic Monomers"* in *Macromolecular Design of Polymeric Materials*, K. Hatada, T. Kitayama and O. Vogl Eds., Marcel Dekker Inc., New York, 1997
8. N. Manolova, J. Libiszowski, R. Szymanski, S. Penczek, *Polymer Int.* **36**, 23 (1995)
9. K. Brzezinska, W. Chwialkowska, P. Kubisa, K. Matyjaszewski, S. Penczek, *Makromol. Chem.* **178**, 2491 (1977)
10. K. Matyjaszewski, S. Penczek, *Makromol. Chem.* **182**, 1735 (1981)
11. K. Matyjaszewski, S. Slomkowski, S. Penczek, *J. Polymer Sci., Polym. Chem. Ed.* **17**, 2413 (1979)