

*Dedicated to the memory of  
Professor Mircea D. Banciu (1941–2005)*

## POLY(ETHYLENE OXIDE-*CO*-TETRAHYDROFURAN) AND POLY(PROPYLENE OXIDE-*CO*-TETRAHYDROFURAN): SYNTHESIS AND THERMAL DEGRADATION

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Copolymers of tetrahydrofuran (THF) and ethylene oxide (EO) (poly(THF-*co*-EO) and THF and propylene oxide (PO) (poly(THF-*co*-PO) were obtained by cationic ring opening polymerization of the monomer mixture at 0°C using boron trifluoride etherate (BF<sub>3</sub>.OEt<sub>2</sub>) as the initiator. From time conversion plots it was concluded that both monomers are consumed from the very beginning of the reaction and random copolymers are obtained. For poly(THF-*co*-PO) the molar ratio of repeating units was varied from [THF]/[PO] = 1 to 10; the molar ratio of monomers in the feed corresponds to the molar ratio of repeating units in the copolymer. Thermogravimetric analysis of the copolymers revealed that both poly(THF-*co*-EO) and poly(THF-*co*-PO) decompose by ca. 50°C lower than poly(THF) and by ca. 100°C lower than poly(EO); 50% mass loss is obtained at  $T_{50} = 375^{\circ}\text{C}$  for poly(EO),  $T_{50} = 330^{\circ}\text{C}$  for poly(THF) and at  $T_{50} = 280^{\circ}\text{C}$  for both copolymers. The [THF]/[PO] ratio does not influence the decomposition temperature significantly as well. For the copolymers the activation energies of the thermal decomposition ( $E_a$ ) were determined experimentally from TGA measurements and by density functional calculations on model compounds on the B3LYP/6-31+G\* level of theory. The results, however, show that lower activation energies do not correlate with lower depolymerisation temperatures.

### INTRODUCTION

Research activities in the field of polymer chemistry mainly focus on materials with high strength and high stability toward extreme environmental conditions such as elevated temperatures, high intensity irradiation or corrosive chemicals. For some applications, however, it is desirable to have a polymeric material available that at one set of environmental conditions retains its physical properties and can be deliberately degraded in a controlled fashion by changing the conditions. In principle several schemes for chemical degradation of polymers are possible such as hydrolysis, oxidation, photolysis and thermolysis. The fields of application for degradable polymers are considerable, as for example polymer matrices for pigments or for drugs in controlled-release pharmaceuticals, polymer resists for the fabrication of integrated circuits, for lithographic processes and for solder pasts for the preparation of electrical or electronic devices.

In the present communication we focus on the preparation of thermally labile copolymers from tetrahydrofuran (THF) and ethylene oxide (EO) or propylene oxide (PO) and their depolymerisation with formation of volatile products. It is our goal to adjust the decomposition temperature of the copolymers by selecting the corresponding copolymer composition.

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## EXPERIMENTAL PART

### Materials

Tetrahydrofuran (purity > 99.8 %, Fluka) was heated over sodium/benzophenone and distilled before use. Ethylene oxide (purity > 99.8 %, Fluka) was used as received. Propylene oxide was heated over calcium hydride and distilled before use. Ethylene glycol (EG) (>99%, Aldrich) was distilled from a solution containing sodium glycolate before use. Boron trifluoride etherate (purity, distilled, Fluka) was used as received.

Polymerisations were carried out in an inert gas atmosphere. Nitrogen (Linde) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminium oxide.

### Measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 MHz and 75 MHz, respectively. Chloroform (CDCl<sub>3</sub>) was used as a solvent, and tetramethylsilane (TMS) served as an internal standard.

Gel permeation chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump (Waters 510) and a refractive index detector (ERC 7515a). The eluting solvent was tetrahydrofuran (stabilized with 2,6-di-tert-butyl-4-methylphenol, 250 mg · L<sup>-1</sup>) with a flow rate of 1 mL · min<sup>-1</sup>. Four columns with PS-DVB gel were applied: length of each column: 300 mm, diameter 8 mm, diameter of gel particles 5 µm, nominal pore width 100Å, 500Å, 10<sup>3</sup>Å and 10<sup>4</sup>Å. Calibration with polystyrene standards was used for the estimation of the molecular weights and the polydispersity.

Thermogravimetric analyses were performed on a TG 209 with a TA-System-controller TASC 414/2 and kinetic software from Netzsch. The measurements were performed in air with a heating rate of 10 K · min<sup>-1</sup>.

### Polymer synthesis

**Poly(tetrahydrofuran):** In a reactor with an automatic heat regulator, THF (100 mL) was polymerized with TfOTf (110 µL, 6.706 · 10<sup>-4</sup> mol) as the initiator at 25 °C. After a selected time *t<sub>p</sub>* the polymerisation was terminated by addition of water (50 mL). THF was removed from the reaction mixture by distillation in vacuum at 30°C. The residue was dissolved in methylene chloride washed with a 10 wt.% solution of sodium carbonate, and with water and dried over sodium sulphate. Evaporation of the solvent resulted in pure telechelic poly(THF). The results obtained are summarised in Table 1.

Table 1

Polymerisation of THF with Tf<sub>2</sub>O as the initiator<sup>a)</sup>; polymer yield, number average molecular weight and polydispersity (PMI =  $M_w/M_n$ ) are given as a function of polymerisation time.

NNo.	<i>t<sub>p</sub></i> min	Yield <sup>b)</sup> in g	$\overline{M}_n$ <sup>c)</sup>	$\overline{M}_w / \overline{M}_n$ <sup>c)</sup>
	20	3.91	13000	1.16
	40	8.98	22600	1.19
	60	14.14	32400	1.21
	80	18.58	45000	1.19
	100	22.14	54400	1.24

<sup>a)</sup> 88.90 g THF with 110 µL Tf<sub>2</sub>O; <sup>b)</sup> determined gravimetrically; <sup>c)</sup> determined by means of GPC with PS standards

### Poly(tetrahydrofuran-co-ethylene oxide)

In a reactor with an automatic heat regulator, a mixture of tetrahydrofuran and ethylene oxide (3 mL, [THF]/[EO] = 1.15) was polymerised with BF<sub>3</sub>·Et<sub>2</sub>O/EG at *T* = 0°C. After a selected time *t<sub>p</sub>* the polymerisation was terminated by addition of water. The polymer was extracted with methylene chloride, the solution washed with a 10 wt.% aqueous solution of sodium carbonate and with water, and dried over sodium sulphate. Evaporation of the solvent resulted in telechelic poly(THF-co-EO). The results obtained are summarised in Tab.2.

Table 2

Copolymerisation of THF with EO: initial conditions and polymer characteristics<sup>a)</sup>

No.	THF+EO g	BF <sub>3</sub> :OEt <sub>2</sub> µL	EG µL	<i>t<sub>p</sub></i> h	Yield <sup>b)</sup> g	[THF]/ [EO] <sup>c)</sup>	$\overline{M}_n$ <sup>d)</sup>	$\overline{M}_w / \overline{M}_n$ <sup>d)</sup>
1	2.97	18.65	8.28	1	0.82	2.14	5900	1.78
2	3.00	18.84	8.37	2	1.53	1.81	10400	1.78
3	3.05	19.15	8.50	3	2.15	1.43	10800	1.85
4	3.12	19.59	8.70	4	2.28	1.35	13400	1.82
5	3.09	19.41	8.62	5	2.70	1.25	13600	1.88
6	2.95	18.53	8.23	6	2.61	1.21	13500	1.84

<sup>a)</sup> The monomer molar ratio was THF/EO = 1.15; <sup>b)</sup> determined gravimetrically; <sup>c)</sup> ratio of repeating units in the copolymer, determined by means of <sup>1</sup>H NMR spectroscopy; <sup>d)</sup> determined by means of GPC with PS standards

**Poly(tetrahydrofuran-co-propylene oxide)**

In a reactor with an automatic heat regulator, a mixture of tetrahydrofuran and propylene oxide (3 mL, [THF]/[PO] = 1.08) was polymerised with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  as the initiator at  $T = 0^\circ\text{C}$ . After a selected time  $t_p$  the polymerisation was terminated by addition of water. The polymer was extracted with methylene chloride, the solution washed with a 10 wt.% aqueous solution of sodium carbonate, and with water and dried over sodium sulphate. Evaporation of the solvent resulted in telechelic poly(THF-co-PO). The results obtained are summarised in Table 3.

Table 3

Copolymerisation of THF with PO<sup>a)</sup>: initial conditions and polymer characteristics

No.	$t_p$ min	Yield <sup>b)</sup> in g	[THF]/[PO] <sup>c)</sup>	$\overline{M}_n$ <sup>d)</sup>	$\overline{M}_w / \overline{M}_n$ <sup>d)</sup>
1	0.5	0.60	1.49	9600	1.29
2	1	1.20	1.47	14400	1.41
3	2	1.96	1.27	15500	1.51
4	3	2.52	1.19	15100	1.62
5	4	2.60	1.28	15200	1.66
6	5	2.77	1.19	15300	1.55
7	6	2.71	1.15	14600	1.55

a) The monomer molar ratio was THF/PO = 1.08 (2.78 g monomer mixture was polymerised with 17.50  $\mu\text{L}$   $\text{BF}_3 \cdot \text{OEt}_2$ ); b) determined gravimetrically; c) ratio of repeating units in the copolymer, determined by means of  $^1\text{H}$  NMR spectroscopy; d) determined by means of GPC with PS standards.

To obtain poly(tetrahydrofuran-co-propylene oxide)s with different compositions polymerisations were performed with selected [THF]/[PO] ratios. The results of these polymerisations are summarized in Table 4.

Table 4

Synthesis of poly(THF-co-PO) samples of various composition: initial conditions and polymer characteristics

No.	THF in mL	PO in mL	$\text{BF}_3 \cdot \text{OEt}_2$ in $\mu\text{L}$	Yield <sup>a)</sup> in g	[THF]/ [PO] <sup>b)</sup>
a	2.43	2.10	24.5	3.90	1.58
b	3.24	1.40	25.4	4.04	2.78
c	3.65	1.05	25.8	4.11	3.94
d	3.89	0.84	26.1	4.10	5.07
e	4.06	0.70	26.3	3.87	6.34
f	4.17	0.60	26.4	3.75	7.29
g	4.26	0.53	26.5	3.48	8.34
h	4.33	0.47	26.6	3.54	9.23
i	4.38	0.42	26.6	3.20	10.78
j	4.42	0.38	26.7	3.20	11.67

a) determined gravimetrically; b) molar ratio of repeating units in the copolymer, determined by means of  $^1\text{H}$  NMR spectroscopy; c) determined by means of GPC with PS standards

**Computational details**

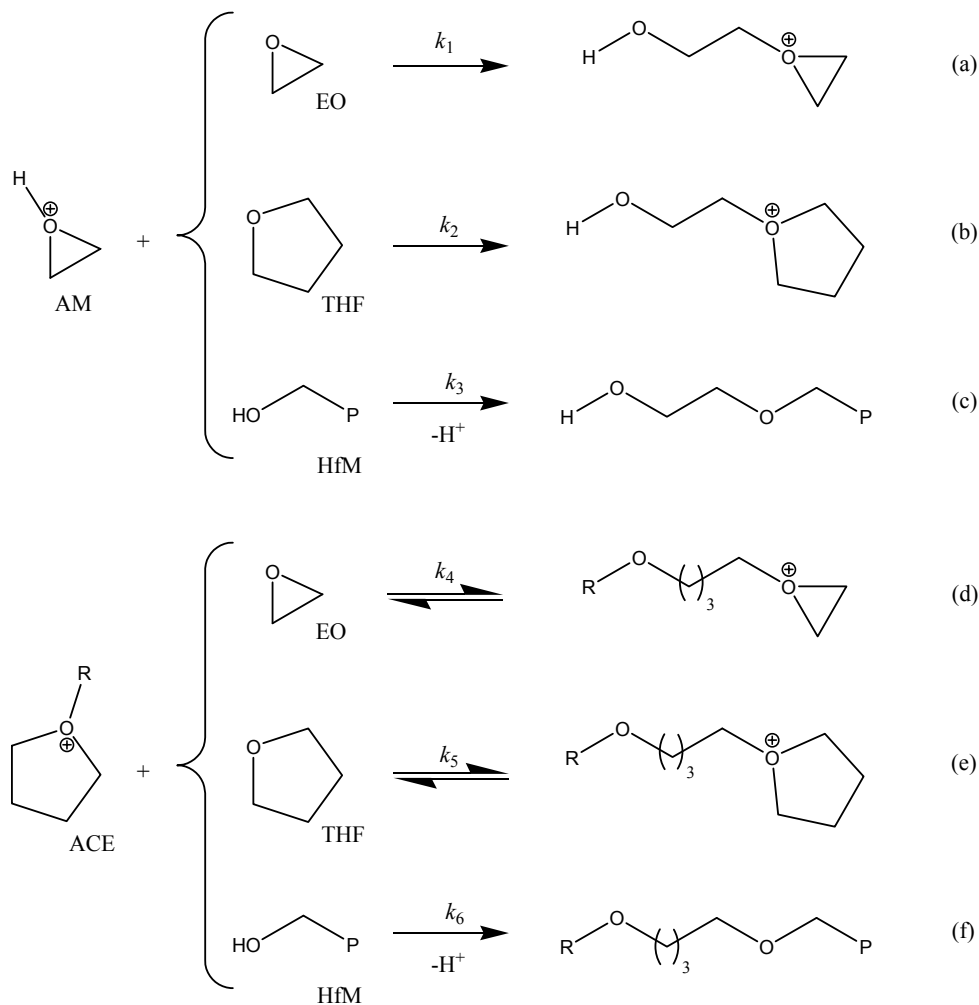
Density functional calculations were carried out using the gaussian98 program package (revision A11) with the B3LYP functional and the 6-31+G\* basis set for all elements involved. All geometries obtained were checked successfully by frequency calculations to ensure that minima (zero imaginary frequencies) or transition states of order one (one imaginary transition state) were obtained. PM3 optimisations as well as HF/6-31+G\* single point energy calculations were carried out using the Hyperchem program package (version 6.03). [Hyperchem]

**RESULTS AND DISCUSSION**

For the cationic ring opening polymerisation of cyclic ethers<sup>1-3</sup> two mechanisms are discussed in the literature: the “active chain end” (ACE)<sup>4,5</sup> and the “active monomer” (AM) mechanism.<sup>6</sup> According to the first mechanism the active species is located at the end of the growing chain while according to the second

one the monomer is activated for a nucleophilic attack. The ring opening polymerisation of THF is the most rigorously studied cationic ring opening polymerisation, following the ACE mechanism. The propagation step involves the nucleophilic attack of a monomer molecule at the methylene group in  $\alpha$ -position to the oxygen atom of the activated chain end (ACE, with a tertiary oxonium ion located at the chain end). (Scheme 1, e). The AM mechanism operates in cationic ring opening polymerisation of ethylene oxide with a Brønsted acid as the catalyst and an alcohol or a diol as the initiator. In the propagation step the protonated monomer (the activated monomer, AM, with a secondary oxonium ion) reacts with the hydroxyl groups of the initiator or of growing chains with formation of a homologous species and regenerating the proton which may protonate the next monomer (Scheme 1, c). In copolymerisation of THF with oxiranes these two mechanisms coexist and lead to a copolymer the microstructure of which is defined by the catalyst used and the polymerisation conditions applied. Characteristic of the copolymerization of THF with EO is, (i) a coexistence of the AM and the ACE mechanism (coexistence of tertiary and secondary oxonium ions). (ii) All reactions with secondary oxonium ions are irreversible, while those of the tertiary oxonium ions with the monomers are reversible. (iii) At low EO concentration the reactions (a) and (d) in Scheme 1 can be neglected.

The copolymerisation of tetrahydrofuran with ethylene oxide was studied mainly by the group in Lodz/Poland.<sup>7-9</sup> These authors polymerised EO and THF using ethylene glycol as the initiator and as the catalyst  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  at temperatures from  $-30$  to  $+60^\circ\text{C}$ . The kinetics of copolymerisation was studied, a mechanism of copolymerisation was proposed, and the influence of copolymerisation conditions on the composition and microstructure of the copolymers was estimated.

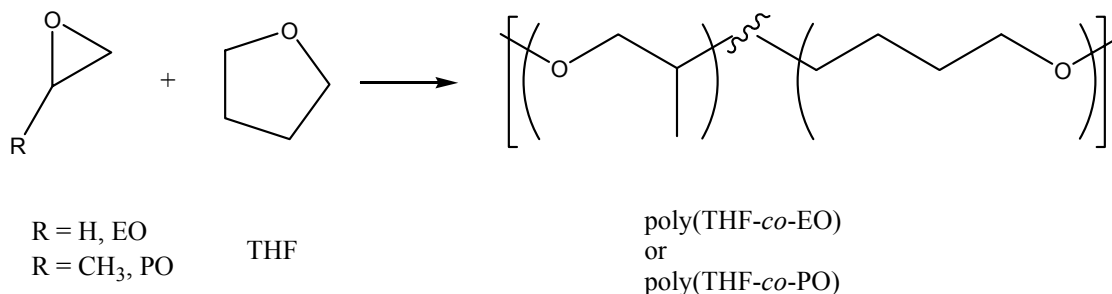


Scheme 1 – Reactions of the activated monomer (AM with a secondary oxonium ion) and the activated chain end (ACE with a tertiary oxonium ion) in the copolymerization of EO with THF.

The copolymerisation of THF with propylene oxide was studied in several laboratories under variable condition. A group from Peking University determined the reactivity ratio of the monomers by using a mixture of acids as the initiator ( $\text{H}_2\text{SO}_4 \cdot \text{SO}_3 \cdot \text{HClO}_4$ ),<sup>10</sup> or an acid chloride in combination with silver perchlorate ( $\text{AgClO}_4$ ).<sup>11</sup> The influence of the monomer ratio, polymerisation temperature was studied for the photochemically initiated copolymerisation of THF and PO in the presence of glycols by a Russian group. The initiator used was triphenylsulfonium hexafluorophosphate.<sup>12</sup> The kinetics of the copolymerisation of THF with PO using antimony pentachloride in combination with 1,2-ethanediol, 1,3-propanediol, 1,2-propanediol, and 1,3-butanediol as initiator was studied by Blanchard *et al.*;<sup>13</sup> a mechanism of cocatalyst effects based on ion-pair solvation was suggested. It is important to note that no poly(THF) is formed in the absence of propylene oxide which readily homopolymerises.<sup>14</sup> The same authors used  $\text{BF}_3$  etherate and 1,2,3-propanetriol as catalyst and cocatalyst, respectively, to copolymerise THF and PO.<sup>15-17</sup> A Russian group studied the copolymerisation of THF with PO in the presence of the  $\text{BF}_3$ -THF complex (0.05 to 0.5 mol%) as a catalyst and ethylene glycol as the initiator in the temperature range of  $-10^\circ$  to  $+20^\circ\text{C}$ . With a PO/THF molar ratio in the feed of 67/33 a 100% yield of the copolymer was obtained. An increase in THF concentration lead to a decrease in copolymer yield.<sup>18-19</sup>

### Polymer synthesis

In this work the copolymers of tetrahydrofuran (THF) with ethylene oxide (EO) and propylene oxide (PO) were prepared by cationic polymerization of the monomer mixture at a temperature of  $T = 0^\circ\text{C}$  (Scheme 2).



Scheme 2 – Copolymerisation of THF with EO or PO by means of cationic polymerization.

Copolymerisation experiments of THF and EO were performed using a 1:1 molar mixture of boron trifluoride etherate ( $\text{BF}_3 \cdot \text{OEt}_2$ )/ethylene glycol (EG) as initiating system. Copolymerisation of THF with PO was performed using only  $\text{BF}_3 \cdot \text{OEt}_2$  as the initiator. It should be mentioned that under these conditions THF/EO did not polymerise. All polymerisation reactions were terminated by addition of water. During work-up the initiator was carefully removed by washing the polymer solution in methylene chloride with aqueous sodium carbonate solution. The polymers were obtained as colourless highly viscous oils.

### Preparation of Poly(THF-co-EO)

In order to obtain information on the microstructure of the copolymers a time conversion analysis was performed with an approx. equimolar monomer mixture THF/EO. The exact composition of the monomer mixture was determined by means of  $^1\text{H}$  NMR spectroscopy.

Six samples were polymerized for 1 to 6 h. The molar ratio of repeating units in the copolymers was determined by means of  $^1\text{H}$  NMR spectroscopy. Figure 1 shows the  $^1\text{H}$  NMR spectra of both the mixture of monomers and the copolymer. The  $^1\text{H}$  NMR spectrum of the copolymer shows the signals of THF repeating units at  $\delta = 1.62$  ppm (4H) and all other methylene signals adjacent to oxygen atoms at  $\delta = 3.40 - 3.65$  ppm. These complex signal patterns are due to different chemical shifts of different triads (THF-THF-THF; EO-THF-THF; THF-EO-THF; EO-EO-THF; EO-THF-EO; EO-EO-EO). From the molar ratio of repeating units and the polymer yield the conversion of each monomer was calculated. The time conversion plots are shown in Figure 2.

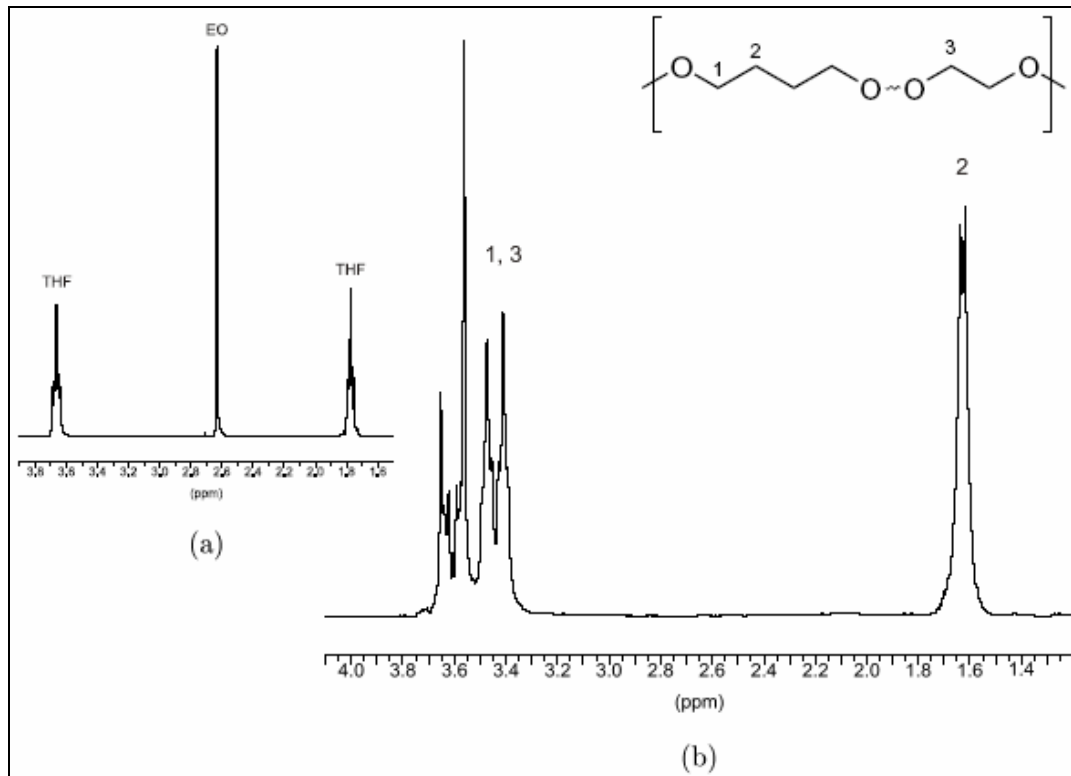


Fig. 1 – <sup>1</sup>H NMR spectra (in CDCl<sub>3</sub>) of (a) the monomer mixture and of (b) poly(THF-co-EO). (Polymerization conditions: T = 0°C, t = 6h).

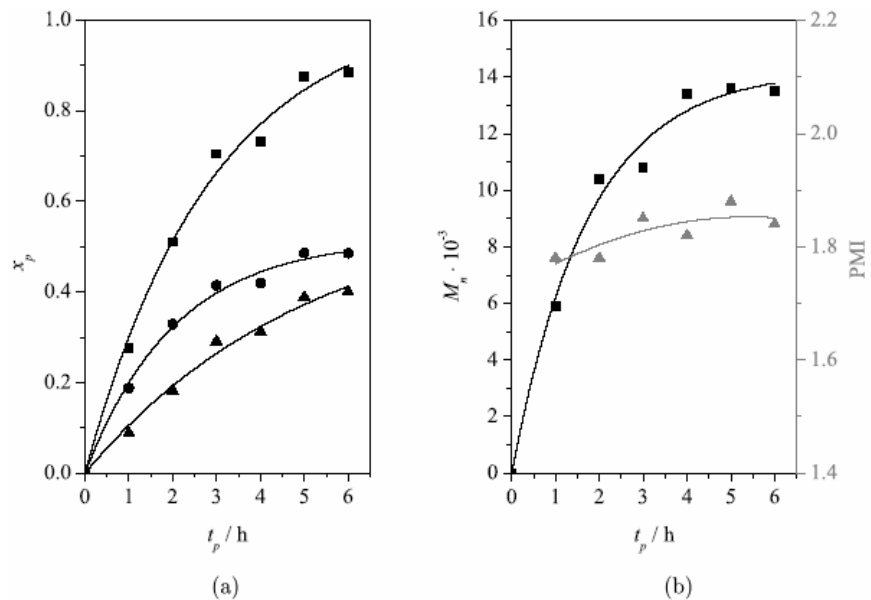


Fig. 2 – (a) Conversion (x<sub>p</sub>) vs. time: over-all conversion (■), conversion of THF (●), conversion of EO (▲) and (b) Number average molecular weight (M<sub>n</sub>) (■) and polydispersity (PMI) (▲) vs. time. Polymerisation conditions: molar ratio THF/EO = 1.15, initiating system I: F<sub>3</sub>OEt<sub>2</sub> / EG = 1 ; [I] = 4.30 × 10<sup>-3</sup> mol/L.

Both monomers are consumed from the very beginning; in accordance with the monomer ratio in the feed, the conversion of THF is always larger than the conversion of EO (Figure 2a). After 6 h a conversion of 90% is obtained. The final composition of the copolymer corresponds to a molar ratio of monomer units

of THF/EO = 1.21 which is slightly higher than the ratio in the feed THF/EO = 1.15. From this result it is concluded that a random copolymer poly(THF-co-EO) is obtained. We have studied the dependence of the molecular weight on time by means of GPC (with PS-standards) (Figure 2b).  $M_n$  increases continuously with time and reaches a value of 13.500 after 6 h. The polydispersity has a value of  $1.8 < M_w/M_n < 1.9$  which is consistent with the coexistence of the AM and ACE mechanism.

### Preparation of Poly(THF-co-PO)

The copolymerisation of THF and PO was performed in analogy to the polymerisation of THF and EO, however, without the use of ethylene glycol in the initiating system. The initial molar monomer ratio was determined by means of NMR analysis of the monomer mixture to be  $[THF]/[PO] = 1.08$ . The copolymer obtained after 6 h (Figure 3) reveals characteristic resonance lines for the methyl groups of the PO repeating units at  $\delta = 1.31$  ppm, the central methylene groups of THF at  $\delta = 1.62$  ppm, and the methylene respectively methine groups of THF and PO adjacent to the oxygen atom as a complex signal at  $\delta = 3.2$ -3.8 ppm.

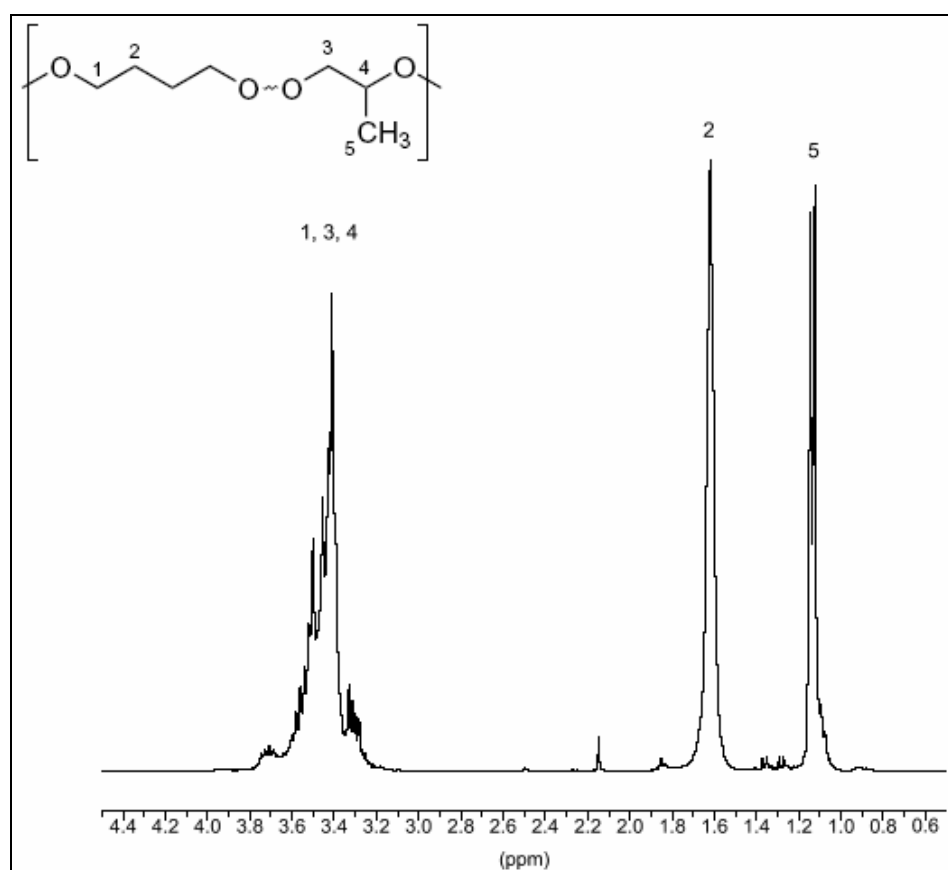


Fig. 3 -  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$ ) of poly(THF-co-PO). (Polymerization conditions:  $T = 0^\circ\text{C}$ ,  $t = 6\text{h}$ ).

The dependence of the monomer conversion on time is shown in Figure 4a. Both monomers are consumed from the very beginning; in correspondence with the monomer ratio in the feed the conversion of THF is always larger than the conversion of PO. After 6 h complete conversion of the monomers is observed. The ratio of repeating units in the copolymer is  $[THF]/[PO] = 1.11$  and hence close to the ratio of the monomers in the feed.

The dependence of  $M_n$  on time shows that after 1 h a value of  $M_n = 15000$  is reached which remains constant till complete conversion. This major difference between the copolymerisation of THF with EO and THF with PO is a consequence of the different initiating systems used.

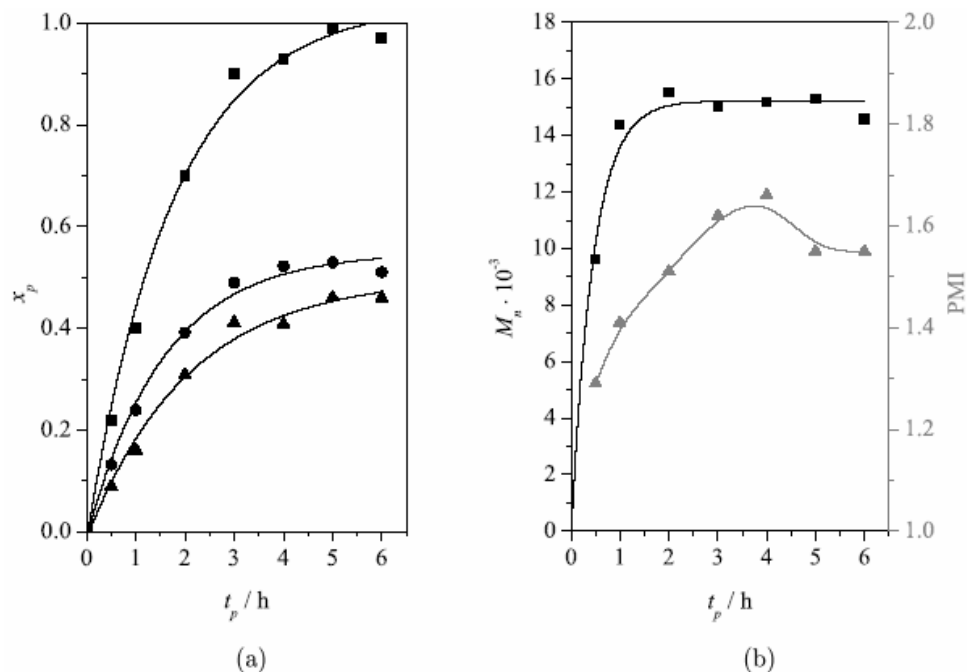


Fig. 4 – (a) Conversion ( $x_p$ ) vs. time: over-all conversion (■), conversion of THF (●), conversion of PO (▲) and (b) Number average molecular weight ( $M_n$ ) (■) and polydispersity (PMI) (▲) vs. time. Polymerisation conditions: THF/PO = 1.08, initiator (I):  $\text{BF}_3\text{OEt}_2$ ;  $[\text{I}] = 4.30 \times 10^{-3}$  mol/L.

Copolymers of THF and PO with different composition were prepared according to the above described procedure. Table 5 shows that with increasing the molar ratio  $[\text{THF}]/[\text{PO}]$  in the feed the overall conversion decreases from 100% to 75% while the  $M_n$  value of the polymer obtained after 6h increases from 15.100 to 39.500. At high THF content in the feed the polymer yield is low because of the increasing concentration of THF at equilibrium. The decrease in molecular weight with increasing PO concentration points to the higher probability of chain transfer reactions when PO active species are present.

Table 5

Poly(THF-co-PO) obtained by copolymerization of THF and PO in different molar ratio using  $\text{BF}_3\text{OEt}_2$  as the initiator. ( $T = 0^\circ\text{C}$ ,  $t_p = 6$  h,  $[\text{I}] = 4.30 \times 10^{-2}$  mol  $\cdot$  L $^{-1}$ ).

P(THF-co-PO)	$[\text{THF}]/[\text{PO}]^{\text{a}}$ repeating units	Yield $^{\text{b}}$ in %	$M_n^{\text{c}}$	$M_w/M_n^{\text{c}}$
<b>a</b>	1.6	100	15100	1.50
<b>b</b>	2.8	100	22800	1.46
<b>c</b>	3.9	99	24600	1.53
<b>d</b>	5.1	98	29100	1.54
<b>e</b>	6.3	92	32100	1.58
<b>f</b>	7.3	89	33300	1.55
<b>g</b>	8.3	83	34900	1.56
<b>h</b>	9.2	84	36100	1.56
<b>i</b>	10.8	75	37000	1.60
<b>j</b>	11.7	75	39500	1.60

<sup>a)</sup> Determined by means of  $^1\text{H-NMR}$  spectroscopy; <sup>b)</sup> determined gravimetrically; <sup>c)</sup> determined by means of GPC, with polystyrene standards.



### Thermal degradation of poly(THF-co-EO) and poly(THF-co-PO)

The thermal degradation of the copolymers of THF with EO and with PO was investigated by means of thermogravimetric analysis (TGA) and by means of density functional calculations. A poly(THF) sample was prepared according to the literature (cf. experimental part) and was used for comparison reasons. The TGA results obtained from poly(THF-co-EO) (molar ratio of the repeating units  $[\text{THF}]/[\text{EO}] = 1.21$ ) and poly(THF-co-PO) (molar ratio of the repeating units  $[\text{THF}]/[\text{PO}] = 1.11$ ) essentially show no difference (Figure 5).

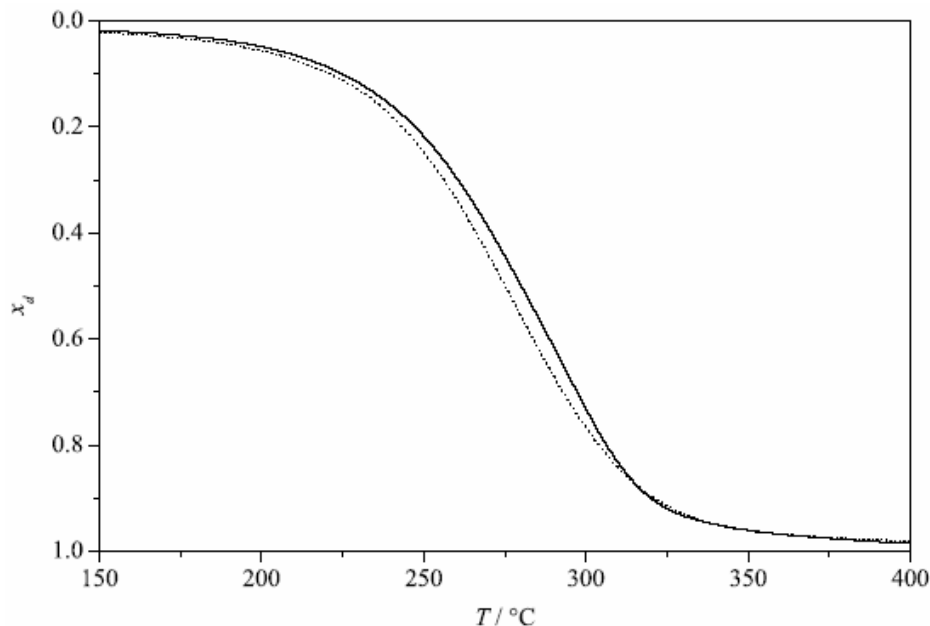


Fig. 5 – Conversion ( $x_d$ ) of poly(THF-co-EO) and poly(THF-co-PO) into volatile products as a function of temperature (heating rate  $10 \text{ K}\cdot\text{min}^{-1}$ ).

In Figure 5 the conversion ( $x_d$ ) of the polymers into volatile products ( $x_d = m_T/m_0$ , with  $m_T$  the remaining mass at temperature  $T$ ,  $m_0$  initial mass) is shown. Both copolymers depolymerise in the temperature range of 225 to 325 °C. At a temperature of 280 °C, 50% of the material is depolymerised; this temperature will be noted as  $T_{50}$ . Compared to poly(THF) or poly(EO) the value of  $T_{50}$  is lower by ca. 50 °C resp. ca. 100 °C. This means that the presence of both tetramethylene-oxy ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$ ) and ethylene-oxy or 1,2-propylene-oxy ( $-\text{CH}_2-\text{CHR}-\text{O}-$ ) repeating units in the polymer chain decreases the stability of the chain. However, no difference is observed for ethylene-oxy and propylene-oxy units.

In order to examine the influence of the concentration of the repeating units on the thermal degradation, samples of poly(THF-co-PO) with a range of molar ratio  $1.5 < [\text{THF}]/[\text{PO}] < 11.7$  were studied by means of TGA. The conversion to volatile products as a function of temperature at a heating rate of  $10 \text{ K}\cdot\text{min}^{-1}$  is shown in Figure 6.

In all cases depolymerisation starts at 225 °C and at 375 °C quantitative decomposition is obtained. The  $T_{50}$  values of the samples show no systematic change with composition of the copolymers; the values of the samples with a molar ratio of  $1.5 < [\text{THF}]/[\text{PO}] < 6.4$  (solid lines in Figure 6) are distributed in the same manner as the values of the samples with  $7.2 < [\text{THF}]/[\text{PO}] < 11.7$  (dotted lines in Figure 6). As a consequence of this investigation it was concluded that the composition of the copolymers in the range studied has no influence on the polymer stability. The observed differences in the thermal stability of the samples are attributed to deviations due to slightly changing conditions in the measuring conditions and in the sample preparation (the fineness of the material used, residual catalyst, etc.).

What is the explanation for the decrease of the thermal stability from poly(THF) to poly(THF-co-EO) and poly(THF-co-PO), why is there no difference in the stability for different propylene oxy ( $-\text{C}_\beta\text{H}_2-\text{C}_\alpha\text{H}(\text{CH}_3)-\text{O}-$ ) repeating units and why is there no difference in thermal stability of the copolymers of THF with EO and with PO? These are some of the questions which will be addressed in the final part of this work. Two working hypotheses were followed:

(i) The decrease in the stability of the copolymers is due to the  $C_{\alpha}$ -O bond and the  $C_{\beta}$ -O bond of the ethylene-oxy repeating unit. Upon cleavage of one of these C-O bonds an active chain is generated leading to a further degradation following a zip mechanism.

(ii) The formation of cycles upon decomposition of poly(THF-co-PO) has a lower activation energy than the formation of cycles from poly(THF). This becomes evident from activation energies and reaction enthalpies determined from TGA experiments and from ab initio density functional calculations.

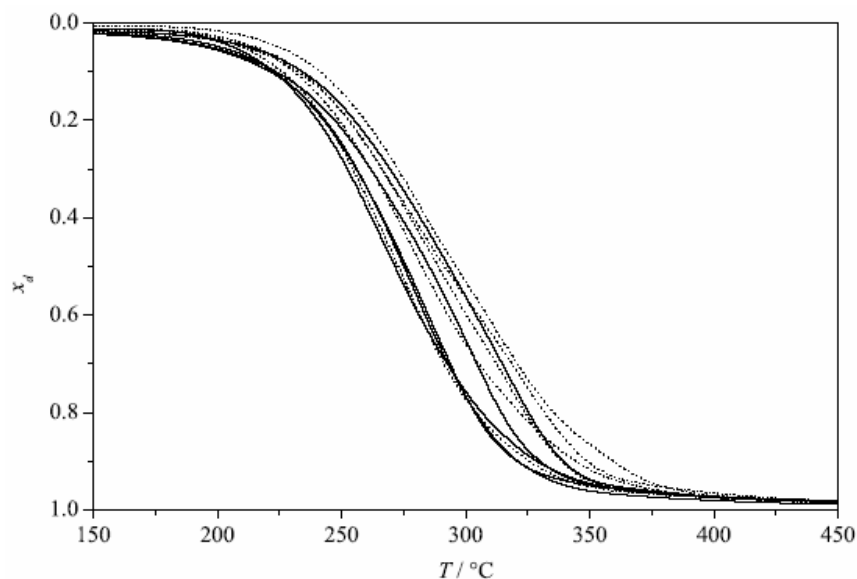


Fig. 6 – Conversion ( $x_d$ ) of poly(THF-co-PO) samples into volatile products as a function of temperature. (An assignment of the curves to a specific polymer is not relevant, solid lines:  $1.5 < [\text{THF}]/[\text{PO}] < 6.4$ ; dotted lines:  $7.2 < [\text{THF}]/[\text{PO}] < 11.7$ ); heating rate  $10 \text{ K}\cdot\text{min}^{-1}$ .

The activation energy for the thermal degradation of poly(THF-co-EO) and poly(THF-co-PO) samples with a molar ratio of monomer units close to 1 was determined from TGA measurements with heating rates of 1, 3, 5, 7, 10, 15, and  $20 \text{ K}\cdot\text{min}^{-1}$  using the two well established models of Friedman and of Ozawa-Flynn-Wall. The results are shown in Figure 7.

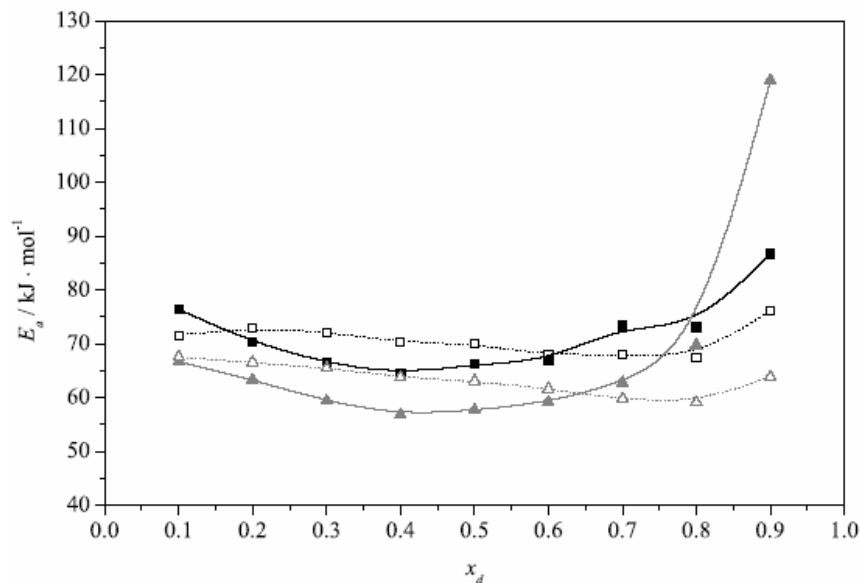


Fig. 7 – Activation energies calculated according to Friedman (■, ▲) and Ozawa, Flynn-Wall (□, Δ) as a function of conversion to volatile products for poly(THF-co-EO) (■, □) and poly(THF-co-PO) (▲, Δ).

In the conversion range of  $0.1 < x_d < 0.8$ ,  $E_a$  is almost constant for poly(THF-*co*-EO), at higher conversion an increase of the activation energy is observed. The arithmetic average value obtained with the Friedman model is  $68.6 \text{ kJ}\cdot\text{mol}^{-1}$  and according to the Ozawa-Flynn-Wall model  $70.1 \text{ kJ}\cdot\text{mol}^{-1}$ . For poly(THF-*co*-PO) the shape of the curves in Figure 7 looks similar. The values of  $E_a$ , however, are by 8 to 10  $\text{kJ}\cdot\text{mol}^{-1}$  lower for both models. The arithmetic average values are  $68.3 \text{ kJ}\cdot\text{mol}^{-1}$  and  $63.3 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively, which are very close to the values obtained for the depolymerisation of poly(THF)  $61.0 \text{ kJ}\cdot\text{mol}^{-1}$  and  $62.6 \text{ kJ}\cdot\text{mol}^{-1}$ .

### Density functional calculations

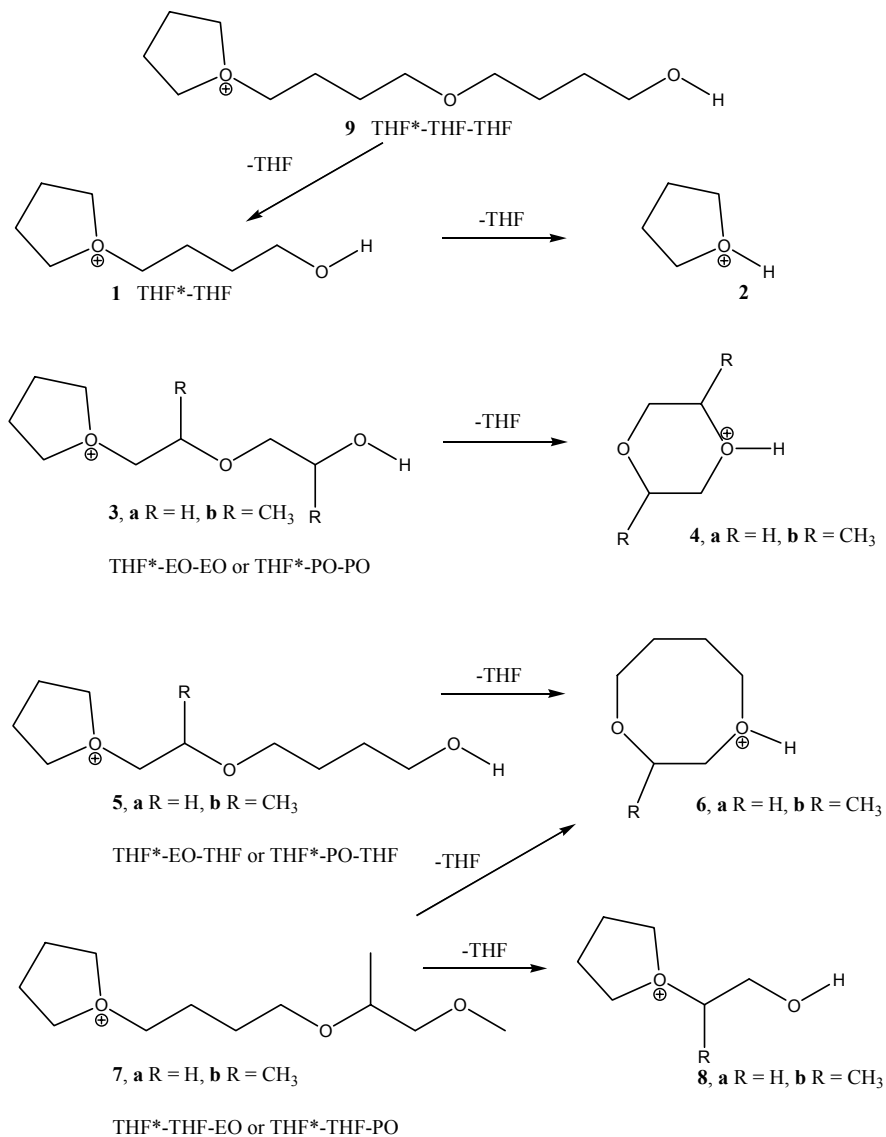
In order to better understand the mechanism of the depolymerisation and - more important - to find a potential relation to the results obtained by means of thermogravimetric analysis we carried out density functional calculations on model compounds on the B3LYP/6-31+G\* level of theory.

For the depolymerisation of poly(THF) we used the model compound **1** as the reactant for our calculations (Scheme 3). Two reaction paths can easily be imagined: (i) the oxonium ion in **1** reacts via an  $S_N2$ -type reaction to give a transition state, which then is cleaved resulting in THF and **2**. To form the final products - THF and **2** -  $+61.49 \text{ kJ}\cdot\text{mol}^{-1}$  are needed which is in full agreement with the experimentally determined values of  $61.0 \text{ kJ}\cdot\text{mol}^{-1}$  (Friedman-model)  $62.6 \text{ kJ}\cdot\text{mol}^{-1}$  (Ozawa-Flynn-Wall-model). The experimentally derived activation energies agree quite well with those calculated for the assumed model reactions.

Encouraged by these results we investigated the depolymerisation mechanisms of poly(THF-*co*-EO) and poly(THF-*co*-PO) by density functional calculations on model compounds on the B3LYP/6-31+G\* level of theory.

It is interesting to note that both poly(THF-*co*-EO) and poly(THF-*co*-PO) are thermally degraded by roughly  $50^\circ\text{C}$  lower than poly(THF). Analyses of samples with different molar ratios of monomer units revealed mean activation energies of  $68.55$  and  $68.26 \text{ kJ}\cdot\text{mol}^{-1}$  for poly(THF-*co*-EO) and poly(THF-*co*-PO), respectively, according to the Friedman-model, whereas the values according to the Ozawa-Flynn-Wall-model are  $70.14$  and  $63.31 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively. Further it turned out, that the composition of the copolymers has no influence on the thermal stability of these copolymers. Decisive for the thermal degradation, which is by ca.  $50^\circ\text{C}$  lower than for pure poly(THF), is the fact that EO or PO is present in these polymers.

Different depolymerisation mechanisms can be envisioned using model compounds as before. Scheme 3 lists the different possible starting species of the depolymerisation; all have an active tetramethylene oxonium species (THF\*) followed by two different repeating units. In compounds **3a** and **3b** two ethylene-oxy repeating units are present in sequence, with a tetramethylene oxonium end group. These compounds can react to give **4a** and **4b**, respectively and in each case one THF molecule is released. Alternatively, a THF ethylene- oxy sequence with a tetramethylene oxonium end group as in **5a** and **5b** can react to give products as **6a** and **6b**, respectively. The third alternative is an ethylene-oxy THF sequence with a tetramethylene oxonium end group as in **7a** and **7b**. These compounds can react either to yield **6a,b** or to **8a,b**, thus forming either an eight membered or a five membered oxonium ion, respectively. Also for reactions of compounds **3** and **5** to **4** and **6**, it can be imagined that upon depolymerisation THF is formed together with a three membered oxonium ion ring. This reaction is not listed in Scheme 4, since our calculations using **3a** on the B3LYP/6-31+G\* level of theory have shown, that the activation energy ( $+157.13 \text{ kJ}\cdot\text{mol}^{-1}$ ) is by far too high to be considered. To save computation time the geometries of other compounds were calculated on the semiempirical PM3 level of theory, and the geometries obtained were used as input for HF/6-31+G\* single point energy calculations (to check if this method is valid, reactions of **3a** to **4a** and reaction of **5a** to **6a** were also calculated on the B3LYP/6-31+G\* level of theory and it turned out, that the HF-6-31G\*//PM3 method is sufficient). The results are summarised in Table 6.



Scheme 3 – Model compounds and model reactions for the thermal depolymerisation of random copolymers of THF and EO or THF and PO, respectively.

Table 6

Reaction enthalpy  $\Delta H$  for selected model reactions

Reaction	R	Level	$\Delta H$ kJ/mol
9 → 1		HF/6-31+G**/PM3	59.12
1 → 2		B3LYP/6-31+G**	61.49
1 → 2		HF/6-31+G**/PM3	62.66
3a → 4a	H	B3LYP/6-31+G**	66.36
3a → 4a	H	HF/6-31+G**/PM3	61.38
3b → 4b	CH <sub>3</sub>	HF/6-31+G**/PM3	41.51
5a → 6a	H	B3LYP/6-31+G**	100.72
5a → 6a	H	HF/6-31+G**/PM3	115.15
5b → 6b	CH <sub>3</sub>	HF/6-31+G**/PM3	88.40
7a → 8a	H	HF/6-31+G**/PM3	59.88
7b → 8b	CH <sub>3</sub>	HF/6-31+G**/PM3	54.03
7a → 6a	H	HF/6-31+G**/PM3	122.75
7b → 6b	CH <sub>3</sub>	HF/6-31+G**/PM3	98.36

With the exception of the reaction to the eight membered oxonium ion rings **6**, all reactions have activation energies very similar to the ones obtained experimentally. This is reasonable, since in the experiment all model reactions will occur at the same time, which leads to a convolution of activation energies. In other words, if the experimentally obtained activation energies are similar to the calculated ones, a mixture of the model reactions mentioned is at work during depolymerisation.

The experimentally obtained activation energies are fairly constant up to conversions of ca. 80%. Then they rise moderately in the case of poly(THF-co-EO) and a little to significantly in the case of poly(THF-co-PO), with the Friedman-model leading to more pronounced increases.

This is reflected qualitatively in the quantum chemical calculations. Significantly higher amounts of energy are needed to form the eight membered oxonium ion ring **6**, with the EO derivative being even richer in energy than with the PO derivative. From the increase in experimentally observed activation energies at conversions over 80% we conclude, that in the final stages of depolymerisation the number of eight membered oxonium ion rings formed increases significantly, i. e. the reaction mechanism changes somewhat to the formation of these cycles.

## CONCLUSIONS

Random copolymers of THF and ethylene oxide or propylene oxide were obtained by cationic polymerization using  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  as the initiator. These polymers were thermally degraded to result in volatile products. The potential for applications will be studied in the future.

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