

The cationic ring-opening polymerization of 7-tetradecene oxide with methyl trifluoromethanesulfonate. An investigation of the mechanism and the kinetics by means of ^1H , ^{13}C and ^{19}F NMR

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Abstract

The polymerization of a mixture of *cis* (ca. 30%) and *trans* (ca. 70%) isomers of 7-tetradecene oxide (7-TDO) with methyl trifluoromethanesulfonate (methyl triflate) as initiator has been investigated. The main reaction products afforded during the polymerization were a linear polyether, a cyclic dimer [2,3,5,6 tetra(*n*-hexyl)dioxane], and 7-tetradecanone. The ketone is formed both via pinacol rearrangement of the monomer and a transfer reaction when all the monomer is consumed, and is favoured by an increase of temperature. Kinetic studies on the ring opening polymerization of this system were performed by means of ^1H and ^{19}F NMR spectroscopies. Approximate rate constants of initiation (k_i) for the *cis* and the *trans* isomers were determined at 298, 314 and 329 K in bulk, and at 298 K in C_6D_6 . The reaction time of the *cis* isomer is faster than that of the *trans* isomer, with an initial molar reactivity ratio of about 11:1 at 298 K, and of about 7:1 at 329 K (in bulk). The activation energies of the initiation reaction for the *cis* and the *trans* isomers were calculated to be 59 and 73 kJ/mol, respectively. By means of ^1H -, ^{19}F - and ^{13}C -NMR the structure of the propagating species is reasonably well identified as an oxonium macroion rather than a linear triflic macroester. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Cationic polymerization; Substituted oxirane; Superacid esters

1. Introduction

The cationic polymerization of cyclic ethers promoted by superacids and their derivatives has been investigated in great detail in recent years [1,2]. The mechanisms of the polymerization of tetrahydrofuran (THF) and ethylene oxide initiated by trifluoromethanesulfonic acid (triflic acid) and its alkyl esters (alkyl triflates) have received wide attention, but much less has been reported on the polymerization of disubstituted oxiranes with these initiators.

By means of extensive NMR investigations, two propagating molecules have been identified in the polymerization of THF, i.e. a cyclic oxonium ion and a linear (covalent) macroester; these two species are in equilibrium, and it was found that the equilibrium position mainly depends on the polarity of the medium [3–7].

In the polymerization of ethylene oxide, a single

propagating species was observed and was assigned to the covalent macroester [8]. It was proposed that this was due to the relative instability of the strained oxonium ion derived from the oxirane ring. More recently however, the same authors found experimental evidence for the involvement of cyclic oxonium species in the reaction [9]. These active species have been directly monitored by ^1H - [9–11] and ^{13}C -NMR [4,6,12] or indirectly by ^{19}F -NMR [6,10,13,14].

The polymerization products are mainly represented by a mixture of linear polymer (polyether) and cyclic oligomers. Their relative ratio depends on the reaction conditions as well as on the ring size of the cyclic monomer. Cyclic oligomers (mainly dimer and tetramer) are formed via the ‘backbiting’ mechanism, an intramolecular reaction which is known to occur in the cationic polymerization of several heterocyclic rings [12,11,15]. In the case of oxirane, the cyclodimerization, leading to the stable 1,4-dioxane, is usually very effective, and under certain conditions it may lead to complete depolymerization of the linear polyether [8].

In the cationic polymerization of substituted epoxides, the reaction products greatly depend on the stability of the

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intermediates in the propagation step. The stability of the propagating species may be determined by several factors, namely whether they are secondary or tertiary oxonium ions, the nature of the counterions, the solvents and the electronic and steric effects of the substituents on the epoxide ring.

Kawakam et al. [16] studied the polymerization of 2,3-epoxybutane and other substituted oxiranes by triflic acid and its derivatives. It was reported that the principal chain carrier would be the oxonium ion due to the instability of the macroester species. Depending on the nature of the initiator and the solvent used, varying amounts of 1,4-dioxanes, 1,3-dioxolanes, methyl ethyl ketone and higher cyclic oligomers were formed. The ketone and the 1,3-dioxolanes are formed as a consequence of a hydrogen transposition. Both the triflic acid and its esters give similar amounts of methyl ethyl ketone and cyclodimers. This fact indicates the importance of the counterion in the determination of the reaction products rather than whether the propagating species is a secondary or tertiary oxonium ion. The electronic effects of the substituents on the epoxide ring are also important factors in determining the reaction products [16]. The electron-donating substituents may easily complete the shift of the hydride ion in the cyclic three-membered oxonium ion intermediate, thus causing its ring-opening to form the oxycarbenium ion which would be responsible for producing dioxolane dimers. On the other hand, epoxides with electron-withdrawing groups such as epichlorohydrin are resistant to isomerization and propagate essentially through a tertiary oxonium ion. Hence the main products of polymerization are dioxane-type dimers and cyclic polyether-type tetramers even with triflic acid as initiator.

In the polymerization of cyclohexene oxide [16], high polymers are exclusively yielded, probably due to the slow rate of the backbiting reaction resulting from the bulky cyclohexane ring on the polymer backbone.

As far as the solvent is concerned, polar solvents promote the hydride ion shift that leads to monomer isomerization or to isomerized oligomeric structures.

In the present study the polymerization of 7-tetradecene oxide (7-TDO), a mixture of *cis* and *trans* isomers, with methyl triflate is reported. The presence of the two long alkylic substituents on the oxirane ring is seen to modify the course of the reaction, in comparison with unsubstituted ethylene oxide.

2. Experimental

2.1. materials

7-tetradecene oxide was prepared from 7-tetradecene in accordance with the procedure reported elsewhere [17]. Unreacted 7-tetradecene (2% by weight) remained in the 7-tetradecene oxide as an impurity. $\text{CF}_3\text{SO}_3\text{CH}_3$ from Fluka was used without further purification. The C_6D_6 was used reagent grade. All procedures were carried out under nitrogen.

2.2. Kinetic procedures

7-tetradecene oxide polymerizations were carried out both in bulk and in benzene solution. 1.9 mmol of 7-TDO and 0.038 mmol of methyl triflate were introduced into an NMR sample tube by using a microsyringe at dry ice temperature in bulk polymerization. In solution polymerization, 1.13 mmol of 7-TDO, 0.023 mmol of methyl triflate and 0.30 ml of C_6D_6 were introduced into the NMR tube at -57°C . The tube was then stirred at the same temperature. The extent of reaction was negligible at -57°C . The tube was placed in the NMR probe insert, which was maintained at a constant temperature. The reaction was then monitored by ^1H -NMR, ^{13}C -NMR and ^{19}F -NMR spectroscopy at 298, 314 and 329 K in bulk. In benzene the reaction was performed at 298 K and some preliminary experiments were performed at 278 and 263 K. The molar ratio initiator:epoxide was 1:50, or alternatively 1:2.5 in a single C_6D_6 experiment.

2.3. NMR measurements

^1H -, ^{19}F - and ^{13}C -NMR were carried out on a Bruker AMX-300 spectrometer operating at a ^1H resonance frequency of 300.130 MHz, ^{19}F resonance frequency of 282.350 MHz and ^{13}C resonance frequency of 75.470 MHz. The reaction temperature was kept constant within $\pm 1^\circ$ and the experimental error of the integration was within 1%.

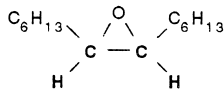
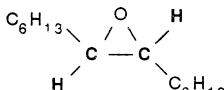
2.4. GC-MS measurements

GC/MS chromatograms were obtained on a Hewlett Packard 5890 gas chromatograph coupled to a VG 70 SQ mass-spectrometer. GC separation was performed using a DB5 fused silica capillary column (J and W Scientific 30 m \times 0.32 mm i.d., 0.25 mm film thickness). Temperature was programmed to hold the column at 60°C for 1 minute, then to increase at 8°C min^{-1} to 280°C , followed by an additional 15 minute period at the maximum temperature. Samples were dissolved in dichloromethane and analysed in a split/splitless injector used in the splitless mode (0.30 min). Injector temperature was set at 260°C , and the GC/MS interface temperature was maintained at 290°C . MS detection was carried out under electron impact ionization conditions (70 eV), acquisition mode in full-scan from 33 to 650 m/e , 1 s per scan. Instrument resolution was 1000 ppm.

2.5. IR measurements

The infra-red spectra of the hydroxy-terminated polymer were performed on the polymerization mixture neutralized with 1 NH_4OH solution as a film coated onto a NaCl plate. A Perkin Elmer FTIR 1760 spectrophotometer was used.

Table 1
 ^1H - and ^{13}C -NMR assignments of the polymerization mixture after 1 min, at 314 K

Compound	Formula	^1H , δ (ppm)	^{13}C , δ (ppm)
<i>cis</i> 7-TDO		2.7 <i>s</i>	56
<i>trans</i> 7-TDO		2.5 <i>s</i>	58
methyl triflate	$\text{CH}_3\text{OSO}_2\text{CF}_3$	4.2 <i>s</i>	61.5
7-tetradecene	$\text{C}_5\text{H}_{11}-\underset{\text{a}}{\text{CH}_2}-\underset{\text{b}}{\text{CH}}=\underset{\text{b}}{\text{CH}}-\underset{\text{a}}{\text{CH}_2}-\text{C}_5\text{H}_{11}$	a. 2.0 <i>m</i> b. 5.8 <i>m</i>	— 130

Multiplicity: *s* = singlet, *t* = triplet, *m* = multiplet.

3. Results and discussion

The cationic polymerization of 7-TDO with methyl triflate as initiator was shown to afford a mixture of polymeric products and a fraction of volatile linear and cyclic compounds. The whole polymerization mixture was characterized by NMR and FTIR spectroscopies while the volatile fraction was separated and identified by gas chromatography / mass spectrometry. ^1H - and ^{13}C -NMR characterizations of the reagent mixture at the beginning of the reaction (after 1 min, 314 K, in bulk) and the polymerization mixture at the end (after 868 min) are reported in Table 1, Table 2. In order to determine the mechanism of polymerization of this system, a kinetic study of the initiation step and the characterization of the propagating species were performed by means of proton, fluorine and carbon NMR techniques.

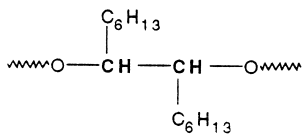
3.1. GC-MS characterization

The GC-MS characterization was afforded for the polymerization reaction carried out at temperature 329 K. The

gas chromatographic scan of the volatile polymerization products shows two different groups of peaks. Early eluted peaks (entry 1–5) correspond to the olefin present in the initial mixture and to products originating from the isomerization of the starting epoxide while later eluted peaks (entry 6) correspond to cyclic isomeric dimers of 7-TDO. The structure and the molecular weight of the compounds corresponding to the different gas chromatographic peaks were identified by electron impact / mass spectroscopy and are summarized in Table 3.

MS-spectra of 2,3,5,6-tetra-*n*-hexyl-dioxane are characterized by a parent peak at *m/e* 424, but each stereoisomer is different from the others because of the different relative abundance of their fragment ions: *n/e* 339 ($\text{M}^+ - \text{C}_6\text{H}_{13}$), *m/e* 311 ($\text{M}^+ - \text{C}_6\text{H}_{13}\text{CO}$) and *m/e* 196 ($\text{M}^+ - \text{C}_6\text{H}_{13}\text{CH} = \text{CHC}_6\text{H}_{13}$). GC chromatographic analysis did not reveal any other cyclic structure larger than the dimer. However their presence in the reaction mixture cannot be excluded because the low volatility of macrocyclic species of high molecular weight could prevent their GC detection. The composition of each volatile by-product is given as a percentage area of the total of the volatile species detectable by

Table 2
 ^1H and ^{13}C NMR assignments of the polymerization mixture after 868 min at 314 K

Compound	Formula	^1H , δ (ppm)	^{13}C , δ (ppm)
Polyether and cyclic oligomers		3–4 <i>m</i>	72–83
7-tetradecanone	$\text{H}_{13}\text{C}_6-\underset{\text{a}}{\text{CH}_2}-\underset{\text{b}}{\overset{\text{O}}{\parallel}{\text{C}}}-\underset{\text{a}}{\text{CH}_2}-\text{C}_5\text{H}_{11}$	2.2 <i>t</i>	a. 42 b. 210

Multiplicity: see Table 1.

Table 3
Composition of the volatile fraction polymerization reaction of 7-TDO with $\text{CH}_3\text{SO}_3\text{OCF}_3$ as percent of total volatile reaction products (GC area)

Entry	<i>m/e</i>	Compound	Composition mol %
1	196	7-tetradecene	0.7
2	194	7,8-tetradecadiene	1.1
3	194	unidentified fraction	3.5
4	212	7-tetradecanone	40.5
5	230	7,8-tetradecandiol	2.6
6	424	2,3,5,6-tetra- <i>n</i> -hexyl-dioxane	51.6

^aPolymerization conditions: $[I]_0 = 0.075 \text{ mol l}^{-1}$, $[7\text{-TDO}]_0 = 3.72 \text{ mol l}^{-1}$, in bulk at 329 K.

gas chromatography under our test conditions. In these calculations, it is assumed that the different species produce approximately the same response factor as measured for the ionic current during analysis. The compounds present in higher concentrations were found to be 7-tetradecanone and cyclic dimers. However, it is important to remember that the relative abundance calculated does not reflect the composition of the polymerization mixture as a whole, but refers only the volatile fraction as it is not possible to have a clear idea of the percentage of volatile species detected in the GC/MS analysis versus the low percentage of undetectable volatile compounds.

3.2. Kinetics and mechanism

Mechanistic studies of the 7-TDO polymerization utilizing methyl triflate as the initiator were performed from the kinetic viewpoint by means of NMR spectroscopies. Schemes 1 and 2 explain the course of the 7-TDO polymerization reaction.

3.2.1. Initiation

From the area of the signals monitored by ^1H – NMR at different times, the consumption of *cis* (δ 2.7 ppm) and *trans*

(δ 2.5 ppm) 7-TDO was detected (Fig. 1). The disappearance of methyl triflate (δ 4.2 ppm) is reported in Fig. 2 and can be written as:

$$-\frac{d[I]}{dt} = k_{i(cis)}[I][E_{cis}] + k_{i(trans)}[I][E_{trans}]_0 + k_{i(trans)}[E_{trans}]_0[I] \quad (1)$$

with $[E_{cis}]_0$, $[E_{trans}]_0$ and $[I]_0$ being the *cis* and *trans* 7-TDO and the initiator feed concentrations respectively and $k_{i(cis)}$ and $k_{i(trans)}$ being the kinetic constant of the initiation step for the two isomers.

The initiator:epoxide concentration ratio employed was 1:50, so a pseudo-first order approximation ($[E_{cis}] = [E_{cis}]_0$ and $[E_{cis}]_0 + [E_{trans}]_0)t$ could be applied to Eq. (1), with its integration giving:

$$\ln \frac{[I]_0}{[I]} = (k_{i(cis)}[E_{cis}]_0 + k_{i(trans)}[E_{trans}]_0)t \quad (1a)$$

The disappearance rate of the two isomers could be written as:

$$-\frac{d[E_{cis}]}{dt} = k_{i(cis)}[E_{cis}][I] + k_{p(cis)}[E_{cis}][P^*] \quad (2)$$

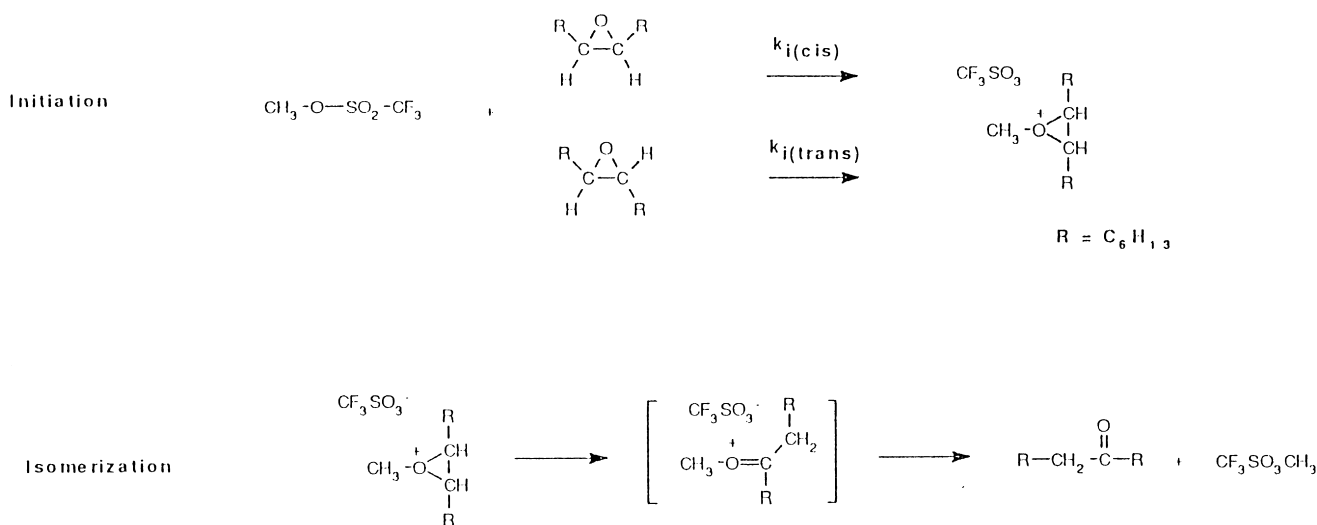
$$-\frac{d[E_{trans}]}{dt} = k_{i(trans)}[E_{trans}][I] + k_{p(trans)}[E_{trans}][P^*] \quad (3)$$

with $[P^*_{cis}]$ being the concentration of the propagating species and $k_{p(cis)}$ and $k_{p(trans)}$ being the kinetic constant of the propagation step for the two isomers.

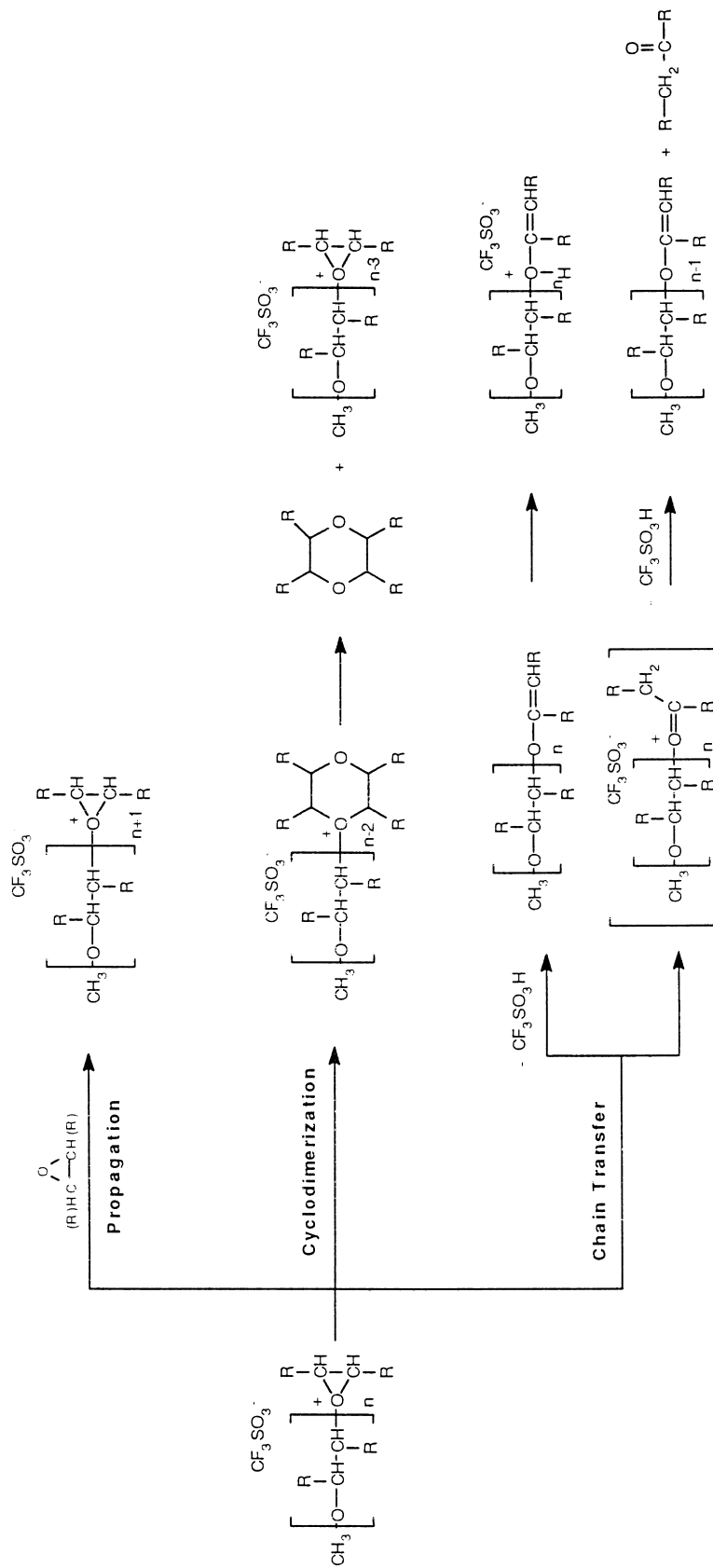
At an early stage of the reaction, we assumed that epoxide consumption due to chain propagation is negligible ($k_{p(cis)}[E_{cis}][P^*] = 0$) and only a negligible amount of the *trans* isomer reacts with the triflic ester ($-\frac{d[E_{trans}]}{dt} \cong 0$). Thus the integration of Eq. (2) gave:

$$\frac{1}{[I]_0 - [E_{cis}]_0} \ln \frac{[I][E_{cis}]_0}{[I]_0[E_{cis}]} = k_{i(cis)}t \quad (2a)$$

From Eq. (2a) $k_{i(cis)}$ was calculated and then inserted in Eq. (1a) to calculate $k_{i(trans)}$. Under this approximation, we



Scheme 1.



Scheme 2.

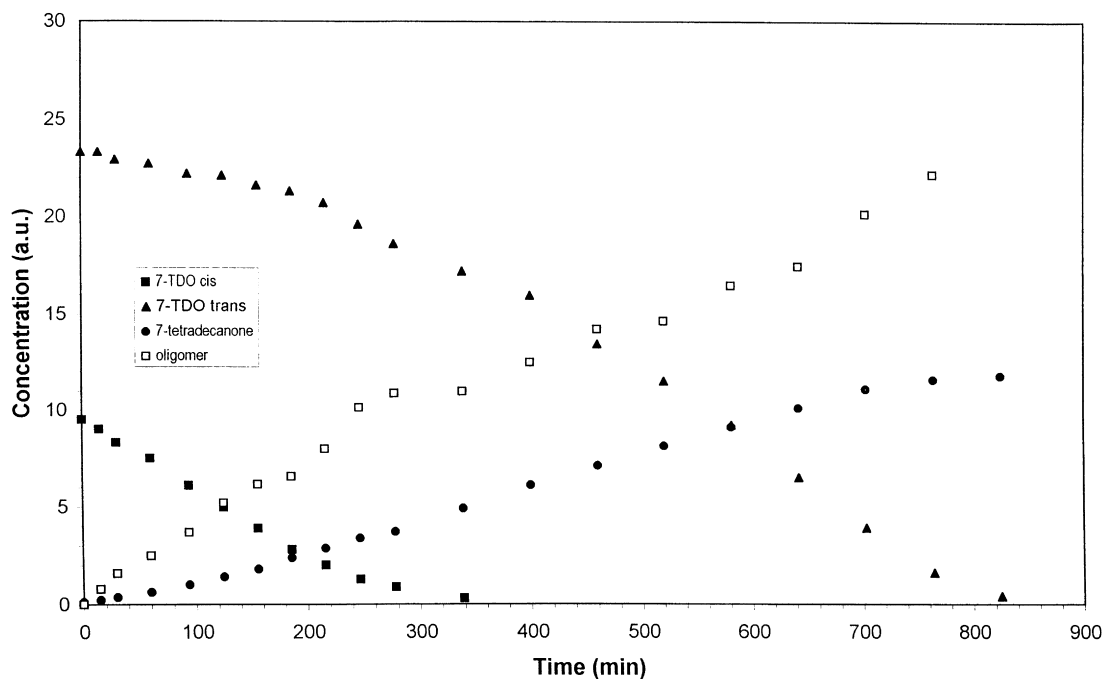


Fig. 1. The concentration–time relationships of *cis* and *trans* 7-TDO, polymer species and 7-tetradecanone in the polymerization carried out in bulk at 314 K, $[I]_0 = 0.075 \text{ mol l}^{-1}$, $[7\text{-TDO}]_0 = 3.72 \text{ mol l}^{-1}$.

obtained second order $k_{i(cis)}$ and their values are reported in Table 4. It is interesting to note that in all testing conditions $k_{i(cis)} > k_{i(trans)}$. This different reactivity behaviour is due, at least partly, to the different ground state energies of the two stereoisomers. In fact the *trans* isomer was calculated to be 2.1 Kcal/mol more stable than the *cis* form³.

Arrhenius plots of k_i for the reaction carried out in bulk at 298, 314 and 329 K lead to the activation energies of 59 kJ mol^{-1} for the *cis* isomer and 73 kJ mol^{-1} for the *trans* isomer (Fig. 3).

3.2.2. Propagation

In order to characterize the propagating species involved in our cationic polymerization system, we carried out the reaction with a molar initiator: monomer ratio of 1:2.5 in C_6D_6 solution (or deuterated toluene in one low temperature experiment). In this way, it was possible to improve the signal to noise ratio and reduce linewidth.

Table 4

Rate constants of initiation (k_i) of the *cis* and *trans* 7-TDO polymerization determined by NMR spectroscopy at three temperatures

Temp. (K)	Solvent	$k_{i \text{ cis}} \times 10^5$ (l/mol s)	$k_{i \text{ trans}} \times 10^5$ (l/mol s)
298	C_6D_6^a	3.8	0.5
298	bulk ^b	4.6	0.4
314	bulk ^b	18	2.4
329	bulk ^b	43	6.3

^a $[I]_0 = 0.70 \text{ mol/l}$, $[E]_0 = 1.74 \text{ mol/l}$.

^b $[I]_0 = 0.075 \text{ mol/l}$, $[E]_0 = 3.72 \text{ mol/l}$.

In all NMR spectra (^1H , ^{13}C and ^{19}F), the assignment of peaks to the propagating species is unambiguously given to those signals which are absent at the beginning of the reaction, grow in intensity during the reaction itself, and then disappear at the end.

The ^1H –NMR spectrum of our reaction system shows two complex multiplets at about 4.9 and 5.0 ppm (Fig. 4) arising during the polymerization reaction. The chemical shifts of these signals have been attributed by various authors alternatively to the oxonium ion or to the linear macroester [6,11,18].

Matyjaszewski et al. were able to see both species during the polymerization of THF with ethyl triflate [6], the resonance at lower fields (4.86 ppm) was assigned to the oxonium ion while the resonance at higher fields (4.58 ppm) was assigned to the ester. A slow equilibrium macroion–macroester was invoked to justify the presence of two distinct peaks in the NMR spectrum. The relative amount of the two species changed with solvent polarity, while their chemical shift did not.

In the polymerization of ethylene oxide with ethyl triflate in CD_2Cl_2 , Kobayashi et al. [9] observed a single peak in the proton spectrum, at 4.6 ppm. It was assigned to the macroester $-\text{CH}_2\text{-O-SO}_3\text{CF}_3$. The same authors could see the two species in equilibrium in the polymerization of oxepane with ethyl triflate [18], where the ester was found at 4.65 ppm and the oxonium ion at 5.0–5.3 ppm.

In order to obtain more information on the signals at δ 4.9 and 5.0 ppm, we recorded a ^1H – ^1H COSY spectrum (Fig.

³Thermodynamical parameters were calculated using a molecular mechanics program based on Allingers MM2 force-field.

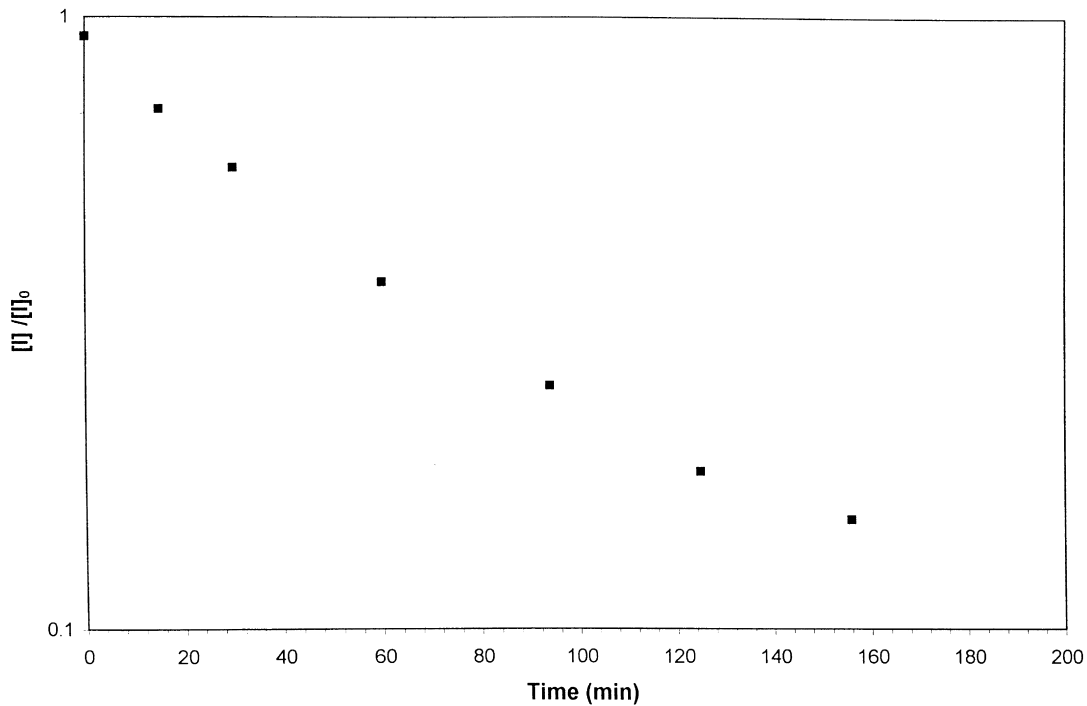


Fig. 2. The concentration–time relationship of methyl triflate in the polymerization carried out in bulk at 314 K, $[I]_0 = 0.075 \text{ mol l}^{-1}$, $[E]_0 = 3.72 \text{ mol l}^{-1}$.

5). As it can be seen, the multiplet at 4.9 ppm shows two distinct cross-peaks, one at about 3.5 ppm, in the ether region, and a second at about 1.2 ppm, in the methylenic region. These signals could arise either from protons of type *b* (polymeric oxonium ion), type *c* (monomeric triflate ester), or type *d* (polymeric triflate ester) (Fig. 6). Other protons adjacent to the active site can be

excluded, as they should not have cross-peaks in the ether region.

On the other hand, the multiplet at 5.0 ppm does not show any cross peak. The only protons which fulfill this requirement are those of type *a* (the methyl of monomeric oxonium ion) (Fig. 6). However it is hard to accept such an assignment, as these protons would be expected to resonate at

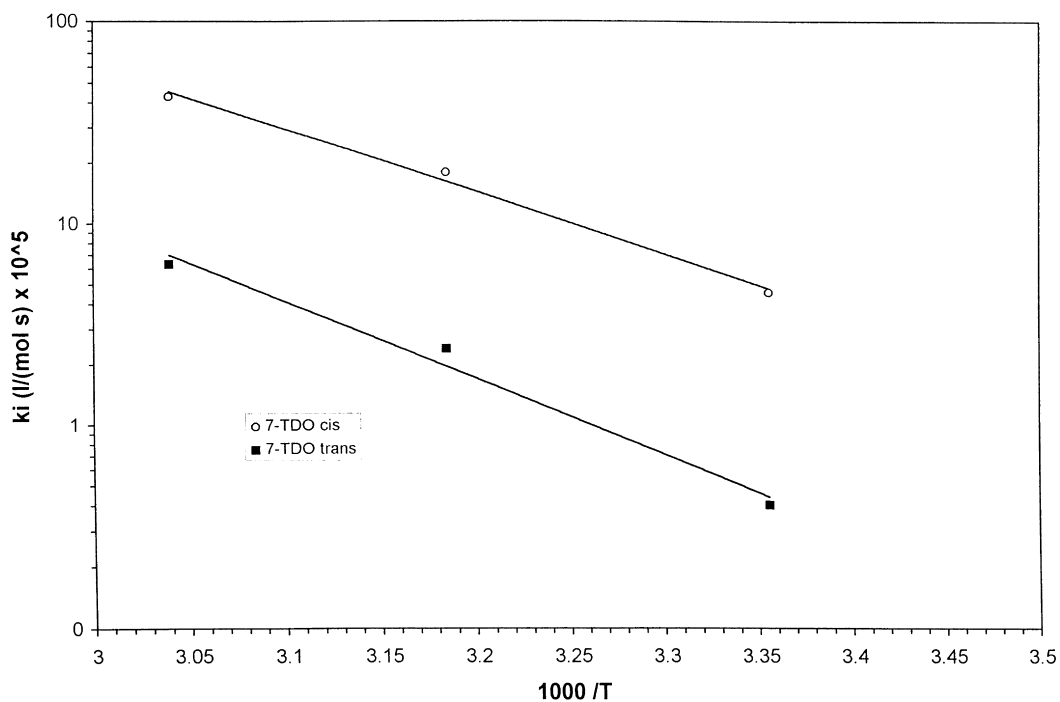


Fig. 3. Arrhenius plot of k_i for the polymerization of *cis* and *trans* 7-TDO in bulk, $[I]_0 = 0.075 \text{ mol l}^{-1}$, $[7\text{-TDO}]_0 = 3.72 \text{ mmol l}^{-1}$.

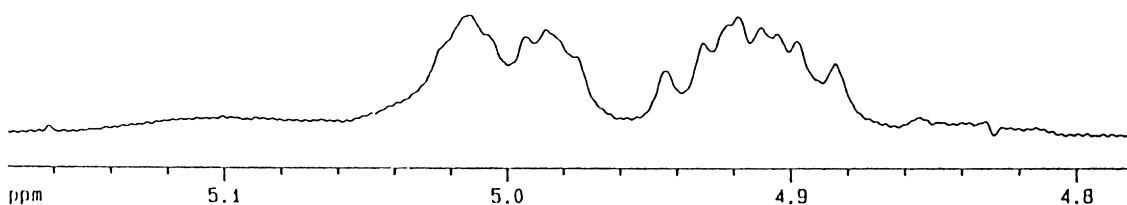


Fig. 4. Partial ^1H -NMR spectrum of 7-TDO polymerization in C_6D_6 after 203 min, at 298 K, $[I]_0 = 0.70 \text{ mol l}^{-1}$, $[E]_0 = 1.74 \text{ mol l}^{-1}$.

higher fields than those of type *b*. The latter, in fact, have an additional oxygen in the β -position and are methynes instead of methyls. Moreover, they should appear as singlets.

Thus we can conclude that the ambiguity of the macroion–macroester cannot be solved with the use of ^1H -NMR, although information on the propagating species can be obtained by the ^{19}F -NMR spectrum. It also offers better resolution, in the case of the oxonium ion, if only the counterion is monitored, and not the propagating chain itself.

As reported in literature, macroester and macroion are well resolved in the fluorine spectrum. In the THF polymerization with ethyl triflate, Kobayashi et al. [10] observed

two sharp singlets, one at -76.08 ppm and one at -79.06 ppm ⁴. They were assigned to the ester and to the oxonium ion, respectively.

Similar results were found by Wu and Pruckmayr [14], as in CCl_4 a peak was seen at $\delta -75.7 \text{ ppm}$, while in CH_3NO_2 a peak was produced at $\delta -78.7 \text{ ppm}$. These observations confirmed that the ester group resonates downfield to ethyl triflate (-77.2 ppm) and the oxonium ion resonates upfield in the ^{19}F -NMR spectra. In the ethylene oxide polymerization Kobayashi et al. [9] found only one peak

⁴ All of the ^{19}F chemical shift (both of literature and ours) are calculated assigning the value of -78.6 ppm to CF_3COOH (external standard), independent of the solvent used.

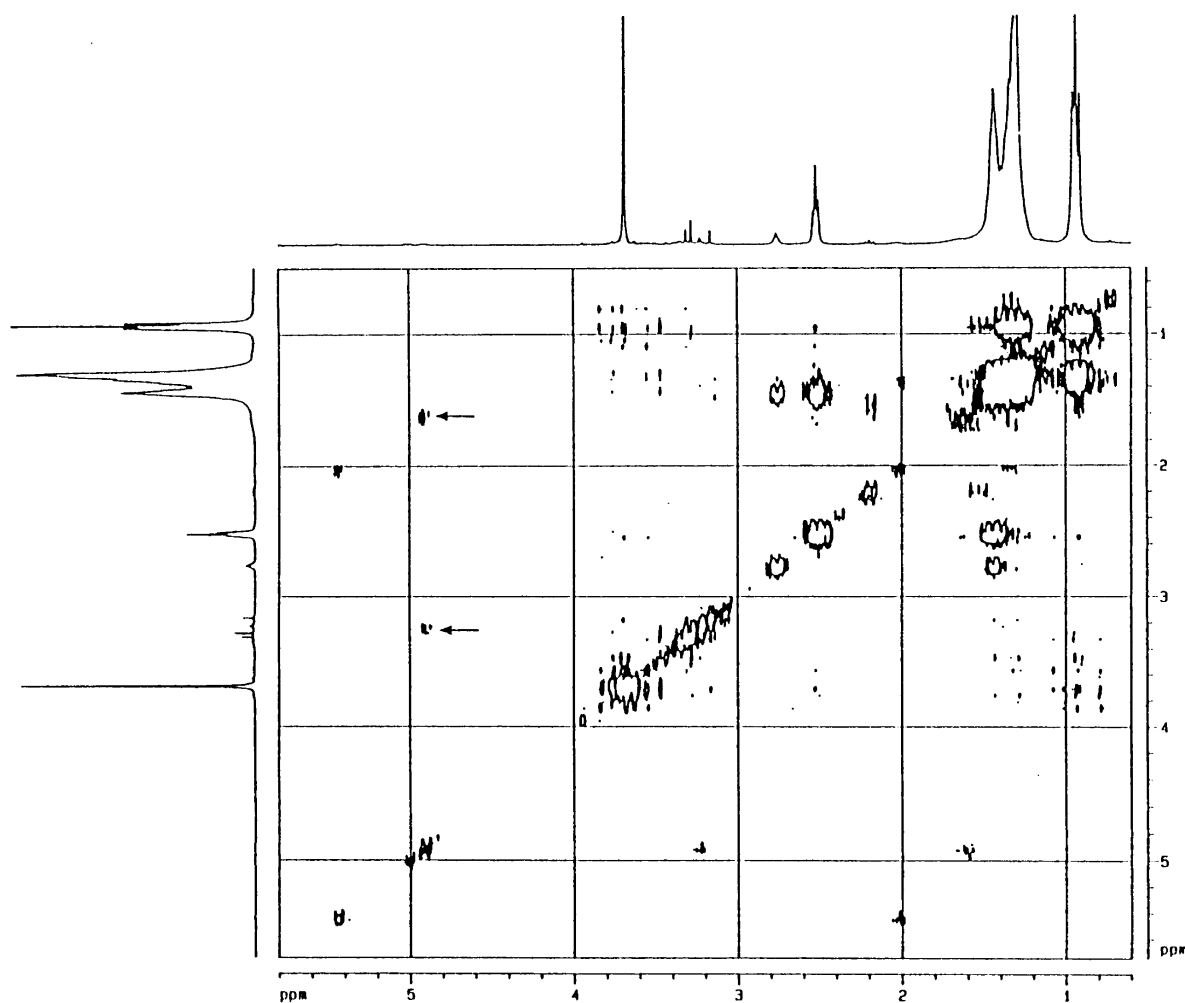


Fig. 5. ^1H - ^1H COSY spectrum during the course of the polymerization reaction in C_6D_6 at 298 K. The arrows show the cross peaks of the resonance at 4.9 ppm.

at -75.62 ppm which was subsequently assigned to the macroester.

The ^{19}F -NMR spectra of our reaction system, at different reaction times, are shown in Fig. 7. No single peak was observed, but as many as three major, along with several minor, resonances in the range -77.6 to -78.0 ppm, all upfield to the initiator chemical shift (-77.2 ppm) were seen. For this reason, they were assigned the macroion propagating specie.

In the ^{13}C -NMR spectrum of the polymerization mixture after the conversion of about 80% of monomer, peaks at 91.9, 93.0 and 96.0 ppm are assigned to the active species (Fig. 8). Pruckmayr [4,19] also found three signals for the THF/ $\text{CF}_3\text{SO}_3\text{CH}_3$ system, and attributed the chemical shifts at 87.5 and 89.6 ppm to the ring- and open-chain methylene carbons adjacent to the oxonium ion, and the signal at 79.1 ppm to the α -methylene carbon of the macroester specie. He also observed a pronounced ring-size effect resulting in a downfield shift of about 1.7 ppm per each ring expansion by one methylene group, going from five to seven-membered rings. It should therefore be expected that an approximate shift of 3.4 ppm upfield in a three-membered ring will be seen. As the methyne carbons rather than methylene carbons were monitored, a downfield shift of approximately 6–9 ppm is expected. A combination of these two effects results in chemical shift values which are in good agreement with the presence of an oxonium ion in the propagating species. The occurrence of the oxonium ion, in the polymerization of 7-TDO, can be justified by the stabilization effect due to the electron release of the two alkyl chains, which are absent in the oxonium ion derived from EO.

It might be postulated that in our reaction, both active species are present in equilibrium, viz. macroion and macroester, as reported by other authors in similar systems. If the equilibrium is obtained rapidly at room temperature on the NMR timescale, the observed chemical shift arises from two species having different chemical shifts. To verify this, we cooled down the reaction system at about 223 K and recorded both the ^{19}F - and ^{13}C -NMR spectra. No significant change was evident in both spectra (data not shown), therefore it is possible to rule out such a fast equilibrium. The observed chemical shift dispersion in our system can be attributed both to the *cis*–*trans* isomerism of 7-TDO and to the different chain lengths of the growing polymer.

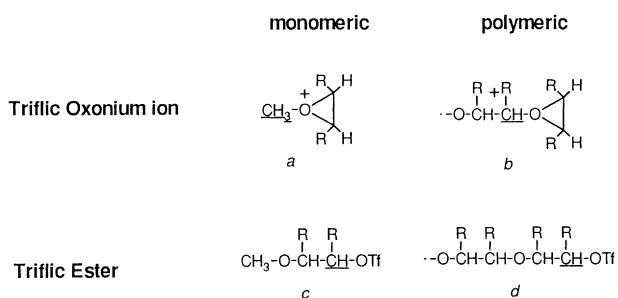


Fig. 6. Structures of the propagating species.

In this work a qualitative kinetic analysis for the actual propagation step was also attempted, but the presence of both *cis* and *trans* 7-TDO isomers made the interpretation of their experimental consumption data quite complicated. In our approach, the reaction was considered a copolymerization where one of the monomers was more reactive than the other toward both propagating species. The *cis* monomer entered the copolymer faster than the *trans* form and tended to self-propagate until it was consumed, at which point the *trans* monomer entered the copolymer.

The consumption data were obtained at 297, 314 and 329 K with an initiator: epoxide ratio of 1:50. If it is assumed that the reactivity of the propagating species is dependent only on the monomer unit at the end of the chain, the following four propagation reactions are possible:



and the rates of disappearance of the two monomers in the

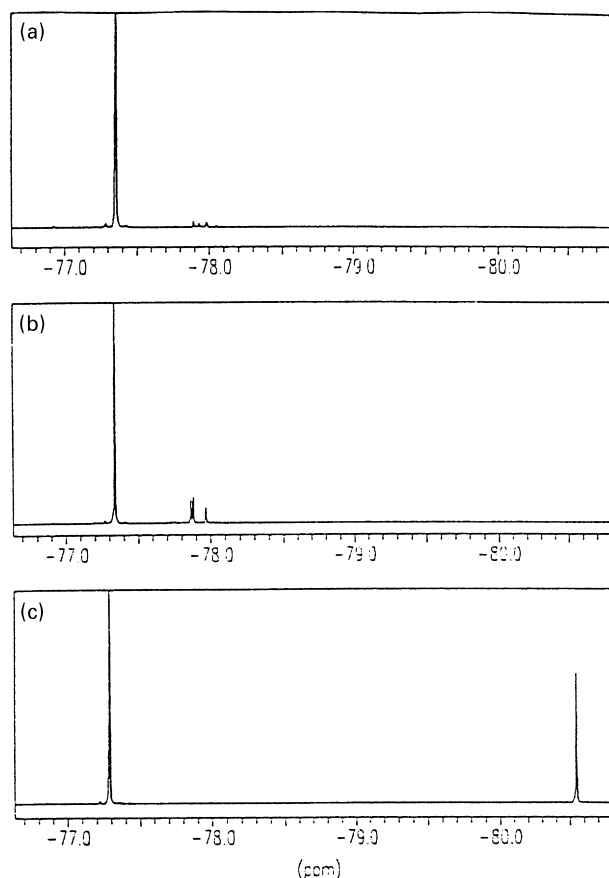


Fig. 7. ^{19}F NMR spectra of the polymerization reaction in C_6D_6 at 298 K: (a) after 11 min; (b) after 203 min; (c) after 443 min.

propagating step were given by:

$$-\frac{d[E_{cis}]}{dt} = k_{p(cis)}[E]_{cis}[P^*] = k_{cc}[P^*_{cis}][E_{cis}] + k_{tc}[P^*_{trans}][E_{cis}] \quad (4)$$

$$-\frac{d[E_{trans}]}{dt} = k_{p(trans)}[E]_{trans}[P^*] = k_{tt}[P^*_{trans}][E_{trans}] + k_{ct}[P^*_{cis}][E_{trans}] \quad (5)$$

with $[P^*_{cis}]$ and $[P^*_{trans}]$ being the concentrations of the propagating species ending with the *cis* and *trans* monomers respectively and k_{cc} , k_{tc} are the propagation kinetic constant of *cis* isomer and k_{ct} , k_{tt} are the propagation kinetic constant of *trans* isomer.

In Fig. 9b both *cis* and *trans* 7-TDO consumption rates are approximately constant until the 200th min of the reaction, that is they followed a pseudo-zero order behaviour. During this step, the concentrations of the two propagating species P^*_{cis} and P^*_{trans} formed during the initiation step remained constant, the concentration of the monomers decreased but remained higher than the concentration of the propagating species so they could be considered constant. After 200 min, the *cis* disappearance rate decreased and the *trans* rate was seen to be slightly increased. It is likely that the *cis* monomer depletion became appreciable and its concentration became comparable with the propagating species. Its disappearance resulted in a decrease in its rate of consumption. Simultaneously the consumption of *trans* monomer by the reaction with P^*_{cis} (Eq. (b)) became important and its disappearance rate accelerated. At the point at which all the *cis* monomer was consumed, the consumption rate of the *trans* isomer slowly increased because both P^*_{cis} and P^*_{trans} reacted with the monomer but with different kinetic constants (Eqs. (b) and (d)).

The same kinetic behaviour was observed at 298 and 329 K, although different disappearance rate values were seen. At 329 K, all reactions were faster and the plateau were very short (Fig. 11c). However, at 298 K (Fig. 11a), the *trans* pseudo-zero order behaviour plateau were larger, the reactions very slow, and the absence of an actual plateau at the beginning of the *cis* reaction may have resulted from a greater difference between k_{cc} and k_{tc} (Eqs. (a) and (b)).

3.2.3. Side-chain reaction

Two main by-products have been observed in the 7-TDO polymerization: cyclic oligomers and 7-tetradecanone.

3.2.3.1. Cyclodimerization. The complex group of signals at δ 3–4 ppm in the proton spectrum and at δ 72–83 ppm in the carbon spectrum are due to methyne groups adjacent to the ether oxygen. Both the methynes of the linear polymer and the cyclic oligomers resonate in this chemical shift range and it is not possible to make a separate assignment for them. The assignment of these signals to the methyne carbons was confirmed by ^{13}C -DEPT 135-NMR experiments.

3.2.3.2. Isomerization. As far as the formation of isomerized products is concerned, pinacol rearrangement is a well-documented reaction in alkyl- and aryl-substituted epoxides under acidic conditions [20–22]. In our case a superacid ester was employed as catalyst so the cyclic oxonium ion formed is tertiary rather than secondary. Moreover, hydrogen is often considered to be a good migrating species [23]. The monomer isomerization could be written as reported in Scheme 1 [23,24].

Further, in the formation of ketone the initiator (methyl triflate) is recovered. The initiator is also recovered during the formation of dioxane, as already observed by Saegusa et al. [9].

The formation of 7-tetradecanone was also confirmed by the IR spectrum of the reaction mixture quenched with 1 N NH_4OH solution. The carbonyl stretching band is visible at 1723 cm^{-1} . The peak at 1090 cm^{-1} and the broad band at $3450\text{--}3550\text{ cm}^{-1}$ are attributed to the ether and hydroxyl groups of the oligomers, respectively (Fig. 10).

There is no clear evidence for the formation of dioxolane type structures. In fact, although according to Kawakami et al. [16] the methynes adjacent to the acetalic function should resonate around 4.5 ppm at proton NMR, only very small peaks were observed in this spectral region. It can therefore be suggested that with the use of our system, monomer isomerization leads entirely to ketone.

As monitored by ^1H -NMR, the amount of ketone increases around 10%–15% with an increase in temperature from 298 to 314 K, and approximately the same amount

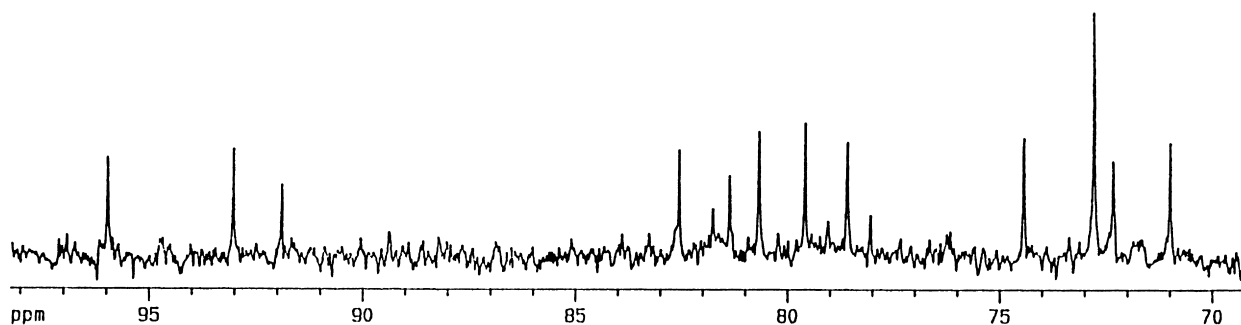


Fig. 8. Partial ^{13}C -NMR spectrum of 7-TDO polymerization in C_6D_6 at 298 K, $[I]_0 = 0.70\text{ mol l}^{-1}$, $[E]_0 = 1.74\text{ mol l}^{-1}$.

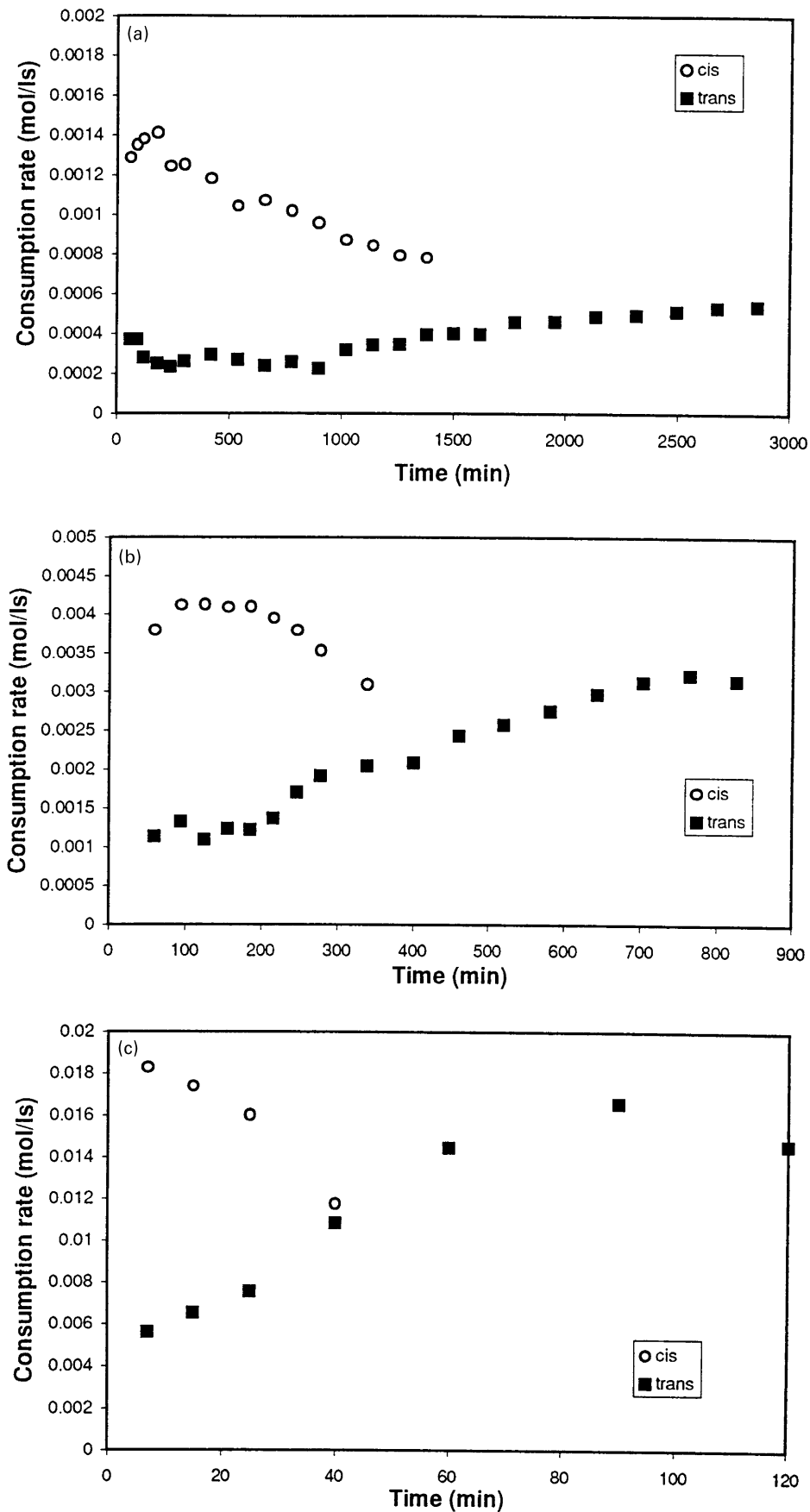


Fig. 9. Consumption rate–time relationships of *cis* and *trans* 7-TDO in the polymerization carried out in bulk, $[I]_0 = 0.075 \text{ mol l}^{-1}$, $[7\text{-TDO}]_0 = 3.72 \text{ mol l}^{-1}$, (a) 298 K; (b) 314 K; (c) 329 K.

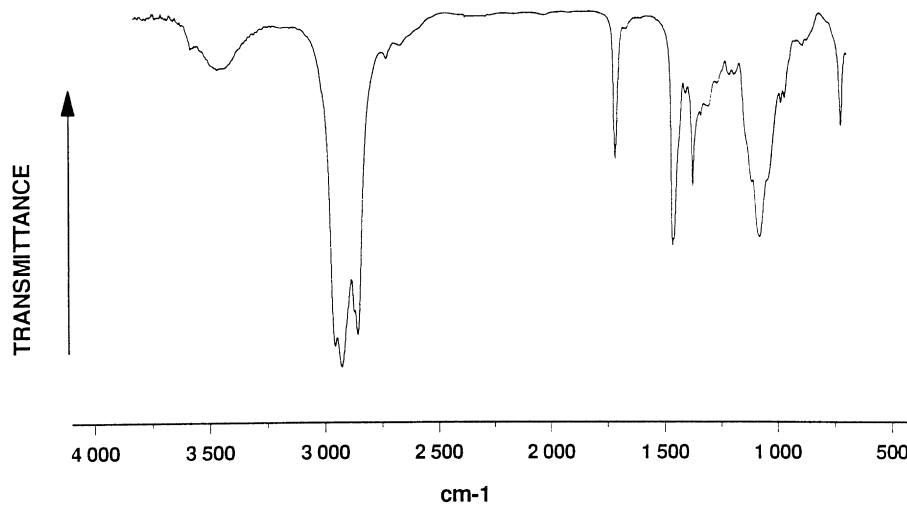


Fig. 10. IR spectrum of 7-TDO polymerization mixture quenched with 1 NH_4OH .

when temperature rises from 314 to 329 K. At temperatures lower than room temperature, only preliminary data are available, but ketone formation seems to be markedly reduced. However, the amount of ketone does not vary significantly between bulk and benzene solution polymerization. Therefore, it can be said that temperature plays a more important role in the formation of ketone. This finding can be explained assuming that 7-tetradecanone is the most thermodynamically stable species formed in the reaction. The approximate heats of formation (H_f) for the main products formed in our reaction⁵ were calculated, and 7-tetradecanone was seen to have a lower enthalpic content ($H_f = -228.0 \text{ kcal mol}^{-1}$) than the most stable stereoisomer of tetrasubstituted dioxane ($H_f = -221.7 \text{ kcal mol}^{-1}$), and

a model linear dimer ($H_f = -220.9 \text{ kcal mol}^{-1}$). The entropic factor is also expected to favour the linear monomeric ketone, when compared to both the cyclic dimer and the linear polymer. As a consequence, it is not surprising that with increasing temperature, the amount of ketone increases significantly. At lower temperatures, it is possible that the reaction proceeds under kinetic control and the linear polymer and cyclic oligomer reaction pathways are favoured. The hydrogen transposition necessary for ketone formation is seen to require a large amount of activation energy.

⁵ Thermodynamical parameters were calculated using a molecular mechanics program based on Allinger's MM2 force-field.

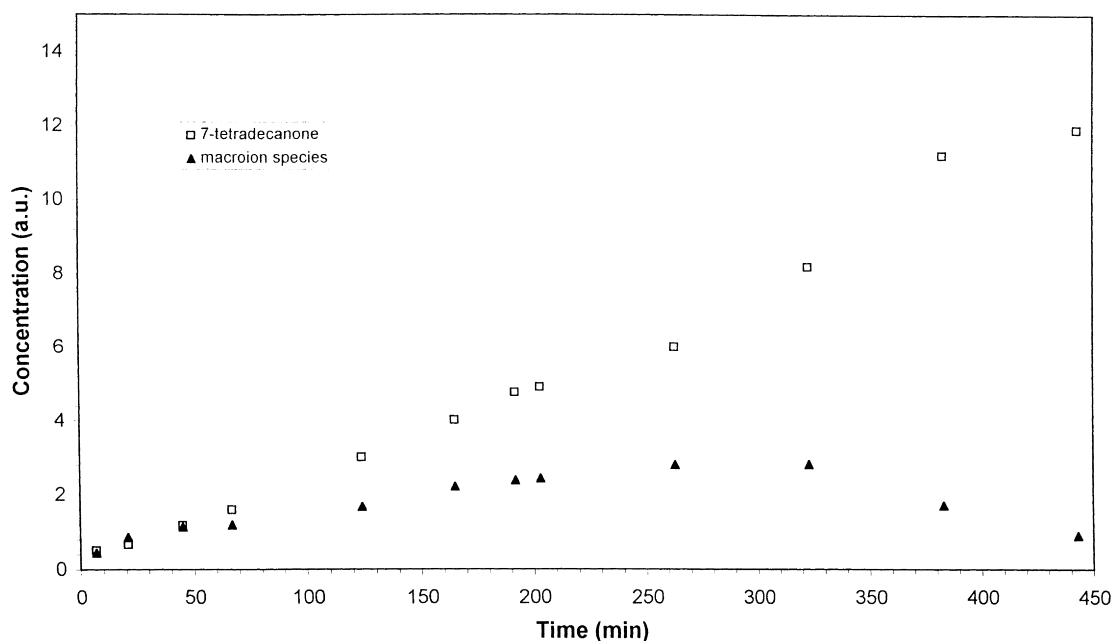


Fig. 11. The concentration–time relationships of the macroion propagating species and 7-tetradecanone in the polymerization carried out in C_6D_6 at 298 K, $[I]_0 = 0.70 \text{ mol l}^{-1}$, $[7\text{-TDO}]_0 = 1.74 \text{ mol l}^{-1}$.

3.2.4. Transfer reaction

At the end of the reaction, large amounts of olefinic protons have been detected in the $^1\text{H-NMR}$ spectrum. As reported in the literature, olefins have already been observed as termination products in the polymerization of cyclic ethers [23,24], and the formation of C—C double bonds could be in good agreement with an E1 termination reaction as shown in Scheme 2. An ‘extra production’ of 7-tetradecanone and a decrease in the macroion concentration were also observed when all monomer was consumed. This effect was more evident when the reaction was carried out with a monomer/initiator ratio of 2.5:1 at 298 K in C_6D_6 (Fig. 11). This finding can be explained if we suggest that the macroion propagating species could rearrange to produce a vinyl terminated polymer and a ketone (Scheme 2). It can be supposed that the propagation and chain transfer reactions are competitive but the latter becomes significant only with a decrease in the monomer concentration. In presence of the more nucleophilic oxirane ring, the transfer reaction is quite negligible.

In the $^{19}\text{F-NMR}$ spectrum a very strong peak at -80.5 ppm abruptly arises (Fig. 7c). The intensity of this signal could be due to a small degree of polymerization (DP) of the oligomer. Its value calculated from GPC data is 3. We could suggest that this signal could be assigned to a linear oxonium ion resulting from the protonation of the vinyl ether group that is formed in the last step (Scheme 2). In order to reproduce similar reaction product a reaction between the ethyl vinyl ether and the methyl triflate was carried out. The $^{19}\text{F-NMR}$ spectrum of the reaction product shows a peak at -79.0 ppm which seems to confirm our previous hypothesis about the presence of a linear oxonium ion derived from the protonation of a vinyl ether terminal group in the reaction mixture of the polymerization of 7-TDO with methyl triflate.

4. Conclusion

Kinetic studies performed on the 7-TDO/methyl triflate polymerization system provide new information about the mechanism of the cation polymerization of disubstituted oxirane rings with superacid derivatives. A different reactivity behaviour was observed for the *cis* and *trans* 7-TDO in the initiation step. The *cis* isomer reacts at a much higher rate than the *trans* form at all temperatures investigated. The activation energies of the two isomers were calculated to be 59 and 73 kJ mol^{-1} for the *cis* and *trans*, respectively. The

propagation step occurs via a nucleophilic attack of the monomer on the the macroion propagating species to give a polyether. However, side-chain reactions produce 1,4-tetrasubstituted dioxane as by-products through a ‘back-biting’ mechanism, and 7-tetradecanone through the isomerization of the 7-TDO. Two kinds of mechanism for the transfer reaction have been suggested: a classical E₁ elimination reaction which leads to a vinyl polyether, and a rearrangement of the macroion which gives the same olefin and the 7-tetradecanone.

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