Kinetics and Thermodynamics of Interconversion of Macroesters and Macroion Pairs in the Cationic Polymerization of Tetrahydrofuran

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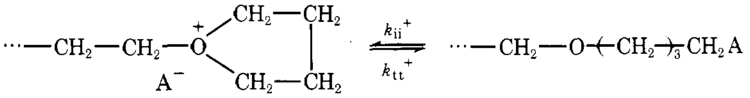
ABSTRACT: The kinetics and thermodynamics of the interconversion governing the equilibrium between the ma-



(where A = FSO_3 or CF_3SO_3)

croion pairs and macroesters in the cationic polymerization of THF were measured by ^1H (300 MHz) and ^{19}F NMR methods. For the triflic anion ΔH_e (kcal/mol) and ΔS_e (cal/(mol K)) are respectively equal to: in CCl_4 −6.0 ± 0.3 and −25 ± 1 and in CH_2Cl_2 −5.6 ± 0.2 and −19.7 ± 0.8. Thus, K_e ($K_e = k_{ii}^{\pm}/k_{tt}^{\pm}$) is equal to 0.07 in CCl_4 and to 0.58 in CH_2Cl_2. The rate constant of internal ionization depends at 25 °C much less on polarity then the rate constant of temporary termination. Thus, the actual position of equilibrium is determined mostly by the rate of the macroion pair collapse, being much higher in the system of low polarity: $k_{ii}^{\pm}$ (25 °C, $s^{-1} \times 10^2$) 0.8 (CCl_4) and 1.9 (CH_2Cl_2); $k_{tt}^{\pm}$ (25 °C, $s^{-1} \times 10^2$) 12.1 (CCl_4) and 3.3 (CH_2Cl_2). The rate constant of the collapse of the ion pair ($k_{tt}^{\pm}$) is comparable to the rate constant of propagation ($k_p^{\pm}$), indicating that monomer and triflic anion are of close nucleophilicity.

In solvolytic reactions,[1] cationic polymerization of vinyl monomers,[2–5] and more recently in the cationic polymerization of heterocyclic monomers, oxazolines,[6] and tetrahydrofuran (THF),[7–9] the simultaneous presence of covalent (e.g., macroester in THF) and ionic reactive species was observed. Some theoretical problems involving these equilibria have also been recently discussed.[10]

It is worth noting that among all of the above listed systems the direct simultaneous spectroscopic determination of both kinds (covalent and ionic) of reactive species has only been accomplished in the polymerization of oxazolines[6] and THF.[9,11–13] This gave an unusual possibility to study various aspects of chemistry involving these two isomeric states of the same species: covalent and ionic.

In the polymerization of THF both macroesters and macroions can contribute in propagation and their individual participations in the chain growth are related to the product of the concentration of given species and the corresponding rate constant of propagation: $k_p^E[E]$ and $k_p^{\pm}[P^{\pm}]$, where the symbols have the self-explanatory meanings.

Thus, in a general scheme of propagation for a system, in which free ions and higher aggregates of ion pairs[14] can be neglected, we have (n denotes a polymerization degree):

$$\begin{tikzcd}
\underset{(E)}{\text{macroester}_n} \arrow[rr, shift left, "k_{ii}^{\pm}"] \arrow[dr, "+M"', "k_p^E"] & & \underset{(P^{\pm})}{\text{macroion pair}_n} \arrow[ll, shift left, "k_{tt}^{\pm}"] \arrow[dl, "+M", "k_p^{\pm}"'] \\
& (\text{macroion pair})_{n+1} &
\end{tikzcd} \tag{1}$$

In our previous paper of this series[15] it has been shown, on the basis of kinetic measurements, that an analogous equilibrium, involving a bimolecular ionization of the macroester

$$\text{macroester}_n + \text{monomer} \underset{k_{et}^{\pm}}{\overset{k_p^E}{\rightleftharpoons}} (\text{macroion pair})_{n+1} \tag{2}$$

contributes much less to the ionization of macroesters than the unimolecular process, given by eq 1. Thus, at the usual concentrations of THF, contribution of an external ionization (according to eq 2) can be neglected.

We have recently measured directly k_p^E and found,[16] in agreement with our earlier assumption,[11] that, at least in CCl_4 solvent, $k_p^{\pm}/k_p^E > 10^2$. Thus, in our hands, the rate constant of propagation on a macroester (triflate) is close to the rate constant of addition of THF to the low esters (methyl, ethyl, propyl) of triflic acid. Kobayashi et al. made a claim that the fluosulfonic macroester is much more reactive in its reaction with THF then the low molecular weight esters.[17] These authors have, however, used unusually high concentrations of active species (up to 1.0 M), when secondary phenomena (heterogeneity of the systems, aggregation of macroion pairs) cast some doubt on the validity of conclusions.

Thus, our previous papers already described quantitatively the contribution of the individual propagations (with rate constants k_p^E and $k_p^{\pm}$) in the chain growth.

In the present paper we report on two other rate constants involved in eq 1, namely $k_{ii}^{\pm}$ and $k_{tt}^{\pm}$: rate constant of an intramolecular ionization, governing formation of macroion pairs from macroesters, and $k_{tt}^{\pm}$, rate constant of temporary termination, describing a rate constant with which a macroion pair collapses into a much less reactive macroester.

Experimental Section

Monomer and Solvents. THF was purified according to the known procedure[18] and kept as a bluish solution over a liquid Na/K alloy in a vacuum container. CCl_4 and CH_2Cl_2 were purified according to ref 18 and stored over CaH_2 in a black-painted round-bottom flask attached to the vacuum line. Both monomer and solvent were volumetrically measured by condensing in the graduated cylinders attached to the hyvac line.

Esters were prepared from the corresponding alcohols and anhydrides[19] and purified according to our published procedure.[11]

Measurements of the Rates of Interconversions. The rates of interconversions were measured in CCl_4, CCl_4/CH_2Cl_2, and CH_2Cl_2 solvents by ^1H and ^{19}F NMR methods. The use of the high resolution equipment (300 MHz for ^1H NMR) allowed us to measure sufficiently low concentrations of macroesters and macroion pairs, when aggregation of the macroion pairs does not upset equilibrium 1 and could be neglected.[14] At these conditions an equilibrium given by eq 1 describes adequately the system under study. At higher concentrations of living ends eq 1 has to be supplemented by an additional equilibrium, involving aggregated ions, which have to be considered in equilibrium with macroion pairs.[14] Free ions are eliminated by low polarity of the studied systems.

The required solutions for kinetic studies were prepared directly

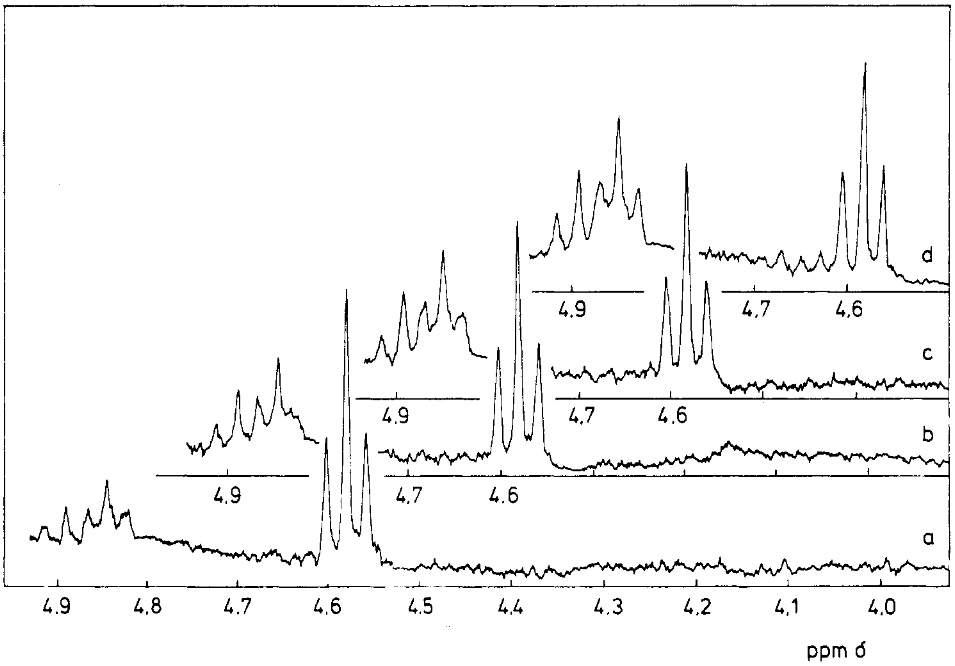


Figure 1. NMR (300 MHz) spectra of the region of living ends in polymerization of THF with $CF_3SO_2O^-$ anion at −18 °C after disrupting an equilibrium established at +18 °C by a sudden change of temperature (after time, s × 10^2): (a) 1.5, (b) 5.7, (c) 13.2, (d) 22.8. CCl_4, $[THF]_0$ = 8.0 mol $l.^{-1}$; initiator, $[CF_3SO_3CH_3]_0$ = 8.10^{-2} mol $l.^{-1}$ in CCl_4 solvent.

in the NMR tubes which were filled up and sealed off in the hyvac line. In experiments, in which CCl_4 was used as a sole solvent, small and precisely known amounts of CH_2Cl_2 were added as internal standards for chemical shifts.

In order to measure rates of conversion of macroesters into macroion pairs polymerization was brought first at 18 °C to equilibrium. When, according to NMR data, the involved equilibria became established, namely the polymer $\rightleftharpoons$ monomer equilibrium and an equilibrium between macroesters and macroions, the tube was immediately inserted into the cavity of the variable temperature probe at the chosen temperature.

It was shown in the independent experiments that thermal equilibrium becomes established for tubes of ϕ = 5 mm within 2–3 min for temperature changes not larger than 50 °C. The reaction half-times observed in this work were not lower than 10 min. Thus, the first spectrum was recorded about 2 min after the initial equilibrium started to change, induced by the change of temperature. Thereafter, spectra were periodically recorded at desired intervals of time.

Concentration of macroesters was determined in ^1H NMR by integrating a triplet due to protons at the carbon atom adjacent to an ester group and absorbing at 4.58 ppm (cf. Figure 1). Integration of the two superimposed triplets at 4.845 and 4.890 ppm (cyclic and linear α-methylene protons of tertiary oxonium ion) gives a concentration of macroions. Reaction was monitored until a new equilibrium between macroesters and macroions was established. This was always much faster than an establishment of a new polymer–monomer equilibrium. Because of the living character of a system, one filled tube could be used several times for various temperatures.

The two superimposed triplets at 4.845 and 4.890 (peak area close to 2:1, after a simple curve resolving) are indeed independent of each other and not a composite multiplet. The double resonance experiment (irradiation at the frequency 747 Hz, upfield from 4.845 triplet (cf. (3)) reduced one of the triplets to a singlet, while the other triplet remained unchanged.

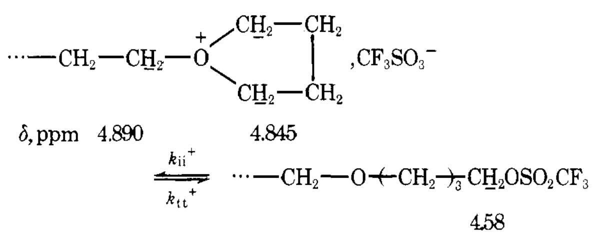
^{19}F NMR was studied with C_6F_6 as an internal standard, and the corresponding chemical shifts of the macroesters and macroion pairs (δ 88.6 and 85.2 ppm, respectively) depended slightly on temperature and concentration of the studied species, as described by us previously.[14]

At the lowest concentration of growing species the ratios between macroesters and macroions were determined from the polymerization kinetics as described by us previously, taking into account that propagation on macroion pairs dominates propagation by macroesters. In this way the proportion of ions could be determined from the measured rate of polymerization.

Results and Discussion

The Actual Picture of a Kinetic Run. A series of ^1H NMR (300 MHz) measurements, taken at various times, for the absorption region from δ 4.5 to 4.9 ppm is shown in Figure 1. Both macroions and macroesters absorb in this region.

The corresponding interconverting species are shown below (for triflic derivatives):



(3)

As is seen in Figure 1, the continuous decrease of the macroester triplet at 4.58 is accompanied by an equivalent increase of the macroion triplets, taking into account the 1:3 ratio of a number of corresponding protons in these species. The sum of the two integrals (with the above mentioned correction) served as an internal standard for individual concentrations of both species.

These data allowed us to determine the momentary concentrations of macroesters and macroions and to study in this way the thermodynamics and kinetics of their interconversion.

Thermodynamics of Equilibrium. The proportions of macroesters (E) and macroion pairs ($P^{\pm}$) have been measured at various temperatures and the obtained equilibrium constants K_e, where $K_e = [P^{\pm}]_e/[E]_e$, were plotted as functions of temperature. The dependence of $\ln K_e$ on $1/T$ is shown in Figure 2 for three different systems at $[M]_0$ (starting concentration of monomer) = 8.0 mol $l.^{-1}$. Concentration of living ends (L.E.), being a sum of macroesters and macroion pairs and equal to the starting concentration of initiator, was kept in the range 6–9 × 10^{-2} mol $l.^{-1}$ in order to avoid an aggregation of macroion pairs.[14] Experimental points in Figure 2 were collected from ^1H and ^{19}F NMR measurements, as well as from dilatometric studies of the polymerization kinetics.

From Figure 2 the corresponding ΔH_e and ΔS_e have been calculated and are given below for a $CF_3SO_3^-$ anion (Chart I).

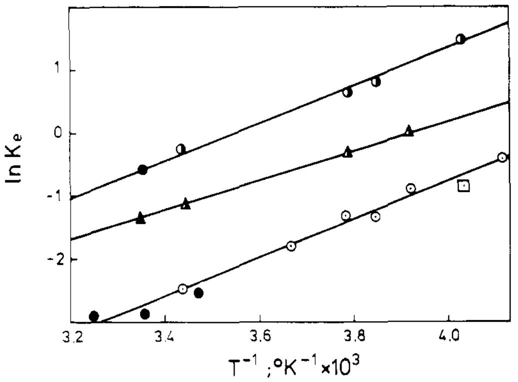


Figure 2. Dependence of ln K_e on T^{-1}. Solvents: (⊙) CCl_4, (▲, ◐) CH_2Cl_2. Anions: (⊙) $CF_3SO_3^-$, (△) FSO_3^-. Full points are from dilatometric measurements.

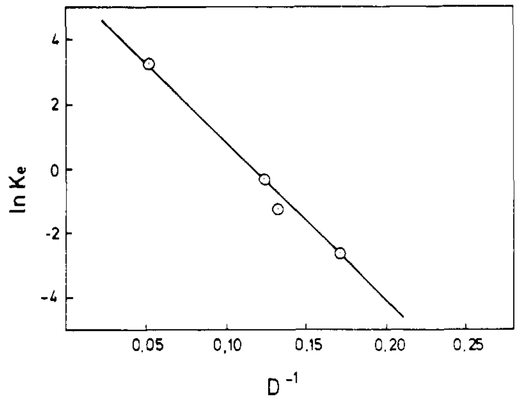


Figure 3. Dependence of ln K_e on D^{-1} at 25 °C for $CF_3SO_3^-$ anion.

Chart I

Solvent	ΔH_e kcal/mol^{-1}	ΔS_e, cal/mol^{-1} K^{-1}
CCl_4	−6.0 ± 0.3	−25 ± 1
CH_2Cl_2	−5.6 ± 0.2	−19.7 ± 0.8

Thus, as could be expected, conversion of macroesters into the macroion pairs is exothermic and endoentropic.

There is a formal analogy in the change of thermodynamic functions in the present ionization and a better known dissociation of ion pairs into free ions.[20] In both processes, apparently solvation factors prevail and are more important than the internal rearrangement of the species involved.

The passage from an ester to the monomer-separated macroion pair[31] should be accompanied by a small decrease of entropy, mostly the translational entropy. Contributions of rotational and vibrational entropies are usually of minor importance. The change of conformational entropy, which can account for a few entropy units in ΔS_e, has its origin in formation of a strained tertiary oxonium ion from a linear ester.

All of these effects cannot account for more than 10–15 entropy units[21,22] and probably even less.

Apparently the highest contribution to the entropy change comes from an additional solvation of the more polar macroion pair by solvent and/or monomer molecules.

Exothermicity of ionization of a macroester is apparently due predominantly to the heat of solvation, in analogy with exothermic dissociation of ion pairs into free ions.

Differences between the entropy change, observed in various solvents, although not too large, are worth noting because they reflect the molecular state of solution of THF in these solvents.

It is known that the heats of interaction (ΔH_m) of THF, being a basic compound, with various acidic solvents are quite high; some of the pertinent values of ΔH_m are given in Chart II.

Chart II

Solvent	ΔH_m, kcal mol^{-1}
$CHCl_3$	−3.2[23]
CH_2Cl_2	−1.2[24]
CCl_4	−0.7[24]

Data shown above mean that, for instance, in CCl_4 solvent there are more free THF molecules available than in $CHCl_3$ solvent, in which a momentary concentration of uncomplexed THF should be lower.

These specific interactions of THF explain differences between the entropy change observed in CCl_4 and CH_2Cl_2.

Macroion pairs are separated and specifically solvated with THF and when a macroester ionizes into a macroion pair in a more polar solvent a smaller number of THF molecules become additionally immobilized than in the less polar one.

This is because in the CH_2Cl_2–THF solution there is already some order established, due to the strong solvent–THF interaction. Thus, formation of the THF shell around the cationic part of a macroion pair means merely a transfer of THF from one ordered state, already existing in solution of a macroester, to another ordered state, in the proximity of cation after its formation. This differs from the CCl_4–THF system, where the solvent–THF interaction is much less pronounced.

Thus, as a result of these differences, ΔS_e is more negative in CCl_4 than in CH_2Cl_2.

The dependence of ln K_e on $1/D$, resulting from the changes of ΔH_e and ΔS_e discussed above, is shown in Figure 3. This relationship shows that, e.g., at 25 °C, $K_e(CH_2Cl_2) = 0.58$, while $K_e(CCl_4) = 0.06$ remembering that K_e = [macroion pairs]/[macroester], the change at 25 °C from CCl_4 to CH_2Cl_2 increases the proportion of macroion pairs by almost one order of magnitude (seven times), i.e., from 5 to 35%. Although the more detailed studies of the system THF–CH_3NO_2 will be published separately, the preliminary results show that the linear dependence of ln K_e on $1/D$ (in Figure 3) passes through a point at $1/D = 0.05$, after a correction for free ions is made,[25] giving $K_e(CH_3NO_2) = 0.9$. All of these data on the proportions of macroion pairs and macroesters in CH_3NO_2, CH_2Cl_2, and CCl_4 solvents are in quantitative agreement with our prediction, based on the polymerization kinetics and reported already in 1973.[8]

Kinetics of Internal Ionization ($k_{ii}^{\pm}$) and of Temporary Termination ($k_{tt}^{\pm}$). The interconversion of macroesters and macroion pairs is described by a following simple unimolecular opposed reaction:

$$E \underset{k_{tt}^{\pm}}{\overset{k_{ii}^{\pm}}{\rightleftharpoons}} P^{\pm}, K_e = [P^{\pm}]/[E] = k_{ii}^{\pm}/k_{tt}^{\pm} \tag{4}$$

Solution of the set of eq 4 leads to the following expression[26]

$$\ln \frac{[E]_0 - [E]_e}{[E]_t - [E]_e} \Bigg/ \frac{(1 + K_e)}{K_e} = k_{ii}^{\pm} \cdot t \tag{5}$$

where t denotes time, $[E]_0$, $[E]_e$, and $[E]_t$ are determined directly from NMR spectra like these in Figure 1, K_e are known from equilibrium experiments (previous paragraph), and, therefore, plotting the left-hand side of eq 5 against time the value of $k_{ii}^{\pm}$ can be determined from a slope.

Typical plots are shown in Figure 4. Rate constants $k_{tt}^{\pm}$

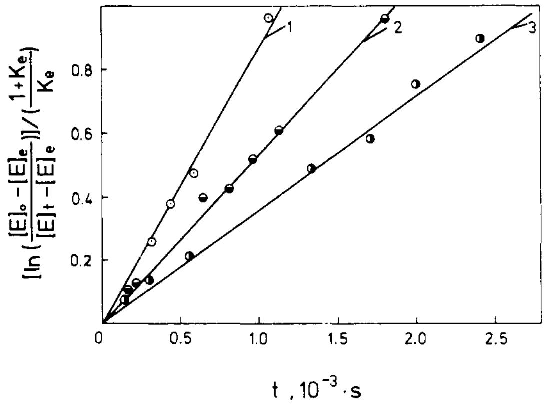


Figure 4. Kinetics of macroester–macroion interconversion at −18 °C for $[THF]_0$ = 8.0 mol l.$^{-1}$: (1) $[CF_3SO_3CH_3]_0$ = 0.10 mol l.$^{-1}$, mixture CH_2Cl_2 with CCl_4; (2) $[FSO_3CH_3]_0$ = 0.09 mol l.$^{-1}$, CH_2Cl_2 solvent; (3) $[CF_3SO_3CH_3]_0$ = 0.08 mol l.$^{-1}$, CCl_4 solvent.

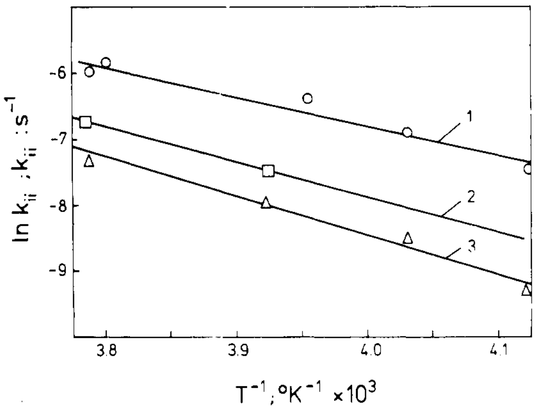
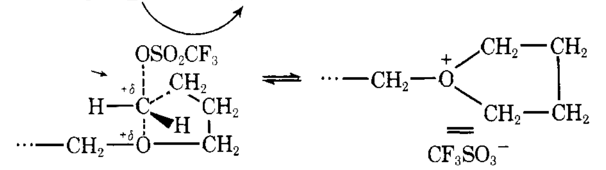


Figure 5. Dependence of ln k_{ii} on T^{-1}: (1) $CF_3SO_3^-$ anion, CH_2Cl_2 solvent; (2) FSO_3^- anion, CH_2Cl_2 solvent; (3) $CF_3SO_3^-$ anion, CCl_4 solvent.

have further been calculated from $k_{ii}^{\pm}$ and K_e, remembering that $K_e = k_{ii}^{\pm}/k_{tt}^{\pm}$.

From linear dependences of ln $k_{ii}^{\pm}$ and ln $k_{tt}^{\pm}$ on $1/T$ (Figures 5 and 6) the corresponding thermodynamical activation parameters have been determined. The dependence of ln $k_{ii}^{\pm}$ and ln $k_{tt}^{\pm}$ on the polarity of the reaction medium (expressed as D) is given in Figure 7.

Before discussing the meaning of numerical values of the thermodynamic activation parameters let us consider again conversion of macroesters into a macroion pair and a structure of the transition state (for triflic derivatives, taken as an example):



(6)

(where ═ denotes a molecule of THF, and an arrow shows a direction of an approach of THF molecule separating an already formed ion pair).

Formation of the $^{+}C{-}^{-\delta}O{-}CH_2$ bond and breaking of the ester $^{+}C{-}^{-\delta}OSO_2{-}CF_3$ bond within a transition state (trigonal bipyramid) are immediately followed by separation of the ions by the THF molecule. The structure of the transition state proposed in eq 6 and its steric arrangement are in agreement with the transition states proposed for the nucleophilic displacement (S_N2) reactions.[27] Thus, a monomer molecule becomes immobilized only in the final ionic state. According to the proposed model, macroester and transition state, behaving as polar molecules, are solvated by components of the system according to their statistical distribution, and only after the ion pair is formed does the cationic part become preferentially solvated by THF.

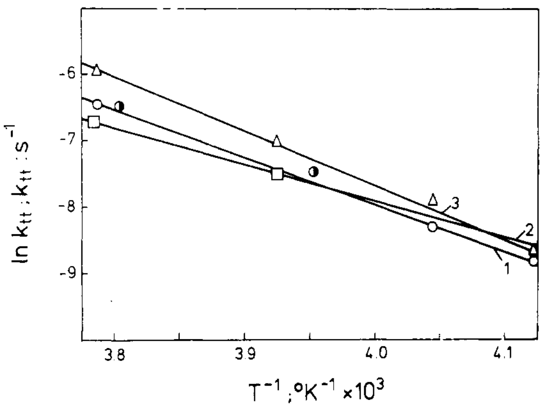


Figure 6. Dependence of ln k_{tt} on T^{-1}: (1, 2, 3) the same as in Figure 5.

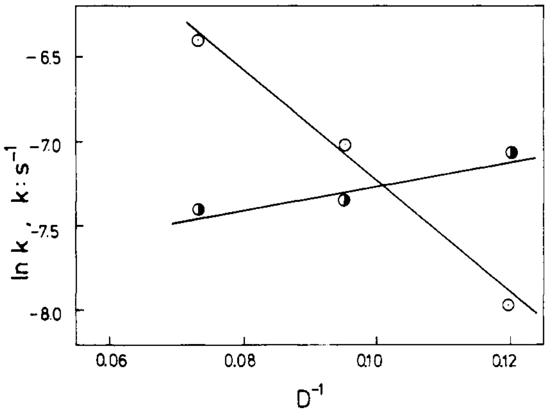


Figure 7. Dependence of ln k_{ii} (⊙) and ln k_{tt} (◐) on D^{-1} at −18 °C.

The data shown in Figures 8 and 9 indicate that the entropy of activation is for both reactions (i.e., internal ionization and temporary termination) more negative in CH_2Cl_2 than in CCl_4. This difference is only slightly compensated by a difference in enthalpies of activation; these are slightly higher in CCl_4 than in CH_2Cl_2.

The large differences in entropies of activation cannot account for structural factors and can only have their origin in the domination of solvation phenomena.

It is also quite unusual that the direction of changes of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with solvent polarity are the same for both considered reactions, going through the same transition state.

This can be explained on the basis of the detailed analysis of differences in solvation of two ground states: macroester and macroion pair. Although structural factors also contribute in the energetics of activation, solvation, as dominating in the whole process, is discussed first.

In our explanation describing activation parameters of the transfer from both ground states, covalent and separated ion pair into a common transition state, an influence of two different kinds of solvation effects will simultaneously be considered: the polarity of the reaction medium and special solvation.

The special solvation is due to the preferential solvation of the cationic part of the ion pair by THF, which is the most

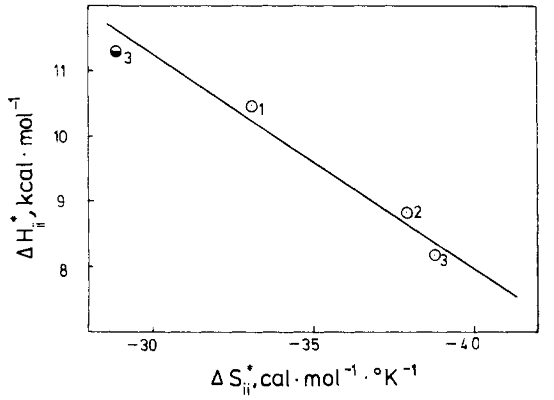


Figure 8. Isokinetic plot for internal ionization for different solvents: (1) CCl_4 solvent, (2) CCl_4:CH_2Cl_2 = 1:3 (molar) mixture, (3) CH_2Cl_2 solvent, (○) $CF_3SO_3^-$, (◑) FSO_3^-.

basic component of the polymerization mixture. This special solvation does not however take place with a macroester, because these species do not have sufficiently separated charges to choose specifically from the components of solution (e.g., THF and CH_2Cl_2); the same applies to the transition state.

The internal ionization process, i.e., a passage from a macroester to the partially ionic transition state, bears resemblance to the complete conversion of a macroester into the macroion pair. Therefore, our discussion of the thermodynamic parameters describing this change does apply at least partially to the internal ionization.

Thus, the entropy of activation is negative mostly because of the more pronounced solvation of the transition state, being more polar than the macroester.

However, in contrast to the macroion pair, which comprises at least one frozen THF molecule, the transition state (cf. (6)), although more polar than the macroester, is not ionic enough to be solvated specifically (i.e., preferentially by THF). Therefore, the transition state is more solvated in a more polar solvent, and, as a result, $\Delta S_{ii}^{\ddagger}$ is more negative in CH_2Cl_2 than in CCl_4.

$\Delta H_{ii}^{\ddagger}$ in CH_2Cl_2 is lower than in CCl_4 (Figure 8), because in a more polar solvent the ester bond is polarized to a larger extent and weakened. The heat of solvation of the transition state is also higher with a more polar solvent. This leads eventually to the lower enthalpy of activation in CH_2Cl_2 solvent.

Structual factors are similar to those already discussed in the previous section (thermodynamics).

In the collapse of a macroion pair into a macroester (temporary termination), solvation factors also dominate in the overall energy change. Recombination of two opposite counterions should proceed with almost no energy loss ($\Delta H_{tt}^{\ddagger}$ should be close to 0) because the energy required for stretching of the O^+–CH_2 bond in the tertiary oxonium ion should be outweighed by partial overlapping of orbitals of an anion and the positively charged transient carbon atom. Thus, the observed large enthalpy of activation ($\Delta H_{tt}^{\ddagger}$) has its origin in the loss of energy due to desolvation.

The structural entropy change should be negative, because mobility of components of an ion pair is less restricted than in a more rigid transition state. On the other hand, a molecule of THF, separating the ion pair, is released increasing the entropy of the system.

According to Figure 9, $\Delta H_{tt}^{\ddagger}(CCl_4) > \Delta H_{tt}^{\ddagger}(CH_2Cl_2)$. This can be explained by an assumption that more desolvation energy is required to desolve an ion pair specifically solvated (by THF) in less polar solvent, in which the THF–solvent interaction is much weaker.

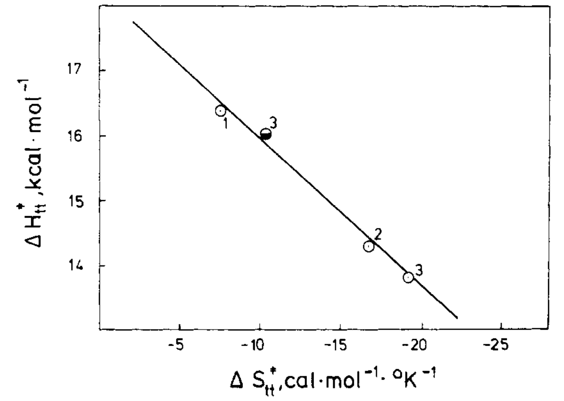


Figure 9. Isokinetic dependence for temporary termination: (1, 2, 3) the same as in Figure 8.

In accordance with this explanation the observed $\Delta S_{tt}^{\ddagger}$ is less negative (only 8 eu) in CCl_4 than in CH_2Cl_2. Apparently, a number of THF molecules released from the solvation shell around a macrocation become in CCl_4 sufficiently large to outweigh almost completely the negative structural components of the entropy change.

Influence of the Structure of an Anion on Thermodynamics and Kinetics of Interconversion. Comparison of the thermodynamic parameters describing the macroester ⇌ macroion equilibrium for fluosulfates and triflates indicates that the fluosulfates prefer, in comparison with triflates, to exist in the form of a macroester. The enthalpy of equilibrium is less negative for fluosulfates (i.e., formation of a fluosulfonic macroion pair is less exothermic) and the entropy of equilibrium is almost the same, namely in CH_2Cl_2 solvent $\Delta S_{e(FSO_3^-)} = -18.5 \pm 0.5$ eu ($\Delta S_{e(CF_3SO_3^-)} = -19.7 \pm 0.8$ eu). The differences in behavior of both anions are due to differences in enthalpies. In CH_2Cl_2 solvent $\Delta H_{e(FSO_3^-)} = -4.7 \pm 0.1$ kcal mol^{-1} (−5.6 for $CF_3SO_3^-$).

The observed difference in ΔH_e for fluosulfates and triflates simply reflects the higher nucleophilicity of fluosulfonic anion; this leads to higher energy needed to break the ester bond lowering in this way the overall exothermicity of the conversion of a macroester into a macroion pair.

Analysis of the activation parameters (cf. Figures 8 and 9) indicates that $\Delta H_{ii}^{\ddagger}$ is higher for fluosulfates, in accordance with the above discussion of differences in ΔH_e. However, in the temporary termination (collapse of an ion pair) the enthalpy of activation for fluosulfonic anion is also higher than for the triflic anion ($\Delta H_{tt}^{\ddagger}(FSO_3^-) > \Delta H_{tt}^{\ddagger}(CF_3SO_3^-)$). Apparently, the smaller FSO_3^- anion is more strongly solvated than a larger $CF_3SO_3^-$ anion and more desolvation energy is needed in formation of the transition state. Thus, the higher tendency of fluosulfates to exist as macroesters has its origin in the more energy consuming breaking of the ester bond and not in the easier collapse of an ion pair, which, actually, proceeds faster for given conditions for triflic anions (Table I).

Propagation on the Macroion Pair Involving Temporary Termination (Collapse of an Ion Pair) and Internal Ionization. As has been shown in this and preceding papers,[11] macroesters are converted into ion pairs (and vice versa) almost exclusively via an intramolecular reaction. Domination of an intramolecular ionization over a bimolecular process, involving reaction between a macroester and a monomer molecule, has its origin in the neighboring group participation effect.[28,29]

Obviously, the neighboring group participation (oxygen atom from a chain is favorably located for a nucleophillic attack (cf. eq 6)) can only be realized if energy gain due to this favorable conformational effect can outweigh the loss of en-

Table I
Rate Constants and Activation Parameters of Internal Ionization (ii) and Temporary Termination (tt) ($[THF]_0$ = 8.0 mol l.$^{-1}$, 25 °C)

Anion	Solvent	$k_{ii}^{\pm}$, 10^2 s^{-1}	$\Delta H_{ii}^{\pm}$, kcal mol^{-1}	$\Delta S_{ii}^{\pm}$, cal mol K^{-1}	$k_{tt}^{\pm}$, 10^2 s^{-1}	$\Delta H_{tt}^{\pm}$, kcal mol^{-1}	$\Delta S_{tt}^{\pm}$, cal mol K^{-1}
$CF_3SO_3^-$	CH_2Cl_2	1.9	8.2 ± 1.0	−39 ± 4	3.3	13.8 ± 1.2	−19 ± 5
$CF_3SO_3^-$	CCl_4	0.8	10.4 ± 1.2	−33 ± 5	12.1	16.4 ± 1.5	−8 ± 6
FSO_3^-	CH_2Cl_2	1.6	11.3	−29	5.9	16.0	−10

ergy due to the strain of the formed ring. The former equals only a few kcal mol^{-1} in THF, while in the three- and four-membered ethers the ring strain approaches 20 kcal mol^{-1}. Because of this tremendous difference, an intramolecular ionization with these monomers is not possible, and in the supposed macroester–macroion equilibrium macroesters are exclusively present.[30]

This, in fact, has been experimentally proved by Saegusa et al.[17] who have shown that in the polymerization of oxiranes and oxetanes the macroesters are (in the polymerization initiated by fluosulfates) the only active species.

In the cationic vinyl polymerization, e.g., in the polymerization of styrene with the ester bond forming anions (e.g., ClO_4^-), the interconversion of a macroester into a macroion pair (and vice versa) is slow and inefficient.[4]

This is again, as in the already discussed polymerization of the three- and four-membered ethers, a result of an absence of a driving force for the ion-forming processes provided in the polymerization of THF by the neighboring group participation.

In our preliminary publication (Roeun, 1973),[8] describing the kinetics of polymerization of THF with $CF_3SO_3^-$ anion, we considered only the bimolecular ionization as others did until now. This treatment should now be supplemented by a faster intramolecular ionization, dominating the bimolecular reaction.

Thus, from a viewpoint of an individual growing living center, the following sequence of consecutive and parallel reactions takes place:

$$\begin{tikzcd}
\text{macroester}_n \arrow[r, shift left, "k_{ii}^{\pm}"] \arrow[rr, bend right=40, "{+M,\ k_{ei}^{\pm} = k_p^E}"'] & \text{macroion pair}_n \arrow[l, shift left, "k_{tt}^{\pm}"] \arrow[r, shift right, "{+M,\ k_p^{\pm}}"'] & \text{macroion pair}_{n+1} \arrow[l, shift right, "{-M,\ k_d^{\pm}}"'] \arrow[ll, bend left=50, "{-M,\ k_{et}^{\pm}}"]
\end{tikzcd}$$

In CCl_4 solvent (25 °C, $[M]_0$ = 8 mol l.$^{-1}$) the scheme given above can be described in the following way (at the monomer–polymer equilibrium): an average macroion pair adds monomer every 7 s and exists as an ion pair, before collapsing into a macroester of the same polymerization degree, during 8.3 s. This is a time sufficient to add 1.2 monomer molecules. After this time the macroion pair converts into a much less reactive macroester, existing in this state during a time equal to 125 s. This is a time sufficient for a rival macroion pair to add 18 molecules of monomer. After conversion of a macroester into the macroion pair the same sequence repeats again.

Macroester can be converted into the macroion pair in a bimolecular reaction (cf. scheme above) with a rate constant $k_{ei}^{\pm}$; this event, however, takes place only once for 32 unimolecular conversions and can thus be practically neglected.

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(31) Evidence will be discussed in our next paper describing the reactivity of ion pairs and "free" ions in the cationic polymerization of THF.