Macroesters and macroions in the polymerization of THF with ClO_4^- anion

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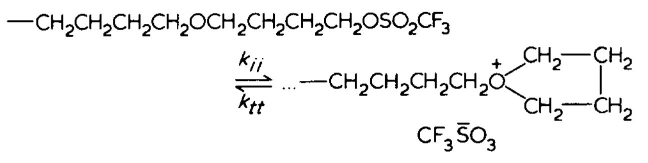
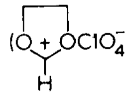
Independent n.m.r. observation of macroesters and macroions in the polymerization of THF [1, 2], for systems initiated with strong acids or their derivatives bearing anions able to form covalent bonds [3, 4] allowed the corresponding thermodynamic equilibrium constants K_e to be determined [5]: e.g.



where $K_e = k_{ii}/k_{tt}$

K_e were measured by us previously[6] for sufficiently low concentration of the growing macrocations to avoid the complicating influence of agglomeration of the macroion-pairs[7] and at conditions when dissociation of macroion-pairs does not upset equilibrium (1).

In order to complete these data and to see whether the nucleophilicities of anions correlate with K_e, we studied polymerization of THF with ClO_4^- anion.



Experimental

1,3-dioxolane-2-ylium perchlorate (I) was prepared from 1,3-dioxolane and $(C_6H_5)_3C^+ClO_4^-$ by H^- transfer method as described previously.[8] *Caution:* I is a powerful explosive when in a dry state and has to be handled with extreme care and only in small quantities. It can be stored below – 20° without noticeable decomposition for at least several days. Initiation of THF with I proceeds with a rate constant k_i comparable to k_p.

THF was purified as previously described.

Solvents: CD_2Cl_2 (IZS, GDR) was dried over D_2SO_4 and then distilled twice over fresh Na-mirrors. CD_3NO_2 was dried with CaH_2 and distilled *in vacuo* into a flask with fresh CaH_2.

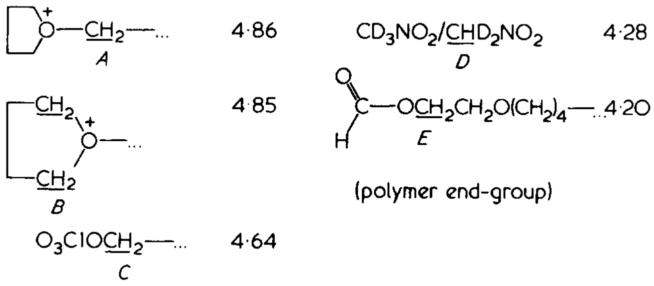
Filling of the n.m.r. tubes was performed *in vacuo* as it was already described.

Measurements were performed by FT-^{1}H-n.m.r. (250 MHz) Cameca.*

Results and Discussion

The 250 MHz FT-^{1}H-n.m.r. spectrum of the region from 4.15 to 5.0 ppm δ is shown in *Figure 1*.

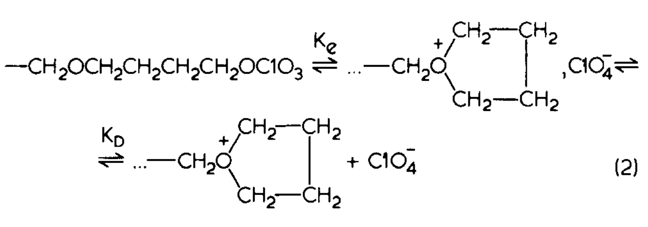
Below, chemical shifts observed in *Figure 1* are assigned to their chemical origins (in ppm δ from TMS).



The ratio of the A/B signals was equal to 1/2 in all of the spectra recorded, and the ratio $(A + B)/C$ depended on the temperature and polarity of the medium as for trifluoric and fluorosulphonic anions [5].

When macroions are practically absent and only macroesters and macroion-pairs are present the equilibrium constant K_e is directly given by ratio of the peak area (cf. equation (1)): $K_e = (A + B)/3C$.

When equilibrium (1) has to be complemented (in more polar solvents) by macroions:



(2)

then

$$[\text{ative species}] = ([I_0]) = [P^+] + [P^\pm] + [E] \tag{3a}$$

$$|I|_0 = [P^+]\left(1 + \frac{[P^+]}{K_D}\,\frac{(1+K_e)}{K_D}\right) \tag{3b}$$

and, eventually:

$$\frac{[P^+] + [P^\pm]}{[I]_0} = \frac{1 + 2/K_e + (1 + 4[I]_0(1+K_e)/K_e{\cdot}K_D)^{1/2}}{1 + (1 + 4[I]_0(1+K_e)/K_e{\cdot}K_D)^{1/2}} \times \frac{K_e}{1+K_e} \tag{3c}$$

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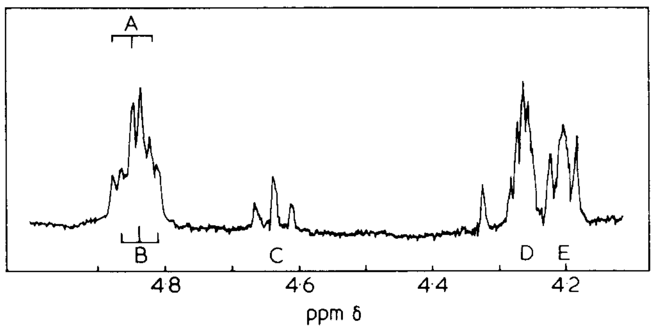

Figure 1 ^{1}H-N.M.R. spectrum of the region of living ends (4.15-5.00 ppm δ) in polymerization of THF with ClO_4^- anion at 20° $[THF]_0 = 8.0\ mol^{-1}$ $CD_3NO_2 : CD_2Cl_2 = 0.89$ (molar ratio) $[I]_0 = 5 \times 10^{-2}\ mol \times 1^{-1}$.

Thus, for conditions including macroions actual values of K_e can be found from equation (3c), if it is assumed that K_D values do not change in the presence of a macroester. K_D is almost independent on anion structure [9]

Below, in *Table 1*, the results of measurements of K_e are given, as measured by ^{1}H-N.M.R. and calculated from equation (3c).

Thus, at 20°C, in CH_2Cl_2 solvent and in CH_3NO_2 solvent ($[THF]_0 = 8.0\ mol \times 1^{-1}$ for both cases) K_e equals 9.5 and .09 respectively.

$$k_p^{app}/k_p^i = \frac{[P^+] + [P^\pm]}{[I]_0} = \frac{K_e'}{1 + K_e'} \tag{4}$$

where

$$K_e' = K_e \frac{1 + 2/K_e + (1 + 4[I]_0(1 + K_e)/K_e \cdot K_D)^{1/2}}{(1 + 4[I]_0(1 + K_e)/K_e \cdot K_D)^{1/2} - 1}$$

and assuming that the rate constant of propagation with ClO_4^- anions (k_p, ClO_4^-) is equal to that with other anions (the dependence of k_p on anion structure is described in *Ref. 6*).

Kinetic measurements allowed also K_e to be determined in CCl_4 solvent, where concentration of macroions is too small to be observed by n.m.r. $K_e = 10^{-2}$ was found for $[THF]_0 = 8.0\ mol \times 1^{-1}$ at 25˘, in CCl_4 solvent.

The values of K_e determined for ClO_4^- anion in CH_3NO_2 and CH_2Cl_2 solvent shown in *Table 1*, can be compared with K_e determined earlier for $CF_3SO_3^-$ and FSO_3^- anions (*Table 2*).

Comparison of acid strength (known to increase in the order $HClO_4 < FSO_3H < CF_3SO_3H$) with the determined K_e values indicates that, as it was supposed, the higher the nucleophilicity of the anion the higher the ability of macroion-pair to collapse into the macroester i.e. the lower the value K_e.

Table 1 Values of macroester ⇌ macroion-pair equilibrium constants in THF polymerization for ClO_4^- anion[a]

$V_{CH_3NO_2}/V_{CH_2Cl_2}$	ϵ	K_D,[b] $mol^{-1} \times 1 \times 10^{-3}$	$(\|P^+\| + \|P^\pm\|)/\|E\|$	K_e
∞	20.2	6.0	11.3	9.5 9.0[c]
2.5	17.0	3.3	3.1	2.2
0.75	13.5	1.4	1.7	1.4
0.425	12.0	0.78	1.2	1.0
0.167	10.0	0.27	0.41	0.33
0	8.1	0.068	0.10	0.9 0.9[c]

[a] $[THF]_0 = 8.0\ mol \times 1^{-1}$, 20°C, $[I]_0$= variable

[b] taken from Ref. 9 for SbF_6^- anion

[c] from kinetic measurements

Table 2 K_e values determined by ^{1}H-n.m.r. for macroester ⇌ macroion pair equilibrium*

Solvent	ClO_4^-	FSO_3^-	$CF_3SO_3^-$
CH_2NO_2	9.5	20	42
CH_2Cl_2	0.09	0.27	0.58

* $[THF]_0 = 8.0\ mol\ 1^{-1}$, 20°C, $[I]_0$ = variable

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