Anionic polymerization of ethylene oxide with cryptates as counterions: 1.

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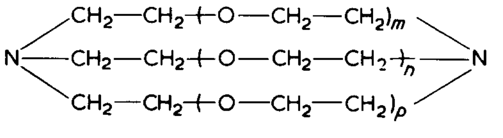
A kinetic study of the anionic polymerization of ethylene oxide has been made in tetrahydrofuran at 20°C, with the cryptate K^+ + [222] as counterion. The ion pair dissociation constant K_D has been deduced from conductivity measurements made on seeds solutions. Some ionic associations higher than cryptated ion pairs could be detected but they are negligible for living end concentrations lower than 6×10^{-4} mol/l. $k_\pm$ and k_- were determined from both sets of kinetic data obtained with and without added salt. Free alkoxide ions are one hundred times more reactive than cryptated ion pairs.

INTRODUCTION

Anionic polymerization of ethylene oxide in the absence of proton donors has been studied in some details by several authors[1–11]. The dependence of the rate of polymerization on the concentration of active centres is complex since associations of ion pairs remain down to low living ends concentrations, and occur even in high polar solvents such as hexamethylphosphoramide[1,3,8]. Dissociation constants of alkoxide ion pairs into free ions are very small in solvents of medium polarity such as tetrahydrofuran (THF) or 1,2-dimethoxyethane[5,6] making the determination of reactivities of different ionic species difficult.

It has been shown that some macroheterobicyclic ligands discovered by Lehn *et al.*[12], which give the so-called 'cryptate' complexes with alkali and alkaline earth cations, lead to the formation of complexed ionic species that are highly reactive[13–15]:



m=n=p=2 designated [222]

Anionic polymerizations of heterocyclic monomers such as propylene sulphide[16,17] and lactones[18] with cryptates as counterions have been examined in some detail, as well as the ring opening of ethylene oxide by several cryptated salts of carbazole and 9-methylfluorene[19,20]. This paper will describe the kinetic results we have obtained for the anionic polymerization of ethylene oxide in THF at 20°C, with the cryptate K^+ + [222] as counterion.

EXPERIMENTAL

All the experiments were made in glass apparatus sealed under high vacuum in order to avoid the destruction of living centres. THF and ethylene oxide were dried over calcium hydride and several sodium mirrors as usual[17,20]. The [222] compound was purified by freeze-drying in benzene and sealed under high vacuum in ampoules fitted with break-seals as described previously[21]. The initiator used in the present study was carbazylpotassium complexed by [222] in THF which was prepared according to the described procedure[22].

Since the initiation is much more rapid than the propagation, conductance and viscosity measurements were performed under vacuum on living poly(ethylene oxide) solutions prepared by reaction of cryptated carbazylpotassium with a small amount of monomer. The conductimetric cell generally used in our previous studies[21,23,24] was slightly modified since it was impossible to change the concentration of the electrolyte by transferring part of the solution to a side tube and distilling the solvent back to the remaining solution, because the living poly(ethylene oxide) precipitate in THF at temperatures lower than 20°C. Thus dilutions were made by successive additions of known amounts of purified THF in a 2000 ml flask fitted with the electrode assembly, two concentric platinum cylinders, in a well at the bottom.

Viscosity measurements were made on active and terminated polymer solutions as described in a previous paper for living poly(propylene sulphide) solutions[25].

Kinetic measurements were made by dilatometry after addition of the monomer to the initiator solution for each experiment. In all cases, concentration in living ends was deduced from that of the initiator which was determined by spectrophotometry using a Cary Model 118 apparatus. Polymerizations of ethylene oxide were stopped by adding a small amount of methanol. Polymers were recovered after precipitation in hexane: their molecular weights were measured by osmometry in toluene at 37°C and by viscometry in water at 25°C using the following relationship[26]:

$$[\eta]\,\text{ml/g} = 2 + 0.027\,(M_v)^{0.725}$$

RESULTS AND DISCUSSION

Anionic polymerization of ethylene oxide initiated by cryptated carbazylpotassium in THF at 20°C gives living polymers, the molecular weight of which can be predicted from the

Table 1 Molecular weights of poly(ethylene oxides) initiated by carbazylpotassium + [222] in THF at 20°C

Initiator [*C*] × 10^4 (mol/l)	[222] × 10^4 (mol/l)	Monomer [*M*] (mol/l)	Yield (%)	Theoretical $\bar{M}_n$ [a]	Experimental $\bar{M}_n$ [b]	Experimental $\bar{M}_v$ [c]
4.8	5.8	1.08	90	89 000	88 000	–
3.7	4.9	0.52	100	62 000	67 000	–
6.2	6.3	1.76	100	125 000	120 000	129 000
1.5	3.0	1.18	100	346 000	337 000	–

[a] Calculated from $\overline{DP}_n = [M]/[C]$; [b] measured by osmometry in toluene at 37°C; [c] measured by viscosity in water at 25°C

Table 2 Conductance date for seeds of poly(ethylene oxide) with K^+ + [222] as counterion in THF at 20°C

Λ	[*C*] × 10^5 (mol/l)
1.09	102.50
1.35	58.40
1.69	30.75
1.97	21.21
2.23	16.47
2.58	10.87
2.97	7.92
3.23	6.43

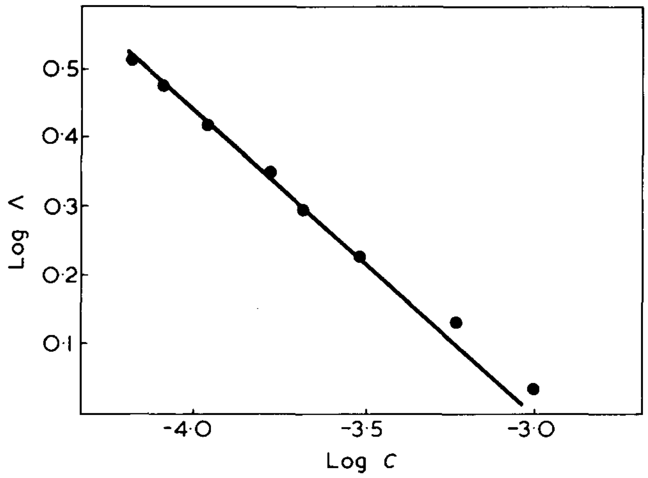


Figure 1 Log Λ vs. log *C* plot for living poly(ethylene oxide) with the cryptate K^+ + [222] as counterion in THF at 20°C

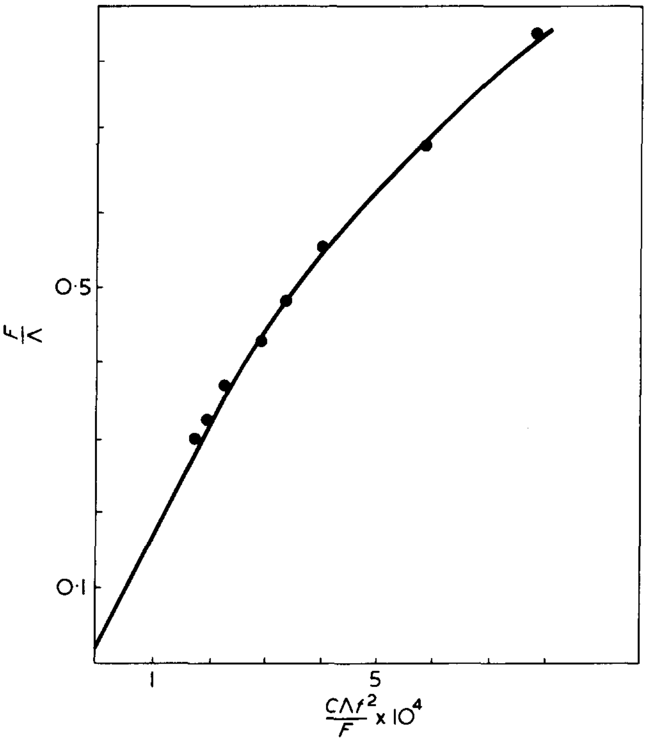


Figure 2 Fuoss conductivity plot for living poly(ethylene oxide) with K^+ + [222] as counterion in THF at 20°C

monomer and initiator concentrations as shown by the results of *Table 1*. There is a good agreement between theoretical molecular weights calculated from the relationship $\overline{DP}_n = [M]/[C]$ and experimental molecular weights measured by osmometry or viscosity, within the experimental errors.

Conductance measurements

Conductance measurements were made on seeds solutions prepared by adding a small amount of ethylene oxide to cryptated carbazylpotassium ($\bar{M}_n \simeq 13\,500$), in THF at 20°C, over a concentration range of 1×10^{-3} to 6×10^{-5} mol/l. The results are given in *Table 2*. Plot of log Λ vs. log *C* is a straight line for living end concentrations lower than 6×10^{-4} mol/l, the slope of which is equal to –0.44 (*Figure 1*). The dissociation constant K_D of the living polymer was estimated applying the Fuoss conductance equation[27–29]: $F/\Lambda = 1/\Lambda_0 + f^2 C\Lambda/FK_D\Lambda_0^2$ and the plot is shown in *Figure 2*. The intercept of the Fuoss line is too small to allow determination of $1/\Lambda_0$. We have assumed that $\Lambda_0 = \lambda_0^+ + \lambda_0^-$ is equal to 41. λ_0^+ for K^+ + [222] has been determined in THF at 20°C from conductance measurements made on ϕ_4BK + [222]: $\lambda_0^+ = 35$[21], and λ_0^- has been deduced from the empirical relationship between $\lambda_0^-\eta$ and the molecular weight of anions[30]: $\lambda_0^- = 6$. Contribution of the polymer anion is small enough so that an error in λ_0^- will not greatly affect Λ_0. The values of the physical constants for THF given by Szwarc *et al.*[31] were used for the calculations. The Fuoss plot is nearly a straight line for low concentrations but becomes slightly curved at higher concentrations indicating the presence of some ionic associations higher than ion pairs. The ion pair dissociation constant K_D was found to be equal to 3×10^{-7}.

Viscosity measurements

The extent of ionic aggregates for high living end concentrations could be detected by viscosity measurements on active and terminated polymers as can be seen in *Table 3*. Some ionic associations still remain though K^+ is complexed by [222], however they become negligible for living end concentrations lower than 3×10^{-4} mol/l. We will see that these associations have not an important influence on the kinetic results even at 7×10^{-4} mol/l.

Table 3 Variations of the ratio of flow times of living (t_l) and terminated (t_t) poly(ethylene oxide) solutions in THF with living ends concentration at 20°C ($\bar{M}_n \simeq 13\,500$)

t_l/t_t	$[C] \times 10^5$ (mol/l)
1.17	100
1.14	58.5
1.07	28.5
1.04	15.9
1.03_5	11.5
1.02	7.1
1.01_5	5.1

Table 4 Kinetic results for anionic polymerization of ethylene oxide with K^+ + [222] as counterion in THF at 20°C ($[222]/[K^+] \simeq 1.2$)

$[C] \times 10^5$ (mol/l)	ϕ_4BK + [222] $\times 10^5$ (mol/l)	$[M] \times 10$ (mol/l)	$\alpha \times 10^2$	k_p (l/mol/min)
74.5	0	2.07	1.98	3.70
67.8	0	2.01	2.10	3.38
35.0	0	2.05	2.90	4.39
11.0	0	1.98	5.10	6.86
4.1_5	0	2.10	8.10	9.90
8.7	0.89_5	2.06	2.80	4.40
8.8_5	2.27	1.87	1.50	3.85
7.6	7.70	1.82	0.61	2.58
14.8	100	2.15	0.12	1.28

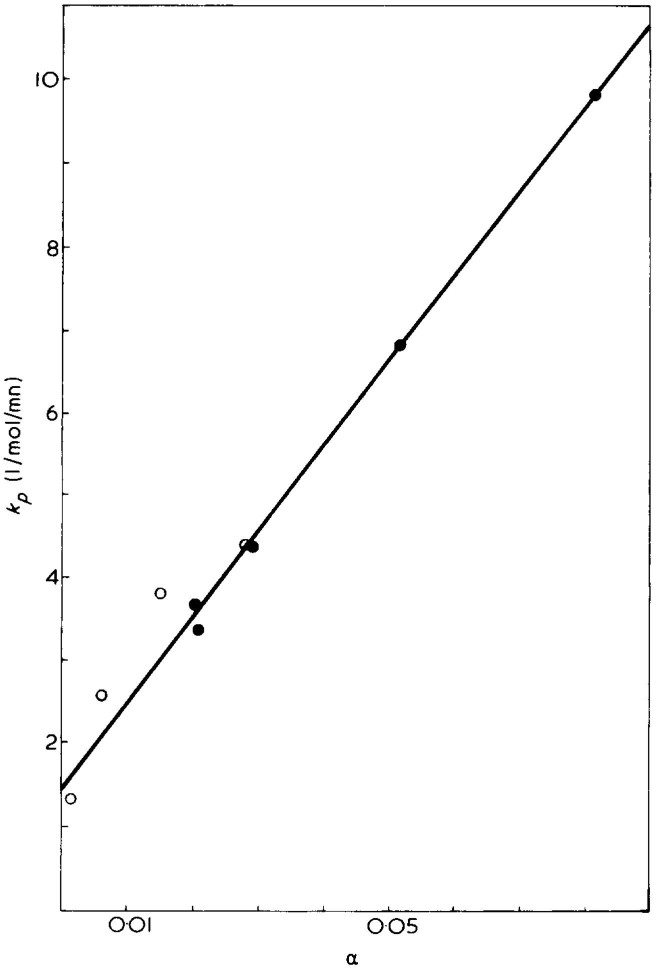


Figure 3 Linear dependence of the apparent bimolecular rate constant of living poly(ethylene oxide) propagation on the fraction of free ions α with the cryptate K^+ + [222] as counterion in THF at 20°C: ●, without added salt; ○, with ϕ_4BK + [222]

Kinetic measurements

Kinetic measurements were performed at several concentrations [*C*] of living ends over a range of 7×10^{-4} to 4×10^{-5} mol/l in THF at 20°C. The values of the apparent propagation rate constant $k_p = R_p/[M]\,[C]$ were determined for each experiment. If the following equilibrium is considered:

$$\sim\!\sim\!\sim O^-K^+ \overset{K_D}{\rightleftarrows} \sim\!\sim\!\sim O^- + K^+$$

the fraction α of the free alkoxide ions is given by the relation:

$$K_D = [C]\alpha^2/(1-\alpha)$$

$$k_p = (1-\alpha)k_\pm + \alpha k_-$$

$k_\pm$ and k_- being the propagation constants of cryptated ion pairs and of free ions respectively. Some results are given in *Table 4*. Addition of ϕ_4BK + [222] suppresses the ionic dissociation of the living polymer and also retards the propagation showing that free ions are more reactive than cryptated ion pairs. This salt is quite convenient because its degree of dissociation is higher than that of the living poly(ethylene oxide)[21]. Several experiments were made with different amounts of this salt. α was thus calculated with measured $K_D = 8.1 \times 10^{-5}$ for ϕ_4BK + [222] [21], according to the classical equation[32]. The results are collected in *Table 4*.

In *Figure 3*, k_p is plotted against α. A straight line is obtained which leads to $k_\pm$ and k_- that are equal to 1.5 and 100 l/mol/min respectively. Other values for K_D have been tried for the calculation of α but the best fit between both sets of data obtained with and without added salt was found for our experimental $K_D = 3 \times 10^{-7}$.

In conclusion use of a macrobicyclic ligand of K^+ such as [222] leads to the formation of living poly(ethylene oxides), in THF at 20°C. For concentrations [*C*] lower than 6×10^{-4} mol/l we can neglect the effect of associated species, and consider that the main ionic species are cryptated ion pairs in equilibrium with free ions. This is the first time k_- could be determined in THF. A comparison with other data of the literature is difficult since the overall rates obtained in ethereal solvents are low, which accounts for the disturbingly high temperatures which have been used (generally 70°C)[6,7]. Kinetic measurements with other cryptates as counterions in ethereal solvents are in progress.

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