Anionic polymerization of ethylene oxide with cryptates as counterions: 2

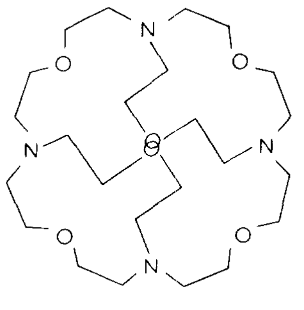
Alain Deffieux
Laboratoire de Chimie Macromoléculaire associé au CNRS, Université Pierre et Marie Curie, T. 44, 4, *place Jussieu,* 75 230 *Paris Cedex* 05, *France*
Ernest Graf
Institut Le Bel, Université Louis Pasteur, 4, *rue Blaise Pascal,* 67 000 *Strasbourg, France*
and Sylvie Boileau
Laboratoire de Chimie Macromoléculaire associé au CNRS, Collège de France, 11, *place Marcelin Berthelot,* 75 231 *Paris Cedex* 05, *France*
(*Received* 15 *July* 1980)

A kinetic study of the anionic polymerization of ethylene oxide has been made in tetrahydrofuran at 20°C, with the cryptate $Cs^+ + [TC]$ as counterion, [TC] being a spheroidal macrotricyclic ligand. Conductance measurements have been made on THF solutions of $\phi_4BCs + [TC]$. Ionic associations higher than cryptated ion pairs are negligible for living end concentrations lower than 3×10^{-4} mol l^{-1}. $k_\pm$ and the alkoxide ion pair dissociation constant K_D were determined from both sets of kinetic data obtained with and without added salt knowing the value of k_- from kinetic data performed with $K^+ + [222]$ as counterion. Free alkoxide ions are about twenty times more reactive than cryptated caesium ion pairs.

INTRODUCTION

Anionic polymerization of ethylene oxide has been studied for a long time by several authors[1-11]. However, the dependence of the rate of polymerization on the concentration of active centres is complex since associations of ion pairs exist down to low living end concentrations, and are not completely destroyed in high polar solvents such as hexamethylphosphoramide[1,3,8]. We have recently examined the anionic polymerization of ethylene oxide with alkali cations complexed by some macroheterobicyclic ligands discovered by Lehn[12], in THF at 20°C [13-16]. Use of the cryptate $K^+ + [222]$ as counterion leads to the formation of living poly(ethylene oxides). For living end concentrations $[C]$ lower than 6×10^{-4} mol l^{-1} the effect of associations of ion pairs can be neglected and the main ionic species are cryptated ion pairs in equilibrium with free ions. The propagation rate constants of cryptated alkoxide ion pairs and of free ions were determined from both sets of kinetic data obtained with and without added salt. At 20°C in THF, $k_\pm$ and k_-, are equal to 1.5 and 100 l mol^{-1} min^{-1} respectively.

This paper will describe the kinetic results obtained for the anionic polymerization of ethylene oxide, in THF at 20°C, with Cs^+ complexed by the spheroidal macrotricyclic ligand synthesized by Lehn *et al.*[17] as counterion.



Designated (TC)

EXPERIMENTAL

All the experiments were made in glass apparatus sealed under high vacuum in order to avoid the destruction of active centres. THF and ethylene oxide were dried over calcium hydride and several sodium mirrors[18,19]. The [TC] ligand was synthesized according to the described procedure[17]. It was purified by freeze drying in benzene and sealed under high vacuum in ampoules fitted with break-seals. The initiator used in the present study was carbazylcaesium in THF which was prepared by adding a solution of carbazole to a solution of caesium dianions of 1,1-diphenylethylene, in stoichiometric proportion[20]. The [TC] compound was added to the carbazylcaesium solution in a ratio $[TC]/[Cs^+]$ slightly higher than 1 in order to insure a complete complexation of the cation.

Conductance measurements were made on THF solutions of caesium tetraphenylboride complexed by the [TC] ligand. Full descriptions of the conductance apparatus and of the procedure used in obtaining the conductance data have been reported elsewhere[21]. Viscosity measurements were performed on active and terminated polymer solutions as described previously[13,22].

Kinetic measurements were made by dilatometry after addition of the monomer to the initiator solution for each experiment since the initiation is much more rapid than the propagation 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

0032-3861/81/040549-04$02.00

Table 1 Molecular weights of poly(ethylene oxides) initiated by carbazylcaesium + [TC] in THF at 20°C ([TC]/[Cs$^+$] ≃ 1.2)

Initiator [C] × 10^5 (mol l^{-1})	Monomer [M] × 10 (mol l^{-1})	Yield (%)	Theoretical $\bar{M}_n$ [a]	Experimental $\bar{M}_n$ [b]	Experimental $\bar{M}_n$ [c]
29.7	1.75	100	26 000	28 000	24 000
20.6	1.78	100	38 000	40 000	40 400
7.2	2.11	98	129 000	120 000	116 000

[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 data for ϕ_4BCs + [TC] in THF ([TC]/[Cs$^+$] = 1.5)

C × 10^5 (mol l^{-1}) at 20°C	Λ +20°C	Λ +10°C	Λ 0°C	Λ −10°C	Λ −20°C	Λ −30°C	Λ −40°C	Λ −50°C	Λ −60°C	Λ −70°C
21.70	38.4	34.8	31.2	27.8	24.4	–	17.7	15.0	12.3	9.9
15.39	41.6	37.4	33.4	29.9	26.1	22.7	19.3	16.2	13.2	10.7
11.64	43.6	39.6	35.5	31.7	27.6	23.8	20.2	17.0	13.9	11.2
8.76	46.7	42.1	37.6	33.4	29.2	25.3	21.5	18.0	14.8	–
6.50	49.0	44.4	39.8	35.4	30.7	26.6	22.5	18.9	15.4	12.2
4.84	51.6	46.8	41.6	36.7	–	27.7	23.4	19.7	16.2	12.9

Concentrations at different temperatures are deduced from those measured at 20°C taking into account the THF density variations with temperature: d ln v/dt = 0.001085, where v is the molar volume of the solvent[26]

following relationship[23]:

$$[\eta]\text{ml g}^{-1} = 2 + 0.027\ (M_v)^{0.725}$$

RESULTS AND DISCUSSION

Anionic polymerization of ethylene oxide initiated by cryptated carbazylcaesium in THF at 20°C gives living monofunctional polymers, the molecular weight of which can be predicted from the 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 $\overline{DP}_n = [\text{M}]/[\text{C}]$ and experimental molecular weights measured by osmometry or viscosity, within experimental errors.

Conductance measurements

Since several kinetic measurements of the anionic polymerization of ethylene oxide were made with different amounts of φ_4BCs + [TC], the knowledge of the dissociation constant of this added salt was necessary in order to determine the fraction of free alkoxide ions. Therefore, conductance measurements were made on THF solutions of φ_4BCs + [TC] over a temperature range of −70°C to +20°C. The concentration range examined was between 2×10^{-4} and 5×10^{-5} mol l^{-1}. The initial concentration of tetraphenylboride solution was determined by weighing. This value was found to be the same as that determined by spectrophotometry on the solution of the cryptated salt ($\varepsilon_{\text{max}} = 2220$ at 274 nm: value found for sodium and quaternary ammonium tetraphenylborides[21]). The data were treated by the method of Fuoss[24,25] in order to determine Λ_0 and K_D by an iterative process. The values of the physical constants for THF given by Szwarc *et al.*[26] were used for the calculations. The results are given in *Tables 2* and *3*.

The Walden product $\Lambda_0\eta$ slightly decreases with temperature as already observed for other tetraphenylborides in THF[21]. The Stokes' radius of Cs$^+$ + [TC] was calculated from the classic equation $R_s^+ = 0.82/\lambda_0^+\eta$. The $\Lambda_0\eta$ value has been determined at 25°C by a linear extrapolation of the $\Lambda_0\eta = f(t)$ plot from the results given in *Table 3*. The limiting equivalent conductance λ_0^- of φ_4B$^-$ is equal to 41.3 in THF at 25°C [21,26]. Thus R_s^+ is found to be equal to 5.5 Å whereas the ionic radius R_i^+ of Cs$^+$ + [TC] evaluated from the radius of the cation located within the central molecular cavity and from the ligand volume[12] is equal to 6.1 Å. These values are in good agreement with the linear relationship found between R_s^+ and R_i^+ for the tetraalkylammonium cations and the cryptates Na$^+$ + [221], K$^+$ + [222][21] and Cs$^+$ + [322][27]. Moreover, the size of the cryptate Cs$^+$ + [TC] is higher than that already observed for the other cryptates. The distance parameter a_K^F which represents the closest distance of approach of ions in solution was calculated from the Fuoss equation:

Table 3 Conductance parameters for ϕ_4BCs + [TC] in THF

T (°C)	Λ_0	$\Lambda_0\eta$	$K_D \times 10^4$	$a_K{}^F$ (Å)
20	68.4	0.332	1.10	8.7
10	62.2	0.337	1.08	8.7
0	54.9	0.334	1.17	8.7
−10	48.2	0.333	1.27	8.7
−20	41.6	0.329	1.37	8.7
−30	35.8	0.328	1.43	8.7
−40	30.4	0.327	1.44	8.7
−50	25.4	0.326	1.49	8.6
−60	20.8	0.322	1.53	8.6
−70	16.2	0.310	1.82	8.8

$$K_D = \frac{3000}{4\pi \text{Na}^3} \exp\left(-\frac{e^2}{a D k T}\right)$$

This distance is the same in the temperature range examined ($a_K^F = 8.7$ Å) as can be seen in the *Table 3*. The value of the enthalpy of dissociation ΔH deduced from the plot of log K_D against $1/T$ is equal to −0.9 kcal mol^{-1}.

Table 4 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 ($\bar{M}_n \simeq 47\,000$)

t_l/t_t	[C] x 10^5 (mol l^{-1})
1.08	36.5
1.02	25.0
1.02	20.0
1.01_5	12.5
1.00	10.0

Table 5 Kinetic results for anionic polymerization of ethylene oxide with Cs^+ + [TC] as counterion in THF at 20°C ([TC]/[Cs^+] $\simeq$ 1.2)

[C] x 10^5 (mol l^{-1})	ϕ_4BCs + [TC] x 10^5 (mol l^{-1})	[M] x 10 (mol l^{-1})	k_p (l mol^{-1} min^{-1})	α x 10^2
29.7	0	1.75	11.5	5.6^a
20.6	0	1.78	13.1	6.7
15.6	0	1.84	14.1	7.7
7.2	0	2.11	17.3	11.1
8.6_5	6.8	2.15	7.8	2.0^b
7.2_5	11.6	1.52	6.5	1.4

[a] Calculated from $K_D = 1 \times 10^{-6}$ for living polymer
[b] Calculated from $K_D = 1 \times 10^{-6}$ for living polymer and $K = 1.1 \times 10^{-4}$ for ϕ_4BCs + [TC]

The conductance parameters of φ_4BCs + [TC] are in good agreement with those found for tetraphenylborides with other cryptates as counterions in THF[21,27].

Viscosity measurements

Depending on the nature of the counterion, alkoxide living ends of poly(ethylene oxides) have a high tendency to form ionic aggregates even in polar media[1,3,8]. The concentration range and the extent of these associations were examined by viscosity measurements on active and terminated polymers prepared by reaction of a small amount of ethylene oxide with carbazylcaesium complexed by [TC]. 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 are given in *Table 4*. Associations of ion pairs may be neglected for [C] lower than 2.5×10^{-4} mol l^{-1} in the case of Cs^+ + [TC] as counterion.

Kinetic measurements

Kinetic measurements were made at several concentrations [C] of living ends over a range of 3×10^{-4} to 7×10^{-5} mol l^{-1} in THF at 20°C. The values of the apparent propagation rate constant $k_p = R_p/[M][C]$ were determined for each experiment. The results are shown in *Table 5*. According to the viscosity measurements, the influence of ionic aggregates may be neglected in the range of concentrations examined and the main ionic species are cryptated ion pairs in equilibrium with free ions:

$$\sim\sim\sim O^-(Cs^+) \overset{K_D}{\rightleftharpoons} \sim\sim\sim O^- + (Cs^+)$$

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

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

and

$$k_p = k_\pm + (k_- - k_\pm)\alpha \qquad (2)$$

$k_\pm$ and k_- being the propagation constants of cryptated ion pairs and of free ions respectively. Since k_- has been determined in the case of K^+ + [222] as counterion[13] ($k_- = 100$ l mol^{-1} min^{-1} in THF at 20°C), equation (2) becomes:

$$k_p = k_\pm + (100 - k_\pm)\alpha \qquad (3)$$

From the results of *Table 5*, it can be seen that k_p increases when [C] decreases showing that cryptated ion pairs are less reactive than free ions. Moreover, the addition of φ_4BCs + [TC] suppresses the ionic dissociation of the living polymer and also retards the propagation.

The dissociation constant K_D of living poly(ethylene oxide) has not been measured in the case of Cs^+ + [TC] as counterion. However, it is possible to determine $k_\pm$ by plotting k_p against α, α being calculated with different hypothetical value of K_D. Such plots give the same intercept for $\alpha = 0$ but a straight line should be obtained only for the real value of K_D. In the case of experiments made with different amounts of φ_4BCs + [TC], α was thus calculated with measured $K = 1.1 \times 10^{-4}$ for this salt, according to the classical equation[28,29]:

$$[M_t^+]^3 + K[M_t^+]^2 - (C_0K + CK_D)[M_t^+] - KK_DC = 0 \qquad (4)$$

with $[M_t^+] = [Cs^+ + TC]$, C_0 equal to the concentration of added salt. In *Figure 1*, k_p is plotted against α using $K_D = 1 \times 10^{-6}$ for the living polymer. A straight line is obtained which leads to $k_\pm$ that is equal to 5.6 l mol^{-1} min^{-1}. Other values for K_D have been tried for the calculation of α but the best fit between both sets of data

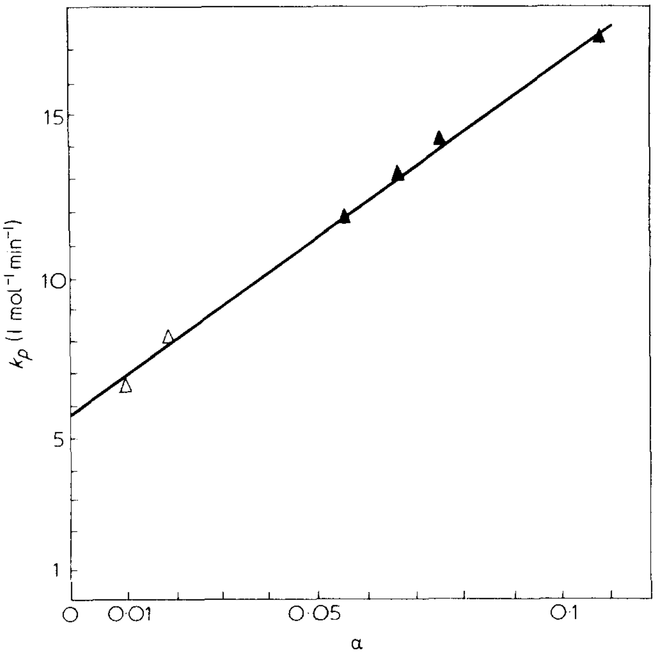


Figure 1 Linear dependence of the apparent bimolecular rate constant of living poly(ethylene oxide) propagation on the fraction of free ions α with the cryptate Cs^+ + [TC] as counterion in THF at 20°C: ▲, without added salt; △, with ϕ_4BCs + [TC]

obtained with and without added salt was found for $K_D = 1 \times 10^{-6}$. This value is higher than that measured for $K^+ + [222]$ as counterion[13] (3×10^{-7}) as expected since the cation is more bulky in the present case.

In conclusion, use of a macrotricyclic ligand of Cs^+ such as [TC] leads to the formation of living poly(ethylene oxides), in THF at 20°C as also observed in the case of $K^+ + [222]$. For concentrations [C] lower than 3×10^{-4} mol l^{-1} we can consider that the main ionic species are cryptated ion pairs in equilibrium with free ions. The reactivity of caesium ion pairs complexed by the [TC] ligand is about 4 times higher than that of potassium ion pairs complexed by the [222]. However the most reactive species are free alkoxide ions. This behaviour is quite different from that observed in the case of the anionic polymerization of propylene sulfide in THF for which cryptated ion pairs have been found more reactive than free ions[14,18]. Kinetic data obtained with alkali metals and other cryptates as counterions[15,16] will be described later. The problem of the reactivities of various alkoxide species for the ring opening of ethylene oxide will be discussed in detail in our next reports.

REFERENCES

1 Figueruelo, J. E. and Worsfold, D. J. *Eur. Polym. J.* 1968, **4**, 439
2 Bawn, C. E. H., Ledwith, A. and McFarlane, N. *Polymer* 1969, **10**, 653
3 Figueruelo, J. E. and Bello, A. *J. Macromol. Sci. (A)* 1969, **3**, 311
4 Solovyanov, A. A. and Kazanskii, K. S. *Vysokomol. Soedin (A)* 1970, **12**, 2114
5 Kazanskii, K. S., Solovyanov, A. A. and Entelis, S. G. *Eur. Polym. J.* 1971, **7**, 1421
6 Solovyanov, A. A. and Kazanskii, K. S. *Vysokomol. Soedin (A)* 1972, **14**, 1063, 1071
7 Kazanskii, K. S., Solovyanov, A. A. and Tzrasov, A. N. *Prepr. IUPAC Int. Symp. Macromolecules, Helsinki* 1972, **2**, 535
8 Price, C. C. and Akkapeddi, M. K. *J. Am. Chem. Soc.* 1972, **94**, 3972
9 Cabasso, I. and Zilkha, A. *J. Macromol. Sci. (A)* 1974, **8**, 1313
10 Rodriguez, M. and Figueruelo, J. E. *Makromol. Chem.* 1975, **176**, 3107
11 Nenna, S. and Figueruelo, J. E. *Makromol. Chem.* 1975, **176**, 3377; *Eur. Polym. J.* 1975, **11**, 511
12 Lehn, J. M. *Struct. Bonding (Berlin)* 1973, **16**, 1 (and references therein)
13 Deffieux, A. and Boileau, S. *Polymer* 1977, **18**, 1047
14 Sigwalt, P. and Boileau, S. *J. Polym. Sci: Polym. Symp.* 1978, **62**, 51
15 Boileau, S., Deffieux, A., Lassalle, D., Menezes, F. and Vidal, B. *Tetrahedron Letters* 1978, 1767
16 Deffieux, A. *Thèse Doctorat d'Etat*, Paris, 1978
17 Graf, E. and Lehn, J. M. *J. Am. Chem. Soc.* 1975, **97**, 5022
18 Hemery, P., Boileau, S. and Sigwalt, P. *J. Polym. Sci.: Polym. Symp.* 1975, **52**, 189
19 Lassalle, D., Boileau, S. and Sigwalt, P. *Eur. Polym. J.* 1977, **13**, 591, 599
20 Hemery, P., Warzelhan, V. and Boileau, S. *Polymer* 1980, **21**, 77
21 Boileau, S., Hemery, P. and Justice, J. C. *J. Solution Chem.* 1975, **4**, 873
22 Guerin, P., Boileau, S. and Sigwalt, P. *Eur. Polym. J.* 1971, **7**, 1119
23 Monnerie, L. and Neel, J. *CR Acad. Sci.* 1963, **256**, 1528
24 Fuoss, R. M. and Accascina, F. 'Electrolytic Conductance', Interscience Publisher, Inc., New York, 1959
25 Fuoss, R. M. *J. Am. Chem. Soc.* 1935, **57**, 488; 1958, **80**, 5059
26 Carvajal, C., Tölle, K. J., Smid, J. and Szwarc, M. *J. Phys. Chem.* 1965, **69**, 612
27 Hemery, P. *Thèse Doctorat d'Etat*, Paris, 1976
28 Szwarc, M. 'Carbanions, Living Polymers and Electron Transfer Processes', Wiley, Interscience, New York, 1968
29 Hostalka, H. and Schulz, G. V. *Z. Phys. Chem.* 1965, **45**, 286