Anionic polymerization of α,α-disubstituted β-propiolactones with cryptates as counter-ions

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A kinetic study of the anionic polymerization of α-methyl-α-propyl-β-propiolactone has been made in tetrahydrofuran at $-20°C$, with the cryptate $K^+ +$ [222] as counter-ion. Conductance measurements have been made on THF solutions of potassium β-naphthoate complexed by [222] as a model of cryptated carboxylates. Propagation reaction proceeds through cryptated ion pairs and free ions. Cryptated carboxylate ion pairs are more reactive than free ions.

Keywords α-Methyl-α-propyl-β-propiolactone; anionic polymerization; cryptates; kinetics; conductivity

INTRODUCTION

The anionic polymerization of α,α-disubstituted β-propiolactones has been studied for many years by several authors[1-7]. Kinetic investigations made in DMSO and in THF have shown that the apparent propagation rate constants were lower in DMSO than in THF, with Et_4N^+ as counter-ion[4-7]. This solvent effect was attributed to a specific solvation of carboxylate anions by DMSO. We have undertaken a detailed study of the propagation reaction in the case of α-methyl-α-propyl-β-propiolactone (MPPL), in THF at $-20°C$, in order to determine the absolute rate constants of ion pairs and of free ions. A similar study has been done recently with β-propiolactone (BPL), in methylene chloride, with K^+ complexed by dibenzo-18 crown-6 ether and with $[(C_6H_5)_3P]_2N^+$ as counter-ions[8,9]. In the present investigation, the cryptated cation $K^+ + [222]$ has been used as counter-ion since it has been shown that the addition of macroheterobicyclic ligands[10] like [222] leads to an increase of the reactivity of ionic species for the anionic polymerization of heterocyclic monomers[11,12] such as propylene sulphide[13,14], ethylene oxide[15] and lactones[16]. Moreover, the aggregates are destroyed and simple kinetic results have been obtained in the case of propylene sulphide, ethylene oxide and cyclosiloxane polymerizations[12].

EXPERIMENTAL

All the experiments were done in glass apparatus sealed under high vacuum in order to avoid the destruction of active centres. Monomer (MPPL) was prepared from 3-bromo-2-methyl-2-propanoic acid according to previously published procedures[2,3]. THF and MPPL were dried over calcium hydride and several sodium mirrors as usual[14]. Potassium β-naphthoate complexed by [222] was prepared by reaction of cryptated 9-methylfluorenylpotassium with β-naphthoic acid solutions in stoichiometric proportion. Carbazylpotassium complexed by [222] in THF was prepared according to the described procedure[17]. In both cases, the ratio $[222]/[K^+]$ was slightly higher than unity in order to ensure a complete complexation of the cation. Conductance measurements were performed under vacuum on THF solutions of cryptated potassium β-naphthoate. Full descriptions of the conductance apparatus and of the procedure used in obtaining the conductance data have been reported elsewhere[18]. The dielectric constant of an MPPL solution in THF was determined from capacitance measurements made in the conductivity cell under vacuum, using pure THF as the reference. 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. The concentration of living ends was deduced from that of the initiator which was determined by spectrophotometry using a Cary model 118 apparatus ($\varepsilon_{398.5\,nm} = 2480$ for carbazylpotassium + [222] in THF[17]). Concentration of potassium β-naphthoate + [222] was deduced from that of the reagents leading to the same value ($\varepsilon_{385\,nm} = 12\,800$ for 9-methylfluorenylpotasium + [222]; $\varepsilon_{281\,nm} = 7100$ for β-naphthoic acid). Polymers were recovered after precipitation in methanol. Their molecular weights were measured by osmometry in toluene at 37°C and by g.p.c. in THF.

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Table 1 Molecular weights of poly(MPPL) initiated by cryptated potassium salts in THF (I = potassium naphthoate + [222]; II = carbazylpotassium + [222])

Runs	1	2	2′	3	4
Initiator [C] × 10^4 (mol l^{-1})	(I) 8.9	(I) 4.6	(I) 4.5	(II) 3.6	(II) 5.0
Monomer [M] (mol l^{-1})	0.59	0.25	a	0.17_5	0.13
t (°C)	−30	20	20	−20	−20
Theoretical $\overline{M}_n$ [b]	79 000	70 000	140 000	62 000	33 000
Experimental $\overline{M}_n$ [c]	82 000	73 000	130 000	87 000	44 000
Experimental $\overline{M}_n$ [d]	66 000	72 500	129 000	–	–
Experimental $\overline{M}_w$ [d]	76 000	87 000	160 000	–	–
$\overline{M}_w/\overline{M}_n$ (g.p.c.)	1.15	1.20	1.24	–	–

[a] A second amount of MPPL was added to the living polymer of run 2

[b] Calculated from $\overline{DP}_n$ = [M]/[C] (quantitative yields were obtained except for run 1:93%)

[c] Measured by osmometry in toluene at 37°C

[d] Measured by g.p.c. in THF

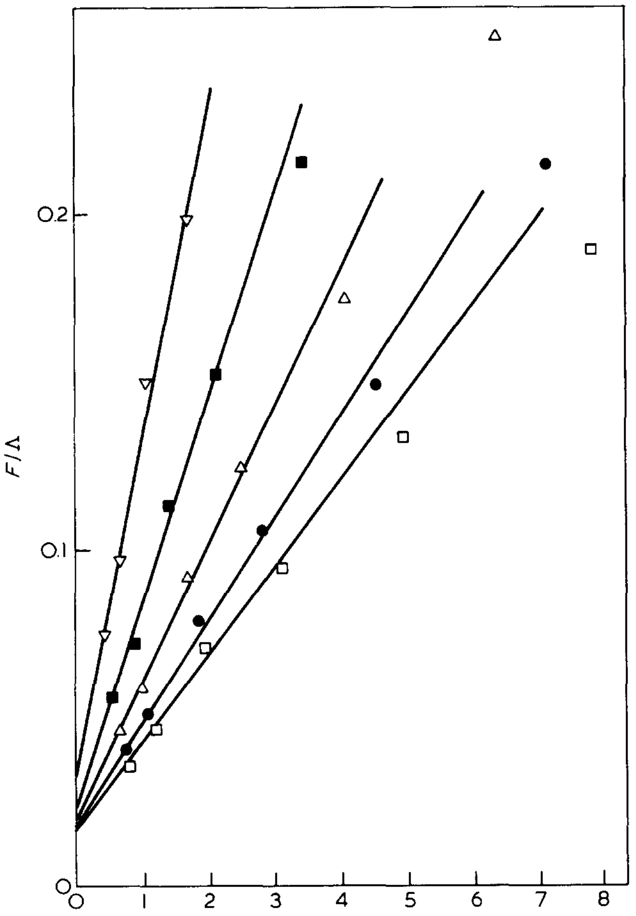

Figure 1 Fuoss conductivity plots for potassium β-naphthoate complexed by [222] in THF: □, 20°C; ●, 0°C; △, −20°C; ■, −40°C; ▽, −60°C

RESULTS AND DISCUSSION

Anionic polymerization of MPPL initiated by cryptated potassium naphthoate or by cryptated carbazylpotassium in THF gives living 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 good agreement between theoretical molecular weights calculated from the relationship $\overline{DP}_n = [\mathrm{M}]/[\mathrm{C}]$ and experimental molecular weights measured by osmometry. Moreover, molecular weights of polymers obtained in runs 1, 2 and 2′ were determined by g.p.c., using the calibration curve of polystyrene. The agreement between $\bar{M}_n$ measured by g.p.c. and by osmometry is quite good and the molecular weight distributions are narrow ($1.15 < \bar{M}_w/\bar{M}_n < 1.24$). It should be mentioned that no low molecular weight by-products were detected in the polymers thus prepared as in the case for the ε-caprolactone polymerization[19,20].

These results indicate that the anionic polymerization of MPPL in THF, with $K^+ + [222]$ as counter-ion, involves living polymer systems with no termination or transfer. Moreover, no intra- or intermolecular attack on the chains by living centres occurs during the propagation. The living polymer character with α,α-disubstituted β-propiolactone monomers has already been demonstrated in the case of tetraalkylammonium counter-ions in THF[3]. The propagation reaction occurs through the attack of the β-carbon–oxygen bond of the monomer by the active centres which are carboxylate species as proposed earlier[4–7].

Conductance measurements

Conductance measurements were made on potassium β-naphthoate complexed by [222], as a model of cryptated carboxylate species, in THF over a temperature range of −60° to +20°C. The concentration range examined was between 5×10^{-4} and 3×10^{-6} mol l^{-1}. The initial concentration of this salt solution was deduced from that of 9-methylfluorenylpotassium + [222] which was used for the salt formation of β-naphthoic acid. The data were treated by the method of Fuoss[21,22]. The values of the physical constants for THF given by Szwarc *et al.*[23] were used for the calculations. The Fuoss conductivity plots

$$F/\Lambda = 1/\Lambda_0 + f^2 C\Lambda / F K_D \Lambda_0^2$$

are straight lines for concentrations lower than 9×10^{-5} mol l^{-1}, but they become slightly curved at higher concentrations, indicating the presence of some ionic associations higher than ion pairs. Some of these plots are shown in *Figure 1* at different temperatures. Λ_0 and K_D were determined by an iterative process from the data corresponding to $C < 8.54 \times 10^{-5}$ mol l^{-1} according to Fuoss[21,22]. The results are given in *Tables 2* and *3*. The distance parameter a_K^F which represents the closest distance of approach of ions in solution was calculated from the Fuoss equation:

Table 2 Conductance data for potassium β-naphthoate +[222] in THF ([222]/[K$^+$] = 1.2)

$C \times 10^6$ (mol l^{-1}) at 20°C	Conductance Λ at temperature indicated								
	+20°C	+10°C	0°C	−10°C	−20°C	−30°C	−40°C	−50°C	−60°C
537.0	3.42	3.17	2.96	2.76	2.51	2.29	2.05	1.82	1.56
208.0	4.96	4.67	4.39	4.09	3.76	3.41	3.06	2.71	2.35
85.4	7.12	6.76	6.42	5.91	5.49	4.99	4.49	4.00	3.43
35.0	10.21	9.60	9.14	8.47	7.81	7.10	6.35	5.66	4.88
16.3	13.74	13.05	12.26	11.47	10.59	9.62	8.64	7.66	6.51
6.0	21.40	20.24	19.12	17.97	16.60	15.40	13.72	11.84	10.18
2.9	27.53	26.30	24.90	23.30	21.52	19.54	17.45	15.33	13.23

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 = 0.001 085, where v is the molar volume of the solvent[23]

Table 3 Conductance parameters for potassium β-naphthoate + [222] in THF

t (°C)	Λ_0	$\Lambda_0\eta$	$K_D \times 10^6$	a_K^F (Å)
20	59.9	0.29	1.1	5.1
10	60.0	0.33	0.9	5.0
0	54.5	0.33	1.0	5.0
−10	54.6	0.38	0.9	4.9
−20	50.6	0.40	0.9	4.8
−30	48.5	0.44	0.8	4.7
−40	42.8	0.46	0.8	4.7
−50	33.8	0.43	1.1	4.8
−60	28.3	0.44	1.2	4.8

$$K_D = \frac{3000}{4\pi N a^3} \exp\left(\frac{e^2}{aDkT}\right)$$

The determination of Λ_0 and K_D is not very accurate because this cryptated carboxylate is not extensively dissociated in THF. K_D does not vary significantly with temperature, and thus the enthalpy of dissociation, ΔH_D, is nearly equal to zero whereas the entropy of dissociation, ΔS_D, is equal to −28 eu. Similar values for ΔH_D and ΔS_D were found for cryptated potassium phenoxides[24]. The interionic distance parameter a_K^F is nearly constant with temperature within the experimental errors. Very few data on conductimetric measurements of carboxylates in aprotic solvents are available in the literature. Several potassium aromatic carboxylates have been examined in methylethyl ketone[25]. Differences between the a_K^F values found for potassium picrate and for potassium carboxylates were found to be between 0.8 and 1.5 Å.

If we compare the interionic distance parameters found for potassium 2,6-dimethylphenolate[24] and potassium β-naphthoate complexed by [222] in THF, the difference, Δa_K^F, is equal to 0.9 Å. Moreover, a similar comparison made between tetraphenyl borides and carboxylates associated with the same counter-ion leads to the following results: $\Delta a_K^F = 3.4$ Å for $(\varphi_3P)_2N^+$ in CH_2Cl_2[8,26] and $\Delta a_K^F = 3.2$ Å for $K^+ + [222]$ in the THF[18]. It can be concluded that the value of a_K^F found for potassium β-naphthoate complexed by [222] in THF is in good agreement with the values found for other potassium carboxylates in methylethyl ketone as well as with other cryptated potassium salts in THF.

The negative charge is equally distributed on both oxygen atoms of carboxylate anion and the contribution of this anion, a^-, in the interionic distance parameter

$$a_K^F = a^- + a^+$$

is much smaller than that of the cryptate. It is smaller than that of the oxyanion in potassium 2,6-dimethylphenolate complexed by [222]. Thus we have assumed that K_D of living cryptated carboxylate centres for the anionic polymerization of MPPL was nearly equal to the K_D value found for potassium β-naphthoate + [222] ($K_D = 9 \times 10^{-7}$ at −20°C in THF).

Kinetic measurements

Kinetic measurements were performed with carbazylpotassium + [222] as initiator, in THF at −20°C, because under these conditions initiation is much more rapid than propagation. Experiments were made at several concentrations, [C], of living ends over a range of 1.7×10^{-4} to 5.0×10^{-4} mol l^{-1}.

The values of the apparent propagation rate constant as obtained from the following equation:

$$k_p = \frac{R_p}{[M] \times [C]}$$

were determined for each experiment (R_p = rate of polymerization, [M] and [C] = monomer and living ends concentrations). The main ionic species involved in the propagation are cryptated carboxylate ion pairs in equilibrium with free ions, as follows:

$$\sim COO^-\ ,\ K^+ + [222] \overset{K_D}{\rightleftarrows} \sim COO^- + K^+ + [222]$$

The fraction of free ions, α, is given by the relations:

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

and

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

$k_{\pm}$ and k_- are the propagation constants of cryptated ion pairs and free ions, respectively.

The dielectric constant of MPPL is much higher than that of THF ($D_{MPPL} = 23$ and $D_{THF} = 9$ at −20°C). Measurements of D_m for an MPPL solution in THF ([MPPL] = 0.44 mol l^{-1}) at different temperatures leads to the following relationship:

$$D_m = -3.15 + 3260/T$$

in which[27]

$$D_m = D_{MPPL}\,y + D_{THF}(1-y)$$

Table 4 Kinetic results for anionic polymerization of MPPL with K^+ + [222] as counter-ion in THF at −20°C ([222]/[K^+] = 1.2)

[C] × 10^4 (mol l^{-1})	[M] (mol l^{-1})	k_p (l mol^{-1} min^{-1})	K_D × 10^6	α × 10^2
4.99	0.130	7.8	1.30	5.0
3.61	0.175	7.7	1.48	6.2
3.37	0.420	7.3	2.87	8.8
1.73	0.357	7.0	2.41	11.1

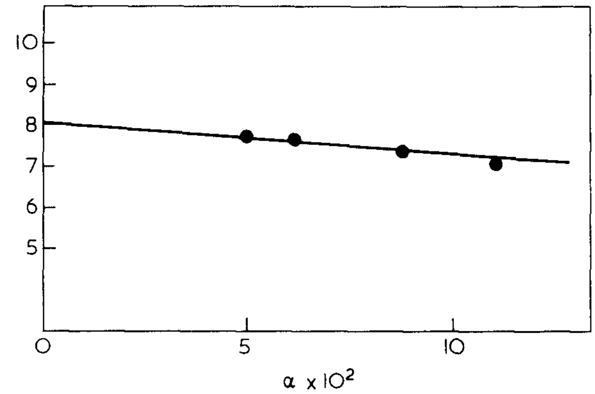

Figure 2 Linear dependence of the apparent bimolecular rate constant of living poly(MPPL) propagation on the fraction of free ions α with the cryptate K^+ + [222] as counter-ion in THF at −20°C

if y is the volume fraction of monomer. The dissociation constant K_D of living ends and the fraction of free ions α were calculated for each experiment taking into account the increase of the dielectric constant of the solution due to MPPL.

The results are given in *Table 4*. When k_p is plotted *versus* α, a straight line is obtained which leads to the values of k_+ and k_- (*Figure 2*): $k_\pm = 8.0 \pm 0.1$ l mol^{-1} min^{-1} and $k_- = 0.8 \pm 0.5$ l mol^{-1} min^{-1}. The precision on the determination of k_- is not very good since the range of variations of α is not large. However, the slope of the straight line which is equal to $k_- - k_\pm$ must lead to a positive value for k_-.

In a general manner, the reactivity of ion pairs is lower than of free ions for the propagation reaction of vinyl and heterocyclic monomers. However, cryptated ion pairs have been found to be more reactive than free ions for the propagation of propylene sulphide, in THF at −30°C[11−14]. It has been assumed that a polarization of the CH_2–S bond in the monomer occurs before ring cleavage and is induced by the ion pair dipole of the living end. Such a modification should increase with the magnitude of the ion pair dipole and also with the size of the counter-ion. These increases lead to an increase of the interaction with the monomer, and thereby to an increase in the reaction rate.

It is understandable that the modification of the polarization of the CH_2–S bond may be quite different when the interaction is with free ions. In the present case, cryptated carboxylate ion pairs are more reactive than free ions. This result might be explained by a push–pull mechanism influenced by dipole–dipole interaction according to the scheme shown in *Figure 3*. The dipole moment of MPPL is not known; however, calculations of molecular structure have been made for β-propiolactone[28,29]. This monomer has a very high dipole moment ($\mu = 3.85$ D at 30°C in benzene[30], $\mu = 4.18$ D in gaseous phase[31]). The calculated partial moments are in good agreement with experiment and the dipole moment is oriented along the CH_2–O bond of the monomer. By assuming that MPPL and β-propiolactone have nearly the same dipole moment, it is probable that a strong dipole–dipole interaction between the monomer and the carboxylate ion pairs occurs before ring opening occurs. Moreover, the attack on the CH_2–O bond of the MPPL is assisted by a transfer of charges through the cation. Such cation assistance as well as dipole–dipole interaction do not occur for the ring opening of MPPL by free carboxylate ions.

If we now consider the kinetic results obtained for MPPL in THF and in DMSO at 37°C, with Et_4N^+ as counter-ion, the apparent rate constant of propagation, k_p, is slightly higher in THF than in DMSO. A specific solvation of carboxylate anions by DMSO was suggested in order to explain this solvent effect. From the conductance data obtained for potassium β-naphthoate + [222] in THF, it can be concluded that the main ionic species involved in the anionic polymerization of MPPL with Et_4N^+ in THF are ion pairs for the experimental conditions of the kinetic study[6]. Moreover, the dissociation constants of some electrolytes have recently been determined in DMSO by using a spectrophotometric method[32]. Most organic salts do not form ion pairs with potassium cations in dilute solutions ([C] < 5 × 10^{-3} mol l^{-1}). K_D was found to be equal to 2 × 10^{-2} for potassium benzoate at 25°C and we can consider that carboxylate living ends with Et_4N^+ as counter-ion are essentially free ions in DMSO. Thus the k_p values determined in THF and in DMSO are those corresponding to ion pairs in THF and to free ions in DMSO.

A possible explanation for the fact that $k_\pm$ in THF is higher than k_- in DMSO would be that tetraethylammonium carboxylate ion pairs might be more reactive than free ions in THF. However, it is difficult to compare the reactivity of free ions in THF and in DMSO since the experiments have been done at different temperatures in both solvents and we do not know the activation energies in THF. In fact, very recent kinetic results obtained in N-methylpyrrolidone and acetone at 34°C with Et_4N^+ as

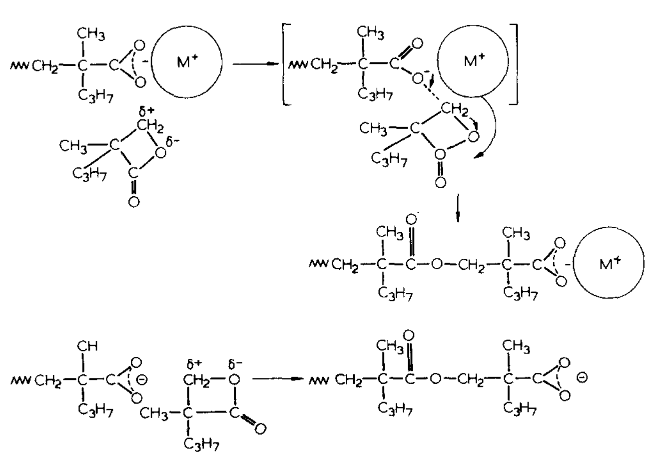

Figure 3 Propagation mechanisms in the anionic polymerization of α-methyl-α-propyl-β-propiolactone

counter-ion lead to k_p values higher than that measured in DMSO, for the same conditions[33]. This result means that the value of k_- determined in DMSO is anomalously low. Moreover, side reactions have been observed during the polymerization of MPPL in this solvent, such as the formation of low molecular weight polymers in the absence of catalyst. Compounds containing hydroxyl groups are presumably formed which could solvate the carboxylate anions, thus lowering the reactivity of these species. Similar behaviour has been found for the anionic polymerization of ethylene oxide in DMSO[34-41] in which chain transfer to the solvent leads to alcohol end groups which solvate living alkoxide centres[42].

In conclusion, use of a macrobicyclic ligand of K^+ such as [222] leads to the formation of living poly(MPPL), in THF. The main ionic species are cryptated carboxylate ion pairs in equilibrium with free ions. The reactivity of cryptated ion pairs is higher than that of free ions. This result can be explained by a push–pull mechanism influenced by a dipole–dipole interaction with the assistance of the cation in the ring opening of the monomer.

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