Kinetics of the anionic polymerization of β-propiolactone in dimethylformamide

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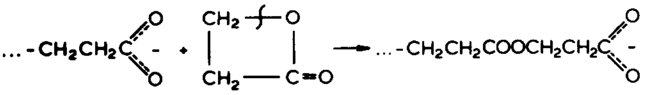
Dissociation constants and thermodynamic parameters of the dissociation of poly(β-propiolactone) macroion pairs (carboxylate anions with $K^+\cdot$dibenzo-18-crown-6 ether counterions) and $CH_3COO^-K^+\cdot$dibenzo-18-crown-6 ether were determined in isodielectric β-propiolactone (βPL)/dimethylformamide (DMF) and ε-caprolactone (εCL)/DMF systems. Stabilization of ion pairs by DMF, due to the $(CH_3)_2N^{+\delta}{=}CHO^{-\delta}$ resonance DMF form was proposed. Rate constants of propagation on macroions, k_p^-, and on macroion pairs, $k_p^\mp$, were measured. The ratio $k_p^-/k_p^\mp$ decreases with decreasing temperature, and at 20°C ($[\beta PL]_0 = 1\ mol\ l^{-1}$) macroion pairs become more reactive than macroions ($k_p^-/k_p^\mp = 7.5 \times 10^{-1}$). This results from a greater enthalpy of activation for propagation on macroions due to the fact that they are more strongly solvated than macroion pairs. Even in practically isodielectric mixtures, activation parameters for propagation on macroions depend on the monomer concentration. The explanation assumes that macroions are strongly solvated with β-propiolactone due to the very high dipole moment ($\mu = 4.18$) of monomer molecules.

(Keywords: β-propiolactone; anionic polymerization; kinetics; ions; ion pairs; solvation)

INTRODUCTION

In the anionic polymerization of β-propiolactone (βPL) it was unequivocally established that propagation proceeds on the carboxylate active centres and that monomer molecules are added with alkyl–oxygen bond scission[1,2]:


$$\ldots\text{-}CH_2CH_2COO^- + \underset{CH_2-C{=}O}{\overset{CH_2-O}{\square}} \longrightarrow \ldots\text{-}CH_2CH_2COOCH_2CH_2COO^- \qquad (1)$$

The present knowledge of the kinetics of anionic polymerization of β-lactones is, however, still very limited and in some cases apparently contradictory. The earlier papers[3–6] provided only values of the overall propagation rate coefficients, without giving insight into the contribution of various forms of active species, e.g. free ions and ion pairs. In a previous paper[7] we presented the first data on the kinetics of propagation on macroions and on macroion pairs in the anionic polymerization of βPL with $K^+\cdot$DB18C6 counterion (DB18C6 = dibenzo-18-crown-6 ether) in CH_2Cl_2 solvent. In these studies we found that macroions are more reactive towards monomer than are macroion pairs. However, the ratio of the corresponding rate constants, $k_p^-/k_p^\mp$, depends on the initial monomer concentration and on the temperature in such a way to suggest that, for high monomer concentrations ($[\beta PL]_0 = 3\ mol\ l^{-1}$) and at low temperatures (< 35°C), $k_p^\mp$ may become higher than k_p^-. To rationalize these results it was proposed that polar monomer molecules contribute significantly to the specific solvation of nonpaired carboxylate active centres. Thus, the enthalpy of activation for propagation on macroions is increased by the energy necessary to destroy the specific solvation during formation of the more charge-delocalized activated complex.

Recently, Haggiage *et al.*[8] published results of kinetic studies of the anionic polymerization of α-methyl-α-propyl-βPL with $K^+\cdot[222]$ counterion in tetrahydrofuran (THF). It was shown that at −20°C the reactivity of macroion pairs is higher than that of carboxylate macroanions ($k_p^-/k_p^\mp = 10^{-1}$). But measurements were carried out only at one temperature, and the dependence of k_p^-/k_p^+ on temperature was not established. The authors proposed the push–pull mechanism whereby the reactivity of macroion pairs is enhanced. From their data it is difficult, however, to conclude whether the observed reactivity ratio $k_p^-/k_p^\mp = 10^{-1}$ results from increased reactivity of macroion pairs, from decreased reactivity of macroions, or from both.

In this paper we present new results of studies on the equilibrium between macroion pairs and macroions and the reactivity of these species in the βPL polymerization in dimethylformamide (DMF). Besides providing new data, our aim was to determine whether the features of βPL polymerization in CH_2Cl_2, namely the specific solvation of carboxylate active centres with monomer molecules, also characterize polymerization of this monomer in the much more polar DMF.

EXPERIMENTAL

Monomer and initiator

Purification of βPL and synthesis of $CH_3COO^-K^+\cdot$DB18C6 and $Ph_4B^-K^+\cdot$DB18C6 are described elsewhere[7].

Solvents

DMF was purified using the following procedure. A mixture of 1.0 l DMF, 20 ml H_2O, and 200 ml benzene was prepared. Water and benzene together with the

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impurities present in DMF (formic acid and dimethylamine) were removed by azeotropic distillation followed by two distillations under reduced pressure (76°C at 40 mmHg) over 4 Å molecular sieves. Finally, portions (~ 100 ml) of DMF were distilled on a high vacuum line to ampoules containing ~ 1 ml of βPL. In this step any traces of formic acid and amine still present in the solvent are removed since they initiate the polymerization of βPL and thus, together with βPL, are incorporated in the nonvolatile polymer. Solvent distilled from this solution was used in further experiments. ε-Caprolactone (εCL) was purified in the same manner as βPL.

Methods

Kinetic measurements were performed using the dilatometric method. Dilatometers with thin-walled glass phials containing a known amount of initiator were filled with βPL/DMF solution under high vacuum. Prior to the experiments, they were stored in liquid nitrogen.

Conductivity measurements were performed using a semiautomatic precision bridge (BM 484, Tesla, Czechoslovakia) and an apparatus[9] equipped with a conductometric cell (cell constant $3.28 \times 10^{-1}\,\mathrm{cm}^{-1}$).

The number-average molecular weight, $\bar{M}_n$ of polymer samples was determined using a 302B vapour pressure osmometer and a 502 high-speed membrane osmometer (both Hewlett-Packard, USA).

Dielectric constants, D, of DMF and εCL were measured using a DK meter (GK 68, PGH Radio und Fernsehen, GDR). For DMF, $D = 13\,050/T - 6.71$; for εCL, $D = 13\,200/T - 4.35$. The dependence of the dielectric constant of βPL on temperature has been determined previously[7] using the same equipment. For βPL, $D = 19\,000/T = 17.97$.

RESULTS

Relation between experimental and calculated $\bar{M}_n$

Polymerizations were carried out as described above. In all experiments the same βPL/DMF solution was used and thus exactly the same initial monomer concentration was maintained ($[\beta\mathrm{PL}]_0 = 9.5 \times 10^{-1}\,\mathrm{mol\,l^{-1}}$). The initiator concentrations were varied from $4.73 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$ to $2.78 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$. When kinetic measurements indicated that polymer formation was complete, the dilatometers were opened and polymer was precipitated in cold (0°C) methanol. Crude polymer was dissolved in CH_2Cl_2, precipitated in methanol and dried under high vacuum for 48 h. Thereafter, $\bar{M}_n$ of polymer samples were determined using the osmometric method.

Values of the number-average molecular weight were also calculated from

$$\bar{M}_n^c = [\beta\mathrm{PL}]_0 \times 72.06/[\mathrm{CH_3COO^-K^+{\cdot}DB18C6}]_0 \quad (2)$$

with the assumption that the polymerization is the living one and thus that chain transfer reactions are unimportant. The correlation between $\bar{M}_n$ and $\bar{M}_n^c$ for poly(βPL) samples is shown in *Figure 1*. It is observed that over the entire region of $\bar{M}_n$ the data fit a straight line with a slope very close to unity (slope = 1.014).

Dissociation of poly(βPL) macroion pairs with $K^+{\cdot}DB18C6$ *counterion and of* $CH_3COO^-K^+{\cdot}DB18C6$ *ion pairs*

The dissociation constant, K_D, of poly(βPL) macroion pairs was determined to estimate the fractions and macroion pairs in the kinetic experiments. Measurements were performed using the conductometric method. Values of K_D were obtained from Fuoss analysis[10,11] of the dependence of equivalent conductance, Λ, on the concentration of the ionic species, c. In each experiment the approximate value of the equivalent conductance at infinite dilution, Λ_0, was evaluated from the dependence of Λ on $c^{1/2}$ extrapolated to $c = 0$. Then, using this value of Λ_0, activity coefficients, γ, and correction coefficients, $F(z)$, were calculated. Finally, values of Λ_0 and K_D were found from the intercept and the slope of the plot of $F(z)/\Lambda$ as a function of $c\gamma^2\Lambda/F(z)$ according to

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{1}{\Lambda_0^2 K_D}\frac{c\gamma^2\Lambda}{F(z)} \quad (3)$$

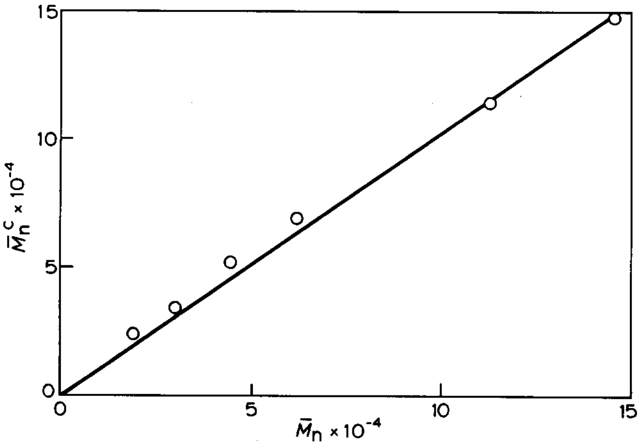


Figure 1 Relation between $\bar{M}_n$ and $\bar{M}_n^c$ for βPL polymerization with $[\beta\mathrm{PL}]_0 = 9.5 \times 10^{-1}\,\mathrm{mol\,l^{-1}}$

Measurements were performed in DMF for the polymerizing systems with $[\beta\mathrm{PL}]_0 = 5 \times 10^{-1}\,\mathrm{mol\,l^{-1}}$ and $1\,\mathrm{mol\,l^{-1}}$, and for $CH_3COO^-K^+{\cdot}DB18C6$ in a model system with βPL replaced by another lactone, namely εCL. The εCL was used in concentrations of $1.42\,\mathrm{mol\,l^{-1}}$ and $2.60\,\mathrm{mol\,l^{-1}}$, giving values of the dielectric constant of the mixtures close to those with $[\beta\mathrm{PL}]_0 = 5 \times 10^{-1}\,\mathrm{mol\,l^{-1}}$ and $1\,\mathrm{mol\,l^{-1}}$ respectively. Additivity of dielectric constants was assumed.

Because carboxylates do not initiate the polymerization of εCL, measurements of the dissociation were easier to perform in the model system, without the limitations imposed by changes in the polymerizing system (e.g. changes in the viscosity during polymerization of βPL). Values of the dissociation constant of poly(βPL)–macroion pairs and of $CH_3COO^-K^+{\cdot}DB18C6$ in the corresponding model systems were similar (see *Figure 2*).

From the dependence of $\ln K_D$ on T^{-1} (*Figure 2*), values of the enthalpy and entropy of dissociation of carboxylate ion pairs with $K^+{\cdot}DB18C6$ counterion were evaluated. For systems with $[\beta\mathrm{PL}]_0 = 5 \times 10^{-1}\,\mathrm{mol\,l^{-1}}$ ($D_{25} = 37.42$) and $[\varepsilon\mathrm{CL}] = 1.42\,\mathrm{mol\,l^{-1}}$ ($D_{25} = 37.41$), it was found that $\Delta H_D = -18 \pm 2\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S_D = -125 \pm 4\,\mathrm{J\,mol^{-1}\,K^{-1}}$ ($K_D^{25} = 4.2 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$). For $[\beta\mathrm{PL}]_0 = 1\,\mathrm{mol\,l^{-1}}$ ($D_{25} = 37.8$) and $[\varepsilon\mathrm{CL}] = 2.6\,\mathrm{mol\,l^{-1}}$ ($D_{25} = 37.7$), the values are $\Delta H_D = -20 \pm 2\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S_D = -136 \pm 3\,\mathrm{J\,mol^{-1}\,K^{-1}}$ ($K_D^{25} = 2.5 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$).

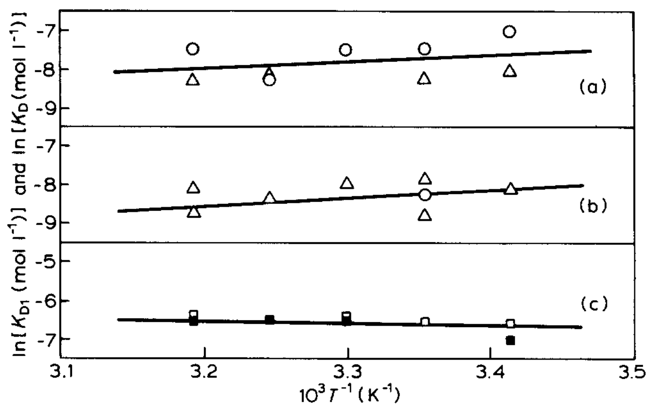


Figure 2 Dependence of $\ln K_D$ ((a) and (b)) and $\ln K_{D1}$ (c) on T^{-1}: (a) $[\beta PL]_0 = 5 \times 10^{-1}$ mol l^{-1} (○), $[\varepsilon CL] = 1.42$ mol l^{-1} (△); (b) $[\beta PL]_0 = 1$ mol l^{-1} (○), $[\varepsilon CL] = 2.60$ mol l^{-1} (△); (c) $[\varepsilon CL] = 1.39$ mol l^{-1} (□), $[\varepsilon CL] = 2.70$ mol l^{-1} (■)

Dissociation of $Ph_4B^-K^+ \cdot DB18C6$ in εCL/DMF

Measurements of the dissociation constants of $Ph_4B^-K^+ \cdot DB18C6$ (K_{D1}) were undertaken because we anticipated that, due to the bulkiness of the cation and anion, this salt may be efficiently dissociated in the polymerizing βPL solution. Efficient dissociation of $Ph_4B^-K^+ \cdot DB18C6$ should raise the concentration of free $K^+ \cdot DB18C6$ cations and affect the position of the equilibrium between the propagating poly(βPL)–macroion pairs and carboxylate macroions by shifting it to the macroion pair side. Thus, it should help to determine the propagation rate constants on macroion pairs.

Experiments and analysis of the data were performed as described earlier in the case of poly(βPL)–macroion pairs and $CH_3COO^-K^+ \cdot DB18C6$. No significant difference was observed between values of K_{D1} for εCL/DMF solutions with $[\varepsilon CL] = 1.39$ mol l^{-1} ($D_{25} = 37.40$) and $[\varepsilon CL] = 2.7$ mol l^{-1} ($D_{25} = 37.7$). Values of dielectric constants matched those of βPL/DMF with $[\beta PL]_0 = 5 \times 10^{-1}$ mol l^{-1} ($D_{25} = 37.42$) and $[\beta PL]_0 = 1$ mol l^{-1} ($D_{25} = 37.8$), respectively. The dependence of $\ln K_{D1}$ on T^{-1} given in *Figure 2* led to the following values of the thermodynamic parameters of dissociation: $\Delta H_{D1} = 11.5 \pm 0.4$ kK mol^{-1} and $\Delta S_D = -16.7 \pm 0.8$ J mol^{-1} K^{-1} ($K_{D1}^{25} = 1.25 \times 10^{-3}$ mol l^{-1}).

Propagation rate constants on poly(βPL) macroions, k_p^-, and on macroion pairs with $K^+ \cdot DB18C6$ counterion, $k_p^\mp$

Kinetic measurements were performed with $[\beta PL]_0 = 5 \times 10^{-1}$ mol l^{-1} and 1 mol l^{-1} in the temperature range 20°C–40°C (at temperatures below 15°C, polymerization becomes heterogeneous due to polymer precipitation). Initiator ($CH_3COO^-K^+ \cdot DB18C6$) concentration was changed from 2.46×10^{-4} mol l^{-1} to 9.80×10^{-3} mol l^{-1}. In some experiments, polymerization was carried out in the presence of $Ph_4B^-K^+ \cdot DB18C6$ dissociation ($K_{D1}^{25} = 1.25 \times 10^{-3}$ mol l^{-1}) and the common cation effect hindered dissociation of the poly(βPL)–macroion pairs.

Conversion of monomer into polymer was monitored dilatometrically. Two typical plots of the semilogarithmic anamorphoses of the kinetic curves are shown in *Figure 3*. It is worth noting that the experimental data are much better approximated by two lines rather than by one straight line.

In all experiments, the apparent propagation rate constants, k_p^{app}, were determined from the initial parts of kinetic plots corresponding to low monomer conversion. Values of the propagation rate constants for poly(βPL) macroions, k_p^-, and macroion pairs, $k_p^\mp$, were deduced from the linear dependence of k_p^{app} on the degree of dissociation, α. The form of this dependence is given by

$$k_p^{app} = k_p^\mp + (k_p^- - k_p^\mp)\alpha \tag{4}$$

The degree of dissociation, α, was calculated for each experiment using values of K_D (if $Ph_4B^-K^+ \cdot DB18C6$ was added also, by using K_{D1}) determined previously and the concentrations of ionic species. Quantitative initiation suggested by agreement between values of $\bar{M}_n$ and $\bar{M}_n^c$ was assumed.

Examples of plots of k_p^{app} as a function of α are given in *Figure 4*. Values of k_p^- and $k_p^\mp$ are collected in *Table 1*. The Arrhenius plots related to the propagation on macroion pairs and macroions in systems with $[\beta PL]_0 = 5 \times 10^{-1}$ mol l^{-1} and 1 mol l^{-1} are presented in *Figure 5*. From them the activation parameters were evaluated (Table 2).

DISCUSSION

Agreement between the number-average molecular weight of poly(βPL) samples measured, $\bar{M}_n$, and calculated

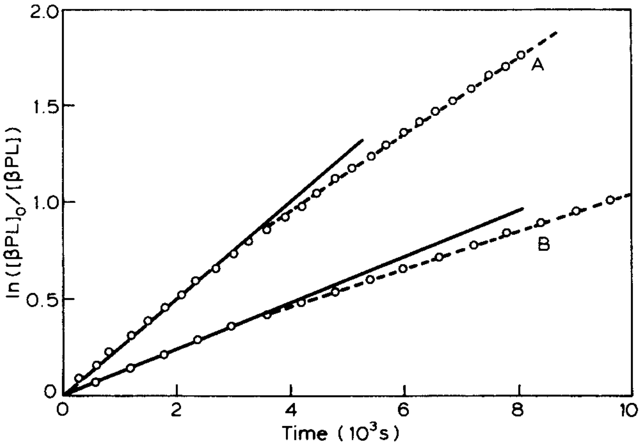


Figure 3 Kinetic plots for βPL polymerization in DMF at 25°C: A, $[\beta PL]_0 = 1$ mol l^{-1}, $[CH_3COO^-K^+ \cdot DB18C6]_0 = 4.09 \times 10^{-3}$ mol l^{-1}, $[Ph_4B^-K^+ \cdot DB18C6] = 2.69 \times 10^{-2}$ mol l^{-1}, $k_p^{app} = 5.7 \times 10^{-2}$ l mol^{-1} s^{-1}; B, $[\beta PL]_0 = 1$ mol l^{-1}, $[CH_3COO^-K^+ \cdot DB18C6]_0 = 1.69 \times 10^{-3}$ mol l^{-1}, $k_p^{app} = 6.21 \times 10^{-2}$ l mol^{-1} s^{-1}

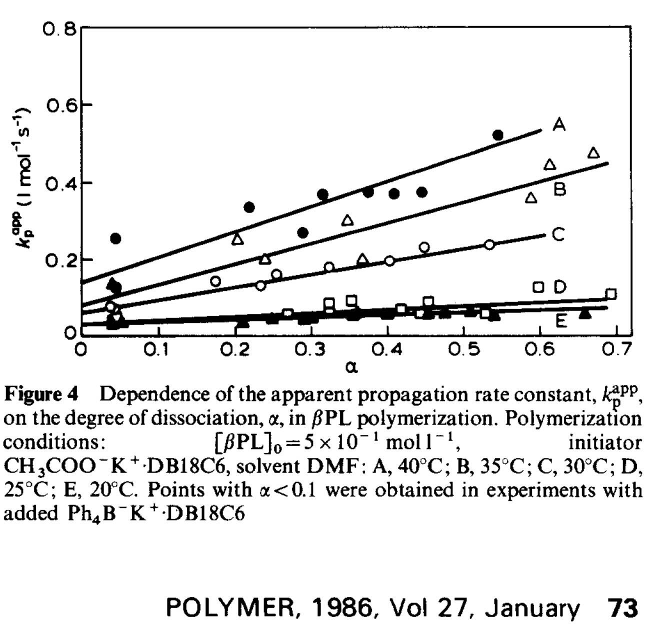


Figure 4 Dependence of the apparent propagation rate constant, k_p^{app}, on the degree of dissociation, α, in βPL polymerization. Polymerization conditions: $[\beta PL]_0 = 5 \times 10^{-1}$ mol l^{-1}, initiator $CH_3COO^-K^+ \cdot DB18C6$, solvent DMF: A, 40°C; B, 35°C; C, 30°C; D, 25°C; E, 20°C. Points with α < 0.1 were obtained in experiments with added $Ph_4B^-K^+ \cdot DB18C6$

according to equation (2), $\bar{M}_n^c$, suggests that:

(a) Initiation is 100% efficient.

(b) The chain transfer reactions are absent.

(c) Even in the case of low initiator concentrations, monomer is completely consumed, indicating that termination reactions are also unimportant.

Thus, measurements of $\bar{M}_n$ provide data conforming to the living polymerization. We are also inclined to accept that the change of the slopes of the kinetic curves presented in *Figure 3* results from the small but noticeable change of the propagation rate coefficients. This presumably occurs due to the change in βPL/DMF properties with conversion of monomer into polymer. Another explanation, namely termination of some fraction of active centres, seems to be less probable because the same reproducible features of the kinetic curves were observed in the whole region of the concentrations of active centres. Any given concentration of impurities killing part of the growing species would have more influence on the kinetics of propagation with lower concentrations of active centres.

Values of K_D were useful not only for estimating the fractions of poly(βPL) macroions and macroion pairs but also for providing some information on the structure of the latter.

According to the simple 'sphere-in-continuum' model, the dissociation constant can be described by

$$K_D = \frac{3000}{4\pi N\tilde{a}^3}\exp\left(-\frac{e^2}{kTD\tilde{a}}\right) \qquad (5)$$

where N is Avogadro's number, k is the Boltzmann constant, e is the elemental charge, and $\tilde{a}$ denotes the distance between ions constituting an ion pair. In the case of systems with $[\beta\text{PL}]_0 = 5\times10^{-1}$ mol l^{-1} ($D_{25} = 37.42$, $K_D^{25} = 4.2\times10^{-4}$ mol l^{-1}) and $[\beta\text{PL}]_0 = 1$ mol l^{-1} ($D_{25} = 37.8$, $K_D^{25} = 2.5\times10^{-4}$ mol l^{-1}), the values of $\tilde{a}$ calculated using equation (5) are 1.12 Å and 1.05 Å, respectively. These values are, however, unreasonably low and therefore cannot be related to the real macroion pair structure.

Dissociation constants determined previously[7] for poly(βPL)-macroion pairs in βPL/CH$_2$Cl$_2$ ($K_D^{25} = 5.6\times10^{-6}$ mol l^{-1} for $[\beta\text{PL}]_0 = 1$ mol l^{-1} and $K_D^{25} = 5.0\times10^{-5}$ mol l^{-1} for $[\beta\text{PL}]_0 = 3$ mol l^{-1}) led to values of $\tilde{a}$ equal to 3.4 Å and 2.7 Å, respectively. Let us assume tentatively that in βPL/DMF and in εCL/DMF the distance between ions in ion pairs does not differ significantly from that in βPL/CH$_2$Cl$_2$. For $\tilde{a} = 3$ Å, $D = 37.4$, and $T = 298.15$ K, we obtain using equation (5) the value K_D(calc.)$\sim10^{-1}$ mol l^{-1}. K_D(calc.) is therefore more than 200 times larger than the measured K_D ($K_D^{25} = 4.2\times10^{-4}$ mol l^{-1}). Hence, we must accept that the simple 'sphere-in-continuum' model cannot realistically describe the dissociation of carboxylate K$^+$·DB18C6 ion pairs in βPL/DMF and εCL/DMF.

Table 1 Propagation rate constants k_p^- and $k_p^{\mp}$ for βPL polymerization with K$^+$·DB18C6 counterion; solvent DMF

	Temperature (°C)				
	20	25	30	35	40
$[\beta\text{PL}]_0 = 5\times10^{-1}$ mol l^{-1}					
$10^2k_p^-$ (l mol^{-1} s^{-1})	9	13	39	60	80
$10^2k_p^{\mp}$ (l mol^{-1} s^{-1})	3.6	3.7	6.3	9	14
$k_p^-/k_p^{\mp}$	2.5	3.5	6.2	6.7	5.7
$[\beta\text{PL}]_0 = 1$ mol l^{-1}					
$10^2k_p^-$ (l mol^{-1} s^{-1})	3	7	–	–	60
$10^2k_p^{\mp}$ (l mol^{-1} s^{-1})	4	5	–	–	20
$k_p^-/k_p^{\mp}$	0.75	1.4	–	–	3

In the past, several attempts have been made to explain the limitations in the applicability of equation (5) and to propose more appropriate modifications. Fuoss[12] pointed out that it is not justified to use the macroscopic dielectric constant for calculations of electrostatic interactions between ions at very short distances. In the initial stage of dissociation of a contact ion pair, there are no solvent molecules between the ions. Thus, along with the separation of ions, the dielectric constant in the space between them changes from unity (dielectric constant of vacuum) to the macroscopic value for a given solvent. Szwarc[13] showed that this can account for dissociation constants much lower than predicted by equation (5). Another approach was proposed by Gilkerson[14], who, besides the electrostatic term $\exp(-e^2/kTD\tilde{a})$, introduced the term $\exp(E_s/RT)$, which is related to the difference in the specific interactions of ions and ion pairs with the nearest solvent molecules. Gilkerson's treatment, however, maintained the oversimplified assumption that, even when ions are in close contact, the macroscopic dielectric constant can be used to describe their electrostatic interactions.

Recently Fuoss[15,16] derived an expression (equation (6)) which yields good agreement between measured and calculated dissociation constants and avoids the above unrealistic assumptions:

$$K_D = \frac{3000}{4\pi Nr^3}\exp\left(-\frac{e^2}{kTDr}\right)\exp\left(\frac{E_s}{RT}\right) \qquad (6)$$

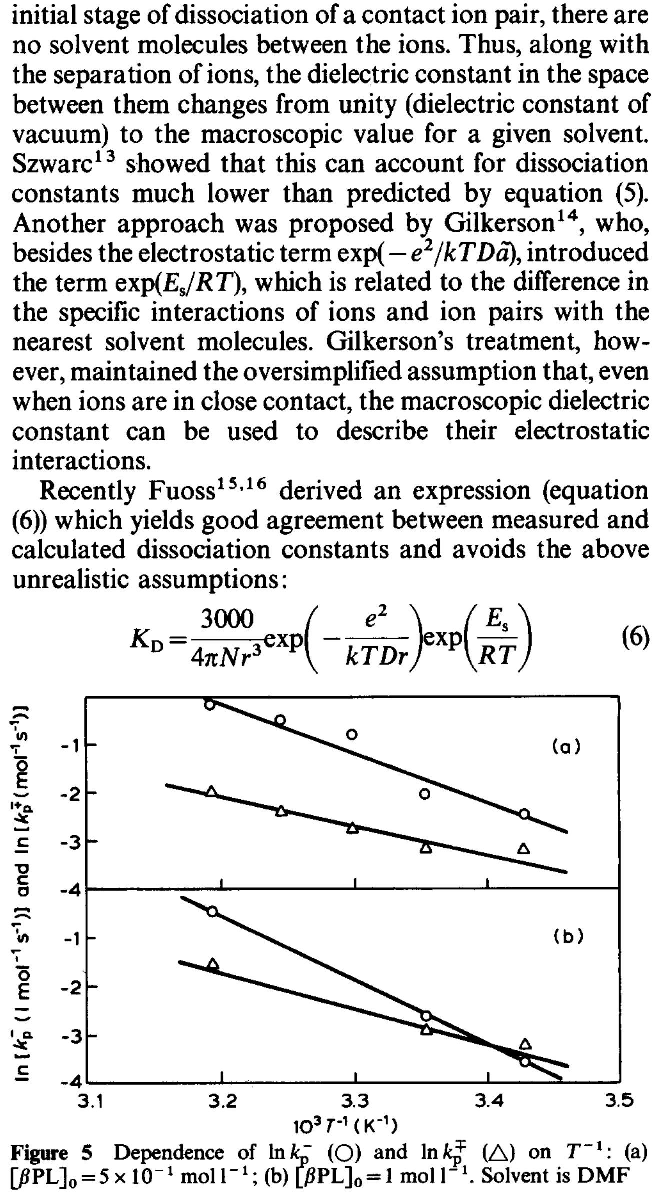


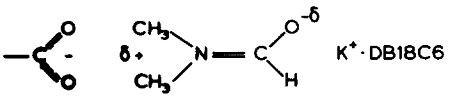
Figure 5 Dependence of ln k_p^- (○) and ln $k_p^{\mp}$ (△) on T^{-1}: (a) $[\beta\text{PL}]_0 = 5\times10^{-1}$ mol l^{-1}; (b) $[\beta\text{PL}]_0 = 1$ mol l^{-1}. Solvent is DMF

Table 2 Enthalpy and entropy of activation for the βPL polymerization with K$^+$·DB18C6 counterion; solvent DMF

	$\Delta H_p^{\ddagger}(-)$ (kJ mol^{-1})	$\Delta S_p^{\ddagger}(-)$ (J mol^{-1} K^{-1})	$\Delta H_p^{\ddagger}(\mp)$ (kJ mol^{-1})	$\Delta S_p^{\ddagger}(\mp)$ (J mol^{-1} K^{-1})
$[\beta\text{PL}]_0 = 5\times10^{-1}$ mol l^{-1}	88±9	34±6	52±8	−95±4
$[\beta\text{PL}]_0 = 1$ mol l^{-1}	114±9	105±9	61±9	−64±6

In equation (6), r is the diameter of the Gurney cosphere characterizing diffusion of ion pairs, i.e. ion pair formation and dissociation which is diffusion-controlled. It was shown[15] that, outside the Gurney cosphere, solvent can be described by its bulk properties and thus, in equation (6), the macroscopic dielectric constant can be used. E_s denotes the change of energy when diffusion ion pairs are converted into closer ion pairs with defined structure (e.g. contact ion pairs) and reflects differences in their interactions with the nearest molecules of the solvation shell.

The value of r for the carboxylate K^+·DB18C6 ion pairs in βPL/DMF and in εCL/DMF is not known but by definition must be larger than the distance between ions at their closest approach. A reasonable lower limit for the distance between carboxylate anion and K^+·DB18C6 in the contact ion pair is ~2.6 Å (crystal radius of K^+ equals 1.33 Å, radius of $-COO^-$ estimated from C=O and C–O bond lengths is ~1.3 Å). Hence, by using $K_D^{25} = 4.2 \times 10^{-4}$ mol l^{-1} ($[\beta PL]_0 = 1$ mol l^{-1}), $T =$ 298.15 K, $D = 37.42$, and $r \geqslant 2.6$ Å, we obtain from equation (6) $E_s \leqslant -12.6$ kJ mol^{-1}. This suggests that the very low dissociation of carboxylate K^+·DB18C6 ion pairs results from their stabilizing solvation, presumably by DMF molecules. It is possible that, due to the 'zwitterionic' nature of its resonance structure, a DMF molecule, when placed between ions, binds them effectively and hinders dissociation:



Activation parameters of propagation also indicate efficient solvation of ion pairs. We did show previously[7] that in βPL polymerization the activated complex with diffuse charge is weakly solvated. In βPL//CH_2Cl_2 when solvation of both macroion pairs and corresponding activated complex is weak, $\Delta H_p^{\ddagger}(\mp) = 25$ kJ mol^{-1} (ref. 7). In βPL/DMF, as follows from *Table 2*, enthalpies of activation for propagation on macroion pairs are much higher: $\Delta H_p^{\ddagger}(\mp) = 52$ kJ mol^{-1} and 61 kJ mol^{-1} for $[\beta PL]_0 = 5 \times 10^{-1}$ mol l^{-1} and 1 mol l^{-1}, respectively. High values of $\Delta H_p^{\ddagger}(\mp)$ in βPL/DMF reflect the expense of energy necessary for desolvation of ion pairs during formation of activated complex.

It is interesting also to compare activation parameters for propagation on macroions in βPL/DMF with $[\beta PL]_0 = 5 \times 10^{-1}$ mol l^{-1} and 1 mol l^{-1}. The dielectric constants of both systems are very close ($D_{25} = 37.41$ and 37.8 for $[\beta PL]_0 = 5 \times 10^{-1}$ mol l^{-1} and 1 mol l^{-1}, respectively), yet the values of $\Delta H_p^{\ddagger}(-)$ and $\Delta S_p^{\ddagger}(-)$ are substantially different (see *Table 2*). Because the only difference between these systems is the initial monomer concentration, it is reasonable to assume that βPL molecules contribute significantly to the solvation of macroanions and affect propagation. In the activated complex, with bonds undergoing rearrangements, negative charge is delocalized to a greater extent than in the parent carboxylate anion. Therefore, the former is much less solvated. The more βPL molecules that are involved in solvation of the carboxylate anions, the higher is the energy necessary for desolvation during formation of an activated complex. Liberation of some molecules from the solvation shell of the macroanion ground state increases the entropy of activation. This results in higher entropy of activation in systems with higher initial monomer concentration (see *Table 2*). In βPL/DMF the influence of desolvation on the propagation on macroions is so strong that, in spite of the loss of translational degrees of freedom during formation of activated complex from macroanion and monomer molecule, the entropies of activation become positive.

Dependences of $\Delta H_p^{\ddagger}(-)$ and $\Delta S_p^{\ddagger}(-)$ on the initial monomer concentration are qualitatively similar in βPL /DMF and βPL/CH_2Cl_2 systems[7]. They conform to the proposal that, even in the case of polar DMF, the solvation shell of propagating macroanion contains a higher fraction of βPL molecules than does the bulk solution. Apparently βPL, with the highest dipole moment ($\mu = 4.18$[17]), solvates carboxylate anions more efficiently than CH_2Cl_2 ($\mu = 1.14$)[18] and even DMF ($\mu = 3.86$)[19].

Over almost the entire temperature range studied, carboxylate macroions are more reactive than macroion pairs, but the difference between the values of the activation parameters for these species results in the dependence of $k_p^-/k_p^{\mp}$ on the temperature of polymerization (*Table 1*). For the polymerizations in DMF, like in CH_2Cl_2 (ref. 7), $k_p^-/k_p^{\mp}$ decreases with decreasing temperature. In DMF with $[\beta PL]_0 = 1$ mol l^{-1}, macroion pairs which at 35°C are less reactive than macroions ($k_p^-/k_p^{\mp} = 3$) become more reactive at 20°C ($k_p^-/k_p^{\mp} = 7.5 \times 10^{-1}$). Our previous studies[7] of βPL polymerization in CH_2Cl_2 suggested that, in the system with $[\beta PL]_0 = 3$ mol l^{-1}, macroion pairs should propagate faster than macroions at temperatures lower than -35°C. It is worth nothing that, in the polymerization of α-methyl-α-propyl-βPL in THF, Haggiage *et al.*[8] found macroion pairs to be more reactive than macroions ($k_p^-/k_p^{\mp} = 10^{-1}$) also at low temperature (-20°C).

Hence, whether the reactivity of macroions is higher (or lower) than the reactivity of the macroion pairs may depend not only on the chemical structure of active centres but also, due to the solvation phenomena, on the nature of monomer and solvent and on the temperature.

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