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lymerized PVK, if indeed the formation of this state depends on the ease of conformational relaxation within the various chain segments which comprise the polymer.

In conclusion, and by way of summary, we simply note that a new vinylcarbazole polymer, P(*N*-ET-4VK), has been prepared and its emission properties compared to those of P(*N*-ET-2VK), P(*N*-ET-3VK), and PVK. The isomeric vinylcarbazole polymers in which bonding to the backbone occurs at one of the ring carbon atoms all display emission spectra characteristic of that from their respective alkylcarbazole monomers and from a low-energy intrachain excimer state. The emission spectra of P(*N*-ET-2VK) and P(*N*-ET-4VK) are virtually indistinguishable; however, fluorescence decay measurements indicate considerable differences in the kinetics of formation and deactivation of the intrachain excimer state. These differences apparently reflect the variations in the preferred ground state geometry between neighboring pendant groups as determined by the position of bonding to the polymer backbone. In the case of P(*N*-ET-4VK) this geometry is such as to require only relatively minor conformational changes to achieve the overlapping sandwich-like geometry appropriate to the intrachain excimer state. The formation of the intrachain excimer state in P(*N*-ET-2VK) requires larger scale conformational changes to achieve the same intrachain excimer geometry. The basic cause leading to the differences in the kinetics of the photophysical processes in P(*N*-ET-2VK) and P(*N*-ET-4VK) appears to be that the geometrical constraints imposed by chain emplacement at the 4 position yield a higher density of ground state chain segment conformations in which achievement of the intrachain excimer geometry requires only small conformational variations. ^{1}H NMR spectroscopic results are in qualitative accord with this assertion. The relatively large amount of intrachain excimer fluorescence observed for P(*N*-ET-3VK), a polymer where interactions between neighboring pendant groups is minimal, is thought to result from an increase in isotactic content in the cationically polymerized sample. PVK, where chain emplacement occurs at the nitrogen atom, exhibits fundamentally different emission properties.

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Macroions and Macroion Pairs in the Anionic Polymerization of β-Propiolactone (β-PL)

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ABSTRACT: The dissociation constants K_D of the poly(β-propiolactone) ion pairs (carboxylate anion paired with crowned K^+) were found to be almost independent of temperature and had the following values at 25 °C: $K_D = 5.6 \times 10^{-6}$ M at [β-PL] = 1.0 M and $K_D = 5.0 \times 10^{-5}$ M at [β-PL] = 3 M (CH_2Cl_2 solvent), the corresponding thermodynamic parameters being equal to (ΔH_D in kcal mol^{-1} and ΔS_D in cal mol^{-1} deg^{-1}) $\Delta H_D = 0.6 \pm 0.5$, $\Delta S_D = -22 \pm 2$, $\Delta H_D = 0 \pm 2$, and $\Delta S_D = -18 \pm 3$, respectively. Rate constants of propagation on macroions (k_p^-) and macroion pairs ($k_p^{\mp}$) were determined, and it was found that the ratio $k_p^-/k_p^{\mp}$ changed with temperature. At −20 °C, $k_p^-/k_p^{\mp} = 5.6$ whereas this ratio increases up to 150 at 35 °C ($[\beta\text{-PL}]_0 = 3.0$ M). Formally this dependence stems from differences in activation parameters ($\Delta H_p^{\ddagger(\mp)} < \Delta H_p^{\ddagger(-)}$); the larger value of the activation enthalpy for macroanions is interpreted in terms of their stronger solvation by highly polar monomer (D_{25} of β-PL equals 45.8). The macroion pair is less solvated because of the shielding effect of the cation.

Anionic polymerization of β lactones has been studied by several authors;[1-10] however until now no rate constants are available for propagation reactions on various kinds of active centers, which are macroion pairs and free ions, that are involved in this process. In the past[11] and more recently[8,12,13] only several rate coefficients, without making distinction between different possible ionic states, were given.

In our previous paper,[9] we described application of crown ethers for complexing counterions in the polymer-

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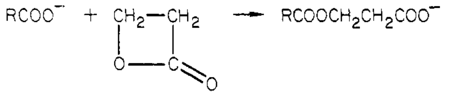
ization of β-PL in CH_2Cl_2 initiated with carboxylate salt. This complexation lead to homogeneous systems because carboxylates with crowned cations have increased solubility in a monomer–solvent mixture even when the active center concentration is as high as 3×10^{-2} mol L^{-1}. Under these conditions, polymerization has been found to proceed without appreciable termination reactions.

It has been shown[14] that the addition of β-PL molecules to the carboxylate anion proceeds with the alkyl–oxygen bond rupture in the monomer and leads to the carboxylate active center. For initiator and active centers of similar



(1)

structure one may suspect the initiation and propagation rate constants to be of the same magnitude. Therefore initiation should not interfere with the study of propagation.

In this work we extend our investigations on the dissociation of the macroion pairs and on the reactivity of free ions and ion pairs in the polymerization of β-PL initiated with I.

Experimental Section

Monomer. β-PL (Fluka, Switzerland) was distilled under reduced pressure (51 °C (10 mmHg)) in a nitrogen atmosphere and finally dried by several (usually three) subsequent distillations on the hy-vac line to the ampules with Na mirrors. Contact of the sodium mirror with β-PL containing traces of H_2O caused polymerization of a part of the monomer. Purified monomer was distilled to the ampules equipped with the break-seals. These were kept in a refrigerator.

Initiator. CH_3COOK–dibenzo-18-crown-6 ether (I) has been prepared by dissolving CH_3COOK and crown ether (1:1 molar) in dry methanol. After evaporation of the solvent, traces of methanol were removed by heating I up to 80 °C in an ampule attached to a hy-vac line for 30 h. The initiator was therefore distributed under vacuum to the thin-walled phials.

$Ph_4B^-K^+$–dibenzo-18-crown-6 ether was prepared from $Ph_4B^-K^+$ and crown ether in the same way as the initiator.

Solvent. Methylene dichloride (POCh, Poland) was purified according to the method elaborated by Sigwalt,[15] and after it was distilled on hy-vac line to ampules equipped with break-seals it was stored in the refrigerator.

Conductivity measurements were performed by using a semiautomatic precision bridge (BM 484, Tesla, Czechoslovakia) and the glass apparatus described previously,[16] equipped with the cell (cell constant 0,760 cm^{-1}) and Teflon (Rotaflo) stopcocks.

Dielectric constants of β-PL were measured with a DK meter (GK 68, PGH Radio und Fernsehen, Karl Marx Stadt, GDR) $D = 1900/T - 17.97$.

The kinetics of polymerization was studied by using the dilatometric method.

For the measurements of the number average molecular weight ($\bar{M}_n$) of polymer samples the 302 B vapor pressure osmometer (Hewlett Packard, USA) has been used.

Results

Dependence of the Apparent Propagation Rate Constants (k_p^{app}) on the Ratio [Dibenzo-18-crown-6 ether]/[CH_3COOK]$_0$. The kinetics of polymerization was studied in CH_2Cl_2 solution with constant initial monomer concentration $[\beta\text{-PL}]_0 = 3$ mol L^{-1}. In all of the experiments, the concentration of CH_3COOK was kept equal to 10^{-2} mol L^{-1}, and the crown ether concentration was changed from 0 to 4×10^{-2} mol L^{-1}. The k_p^{app} values were determined at 25 °C from the plots of ln ($[\beta\text{-PL}]_0/[\beta\text{-PL}]$) vs. time.

In Figure 1 the dependence of k_p^{app} on [dibenzo-18-crown-6 ether]/$[CH_3COOK]_0$ is given. k_p^{app} increases with the addition of crown ether until its concentration becomes equal to that of CH_3COOK. Therefore in all further experiments the 1:1 molar complex (I) was used.

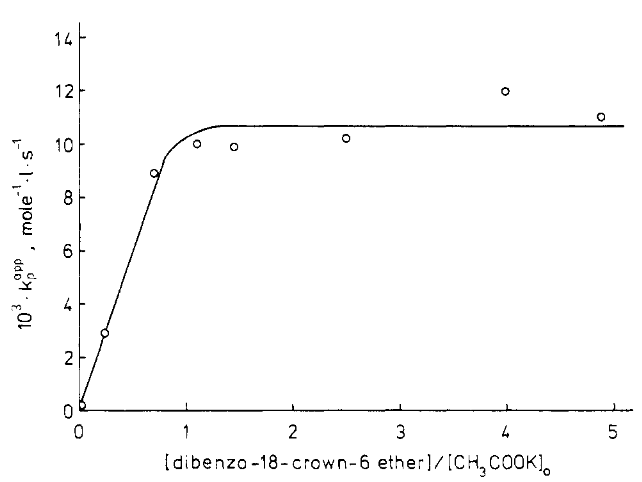


Figure 1. Dependence of k_p^{app} on [dibenzo-18-crown-6 ether]/$[CH_3COOK]_0$ with $[\beta\text{-PL}]_0 = 3$ mol L^{-1}, $[CH_3COOK]_0 = 10^{-2}$ mol L^{-1}, 25 °C, and CH_2Cl_2 solvent.

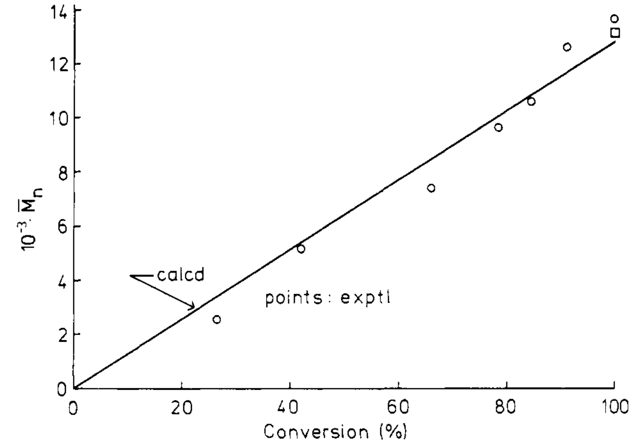


Figure 2. Dependence of $\bar{M}_n$ on conversion for β-PL polymerization with $[\beta\text{-PL}]_0 = 3$ mol L^{-1}, $[I]_0 = 1.67 \times 10^{-2}$ mol L^{-1}, 35 °C: ○, experimental; □, calculated as $[\beta\text{-PL}]_0 M_w(\beta\text{-PL})/[I]_0$.

Molecular Weights ($\bar{M}_n$) of Poly-β-PL. The dependence of $\bar{M}_n$ on monomer conversion for the poly-β-PL samples taken from the polymerizing mixture at various times has been investigated to confirm the living character of the anionic polymerization of β-PL.

In each sample the living centers have been deliberately killed by addition of CH_2Cl_2 containing HCl. Then the polymer was precipitated in methanol and after filtration dried to the constant weight. The $\bar{M}_n$ of each sample was determined by using Vapor Pressure osmometry.

In Figure 2 the dependence of $\bar{M}_n$ on conversion is given. From the same experimental data a kinetic plot has been made (Figure 3), which gave the $k_p^{app} = 1.88 \times 10^{-2}$ mol^{-1} L s^{-1} conforming to the k_p^{app} obtained by the dilatometric method (cf. Figure 5). Dissociation degree $\alpha = 0.05$ for experiment; results which are given in Figure 3 were calculated by using the dissociation constant $K_D = 5 \times 10^{-5}$ mol L^{-1} (see the following text) and the active centers concentration 1.67×10^{-2} mol L^{-1}.

Dissociation Constant (K_{D1}) of the Ph_4B^-,K^+-Dibenzo-18-crown-6 Ether. The K_{D1} values were determined conductometrically from the dependence of equivalent conductance (Λ) on the salt concentration (c) according to Fuoss' method.[17,18] After the determination of the first approximation of Λ_0 (equivalent conductance at infinite dilution) from the $\Lambda = f(c^{1/2})$ plot, Λ_0 and K_{D1} were evaluated from eq 2 by plotting $F(z)/\Lambda$ as a function of

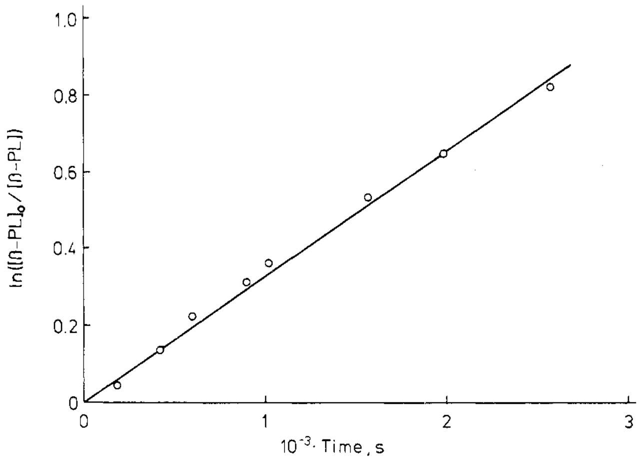


Figure 3. Kinetic plot for the polymerization of β-PL (conversion determined gravimetrically) with $[\beta\text{-PL}]_0 = 3$ mol L^{-1}, $[I]_0 = 1.67 \times 10^{-2}$ mol L^{-1}, 35 °C, CH_2Cl_2 solvent, and $k_p^{app} = 1.88 \times 10^{-2}$ mol^{-1} L s^{-1}.

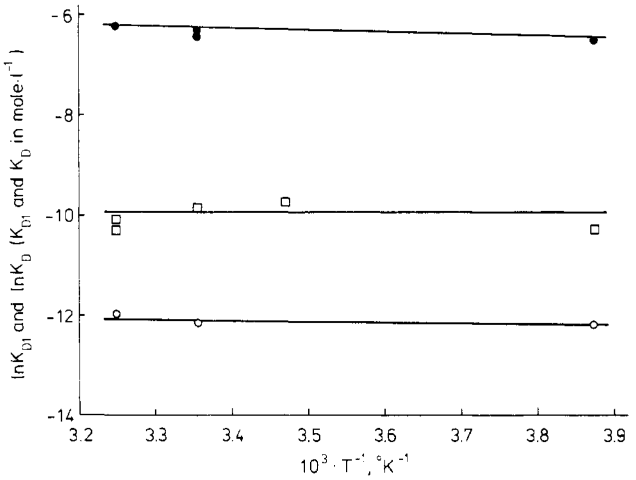


Figure 4. Dependence of ln K_{D1} (●, $[\beta\text{-PL}]_0 = 3$ mol L^{-1}) and of ln K_D (□, $[\beta\text{-PL}]_0 = 3$ mol L^{-1}; ○, $[\beta\text{-PL}]_0 = 1$ mol L^{-1}) on T^{-1} with CH_2Cl_2 solvent.

$c\gamma^2\Lambda/F(z)$, where γ is the activity coefficient, and $F(z)$ is a correction factor.

$$F(z)/\Lambda = 1/\Lambda_0 + c\gamma^2\Lambda/(\Lambda_0^2 K_{D1} F(z)) \qquad (2)$$

The K_{D1} values were determined in the CH_2Cl_2/β-PL solvent in the temperature region −15 to 35 °C. Tentatively the additivity of monomer and CH_2Cl_2 dielectric constants has been assumed. The solvent contained $[\beta\text{-PL}]_0 = 3$ mol L^{-1}, ensuring the same dielectric constant of the medium as in one set of measurements of the dissociation constant for poly-β-PL macroion pairs.

In Figure 4 the Van't Hoff's plot for K_{D1} is given. The enthalpy $\Delta H_{D1} = 0.6 \pm 0.5$ kcal mol^{-1} and entropy $\Delta S = -10 \pm 2$ eu were determined. At 25 °C K_{D1} was equal to 1.8×10^{-3} mol L^{-1}.

Dissociation Constant (K_D) of the Poly-β-PL Macroion Pairs. The K_D values for poly-β-PL macroion pairs were determined in the same way as K_{D1}. The measurements were performed in the temperature region from −15 to 35 °C for the living poly-β-PL in CH_2Cl_2/β-PL solution with initial monomer concentrations equal to 1 and 3 mol L^{-1}. The initiator concentration was low enough (less than 2×10^{-4} mol L^{-1}) to ensure that during conductivity measurements no more than 5% of the monomer was converted into polymer and that the dielectric constant of the medium does not change appreciably.

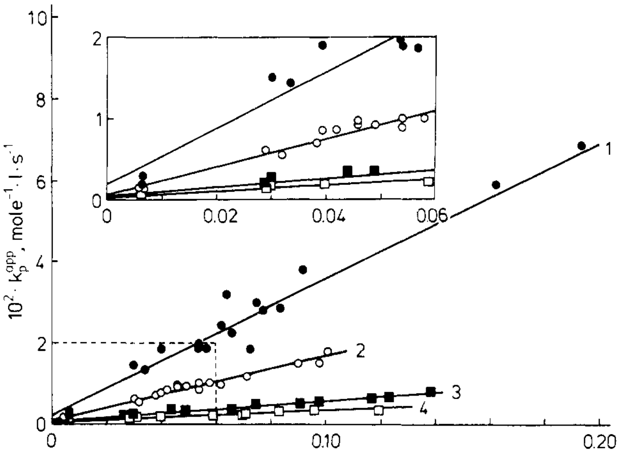


Figure 5. Dependence of the apparent rate constants of propagation (k_p^{app}) on the dissociation degrees (α) with $[\beta\text{-PL}]_0 = 3$ mol L^{-1}, initiator CH_3COOK–dibenzo-18-crown-6 ether, CH_2Cl_2 solvent: 1, 35 °C; 2, 25 °C; 3, 15 °C; 4, 10 °C. Points for α lower than 0.01 correspond to experiments with addition of $Ph_4B^-K^+$–dibenzo-18-crown-6 ether.

Table I
Propagation Rate Constants k_p^- and $k_p^{\mp}$ for the Polymerization of β-PL with K^+–Dibenzo-18-crown-6 Ether Counterion in CH_2Cl_2 Solvent

	temp, °C						
	−20	−15	0	10	15	25	35
$[\beta\text{-Pl}]_0 = 3$ mol L^{-1}							
$10^4 k_p^-$, mol^{-1} L s^{-1}	6.2	49	120	340	524	1600	3380
$10^4 k_p^{\mp}$, mol^{-1} L s^{-1}	1.1	2.7	5.5	5.6	6.5	7	22
$[\beta\text{-PL}]_0 = 1$ mol L^{-1}							
$10^4 k_p^-$, mol^{-1} L s^{-1}		490				2100	4900
$10^4 k_p^{\mp}$, mol^{-1} L s^{-1}		1.7				17	23

The plots of K_D vs. reciprocal absolute temperature are given in Figure 4. From this dependence, $\Delta H_D = 0.6 \pm 0.5$ kcal mol^{-1} and $\Delta S_D = -22 \pm 2$ eu for the solution with $[\beta\text{-PL}]_0 = 1$ mol L^{-1} and $\Delta H_D = 0 \pm 2$ kcal mol^{-1} and $\Delta S_D = -18 \pm 3$ eu for $[\beta\text{-PL}]_0 = 3$ mol L^{-1} were determined. Therefore K_D practically does not depend on temperature. At 25 °C, $K_D = 5.6 \times 10^{-6}$ mol L^{-1} at $[\beta\text{-PL}]_0 = 1$ mol L^{-1} and $K_D = 5.0 \times 10^{-5}$ mol L^{-1} at $[\beta\text{-PL}]_0 = 3$ mol L^{-1}. Thus, for similar conditions (25 °C, $[\beta\text{-PL}]_0 = 3$ mol L^{-1}) the dissociation constant of Ph_4B^-,K^+–dibenzo-18-crown-6 ether is 36 times higher than that for a living poly-β-PL with the same cation.

Determination of the Propagation Rate Constants for Macroions (k_p^-) and Macroion Pairs with Crowned Cations ($k_p^{\mp}$). The k_p^{app} was measured in the temperature region ranging from −20 to 35 °C for the initiator concentrations from $[I]_0 = 10^{-4}$ to 3×10^{-2} mol L^{-1}. Two sets of experiments were made, with $[\beta\text{-PL}]_0 = 1$ mol L^{-1} and $[\beta\text{-PL}]_0 = 3$ mol L^{-1}. The absolute propagation rate constants k_p^- and $k_p^{\mp}$ were determined from the general dependence of k_p^{app} on the dissociation degree (α) of the active centers

$$k_p^{app} = k_p^{\mp} + \alpha(k_p^- - k_p^{\mp}) \qquad (3)$$

(where $k_p^{\mp}$ denotes a rate constant of propagation on macroion pairs with crowned cation).

Dissociation degree (α) was calculated by using the K_D values and the active centers concentration, assuming the initiation to be quantitative. In several experiments the polymerization was carried on in the presence of $Ph_4B^-K^+$–dibenzo-18-crown-6 ether in order to suppress the concentration of the macroanions. Because of its high

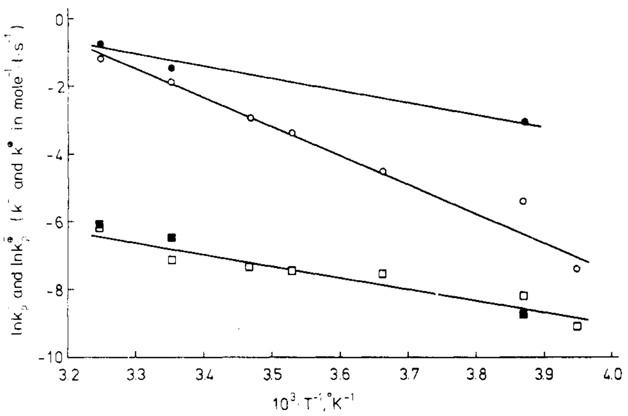


Figure 6. Dependence of ln k_p^- (●, $[\beta\text{-PL}]_0 = 1$ mol L^{-1}; ○, $[\beta\text{-PL}]_0 = 3$ mol L^{-1}) and ln $k_p^{\mp}$ (■, $[\beta\text{-PL}]_0 = 1$ mol L^{-1}; □, $[\beta\text{-PL}]_0 = 3$ mol L^{-1}) on T^{-1}.

Table II
Activation Parameters for the Polymerization of β-PL with K^+-Dibenzo-18-crown-6 Ether Counterion in CH_2Cl_2 Solvent

	$\Delta H_p^{\ddagger(-)}$, kcal mol^{-1}	$\Delta S_p^{\ddagger(-)}$, eu
$[\beta\text{-PL}]_0 = 3$ mol L^{-1}	16 ± 1	−10 ± 4
$[\beta\text{-PL}]_0 = 1$ mol L^{-1}	6 ± 1	−40 ± 5
	$\Delta H_p^{\ddagger(\mp)}$, kcal mol^{-1}	$\Delta S_p^{\ddagger(\mp)}$, eu
$[\beta\text{-PL}]_0 = 1$ and 3 mol L^{-1}	6 ± 1	−52 ± 4

dissociation constant (K_{D1}), the addition of this salt in concentrations of approximately 4×10^{-2} mol L^{-1} shifted the equilibrium between the two types of active centers considerably to the macroion pairs side.

In Figure 5 plots of k_p^{app} vs. α at several temperatures are given. All are represented by straight lines. From intercepts $k_p^{\mp}$ and from slopes k_p^- have been calculated. These values are given in Table I.

In Figure 6 the dependence of ln (k_p^-) and ln ($k_p^{\mp}$) vs. T^{-1} is plotted, and the eventually determined activation parameters are given in Table II.

Discussion

From the dependence of k_p^{app} on the [dibenzo-18-crown-6 ether]/$[CH_3COOK]_0$ ratio (cf. Figure 1), it follows that starting from a crown ether concentration equal to that of the potassium cations (1:1 molar) practically all of the cations are complexed. This reflects the known high value of the equilibrium constant of complexation of K^+ ions with dibenzo-18-crown-6 ether (e.g., it equals 10^5 mol L^{-1} in methanol at 25 °C[19]). In our previous paper on the β-PL polymerization with Na^+ counterion, we have shown that at similar conditions these cations are completely complexed only with approximately threefold excess of dibenzo-18-crown-6 ether, and indeed it is known that this particular ether fits the K^+ cations much better than the Na^+ cations.[19]

Linearity of the corresponding semilogarithmic kinetic plots (cf. Figure 3) indicates that concentration of the active centers does not change up to high conversion; dependence of $\bar{M}_n$ on conversion (Figure 2) also shows that transfer is eliminated. Therefore polymerization of β-PL initiated with I may be considered as the living process.

The enthalpy of dissociation of the poly-β-PL macroion pairs close to zero and the entropy of dissociation equal to −22 and −18 eu, for solutions with β-PL concentrations 1 and 3 mol L^{-1}, respectively, are characteristic for the loose ion pairs[20,21] and indicate a small change of the solvation state in going from ion pairs to free ions. This is probably due to the bulkiness of the complexed K^+ counterion.

It is known that with an increase in the size of the ions the enthalpy of dissociation becomes less negative. Indeed, for the dissociation of the tight poly(styrylsodium) ion pairs in THF $\Delta H_D = -9$ kcal mol^{-1} whereas for the poly(styrylcaesium) ion pairs in the same solvent $\Delta H_D = -1.8$ kcal mol^{-1} (the corresponding crystallographic radii are 0.95 and 1.69 Å for Na^+ and Cs^+, respectively).[22] In THF solution for the solvent-separated poly(styrylsodium) ion pair with solvated cation (Stokes' radius ≈ 4.2 Å[23]), the enthalpy of dissociation equals 0.1 kcal mol^{-1}.[21] Enthalpies of dissociation of fluorenyl salts with large, complexed crown ether Na^+ cations are close to 0 kcal mol^{-1}.[24]

The relation between the dimensions of the ions constituting the ion pair and the dissociation constant is very strongly pronounced also when passing from salts with poly(styrylium) anions to those with larger Ph_4B^- anions. In the 3-Me-THF solvent at 20 °C, the dissociation constants of the poly(styrylsodium) ion pair and of Ph_4B^-,K^+ determined by conductivity measurements are equal to 4.56×10^{-9} mol L^{-1} and 1.12×10^{-5} mol L^{-1}, respectively.[21]

Similar behavior was observed in this work for carboxylates ($K_D = 5.0 \times 10^{-5}$ mol L^{-1}, in CH_2Cl_2/β-PL mixture, $[\beta\text{-PL}]_0 = 3$ mol L^{-1}, 25 °C) and tetraphenylborates ($K_{D1} = 1.8 \times 10^{-3}$ mol L^{-1}, at the same conditions) with K^+ complexed with crown ether cations.

As one can see from Table I, for the polymerizations with $[\beta\text{-PL}]_0 = 3$ mol L^{-1} at high temperatures, the rate constants of propagations on macroions (k_p^-) are considerably higher than those for the crowned ion pairs ($k_p^{\mp}$) ($k_p^-/k_p^{\mp} = 150$ at 35 °C) whereas at low temperatures the reactivities of both kinds of active centers toward monomer differ less than by one order of magnitude ($k_p^-/k_p^{\mp} = 5.6$ at −20 °C). Formally it results from the significantly lower value of $\Delta H_p^{\ddagger(\mp)}$ than that of $\Delta H_p^{\ddagger(-)}$ (cf. Table II).

Different types of ion pairs (e.g., contact and solvent separated) are known to exist in equilibrium.[21,25] Thus, two kinds of ion pairs were found for fluorenyl salts with Na^+ and K^+ cations complexed with crown ether, namely, crown complexed tight ion pairs (fluorenyl$^-$, K^+, crown ether) and crown separated ion pairs (fluorenyl$^-$, crown ether, K^+).[26] Therefore, before drawing mechanistic conclusions, it is necessary to make certain that what has been designated enthalpy of activation for propagation by crowned macroion pairs corresponds to the elementary reaction with only one type of ion pair being involved and that it is not a complex parameter composed of activation and thermodynamic equilibrium parameters for different ion pairs.

Let us tentatively assume that the crown separated macroion pairs and crown complexed tight macroion pairs, the latter ones being much less reactive, are simultaneously present in the system. In this case the lowering of the temperature shifts the equilibrium toward separated ion pairs (equilibrium between tight and separated ion pairs was always found to be exothermic[21,26]) and it might indeed result in apparently lower enthalpy of activation (e.g., anionic polymerization of styrene in THF, THP, and DME[21]). However, the equilibrium between two types of ion pairs is influenced not only by temperature but also by polarity of the medium. This is, for instance, manifested in the case of the equilibrium between crown complexed fluorenylsodium tight ion pairs and the corresponding crown separated ion pairs. An important increase from 0.52 to 1.8 was observed when the solvent was changed from THP ($D_{25°C} = 6.61$) to only slightly more polar THF ($D_{25°C} = 7.39$). Hence, in the kinetic experi-

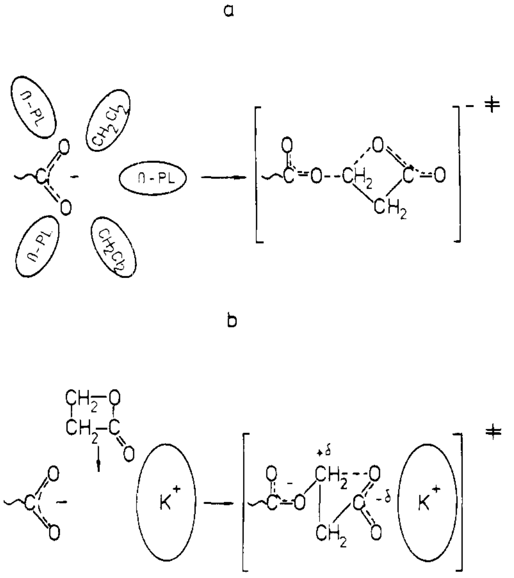


Figure 7. (a) Formation of the activated complex for the propagation on macroions. The solvation shell is represented schematically by monomer and solvent molecules (the actual number of monomer molecules in the solvation shell is not known and this value shown in the picture may not correspond to the actual value). (b) Formation of the activated complex for the propagation on macroion pairs.

ments performed with $[\beta\text{-PL}]_0 = 1$ mol L^{-1} ($D_{25\,°C} = 11.4$ for the solution), the proportion of crown complexed tight macroion pairs should be higher than that for $[\beta\text{-PL}]_0 = 3$ mol L^{-1} ($D_{25\,°C} = 16.1$ for the solution). This should result in influencing the kinetically determined propagation rate constants for macroion pairs $k_p^{\mp}$.

From Table I and from Figure 6 one can see, however, that there are practically no differences in the $k_p^{\mp}$ for $[\beta\text{-PL}]_0 = 1$ and 3 mol L^{-1} in the whole temperature region. In effect it is reasonable to assume that $\Delta H_p^{\ddagger(\mp)}$ is a genuine enthalpy of the simple elementary reaction. The high polarity of the CH_2Cl_2/β-PL solutions enables us to expect the macroion pairs to be crown separated ones (even in moderately polar THF the proportion of crown separated fluorenylsodium ion pairs approaches 60%).[26]

Large differences of $\Delta H_p^{\ddagger(-)}$ and $\Delta H_p^{\ddagger(\mp)}$, for $[\beta\text{-PL}]_0 = 3$ mol L^{-1}, and a very low value of $\Delta S_p^{\ddagger(\mp)} = -52$ eu may be explained when the solvation phenomena are taken into account.

In Figure 7a the transition from substrate to activated complex in the propagation is shown schematically. The active center, carboxylate anion, should be strongly solvated with polar (predominantly monomer) molecules. In the activated complex, in which some bonds are partially broken and some new ones are partially formed, the negative charge is delocalized to a great extent and consequently the solvation is less efficient. Hence, when passing from the carboxylate anion to the activated complex it is necessary to provide enough energy for desolvation. This energy increases the enthalpy of activation. Furthermore, desolvation results in an increase in the number of degrees of freedom, which is what makes the entropy of activation less negative.

For the propagation on macroion pairs, in the ground state and in the corresponding activated complex the charge distributions do not differ significantly and the bulkiness of the cation causes the solvation of both structures to be low. The enthalpy of activation ($\Delta H_p^{\ddagger(\mp)}$), not being influenced considerably by the solvation phenomena, is much lower than that for free macroions. The entropy of activation is determined by the necessity of proper orientation of both ions and monomer molecule in the activated complex. Thus, the rigidity of this structure should result in lowering the number of degrees of freedom when passing from the ground state to the activated complex and can be a sufficient reason for a substantially negative entropy of activation ($\Delta S_p^{\ddagger(\mp)} = -52 \pm 4$ eu). In the activated complex for propagation on the macroion pairs, the monomer molecule is probably already placed properly oriented between cation and anion, therefore the push-pull mechanism may enhance the corresponding rate constant as earlier proposed for other systems.[27]

For propagation on macroions with $[\beta\text{-PL}]_0 = 1$ mol L^{-1}, the solvation of carboxylate anions becomes less efficient than that for $[\beta\text{-PL}]_0 = 3$ mol L^{-1}, which results in much lower values of enthalpy and more negative entropy of activation ($\Delta H_p^{\ddagger(-)} = 6 \pm 1$ kcal mol^{-1} and $\Delta S_p^{\ddagger(-)} = -40 \pm 5$ eu).

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