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SPECIFIC SOLVENT EFFECTS OF DIOXANE AND N,N,N',N'-TETRAMETHYLETHYLENEDIAMINE IN THE ANIONIC POLYMERIZATION OF STYRENE WITH Li^+ AS COUNTERION

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Abstract

The anionic propagation of living polystyryllithium shows a distinctly different behavior depending on the nature of the solvent used (polar or non-polar). To demonstrate the transition of one type of behavior to the other, studies have been carried out in the past in mixtures of benzene and tetrahydrofuran (THF) and mixtures of dioxane and THF.

The results found in mixtures of benzene and THF could entirely be accounted for in terms of classical dielectric theory.

In contrast to this the reactivity of the ion pair in dioxane -THF mixtures cannot be explained in these simple terms.

In order to elucidate this controversy, similar experiments were carried out in this work in mixtures of N,N,N',N'-tetramethylethylene diamine (TMEDA) and THF and the results are compared with those previously found in the other mixtures.

From this comparison it can be concluded that in all cases the specific solvation of Li^+ is of utmost importance and that it is the solvent-separated ion pairs, the concentration of which is always small compared to that of the externally solvated contact ion pairs, which are mainly responsible for the observed propagation. A direct comparison between dioxane and TMEDA does not seem to hold.

Indeed, whereas the bidentate TMEDA replaces equally well two THF molecules in the externally solvated contact ion pairs as in the solvent-separated ion pairs, one must conclude from the comparison of the results that dioxane cannot enter the solvation shell of the solvent-separated ion pair without destroying it. On top of that, recent results show that unlike TMEDA, which can act as a bidentate ligand , dioxane, even in its boat-form, cannot do this, since the free electron pairs on the oxygen atoms remain too far away from the Li^+-cation.

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1. Introduction

It has been known for some time that the anionic polymerization of living polystyrene shows a entirely different behavior depending on the nature of the solvent (polar or non-polar) [1-5].

In order to demonstrate the transition from one type of behavior to the other, Bywater et al. measured the propagation rate constants and the equilibrium constants of dissociation into free ions of polystyryllithium in mixtures of benzene and tetrahydrofuran (THF) [6]. In these mixtures the ion pair rate constant falls fairly rapidly as the dielectric constant (ε) of the medium decreases. Plots of the logarithm of the dissociation constant into free ions K_d against $1/\varepsilon$ give a good straight line as expected from the classical model of spherical ions in a continuous diëlectric. Plots of the logarithm of the ion-pair rate constant $k_{p\pm}$ against $1/\varepsilon$ or against the Kirkwood function $(\varepsilon-1)/(2\varepsilon+1)$ show in both cases a linear dependence. These investigators concluded therefore that the increase in rate at higher dielectric constants would formally correspond to an increase in dipole moment during the formation of the transition state, and that with both approaches most of the change should occur in the activation energy term.

A simular study by Van Beylen et al. was devoted to the kinetics of propagation of polystyryllithium in mixtures of dioxane (DOX) and THF [7].

In THF [2-5] a decrease of living ends results in an increasing propagation rate constant k_p indicating the presence of two propagating species in fast equilibrium with each other, namely ion pairs (contact- and solvent-separated ion pairs) and free ions.

In dioxane however [8-11] the observed rate constant is independent of the concentration of living ends. The polymerization reaction is first order with respect to the monomer and to the living ends, which indicates that polystyryllithium ion pairs are not aggregated in dioxane as they are in non-polar medium such as benzene.

The strikingly different behavior of living polystyrene in THF and in dioxane and the surprisingly large effects of these solvents upon both the rate of polymerization and the order of reactivities of ion pairs induced Van Beylen et al. to investigate the anionic propagation of polystyryllithium in mixtures of THF and dioxane. In this study a perfect linear relation is obtained when the logarithm of the ionic dissociation constant

K_d is plotted versus $1/\varepsilon$. In contradistinction to the ion dissociation process, the reactivity of the ion pairs however cannot be explained in these simple terms. The kinetic study shows that the situation in these mixtures is much more complex. Plots of the logarithm of the ion-pair rate constant $k_\pm$ against $1/\varepsilon$ or against the Kirkwood function $(\varepsilon-1)/(2\varepsilon+1)$ deviate markedly from linearity. On the other hand, a plot of the logarithm of the ion-pair rate constant $k_\pm$ versus the mole fraction of dioxane seems to be less curved although its concave shape is indisputable. As pointed out by these authors, these concave shapes of the plots are surprising because they indicate that adding a small amount of dioxane to THF results in a large drop of the reactivity of the ion pairs, while a much higher amount of THF has to be added to dioxane to produce a noticeable increase of the ion pair rate constant. This could indicate that in the vicinity of the ion pair the proportion of dioxane is higher than in the bulk of the solution, which would be surprising as one would expect the better solvating compound, THF, to interact more strongly with the ion pair than dioxane, because it was found that THF, but not dioxane, forms solvent-separated ion pairs with lithium and sodium salts of fluorenyl carbanions [12]. Here however one has the impression that dioxane solvates the ion pair better than THF, but instead of increasing its reactivity it appears to retard the propagation. Alternatively, the results may indicate that the high reactivity of the polystyryllithium ion pair in THF is due to the participation of several THF molecules (probably four) in the transition state of the reaction, and this beneficial solvation is destroyed even if one of them is replaced by dioxane. One might think that dioxane could become a good solvating agent for the cation by isomerizing from its normal chair conformation to that of the boat, but no further investigation was made to see whether such an isomerization can take place in the course of solvation of an ion pair.

During the last several years a lot of research has been done on adding and using complexing agents in anionic polymerization systems. Very spectacular results were obtained by Langer [13,14] who used N,N,N',N'-tetramethylethylene diamine (TMEDA) to form relatively stable organolithium complexes for the anionic polymerization of monomers with low reactivity such as ethylene. The results of a kinetic study by Langer, carried out for the purpose of identifying the propagating species and their reactivities, show that the living ends are complexed with only one

TMEDA molecule and that these organolithium complexes possess remarkable higher carbanion reactivity in comparison with the non-complexed living ends. These results were later confirmed by Schué et al. [15-18].

Hélary and Fontanille [19-21] showed that this complexation of the ion pair with TMEDA is a 1:1 external solvation by which only non-associated, externally solvated contact ion pairs are formed (figure 1). This external solvation of the ion pairs by TMEDA was shown by these authors to hardly affect the interionic distance.

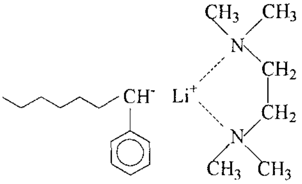

Figure 1 : Complexation of PStLi with TMEDA.

The comparable properties of TMEDA and dioxane, neither of which form solvent-separated ion pairs with fluorenyl salts and the dielectric constant of which are 2.8 and 2.2 respectively, induced us to investigate the anionic polymerization of polystyryllithium in mixtures of THF and TMEDA. In order to explain the controversy of the exact role of dioxane, the purpose of this investigation was, to use TMEDA as some kind of a substitute for dioxane and to study how the ion-pair rate constant of polystyryllithium changes in mixtures of THF and TMEDA, and also to determine the value of the ion-pair rate constant in pure TMEDA. The results have been compared with those found in the other mixtures. A model, explaining the three series of experiments, based on solvent-separated ion pairs as the most important carrier of the ion pair reactivity, instead of in terms of dielectric constants, is proposed.

II. Experimental section

All monomer and solvent purifications were carried out under high vacuum.

-Benzene was purified by refluxing with sodium-potassium (1/3) alloy. It was then stirred and degassed on the vacuum line.

-Tetrahydrofuran (THF) was refluxed with and fractionally distilled from sodium-potassium (1/3) alloy. The solvent was then put upon new sodium-potassium alloy. After stirring and repeatedly degassing on the vacuum line the characteristic blue color appears.

-N,N,N',N'-Tetramethylethylene diamine (TMEDA) was first dried over molecular sieves 4Å and then distilled over n-BuLi.

-Styrene was fractionally distilled to remove the inhibitor and stirred for 48h over calcium hydride and before use finally distilled from polystyryllithium.

-Sec-butyllithium was used after sublimation under vacuum.

-Polystyryllithium was synthesized in benzene by reaction of sec BuLi with styrene. The reaction mixture was stirred for 24h at room temperature producing PStLi with its typical yellow orange color in benzene ($\lambda_{max} = 330$ nm).

-The physical properties of the solvent mixtures, prepared by distilling the correct amounts of the two solvents into the reaction vessel, were measured at 20°C. The densities were measured on a hydrostatic balance and the viscosities in a Ubbelohde viscometer which was calibrated with liquids of known viscosity including pure THF and TMEDA. A decameter was used to determine the dielectric constants of the solvent mixtures.

-The conductances of polystyryllithium were measured between -60°C and 20°C with a Wayne - Kerr Bridge. Dilution was achieved by leaving part of the solution in the required compartment and distilling into it the solvent from the remaining solution. Since the dilution is achieved by removing the solute and not by adding more solvent, highly dilute solutions may be obtained without introducing any impurities. To avoid polarization on the platina electrodes an alternating current was used during the experiments.

-The kinetics of the propagation reactions were determined by following the disappearance of styrene spectrophotometrically at 291.5 nm on a Cary 2200 at 20°C.

III. Results

Before starting the conductivity and the kinetic study of polystyryllithium it was necessary to characterize our solvent system. Consequently the densities, viscosities and the dielectric constants of several THF-TMEDA solvent mixtures were experimentally determined. The results are listed in table I. A detailed knowledge of these physical properties is indispensable in order to evaluate the conductance and kinetic measurements correctly.

Table I : Physical properties of THF-TMEDA mixtures and K_d values of PStLi at 20°C.

Vol % of TMEDA	ρ (g/cm^3)	η (poise)	ε	K_d (M)
0.0	0.8800	$4.60\ 10^{-3}$	7.51	$1.9\ 10^{-7}$
10.0	0.8416	$4.95\ 10^{-3}$	7.04	$8.3\ 10^{-8}$
24.4	0.8576	$5.20\ 10^{-3}$	6.18	$7.1\ 10^{-9}$
33.7	0.8483	$5.22\ 10^{-3}$	5.77	$1.2\ 10^{-9}$
47.0	0.8295	$5.47\ 10^{-3}$	5.22	$9.0\ 10^{-11}$
65.4	0.8025	$5.12\ 10^{-3}$	4.35	$1.1\ 10^{-11}$
100.0	0.7700	$6.01\ 10^{-3}$	2.83	---

The ionic dissociation behavior of polystyryllithium in various mixtures of THF and TMEDA can be studied from the conductance measurements of the solutions. The dissociation constants K_d were determined from Kraus and Bray plots [22]. The values of these constants are also given in table I. From these measurements we can deduce that the dissociation of ion pairs into free ions increases progressively with increasing amounts of THF in the solvent mixtures as a result of the increasing polarity of the medium. A plot of the logarithm of K_d versus $1/\varepsilon$ gives a straight line (figure 2).

From these conductances we may conclude that the overall dissociation behavior of polystyryllithium in mixtures of THF and TMEDA can be explained in terms of the macroscopic dielectric constant. The same conclusion could be made in the previously studied THF-benzene [6] and THF-dioxane mixtures [7]. But in the latter it was shown that in contradistinction to the ionic dissociation process, the reactivity of the PStLi ion pairs could not be accounted for in these simple terms.

The study of the kinetics of polystyryllithium in mixtures of THF and TMEDA shows that for all the measured reactions there is a first-order disappearance of styrene. The results are given in table II.

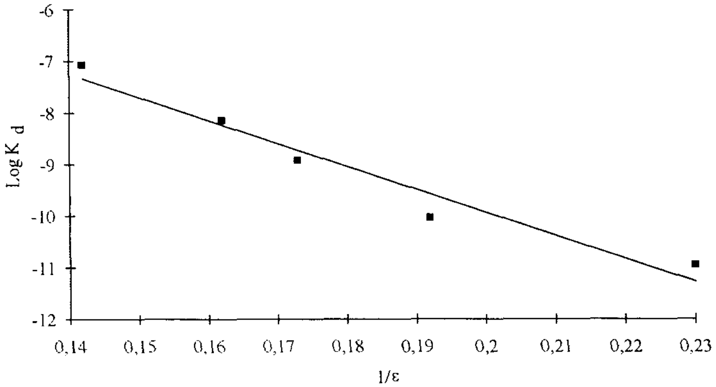

Figure 2 : Log K_d versus 1/ε for THF-TMEDA mixtures at 20°C.

For the first three mixtures (100, 85 and 70 Vol % TMEDA) the rate constants seem to be independent of the concentration of the living ends. This proves that in these mixtures only the PStLi ion pairs are responsible for the propagation reaction. In these solvent mixtures the concentrations of free ions are too small to have any influence on the results. Consequently, the propagation rate constant of the ion pair $k_{\pm}$ is given directly by the experimental k_p. In the solvent mixtures with a higher amounts of THF, where there is a noticeable dissociation of the polystyryllithium ion pairs into free ions, we establish a totally different behavior. In these mixtures the polymerization reaction takes place not only via ion pairs but also via the much more reactive free ions, each with there own rate constant. Consequently the over-all propagation rate constant k_p is no longer independent of the concentration of the living ends. In these cases the rate constant k_p is complex and contains the rate constant of the ion pairs $k_{\pm}$ and the rate constant of the free ions k_- according to the equation:

$$k_p = k_{\pm} + (k_- - k_{\pm})\left(\frac{K_d}{[LE]}\right)^{1/2}$$

The dependence of the over-all propagation rate constant, k_p, on the concentration of the living ends is shown in figure 3 for the solvent mixture containing 50 vol.% of TMEDA.

Table II : results of the kinetic study of PStLi in THF-TMEDA mixtures at 20°C.

Vol % TMEDA	[PStLi] mol l^{-1}	dielec. Constant (ε)	k_p L mol^{-1} s^{-1}
100.0	$2.56\ 10^{-3}$	2.83	3.64
100.0	$2.26\ 10^{-3}$	2.83	3.24
85.0	$2.21\ 10^{-3}$	3.46	7.22
85.0	$3.72\ 10^{-4}$	3.46	6.97
70.0	$1.13\ 10^{-3}$	4.16	20.15
70.0	$5.45\ 10^{-4}$	4.16	18.62
70.0	$6.0\ 10^{-5}$	4.16	18.34
50.0	$8.54\ 10^{-4}$	5.09	57.66
50.0	$7.23\ 10^{-4}$	5.09	61.85
50.0	$5.01\ 10^{-4}$	5.09	66.22
50.0	$4.65\ 10^{-4}$	5.09	69.07
50.0	$1.76\ 10^{-4}$	5.09	82.27
50.0	$5.0\ 10^{-5}$	5.09	130.82
25.0	$1.95\ 10^{-3}$	6.26	127.62
25.0	$7.8\ 10^{-4}$	6.26	126.2
25.0	$6.45\ 10^{-4}$	6.26	123.84
0.0	---	7.51	176.0

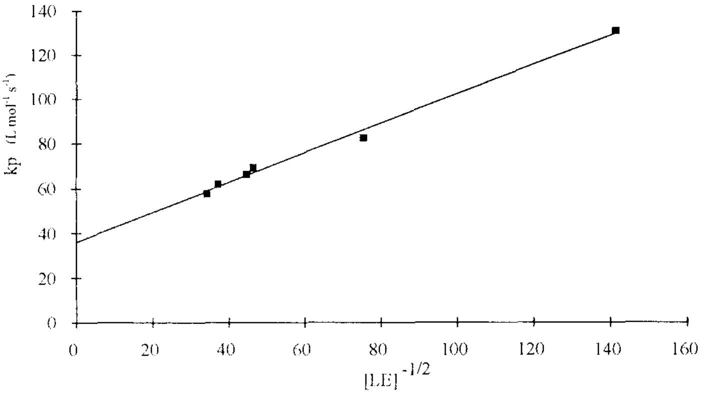

Figure 3 : Dependence of the propagation rate constant on PStLi concentration in THF-TMEDA mixture (50 vol.% TMEDA) at 20°C.

The experimental points conform very well to a linear relation. The intercept of the line is the ion-pair rate constant $k_{\pm}$ and has a value of 36.2 L mol^{-1} s^{-1}. The slope equals k_- $(K_d)^{1/2}$ and has a value of 0.73. Since at this composition of the solvent mixture $K_d \approx$ 7.7 10^{-11} M, $k_- \approx$ 83,000 L mol^{-1} s^{-1}. In pure THF at 20°C the propagation rate constant of the free polystyryl ions was determined to be k_- = 115,000 L mol^{-1} s^{-1}, whereas that of the polystyryllithium ion pairs $k_{\pm}$ seems to be 176 L mol^{-1} s^{-1} [23]. It seems, therefore, that in THF - TMEDA solvent mixtures containing 50 vol% or more of THF the reactivity of the free polystyryl ions is only slightly affected by the solvent composition. This is not surprising since the negative polystyryl ions are not expected to coordinate with either THF or TMEDA. The k_p values for the mixtures with 25 vol% of TMEDA were determined in the presence of an excess of $LiBPh_4$ (1.10^{-2} M) and correspond therefore to $k_{\pm}$. In contrast to the above mentioned THF - dioxane mixtures, plotting log $k_{\pm}$ as a function of 1/ε or of (ε-1)/(2ε+1) for the THF - TMEDA mixtures results in straight lines as shown in figure 4.

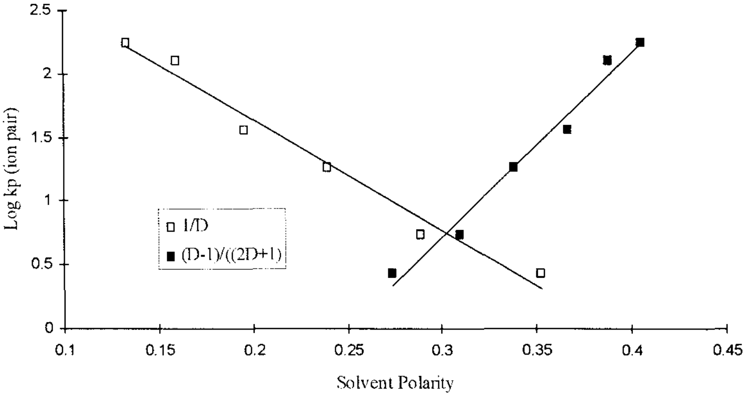

Figure 4 : Log $k_{p\pm}$ versus 1/ε and (ε-1)/(2ε+1) in TMEDA-THF mixtures.

IV. Discussion

In order to understand and to explain the different behavior of polystyryllithium in THF - TMEDA mixtures, as well as in the previously studied THF - benzene mixtures [6] and THF - dioxane mixtures [7], it is necessary to consider the different types of polystyrylllithium ion pairs which can occur in the various solutions.

* In pure benzene PStLi forms, besides aggregated ion pairs, only what we call normal contact ion pairs (PLi).

* In solvents however with specific electron donor sites, like THF, coordination of the Li^+-ion with solvent molecules may lead to solvent - separated ion pairs. For this to happen the THF molecules transfer some of their electronic charge to Li^+, thereby conferring some covalent character to the Li^+ - O bounds. Because of the low difference in energy between 2s and 2p orbitals the Li^+-ion will therefore be sp^3 hybridized. For solvent-separated ion pairs of PStLi we accept a coordination number of four for Li^- which agrees with a sp^3-hybridization. This formation of solvent-separated ion pairs by coordination of the Li^+-ion with the lone electron pairs of the solvent is to be distinguished from the non-specific electrostatic interactions between the positive charge of the cation and the dipoles of the solvent molecules, since this formation requires some transfer of electronic charge from the four solvent molecules towards Li^+ ion. These THF separated PStLi ion pairs will henceforth be denoted LiT_4P.

* Some anions can be taken up in the coordination sphere around the Li^+ ion thereby releasing some of the electron donating ligands. In this way ion pairs which are usually referred to as externally solvated contact ion pairs, and which will be denoted as $LiPT_n$, are formed. One of such anions with specific electron donor sites is the polystyryl anion PSt^- [24].

In pure THF, three different PStLi ion pairs can therefore in principle be considered:

- LiP: non-solvated contact ion pairs
- $LiPT_n$: externally solvated contact pairs
- LiT_4P: solvent-separated ion pairs

In pure THF and in mixtures containing sufficient amounts of THF or of the other complexing agents considered in this paper we can neglect the presence of the non solvated LiP ion pairs because of their extremely low concentration [25]. The solvent-separated ion pairs however cannot be neglected in spite of their very low concentration, because they have a very high reactivity and play therefore a very important role in the global reaction. If, for convenience, we consider the formation of the externally solvated contact pairs and the solvent-separated ion pairs starting from the non-solvated contact-ion pairs LiP, in spite of the fact that the latter are virtually absent in the mixtures we consider, the following constants b can be defined:

$$b^{o}_{PT_n} = \frac{[LiPT_n]}{[LiP]} = \frac{[\text{externally solvated contact-pairs}]}{[\text{non solvated contact ion pairs}]} = K_{PT_n}[T]^n = \frac{K_{PT_n}}{V_T^n} \quad (1)$$

$$b^{o}_{T_4P} = \frac{[LiT_4P]}{[LiP]} = \frac{[\text{solvent - separated ion pairs}]}{[\text{non solvated contact ion pairs}]} = K_{T_4P}[T]^4 = \frac{K_{T_4P}}{V_T^4} \quad (2)$$

Where [T] stands for the formal concentration of THF solvent molecules in the pure solvent (M), which is equal to the reciprocal of its molar volume V_T and where K_{PT_n} and K_{T_4P} represent the formation constants of the externally solvated contact pairs and the solvent-separated ion pairs respectively. The superscript ^{o} refers to the value of b in the pure solvent.

In comparing the reactivities of the different ion pairs we see that for the solvent-separated ion pairs LiT_4P the bonding between anion and cation is rather weak because of the great distance between the two ions. For the non-solvated contact ion pairs LiP this distance is much shorter and consequently the bonding between anion and cation is much stronger. Nevertheless their reactivity is usually assumed to be greater than that of the externally solvated contact ion pairs $LiPT_n$ [25] possibly due to the participation of the Li^+-cations in the propagation step [26] which becomes impossible if the Li^+-cation is specifically solvated. The following sequence for the rate constants of the ion pairs can thus be predicted:

$$k_{LiT_4P} >> k_{LiP} > k_{LiPT_n}$$

In pure THF where, for the reasons explained above, only two different types of ion pairs are of importance (externally solvated contact ion pairs and solvent-separated ion pairs), the following equation for the propagation rate constant of the ion pairs can be written:

$$k^{o}_{\pm} = \alpha_{PT_n} \cdot k_{LiPT_n} + \alpha_{T_4P} \cdot k_{LiT_4P} \quad (3)$$

where α_{PT_n} and α_{T_4P} represent the molar fraction of the externally solvated contact pairs and the solvent-separated ion pairs respectively, and k_{LiPT_n} and k_{LiT_4P} their propagation rate constants.

Since on the other hand we can write that in general

$$\alpha_i = \frac{b_i}{\sum b_i}$$

where b_i refers to the above defined b constants and i indicates the different kinds of ion pairs, the equation for the experimentally observed rate constants can in general also be written as

$$k_{\pm} = \frac{\sum k_i b_i}{\sum b_i}$$

which in the case of pure THF, where only the two above mentioned ion pairs are of importance, becomes

$$k_{\pm}^{o} = \frac{k_{LiPT_n} \cdot b_{PT_n}^{o} + k_{LiT_4P} \cdot b_{T_4P}^{o}}{b_{PT_n}^{o} + b_{T_4P}^{o}} \qquad (4)$$

According to the literature, an acceptable value at room temperature for k_{LiT_4P} is 70,000 L mol^{-1} s^{-1} [3], and for k_{LiPT_n} 0.5 L mol^{-1} s^{-1} [6, 25]. Filling in these values in equation (4) together with $k_{\pm}^{o}$ = 176 L mol^{-1} s^{-1} as previously found in our laboratory [23] we can write that :

$$k_{\pm}^{o} = 176 = \frac{0.5 b_{PT_n}^{o} + 70{,}000 b_{T_4P}^{o}}{b_{PT_n}^{o} + b_{T_4P}^{o}}$$

Dividing by $b_{PT_n}^{o}$ gives $$176 = \frac{0.5 + 70{,}000 \dfrac{b_{T_4P}^{o}}{b_{PT_n}^{o}}}{1 + \dfrac{b_{T_4P}^{o}}{b_{PT_n}^{o}}} \quad \text{or} \quad \frac{b_{T_4P}^{o}}{b_{PT_n}^{o}} = \frac{[LiT_4P]}{[LiPT_n]} = 2.5\ 10^{-3}$$

This value was previously estimated to be 3.5 10^{-3} by J. Smid [24]. The agreement is quite gratifying and corroborates the assumption that in pure THF apart from the free ions, which are not considered here, the species responsible for propagation are indeed externally solvated contact ion pairs and solvent-separated ion pairs and that

$$[LiPT_n] >> [LiT_4P] >> [LiP]$$

The rate constants of the ion-pairs of polystyryllithium, determined experimentally, for the solvent mixtures benzene-THF, dioxane-THF and TMEDA-THF are compared with each other in a plot of the rate constants of the ion pairs versus the square of the volume fraction of THF (Φ^2) (figure 5). This plot shows that for the benzene-THF and the TMEDA-THF mixtures almost the same linear relation is obtained. For the dioxane-THF mixtures however, the relation deviates completely from linearity.

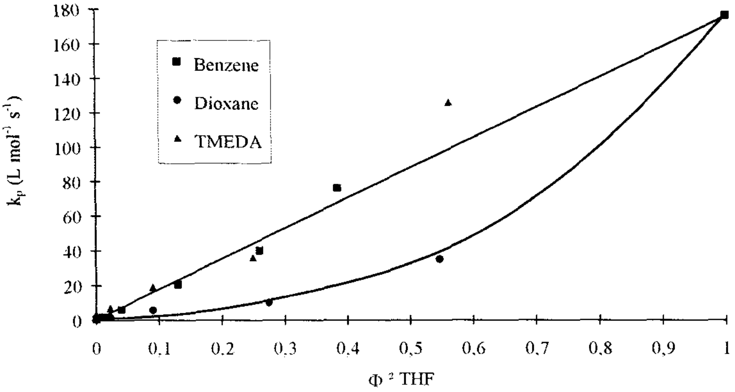

Figure 5 : Rate constants of PStLi ion pairs versus the square of the volume fraction of THF Φ^2.

In the benzene-THF mixtures, the smallest mole fraction of THF used by Bywater and Worsfold [6] is 0.05. From a previous study by the same authors [25] J. Smid deduced that under these conditions only externally solvated contact ion pairs, $LiPT_n$, and possibly solvent-separated ion pairs, LiT_4P, are present [24]. In general, the equation of the rate constant of the PStLi ion pairs in benzene-THF mixtures can again be written as :

$$k_{\pm} = \alpha_{PT_n} . k_{LiPT_n} + \alpha_{T_4P} . k_{LiT_4P} \tag{5}$$

and since $\alpha_{PT_n} = \dfrac{[LiPT_n]}{[LiPT_n]+[LiT_4P]}$ and $\alpha_{T_4P} = \dfrac{[LiT_4P]}{[LiPT_4]+[LiT_4P]}$

$k_{\pm}$ can according to the definition (1) and (2) also be written to be equal to

$$k_{\pm} = \frac{k_{LiPT_n} . K_{PT_n} . [T]^n + k_{LiT_4P} . K_{T_4P} . [T]^4}{K_{PT_n} . [T]^n + K_{T_4P} . [T]^4} \tag{6}$$

or denoting , as above, the volume fraction of THF by Φ_T and the molar volume of THF by V_T

$$k_{\pm} = \frac{k_{LiPT_n}.K_{PT_n}\frac{\Phi_T^n}{V_T^n} + k_{LiT_4P}.K_{T_4P}\frac{\Phi_T^4}{V_T^4}}{K_{PT_n}\frac{\Phi_T^n}{V_T^n} + K_{T_4P}\frac{\Phi_T^4}{V_T^4}} \qquad (7)$$

and since $\frac{K_{PT_n}}{V_T^n} = b^{\circ}_{PT_n}$ and $\frac{K_{T_4P}}{V_T^4} = b^{\circ}_{T_4P}$ according to the same definitions the equation for $k_{\pm}$ becomes :

$$k_{\pm} = \frac{k_{LiPT_n}.b^{\circ}_{PT_n}.\Phi_T^n + k_{LiT_4P}.b^{\circ}_{T_4P}.\Phi_T^4}{b^{\circ}_{PT_n}.\Phi_T^n + b^{\circ}_{T_4P}.\Phi_T^4} \qquad (8)$$

with n = 2 or 3, provided that the change in dielectric constant has no influence on the formation constants of externally solvated contact ion pairs and of solvent-separated ion pairs, so that

$$k_{\pm} = \frac{k_{LiPT_n}.b^{o}_{PT_n}.\Phi_T^n + k_{LiT_4P}.b^{o}_{T_4P}.\Phi_T^4}{b^{o}_{PT_n}.\Phi_T^n + b^{o}_{T_4P}.\Phi_T^4} \qquad (9)$$

Since the externally solvated contact ion pairs are the least reactive ones of all the ion pairs, the first term in the numerator of equation (9) can be neglected. In the denominator, the second term can be neglected because the value of $b^{o}_{T_4P}$ is negligibly small compared to the others and multiplying it with Φ_T^4 makes it even smaller. Equation (9) can thus be simplified to:

$$k_{\pm} = \frac{k_{LiT_4P}.b^{o}_{T_4P}.\Phi_T^4}{b^{o}_{PT_n}.\Phi_T^n} \qquad (10)$$

From the value of the experimental rate constant of PStLi ion pairs in pure THF (176 L mol^{-1} s^{-1}, or which is the same putting k_{LiT_4P} equal to 70,000 and $\frac{b^{\circ}_{T_4P}}{b^{\circ}_{PT_n}}$ equal to 2.5 10^{-3} equation (5) can be transformed to

$$k_{\pm} = 176.\frac{\Phi_T^4}{\Phi_T^n} \qquad (11)$$

Figure 6 shows a plot of $k_{\pm}$ versus Φ_T (equation 11) calculated respectively for n=2 and n=3. If we compare this plot with the experimental values, we see that they match pretty well with the equation (11) for n = 2.

This shows that the externally solvated contact ion pair is solvated with two THF molecules. A similar explanation in terms of not very reactive dietherates in equilibrium with very reactive solvent-separated ion pairs instead of in terms of the overall dielectric constant of the different mixtures was also suggested previously by J. Smid [24].

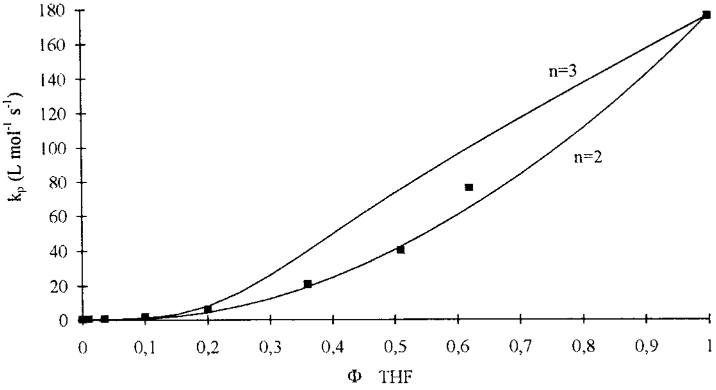

Figure 6 : $k_\pm$ versus Φ_T for PStLi in mixtures of benzene and THF.

In TMEDA-THF and dioxane-THF mixtures the situation is much more complex because here the formation of mixed ion pairs, whereby one or more THF molecules are replaced by one or more molecules of the other solvent, must be considered.

In TMEDA-THF mixtures the change of $k_\pm$ with Φ_T^2 was practically the same as for the benzene-THF mixtures (figure 5) where are explanation by classic dielectric theory was shown to be possible [6]. At first sight this could be explained by assuming that there are no specific interactions between Li^+ and TMEDA and that the results can be explained on basis of the classic dielectric theory as was originally also done for the benzene-THF mixtures. However, this is very unlikely because it has been shown that TMEDA forms strong complexes with Li^+ and that in fact TMEDA is an even stronger electron donor than THF [19-21]. An alternative explanation for this phenomenon is that the replacement of THF molecules by TMEDA molecules has no effect on the ratios of the b parameters in the rate constant equation. In other words, TMEDA is able to penetrate in the same way into the externally solvated contact ion pairs and into the solvent-separated ion pairs and replace two THF molecules by one TMEDA molecule in either kind of ion pairs. In the investigated TMEDA-THF mixtures the following PStLi ion pairs can then occur:

LiPA: contact ion pairs externally solvated with one TMEDA molecule

$LiPT_2$: contact ion pairs externally solvated with two THF molecules

$LiAT_2P$: mixed solvent-separated ion pairs with one TMEDA and two THF molecules

LiT_4P: solvent-separated ion pairs with four THF molecules

In general, for the TMEDA-THF mixtures, the following equation for the ion-pair rate constant can then be written:

$$k_{\pm} = \alpha_{PA} \cdot k_{LiPA} + \alpha_{PT_2} \cdot k_{LiPT_2} + \alpha_{AT_2P} \cdot k_{LiAT_2P} + \alpha_{T_4P} k_{LiT_4P} \qquad (12)$$

On the basis of similar definitions as previously given for the benzene-THF mixtures one can also write this equation in the following form :

$$k_{\pm} = \frac{k_{LiPA} \cdot K_{PA}[A] + k_{LiPT_2} \cdot K_{PT_2}[T]^2 + k_{LiAT_2P} \cdot K_{AT_2P}[A][T]^2 + k_{LiT_4P} \cdot K_{T_4P}[T]^4}{K_{PA}[A] + K_{PT_2}[T]^2 + K_{AT_2P}[A][T]^2 + K_{T_4P}[T]^4} \qquad (13)$$

and denoting, as above, the volume fraction of TMEDA and THF by Φ_A and Φ_T respectively and their molar volumes by V_A and V_T the equation for $k_{\pm}$ becomes :

$$k_{\pm} = \frac{k_{LiPA} \cdot K_{PA} \frac{\Phi_A}{V_A} + k_{LiPT_2} \cdot K_{PT_2} \frac{\Phi_T^2}{V_T^2} + k_{LiAT_2P} \cdot K_{AT_2P} \frac{\Phi_A \Phi_T^2}{V_A V_T^2} + k_{LiT_4P} \cdot K_{T_4P} \frac{\Phi_T^4}{V_T^4}}{K_{PA} \frac{\Phi_A}{V_A} + K_{PT_2} \frac{\Phi_T^2}{V_T^2} + K_{AT_2P} \frac{\Phi_A \Phi_T^2}{V_A V_T^2} + K_{T_4P} \frac{\Phi_T^4}{V_T^4}} \qquad (14)$$

and replacing respectively $\frac{K_{PA}}{V_A}$ by b°_{PA}, $\frac{K_{PT_2}}{V_T^2}$ by $b^{\circ}_{PT_2}$, $\frac{K_{AT_2P}}{V_A V_T^2}$ by b_{AT_2P} and $\frac{K_{T_4P}}{V_T^4}$ by $b^{\circ}_{T_4P}$, one obtains finally

$$k_{\pm} = \frac{k_{LiPA} \cdot b^{\circ}_{PA} \cdot \Phi_A + k_{LiPT_2} \cdot b^{\circ}_{PT_2} \cdot \Phi_T^2 + k_{LiAT_2P} \cdot b_{AT_2P} \cdot \Phi_A \cdot \Phi_T^2 + k_{LiT_4P} \cdot b^{\circ}_{T_4P} \cdot \Phi_T^4}{b^{\circ}_{PA} \cdot \Phi_A + b^{\circ}_{PT_2} \cdot \Phi_T^2 + b_{AT_2P} \cdot \Phi_A \cdot \Phi_T^2 + b^{\circ}_{T_4P} \cdot \Phi_T^4} \qquad (15)$$

assuming again that the change in dielectric constant has no influence on the formation constants of the different kinds of ion pairs.

Since in the numerator we can neglect all externally solvated ion pairs on account of their low reactivity and that in denominator the two last terms pertaining to the solvent-separated ion pairs can be neglected because their b values, which we suppose to be of similar magnitude, are small compared to the other b parameters, the above equation reduces to :

$$k_{\pm} = \frac{k_{LiAT_2P} \cdot b_{AT_2P} \cdot \Phi_A \cdot \Phi_T^2 + k_{LiT_4P} \cdot b^o_{T_4P} \cdot \Phi_T^4}{b^o_{PA} \cdot \Phi_A + b^o_{PT_2} \cdot \Phi_T^2} \tag{16}$$

Supposing further that $k_{LiT_4P} \approx k_{LiAT_2P}$ and $b^o_{PT_2} \cong b^o_{PA}$, equation (16) can be written as:

$$k_{\pm} = \frac{k_{LiT_4P} \cdot b^o_{T_4P}\left(\Phi_A + \Phi_T^2\right)\Phi_T^2}{b^o_{PT_2}\left(\Phi_A + \Phi_T^2\right)} = \frac{176\left(\Phi_A + \Phi_T^2\right)\Phi_T^2}{\left(\Phi_A + \Phi_T^2\right)} \tag{17}$$

Figure 7 shows a plot of equation (17) compared with the experimental results determined in TMEDA-THF mixtures. Also in these mixtures theory and experiment match very well.

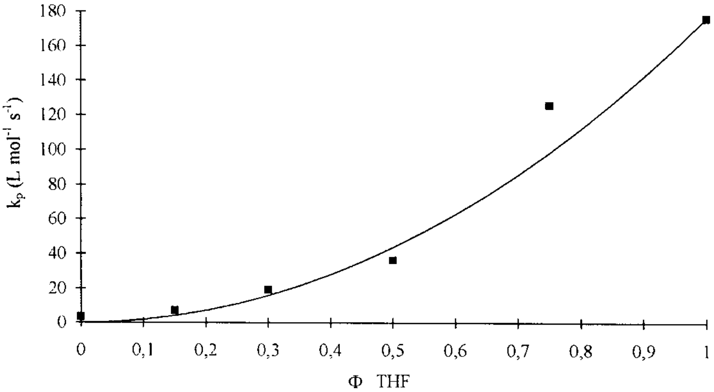

Figure7 : $k_{\pm}$ versus Φ_T for PStLi in mixtures of TMEDA and THF.

Finally, in dioxane-THF mixtures the formation of mixed ion pairs must also be considered. As shown before in figure 5, here the situation is even more complex than in the other mixtures because in figure 5 the change of $k_{\pm}$ with Φ^2 for dioxane -THF mixtures is completely different from the other ones.

A possible explanation for this behavior is that dioxane can replace THF molecules in the externally solvated contact ion pairs, leaving the b parameter constant, but that, on the other hand, dioxane, in contrast to TMEDA, is not able to do so in the solvent-separated ion pairs without destroying the latter. In other words, in dioxane-THF mixtures the following ion pairs can be present:

$LiPD_2$: contact ion pairs externally solvated with two dioxane molecules

$LiPT_2$: contact ion pairs externally solvated with two THF molecules

LiPTD: mixed contact ion pairs externally solvated with one dioxane and one THF molecule

LiT_4P: solvent-separated ion pairs with THF

In general, the equation for the rate constant of PStLi ion pairs in dioxane-THF mixtures can then, in analogy with equation 8 and equation 15, be written as:

$$k_{\pm} = \frac{k_{LiPT_2} \cdot b^{o}_{PT_2} \cdot \Phi_T^2 + 2k_{LiPTD} \cdot b_{PTD} \cdot \Phi_T \cdot \Phi_D + k_{LiPD_2} \cdot b^{o}_{PD_2} \cdot \Phi_D^2 + k_{LiT_4P} \cdot b^{o}_{T_4P} \cdot \Phi_T^4}{b^{o}_{PT_2} \cdot \Phi_T^2 + 2b_{PTD} \cdot \Phi_T \cdot \Phi_D + b^{o}_{PD_2} \cdot \Phi_D^2 + b^{o}_{T_4P} \cdot \Phi_T^4} \quad (18)$$

The statistical factor 2 in the second term of the numerator and the denominator stems from the two possibilities of replacing one THF molecule by one dioxane molecule. Just like for the two other mixtures equation (18) can be rewritten as:

$$k_{\pm} = \frac{k_{LiT_4P} \cdot b^{o}_{T_4P} \cdot \Phi_T^4}{b^{o}_{PT_2} \cdot \Phi_T^2 + 2b_{PTD} \cdot \Phi_D \cdot \Phi_T + b^{o}_{PD_2} \cdot \Phi_D^2} \quad (19)$$

If $b^{o}_{PT_2} \approx b_{PTD} \approx b^{o}_{PD_2}$ then:

$$k_{\pm} = \frac{k_{LiT_4P} \cdot b^{o}_{T_4P} \cdot \Phi_T^4}{b^{o}_{PT_2}\left(\Phi_T^2 + 2\Phi_T\Phi_D + \Phi_D^2\right)} = \frac{k_{LiT_4P} \cdot b^{o}_{T_4P} \cdot \Phi_T^4}{b^{o}_{PT_2}\left(\Phi_T + \Phi_D\right)^2} \quad (20)$$

and since $\Phi_T + \Phi_D = 1$ one obtains finally

$$k_{\pm} = \frac{k_{LiT_4P} \cdot b^{o}_{T_4P} \cdot \Phi_T^4}{b^{o}_{PT_2}} = 176.\Phi_T^4$$

A plot of $k_{\pm}$ versus Φ_T for this equation, compared with the experimental results, gives also in this mixture a very good agreement (figure 8).

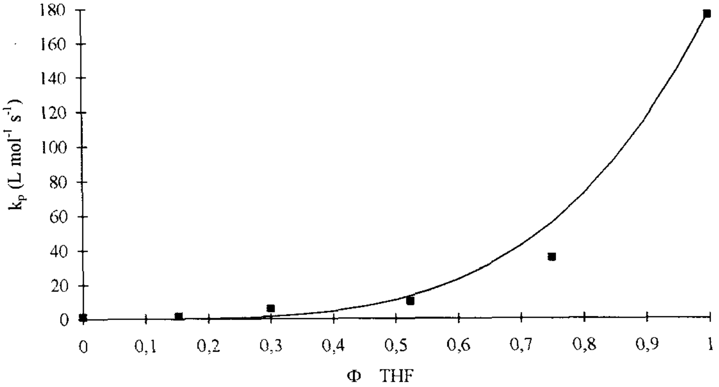

Figure 8 : $k_{\pm}$ versus Φ_T for PStLi in mixtures of dioxane and THF.

Unlike one might expect at first sight, dioxane behaves quite differently from TMEDA. Indeed recent MNDO calculations by A. Yakimanski have clearly indicated that, in contrast to TMEDA, dioxane cannot act as a bidentate ligand for the Li^+-cation [27]. The main reason for this is not a high chair-to-boat transformation energy but the fact that in a boat-like conformation the two oxygen atoms of dioxane cannot bind effectively with the Li^+-cation simultaneously, because the direction of their electron pairs is unsuitable for this. Therefore all dioxane molecules are in chair-like conformation and act as monodentate ligands. Dioxane is in that respect quite different from dimethoxyethane, which is capable of turning two lone electron-pairs towards the center of the Li^+-cation as illustrated in figure 9.

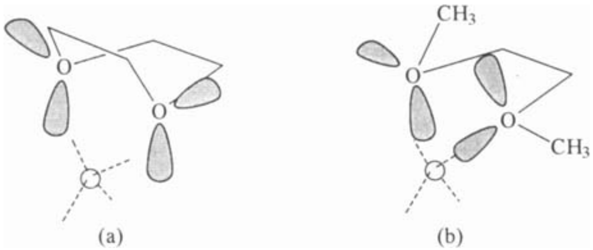

Figure 9 : Orientation of the free electron pairs of two oxygen atoms with respect to a central Li^+-cation in (a) dioxane and in (b) dimethoxyethane.

It should also be stressed that when TMEDA replaces two THF molecules in the solvent-separated ion pair, it is most likely the two outer THF molecules that are replaced as in the externally solvated contact ion pair. Indeed TMEDA is known not to form solvent-separated ion pairs to any significant extent [28] probably for steric reasons [28, 29]. This lends additional credibility to the above made assumption that TMEDA replaces equally well two THF molecules in the externally solvated contact ion pair and in the solvent-separated ion pair in TMEDA-THF mixtures.

V. Conclusion

From this study we can conclude that the proposed mechanisms, based on the existence in the different solvent mixtures of a majority of not very reactive externally solvated contact ion pairs and a small amount of very reactive solvent-separated ion pairs, in which the Li^+-cation is tetrahedrally coordinated by donor ligand molecules, allows us to account for the observed behavior in all cases rather than any considerations based on classical dielectric theory. We feel therefore that in all cases the strong specific solvation of the Li^+ ion, leading to well defined entities, offers a more attractive explanation than the effect of the macroscopic dielectric constant. The solvent-separated ion pairs are the ones which are responsible for the observed polymerization rate, in spite of their very low concentration compared to that of the externally solvated contact ion pairs which form the large majority of all the ion pairs present in the solutions. Finally we can conclude that a comparison between dioxane and TMEDA, on which this study was initially based does not hold. Apparently the bidentate TMEDA can replace two THF molecules equally well in the externally solvated contact ion pairs as in the solvent-separated ion pairs, and dioxane is not able to penetrate into the solvation shell of the solvent-separated ion pairs without destroying them. Moreover unlike TMEDA, which can act as a bidentate ligand for Li^+, dioxane, even in its boat conformation, cannot do this, because the free electron pairs on its oxygen atoms are not properly oriented and therefore it will remain in its chair-like conformation and act as a monodentate ligand.

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