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Effect of lithium butoxide additives on the anionic propagation of polystyryllithium in ethereal solvents

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Abstract

The addition of tertiary butoxide lithium (*t*-BuOLi) was found to slow down the anionic propagation of polystyryllithium (PStLi) in tetrahydropyran (THP), whereas, the addition of normal butoxide lithium (*n*-BuOLi) increases the rate over the investigated ranges of PStLi concentrations. Both lithium butoxides, which are tetrameric in ethereal solvents, also increase the conductance of PStLi in THP solution much more than expected on the basis of the separate conductances of PStLi and the lithium alkoxides and the increase is more important in the case of the addition of *n*-BuOLi than in that of *t*-BuOLi.

These phenomena are fully accounted for by a similar mechanism as that invoked to explain the influence of the addition of lithium chloride (LiCl), which contrasts at first sight with the lithium alkoxides by displaying both a retarding and an accelerating effect at the lower and the higher concentrations respectively of the investigated PStLi concentration domain.

This common cause of the observed phenomena consists of the dissociation of the dimers of LiCl or the tetramers of the lithium alkoxides into the free Li^+-ion and the multiple anions ($ClLiCl^-$ in the case of LiCl and $(BuOLi)_3BuO^-$ in the case of the lithium alkoxides) but also of the often overlooked Li^+-ion scavenging reaction by the LiCl dimers or the lithium alkoxide tetramers producing multiple cations. The first reaction providing Li^+-ions represses the ionic dissociation of PStLi by a common ion effect reducing thereby the amount of free PSt^--anions which are the main contributors to the rate of propagation and resulting therefore, in retardation. The second one scavenging Li^+-ions reduces the concentrations of free Li^+-ions and increases therefore, the concentration of reactive free polystyryl anions and as a consequence accelerates the propagation reaction.

The concentration of PStLi at which a crossover occurs from retardation to acceleration lies for the addition of LiCl in the investigated range of PStLi concentrations. For the addition of *t*-BuOLi calculations show that this crossover concentrations lies above the highest investigated PStLi concentration, whereas, for the addition of *n*-BuOLi it lies below the lowest investigated PStLi concentration giving the impression that *t*-BuOLi only retards the propagation and that *n*-BuOLi only accelerates but in actual fact the same mechanism is operating in all three cases.

Keywords: Influence of lithium alkoxide additives; Anionic polymerization; Propagation of polystryryllithium

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1. Introduction

In a previous paper [1] we showed that the addition of lithium chloride (LiCl) to a solution of polystyryllthium (PStLi) in tetrahydropyran (THP) reduces the rate of propagation of PStLi at low concentration of the latter but accelerates it at higher concentrations of PStLi. On top of that the addition of LiCl, which was shown to be dimeric in ethereal solution, increased the conductance of PStLi in THP over and above the sum of the separate conductances of PStLi and LiCl. These observations were fully accounted for by the dissociation of LiCl dimers into Li^+ and $ClLiCl^-$-triple ions but also by the ability of these dimers to scavenge Li^+-ions forming quintuple cations $Li(LiCl)_2^+$ according to the following set of equations

$$(LiCl)_2 \rightleftharpoons Li^+ + ClLiCl^- \tag{1}$$

$$Li^+ + (LiCl)_2 \rightleftharpoons (LiCl)_2Li^+ \tag{2}$$

This explanation was further substantiated by density functional theoretical calculations [2].

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This dissociation of LiCl dimers suppresses the dissociation of PStLi into Li^+ and PSt^--ions by a common ion effect and results therefore, in a retardation since the rate of propagation of PStLi in ethereal solvents is mainly determined by the very reactive free PSt^--ions while the scavenging reaction (2) reduces the amount of Li^+-ions thereby increasing the dissociation of PStLi and therefore, also the rate of propagation.

In contrast to this dual influence of LiCl, lithium alkoxides were reported either only to retard (*t*-BuOLi) or only to accelerate (*n*-BuOLi) the anionic propagation of PStLi in tetrahydrofuran (THF) [3,4]. Unlike LiCl, which is dimeric in ethereal solvents [5], lithium alkoxides where shown to be tetrameric [6].

Therefore, in the case of the lithium alkoxides the above equilibria (1) and (2) could be written as

$$(BuOLi)_4 \rightleftharpoons Li^+ + (BuOLi)_3BuO^- \tag{3}$$

$$Li^+ + (BuOLi)_4 \rightleftharpoons (BuOLi)_4Li^+ \tag{4}$$

The addition of both lithium alkoxides to THP solution of PStLi increases the conductance of the solution, more so in the case of *n*-BuOLi than in the case of *t*-BuOLi.

Previously published quantum-chemical DFT calculations [7] indicated that the dissociation of PStLi into Li^+-ions and very reactive PSt^- free ions is differently affected by the dissociation reaction and the Li^+-scavenging reaction of the alkoxides in the case of *n*-BuOLi and that of *t*-BuOLi, the dissociation reaction of *t*-BuOLi supplying free Li^+-cations and repressing the dissociation of PStLi and therefore, decreasing the rate of polymerization prevailing for *t*-BuOLi while the reaction of Li^+-ion scavenging increasing the dissociation of PStLi predominates for *n*-BuOLi.

In the present paper we wish to report some of the experimental conductances and the experimentally observed retardation of the propagtion of PStLi in THP in the case of the addition of *t*-BuOLi and acceleration in the case of *n*-BuOLi as well as the mathematical derivations as given in [1] for the above given Eqs. (3) and (4). We will show that these very similar derivations not only clearly indicate that a similar reasoning as that given for LiCl as an additive in [1] is capable of fully explaining the phenomena observed in the presence of lithium alkoxides taking due account of their different degrees of aggregation, but also permit the determination of all the equilibrium and rate constants both upon the addition of *n*-BuOLi and *t*-BuOLi and a direct comparison with the case of LiCl addition.

2. Experimental section

2.1. Materials

Styrene was dried twice under high vacuum on CaH_2 and was distilled over dry PStLi oligomer before use. *sec*-Butyllithium (*s*-BuLi) was purified by a short path distillation under high vacuum. Tetrahydropyran (THP) was refluxed over an alloy of Na and K. It was then stirred and degassed over a fresh Na–K alloy on a vacuum line and was subsequently distilled over dry PStLi oligomer. Normal butoxide lithium (*n*-BuOLi) and tertiary butoxide lithium (*t*-BuOLi) were synthesized by reacting highly purified *n*-butanol and *t*-butanol with *s*-BuLi in benzene at room temperature during 24 h under high vacuum. Afterwards benzene is distilled off and replaced by THP and divided over calibrated ampules under high vacuum. Their concentration is determined by AAS-spectroscopy.

PStLi was synthesized by the reaction of purified styrene with the required amount of *s*-BuLi in benzene as a solvent to produce a polymer with a molecular weight of about 4000. Its concentration was determined by UV-spectroscopy.

2.2. Measurements

Conductance measurements were carried out with a Wayne Kerr B642 universal bridge. Kinetic measurements of the propagation rates were made by monitoring the disappearance of styrene spectrophotometrically at 291.5 nm on a Cary 2200 at 20 °C. All measurements were carried out under high vacuum in all-glass apparatus prewashed with living polymer solutions.

3. Results and discussion

3.1. Conductance measurements

In the previous paper on the dual effect of LiCl on the propagation of PStLi [1] conductances of PStLi in THP were measured at 20 °C. They showed a linear dependence of the square of the specific conductance κ on the concentration of PStLi, indicative of a simple ionic dissociation of a weak electrolyte for which the following equation can be shown to hold

$$\kappa^2 = \Lambda_0^s K_d C$$

where Λ_0^s denotes the overall ionic conductance equal to the sum of the ionic conductances of the cation (λ_0^+) and of the anion (λ_0^-) and C is the overall concentration of the electrolyte, whereas, K_d is the equilibrium constant of dissociation. The values of λ_0^+ and λ_0^- for PStLi were taken from the literature and K_d for PStLi in THP at 20 °C was determined as 3.7×10^{-10} M.

In analogy with LiCl in ethereal solvents the plots of κ^2 vs. C both for *t*-BuOLi and *n*-BuOLi in THP are strongly curved, whereas, a plot of κ vs. C is linear as shown for *t*-BuOLi and for *n*-BuOLi in Fig. 1.

This is indicative of a weak electrolyte forming one kind of triple ion according to the equation

$$AB \overset{K_d}{\rightleftharpoons} A^+ + B^-$$

$$A^+ + AB \overset{K_t}{\rightleftharpoons} ABA^+$$

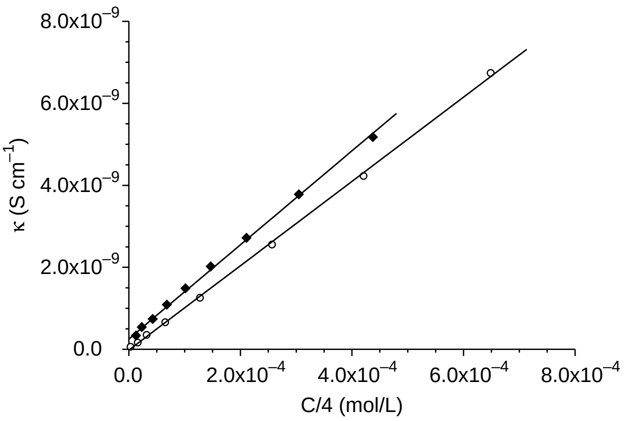

Fig. 1. Specific conductance κ (S cm^{-1}) as a function of the concentration of *t*-BuOLi and *n*-BuOLi in THP at 20 °C. The formal concentration is divided by 4 because *t*-BuOLi and *n*-BuOLi are tetrameric in THP. ◆: *t*-BuOLi; ○: *n*-BuOLi.

for which a conductance equation can be derived of the form

$$\kappa^2 = (\Lambda_0^{\mathrm{t}})^2 K_{\mathrm{d}} K_{\mathrm{t}} [\mathrm{AB}]^2 \left\{ \frac{1}{K_{\mathrm{t}}[\mathrm{AB}]} + 1 \right\}$$

which in the domain where triple ions dominate can be simplified to

$$\kappa = \Lambda_0^{\mathrm{t}} (K_{\mathrm{d}} K_{\mathrm{t}})^{1/2} [\mathrm{AB}]$$

where Λ_0^{t} stands for the sum of the ionic conductance $\lambda_0^{\mathrm{t}+}$ of the triple ion and λ_0^- of the anion.

However, in analogy with the case of LiCl in ethereal solvents [1] where AB in the aforementioned equilibria was assumed to represent not LiCl but its dimer $(\mathrm{LiCl})_2$, we took AB to represent in this case not *t*-BuOLi or *n*-BuOLi but their tetrameric aggregates $(t\text{-BuOLi})_4$ and $(n\text{-BuOLi})_4$ as represented in the following equations

$$(\mathrm{BuOLi})_4 \overset{K_{\mathrm{d}}}{\rightleftharpoons} \mathrm{Li}^+ + (\mathrm{BuOLi})_3\mathrm{BuO}^-$$

$$\mathrm{Li}^+ + (\mathrm{BuOLi})_4 \overset{K_{\mathrm{t}}}{\rightleftharpoons} (\mathrm{BuOLi})_4\mathrm{Li}^+$$

This is also in agreement with the above mentioned density functional theory study concerning the aggregation and dissociation behavior of lithium butoxide in ethereal solvents by Yakimansky et al. [7] indicating that $\mathrm{Li}^+(\mathrm{THP})_4$ cations are supplied by the dissociation of $(\mathrm{BuOLi})_4$ tetramers and that scavenging reaction of $\mathrm{Li}^+(\mathrm{THF})_4$ by $(\mathrm{BuOLi})_4$ tetramers occurs to form a solvated multiple cation.

The addition of both lithium alkoxides to THP solutions of PStLi increases the conductance of these solutions to a much greater extent than expected on the basis of the separate conductances of PStLi and the lithium alkoxides, which are themselves even less dissociated than PStLi. This is shown in Fig. 2 for *t*-BuOLi and Fig. 3 for *n*-BuOLi.

In both these figures where κ^2 is plotted vs. the concentration C for pure lithium alkoxides (coinciding with the abscissa at the chosen scale), for pure PStLi and for different mixtures of PStLi and the alkoxides. It is noteworthy, that in both Figs. 2 and 3 there is an upward curvature of κ^2 as a function of C for the mixtures. Note also that the increase in conductivity is more pronounced for the mixtures of PStLi and *n*-BuOLi than for PStLi and *t*-BuOLi.

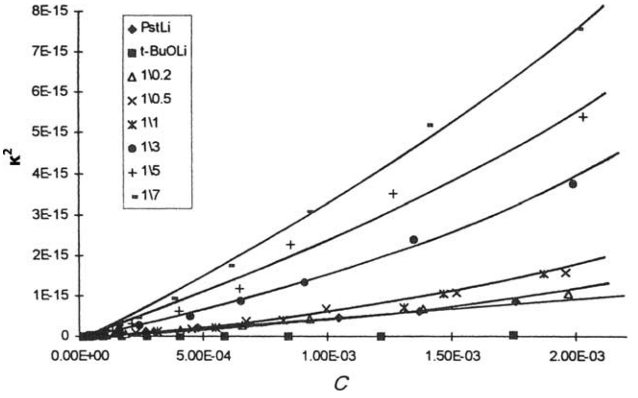

Fig. 2. Square of the specific conductance (S^2 cm^{-2}) as a function of the concentration of PStLi at different [*t*-BuOLi]/[PStLi] ratios or as a function of the concentration of PStLi or *t*-BuOLi in THP at 20 °C.

3.2. Kinetic measurements

Kinetic measurements of the propagation rate constants for different concentrations of PStLi in the absence and presence of various amounts of *t*-BuOLi and *n*-BuOLi were carried out in THP at 20 °C. Since both ion pairs and free ions are known to contribute to the reaction, the pseudo first order rate constant of propagation can be written as

$$k_1 = -\frac{1}{[\mathrm{Sty}]}\frac{\mathrm{d}[\mathrm{Sty}]}{\mathrm{d}t} = k_{\mathrm{PSt}^-}[\mathrm{PSt}^-] + k_{\mathrm{PStLi}}[\mathrm{PStLi}]$$

The concentration of free carbanions is much smaller than that of the undissociated ion pairs. Since, however, the rate constant of free ions k_{PSt^-} is by several orders of magnitude greater than that of the ion pairs κ_{PStLi}, the contribution of the ion pairs to the first order rate constant is to a first approximation neglected next to that of the free ions.

The rates expressed in terms of k_1 for different concentrations of PStLi and varying ratios of [BuOLi]/[PStLi] are

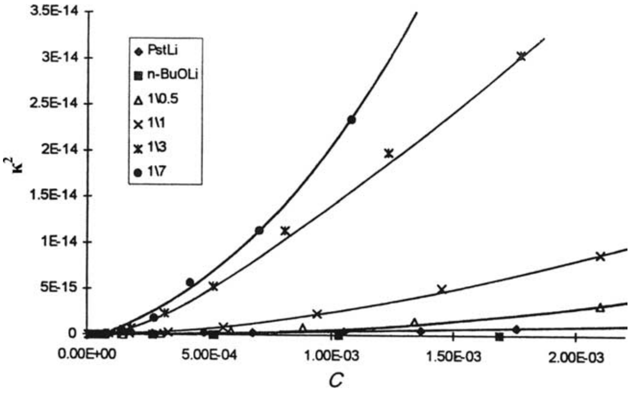

Fig. 3. Square of the specific conductance (S^2 cm^{-2}) as a function of the concentration of PStLi at different [*n*-BuOLi]/[PStLi] ratios or as a function of the concentration of PStLi or *n*-BuOLi in THP at 20 °C.

Table 1
Kinetic measurements in the presence of *t*-BuOLi at different concentrations of PStLi and at different ratios $r=[t\text{-BuOLi}]/[\text{PStLi}]$ in THP at 20 °C

[PStLi] (M)	$r=[t\text{-BuOLi}]/[\text{PStLi}]$	k_1 (s^{-1})
3.66×10^{-5}	0	4.76×10^{-3}
4.89×10^{-5}	0.55	3.31×10^{-3}
4.31×10^{-5}	0.71	2.85×10^{-3}
3.75×10^{-5}	1.24	2.09×10^{-3}
4.02×10^{-5}	2.37	1.92×10^{-3}
3.00×10^{-5}	5.29	1.23×10^{-3}
3.92×10^{-5}	6.60	1.53×10^{-3}
9.82×10^{-4}	0	2.98×10^{-2}
9.90×10^{-4}	0.21	2.35×10^{-2}
9.58×10^{-4}	0.67	2.03×10^{-2}
1.07×10^{-3}	1.09	1.77×10^{-2}
9.37×10^{-4}	2.50	1.46×10^{-2}
8.57×10^{-4}	8.27	1.27×10^{-2}

given in Table 1 for the addition of *t*-BuOLi and in Table 2 for the addition of *n*-BuOLi.

In both tables two different concentration domains of PStLi (each of approximately the same concentration) were used and lithium butoxides were added in varying ratios $r=[\text{BuOLi}]/[\text{PStLi}]$.

In the table concerning the addition of *t*-BuOLi it is clearly seen that, in analogy to the addition of LiCl to PStLi in THP as described in [1], in the lower concentration domain ($\sim 4\times10^{-5}$ M), addition of *t*-BuOLi slows down the propagation as increasing ratios of [*t*-BuOLi]/[PStLi] are used. Unlike in the case of LiCl addition, however, no acceleration is observed in the higher concentration domain of PStLi ($\sim 10^{-3}$ M) but again a slowing down of the propagation reaction. This is in agreement with the effects of the addition of *t*-BuOLi to the anionic polymerization of styrene reported by Ogle et al. [3,4].

It should be pointed out that the retardation in the lower PStLi concentration domain is stronger than in the domain of about 10^{-3} M PStLi.

On the other hand kinetic measurements in which *n*-BuOLi in different ratios $r=[n\text{-BuOLi}]/[\text{PStLi}]$ is added to PStLi in two different concentration domains of PStLi (again each of approximately the same concentration) clearly show an acceleration in both PStLi concentration domains.

At first sight this retardation of the PStLi propagation by *t*-BuOLi over the complete investigated concentration domain of PStLi and the acceleration by *n*-BuOLi over the complete investigated PStLi concentration domain may seem rather surprising when compared to the dual effect of LiCl which was found to reduce the rate of propagation of PStLi in THP at low concentration of the latter, but to accelerate it at higher concentrations of PStLi.

Table 2
Kinetic measurements in the presence of *n*-BuOLi at different concentrations of PStLi and at different ratios $r=[n\text{-BuOLi}]/[\text{PStLi}]$ in THP at 20 °C

[PStLi] (M)	$r=[n\text{-BuOLi}]/[\text{PStLi}]$	k_1 (s^{-1})
8.37×10^{-4}	0	5.01×10^{-2}
8.61×10^{-4}	0.31	9.30×10^{-2}
7.76×10^{-4}	1.32	2.18×10^{-1}
5.28×10^{-5}	0	1.69×10^{-2}
5.70×10^{-5}	0.40	1.05×10^{-2}
4.83×10^{-5}	1.23	8.14×10^{-3}
5.32×10^{-5}	1.90	1.23×10^{-2}
3.85×10^{-5}	3.53	1.10×10^{-2}
4.85×10^{-5}	4.99	2.09×10^{-2}
3.81×10^{-5}	6.81	2.03×10^{-2}

This reduction of the rate was attributed to the dissociation of LiCL dimers producing free Li^+-ions, which repress by the common ion effect the ionic dissociation of PStLi into Li^+-ions and free PSt^- anions, which are the main contributors to the propagation reaction. The acceleration on the other hand is ascribed to the Li^+ scavenging action of LiCl dimers leading to multiple ions and reducing the Li^+ concentration and increasing thereby, the dissociation of PStLi and thus the formation of reactive PSt^--anions.

Nevertheless, the behavior observed when lithium butoxides (only reduction of the rate by addition of *t*-BuOLi and only enhancement by addition of *n*-BuOLi and increase in conductance upon addition of either, although higher in the case of *n*-BuOLi) are added to the THP solution of PStLi can be fully accounted for by the same mathematical treatment as given previously in the case of LiCl [1].

Taking into account the high degree of association of both *t*-BuOLi and *n*-BuOLi to tetramers in ethereal solution, as revealed by colligative measurements, the following set of equilibria is considered

$$\text{PStLi} \overset{K_1}{\rightleftharpoons} \text{Li}^+ + \text{PSt}^- \tag{5}$$

$$(\text{BuOLi})_4 \overset{K_2}{\rightleftharpoons} \text{Li}^+ + (\text{BuOLi})_3\text{BuO}^- \tag{6}$$

$$\text{Li}^+ + (\text{BuOLi})_4 \overset{K_3}{\rightleftharpoons} (\text{BuOLi})_4\text{Li}^+ \tag{7}$$

Without going through the detailed mathematics, which were dealt with extensively in the paper on addition of LiCl [1] and published there, let it suffice here to say that the concentrations of all species occurring in the above set of equilibria have been calculated for all the initial concentrations of PStLi and BuOLi, respectively, by expressing the concentrations of these species as a function of the Li^+-ion concentration for which the following approximate equation was derived

$$[\text{Li}^+] \approx \left(\frac{aK_1 + \frac{b}{4}K_2}{1 + \frac{b}{4}K_3}\right)^{1/2}$$

where a and b are the initial concentrations of PStLi and BuOLi (*t*- or *n*-) respectively and which is a similar equation to that derived in the case of LiCl [1] taking, however, into account that the lithium butoxides are aggregated to tetramers in THP, whereas, LiCl was associated to dimers.

For the specific conductances, we can write that:

$$\kappa = \lambda^0_{\text{PSt}^-}[\text{PSt}^-] + \lambda^0_{\text{Li}^+}[\text{Li}^+] + \lambda^0_{(\text{BuOLi})_3\text{BuO}^-}[(\text{BuOLi})_3\text{BuO}^-] + \lambda^0_{(\text{BuOLi})_4\text{Li}^+}[(\text{BuOLi})_4\text{Li}^+] \tag{8}$$

$\lambda^0_{\text{PSt}^-}$ and $\lambda^0_{\text{Li}^+}$ were taken from our paper on LiCl addition to PStLi solutions, which were themselves taken from

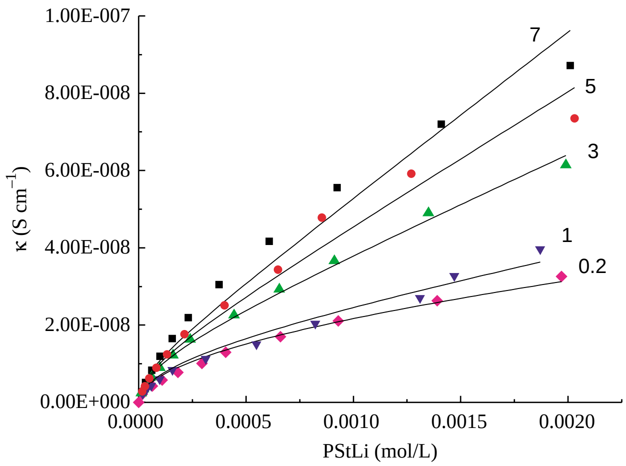

Fig. 4. Specific conductance κ (S cm^{-1}) as a function of the concentration of PStLi at different [*t*-BuOLi]/[PStLi] ratios ($r=0.2$, 1, 3, 5 and 7). The experimental points were fitted by the curves calculated with $K_1=3.7\times 10^{-10}$ M, $K_2=1.7\times 10^{-9}$ M and $K_3=1.8\times 10^3$ M^{-1}.

the literature as 7.7 and 12.6 S equiv^{-1} cm^2, respectively. For $\lambda^0_{(\mathrm{BuOLi})_3\mathrm{BuO}^-}$ and $\lambda^0_{(\mathrm{BuOLi})_4\mathrm{Li}^+}$ the values were estimated on the basis of the molecular weights of the charged species with due account taken of their most probable solvation state and as compared to charged species of known molecular weight and known λ^0. They were taken as 9.8 and 7.4 S equiv^{-1} cm^2, respectively.

The least squares method was then used to determine the equilibrium constants K_1, K_2 and K_3 to obtain the best fit of the experimental points.

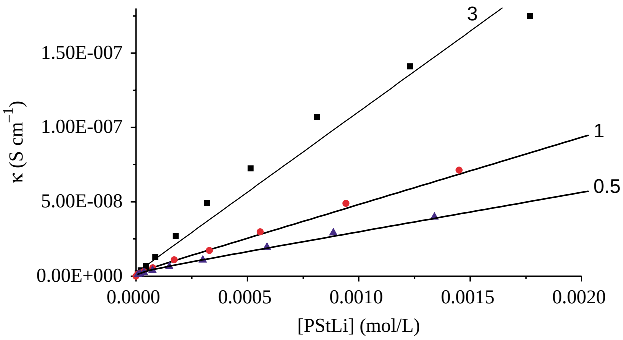

Fig. 5. Specific conductance κ (S cm^{-1}) as a function of the concentration of PStLi at different [*n*-BuOLi]/[PStLi] ratios ($r=0.5$, 1 and 3). The experimental points were fitted by the curves calculated with $K_1=3.7\times 10^{-10}$ M, $K_2=1.1\times 10^{-9}$ M and $K_3=5\times 10^4$ M^{-1}.

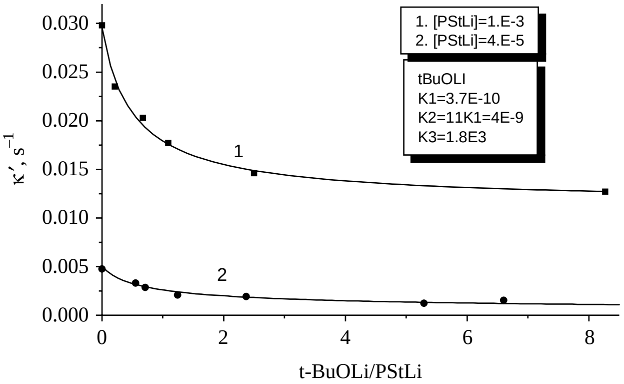

Fig. 6. Kinetic experiments in the presence of *t*-BuOLi at different concentrations of PStLi and at different ratios $r=[t\text{-BuOLi}]/[\text{PStLi}]$ in THP at 20 °C. The points are the experimental ones and they were fitted by the curves calculated with $K_1=3.7\times 10^{-10}$ M, $K_2=4\times 10^{-9}$ M and $K_3=1.8\times 10^3$ M^{-1}.

Such a fit for the specific conductance κ as a function of the concentration of PStLi and for different $r=[\text{BuOLi}]/[\text{PStLi}]$ values in THP is shown in Fig. 4 for the addition of *t*-BuOLi and in Fig. 5 for the addition of *n*-BuOLi to PStLi solutions. The points are the experimental ones and the curves are calculated with $K_1=3.7\times 10^{-10}$ M, $K_2=1.7\times 10^{-9}$–4×10^{-9} M (the value of $K_2=1.7\times 10^{-9}$ M is the one that gave the best fit for the conductance data in Fig. 5, whereas, the value $K_2=4\times 10^{-9}$ M is the one that gave the best fit for the kinetic data Fig. 6) and $K_3=1.8\times 10^3$ M^{-1} for *t*-BuOLi and with $K_1=3.7\times 10^{-10}$ M, $K_2=1.1\times 10^{-9}$ M and $K_3=5\times 10^4$ M^{-1} for *n*-BuOLi. It is seen that, whereas, the K_2 values (disaggregation) for *n*-BuOLi and *t*-BuOLi are comparable, the K_3 value (scavenging reaction) for *n*-BuOLi is almost 30 times greater than that for *t*-BuOLi. This is probably due to the steric hindrance in the tertiary isomer by the tertiary butoxy groups. It is noteworthy that this difference in the K_3 value is the main cause for the difference in behavior of the butoxides (only retardation with *t*-BuOLi and only acceleration with *n*-BuOLi) to be discussed further.

In view of the procedure used to determine the different constants and the possible errors in the estimation of the λ^0 values we think the agreement is quite satisfying.

For *n*-BuOLi an association degree of 6 was considered but the results of the fitting procedure were much less satisfying.

As for the kinetic experiments, the data of which are summarized in Table 1, the experimental points were fitted by the curves calculated with the constants deduced from the conductances and attributing the observed rates entirely to free anions, thus neglecting the contribution of the ion pairs, which was shown in the past to be an acceptable assumption in most anionic polymerizations. The pseudo first order rate constants for propagation are shown as a function of the [BuOLi]/[PStLi] ratio for *t*-BuOLi in Fig. 6 and for *n*-BuOLi in Fig. 7.

The points are the experimental ones and the curves those obtained by the above mentioned procedure.

Again the agreement between experimental points and the calculated curves, obtained with the aforementioned constants is quite gratifying and seen as support for the validity of the assumed mechanism and the procedure used to prove it. The above mentioned retardation by the addition of *t*-BuOLi over the investigated high and low concentration domain of PStLi and the acceleration on addition of *n*-BuOLi is clearly seen from these figures.

If we compare the case of the addition of *t*-BuOLi (only retardation) to the PStLi domain where addition of LiCl also slows down the propagation reaction, we must conclude that the dissociative behavior of $(t\text{-BuOLi})_4$ (6) produces enough Li$^+$-ions to repress the ionization of PStLi, thereby causing ion pairing of PSt$^-$ with Li$^+$-ions and thus reducing the number of

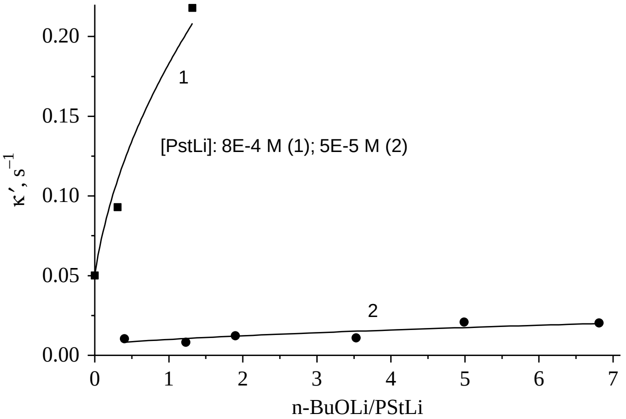

Fig. 7. Kinetic experiments in the presence of *n*-BuOLi at different concentrations of PStLi and at different ratios $r=[n\text{-BuOLi}]/[\text{PStLi}]$ in THP at 20 °C. The points are the experimental ones and they were fitted by the curves calculated with $K_1=3.7\times10^{-10}$ M, $K_2=4\times10^{-9}$ M and $K_3=1.8\times10^3$ M^{-1}.

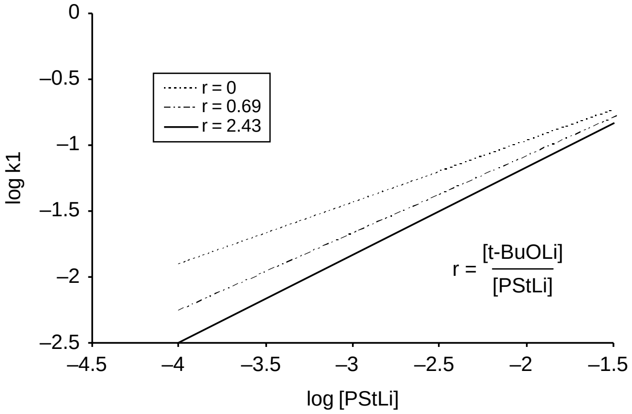

Fig. 8. Log k_1 as a function of log[PStLi] for the propagation of PStLi in THP at 20 °C in the absence and presence of *t*-BuOLi; $r=0$, 0.69 and 2.43.

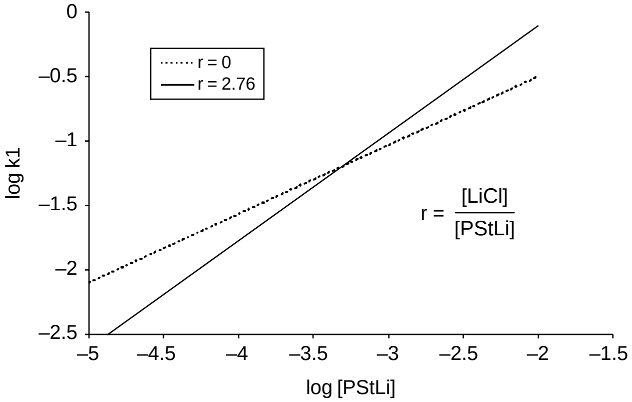

Fig. 9. Log k_1 as a function of log[PStLi] for the propagation of PStLi in THP at 20 °C in the absence and presence of LiCL [1]; $r=0$ and 2.76.

PSt$^-$-ions, which are the main contributors to the rate of propagation.

In contrast, however, with the case of LiCl, where a ‘crossover’ concentration of PStLi was found at which any amount of added LiCl does not affect the polymerization rate [1] and below which addition of LiCl only retards the rate and above which addition of LiCl only accelerates the propagation, no such point was observed in the investigated concentration domain of PStLi upon addition of *t*-BuOLi. This is easily understood since this ‘crossover’ concentration of PStLi, which as shown in the paper on the influence of LiCl is given by K_2/K_1K_3 and for LiCl lies around 2–4$\times10^{-4}$ M, for addition of *t*-BuOLi only occurs at $\sim6\times10^{-3}$ M and lies above and therefore, outside the investigated domain of PStLi as estimated from the above determined constants.

Similarly, if we compare the case of addition of *n*-BuOLi (acceleration) to the PStLi domain where addition of LiCl was shown to accelerate the propagation reaction, the reaction of scavenging Li$^+$-cations by $(n\text{-BuOLi})_4$ (7) prevails thereby reducing the number of Li$^+$-ions and therefore, shifting the dissociation of PStLi (5) to the right and thus increasing the amount of very reactive PSt$^-$-ions.

Again no ‘crossover’ concentration of PStLi at which the acceleration switches over to a retardation, as with LiCl, is observed since with *n*-BuOLi this crossover concentration of PStLi lies below the investigated concentration domain of PStLi viz. at $\sim6\times10^{-5}$ M PStLi as calculated from the above equation.

The three situations, that of addition of *t*-BuOLi, the previously reported one of LiCl and that of *n*-BuOLi are graphically represented in Figs. 8–10.

Thus it is seen that in fact the same mechanism is operative in the three systems viz. the anionic propagation of PStLi in the presence of LiCl, as described in a previous paper [1], and that in the presence of both *t*-BuOLi and *n*-BuOLi, described in this paper, and that the retardation by *t*-BuOLi and the enhancement of the rates by *n*-BuOLi as well as these two phenomena occurring in the presence of LiCl can be fully rationalized in terms of the repression or the enhancement of the dissociation of PStLi into free Li$^+$ and free PSt$^-$-anions, the latter being the main contributors to the propagation rate.

As mentioned before, the retardation by *t*-BuOLi and the acceleration by *n*-BuOLi described in this paper were also found by Ogle et al. [3,4] but they did not recognize the real reasons for their findings since they did not perform any conductance measurements and did therefore, not realize that it

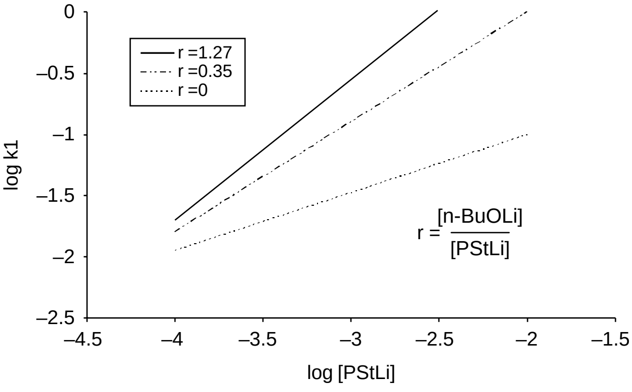

Fig. 10. Log k_1 as a function of log[PStLi] for the propagation of PStLi in THP at 20 °C in the absence and presence of *n*-BuOLi; $r=1.27$, $r=0.35$ and $r=0$.

are mainly the free PSt$^-$-anions that are responsible for the observed rates and not as they claim, mixed aggregates of ion pairs with different reactivities, whose contribution, even in the presence of these lithium alkoxide salts, is negligible.

4. Conclusions

The experiments reported in this paper clearly demonstrate that the retardation of the propagation of PStLi in THP over the investigated PStLi concentration domain by the addition of *t*-BuOLi as well as the acceleration observed over the investigated PStLi concentration domain upon addition of *n*-BuOLi can both be fully accounted for by a similar mechanism as that earlier invoked in a previous publication to explain the dual i.e. retarding and accelerating effect of the addition of LiCl at low respectively high PStLi concentration viz. not only the dissociation of the lithium alkoxide tetramers into Li$^+$-ions and $(BuOLi)_3BuO^-$ ions, but also theLi$^+$-ion scavenging capacity of these alkoxide tetramers (much like the dimers in the case of LiCl).

However, in the case of *t*-BuOLi the predominant effect of the dissociation reaction of *t*-BuOLi tetramers represses the ionization of PStLi by a common ion effect diminishing also the amount of free PSt$^-$-anions and therefore, also the propagation rate since the free ions are known to be the main contributors to this reaction. On the other hand, in the case of *n*-BuOLi the Li$^+$-ion scavenging reaction of the *n*-BuOLi tetramers to form multiple cations, prevails over that of *t*-BuOLi and reduces the concentration of Li$^+$-ions thereby, increasing the amount of free PSt$^-$-anions through the increasing dissociation of PStLi leading to more of the reactive free PSt$^-$-anions. The concentration of the crossover reaction from retardation to acceleration as observed for LiCl when the PStLi concentration increases, does also occur for both alkoxides but as clearly shown from the pertinent equilibrium constants at concentrations above those of the investigated concentrations of PStLi in the case of *t*-BuOLi and at concentrations below those investigated in the case of *n*-BuOLi.

It should be stressed that the Li$^+$-scavenging reaction of both LiCl dimers and lithium alkoxide tetramers is often overlooked but is essential to explain the observed phenomena.

Therefore, when salts are being added to polymerization systems, polymerizing anionically in ethereal solvents, the mechanism described in this paper including the latter possibility should be taken into account. With this in mind we looked at the anionic polymerization of polymethylmethacrylate lithium which is frequently being carried out in ethereal solvents in the presence of LiCl and lithium butoxides. However, the ionic dissociation of polymethylmethacrylate lithium is so low that the mechanism shown above probably does not apply.

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