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The influence of π-complexing additives on the dissociation of organolithium compounds in non-polar medium: a long time unexplored area in anionic polymerization

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Abstract

In 1965 0'Driscoll et al. showed that the addition of a π-complexing agent such as 1,2,4,5-tetramethylbenzene (durene) has a marked effect on the anionic propagation of polystyryllithium (PStLi) in benzene, comparable to but much weaker than the effect of tetrahydrofuran (THF) on this polymerization described by Worsfold and Bywater. Indeed much higher quantities of durene than of THF were necessary to bring about a similar effect i.e. an initial increase in the rate of propagation, passing then through a maximum to decrease afterwards with increasing amounts of durene or THF. In analogy with THF, dissociating the ionic aggregates through formation of a σ-complex with the Li^+-cation, this behavior was attributed to a similar dissociating effect of durene, forming a π-complex with the Li^+-cation. A similar behavior was found for PStLi in cyclohexane, requiring however, even higher quantities of durene than in benzene. In order to further substantiate this dissociative capacity of π-complexing agents in general and of durene in particular, a preliminary study of the kinetics of propagation of PStLi in cyclohexane in the presence of 0.27 M durene was carried out. We could show that in these circumstances the dissociation constant (K_d) of the dimers of PStLi, which is estimated to be around 10^{-7} M in pure cyclohexane, was equal to about 4×10^{-3} M when 0.27 M durene was added. This means that at a formal concentration of PStLi of 10^{-3} M, 75% of the dimeric aggregates are disrupted. Also other π-complexing agents are studied in this work, such as benzene, hexamethylbenzene (HMB), tertamethylethylene (TME) and tetraphenylethylene (TPhE).

Keywords: π-Complexing additives; Anionic polymerization; Organolithium compounds

1. Introduction

In non-polar solvents organolithium compounds tend to form unreactive aggregated species. These include initiating species as well as propagating organolithium polymer ends. Many of the alkyllithium aggregates are formed through association of two, four or six molecules, depending on their structure [1]. This has led to kinetics of initiation and propagation with a fractional order with respect to these alkyllithium compounds, related to their state of association. This observation is accounted for by the assumption that, usually only the dissociated form is able to react with the monomer, whereas the associated species are not or very much less reactive.

Polar solvents, which are used very often in anionic polymerization, are mostly ether solvents often cyclic ethers such as tetrahydrofuran (THF) and tetrahydropyran (THP), but also linear ethers such as dimethoxyethane (DME). These ethers can be used as pure solvents but also as additives to anionic systems in non-polar solvents. For the latter purpose also amines such as triethylamine or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) can be used.

Both in pure polar solvents and in non-polar solvents but in the presence of sufficient amounts of polar additives, the association of the living ends is disrupted. Also in weak polar solvents, such as dioxane, the associates that occur in non-polar solvents are broken. The disappearance of the aggregates was proven spectrophotometrically by Waack

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[2,3]. This is undoubtedly due to the ability of such ethers to solvate the lithium cation. It is interesting to study the 'specific' solvent effect, which results in the solvation of the lithium cation by the polar solvent by observing the change of the state of association with increasing amounts of the polar solvent. This was studied for PStLi in benzene [4] by Morton et al. and for polyisoprenyllithium (PIsLi) in hexane [5] by Stavely using viscometric measurements at 30 °C. It was obvious that the degree of association decreases when THF is added and the solution becomes more and more polar. The association is clearly disrupted by the added THF. It was determined that only trace amounts of THF ([THF]/[PStLi] ≅ 10) are required to dissociate PStLi completely, while relative large amounts of THF ([THF]/[PIsLi] ≅ 2600) are required for the dissociation of PIsLi. These results are consistent with the previously discussed higher degrees of association of polydienyllithium.

Welch [6] reported an accelerating effect on the overall rates of polymerization with added THF, diethyl ether and triethylamine. Addition of small amounts of ethers such as dioxane [7] and THF [8–11] causes initial increases in propagation rate for isoprene and styrene polymerization in non-polar solvents. With increasing amounts of THF the rate of propagation of PStLi passes through a maximum and then decreases when more THF is added. With dioxane a similar maximum is observed as with THF.

Another kind of interaction is that of the Li^+-cation with the vinyl monomers which is proposed to explain the changing microstructure of anionically polymerized polydienes. Polar solvents can drastically alter the polyisoprene structure from 70–90% *cis*-1,4 obtained in pure hydrocarbon solvent to mainly 3,4. A similar effect is noted for polybutadiene, where changes from a very high (>90%) 1,4 content occur to a substantial 1,2 content occur, even when low concentrations of THF are added. An illustration of this trend is given by Huang [12], the vinyl content increasing from 20 to 64% with an increase in the amount of THF from 200 ppm to 1 wt%. It is to be noted that other ether or amine co-solvents may not have such a dramatic effect [13], although very small amounts of amine increase the amount of 1,2 or 3,4 units extensively [14].

A simple mechanism was proposed initially to explain the *cis*-stereochemistry of diene polymerization with lithium as a counter-ion [15]. According to this, PIsLi first complexes with isoprene in the *cis*-form. The complex subsequently rearranges to form a transition state in the form of a six-membered ring. The configuration of each monomer unit in the chain is thus fixed at its point of entry. The cyclic transition state was already proposed by Stearn and Foreman in 1959 [16]. Such a cyclic transition state explains the stereochemistry of isoprene homopolymerization with a lithium counter-ion. Medvedev and co-workers [17] have postulated the formation of a π-complex between the monomer and the positive counter-ion of the chain in order to explain the co-polymerization behavior in diene–vinyl systems. In a study of polymerization reactions which take place in hydrocarbon solutions in the presence of organolithium compounds they pointed out the possibility of solvation of the lithium cation of the growing chain end or its associated complex with its own monomer. One may suppose that the electron donating capacity of the double bonds in the monomer is the basis for the interaction between the monomer and the lithium component of the growing chain resulting in a π-complex. The suggestions of Stearns–Forman and Medvedev et al. are not at all contradictory, since the complex formation would presumably precede the transition state which determines the stereochemistry.

Another indication of the electron donating capacity of the double bonds of π-complexing agents can be found for alkyllithium species, which are used as initiator. Initial rates of initiation in cyclohexane were found to be several orders of magnitude smaller than those observed, under equivalent conditions, when cyclohexane was replaced with benzene [18,19]. The effect of the aromatic solvent is consistent with the known ability of these solvents to promote dissociation of organolithium aggregates [20].

Also the rates of alkyllithium initiation reactions with monomers are faster in aromatic than aliphatic solvents. Roovers and Bywater [21] e.g. reported that the rate of initiation of isoprene by *s*-BuLi is 2000 times faster in benzene than in hexane at a concentration of 10^{-3} M.

In the propagation of styrene and diene monomer in non-polar solvents with lithium as the counter-ion similar association phenomena are operative as in the initiation. Thus during propagation the carbanionic species also tend to form aggregates. PStLi e.g. appears as a dimer in cyclohexane or benzene. Worsfold and Bywater [22] attributed the observed one-half kinetic order dependence on chain-end concentration to a predominant association of PStLi in hydrocarbon solutions to unreactive dimers in rapid equilibrium with a small amount of reactive unassociated ion-pairs.

O'Driscoll [23] proposed two mechanisms for anionic propagation: (1) direct addition of monomer to an ion-pair wherein the positive counter-ion is complexed by either solvent or another monomer molecule, (2) formation of a π-complex between the entering monomer and the positive counter-ion, followed by bond formation between the negative chain-end and the complexed monomer. When benzene and THF are compared as solvents in the propagation of PStLi, it is likely that in benzene a common moiety of the different chain-ends is controlling the rate of addition of monomer, while in THF monomer is adding to two different ion-pairs. Therefore, O'Driscoll proposed that the positive counter-ion of a chain-end could form a π-complex with a monomer (whether vinyl or diene) or it can form a σ- or π-complex with the solvent, depending on the nature of the solvent.

As a test of the proposed mechanism, the authors examined whether a non-polymerizable, electron-rich π-complexing agent such as 1,2,4,5-tetramethylbenzene (durene) has a marked effect on polymerization by polymerizing 0.7 M styrene in benzene as a solvent, at a constant chain-end concentration of 0.021 M styrene with various durene concentrations. An increase in propagation rate followed by a decrease with increasing amounts of durene was obtained. The increase in the observed rate constant at low durene concentration may be interpreted as due to an increase in the number of dissociated chain-ends. Further increase in durene resulted in a depression of the rate due the formation of durene complexed chain-ends of lower reactivity than the unassociated, uncomplexed ones. It is noted that durene is exhibiting a similar behavior to that of THF, a strong σ-complexing agent, the amounts of THF, necessary to bring about the observed behavior, being however, much smaller [10]. When higher amounts of THF are present, a second THF molecule is added to the propagating chain-end. All these species had their own rate of propagation. The reactivity of the dietherate is comparatively low compared with the monoetherate or the bare ion-pair [10].

Later the interaction between π-complexing additives and the Li^+-cation was confirmed by spectroscopic analysis [24–26].

2. Experimental section

In this work we carried out living anionic polymerizations, characterized by the absence of termination or chain transfer. To obtain such a living system, it is imperative to work in an environment free of impurities, such as O_2, CO_2, water and any other proton donors. The best condition to obtain such an environment is working under high vacuum in all glass apparatuses.

2.1. Chemicals

The solvent, cyclohexane in this research, is first distilled, degassed several times and refluxed under high vacuum using a Na/K alloy. Prior to use the solvent is distilled through the vacuum line into a flask onto which an ampulle with some PStLi had previously been connected. When the orange color of PStLi remains after addition to the cyclohexane, the latter is considered pure.

Styrene (Fluka) is poured through a column containing aluminum oxide to remove the stabilizer it contains. It is brought into a flask of an all glass apparatus, which contains CaH_2 and stirred for a day. This procedure is repeated a second time. Styrene is distilled over PStLi prior to use. Butadiene, purchased from Fluka, is dried twice over CaH_2 and in a second step it is dried twice over K-mirrors in a similar apparatus. In a third step it is dried over PStLi. Other liquid agents are purified in a similar way.

Durene, hexamethylbenzene and tetraphenylethylene are recrystallized in ethanol and sublimed onto a cold finger under reduced pressure using liquid nitrogen. Finally it is brought under high vacuum in an all glass apparatus. Secondary-butyllithium (*s*-BuLi) or tertiary-butyllithium (*t*-BuLi), which are used as initiator for the synthesis of a pre-polymer, are purified by a short distance distillation using a cold finger under dynamic vacuum. The pre-polymer is synthesized using an exact amount of this initiator and a fixed amount of monomer. This procedure is necessary to exclude the kinetic step of initiation during the measurements of propagation.

2.2. Kinetic measurements

In living anionic polymerization the concentration of reactive centers remains constant during reaction. It is therefore, possible to write the kinetic equation of propagation as a pseudo-first-order reaction.

$$-\frac{d[M]}{dt} = k_{obs}[M]$$

with

$$k_{obs} = k_p\left(K_d\frac{[PLi]_{form}}{n}\right)^{\frac{1}{n}}$$

where $n = 2$ for PStLi in cyclohexane and benzene in which it occurs almost entirely as dimers ($n = 2$) and $n = 4$ for polybutadienyllithium (PBuLi) which in the same conditions appears as tetramers ($n = 4$). The rates of styrene polymerization are measured by observing at a constant temperature of 20 °C the absorbance of styrene at 291 nm, which is the λ_{max} of absorbance of styrene monomer, as a function of time using an UV–VIS spectrophotometer (Varian CARY 2000). Since styrene is the species of which the concentration changes during time in the propagation step, the decrease in absorbance is solely due to the disappearance of styrene. According to the equation above concerning the propagation, one can obtain k_{obs} (observed rate constant of propagation) from a graph where $ln(A_{obs} - A_{inf})$ is plotted as a function of time. The slope of the straight line through the measured points is equal to k_{obs}. A_{obs} represents the absorbance observed at different times and A_{inf} is the absorbance when the reaction is completely over. This is the remaining absorbance of the other compounds in the solution. In kinetic studies in which butadiene is used as a monomer, the decrease in absorbance is followed at 236.5 nm.

3. Results and discussion

Organolithium species are the only kind of organometallic compounds used in this research because next to the polymerization of styrene, butadiene is also studied in this work and, apart from their easy complexation, they are the only carbanion salts that result mainly in 1,4 microstructure of the polydienes synthesized, which is the desired structure for possible use in rubber applications. The use of π-complexing agents in such synthesis is the topic of a forthcoming paper. It has been previously, repeatedly emphasized that these organolithium species tend to form aggregates in non-polar solvents. These associations are based on the strong interaction of ionic charges in non-polar medium i.e. of the positive charge of the Li^+-cations with the negative charges of the carbanionic species leading to clusters of the ionic charges screened from the non-polar medium by the surrounding organic residues that provide the solubility of the compounds.

In the viewpoint concerning the mechanism of 1,4 propagation of dienes, it is proposed that in non-polar medium the Li^+-cation can interact with the π-cloud of a monomer and can bring the monomer towards the reactive chain-ends in the required arrangement [17]. Illustrated in Fig. 1 is the Li^+-cation which keeps the monomer, e.g. butadiene, in such a conformation that it will be built into the polymer in a 1,4 fashion. When polar additives, such as THF, are used the Li^+-cation will be solvated by these σ-complexers and will not be able to anymore interact with other compounds including the propagating monomer. As a consequence the propagation will not result anymore in a mainly 1,4 content of the polymerized polydiene but a lot of 1,2 units in polybutadiene and 3,4 units in polyisoprene will be obtained.

With these mechanisms in mind, i.e. the association–dissociation equilibrium of organolithium species and the interaction of the Li^+-cation with the monomer, the anionic polymerization and especially the one of dienes, would benefit from an additive that would shift the association equilibrium to the unassociated form and that would not render impossible or interfere unfavorably with the interaction of the Li^+-cation with the propagating monomer.

Such a possible additive was studied by O'Driscoll et al. [23]. In a study to prove the proposed interaction of π-bond-containing compounds with the Li^+-cation, they have chosen durene as the non-polymerizable π-complexing agent. It was shown that a low concentration of this compound (up to 0.15 M) caused the rate of propagation of PStLi in benzene to increase, whereas, higher concentrations of durene brought about a decrease.

3.1. Influence of tetrahydrofuran on the rate of propagation

In analogy to the study by Worsfold and Bywater [8] the effect of added THF on the rate of propagation of PStLi in benzene, Huang and Tsiang [12] measured the rate of propagation of styrene and of butadiene in cyclohexane with Li^+ as a counter-ion and in the presence of small amounts of THF.

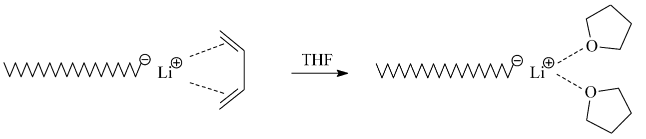

Fig. 1.

In both experiments an increase in the observed reaction rate is followed by a decrease, completely in agreement with the previously described mechanism of this kind of reaction mixtures.

3.2. Tetramethylethylene as dissociating additive

The possible influence of tetramethylethylene (TME) was investigated in our laboratory by different researchers; all the results are included in Fig. 2. In this figure it can be clearly seen that, although there is a lot of undesirable scatter of the experimental points, TME had no effect on the reaction rate. TME is one of the simplest structures of π-complexing agents that do not cause termination or do not polymerize. In spite of the electron-giving methyl groups onto the central double bond, apparently it does not constitute a sufficiently strong complexing agent to cause any detectable influence on the rate of propagation of styrene in cyclohexane at 20 °C with chain-end concentration in the region of 10^{-3} M. To eliminate the small differences in the living end concentrations used and since it is not a priori known whether the presence of TME changes the order 1/2 found for PStLi in pure cyclohexane, $k$obs/[PStLi] is given in the ordinate.

3.3. Benzene as dissociating additive

From the results of the former additive it seemed that TME was not strong enough to result in a noticable dissociation of PStLi. Therefore, another kind of π-electron-containing compound, i.e. benzene as well as some other phenyl derivatives were chosen. The π-cloud of a phenyl compound is of course much more electron-rich than a common double bond. Increasing amounts of benzene were added to propagating PStLi in cyclohexane at 20 °C. The

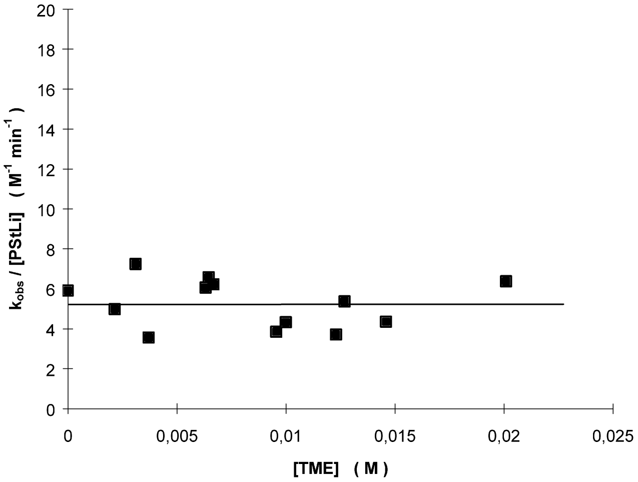

Fig. 2. Observed rate constants divided by [PStLi] for the propagation of PStLi at 20 °C with varying amounts of TME in cyclohexane; [PStLi] ≅ 2×10^{-3} M.

results are shown in Fig. 3. Since it is known from the literature that the order with respect to the PStLi-concentration even in pure benzene is strictly 1/2, $k_{\mathrm{obs}}/[\mathrm{PStLi}]^{1/2}$ is plotted as a function of the benzene concentration instead of $k_{\mathrm{obs}}/[\mathrm{PStLi}]$ as for the other additives.

Because benzene is fully miscible with cyclohexane it is possible to go up to very high benzene concentrations, even to pure benzene. This is the last measured point in the plot of the series, i.e. 11 M. One can see that there is an increase in the rate of propagation with increasing concentration of benzene. However, no maximum is observed. This is because benzene is a strong enough π-complexing agent to dissociate part of the aggregates present in the reaction mixture, but it is apparently not strong enough to lead to a sufficiently important dissociation of the aggregates to cause an increase in the one-half-order dependence of the rate of propagation on the PStLi concentration. Moreover, it is well known that organolithium compounds are still largely associated in pure benzene. Therefore, benzene cannot be used for the purposes needed in this research, but it can be seen as an indication in the right direction. Indeed estimates (since they cannot be measured directly) of the true k_p value of PStLi in pure cyclohexane and pure benzene indicate that the true k_p value is smaller in benzene than in cyclohexane. This could be interpreted as due to the fact that the weak π-complexing agent benzene interacts with the Li^+-cation of the chain-end and interferes therefore, to some extent with the interaction of the Li^+-cation with the monomer. This interference could cause the true rate constant k_p to be smaller in benzene than in cyclohexane. The greater observed reaction rate in benzene must then be attributed to the greater number of non-associated chain-ends in benzene, although not great enough to result in a observable increase in the reaction order.

3.4. Durene as dissociating additive

In view of the results reported by O'Driscoll et al. [23], a study was performed of the influence of increasing amounts of durene on the propagation of styrene in cyclohexane, which is illustrated in Fig. 4. Although some scatter of the experimental points is often observed in these experiments (see e.g. also Fig. 2) it should be noted that another possible reason for the scatter of points in Fig. 4 may be the fact that the concentration of living ends varied somewhat in some experiments. Nevertheless it is shown that a very similar effect was detected as in O'Driscoll's study, performed in benzene. The maximum of the rate of propagation was situated at 0.15 M in benzene and is situated at 0.7 M in cyclohexane. This difference is due to the fact that benzene itself has already a dissociating effect, as described in the former paragraph. As a consequence less durene was needed to reach the maximum increase in rate followed by its decrease afterwards in benzene than in our study in cyclohexane.

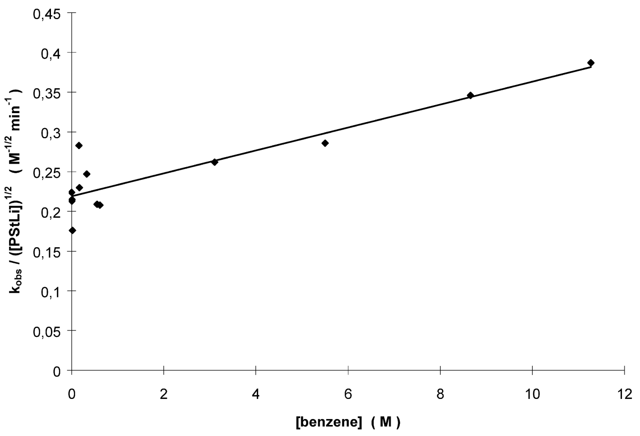

Fig. 3. Observed rate constants divided by $[\mathrm{PStLi}]^{1/2}$ for the propagation of PStLi at 20 °C with varying amounts of benzene in cyclohexane; $[\mathrm{PStLi}] \cong 1 \times 10^{-3}$ M.

To assess the dissociating effect of durene on PStLi more quantitatively a number of preliminary kinetic measurements of the rate of propagation of PStLi in cyclohexane in the presence of durene were carried out. The concentration of PStLi was varied from 3.6×10^{-3} M to 5.1×10^{-4} M and the concentration of durene was 0.27 M. The results of this study gave a value for the dissociation constant (K_d) equal to $K_d \approx 4 \times 10^{-3}$ M and for the rate constant (k_p) equal to $k_p \approx 9\ \mathrm{M\ min}^{-1}$.

The calculation is based on an equation proposed by S. Bywater [27]:

$$\frac{[\mathrm{LE}]}{k_{\mathrm{obs}}} = \frac{1}{k_p} + \frac{2k_{\mathrm{obs}}}{k_p^2 K_d}$$

This equation from the intercept and the slope of which the values and k_p and K_d can in principle be obtained, is a

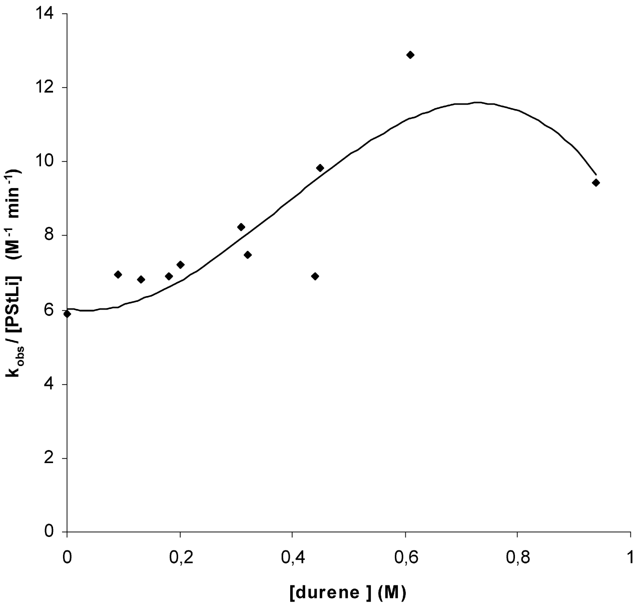

Fig. 4. Observed rate constants divided by [PStLi] for the propagation of PStLi at 20 °C with varying amounts of durene in cyclohexane; $[\mathrm{PStLi}] \cong 5$ to 9×10^{-4} M.

linearized form of the relation between log k_{obs} and log[LE] and is particularly useful when the logk_{obs} − log[LE] relation is not completely linear or gives apparent orders between 0.5 and 1 i.e. when non-negligible amounts of not too reactive non-associated species are present. In the usual case of negligible dissociation of the associated species into highly reactive non-associated species, as in pure benzene or cyclohexane, the intercept is indistinguishable from zero and K_d and k_p can not be obtained separately from this plot. The value of K_d obtained in the presence of 0.27 M durene is much bigger than the dissociation constant that was reported in the literature [28] concerning dimers of PStLi in pure cyclohexane, which is estimated to be 10^{-6} or 10^{-7} M. The K_d of 4×10^{-3} M which we obtained results in over 75% of the associates of PStLi being broken at a formal concentration of PStLi of 10^{-3}. Increasing the concentration of durene would most probably result in an even higher percentage of dissociated species. However, as can be seen from the low rate constant and as will be shown in more detail in a following paper the addition of durene produces durene-complexed species of much lower reactivity than the non-associated non-complexed ion pairs. The gradual replacement of the latter by the complexed ion pairs upon addition of durene therefore, only gives a limited increase in the rate and after a maximum at about 0.7 M of durene leads to a gradual decrease in the rate.

Because other organolithium compounds than PStLi also tend to form aggregates in non-polar solvents, a similar study as the one above, was made for PBuLi as the organolithium compound. The results are shown in Fig. 5. Although PBuLi is more associated in cyclohexane than PStLi, the addition of durene had a similar influence on the rate of propagation, i.e. an increase followed by a maximum and subsequently by a decrease. Durene is thus strong enough to break down the association of PBuLi in cyclohexane. However, in view of the tetrameric or even hexameric association of PBuLi in cyclohexane, it is not possible from these results to decide to which level of dissociation this break-down leads and a direct comparison with the case of PStLi may therefore, not be justified.

Nevertheless, it should be stressed that, as will be shown in detail in a forthcoming publication the addition of durene had no influence on the 1,4 content of the polybutadiene obtained.

3.5. Hexamethylbenzene as dissociating additive

In view of the very good results of durene compared to benzene, hexamethylbenzene (HMB) was proposed as another possible dissociating agent in the system.

Durene has four electron donating groups attached to the phenyl ring, and as experimentally proven this is enough to result in a significant effect. HMB has six such electron donating groups attached to the phenyl ring and should therefore, be an even better dissociating additive.

The results are shown in Fig. 6 [29]. The maximum rate is reached after 0.3 M HMB compared to 0.7 M durene in a same system, suggesting that it has a bigger dissociating ability than durene. Unfortunately 0.3 M is the maximum solubility of HMB in cyclohexane. It was therefore, not possible to add more HMB in order to investigate a higher concentration region. Also an important transfer reaction, i.e. the metalation of the methyl groups, occurred.

3.6. Tetraphenylethylene as dissociating additive

Tetraphenylethylene (TPhE) is an additive that consists of a double bond, as in TME, but with phenyl groups as substituents. Again an increase in the rate of propagation at

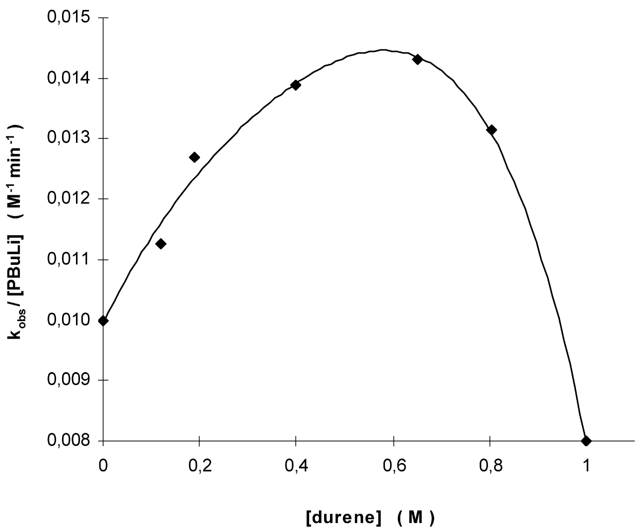

Fig. 5. Observed rate constants divided by [PBuLi] for the propagation of PBuLi at 20 °C with varying amounts of durene in cyclohexane; [PBuLi] ≅ $1{,}2 \times 10^{-3}$ M.

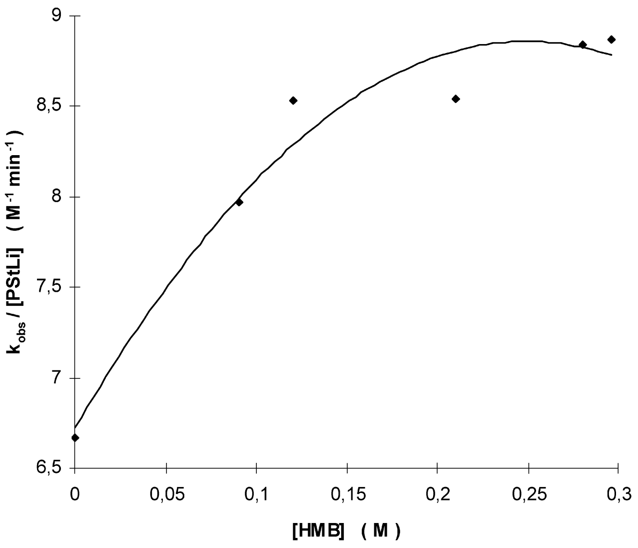

Fig. 6. Observed rate constants divided by [PStLi] for the propagation of PStLi at 20 °C with varying amounts of HMB in cyclohexane; [PStLi] ≅ 6 to 9×10^{-4} M.

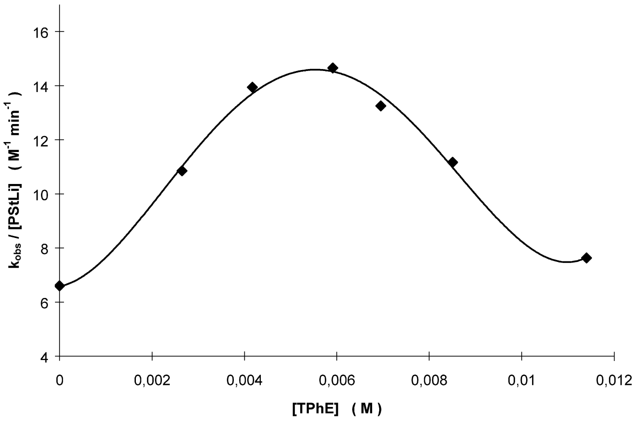

Fig. 7. Observed rate constants divided by [PStLi] for the propagation of PStLi at 20 °C with varying amounts of TPhE in cyclohexane; [PStLi] ≅ 4 to 8×10^{-4} M.

lower TPhE concentrations is found, followed by a maximum and a subsequent decrease at the higher concentration region of TPhE. The most striking difference with the other additives is the amount of TPhE necessary to bring about a similar effect as durene. This amount is a 100 times smaller than that of durene to obtain a similar effect, suggesting that the strength is a 100 times greater than that of durene or HMB. The evolution of the rate of propagation as a function of increasing amounts of TPhE is shown in Fig. 7.

The influence of TPhE is probably due to the interaction of the two adjacent phenyl rings with the Li^+-cation. This explains the increased strength in the interaction of TPhE with the Li^+-cation as compared with TME and with durene or HMB.

4. Conclusion

In this research different kind of additives capable of acting as π-complexing agents were considered and their capacity to dissociate the aggregates of the carbanion-Li^+ chain-ends of living polymers that are present in non-polar solvents was studied by measurements of the propagation rates in the presence of these additives. It is shown that different additives resulted into actual dissociation, viz. durene, HMB and TPhE. Benzene and TME seemed too weak to result in a significant change of the rate of propagation.

The mechanism of the dissociating capacity of the π-complexing additives is based on the interaction of the π-electrons of the agent with the Li^+-cation. Indeed this effect was strong enough to result in an increase in the rate of propagation. Using higher concentrations of durene and TPhE this led to a decrease in the rate of propagation, completely in agreement with the mechanism that was proposed for the addition of small amounts of THF in the reaction medium of PStLi in cyclohexane and benzene. This decrease is due to a lower reactivity of the complexed ion-pairs caused by the complexation of the lithium cation. This complexation hinders or in the case of σ-additives may even exclude the interaction of the Li^+-cation with the π-cloud of the monomer, which is considered to form a pre-reactive complex or a coordinated state of the monomer in a single reaction step, in which the monomer is activated for a nucleophilic attack by the propagating anion.

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