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Influence of π-complexing agents on the anionic polymerization of styrene with lithium as counterion in cyclohexane 1. Effect of durene

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Dedicated to the memory of Prof. Dr. S. Bywater

Abstract

The propagation reaction in the anionic polymerization of styrene with lithium as counter ion in cyclohexane has been investigated for six different concentrations of 1,2,4,5-tetramethylbenzene (durene) in the range of living ends concentration between 10^{-5} and 10^{-3} M at 20 °C. The values of the apparent dissociation constant of PStLi dimer and the weighted rate constants of all unassociated species were obtained for all six investigated concentrations of durene. The apparent dissociation constant increases several orders and the weighted rate constants of all unassociated species decreases one or two orders depending on the concentration of durene. A new mechanism was proposed and the values of the relevant absolute propagation rate constants of the three reactive monomeric species have been for the first time derived from the kinetic results. The absolute propagation rate constants of PStLi·D and PStLi·2D are comparable but much lower than that of PStLi. The complexation constant of PStLi with one molecule of durene is much larger than that of PStLi with a second molecule of durene.

Keywords: Anionic polymerization; Kinetics and mechanism; Durene

1. Introduction

The mechanism of the anionic polymerization of styrene with lithium as a counter ion in non-polar solvents has been well established [1–3]. A kinetic order of 0.5 with respect to the living end concentration of polystyryllithium (PStLi) was found for the observed rate constants in non-polar solvents, i.e. benzene [4] and cyclohexane [5]. This behavior is in agreement with the coexistence of dimeric associates with a small fraction of monomeric PStLi species, the latter being the only species capable of propagating.

The addition of σ-type additives, such as ethers, has a large effect on the propagation kinetics of styrene with lithium as counter ion. Addition of small amounts of THF initially causes the increase of propagation rate of PStLi in benzene; however, with increasing amounts the rate passes through a maximum and then decreases to a value which is higher than the original one [6,7].

1,4-dioxane [8,9] was shown to be an efficient complexing agent, but slightly weaker than THF. Recently, the influence of π-complexing agents on the anionic polymerization of styrene with lithium as a counterion in non-polar solvents was studied by Maeseele et al. [10] and Van Beylen et al. [11,12] have successfully developed an improved method for the synthesis of triblock SBS copolymers through the novel use of such π-complexing agents. Durene is one of the series of π-complexing agents, which was first investigated by O'Driscoll [13] for the anionic polymerization of styrene in benzene. The observed propagation rate constant increases at low durene concentration and after going again through a maximum further increase in durene concentration results in a decrease of rate. In comparison with THF and Dioxane, more durene is needed for the dissociation of PStLi aggregates in benzene.

In this work, the influence of durene in the propagation rate of PStLi in cyclohexane at 20 °C was investigated in detail and the relevant mechanism was proposed.

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2. Experimental section

All the purifications were carried out under high vacuum. Styrene was dried by distillation from CaH_2(2 ×) and distilled over PStLi oligomer. *Sec*-BuLi was purified by a short-path vacuum distillation. Polystyrene oligomer was obtained by the initiation of styrene with *sec*-BuLi in cyclohexane, and its measured molecular weight is 5000. Cyclohexane was refluxed with Na–K alloy, then stirred and degassed on the vacuum line, finally distilled over PStLi oligomer. Durene was initially recrystallized from ethanol, then vacuum-sublimed and finally further dried on the high vacuum line. The kinetics of the propagation reaction were determined by following the disappearance of styrene spectrophotometrically at 291 nm on a Cary 2200 at 20 °C.

3. Results and discussion

The influence of durene on the observed propagation rate of PStLi in cyclohexane was first investigated at two nearly constant PStLi concentrations, i.e. $C^* = 5.2 \times 10^{-4}$ M and $C^* = 3.0 \times 10^{-3}$ M and the result is shown in Fig. 1.

It is shown that for two concentrations of PStLi, increasing the amount of durene leads initially to an increase of k_{obs}/C^* where k_{obs} represents the observed monomolecular propagation rate constant given by $-\mathrm{d}\ln[\mathrm{M}]/\mathrm{d}t$ and C^* is the formal concentration of active ends, passing then through a maximum, and finally decreases with further addition of durene. This phenomenon is consistent with a reaction scheme whereby the initial unreactive dimeric ion-pair, $(\mathrm{PStLi})_2$, is in equilibrium with the reactive monomeric ion-pair, PStLi, which in turn is in equilibrium with a complex of this ion-pair with one molecule of durene(PStLi·D), and the latter in turn

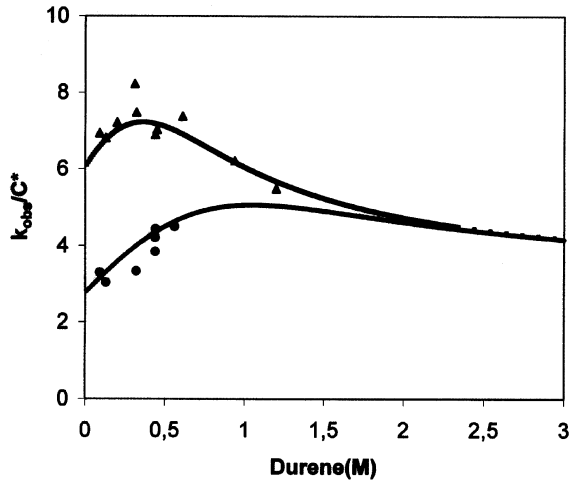

Fig. 1. The effect of durene on the propagation rate of PStLi with lithium as counter ion in cyclohexane at 20 °C. ▲ $[\mathrm{PStLi}] = 5.2 \times 10^{-4}$ M; ● $[\mathrm{PStLi}] = 3.0 \times 10^{-3}$ M. Solid line: calculated curve (the detailed procedures are shown in Appendix A).

$$(\mathrm{PStLi})_2 \underset{}{\overset{K_D}{\rightleftharpoons}} 2\mathrm{PStLi}$$

$$\mathrm{PStLi} + \mathrm{D} \overset{Ks_1}{\rightleftharpoons} \mathrm{PStLi{\cdot}\,D}$$

$$\mathrm{PStLi{\cdot}D} + \mathrm{D} \overset{Ks_2}{\rightleftharpoons} \mathrm{PStLi{\cdot}\,2D}$$

$$\mathrm{PStLi} + \mathrm{Sty} \xrightarrow{kp} (\mathrm{PSt})\mathrm{StyLi}$$

$$\mathrm{PStLi{\cdot}\,D} + \mathrm{Sty} \xrightarrow{kp_1} (\mathrm{PSt})\mathrm{StyLi{\cdot}\,D}$$

$$\mathrm{PStLi{\cdot}\,2D} + \mathrm{Sty} \xrightarrow{kp_2} (\mathrm{PSt})\mathrm{StyLi{\cdot}\,2D}$$

Scheme 1.

complexes with one more molecule of durene (PStLi·2D). The reactivities of PStLi·D, PStLi·2D are lower than that of uncomplexed PStLi, as shown in Scheme 1.

This preliminary result clearly shows that durene is an efficient π-complexing agent leading to the dissociation of the associated PStLi dimer. A similar behavior has also been found in THF [6,7] and dioxane [8] and several complex constants for the three different reactive species were derived from the kinetic results of the relatively low and high concentrations of these two σ-complexing agents [6,8]. However, with the exception of k_{p_2}, the values of K_D, K_{S_1}, K_{S_2}, k_p, k_{p_1} could not be determined in these cases. A similar mechanism as represented in Schemes 1 and 2 is proposed to allow the determination of these values in the case of durene. Moreover, it can allow us to check whether there are two or three reactive monomeric species in the presence of durene.

K_D^{app} is the apparent dissociation constant of the PStLi dimers and k_p^{app} is the weighted rate constant of all unassociated species in the presence of durene analogous to the constants K_D and k_p in pure cyclohexane.

Here, the reactive monomeric species remain in equilibrium with the unreactive associated PStLi dimer and only the former contribute to the propagation step. If three monomeric species, that is, PStLi, PStLi·D, PStLi·2D, are involved we can define:

$$k_p^{app} = (1 - \alpha - \beta)k_p + \alpha k_{p_1} + \beta k_{p_2} \quad (1)$$

$$\text{Dimeric Species} \overset{K_D^{app}}{\rightleftharpoons} \text{Monomeric Species}$$

$$\text{Monomeric Species} + \text{Styrene} \xrightarrow{k_p^{app}} \text{Monomeric Species}$$

Scheme 2.

$$\alpha = \frac{[\text{PStLi·D}]}{[\text{PStLi}] + [\text{PStLi·D}] + [\text{PStLi·2D}],}$$
$$\beta = \frac{[\text{PStLi·2D}]}{[\text{PStLi}] + [\text{PStLi·D}] + [\text{PStLi·2D}]} \quad (2)$$

On one hand, according to Scheme 1

$$[\text{PStLi·D}] = K_{S_1}[\text{PStLi}][\text{D}], \text{ and } [\text{PStLi·2D}] = K_{S_1}K_{S_2}[\text{PStLi}][\text{D}]^2 \quad (3)$$

From Eqs. (1)–(3), k_p^{app} can be expressed as follows:

$$k_p^{app} = \frac{k_p + K_{S_1}[\text{D}]k_{p_1} + K_{S_1}K_{S_2}[\text{D}]^2k_{p_2}}{1 + K_{S_1}[\text{D}] + K_{S_1}K_{S_2}[\text{D}]^2} \quad (4)$$

On the other hand,

$$K_D^{app} = \frac{([\text{PStLi}] + [\text{PStLi·D}] + [\text{PStLi·2D}])^2}{[(\text{PStLi})_2]} \quad (5)$$

Combining Eqs. (3) and (5), we can obtain:

$$K_D^{app} = K_D(1 + K_{S_1}[\text{D}] + K_{S_1}K_{S_2}[\text{D}]^2)^2$$

then

$$\sqrt{K_D^{app}} = \sqrt{K_D}(1 + K_{S_1}[\text{D}] + K_{S_1}K_{S_2}[\text{D}]^2) \quad (6)$$

From Eqs. (4) and (6),

$$\sqrt{K_D^{app}}k_p^{app} = \sqrt{K_D}(k_p + K_{S_1}[\text{D}]k_{p_1} + K_{S_1}K_{S_2}[\text{D}]^2k_{p_2}) \quad (7)$$

In combination with the plots of $\sqrt{K_D^{app}}$ vs. [D] and $\sqrt{K_D^{app}}k_p^{app}$ vs. [D], the values of K_D, K_{S_1}, K_{S_2}, k_p, k_{p_1}, k_{p_2} can be determined, respectively, if the values of K_p^{app} and K_D^{app} can be obtained for several different concentrations of durene. In this work, six different concentrations of durene ranging from 0.09 to 0.56 M were investigated and the detailed kinetic results are shown in Table 1.

The values of K_p^{app} and K_D^{app} can be obtained by the recently developed linear equation [14,15] shown below, which was derived for the case where non-negligible amounts of unassociated species (complexed and/or non-complexed) occur, leading to a non-linear log k_{obs} − log $C*$ relationship.

$$\frac{C^*}{k_{obs}} = \frac{1}{k_p^{app}} + \frac{2k_{obs}}{(k_p^{app})^2K_D^{app}} \quad (8)$$

The values of K_D^{app} and k_p^{app} were obtained from the values of the slope and intercept of the plot of C^*/k_{obs} vs. k_{obs} for all six concentrations of durene and the results are generalized in Table 2. At each constant concentration of durene the experimental data fit the straight line very well and a typical example is shown in Fig. 2.

It was found, as shown in Table 2, that the apparent dissociation constant of PStLi dimer increases and the weighted rate constant of all unassociated species decreases with increasing concentration of durene. In pure cyclohexane the K_D was estimated to be of the order of 10^{-7} M. The addition of durene increases the apparent dissociation constant K_D^{app} several orders, viz. from 6.52×10^{-5} M at [durene] = 0.09–6.22×10^{-3} M at [durene] = 0.56 M. These quantitative results show that durene is able to dissociate the PStLi dimer into the monomeric species.

In Table 2 it can also be seen that in this more systematic kinetic study the value of K_D^{app} at [durene] = 0.32 M is somewhat lower and that of k_p^{app} somewhat higher than in the preliminary measurements at [durene] = 0.27 M reported in

Table 1
Kinetic results of styrene polymerization in cyclohexane with lithium as a counter ion in the presence of durene at 20 °C

Durene (M)	C^* (M)	k_{obs} (min^{-1})	Durene (M)	C^* (M)	k_{obs} (min^{-1})
0.09	3.00×10^{-5}	6.00×10^{-4}	0.13	6.50×10^{-5}	8.80×10^{-4}
	8.20×10^{-5}	1.10×10^{-3}		1.43×10^{-4}	1.50×10^{-3}
	8.50×10^{-5}	1.20×10^{-3}		1.50×10^{-4}	1.90×10^{-3}
	1.40×10^{-4}	2.10×10^{-3}		1.73×10^{-4}	1.60×10^{-3}
	3.76×10^{-4}	2.90×10^{-3}		1.80×10^{-4}	1.70×10^{-3}
	5.38×10^{-4}	4.00×10^{-3}		2.53×10^{-4}	2.50×10^{-3}
	1.12×10^{-3}	6.10×10^{-3}		5.45×10^{-4}	3.50×10^{-3}
	1.50×10^{-3}	6.90×10^{-3}		5.72×10^{-4}	3.70×10^{-3}
	2.33×10^{-3}	8.10×10^{-3}		8.90×10^{-4}	4.50×10^{-3}
				1.40×10^{-3}	6.70×10^{-3}
				2.90×10^{-3}	8.80×10^{-3}
0.2	2.52×10^{-4}	2.30×10^{-3}	0.32	7.00×10^{-5}	7.00×10^{-4}
	3.72×10^{-4}	3.10×10^{-3}		1.58×10^{-4}	1.80×10^{-3}
	5.07×10^{-4}	3.90×10^{-3}		2.09×10^{-4}	1.80×10^{-3}
	5.96×10^{-4}	4.30×10^{-3}		3.35×10^{-4}	3.00×10^{-3}
	8.00×10^{-4}	5.20×10^{-3}		4.96×10^{-4}	4.00×10^{-3}
	1.16×10^{-3}	6.30×10^{-3}		1.00×10^{-3}	6.00×10^{-3}
				1.70×10^{-3}	8.00×10^{-3}
				1.80×10^{-3}	8.20×10^{-3}
				3.33×10^{-3}	1.25×10^{-2}
0.44	1.28×10^{-4}	1.40×10^{-3}	0.56	1.30×10^{-3}	7.00×10^{-3}
	2.00×10^{-4}	1.60×10^{-3}		2.50×10^{-3}	1.26×10^{-2}
	2.11×10^{-4}	1.60×10^{-3}		8.35×10^{-4}	5.30×10^{-3}
	2.95×10^{-4}	2.50×10^{-3}		1.50×10^{-4}	1.10×10^{-3}
	5.54×10^{-4}	4.00×10^{-3}		3.00×10^{-4}	2.10×10^{-3}
	7.32×10^{-4}	4.80×10^{-3}			
	8.05×10^{-4}	5.30×10^{-3}			
0.44	1.11×10^{-3}	6.10×10^{-3}			
	1.40×10^{-3}	7.10×10^{-3}			
	1.58×10^{-3}	7.60×10^{-3}			
	2.85×10^{-3}	1.20×10^{-2}			
	2.93×10^{-3}	1.30×10^{-2}			
	3.20×10^{-3}	1.20×10^{-2}			

Table 2
Summary of the values of K_D^{app} and k_p^{app} in the presence of durene

Durene (M)	K_D^{app} (M)	k_p^{app} (M^{-1} min^{-1})
0.09	6.52×10^{-5}	32.79
0.13	1.28×10^{-4}	22.73
0.20	4.40×10^{-4}	15.80
0.32	7.00×10^{-4}	13.39
0.44	1.56×10^{-3}	10.27
0.56	6.22×10^{-3}	7.55

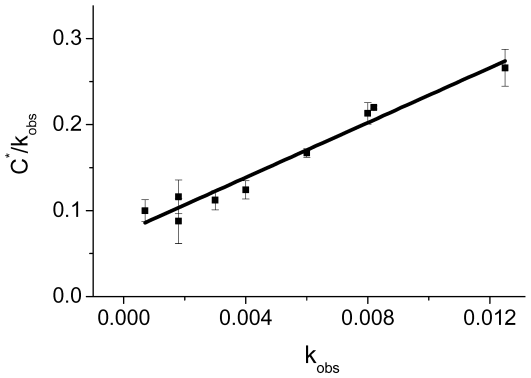

Fig. 2. Plot of C^*/k_{obs} vs. k_{obs} at [durene] = 0.32 M.

the previous publication [10]. In view of the greater concentration range covered and of the values obtained at the other durene-concentrations in this work we feel that those reported in this paper are the more accurate ones.

The values of K_D^{app} and k_p^{app} allow the reconstruction of the non-linear dependence of $\log k_{obs}$ vs. $\log C^*$ found experimentally. For all six investigated concentrations of durene the calculated dependences of $\log k_{obs}$ vs. $\log C^*$ reproduce the experimental data very well and one of the calculation results is shown in Fig. 3.

A manifest curvature is clearly seen in Fig. 3. The curvature of the order in living ends plot is attributed to the coexistence of unreactive PStLi dimer and reactive monomeric species in the presence of durene. The slope of the bilogarithmic plot of k_{obs} vs. [C*] shows a decrease of the reaction order from 0.91 to 0.59 for [C*] increasing from 7.0×10^{-5} to 3.3×10^{-3} M, which indicates the increase of the mole fraction of the monomeric species. Actually the exact fraction of monomeric species in the presence of durene can be obtained by the following equation:

$$\frac{[\text{monomeric}]}{C^*} = \frac{-K_D^{app} + \sqrt{(K_D^{app})^2 + 8C^* K_D^{app}}}{4C^*} \quad (9)$$

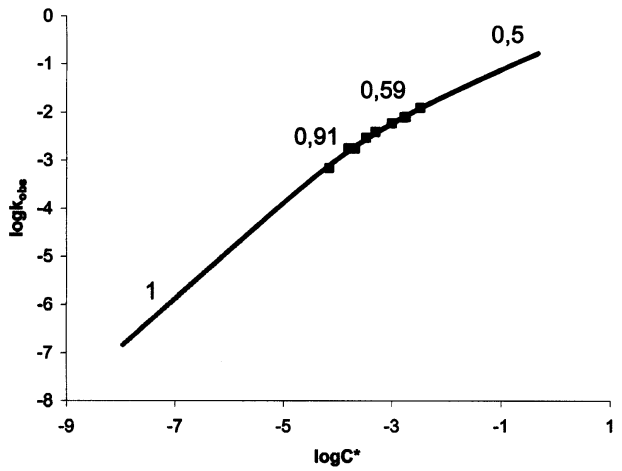

Fig. 3. Dependence of $\log k_{obs}$ vs. $\log C^*$ at [durene] = 0.32 M. ■, experimental points; solid line, calculated line with $K_D^{app} = 7.00 \times 10^{-4}$ M, $k_p^{app} = 13.39$ M^{-1} min^{-1}.

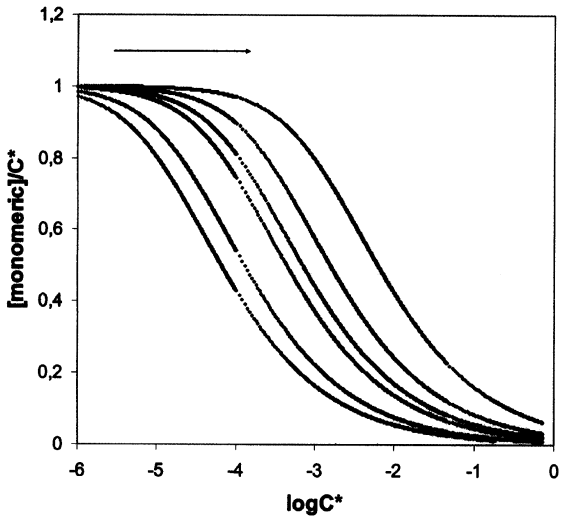

Fig. 4. Dependencies of the mole fractions of the monomeric species on the total concentration of PStLi for six different concentrations of durene. The durene concentration is 0.09, 0.13, 0.20, 0.32, 0.44, 0.56 M, respectively, in the direction of the arrow.

The dependencies of the mole fractions of the monomeric species on the total concentration of PStLi for six different concentrations of durene are shown in Fig. 4. It is clearly seen that the mole fraction of monomeric species increases with increasing amounts of durene at a constant concentration of PStLi. On the other hand, the determined values of K_D^{app} and k_p^{app} at six different concentrations of durene allow us to find the dependence of $\sqrt{K_D^{app}}$ vs. [durene] and $\sqrt{K_D^{app} k_p^{app}}$ vs. [durene], as shown in Figs. 5 and 6. Through the fitting procedures the values of $K_D = 2.0 \times 10^{-7}$ M, $K_{S_1} = 140$ M^{-1}, $K_{S_2} = 1$ M^{-1}, $k_p = 480$ M^{-1} min^{-1}, $k_{p_1} = 6.7$ M^{-1} min^{-1}, and $k_{p_2} = 3$ $M^{-1}\text{min}^{-1}$ are determined. The simulation results indicate that there are three reactive monomeric species in this system. But it should be noted that the dependence of $\sqrt{K_D^{app}}$ and $\sqrt{K_D^{app} k_p^{app}}$ on [durene] can be fitted very well with a linear regression equation if the last point ([durene] = 0.56 M) is neglected. But the later

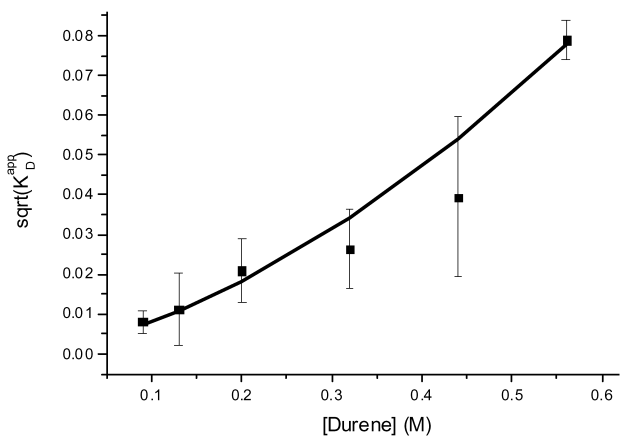

Fig. 5. Plot of $\sqrt{K_D^{app}}$ vs. [durene] for six concentrations of durene. ■, experimental points; solid line, weighted simulation results.

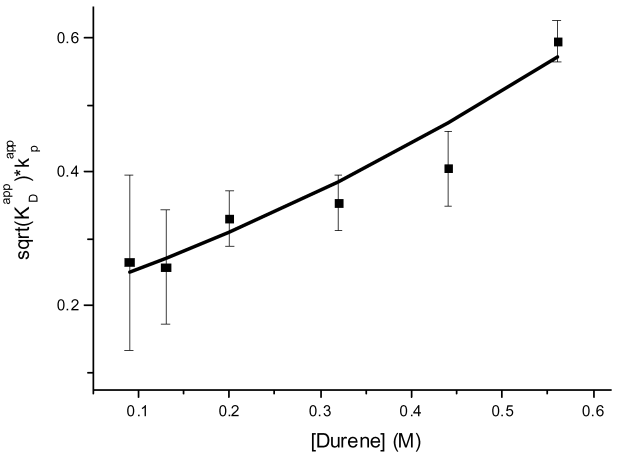

Fig. 6. $\sqrt{K_D^{app}} \cdot k_p^{app}$ vs. [durene] for six concentrations of durene. ■, experimental points; solid line, weighted simulated results.

described simulation of the curves of k_{obs}/C^* plotted as a function of [durene] (see Appendix A) and the quantum chemical calculation results, to be reported in the next paper [16], indicate that this point can not be neglected and that there are indeed three reactive monomeric species involved in the propagation step.

With the determined values of K_D, K_{S_1}, K_{S_2}, k_p, k_{p_1}, k_{p_2} we can in turn check the dependence of k_p^{app} vs. [durene]. The result is shown in Fig. 7. It is clearly seen that the calculated line fits the values of k_p^{app} determined by the linear analytical method very well. Moreover, as mentioned above, the validity of the determined values of these parameters can be checked by fitting the original experimental data of k_{obs}/C^* vs. [durene] and the detailed calculation procedures as shown in Appendix A. The calculation result is shown in Fig. 1 (solid line) at [PStLi] $= 5.2 \times 10^{-4}$ M and [PStLi] $= 3.0 \times 10^{-3}$ M with the determined values of K_D, K_{S_1}, K_{S_2}, k_p, k_{p_1} and k_{p_2}. The simulated lines reproduce the original dependencies very well. It can also be seen from Fig. 1 that at sufficiently high

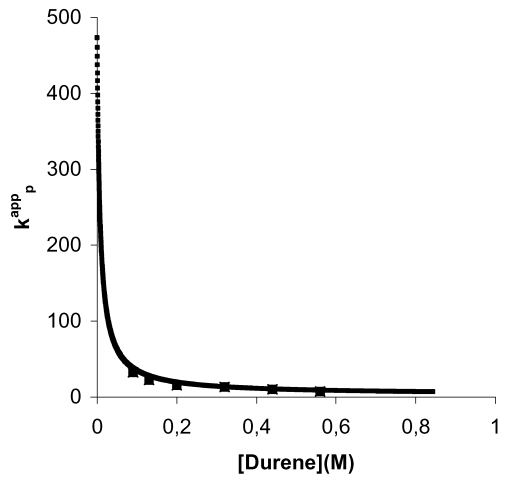

Fig. 7. Simulation of Plot of k_p^{app} vs. [durene] with determined values of $K_D = 2.0 \times 10^{-7}$ M, $K_{S1} = 140$ M^{-1}, $K_{S2} = 1$ M^{-1}, $k_p = 480$ M^{-1} × min^{-1}, $k_{p1} = 6.7$ M^{-1} min^{-1}, and $k_{p2} = 3$ M^{-1} min^{-1}.

concentrations of durene, which in actual practice cannot be reached for solubility reasons of durene, a common line will result for the two concentrations of PStLi when all the dimeric species are dissociated and complexed. The reaction will then be first order in PStLi. The calculation results show that this point is reached at about [durene] = 2.5 M. Considering the fact that the maximum solubility of durene in cyclohexane is around 1.2 M, the reaction order will never be entirely unity within all the investigated concentrations of durene. The influence of σ-complexing agents such as THF and dioxane on the anionic polymerization of styrene with lithium as a counter ion in benzene was investigated and a similar point was found at [THF] = 0.015 M [6] and [dioxane] = 0.05 M [8].

On the other hand, with the determined values of K_D, K_{S_1}, K_{S_2}, k_p, k_{p_1}, k_{p_2}, the mole fraction of the four ionic species involved in the presence of durene can be calculated, as shown in Fig. 8. The concentration of PStLi dimeric aggregates decreases gradually and the PStLi decreases slightly. The concentration of PStLi·D first increases, then passing through a maximum, then decreases with the further addition of durene. The concentration of PStLi·2D increases gradually.

4. Conclusions

The efficient dissociating ability of the π-complexing agent, durene, is qualitatively found by the fact that the increase of the initial concentration of durene increases the observed propagation rate constant, which passes through a maximum and then decreases with the further addition of durene. It is explained by the coexistence of PStLi dimer and three reactive monomeric species.

The propagation reaction in anionic polymerization of styrene in cyclohexane with lithium as a counterion has been investigated for six different concentrations of durene in the range of an active-center concentration between 10^{-3} and 10^{-5} M at 20 °C. Within the investigated concentrations of durene, the plot of log k_{obs} vs. log C^* is curved, indicating

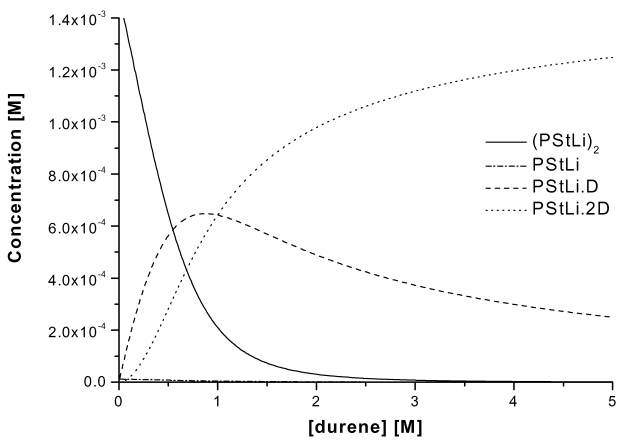

Fig. 8. Calculated concentration of ionic species involved in the presence of durene.

a change in the order with respect to the living ends concentration of PStLi. The reaction order with respect to the active centers is found in all cases to be greater than 0.5, which is attributed to the increasing dissociation of the PStLi dimeric species into the monomeric species. The exact fraction of monomeric species is quantitatively calculated and increases with increasing amount of durene. Further investigation shows that there are three reactive monomeric species, PStLi, PStLi·D, PStLi·2D in the presence of durene. A recently developed linear analytical method was used to determine the weighted rate constants of all unassociated species and the apparent dissociation constants of PStLi dimers. In comparison with the situation in pure cyclohexane, the apparent dissociation constant increases while the weighted rate constant decreases with increasing concentrations of durene. Based upon the extensive kinetic study a new mechanism was proposed and the values of the absolute propagation rate constant of each monomeric species involved is derived. The absolute propagation rate constant of PStLi·D and PStLi·D_2 are much lower than that of PStLi. The complexation constant of PStLi with one molecule of durene is more than 100 times higher than that of PStLi with a second molecule of durene. The excellent agreement of the simulated curves with the original data supports the proposed mechanism and the validity of the values of the absolute propagation rate constants of the monomeric species as well as the complexation constants of PStLi with durene.

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Appendix A

In the presence of durene, the total concentration of PStLi is the sum of associated dimeric species and three reactive monomeric species, that is, PStLi, PStLi·D, PStLi·2D.

$$2[(\mathrm{PStLi})_2] + [\mathrm{PStLi}] + [\mathrm{PStLi{\cdot}D}] + [\mathrm{PStLi{\cdot}2D}] = C^* \quad (10)$$

According to Scheme 1,

$$K_{S_2} = \frac{[\mathrm{PStLi{\cdot}2D}]}{[\mathrm{PStLi{\cdot}D}][\mathrm{D}]}$$

and putting $[\mathrm{PstLi{\cdot}2D}] = B$ yields:

$$[\mathrm{PStLi{\cdot}D}] = \frac{B}{K_{S_2}[\mathrm{D}]} \quad (11)$$

On the other hand:

$$K_{S_1} = \frac{[\mathrm{PStLi{\cdot}D}]}{[\mathrm{PStLi}][\mathrm{D}]},$$

which after rearranging gives:

$$[\mathrm{PStLi}] = \frac{B}{K_{S_1}K_{S_2}[\mathrm{D}]^2} \quad (12)$$

$$\text{Since } K_D = \frac{[\mathrm{PStLi}]^2}{[(\mathrm{PStLi})_2]},$$

we obtain:

$$[(\mathrm{PStLi})_2] = \frac{B^2}{K_D K_{S_1}^2 K_{S_2}^2[\mathrm{D}]^4} \quad (13)$$

Thus, Eq. (10) can be changed to below from Eqs. (11)–(13):

$$\frac{2B^2}{K_D K_{S_1}^2 K_{S_2}^2[\mathrm{D}]^4} + \frac{B}{K_{S_1}K_{S_2}[\mathrm{D}]^2} + \frac{B}{K_{S_2}[\mathrm{D}]} + B = C^*$$

and after rearranging:

$$\frac{2B^2}{K_D K_{S_1}^2 K_{S_2}^2[\mathrm{D}]^4} + \left(\frac{1}{K_{S_1}K_{S_2}[\mathrm{D}]^2} + \frac{1}{K_{S_2}[\mathrm{D}]} + 1\right)B - C^* = 0 \quad (14)$$

Since the values of K_D, K_{S_1}, K_{S_2} are known, the solution of B can be numerically solved.

On the other hand:

$$-\frac{\mathrm{d}\ln[\mathrm{M}]}{\mathrm{d}t} = k_{obs} = \frac{k_p B}{K_{S_1}K_{S_2}[\mathrm{D}]^2} + \frac{k_{p_1}B}{K_{S_2}[\mathrm{D}]} + k_{p_2}B \quad (15)$$

Since the value of B can be determined for all investigated concentrations of durene at a certain concentration of PStLi, the simulated line of plot of k_{obs}/C^* vs. k_{obs} can be obtained.

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