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Influence of π-complexing agents on the anionic polymerization of styrene with lithium as counterion in cyclohexane. 3. Effect of tetraphenylethylene

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Abstract

The propagation reaction in anionic polymerization of styrene with lithium as counterion in cyclohexane has been investigated for four different concentrations of tetraphenylethylene (TPhE) in the range of living end concentrations 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 four investigated concentrations of TPhE. The mechanism, already used in the case of durene, was also applied in this system and the values of the relevant absolute propagation rate constants of the two reactive monomeric species have been derived from the kinetic results. The absolute propagation rate constant of PStLi·TPhE is much lower than that of PStLi. The complexation constant of PStLi with one molecule of TPhE is more than 100 times larger than that of PStLi with one molecule of durene.

Keywords: Anionic polymerization; Kinetics and mechanism; Tetraphenylethylene

1. Introduction

The kinetics of anionic polymerization of styrene with lithium as a counter ion has been studied in a number of non-polar solvents, including benzene [1], toluene [2], cyclohexane [3]. In all these cases, a kinetic order of 0.5 with respect to the living end concentration of polystyryllithium (PStLi) has been found for the apparent polymerization rate constants. This behavior has been unambiguously attributed to the coexistence of dimeric associates, $(PStLi)_2$, with a small fraction of monomeric species, PStLi, only the latter being able to propagate [4–6]. The equilibrium between the dimeric and monomeric living chain ends is shifted towards monomeric species in the presence of different agents capable of complex formation with PStLi. Until now, four series of complexing agents have been investigated, including inorganic salt such as metal alkoxide [7,8] (μ-type), THF [9], dioxane [10], *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (TMEDA) [11], tetramethyltetraazacyclotetradecan (TMTCT) [12] (σ-type), polyether metal alkoxides [13–15], lithium aminoalkoxides [16] (μ-σ type), 1,2,4,5-tetramethylbenzene (durene) [17], tetraphenylethylene (TPhE) (π-type).

In an earlier paper [17], the influence of durene, one of the π-type additives, on the anionic polymerization of styrene was studied. In this work, the effect of TPhE on the propagation rate of PStLi in cyclohexane at 20 °C was investigated in detail.

2. Experimental section

All the purifications were carried out under high vacuum.

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Styrene was dried by distillation from CaH_2 (2×) and distilled over oligomeric lithium polystyrene. Sec-BuLi was purified by a short-path vacuum distillation. Cyclohexane was refluxed with Na–K alloy, then stirred and degassed on the vacuum line, finally distilled over oligomeric lithium polystyrene. TPhE was firstly recrystallized from ethanol, then vacuum-sublimed and finally further dried on the high vacuum line.

Oligomeric lithium polystyrene used at the start of the reaction was obtained by the initiation of styrene with sec-BuLi in cyclohexane, and its measured molecular weight is 5000. The initial monomer concentration was such that for the lowest concentration of active centers the molecular weight after reaction was around 50,000 to 60,000. The kinetics of the propagation reaction was determined by following the disappearance of styrene spectrophotometrically at 291 nm on a Cary 2200 at 20 °C.

Quantum-chemical calculations of equilibrium structures and energies of TPhE complexes with the model living chain end, 1-phenyl-ethyllithium (HStLi), were performed using the DFT approach [18] implemented into the TURBOMOLE package [19] of ab initio quantum-chemical programs. BP86 set of potentials, consisting of Becke's exchange potential [20] and Perdew's correlation potential [21], was used with TURBOMOLE split valence plus polarization (SVP) basis sets [22] of 6-31G* quality. Detailed description of calculation methods is published in Part 2 of this series [23].

3. Results and discussion

Fig. 1 shows the effect of TPhE on the observed propagation rate of PStLi in cyclohexane at two nearly constant total living end concentrations, $C^* = 5.4\times10^{-4}$ M and $C^* = 2.5\times10^{-3}$ M.

At $C^* = 5.4\times10^{-4}$ M, the k_{obs}/C^* value decreases monotonically with increasing concentration of TPhE. At $C^* = 2.5\times10^{-3}$ M, it increases initially, passes through a maximum, and then decreases with increasing concentration of TPhE. A similar behavior has been found in the presence of durene (D) as the π-donor and it has been explained by the existence of three types of reactive species, PStLi, PStLi·D, and PStLi·2D [17]. However, extensive kinetic results and quantum chemical calculations seem to indicate that in the presence of TPhE, the observed non-monotonic dependence of k_{obs}/C^* on $[TPhE]_0$ is due to only two reactive monomeric species, as shown in Scheme 1.

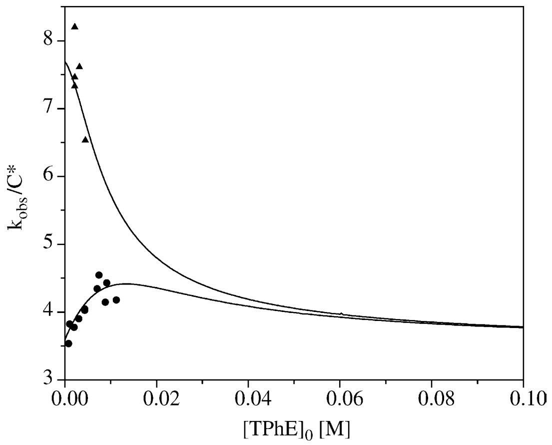

Fig. 1. The effect of TPhE on the propagation rate of PStLi in cyclohexane at 20 °C. (▲), $C^*=0.54$ mM; (●), $C^*=2.5$ mM; Solid line: calculated curve (the detailed procedures are shown in Appendix A).

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

$$PStLi + TPhE \overset{Ks_1}{\rightleftharpoons} PStLi\cdot TPhE$$

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

$$PStLi\cdot TPhE + Sty \xrightarrow{kp_1} (PSt)StyLi\cdot TPhE$$

Scheme 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.

In the presence of TPhE, the dissociative mechanism still holds, as shown in Scheme 2.

(K_D^{app} is the apparent dissociation constant of the PStLi dimers and k_p^{app} is the weighted rate constant of all non-associated species in the presence of TPhE analogous to the constants K_D and k_p in pure cyclohexane).

If only two monomeric species, PStLi and PStLi·TPhE, are involved into propagation reaction k_p^{app} can be defined as:

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

where

$$\alpha = \frac{[PStLi\cdot TPhE]}{[PStLi] + [PStLi\cdot TPhE]} \tag{2}$$

Taking into account that

$$[PStLi\cdot TPhE] = K_{S_1}[PStLi][TPhE] \tag{3}$$

k_p^{app} is determined from Eqs. (1)–(3) by the following Eqs.:

$$k_p^{app} = \frac{k_p + K_{S_1}[TPhE]k_{p_1}}{1 + K_{S_1}[TPhE]} \tag{4}$$

On the other hand,

$$K_D^{app} = \frac{([PStLi] + [PStLi\cdot TPhE])^2}{[(PStLi)_2]} \tag{5}$$

Combining Eqs. (3) and (5), one can derive:

$$\sqrt{K_D^{app}} = \sqrt{K_D}(1 + K_{S_1}[TPhE]) \tag{6}$$