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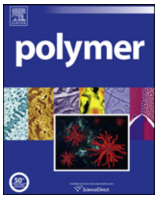

Kinetic study of the initiation reaction by a dilithium initiator used for the preparation of ABA triblock copolymers in non-polar medium

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ABSTRACT

The kinetics of the reaction of the bifunctional lithium initiator, Li-DIB-Li, with DPE was studied. It was shown that the kinetic order of this reaction with respect to the reactive ends of the dilithium initiator is close to zero, indicating a rather high degree of aggregation of the dilithium initiator. Possible structures of these highly aggregated species are illustrated by DFT quantum-chemical calculations and their relative stabilities are analyzed. It is concluded that the solubilization through breaking up of long intermolecular aggregates of dilithium initiator chains into small soluble ones by complexation with durene is certainly as important or more than the dissociation of the active centers of the dilithium initiator, as originally thought.

1. Introduction

In the past we reported on the complexing capacity of π-donating agents, such as durene, for Li^+-cations of organolithium compounds in non-polar medium [1–4] and its beneficial use for the initiation of dienes by dilithium initiators in non-polar medium (cyclohexane) for the preparation of well characterized triblock copolymers of the type styrene-butadiene-styrene (SBS) with high 1,4-structure in the difunctionally growing diene block [5].

Indeed, the synthesis of triblock copolymers SBS with high 1,4- and low 1,2-units content in the diene block has been the subject of a lot of research as they lead to good elastomeric properties [6]. This can in general be obtained by carrying out the polymerization in non-polar medium. However, the dilithium initiators used for their synthesis are rather insoluble in this non-polar medium, probably because of aggregation of the living ends. Therefore, polar σ-additives are usually added to disrupt this aggregation, but their addition raises the problem of the unfavorable increase of 1,2-units in the diene block.

We demonstrated in our laboratory that some rather non-polar additives, having π-donor properties, can lead to soluble dilithium initiators, when added in sufficient amounts. Thus it was shown that with a dilithium initiator, prepared by the reaction of *t*-BuLi with *m*-diisopropenylbenzene, in the presence of durene well characterized SBS-triblock copolymers could be obtained, whose diene block had a 1,4-content as high as those prepared in pure non-polar medium [5]. An in depth kinetic study of the initiation of butadiene by the dilithium initiator in the presence of durene (1,2,4,5-tetramethylbenzene), presented here, leads to the completion of this research in our laboratory.

2. Experimental section

2.1. Chemicals

The reagents are purified in a similar way as described in our previous papers [1, 2]. All the purifications were carried out under high vacuum. 1,1-diphenylethylene is a liquid with a very high boiling point (270–271 °C). It was therefore dried once on CaH_2 and subsequently distilled onto a K mirror under high vacuum, until a yellow color develops, typical of the DPE^-K^+ salt, and divided by distilling into graduated ampoules.

2.2. Synthesis of the dilithium initiator

1,3-diisopropenylbenzene (DIB) was reacted in cyclohexane with a twofold excess of *t*-BuLi, which was shown by Yu et al. [7] to be more effective than *s*-BuLi for the synthesis of a dilithium initiator (Li-DIB-Li) in the presence of durene.

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2.3. Kinetic measurements

Since the initiation of butadiene with the dilithium initiator was much too fast to be followed spectroscopically, the kinetics of the reaction with the dilithium initiator in the presence of durene were studied for its reaction with 1,1-diphenylethylene (DPE). The advantage of using DPE as a monomer instead of butadiene consists in its strong steric hindrance, such that after its initiation, it will not polymerize any further. In other words, it is possible to follow the initiation by the dilithium initiator spectroscopically without having to take a possibly occurring propagation into account. On top of that, whereas the absorption maximum of polybutadienyllithium (PButLi) in cyclohexane formed through the addition of the organolithium initiator is covered by the absorbance of durene and that the initiation can therefore only be followed by the disappearance of the slightly yellow colored dilithium initiator, the Li-salt of the carbanion of DPE is characterized by a strong absorption maximum at 440 nm permitting the spectral assessment of the increase in concentration of this salt during the initiation.

The measurements were carried out at a durene concentration of 0.8 M and at a constant concentration of DPE with varying concentrations of dilithium initiator at 20 °C. The initial concentration of DPE at the various measurements was lower than 10^{-4} M such that the dilithium initiator was always present in excess [8]. By monitoring the increase in absorption at 440 nm until a maximum absorption value is obtained, a plot is obtained as shown in Fig. 1, from which the apparent rate constant of initiation of DPE by the bifunctional initiatior can be determined.

The concentration of 0.8 M of durene was chosen to have the highest possible rate based on our earlier data [2] on the influence of durene on the anionic polymerization of styrene in cyclohexane with Li^+ as a counterion. The limit of solubility of durene is cyclohexane is 1.2 M but it was found [2] that at this concentration the rate diminished again. Therefore, 0.8 M of durene was chosen throughout this paper.

The reaction of the dilithium initiator with DPE is a bimolecular reaction. Therefore, and since the monomer is not going to polymerize any further, the dilithium initiator is used in excess, so that the change of its concentration, even when DPE is reacted to 100% conversion, may be neglected, resulting in a first-order reaction. Besides, when the DPE reacts with the Li-DIB-Li, an ion-pair is formed which might give rise to cross-association with the Li-DIB-Li and influence the kinetics. However, when the Li-DIB-Li is in excess, such cross-association may be neglected.

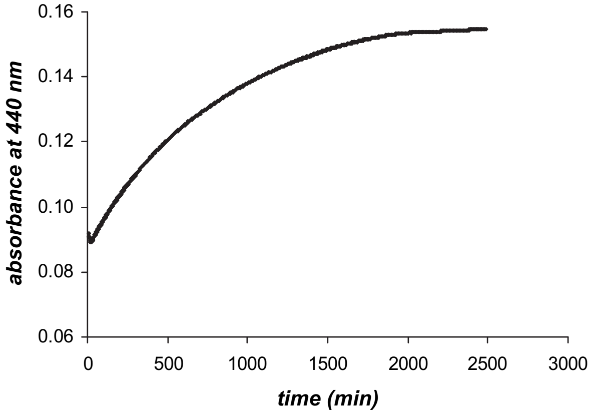

Fig. 1. Change in absorbance at 440 nm as a function of time at 20 °C in cyclohexane [Li-DIB-Li] = 0.56 10^{-3} M, [DPE] = 1.07 10^{-4} M and 0.8 M durene.

The rate constants of butadiene polymerization by PButLi were determined by measuring the decrease of butadiene concentration through the observation of the absorbance at 236.5 nm (located outside the absorption of durene) at different times. Plotting the $\ln(A_{obs} - A_\infty)$ in which A_{obs} is the absorbance observed at each time and A_∞ is the absorbance at the end of the reaction (when all the butadiene has been consumed) as a function of time gives a straight line, the slope of which is equal to the apparent propagation rate constant k_p^{app}.

The initial concentration of butadiene was about 10–20 times the concentration of the initiator or the initiating species (as the order with respect to monomer in anionic polymerizations is almost always one, it is not necessary to exactly determine the initial monomer concentration). As for the concentration of polybutadienyllithium (which remains constant during the reaction), this was determined at the end of the reaction by adding a small amount of THF, shifting the absorption maximum of polybutadienyllithium (originally covered by the absorption of durene) to 320 nm, i.e. next to the absorption of durene.

2.4. Quantum-chemical calculations

All quantum-chemical calculations of the Li-DIB-Li aggregates and their complexes with durene (D) were performed using the density functional theory (DFT) approach [9] implemented into the TURBOMOLE package [10] of *ab initio* quantum-chemical programs. The geometries of all structures studied were completely optimized with the convergence criteria of 10^{-8} Hartree for total energy and 10^{-4} Hartree/(Bohr or radian) for the largest component of the total energy gradient.

For the DFT geometry optimizations, Becke's exchange potential [11] and Perdew's correlation potential [12] were used. This set of DFT-potentials, hereafter referred to as BP86, was used in the "resolved identity" (RI) formalism [13–15] to avoid the *calculations* of all four-centered two-electron integrals. TURBOMOLE split valence plus polarization (SVP) basis sets [16] of 6-31G* quality were employed. For the fitting of the Coulomb potential within the RI formalism, Ahlrichs' auxiliary basis sets [14, 17] have been used. The details about contraction schemes and polarization function exponents for each element is described elsewhere [18].

For all optimized structures of the type $(\text{Li-DIB-Li})_n(\text{D})_x$, vibrational frequencies, zero-point energy corrections and entropic contributions and free energies (at 300 K) were calculated. For these structures, average energies, $\overline{E}$, and free energies, $\overline{G}$, per one Li-DIB-Li molecule were calculated as:

$$\overline{E}\left[(\text{Li-DIB-Li})_n(\text{D})_x\right] = \left\{E\left[(\text{Li-DIB-Li})_n(\text{D})_x\right] - x \cdot E(\text{D})\right\}/n \qquad (1)$$

$$\overline{G}\left[(\text{Li-DIB-Li})_n(\text{D})_x\right] = \left\{G\left[(\text{Li-DIB-Li})_n(\text{D})_x\right] - x \cdot G(\text{D})\right\}/n \qquad (2)$$

where $E[(\text{Li-DIB-Li})_n(\text{D})_x]$ and $G[(\text{Li-DIB-Li})_n(\text{D})_x]$ denote the minimized total energy and calculated free energy, respectively, for the particular structure. $E(\text{D})$ and $G(\text{D})$ are, respectively, minimized total energy and calculated free energy of the isolated durene molecule. Relative stabilities of different structures are characterized by their $\Delta\overline{E}$ and $\Delta\overline{G}$ values with respect to the most stable structure for which $\Delta\overline{E} = \Delta\overline{G} = 0$.

3. Results and discussion

3.1. Kinetics of the reaction of Li-DIB-Li with DPE

Fig. 1 presents the observed time dependence of the concentration of the DPE^-Li^+ salt forming in the reaction of Li-DIB-Li with DPE, being monitored by the absorption at 440 nm.

Taking into account that the two carbanionic sites of Li-DIB-Li can both react with DPE, we can write for the reaction rate:

$$R_{\mathrm{i}} = -\frac{d[\mathrm{DPE}]}{dt} = k_{\mathrm{i}}[\mathrm{DPE}]\ [\mathrm{DIB\text{-}Li}] \tag{3}$$

where [DIB-Li]=2[Li-DIB-Li].

If it is assumed that even in the presence of durene, the concentration of non-associated ion-pairs is small compared to that of all living ion-pairs, one can write:

$$\left[(\mathrm{Li\text{-}DIB\text{-}Li})_n\right] = \frac{[\mathrm{DIB\text{-}Li}]_{\mathrm{form}}}{2n} \tag{4}$$

where$[\mathrm{DIB\text{-}LI}]_{\mathrm{form}}$ represents the formal concentration of the dilithium initiator.

With the following expression for the equilibrium dissociation constant of Li-DIB-Li aggregates,

$$K_{\mathrm{diss}} = \frac{[\mathrm{Li\text{-}DIB\text{-}Li}]^n}{\left[(\mathrm{Li\text{-}DIB\text{-}Li})_n\right]} \tag{5}$$

Eq. (3) can be rewritten as

$$-\frac{d[\mathrm{DPE}]}{dt} = k_{\mathrm{i}}^{\mathrm{app}}[\mathrm{DPE}] \tag{6}$$

with the apparent rate constant

$$k_{\mathrm{i}}^{\mathrm{app}} = 2k_{\mathrm{i}}\left(\frac{K_{\mathrm{diss}}}{2n}\right)^{1/n}[\mathrm{DIB\text{-}Li}]_{\mathrm{form}}^{1/n} \tag{7}$$

A pseudo-first-order reaction with respect to [DPE] is thus obtained since the concentration of carbanionic centers is taken in excess with respect to [DPE] and can, therefore, be considered to be constant. In other words,

$$\int_{[\mathrm{DPE}]_0}^{[\mathrm{DPE}]_t} \frac{d[\mathrm{DPE}]}{[\mathrm{DPE}]} = -k_{\mathrm{i}}^{\mathrm{app}}\int_0^t dt$$

and

$$[\ln[\mathrm{DPE}]\,]_0^t = -k_{\mathrm{i}}^{\mathrm{app}}t \tag{8}$$

The equation of mass balance for DPE is

$$[\mathrm{DPE}]_t = [\mathrm{DPE\text{-}Li}]_\infty - [\mathrm{DPE\text{-}Li}]_t \tag{9}$$

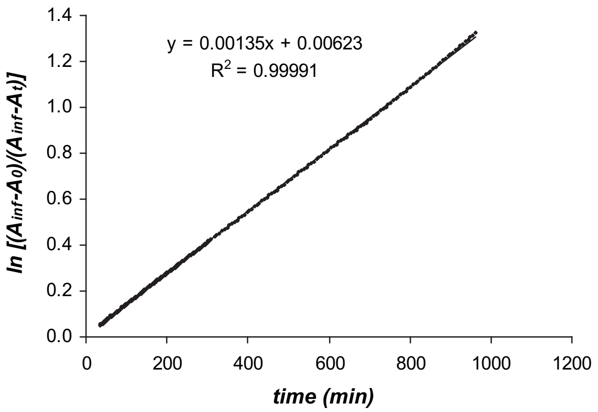

Fig. 2. $\ln[A_\infty - A_0/A_\infty - A_t]$ as a function of time for the determination of $k_{\mathrm{i}}^{\mathrm{app}}$ in cyclohexane at 20 °C, [Li-DIB-Li] = 0.56 10^{-3} M, [DPE] = 1.07 10^{-4} and 0.8 M durene.

Table 1
Kinetic experiments and $k_{\mathrm{i}}^{\mathrm{app}}$ values for the initiation of DPE with the bifunctional Li-DIB-Li initiator in cyclohexane with 0.8 M of durene at 20 °C.

[DIB-Li] (mol L^{-1})	$k_{\mathrm{i}}^{\mathrm{app}}$ ($\min^{-1}$)
$2.13\cdot10^{-4}$	$1.14\cdot10^{-3}$
$2.23\cdot10^{-4}$	$1.25\cdot10^{-3}$
$3.90\cdot10^{-4}$	$0.86\cdot10^{-3}$
$6.70\cdot10^{-4}$	$0.90\cdot10^{-3}$
$1.12\cdot10^{-3}$	$1.35\cdot10^{-3}$
$1.20\cdot10^{-3}$	$1.32\cdot10^{-3}$
$1.86\cdot10^{-3}$	$0.95\cdot10^{-3}$

where [DPE-Li] is proportional to the absorbance, A, at 440 nm. Then Eq. (8) can be rewritten as

$$\ln\left[\frac{A_\infty - A_0}{A_\infty - A_t}\right] = k_{\mathrm{i}}^{\mathrm{app}}t \tag{10}$$

Plotting $\ln[A_\infty - A_0/A_\infty - A_t]$ as a function of time will then yield a straight line, whose slope will be equal to the apparent rate constant of initiation of DPE by Li-DIB-Li. This is graphically illustrated in Fig. 2 and the respective values of $k_{\mathrm{i}}^{\mathrm{app}}$ are given in Table 1.

The values of $k_{\mathrm{i}}^{\mathrm{app}}$ are seen to change only slightly with the concentration of living initiator chain ends. When graphically plotted as in Fig. 3, an order with respect to the dilithium initiator close to zero seems therefore to be obtained.

This almost zero order with respect to the dilithium initiator thus indicates that the n value is rather large and $1/n$ is, therefore, small. Since in the absence of durene the dilithium initiator is rather insoluble in cyclohexane, this seems to be due to a strong association of the Li-DIB-Li molecules to insoluble associates. This is illustrated by DFT calculations presenting possible $(\mathrm{Li\text{-}DIB\text{-}Li})_n(\mathrm{D})_x$ structures (Figs. 4–7).

In the absence of durene, lithium ions tend to be hidden within $(\mathrm{Li\text{-}DIB\text{-}Li})_n$ clusters as shown for $n = 2$ (Fig. 5) and $n = 4$ (Fig. 7). It is seen from Table 2 that the $(\mathrm{Li\text{-}DIB\text{-}Li})_4$ cluster is the most stable among the studied structures. It is clear that rather long similarly arranged chain-like clusters could form. In the present paper, $(\mathrm{Li\text{-}DIB\text{-}Li})_n$ structures with $n > 4$ were not calculated due to computational limitations.

The data presented in Table 2 also show that the $\Delta\overline{E}$ and $\Delta\overline{G}$ values for the $(\mathrm{Li\text{-}DIB\text{-}Li})_n(\mathrm{D})_2$ clusters are lower for $n = 2$ (Fig. 4) than for $n = 1$ (Fig. 6), being in the case $n = 2$ not very high. Therefore, it may be concluded that durene induces a fragmentation of long $(\mathrm{Li\text{-}DIB\text{-}Li})_n$ chains into shorter ones, “extracting” terminal lithium ions of a shorter cluster out of its interior and forming complexes with these terminal lithium ions. This is in accordance with the above presented experimental data on the

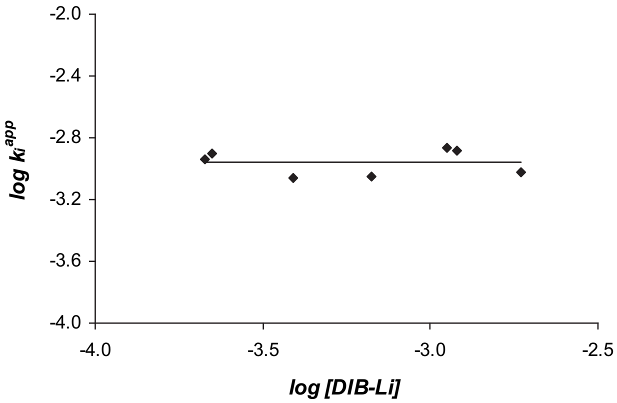

Fig. 3. log $k_{\mathrm{i}}^{\mathrm{app}}$ for the initiation of DPE with Li-DID-Li as a function of log [DIB-Li] in cyclohexane with 0.8 M durene at 20 °C.

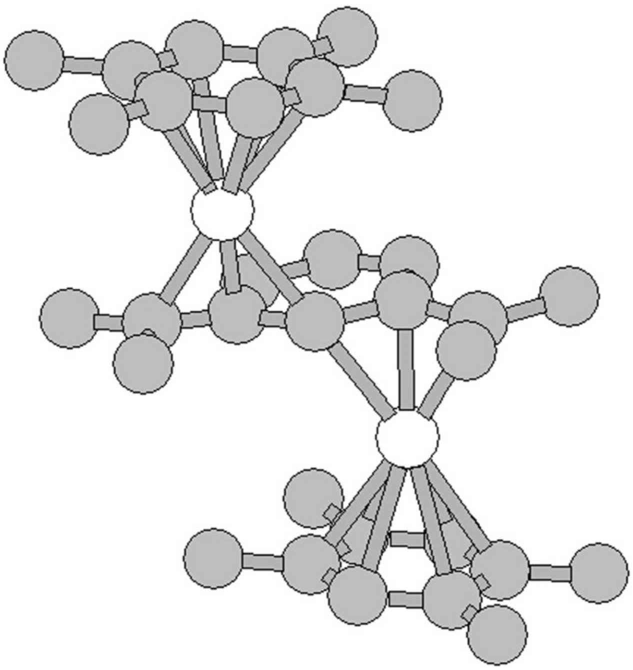

Fig. 4. DFT optimized structure $(Li\text{-}DIB\text{-}Li)_1(D)_2$. Carbon and lithium atoms are shown by grey and white circles, respectively. Hydrogen atoms are not shown for clarity.

solubilization of the bifunctional initiator Li-DIB-Li by durene. It should be noted that the $(Li\text{-}DIB\text{-}Li)_n(D)_2$ clusters "end-capped" with durene molecules can, of course, have $n > 2$, but such systems were beyond the computational limitations. However, it is clear that this terminal solvation by durene limits the aggregation degree to some extent and increases the solubility of the dilithium initiator.

3.2. Reaction of α-methylstyryllithium with DPE

It seems that not just the dissociation into unassociated ion-pairs, as observed for PStyLi [2], but also the solubilization of the dilithium initiator by complexation with durene appears to be an important step in the synthesis of triblock copolymers in non-polar medium. This hypothesis was checked by reacting DPE with monofunctional α-methylstyryllithium (α-MeStyLi) in the presence of durene (α-MeStyLi was prepared through reaction of α-methylstyrene with t-BuLi at 40 °C, its formation being monitored spectroscopically by absorption maximum at 312 nm with molar extinction coefficient $\epsilon = 14000\ \mathrm{L\,mol^{-1}\,cm^{-1}}$).

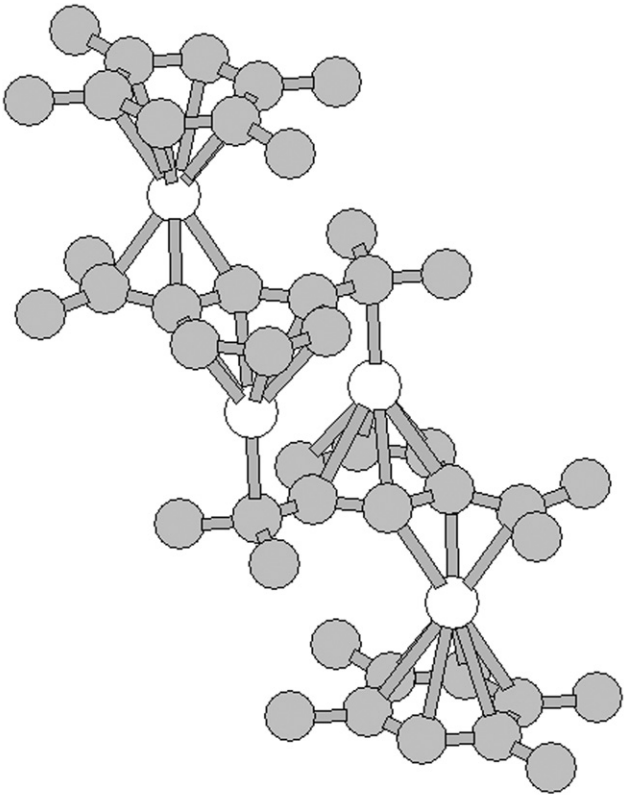

Fig. 6. DFT optimized structure $(Li\text{-}DIB\text{-}Li)_2(D)_2$. Carbon and lithium atoms are shown by grey and white circles, respectively. Hydrogen atoms are not shown for clarity.

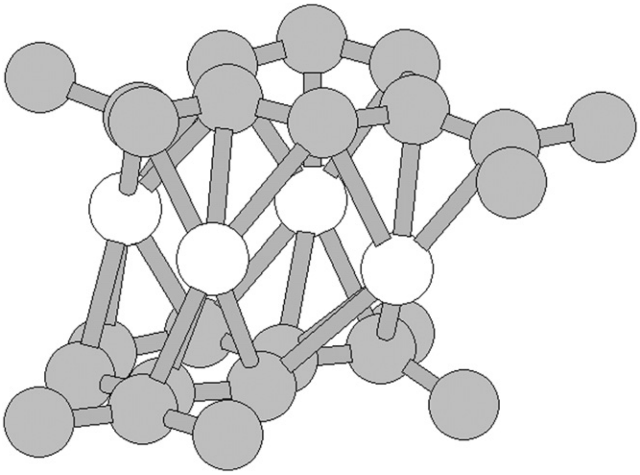

Fig. 5. DFT optimized structure $(Li\text{-}DIB\text{-}Li)_2$. Carbon and lithium atoms are shown by grey and white circles, respectively. Hydrogen atoms are not shown for clarity.

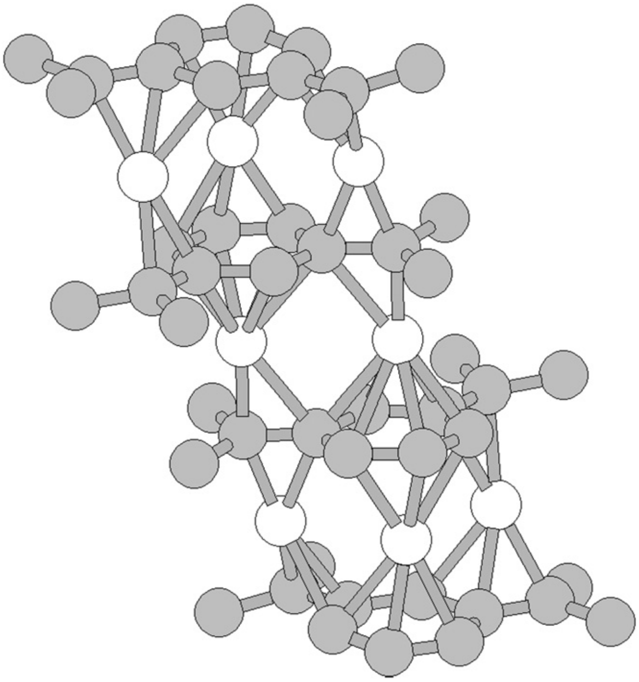

Fig. 7. DFT optimized structure $(Li\text{-}DIB\text{-}Li)_4$. Carbon and lithium atoms are shown by grey and white circles, respectively. Hydrogen atoms are not shown for clarity.

Table 2

Calculated total energies, E, combined zero-point energies, $G-E$, average total energies, $\overline{E}$, and free energies, $\overline{G}$, per one Li-DIB-Li molecule, and relative total energies, $\Delta\overline{E}$ (Eq. (1)), and free energies, $\Delta\overline{G}$ (Eq. (2)), for the considered structures $(\text{Li-DIB-Li})_n(\text{D})_x$.

Structure	Symmetry	E, Hartree	$G-E$ (300 K), kcal/mol	$\overline{E}$, Hartree	$\overline{G}-\overline{E}$ (300 K), kcal/mol, per one Li-DIB-Li	$\Delta\overline{E}$, kcal/mol	$\Delta\overline{G}$, kcal/mol
Durene	C_{2h}	−389.2134479692	92.8	–	–	–	–
$(\text{Li-DIB-Li})_1(\text{D})_2$ (Fig. 4)	C_2	−1260.023695457	315.6	−481.5967995186	130.0	11.5	24.2
$(\text{Li-DIB-Li})_2$ (Fig. 5)	C_2	−963.2158241366	229.1	−481.6079120683	114.6	4.5	1.8
$(\text{Li-DIB-Li})_2(\text{D})_2$ (Fig. 6)	C_i	−1741.653879038	431.6	−481.6134915498	123.0	1.0	6.7
$(\text{Li-DIB-Li})_4$ (Fig. 7)	C_i	−1926.460337612	469.1	−481.615084403	117.3	0	0

In order to check the association of α-MeStyLi in the presence of durene, the order with respect to α-MeStyLi was examined in its reaction with DPE in the presence of 0.8 M durene at 40 °C.

In analogy with the equations written for the anionic propagation of styrene with PStyLi in cyclohexane and benzene [1], the equation for the initiation of DPE by α-MeStyLi can be written as

$$R_\text{i} = k_\text{i}\left(\frac{K_\text{d}}{n}[\alpha\text{-MeStyLi}]\right)^{1/n}[\text{DPE}] \tag{11}$$

with

$$\log k_\text{i} = \log\left[k_\text{i}\left(\frac{K_\text{d}}{n}\right)^{1/n}\right] + \frac{1}{n}\log\,[\alpha\text{-MeStyLi}]_\text{form} \tag{12}$$

The pertinent data are given in Table 3 and graphically represented in Fig. 8.

From the slope of the straight line in Fig. 8 it can be derived that the order with respect to α-MeStyLi at a concentration of durene 0.8 M is for all practical purposes equal to ½. This indicates that, in contrast to PStyLi, α-MeStyLi is still almost completely associated to dimers, in the presence of 0.8 M durene, supporting the high association of the dilithium initiator at this durene concentration proposed in the explanation for the data in paragraph 3.1.

3.3. *Propagation of monofunctional polybutadienyllithium*

To complete the study of the synthesis of the well characterized triblock copolymers in non-polar medium, which could be synthesized using bifunctional dilithium initiators in the presence of durene and other π-donors with full conservation of the 1,4-units content in the diene block, in contrast with those made in the presence of more polar σ-additives, the kinetic study of propagation of monofunctional polybutadienyllithium (PButLi) in the presence of durene was carried out.

The anionic propagation of PButLi with butadiene in cyclohexane without any additive is known to proceed with PButLi mainly present in tetrameric form. In analogy with the propagation of PStyLi with styrene in non-polar medium as described above, the polymerization rate could be presented as

Table 3

Kinetic experiments and k_i^app values for the initiation of DPE with monofunctional α-MeStyLi in cyclohexane with 0.8 M durene at 40 °C.

[α-MStyLi] (mol L^{-1})	k_i^app (min^{-1})
$1.02\cdot10^{-4}$	$2.38\cdot10^{-3}$
$1.77\cdot10^{-4}$	$1.72\cdot10^{-3}$
$1.97\cdot10^{-4}$	$2.12\cdot10^{-3}$
$4.56\cdot10^{-4}$	$1.87\cdot10^{-3}$
$9.24\cdot10^{-4}$	$5.87\cdot10^{-3}$
$1.58\cdot10^{-3}$	$7.86\cdot10^{-3}$
$1.78\cdot10^{-3}$	$5.49\cdot10^{-3}$

$$R_\text{p} = -\frac{d[\text{But}]}{dt} = k_\text{p}[\text{PButLi}]\ [\text{But}] \tag{13}$$

if it is assumed that only the non-associated ion-pairs are reactive and that the equilibrium dissociation constant

$$K_\text{D} = \frac{[\text{PButLi}]^4}{[(\text{PButLi})_4]} \tag{14}$$

Since the concentration of PButLi remains constant, Eq. (13) can be rewritten as:

$$-\frac{d[\text{But}]}{dt} = k_\text{p}^\text{app}[\text{But}] \tag{15}$$

with

$$k_\text{p}^\text{app} = k_\text{p}\left(\frac{K_\text{D}}{4}[\text{PButLi}]_\text{form}\right)^{1/4} \tag{16}$$

After integration of Eq. (16) one obtains for the apparent polymerization rate constant:

$$\log k_\text{p}^\text{app} = \log\left[k_\text{p}\left(\frac{K_\text{D}}{4}\right)^{1/4}\right] + \frac{1}{4}\log\,[\text{PButLi}]_\text{form} \tag{17}$$

Plotting $\log k_\text{p}^\text{app}$ as a function of $\log\,[\text{PButLi}]_\text{form}$, a straight line should be obtained with a slope equal to ¼, indicative of a degree of association equal to 4.

The pertinent data from the experimental measurements carried out in cyclohexane in the presence of 0.8 M of durene at 40 °C are given in Table 4 and graphically represented in Fig. 9.

It appears from Fig. 9 that in the presence of 0.8 M of durene in cyclohexane, the slope is not ¼, as in pure cyclohexane, but situated between ¼ and ½. The monofunctional PButLi appears, therefore, to be still aggregated to a mixture of tetramers and dimers in cyclohexane in the presence of 0.8 M of durene.

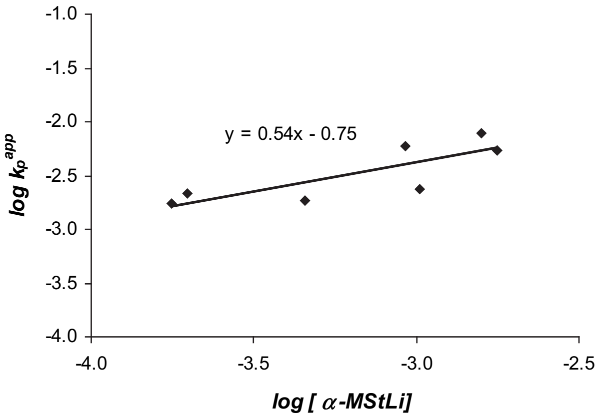

Fig. 8. $\log k_\text{i}^\text{app}$ for the reaction of α-MeStyLi with DPE as a function of log [α-MeStyLi] in cyclohexane with 0.8 M durene at 40 °C.

Table 4
Kinetic experiments and k_p^{app} values for the propagation of butadiene with monofunctional PButLi in cyclohexane with 0.8 M of durene at 40 °C.

[PButLi] (mol L^{-1})	k_p^{app} (min^{-1})
$3.67 \cdot 10^{-4}$	$0.75 \cdot 10^{-2}$
$7.65 \cdot 10^{-4}$	$1.07 \cdot 10^{-2}$
$9.40 \cdot 10^{-4}$	$1.15 \cdot 10^{-2}$
$2.28 \cdot 10^{-3}$	$1.57 \cdot 10^{-2}$
$3.04 \cdot 10^{-3}$	$1.58 \cdot 10^{-2}$

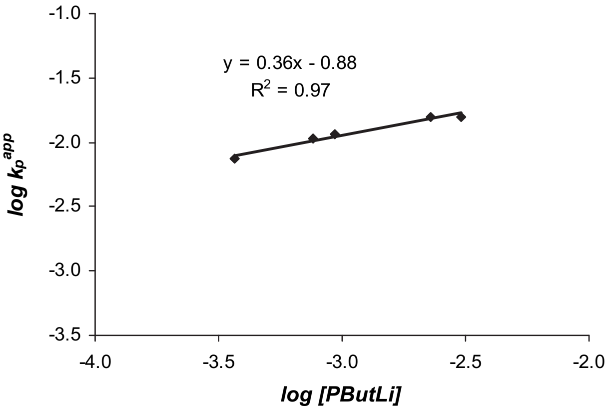

Fig. 9. log k_p^{app} for the reaction of monofunctional polybutadiene as a function of log [PButLi] in cyclohexane with 0.8 M durene at 40 °C.

4. Conclusion

The reaction of *m*-diisopropenylbenzene with twice the amount of t-butyllithium in non-polar medium such as cyclohexane, to produce a bifunctional Li-initiator as frequently used for the synthesis of SBS-triblock copolymers, results in the formation of a rather insoluble dilithium initiator in this non-polar medium probably because of intermolecular aggregation of the living ends. Since polar additives which are usually added to dissolve the initiator, raise the problem of the unfavorable increase of 1,2-units in the diene block, π-complexing agents such as 1,2,4,5-tetramethylbenzene (durene), which were shown previously to be able to break up significantly, although less than polar agents, the aggregation of polystyryllithium in cyclohexane, were used in our laboratory and permitted to obtain the bifunctional Li-initiator in a soluble form. On top of that in the presence of durene, well characterized SBS-triblock copolymers could be obtained in non-polar medium (cyclohexane) whose diene block had a 1,4-content as high as those prepared in pure non-polar medium.

To check whether the dilithium initiator is associated or not, the kinetics of the initiation with this initiator was studied. However, as the initiation of butadiene is very rapid with this initiator, another non-polar monomer, 1,1-diphenylethylene (DPE), was chosen. For this reaction, an order close to zero was found with respect to the reactive ends of the dilithium initiator, indicating a rather high degree of aggregation of the dilithium initiator. Possible structures of these highly aggregated species are illustrated by DFT quantum-chemical calculations.

To further corroborate this finding, the order of the reaction of a monofunctional model of the initiator, viz. the salt of the reaction product of *t*-BuLi and α-methylstyrene, with DPE was also investigated. The order of this reaction with respect to the α-methylstyryllithium ion-pairs was close to ½, indicating that the latter were still mostly associated to dimers in the presence of durene in contrast to those of PStyLi.

To complete this study, the homopolymerization of butadiene with *t*-BuLi as an initiator in the presence of durene was examined and the order of the propogation reaction with respect to butadienyllithium was between ¼ and ½. DFT calculations showed that durene solubilizes the dilithium initiator, breaking its long intermolecular aggregates into small soluble ones.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.polymer.2009.09.045.

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