Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 44 (2003) 6457–6463

polymer

www.elsevier.com/locate/polymer

Influence of π-complexing agents on the anionic polymerization of styrene with lithium as counterion in cyclohexane. 2. Quantum-chemical density functional theory calculations

Alexander Yakimansky[a,*], Guoming Wang[b], Kristof Janssens[b], Marcel Van Beylen[b,1]

[a]*Laboratory of thermostable polymers, Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi prospect 31, 199004 St. Petersburg, Russian Federation*
[b]*Laboratory of Macromolecular and Physical Organic Chemistry, Catholic University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium*

Received 6 May 2003; received in revised form 4 August 2003; accepted 5 August 2003

Abstract

For the interpretation of the effect of such π-donors as durene and tetraphenylethylene on the observed rate constant of the styrene anionic polymerization in cyclohexane, quantum-chemical DFT calculations of the structures and relative stabilities of the polymerization active sites, their dimeric associates and complexes with the π-donors were performed. It was shown that π-donors stabilize the propagating monomeric chain-ends, PStLi, facilitating the deaggregation of the $(PStLi)_2$ dimers. The calculations showed that the formation of the PStLi complexes with one and two durene molecules is possible. In agreement with the experimental kinetic data, it was shown that the higher is the number of durene molecules complexed to the active site, the lower are its ability to bind styrene and, thus, its propagating activity. Therefore, addition of π-donors initially leads to an increase in the observed polymerization rate constant due to active chain-ends being deaggregated. However, after a maximum, further addition of π-donors decreases the observed polymerization rate constant due to decreasing propagating ability of active sites complexed with π-donors.

Keywords: Styrene; Anionic polymerization; Durene

1. Introduction

It is well established that the polystyryllithium (PStLi) growing chains during the anionic polymerization of styrene in non-polar solvents are mostly associated into $(PStLi)_2$ dimers, being in an equilibrium with a low proportion of non-associated PStLi chains [1–4]. A kinetic order of 0.5 with respect to [PStLi] for the observed rate constants in benzene [1], toluene [5], and cyclohexane [6] is in agreement with the assumption that only monomeric PStLi ion-pairs are able to propagate.

Recently, such π-complexing agents as durene (1,2,4,5-tetramethylbenzene) (D) and tetraphenylethylene (TPhE) have been successfully employed for the syntheses of triblock SBS copolymers in non-polar solvents [7]. The π-donors effect on the anionic polymerization of styrene has been first investigated by O'Driscoll [8]. In the case of durene as the π-additive, the observed rate constant increases at low [D] values and further increase in [D] results in a decrease of rate [8].

In comparison with such σ-complexing additives as THF and dioxane, more durene is needed for the dissociation of PStLi aggregates in benzene solution. In cyclohexane, even higher amounts of durene is needed to result in the same effect as that observed in benzene [7].

If the polymerization proceeds in benzene with addition of THF [9] or dioxane [10], there is a very narrow range of σ-donor concentrations where the kinetic order with respect to [PStLi] changes from 0.5 to 1. Such a transition range of [D] values also exists when polymerization proceeds in cyclohexane in the presence of durene [11]. However, compared to THF or dioxane, π-donors are relatively weaker complexing agents and, therefore, the transition range is wider [11].

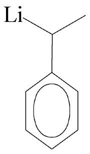
---

[*] Corresponding author. Tel.: +7-812-323-5025; fax: +7-812-328-6869.
E-mail addresses: yak@imc.macro.ru (A. Yakimansky), marcel.vanbeylen@chem.kuleuven.ac.be (M. Van Beylen).
[1] Tel.: +32-16-327-418/424; fax: +32-16-327-990.

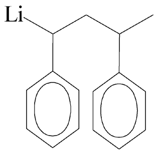
0032-3861/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0032-3861(03)00730-4

In order to explain the observed maximum on the [D]-dependence of the observed rate constant of the styrene polymerization in cyclohexane with addition of durene, we have suggested a new mechanism. It assumes the formation of new propagating species of differing activity, 1:1 and 2:1 complexes of the active centers with durene, that is, PStLi·D and PStLi·2D, in addition to the durene-free monomeric chain-end, PStLi, the three reactive species being in equilibrium with each other and with dimeric chain-end associates, $(PStLi)_2$ [11]. A detailed styrene polymerization kinetic study in cyclohexane at 20 °C for six different [D] allowed us to determine all the relevant equilibrium and propagation rate constants for all propagating species. With these values, the experimental [D]-dependence of the observed polymerization rate constant was reproduced with a reasonable precision [11].

The aim of the present paper was to determine the structure of different PStLi complexes with styrene (St) and/or π-additive (durene or TPhE) and to estimate their relative stability with respect to each other and to different additive-free forms of active sites. For this purpose, quantum-chemical DFT methods were employed. As the models of the PStLi chain-end, 1-phenyl-ethyllithium (HStLi) and 1,3-diphenyl-*n*-butyllithium (HSt_2Li) were used:



(HStLi)



(HSt_2Li)

2. Methods

All quantum-chemical calculations were performed using the DFT approach [12]. The geometries of all structures studied were completely optimized using the TURBOMOLE program [13] with the BP86 exchange-correlation potential [14,15] and TURBOMOLE split valence plus polarization (SVP) basis sets [16] of 6-31G* quality. The 'resolved identity' (RI) formalism [17–19] was used to avoid the calculations of all four-centered two-electron integrals. For the fitting of the Coulomb potential within the RI formalism, Ahlrichs' auxiliary basis sets [17, 20] have been used. The details about contraction schemes and polarization function exponents for each element are described elsewhere [21].

For all considered structures of the type $(HSt_mLi)_n(\pi\text{-donor})_x(St)_y$ ($m = 1, 2$; $n = 1, 2$; $x = 0, 1, 2$; $y = 0, 1$; π-donor is either D or TPhE), the values of the averaged energy per one active chain-end $\bar{E}[(HSt_mLi)_n(\pi\text{-donor})_x(St)_y]$, were calculated as a comparable stability parameter:

$$\bar{E}[(HSt_mLi)_n(\pi\text{-donor})_x(St)_y] = \frac{E[(HSt_mLi)_n(\pi\text{-donor})_x(St)_y] - xE(\pi\text{-donor}) - yE(St)}{n} \tag{1}$$

where $E[(HSt_mLi)_n(\pi\text{-donor})_x(St)_y]$ denotes the minimized total energy of the particular structure and $E(\pi\text{-donor})$ and $E(St)$ are minimized total energies of the isolated molecules of the given π-donor and styrene, respectively. The calculated E values for all structures are presented in Table 1. Relative stabilities of different structures are characterized by their $\Delta\bar{E}$ values with respect to the most stable structure for which $\Delta\bar{E} = 0$. The calculated $\Delta\bar{E}$ values for the studied complexes of the HStLi and HSt_2Li model active sites are given in Tables 2 and 3, respectively.

To estimate the effect of the basis set and DFT exchange-correlation potential, for all structures optimized at the BP86/SVP level, single-point energy calculations at the B3LYP/TZVP level were performed using Karlsruhe TZVP basis sets (triple-ζ for valence shells plus polarization for non-hydrogen atoms [22]) and the B3LYP exchange-correlation potential which partially accounts for the non-locality of exchange [23,24]. This approach has been multiply justified by DFT calculations of polymer anionic chain-ends with lithium counterion [21,25–28]. It has been shown that the performance of the B3LYP potential for organometallic aggregates complexed with electron-donating ligands is comparable to that of the MP2 method [29].

For most of the $(HSt_mLi)_n(\pi\text{-donor})_x(St)_y$ ($m = 1$) complexes, normal vibrations were calculated at the BP86/SVP level using the GAUSSIAN-98 program [30]. All these structures have no imaginary vibration frequencies and, thus, are true local minima. Zero-point energies, ZPE, and Gibbs free energies, G, calculated for these structures are presented in Table 1. Also, for several complexes basis set superposition errors (BSSE) were evaluated by the counterpoise method [31] (Table 1). Averaged total energies including the BSSE correction, $\bar{E}_{BSSE}$, and the ZPE correction, $\bar{E}_{ZP}$, and averaged Gibbs free energies, $\bar{G}$, are shown in Table 2. The $\bar{E}_{BSSE}$, $\bar{E}_{ZP}$, and $\bar{G}$, values were calculated using the values of $E + BSSE$, $E + ZPE$ and G, respectively, instead of the E values in Eq. (1).

3. Results and discussion

One can see from Table 2 that the ZPE effect on the relative stabilities of the complexes studied is negligible because the $\Delta\bar{E}_{ZP}$ and $\Delta\bar{E}$ values calculated at the BP86/SVP//BP86/SVP level are almost the same. Therefore, the obtained differences between the $\Delta\bar{E}$ and $\Delta\bar{G}$ values are of purely entropic nature.

It is expectable that the BSSE correction is the largest for triple complexes like HStLi·2D and HStLi·D·St

Table 1
Calculated total energies, *E*, zero-point energies, ZPE, differences between Gibbs free energies, *G*, and *E* values at 25 °C, basis set superposition errors, BSSE, for associates of HStLi, HSt_2Li, and their complexes with durene (D), tetraphenylethylene (TPhE), and styrene (St)

			BP86/SVP//BP86/SVP				B3LYP/TZVP//BP86/SVP
Structure	Figure	Symmetry	*E* (Hartree)	ZPE (Hartree)	$G-E$ (Hartree)	BSSE (kcal/mol)	*E* (Hartree)
Styrene	–	C_1	−309.41795	0.12941	0.09813	0	−309.54423
Durene	–	C_{2v}	−389.21344	0.20413	0.16861	0	−389.37144
TPHE	–	D_2	−1002.08687	0.36551	0.31358	0	−1002.46422
HstLi	Fig. 1(a)	C_1	−317.52948	0.14000	0.10725	0	−317.65854
$(HStLi)_2$	Fig. 1(b)	C_2	−635.13822	0.28267	0.23664	3.8	−635.39146
$(HStLi)_2$	Fig. 1(c)	C_2	−635.13376	0.28184	0.23480	–	−635.38633
HStLi·HstLi	Fig. 1(d)	C_1	−635.08612	0.28070	0.23184	2.6	−635.34071
HStLi·D	Fig. 2(a)	C_1	−706.76701	0.34493	0.29363	3.1	−707.05164
HStLi·TphE	Fig. 2(b)	C_1	−1319.63862	0.50618	0.44052	3.5	−1320.13756
HStLi·St	Fig. 2(c)	C_1	−626.97061	0.27034	0.22236	2.4	−627.21978
HStLi·HStLi·D	Fig. 3(a)	C_1	−1024.32765	0.48562	0.41687	–	−1024.73872
HStLi·D·LiStH	Fig. 3(b)	C_2	−1024.31267	0.48538	0.41882	–	−1024.72120
HStLi·HStLi·TphE	Fig. 3(c)	C_1	−1637.20204	–	–	–	−1637.82262
HStLi·HStLi·St	Fig. 3(d)	C_1	−944.53018	–	–	–	−944.90272
HStLi·2D	Fig. 4(a)	C_1	−1095.97963	0.55006	0.48257	5.7	−1096.41974
HStLi·D·St	Fig. 4(b)	C_1	−1016.19125	0.47561	0.41185	5.5	−1016.59615
HSt_2Li^a	Fig. 5(a)	C_1	−626.99381	–	–	–	−627.23555
$(HSt_2Li)_2{}^a$	Fig. 5(b)	C_2	−1254.02962	–	–	–	−1254.51544
$(HSt_2Li)_2{}^b$	Fig. 5(c)	C_2	−1254.03218	–	–	–	−1254.52127
$HSt_2Li{\cdot}D^a$	Fig. 6(a)	C_1	−1016.21155	–	–	–	−1016.61161
$HSt_2Li{\cdot}D^b$	Fig. 6(b)	C_1	−1016.21475	–	–	–	−1016.61745
$HSt_2Li{\cdot}St^a$	Fig. 6(c)	C_1	−936.42027	–	–	–	−936.78613
$HSt_2Li{\cdot}St^b$	Fig. 6(d)	C_1	−936.41772	–	–	–	−936.78583
$HSt_2Li{\cdot}2D^b$	Fig. 7(a)	C_1	−1405.42957	–	–	–	−1405.98728
$HSt_2Li{\cdot}D{\cdot}St^b$	Fig. 7(b)	C_1	−1325.64038	–	–	–	−1326.16357

[a] Aromatic ring of the penultimate unit is coordinated to Li.
[b] Aromatic ring of the penultimate unit is not coordinated to Li.

($\Delta\bar{E}_{BSSE} - \Delta\bar{E} = 3.8$ and 3.6 kcal/mol, respectively, Table 2). However, these triple complexes have rather high $\Delta\bar{G}$ values, i.e. they are much more destabilized due to entropic reasons than due to the BSSE effect. As far as the non-associated chain-end, HStLi, and the complexes, consisting of two components, are compared at the BP86/SVP//BP86/SVP level, their $\Delta\bar{E}_{BSSE}$ and $\Delta\bar{E}$ values give generally the same order of relative stabilities: $(HStLi)_2 \gg$ HStLi·D ≈ HStLi·St ≥ HStLi·TPhE > (HStLi·HStLi ≫ HStLi. Therefore, below only the $\Delta\bar{E}$ and $\Delta\bar{G}$ values are discussed.

As seen from Table 2, the dimer, $(HStLi)_2$, is the most stable structure of the studied complexes and associates of HStLi. Formation of dimers and even higher aggregates is typical of organolithium compounds [32]. However, the optimized $(HStLi)_2$ structure differs from what could be expected for dimers of alkyllithium compounds which usually contain 4-membered cycles formed by two C–Li bonds [33–35]. There is no such a 4-membered cycle in the C_2-symmetric $(HStLi)_2$ structure (Fig. 1(b)). In this structure, each of two lithium atoms is intramolecularly η^1-coordinated and intermolecularly η^6-coordinated, leading to a 'sandwich' structure with the Li–Li distance of ca. 3.4 Å. Recently, a rather similar structure with the C_i-symmetry has been shown to be the most stable one for the dimer of 1-phenyl-*n*-propyllithium at the B3LYP/DZVP level of theory [36]. Our attempts to localize a dimeric $(HStLi)_2$ structure similar to that of, e.g. methyllithium dimer (Li–Li distance of ca. 2.2 Å [35]) failed at both BP86/SVP and B3LYP/TZVP levels.

The 'classical' η^3 lithium arrangement was found for the optimized non-aggregated HStLi structure (Fig. 1(a)), in agreement with ab initio 3-21G calculations for benzyllithium by Sygula and Rabideau [37]. These authors have

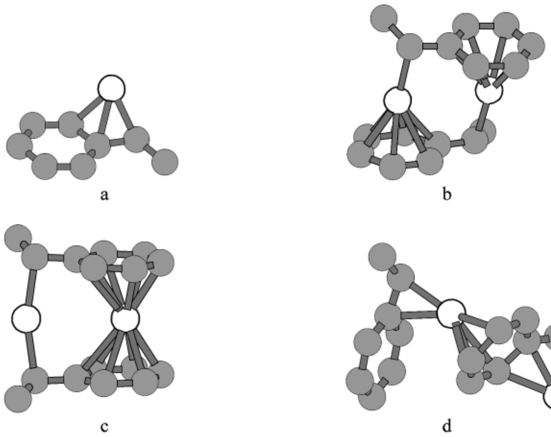


Fig. 1. Optimized geometries of the model active site HStLi (a) and its different dimeric forms $(HStLi)_2$ (b–d). Hydrogen atoms are not shown. Li–C distances shorter than 2.6 Å are marked as covalent bonds.

Table 2
Averaged energies per one active chain-end and relative stabilities for different associates of HStLi and its complexes with durene (D), tetraphenylethylene (TPhE), and styrene (St) calculated at the BP86/SVP//BP86/SVP and B3LYP/TZVP//BP86/SVP (marked bold) levels of theory

Structure	Figure	$\bar{E}$ (Hartree)	$\bar{E}_{BSSE}$ (kcal/mol)	$\bar{E}_{ZP}$ (Hartree)	$\bar{G}$ (Hartree)	$\Delta\bar{E}$ (kcal/mol)	$\Delta\bar{E}_{BSSE}$ (kcal/mol)	$\Delta\bar{E}_{ZP}$ (kcal/mol)	$\Delta\bar{G}$ (kcal/mol)
HstLi	Fig. 1(a)	−317.52948	0	−317.38948	−317.42223	24.9	23.0	24.0	17.9
		−317.65854	–	–	–	**23.3**	–	–	–
$(HStLi)_2$	Fig. 1(b)	−317.56911	1.9	−317.42778	−317.45079	0	0	0	0
		−317.69573				**0**	–	–	–
$(HStLi)_2$	Fig. 1(c)	−317.56688	–	−317.42596	−317.44948	1.4	–	1.1	0.8
		−317.69317	–	–	–	**1.6**	–	–	–
HStLi·HStLi	Fig. 1(d)	−317.54306	1.3	−317.40271	−317.42714	16.3	15.7	15.7	14.8
		−317.67035	–	–	–	**15.9**	–	–	–
HStLi·D	Fig. 2(a)	−317.55357	3.1	−317.41277	−317.42855	9.8	11.0	9.4	14.0
		−317.68020	–	–	–	**9.7**	–	–	–
HStLi·TPhE	Fig. 2(b)	−317.55175	3.5	−317.41108	−317.42481	10.9	12.5	10.5	16.3
		−317.67334	–	–	–	**14.0**	–	–	–
HStLi·St	Fig. 2(c)	−317.55266	2.4	−317.41174	−317.42843	10.3	10.8	10.1	14.0
		−317.67555	–	–	–	**12.7**	–	–	–
HStLi·HStLi·D	Fig. 3(a)	−317.55710	–	−317.41636	−317.43298	7.5	–	7.2	11.2
		317.68364	–			**7.6**	–	–	–
HStLi·D·LiStH	Fig. 3(b)	−317.54960	–	−317.40899	−317.42451	12.2	–	11.8	16.5
		−317.67488	–	–	–	**13.1**	–	–	–
HStLi·HStLi·TphE	Fig. 3(c)	−317.55106	–	–	–	11.3	–	–	–
		−317.67920	–	–	–	**10.4**	–	–	–
HStLi·HStLi·St	Fig. 3(d)	−317.55612	–	–	–	8.2	–	–	–
		−317.67924	–	–	–	**10.3**	–	–	–
HStLi·2D	Fig. 4(a)	−317.55275	5.7	−317.41095	−317.40740	10.3	14.1	10.6	27.2
		−317.67685	–	–	–	**11.8**	–	–	–
HStLi·D·St	Fig. 4(b)	−317.55986	5.5	−317.41779	−317.41475	5.8	9.4	6.3	22.6
		−317.68048	–	–	–	**9.6**	–	–	–

Table 3
Averaged energies per one active chain-end and relative stabilities for different associates of HSt_2Li and its complexes with durene (D) and styrene (St) calculated at the BP86/SVP//BP86/SVP and B3LYP/TZVP//BP86/SVP (marked bold) levels of theory

Structure	Figure	$\bar{E}$ (Hartree)	$\Delta\bar{E}$ (kcal/mol)
HSt_2Li^a	Fig. 5(a)	−626.993809	14.0
		−627.235549	**15.7**
$(HSt_2Li)_2{}^a$	Fig. 5(b)	−627.014812	0.8
		−627.257722	**1.8**
$(HSt_2Li)_2{}^b$	Fig. 5(c)	−627.016089	0
		−627.260633	**0**
$HSt_2Li{\cdot}D^a$	Fig. 6(a)	−626.998111	11.3
		−627.240163	**12.8**
$HSt_2Li{\cdot}D^b$	Fig. 6(b)	−627.001308	9.3
		−627.246003	**9.2**
$HSt_2Li{\cdot}St^a$	Fig. 6(c)	−627.002319	8.6
		−627.241895	**11.8**
$HSt_2Li{\cdot}St^b$	Fig. 6(d)	−626.999771	10.2
		−627.241595	**11.9**
$HSt_2Li{\cdot}2D^b$	Fig. 7(a)	−627.002687	8.4
		−627.244393	**10.2**
$HSt_2Li{\cdot}D{\cdot}St^b$	Fig. 7(b)	−627.008984	4.5
		−627.247894	**8.0**

[a] Aromatic ring of the penultimate unit is coordinated to Li.
[b] Aromatic ring of the penultimate unit is not coordinated to Li.

also found an η^5 local minimum for benzyllithium, similar to the intermolecular η^6 lithium arrangement in $(HStLi)_2$ found here. Moreover, they have shown that the η^1-coordination is the global minimum when the C–Li bond is artificially made purely ionic [37]. It could be a hint for a higher ionic character of the C–Li bond in the presented 'sandwich' $(HStLi)_2$ structure as compared to the non-associated HStLi. Indeed, Mulliken atomic C and Li charges calculated at the B3LYP/TZVP//BP86/SVP level are −0.39 and 0.63 for HStLi and −0.60 and 0.57 for $(HStLi)_2$. It is noteworthy in this context that the crystal structure of lithium 7bH-indeno[1,2,3-jk]fluorenide, consisting of two Li^+ ions 'sandwiched' between two parallel carbanions, has been reported [38].

It is interesting to note that another $(HStLi)_2$ structure, having non-equivalent lithium atoms (one is doubly η^1-coordinated and the other is doubly η^5-coordinated) was optimized (Fig. 1(c)). It is a kind of 'inner' triple ion pair (atomic C and η^1-coordinated Li Mulliken charges are −0.54 and 0.67) which is only slightly less stable ($\Delta\bar{E} = 1.5$ kcal/mol, Table 2) than the structure shown in Fig. 1(b). Also, the structure of a 'linear' dimer, HStLi·HStLi (Fig. 1(d)), was optimized ($\Delta\bar{E} = 15.9$ kcal/mol, Table 2).

The non-associated chain-end, HStLi, is rather unstable ($\Delta\bar{E} = 23.3$ kcal/mol, Table 2) with respect to the dimer, $(HStLi)_2$, i.e. the dissociation of $(HStLi)_2$ into two HStLi molecules is an unfavorable reaction. It was not possible to find a stabilized complex of the $(HStLi)_2$ 'sandwich'-like dimer with either TPhE or durene or styrene, because the lithium atoms inside the 'sandwich' structure are not accessible for such bulky complexing agents. Therefore, complexation of HStLi with either durene or TPhE or styrene facilitates the deaggregation of $(HStLi)_2$, considerably stabilizing the monomeric active site: $\Delta\bar{E} = 9.7$, 14.0, and 12.7 kcal/mol (Table 2) for HStLi·D (Fig. 2(a)), HStLi·TPhE (Fig. 2(b)), and HStLi·St (Fig. 2(c)), respectively. A lower but still considerable stabilization effect was found when the outer lithium atom of HStLi·HStLi is complexed to a π-donor: $\Delta\bar{E} = 7.6$, 10.4, and 10.3 kcal/mol, for HStLi·HStLi·D (Fig. 3(a)), HStLi·HStLi·TPhE (Fig. 3(c)), and HStLi·HStLi·St (Fig. 3(d)), respectively. It should also be noted that the 'linear' dimer HStLi·HStLi·D ($\Delta\bar{E} = 7.6$ kcal/mol, $\Delta\bar{G} = 11.2$ kcal/mol) is more stable than the structure HStLi·D·LiStH ($\Delta\bar{E} = 13.1$ kcal/mol, $\Delta\bar{G} = 16.5$ kcal/mol) in which two HStLi chain-ends are arranged symmetrically on the opposite sides of the durene molecule (Fig. 3(b)).

It is predictable that the complexation of π-ligands to HStLi is unfavorable entropically. Therefore, the differences in the $\Delta\bar{G}$ values between the HStLi·D, HStLi·TPhE, HStLi·St complexes ($\Delta\bar{G} = 14.0$, 16.3,14.0 kcal/mol, respectively) and the ligand-free non-associated active site HStLi ($\Delta\bar{G} = 17.9$ kcal/mol) are lower than the corresponding differences in the $\Delta\bar{E}$ values.

Kinetic data on the anionic polymerization of styrene in cyclohexane in the presence of durene imply that with the increase in [D], durene-free and the most active propagating species, PStLi, should be transformed into less active but still propagating complexes of the PStLi chain-ends with one and two durene molecules [11]. We managed to optimize the structures HStLi·2D (Fig. 4(a), $\Delta\bar{E} = 11.8 \times$ kcal/mol, $\Delta\bar{G} = 27.2$ kcal/mol) and HStLi·D·St (Fig. 4(b), $\Delta\bar{E} = 9.6$ kcal/mol, $\Delta\bar{G} = 22.6$ kcal/mol) but failed to find a complex HStLi·2D·St. An obvious reason is that so many bulky aromatic ligands cannot be arranged around lithium atom due to their strong steric interactions.

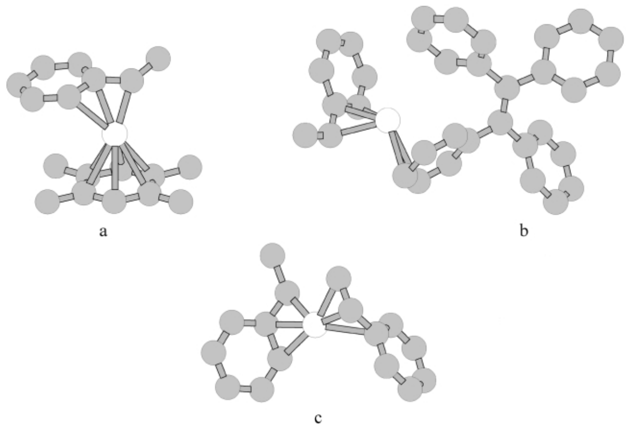


Fig. 2. Optimized geometries of the complexes of HStLi with durene (a), tetraphenylethylene (b), and styrene (c). Hydrogen atoms are not shown. Li–C distances shorter than 2.6 Å are marked as covalent bonds.

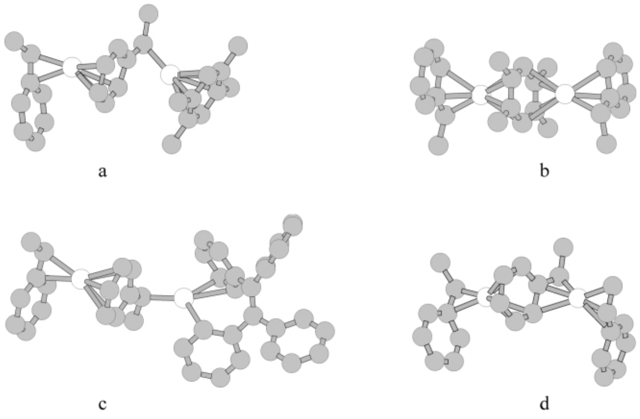


Fig. 3. Optimized geometries of the complexes of HStLi·HStLi with durene (a,b), tetraphenylethylene (c), and styrene (d). Hydrogen atoms are not shown. Li–C distances shorter than 2.6 Å are marked as covalent bonds.

One can see that the styrene complexation to HStLi·D is an almost thermoneutral ($\Delta\bar{E}$[HStLi·D·St] − $\Delta\bar{E}$[HStLi·D] = −0.1 kcal/mol) and entropically unfavorable ($\Delta\bar{G}$[HStLi·D·St] − $\Delta\bar{G}$[HStLi·D] = 8.6 kcal/mol) reaction, while its complexation to the ligand-free model active site, HStLi, is rather exothermic ($\Delta\bar{E}$[HStLi·St] − $\Delta\bar{E}$[HStLi] = −10.6 kcal/mol) and favorable by free energy ($\Delta\bar{G}$[HStLi·St] − $\Delta\bar{G}$[HStLi] = −3.9 kcal/mol). Therefore, it is possible to conclude that the affinity of propagating sites towards styrene decreases in the series HStLi, HStLi·D, HStLi·2D, in agreement with the experimental findings [11].

In the case of HSt_2Li model active sites, the penultimate styrene unit can be non-coordinated to the counterion or coordinated to it (except for the non-associated HSt_2Li (Fig. 5(a)), for which such a coordination is strongly preferable [36,39,40], and the $HSt_2Li·2D$ (Fig. 7(a)) and $HSt_2Li·D·St$ (Fig. 7(b)) structures, for which this coordination is impossible). Accordingly, two structures of $(HSt_2Li)_2$ were found. The structure shown in Fig. 5(b) has a 4-membered cycle formed by two C–Li bonds, lithium atoms being coordinated by aromatic rings of penultimate styrene units. However, this structure is less stable ($\Delta\bar{E} = 1.8$ kcal/mol, Table 3) than the most stable

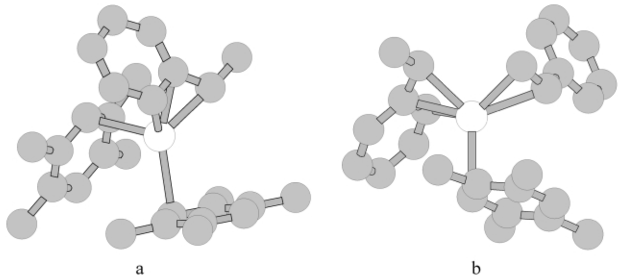


Fig. 4. Optimized geometries of the HStLi complexes with two durene molecules (a) and with one durene and one styrene molecule (b). Hydrogen atoms are not shown. Li-distances shorter than 2.6 Å are marked as covalent bonds.

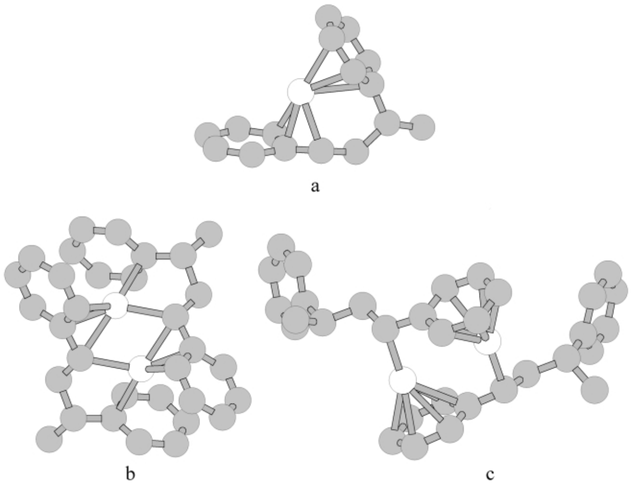


Fig. 5. Optimized geometries of the HSt_2Li (a) and $(HSt_2Li)_2$ dimers with (b) and without (c) the coordination of the penultimate styrene unit to lithium counterion. Hydrogen atoms are not shown. Li–C distances shorter than 2.6 Å are marked as covalent bonds.

‘sandwich’-like dimer without the penultimate unit coordination (Fig. 5(c)). In general, as seen from Table 3, the $\Delta\bar{E}$ values for systems with Li-coordinated penultimate units are not lower than for the corresponding systems without such coordination. Only for the least sterically hindered $HSt_2Li\cdot St$ system (Fig. 6(c) and (d)), the $\Delta\bar{E}$ values in both cases are almost the same. Comparing the data in Tables 2 and 3, it is seen that for the complexes $HSt_mLi\cdot D$, $HSt_mLi\cdot St$, and, especially, for the complexes $HSt_mLi\cdot 2D$, $HSt_mLi\cdot D\cdot St$, the calculated $\Delta\bar{E}$ values are lower for $m = 2$ (Figs. 6 and 7; Table 3) than for $m = 1$ (Figs. 2(a) and (c) and 4; Table 2).

It is important to emphasize that the dissociation of the $(HSt_2Li)_2$ dimer into the non-associated HSt_2Li structure ($\Delta\bar{E} = 15.7$ kcal/mol, Table 3) is, due to the coordination of the penultimate unit to the lithium counterion in the latter (unlike in the former), much less endothermic than that of the $(HStLi)_2$ dimer into the monomeric HStLi ($\Delta\bar{E} = 23.3$ kcal/mol, Table 2). In contrast, the complexation of styrene with the non-associated species HSt_mLi is much less exothermic for $m = 2$ ($\Delta\bar{E}[HSt_2Li\cdot St] - \Delta\bar{E}[HSt_2Li] = -3.9$ kcal/mol, Table 3) than for $m = 1$ ($\Delta\bar{E}[HStLi\cdot St] - \Delta\bar{E}[HStLi] = -10.6$ kcal/mol, Table 2). These results are in a good agreement with experimental data on the influence of the penultimate unit [39,40].

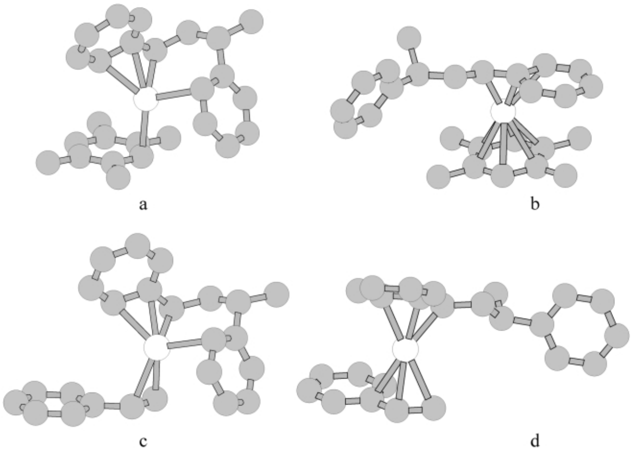


Fig. 6. Optimized geometries of the HSt_2Li complexes with durene (a,b) and styrene (c,d). Hydrogen atoms are not shown. Li–C distances shorter than 2.6 Å are marked as covalent bonds.

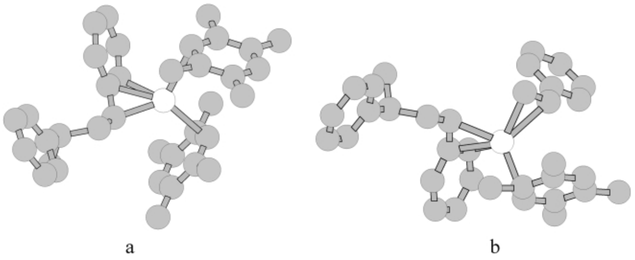


Fig. 7. Optimized geometries of the HSt_2Li complexes with two durene molecules (a) and with one durene and one styrene molecule (b). Hydrogen atoms are not shown. Li–C distances shorter than 2.6 Å are marked as covalent bonds.

4. Conclusions

The presented data of quantum-chemical DFT calculations are useful in two aspects. Firstly, some unusual structures (Figs. 1(b) and (c), 5(c)) of dimeric associates, $(PStLi)_2$, were found, which, to our knowledge, have not been discussed in literature. Secondly, it was shown that π-donors, like durene, cause a dualistic effect on the styrene anionic polymerization rate in non-polar solvents. On one hand, they strongly facilitate the deaggregation of the chain-end dimers, $(PStLi)_2$, increasing the number of propagating active centers. On the other hand, being complexed to the monomeric propagating species, PStLi, they markedly reduce the ability of the active sites to bind styrene and, thus, to propagate. These data are in agreement with the maximum found on the [D]-dependence of the observed rate constant of the styrene anionic polymerization in cyclohexane [11].

Acknowledgements

The authors are grateful to Prof. Alain Deffieux (Laboratoire de Chimie des Polymères Organiques, CNRS-ENSCPB-Université Bordeaux I) for helpful discussions and Dr Pierre Verstraete (Laboratoire de Physico-Chimie Moléculaire, l'Université Bordeaux I) for discussions and sharing with them the results of his PhD work.

References

[1] Worsfold DJ, Bywater S. Can J Chem 1960;38:1891.

[2] Szwarc M, Van Beylen M. Ionic polymerization and living polymers. London: Chapman & Hall; 1993.

[3] Van Beylen M, Bywater S, Smets G, Szwarc M, Worsfold DJ. Adv Polym Sci 1988;86:87.

[4] Hsieh HL, Quirk RP. Anionic polymerizaiton, principles and pratical applications. New York: Marcel Dekker; 1996.

[5] Spirin YuL, Gantmakher AR, Medvedev SS. Dokl Akad Nauk SSSR 1962;46:368.

[6] Johnson AF, Worsfold DJ. J Polym Sci Part A 1965;3:449.

[7] Hofmans J. PhD dissertation, Catholic University of Leuven, 1999.

[8] O'Driscoll KF, Patsiga R. J Polym Sci Part A 1965;3:1037.

[9] Bywater S, Worsfold DJ. Can J Chem 1962;40:1564.

[10] Bywater S, Alexander IJ. J Polym Sci Part A-1 1968;6:3407.

[11] Wang G, Van Beylen M. Part 1. 2003;44:5527.

[12] Parr RG, Yang W. Density-functional theory of atoms and molecules. Oxford, England: Oxford University Press; 1989.

[13] Ahlrichs R, Bär M, Häser M, Horn H, Kölmel C. Chem Phys Lett 1989;162:165.

[14] Becke AD. Phys Rev A 1988;38:3098.

[15] Perdew JP. Phys Rev B 1986;33:8822.

[16] Schäfer A, Horn H, Ahlrichs R. J Chem Phys 1992;97:2571.

[17] Vahtras O, Almlöf J, Feyereisen MW. Chem Phys Lett 1993;213:514.

[18] Eichkorn K, Treutler O, Öhm H, Häser M, Ahlrichs R. Chem Phys Lett 1995;242:652.

[19] Eichkorn K, Weigand F, Treutler O, Ahlrichs R. Theor Chem Acc 1997;97:119.

[20] Eichkorn K, Treutler O, Öhm H, Häser M, Ahlrichs R. Chem Phys Lett 1995;240:283.

[21] Yakimansky AV, Müller AHE. Macromolecules 1999;32:1731.

[22] Schäfer A, Huber C, Ahlrichs R. J Chem Phys 1994;100:5829.

[23] Becke AD. J Chem Phys 1993;98:5648.

[24] Lee C, Yang W, Parr RG. Phys Rev B 1988;37:785.

[25] Yakimansky AV, Müller AHE. J Am Chem Soc 2001;123:4932–7.

[26] Yakimansky AV, Müller AHE, Van Beylen M. Macromolecules 2000;33:5686.

[27] Yakimansky AV, Van Beylen M. Polymer 2002;43:5797–805.

[28] Abbotto A, Streitwieser A, Schleyer PvR. J Am Chem Soc 1997;119:11255.

[29] Carvajal A, Liu X-Y, Alemany P, Novoa JJ, Alvarez S. Int J Quant Chem 2002;86:100–5.

[30] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pople JA. GAUSSIAN-98, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.

[31] Boys SF, Bernardi J. Mol Phys 1970;19:53.

[32] Sapse A-M, Schleyer PvR, editors. Lithium chemistry: a theoretical and experimental overview. New York: Wiley; 1995.

[33] Kwon O, Sevin F, McKee ML. J Phys Chem A 2001;105:913–22.

[34] Bickelhaupt FM, van Eikema Hommes NJR, Guerra CF, Baerends EJ. Organometallics 1996;15:2923–31.

[35] Kaufmann E, Raghavachari K, Reed AE, Schleyer PvR. Organometallics 1988;7:1597–607.

[36] Verstraete P. PhD Thesis, l'Université Bordeaux I, 2002.

[37] Sygula A, Rabideau RW. J Am Chem Soc 1992;114:821–4.

[38] Bladauski D, Dietrich H, Hecht HJ, Rewicki D. Angew Chem 1997;89:490–1.

[39] Walckiers E, Van Beylen M, Macromolecular preprints XXIII IUPAC congress, Boston, USA, vol. II.; 1971. p. 1199.

[40] Dils J, Van Beylen M, Proceedings international symposium on macromolecules, Dublin, Ireland, vol. I.; 1977. p. 69.