polymer

Quantum-chemical DFT calculations to interpret the effect of lithium butoxide additives on the anionic polymerization of styrene in polar solvents

Alexander V. Yakimansky[a,b,*], Marcel Van Beylen[a,1]

[a]*Katholieke Universiteit Leuven, Celestijnenlaan 200 F, B-3001 Heverlee, Belgium*
[b]*Polymer Theory Laboratory, Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi prospect 31, 199004 St Petersburg, Russian Federation*

Abstract

For the interpretation of the effect of lithium butoxides on the rate of the styrene anionic polymerization, quantum-chemical DFT calculations of their aggregation and dissociation behavior in polar solvents were performed. The calculations showed that addition of n-BuOLi should lead to the preferable scavenging of free Li^+-cations by the tetrameric THF-solvated aggregates of the alkoxide, thus increasing through the common ion effect the concentration of the free anionic PSt^- sites, which are the main contributors to the rate of polymerization. In contrast, addition of t-BuOLi should mostly lead to the decrease of the concentration of the PSt^- active sites which abstract Li^+-cations from the tetrameric aggregate of the additive, resulting in slowing down the polymerization. These results agree with the observed effects of n-BuOLi and t-BuOLi on the polymerization rate in polar solvents like THP or THF and with the increase in the solution conductivity observed upon the addition of both lithium butoxides to the solution of PSt–Li chains. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

Li-containing additives are known to affect the anionic polymerization rates of styrene (St), the effect observed being dependent on concentrations of both polystyrene living chain ends (PSt–Li) and that of the additive as well as on its chemical structure [1–3]. A recent quantum-chemical density functional theory (DFT) study of the effect of LiCl on the rate of styrene (St) polymerization in polar solvents [4] has indicated that the observed retardation or acceleration in the rates of polymerization is due to the domination of LiCl dissociation, producing free Li^+ cations and repressing the dissociation of PSt–Li through the common ion effect, or to the scavenging of free Li^+ cations by LiCl,

promoting the dissociation of PSt–Li. It was emphasized [4] that at the constant value of molar ratio r = [LiCl]/[PSt–Li] = 7, the polymerization is retarded (accelerated) at low (high) concentrations of both LiCl and PSt–Li. Although this conclusion is qualitatively true for any fixed value of r, we found later [2] that there exists a 'crossover' concentration of PSt–Li at which any amount of added LiCl does not affect the polymerization rate. Below (above) this crossover concentration, addition of LiCl only retards (accelerates) the polymerization, the magnitude of the effect increasing with the amount of LiCl added [2].

In contrast to this dual effect of LiCl, only enhancement (retardation) of the styrene polymerization is observed when n-BuOLi (t-BuOLi) is added at any experimentally attainable concentration of PSt–Li in tetrahydrofuran (THF) [5,6] or tetrahydropyran (THP) [3] solutions. It should be noted that addition of both lithium alkoxides to THP solution of PSt–Li was found to lead to an increase in the solution conductivity, the effect being more pronounced in the case of n-BuOLi. In the present paper, quantum-chemical DFT

* Corresponding author. Address: Polymer Theory Laboratory, Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi prospect 31, 199004 St Petersburg, Russian Federation. Tel.: +7-8123285601; fax: +7-8123286869.
E-mail addresses: yak@imc.macro.ru (A.V. Yakimansky), marcel.vanbeylen@chem.kuleuven.ac.be (M.V. Beylen).
[1] Tel.: +32-16-327-418/424; fax: +32-16-327-990.

calculations are used in order to explain the differences between the effects of n-BuOLi and t-BuOLi on the styrene polymerization rates and solution conductivities.

2. Methods

All quantum-chemical calculations were performed using the DFT approach [7] implemented into the TURBOMOLE package [8] of ab initio quantum-chemical programs. The structures studied here are different neutral or ionic THF-solvated aggregates of n-BuOLi and t-BuOLi. Their geometries were completely optimized with the convergence criteria of 10^{-6} hartree for total energy and 10^{-3} hartree/(bohr or radian) for the largest component of the total energy gradient. Their initial geometries, to start the geometry optimization with, were chosen in a way to preserve to the highest possible extent the central core of pseudo-cubic lithium butoxide tetrameric aggregates [9]. Each of the Li atoms within a given structure was initially saturated with the necessary amount of THF molecules to be in an approximately tetrahedral environment of four oxygen atoms.

For the DFT geometry optimizations, Becke's exchange potential [10] and Perdew's correlation potential [11] were used. This set of DFT-potentials, hereafter referred to as BP86, was used in the 'resolved identity' (RI) formalism [12–14] to avoid the *calculations* of all four-centered two-electron integrals. TURBOMOLE split valence plus polarization (SVP) basis sets [15] of 6-31G* quality were employed. For the fitting of the Coulomb potential within the RI formalism, Ahlrichs' auxiliary basis sets [13,16] have been used. No frequency calculations were made. The details about contraction schemes and polarization function exponents for each element is described elsewhere [17].

In addition to the specific solvation, taken into account by the explicit inclusion of THF molecules into the considered complexes, their non-specific solvation energies, E_{nss}, due to the solvent continuum were calculated semi-empirically at the BP86/SVP-optimized geometries using the solvent-continuum model [18] implemented into the modified MOPAC 6.0 program using MNDO parametrization [19]. The solvent polarity was characterized by its dielectric constant, ε. This semi-empirical solvent-continuum model has been successfully employed in combination with DFT-methods to study the dissociation of PSt–Li in ethereal solvents [4] and the relative stabilities of different forms of PMMA–Li chain ends [20]. The results presented in this paper were obtained for $\varepsilon = 5.71$, corresponding to the dielectric constant of THP at room temperature.

To estimate the effect of the basis set and DFT exchange-correlation potential on the calculated reaction enthalpies for aggregates of n-BuOLi and t-BuOLi, the calculations were first reproduced for similar aggregates of lithium methoxide (MeOLi). For all the aggregated structures of MeOLi optimized at the BP86/SVP level, single-point energy calculations at the B3LYP/TZVP level were performed using Karlsruhe TZVP basis sets, consisting of TZV basis sets of triple-ζ quality [21] augmented with polarization functions for all non-hydrogen atoms [17], and Becke's three-parameter functional [22] with the correlation potential by Lee, Yang, and Parr [23]. It should be noted that calculating B3LYP energies at the geometries optimized at a lower level of theory was justified by Abbotto, Streitwieser, and Schleyer in their studies on the aggregation behavior of lithium enolate of acetaldehyde [24]. On the other hand, the performance of the B3LYP method for organometallic aggregates complexed with electron-donating ligands was recently shown to be comparable to that of the MP2 method [25].

3. Results and discussion

It is well established [26] that the rate of the anionic polymerization of styrene in ethereal solvents (except dioxane) depends mainly on the concentration of free anions, PSt^-, being determined by the equilibrium

$$PSt\text{–}Li \rightleftharpoons PSt^- + Li^+ \qquad (1)$$

The effect of lithium alkoxides additives on the rate of styrene polymerization should, therefore, be realized through either (i) their direct interactions with all the participants of equilibrium (1) or (ii) their self-dissociation reactions that shift the equilibrium towards the left by generation of Li^+ cations.

Considering possible reactions of these types (Table 1), one should take into account that, even in polar solvents, lithium alkoxides, ROLi, are aggregated into tetramers [9]. Calculated products of the reactions of these tetramers, $(ROLi)_4$, in THF solutions of PSt–Li chains are rather complicated three-dimensional structures with central cores of multi-valent lithium–oxygen bonds and several THF molecules around each Li ion (Figs. 1–5). The maximum coordination number for Li ions is four. However, the total number of solvating THF molecules, n, is generally lower in the case of R = t-Bu than in the case of R = n-Bu (Table 1) as a result of the steric constraint of the t-Bu groups.

Calculated total energies, E, and non-specific solvation energies, E_{nss}, for all the structures studied are collected in Table 2. The completely optimized DFT structures of THF-solvated tetramers of n-BuOLi and t-BuOLi are shown in Fig. 1. They represent pseudo-cubic structures with S_4-symmetry. The calculated heat effects per one lithium alkoxide molecule, ΔE, for the reactions (1)–(8) (Table 1) are given in Table 3:

$$\Delta E = \sum_{products} (E + E_{nss}) - \sum_{reagents} (E + E_{nss}) \qquad (2)$$

ZPE-corrections were not included into the ΔE values, because a reliable estimation of vibrational frequencies for systems with so many 'soft' bonds, as those between Li ions

Table 1
Considered reactions of lithium alkoxides, ROLi, in THF solutions of PSt–Li chain ends and their expected effect on the solution conductivity and the rate of St polymerization

No.	Reaction	n		Effect of the reaction on the conductivity	Effect of the reaction on the polymerization rate
		R = n-Bu	R = t-Bu		
Generation of polymerization active sites, PSt⁻, by the reactions of lithium alkoxides, ROLi, with PSt–Li chain ends					
(1)	$3/4(ROLi·THF)_4 + 1\text{-PhEtLi(THF)}_3 + (n-6)THF(ROLi)_3Li^+(THF)_n + 1\text{-PhEt}^-$	5, 7, 8	5, 6	Increasing[a]	Increasing[b]
(2)	$(ROLi·THF)_4 + 1\text{-PhEtLi(THF)}_3 + (n-7)THF(ROLi)_4Li^+(THF)_n + 1\text{-PhEt}^-$	8	5	Increasing[a]	Increasing[b]
Neutralization of polymerization active sites, PSt⁻, by their reactions with lithium alkoxides, ROLi					
(3)	$5/4(ROLi·THF)_4 + 1\text{-PhEt}^- + (n-2)THF(ROLi)_4(RO)^-(THF)_n + 1\text{-PhEtLi(THF)}_3$	3	3	Increasing[c]	Decreasing[d]
(4)	$(ROLi·THF)_4 + 1\text{-PhEt}^- + (n-1)THF(ROLi)_3(RO)^-(THF)_n + 1\text{-PhEtLi(THF)}_3$	3	2	Increasing[c]	Decreasing[d]
Scavenging of free Li⁺(THF)₄ cations by lithium alkoxides, ROLi					
(5)	$3/4(ROLi·THF)_4 + Li^+(THF)_4 + (n-7)THF(ROLi)_3Li^+(THF)_n$	5, 7, 8	5, 6	Decreasing[e]	Increasing[f]
(6)	$(ROLi·THF)_4 + Li^+(THF)_4 + (n-8)THF(ROLi)_4Li^+(THF)_n$	8	5	Decreasing[e]	Increasing[f]
Self-dissociation of lithium alkoxides, ROLi					
(7)	$5/4(ROLi·THF)_4 + (n-1)THF(ROLi)_4(RO)^-(THF)_n + Li^+(THF)_4$	3	3	Increasing[a]	Decreasing[g]
(8)	$(ROLi·THF)_4 + nTHF(ROLi)_3(RO)^-(THF)_n + Li^+(THF)_4$	3	2	Increasing[a]	Decreasing[g]

[a] The reaction produces free ions.
[b] Anionic active site of the polymerization is generated in the reaction.
[c] For a sufficiently long chain of PSt⁻, being simulated by 1-PhEt⁻, the reaction leads to the formation of lighter and, thus, more mobile anion.
[d] Anionic active site of the polymerization is neutralized in the reaction.
[e] The reaction produces heavier, and thus, less mobile cation.
[f] The reaction reduces the concentration of free Li⁺(THF)₄ cations, promoting the dissociation of PSt–Li chain ends through the common-ion effect.
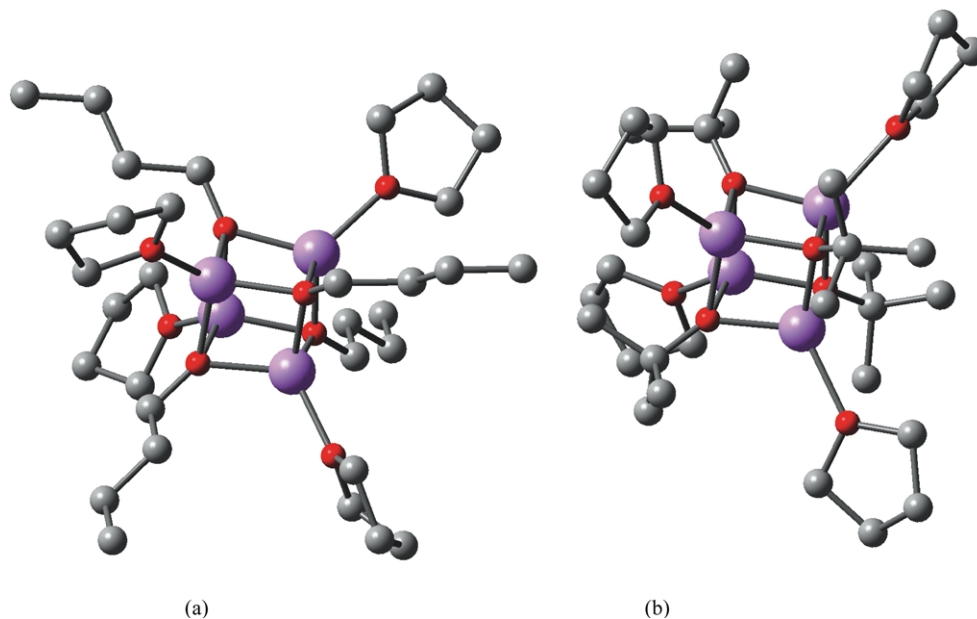[g] The reaction produces free Li⁺(THF)₄ cations, suppressing the dissociation of PSt–Li chain ends.

Fig. 1. Optimized geometries of the THF-solvated tetrameric aggregates of n-BuOLi (a) and t-BuOLi (b) (hydrogen atoms are not shown).

and solvent molecules, is, in our opinion, impossible within harmonic the approximation.

The expected effects of all the analyzed reactions on the solution conductivity and the rate of styrene polymerization are indicated in Table 1.

As seen from Table 3, the self-dissociation reactions of all lithium alkoxides are strongly endothermic and, thus, unfavorable. Therefore, the observed changes of both the solution conductivities and the polymerization rates in the presence of the additives cannot be due to their self-dissociation in polar solvents like THF or THP.

3.1. The basis set and DFT potential effect on the calculated reaction enthalpies

The values of total energies, E, and non-specific solvation energies, E_{nss}, calculated for the aggregates of MeOLi at the BP86/SVP//BP86/SVP and B3LYP/TZVP//BP86/SVP levels, are shown in Table 2. The data presented in Table 3 for the reactions of MeOLi aggregates show that the differences between the ΔE values calculated at the BP86/SVP//BP86/SVP and B3LYP/TZVP//BP86/SVP levels of theory do not exceed 1.6 kcal/mol (reaction
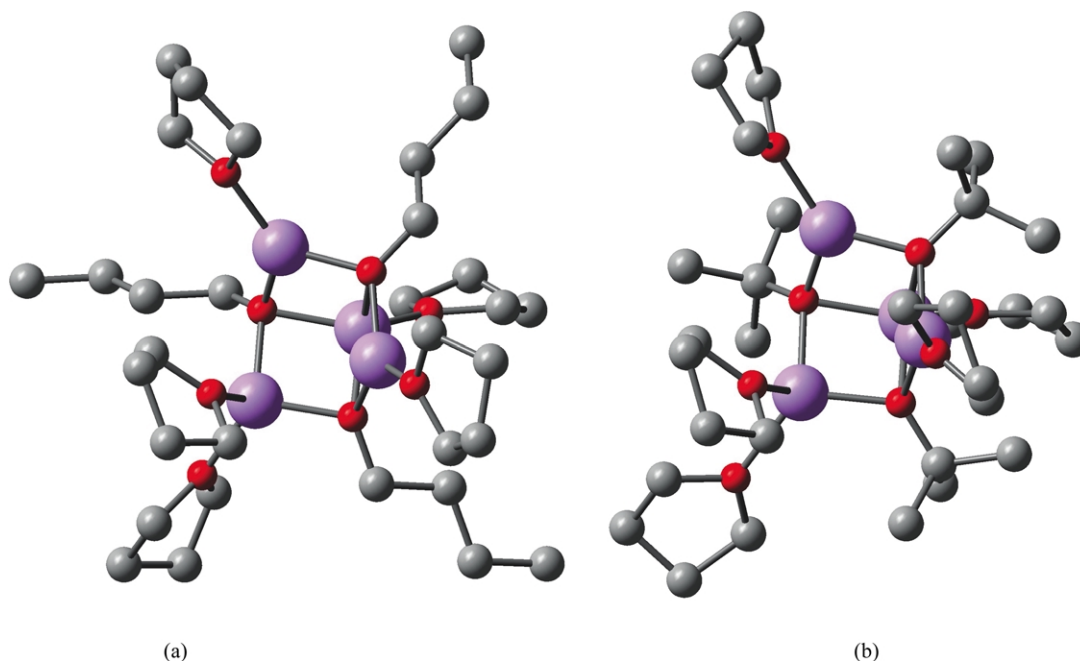

Fig. 2. Optimized geometries of the cations $(n\text{-BuOLi})_3\text{Li}^+(\text{THF})_5$ (a) and $(t\text{-BuOLi})_3\text{Li}^+(\text{THF})_5$ (b) (hydrogen atoms are not shown).
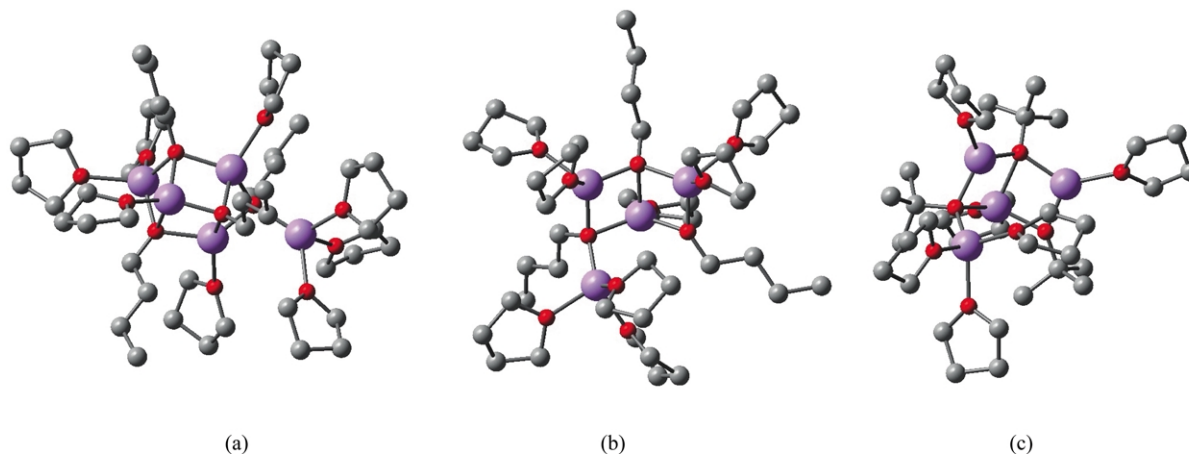
(a) (b) (c)

Fig. 3. Optimized geometries of the cations $(n\text{-BuOLi})_4\text{Li}^+(\text{THF})_8$ (a), $(n\text{-BuOLi})_3\text{Li}^+(\text{THF})_8$ (b), and $(t\text{-BuOLi})_3\text{Li}^+(\text{THF})_6$ (c) (hydrogen atoms are not shown).

(a) (b)

Fig. 4. Optimized geometries of the anions $(n\text{-BuOLi})_4(n\text{-BuO})^-(\text{THF})_3$ (a) and $(t\text{-BuOLi})_4(t\text{-BuO})^-(\text{THF})_3$ (b) (hydrogen atoms are not shown).

(a) (b)

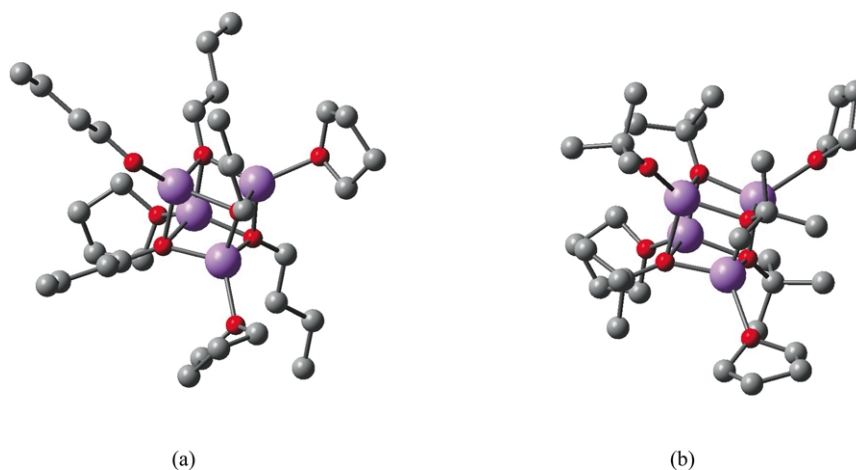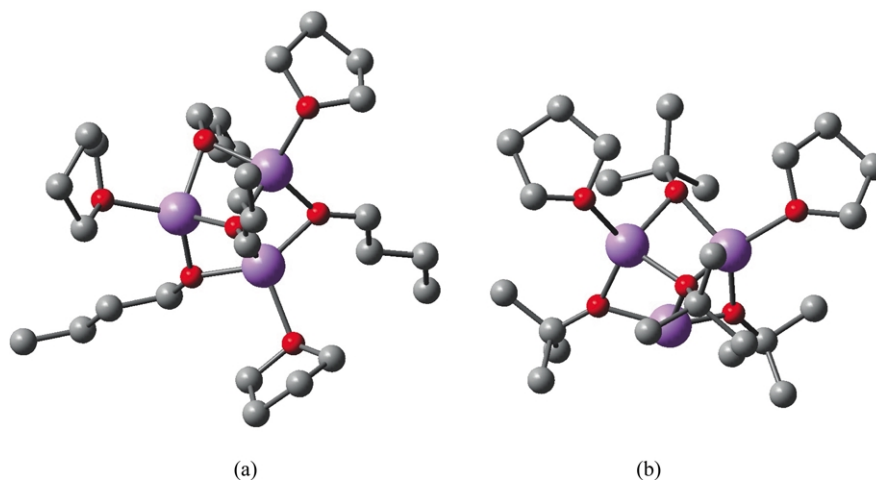Fig. 5. Optimized geometries of the anions $(n\text{-BuOLi})_3(n\text{-BuO})^-(\text{THF})_3$ (a) and $(t\text{-BuOLi})_3(t\text{-BuO})^-(\text{THF})_2$ (b) (hydrogen atoms are not shown).

Table 2
Calculated total energy values, E, and non-specific solvation energies, E_{nss} ($\varepsilon = 5.71$), for the structures involved into reactions (1)–(8)

Structure	Figure (R)	R						
		Me			n-Bu		t-Bu	
		E (hartree)		E_{nss}, (kcal/mol)	E (hartree), BP86/SVP//BP86/SVP	E_{nss}, (kcal/mol)	E (hartree), BP86/SVP//BP86/SVP	E_{nss}, (kcal/mol)
		BP86/SVP//BP86/SVP	B3LYP/TZVP//BP86/SVP					
$(ROLi \cdot THF)_4$	1	−1419.710085	−1420.462015	−10.9	−1891.103638	−11.0	−1891.110175	−5.8
$(ROLi)_3Li^+(THF)_5$	2	−1536.786043	−1537.584818	−25.8	−1890.331149	−25.1	−1890.333818	−24.4
$(ROLi)_3Li^+(THF)_6$	3c (R = t-Bu)	–	–	–	–	–	−2122.593925	−24.9
$(ROLi)_3Li^+(THF)_7$		−2001.350984	−2002.369964	−25.7	−2354.890666	−24.8	–	–
$(ROLi)_3Li^+(THF)_8$	3b (R = n-Bu)	−2233.621979	−2234.751097	−25.8	−2587.157801	−25.4	–	–
$(ROLi)_4Li^+(THF)_5$		–	–	–	–	–	−2130.823778	−23.6
$(ROLi)_4Li^+(THF)_8$	3a (R = n-Bu)	−2356.277683	−2357.483390	−26.2	−2827.656256	−24.9	–	–
$(ROLi)_4(RO)^-(THF)_3$	4	−1302.491669	−1303.199769	−52.6	−1891.744100	−47.3	−1891.762137	−37.5
$(ROLi)_3(RO)^-(THF)_2$	5b (R = t-Bu)	–	–	–	–	–	−1418.980320	−37.6
$(ROLi)_3(RO)^-(THF)_3$	5a (R = n-Bu)	−1179.847454	−1180.476707	−49.5	−1651.244290	−44.1	–	–
1-PhEtLi(THF)_3		−1014.410443	−1014.874294	−9.5				
1-PhEt$^-$		−310.021933	−310.144613	−43.7				
$Li^+(THF)_4$		−936.545041	−937.003802	−28.3				
THF		−232.270698	−232.384733	−1.3				

Table 3
Calculated enthalpies per one lithium alkoxide molecule, ΔE (kcal/mol), for reactions (1)–(8) as presented in Table 1 (with different number, n, of THF molecules in the reaction products)

Reaction	n	R							
		Me				n-Bu		t-Bu	
		BP86/SVP//BP86/SVP		B3LYP/TZVP//BP86/SVP		BP86/SVP//BP86/SVP			
		$\varepsilon = 1$	$\varepsilon = 5.71$	$\varepsilon = 1$	$\varepsilon = 5.71$	$\varepsilon = 1$	$\varepsilon = 5.71$	$\varepsilon = 1$	$\varepsilon = 5.71$
Generation of polymerization active sites, PSt⁻, by the reactions of lithium alkoxides, ROLi, with PSt−Li chain ends									
(1)	5	23.9	6.2	22.3	4.6	23.9	6.5	24.4	5.9
	6	–	–	–	–	–	–	26.6	8.4
	7	19.0	2.2	19.0	2.2	20.1	3.6	–	–
	8	18.9	2.5	19.8	3.4	20.9	4.7	–	–
(2)	5	–	–	–	–	–	–	20.9	7.3
	8	14.4	2.4	14.6	2.6	16.7	5.0	–	–
Neutralization of polymerization active sites, PSt⁻, by their reactions with lithium alkoxides, ROLi									
(3)	3	3.5	2.8	4.1	3.4	2.2	2.6	1.0	2.0
(4)	2	–	–	–	–	–	–	1.9	2.8
	3	2.4	2.0	3.9	3.5	1.9	2.8	–	–
Scavenging of free Li⁺(THF)₄ cations by lithium alkoxides, ROLi									
(5)	5	0.0	2.7	− 0.8	1.9	0.0	3.0	0.5	2.4
	6	–	–	–	–	–	–	2.7	4.9
	7	− 4.9	− 1.3	− 4.1	− 0.5	− 3.7	− 0.1	–	–
	8	− 5.0	− 1.0	− 3.4	0.6	− 3.0	1.0	–	–
(6)	5	–	–	–	–	–	–	3.0	4.7
	8	− 3.5	− 0.3	− 2.8	0.4	− 1.2	2.1	–	–
Self-dissociation of lithium alkoxides, ROLi									
(7)	3	75.2	13.3	73.5	11.6	73.9	13.1	72.7	12.5
(8)	2	–	–	–	–	–	–	73.6	13.3
	3	74.1	12.5	73.3	11.7	73.6	13.3	–	–

(1) at $n = 5$). At both levels, the most favorable reaction is reaction (5) at $n = 7$: the ΔE values (with non-specific solvation effects taken into account) are -1.3 and -0.5 kcal/mol for the BP86/SVP//BP86/SVP and B3LYP/TZVP//BP86/SVP levels, respectively. Thus, further using the BP86/SVP data for the reactions of aggregated n-BuOLi and t-BuOLi is justified.

3.2. n-BuOLi

It may be seen from Table 3 that the reactions of generation of polymerization active sites, PSt^-, from the living chain ends, PSt–Li, by their reaction with tetramers $(n\text{-BuOLi})_4$ (the most favorable of them is reaction (1) at $n = 7$: $\Delta E = 3.6$ kcal/mol) and the reverse reactions of the active site deactivation ($\Delta E = 2.6$ kcal/mol for reactions (3)) are thermodynamically almost equally probable. Taking into account that the ΔE values for both reactions are reasonably low, they should contribute to an increase in the solution conductivity (Table 1) observed in the presence of n-BuOLi [3].

However, the most favorable reaction with the participation of the n-BuOLi tetrameric aggregate is reaction (5) at $n = 7$, i.e. the scavenging of THF-solvated Li^+-cations by the aggregated alkoxide additive: with non-specific solvation energy taken into account $\Delta E = -0.1$ kcal/mol (Table 3). It may be concluded that the n-BuOLi influence on the dissociation equilibrium of PSt–Li living chain ends is dominated by this almost thermoneutral reaction, promoting an increase in the concentration of PSt^- ions, through the common ion effect. The decrease in the solution conductivity should not be very high (if any), because the mobilities of the original $Li^+(THF)_4$ cation and the formed $(n\text{-BuOLi})_3Li^+(THF)_7$ cation, being inversely proportional to square roots of their molecular weights, differ by only 30%. The experimental fact that the conductivity increases upon the addition of n-BuOLi [3], can be explained by the influence of the above considered reaction (1), enhancing the concentration of free ions, and reaction (3), producing much lighter and more mobile anions, $(n\text{-BuOLi})_4(n\text{-BuO})^-(THF)_3$, than the original PSt^- ones.

3.3. t-BuOLi

As shown in Table 3, activation of the PSt–Li through the Li^+-abstraction by tetrameric t-BuOLi is rather endothermic (the lowest $\Delta E = 5.9$ kcal/mol is obtained for reaction (1) at $n = 5$). Reaction (5) of scavenging free Li^+-cations by the tetramer $(t\text{-BuOLi})_4$ is not as endothermic ($\Delta E = 2.4$ kcal/mol at $n = 5$). However, the corresponding increase in PSt^- concentration should to a large degree be compensated for by reaction (3) ($\Delta E = 2.0$ kcal/mol), which has virtually the same ΔE value as reaction (5) but leads to a decrease in PSt^- concentration.

The increase in the solution conductivity in the presence of t-BuOLi is much lower than that found in the presence of n-BuOLi [3]. This difference can be explained by the much higher endothermicity of reactions (1) and, consequently, by their much lower enhancing contribution into the solution conductivity, in the case of t-BuOLi compared to that in the case of n-BuOLi (Table 3). The slight but still observable overall increase of the solution conductivity in the presence of t-BuOLi may be related to the dominating contribution of reaction (3) compared to that of reaction (5).

It has been claimed that the anionic polymerization of styrene in the presence of lithium alkoxides occurs largely through mixed aggregates of ion pairs with different reactivities rather than through free ions [5,6]. A more accurate statement is that dissociation of both n-BuOLi and t-BuOLi additives in THF or THP shift equilibrium (1) to ion pairs and repress the formation of free PSt^- ions, and therefore, decrease the propagation reaction [6].

However, it was shown in this paper that an overall effect of the particular alkoxide additive on the polymerization rate is determined by an interplay between its (predominating for t-BuOLi) dissociation reaction, supplying free Li^+-cations and shifting equilibrium (1) to the left, and (prevailing in the case of n-BuOLi) the reaction of scavenging Li^+ cations, shifting equilibrium (2) to the right. Moreover, the presence of the Li^+-ion scavenging reaction is confirmed by a considerable increase of the conductance of PSt–Li solutions in THP upon addition of both Li-alkoxides compared to the conductances of both pure alkoxide and pure PSt–Li solutions.

4. Conclusions

Quantum-chemical DFT calculations clearly indicate that lithium butoxides affect the dissociation equilibrium of the PSt–Li living chain ends in different ways, depending on the alkoxide structure. In the case of n-BuOLi (t-BuOLi), thermodynamically the most favorable reactions of the tetrameric lithium alkoxide on the PSt–Li dissociation equilibrium are scavenging reactions of free Li^+-cations. Thus, addition of n-BuOLi enhances the concentration of PSt^-, the main species responsible for the rate of polymerization. On the other hand, addition of t-BuOLi is predicted to slow the polymerization due to ion pairing of PSt^- with Li^+-ion. These major conclusions are in a perfect agreement with the experimentally observed effects of both lithium butoxide additives on the rate of the anionic polymerization of styrene [3,5,6].

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