Density Functional Theory Study on the Aggregation and Dissociation Behavior of Lithium Chloride in THF and Its Interaction with the Active Centers of the Anionic Polymerization of Methyl Methacrylate and Styrene

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ABSTRACT: The structure of LiCl in tetrahydrofuran (THF) solution and its effect on the structure and stability of active sites of the anionic polymerization of methyl methacrylate (MMA) and styrene (St) was studied using the quantum-chemical density functional theory (DFT) approach. In the case of MMA anionic polymerization, it was found that LiCl forms stable mixed aggregates with ester enolates which model the PMMA living chain ends, thus preventing them from self-aggregation. They may even stabilize more reactive zwitterionic structures of these chain ends. The dissociation of solvated LiCl dimers to form Li⁺(THF)₄ cations is slightly endothermic in THF, while scavenging of Li⁺(THF)₄ by LiCl dimers to produce more stable quintuple cations [Li⁺(THF)₃Li⁺(LiCl)₂] is exothermic. Therefore, if the concentration of LiCl exceeds a certain threshold value, Li⁺(THF)₄ cations should effectively be scavenged by LiCl dimers. Thus, increasing LiCl concentration below the threshold concentration should lead to an increase in the concentration of free Li⁺(THF)₄ cations. In the anionic polymerization of styrene in the presence of LiCl, this results in the suppression of PSt–Li chain end dissociation due to the common ion effect, slowing down the polymerization. Further addition of LiCl above the threshold concentration should decrease the concentration of free Li⁺(THF)₄ cations, leading to enhanced PSt–Li chain end dissociation, thus increasing the polymerization rate, in agreement with kinetic data reported in the literature.

Introduction

Lithium chloride is known to affect the anionic polymerization of methyl methacrylate (MMA) in ethereal solvents such as THF. ¹ There is evidence that PMMA living chain ends form mixed aggregates with LiCl, predominantly existing in a dimeric form in THF solution,² of 1:1 and 2:1 compositions:¹

(RLi)₂ + (LiCl)₂ ⇄ 2(RLi)(LiCl)
2(RLi)(LiCl) + (LiCl)₂ ⇄ 2(RLi)(LiCl)₂

Extensive NMR studies of possible equilibria were published.³

The aggregation behavior in THF of methylα-lithioisobutyrate (MIB–Li), simulating PMMA living chain ends, has been fully studied experimentally, using vapor phase osmetry⁴ and NMR methods.⁵,⁶ It has been well established⁴–⁶ that in THF solution there is an equilibrium between dimeric and tetrameric MIB–Li aggregates, the former prevailing at low and the latter at higher temperatures. Therefore, it has been reasonably suggested⁵,⁶ that the dimer is specifically solvated with THF molecules, unlike the tetramer, and is, therefore, energetically favorable but entropically unfavorable compared to the tetramer.

Experimental data on the effect of LiCl on the anionic polymerization of styrene (St) in tetrahydropyran (THP) solution show⁷ that addition of a 7-fold molar excess of LiCl retards the polymerization if LiCl concentration is low (about 10⁻⁴ mol/L for THP case) and accelerates it if LiCl concentration is high enough (about 10⁻² mol/L in THP). These data were interpreted in terms of a prevailing ionogenic equilibrium into which LiCl is involved in an ethereal solvent, like THP or THF, depending on its concentration. Thus, if the LiCl concentration is low, Li⁺ cations are mainly supplied into the solution via unimolecular dissociation of LiCl dimers:

(LiCl)₂ ⇄ Li⁺ + (Cl⁻–Li–Cl)⁻

suppressing the dissociation of living polymer chain ends, PSt–Li, by a common ion effect. As styrene polymerization in ethereal solvents is mainly propagated by free anions, PSt⁻,⁸ this results in slowing down the polymerization. On the other hand, at sufficiently high LiCl concentration, a bimolecular scavenging reaction of Li⁺ by LiCl was proposed to dominate

Li⁺ + (LiCl)₂ ⇄ (Li–Cl–Li–Cl–Li)⁺

thus promoting PSt–Li dissociation and enhancing the polymerization rate.

The aim of the present paper is 2-fold: using the modern quantum-chemical density functional theory (DFT) approach, (1) to analyze the energetics of possible ionogenic reactions of LiCl itself in an ethereal solvent (THF) and (2) to study the solvent (THF) and the additive (LiCl) effects on the stability and structure of
models of PMMA-Li and PSt-Li living chain ends and their reactivities as anionic polymerization propagation centers.

It should be noted that the reactivity of PSt-Li living chain ends is considered to be determined by their ability to dissociate into free anions, PSt chains ends is supposed to be dependent only on their aggregation state, because the equilibrium constant of their dissociation into free ions is very low.²⁸ Earlier, some of us reported on ab initio Hartree-Fock calculations of MIB-Li aggregates.¹⁰ However, in that work, effects of the specific solvation by THF on the MIB-Li aggregation state were estimated only semiempirically.

**Methods**

All quantum-chemical calculations were carried out employing the TURBOMOLE package²³ of ab initio quantum chemical programs within the framework of the DFT approach.¹²

The geometries of all studied structures of the type (R-Li)_n(THF)_y were completely optimized. Active sites of MMA polymerization were simulated by ω-lithiobenzyl isobutylate (MIB-Li) in both nonaggregated (n = 1) and aggregated (n = 2) states and those of St polymerization by 1-lithioethylbenzene (EB-Li) in a nonaggregated state (n = 1). Specific solvation by THF molecules was taken into account by adding the necessary amount of THF molecules so as to create a tetrahedral arrangement of electron donors (oxygen and/or chlorine atoms) around each of Li atoms.

For the DFT geometry optimizations, Becke’s exchange potential¹³ and Perdew’s correlation potential¹⁴ were used. This set of DFT potentials is hereafter referred to as BP86.

TURBOMOLE split valence plus polarization (SVP) basis sets¹⁵ of 6-31G* quality were employed. The details about contraction schemes and polarization function exponents for each element are described in the recently published paper.¹⁶ For all the structures optimized at the SVP/BP86 level, single-point energy calculations at the TZVP/B3-LYP level were performed using Karlsruhe TZVP basis sets, consisting of TZV basis sets¹⁷ of triple-zeta quality augmented with polarization functions for all atoms,¹⁸ and Becke’s three-parameter functional¹³ with the correlation potential by Lee, Yang, and Parr.¹⁹

Calculating B3-LYP energies at the geometries optimized at a lower level of theory (including even semiempirical one) was recently justified by Abbott, Streitwieser, and Schleyer in a lower level of theory (including even semiempirical one) was recently published paper.¹⁶

RI approximation,²¹ allowing one to approximate the Coulomb potential with high accuracy without calculations of four-centered two-electron integrals, was used at the SVP/BP86 level. The set of atom-centered auxiliary basis set (ABS) utilized by the RI approximation was the same as in ref 16.

In some cases, ³¹C NMR shifts, δ, on atoms of interest (mainly Li atoms or carbons of MIB-Li monomers) were calculated by the GIAO–SCF method²² implemented into the TURBOMOLE program²³ and compared with relevant experimental data. For the NMR calculations of all structures studied, Hartree–Fock molecular orbitals were calculated at the SVP/BP86-optimized geometries with the TZVP basis sets. Although no transition state structures were calculated in the present paper, we attempted to estimate the relative reactivity of MIB-Li aggregates as MMA propagation centers by comparing their chemical shifts for α-carbons and, thus, to their reactivity with respect to the monomer.

For all LiCl-aggregated complexes with THF of the type (LiCl)_n(THF)_y, the values of a comparable stability parameter, the averaged energy per one LiCl molecule, E[(LiCl)_n(THF)_y], were calculated via eq 1, where E[(LiCl)_n(THF)_y] and E(THF)

\[
\frac{E[(LiCl)_n(THF)_y]}{n} - \frac{E[(LiCl)_n(THF)_y]}{n} - \frac{E(THF)}{x}
\]

are the minimized total energy of the particular complex (LiCl)_n(THF)_y, and THF molecule, respectively.

For all considered structures of the type (R-Li)_n(LiCl)_y(THF)_z, the values of the averaged energy per one active site, E[(R-Li)_n(LiCl)_y(THF)_z], were calculated as a comparable stability parameter

\[
\frac{E[(R-Li)_n(LiCl)_y(THF)_z]}{n} - \frac{E[(R-Li)_n(LiCl)_y(THF)_z]}{n} - \frac{E(THF)}{x}
\]

are the minimized total energy of the particular complex (R-Li)_n(LiCl)_y(THF)_z, and THF molecule, respectively.

The results presented in this paper were obtained for ϵ = 12.13, corresponding to the dielectric constant of THF at low temperature, about −70 °C, at which MMA anionic polymerization typically proceeds. It should be noted that (1) the anionic polymerization of St is usually being carried out at higher temperatures (between 20 and 200 °C) and (2) the ε value for THF is lower than that for THF. However, no qualitative changes in the obtained results were found when ε = 7.42, which corresponds to the dielectric constant of THF at room temperature and is close to the ε value of THF at room temperature (5.71), was used.

**Results and Discussion**

1. **LiCl Behavior in THF.** Calculated DFT values of total energies, E, stability indices, E, and MNDO-estimated nonspecific solvation energies, E_{nss}, for all studied (LiCl)_n(THF)_y complexes are summarized in Table 1.

Table 1 presents the data concerning the energetics of gradual deaggregation of LiCl from dimeric to unimeric form upon increasing specific solvation by THF.
molecules per one LiCl molecule is, in general, favorable.

1) and in polar medium (Figure 1b) which is rather stable both in a vacuum (Figure 2a) and a quintuple cation [(THF)3Li—Cl—Li—(THF)2—Cl—Li(THF)3]+ (Figure 2b). At the higher level of theory, this dissociation reaction is almost thermoneutral if nonspecific solvation is taken into account.

According to NMR data for allylic lithium compounds,26–28 the Li atom in triple anions of the (allyl—Li—allyl)- kind is not solvated. Conductivity studies of THF solution of LiCl also showed that the data are better reproduced theoretically if one assumes that in a triple anion (Cl—Li—Cl)— the central Li atom is not solvated.29 The reason for this is, probably, of entropic nature, as our DFT data show that THF solvation of the Li atom within the triple anion is energetically favorable.

Table 1 DFT Results Related to LiCl Aggregation and Dissociation Behavior in THF

<table>
<thead>
<tr>
<th>structure</th>
<th>$E$, hartree</th>
<th>$E$, kJ/mol</th>
<th>$\Delta E$, kJ/mol</th>
<th>$E_{\text{nss}}$, kJ/mol</th>
<th>$\Delta (E + E_{\text{nss}})$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LiCl)2(THF)4</td>
<td>a</td>
<td>-1864.636073</td>
<td>-467.776405</td>
<td>0</td>
<td>-63.7</td>
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<tr>
<td>(LiCl)2(THF)5</td>
<td>b</td>
<td>-1865.205806</td>
<td>-467.833437</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(LiCl)(THF)4</td>
<td>a</td>
<td>-1896.912118</td>
<td>-467.78864</td>
<td>-6.4</td>
<td>-80.3</td>
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<tr>
<td>(LiCl)(THF)5</td>
<td>a</td>
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<td>-467.772459</td>
<td>10.4</td>
<td>-52.3</td>
</tr>
<tr>
<td>(LiCl2(THF)4</td>
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<td>-467.76979</td>
<td>-1.5</td>
<td>-51.2</td>
</tr>
<tr>
<td>(LiCl2(THF)5</td>
<td>a</td>
<td>-1869.936299</td>
<td>-467.827697</td>
<td>15.0</td>
<td>8.5</td>
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</table>

Table 4 contains calculated DFT values of total energies, $E$, stability indices, $E$, and MNDO-estimated nonspecific solvation energy, $E_{\text{nss}}$, values for all (MIB—Li)+ by (LiCl2(THF)4). The results are qualitatively similar at both levels of theory. It is seen that the formation of a quintuple cation [(THF)3Li—Cl—Li—(THF)2—Cl—Li(THF)3]+, as a result of the scavenging, is thermodynamically favorable (the enthalpy is negative) both in a vacuum and in the polar solvent. The formation of triple cation, [(THF)3Li—Cl—Li(THF)3]+, being most preferable in a vacuum, is thermodynamically unfavorable in the polar medium.

2. Aggregation Behavior of MIB—Li, as a Model of the PMMA Living Chain End, in THF Solution

Table 2 presents the DFT enthalpies of dissociation reactions of the (LiCl2(THF)4) complex calculated per LiCl molecule as differences in the $E$ values between the products (pairs of free ions) and reagent ((LiCl2(THF)4 complex of contact ion pair type) of these reactions. As seen from the data of Table 2, the dissociation enthalpies are systematically lower at the TZVP/B3—LYP level than at the SVP/BP86 level. The most energetically favorable dissociation of (LiCl2 — THF)4 is that into a triple anion [Cl—Li(THF)2—Cl]+ (Figure 2a) and a quintuple cation [(THF)3Li—Cl—Li—(THF)2—Cl—Li(THF)3]+ (Figure 2b). At the higher level of theory, this dissociation reaction is almost thermoneutral if nonspecific solvation is taken into account.
The calculated 13C NMR α-carbon signal for the (MIB–Li)(LiCl)2(THF)6 1:2 complex (Figure 5a) is by ca. 2.3 ppm downfield shifted compared to that of the (MIB–Li)(LiCl)(THF)4 1:1 complex (Figure 4a), in agreement with slowing down MMA polymerization upon further LiCl addition (1 ≤ R ≤ 10).1 Downfield shifts of the α-carbon 13C NMR signal of di-tert-butyl 2-lithio-2,4,4-trimethylglutarate were also found upon its mixing with LiCl.3 MNDO calculations indicated the possible formation of both 2:2 and 2:4 mixed complexes of α-lithio ester enolates with LiCl, which may be considered as dimerized 1:1 (Figure 4a) and 1:2 (Figure 5a) complexes studied here. The lack of accounting for solvation effects, both specific and nonspecific, should be noted with regard to these MNDO data. In particular, it could be the reason for the considerably higher MNDO-predicted stability of the 1:2 complex between ester enolate and LiCl compared to that of 1:1 complex (by >100 kJ/mol). This is obviously not the case for the DFT data obtained in the present work: the 1:2 complex (ΔE = E_{1s}) is 7.8 and 17.4 kJ/mol at the SVP/BP86 and TZV/B3–LYP levels, respectively) is by more than 16 kJ/mol less stable than the 1:1 complex (ΔE = E_{1s}) = 9.4 and 4.3 kJ/mol at the SVP/BP86 and TZV/B3–LYP levels, respectively). Moreover, the 2:2 cubelike mixed complex (MIB–Li)2(LiCl)(THF)4 (Figure 5c) has a very high relative energy (more than 25 kJ/mol) at both theory levels and a rather low electron density at the α-carbon atoms (Δδ = 6.93 ppm). The experimentally found presence of associated PSt MMA living chains at very high LiCl concentrations32 may be due to formation of 2:1 complexes (Figure 5b).

4. Effect of LiCl on Ionogenic Reactions of PSt–Li Active Sites in THF Solution. 1-Lithioethylben-
zene (EB–Li) was used as a model compound for PST–Li chain ends. Calculated DFT values of total energies, \( E \), stability indices, \( \delta \), and MNDO-estimated nonspecific solvation energy, \( E_{\text{nss}} \), values for all studied (EB–Li)–(LiCl)\(_2\)(THF)\(_x\) complexes are collected in Table 5. It is seen that the formation of the THF-separated ion pair, EB\(^+\)[Li(THF)\(_x\)]\(^+\) (Figure 6a), is thermodynamically favorable in THF solution. However, from the experimental point of view, such ion pairs are only indirectly observed for PST–Li in THF through kinetic measurements.\(^{33,34}\) According to the calculated data presented in Table 6, their dissociation is endothermic (for \( \epsilon = 12.13 \), \( \Delta H = 31.5 \) and 15.7 kJ/mol at the SVP/BP86 and TZVP/B3–LYP/SVP/BP86 levels, respectively). It means that gain in the nonspecific solvation energy due to the dissociation is small compared to the Coulomb attraction energy within the ion pair. Therefore, the ion pair dissociation into free ions should lead to no considerable solvent confinement, and can be entropically favorable.

Experimentally, PST–Li chain ends were shown to be solvated with only two THF molecules,\(^{34,35}\) and their overall dissociation into free ions in THF was found to be slightly exothermic.\(^{36}\) Our calculations confirm the exothermicity of the dissociation of the (EB–Li)(THF)\(_2\) complex (Table 6). However, the DFT data presented in Table 5 show that the (EB–Li)(THF)\(_2\) complex is enthalpically less stable than (EB–Li)(THF)\(_3\), at both
Table 5. DFT Results Related to the Effect of LiCl on Ionogenic Reactions of PST–Li Active Sites in THF Solution

<table>
<thead>
<tr>
<th>structure</th>
<th>$E_{\text{hartree}}$</th>
<th>$E_{\text{hartree}}$</th>
<th>$\Delta E$, kJ/mol</th>
<th>$E_{\text{int}},$ kJ/mol</th>
<th>$E_{\text{int}},$ kJ/mol</th>
<th>$\Delta (E + E_{\text{int}})$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_5$-CH(CH$_3$)$_3$-Li(THF)$_2$+</td>
<td>a</td>
<td>-1014.410443</td>
<td>-317.589349</td>
<td>0</td>
<td>-47.7</td>
<td>-28.6</td>
</tr>
<tr>
<td>C$_6$H$_5$-CH(CH$_3$)$_3$-Li(THF)$_2$+</td>
<td>b</td>
<td>-1014.874294</td>
<td>-317.720095</td>
<td>0</td>
<td>30.5</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_5$-CH(CH$_3$)$_3$-Li(THF)$_2$+</td>
<td>a</td>
<td>-782.129776</td>
<td>-317.588380</td>
<td>26.2</td>
<td>-37.0</td>
<td>-24.3</td>
</tr>
<tr>
<td>C$_6$H$_5$-CH(CH$_3$)$_3$-Li(THF)$_2$+</td>
<td>b</td>
<td>-782.468090</td>
<td>-317.712624</td>
<td>19.6</td>
<td>23.9</td>
<td></td>
</tr>
</tbody>
</table>

The data of Table 6 show that the dissociation of (EB–Li)$^+$ (2, 3) is not promoted by EB$^-$ ion complexation with the LiCl molecule (the geometry of this complex is shown in Figure 6b). This result was obtained at both levels of theory. Thus, LiCl should not affect styrene anionic polymerization rate only through the change of the concentration of PST$^-$ polymerization active centers due to Li$^+$ scavenging from PST$^-$ or suppression of the dissociation of PST$^-$–Li into PST$^-$ anion and Li$^+$ (THF)$_2$ cation.

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References and Notes