

DFT Study of the Effect of σ -Ligands on the Structure of Ester Enolates in THF, as Models of the Active Center in the Anionic Polymerization of Methyl Methacrylate

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Abstract: A Density Functional Theory (DFT) study was carried out on structures of the lithium ester enolate of methyl isobutyrate (MIB-Li) in THF solution, in the presence of TMEDA, dimethoxyethane (DME), crown ether 12-crown-4, and cryptand-2,1,1, as electron donor ligands (σ -ligands). Both specific solvation with THF and/or ligand molecules and nonspecific solvation by the solvent continuum were taken into account. The possibility of ligand-separated ion pair formation was analyzed for each of the ligands, including THF alone. In most cases peripherally solvated dimers are the most stable species. Only in the presence of cryptand-2,1,1 was a ligand-separated triple ion pair, (MIB-Li-MIB)⁻(THF)₂Li(2,1,1)₁⁺, shown to be comparable in stability to the THF-solvated dimer, (MIB-Li)₂(THF)₄. These results are in agreement with experimental NMR data on the structure of MIB-Li in the presence of DME, 12-crown-4, and cryptand-2,1,1. An upfield shift of the ¹³C NMR signal of the α -carbon of MIB-Li observed in the presence of cryptand-2,1,1, originally attributed to a ligand-separated monomer, MIB⁻Li(2,1,1)⁺, was well reproduced by Hartree–Fock calculated NMR shifts for the predicted ligand-separated triple ion pair.

Introduction

Enolate ions and ion pairs are ubiquitous intermediates in many organic reactions.¹ Among them, lithiated ester enolates are most important in polymer chemistry as initiators and active centers of the anionic polymerization of (meth)acrylic monomers, e.g., methyl methacrylate (MMA).^{2,3} Thus, lithiated isobutyrate and propionate have been extensively studied as monomeric models structurally corresponding to a living chain end in these polymerization processes. Their strong tendency to aggregate in both crystalline state^{4,5} and solution^{6,7} has been widely recognized as the most important property determining the polymerization rate and molecular weight distribution.⁸

In nonpolar solvents, polymerization of MMA by α -lithio esters does not have controlled character as indicated by very broad and multimodal molecular weight distributions.^{9–11} In addition to side reactions, this may be attributed to the coexistence of various aggregated species of different reactivity

which exchange only slowly on the polymerization time scale. According to a recent DFT study on the aggregation of methyl α -lithio isobutyrate (MIB-Li) in nonpolar media,¹² the hexamer (MIB-Li)₆ is the most stable among such aggregates, in agreement with high aggregation degrees observed by vapor-phase osmometry⁶ and NMR.¹³ Moreover, an intramolecular Claisen condensation is an important terminating (“back-biting”) reaction,¹⁴ especially remarkable in nonpolar solvents due to the solvation of terminal counterions by ester groups of penultimate monomer units.¹⁵ Therefore, polar solvents, like THF, with strong affinity to the counterion are necessary to achieve a control in the polymerization of MMA.^{16–19} Vapor-pressure osmometry⁶ shows that lithiated isobutyrate are less aggregated in polar solvents, the average degree of aggregation being $n = 2–4$ in THF. These findings were confirmed by ¹³C and ⁷Li NMR studies of Wang and Teyssié,⁷ who found a dynamic equilibrium between MIB-Li dimers and tetramers in THF, the tetramer being more stable at higher temperatures. NMR measurements of Kříž et al.²⁰ even indicate the presence of trimers.

The reactivity of ester enolate chain ends should be related to the negative charge density on the C _{α} atom. Ab initio

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(Hartree–Fock) and semiempirical studies of $(\text{MIB-Li})_n$ aggregates ($n = 1, 2,$ and 4)²¹ have shown that aggregation stabilizes the structures but reduces the electron densities on the C_α atoms of the enolates, leading to (calculated) downfield ¹³C NMR shifts for these atoms, in reasonable agreement with the observed shifts. However, specific solvation of $(\text{MIB-Li})_n$ aggregates with THF molecules was studied only semiempirically in that paper. Recently performed DFT calculations of different MIB-Li aggregates with explicit inclusion of THF solvation²² have confirmed the experimental findings^{7,20,23} that the MIB-Li dimer, solvated with 4 THF molecules, $-(\text{MIB-Li})_2(\text{THF})_4$, is enthalpically the most stable aggregate in THF solution.

Aggregation of ester enolates results in a drastic decrease of their reactivity as initiators of anionic polymerization. In particular, in the anionic polymerization of MMA, initiated by MIB-Li in THF, aggregates of the active chain ends have been shown to be some orders of magnitude less reactive than nonaggregated ion pairs.⁸ Furthermore, a rather slow exchange between aggregated and nonaggregated chain ends has been shown to lead to a considerable broadening of the molecular weight distribution.^{8,24} There are a number of successful attempts to cope with these problems with ligand additives of the μ -type (e.g., Li or Na alkoxides,^{2,10,25,26} LiCl,^{8,27,28} LiClO₄,^{29,30} Al alkyls^{31–33}), σ -type (electron donors, e.g., linear and cyclic oligoethers^{23,34–36} and oligoamines,^{37–39} cryptands^{23,40}), and σ_μ -type (e.g., alkoxyalkoxides^{41,42}). As indicated by kinetic⁴⁰ and NMR²³ data, some of the σ -ligands, especially cryptands, seem to promote the formation of ligand-separated MIB-Li ion pairs as the only type of active site, thus enhancing both reactivity of the initiator and control of the polymerization.

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DFT calculations of MIB-Li in the presence of LiCl in THF²² have shown that LiCl forms stable mixed aggregates with ester enolates which model the PMMA living chain ends, thus preventing them from self-aggregating. It was also found that mixed dimers of MIB-Li with LiCl may adopt (without high energy losses) a rather reactive zwitterionic form.

The main focus of the present paper is on the quantum-chemical DFT study of the structures and relative stabilities of MIB-Li ion pairs in the presence of various σ -ligands. Correlation of results obtained with kinetic and spectroscopic data for THF solutions of ester enolates in the presence of cryptands, crown ethers, glymes, or diamines is established.

Methods

All quantum-chemical calculations were carried out employing the TURBOMOLE package⁴³ of ab initio quantum chemical programs within the framework of the DFT approach.⁴⁴ The geometries of all studied structures of the type $(\text{MIB-Li})_n(\text{ligand})_x(\text{THF})_y$ were completely optimized.

For the DFT geometry optimizations, Becke's exchange potential⁴⁵ and Perdew's correlation potential⁴⁶ were used. This set of DFT potentials, hereafter referred to as BP86, was used in the RI formalism.^{47–49} TURBOMOLE split valence plus polarization (SVP) basis sets⁵⁰ of 6-31G* quality were employed. For the fitting of the Coulomb potential within the RI formalism, Ahlrichs' auxiliary basis sets^{48,51} have been used. No frequency calculations were made. The details about contraction schemes and polarization function exponents for each element are described in a recently published paper.¹²

For all the structures optimized at the SVP/BP86 level, single-point energy calculations at the TZVP/B3-LYP level were performed with Karlsruhe TZVP basis sets, consisting of TZV basis sets⁵² of triple- ζ quality augmented with polarization functions for all non-hydrogen atoms,¹² and Becke's 3-parameter functional⁵³ with the correlation potential by Lee, Yang, and Parr.⁵⁴ For some of the considered systems emphasized in the discussion, the effect of inclusion of diffuse s-functions into the TZVP basis on the stability of ligand-separated ion pairs was checked. This level of calculation will be referred to as TZVP+/B3LYP. The diffuse s-functions added had the exponents of 0.024, 0.046, 0.034, and 0.026 for carbon, oxygen, nitrogen, and hydrogen atoms, respectively, corresponding to $1/4$ of the lowest s-exponent in the TZVP basis sets for these atoms. As the TZVP basis set for lithium contains a rather diffuse s-function with the exponent of 0.029, no other diffuse functions for lithium atoms were added.

In some cases, ¹³C NMR shifts on atoms of interest (mostly α -carbons of MIB-Li moieties) were calculated by the GIAO-SCF method⁵⁵ implemented into the TURBOMOLE program⁵⁶ and compared with relevant experimental data. For the NMR shift calculations of all structures studied, Hartree–Fock molecular orbitals were calculated at the SVP/BP86-optimized geometries with the TZVP basis sets.

For all considered structures of the type $(\text{MIB-Li})_n(\text{ligand})_x(\text{THF})_y$, the values of the averaged energy per one MIB-Li molecule $\bar{E}[(\text{MIB-Li})_n(\text{ligand})_x(\text{THF})_y]$

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Table 1. Calculated Nonspecific Solvation Energies, E_{NSS} , for Isolated Ligand Molecules

ligand	symmetry	E_{NSS} , kJ/mol
THF	C_2	-6.4
TMEDA	C_2	-2.9
DME	C_2	-9.7
12-crown-4	C_1	-18.1
cryptand-2,1,1	C_1	-18.0

$\text{Li})_n(\text{ligand})_x(\text{THF})_y]$, were calculated as a comparable stability parameter:

$$\bar{E} = (1/n)\{E[(\text{MIB-Li})_n(\text{ligand})_x(\text{THF})_y] - x \cdot E(\text{ligand}) - y \cdot E(\text{THF})\} \quad (1)$$

where $E[(\text{MIB-Li})_n(\text{ligand})_x(\text{THF})_y]$ denotes the minimized total energy of the particular structure and $E(\text{ligand})$ and $E(\text{THF})$ are minimized total energies of the isolated molecules of the given ligand and THF, respectively.

In addition to the specific solvation, taken into account by the explicit inclusion of THF molecules into the considered complexes, their nonspecific solvation by the solvent continuum is of importance, as far as the stability of solvent- or ligand-separated ion pairs is concerned. Nonspecific solvation energies, E_{NSS} , of all structures were calculated semiempirically at the SVP/BP86-optimized geometries by using the solvent-continuum model⁵⁷ implemented into the modified MOPAC 6.0 program. MNDO parametrization⁵⁸ was used. The solvent polarity was characterized by its dielectric constant, ϵ . The results presented in this paper were obtained for $\epsilon = 12.13$, corresponding to the dielectric constant of THF at low temperature, about -70°C , at which MMA anionic polymerization typically proceeds. Average values of nonspecific solvation energies per MIB-Li molecule, \bar{E}_{NSS} , were calculated analogously to eq 1:

$$\bar{E}_{\text{NSS}} = (1/n)\{E_{\text{NSS}}[(\text{MIB-Li})_n(\text{ligand})_x(\text{THF})_y] - x \cdot E_{\text{NSS}}(\text{ligand}) - y \cdot E_{\text{NSS}}(\text{THF})\} \quad (2)$$

The E_{NSS} values for isolated THF and other ligand molecules are presented in Table 1.

Results and Discussion

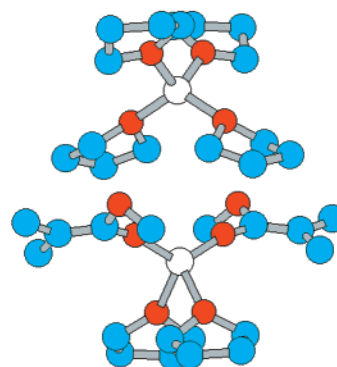
As mentioned in the Introduction, our recent DFT studies of the aggregation behavior of MIB-Li in THF solution²² have shown that the MIB-Li dimer solvated with 4 THF molecules, $(\text{MIB-Li})_2(\text{THF})_4$, is enthalpically the most stable structure of contact ion pair type, in agreement with the experimental data.^{7,20,23} Our calculations showed that addition of one more THF molecule to this aggregate leads to breakage of one Li-O bond and formation of a zwitterionic complex, $(\text{MIB-Li})_2(\text{THF})_5$. The latter was calculated to be less stable than $(\text{MIB-Li})_2(\text{THF})_4$ by ca. 5 kJ/mol per MIB-Li molecule, but had a higher electron density on the α -carbon atoms. The calculated ^{13}C NMR shifts for the α -carbon atoms are by 2.5–3.5 ppm to higher field compared to $(\text{MIB-Li})_2(\text{THF})_4$.²² These data are reproduced in Table 2 for the sake of comparison with corresponding data for solvent- and ligand-separated ion pairs of MIB-Li discussed below.

Stabilities of Solvent-Separated Ion Pairs in Ligand-Free THF Solution of MIB-Li. It is clear that any structure of a solvent-separated ion pair should include the $[\text{Li}(\text{THF})_4]^+$ cation. Approximate semiempirical estimations have shown⁵⁹ that solvent-separated ion pairs with the monomeric MIB⁻ coun-

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**Figure 1.** Optimized structure of a THF-separated ion pair $(\text{MIB-Li-MIB})^-(\text{THF})_2/\text{Li}(\text{THF})_4^+$ (hydrogens are not shown).

teranion are far less stable than the dimeric contact ion pair $(\text{MIB-Li})_2(\text{THF})_4$, while those with the $(\text{MIB-Li-MIB})^-$ triple anion may have a comparable and (as will be shown later) even higher stability than that of the contact ion pairs. The crucial role of similar triple anions, $(\text{Cl-Li-Cl})^-$ for the ionogenic equilibria of LiCl in polar solvents has been found experimentally⁶⁰ and confirmed by DFT calculations.²² Triple ions have also been observed in the anionic polymerizations of styrene^{61,62} and vinyl pyridine.⁶³ Triple anions of organolithium compounds were found by X-ray structural analysis for some of their ate complexes with electron donor ligands.^{64,65} Thus, tris(trimethylsilyl)methylolithium forms with THF⁶⁴ and TMEDA⁶⁵-separated ion pair adducts of the form $(\text{SiMe}_3)_3\text{C-Li-C}(\text{SiMe}_3)_3, \text{Li}(\text{THF})_4^+$ and $(\text{SiMe}_3)_3\text{C-Li-C}(\text{SiMe}_3)_3, \text{Li}(\text{TMEDA})_2^+$, respectively.

The optimized structure of a THF-separated ion pair $(\text{MIB-Li-MIB})^-(\text{THF})_2, \text{Li}(\text{THF})_4^+$ is shown in Figure 1. The Li atom in the triple anion is specifically solvated with 2 THF molecules as has also been found energetically favorable for the $(\text{Cl-Li-Cl})^-$ triple anion.²² The structure is characterized by the C_2 symmetry axis passing through the two Li atoms, which is also a structural feature for all ion pairs discussed below. The calculated relative energies for this and other ion pairs are collected in Table 2.

It is seen from Table 2 that even at $\epsilon = 12.13$, the solvent-separated ion pair $(\text{MIB-Li-MIB})^-(\text{THF})_2, \text{Li}(\text{THF})_4^+$ is by ca. 20 kJ/mol (at the TZVP/B3LYP level of theory) per one MIB-Li molecule less stable than the contact ion pair $(\text{MIB-Li})_2(\text{THF})_4$.

Stabilities of Ligand-Separated Ion Pairs in THF Solution of MIB-Li in the Presence of TMEDA. The dimeric contact ion pair $(\text{MIB-Li})_2(\text{TMEDA})_2$ (Figure 2a) and two structures of TMEDA-separated ion pairs of MIB-Li (Figure 2b,c) were calculated. In one of the latter two, the Li atom in the triple anion is solvated with two THF molecules (Figure 2b) and in the other one with one TMEDA molecule (Figure 2c). As seen from Table 2, the former of these two TMEDA-separated ion pairs, $(\text{MIB-Li-MIB})^-(\text{THF})_2/\text{Li}(\text{TMEDA})_2^+$, is more stable than the latter, but it is of almost the same stability as the

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Table 2. Relative DFT Energies for the Ion Pairs of MIB-Li Calculated at the SVP/BP86, **TZVP/B3LYP** (in bold), and ***TZVP+/B3LYP*** (in bold italic) Levels^d

structure	figure no. or ref	sym / δ , ppm ^c	$\Delta\bar{E}$, kJ/mol	E_{nss} , kJ/mol	\bar{E}_{nss} ^b , kJ/mol	$\Delta(\bar{E} + \bar{E}_{\text{nss}})$, kJ/mol
(MIB-Li) ₂ (THF) ₄ ^a	ref ²²	C ₂ 74.2	0 0 <i>0</i>	-44.2	-9.4	0 0 <i>0</i>
(MIB-Li) ₂ (THF) ₅ ^a	ref ²²	C ₁ 70.6; 71.6	5.7 10.7	-52.6	-10.4	4.7 9.7
(MIB-Li-MIB) ⁻ (THF) ₂ /(THF) ₄ Li ⁺	1	C ₂	26.9 32.2	-81.9	-21.8	14.5 19.8
(MIB-Li) ₂ (TMEDA) ₂	2a	C ₂	17.0 7.0	-36.7	-15.5	10.9 0.9
(MIB-Li-MIB) ⁻ (THF) ₂ /Li(TMEDA) ₂ ⁺	2b	C ₂	36.3 36.6	-75.1	-28.3	17.4 17.7
(MIB-Li-MIB) ⁻ (TMEDA) ₁ /Li(TMEDA) ₂ ⁺	2c	C ₂	47.7 42.0	-66.0	-28.7	28.4 22.7
(MIB-Li) ₂ (DME) ₂	3a	C ₂	22.3 18.8	-59.5	-20.0	11.7 8.2
(MIB-Li-MIB) ⁻ (THF) ₂ /Li(DME) ₂ ⁺	3b	C ₂	33.9 38.0	-97.6	-32.7	10.6 14.7
(MIB-Li-MIB) ⁻ (DME) ₁ /Li(DME) ₂ ⁺	3c	C ₂	36.9 40.1	-78.0	-24.5	21.8 25.0
(MIB-Li) ₂ (12-crown-4) ₂	4a	C ₂	25.7 35.8	-60.3	-12.0	23.1 33.2
(MIB-Li-MIB) ⁻ (THF) ₂ /Li(12-crown-4) ₂ ⁺	4b	C ₂	15.5 30.4	-89.0	-20.0	4.9 19.8
(MIB-Li-MIB) ⁻ (12-crown-4) ₁ , Li(12-crown-4) ₂ ⁺	4c	C ₂	31.3 50.6	-86.1	-15.9	24.8 44.1
(MIB-Li-MIB) ⁻ (THF) ₂ /Li(2,1,1) ₁ ⁺	5a	C ₂ 66.4	15.5 20.0 <i>20.7</i>	-83.1	-26.2	-1.3 3.2 <i>3.9</i>
MIB ⁻ /Li(2,1,1) ₁ ⁺ (ligand-separated ion pair)	5b	C ₁ 59.9	78.9 81.2 <i>82.2</i>	-99.9	-81.9	6.4 8.7 <i>9.7</i>
(MIB-Li)(2,1,1) ₁ (contact ion pair)	5c	C ₁ 68.3	38.8 49.7 <i>51.1</i>	-47.4	-29.4	18.8 28.7 <i>30.1</i>

^a Taken from ref 22. ^b Calculated via eq 2. ^c Calculated ¹³C NMR shift at α -carbon atoms. ^d The absolute energies and absolute values of \bar{E} (according to eq 1) in hartrees are given as Supporting Information.

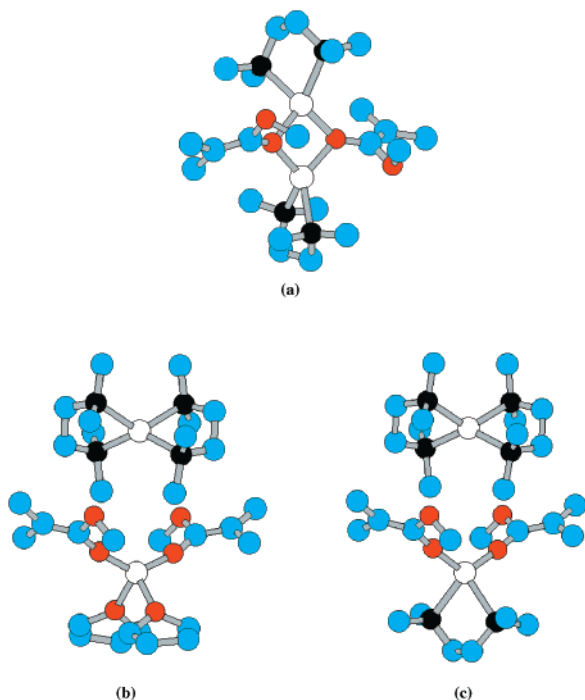


Figure 2. Optimized structures of MIB-Li complexes with TMEDA (hydrogens are not shown): (a) contact ion pair (MIB-Li)₂(TMEDA)₂, (b) TMEDA-separated ion pair (MIB-Li-MIB)⁻(THF)₂/Li(TMEDA)₂⁺, and (c) TMEDA-separated ion pair (MIB-Li-MIB)⁻(TMEDA)₁/Li(TMEDA)₂⁺.

solvent-separated ion pair, (MIB-Li-MIB)⁻(THF)₂/Li(THF)₄⁺ (at the TZVP/B3LYP level of theory, $\Delta(\bar{E} + \bar{E}_{\text{nss}})$ values are ca. 18 and 23 kJ/mol, respectively). This result is in obvious agreement with the experimental data revealing no accelerating effect of TMEDA addition on the rate of MMA polymerization in THF solution.³⁹ The MIB-Li dimer, solvated with two TMEDA molecules, (MIB-Li)₂(TMEDA)₂, was found (at the SVP/BP86 level of calculations) to be less stable than the THF-solvated dimer, (MIB-Li)₂(THF)₄. At the TZVP/B3LYP level, the stabilities of the two contact ion pairs are comparable.

Stabilities of Ligand-Separated Ion Pairs in THF Solution of MIB-Li in the Presence of DME. The two most stable structures of DME-separated ion pairs of MIB-Li are shown in Figure 3b,c. In one of them, which could be denoted as (MIB-Li-MIB)⁻(THF)₂/Li(DME)₂⁺, the Li atom in the triple anion is solvated with two THF molecules (Figure 3b) and in the other one with one DME molecule (Figure 3c). At both levels of theory, the former is by more than 10 kJ/mol and the latter by more than 20 kJ/mol per one MIB-Li molecule less stable than the dimeric contact ion pair (MIB-Li)₂(THF)₄ (Table 2). The dimeric contact ion pair solvated with two DME molecules, (MIB-Li)₂(DME)₂ (Figure 3a), is also by almost 10 kJ/mol less stable than the THF-solvated contact ion pair. Generally, the stabilities of DME-separated ion pairs are similar to those of the corresponding TMEDA-separated ion pairs, at least at the TZVP/B3LYP level of calculations (Table 2). This coincides with the lower reactivity of PMMA-Li in pure DME.⁶⁶

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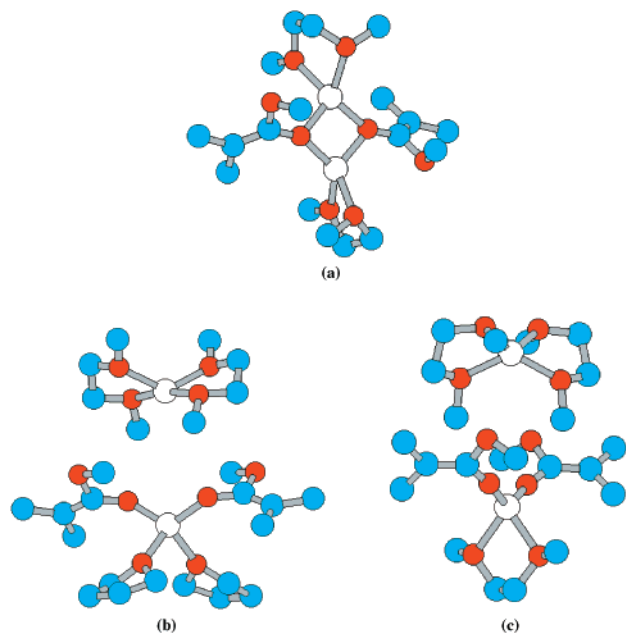


Figure 3. Optimized structures of MIB-Li complexes with DME (hydrogens are not shown): (a) contact ion pair $(\text{MIB-Li})_2(\text{DME})_2$, (b) DME-separated ion pair $(\text{MIB-Li-MIB})^-(\text{THF})_2/\text{Li}(\text{DME})_2^+$, and (c) DME-separated ion pair $(\text{MIB-Li-MIB})^-(\text{DME})_1,\text{Li}(\text{DME})_2^+$.

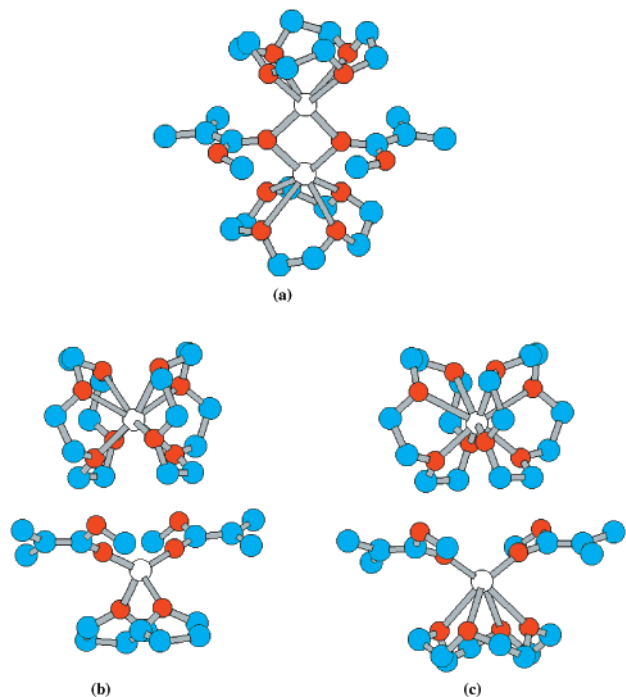


Figure 4. Optimized structures of MIB-Li complexes with 12-crown-4 (hydrogens are not shown): (a) contact ion pair $(\text{MIB-Li})_2(12\text{-crown-4})_2$, (b) 12-crown-4-separated ion pair $(\text{MIB-Li-MIB})^-(\text{THF})_2/\text{Li}(12\text{-crown-4})_2^+$, and (c) 12-crown-4-separated ion pair $(\text{MIB-Li-MIB})^-(12\text{-crown-4})_1,\text{Li}(12\text{-crown-4})_2^+$.

Stability of Ligand-Separated Ion Pairs in THF Solution of MIB-Li in the Presence of 12-Crown-4. Figure 4 presents the completely DFT-optimized structures of the MIB-Li dimeric contact ion pair solvated with two 12-crown-4 molecules (Figure 4a) and 12-crown-4-separated ion pairs, $(\text{MIB-Li-MIB})^-(\text{THF})_2/\text{Li}(12\text{-crown-4})_2^+$ (Figure 4b) and $(\text{MIB-Li-MIB})^-(12\text{-crown-4})_1,\text{Li}(12\text{-crown-4})_2^+$ (Figure 4c). As seen from Table 2, the ligand-separated ion pair with two 12-crown-4 and two THF molecules, $(\text{MIB-Li-MIB})^-(\text{THF})_2,\text{Li}(12\text{-crown-4})_2^+$, is the most

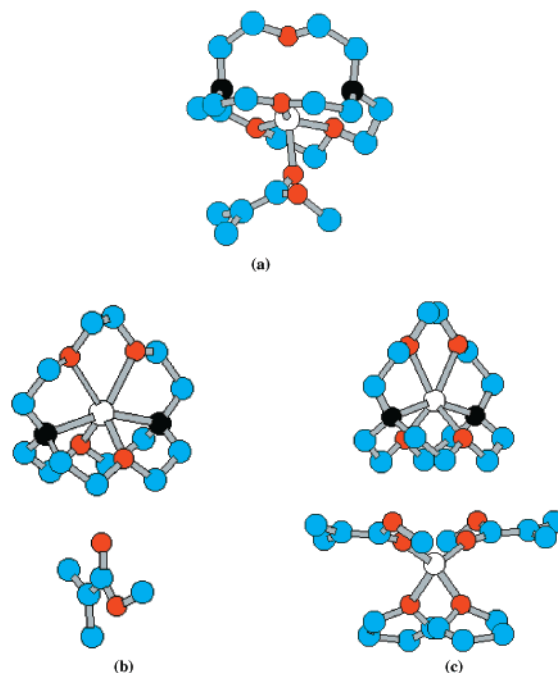


Figure 5. Optimized structures of MIB-Li complexes with cryptand-2,1,1 (hydrogens are not shown): (a) contact ion pair $(\text{MIB-Li})(2,1,1)_1$, (b) $(2,1,1)$ -separated ion pair $\text{MIB}^-/\text{Li}(2,1,1)_1^+$, and (c) $(2,1,1)$ -separated triple ion pair $(\text{MIB-Li-MIB})^-(\text{THF})_2,\text{Li}(2,1,1)_1^+$.

stable among the three structures, the other two being strongly sterically destabilized due to bulkiness of the ligand molecules. At the SVP/BP86 level of theory, the $(\text{MIB-Li-MIB})^-(\text{THF})_2/\text{Li}(12\text{-crown-4})_2^+$ structure is of slightly lower (although comparable) stability than the contact ion pair $(\text{MIB-Li})_2(\text{THF})_4$ ($\Delta(\bar{E} + \bar{E}_{\text{NSS}}) = 4.9$ kJ/mol). However, at the TZVP/B3LYP level, it is much less stable ($\Delta(\bar{E} + \bar{E}_{\text{NSS}}) = 19.8$ kJ/mol, Table 2). It should be noted that this ligand-separated ion pair could also be disfavored by entropic contributions due to two fixed ligand molecules. The combination of enthalpic and entropic reasons can explain why ^{13}C and ^7Li NMR studies of MIB-Li aggregates in THF solution in the presence of 12-crown-4²³ have revealed only contact ion pairs with degrees of aggregation 2 and 4. No kinetic data for MMA polymerization in the presence of crown ethers have been reported. Our results suggest that the effect of crown ethers on the kinetics should not be very pronounced.

Stability of Ligand-Separated Ion Pairs in THF Solution of MIB-Li in the Presence of Cryptand-2,1,1. Figure 5 shows the completely optimized geometries of the three structures: $(\text{MIB-Li})(2,1,1)_1$ contact ion pair (Figure 5a) and cryptand-2,1,1-separated ion pairs, including the monomeric anion, MIB^- , $\text{Li}(2,1,1)_1^+$ (Figure 5b), and triple anion, $(\text{MIB-Li-MIB})^-(\text{THF})_2,\text{Li}(2,1,1)_1^+$ (Figure 5c).

As seen from Table 2, at both levels of theory the triple ion pair shown in Figure 5c is the most stable among these three structures. It is also very close in stability to the THF-solvated contact ion pair, $(\text{MIB-Li})_2(\text{THF})_4$ ($\Delta(\bar{E} + \bar{E}_{\text{NSS}}) = -1.3$ and 3.2 kJ/mol at the SVP/BP86 and TZVP/B3LYP levels of calculations, respectively). A rather similar structure with a caged Li^+ cation was determined by X-ray structural analysis of the complex of 2,1,1 with LiI .⁶⁷ A virtually complete dissociation of the Li-I bond was found, the distance between these atoms exceeding 6.5 Å. The distance of inter-ion separation in the $(\text{MIB-Li-MIB})^-(\text{THF})_2,\text{Li}(2,1,1)_1^+$ ion pair, which could

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be approximately characterized by the distance between the Li atoms, slightly exceeds 6 Å (Figure 5). Moreover, it should be stressed that the Li and I atoms in the crystal structure of the ion pair $\text{I}^-, \text{Li}(2,1,1)_1^+$ lie on the C_2 symmetry axis of the complex, exactly as the two Li atoms do in the calculated structure of the $(\text{MIB-Li-MIB})^-(\text{THF})_2, \text{Li}(2,1,1)_1^+$ ion pair.

The calculated comparable stability of the $(\text{MIB-Li-MIB})^-(\text{THF})_2, \text{Li}(2,1,1)_1^+$ ion pair with respect to that of $(\text{MIB-Li})_2(\text{THF})_4$ agrees with the experimental evidence for a much more polar complex found by ^{13}C and ^7Li NMR studies of THF solutions of MIB-Li in the presence of 2,1,1.²³ The ^{13}C NMR signal for the α -carbon found for this very polar structure was shifted by 5.5 ppm to higher field with respect to the signal of the MIB-Li dimer in the absence of the additive. As presented in Table 2, the difference, $\Delta\delta$, in the calculated ^{13}C NMR shifts of the α -carbon atoms between the $(\text{MIB-Li})_2(\text{THF})_4$ and $(\text{MIB-Li-MIB})^-(\text{THF})_2, \text{Li}(2,1,1)_1^+$ structures is ca. 8 ppm. The agreement with the experimental result mentioned above is excellent, taking into account the reported accuracy of the theoretical approach (7–10 ppm).⁶⁸

In the $(\text{MIB-Li})(2,1,1)_1$ contact ion pair (Figure 5a) the calculated ^{13}C NMR shift of the α -carbon atom is rather similar to that of the $(\text{MIB-Li-MIB})^-(\text{THF})_2, \text{Li}(2,1,1)_1^+$ triple ion pair. However, this contact ion pair is of rather low stability ($\Delta(\bar{E} + \bar{E}_{\text{nss}}) = 18.8$ and 28.7 kJ/mol at the SVP/BP86 and TZVP/B3LYP levels of theory, respectively). In contrast, the $\text{MIB}^-, \text{Li}(2,1,1)_1^+$ ion pair (Figure 5b) is of comparable stability ($\Delta(\bar{E} + \bar{E}_{\text{nss}}) = 6.4$ and 8.7 kJ/mol at the SVP/BP86 and TZVP/B3LYP levels of theory, respectively) with respect to the $(\text{MIB-Li-MIB})^-(\text{THF})_2, \text{Li}(2,1,1)_1^+$ triple ion pair, but its calculated $\Delta\delta \approx 14$ ppm (Table 2) is unrealistically large compared to the experimental value ($\Delta\delta \approx 5.5$ ppm).²³

To check the reliability of the results for the cryptated systems discussed in this paragraph, we performed single-point energy calculations for these systems and for the $(\text{MIB-Li})_2(\text{THF})_4$ at the TZVP+/B3-LYP level using the TZVP basis set augmented with diffuse s-functions at all but Li atoms. As seen from Table 2, the effect of the diffuse s-functions on the stability of the cryptated ion pairs compared to the $(\text{MIB-Li})_2(\text{THF})_4$ does not exceed 1.5 kJ/mol and it does not change the results qualitatively.

Conclusions

The data of DFT calculations presented above clearly demonstrate that TMEDA-, DME- and 12-crown-4-separated ion pairs of MIB-Li are not sufficiently stable in THF solution to cause an accelerating effect on the anionic polymerization of MMA by MIB-Li in the presence of these σ -ligands. This

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result agrees with the experimental data for both TMEDA³⁹ and oligoether ligands.²³ In contrast, the formation of the cryptand-2,1,1-separated triple ion pair of MIB-Li (Figure 5c) was shown to be energetically quite favorable in THF solution at all considered levels of theory, including calculations at the TZVP+/B3LYP level with diffuse s-functions. These data are in general agreement with the experimental ^{13}C and ^7Li NMR data by Wang et al.²³ It is important to emphasize that the structural features of the ion pair (C_2 -symmetry and interionic separation) are in excellent agreement with those found experimentally for 2,1,1-cryptated lithium iodide.⁶⁷ A tremendous increase in rate was also observed in the polymerization of MMA in the presence of $\text{Na}^+(2,2,2)$ counteraction.⁴⁰

Wang et al.²³ have postulated that the counteranion within the ion pair formed in the presence of cryptand-2,1,1 is the monomeric MIB^- anion. However, our data on the calculated stabilities and ^{13}C NMR chemical shifts of α -carbons for the 2,1,1-cryptated complexes of MIB-Li point to the $(\text{MIB-Li-MIB})^-(\text{THF})_2, \text{Li}(2,1,1)_1^+$ triple ion pair as the most probable one. Moreover, experimental X-ray data confirm the ability of organolithium compounds to form THF-separated ion pairs containing triple counteranions with respect to the $\text{Li}(\text{THF})_4^+$ cation.^{64,65} As further arguments for triple anions, it could also be added that solutions of phenyllithium have been postulated to contain $\text{Li}^+, \text{Ph-Li-Ph}^-$ ion pairs,⁶⁹ and those of 1:1 PhM-PhLi adducts to contain ion pairs $\text{M}^+, \text{Ph-Li-Ph}^-$ ($\text{M} = \text{Na, K, Cs}$),^{70,71} and a crystalline complex with the suggested⁷² structure of $\text{NaOEt}_2^+, \text{Ph-Li-Ph}^-$ is known.^{70,71}

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Supporting Information Available: Calculated absolute total energy values, \bar{E} and (in hartrees), at the SVP/BP86, TZVP/B3LYP, and (where available) TZVP+/B3LYP levels and the SVP/BP86-optimized Cartesian coordinates (in atomic units) for all the structures mentioned in Tables 1 and 2 and input files for visualization with the HYPERCHEM software (extension-.hin), containing the atomic coordinates (in Å) of the structures in Figures 1–5 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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