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Anionic Polymerization of Acrylic Monomers. 18. NMR Characterization of a Unique Complex between Lithium 2-(2-Methoxyethoxy) Ethoxide and Methyl α-Lithioisobutyrate

Jin-Shan Wang, Robert Jérôme, and Philippe Teyssié[*]

Centre for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium

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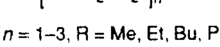
ABSTRACT: A unique ligand-promoted-loose mixed complex MIB$^-$(Li$_3$(OEEM)$_2$)$^+$ has been characterized for the first time by means of NMR spectroscopy in solution. This new complex, which is a dual μ/σ one, is obviously different from either a simple tight μ-mixed complex, such as nMIBLi·mX (X = Cl or OtBu), or a σ-cation-binding one with more charge separation, such as K211/MIBLi. It originates from a simultaneous dual complexation (μ/σ) of MIBLi by both the lithium alkoxide (μ-mixed complexation) and the chelating polyether components (σ-cation-binding complexation) of LiOEEM. Furthermore, it has been demonstrated that, whichever the solvent, i.e., toluene, a 9/1 toluene/THF mixture, or THF, complexation of MIBLi by $\geq$ 2 mol equiv of LiOEEM produces the same type of complex, i.e., MIB$^-$(Li$_3$(OEEM)$_2$)$^+$, suggesting that, in this strong complex, the lithium cations are strongly coordinated by the ligand.

Introduction

Very recently, it has been demonstrated from this laboratory that a new family of lithium polydentate alkoxides (1) affords the living anionic (co)polymerization of methacrylates and acrylates.[1] In comparison with other ligands discovered to date by us[2] and others,[3] this family of additives has several definite advantages, which included (1) direct living anionic polymerization of some acrylates including primary ones such as nBuA and 2EtHA,[4] (2) direct anionic block copolymerization of methacrylates and primary acrylates whichever monomer is first polymerized,[5] (3) control of a high syndiotacticity of PMMA (*rr*: 75–85%) even in toluene at relatively high temperatures (e.g., 0 °C),[6] and (4) living random copolymerization of MMA and tBuA.[7] Furthermore, ligands 1, which combine two different types of complexing groups in the same molecule, i.e., lithium alkoxide (μ-type) and polyether (σ-chelating type), should display a special character in coordinating with lithium-containing initiators.

On the other hand, in order to elucidate the mechanism of ligated anionic living polymerizations, we have systematically carried out investigations on the structure and equilibrium of ion pairs and related complexes by means of NMR spectroscopy.[8–11] Accordingly, the formation of the so-called μ-mixed[9,10] and σ-cation-binding[11] complexes has been well characterized, thanks to the use of a suitable model compound,[8] i.e., methyl α-lithioisobutyrate (MIBLi), combined with various ligands, such as lithium chloride (LiCl),[9] lithium *tert*-butoxide (LiOtBu),[10] polyethers,[11] and 211 cryptand (K211).[11] Therefore, it seemed timely and also of great importance to extend our study to the complexation between MIBLi and ligand 1.


$\mathrm{R{+}OCH_2CH_2{+}_{\mathit{n}}OLi}$

1 (n = 1–3, R = Me, Et, Bu, Ph)

This paper accordingly deals with the ^{7}Li and/or ^{13}C NMR characterization of a specific complexation of MIBLi by lithium 2-(2-methoxyethoxy) ethoxide (LiOEEM, for 1, n = 2, R = Me) in various solvents, i.e., THF, a 9/1 toluene/THF mixture, and toluene. Special attention will be paid to the significance of both the lithium alkoxide and the polyether components of LiOEEM in forming a new unique dual (μ/σ) complex.

Experimental Section

N-Lithiodiisopropylamide (97%) was a commercial product from Aldrich and was used as received. Lithium 2-(2-methoxyethoxy)ethoxide (LiOEEM) was prepared by reacting equimolar amounts of the corresponding polyether alcohol and n-BuLi in hexane at 0 °C.[1] Purification of solvents (hexane, THF, THF-d_8, toluene, toluene-d_8, and benzene-d_6) and 2-(2-methoxyethoxy)ethanol was described in detail elsewhere.[1,8]

Methyl α-lithioisobutyrate (MIBLi) was prepared under pure nitrogen from equimolar amounts of methyl isobutyrate and *N*-lithiodiisopropylamide in hexane at −78 °C.[8] The resulting white MIBLi solid was dissolved in the desired volume of LiOEEM-containing solvent at −78 °C and then directly filtered into NMR tubes which were sealed under vacuum.

The ^{13}C and ^{7}Li NMR spectra were obtained with a Bruker AM 400 superconducting magnet system operating in the FT mode at 100.6 and 155.5 MHz, respectively, using a deuterium lock. The ^{13}C spectral assignments were aided by an off-resonance technique, and all chemical shifts were referenced to high-field resonance of THF-d_8 or toluene-d_8, whose chemical shifts were separately determined to be 25.3 and 21.0 ppm, respectively, relative to (CH$_3$)$_4$Si. Lithium-7 NMR spectra were referenced to a 0.2 M LiCl solution in THF. To perform a quantitative analysis of ^{13}C NMR spectra, an inverse-gated proton decoupling technique with a $\pi/4$ pulse width and a 5s relaxation delay was applied in order to suppress nuclear Overhauser enhancement.

Results

Lithium-7 NMR Data for MIBLi (0.2 M) in THF in the Presence of LiOEEM at −60 °C. The occurrence of spontaneous complexation between MIBLi and LiOEEM in THF was first monitored through ^{7}Li NMR spectra of MIBLi added with varying amounts of LiOEEM at −60 °C. As illustrated in Figure 1, in the absence of LiOEEM, ^{7}Li resonances of 0.2 M MIBLi consist of two well-separated peaks at ca. −0.52 and −0.71 ppm (relative to 0.2 M lithium chloride in THF), characteristic of tetrameric and dimeric MIBLi species,[8] respectively (Figure 1A). However, while adding 0.5 mol equiv of LiOEEM, three

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[*] To whom all correspondence should be addressed.

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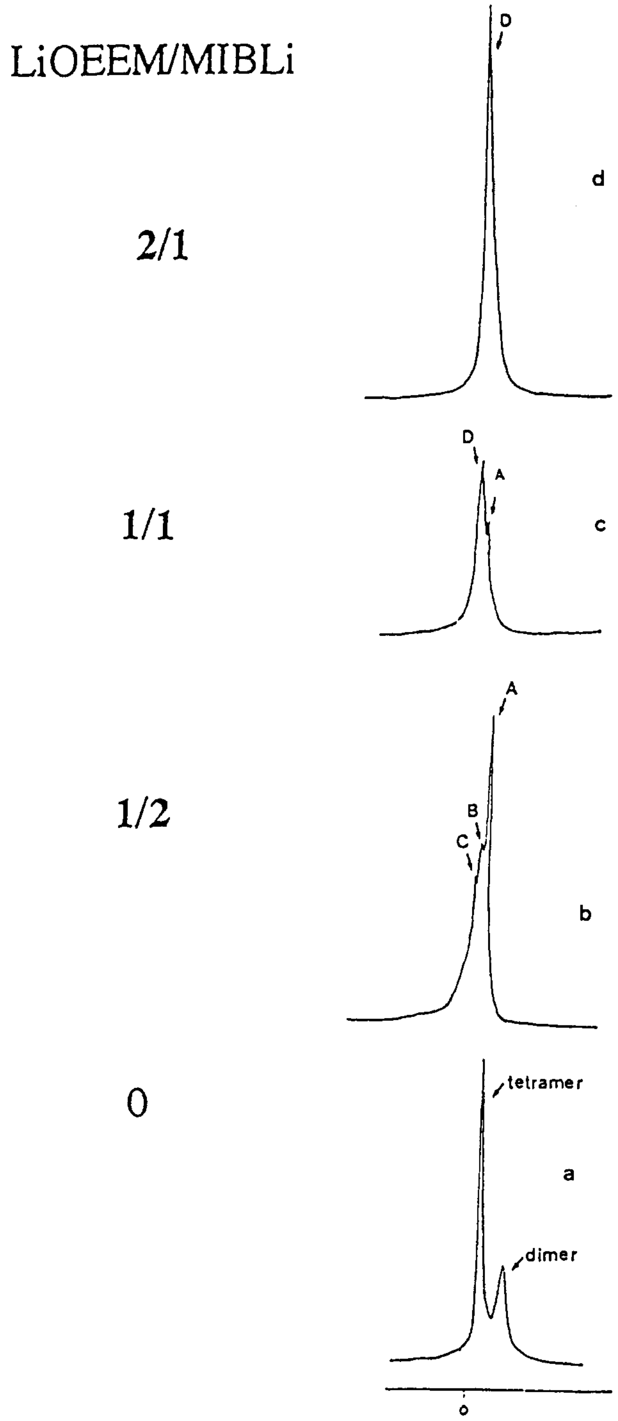


Figure 1. Lithium-7 NMR spectra of 0.2 M MIBLi added with varying amounts of LiOEEM in THF at −60 °C.

new well-resolved signals, one at −0.39 ppm (A) and the other two, B and C, at −0.20 and −0.03 ppm, respectively, immediately show up in the ^{7}Li NMR spectrum (Figure 1B), indicating the existence of at least three types of species.

With increasing LiOEEM/MIBLi ratio up to 1/1, the area of resonance A decreases and a new broad signal D at −0.14 ppm conversely emerges in the ^{7}Li NMR spectrum (Figure 1C). Furthermore, only this singlet resonance D is visible at a 2/1 LiOEEM/MIBLi ratio (Figure 1D). Since the ^{7}Li signal for LiOEEM in THF may also resonate in this region (−0.12 ppm, at −60 °C), it is hard at this point to tell whether the broad resonance D corresponds to the sole LiOEEM-complexed MIBLi species or to a weight-averaged one resulting from a fast exchange between complex(s) and free LiOEEM.

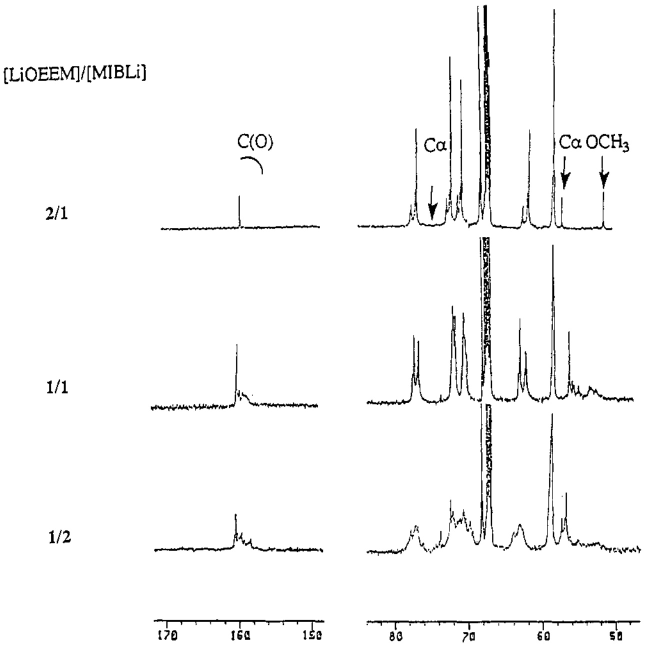


Figure 2. Partial carbon-13 NMR spectra of MIBLi (0.5 M) in the presence of various amounts of LiOEEM in THF at −60 °C.

Nevertheless, these pertinent ^{7}Li results safely allow the preliminary conclusion that LiOEEM is very efficient in complexing with MIBLi in THF.

Carbon-13 NMR Spectra of Methyl α-Lithioisobutyrate (MIBLi) Solution Added with Varying Amounts of Lithium 2-(2-Methoxyethoxy) Ethoxide (LiOEEM). (a) In THF. Although ^{7}Li NMR, to some extent, affords a suitable probe in characterizing the complexation between MIBLi and LiOEEM, as noted above, it is somewhat difficult to obtain detailed information about either complex composition or charge distribution around the carbanion from lithium cation NMR data. For this reason, our attention focused upon ^{13}C NMR.

Recent experimental evidence from ^{7}Li and ^{13}C NMR spectroscopy has accumulated to suggest that an association equilibrium between tetrameric and dimeric species dominates in a MIBLi/THF solution (eq 1).[8] Moreover, the exchange between these two aggregated species is slow on the ^{13}C and ^{7}Li time scale, thereby allowing the observation of the NMR signals due to the differently aggregated species.

$$\mathrm{MIB_4Li_4S}_n + n\mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\mathrm{MIB_2Li_2S}_n \ (\mathrm{S} = \mathrm{THF}) \qquad (1)$$

As expected, addition of LiOEEM has a profound effect on the ^{13}C NMR spectrum of 0.5 M MIBLi in THF, i.e., on the aggregation equilibrium and the negative charge distribution around the MIBLi carbanion. This is clearly demonstrated in Figure 2 and Table 1.

Considering the data for systems at LiOEEM/MIBLi ≥ 2, several very remarkable features immediately stand. First, instead of two sets of ^{13}C resonances for MIBLi characteristic of coexisting tetramer and dimer species, injection of LiOEEM brings about a single set of resonances, supporting the idea of the occurrence of complexation between MIBLi and LiOEEM in THF.

Second, the ^{13}C resonance at metalated carbon (C_α), the most sensitive atom in MIBLi, surprisingly moves to very high field (Table 1). Indeed, its chemical shift is found to be ca. 57.7 ppm, i.e., c.a. 16 and 8 ppm upfield from those of the tetrameric and dimeric MIBLi, respectively, corresponding to a substantial increase in charge density

Table 1. ^{13}C Chemical Shifts (ppm) of a MIBLi/THF Solution (M) (0.5 M) in the Presence of Various Amounts of LiOEEM (L)[a]

T (°C)	L/M (mol/mol)	C(O)	C_α	OCH_3	$(CH_3)_2$
25	*c*	176.8	34.3	51.3	19.2
−60	*d*	160.5 (T),[b] 158.9 (D)	73.5, (T), 65.4 (D)	57.0, 56.0	18.3, 18.0 (T); 18.9, ? (D)
	0.5/1	158.9–160.8[f]	73.5, ?; 57.9	57.5, 56.3, ?	18.0–19.4[f]
	1/1	158.8–160.3[f]	?, 57.9	56.7, 53.3, ?	18.0, 18.2; 18.5, 19.4; ?
	2/1	160.2	57.7	50.9	19.5, 18.4
	3/1	160.2	57.7	50.9	19.6, 18.4
	5/1	160.1	57.8	50.7	19.3, 18.2
	1.5/1[e]	159.3	59.9	50.9	18.6, 19.9
0	2/1	160.3	58.0	50.8	19.5, 18.9

[a] Relative to the high-field signal of THF-d_8, 25.3 ppm. [b] T, tetramer; D, dimer. [c] Corresponding parent ester, i.e., methyl isobutyrate, $(CH_3)_2CHCOOCH_3$. [d] LiOMEEM-free MIBLi. [e] In the presence of 1.5 mol equiv of K211 instead of LiOEEM.[7] [f] Multi-peak.

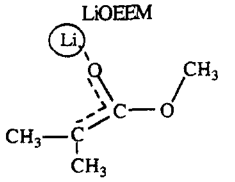
Table 2. ^{13}C Chemical Shifts (ppm) of 0.5 M MIBLi (M) in the Presence of LiOEEM (L) in Toluene (tol) and a 9/1 Toluene/THF Mixture (9/1)[a]

solv	L/M (mol/mol)	C(O)	C_α	OCH_3	$(CH_3)_2$
THF	*c*	176.8	34.3	51.3	19.2
THF	*d*	160.5 (T),[b] 158.9 (D)	73.5 (T), 65.4 (D)	57.0, 56.0	18.3, 18.0 (T); 18.9, ? (D)
tol	2/1 (−60 °C)	160.3	57.8	50.9	20.1, *e*
	2/1 (0 °C)	160.6	57.9	51.0	20.2, *e*
	5/1 (−60 °C)	160.6	57.7	50.7	20.2, *e*
9/1	2/1 (−60 °C)	160.3	58.0	50.9	20.0, *e*

[a] Relative to the high-field signal of THF-d_8, 25.3 ppm, or to the high-field signal of toluene-d_8, 21.0 ppm. [b] T, tetramer; D, dimer. [c] Corresponding parent ester, i.e., methyl isobutyrate, $(CH_3)_2CHCOOCH_3$. [d] LiOEEM-free MIBLi. [e] Obscured.

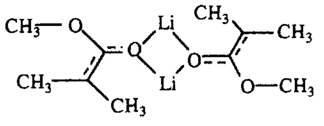
at that position. Interestingly enough, a similar situation has already been demonstrated for MIBLi in the presence of 1.5 mol equiv of K211 in THF (also see Table 1),[11] where a K211-complexed *monomeric* MIBLi might be present. Since a change in the aggregation degree of lithium enolates usually leads to a large difference in ^{13}C chemical shift of metalated carbon,[12] similarly to the MIBLi/K211 complex,[11] the present results might give the credit to a complete deaggregation of the highly aggregated MIBLi with the formation of a complex in which only one MIBLi molecule is incorporated, i.e., MIBLi·xLiOEEM.

In addition, also noteworthy is the observation of a negative (*upfield*) chemical shift at the OCH_3 group (ca. 0.4 ppm) in MIBLi·xLiOEEM compared to the same group in the parent ester, i.e., methyl isobutyrate (Table 1), again well consistent with monomeric K211-complexed MIBLi in THF.[11] This is indeed a surprising behavior, since in either tetrameric or dimeric MIBLi, a ca. 5 ppm *downfield* shift was detected at the same carbon atoms (Table 1).[8] In agreement with the suggestion by Corest et al.[13] the negative shift at the methoxy group might imply that LiOEEM-complexed MIBLi displays a *s-cis* conformation (OCH_3 cis to the carbonyl group as in **2a**), which usually occurs to the monomeric enolate species,[13] whereas a *s-trans* structure is involved in tetrameric and dimeric MIBLi (e.g., **2b**).



s-cis

2a



s-trans

2b

Finally, increasing the temperature does not seem to significantly modify the ^{13}C spectra, as indicated by the almost identical chemical shifts at all carbons for MIBLi between −60 and 0 °C (Table 1), in strong support for the existence of a very stable complex. Noticeably however, MIBLi undergoes a decomposition reaction above 0 °C, due to the occurrence of the autocondensation reaction.[14]

In contrast to the above-described results at LiOEEM/MIBLi ≥ 2, a much more complicated scenario prevails in the ^{13}C spectra at LiOEEM/MIBLi ≤ 1 (Figure 2). Actually, multipeak resonances are recorded, for which it appears difficult to make precise assignments. In agreement with the above-discussed ^7Li results, it may not be impossible that several types of LiOEMM-complexed or even LiOEMM-free species coexist in these systems under slow exchange.

(b) In Toluene and a 9/1 Toluene/THF Mixture. Although MIBLi is virtually insoluble in nonpolar solvents, it was found that addition of more than 2 mol equiv of LiOEEM affords a homogeneous MIBLi/toluene solution. Even more surprising is the finding that the overall pattern of the ^{13}C NMR spectrum of 0.5 M MiBLi in the presence of more than 2 mol equiv of LiOEEM in toluene is very similar to the one observed in pure THF, the chemical shifts at all carbons being almost identical as well (Table 2).

In addition, the same spectra were also recorded in a 9/1 toluene/THF mixture, while adding 2 mol equiv of LiOEEM to MIBLi (Table 2). Clearly enough, these results provide unambiguous evidence that MIBLi is strongly coordinated by LiOEEM and the same type of LiOEEM-complexed species, i.e., MIBLi·xLiOEEM, is formed, whichever the solvent, when more than 2 equiv of LiOEEM is added.

Ligand Carbon-13 NMR Spectra in THF. Thus far the complex formation between LiOEEM and MIBLi in various solvents is firmly supported by ^{13}C NMR data of the MIBLi anion and/or ^7Li NMR. Interestingly, the same type of complex MIBLi·xLiOEEM can be formed upon addition of more than 2 mol equiv of LiOEEM to MIBLi in THF, toluene, and a 9/1 toluene/THF mixture. Although these results are very helpful in understanding the nature of the MIBLi anion partner in the complex formed, it is still difficult to get pertinent information concerning the ligand side. This is the reason why attention was paid to ligand **3** ^{13}C spectra for at least systems of interest, i.e., those at LiOEEM/MIBLi $\geq 2/1$;

Table 3. ^{13}C Chemical Shifts (ppm) of LiOEEM (3) at Various LiOEEM/MIBLi (L/M) Ratios in THF at −60 °C[a,b]

L/M (mol/mol)	C1	C2	C3	C4	C5
c	78.7	72.4	70.6	64.1	58.8
2/1	77.8	72.0	70.3	63.4	59.0
3/1	77.8, 78.7	72.0, 72.4	70.2, 70.6	63.4, 64.1	59.0, 58.8
5/1	77.9, 78.8	72.0, 72.4	70.3, 70.6	63.3, 64.0	59.0, 58.7

[a] MIBLi in THF: 0.5 M. [b] Relative to the high-field signal of THF-d_8, 25.3 ppm. [c] Free LiOEEM.

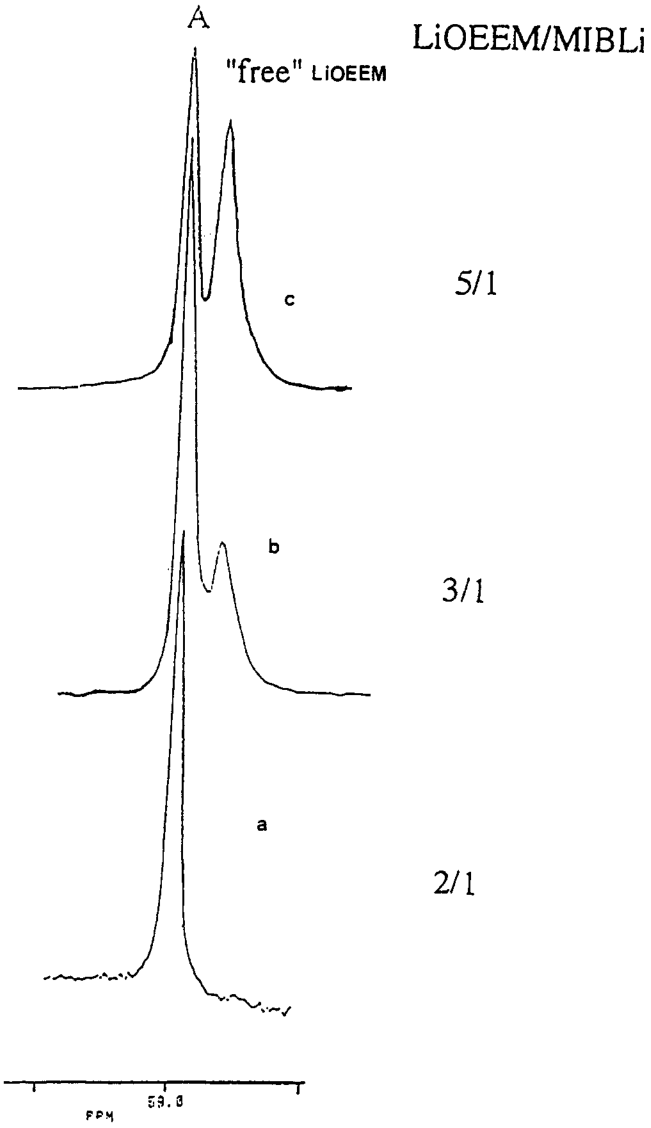
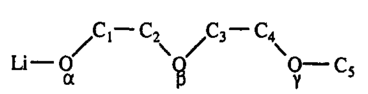


Figure 3. Carbon-13 NMR spectra of LiOEEM (3) at the C_5 carbon added with different amounts of MIBLi in THF (0.5 M) at −60 °C.

the results are presented in Table 3.



3

Figure 3 also illustrates how the ^{13}C spectrum of LiOEEM at C_5 changes while mixing with varying amounts of MIBLi (0.5 M) in THF at −60 °C. As seen in Table 3 and Figure 3, at a 2/1 LiOEEM/MIBLi ratio, only one set of ^{13}C resonances, namely, A, is recorded (Table 3 and Figure 3a). Moreover, when that ratio is increased to 3/1, the signal A still resonates at a similar position, while another set of peaks corresponding to free LiOEEM clearly shows up in the spectrum (Table 3 and Figure 3b). Furthermore, addition of 5 mol equiv of LiOEEM only induces an increase in the relative intensity of the resonance typical of the free ligand (Figure 3c). In agreement with the above-described ^{13}C data for the MIBLi anion, it seems obvious that signal A may be regarded as characteristic of the complex species MIBLi·xLiOEEM.

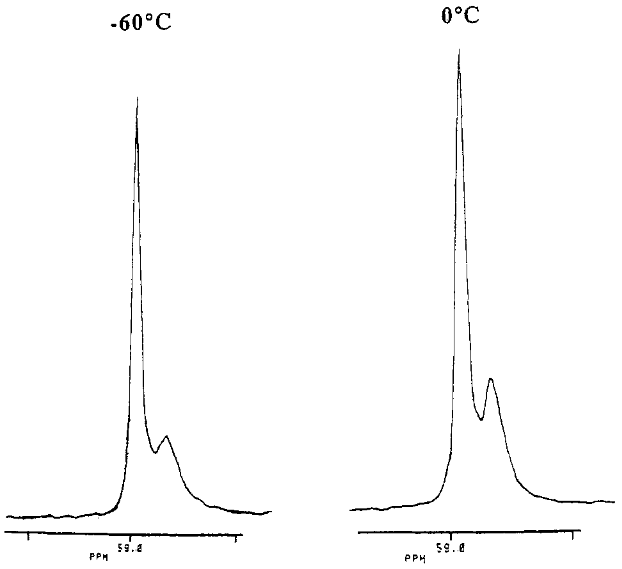


Figure 4. Carbon-13 NMR spectra of LiOEEM at C_5 in THF and in the presence of 3 mol equiv of MIBLi (0.5 M) at different temperatures.

Thanks to a slow-exchange process between "free" and "complexed" LiOEEM on the ^{13}C NMR time scale, measurement of the relative area ratio of free to complexed LiOEEM peaks should provide a precise number x for LiOEEM-complexed species. Accordingly, a direct integration of the two well-separated signals in Figure 3, i.e., species A and free LiOEEM, indicated that a 3/1 LiOEEM/MIBLi mixture contained 34% of "free" LiOEEM, while a 5/1 one contained ca. 58% of the same form, i.e., the mole ratios of free to complexed LiOEEM are very close to 1/2 and 3/2 and 5/1 LiOEEM/MIBLi systems, respectively. Together with the 0% of "free" LiOEEM detected at 2/1 LiOEEM/MIBLi, these data are perfectly consistent with the existence of a unique strong complex, i.e., MIBLi·2LiOEEM at LiOEEM/MIBMLi ≥ 2/1. Actually, the formation of such a MIBLi·2LiOEEM complex is convincingly supported by a recent quantum calculation carried out by Müller et al.[17]

Moreover, in the case of a 3/1 LiOEEM/MIBLi system, the resonances for free and complexed LiOEEM are still obtained as discrete signals up to at least 0 °C (Figure 4) suggesting a very strong interaction between ligand and Li^+.[15] The same behavior has been observed by Smid in the case of a 2/1 mixture of dimethyldibenzo-18-crown-6- and fluorenylsodium,[15] where the coalescence temperature for the polyether ring protons was found to be 2 °C.

Discussion

Significance of Both the Lithium Alkoxide and the Polyether Components in LiOEEM for Its Powerful Complexation to Lithium Ester Enolate in Solution. The high propensity of LiOEEM to form a unique complex MIBLi·2LiOEEM in solutions is thus obvious, since addition of 2 equiv of LiOEEM to a MIBLi solution spontaneously leads to the formation of the MIBLi·2LiOEEM complex as well in THF as in toluene, that complex being stable between −60 °C and at least 0 °C.

Table 4. Comparison of ^{13}C Chemical Shifts (ppm) of MIBLi (M) (0.5 M) in THF at −60 °C, in the Presence of Various Types of Ligand (L)

ligand	L/M (mol/mol)	C(O)	C_α
		160.5 (T),[a] 158.9 (D)[b]	73.9 (T), 65.8 (D)
$LiO(CH_2CH_2O)_2CH_3$	≥2/1	160.2	57.7
K211	1.5/1	159.1	59.9
$CH_3O(CH_2CH_2O)_2CH_3$	10/1	160.6 (T), 158.8 (D)	73.5 (T), 65.5 (D)
12-CE-4	5/1	160.6 (T), 159.2 (D)	73.2 (T), 65.1 (D)
LiCl	≥1/1	ca. 159.3	ca. 66.5
$LiOC(CH_3)_3$	2/1	161.0, 161.8	72.2, 71.3

[a] T, tetramer. [b] D, dimer.

Moreover, injection of 3 or 5 mol equiv of LiOEEM does not produce other types of complexes.

For comparison purposes, Table 4 also lists the ^{13}C data at C_α and C(O) for MIBLi complexed by different types of ligands in THF.

In striking contrast to $LiO(CH_2CH_2O)_2CH_3$ (LiOEEM), it can be noted from Table 4 that addition of 10 mol equiv of glyme-3, i.e., $CH_3O(CH_2CH_2O)_2CH_3$, a polydentate-type structure analogous to LiOEEM, does not have any significant influence on ^{13}C spectra of MIBLi in THF. Actually, in the presence of glyme-3, tetrameric and dimeric enolate species still coexist in a MIBLi/THF solution, although there appears a slight increase in dimeric population.[11] Moreover, the same situation also prevails upon addition of 5 equiv of 12-CE-4 (Table 4 and ref 11). These results indicate that most lithium cation-binding ligands are not powerful enough to destroy the aggregation of lithium ester enolate, probably due to the presence of a very strong O–Li bond in aggregated lithium enolate.[11]

Undoubtedly its lithium alkoxide moiety powerfully helps polydentate LiOEEM to interact with MIBLi, due to the electrostatic advantage of stabilization through a typical 4-membered μ-type mixed aggregate.[9,10]

Indeed, as reported elsewhere,[10] a simple lithium alkoxide-type structure analogous to that of LiOEEM, $LiOC(CH_3)_3$ (LiOtBu), has been proven to efficiently coordinate with MIBLi in THF. However, LiOtBu only has the ability of incrementally replacing MIBLi in its tetramer with the formation of new mixed tetrameric complex $MIB_{4-x}Li_4(OtBu)_x$ (x = 1–3).[10] Moreover, ^{13}C resonances at C_α in $MIB_{4-x}Li_4(OtBu)_x$ (x = 1–3) are only progressively shifted *upfield* by about 2.6 ppm compared to that in tetrameric MIBLi,[10] as number x changes from 0 to 3 (also see Table 4).

Conversely, although another μ-ligand, LiCl, can induce the formation of the less aggregated mixed complexes such as MIBLi·nLiCl (n = 1, 2, or 3), there only appears a slight *downfield* shift of ca. 1.0 ppm at C_α with respect to that in dimeric MIBLi species (Table 4).[9]

So, apparently, the mixed complexation of MIBLi by LiCl or LiOtBu does not largely modify the charge distribution around the MIBLi carbanion in the mixed complex.

By contrast, as already discussed in the preceding sections, LiOEEM not only gives rise to a complete deaggregation of MIBLi resulting in the mixed complex MIBLi·2LiOEEM but also induces a very large upfield shift at C_α (16 and 8 ppm upfield compared to tetrameric and dimeric MIBLi, respectively!). Moreover, that situation is surprisingly comparable to the behavior of MIBLi complexed with K211, to date one of the most powerful lithium-cation complexing agents known (Table 4).

In other words, the chelating polyether moiety in LiOEEM also clearly plays a very important role, typical of σ-cation-binding complexation, in simultaneously coordinating with lithium cations. This might be at the origin of the significant modification of the charge density in the carbanion.

Therefore, LiOEEM clearly behaves as a dual ligand (μ/σ type), and the complex between MIBLi and this μ/σ ligand, i.e., MIBLi·2LiOEEM, may be regarded as a characteristic μ/σ type of complex.

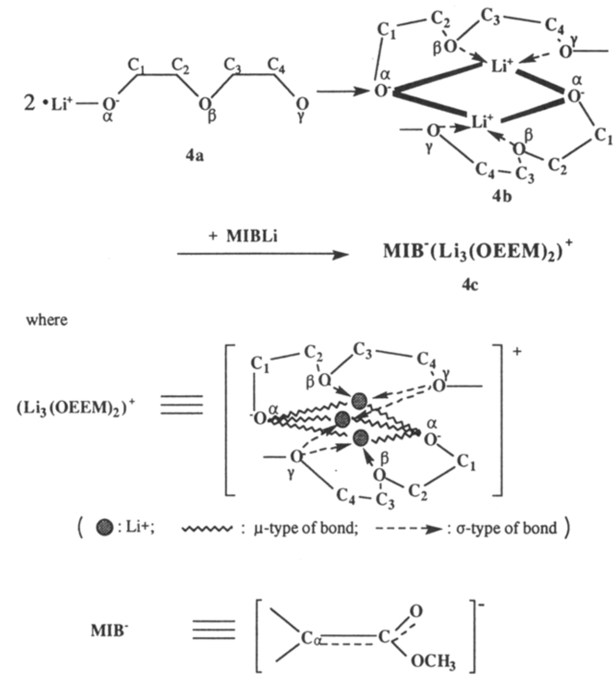
Structure of the MIBLi·2LiOEEM Mixed Complex. In order to distinguish between two types of mixed complex, i.e., LiOtBu (or LiCl)–MIBLi and LiOEEM–MIBLi, we feel justified in proposing that the former one may be regarded as a tight one $MIB_xLi_yX_z$ (X = Cl and $OC(CH_3)_3$); similar to the parent MIBLi in terms of ion-pair "solvation" behavior, the lithium cations in this tight mixed complex are strongly bound to both the parent (MIB) and ligand anions. Conversely, the later one might be reasonably ascribed as a ligand-promoted–loose mixed complex, i.e., $MIB^-(Li_3(OEEM)_2)^+$, in which the lithium cations are strongly coordinated by the chelating polyether in the ligand and the interaction between these cations and the MIBLi anion is somewhat weakened.

In terms of ^{13}C data in Tables 1 and 2, it seems likely that the MIB^- anion displays a charge-delocalized character. Support for this conclusion is the observation of two nonequivalent methyl resonances and of the highly upfield/downfield shifts at C(O)/C_α with respect to those of the parent ester, i.e., methyl isobutyrate.[8]

A further examination of data in Table 3 also provides useful information regarding the structure of the $(Li_3(OEEM)_2)^+$ partner. It is worth noting that the complexation of LiOEEM with MIBLi leads to upfield shifts of ca. 0.9, 0.7, and 0.4 ppm from normal positions at C_1 and C_4 as well as C_2 (and C_3) in **3**, respectively (Table 3). This might indicate an increase in the charge density at oxygens in the order $\alpha > \gamma > \beta$.

Presumably, these results point toward a complexation process as in Scheme 1. Supposing a coordination number of 4 for the lithium cation[16] and that LiOEEM exists as a dimeric species as in **4b**,[17] the preferential coordination of Li^+ from MIBLi to oxygen α might benefit from the electrostatic advantage bonded to the formation of a stable μ-mixed complex.[9,10] From a steric point of view, compared to less accessible β oxygens, the simultaneous coordination of that Li^+ with two γ oxygens (σ-cation-binding) might be easier. Clearly, such a σ-cation-binding complexation must to some extent weaken the interaction between the Li cation and the MIB anion, resulting in the so-called ligand-promoted–loose mixed complex **4c**. It must be reminded here that a solvent-separated mixed complex between lithium 2,6-dimethylphenolate and $LiBPh_4$ in dioxolane has been well established by Jackman in terms of NMR spectroscopy.[18] Again, it is obvious that this ligand-promoted–loose mixed complex is also very bulky. At this point, it is tempting to make a parallel, at least formal, between this complex composed of two large-extension components, displaying a high electron delo-

Scheme 1



calization and a rather "soft" character with the metal-free organic initiator systems described by Reetz[19] (tetraalkylammonium-containing species, e.g., $R^-N^+Bu_4$) and by Seebach[20] (P4-phosphazene base). However, more detailed structural analyses, whatever the technique, are obviously requested for the structure of the complex **4c** to be more cleared up.

At the end of this discussion, it is necessary to point out that there appears a fairly good correlation between the structural characteristics of the LiOEEM-complexed MIBLi and the main features of the anionic polymerization processes of (meth)acrylates, which might be summarized as follows:

(i) The exceptionally fast kinetics[17,21] of the MMA anionic polymerization even in pure toluene at low temperatures using LiOEEM-complexed Li-containing initiator was surprisingly found to be very comparable to that in THF using a K222-complexed Na-containing one,[17] which could only be understood if a loose ion pair is involved in the propagation.

(ii) Similar to a DB 18-CE-6/Na system, a LiOEEM-modified initiator can effectively diminish a backbiting termination reaction in the anionic copolymerization of MMA and tBuA mixtures in THF at −78 °C.[7] This has indeed been accounted for by the presence of a bulky active complex.[22]

(iii) The stereochemistry of the LiOEEM-complexed MMA anionic polymerization at −78 °C is almost identical as well in THF as in toluene and toluene/THF mixtures,[6] well consistent with the involvement of the same type of LiOEEM-modified active species.

Conclusion. It has been shown that addition of a new type of polydentate lithium alkoxide ligand, i.e., a μ/σ dual ligand, LiOEEM, to MIBLi, whichever the solvent, induces the formation of the same type of stable and bulky mixed complex $MIB^-(Li(OEEM)_2)^+$, also a μ/σ complex. The structure of that complex is well related to its remarkable efficiency in controlling the anionic polymerization of (meth)acrylic esters.

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