Macromolecules **1994,** *27,* 1691-1696

Anionic Polymerization of Acrylic Monomers. 13. Carbon-13 NMR Characterization of the Mixed Complexation of Methyl α-Lithioisobutyrate by Lithium *tert*-Butoxide in Tetrahydrofuran

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Received August 3, 1993; Revised Manuscript Received December 12, 1993[⊗]

ABSTRACT: The mixed complexation of methyl α-lithioisobutyrate (MIBLi) (a monomeric model structurally corresponding to the living end of PMMA$^-$Li$^+$) with lithium *tert*-butoxide (LiOtBu) in THF has been studied for the first time by using ^{13}C NMR spectroscopy. It is shown that LiOtBu, like LiCl, is very effective in coordinating with MIBLi tetramer in THF, incrementally replacing MIBLi with the formation of other tetrameric complexes, $\mathrm{MIB}_x\mathrm{Li}_4(\mathrm{OtBu})_{4-x}$ (x = 1–3). Complextion of MIBLi by LiOtBu induces a shielding ^{13}C shift of the MIBLi C_α resonance, which might suggest that lithium cations associated with the electron-rich ligands, i.e., LiOtBu, can also form weaker bonds with the carbonyl oxygen of MIBLi (i.e., μ-type complexes), thereby decreasing the localization of the negative charge on that latter atom. In comparison with LiCl, one of the most significant features is that only one single type of species results from mixed complexation of MIBLi and LiCl at LiCl/MIBLi = 1, 2, and $\geq$3, respectively, at low temperature, whereas several LiOtBu-complexed species may coexist, whatever the LiOtBu/MIBLi ratio; furthermore, their exchange is found to be very slow at a temperature as high as 0 °C. Tentatively, this striking feature may explain nicely the large difference in molecular weight distribution of poly(meth)acrylates anionically prepared in the presence of LiOtBu and LiCl, respectively.

Introduction

Although the anionic polymerization of (meth)acrylates is still nowadays a very difficult challenge, the use of suitable ligands interacting with the growing species to efficiently minimize the secondary reactions or to possibly displace the classical equilibria between different ion pairs (and/or aggregates) has allowed much better control of these propagation processes.[1] Documented examples of living systems already abound in the literature, and the efficient ligands discovered to date can be divided into two main classes: inorganic (or organometallic) μ-bonded additives such as alkali and alkaline-earth metal salts, metal alkoxides, and Lewis acids such as trialkyl aluminium derivatives on one side;[2–4] cation σ-binding organic ligands such as polyethers (including crowns) and polyamine (including cryptands) on the other.[5]

Furthermore, the ligated (ligand-modified) process promisingly represents a useful probe for better understanding the mechanism of anionic polymerization of (meth)acrylates. Thanks to the efficiency of lithium chloride (LiCl) and lithium *tert*-butoxide (LiOtBu) as ligands, kinetic studies by Müller et al. have recently revealed the important role of association/complexation equilibria in the anionic polymerization of methyl methacrylate (MMA) and *tert*-butyl acrylate (tBuA) associated with lithium countercation in THF at low temperature.[6]

We have previously carried out an NMR study of methyl α-lithioisobutyrate (MIBLi) in THF, a monomeric model structurally comparable to the living end of PMMA$^-$Li$^+$.[7] An equilibrium between tetrameric and dimeric MIBLi's with a slow exchange process was accordingly established. It was also shown that the addition of μ-type inorganic ligand, i.e., lithium chloride (LiCl), into coexisting tetrameric and dimeric MIBLi's in THF causes mixed complexation.[8] A preliminary attempt to correlate the structure and dynamics of LiCl-modified with the main features of the MMA polymerization process suggests that the formation of one single type of LiCl-complexed species likely plays an important role in controlling the perfect living polymerization of MMA in THF at low temperature, in agreement with kinetics studies developed by Müller et al.[6] on related systems.

In the course of these NMR studies, it appeared of great interest to compare the effects of different types of ligands on the same original species, i.e., MIBLi, since that might provide more extensive insight into the nature of active species modified by various types of ligands and a better understanding of the mechanism of the resulting living process. In this paper, we present the results of the ^{13}C NMR characterization of mixed complex formation between MIBLi and LiOtBu in THF.

Experimental Section

Materials. Solvents (THF, THF-d_8, and hexane) were purified and dried as previously described.[7,8] Methyl isobutyrate from Aldrich was purified and dried by distillation from $\mathrm{CaH_2}$ (twice). *N*-Lithiodiisopropyl amide (97%) was a commercial product used as received, also from Aldrich. Lithium *tert*-butoxide was prepared according to a literature method.[9]

Sample Preparation. The method for preparing moisture- and air-free, sealed, 5-mm ^{13}C NMR samples of MIBLi has been previously described.[7] In the present experiments, the resulting white MIBLi solid was dissolved at −78 °C in the desired volume of solvent containing a definite amount of ligand and then directly filtered into NMR tubes which were degassed using freeze–thaw cycles before sealing under vacuum.

NMR Spectroscopy. The ^{13}C spectra were obtained with a Bruker AM-400 spectrometer operating in the FT mode at 100.6 MHz using a deuterium lock. The ^{13}C chemical shifts were referenced to the high-field resonance of internal THF-d_8, whose chemical shift was separately determined to be 25.3 ppm relative to $\mathrm{Me_4Si}$ in the same solvent.

Results and Discussion

Evidence for Mixed Complex Formation between MIBLi and LiOtBu. Figure 1 depicts partial ^{13}C NMR spectra of LiOtBu for the $(\mathrm{O})\underline{\mathrm{C}}(\mathrm{CH_3})_3$ carbon located in the region 66.0–66.8 ppm for various mixtures of MIBLi

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1994.

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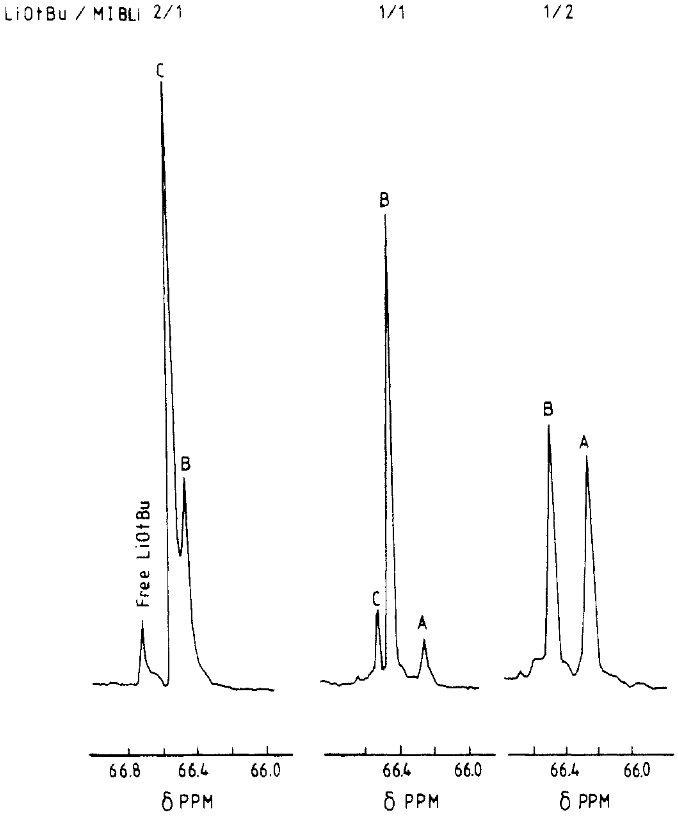


Figure 1. Partial ^{13}C NMR spectra of LiOtBu at the $(O)\underline{C}(CH_3)_3$ carbon for various mixtures of MIBLi (0.8 M) and LiOtBu in THF at -40 °C.

Table 1. ^{13}C Chemical Shifts^a of Lithium *tert*-Butoxide at the $(O)\underline{C}(CH_3)_3$ Carbon at Different LiOtBu/MIBLi^b Ratios at -60 °C

L/M^c	species	δ, ppm	L/M^c	species	δ, ppm
d		66.7		C	66.5
0.5	A	66.2	2	B	66.4
	B	66.4		C	66.5
1	A	66.2			66.7^d
	B	66.4			

^{a} At -40 °C. ^{b} MIBLi: methyl α-lithioisobutyrate. ^{c} Molar ratio of LiOtBu/MIBLi. ^{d} "Free" LiOtBu.

(0.8 M) and LiOtBu in THF at -40 °C. It is obvious that these 100.6-MHz ^{13}C spectra vary considerably with the LiOtBu/MIBLi molar ratio (Table 1). Accordingly, when 0.5 M equiv LiOtBu was introduced into the MIBLi solution, two peaks at δ 66.2 and 66.4 ppm, namely, A and B, respectively, immediately emerged upfield of the single former position at 66.7 ppm, providing the first unambiguous evidence for mixed complexation, not accompanied by fast exchange. Moreover, the fact that a ^{13}C signal responsible for the "free" LiOtBu species could not be detected might indicate quantitative formation of that complex. As the molar ratio LiOtBu/MIBLi was further increased to 1/1, the peak at lower field (B, 66.4 ppm) increased in intensity at the expense of the other one (A, 66.2 ppm), and a new ^{13}C resonance (C) further appeared at ca. δ 66.5 ppm, indicative of the presence of a third type of complex species. Finally, at a relatively higher LiOtBu/MIBLi ratio, i.e., 2/1, the only resonances visible were those at 66.7, 66.5, and 66.4 ppm, clearly corresponding to free LiOtBu, C, and B species, respectively.

Conversely, three sets of new resonances are also recorded in the ^{13}C spectra of MIBLi in the presence of various amounts of LiOtBu (Figure 2). The ^{13}C chemical shifts of these new species are reported in Table 2. By comparing the variation in relative intensity of the ^{13}C resonances at various carbons of the metalated methyl isobutyrate moiety to that at the $(O)\underline{C}(CH_3)_3$ carbon with the same LiOtBu/MIBLi ratio, it is quite feasible to assign them to species A, B, and C, respectively.

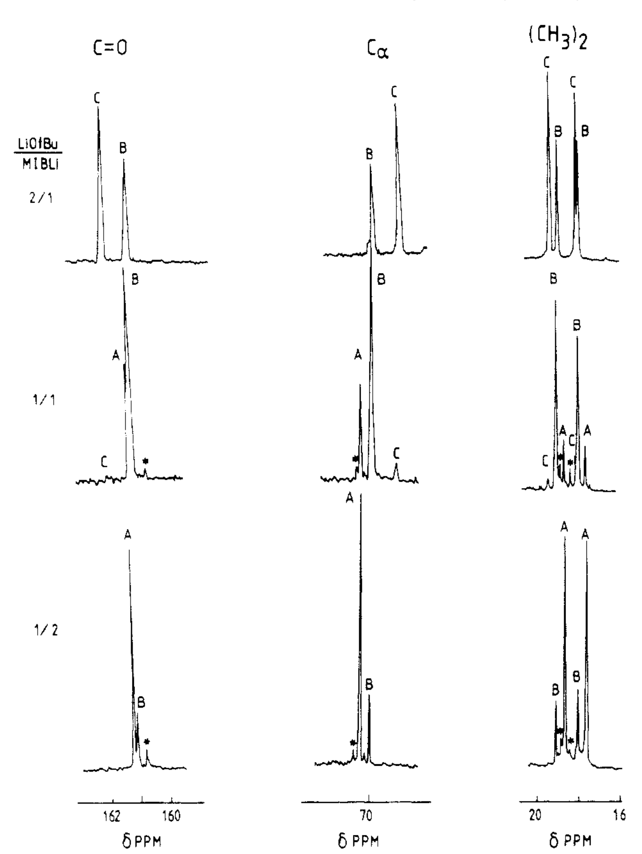


Figure 2. Partial carbon-13 spectra of MIBLi (0.8 M) in the presence of different amounts of LiOtBu in THF at -40 °C. (*) "Free" MIBLi species.

Table 2. ^{13}C Chemical Shifts for Methyl α-Lithioisobutyrate with and without Added Lithium *tert*-Butoxide in THF^a

L/M^b	species	C(O)	C$_\alpha$	(O)CH$_3$	(CH$_3$)$_2$
c		176.8	34.3	51.3	19.2
0		160.5	72.8, 72.5	56.7	18.4, 17.9
0.5		160.5	72.8	56.7	18.4, 17.9
	A	161.2	72.4	56.7	18.7, 17.6
	B	161.0	72.2	56.2	19.1, 18.1
1		160.5	72.8	56.7	18.4, 18.1
	A	161.2	72.4	56.7	18.7, 17.6
	B	161.0	72.2	56.2	19.1, 18.1
	C	161.8 (?)	71.3	55.8	19.5, 18.2
2	B	161.0	72.2	56.2	19.1, 18.1
	C	161.8	71.3	55.8	19.5, 18.2

^{a} At -40 °C. ^{b} LiOtBu/MIBLi (mol/mol). ^{c} Corresponding methyl isobutyrate, i.e., $(CH_3)_2CHCOOCH_3$.

McGarrity and Ogle had already made a similar observation in terms of ^{1}H and ^{7}Li resonances by adding lithium butoxide (LiOBu) to butyllithium (nBuLi) in THF.[10] In the ^{1}H spectrum of the mixture, they observed three new peaks, which have been reasonably ascribed to three types of tetrameric LiOBu-complexed BuLi species, i.e., $Bu_xLi_4(OBu)_{4-x}$, $x = 1$–3. This is remarkably similar to the present system where three and *only three* sets of new peaks were detected while increasing the molar ratio LiOtBu/MIBLi; it might be consistent with successive replacements of MIBLi by LiOtBu in the MIBLi tetramer with the formation of mixed complexes $MIB_xLi_4(OtBu)_{4-x}$ ($x = 1$–3) (eqs 1-3). In fact, it has previously been shown that only a tetrameric species is involved in the 0.8 M MIBLi/THF solution[7] and that LiOtBu generally is also

$$3MIB_4Li_4{\cdot}4THF + Li_4(OtBu)_4{\cdot}4THF \rightleftharpoons 4MIB_3Li_4OtBu{\cdot}4THF \quad (1)$$

A, 1

$$2MIB_3Li_4OtBu{\cdot}4THF + Li_4(OtBu)_4{\cdot}4THF \rightleftharpoons 3MIB_2Li_4(OtBu)_2{\cdot}4THF \quad (2)$$

B, 2

$$MIB_2Li_4(OtBu)_2{\cdot}4THF + Li_4(OtBu)_4{\cdot}4THF \rightleftharpoons 2MIBLi_4(OtBu)_3{\cdot}4THF \quad (3)$$

C, 3

tetrameric in THF and tends to form mixed tetramers with organolithium compounds.[10]

Up to this point, we also see that species A, B, and C may represent $MIB_3Li_4(OtBu)_1$ (**1**), $MIB_2Li_4(OtBu)_2$ (**2**), and $MIB_1Li_4(OtBu)_3$ (**3**), respectively.

Charge Distribution in the Complexed Species $MIB_xLi_4(OtBu)_{4-x}$. Having obtained evidence for the mixed complexation of MIBLi by LiOtBu in THF, we first discuss the charge distribution in these mixed complexes and then tentatively draw a probable picture for LiOtBu-complexed MIBLi species in terms of available ^{13}C data.

First of all, as clearly seen in Table 2, the C_α/C(O) signals of MIBLi in all three complexes move to much lower/higher fields (ca. 37/15 ppm, respectively) vs the parent ester, i.e., methyl isobutyrate. In addition, it might also be noted that, within each complex, the methyl groups bound to C_α are magnetically nonequivalent over a large temperature range (see below). This is consistent with a pronounced double-bond character about the C_α–C(O) bond.[7,11] As already demonstrated in the MIBLi/THF solution,[7,11] these results suggest a charge-delocalized character of MIBLi in solution. It seems likely that complexation of MIBLi by LiOtBu will not change its charge-delocalized character, except in its extent.

In addition, a further examination of the ^{13}C spectra in different mixed complexes $MIB_xLi_4(OtBu)_{4-x}$ reveals several intriguing features. Table 2 shows that ^{13}C resonances at C_α of MIBLi shift progressively upfield (about 1.5 ppm) as the number of *tert*-butoxide ligands increases from 0 to 3. This clearly indicates that the negative charge density at C_α increases with an increase in the number of LiOtBu ligands in the mixed complexes.

Jackman et al. have recently shown that the formation of mixed tetramer between lithium 3,5-dimethylphenolate and lithium perchlorate ($LiClO_4$) in dioxolane at −80 °C results in a deshielding (i.e., downfield shift) of the C_α of the phenolate in ^{13}C spectra (ca. 1 ppm), relative to that of the parent tetramer.[12a] Similarly, it has been also reported by us that the mixed complexation of MIBLi by LiCl in THF at −60 °C causes a ca. 1.3 ppm deshielding of C_α from the parent dimeric MIBLi.[8] These are to be expected since lithium cations associated with the weakly basic inorganic ions (ClO_4^- or Cl^-) can form stronger bonds with the phenolate or enolate oxygens, which should increase the localization of the negative charge on those atoms.[12a] Actually, this stronger interaction in the mixed complex is apparent in the observed bond length of the PhLi/LiBr mixed tetramer, in which the appropriate C–Li bond lengths are 0.05-Å shorter than in the phenyllithium tetramer.[12b]

At this point, it is obvious that the mixed complexation of MIBLi by LiOtBu affects the negative charge distribution around the carbanion in a quite different manner from that of phenolate by $LiClO_4$ and MIBLi by LiCl. It seems clear that, in $MIB_xLi_4(OtBu)_{4-x}$ (x = 1–3), lithium cations form relatively weaker additional bonds with the carbonyl oxygens of MIBLi, most probably due to the presence of more electron-rich ligands, i.e., LiOtBu. This weaker interaction may accordingly lead to a decreased localization of the negative charge at carbonyl oxygens, resulting in upfield shifts at C_α.

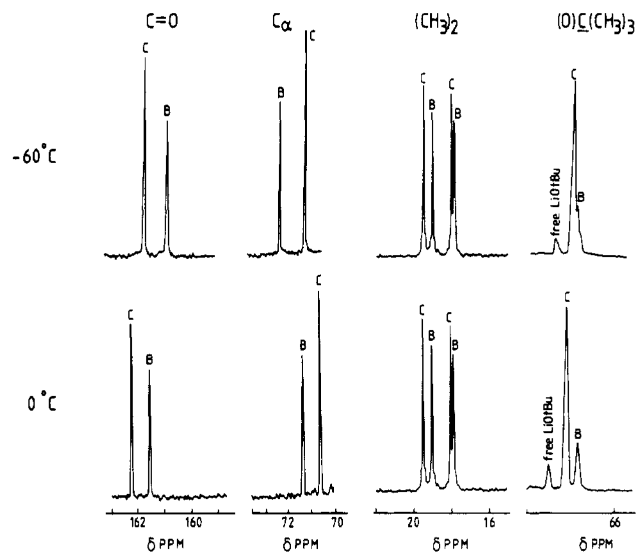


Figure 3. Temperature-variable ^{13}C NMR spectra of MIBLi (0.8 M) in the presence of 2 equiv of LiOtBu in THF.

The observation of upfield shifts at $(O)\underline{C}(CH_3)_3$ in mixed complexes compared to the one in free LiOtBu might strongly support the above conclusions (Table 1): a relatively stronger interaction between lithium cation and *tert*-butoxide oxygen increases the localization of the negative charge at $(O)\underline{C}(CH_3)_3$ atoms, leading to shield shifts. Moreover, it is further interesting to note that, as the number of MIBLi moieties in the mixed complexes decreases from 3 to 1, the carbons at $(O)\underline{C}(CH_3)_3$ become less shielded by 0.5, 0.3, and 0.2 ppm, respectively. It is tempting to correlate this variation with a decreased localization of the negative charge at the $(O)\underline{C}(CH_3)_3$ group. Since the additional negative charge located at the $(O)C(CH_3)_3$ group in the mixed complexes $MIB_xLi_4(OtBu)_{4-x}$ originates from the presence of relatively weaker additional bonding between lithium and the carbonyl oxygen than that between lithium and the alkoxy one, the localization of the negative charge at the $(O)\underline{C}(CH_3)_3$ group would be reduced by incorporation of less metalated methyl isobutyrate groups into mixed complexes, leading to less shielded shifts.

Furthermore, it may be seen from Table 2 that the ^{13}C signals at the carbonyl group (C(O)) in LiOtBu-complexed MIBLi conversely shift downfield compared to that in the LiOtBu-free one. This is again very consistent with the decreased localization of the negative charge at the C(O) group due to relatively weaker additional interaction between lithium and the carbonyl oxygen. However, the change in ^{13}C chemical shifts at the C(O) carbon with number x follows a surprisingly irregular order $\delta_{C(O),B} < \delta_{C(O),A} < \delta_{C(O),C}$ (Table 2 and Figure 2), which has not found a satisfactory explanation as yet.

On the basis of IR studies, Lochmann et al. have previously proposed a six-membered-ring structure (i.e., "enveloped" complex, **4**) for the mixed complex of lithium alkoxide and lithium ester enolate.[13] As rightly pointed out by them, the actual structure of these mixed complexes is certainly more complicated. Anyhow, the present ^{13}C data obviously disagree with that proposal of Lochmann et al., the simplest reason for that discrepancy being that there is double-bond rather than single-bond character

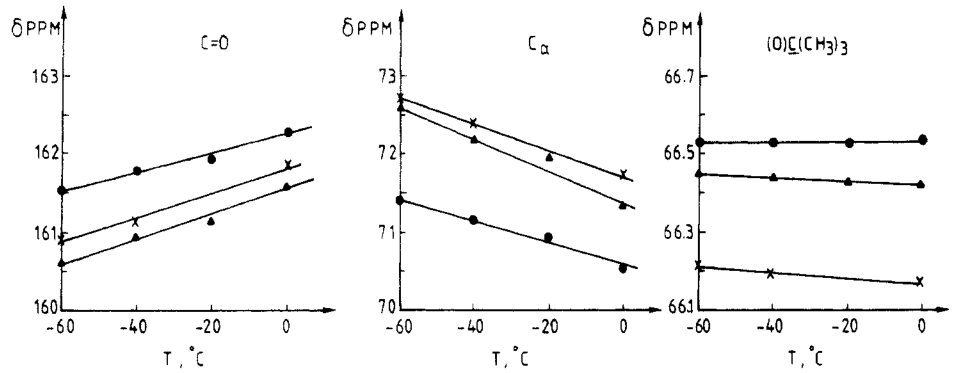
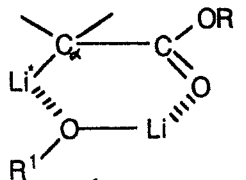


Figure 4. Variation of ^{13}C chemical shifts of various LiOtBu-added complexes (MIBLi: 0.8 M) with temperature. (×) $MIB_3Li_4(OtBu)_1$; (▲) $MIB_2Li_4(OtBu)_2$; (●) $MIB_1Li_4(OtBu)_3$.



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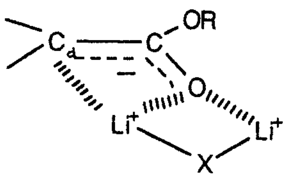
about the C_α–C(O) bond. Moreover, although the complexation of MIBLi by LiOtBu leads to a upfield shift at C_α and a downfield one at the C(O) carbon (characteristic of decreased coordination between Li^+ and the carbonyl oxygen), it seems very unlikely that a lithium ion (Li^* in 4) in the mixed complexes is solely coordinated to α-carbon rather than at least in part to the still electron-richer carbonyl oxygen.

It appears accordingly more reasonable to describe the partial structure of these mixed complexes in 5, where a four-membered ring involving two lithium cations and two oxygen atoms is connected to a delocalized metalated methyl isobutyrate anion, i.e., a more typical μ-type coordination. Indeed, such a structure has been already proposed for MIBLi/LiCl mixed complexes.[8] Moreover, in LiOtBu-complexed species, the extent of charge redistribution is likely to be small given relationships of ~150 ppm per π-electron charge at the carbon in other delocalized systems, which might also give the credit to the partial structure of the mixed complexes as in 5.



R: CH_3; X: Cl, $OC(CH_3)_3$

5

Temperature-Variable ^{13}C NMR Spectra of the Mixed Complexes $MIB_xLi_4(OtBu)_{4-x}$. The typical temperature-variable ^{13}C NMR spectra are illustrated in Figure 3, their most striking feature being that the ^{13}C resonances for different LiOtBu-added complexes are still observed as discrete signals, even without significant line broadening up to at least 0 °C. This provides very strong evidence that the exchange between the different complexes is extremely slow.

It is also remarkable that the ^{13}C shifts at various carbons of the metalated methyl isobutyrate moiety in all three mixed complexes slightly vary with temperature in a linear fashion: see, for example, Figure 4A,B. Indeed, the α-carbons move upfield by ca. 0.5–1.0 ppm upon an increase in temperature of 60 °C. This variation is, however, compensated by a downfield shift of ca. 0.8–1.3 ppm at the carbonyl carbon (C(O)). These results strongly suggest that, upon increasing the temperature, the negative charge density increases at C_α but decreases at C(O).

One must, however, stress that the observed changes were an order of magnitude smaller than those caused at C_α by changes in the aggregation state, i.e., ca. 7 ppm difference between tetrameric and dimeric MIBLi's,[7] ruling out an association-dependent mechanism for the explanation of the temperature-dependent chemical shifts. On the other hand, another NMR study[14b] has revealed a similar temperature-dependent chemical shift for several types of aromatic carbanions. Such behavior has been ascribed to systems where a temperature-dependent equilibrium exists between two types of ion pairs, i.e., tight and solvent-separated ones. For the present systems, formation of solvent-separated species is implausible since they are highly aggregated mixed complexes in which a strong Li–O bond is involved.

However, there is evidence from a kinetic investigation developed by Müller et al. that a living $PMMA^-Li^+$ end exists as a contact ion pair in several ether solvents. In such a more powerful solvating medium, the lithium counterion is, of course, supposed to be more separated from the carbanion by solvent molecules, while still being in strong contact with the enolate oxygen.[15] This might imply that the lithium cation could shift from C_α to the C(O) carbons due to solvation effects. In that respect, the charge density would be reduced at C_α and correspondingly enhanced at the C(O) carbon when lithium cation is more solvated. It is also well-known that this solvation of lithium cation can also be affected by varying the temperature. In fact, coordination of Li^+ by a solvent, e.g., THF, is essentially favored at low temperature. Hence, one may speculate that the present situation might correspond to a solvation effect on the charge distribution around the metalated methyl isobutyrate moiety, typically at C_α and C(O), by varying the temperaure: at higher temperature, the lithium cation is somewhat less solvated by THF, resulting in a relatively closer interaction between C_α and Li^+ and a decreased interaction between Li^+ and the C(O) group. However, it is necessary to point out that such a solvation effect does not necessarily mean that lithium is separated from C_α by THF.

In striking contrast to the results described above, only very slight changes are observed at the $(O)\underline{C}(CH_3)_3$ carbon in the same temperature range (Figure 4C). This might imply that the solvation of lithium ion has very little effect on the LiOtBu moeities, due to some still unclear reasons.

Equilibrium Constants for the Mixed Complex Formation. As with LiOtBu-complexed systems, the exchange between various species is slow on the ^{13}C NMR

Table 3. Concentration of Mixed Complexes $MIB_xLi_4(OtBu)_{4-x}$ at Various LiOtBu/MIBLi Ratios

MIBLi, mM	LiOtBu, mM	T, °C	x = 4	x = 3	x = 2	x = 1	$Li_4(OtBu)_4$, mM
3.2	1.6	−40	0.09	0.61	0.50		
3.2	3.2	−40	0.08	0.15	1.06	0.31	
3.15	6.4	−60			0.85	1.44	0.10
		−40			0.87	1.39	0.12
		−20			0.91	1.33	0.15
		0			0.93	1.30	0.16

Table 4. Equilibrium Constants for the Formation of $MIB_xLi_4(OtBu)_{4-x}$ (x = 1–3) Mixed Complexes at −40 °C

K_1	K_2	K_3
200	1.1×10^4	18.5

time scale, in a broad temperature range of −60 to 0 °C; it was accordingly possible, using direct integration, to determine the population of each species at different LiOtBu/MIBLi ratios. These results are presented in Table 3.

The high propensity of LiOtBu to form mixed complexes with MIBLi in THF is clearly apparent from these data. At LiOtBu/MIBLi < 1/1, all LiOtBu have reacted with MIBLi, mainly forming 1 and 2. At a relatively high LiOtBu/MIBLi ratio, e.g., 2/1, the species 3 becomes predominant.

Although it is impossible to directly calculate the equilibrium constants K_1 and K_2 for eqs 1 and 2, respectively, due to the difficulty in detecting free LiOtBu at LiOtBu/MIBLi < 2, in the case of LiOtBu/MIBLi = 2/1, fortunately, as one can estimate the concentration of free lithium *tert*-butoxide (presumed to be present as a tetrameric aggregate), an equilibrium constant for the formation of mixed complex 3 (eq 3) can be evaluated:

$$K_3 = \frac{[MIB_1Li_4(OtBu)_3]^2}{[MIB_2Li_4(OtBu)_2][Li_4(OtBu)_4]} \tag{4}$$

In this regard, K_1 and K_2 can be easily obtained from eqs 5 and 6.[16a]

$$\frac{K_3}{K_2} = \frac{[MIB_1Li_4(OtBu)_3]^2[MIB_3Li_4(OtBu)_1]^2}{[MIB_2Li_4(OtBu)_2]^4} \tag{5}$$

$$\frac{K_2}{K_1} = \frac{[MIB_2Li_4(OtBu)_2]^3[MIB_4Li_4]^3}{[MIB_3Li_4(OtBu)]^6} \tag{6}$$

Accordingly, three equilibrium constants at −40 °C are tabulated in Table 4. It is quite evident that the formation of LiOtBu-complexed MIBLi is more favorable in the order $MIB_2Li_4(OtBu)_2 > MIB_3Li_4(OtBu)_1 > MIB_1Li_4(OtBu)_3$.

In addition, the corresponding thermodynamic parameters for eq 3 have also been determined from a van't Hoff plot (Figure 5), as $\Delta H = -1.5$ kcal/mol and $\Delta S = -0.8$ cal/(mol K), very close to those of $\Delta H = -1.2$ kcal/mol and $\Delta S = -1.3$ cal/(mol K) reported by Jackman et al. for the mixed-dimer formation between lithium 2,6-dimethylphenolate and lithium tetraphenylborate in dioxolane.[16b]

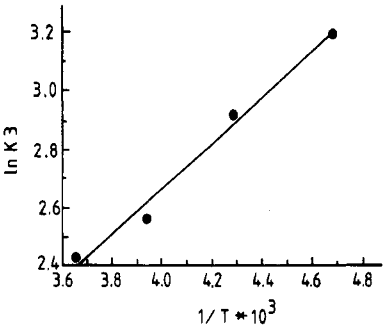


Figure 5. van't Hoff plot for the formation of mixed complex $MIB_1Li_4(OtBu)_3$ (MIBLi: 0.8 M) in THF.

Comparison of the Mixed Complexation Behavior of MIBLi by LiOtBu or by LiCl in THF. As established above, and similarly to LiCl,[8] LiOtBu is found to be also very effective in coordinating with MIBLi to form various mixed complexes $MIB_xLi_4(OtBu)_{4-x}$ (x = 1–3).

However, we still note several important and significant differences between these two ligands. First, LiOtBu has the ability to incrementally replace metalated methyl isobutyrate ligands in MIBLi tetramer to form tetrameric mixed complexes in THF, whereas the addition of LiCl into MIBLi in THF instantaneously forms the mixed dimer 1LiCl·1MIBLi at LiCl/MIBLi 1/1, trimer 2LiCl·1MIBLi at LiCl/MIBLi 2/1, and possibly tetramer 3LiCl·1MIBLi at LiCl/MIBLi ≥3/1.[8] It seems obvious that LiCl can promote less aggregated mixed complexes than LiOtBu. Such a difference most probably results from the different solvation degree of these ligands by THF. In support of this explanation, it has been shown that LiCl is exclusively dimeric in THF,[17] while LiOtBu is essentially tetrameric.[10]

On the other hand, when studying the process of incorporation of a third ligand into mixed complexes in these two systems, it is inrewarding to compare the essentially zero entropy change (ca. −0.8 cal/(mol K)) for the formation of mixed LiOtBu/MIBLi tetramer 3 (see above) and the highly negative one (ca. −46.5 cal/(mol K))[8] for the formation of mixed LiCl/MIBLi 3:1 complex. In a multinuclear NMR investigation of mixed aggregation between various lithium salts and lithium phenolates, Jackman et al. have previously demonstrated that the solvation effect on the mixed complexation process is essentially entropic in origin, reflecting the relative solvation degree of the added salt vs the mixed aggregate.[16] By analogy, the quite different entropies observed here for complexation of MIBLi by LiCl or LiOtBu may thus be a consequence of a changing solvation degree in the two systems. Actually, it is obvious from eq 3 that the formation of mixed tetramer 3 involves no change in solvation, whereas the production of the LiCl/MIBLi 3:1 complex by reacting LiCl/MIBLi 2:1 with dimeric LiCl possibly involves a formal release of several units in the total number of solvent molecules.[8]

Finally, the difference in dynamic behavior of these two mixed complexed systems probably provides the most striking feature of this comparison. As noted above, several LiOtBu/MIBLi mixed complexes may coexist in solution with a very slow exchange process even at temperatures as high as 0 °C. By contrast, even at a low temperature (e.g., −80 °C), only one single type of LiCl-complexed species prevails at LiCl/MIBLi = 1, 2, and ≥3, respectively.[8] Recently, in the course of a kinetic study of the anionic polymerization of MMA abd tBuA, Müller et al. have well established[6,18] that, although LiOtBu stabilizes the active center by decreasing the termination rate, the molecular weight distributions (MWDs) obtained by them and by us are considerably broader than those in the presence of LiCl (1.77 against 1.08 for PtBuA). It seems obvious now that these differences in MWDs can be connected with the different dynamic behaviors discussed here for the two ligated systems, supporting the important role of association/complexation equilibria in the anionic living polymerization of (meth)acrylates.[8,19]

In conclusion, once again, it has been shown that NMR investigation of model systems is very helpful for mechanistic studies of the anionic polymerization of (meth)-acrylates. By comparing different ligands/MIBLi complexing behaviors, one may gain further insight into the intimate course of these processes. Additional results involving other types of ligands will be reported in due course.

Acknowledgment. We are deeply indebted to ATOCHEM-ELF (France) for generous financial and scientific support, as well as to the "Services de Programmation de la Politique Scientifique" (Brussels, Belgium). We also thank Mrs. C. Henrard-Schouille for her skillful technical assistance. NMR spectra were recorded at the CREMAN facility at the University of Liége (Belgium).

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