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Anionic Polymerization of Acrylic Monomers. 14. Carbon-13 and Lithium-7 NMR Characterization of the Complexation of Methyl α-Lithioisobutyrate with Various Lithium Cation-Binding Ligands in Tetrahydrofuran

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ABSTRACT: The aggregation equilibrium and electronic structure of methyl α-lithioisobutyrate (MIBLi), a monomeric model structurally corresponding to a living poly(methyl methacrylate) chain end associated with a lithium countercation, has been examined by ^{7}Li and/or ^{13}C NMR spectroscopy in tetrahydrofuran (THF) in the presence of various lithium cation-binding ligands. The addition of dimethoxyethane (DME), triglyme (glyme-3), 12-crown-4 (12-CE-4), and hexamethylphosphoric triamide (HMPA) to coexisting tetrameric and dimeric MIBLi in THF induces an increase in dimeric population in the order DME < glyme-3 < 12-CE-4 < HMPA. That order corresponds to an increasing strength of complexation between MIBLi (lithium cation) and the (solvating) ligands. For either tetrameric or dimeric species, moreover, the negative charge distribution around MIBLi does not seem to be significantly modified due to the presence of these complexing agents. In striking contrast, complexation of MIBLi by cryptand 211 (K211) does shift the equilibrium between tetramer and dimer toward the formation of a single monomeric K211-complexed species, which gives rise to ca. 13 and 5 ppm upfield shifts at C_α in the ^{13}C NMR spectra, compared to tetrameric and dimeric species, respectively. The effect of 12-CE-4/K211 on the original aggretation equilbrium for MIBLi in THF nicely explains the significantly different MWD of PMMA anionically prepared in the presence of each of these ligands.

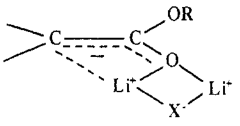
Introduction

The so-called ligated (ligand modified) polymerization has steadily emerged as an efficient pathway toward the control of anionic living polymerization of (meth)acrylic monomers,[1] thanks to the use of several ligated initiators recently discovered by us[2] and others.[3] However, the underlying mechanism of these processes is still unclear. Indeed, even for ligand-free (meth)acrylate anionic polymerization systems, to date direct spectroscopic investigation has rarely been carried out, most available information largely originates from the kinetic studies.[4] The main reasons for such a sluggish development are most likely due to the difficulties in obtaining suitable and stable living poly(meth)acrylate solutions and to the lack of characteristic spectra (e.g., UV–visible) that are useful in terms of interpretation of the ion-pairing structure.

In order to overcome these difficulties and to gain deeper insights into the nature of the ligated living processes, we have recently set up systematic studies of ion pairs and related complexes with different kinds of ligands by means of NMR spectroscopy. Although it is rather difficult to perform an investigation on a "real" living poly[alkyl (meth)acrylate] system, the use of models has been found to be very helpful. Indeed, we have previously reported[5] on the utility of both ^{13}C and ^{7}Li NMR for the characterization and quantitative description of differing ion pairs (and aggregates) of methyl α-lithioisobutyrate (MIBLi; 1) in THF, a monomeric model structurally corresponding to a living poly(methyl methacrylate) chain end. Moreover, the complexation of MIBLi by two broadly used ligands, lithium chloride (LiCl)[6] and lithium *tert*-butoxide (LiOtBu),[7] has also been investigated by using ^{7}Li and/or ^{13}C NMR spectroscopy. A mixed μ-type complex (**2**) between MIBLi and LiX (X = Cl, OtBu) has been accordingly put in evidence.

$(CH_3)_2C(Li)COOCH_3$

1



X = Cl, OtBu

R = CH$_3$

2

It is also well-known that polyethers (including crown ethers) and polyamines (including cryptands) present another type of ligand (i.e., σ-type cation binding) useful in the course of anionic polymerization of (meth)acrylates.[1] It thus seemed of great interest to perform an additional NMR investigation of complexation of MIBLi with these ligands. Furthermore, by comparing the complexation behavior of MIBLi with different types of ligands, one may expect to gain a better understanding of the nature of complexed active species in ligated living anionic polymerization of (meth)acrylates and hopefully to tailor new useful additives for that process.

In this paper, we report ^{13}C and ^{7}Li NMR studies of methyl α-lithioisobutyrate (MIBLi)/THF solutions in the presence of various lithium cation-binding ligands. It is indeed essential to know whether and how these σ-type ligands affect the electronic structure and dynamics of the MIBLi/THF solution in relation to the polymerization process characteristics.

For convenience the structures of these potential ligands used in this work are listed as **3**–**7** together with their common abbreviations.

Experimental Section

Methyl isobutyrate from Aldrich was purified and dried by distillation from CaH_2 (two times). It was then stored under a

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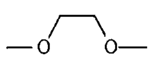
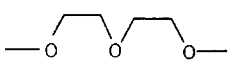
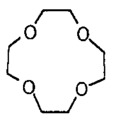


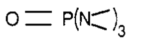
3, DME



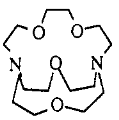
4, Glyme 3



5,12-CE-4



6, HMPA



7, K211

nitrogen atmosphere. N-Lithiodiisopropylamide (97%) was a commercial product from Aldrich and was used as received. THF, THF-d_8, dimethoxyethane (DME), and triglyme (glyme-3) also from Aldrich were refluxed over benzophenone sodium ketyl and distilled immediately prior to use. Hexane, toluene, and benzene-d_6 were refluxed over CaH_2 and distilled over styryllithium living oligomer just before use. Hexamethylphosphoric triamide (HMPA) and 12-crown-4 (12-CE-4) were distilled from CaH_2 prior to use. The cryptand 211 (K211) was used without purification.

Pure methyl α-lithioisobutyrate (MIBLi) was prepared under dry nitrogen from equimolar amounts of methyl isobutyrate and N-lithiodiisopropylamide in hexane at −78 °C as reported previously.[5] The resulting white MIBLi solid was dissolved in the desired volume of ligand solution at −78 °C and then directly filtered under nitrogen 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, whose chemical shift was separately determined to be 25.3 ppm relative to $(CH_3)_4Si$. Lithium-7 NMR spectra were referenced to a 0.2 M LiCl solution in THF.

Results

Complexation of Linear Polyethers [DME (3) and Glyme-3 (4)] and a Macrocyclic Polyether [12-CE-4 (5)] to Methyl α-Lithioisobutyrate [MIBLi, (1)] in THF. (a) General Behavior. It has been previously shown that a coordination equilibrium exits between tetrameric and dimeric MIBLi in THF solution (eq 1).[5]

$$2Li_2MIB_2S_4 \rightleftharpoons Li_4MIB_4S_4 + 4S \qquad (1)$$

$$S = THF$$

The exchange between these two aggregated species was found to be slow on the ^{13}C and ^{7}Li NMR time scales, thereby allowing observation of spectra due to different species. The ^{13}C NMR spectra also revealed that both species display charge-delocalized character and that the dimeric species possesses a more negative charge density at metalated carbon (C_α) than the tetrameric one.

When three potential lithium cation-binding polyethers, DME (3), glyme-3 (4), and 12-CE-4 (5), are added into a MIBLi/THF solution, the ^{7}Li NMR data for MIBLi fall altogether into a common pattern which is typical of the one observed for a MIBLi/THF solution (Figure 1): under all circumstances so far we observe no more than three lithium resonances, and their shifts are close to those seen for MIBLi in THF. This might indicate a coexistence of tetrameric and dimeric MIBLi in the presence of these ligands (Table 1).

As also noted in Table 1, addition of DME (3) and glyme-3 (4) into the MIBLi/THF solution leads to rather small changes in ^{7}Li chemical shifts (ca. 0.01–0.02 ppm) compared to "free" MIBLi, whereas 12-CE-4 (5) gives rise to relatively larger downfield shifts of ca. 0.07 and 0.03

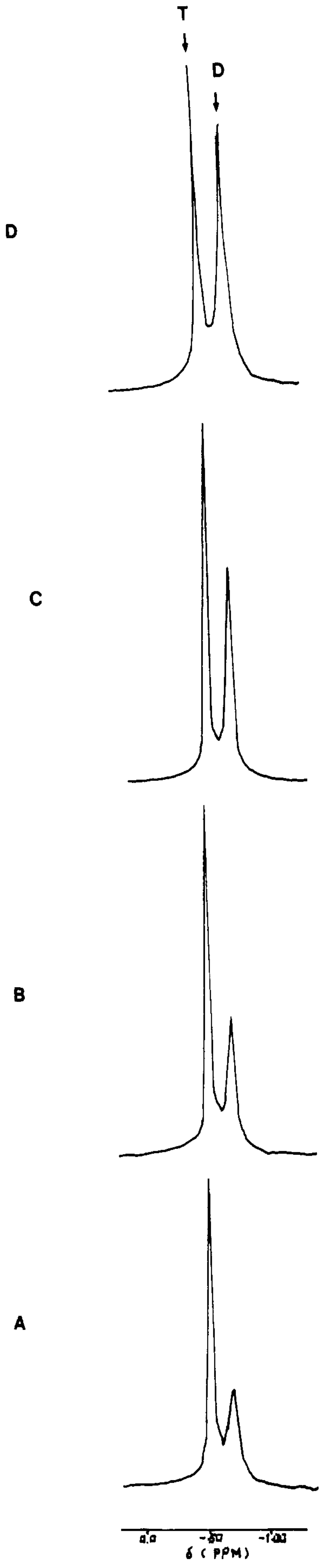


Figure 1. Lithium-7 (155.6-MHz) spectra of 0.2 M methyl α-lithioisobutyrate (MIBLi) in THF and in the presence of various polyether type ligands at 203 K. T: tetramer. D: dimer. (A) THF. (B) In the presence of 10 mol equiv of DME. (C) In the presence of 10 mol equiv of glyme-3. (D) In the presence of 5 mol equiv of 12-CE-4.

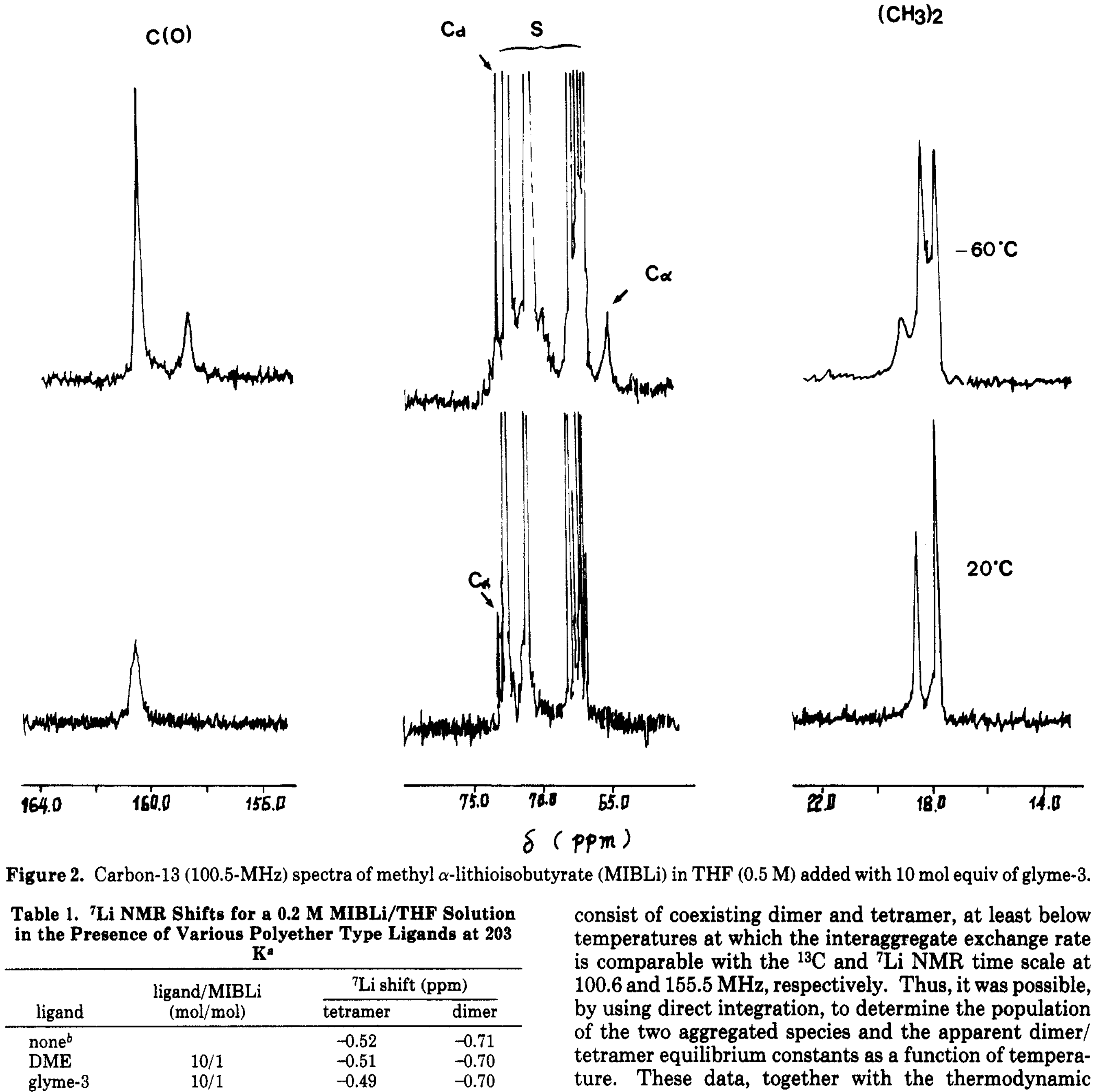


Figure 2. Carbon-13 (100.5-MHz) spectra of methyl α-lithioisobutyrate (MIBLi) in THF (0.5 M) added with 10 mol equiv of glyme-3.

Table 1. ^{7}Li NMR Shifts for a 0.2 M MIBLi/THF Solution in the Presence of Various Polyether Type Ligands at 203 K[a]

ligand	ligand/MIBLi (mol/mol)	^{7}Li shift (ppm)	
		tetramer	dimer
none[b]		−0.52	−0.71
DME	10/1	−0.51	−0.70
glyme-3	10/1	−0.49	−0.70
12-CE-4	5/1	−0.47	−0.69

[a] Relative to 0.2 M LiCl in THF at 298 K. [b] Reference 4.

ppm from uncomplexed tetrameric and dimeric MIBLi, respectively. These results might indicate a change in the coordination environment of lithium, more likely in the first solvation shell. 12-CE-4 might accordingly be more powerful than DME and glyme-3 in competing with THF for coordination to lithium cations in MIBLi.

Furthermore, three polyether ligand-added systems, which give rise to two resonances in the ^{7}Li NMR spectra at low temperatures, have ^{13}C shifts analogous to those obtained in the free MIBLi/THF system. Figure 2 shows the typical ^{13}C NMR spectra of MIBLi in THF containing 10 equiv of glyme-3 at −60 and +20 °C, and Table 2 lists carbon-13 shifts of MIBLi in the presence of DME, glyme-3, and 12-CE-4. Comparison with ^{13}C NMR data for the MIBLi/THF solution, it is obvious that two types of aggregated species, i.e., tetrameric and dimeric MIBLi, are still involved in these three polyether-added systems at a low temperature, e.g., −60 °C. This is in good agreement with the above-described ^{7}Li results.

(b) Aggregation Equilibrium between Tetrameric and Dimeric MIBLi. All polyether–MIBLi complexes consist of coexisting dimer and tetramer, at least below temperatures at which the interaggregate exchange rate is comparable with the ^{13}C and ^{7}Li NMR time scale at 100.6 and 155.5 MHz, respectively. Thus, it was possible, by using direct integration, to determine the population of the two aggregated species and the apparent dimer/tetramer equilibrium constants as a function of temperature. These data, together with the thermodynamic parameters obtained from a van't Hoff plot, are presented in Table 3.

It is evident from Table 3 that the proportion of dimer increases in the order THF < DME < glyme-3 < 12-CE-4, which corresponds to an increasing strength of complexation between the lithium-containing ion pairs and the cation-binding (solvating) ligands.[8] This is expected since it has been well established that dissociation behavior of methyl α-lithioisobutyrate (MIBLi) is similar to the one generally observed for solvated organolithium compounds;[5] i.e., their dissociation into smaller aggregates in coordinating solvents is accompanied by increased coordination (solvation) to lithium and thus favored in the presence of stronger cation-binding (solvating) reagents.[9]

It is also quite standard that these systems are all characterized by negative dissociation enthalpies, indicating that the solvation-assisted dissociation process is favored at lower temperatures, this is again in good agreement with many previously reported data for the dissociation of organolithium compounds to smaller aggregates in coordinating solvents.[9] Furthermore, the enthalpy toward dimer formation becomes more negative again in the order THF < DME < glyme-3 < 12-CE-4,

Table 2. ^{13}C Chemical Shifts (in ppm) of MIBLi (0.5 M) in THF Added with Several Lithium Cation-Binding Polyethers[a]

ligand	L/M[b] (mol/mol)	*T* (°C)	C(O) T[c]	C(O) D[d]	C_α T	C_α D	OCH_3 T	OCH_3 +	OCH_3 D	$(CH_3)_2$ T	$(CH_3)_2$ D
e		25	176.8		34.3			51.3		19.2	
no[f]		−60	160.5	158.9	73.5	65.4	57.0		56.0	18.3, 18.0	18.9
		20	160.6		72.7[g]			56.7		18.3, 17.7	
DME	10/1	−60	160.6	158.9	73.4	65.5		57.0		18.7, 17.9	18.9
		20	160.8		72.4			56.7		18.7, 17.8	
glyme-3	10/1	−60	160.6	159.0	73.4	65.5		57.1		18.4, 17.9	19.1, 18.2
		20	160.6		*h*			56.8[g]		18.5, 17.8	
12-CE-4	5/1	−60	160.6	159.3	73.2	65.2		57.0		18.4, 17.9	18.9, 18.1
		20	160.8		72.7			56.7[g]		18.4, 17.7	

[a] Relative to the high field signal of THF-d_8, 25.3 ppm. [b] Mole ratio of ligand (L) to MIBLi (M). [c] Tetramer. [d] Dimer. [e] Corresponding parent ester, i.e., methyl isobutyrate, $(CH_3)_2CHCOOCH_3$. [f] Reference 4. [g] Broad. [h] Obscured.

Table 3. Equilibrium Constants for $(MIBLi)_4$ (T) ⇌ 2 $(MIBLi)_2$ (D) as a Function of Temperature for 0.2 M MIBLi in THF Added with Various Polyether-Type Ligands[a]

T (K)	T	D	D/T	K_{eq}
		THF[b]		
	$\Delta H = -2.1$ kcal/mol		$\Delta S = -13.7$ cal/mol·K	
		DME		
193	0.0255	0.0490	1.922	0.0941
197	0.0267	0.0466	1.745	0.0813
203	0.0280	0.0440	1.571	0.0691
207	0.0294	0.0412	1.401	0.0577
	$\Delta H = -2.8$ kcal/mol		$\Delta S = -19.1$ cal/mol·K	
		Glyme-3		
193	0.0215	0.0570	2.651	0.151
198	0.0228	0.0544	2.386	0.130
202	0.0234	0.0532	2.274	0.121
208	0.0271	0.0458	1.690	0.0774
	$\Delta H = -3.4$ kcal/mol		$\Delta S = -21.3$ cal/mol·K	
		12-CE-4		
193	0.0210	0.0570	2.762	0.160
203	0.0225	0.0550	2.444	0.134
208	0.0265	0.0470	1.774	0.083
213	0.0310	0.0380	1.226	0.047
218	0.0340	0.0320	0.941	0.030
	$\Delta H = -5.7$ kcal/mol		$\Delta S = -31.4$ cal/mol·K	

[a] ^{7}Li data. [b] Reference 5.

Table 4. ^{13}C Chemical Shifts (in ppm) of MIBLi (0.5 M) in THF in the Presence of 4 mol equiv of HMPA[a]

T (°C)	C(O) T[b]	C(O) D[c]	C_α T	C_α D	OCH_3 T	OCH_3 +	OCH_3 D	$(CH_3)_2$ T	$(CH_3)_2$ D
25[d]	176.8		34.3			51.3		19.2	
−60[e]	160.5	158.9	73.4	65.4	57.0		56.0	18.3, 18.0	18.9
−60	160.5	159.0	73.3	65.2	56.9		56.0	18.3, 17.9	18.9, 18.2
−50	160.5	159.0	73.3	65.2	57.0		55.9	18.3, 17.9	18.9, 18.2
−40	160.6[f]		73.3			57.0[f]		18.3, 17.8	

[a] Relative to the high-field signal of THF-d_8, 25.3 ppm. [b] Tetramer. [c] Dimer. [d] Corresponding parent ester, i.e, methyl isobutyrate, $(CH_3)_2CHCOOCH_3$. [e] Data for HMPA-free MIBLi in THF; see ref 4. [f] Broad.

which might suggest that solvent-mediated breakdown of the aggregate is more favored enthalpically in the presence of relatively stronger lithium cation-binding (solvating) reagents. Similar results have also been obtained by Jackmann et al.,[9a] who reported that the enthalpy for the tetramer ⇌ dimer equilibrium for lithium 2,6-di-*tert*-butylphenolate is more negative in pyridine than in dioxolane, a consequence of a stronger solvating power of the former solvent over the latter one.

Moreover, it is worth noting that in all systems studied here the entropies increase on going from dimer to tetramer. This is qualititively consistent with the liberation of solvent molecules[9b] as, for example, in eq 1, where S may represent other cation-binding ligands.

(c) Effect of Polyether Ligands in THF on the Charge Distribution in MIBLi. Another approach is to evaluate the effect of the addition of various polyether ligands on the charge distribution around the carbanion of MIBLi in THF, as provided by a further examination of the related ^{13}C NMR spectra.

Considering these spectra (Table 2), one may conclude as a first approximation that they follow the pattern expected for a highly charge-delocalized MIBLi carbanion as already demonstrated in the MIBLi/THF solution.[5] First, the methyls bound to C_α are magnetically nonequivalent in a broad temperature range, consistent with a pronounced double-bond character about the C_α–C(O) bond.[5,10] Second, the ^{13}C resonance at C(O) carbon shifts upfield ca. 17 ppm from that of the parent ester, i.e., methyl isobutyrate, indicating a significant charge delocalization at this carbon atom. Finally, although suitable reference compounds for MIBLi having pure sp^2 carbons are not available, the hybridization change from sp^3 to sp^2 has been established to result in a ca. 100 ppm downfield shift in ^{13}C NMR spectra.[11] In that respect, the ca. 30–40 ppm downfield shift of MIBLi from the parent ester (ca. 65.2 and 73.5 ppm against 34.3 ppm) at the metalated carbon atom (C_α) strongly suggests that the negative charge is also delocalized to this atom.[5,10]

Again, from Table 2, it is clear that complexation of the lithium cation by stronger cation-binding polyether ligands (relative to THF) causes a very slight modification of the negative charge distribution around the MIBLi carbanion, as indicated by very small observable changes in the ^{13}C chemical shifts at all carbons (ca. 0.1–0.4 ppm). House et al. examined the effect of DME and several crown ethers on the ^{13}C spectra of alkali-metal enolates in THF, e.g., 8. The spectra showed that, if complexation occurred at all, it was to an extent insufficient to produce observable changes in the chemical shifts.[12a] Jackmann et al.[12b,c] have also carried out a similar study of lithium isobutylphenone (9) in dioxolane or DME with glyme-3, 12-CE-4, or 15-CE-5, confirming the findings of House et al. The present results then appear to be consistent with all the published data.

$\mathrm{PhC(OLi){=}CH_2}$

8

$\mathrm{PhC(OLi){=}C(CH_3)_2}$

9

Complexation of Hexamethylphosphoric Triamide [HMPA (6)] to Methyl α-Lithioisobutyrate (MIBLi) in THF. The ^{13}C chemical shifts of a 0.5 M MIBLi/THF solution in the presence of 4 mol equiv of HMPA are listed in Table 4. Here again, it is obvious that two species are present below ca. −40 °C, the ^{13}C chemical shifts of which are obviously very close to those for tetrameric and dimeric ones observed in the HMPA-free MIBLi/THF solution. This clearly indicates that two coordination aggregates still coexist in the HMPA-added MIBLi in a THF solution.

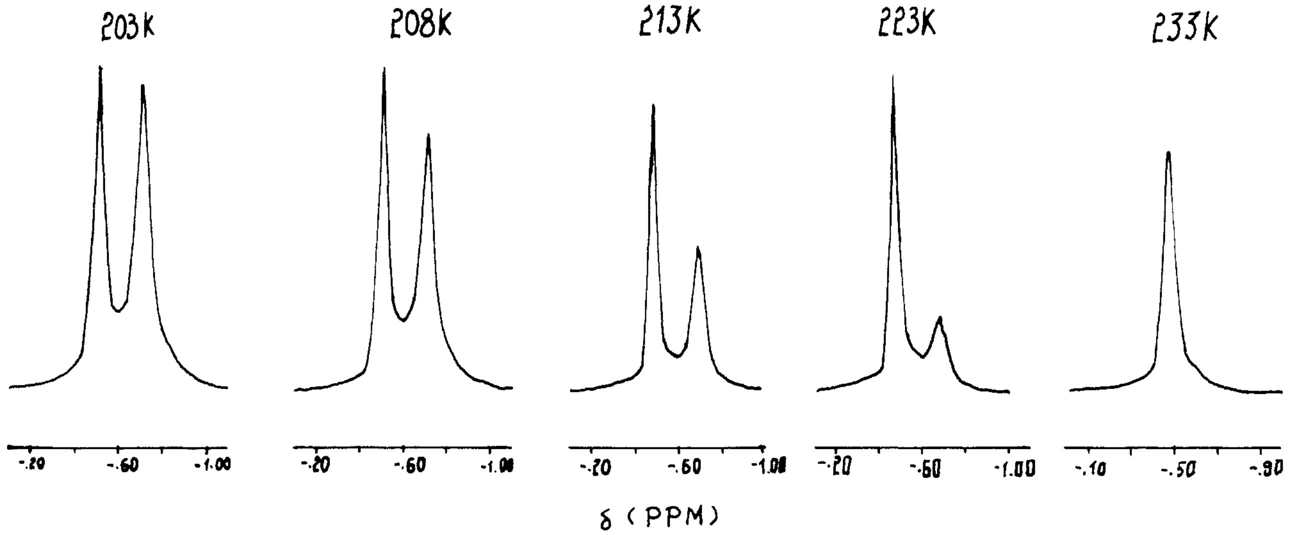


Figure 3. Lithium-7 (155.6-MHz) spectra of 0.2 M methyl α-lithioisobutyrate (MIBLi) in THF added with 4 mol equiv of HMPA at different temperatures.

Table 5. Concentration of Tetrameric Species (T, δ −0.69 ppm) and Dimeric Species (D, δ −0.49 ppm) in a 0.2 M MIBLi in THF in the Presence of 4 mol equiv of HMPA as a Function of Temperature[a]

T (K)	T	D	D/T	K_{eq}
203	0.0215	0.0570	2.651	0.151
208	0.0240	0.0516	2.132	0.110
213	0.0285	0.0431	1.512	0.0652
218	0.0322	0.0356	1.106	0.0394
	$\Delta H = -7.9$ kcal/mol		$\Delta S = -42.6$ cal/mol·K	

[a] ^{7}Li NMR data.

The lithium-7 NMR data confirm and extend the above observations. Upon addition of 4 mol equiv of HMPA into a 0.2 M MIBLi/THF solution, two well-separated ^{7}Li resonances are recorded below ca. −40 °C (Figure 3), showing that exchange between these two species is slow on the ^{7}Li NMR time scale at low temperatures. As already discussed in the preceding sections, these two ^{7}Li signals might correspond to the tetrameric and dimeric MIBLi.

In addition, Table 5 shows that HMPA gives rise to a larger increase in the fraction of dimer species and a more negative enthalpy change toward the dimer formation, compared to various polyether ligands. This probably reflects the fact that HMPA is a stronger complexing reagent than the above-mentioned polyethers.[8]

It is worthwhile to mention here that House and Jackmann have previously reported that addition of ca. 4 equiv of HMPA caused significant upfield shifts of the C_α resonance in lithium enolates **8** and **9**, in several ether solvents at room temperature. For example, House showed that addition of 3.9 equiv of HMPA to **8** in THF leads to a 2.7 ppm upfield shift at metalated carbon.[12a] Similarly, in dioxolane and DME, Jackmann et al. observed that the resonances of the α-carbon atom in **9** are shifted upfield by almost 4.3 and 1.9 ppm, respectively.[12b] Due to the lack of detailed studies of the aggregation equilibrium for **8** by House et al., it is hard to make a further comparison between their results and the present ones. Nevertheless, Jackmann has shown that **9** may exist as a tetramer in dioxolane and as a mixture of tetramer and dimer in DME at room temperature. Since the complexation of **9** by HMPA in both solvents gives rise to an almost identical shielding ^{13}C chemical shift typical of a dimeric **9** in DME,[12c] one may suspect that the situation reported by Jackmann et al. corresponds to a deaggregation process of lithium phenolate **9** as promoted by HMPA. The same conclusion might then also be reasonably drawn for the complexation of lithium phenolate **8** by HMPA as reported by House et al.

Complexation between Cryptand 211 [K211 (7)] and Methyl α-Lithioisobutyrate (MIBLi) in THF. As discussed above, the equilibrium observed between tetrameric and dimeric species in a MIBLi/THF solution still persists in the presence of DME, glyme-3, 12-CE-4, and HMPA. However, in striking contrast, only one kind of species is recorded in the ^{13}C NMR spectra when 1.5 mol equiv of K211 is added into the 0.5 M MIBLi/THF solution (Table 6). It is worth noting from Table 6 that this powerful lithium ion complexing reagent, K211, also has a profound influence on the negative charge distribution around a carbanion of MIBLi. In fact, the resonance of the α-carbon atom is shifted upfield by almost 5 and 13 ppm from dimeric and tetrameric MIBLi species, respectively, corresponding to a substantial increase in the charge density at that position. Again, similar results have also been reported by Jackmann et al., who observed that, in dioxolane, the C_α resonance of lithioisobutylphenone (**9**) is shifted by 8 ppm to higher field on addition of 1.13 mol equiv of K211.[12b] Moreover, the X-ray structure of K211-complexed lithium iodide (LiI) reveals virtually complete dissociation of the LiI ionic bond, the lithium cation being encapsulated by the cryptand ligand.[13] Thus, the ^{13}C spectrum of MIBLi in the presence of K211 presumably corresponds to that of the MIBLi anion only slightly perturbed by very weak ion pairing associated with the lithium countercation.[12b] Most probably, such a cryptand-added MIBLi ion pair exists as a monomeric species;[12b] it is however difficult to estimate at this point whether this monomeric complexed species consists of a K211-separated ion pair or of free ions.

In addition, it is intriguing to observe that, in the ^{13}C NMR spectra of K211-complexed MIBLi in THF, there appears a negative chemical shift at OCH_3 carbon compared to the one of the parent ester, i.e., methyl isobutyrate (Table 6). This is obviously in contrast to the results obtained for K211-free MIBLi in THF[5] where the OCH_3 resonance conversely resonates ca. 5 ppm downfield of that of the parent ester.

Recently, the lithium enolate of methyl phenyl acetate (**10**) in THF has been carefully investigated by Corset et

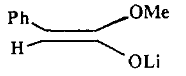


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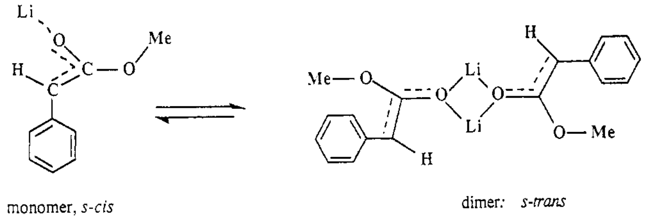
Table 6. ^{13}C Chemical Shifts (in ppm) of a 0.5 M MIBLi/THF Solution in the Presence of 1.5 mol equiv of K211[a]

T (°C)	C(O)	C_α	OCH_3	$(CH_3)_2$
25[b]	176.8	34.3	51.3	19.2
−60[c]	160.5 (T), 158.9 (D)	73.4 (T), 65.4 (D)	57.0, 56.0 (T + D)	18.3, 18.0 (T), 18.9, ?(D)
−60	159.3	59.9	50.9	18.6, 19.9
−50	159.4	59.9	50.9	18.6, 19.9
−30	159.4	59.9	50.9	18.6, 19.9

[a] Relative to the high-field signal of THf-d_8 25.3 ppm. [b] Corresponding parent ester, i.e., methyl isobutyrate, $(CH_3)_2CHCOOCH_3$. [c] K211-free MIBLi in THF (0.5 M): T, tetramer species; D, dimer species.

Scheme 1



al. by IR and ^{13}C NMR spectra. It has been accordingly demonstrated that[14] two differently aggregated species, i.e., monomer and dimer, coexist. Moreover, two types of different ^{13}C resonances at OCH_3, characteristic of two differently aggregated species, have been observed, one moving upfield (ca. 1.6 ppm) and the other one downfield (ca. 2.3 ppm) from the neutral compound. They are likely related to the presence of different conformers around the C–OMe bond in differently aggregated species[14] as sketched in Scheme 1.

According to the observations by Corset et al.,[14] the *s-cis* confomer, responsible for the negative OCH_3 shift, is more populated in the monomeric lithium enolate species, compared to the *s-trans* confomer that gives rise to a positive shift. The reverse occurs for the more aggregated species (i.e., dimer in Scheme 1), probably in order to avoid steric hindrance. In agreement with this explanation, it might be suggested that K211-complexed MIBLi has a predominant *s-cis* conformation, whereas the *s-trans* conformer dominates in K211-free tetrameric and dimeric MIBLi species. This also gives further support to the monomeric nature of the K211-complexed species.

Anionic Polymerization of Methyl Methacrylate (MMA) in THF at −78 °C Initiated with DPMLi in the Presence of 12-CE-4 and K211, respectively. Study of the complexation of MIBLI by a macrocyclic polyether (12-CE-4) and a cryptand (K211) has been completed by the effect of these lithium cation-binding σ-ligands on the course of the anionic polymerization of MMA, in THF, at −78 °C. Diphenylmethyllithium (DPMLi) has been used as an initiator and the effect of the Lσ/DPMLi (Lσ = 12-CE-4 or K211) on the molecular weight distribution (MWD) of PMMA has been investigated. Figure 4 shows that 12-CE-4 has no very significant effect on the MWD of PMMA. M_w/M_n drops from 1.15 to ca. 1.12, when the Lσ/DPMLi (Lσ = 12-CE-4) ratio is increased up to 2. Any further increase in the relative amount of the macrocyclic polyether compared to the initiator has no additional effect on the MWD of the final polymer. In contrast, M_w/M_n sharply decreases from 1.15 down to 1.01_5 when the K211 is used up to a 2-fold molar excess with respect to the initiator. A larger excess of K211 is again useless. There is a striking similarity in the effect of K211 and LiCl on the MWD of PMMA prepared under the same experimental conditions. When LiCl is used as a μ-type of ligand, a value of M_w/M_n as low as 1.02 is also observed for LiCl/DPMLi molar ratios that exceed 3.[15] This effect has indeed been accounted for by an interplay of an association/complexation equilibria mechanism.[1b,6] LiCl is responsible for the formation of mixed aggregates with the living ends, that shifts a relatively slow equilibrium[4b] between dimeric and monomeric PMMA$^-$Li$^+$ active species toward a single active complex.[6] As a result, a polymerization of an extremely narrow MWD results. This explanation can be now extended to K211, which is thus assumed to coordinate to the living chain ends with the formation of a single complexed active species, in perfect agreement with the NMR analysis of the K211/MIBLi complexation. Still in accordance with the NMR data reported in this work for complexation of 12-CE-4 with MIBLi, this macrocyclic polyether does not perturb significantly the slow association equilibrium of a living PMMA$^-$Li$^+$ chain, thus leading to a polydispersity of ca. 1.12.[16]

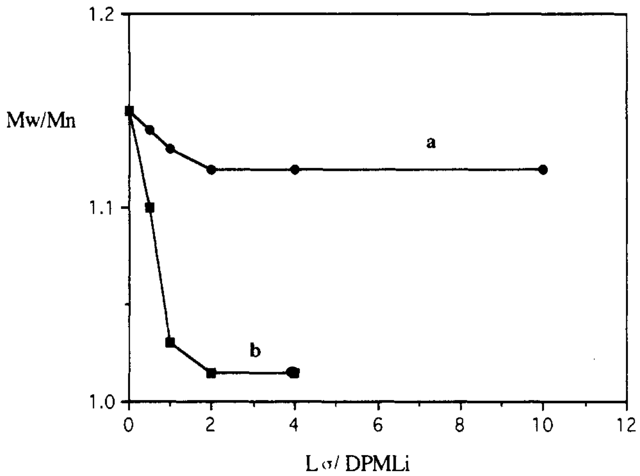


Figure 4. Effect of the Lσ/initiator molar ratio on the polydispersity index (M_w/M_n) of PMMA synthesized in THF at −78 °C in the presence of a Li counterion. Initiator = DPMLi, at a 4×10^{-4} mol/L concentration. (a) Lσ = 12-CE-4. (b) Lσ = K211.

Discussion

Complexaion Behavior of MIBLi by σ-Type of Ligands in THF. The main driving force for aggregation in a coordination solvent is, of course, the maximization of associative electrostatic interactions between cations and anions.[9] Aggregation, however, generally occurs at the expense of solvation of the ions (principally the lithium cation). The overall process may, therefore, be viewed as a competition between anions, ligands, and solvent for coordination with lithium cations. It is thus expected that the tendency toward less aggregated species, e.g., dimer formation in the present systems, is greater in the presence of a more powerful cation-binding ligand. The results of this work are consistent with such qualitative prediction.

However, it is worth noting that, except for K211, the complexation of MIBLi by the above-reported lithium cation-binding ligands, i.e., DME, glyme-3, 12-CE-4, and HMPA, does not lead to complete dissociation but only gives rise to an increase in population of dimeric species. Furthermore, no significant influence on the charge distribution in MIBLi was observed in these ligated systems, as indicated by a little change in ^{7}Li and ^{13}C spectra. This strongly suggests that coordination between anion and lithium is still relatively strong in MIBLi, more likely in relation to the strength of the O–Li bond present.

On the other hand, we have previously shown that some organic and inorganic salts, such as lithium *tert*-butoxide (LiOtBu) and lithium chloride (LiCl), are very effective as ligands of MIBLi in THF.[6,7] A ^{13}C NMR investigation has established that LiOtBu can incrementally replace methyl α-lithioisobutyrate moieties in MIBLi tetramer with the formation of coexisting tetrameric mixed complexes $\mathrm{MIB}_x\mathrm{Li}_4(\mathrm{OtBu})_{4-x}$ (x = 1–3). Moreover, a combination of ^{7}Li and ^{13}C NMR has shown that complexation of MIBLi by LiCl leads to the formation of mixed dimer 1/1 LiCl/MIBLi, trimer 2/1 LICl/MIBLi, and possibly tetramer 3/1 LiCl/MIBLi at LiCl/MIBLi = 1,2, and ≥3, respectively. In both mixed complexation systems, the negative charge distribution around MIBLi is somewhat modified.

The difference between the mixed complexation of MIBLi by inorganic or organic salts, and the cation-binding complexation by various polyether ligands and HMPA in THF is thus very clear. It seems most likely that the mixed complexation benefits from the electrostatic advantage of having all lithium cations in the system associated with MIBLi oxygens while also in close contact with the ligand ions (OtBu$^-$ or Cl$^-$), whereas the coordination of lithium by even quite powerful lithium cation-binding ligands, e.g., 12-CE-4 and HMPA, cannot largely perturb the aggregation of MIBLi most probably because of the presence of stable coordinative O–Li bonds, except for the extremely strong K211 ligand, the only one able to redistribute the banding situation.

On the Role of Lithium-Binding Ligands on Living Anionic Polymerization of MMA in THF at −78 °C. Once again, it is important to point out that, although there are some differences between model and real living systems, the analysis of the structure and dynamics of model active complexes may be very useful to understand the main characteristic features of the ligated anionic polymerization of (meth)acrylates.[15] Indeed, the picture of a slow aggregation equilibrium between tetramers and dimers of MIBLi in THF at a low temperature has emerged from a NMR study.[5] This conclusion is quite comparable to the proposal by Müller et al. for a slow equilibrium between dimeric and monomeric PMMA$^-$Li$^+$ under the same experimental conditions.[1b] The fast addition of MMA is thus expected to lead to a rather broad MWD.[16] Moreover, a ^{7}Li and/or ^{13}C NMR investigation of μ-mixed complexation of MIBLi by LiCl and LiOtBu, respectively, has shown that, although these two μ-type of ligands are very efficiently complexed to MIBLi,[6,7] LiCl induces a single complexed species at LiCl/MIBLi ≥ 3, whereas several types of complexed species coexist in the LiOtBu-added system and the exchange among them is still slow. Quite importantly, the difference in the dynamics of these two systems may nicely explain the significant difference in MWD for the anionically prepared PMMA in the presence of LiCl ($M_\mathrm{w}/M_\mathrm{n} \sim 1.02$)[6] and LiOtBu ($M_\mathrm{w}/M_\mathrm{n} \sim 1.10$)[17] under the same experimental conditions.

Results of this study give credit to a remarkable correlation between the dynamics of MIBLi complexed by σ-ligands, e.g., K211 and 12-CE-4, and the MWD of PMMA prepared in the presence of these ligands. Indeed, 12-CE-4 is not powerful enough to perturb the MIBLi aggregation and a slow exchange between aggregated species persists. In contrast, a monomeric K211-complexed MIBLi species is formed. Quite consistently, the MWD of PMMA is found to remain almost unchanged in the presence of 12-CE-4 (1.15 against 1.12), whereas an extremely narrow MWD (down to 1.01_5) is obtained when K211 is the ligand.

In conclusion, in comparison with a μ-type of ligand (LiCl and tBuOLi), complexation of MIBLi by various lithium cation-binding ligands of a σ-type in THF (DME, glyme-3, 12-CE-4, and HMPA) is less effective in perturbing the strong aggregating O–Li bonds. Nevertheless, K211 leads to the formation of monomeric K211-complexed MIBLi species, which is at the origin of an extremely narrow MWD of PMMA anionically prepared in the presence of this ligand in THF at −78 °C.

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