Anionic Polymerization of Acrylic Monomers. 11. NMR Investigation of the Mixed Complexation of Methyl α-Lithioisobutyrate and Lithium Chloride

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ABSTRACT: Solutions of methyl α-lithioisobutyrate (MIBLi) in THF added with various amounts of lithium chloride (LiCl) have been analyzed by ^{7}Li NMR spectroscopy in a wide range of temperatures. Although below ca. 205 K tetramers of MIBLi have been reported to be in equilibrium with dimers, 1/1 and 2/1 LiCl/MIBLi mixed complexes instantaneously form upon the addition of 1 and 2 mol equiv of LiCl, respectively. Further addition of LiCl more likely promotes the formation of a less stable 3/1 complex. Both 1/1 and 2/1 adducts are stable between −80 °C and at least +12 °C. From ^{13}C NMR spectroscopy, it appears that the addition of an equimolar amount of LiCl to the MIBLi solution in THF is at the origin of a ca. 7.0 ppm upfield shift of the metalated α-carbon compared to the tetrameric MIBLi species and a ca. 1.0 ppm downfield shift with respect to the dimeric MIBLi. However, the charge distribution over the carbanion does not change anymore when the amount of LiCl exceeds 1 mol equiv. In contrast to nonligated MIBLi, the OR group has a considerable rotational freedom in LiCl-modified MIBLi. A comparison of the structure and dynamics of the LiCl-modified MIBLi species in THF at 197 K with the characteristic features of the anionic polymerization of MMA under the same conditions suggests that the formation of one type of LiCl-complexed species has a decisive effect on the control of the living polymerization of MMA. This conclusion is in agreement with a kinetic study carried out by Müller for the same system.

Introduction

The industrial importance of a large range of poly[alkyl (meth)acrylate]-based products[1] has raised a steadily increasing interest for the precisely-controlled polymerization of (meth)acrylic ester monomers.

Although the anionic polymerization of hydrocarbon monomers such as styrene and dienes is a well-controlled process, one of the polar monomers is still a difficult challenge, because of the occurrence of side termination reactions.[2] A research team from Du Pont Co. has, however, demonstrated that the nucleophile-assisted group-transfer polymerization (GTP) reaction of silylketene acetals can be turned into an efficient living polymerization process for alkyl (meth)acrylates.[3] Although that "living" polymerization process is now available to the molecular engineering of alkyl (meth)acrylate based polymers and block copolymers, it is still quite a problem to copolymerize these compounds with comonomers missing a carbonyl conjugated group.

In an attempt to modify and hopefully improve that situation, a literature scan has been performed in order to evaluate the possible control of the anionic polymerization of (meth)acrylates. The main conclusion is that most of the positive (if not completely successful) attempts are all related to the use of ligands interacting with the growing ion pairs, which could be divided into two main classes:[4] inorganic or organometallic μ-bonded additives such as alkali and alkaline-earth metal salts, alkyl metal, and metal alkoxides, on the one hand, cation σ-bonding organic ligands, such as polyethers (including crowns) and polyamines (including cryptands), on the other hand. Very recently, a remarkable work has been carried out by Dr. Ballard,[4d] since the controlled anionic polymerization of MMA can be achieved in toluene, even at 40 °C, by using bulky aluminum phenolates as ligands.

It has been reported from this laboratory that some LiCl-modified organolithium initiators can promote the perfectly living anionic polymerization of *tert*-butyl acrylate (tBA) and methyl methacrylate (MMA): that discovery has opened new practical avenues for producing interesting (meth)acrylate-based products, i.e., pure block copolymers, end-functionalized oligomers, star-shaped (co)polymers, with high efficiency (>90%) and low polydispersity (M_w/M_n down to ca. 1.02).[5,6]

Preliminary ^{7}Li NMR analyses of αMSt$^-$Li$^+$/LiCl and oligomeric PMMA$^-$Li$^+$/LiCl systems have shown that the experimental chemical shifts, although intermediate between those of the ion pair and pure LiCl, do not match the weight-average value expected for a statistical ion exchange.[5a,7a] Moreover, these shifts are independent of temperature, in contrast to what happens in the absence of LiCl. Clearly, the addition of LiCl shifts the classical equilibrium between different ion pairs (and aggregates), notwithstanding the fact that this salt is potentially able to form a μ-type complex (mixed aggregate) with the ion pair.

We have also reported on the ^{7}Li and ^{13}C NMR investigation of methyl α-lithioisobutyrate (MIBLi) in THF, i.e., a model compound for the active chain ends of PMMA.[7b] An aggregation equilibrium between tetramer and dimer coordinative aggregates has been clearly established. In order to get a better insight on the structure and dynamics of the LiCl-modified species active in the living polymerization system, a NMR characterization of the closely related nuclei is in order.

This paper deals with the ^{7}Li and ^{13}C NMR spectroscopic study of MIBLi solutions in THF added with various amounts of LiCl. The question of the formation of μ-type mixed complexes is addressed. It is indeed essential to know how LiCl affects the structure and dynamics of the ion pairs in relation to the polymerization process itself.

Experimental Section

Methyl isobutyrate from Aldrich was purified and dried by distillation from CaH_2 (2×). It was then stored under a nitrogen atmosphere. *N*-Lithiodiisopropylamide (97%) was a commercial product from Aldrich and used as received. THF and THF-d_8

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also from Aldrich were refluxed over benzophenone sodium and distilled immediately prior to use. Hexane, toluene, and benzene-d_6 were refluxed over CaH$_2$ and distilled over styryllithium oligomers just before use.

Methyl α-lithioisobutyrate (MIBLi) was prepared under pure nitrogen from equimolar amounts of methyl isobutyrate and *N*-lithiodiisopropylamide in hexane at -78 °C as previously reported.[7b,8] The white MIBLi solid was dissolved in the appropriate volume of solvent added with the desired amount of LiCl at -78 °C and then directly filtered into NMR tubes which were degassed by freeze–thaw cycles and sealed under vacuum.

All spectra were obtained with a Bruker AM 400 superconducting magnet system operating in the FT mode at 100.6 MHz (^{13}C) and 155.5 MHz (^{7}Li), using a deuterium lock. ^{13}C chemical shifts were referred to the high-field resonance of THF-d_8, the chemical shift of which was previously measured as 25.3 ppm relative to (CH$_3$)$_4$Si. ^{7}Li NMR shifts were referred to a 0.2 M LiCl solution in THF.

All the spectroscopic measurements were carried out with freshly prepared solutions of MIBLi in THF. The concentration of MIBLi was determined after the NMR experiments by reacting MIBLi with an excess of a standard HCl solution and back-titrating HCl with a standard NaOH solution. Most of the nuclear magnetic resonance (NMR) spectra were recorded two to three times by using independently prepared samples. Mixtures of x mol equiv of LiCl and y mol equiv of MIBLi will be referred to as x/y LiCl/MIBLi. A complex comprising equimolar amounts of LiCl and MIBLi is labeled 1LiCl·1MIBLi.

Results and Discussion

^{7}Li and ^{13}C NMR Spectra at LiCl/MIBLi Ratios Smaller than 1/1. Evidence for Mixed Complex Formation between LiCl and MIBLi in THF. Formation of mixed complexes of lithium halides and various kinds of organolithium compounds, such as alkyllithium,[9a] lithium amide,[9b] lithium keto(ne)-enolate,[9c] and lithium phenolate,[9d] is well documented in the scientific literature. The stoichiometry, structure, and dynamics of these mixed complexes have been mainly investigated by NMR techniques. Nevertheless, the analysis of the possible complexation of lithium ester enolate with a lithium halide has not yet been reported. It is therefore an important step to probe any interactions between LiCl and MIBLi in THF. In this respect, ^{7}Li NMR is a very valuable tool, since it is sensitive to the "local environment" in both MIBLi and LiCl.

A previous ^{7}Li NMR spectroscopic study of MIBLi solutions in THF has shown that tetrameric and dimeric MIBLi aggregates coexist over a large concentration range (0.05–2.0 M) below ca. 205 K.[7b] Two well-separated peaks are observed at δ -0.71 ppm for the dimer and at δ -0.52 ppm for the tetramer. As expected, the addition of LiCl has a significant effect on the ^{7}Li NMR spectrum of a 0.133 M solution of MIBLi in THF. Figure 1 clearly illustrates the modifications in the ^{7}Li spectrum when the LiCl/MIBLi molar ratio is changed at 197 K.

At LiCl/MIBLi ratios smaller than 1, i.e., 0.25/1, 0.5/1, and 0.72/1, two well-resolved ^{7}Li signals are observed, which indicates a slow exchange between the underlying species at least within the NMR time scale. The assignment of these spectra is straightforward and directly supports the mixed complexation of LiCl with MIBLi.

As an example, the ^{7}Li NMR spectrum for the 0.5/1 LiCl/MIBLi ratio (Figure 1C) shows two signals which resonate at δ -0.43 ppm (peak on the left) and at δ -0.52 ppm (peak on the right). Compared to the ^{7}Li spectrum of MIBLi in THF at the same concentration (Figure 1A), the new species associated to the downfield shift at δ -0.43 ppm is an unequivocal proof of a mixed complex between LiCl and MIBLi, whereas the signal at δ -0.52 ppm is the typical resonance of the MIBLi tetramer.[7b] Similarly, the ^{7}Li spectrum for a LiCl/MIBLi ratio of either 0.25/1 or 0.72/1 exhibits two resolved resonances characteristic of a mixed complex and the MIBLi tetramer (Figure 1B,D).

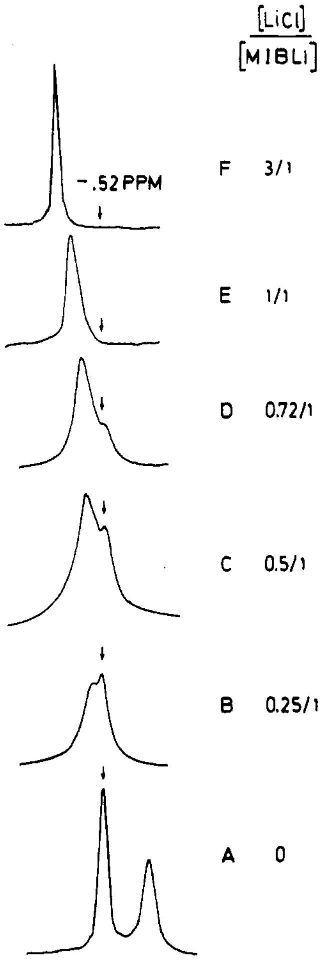


Figure 1. ^{7}Li NMR spectra of MIBLi, in THF at 197 K, at various LiCl/MIBLi molar ratios.

The ^{13}C NMR data further confirm the formation of a mixed LiCl/MIBLi complex. From Figure 2, it appears that the addition of 0.75 mol equiv of LiCl to MIBLi is responsible for a new set of ^{13}C resonances, at ca. 159.3/66.7/52.5/18.1 and 18.8 (in ppm) for C(O)/C$_\alpha$/OCH$_3$/(CH$_3$)$_2$ carbon atoms (indicated by arrows in Figure 2), at the expense of the signals characteristic of the "free" MIBLi species. Therefore, both ^{7}Li and ^{13}C NMR give credit to the formation of mixed complexes when lithium chloride (LiCl) is added to a MIBLi solution in THF.

It is worth noting that the ^{7}Li NMR spectra of the three LiCl/MIBLi ratios smaller than 1 (Figure 1B–D) have one common striking feature, i.e., the complete disappearance of the signal at δ -0.71 ppm, characteristic of the dimeric MIBLi species. This observation is surprising since a LiCl-free solution of MIBLi in THF contains at least 50% dimeric species under the same experimental conditions.[7b] This suggests a complicated complexation process at low LiCl/MIBLi molar ratios, in relation to the preferential complexation of LiCl with dimeric MIBLi compared to the less accessible tetrameric one.

Furthermore, the ^{7}Li line width at half-height is larger for the complex (Table I), supporting the idea of a definite modification in the first solvation shell of lithium ions in LiCl-complexed species.

Mixed Complex Formation at LiCl/MIBLi Molar Ratios Larger Than 1. Since the addition of small but increasing amounts of LiCl to MIBLi in THF has

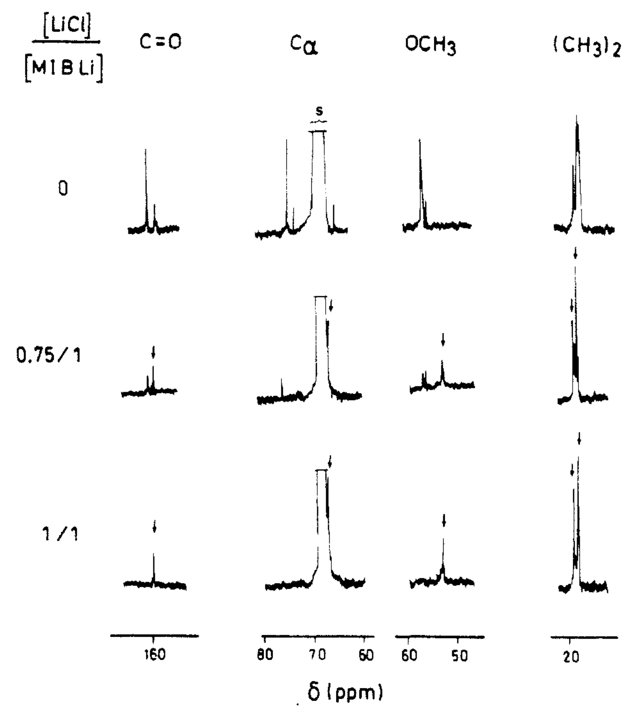


Figure 2. Partial ^{13}C NMR spectra of MIBLi in THF (0.2 M) at 193 K in the presence of various amounts of LiCl.

Table I. ^{7}Li Data Line Width[a] of LiCl-Complexes MIBLi (δ −0.36 ppm) and LiCl-"Free" MIBLi (δ −0.52 ppm), at 0.72/1 LiCl/MIBLi[b]

	MIBLi	
T, °C	complexed	free
−70	26.7	15.7
−65	20.1	18.1

[a] At half-height ($\Delta\nu_{1/2}$, Hz). [b] MIBLi in THF: 0.133 M.

supported a coordinative mixed association, it is of the utmost importance to consider the ^{7}Li NMR spectra for LiCl/MIBLi ratios ≥ 1/1, i.e., for the systems which have been reported to affect deeply the anionic polymerization of MMA in THF at 195 K.

When the molar ratio of LiCl to MIBLi is 1 or higher, the situation changes deeply since, as shown by Figure 1E, instead of two resolved peaks indicative of coexisting and slowly exchanging LiCl-complexed and LiCl-free MIBLi species (at LiCl/MIBLi < 1/1; Figure 1B–D), a singlet ^{7}Li resonance at δ −0.29 ppm shows up in the ^{7}Li NMR spectrum of the 1/1 LiCl/MIBLi system. A lack of signal typical of LiCl-free MIBLi at δ −0.52 ppm might thus suggest that only a mixed complex prevails upon the addition of 1.0 equiv of LiCl to MIBLi.

Furthermore, Figure 3 shows that there is a discontinuity in the downfield chemical shift of the ^{7}Li NMR resonance of the mixed complex versus the LiCl/MIBLi ratio at 197 K. The discontinuity at a 1/1 LiCl/MIBLi molar ratio strongly supports the formation of a well-defined mixed adduct. It must be pointed out that the ^{7}Li chemical shift for the 1/1 LiCl/MIBLi system is essentially independent of temperature from 193 to 285 K (Figure 4A), which stresses the stability of this 1/1 adduct. As mentioned in the Introduction, a similarly stable LiCl/αMSt$^-$Li$^+$ complex has been observed for the 1/1 LiCl/αMSt$^-$Li$^+$ solution in THF.[5a] In agreement with Seebach et al.,[10a] the 1/1 LiCl/MIBLi complex will be referred as the 1LiCl·1MIBLi (1) mixed dimer.

^{7}Li NMR analyses of MIBLi added with a molar excess of LiCl reveal some intriguing scenarios. At a 2/1 LiCl/MIBLi ratio, the ^{7}Li chemical shift is also found to be constant in the temperature range from 193 to 285 K (Figure 4B). In contrast, the chemical shift observed for the 3/1 system is only stable up to ca. 218 K; then it is downfield shifted upon increasing temperature (Figure 4C). The same behavior seems to prevail when 5.4 equiv of LiCl are added to MIBLi (Figure 4D). These results might indicate the formation of new complexes at the expense of the 1/1 mixed dimer. Indeed the temperature independence of the ^{7}Li chemical shift when the LiCl over MIBLi ratio is 2 could be explained either by the formation of a stable 2/1 mixed complex or by a weight-average resonance resulting from the statistical exchange of the stable 1/1 complex and free LiCl. On the basis of the fast-exchange hypothesis, the theoretical weight-average

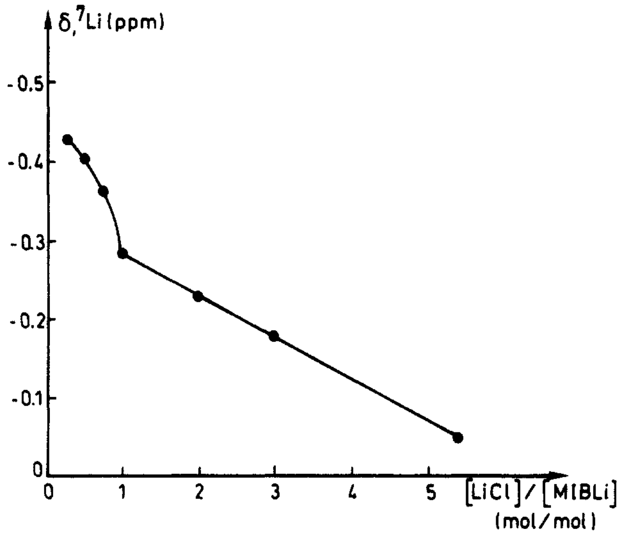


Figure 3. Dependence of the ^{7}Li chemical shift of the LiCl-added species on the LiCl/MIBLi molar ratio at 197 K.

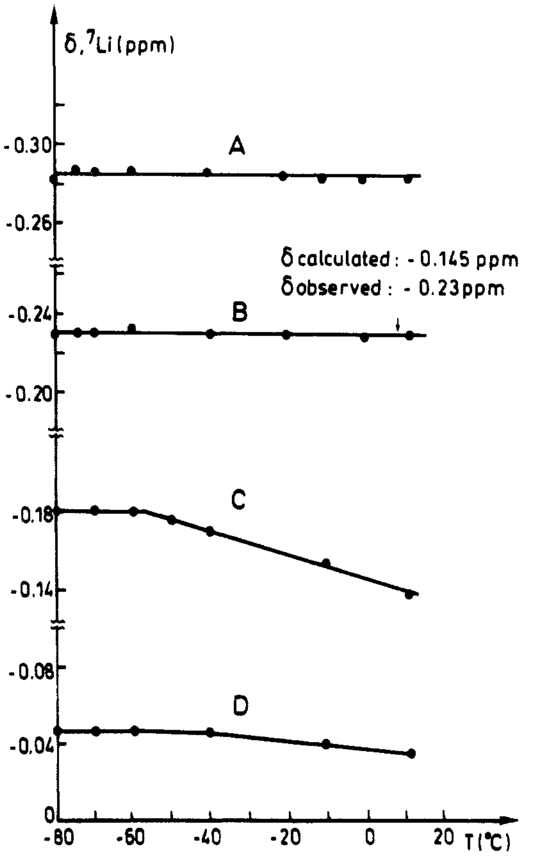


Figure 4. Temperature dependence of the ^{7}Li chemical shift associated to various LiCl/MIBLi molar ratios in THF: (A) 1/1; (B) 2/1; (C) 3/1; (D) 5.4/1.

Table II. Concentration of Mixed Trimer (2), Mixed Tetramer (3), and "Free" LiCl (0) in the 3/1 LiCl/MIBLi System, in THF at Different Temperatures[a]

T, °C	3	2	0
−80	100	0	0
−60	100	0	0
−55	100	0	0
−50	96.8	1.6	1.6
−30	88.2	5.9	5.9
−10	71.0	14.5	14.5
+12	58.0	21.0	21.0

[a] On the basis of eq 5 (see text).

^{7}Li resonance should be given by eq 1 where δ_{LiCl} and δ_1

$$\delta_{\mathrm{th}} = \delta_{\mathrm{LiCl}}X_{\mathrm{LiCl}} + \delta_1\mathbf{X}_1 \qquad (1)$$

are the ^{7}Li chemical shifts of the free LiCl and 1LiCL·1MIBLi (1), respectively, and X_{LiCl} and X_1 are the populations of the lithium ion at each site. From $X_{\mathrm{LiCl}} = X_1 = 0.5$ and $\delta_1 = -0.29$ ppm and $\delta_{\mathrm{LiCl}} = 0$ ppm (LiCl is the reference), δ_{th} amounts to −0.145 ppm, which is exceedingly higher than the observed value of δ −0.23 ppm, and thus rules out the possible coexistence of equimolar amounts of free LiCl and a stable 1/1 adduct. Then, it seems reasonable that a relatively stable mixed trimer, i.e., 2LiCl·1MIBLi (2), forms spontaneously upon the addition of 2 equiv of LiCl to MIBLi in a THF solution. This situation actually compares well with the 2/1 adduct between LiCl (2 equiv) and PMMA$^-$Li$^+$ (1 equiv) as proposed by Müller et al.[10b]

On a similar basis, the formation of a 3/1 adduct, i.e., 3LiCl·1MIBLi, might be assumed to occur upon the addition of an additional 1 equiv of LiCl to the MIBLi solution in order to account for the temperature dependence of the ^{7}Li chemical shift. Thus the constant ^{7}Li chemical shift below ca. 218 K (Figure 4C) might correspond to a 3LiCl·1MIBLi (3) adduct, and the stepwise downfield shift of the ^{7}Li resonance upon increasing temperature above 218 K would result from the progressive dissociation of the mixed tetramer (3) into the temperature-independent 2LiCl·1MIBLi trimer (2) and free LiCl (eq 2).

$$\mathrm{2LiCl{\cdot}1MIBLi + LiCl} \underset{k'_{c3}}{\overset{k_{c3}}{\rightleftharpoons}} \mathrm{3LiCl{\cdot}1MIBLi} \qquad (2)$$

Assuming a fast-exchange above 218 K for the 3/1 LiCl/MIBLi ratio, populations and ^{7}Li chemical shifts of species involved in eq 2 are expressed by eq 3. where δ_2 and δ_3 are

$$\delta_{\mathrm{ob}} = \delta_3X_3 + \delta_2X_2 + \delta_{\mathrm{LiCl}}X_{\mathrm{LiCl}} \qquad (3)$$

the ^{7}Li chemical shifts of the mixed trimer 2LiCl·1MIBLi (2) and mixed tetramer 3LiCl·1MIBLi (3), respectively, and X_2 and X_3 are the related populations, i.e., molar fractions.

$$X_2 + X_{\mathrm{LiCl}} + X_3 = 2X_2 + X_3 = 1 \quad \text{and} \quad \delta_{\mathrm{LiCl}} = 0 \qquad (4)$$

Equation 5 results easily from eqs 3 and 4.

$$\delta_{\mathrm{ob}} = \delta_3 + (\delta_2 - 2\delta_3)X_2 \qquad (5)$$

The molar fractions of each species are easily calculated from eqs 4 and 5, provided that δ_2 equals −0.23 ppm and that δ_3 is the value observed at low temperature (−0.18 ppm; Table II).

From data in Table II, the equilibrium constant ($K_3 = k_{c3}/k'_{c3}$) between the mixed trimer 2 and mixed tetramer 3 can be calculated. The plot of K_3 versus temperature provides the thermodynamic parameters for that equilibrium, i.e., $\Delta H = -11.8$ kcal mol^{-1} and $\Delta S = -46.5$ cal mol^{-1} K^{-1}, respectively (Figure 5). It is obvious that the formation of the mixed tetramer 3 from the mixed trimer 2 results from a favorable enthalpic effect.

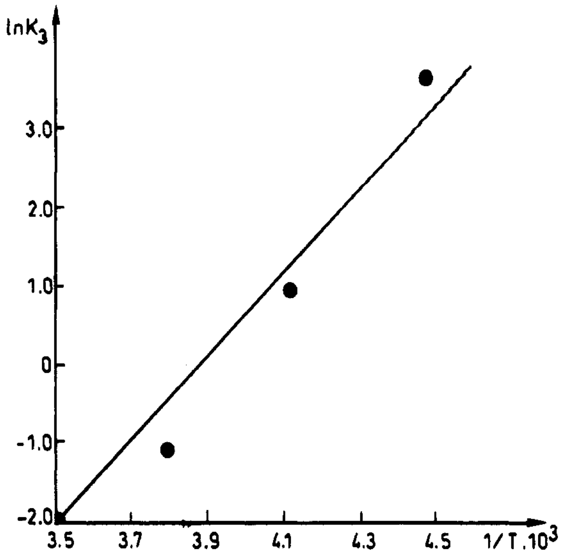
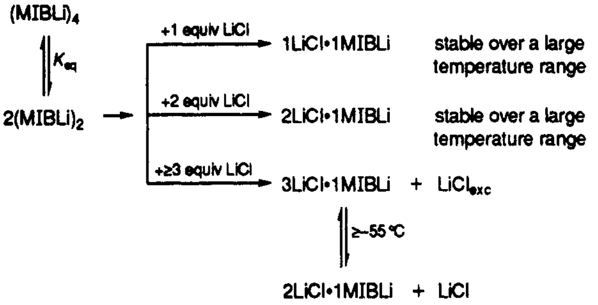


Figure 5. van't Hoff plot for the 2LiCl·1MIBLi/3LiCl·MIBLi equilibrium in THF at 197 K.

The high propensity of LiCl to form mixed complexes with MIBLi in THF is thus clear. For example, the mixed dimer 1 or the mixed trimer 2 forms spontaneously upon addition of 1 or 2 equiv of LiCl to MIBLi in a THF solution. Formation of a less stable mixed tetramer 3 might also further result from a 3/1 LiCl/MIBLi ratio (eq 6).



(6)

The mixed LiCl/MIBLi complexation appears to be a competitive process for the coordinative aggregation of MIBLi. The extent to which mixed complexes are formed would thus be the result of a complex interplay involving the electronic and steric properties of the MIBLi carbanion, the chloride ion, and the solvent. It has been demonstrated that the tendency to form mixed complexes between lithium halides and lithium keto-enolates or phenolates would increase upon decreasing interactions between lithium and oxygen of phenolates or enolates.[9b,c] The present results may thus point to a somewhat stronger interaction between the lithium cation and the chloride ion in mixed complexes than the interaction between lithium and oxygen, or lithium and carbanion in MIBLi aggregates, a situation typical of μ-type complexes. In addition, mixed complex formation is also favored by the low solvation of lithium halide by solvent.[9c] Indeed, there is evidence from colligative measurements that LiCl in THF in the concentration range 0.04–0.14 M is extensively dimerized,[11] suggesting that LiCl is poorly solvated by THF, which probably provides the main driving force for the formation of mixed complexes of higher nuclearity at high LiCl/MIBLi ratios.

Table III. Influence of LiCl on ^{13}C Chemical Shifts of Methyl α-Lithioisobutyrate (MIBLi) in THF at −80 °C[a]

L/M[b]	C(O)	C_α	OCH_3	$(CH_3)_2$
0[c]	160.5, 158.9	73.5, 71.8; 65.4	57.0, 56.0	18.0, 18.3; 18.9(?)
0.75/1	160.4, 159.3	73.9, 71.8(?); 66.7	56.5, 56.0; 52.5	18.0(?), 18.5; 18.1,18.8
1/1	159.1	66.7	52.5	18.1, 18.8
2/1	159.3	66.5	52.6	18.1, 18.7

[a] Relative to the high-field signal of THF-d_8, 25.3 ppm. [b] LiCl/MIBLi (mol/mol). [c] See ref 7b.

Comparison of Charge Distribution in LiCl-Complexed and -Free Ion Pairs. Thus far the mixed complex formation between LiCl and MIBLi in THF is firmly supported by ^{7}Li NMR spectroscopy. Although this technique has been very useful in probing the formation of various types of mixed complexes and related equilibria, it is quite difficult to get pertinent structural–electronic information. It is the reason why attention has been paid to ^{13}C NMR for at least two systems of interest, i.e., the mixed dimer 1LiCl·1MIBLi (1) and the mixed trimer 2LiCl·1MIBLi (2), for which ^{13}C chemical shifts are reported in Table III.

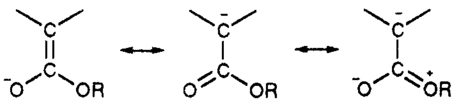
According to Figure 2 and Table III, the addition of 1 or 2 mol equiv of LiCl into MIBLi in THF causes the substitution of three sets of ^{13}C resonances indicative of coexisting tetrameric and dimeric MIBLi[7b] by one set of new resonances characteristic of the corresponding mixed aggregate. This effect is very well consistent with the aforementioned ^{7}Li NMR results. However, there is a small difference in chemical shift at all carbons (0.1–0.3 ppm) between mixed dimer 1 and mixed trimer 2, which might be an indication that complexation of one additional LiCl to mixed dimer 1LiCl·1MIBLi has only a slight influence on the charge distribution around the carbanion.

Furthermore, the ^{13}C NMR spectrum of mixed dimer 1 or mixed trimer 2 supports that the two methyl groups are nonequivalent, since two roughly equal resonances at 18.1 and 18.7 ppm are still observed (Figure 2 and Table III). This suggests that a pronounced double-bond character about the C_α–C(O) bond also occurs in the LiCl-added species[7b] and that complexation of LiCl does not change the predominant enolate character of MIBLi in THF.

In comparison with LiCl-free MIBLi, complexation with 1 or 2 mol equiv of LiCl, however, modifies the charge distribution over the carbanion. It can indeed be seen from Table III that there is a considerable shielding of C_α with respect to tetrameric MIBLi since the chemical shift for LiCl-complexed species is ca. 66.5 ppm instead of 73.5 ppm for LiCl-free MIBLi. Although smaller, there is also a downfield chemical shift at the α-carbon, ca. 1.0 ppm, and at the carbonyl carbon, 0.3 ppm, while going from the dimeric MIBLi to the LiCl-complexed MIBLi (Table III). This might reflect the facts that the mixed complexes are less aggregated than the LiCl-free tetrameric MIBLi and that the interaction between LiCl and Li$^+$ in LiCl-complexed species more likely reduce polarization of the carbanion by the lithium cation.

The addition of LiCl to MIBLi is also responsible for some significant changes at the OCH_3 carbon. Figure 2 shows a singlet resonance for the OCH_3 carbon of 1LiCl·1MIBLi in THF even at 193 K. This resonance is actually slightly shifted to lower field with respect to the corresponding parent ester (ca. 1.2 ppm; Table III).

In striking contrast to the above-mentioned results, previous data have shown that MIBLi exhibits two resonances for the OCH_3 carbon,[7b] which are observed ca. 5.4 ppm downfield compared to the parent ester, i.e., methyl isobutyrate (56.7 ppm against 51.3 ppm). These results can be accounted for by the predominant participation of the canonical resonance structure **7c**, in which the C–OR bond of the ester has a partial double-bond character, responsible for a restricted rotation around the C(O)–OR bond and thus for two sets of nonequivalent resonances at the OCH_3 atom.[7b]



7a **7b** **7c**

Clearly enough, this study strongly suggests that the contribution of the canonical resonance structure **7c** is negligible in LiCl-complexed MIBLi species, where the OR group enjoys a considerable freedom of rotation.

On the Role of LiCl in a Perfectly Living Polymerization of MMA in THF at a Low Temperature. Although there exist some differences between the model MIBLi compound and the actual living polymerization of MMA, it is worthwhile to look for a correlation between the structural characteristics of the LiCl-complexed MIBLi and the main features of the MMA polymerization processes. Let us first recall several published results.

McGrath et al. have demonstrated that the side reactions usually observed in the anionic polymerization of MMA can be limited, when a sterically hindered initiator, e.g., (diphenylhexyl)lithium, is used in a polar solvent (THF) at a low temperature, such as 195 K. MMA polymerization is then a "living" process.[12a]

It has been reported from this laboratory that the LiCl-modified ion pairs have the most beneficial influence on the polydispersity (M_w/M_n).[5,6] PMMA of an extremely narrow molecular weight distribution (ca. 1.02) can be obtained in THF at −78 °C, when the DPHLi is added with more than 3 equiv of LiCl.

On the other hand, Müller et al. have found that the addition of LiCl modifies to some extent the propagation rate of alkyl (meth)acrylate polymerization in contrast to the termination rate.[10b,c]

All these experimental data reasonably point to the fact that LiCl has a significant effect on the initiation and propagation step rather than on the termination step.

Recently, Müller et al. have focused on the kinetics of the related polymerization systems and proposed that association/complexation equilibria dominate in the anionic polymerization of MMA.[10b,c] An equilibrium between dimeric and monomeric living PMMA$^-$Li$^+$ chains in THF would occur. However, complexation of the active centers by LiCl competes with the association of living PMMA$^-$Li$^+$ and strongly affects kinetics and polydispersity of the living PMMA chains. This work also gives credit to the key effect of the association/complexation equilibria in the anionic polymerization of MMA, in THF, at a low temperature. As previously shown,[7b] there is an aggregation equlibrium between tetramer and dimer in MIBLi solutions in THF, in the absence of LiCl. There is a slow exchange between the two species. This *dynamics* behavior is quite comparable to the proposal by Müller et al. of an equilibrium between dimeric and monomeric PMMA$^-$Li$^+$ in THF at a low temperature.[10b,c] The fast addition of MMA to living PMMA$^-$Li$^+$ must then lead to a rather large polydispersity.[12b] In contrast, the mixed complexation by LiCl does shift this aggregation equilibrium toward the formation of a unique mixed aggregate species (eq 6), which thus gives to a living polymer of a very low polydispersity, i.e., close to 1.

In summary, it can be concluded that a multinuclei NMR investigation of MIBLi chosen as a model for living PMMA$^-$Li$^+$ is a very useful tool for the mechanistic study of the anionic polymerization of (meth)acrylates. It particularly provides extensive valuable insights into the structure and fate of the species active in the polymerization which allows us to account for the polymerization kinetics and the polymer characteristics.

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