NMR and Quantum-Chemical Study on the Structure of Ester Enolate−Aluminum Alkyl Complexes as Models of the Active Center in the Anionic Polymerization of Methacrylates in Toluene

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ABSTRACT: ^{6}Li and ^{13}C NMR on ethyl α-lithioisobutyrate (EiBLi) and quantum-chemical (DFT) calculations on methyl α-lithioisobutyrate (MiBLi) were used to elucidate the structure of the active center in the anionic polymerization of methacrylates in the presence of triethylaluminum ($AlEt_3$) in toluene. This study reveals ester enolate/aluminum alkyl complexes with different degrees of association, $(MiBLi\cdot AlEt_3)_n$ ($n = 1, 2, 4$), and different stoichiometries, $MiBLi\cdot xAlEt_3$ ($x = 1, 2$). In the presence of methyl pivalate (MPiv), which is taken as a model compound for the monomer and polymer, complexes such as $(MiBLi\cdot MPiv\cdot AlEt_3)_n$ ($n = 1, 2$) are formed. These complexes can dissociate into $MiBLi\cdot 2AlEt_3$ and $MPiv\cdot AlEt_3$ when $AlEt_3$ is used in excess.

Introduction

The anionic polymerization of acrylic monomers in nonpolar solvents at or near ambient temperatures is of general interest, provided that it has controlled character. A few such reactions have been reported at this time,[1−5] one of which is the polymerization initiated by organolithium compounds in the presence of aluminum alkyls in toluene.[4] This system enabled a living anionic polymerization of, e.g., methyl methacrylate (MMA) up to 0 °C using readily available and inexpensive reagents. However, according to kinetic studies of Müller et al.,[6,7] its control was somewhat deficient: a gel was precipitating from the reaction solution soon after the monomer was added, the polymerization did not follow conventional first-order kinetics, and the polymers displayed fairly broad molecular-weight distributions.

This precipitate was found to consist of living chains that were capable to reinitiate MMA polymerization in tetrahydrofuran (THF). The solid-state ^{13}C NMR spectrum of an unquenched gel sample showed, besides all expected signals for PMMA−Li at $\delta = 19$, 45, 53, and 178 ppm, a further ester carbonyl signal at 184 ppm suggesting that some in-chain ester groups are coordinated to the gegenion of the living chain end. Evidently, any intermolecular coordination of this kind will end up in a coordinative network of living polymer chains which then might cause all of the mentioned deficiencies.[7,8]

Esters such as methyl pivalate or diisooctyl phthalate were thus used as cosolvents in order to prevent the coordination of in-chain ester groups to the living chain end. In fact, gelation did not occur when MMA was polymerized in, e.g., 2:1 toluene/methyl pivalate (v/v), and then the first-order time−conversion plots were linear and the molecular-weight distributions of the polymers were unimodal and narrow. The so-achieved gain in control (indirectly) demonstrates the validity of the above-described mechanism of the anionic polymerization in the presence of aluminum alkyls.[8,9]

What, then, is the structure of the living polymer end group? Alkyl α-lithioisobutyrates have been extensively used as model compounds to examine the structure of living polymethacrylate chain ends.[10−15] ^{13}C NMR investigations showed that alkyl α-lithioisobutyrates are ester enolates rather than carbanions which predominantly form dimeric and tetrameric aggregates in polar solvents.[15,16] In nonpolar solvents,^{13}C NMR investigations[17] in conjunction with vapor pressure osmometric measurements[10] indicate that tetramers and hexamers are the predominant species. These results are supported by quantum-chemical calculations,[18,19] which show the hexameric structure as the most stable one. In addition, there is a difference in the degree of aggregation between the model compound (MiBLi)[10] and the polymer chain (PMMA−Li),[20] in THF. The degree of aggregation is lower for the polymer chain ends, mainly due to steric effects and because it is stabilized by intramolecular coordination ("penultimate coordination") to in-chain ester carbonyl groups. This coordination was found by IR[12] and ^{13}C NMR[21] investigations of di-*tert*-butyl α-lithioglutarate, a model compound for a dimeric methacrylic polymer chain, also in the presence of aluminum alkyls.[8]

According to our earlier ^{13}C NMR studies on ethyl α-lithioisobutyrate (EiBLi) in toluene,[17] the signal of the carbonyl carbon shifts from 159 to 150 ppm upfield and that of the α-carbon from 77 to 91 ppm downfield upon the addition of, e.g., triethylaluminum in equimolar amounts. These shifts were attributed to an $EiBLi\cdot AlR_3$ "ate" complex which has a significantly lower reactivity than EiBLi−this is in agreement with the observed respective polymerization rates.[6,8] However, these NMR measurements could not provide the structure of this complex or its degree of association. Kinetic studies suggest that the active polymer chain ends may coexist

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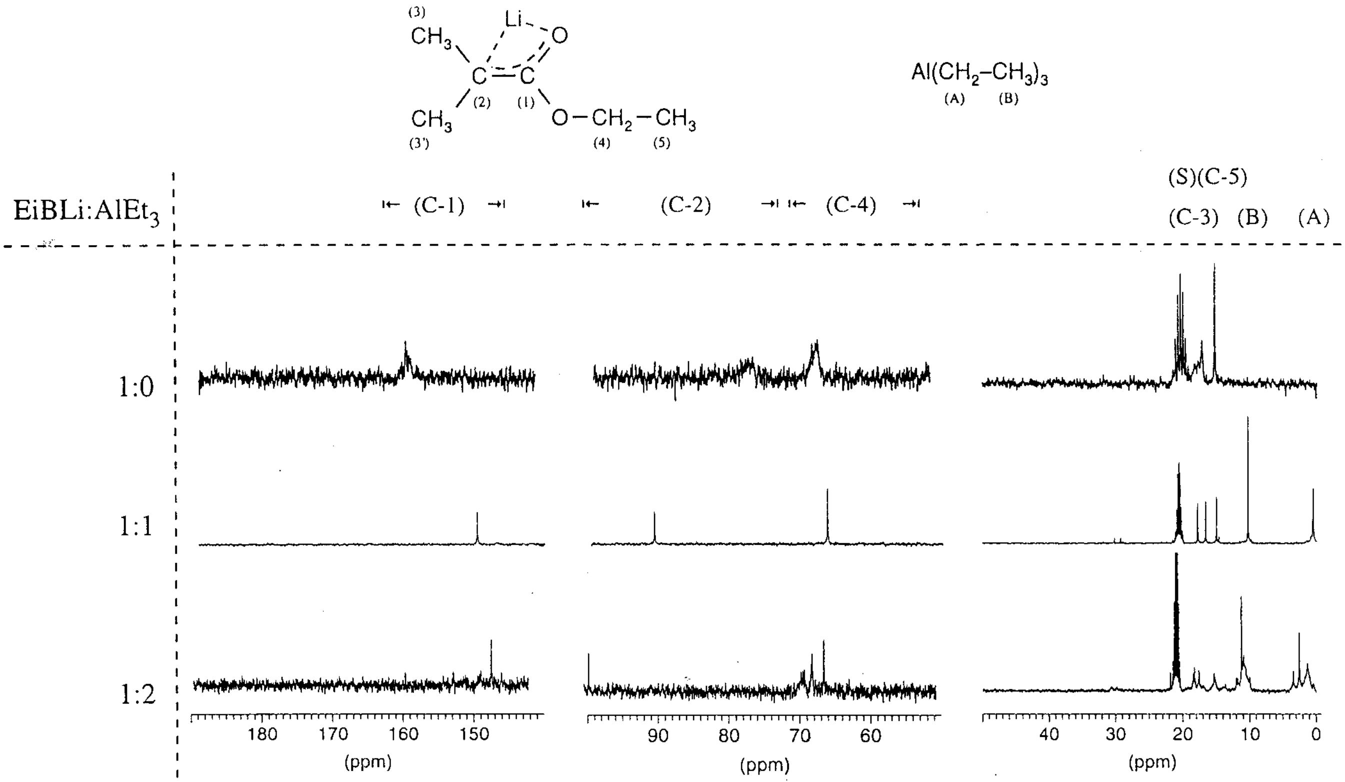


Figure 1. ^{13}C NMR spectra of ethyl-α-lithioisobutyrate and its complexes with triethylaluminum at $T = -20$ °C in toluene-d_8. S = solvent.

as tight ion pairs and as dimeric associates, the first being the major monomer-adding species.[8,9]

In the present work we wish to present the results of ^{6}Li and ^{13}C NMR studies combined with those of quantum-chemical (DFT) calculations, which should give more precise information on the structure of active chain ends in the polymerization of MMA in the presence of $AlEt_3$ in toluene and the effect of in-chain ester groups, as modeled by methyl pivalate. Although the natural occurrence of ^{6}Li is much lower than that of ^{7}Li, we prefer the former nucleus because the signals are sharper within the same ppm range. Because of the small chemical shifts (δ < 2 ppm), assignments are difficult. However, the number of peaks indicates the minimum number of different coexisting species.

Experimental Part

NMR Experiments. Toluene-d_8 (99% d, Aldrich) was stirred over sodium/potassium alloy, degassed, and distilled in a high vacuum. Pure ethyl α-lithioisobutyrate (EiBLi) was prepared according to the method of Lochmann and Lím,[22] and di-*tert*-butyl α-lithioglutarate (DtBGLi) was kindly supplied by Dr. L. Lochmann, Prague, as a white crystalline powder. Methyl pivalate (MPiv, Aldrich) was stirred over CaH_2, degassed and distilled in high vacuum. Triethylaluminum ($AlEt_3$) was purchased as 25 wt % solution in toluene (Aldrich); the nondeuterated solvent was stripped off in high vacuum and replaced by toluene-d_8. All samples were prepared under inert conditions at −78 °C, and every series of measurements was started at low temperature. The concentration of EiBLi was ca. 30 mg/mL. ^{13}C and ^{6}Li NMR spectra were recorded with a Bruker AM-400 instrument. The ^{13}C NMR chemical shifts were determined with respect to the CD_3 multiplet of the solvent at $\delta = 20.4$ ppm. For the ^{6}Li NMR measurements, a saturated LiCl solution in THF-d_8 was used as external standard.

Density Functional Theory (DFT) Calculations. All density functional theory (DFT) geometry optimizations were performed using the parallel Karlsruhe TURBOMOLE[23] quantum chemistry package on a 12-processor SGI Power Challenge system and a 20 processor Pentium Pro Cluster. A B-P86[24−26] gradient corrected functional in the RI-formalism[27−29] was used throughout for the geometry optimizations. The energetics for the different stages of the insertion reaction was checked by single-point calculations with a B3[30,31]-LYP functional. The employed numerical integration scheme using an "m3" grid was described in ref 32. For the fitting of the Coulomb potential within the RI formalism, Ahlrichs' auxiliary basis sets[28,33] were used. The geometry optimizations were carried out using a *split valence* (SV) (7s3p)/[3s2p] basis augmented with a d-polarization function (exponent 0.8) for carbon and oxygen (d-exponent 1.2),), a *split valence* (SV) (7s)/[3s] basis augmented with a p-polarization function (exponent 0.17) for lithium, a *double-ζ* (6s)/[2s] basis set for hydrogen and a *split valence* (SV) (10s7p)/[4s3p] basis set for aluminum with one additional d-function (exponent 0.3). This basis (which is comparable to a 6-31G*) is referred to as SV(P).[34]

For the single-point energy calculations with the B3-LYP functional, a larger basis set named TZV(P)][35] was used for C, O, H, Li, and Al. This basis set is of *triple-ζ* quality for the valence shells. The polarization functions are as described above, the contraction patterns are (5s)/[3s] for hydrogen (again, the (P) denotes polarization functions everywhere except on H), (11s)/[5s] for lithium, (11s6p)/[5s3p] for carbon and oxygen, and (15s9p)/[6s4p] for aluminum.

As in standard nomenclature, B3-LYP/TZV(P)//B-P86/SV-(P) denotes a single-point energy calculation with a B3-LYP functional employing the TZV(P) basis at a geometry optimized with a B-P86 functional obtained with a SV(P) basis. All reported energies refer to this method.

Currently, calculation of DFT−NMR shifts is not supported in TURBOMOLE. NMR shifts have been calculated using deMon (Version 1)[36] with the Malkin's SOS approach[37]at the B-P86/SV(P) optimized geometries. IGLO_II-basis sets[38] have been employed throughout. A Perdew-Wang 91[39] functional has been used.

Absolute energies of structures (in hartrees) are summarized in Table 4. Cartesian coordinates, Mulliken charges, and calculated NMR shifts are given as Supporting Information.

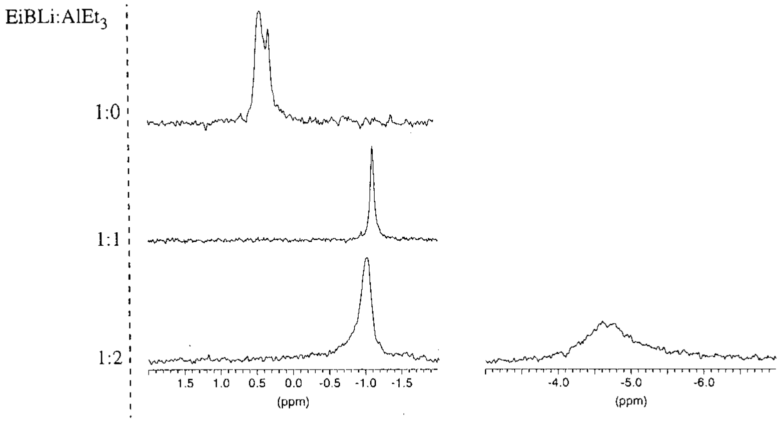


Figure 2. ^{6}Li NMR spectra of ethyl-α-lithioisobutyrate and its complexes with triethylaluminum at $T = -20$ °C in toluene-d_8.

Table 1. ^{13}C and ^{6}Li NMR Signals of Ethyl α-lithioisobutyrate in the Presence of Triethylaluminum in Toluene-d_8 (δ/ppm) and, in Addition, Quantum-Chemical (DFT) Calculated ^{13}C NMR Signals of 1:1, 2:2, and 1:2 Complexes

substance	T/°C	C-1	C-2	C-3	C-4	C-5	A (Al−CH$_2$−)	B (Al−CH$_3$)	^{6}Li
EiBLi	−20	158.4	76.4	17.2	66.7	15.3	...	...	0.31
		158.7	77.0	17.6	66.8				0.43
		158.9	77.4	17.8	67.1				
		159.2		18.1	67.6				
				18.2					
				18.4					
				18.6					
(MiBLi)$_4$	calcd	158.8	77.7	18.0	55.7	...	...	...	...
		159.0	78.5	18.1	56.0				
		159.1	78.6	18.2	56.4				
				18.4					
				18.5					
AlEt$_3$	−20	...	...	...	...	...	0.0	8.6	...
EiBLi + AlEt$_3$	−20	149.7	91.4	16.4	67.9	14.8	**0.2**	**10.0**	−1.11
				17.6		14.4	0.5		
EiBLi·AlMe$_3$[a]	calcd	155.8	88.1	19.0	70.2	18.3	...	...	...
(EiBLi·AlMe$_3$)$_2$[a]	calcd	157.6	83.1	21.2	75.0	19.0	...	...	...
(MiBLi·AlEt$_3$)$_2$	calcd	157.4	83.8	19.3	59.6	...	...	...	...
EiBLi + 2AlEt$_3$	−20	145.3	100.6	17.0	58.9	14.6	−0.6	9.1	−1.01
				17.8	65.6		**0.2**	**9.3**	−4.61
					66.0		**0.8**	10.2	−4.77
					67.9		1.6	**10.5**	
EiBLi·2AlMe$_3$[a]	calcd	150.9	93.1	19.2	74.3	16.6	...	...	...

[a] Reference 8.

Energies of structures in the text reflect the differences of the energies of formation of products and educts ($\Delta E = H_{\mathrm{f,products}} - \Delta H_{\mathrm{f,educts}}$). In all energy comparisons entropies are not taken into account, although their influence on the free energies certainly cannot be excluded.

Results and Discussion

Ethyl α-Lithioisobutyrate. The model of the living polymer chain end of PMMA, ethyl α-lithioisobutyrate (EiBLi), was used to investigate the structure of the active center of the polymerization of MMA in toluene by ^{6}Li and ^{13}C NMR spectroscopy. The ^{13}C NMR signal of the carbonyl carbon is found at 159 ppm and that of the α-carbon at 77 ppm (see Figure 1, top).[17] The multiple signals at 0.3 ppm observed in the ^{6}Li NMR spectra confirm the earlier ^{13}C NMR measurements,[6] which already indicated the coexistence of various aggregates (see Figure 2, top). Quantum-chemical calculations of MiBLi[18,19] in fact demonstrate that tetramers and hexamers are the most stable structures in a vacuum. It is supposed that this is also true in nonpolar solvents[10,13,18] like toluene. To minimize the computational effects, all calculations were performed on the methyl ester. It was shown earlier[18] that the nature of the ester group has negligible effects only on the stability of aggregates and NMR shifts of the carbonyl carbon and α-carbon. Although hexamers of MiBLi are slightly more stable than tetramers ($\Delta E = -16$ kJ/mol per MiBLi unit),[19] they could not be considered in the following calculations due to the large number of atoms.

Mixtures of Ethyl α-Lithioisobutyrate and Triethylaluminum. Upon addition of AlEt$_3$ to EiBLi in equimolar amounts, the ^{13}C NMR signal of the carbonyl carbon shifts upfield from 159 to 150 ppm and the α-carbon shifts downfield from 77 to 91 ppm. All other signals of EiBLi are not significantly affected, and those of the aluminum alkyl are slightly shifted downfield (Figure 1 and Table 1).[17] In addition, the ^{6}Li NMR signal of the sample arises at −1.1 ppm, i.e., at a much higher field (Figure 2 and Table 1), indicating a somewhat higher electron density at the lithium ion of the ester enolate. The latter two findings suggest that there might be a weak coordination between the methylene groups next to the aluminum and the lithium ion. In contrast to the broad signals in the ^{13}C and ^{6}Li NMR spectra of pure EiBLi, the peaks are narrow when AlEt$_3$ is present. This indicates that either just one active species is formed or that the rate of exchange of the association equilibrium is relatively fast.

Quantum-chemical calculations reveal that, in the unimeric MiBLi·AlEt$_3$ adduct, the aluminum alkyl is coordinated to the carbonyl oxygen forming an "ate" complex (see Figure 3a). In the dimeric (Figure 3b) and tetrameric (Figure 3c) aggregates, (MiBLi·AlEt$_3$)$_2$ and (MiBLi·AlEt$_3$)$_4$, instead, AlEt$_3$ is coordinated to the

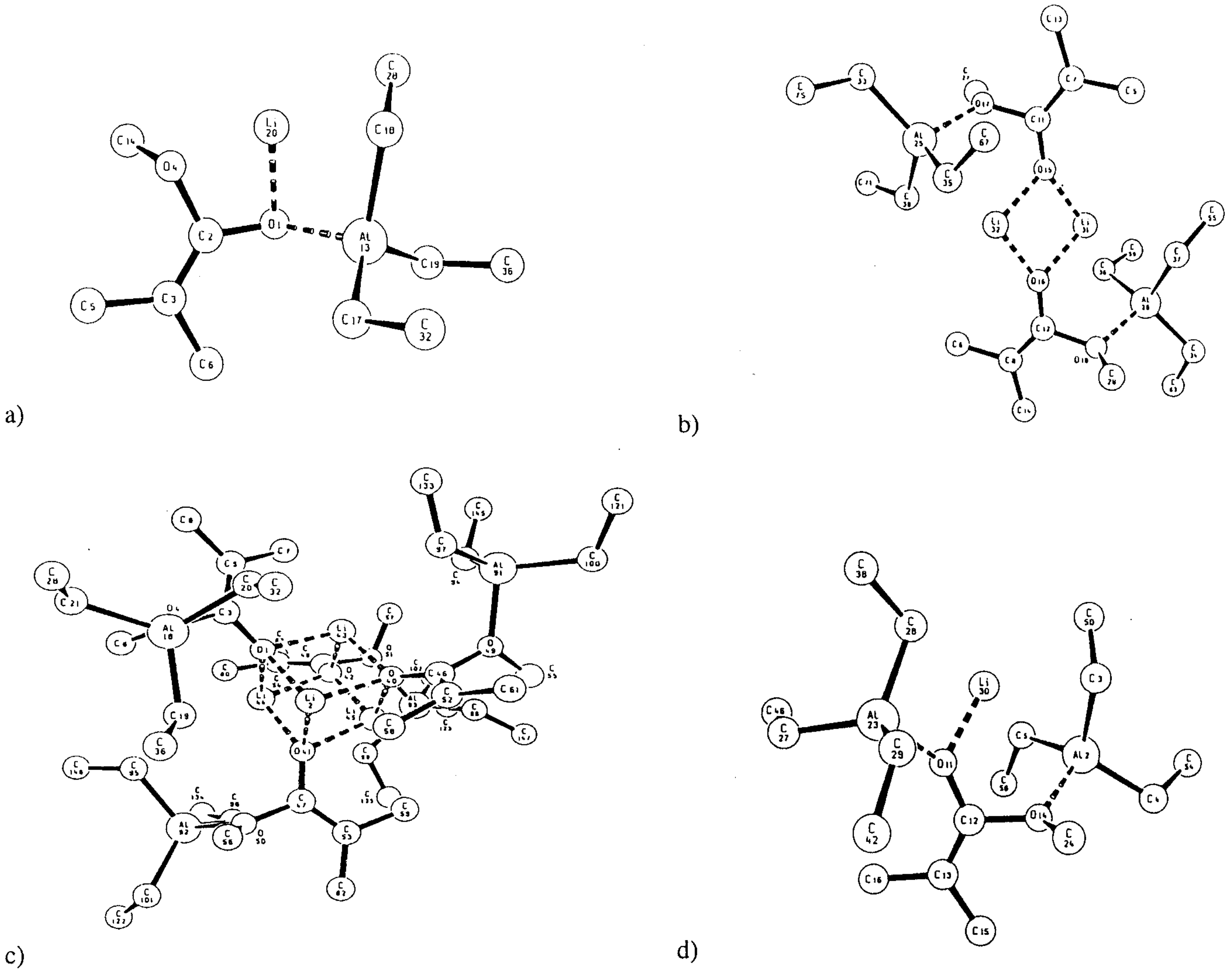


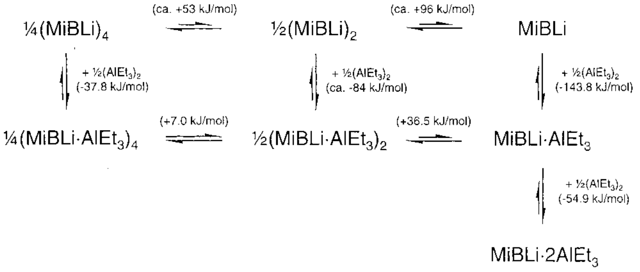
Figure 3. Calculated structures of the complexes MiBLi·AlEt$_3$ (a), (MiBLi·AlEt$_3$)$_2$ (b), (MiBLi·AlEt$_3$)$_4$ (c), and MiBLi·2AlEt$_3$ (d).

Table 2. Energy and Differences of the ^{13}C NMR Shifts Relative to the Pure Tetrameric Ester Enolate and a Comparison of Experimental and Calculated Data for Ester Enolate/Aluminum Alkyl Complexes

EiBLi/AlEt$_3$/ MiBLi/AlEt$_3$	ΔE/(kJ/mol)	$\Delta\delta_{(C(O))}$/ppm		$\Delta\delta_{(C(\alpha))}$/ppm	
		exptl	calcd	exptl	calcd
1:0 (tetramer)	0	0	0	0	0
1:1 (unimer)	8.7		−3.1		9.8
1:1 (dimer)	−27.8	−9.0	−1.5	14.6	5.5
1:1 (tetramer)	−37.8		*a*		*a*
1:2 (unimer)	−46.2	−13.4	−8.0	22.8	14.8

[a] Not calculated.

Scheme 1. Interactions of Ester Enolate with Aluminum Alkyl



alcohol oxygen, and the lithium and carbonyl oxygen atoms form rhombic (dimer) and cubic (tetramer) centers, respectively. The energies of the dimeric and tetrameric structures of ester enolate/aluminum alkyl complexes are comparable, supporting the coexistence of different aggregates within a fast equilibrium. The aggregated structures are considerably more stable than the unimeric ate complex (Scheme 1) due to the higher coordination of the lithium ion.

Increasing the molar ratio aluminum alkyl/ester enolate (Al/Li = 2) leads to a further 5 ppm upfield shift of the carbonyl carbon to 145 ppm, while the α-carbon shifts 9 ppm downfield to 100 ppm. Besides the ^{6}Li NMR signal at −1.1 ppm, a second, extremely broad signal arises at −4.7 ppm (see Figure 1 and Table 1). Quantum-chemical calculations provide an unimeric structure (EiBLi·2AlEt$_3$) with each oxygen coordinated to AlEt$_3$ (see Figure 3d). This species is even more stable than the aggregated ester enolate/aluminum alkyl complexes (see Table 2). The energetics of the various interactions of AlEt$_3$ with MiBLi are summarized in Scheme 1. Although the absolute values of the experimentally obtained NMR shifts deviate significantly from the calculated ones, the relative shifts show good agreement (see Table 2).

The high tendency of the ester enolate/aluminum alkyl complexes to associate is obviously caused by an electron deficiency in the coordination sphere of the lithium ion. Apparently, the electron-donating capability of toluene is quite insufficient, and the lithium ion

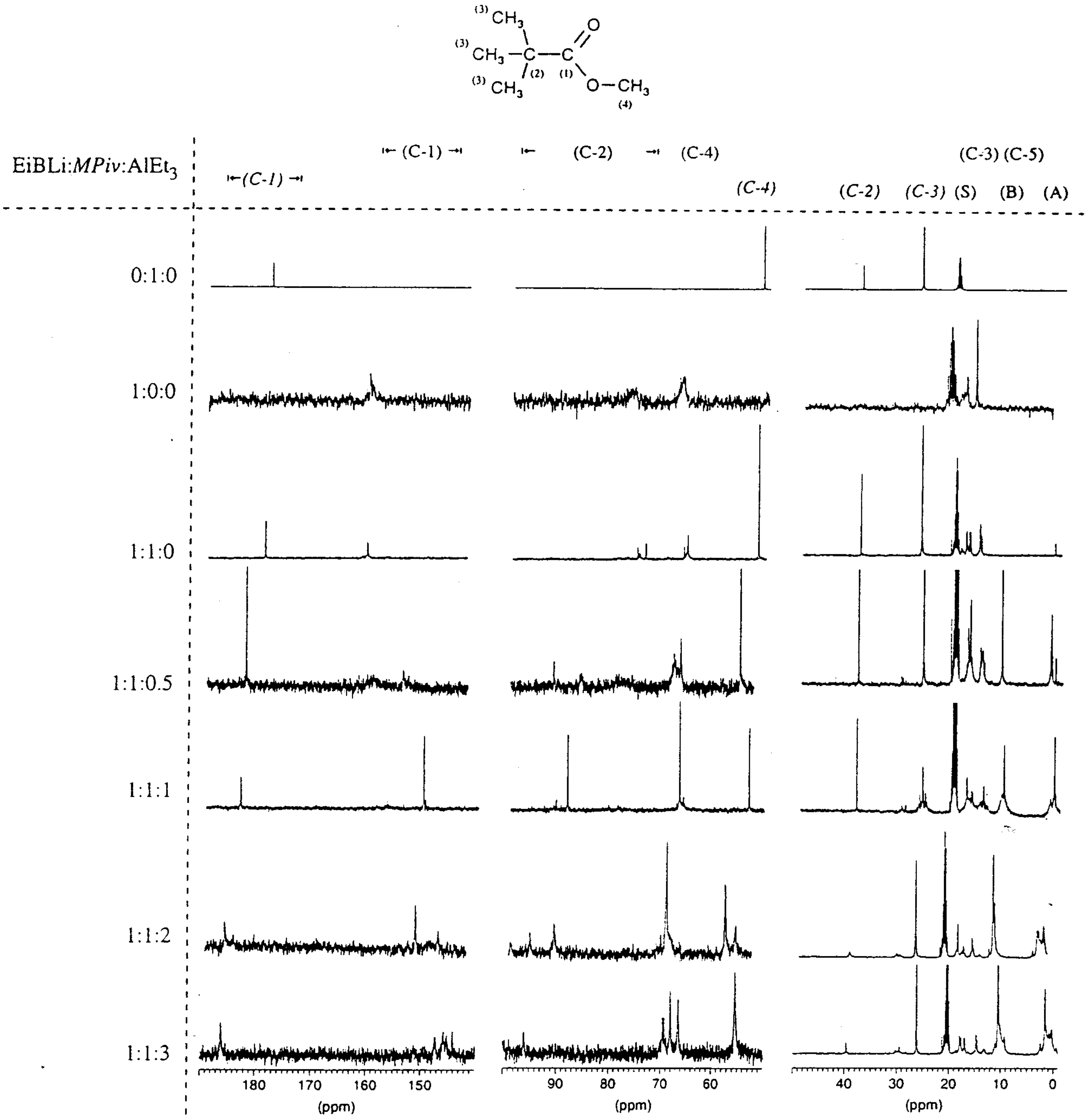


Figure 4. ^{13}C NMR spectra of mixtures of ethyl α-lithioisobutyrate and methyl pivalate with different concentrations of aluminum alkyl at $T = -20$ °C (MPiv at 25 °C) in toluene-d_8.

therefore coordinates to the ester carbonyl groups of the monomer or polymer instead. This leads to the above-mentioned formation of a coordinative network of living polymer chains.[7] To gain a deeper insight into the corresponding reactions and equilibria, methyl pivalate (MPiv) was introduced as a model for the monomer and the polymer chain.

Mixtures of Ethyl α-Lithioisobutyrate, Triethylaluminum, and Methyl Pivalate. Müller et al.[17] showed that aluminum alkyls form adducts with the ester groups of both MMA and MPiv. The formation of the complex of AlEt$_3$ with monomer leads to a downfield shift of the methylene, carbonyl, and methoxy groups, whereas the α-carbon shifts upfield. Addition of AlEt$_3$ to MPiv only leads to a downfield shift of the carbonyl and methoxy groups, while the *tert*-butyl group is not affected. Quantum-chemical calculations show that the formation of the complexes of AlEt$_3$ with methyl methacrylate ($\Delta E = -52$ kJ/mol) or methyl pivalate ($\Delta E = -40$ kJ/mol) is highly exothermic, even more than that of the formation of (EiBLi·AlEt$_3$)$_4$ ($\Delta E = -38$ kJ/mol). Thus, an excess of aluminum alkyl in the real polymerization solution (Al/Li > 1) will not result in the formation of an active center complexed by 2 equiv of aluminum alkyl but will result in the coordination of excess aluminum alkyl with monomer or polymer. Moreover, since the carbonyl groups of the enolate, the monomer, and the polymer chain compete for the coordination to the aluminum alkyl, it might be argued that the enolate is not coordinated at all in real polymerization systems. However, this is very unlikely, because of the strong effect of AlEt$_3$ on the polymerization kinetics and the tacticities of the polymers obtained. So, what kind of complexes are formed finally?

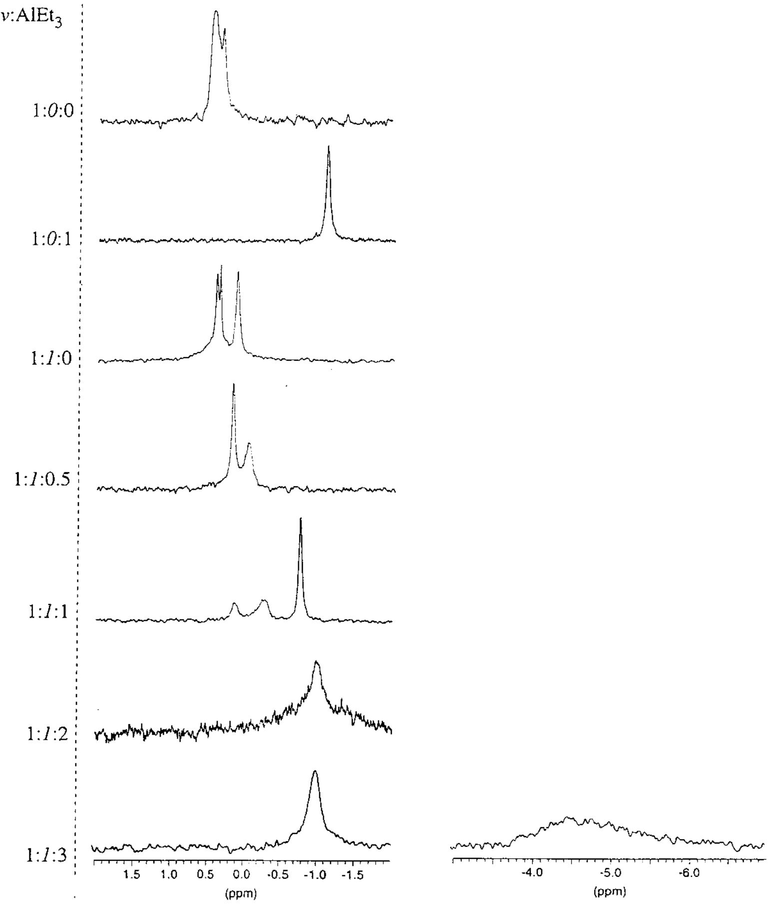


Figure 5. ^{6}Li NMR spectra of mixtures of ethyl α-lithioisobutyrate and methyl pivalate with different concentrations of aluminum alkyl at $T = -20$ °C in toluene-d_8.

First we examined a mixture of EiBLi and MPiv and obtained much sharper ^{13}C NMR signals than in the spectrum of the pure ester enolate; the chemical shifts move only very slightly (Figure 4). The ^{6}Li NMR spectrum shows one signal shifted upfield at 0.1 ppm and the other one splitted at 0.4 ppm (Figure 5). These results can be explained by a weak coordination of the carbonyl oxygen of methyl pivalate with the lithium ion of the ester enolate. Because of the small changes in chemical shifts in ^{13}C NMR, the occurrence of separated signals in ^{6}Li NMR, and the sharpness of the signals, we propose the existence of only one ester enolate/methyl pivalate complex whose structure might be similar to the one of the pure ester enolate. These complexes are supposed to play an important role in the polymerization of (meth)acrylates in toluene in the absence of AlR_3, which is known to be uncontrolled.[40]

In a competition experiment, we tried to find out whether MPiv or EiBLi coordinate stronger to the aluminum alkyl. Adding a small amount of aluminum alkyl to an equimolar mixture of EiBLi and MPiv (Al/ester = 0.25) causes two additional ester enolate peaks in the ^{13}C NMR spectrum (Figure 4, Table 3), one shifted upfield of the carbonyl carbon (δ = 151 ppm) and another one shifted downfield of the α-carbon (δ = 91 ppm). The ^{6}Li NMR spectrum (Figure 5) shows slightly upfield shifted signals. These results indicate the coexistence of EiBLi and its aluminum alkyl complex, EiBLi·$AlEt_3$, in a slow equilibrium. Additionally, a downfield shift of the carbonyl carbon of methyl pivalate was found, corresponding to the formation of an MPiv·$AlEt_3$ adduct. However, we also have to take into account the formation of a complex containing all compounds, EiBLi·MPiv·$AlEt_3$.

If the three compounds are mixed in equimolar amounts (Al/ester = 0.5), new sharp signals are found in the ^{13}C NMR spectrum at 150 and 89 ppm for EiBLi, similar to those of the EiBLi·$AlEt_3$ complex. The ^{6}Li NMR spectrum also shows a new signal, but it is different from that of the EiBLi·$AlEt_3$ complex. The ^{13}C NMR signal of the methyl pivalate carbonyl carbon is further shifted downfield. Again, these results indicate an equilibrium of different aluminum alkyl adducts or a complex of all compounds.

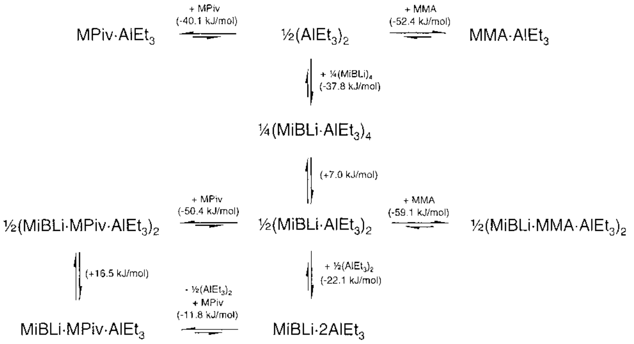
At a molar ratio Al/ester = 1, ^{13}C NMR chemical shifts are observed in the ester enolate region which correspond to the EiBLi·$AlEt_3$ complex. Additional signals of the carbonyl and the α-carbon arise at 145 ppm and 96/99 ppm, respectively, which can be assigned to EiBLi·2$AlEt_3$. The peak in the ^{6}Li NMR spectrum is fairly broad, indicating different species in coalescence. Further, two signals of the carbonyl carbon of MPiv are observed, indicating the coexistence of a MPiv·$AlEt_3$ complex and a complex of all three compounds (see Scheme 2). All these observations force the assumption of a new species containing EiBLi, $AlEt_3$, and MPiv in equimolar amounts. The residual $AlEt_3$ seems to partially break up this complex to form the complexes EiBLi·2$AlEt_3$ and MPiv·$AlEt_3$.

When the aluminum alkyl is present in excess (Al/ester = 1.5), at least four signals of the carbonyl, the α-carbon, and the oxomethylene carbon of the ester enolate are observed which are due to species with different degrees of association and different stoichi-

Table 3. ^{13}C and ^{6}Li NMR Signals of Mixtures of Ethyl α-Lithioisobutyrate and Methyl Pivalate with Respect to the Triethylaluminum Concentration in Toluene-d_8 at $T = -20$ °C (MPiv at 25 °C) (δ/ppm)

EiBLi:*MPiv*:AlEt$_3$	C-1	C-2	C-3	C-4	C-5	*A* (Al−CH$_2$−)	*B* (Al−CH$_3$)	^{6}Li
0:*1*:0	*177.5*	*38.7*	*27.3*	*51.2*	...	...	...	...
1:*0*:0	158.4	76.4	17.2	66.7	15.3	...	...	0.31
	158.7	77.0	17.6	66.8				0.43
	158.9	77.4	17.8	67.1				
	159.2		18.1	67.6				
			18.2					
			18.4					
			18.6					
1:*1*:0	159.3	74.0	19.3	65.8	15.4	...	...	0.12
	159.4	75.3	18.4	65.9	15.7			0.35
		75.6	17.8	66.4	15.8			0.40
			17.7					
	178.9	*38.7*	*27.0*	*51.7*				
1:*1*:0.5	151.3	75.3	17.3	65.2	14.9	1.4	**11.4**	−0.03
	151.4	77.9	17.6	65.8	15.2	**2.2**		0.18
	152.4	78.5	17.3	66.3	15.4	2.3		
	158.2	85.7	17.9	66.6	15.6			
	158.6	86.1	18.0	67.1				
	159.3	91.3	18.3					
	182.4	*39.0*	*26.6*	*52.8*				
1:*1*:1	149.8	88.9	16.9	66.1	14.4	**1.2**	**10.7**	−0.77
		91.1	17.0	66.9	14.8	2.0	11.1	−0.25
			17.3		15.0			0.14
			17.6		15.3			
			18.0		15.5			
	183.6	*39.1*	*26.4*	*53.2*				
1:*1*:2	145.4	91.0	16.2	65.1	14.5	0.4	10.2	−0.99
	149.7	95.9	16.5	67.8	14.7	1.1	**10.5**	
		99.9	16.9	69.1		1.4	11.3	
			17.0			**1.7**		
			17.7			2.6		
			18.0					
	184.4		17.9	53.3				
	186.1	*39.6*	*26.6*	*55.5*				
1:*1*:3	144.1	95.3	16.9	66.4	14.5	0.4	9.3	−1.05
	145.1	100.2	17.7	68.1	14.7	0.9	**10.5**	−4.47
	145.7	101.2	17.9	69.3		**1.6**	11.1	
	147.2			69.6		2.5		
	186.1	*39.6*	*26.2*	*55.4*				

Scheme 2. Interactions of Aluminum Alkyl with Esters and Ester Enolates



ometries. Furthermore, the ^{6}Li NMR spectrum shows a second, upfield-shifted signal, as it was observed in the respective spectra without MPiv. The ^{13}C NMR chemical shifts of the carbonyl carbon of methyl pivalate overlap with those of the MPiv•AlEt$_3$ complex. Therefore, we assume a further dissociation of the complex EiBLi·MPiv·AlEt$_3$ (see Scheme 2).

Our conclusions are confirmed by the correlation of the sum of the differences of the chemical shifts with respect to the pure ester with the molar ratio aluminum alkyl/ester (Figure 6). Up to equimolar amounts of the compounds (Al/ester = 0.5), the aluminum alkyl is bound somewhat more strongly to both esters than to the pure compounds. A similar effect is observed in the shifts of the α-carbon and the carbonyl carbon. This synergetic effect is due to the new species. Increasing the molar ratio leads to a stronger complexation of AlEt$_3$ and EiBLi. The sum of chemical shifts of MPiv in the mixture slowly approaches that of the pure esters. Both increase and final values are in agreement with the dissociation of the complex.

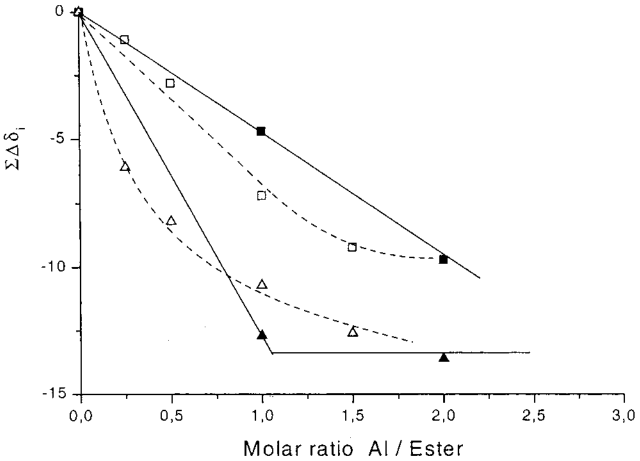


Figure 6. Effect of molar ratio AlEt$_3$/(EiBLi, MPiv) on the chemical shifts of EiBLi (■, □) and MPiv (▲, △) in toluene at $T = -20$ °C: (■) EiBLi + AlEt$_3$; (▲) MPiv + AlEt$_3$; (□, △) EiBLi + MPiv + AlEt$_3$ ($\Sigma\Delta\delta_i$: sum of the differences of the chemical shifts with respect to the pure ester).

Quantum-chemical calculations in fact provide unimeric and dimeric complexes (EiBLi·MPiv·AlEt$_3$)$_n$ (n

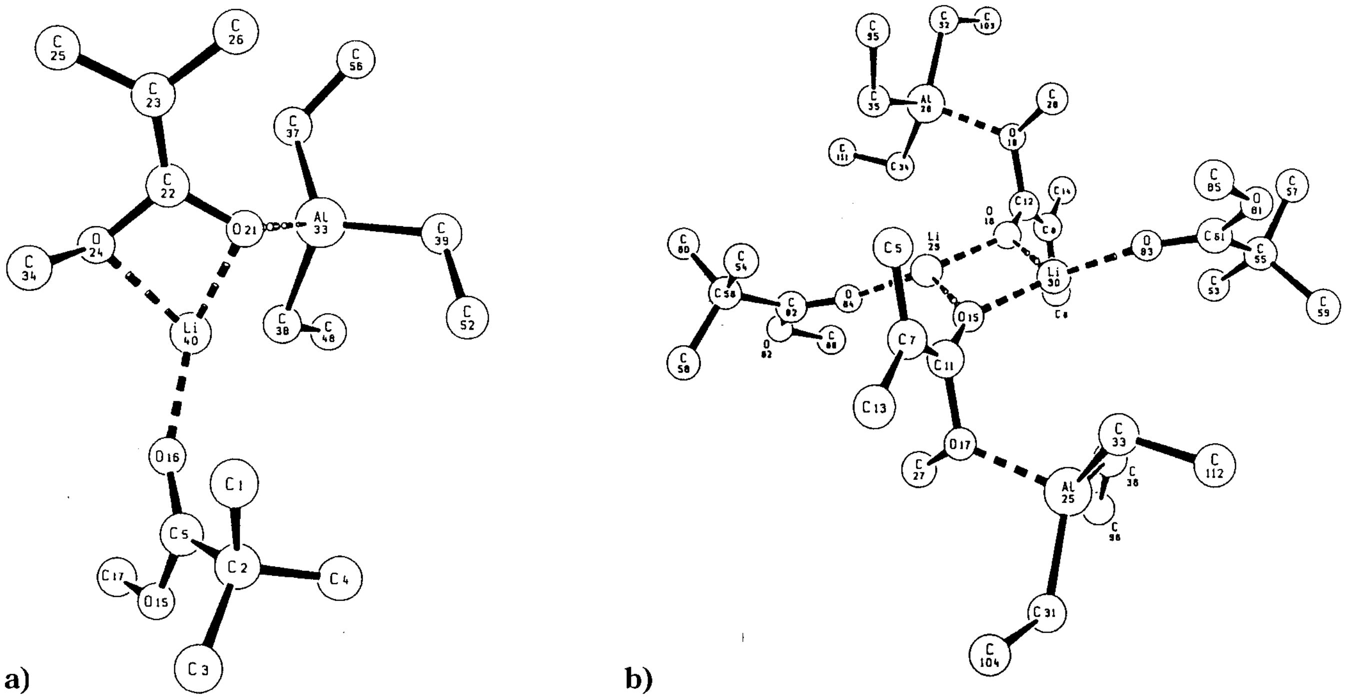


Figure 7. Calculated structure of the unimeric (a) and dimeric (b) complexes $(\mathrm{MiBLi\cdot AlEt_3\cdot MPiv})_n$ ($n = 1, 2$).

Scheme 3. Possible Interactions of the Complex $(\mathrm{EiBLi\cdot MPiv\cdot AlEt_3})_2$ with Aluminum Alkyl

$$\tfrac{1}{2}\,(\mathrm{MiBLi\cdot MPiv\cdot AlEt_3})_2 \rightleftharpoons \tfrac{1}{4}\,(\mathrm{MiBLi\cdot AlEt_3})_4 + \mathrm{MPiv} \qquad (\Delta E = +40\ \mathrm{kJ/mol})$$

$$\tfrac{1}{2}\,(\mathrm{MiBLi\cdot MPiv\cdot AlEt_3})_2 \rightleftharpoons \tfrac{1}{4}\,(\mathrm{MiBLi})_4 + \mathrm{MPiv\cdot AlEt_3} \qquad (\Delta E = +38\ \mathrm{kJ/mol})$$

$$\tfrac{1}{2}\,(\mathrm{MiBLi\cdot MPiv\cdot AlEt_3})_2 + \tfrac{1}{2}\,(\mathrm{AlEt_3})_2 \rightleftharpoons \mathrm{MiBLi\cdot 2AlEt_3} + \mathrm{MPiv} \qquad (\Delta E = +28\ \mathrm{kJ/mol})$$

$$\tfrac{1}{2}\,(\mathrm{MiBLi\cdot MPiv\cdot AlEt_3})_2 + \tfrac{1}{2}\,(\mathrm{AlEt_3})_2 \rightleftharpoons \tfrac{1}{4}\,(\mathrm{MiBLi\cdot AlEt_3})_4 + \mathrm{MPiv\cdot AlEt_3} \qquad (\Delta E = \pm 0\ \mathrm{kJ/mol})$$

$$\tfrac{1}{2}\,(\mathrm{MiBLi\cdot MPiv\cdot AlEt_3})_2 + (\mathrm{AlEt_3})_2 \rightleftharpoons \mathrm{MiBLi\cdot 2AlEt_3} + \mathrm{MPiv\cdot AlEt_3} \qquad (\Delta E = -12\ \mathrm{kJ/mol})$$

Table 4. Calculated Total Energies (in hartrees)

substance, point group	Figure	*E* (hartrees)
$\mathrm{AlEt_3}$ (dimer), C_i		−959.925027
Mpiv, C_s		−386.216327
MMA, C_s		−345.697070
$\mathrm{MPiv\cdot AlEt_3}$, C_1		−866.194092
$\mathrm{MMA\cdot AlEt_3}$, C_1		−825.679526
MiBLi (unimer), C_1		−353.842708
MiBLi (tetramer), C_1		−1415.597538
$\mathrm{MiBLi\cdot AlEt_3}$ (unimer), C_1	3a	−833.859978
$\mathrm{MiBLi\cdot AlEt_3}$ (dimer), C_1	3b	−1667.744976
$\mathrm{MiBLi\cdot AlEt_3}$ (tetramer), D_2	3c	−3335.505214
$\mathrm{MiBLi\cdot 2AlEt_3}$, C_1	3d	−1313.843432
$\mathrm{MiBLi\cdot MPiv\cdot AlEt_3}$ (unimer), C_1	7a	−1220.101680
$\mathrm{MiBLi\cdot MPiv\cdot AlEt_3}$ (dimer), C_i	7b	−2440.216016
$\mathrm{MiBLi\cdot MMA\cdot AlEt_3}$ (dimer), C_i		−2359.184094

= 1, 2) as the most stable structures ($\Delta E = -62$ kJ/mol for $n = 1$, $\Delta E = -78$ kJ/mol for $n = 2$). These structures are even more stable than the tetrameric ester enolate/aluminum alkyl complex $(\mathrm{EiBLi\cdot AlEt_3})_4$ ($\Delta E = -38$ kJ/mol).

As shown in Figure 7, the carbonyl oxygen of methyl pivalate saturates the coordination sphere of lithium. Thus, the quantum-chemical calculations explain why the addition of MPiv to the living aluminum alkyl/ester enolate chain ends can break up the coordinative network. The unimeric complex $\mathrm{EiBLi\cdot MPiv\cdot AlEt_3}$ is less stable by only 16 kJ/mol. These results agree with kinetic data, where an equilibrium between unimeric and dimeric chain ends was postulated.[9] Quantum-chemical calculations also show that any excess aluminum alkyl would lead to formation of $\mathrm{MiBLi\cdot AlEt_3}$ and $\mathrm{MPiv\cdot AlEt_3}$ (Scheme 3). The energies of formation (in hartrees) of the compounds and the different structures are summarized in Table 4.

Di-*tert*-butyl α-Lithioglutarate. Di-*tert*-butyl α-lithioglutarate (DtBGLi) is a better model compound of the active polymer chain ends since it contains a penultimate ester group. ^{13}C NMR investigations on DtBGLi in toluene-d_8 show that addition of $\mathrm{AlEt_3}$ shifts the signal of the enolate carbonyl carbon of DtBGLi upfield from 158 to 154 ppm and that of the α-carbon downfield from 72 to 91 ppm (Figure 8 and Table 5), similar to that for EiBLi. Moreover, the signal of the carbonyl carbon of the penultimate ester group shifts downfield from 176 to 183 ppm, as was observed for the complex $\mathrm{MPiv\cdot AlEt_3}$.[8,9]

The latter observation can only be explained by a coordination of the penultimate carbonyl group to one of the metal atoms. It was first suggested that they coordinate to the aluminum atoms.[7] However, a ^{27}Al NMR signal at $\delta = 160$ ppm[8] shows a 4-fold coordination at the aluminum atom, and ^{13}C NMR shifts indicate that the aluminum alkyl is coordinated to the alcohol oxygen of the active center. Thus, the only explanation for the change in chemical shifts is the coordination with lithium. Consequently, any inter- and/or intramolecular coordination of the penultimate ester group should occur via the lithium ion of the active center (see Figure 9).

Therefore, the formation of a coordinative polymer network during the polymerization of methacrylates in the presence of aluminum alkyls is to be expected. Prevention of the polymer network is possible by adding excess methyl pivalate or other Lewis bases, as shown in the kinetic studies.[9]

Table 5. ^{13}C NMR Signals of Di-*tert*-butyl α-Lithioglutarate and Its Complex with Triethylaluminum in Toluene-d_8 at T = −20 °C (δ/ppm)[a]

DtBGLi:AlEt$_3$	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11/12	*A*	*B*
1:0	158.1	72.4	44.1	67.6	30.3	19.1	47.1	176.2	80.0	27.5	25.6	...	...
1:1	153.8	90.5	43.3	68.9	29.5	18.9	46.0	183.4	82.1	27.1	24.7	−0.2	10.6
											25.1	1.5	11.6

[a] Unknown signal: δ/ppm = 76.0.

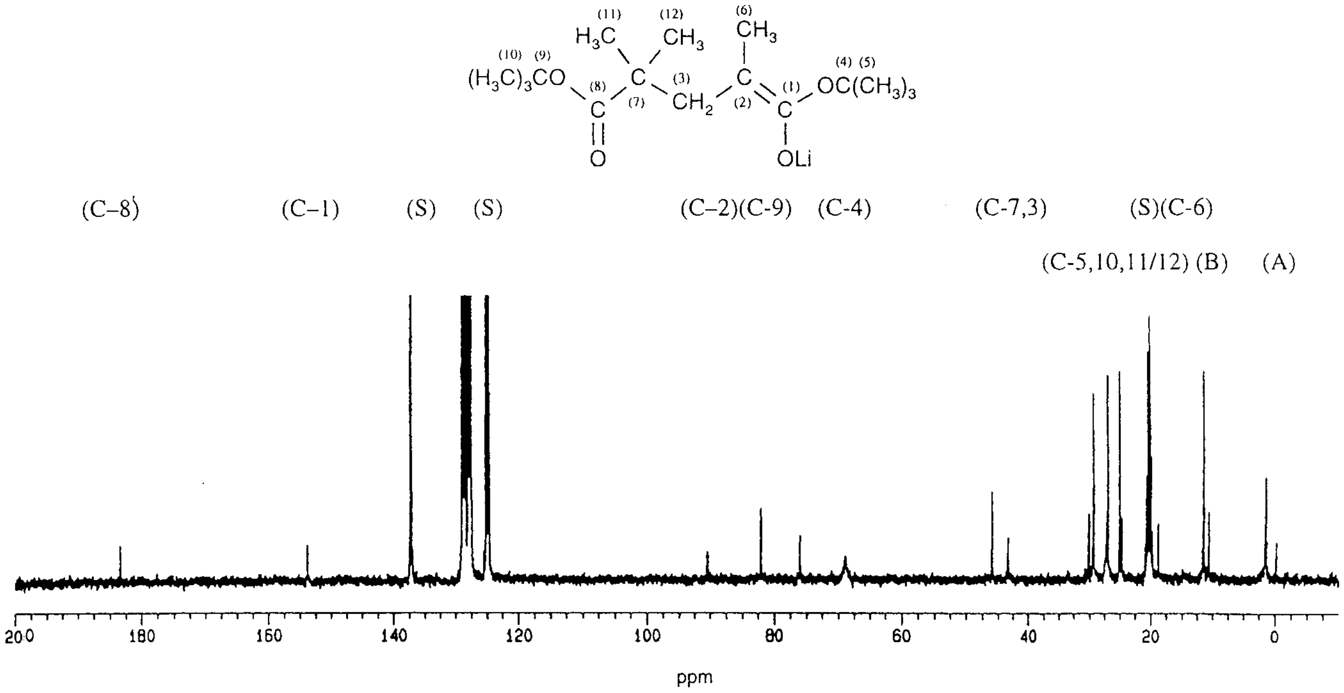


Figure 8. ^{13}C NMR spectrum of the di-*tert*-butyl α-lithioglutarate/triethylaluminum complex (Al/Li = 1) at T = −20 °C in toluene-d_8.

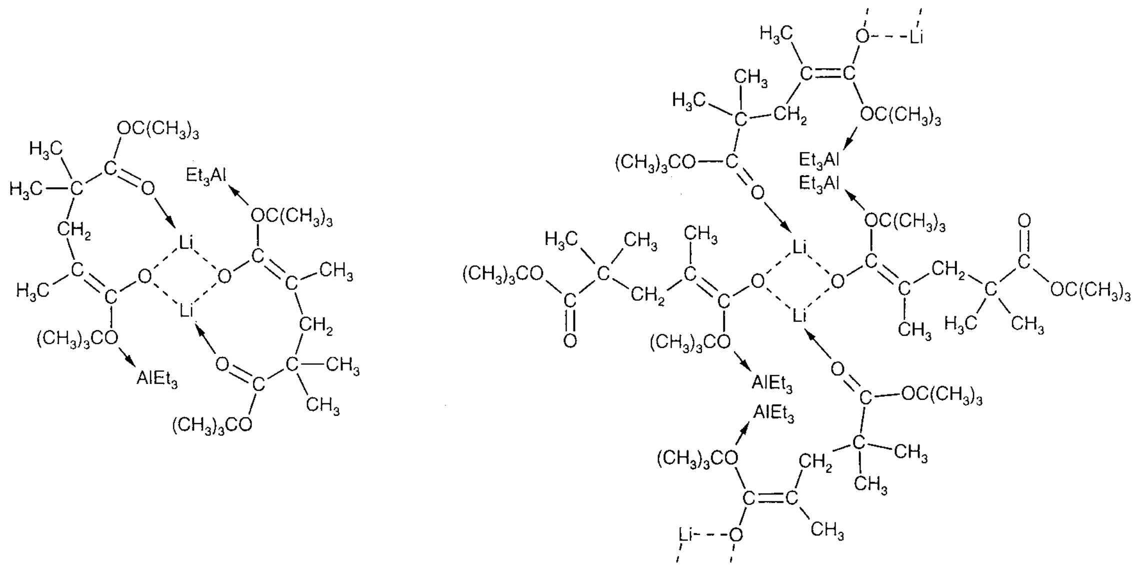


Figure 9. Intra- (a) and intermolecular (b) coordination of the penultimate ester carbonyl group to the lithium ion of the living end group of the dimeric complex (DtGBLi·AlEt$_3$)$_2$.

Conclusions

Multinuclear NMR and quantum-chemical investigations made it possible to determine the structure of active species in methacrylate polymerization in the presence of aluminum alkyls in nonpolar solvents. Reaction of EiBLi and aluminum alkyl with methyl pivalate in equimolar amounts leads to an equilibrium of unimeric and dimeric complexes (EiBLi·MPiv·AlEt$_3$)$_n$ (n = 1, 2), consistent with kinetic studies. Methyl pivalate is able to fill up the coordination sphere of lithium, leading to highly stabilized active chain ends without the tendency to associate with polymer ester groups. Thus, network formation is prevented. Although excess aluminum alkyl destroys these species, forming separate adducts of each ester (EiBLi·2AlEt$_3$ and MPiv·AlEt$_3$), this reaction is not important in real polymerization systems, where the concentration of the ester groups is much higher than that of the aluminum alkyl.

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Supporting Information Available: Cartesian coordinates (in atomic units) of the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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