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Anionic Polymerization of (Meth)acrylates in the Presence of Tetraalkylammonium Halide−Trialkyl Aluminum Complexes in Toluene. 2.[†] NMR and Quantum-Chemical Study on the Structure of Ester Enolate Complexes as Models of the Active Center

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ABSTRACT: ^{6}Li and ^{13}C NMR investigations on ethyl α-lithioisobutyrate (EiBLi) and quantum-chemical (DFT) calculations on methyl α-lithioisobutyrate (MiBLi) were performed to study the structure of active centers in anionic polymerization of methacrylates in toluene in the presence of tetramethylammonium chloride/triethylaluminum complexes $NMe_4[Al_nEt_{3n}Cl]$ ($n = 1, 2$). The results support the existence of several complex species ($([EiBLi\cdot Al_nEt_{3n}Cl]NMe_4)_m$) varying in composition ($n = 1, 2$) and degree of association ($m = 1, 2$). In the presence of methyl pivalate (MPiv), a model compound for monomer/polymer ester groups, a nonassociated complex $NMe_4[EiBLi\cdot MPiv\cdot AlEt_3Cl]$ is preferably formed.

Introduction

The anionic polymerization of acrylic monomers in the presence of tetraalkylammonium halide−trialkyl aluminum (THTA) complexes in toluene proceeds in a living and controlled manner at temperatures as high as 0 °C for methacrylates and at low temperatures for acrylates.[1] Quantitative monomer conversions are usually reached within a few minutes, and the polymers obtained have narrow molecular weight distributions. The reaction follows first-order kinetics with respect to the initial concentration of initiator, monomer, and THTA complex. Nevertheless, at low concentrations of the THTA complex the first-order time−conversion plots are curved, and the polymers obtained at low conversions show a bimodal molecular weight distribution. Therefore, we consider that there must be at least two active species with different reactivities, the equilibrium between which being established rather slow during polymerization.[2]

Up to now, very little is known about the structure of active species in this polymerization system. We earlier reported on ^{6}Li and ^{13}C NMR studies together with quantum-chemical calculations on ester enolate model substances in the presence of aluminum alkyls.[3] We found that ethyl α-lithioisobutyrate (EiBLi) and triethyl aluminum ($AlEt_3$) form various complexes having different stoichiometries and degrees of association: $(EiBLi\cdot nAlEt_3)_m$ ($n = 1, 2$; $m = 1, 2, 4$). The driving force toward association was attributed to an electron deficiency at the lithium atom which, in real polymerization systems, will be effectively compensated by the coordination to ester carbonyl groups of either monomer or polymer. As a matter of fact, this coordination process can promote the incorporation of the living polymer chains into a coordinative network and their precipitation from reaction solution. For NMR studies, "real" polymerization conditions were imitated by employing a model compound not only of the living chain end, EiBLi, but also of the monomer/polymer, namely methyl pivalate (MPiv). These investigations supported the existence of ternary complexes $(EiBLi\cdot MPiv\cdot AlEt_3)_m$ ($m = 1, 2$).

In the present paper we are reporting ^{6}Li and ^{13}C NMR studies and the results of quantum-chemical (DFT) calculations on the structure of living chain ends during the polymerization of methyl methacrylate (MMA) in the presence of the THTA complexes $NMe_4[Al_nEt_{3n}Cl]$ ($n = 1, 2$) in toluene. The effect of ester groups on the structure of living chain ends is also described.

Experimental Part

The preparation and purification of reagents and NMR measurements as well as the methods and tools employed for DFT calculations have previously been described in ref 3; except for the following.

NMR Experiments. Tetramethylammonium chloride (NMe_4Cl, Aldrich) was freeze-dried from benzene.

DFT Calculations. The geometry optimizations were carried out using a *split valence* (7s3p)/[3s2p] basis augmented with a d-polarization function (exponent 1.0) for nitrogen. For the single-point energy calculations with a B3-LYP functional, a TZV(P) basis set was used for C, O, H, Li, N, Cl, and Al; the contraction patterns are (5s)/[3s] for H, (11s)/[5s] for Li, (11s6p)/[5s3p] for C, O, and N, and (14s9p)/[5s4p] for Cl and Al.

Results and Discussion

Mixtures of EiBLi and $NMe_4[AlEt_3Cl]$. Upon addition of the THTA complex $NMe_4[AlEt_3Cl]$ to EiBLi in equimolar amounts, at least four main ^{13}C NMR signals of carbonyl carbons (C-1) are observed (Figure 1c): a group of three signals at $\delta = 158−159$ ppm very similar

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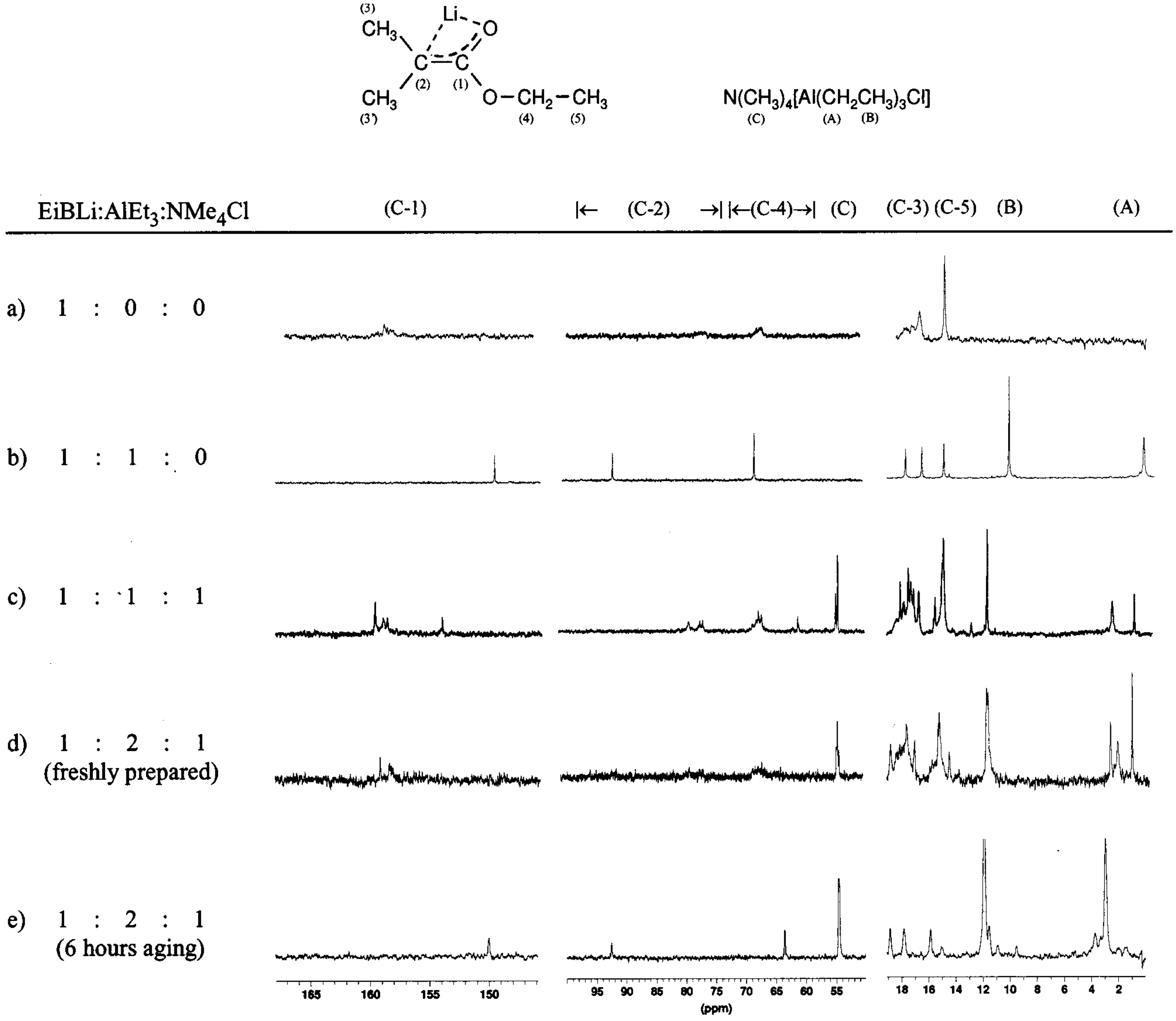

Figure 1. ^{13}C NMR spectra of EiBLi and its complexes with THTA complexes at −20 °C in toluene-d_8.

to that arising from pure EiBLi (Figure 1a) and one at 153.5 ppm which can be assigned to a newly formed species. For the α-carbon atom (C-2) a multiple signal at 77 ppm is found like the one observed for EiBLi; the same goes for all other signals of ester enolate carbons. The signals of $AlEt_3$ are slightly shifted downfield due to the complex formation with NMe_4Cl (see Table 1). The ^{6}Li NMR signal of the complex sample arises at 0.2−0.5 ppm, very similar to that of EiBLi (Figure 2a,c). The multiplicity and the width of all ^{13}C and ^{6}Li NMR signals indicate the existence of at least two species in equilibrium, but a definite assignment of signals could not be achieved.

Quantum-chemical calculations provide a structure for the newly formed species in the presence of $NMe_4[AlEt_3Cl]$ shown in Figure 3. However, the lithium ion is coordinated to both the enolate oxygen and the aluminate complex $[AlEt_3Cl]^-$, while the tetramethylammonium ion stays in the vicinity of the α-carbon atom (C-2). Thus, it is not a simple exchange of counterions yielding $EiB^-NMe_4^+$ that will take place upon adding the THTA complex to EiBLi but the formation of a far more complex species, $[EiBLi{\cdot}AlEt_3Cl]NMe_4$. The calculated ^{13}C NMR shifts, however, deviate significantly from the experimentally observed ones (Table 2); the relative shifts on the other hand agree quite well (Table 3). The formation of the unimeric complex $[EiBLi{\cdot}AlEt_3Cl]NMe_4$ from $(EiBLi)_4$ is calculated to be an endothermic process ($\Delta E = +12.6$ kJ/mol) while that of the corresponding dimeric associate, $([EiBLi{\cdot}AlEt_3Cl]NMe_4)_2$, is exothermic ($\Delta E = -34.2$ kJ/mol) (see Table 3). We suppose that the high tendency toward association ($\Delta E_{\mathrm{unimer/dimer}} = -47$ kJ/mol) is caused by the low electron density at the lithium ion. The different heats of formation could explain the existence of the different species observed by NMR.

Mixtures of EiBLi and $NMe_4[Al_2Et_6Cl]$. In the ^{13}C NMR spectrum of a freshly prepared mixture of EiBLi and $NMe_4[Al_2Et_6Cl]$ (Figure 1d and Table 1), only the shifts for C-1 and C-2 of the parent ester enolate can be seen at 158−159 and 77−79 ppm, respectively. In ^{6}Li NMR, we find a broad signal originating from EiBLi (0.4−0.5 ppm) and an additional signal at higher field (−0.3 ppm, Figure 2d). After 6 h of sample aging, the ^{13}C NMR spectrum shows a single and rather narrow peak for C-1 at 150.0 ppm and one for C-2 at 92.6 ppm (Figure 1e). In the ^{6}Li NMR spectrum, however, two distinct peaks at −0.31 and −0.36 ppm can be observed (Figure 2e). The NMR spectra of this sample are different from from those of $EiBLi{\cdot}AlEt_3$ and $[EiBLi{\cdot}AlEt_3Cl]NMe_4$ (see Figures 1 and 2), which means that we are now dealing with another new species. The NMR

Table 1. ^{13}C and ^{6}Li NMR Signals (δ/ppm) of Ethyl α-lithioisobutyrate (EiBLi) in the Presence of THTA Complexes ($NMe_4Cl/AlEt_3$) in Toluene-d_8 at −20 °C

		^{13}C								
EiBLi:$AlEt_3$:Me_4NCl	Figure	C-1	C-2	C-3	C-4	C-5	Al−CH_2	Al-•-CH_3	N−CH_3	^{6}Li
1:0:0	1a	158.4	76.4	17.2	66.7	15.3				0.31
	2a	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	1b	149.7	91.4	16.4	67.9	14.8	0.2	10.0		−1.11
	2b			17.6		14.4	(0.5)			
1:1:1	1c	153.5	76.4	17.1	60.8	15.3	1.5	11.6	54.3	0.28
	2c	158.6	76.9	17.9	63.6	15.9	3.6		54.7	0.33
		159.0	78.7	18.4	66.7					0.43
		159.3	79.5	18.9	67.2					
					68.5					
1:2:1[a]	1d	158.4	76.4	17.0	66.7	14.6	1.3	11.8	54.0	−0.31
	2d	158.7	76.9	17.7	67.3	15.3	2.4	11.9	54.3	0.46
		159.2	78.7	18.2	67.8	15.8	2.9		54.5	
				18.4	68.2					
				18.7						
1:2:1[b]	1e	150.0	92.6	17.9	63.6	15.1	1.4	10.9	54.6	−0.36
	2e			18.8		15.9	2.1	11.5		−0.31
							2.9	11.9		
							3.7			
$AlEt_3$							0.5	8.8		
$NMe_4[AlEt_3Cl]$							3.7	11.4	55.1	
									55.4	
$NMe_4[Al_2Et_6Cl]$							3.1	10.8	55.0	
									55.1	

[a] Freshly prepared. [b] After 6 h aging.

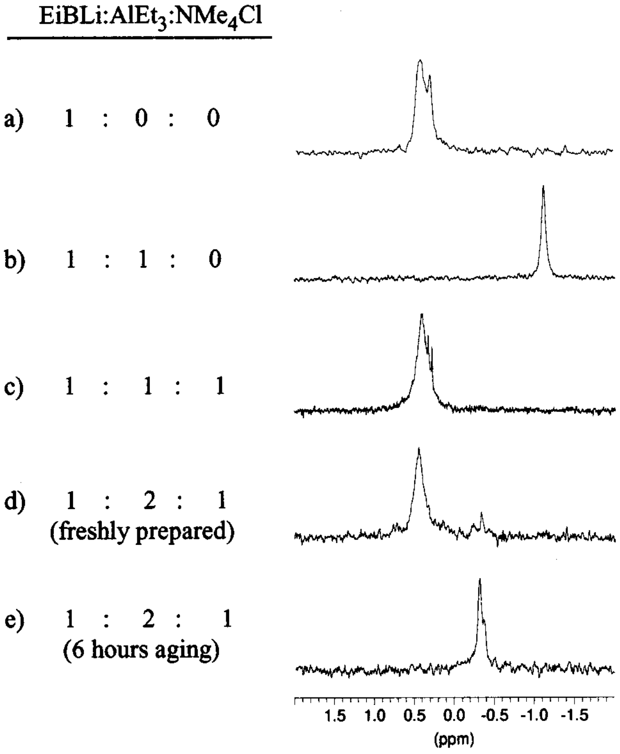

Figure 2. ^{6}Li NMR spectra of EiBLi and its complexes with THTA complexes at −20 °C in toluene-d_8.

Table 2. Calculated ^{13}C NMR Signals (δ/ppm) of Methyl α-Lithioisobutyrate (MiBLi) in the Presence of $AlEt_3$ and of $NMe_4[AlEt_3Cl]$

	C-1	C-2	C-3	C-4 (−OCH_3)	Al−CH_2	Al-•-CH_3	N−CH_3
$(MiBLi)_4$	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				
$(MiBLi\cdot AlEt_3)_2$	156.7	82.6	18.7	59.2	−0.6	11.8	
	157.9	83.0	19.6	60.1	0.5	12.4	
			20.0		4.9	12.5	
					5.6	12.6	
					7.0	13.1	
					9.0	14.2	
$[MiBLi\cdot AlEt_3Cl]$-NMe_4	155.4	79.2	19.0	54.9	2.5	12.0	56.5
			19.7		2.6	12.1	56.9
					5.1	12.5	57.0
							57.4

Table 3. Calculated Heats of Formation (ΔE) and Relative ^{13}C NMR Shifts ($\Delta\delta$) of Ester Enolates Complexes with $AlEt_3$ and $NMe_4[Al_nEt_{3n}Cl]$ (n = 1, 2) with Respect to $(MiBLi)_4$

		$\Delta\delta_{C-1}$/ppm		$\Delta\delta_{C-2}$/ppm	
	ΔE/(kJ/mol)	calcd	exptl	calcd	exptl
$(MiBLi)_4$					
$(MiBLi\cdot AlEt_3)_2$	−27.8	−1.5	−9.0	5.5	14.6
$MiBLi\cdot AlEt_3\cdot NMe_4Cl$	+12.6	−3.5	−5.1	0.9	0.4
$(MiBLi\cdot AlEt_3\cdot NMe_4Cl)_2$	−34.2		−5.1		0.4
$MiBLi\cdot 2AlEt_3\cdot NMe_4Cl$	−35.5		−8.7		15.8

results also suggest that the reaction between EiBLi and the THTA complex $NMe_4[Al_2Et_6Cl]$ is a rather slow process, which is in accordance with conclusions drawn from earlier kinetic investigations.[2]

Quantum-chemical calculations provide a structure of the new species, $[EiBLi\cdot AlEt_3\cdot AlEt_3Cl]NMe_4$ (Figure 4a), which is very similar to that of $[EiBLi\cdot AlEt_3Cl]$-NMe_4 but has an additional $AlEt_3$ molecule at the oxygen atom of the ester alcohol. It is known that THTA complexes such as $NMe_4[Al_2Et_6Cl]$ will lose their second mole $AlEt_3$ in the presence of even weak Lewis bases such as diethyl ether[5] or methyl pivalate.[6] Thus, the

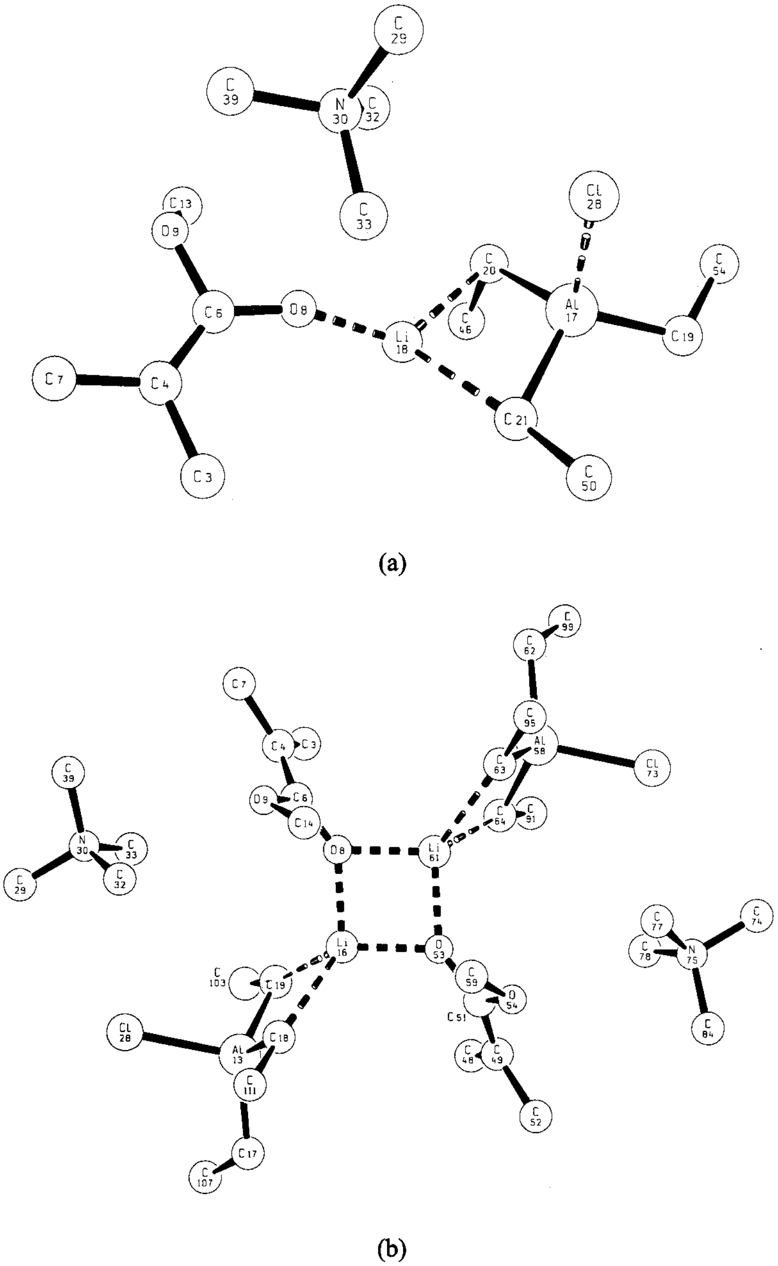

Figure 3. Calculated structures of [MiBLi$\cdot$AlEt$_3$Cl]NMe$_4$: (a) nonassociated and (b) dimeric structures.

formation of [EiBLi$\cdot$AlEt$_3\cdot$AlEt$_3$Cl]NMe$_4$ from EiBLi and NMe$_4$[Al$_2$Et$_6$Cl] might be a two-step process with EiBLi$\cdot$AlEt$_3$ and NMe$_4$[AlEt$_3$Cl] as intermediate products.[6] Compared to [EiBLi$\cdot$AlEt$_3$Cl]NMe$_4$, the complex [EiBLi$\cdot$AlEt$_3\cdot$AlEt$_3$Cl]NMe$_4$ is $\Delta E = -48$ kJ/mol more stable (cf. Table 3). The corresponding dimeric associate is considered to be even more so, but its structure was not calculated because of the large number of atoms.

According to previous studies,[2,6] ammonium enolates MiB$^-$NMe$_4^+$ and [MiB$\cdot$AlEt$_3$]$^-$NMe$_4^+$ (Figure 4b,c) might play a considerable role for polymerization kinetics even at very low concentrations because of their high reactivity. These enolates are expected to be formed in the course of dissociation of either [EiBLi$\cdot$AlEt$_3$Cl]NMe$_4$ or [EiBLi$\cdot$AlEt$_3\cdot$AlEt$_3$Cl]NMe$_4$ with the release of Li[AlEt$_3$-Cl] (see Scheme 1). However, the respective formation energies are so high ($\Delta E = +165$ and $+77$ kJ/mol, respectively) that MiB$^-$NMe$_4^+$ and [MiB$\cdot$AlEt$_3$]$^-$NMe$_4^+$ should only be formed with extremely low yield. On account of such low concentrations, the ammonium enolates are out of the range of detection by NMR. The energies of formation (in hartree units) of every calculated compound or structure are summarized in Table 4.

The quantum-chemical calculations support the existence of associated species, since all nonassociated structures display an electron deficiency in the coordination sphere of lithium. The electron-donating capacity of the solvent molecules (toluene) cannot compensate this deficiency but, according to earlier studies,[3,6–8] the ester carbonyl groups of the monomer and the polymer can do so. Therefore, we expect that the active species will be less associated or even nonassociated during a polymerization process. To mimic "real" polymerization conditions, the products formed from EiBLi and THTA complexes were examined in the presence of methyl pivalate (MPiv).

Mixtures of EiBLi, NMe$_4$[Al$_n$Et$_{3n}$Cl] ($n = 1, 2$), and MPiv. The addition of MPiv in equimolar amounts to the complex [EiBLi$\cdot$AlEt$_3$Cl]NMe$_4$ has a considerable

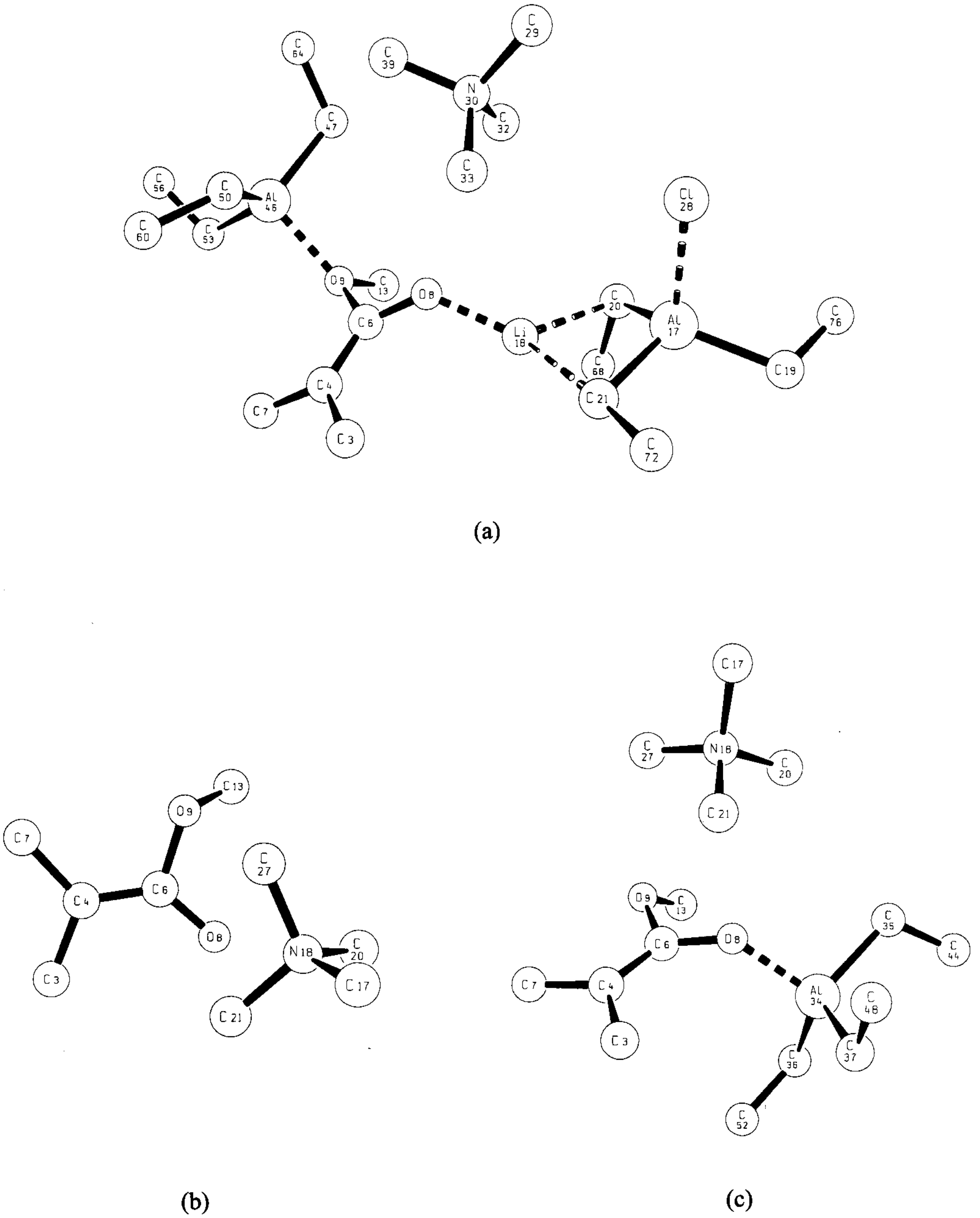

Figure 4. Calculated unimeric structures of (a) [MiBLi·AlEt$_3$Cl·AlEt$_3$]NMe$_4$, (b) MiB$^-$NMe$_4^+$, and (c) [MiB·AlEt$_3$]$^-$NMe$_4^+$.

effect on both ^{13}C and ^{6}Li NMR signals. We observe in ^{13}C NMR a single peak for the ester enolate C-1 at 153.3 ppm, whereas the signals of C-2 and C-4 vanish in the noise (Figure 5b); the ^{6}Li NMR spectrum shows not just one but three groups of signals at 0.12, 0.45, and 0.72 ppm (Figure 6b). The width and multiplicity of the signals indicate the presence of various species in slow equilibrium. The NMR signal of C-1 and the ^{6}Li NMR signals at 0.1−0.5 ppm can be assigned to [EiBLi·AlEt$_3$Cl]NMe$_4$ (cf. Table 5). The downfield shift of the ^{13}C NMR signal of the MPiv carbonyl carbon by 2.5 ppm (see Table 5) indicates that the ester might be coordinated to either Li$^+$ or AlEt$_3$ yielding [EiBLi·MPiv·AlEt$_3$Cl]NMe$_4$; due to the large variety of ^{6}Li NMR signals and earlier results,[8] we presume that MPiv is bound to the lithium ion.

For the mixture of EiBLi and NMe$_4$[Al$_2$Et$_6$Cl] in the presence of MPiv, we observe two ^{13}C NMR signals for C-1 at 150.1 and 153.2 ppm and two for C-2 at 79.8 and 92.4 ppm (Figure 5d). The signals at 153.2 and 79.8 ppm can be assigned to [EiBLi·MPiv·AlEt$_3$Cl]NMe$_4$ as the predominant species, and the others are very similar to those of EiBLi·AlEt$_3$, EiBLi·AlEt$_3$·MPiv or [EiBLi·AlEt$_3$·AlEt$_3$Cl]NMe$_4$ (see Table 5). When we take into account the shifts of the carbonyl carbon of MPiv at 181.2 and 182.2 ppm, [EiBLi·MPiv·AlEt$_3$Cl]NMe$_4$ and EiBLi·AlEt$_3$·MPiv should be the two other active species; the peak at 183.5 ppm might arise from MPiv·AlEt$_3$. This interpretation of the spectra is in accordance with the results of kinetic investigations.[2,7] The ^{6}Li NMR spectrum of the sample shows, however, just one major signal at 0.0 ppm.

Quantum-chemical calculations should give more precise information about the structures formed in the presence of MPiv, but they could not be performed for capacity reasons. However, we can assume that a complex [EiBLi·MPiv·AlEt$_3$Cl]NMe$_4$ is highly stable and does not form dimeric or higher associates. The living

Scheme 1. Calculated Reaction Enthalpies of Interactions of Ester Enolates with THTA Complexes (Dimeric Associates Not Taken into Account)

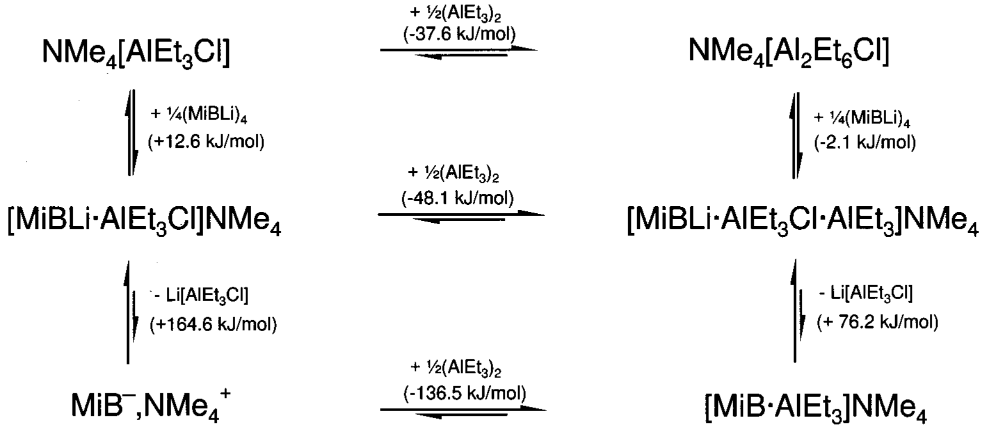

Table 4. Calculated Total Energies *E* (in Hartree Units) of All Considered Complexes and Structures

substance	point group	*E*	substance	point group	Figure	*E*
$(AlEt_3)_2$	C_i	−959.925027	MiBLi·$AlEt_3$	C_1		−833.859978
NMe_4Cl	C_1	−674.437634	(MiBLi·$AlEt_3)_2$	C_1		−1667.744976
$NMe_4[AlEt_3Cl]$	C_1	−1154.437767	(MiBLi·$AlEt_3)_4$	D_2		−3335.505214
$NMe_4[Al_2Et_6Cl]$	C_1	−1634.414455	[MiBLi·$AlEt_3Cl]NMe_4$	C_1	3a	−1508.332328
$Li[AlEt_3Cl]$	C_1	−947.747298	([MiBLi·$AlEt_3Cl]NMe_4)_2$	C_1	3b	−3016.700192
$Li[Al_2Et_6Cl]$	C_1	−1427.726663	[MiBLi·$AlEt_3Cl$·$AlEt_3]NMe_4$	C_1	4a	−1988.313062
MiBLi	C_1	−353.842708	$MiB^-NMe_4^+$	C_1	4b	−560.522333
$(MiBLi)_4$	C_1	−1415.597538	[MiB·$AlEt_3]NMe_4$	C_1	4c	−1040.536793

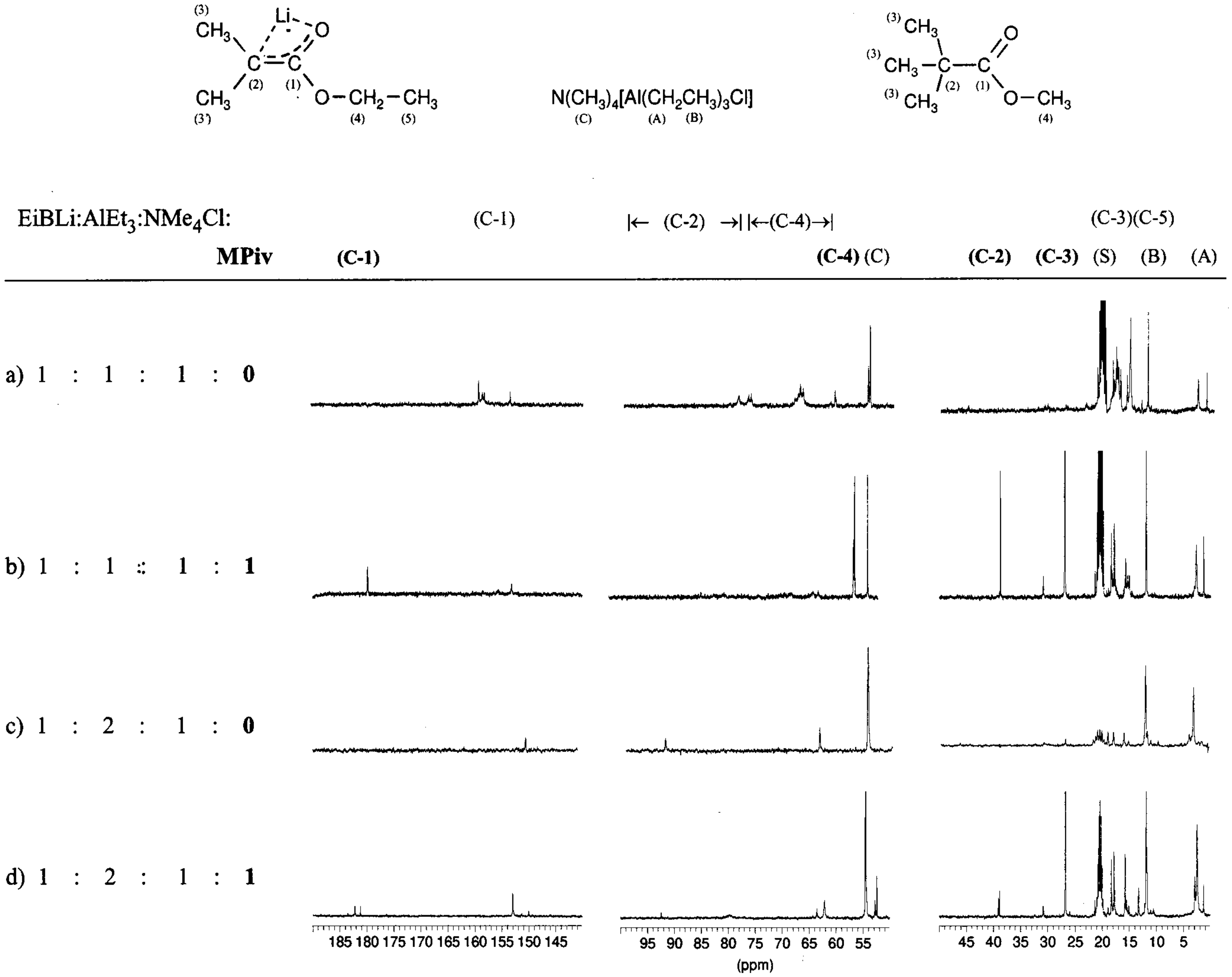

Figure 5. ^{13}C NMR spectra of mixtures of EiBLi, THTA complexes, and MPiv at −20 °C in toluene-d_8. S = solvent.

Table 5. ^{13}C and ^{6}Li NMR Signals (δ/ppm) of Mixtures of Ethyl α-Lithioisobutyrate (EiBLi), THTA Complexes ($NMe_4Cl/AlEt_3$), and Methyl Pivalate (MPiv, in Bold) in Toluene-d_8 at −20 °C

		^{13}C								
EiBLi:$AlEt_3$:NMe_4Cl:**MPiv**	Figure	C-1	C-2	C-3	C-4	C-5	Al−CH_2	Al-•-CH_3	N−CH_3	^{6}Li
1:1:0:**0**[a]		149.7	91.4	16.4	67.9	14.8	0.2	10.0		−1.11
				17.6		14.4	(0.5)			
1:1:0:**1**[a]		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	**39.0**	**26.6**	**52.8**					
1:1:1:**0**	5a/1c	153.5	76.4	17.1	60.8	15.3	1.5	11.6	54.3	0.28
	6a/2c	158.6	76.9	17.9	63.6	15.9	3.6		54.7	0.33
		159.0	78.7	18.4	66.7					0.43
		159.3	79.5	18.9	67.2					
					68.5					
1:1:1:**1**	5b	153.3	(77)	17.8	(61)	15.1	1.3	11.9	54.6	0.12
	6b			17.9		15.4	2.7	12.0		0.45
				18.3		15.6				0.72
				18.5		15.9				
		180.1	**38.8**	**26.9**	**52.1**					
1:2:1:**0**	5c/1e	150.0	92.6	17.9	63.6	15.1	1.4	10.9	54.6	−0.36
	6c/2e			18.8		15.9	2.1	11.5		−0.31
							2.9	11.9		
							3.7			
1:2:1:**1**	5d	150.1	79.8	17.7	62.2	15.1	1.3	11.7	54.6	−0.06
	6d	153.2	92.4	17.8	63.6	15.4	2.5	12.0		0.03
				18.2		15.5	3.0	13.3		
				18.3		15.8				
		181.2	**38.9**	**26.8**	**52.5**					
		182.2								
		183.5								
MPiv[b]		177.9	38.7	27.3	51.2					
MPiv·AlR_3[b,c]		182.3	39.4	27.0	53.8					

[a] Data taken from ref 3. [b] Measured at 25 °C. [c] Data taken from ref 7 (R = Bu^i).

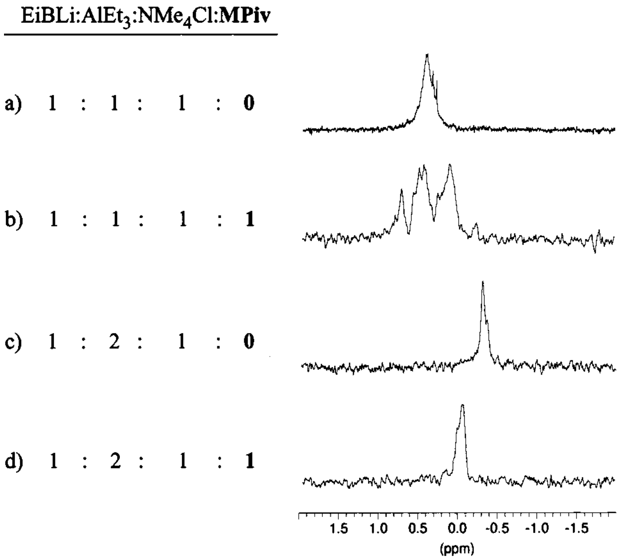

Figure 6. ^{6}Li NMR spectra of mixtures of EiBLi, THTA complexes, and MPiv at −20 °C in toluene-d_8.

chain ends during methacrylate polymerization in the presence of THTA complexes should therefore be unimeric as well.

Conclusions

Multinuclear NMR and quantum-chemical investigations were used to investigate the structure of ester enolate species in the presence of THTA complexes during methacrylate polymerization in toluene. The reaction of EiBLi with equimolar amounts of $NMe_4[AlEt_3Cl]$ or $NMe_4[Al_2Et_6Cl]$ yields $[EiBLi·AlEt_3Cl]NMe_4$ and $[EiBLi·AlEt_3·AlEt_3Cl]NMe_4$, respectively, and is a rather slow process. These species tend to form associates because of an electron deficiency in the coordination sphere of lithium. MPiv, a model compound for the monomer and the polymer, is capable of compensating this deficiency yielding $[EiBLi·MPiv·AlEt_3Cl]NMe_4$ as the major species—this structure is supposed to be highly stable and does not associate.

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Supporting Information Available: A table of Cartesian coordinates (in atomic units) of the structures. A table of Mulliken charges and NMR shifts (in part) including structural diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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