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Anionic Polymerization of Acrylic Monomers. 17. Ligated Anionic Living Polymerization of 2-Ethylhexyl Acrylate As Promoted by Polydentate Lithium Alkoxides

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ABSTRACT: Different initiators combined with a new family of μ/σ dual ligands, i.e., polydentate alkoxides, were used to initiate the anionic polymerization of 2-ethylhexyl acrylate (2EtHA) at low temperatures. It has been found that lithium 2-(2-methoxyethoxy) ethoxide (LiOEEM) is the most efficient μ/σ ligand in promoting a living polymerization of that monomer. Although LiOEEM gives rise to a molecularly well-controlled P2EtHA at −78 °C in a 9/1 toluene/THF mixture, i.e., quantitative yield, high initiator efficiency (>90%), and narrow molecular weight distribution (M_w/M_n down to 1.05), two-step monomer resumption experiments always lead to a bimodal distribution, suggesting that the LiOEEM-complexed P2EtHA anions are not stable. Nevertheless, a perfectly living 2EtHA anionic polymerization process has been obtained at −100 °C, keeping other conditions unchanged. In comparison with other types of ligands, such as LiCl and LiOtBu (both μ-ligands) and DB18CE6 and K222 (both σ-ligands), it has been further demonstrated that the formation of a stable and bulky active complex is at the origin of the anionic living polymerization of 2EtHA, in agreement with our findings in the case of anionic statistical copolymerization of methacrylate and acrylate.

Introduction

Devising a living system for the anionic (co)polymerization of (meth)acrylates has been a long-standing problem sin polymer synthesis.[1] Partial answers have already come from the discoveries of "group-transfer polymerization" (GTP) by a DuPont research team,[2] "metal-free anionic polymerization" by Reetz,[3] "ligated" anionic polymerization by us[4] and others,[5] and the so-called covalent living polymerization by several groups.[6] We have been intrigued for some time in the ligated polymerization, since only that technique might achieve simultaneously the general goals of the field, e.g., copolymerization of (meth)acrylates with various types of classical monomers, stereochemical control, etc.

Documented examples of efficient ligands discovered up-to-date can be divided into two main classes:[1] inorganic or organometallic μ-bonded additives such as alkali and alkaline-earth metal salts, metal alkyls, alkoxides, and amides, on the one hand, and cation-σ-binding organic ligands, such as polyethers (including crowns) and polyamines (including cryptands), on the other. These ligands are mostly effective in promoting the living anionic polymerization of alkyl methacrylates and bulky acrylates; the one of primary acrylates is however still a difficult challenge.

It has been recently claimed that the use of lithium alkyl isobutyrate combined with lithium *tert*-butoxide as an initiator affords the anionic polymerization of some primary acrylates, such as 2-ethylhexyl acrylate (2EtHA)[5b] and *n*-butyl acrylate (n-BuA),[5c] in high yield and with narrow molecular weight distribution. Unfortunately, the initiator efficiency is still very low (<0.60), a critical problem in producing well-controlled block copolymers.

Very recently, a new family of ligands, i.e., polydentate lithium alkoxides, has been discovered in this laboratory and proven to be very effective in anionic living polymerization of (meth)acrylates.[4e-g] In comparison with other types of ligands invented up-to-date, they provide several definite advantages, including anionic living polymerization of several primary acrylates,[4f] well-controlled anionic sequential copolymerization of methyl methacrylate and primary acrylates irrespective of the addition order of the monomers,[7] synthesis of controlled highly syndiotactic poly(methyl methacrylate) even in toluene at elevated temperatures,[8] and living anionic statistical copolymerization of methyl methacrylate (MMA) and *tert*-butyl acrylate (tBuA).[4g,9]

Furthermore, a ^{13}C and ^7Li NMR study clearly revealed that ligands 1, combining both μ- and σ-complexing character, have a high propensity to coordinate with lithium ester enolates in solution with the formation of a very strong and bulky μ/σ dual complex,[10] which actually accounts very well for the kinetics,[11] stereochemistry,[12] and livingness of the resulting anionic polymerization processes.[9]

The present paper aims to show in detail how a series of μ/σ dual ligands, mainly polydentate lithium alkoxides (1), affect the anionic polymerization of 2-ethylhexyl acrylate (2EtHA) at low temperature. In order to demonstrate the importance of μ/σ dual complexation, the 2EtHA anionic polymerization in the presence of various types of ligands will be discussed.

$$CH_3-\!\!\left[OCH_2CH_2\right]_2\!\!-OLi$$

1, LiOEEM

Experimental Section

Reagents and Solvents. 2EtHA obtained from Norsolor (France) was first vacuum distilled from CaH_2 after reflux and stored under a pure nitrogen atmosphere at −20 °C. Before polymerization, it was added with a 10 wt % $AlEt_3$ solution in hexane until a persistent yellowish green color was observed and then distilled under reduced pressure. THF was purified by refluxing over a fresh sodium benzophenone complex. Toluene and hexane were refluxed over CaH_2 for 48 h and redistilled over oligo(styryllithium) immediately prior to use. Alcohols from Aldrich were distilled from CaH_2 and stored under nitrogen.

Initiators. Diphenylhexyllithium (DPHLi) was prepared at room temperature by reacting *n*-butyllithium and diphenyleth-

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Table 1. Anionic Polymerization of 2EtHA Initiated by DPHLi in the Presence of LiOEEM in a 9/1 Toluene/THF Mixture at −78 °C[a]

[DPHLi] (mol/L)	[2EtHA] (mol/L)	[LiOEEM]/[DPHLi]	yield (wt %)	$\bar{M}_n$ cal	$\bar{M}_n$ SEC	initiator efficiency (*f*)	M_w/M_n
0.01	0.465	0	45	4000	2000	2.0	3.2
0.01	0.465	2	90	7900	24000	0.33	1.70
0.01	0.528	10	100	10000	11000	0.91	1.05
0.005	0.233	10	99	8800	9000	0.97	1.06
0.00125	0.233	10	98	32500	36000	0.90	1.10

[a] Polymerization time: 1–5 min.

ylene in toluene for 24 h. The (diphenylmethyl)lithium (DPMLi), (diphenylmethyl)sodium (DPMNa), and (diphenylmethyl)potassium (DPMK) were obtained by reacting diphenylmethane with lithium, sodium, and potassium naphthalene, respectively, in THF at room temperature for 24 h. Ethyl α-lithioisobutyrate (EIBLi) was synthesized from equimolar amounts of lithium diisopropylamide (LDA, from Aldrich, used as received) and ethyl isobutyrate in hexane at −78 °C according to a literature method.[5a]

Preparation of Polydentate Alkoxides. Two different methods were envisioned to prepare the ligands 1 and other polydentate metal alkoxides. (1) Under oxygen and moisture-free argon equimolar amounts of metal and corresponding alcohol were added into THF in a dry flask equipped with an inert gas inlet, magnetic stir bar, and water-cooled condenser. The solution was heated to reflux and the reaction allowed to continue at reflux conditions overnight. (2) Lithium alkoxides were generated by reacting the suitable alcohol in dry hexane with an equimolar amount of n-BuLi at 0 °C. In this case, a few drops of 1 M diphenylethylene in hexane were used as indicator. It was found that ligands prepared by two these different methods give comparable results.

Polymerization. Anionic polymerization of 2EtHA was carried out in a flamed glass reactor under a nitrogen atmosphere. Solvent, ligand, and initiator were transferred into the glass reactor by using a rubber septum and a stainless steel capillary or a syringe. The initiator solution was added dropwise to the solvent containing the polydentate lithium alkoxide ligand until the initiator color persisted; ca. 5 drops of a 0.2 M initiator solution was generally required to get a persistent color in 100 mL of solution, i.e., a highly pure medium. After adding the calculated amount of initiator, the solution was cooled to the desired temperature, the required quantity of monomer was introduced, and the polymerization was performed at that temperature. It was then stopped by adding acidic methanol, and the polymer was recovered by precipitation into methanol. The crude polymer was dried under vacuum at 40 °C for 48 h.

Characterization. SEC was carried out by using a Hewlett-Packard 1090 liquid chromatograph equipped with four columns (10^5, 10^3, 500, and 100 Å) and a Hewlett-Packard 1037A refractive index detector. Polystyrene standards were used for calibration of the number- (M_n) and weight-average (M_w) molecular weights as well as polydispersity of the polymer accordingly calculated.

Results and Discussion

Anionic Polymerization of 2EtHA Initiated with LiOEEM-Complexed DPHLi in a 9/1 Toluene/THF Mixture. Table 1 and Figure 1 clearly show how a polydentate lithium alkoxide, i.e., lithium 2-(2-methoxyethoxy) ethoxide (LiOEEM), provides definite beneficial effects in the anionic polymerization of 2EtHA in that mixed solvent at −78 °C. Indeed, in the absence of LiOEEM, the polymerization is a rather complicated and poorly controlled process (Figure 1A), as evidenced by a very broad multimodal distribution ($M_w/M_n > 3.0$) and a limited conversion (<50%), clearly indicating that side reactions occur in a possible relation with several types of active species. That situation was largely improved when only 2 mol equiv of LiOEEM was used per mole of initiator. The yield in polymer significantly increases from 45% to 90%; at the same time, the molecular weight distribution (MWD) has been reduced from 3.2 to 1.7 (Figure 1B). However, it should be noted from Table 1 that the initiation efficiency is still not satisfactory (*f* = 0.33).

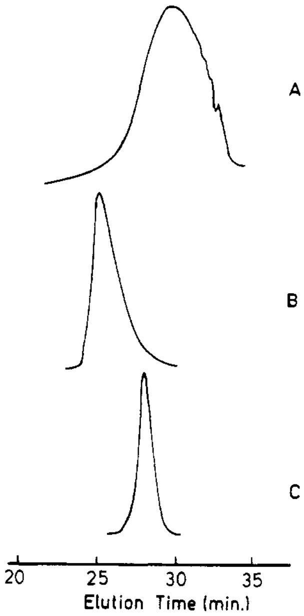

Figure 1. Size-exclusion chromatograms of P2EtHA synthesized in a 9/1 toluene/THF mixture at −78 °C. The initiator was (diphenylhexyl)lithium as modified by lithium 2-(2-methoxyethoxy) ethoxide ligand: (A), without ligand; (B) with 2 mol equiv of ligand; (C) with 10 mol equiv of ligand.

A further increase in the relative amount of LiOEEM over initiator up to 10 or more again improves the situation to the point where monomer conversion is quantitative, initiator efficiency becomes very high (>90%), and MWD is very narrow ($M_w/M_n < 1.10$) and symmetrical (Figure 1C).

In order to demonstrate the living character of that polymerization at −78 °C, a series of 2EtHA polymerizations were carried out using various monomer/initiator molar ratios and a constant LiOEEM/DPHLi molar ratio of 10. Figure 2 compares the experimental molecular weight ($M_{n,exp}$) and the theoretical one ($M_{n,cal}$). A linear plot is obtained in a molecular weight range between 4.5×10^3 and 3.5×10^4. Moreover, the slope of the straight line is 0.91, in good agreement with the initiator efficiency reported in Table 1. It must be recalled that a previous study has shown that molecular weights of PMMA and PtBuA, as measured by SEC on the basis of a polystyrene calibration, are in very close agreement with the absolute molecular weight, at least in the range smaller than 30 000.[13]

Up to this point, one may already conclude that this LiOEEM-modified active species is very effective in protecting the anionic polymerization of 2EtHA from noxious termination reactions in a 9/1 toluene/THF mixture at −78 °C. The μ/σ dual ligand, LiOEEM, seems to stabilize the active species and to make it bulky enough for preventing the secondary attacks.[10]

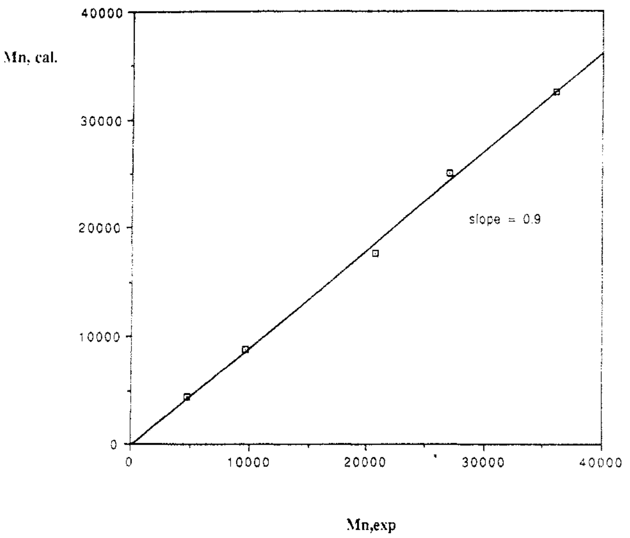

Figure 2. Dependence of experimental M_n as determined by SEC on M_n values calculated from the monomer/initiator ratio and the monomer conversion. Experimental conditions: 9/1 toluene/THF mixture; −78 °C; initiator, (diphenylhexyl)lithium as modified by a 10-fold molar excess of LiOEEM.

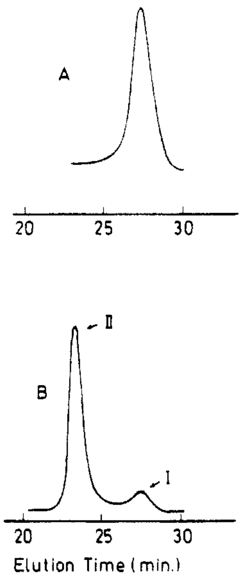

Figure 3. SEC traces of P2EtHA samples synthesized in a 9/1 toluene/THF mixture of −78 °C using a 10 molar ratio LiOEEM/DPHLi initiator system: (A) after polymerization of a first monomer dose; (B) after polymerization of a second monomer dose. Total conversion 100%.

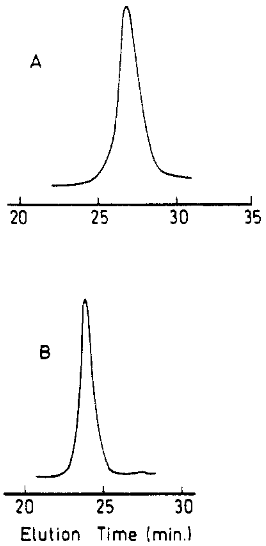

Figure 4. SEC traces of P2EtHA samples synthesized in a 9/1 toluene/THF mixture at −100 °C using a 10 molar ratio LiOEEM/DPHLi initiator system: (A) after polymerization of a first monomer dose; (B) after polymerization of a second monomer dose. Total conversion 100%.

Table 2. Anionic Polymerization of 2EtHA in Various Toluene/THF Mixtures at −78 °C, Using DPHLi as an Initiator and in the Presence of 10 Mol Equiv of LiOEEM[a]

tol/THF (mL/mL)	[DPHLi] (mol/L)	[2EtHA] (mol/L)	yield (wt %)	$\bar{M}_n$ cal	$\bar{M}_n$ SEC	f	M_w/M_n
95/5	0.00125	0.233	100	35200	36000	0.94	1.09
90/10	0.01	0.466	100	8800	9900	0.91	1.05
70/30	0.01	0.212	99	4000	4500	0.89	1.15
60/40	0.01	0.212	98	4000	4700	0.85	1.30
0/100	0.005	0.466	100	17600	21500	0.82	2.55

[a] Polymerization time: 1–5 min.

A further insight in the livingness of 2EtHA anionic polymerization at −78 °C is given by means of two-step monomer resumption experiments. Accordingly, a first dose of 2EtHA (0.021 mol) is polymerized (DPHLi, 4 × 10^{-4} mol) and 1 min later the same molar amount of 2EtHA added. As a result, and somewhat surprisingly, two well-separated peaks I and II clearly show up in the SEC of the final raw product (Figure 3B). Since the elution time of peak I in Figure 3B is almost identical to that for the first P2EtHA crop (Figure 3A), peak II in Figure 3B obviously corresponds to the final P2EtHA–P2EtHA polymer. It seems most likely that some of the initial living P2EtHA chains have already been killed, whatever the reason, before adding the monomer second dose. Actually, the M_n of the first P2EtHA sample was 9000 (M_w/M_n = 1.06, f = 0.91) and that of the final polymer (peak II in Figure 3B) was 37 000 (M_w/M_n = 1.07, f = 0.53), clearly indicating that the concentration of active species during the course of propagation of the 2EtHA second dose is much less than that of the first one. In view of the fact that side termination reactions are not likely involved during that propagation of 2EtHA (see above), the present results may only be understood if the LiOEEM-complexed P2EtHA anions are relatively unstable and undergo termination reactions during the interval between the two doses of polymerization. Indeed, compared to the first dose polymer, the MWD of the final one remains almost unchanged, also with a symmetrical distribution, which gives additional credit to this conclusion. Actually, termination seems to occur when the monomer is consumed. As soon as a new monomer feed is added, propagation completely prevails over termination and the newly formed polymer is of a narrow MWD.

For such fast polymerizations, polymerization temperature should obviously be a critical parameter for improving that situation. Figure 4 accordingly shows that, when the monomer resumption experiment is carried out at −100 °C while keeping other parameters unchanged, there is practically no original P2EtHA present anymore within the limit of detection in SEC measurements. Quite consistently, the final experimental molecular weight (M_n = 20 000) is now found to be very close to the calculated one (M_n = 18 000), i.e., f = 0.90. It might be thus suggested that a decrease in the polymerization temperature promisingly enhances the stability of P2EtHA anions, leading to a perfectly "living" anionic polymerization of 2EtHA at −100 °C.

Effect of the Reaction Medium Polarity on the Livingness of 2EtHA Anionic Polymerization at −78 °C. Table 2 illustrates the effect of the THF content in a toluene/THF mixed solvent, i.e., the polarity of the reaction medium, on the yield, initiator efficiency (*f*), and molecular weight distribution (MWD) of the P2EtHA obtained in a polymerization at −78 °C using DPHLi as an initiator and LiOEEM (10 mol equiv) as a ligand. It immediately appears from Table 2 that changing the medium polarity does not significantly affect the polymerization yield, although slightly decreasing the initiator efficiency. However, an increase in the THF content results in a substantial increase in the MWD. Typically, a MWD of ca. 2.55 is observed in pure THF at −78 °C, much broader than the one of 1.06 found in a 9/1 toluene/THF mixture at the same temperature. Moreover, a large tailing on the lower molecular weight side clearly shows up in the SEC of the final product produced in pure THF, again in sharp contrast to the symmetrical distribution when using a 9/1 toluene/THF mixture.

According to Szwarc,[14] the observed broadening of the MWD caused by increasing the medium polarity might likely be due to the following reasons, provided initiation is fast and identical experimental conditions, i.e., concentration and temperature, prevail and remain uniform through the whole reactor: (i) coexistence of several different types of propagating species, the exchange among them being slow compared to the propagation process; (ii) presence of chain transfer or termination side reactions throughout the polymerization reactions.

Recently, we have already demonstrated that,[10] according to ^{13}C and ^{7}Li NMR analysis of model systems, LiOEEM is very effective in complexing with lithium ester enolates with the formation of a unique single type of μ/σ complex in toluene, THF, and various toluene/THF mixtures at [LiOEEM]/[ester enolate] ≥ 2. The presence of the same type of LiOEEM-complexed active species is further well substantiated by the fact that the stereochemistry of the MMA anionic polymerization remains almost identical as well in pure THF as in pure toluene and in various mixtures of these two solvents.[12] Assuming the same situation prevails in the LiOEEM-modified anionic polymerization of 2EtHA at −78 °C, one may reasonably rule out the coexistence of several types of active species.

As already demonstrated above and elsewhere,[7] the shelftime of the living P2EtHA chains seems to be short enough, so that monomer resumption experiments and sequential anionic polymerization at −78 °C unavoidably induce the formation of considerable amounts of the first dose P2EtHA or of homo-P2EtHA, respectively. It might then be suggested that an increase in the polarity of the solvent further reduces the shelftime of the living P2EtHA anions, some of which might consequently terminate even before the end of a one-step polymerization. If so, a broader MWD must result; and at the same time, the tailing visible in the SEC diagram should of course occur on the lower molecular weight side. A detailed investigation on the shelftime of the living P2EtHA is in progress and will be the subject of a forthcoming paper.

Anionic Polymerization of 2EtHA in a 9/1 Toluene/THF Mixture at −78 °C Initiated with Various Types of Organolithium Initiators (Other Than DPHLi) in the Presence of 10 Mol Equiv of LiOEEM. The characterization data for P2EtHA samples prepared under such conditions are reported in Table 3. Quite comparable to DPHLi, most monofunctional initiators studied, i.e., (diphenylmethyl)lithium (DPMLi), lithium ethyl isobutyrate (EIBLi), and lithium diisopropylamide (LDA), afford a well-controlled polymerization of 2EtHA, leading to quantitative monomer conversion (>95%), very narrow MWD (<1.1), and high initiator efficiency (>0.91), suggesting a termination-free process. By contrast, a LiOEEM-added simple alkyllithium initiator, i.e., *s*-BuLi, gives rise to an ill-controlled product (Table 3). This might result from the occurrence of termination reactions at earlier stages of the polymerization, probably because LiOEEM-complexed *s*-BuLi still displays a high nucleophilicity and a less sterically hindered structure.

Table 3. Characterization of Samples from Anionic Polymerization of 2EtHA in a 9/1 Toluene/THF Mixture at −78 °C, Using Various Types of Organolithium Initiators As Modified by 10 Mol Equiv of LiOEEM[a]

initiator	yield (wt %)	$M_{n,cal}$	$M_{n,SEC}$	M_w/M_n	*f*
s-BuLi	35	10 000	27 500	3.55	0.36
DMPLi	100	10 000	10 500	1.08	0.95
EIBLi	99	10 000	11 000	1.12	0.91
LDA	98	10 000	10 800	1.10	0.93
NaphLi[b]	100	10 000	10 600	1.08	0.94

[a] Initiator concentration: 0.005 mol/L. Monomer concentration: 0.265 mol/L. Polymerization time: 1–10 min. [b] Added with 1.1 mol equiv of DPE in the presence of LiOEEM.

It is also interesting to note that a difunctional initiator system, i.e., the reaction adduct of lithium naphthalene and diphenylethylene (DPE), also includes a well-defined P2EtHA in the presence of 10 mol equiv of LiOEEM. Actually, well-controlled triblock copolymers P2EtHA-*b*-PMMA-*b*-P2EtHA have been successfully prepared using that difunctional initiator system.[7]

Effect of Various Types of Polydentate Lithium Alkoxides on 2EtHA Anionic Polymerization in a 9/1 Toluene/THF Mixture at −78 °C. Having demonstrated the effectiveness of LiOEEM on the anionic living polymerization of 2EtHA in a 9/1 toluene/THF mixture, it was logical to further examine the livingness of such a polymerization in the presence of other types of polydentate alkoxides, listed in Table 4. Characterization data for these polymerizations are tabulated in Table 5, from which several interesting features immediately emerge.

First, in striking contrast to the LiOEEM-complexed DPMLi, an NaOEEM-added DPMNa initiator initiator induces very poor results: i.e., low yield (ca. 50%), very low initiator efficiency (*f* = 0.34), and broad MWD (M_w/M_n = 1.84). This might reflect the fact that complexation of a sodium-containing ion pair with NaOEEM is much less efficient than that of a lithium-containing one with LiOEEM in promoting anionic living polymerization of 2EtHA. In fact, it has been found that NaOEEM itself initiates the anionic polymerization of 2EtHA under the same conditions,[15] which might result in at least two types of initiating species and a less efficient complexation of DPMNa by NaOEEM.

Second, when LiOEM or LiOEEEM is used instead of LiOEEM, the 2EtHA polymerization does not seem to proceed in a really living manner, as indicated by a very broad MWD (M_w/M_n > 2.0), although the initiator efficiency is found to be close to 1 in the case of the LiOEEEM-complexed system, in sharp contrast to the LiOEM-complexed one ($f \sim 0.30$). It is indeed intriguing that the most beneficial effects of LiO(E)$_n$M's on 2EtHA anionic polymerization are only found in the case where $n = 2$, a striking selectivity which is currently under investigation in this laboratory.

Finally, also noteworthy from Table 5 is that either a poly(propylene oxide) based lithium alkoxide (e.g., LiOPPM) or a lithium (dimethylamino)ethoxy ethoxide (e.g., LiOEEN) gives much poorer results compared to LiOEEM, in terms of yield and MWD of resulting polymers. It is well-known that the complexation between lithium cations and polyether units will be considerably weakened, when

Table 4. List of Polydentate Alkoxides Used in the Present Work

lithium 2-(2-methoxyethoxy) ethoxide	$LiOCH_2CH_2OCH_2CH_2OCH_3$	LiOEEM
lithium triethylene glycol monomethyl ether alkoxide	$LiOCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$	LiOEEEM
lithium 2-methoxy ethoxide	$LiOCH_2CH_2OCH_3$	LiOEM
sodium 2-(2-methoxyethoxy) ethoxide	$NaOCH_2CH_2OCH_2CH_2OCH_3$	NaOEEM
lithium dipropylene glycol monomethyl ether alkoxide	$LiOCH_2CH(CH_3)OCH_2CH(CH_3)OCH_3$	LiOPPM
lithium (dimethylamino)ethoxy ethoxide	$LiOCH_2CH_2OCH_2CH_2N(CH_3)_2$	LiOEEN

Table 5. Characterization of Samples from Anionic Polymerization of 2EtHA in a 9/1 Toluene/THF Mixture at −78 °C, Using Various Types of Polydentate Alkoxide-Modified Organoalkali Initiators[a]

polydentate alkoxide/initiator[b]	yield (wt %)	$M_{n,cal}$	$M_{n,SEC}$	M_w/M_n	f
NaOEEM/DPMNa	55	4840	13 080	1.84	0.37
LiOEM/DPMLi	92	7220	23 000	2.30	0.31
LiOEEEM/DPMLi	97	8800	9 100	2.10	0.97
LiOPPM/DPMLi	41	4660	17 900	1.58	0.26
LiOEEN/DPMLi	55	4840	8 810	1.75	0.55

[a] Initiator concentration: 0.005 mol/L. Monomer concentration: 0.265 mol/L. Polymerization time: 1–10 min. [b] 10/1.

Table 6. Characterization of Samples from Anionic Polymerization of 2EtHA in a 9/1 Toluene/THF Mixture at −78 °C, Using Various "Ligated" Initiators[a]

ligand/initiator (mol/mol)	time (min)	yield (wt %)	$M_{n,cal}$	$M_{n,SEC}$	M_w/M_n	f
Glyme-3/DPHLi (10/1)	60					
LiCl/DPHLi (5/1)	60	65	5700	15 400	2.65	0.37
LiOtBu/DPHLi (10/1)	60	95	8800	56 400	1.78	0.16
DB18CE6/DPMNa (2/1)	10	77	6780	12 800	1.84	0.53
K222/DPMK (2/1)	10	95	8800	26 000	1.91	0.38

[a] Initiator concentration: 0.005 mol/L. Monomer concentration: 0.265 mol/L.

poly(propylene oxide) is used instead of poly(ethylene oxide), due to the steric hindrance from the methyl group. This might also be the case for the μ/σ complexation between LiOPPM and $P2EtHA^-Li^+$. In that respect, the σ-coordination promoted by the polyether moiety might be largely disturbed, resulting in a less controlled reaction. However, the low efficiency of LiOEEN in this 2EtHA anionic polymerization is still very puzzling and has not found satisfactory explanation as yet.

Anionic Polymerization of 2EtHA Using Other Types of Ligand-Modified Initiator Systems. In order to demonstrate the significance of μ/σ dual ligands, e.g., LiOEEM, in the anionic polymerization of 2EtHA, several different types of ligated (ligand-modified) initiator systems, glyme-3/DPHLi, DB18-CE-6/DPMNa, K222/DPMK, LiCl/DPHLi, and LiOtBu/DPHLi, have been used to initiate the polymerization of 2EtHA at −78 °C. The results are listed in Table 6.

It is first intriguing to note that addition of 10 mol equiv of glyme-3, a polydentate-type structure analogous to LiOEEM, does not provide any beneficial effects on the anionic polymerization of 2EtHA in a 9/1 toluene/THF mixture at −78 °C. In fact, in the presence of glyme-3, no polymer at all was recovered, in sharp contrast to the living process obtained in the presence of LiOEEM. Nevertheless, this is perfectly consistent with an NMR investigation of the complexation behavior between lithium ester enolates and two ligands: unlike LiOEEM, glyme-3 is not powerful enough to coordinate with lithium ester enolate, due to the presence of strong associative O–Li bonds.[16] Conversely, the lithium alkoxide component in LiOEEM is very effective in complexing with the enolate with the formation of a μ-type complex.[10]

On the other hand, it can be seen from Table 6 that LiCl, a very effective μ-ligand in promoting a perfectly anionic living polymerization of MMA and tBuA in THF at −78 °C,[4a–c] cannot induce a living polymerization of 2EtHA. As already demonstrated in the case of anionic copolymerization of MMA and tBuA mixtures,[18] a LiCl complexed active species is not soft and bulky enough so as to eliminate side termination reactions in the anionic polymerization of (meth)acrylates. By contrast, as far as another type of μ-ligand, i.e., LiOtBu, is used, the anionic polymerization of 2EtHA becomes somewhat better controlled compared to that using LiCl as a ligand. Although initiator efficiency is still extremely low and MWD not very narrow, the polymerization is indeed almost quantitative (Table 6). Such a discrepancy between two ligated systems might result from the difference of the steric hindrance in two types of active μ-complexes,[18b] knowing the fact that a LiOtBu-complexed species is bulkier than a LiCl-complexed one.[18b]

Up to this point, it seems that the bulkiness of an active complex plays a very important role in controlling the anionic living polymerization of 2EtHA. Since the polyether moiety in LiOEEM is also very effective in simultaneously forming a bulkier σ-complex with lithium ester enolate in addition to the above-mentioned μ-type one,[10] it might be concluded that the resulting very bulky μ/σ dual active species is at the origin of precise control exerted on that type of anionic polymerization.

However, when such a polymerization was carried out using two even bulkier initiator systems, i.e., DB18CE6/DPMNa or K222/DPMK, the data in Table 6 indicate a very complex process, leading to a limited conversion and a broad multimodal MWD. This may be puzzling, since it has been demonstrated that, similar to $LiOEEM/Li^+$, at least the $DB18CE6/Na^+$ active complex can completely suppress the so-called back-biting termination reactions in anionic statistical copolymerizations of MMA and tBuA in THF at −78 °C, giving a perfectly living P(MMA-*co*-tBuA).[19] It was also reported that this very bulky active species can induce a living anionic polymerization of MMA in pure toluene at 5 °C.[4d] All of these results have indeed been accounted for by the presence of a very bulky active species.[1b] Clearly, other factors might also strongly affect the anionic polymerization of 2EtHA. As discussed above, LiOEEM-complexed P2EtHA anions are not very stable. Consequently, termination reactions may occur when that polymerization is carried out in pure THF. It is thus not impossible that the complexation of P2EtHA ion pairs by very strong cation-binding ligands, i.e., DB18-CE-6 or K222, may induce more ion separation in complexed ion pairs (e.g., ligand-separated ion pairs or even free ions). These active species might then become even less stable, leading to termination reactions during the propagation.[1b]

As a general conclusion, the above-discussed results might point toward the fact that the formation of a stable and bulky active complex, without important charge separation, presents an efficient pathway toward the control of 2EtHA anionic living polymerization. LiOEEM is the best ligand found up-to-date to achieve that strategy.

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