Anionic Polymerization of (Meth)acrylic Monomers. 4.[†] Effect of Lithium Salts as Ligands on the "Living" Polymerization of Methyl Methacrylate Using Monofunctional Initiators

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Received June 14, 1989; Revised Manuscript Received November 6, 1989

ABSTRACT: The low-temperature polymerization of methyl methacrylate initiated with monofunctional lithium carbanionic species has been studied in THF and in a 9:1 toluene-THF mixture. Various types of "ligand" lithium salts have been purposely added to modify the active growth species. Quite interestingly, it has been found that lithium chloride, although not influencing the stereochemistry of the propagation, has an important beneficial effect on the "living" character of the process. That approach provides for a straightforward high-yield synthesis of PMMA samples displaying a predetermined molecular weight and a very low polydispersity. The LiCl:initiator molar ratio and the polarity of the solvent have been shown to be determinant parameters in the association equilibrium involved in these controls.

Introduction

The anionic polymerization of vinyl aromatics, 1,4-conjugated dienes, and heterocyclics (such as oxirane and lactones) has received a great deal of attention since Szwarc's discovery of a possibly "living" mechanism.[1] Despite the rapidly growing importance of (meth)acrylate monomers,[2] their anionic polymerization has not been developed so extensively due to inherent side reactions associated with the ester group in the presence of very basic carbanions.[3] These limitations have been discussed in detail in terms of mechanism and kinetics.[4-11] Under a given set of experimental conditions, kinetic results indicate that polymerization proceeds from more than one kind of species;[12,13] impurities unavoidably present in commercial-grade monomers may also perturb the course of the polymerization, although that problem has been practically overcome by a purification methodology involving alkylaluminum reagents.[14]

In methyl methacrylate (MMA) anionic polymerization, the nature of the solvent and the reaction temperature have been shown to deeply affect polymer yield and chain tacticity.[15] Nucleophilic attack on the carbonyl group is the most usual secondary reaction, leading to limited monomer conversion and metal methoxide formation.[16,17] This reaction can be limited when a sterically hindered initiator, e.g., (diphenylhexyl)lithium, is used in a polar solvent (THF) below -70 °C; MMA polymerization may then become a "living" process.[16,18]

At higher temperature, i.e., -45 °C, the enolate PMMA anion is no longer stable, and the molecular weight distribution is significantly broadened.[15] Furthermore, when the dielectric constant of the medium is decreased, the kinetics become more complex, to such an extent that the molecular weight distribution of the polymer may become multimodal.[19]

Several strategies have been proposed in order to eliminate these drawbacks.[5,9,16-22] Lochmann[23] et al. reported that MMA polymerization in toluene is still controlled at 20 °C, provided the initiator is added with alkali metal *tert*-butoxide as a ligand. Pyridine has been recommended as a solvent or cosolvent (<10 vol %) by Huynh-Ba[24] and Andrews.[25] These authors propose the formation of a "σ complex" at the end of the growing chain, resulting in a living polymerization at -45 °C. Another milestone was reached recently when a Du Pont Co. research team demonstrated that the nucleophile-assisted "group-transfer" reaction of silyl ketene acetals could be turned into a living polymerization process, specifically for unsaturated carbonyl-conjugated monomers.[26-28] This discovery promoted a precise molecular engineering of (meth)acrylate-based polymers and block copolymers. Nevertheless, it does not allow for the direct block copolymerization of the (meth)acrylates with comonomers lacking conjugated carbonyl groups, i.e., vinyl aromatics, dienes, and heterocyclics, by a multistep living process. In order to fill this gap, we have reconsidered the use of ligands able to control the reactivity of the anionic species involved and to prevent the occurrence of secondary reactions.[29-32] The purpose of the present paper is to report on the effect of simple lithium salts on the anionic polymerization of MMA as initiated by lithium alkyls in polar solvents at low temperature.

Experimental Section

MMA obtained from Aldrich was first vacuum distilled from CaH_2 after reflux and then stored under a nitrogen atmosphere at -20 °C. Before polymerization, it was added to a 10 wt % triethylaluminum solution in hexane until a persistent yellowish green color was observed.[14] It was then redistilled under reduced pressure just prior to polymerization.

LiCl (99.99% purity, Aldrich) was dried overnight at 130 °C and then dissolved in dry THF. After introduction into the reactor, the THF was removed under reduced pressure prior to use. The THF was purified by refluxing over fresh sodium-benzophenone complex (a deep purple color indicating an oxygen- and moisture-free dried solvent). It was further distilled under dry nitrogen over styryllithium, as was toluene after refluxing over CaH_2.

Initiators used in this study were the reaction products of *n*- or *sec*-butyllithium with a few units of α-methylstyrene (αMS)[33] or one unit of 1,1-diphenylethylene (DPE), respectively. A deep red color developed in THF at room temperature.

MMA polymerization was carried out in a glass reactor under an inert atmosphere, the monomer, solvent, and initiator being transferred by a syringe and capillary technique. Purified MMA was then added to the initiator solution, previously cooled to -78 °C with a dry ice-acetone bath. About 10-15 s was usually required to add 5 mL of monomer through the stainless steel capillary. Monomer conversion was determined gravimetrically after terminating the polymerization with cold methanol, precipitating the polymer in heptane, and drying it care-

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[†] For preceding papers, see refs 29-32.

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Table I
Characteristic Data for Anionic Polymerization of MMA in THF at −78 °C Using αMS$^-$Li$^+$ Initiator in the Presence of Different Ligands Containing a Lithium Counterion[a]

							microstructure		
ligand	polymn time, s	conv, %	$\bar{M}_{n,SEC} \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_{n,SEC}/\bar{M}_{n,calc}$	init eff	% s	% h	% i
	25	32	14.0	1.30	1.55	0.64	80	20	
	50	52	22.0	1.22	1.51	0.66			
	70	81	33.0	1.20	1.50	0.66			
	100	99	41.0	1.20	1.50	0.66	79	19	2
LiCl	25	25.6	8.0	1.18	1.16	0.86	78	19	3
LiCl	41	56.5	18.0	1.09	1.16	0.86			
LiCl	80	70.0	22.0	1.09	1.15	0.86			
LiCl	100	99.5	32.5	1.09	1.17	0.85	81	19	
LiF	40	56	28.5	1.24	1.83	0.54			
LiF	80	75	38.0	1.24	1.83	0.54	80	19	1
LiF	100	99	46.5	1.17	1.70	0.58			
LiBr	40	49	22.0	1.20	1.60	0.60			
LiBr	80	91	36.0	1.18	1.44	0.69			
LiBr	100	96	38.0	1.16	1.43	0.69	81	18	1
Li(Ph)$_4$B	30	30	10.5	1.30	1.26	0.78			
Li(Ph)$_4$B	50	47	17.5	1.30	1.34	0.74			
Li(Ph)$_4$B	100	68	25.5	1.24	1.34	0.74	79	19	2

[a] [αMS$^-$Li$^+$] = 1.7 × 10^{-3} mol/L, [ligand] = 1.8 × 10^{-3} mol/L, [monomer] = 0.468 mol/L.

fully at 80 °C for 24 h under reduced pressure.

The presence of LiCl (2.5 × 10^{-3} M) in a toluene–THF (9:1 v/v) solvent mixture causes a cloudiness to develop, indicating saturation. However, the cloudiness disappears progressively upon addition of initiator solution, the final solution being completely clear. The living character of the PMMA anions was evidenced by monomer resumption experiments, in which a second monomer dose was added after 90 min of polymerization of the first monomer dose.

The dependence of the experimental molecular weight ($\bar{M}_{n,exp}$) on the monomer:initiator molar ratio (i.e., $\bar{M}_{n,calc}$) was investigated by determining plymer molecular weights with a Waters 501 size exclusion chromatograph (SEC) equipped with linear Styragel columns and applying the universal calibration method.[34] Samples were analyzed before precipitating the polymer in heptane to limit as much as possible the loss of oligomers in the workup procedure.

The glass transition temperature (T_g) of the polymer samples was determined by differential scanning calorimetry (DSC) on a Du Pont 9000 instrument, calibrated with indium and mercury. Samples were heated at 170 °C, cooled to 20 °C, and scanned repeatedly at 20 °C/min.

Chain tacticity was determined by ^{1}H NMR using a Bruker AN 400 spectrometer.

Results and Discussion

Table I reports a number of characteristic data for the **polymerization of MMA in THF at −78 °C using αMSLi as an initiator**, further combined with various lithium salts that are believed to possibly act as μ ligands of the active ion pair (see below), i.e., LiF, LiCl, LiBr, and Li(C_6H_5)$_4$B. Although these lithium-based additives are not by themselves initiators, they will strikingly affect the course of that anionic process. It is also worth noting here that the use of *sec*-butyllithium as an initiator under the same conditions does not produce any polymer from MMA in the presence or absence of lithium halides, as also mentioned by Andrews et al.[18] MMA polymerization by itself is an extremely fast reaction under the conditions stated above, typically ensuring a quantitative monomer conversion within 100 s. Initiation is obviously very rapid since the red color of the initiator disappears instantaneously upon monomer addition and probably faster than propagation considering the rather low polydispersity of the products ($\bar{M}_w/\bar{M}_n \simeq 1.25$). It is typically free from significant self-termination and chain-transfer reactions since the degree of polymerization follows a linear correlation versus monomer conversion, indicating the living nature of the system (Figure 1). The addition of a lithium salt has some influence on the polymerization rate; i.e., LiCl depresses the rate of polymerization by ca. 15% and Li(C_6H_5)$_4$B by ca. 35%, as far as one can judge properly for such fast exothermic reactions. In any case, their living character is maintained (Figure 1), and compared to the other additives investigated here, LiCl leads to a particularly narrow molecular weight distribution (Table I).

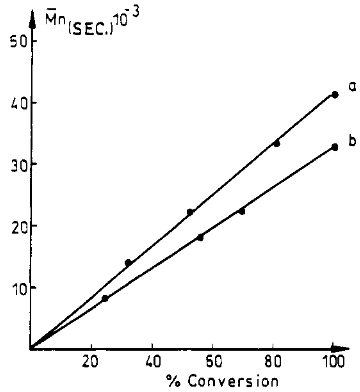

Figure 1. Dependence of $\bar{M}_n$ upon conversion for MMA polymerization by αMSLi in THF at −78 °C (a) in the absence and (b) in the presence of an equimolar amount of LiCl.

Figure 2 compares the experimental $\bar{M}_n$ values to the theoretical ones ($\bar{M}_{n,calc}$), calculated from monomer:initiator molar ratio and conversion assuming a perfectly living system ($\bar{M}_{n,calc} = 100[M]_0/[I]_0 \times$ % conv). Experimental data indicate that some fraction of the initiator is lost, most likely because of side reactions with impurities or ester groups during the initiation step: the measured $\bar{M}_n$ is indeed systematically higher than the theoretically expected value. However, the initiation efficiency f (given by the concentration of growing chains divided by the concentration of the initiator, i.e., $[P]/[I]_0$), is clearly improved by the addition of an equimolar amount of LiCl versus initiator (Table I). Furthermore, increasing the LiCl:initiator molar ratio to a value of 10 leads to a still higher efficiency, well over 90% (see Figure 2 as well as Tables II and III).

Significantly, the molecular weight distribution narrows as the LiCl:initiator ratio increases, and polydispersity values as low as 1.02 can be reproducibly obtained (Table II and Figure 3). It is interesting to note that

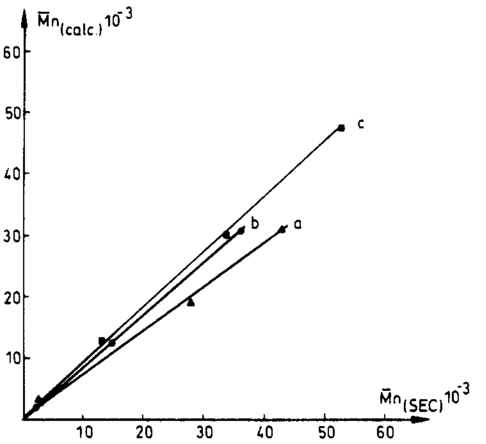

Figure 2. Plots of calculated $\bar{M}_n$ vs experimental values obtained from SEC: (a) without LiCl, $f = 0.70$; (b) with $[LiCl]/[I]_0 = 1$, $f = 0.83$; (c) with $[LiCl]/[I]_0 = 10$, $f = 0.92$. Conditions as in Table II.

when αMS^-Li^+ is used as an initiator in the absence of LiCl, the molecular weight distribution is found to be 1.30 in the initial stage of MMA polymerization and then decreases to 1.20 as the polymerization continues. In the presence of LiCl, the initial molecular weight distribution of the polymer is narrower (1.18 at ca. 25.6% conversion) and then it further narrows to 1.09 at conversion >50%. A similar trend is observed for the other additives reported in Table I. At any rate, SEC data for products obtained at different degrees of conversion clearly prove that polymerization obeys a straightforward living mechanism resulting in narrow molecular weight distribution polymers. These results are in contrast to the observations[12] of Müller and Jeuck, who reported two kinds of active species in the initial stage of MMA polymerization using (1,1-diphenylhexyl)lithium as initiator in THF at −88 °C in the presence of $Li(C_6H_5)_4B$ as a common cation salt. Under these conditions and using a stopped-flow reactor, these authors observed a bimodal distribution for the polymer produced up to 30% conversion, a value only attained in 80 s, while the present systems ensure a quantitative yield in 100 s. At −73 °C, they also reported a rate constant of ca. 15 L mol^{-1} s^{-1}, which is very close to the value of ca. 17 L mol^{-1} s^{-1} obtained from data in Table I.

All of these data demonstrate the remarkable ability and efficiency of such single systems in precisely controlling the synthesis of PMMA's of predetermined molecular weight and very low polydispersity, allowing straightforward preparation of standard samples.

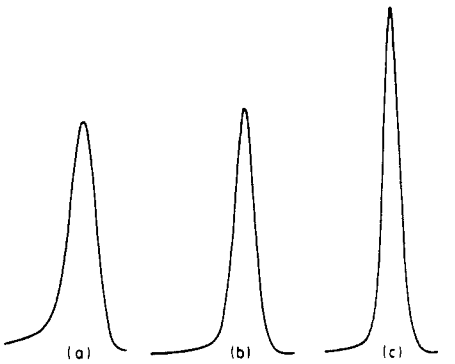

Figure 3. SEC traces for PMMA's prepared as in Table II: (a) without LiCl, $\bar{M}_n = 28\,000$, $\bar{M}_w/\bar{M}_n = 1.20$; (b) $[LiCl]/[I]_0 = 1$, $\bar{M}_n = 15\,000$, $\bar{M}_w/\bar{M}_n = 1.06$; (c) $[LiCl]/[I]_0 = 10$, $\bar{M}_n = 13\,000$, $\bar{M}_w/\bar{M}_n = 1.02$.

Other more sterically hindered initiators have also been considered, i.e., (1,1-diphenyl-3-methylpentyl)lithium and (1,1-diphenylhexyl)lithium (from *sec*-butyllithium + DPE and *n*-butyllithium + DPE, respectively). As expected, they are characterized by an efficiency of ca. 0.95, definitely higher than the one observed for the less hindered αMSLi initiator (Table III). Practically, the initiation efficiency f is the same in the presence or absence of LiCl using such sterically hindered initiators. The effect of LiCl is thus less pronounced when steric hindrance is brought in by the initiator (compared to the less hindered ones in Table I), which might indicate that this ligand has a determinant effect on the initiation step, resulting in PMMA samples of a very narrow molecular weight distribution.

The polarity of the solvent used for these polymerizations is obviously another factor of paramount importance. Indeed, MMA polymerization in a toluene–THF (9:1 v/v) mixture seems to be a complicated and slow process, as evidenced by a broad multimodal distribution, an incomplete conversion (≤50%) after 90 min, and the formation of a gel during the reaction. Again, this situation was modified when polymerization was performed in the presence of an equimolar amount of LiCl with respect to the initiator (Table IV), probably due to its influence on the active species association, as suggested by the practical disappearance of the gel phase. Figure 4 presents a kinetic comparison between the two situations, and clearly illustrates this beneficial effect of the additive on the polymer yield.

SEC data for PMMA's prepared in such a solvent mixture of lower polarity show (Figure 5) that LiCl addition still does not allow for a definitive control of the molecular polydispersity and again leads to a bimodal distribution up to 50% monomer conversion. The data indicate that more than one kind of species is present in the course of the reaction and clearly imply that lower molec-

Table II
Effect of LiCl on the Anionic Polymerization in THF at −78 °C Using αMS^-Li^+ Initiator[a]

[ligand] × 10^{-3}, mol	[αMS^-Li^+] × 10^{-3}, mol	$\bar{M}_{n,calc} \times 10^{-3}$	$\bar{M}_{n,SEC} \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_{n,SEC}/\bar{M}_{n,calc}$	T_g,[b] °C i	T_g,[b] °C m	microstructure % s	microstructure % h	microstructure % i
	1.90	2.5	3.5	1.20	1.41	116	120	79	19.5	1.5
	0.25	19.0	28.0	1.20	1.47	127	132.7	78.5	19.0	2.5
	0.15	30.0	43.0	1.18	1.44	127	132.7			
2.4	2.5	1.9	2.4	1.10	1.26	106	113	73.2	23.0	3.8
0.87	0.87	5.0	6.0	1.08	1.20					
0.38	0.37	12.5	15.0	1.06	1.20	130	133			
0.11	0.12	31.0	36.0	1.06	1.18					
23.5	2.0	2.5	3.0	1.03	1.20	106	113	76.6	19.8	3.6
3.8	0.38	12.5	13.0	1.02	1.04	127	132			
1.1	0.10	47.0	53.0	1.02	1.12	127	134			

[a] Polymerization time 5 min; MMA = 5 mL; THF = 150 mL. [b] T_g's were recorded from second runs; i and m designate beginning and middle of the second-order transition.

Table III
Polymerization of MMA in THF at -78 °C Using (a) (1,1-Diphenylhexyl)lithium or (b) (1,1-Diphenyl-3-methylpentyl)lithium Initiator[a]

ligand	[initiator] × 10^{-3}, mol/L	polymn time, s	conv, %	$\bar{M}_{n,SEC} \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_{n,SEC}/\bar{M}_{n,calc}$	init eff	microstructure		
								% s	% h	% i
	3.0(a)	30	64	11.5	1.15	1.09	0.92			
	3.0(a)	100	100	16.0	1.13	1.04	0.94	81	18	1
$Li(Ph)_4B$	3.0(a)	25	47	9.0	1.16	1.20	0.83			
$Li(Ph)_4B$	3.0(a)	50	75	15.0	1.13	1.25	0.80			
$Li(Ph)_4B$	3.0(a)	100	100	18.0	1.12	1.16	0.86	78	20	2
LiCl	2.2(b)	30	44	10.0	1.09	1.05	0.94			
LiCl	2.2(b)	50	67	15.0	1.09	1.03	0.97			
LiCl	2.2(b)	100	93	22.0	1.09	1.10	0.93	81	18	1

[a] $[Li(Ph)_4B] = 3.0 \times 10^{-3}$ mol/L; $[LiCl] = 2.4 \times 10^{-3}$ mol/L; [monomer] = 0.468 mol/L.

Table IV
Characteristic Data for PMMA's Synthesized in Toluene-THF (9:1 v/v) at -78 °C Using αMS^-Li^+ Initiator[a]

ligand	polymn time, min	conv, %	$\bar{M}_{n,calc} \times 10^{-3}$	$\bar{M}_{n,SEC} \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	T_g, °C		microstructure		
						i	m	% s	% h	% i
	5	14.0	2.5	7.5	2.52	102	111	45	27	28
	15	17.0	3.0	10.5	2.80	86.5	111	56	24	20
	30	24.0	4.5	15.5	2.52			57.4	25.3	17.3
	90	48.0	9.0	18.0	2.52	108.5	117	56	27	17
	300	57.0	10.5	21.0	2.50	107	117			
LiCl	5	9.0	1.7	7.5	2.77	100	109	52.2	26.7	21.1
LiCl	15	25.0	4.7	15.0	2.36	116	123	62.3	25	12.7
LiCl	60	58.0	11.0	19.5	2.35	117	126			
LiCl	90	80.0	15.0	26.0	1.50	117	126	62	25	13

[a] $[\alpha MS^-Li^+] = 2.56 \times 10^{-3}$ mol/L; $[LiCl] = 2.57 \times 10^{-3}$ mol/L; [monomer] = 0.468 mol/L.

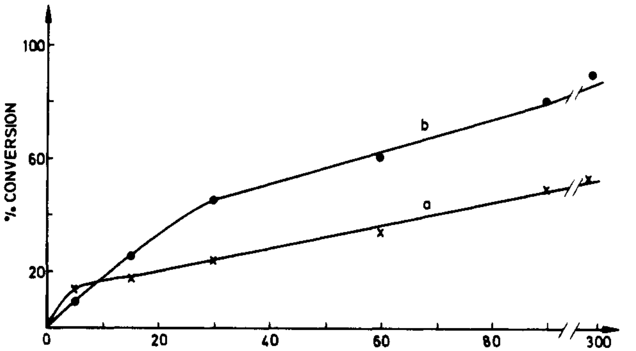

Figure 4. Effect of LiCl on MMA polymerization rate in toluene-THF (9:1 v/v) solvent mixture: (a) without LiCl; (b) with $[LiCl]/[I]_0 = 1$. Conditions as in Table IV.

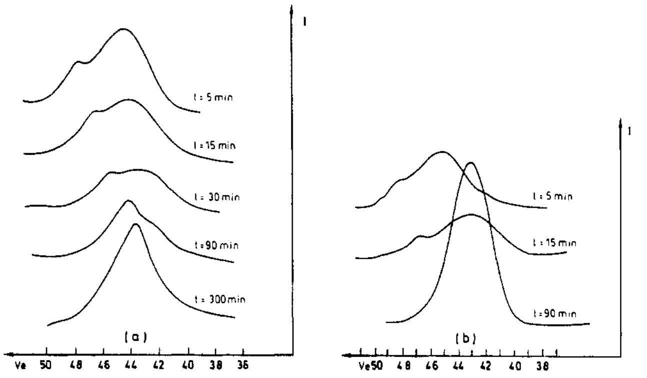

Figure 5. SEC diagrams for PMMA synthesized in a toluene-THF mixture at different conversions: (a) without LiCl; (b) with $[LiCl]/[I]_0 = 1.0$. Conditions as in Table IV.

ular weight species participate in the propagation. However, as that propagation goes on, the polymer produced in the presence of LiCl tends to a unimodal symmetrical distribution with a $\bar{M}_w/\bar{M}_n$ value of 1.5. In order to ascertain whether the polymerization was still a living process under these conditions, we carried out a monomer resumption experiment. SEC traces presented in Figure 6 show that upon addition of the second dose of monomer, the mean molecular weight increased (found: 90×10^{-3}; expected: 38×10^{-3}), while an 87% total conversion was obtained in a 2-h reaction time. This piece of information demonstrates at least a partially living character of the process.

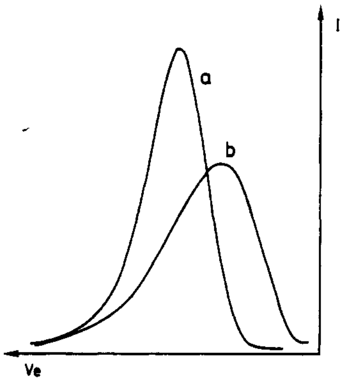

Figure 6. SEC traces for PMMA samples synthesized in a toluene-THF mixture in the presence of LiCl: (a) after polymerization of first monomer dose; (b) after polymerization of second monomer dose. Total conversion 87%. Conditions as in Table IV.

Association-dissociation phenomena are a well-known and determinant feature of lithium-initiated anionic polymerizations.[8,35] To postulate a structure for the possibly complexed growth center in these systems is obviously too hazardous, for the situation is undoubtedly very complicated. Indeed, the simple presence of the additive is certain to shift the classical equilibrium between free ions and ion pairs (solvent-separated or contact ion pairs), notwithstanding the fact that these salts are potentially able to form μ-type complexes with the ion pair, i.e. four-center electron-delocalized entities. Moreover, coordination to carbonyl groups present is probable and has been partially documented.[23,36]

Preliminary ^7Li NMR analyses[29-31] carried out on

αMSLi and oligomeric PMMA-Li have shown that the recorded chemical shifts although intermediate between those of the ion pair and of pure LiCl, do not correspond to the weighted average value expected for a simple statistical ion exchange. Moreover, these shifts do not vary with temperature, in contrast with initiators without LiCl, thus supporting the idea of a true (if reversible) complexation. The growth center in this type of polymerization would thus be "protected" by one (or even two) LiCl molecules, thus decreasing the importance of the secondary reactions. This simple picture obviously calls for further and more in-depth studies, presently being carried out,[37] but as such it is already in close qualitative agreement with all of the data presented above, i.e., the influence of the LiCl:initiator ratio and the effect of solvent on the various kinetic and molecular characteristics of these reactions. It also is in full agreement with Lochmann's studies[23,36] on the formation and properties of adducts between metalloesters and alkali metal alkoxides, in which mechanistic and microstructure considerations confirm complexation and stabilization of the growth center in a nonpolar solvent.

In the present investigation, however, and whatever the solvent used, the added ligand salt does not have any detectable influence on the chain tacticity of the polymers formed. ^{1}H NMR spectra of PMMA samples prepared in THF at −78 °C using αMSLi with or without LiCl are identical (see also microstructure data in all tables) and indicate that the expected complexation of LiCl on the active sites is not tight enough, or does not provide for enough steric hindrance, as to have a significant influence on the stereoselectivity of the propagation reaction. The T_g's of the polymers obtained mainly depend either on the $\bar{M}_n$ (Table II) or on the solvent-controlled microstructure of the polymers (Table IV).

In summary, one can conclude that the addition of common cation salts with proper electronic characteristics represents an interesting and probably quite general strategy for a better control of growth centers in anionic polymerization of (meth)acrylic esters. It may lead to perfect control of polymer molecular weights, while ensuring very low polydispersity, at least when working in polar solvents at low temperature. It also has some beneficial influence on the rate and living character of these processes in lower polarity media.

Up to now, and rather surprisingly, no significant influence of simple salts on the reaction stereoselectivity has been observed, the microstructure being essentially controlled by solvent polarity and temperature.

Acknowledgment. We are deeply indebted to CIPARI and NORSOLOR for their generous help and collaboration as well as to the Services de la Programmation de la Politique Scientifique (Brussels) for their general support. We also express our sincere appreciation to M. C. Guesse and A. M. Vincent for their skilful technical assistance. NMR data were obtained through the facilities of the CREMAN center at the University of Liège, thanks to the helpful collaboration of Dr. R. Warin.

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Registry No. PMMA, 9011-14-7; LiCl, 7447-41-8; LiF, 7789-24-4; LiBr, 7550-35-8; Li(Ph)$_4$, 14485-20-2; α-MSt$^-$Li$^+$, 66050-73-5; (1,1-diphenylhexyl)lithium, 3462-81-5; (1,1-diphenyl-3-methylpentyl)lithium, 66014-41-3.