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Anionic Polymerization of (Meth)acrylic Monomers. 12. Effect of Lithium Chloride on the Stereochemistry of the Anionic Polymerization of Methyl Methacrylate in THF and in a 9/1 Toluene/THF Mixture

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ABSTRACT: The effect of LiCl on the stereochemistry of the anionic polymerization of methyl methacrylate in the presence of a lithium counterion at −78 °C in THF and in a 9/1 toluene/THF mixture, has been studied by ^{13}C and ^{1}H NMR spectroscopy. It has been found that LiCl has an important effect on the *E*/*Z* ratio of the living chain ends in THF, in contrast to the main-chain tacticity. In contrast, LiCl has a significant influence on the stereoregularity of the anionic polymerization of MMA in a 9/1 toluene/THF mixture. When the LiCl/initiator molar ratio is increased, the syndiotactic placements (rr) are favored at the expense of the isotactic ones (mm). This effect can be accounted for by a multistate propagating mechanism controlled by association/complexation equilibria among associated, nonassociated, and LiCl-complexed species. These association/complexation equilibria, which were originally proposed by Müller, appear to have a decisive effect not only on the livingness (molecular weight distribution (MWD)) but also on the stereochemistry of the anionic polymerization of MMA in a 9/1 toluene/THF mixture at −78 °C, confirming the involvement of the ligand in propagation control.

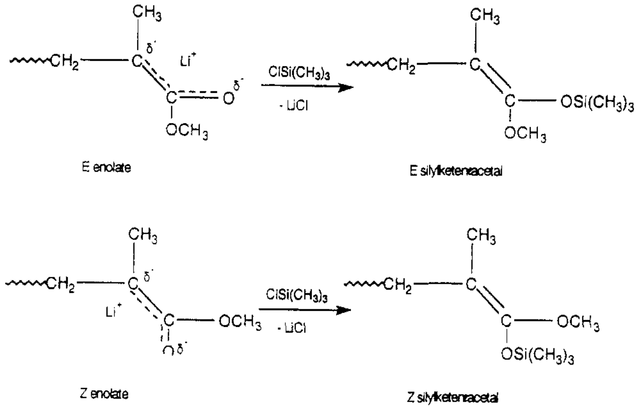
Introduction

It has been shown from this laboratory that μ-coordinating inorganic salts such as lithium chloride (LiCl) are effective in promoting the perfectly "living" anionic polymerization of methacrylic esters (e.g., methyl methacrylate (MMA)) and hindered acrylic esters (e.g., *tert*-butyl acrylate (tBuA)) in THF at low temperatures. That discovery has opened new practical avenues for producing valuable (meth)acrylate-based products,[1] i.e., block copolymers, end-functionalized oligomers, and star-shaped polymers, with a high efficiency (>90%) and a very narrow molecular weight distribution (M_w/M_n down to ca. 1.02).

In addition, the ligated (ligand-modified) polymerization has proven to be useful in studying the mechanism of the anionic polymerization of (meth)acrylates. Indeed, Müller et al. have used LiCl as a probe in the kinetic study of MMA and tBuA living anionic polymerization in the presence of a lithium counterion in THF at low temperatures[2] and accordingly revealed the important role of association/complexation equilibria among associated, nonassociated, and LiCl–complexed species. Furthermore, ^{13}C and ^{7}Li NMR analyses of methyl α-lithioisobutyrate (MIBLi) in THF i.e., a monomeric model for the living $PMMA^-Li^+$ chain end, have shown that addition of LiCl to coexisting tetrameric and dimeric MIBLi species causes a spontaneous mixed complexation with formation of a single type of LiCl-complexed species at LiCl/MIBLi = 1, 2, and ≥3.[3] It has been suggested that the fast addition of the monomer to that unique type of LiCl-complexed propagating species is at the origin of the perfectly living anionic polymerization of MMA in THF at low temperatures.

To gain a deeper insight into LiCl-modified anionic polymerization of MMA, it is thus of great interest to further investigate how LiCl affects the stereochemistry of the polymerization. This paper is concerned with the stereochemistry of MMA anionic polymerization at −78 °C in THF and in a 9/1 toluene/THF mixture in the presence of lithium as a counterion and LiCl as a ligand.

Scheme I



Experimental Section

Methyl methacrylate was polymerized under moisture- and air-free conditions (usually 5 g of monomer in 100 mL of solvent) using (diphenylmethyl)lithium (DPMLi), (diphenyhexyl)lithium (DPHLi), or αMSt^-Li^+ as an initiator. Purification of monomer and solvents and polymerization techniques were described in detail elsewhere.[1b]

The analysis of the *E*/*Z* isomerism of the chain ends relied upon the silylation of the living $PMMA^-Li^+$ chains with a 10-fold molar excess of $ClSi(CH_3)_3$ (Scheme I).[4] After the solvent was evaporated, the silylated polymer was dissolved in dry $CDCl_3$ (25 wt %) and transferred into an NMR tube, which was sealed under vacuum. It is important to state here that it has been established that silylation of the ester is very fast and renders information on the instantaneous *E*/*Z* ratio.[4]

The ^{1}H and ^{13}C NMR spectra were recorded at 20 °C with a Bruker AM-400 spectrometer operating at 400 and 100 MHz, respectively. An inverse-gated proton decoupling technique was applied to perform quantitative analysis of ^{13}C NMR spectra.

Size exclusion chromatography (SEC) was carried out with a Hewlett-Packard 1090 liquid chromatography equipped with four columns (10^5, 10^3, 500, and 100 Å) and a Hewlett-Packard 1030A refractive index detector.

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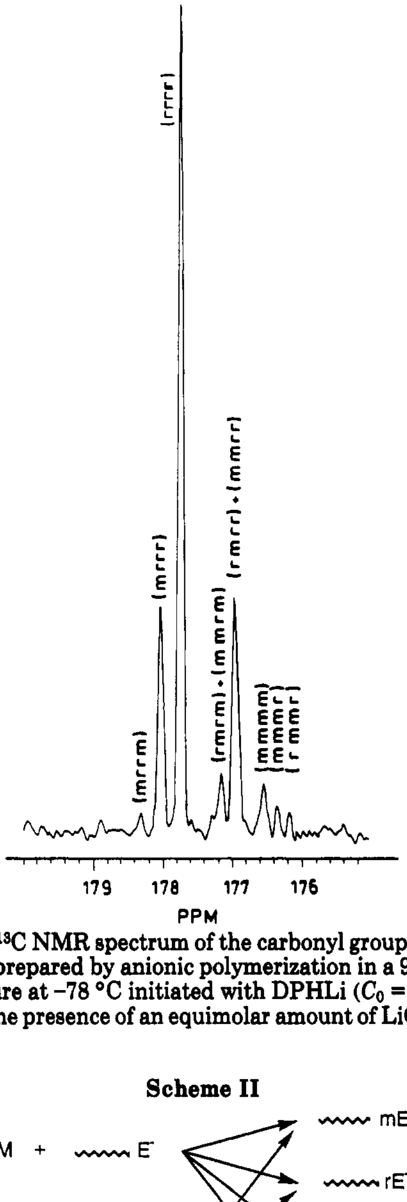
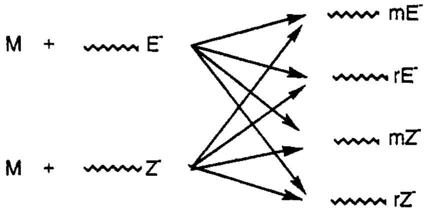


Figure 1. ^{13}C NMR spectrum of the carbonyl group (100 MHz) of PMMA prepared by anionic polymerization in a 9/1 toluene/THF mixture at −78 °C initiated with DPHLi ($C_0 = 2.56 \times 10^{-3}$ mol/L) in the presence of an equimolar amount of LiCl. Solvent = $CDCl_3$.

Scheme II



Results and Discussion

The main-chain tacticity of PMMA was calculated from the ^{13}C NMR of the C═O group and/or the ^1H NMR of the α-methyl group. The ^{13}C NMR resonance of the ester carbonyl group is recorded in the region 176–179 ppm with respect to the central peak of $CDCl_3$ at 77.2 ppm. It is well split into pentads (Figure 1), the assignment of which has been proposed by Peat and Reynolds.[5] The underlying tetrad placements can be calculated from the intensities of pentads according to the following equations.[6]

$$\begin{gathered}(\mathrm{mmm}) = (\mathrm{mmmm}) + {}^1/_2(\mathrm{mmmr})\\ (\mathrm{mmr}) = (\mathrm{mmmr}) + 2(\mathrm{rmmr})\\ (\mathrm{mrm}) = {}^1/_2(\mathrm{mmrm}) + {}^1/_2(\mathrm{mrmr})\\ (\mathrm{mrr}) = 2(\mathrm{mrrm}) + (\mathrm{mrrr})\\ (\mathrm{rrr}) = (\mathrm{rrrr}) + {}^1/_2(\mathrm{mrrr})\\ (\mathrm{mmm}) + (\mathrm{mmr}) + (\mathrm{mrm}) + (\mathrm{mrr}) + (\mathrm{rmr}) + (\mathrm{rrr}) = 1\end{gathered} \tag{1}$$

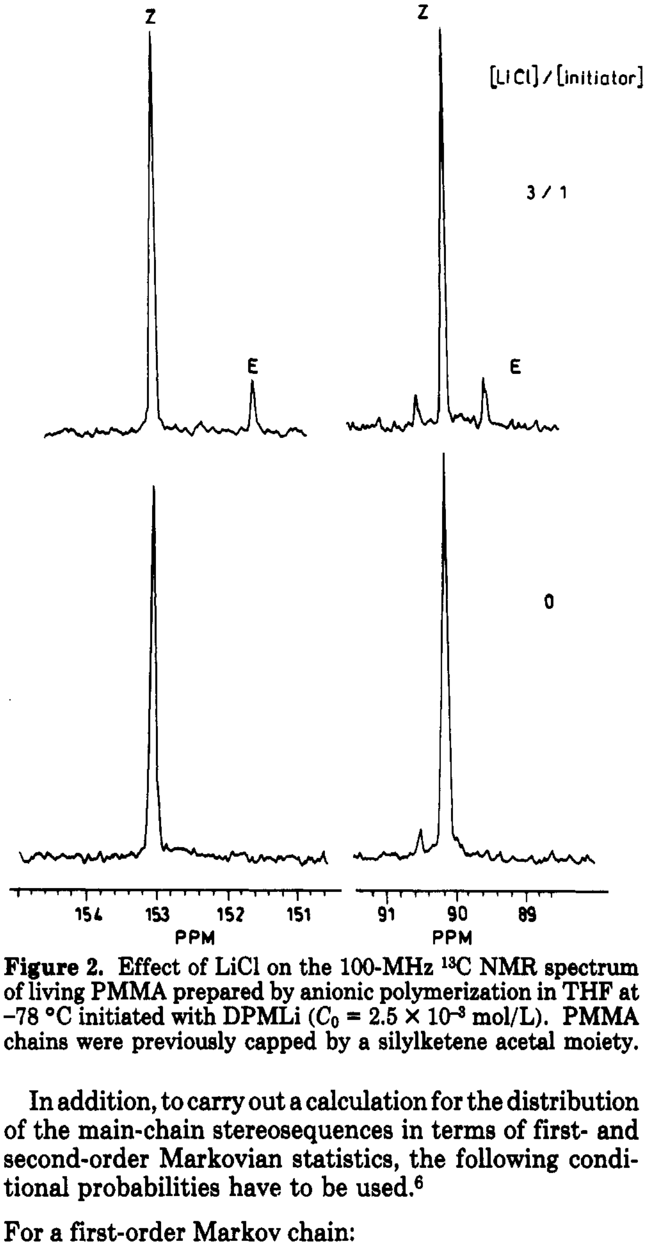


Figure 2. Effect of LiCl on the 100-MHz ^{13}C NMR spectrum of living PMMA prepared by anionic polymerization in THF at −78 °C initiated with DPMLi ($C_0 = 2.5 \times 10^{-3}$ mol/L). PMMA chains were previously capped by a silylketene acetal moiety.

In addition, to carry out a calculation for the distribution of the main-chain stereosequences in terms of first- and second-order Markovian statistics, the following conditional probabilities have to be used.[6]

For a first-order Markov chain:

$$\begin{gathered}P_{\mathrm{mr}} = 1 - P_{\mathrm{mm}} = (\mathrm{mr})/2(\mathrm{m})\\ P_{\mathrm{rm}} = 1 - P_{\mathrm{rr}} = (\mathrm{mr})/2(\mathrm{r})\end{gathered} \tag{2}$$

where P_{mr} is the probability of a monomer adding in r fashion to a chain ending in m, and so on.

For a second-order Markov chain:

$$\begin{gathered}P_{\mathrm{mmm}} = (\mathrm{mmm})/(\mathrm{mm})\\ P_{\mathrm{mmr}} = (\mathrm{mmr})/2(\mathrm{mm})\\ P_{\mathrm{mrm}} = 2(\mathrm{mrm})/(\mathrm{mr})\\ P_{\mathrm{mrr}} = (\mathrm{mrr})/(\mathrm{mr})\\ P_{\mathrm{rmm}} = (\mathrm{mmr})/(\mathrm{mr})\\ P_{\mathrm{rmr}} = 2(\mathrm{rmr})/(\mathrm{mr})\\ P_{\mathrm{rrm}} = (\mathrm{mrr})/2(\mathrm{rr})\\ P_{\mathrm{rrr}} = (\mathrm{rrr})/(\mathrm{rr})\end{gathered} \tag{3}$$

where P_{mmm} is the probability of a monomer adding in m fashion to a chain ending in mm, and so on.

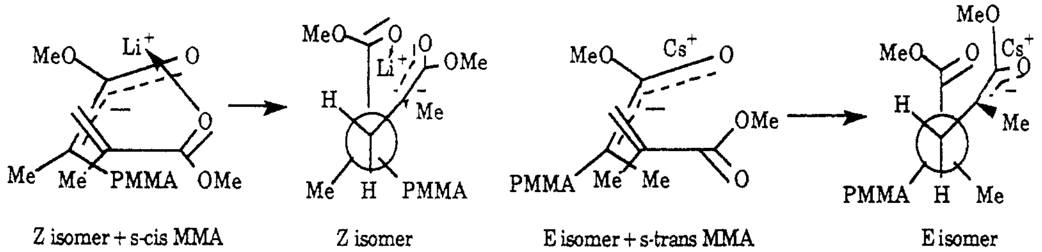
Stereochemistry of the MMA Anionic Polymerization in THF at −78 °C by Using DPMLi as an Initiator. The effect of LiCl on the tacticity of PMMA

Table I. Fractions of Pentads, Triads, and Diads in Poly(methyl methacrylate) (PMMA) Anionically Prepared in THF at -78 °C Using DPMLi as an Initiator (I) and Lithium Chloride as a Ligand and Fit of Pentads to First-Order Markovian Statistics[a]

	LiCl/I[b] = 0		LiCl/I = 1		LiCl/I = 5	LiCl/I = 10	
	exptl	calcd	exptl	calcd	exptl	exptl	calcd
(mmmm)	0	0	0	0		0	0
(mmmr)	0	0	0	0		0	0
(rmmr)	0.01	0.01	0.01	0.01		0.01	0.01
(rmrm)							
(mmrm)	0.03	0.03	0.03	0.03		0.04	0.04
(rmrr)							
(mmrr)	0.18	0.19	0.19	0.19		0.17	0.17
(mrrm)	0.02	0.01	0.01	0.01		0.02	0.01
(mrrr)	0.17	0.16	0.17	0.16		0.16	0.16
(rrr)	0.59	0.60	0.59	0.60		0.60	0.61
(mm)	0.01		0.01		0.01	0.10	
(mr)	0.21		0.21		0.20	0.20	
(rr)	0.78		0.78		0.79	0.79	
(m)	0.115		0.115		0.11	0.11	
(r)	0.885		0.885		0.89	0.89	
ρ[c]	0.97		0.97		0.98	0.98	

[a] Initiator concentration = 2.5×10^{-3} mol/L. [b] mol/mol. [c] The persistence ratio, $\rho = 2(m)(r)/(mr)$.

Scheme III



prepared in THF at -78 °C is shown in Table I. In the absence of LiCl, there is a marked preference for a syndiotactic (rr) placement (ca. 78%), in accordance with numerous other works.[4] Moreover, a fit of pentads to first-order Markovian statistics is given, also in good agreement with the results of most other investigations on the same system.[4]

The addition of LiCl to the polymerization system (up to a 10/1 LiCl/initiator molar ratio) has no significant effect on the main-chain tacticity of the resulting PMMA (Table I). Changes in the content of diads, triads, and pentads as well as the persistence ratio, ρ (=2(m)(r)/(mr)), are within the limits of experimental error.

It is thus clear that LiCl has no effect on the stereoregularity of the anionic polymerization of MMA in THF at -78 °C. This is surprising, since LiCl has been shown to perturb the negative charge distribution on the active center,[3b] the polymerization kinetics,[2] and the molecular weight distribution[1b,2] under the same experimental conditions.

It is worth recalling that Müller and Hogen-Esch have recently demonstrated that the PMMA main-chain tacticity could be determined by the *E*/*Z* stereoisomerism of the living chain ends (Scheme II).[4] When Li is the counterion, the living chain ends essentially exist as the *Z* isomer, which mainly produces racemic placements.

To understand why the stereoregularity of the anionic polymerization of MMA in THF is unaffected by LiCl, the *E*/*Z* ratio of the chain ends has been measured by ^{13}C NMR analysis of the quaternary carbon at 89–91 ppm and the carbonyl carbon at 151–154 ppm of the parent silylated adducts. It is obvious from Figure 2 that the complexation of active chain ends by LiCl leads to a considerable increase in the *E*/*Z* ratio. The percentage of *Z* enolate indeed decreases from ca. 100% to 88.5% upon the addition of 3 equiv of LiCl per initiator (Table II).

Table II. Effect of LiCl on the *E*/*Z* Ratio of Chain Ends and the Triad Fraction of PMMA Prepared in THF at -78 °C in the Presence of a Lithium Counterion[a]

LiCl/initiator (mol/mol)	*E*/*Z*[b]	(mm)[c]	(mr)[c]	(rr)[c]
0	ca. 0/100	1.2	20.8	78.0
3	11.5/88.5	1.0	20.0	79.0

[a] Initiator = DPMLi, concentration = 7×10^{-3} mol/L. [b] ^{13}C NMR data characteristic of the C═O group. [c] ^{13}C NMR data characteristic of the quaternary carbon atom of silylated and subsequently hydrolyzed PMMA.

At this point, these results clearly lead to two important questions. First, why does the complexation of living ends by LiCl significantly increase its *E*/*Z* ratio? According to Müller and Hogen-Esch, the *E*/*Z* ratio of the living PMMA ends is critically determined by the *s-cis* or *s-trans* monomer approach.[4] For the smallest counterion, i.e., Li^+, the *s-cis* approach (leading to *Z* chain ends) would be favored due to coordination of the monomer carbon group to the counterion in the transition state, whereas for larger counterions, e.g., Cs^+, *s-trans* results from steric reasons (leading to *E* chain ends) (Scheme III). In reference to the above explanation, the complexation of active species by LiCl might perturb the coordination of monomer to the lithium counterion by a steric effect and/or a competitive coordination. In that respect, the *s-trans* monomer approach should be somewhat more favorable and consequently lead to the formation of a considerable amount of *E* isomer.

Although the increase in *E*/*Z* ratio for LiCl-complexed chain ends seems to be reasonably explained in the way described above, the poor correlation between the *Z*/*E* ratio and the main-chain tacticity is still very puzzling (Table II). A possible, although speculative, interpretation might be that the LiCl-complexed Li^+/E isomer displays a very low reactivity and, to some extent, would accordingly

Table III. Experimental and Calculated Pentad Composition of Poly(methyl methacrylate) Anionically Prepared in a 9/1 Toluene/THF Mixture at −78 °C in the Presence of a Lithium Counterion[a]

	exptl	Bernoullian	1st-order Markov	2nd-order Markov
(mmmm)	0.14	0.01	0.06	0.15
(mmmr)	0.03	0.04	0.08	0.05
(rmmr)	0.01	0.04	0.03	0.00
(rmrm)				
(mmrm)	0.11	0.13	0.05	0.11
(rmrr)				
(mmrr)	0.16	0.29	0.21	0.16
(mrrm)	0.02	0.04	0.02	0.01
(mrrr)	0.13	0.21	0.17	0.14
(rrrr)	0.40	0.24	0.38	0.38
(mmm)[b]	0.16			
(mmr)	0.05			
(mrm)	0.06			
(mrr)	0.17			
(rmr)	0.09			
(rrr)	0.47			
(mm)	0.17			
(mr)	0.25			
(rr)	0.58			
(m)	0.30			
(r)	0.70			
ρ	1.68			

[a] Initiator = αMStLi, initiator concentration = 2.56×10^{-3} mol/L, monomer conversion = 48%. [b] Calculated from eq 1.

Table IV. Effect of the Initiator (I) Concentration on the Triad Composition of PMMA Anionically Prepared in a 9/1 Toluene/THF Mixture at −78 °C in the Presence of a Lithium Counterion[a,b]

(I) (mol/L)	(rr)	(mr)	(mm)	ρ
3.0×10^{-4}	62.4	28.1	9.5	1.28
2.56×10^{-3}	57.5	25.4	17.1	1.65
1.0×10^{-2}	47.7	32.2	20.1	1.43

[a] Initiator = DPHLi. [b] Monomer conversion = ca. 50%. $\overline{M}_n \simeq$ 25000.

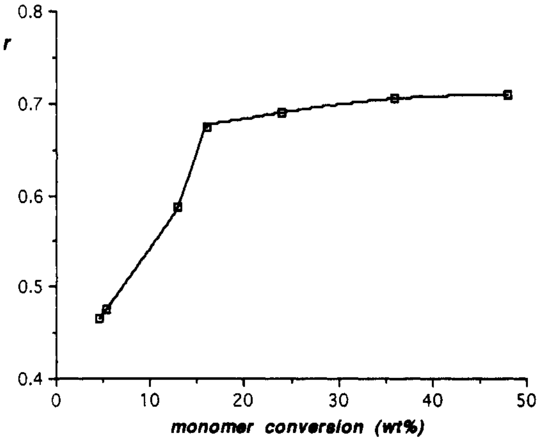


Figure 3. Effect of monomer conversion on the racemic placement in the anionic polymerization of MMA in a 9/1 toluene/THF mixture at −78 °C in the presence of Li counterion. Initiator = αMSt$^-$Li$^+$, concentration = 2.56×10^{-3} mol/L.

Table V. Dependence of Microtacticity of PMMA Anionically Prepared in a 9/1 Toluene/THF Mixture at −78 °C on Monomer Conversion (conv) and Polymerization Degree (DP)[a]

conv	DP[b]	(mm)	(mr)	(rr)	(m)	(r)
5.4	20	0.36	0.33	0.30	0.54	0.46
13.0	82	0.28	0.28	0.44	0.42	0.58
17.0	100	0.19	0.24	0.57	0.31	0.69

[a] Initiator = αMStLi, concentration = 2.56×10^{-3} mol/L. [b] SEC data.

behave as a "stereoselectively dormant species".

Moreover, the results in Table II are in a sharp contrast to the observation that, in the anionic polymerization of MMA in THF, both main-chain tacticity and *E*/*Z* isomerism of the chain ends are simultaneously modified when a K counterion is complexed by K222 in THF.[4] Therefore, one may conclude that mixed complexation (LiCl/PMMA$^-$Li$^+$), i.e., a μ-type complexation, and cation-binding complexation (cryptand 222/PMMA$^-$K$^+$), i.e., a σ-type complexation, affect quite differently the stereochemistry of the anionic polymerization of MMA in THF at a low temperature.

Stereochemistry of MMA Anionic Polymerization by Using αMStLi as an Initiator in a 9/1 Toluene/THF Mixture at −78 °C in the Absence of LiCl. To get a better understanding of the effect of LiCl on the stereochemistry of MMA anionic polymerization, THF was replaced by a 9/1 toluene/THF mixture. It is indeed well known that the stereochemistry of that anionic polymerization is quite different in toluene/10% THF as compared to that in pure THF or in pure toluene.[7] Furthermore, LiCl considerably enhances the livingness of the MMA anionic polymerization in such a mixture at −78 °C.[1b]

Table III shows that, in a 9/1 toluene/THF mixture and in the absence of LiCl, the isotactic fraction (mm) dramatically increases compared to the isotactic fraction observed in THF. The increase in the (mm) content from 0.01 to 0.17 is essentially observed at the expense of the (rr) triads that decline from 0.78 to 0.58, in agreement with previously reported data.[7]

Furthermore, the stereochemistry of the MMA polymerization in a 9/1 toluene/THF mixture appears to be inconsistent with a Bernoullian process since the persistence ratio, ρ, is much larger than 1 (Table III). The comparison of the observed pentads with the calculated ones, however, gives credit to a second-order Markovian statistics, not to a first-order one (Table III). At this point, it is necessary to stress that the validity of second-order Markovian statistics only means consistency with such a process that can accommodate virtually all non-Bernoullian processes. Coleman-Fox[9] or *E*–*Z*[4] processes (or a combination) should readily accommodate the data as well.

Suzuki et al. have also analyzed the distribution of the stereosequences in PMMA anionically prepared at −78 °C by using BuLi as an initiator in toluene–THF mixtures varying from 100/1 to 10/30 by volume. In contrast to the present results, they reported that the process obeyed neither Bernoullian nor any order Markovian statistics.[7a] They concluded, however, that the PMMA microstructures were very simply approximated by combinations of the structures found for polymers formed in pure toluene and in pure THF, respectively. We do not have a definite reason for the apparent disagreement between the results of Suzuki et al. and this study but suspect that the difference in the initiators employed in the two studies might be a reasonable explanation.

Effects of Initiator Concentration and Monomer Conversion on the Microtacticity of PMMA Prepared by Using αMStLi as an Initiator in 9/1 Toluene/THF Mixture at −78 °C in the Absence of LiCl. It is worth pointing out that the tacticity of PMMA prepared in the 9/1 toluene/THF mixed solvent is strongly dependent on both the initiator concentration (Table IV) and the monomer conversion (Figure 3 and Table V). Actually, syndiotactic triads (rr) drop from ca. 0.62 to 0.48 as the initiator concentration increases from 3×10^{-4} to 10^{-2} mol/L (Table IV). Conversely, the fraction of isotactic triads

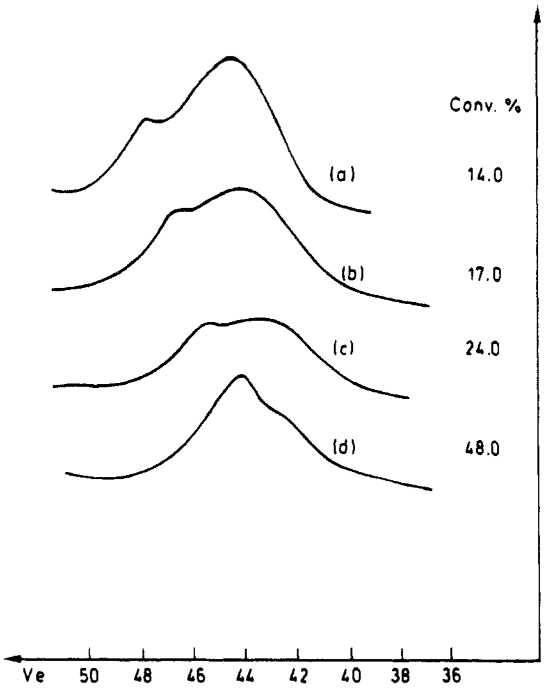


Figure 4. Effect of monomer conversion on the size exclusion chromatogram of PMMA synthesized in a 9/1 toluene/THF mixture, at −78° C in the presence of Li counterion (see ref 1b). Initiator = αMSt$^-$Li$^+$; concentration = 2.56 × 10^{-3} mol/L.

increases from 0.10 to 0.20. Moreover, it must be pointed out that the persistence ratio, ρ, goes through a maximum as a function of the initiator concentration (Table IV), for which no satisfactory explanation can be proposed now. Furthermore, it can be clearly noted from Table V and Figure 3 that an increase in the monomer conversion from 5% (polymerization degree (DP) of ca. 20) to 17% (DP close to 100) results in a rapid increase in the racemic fraction (r), from 0.46 to 0.70. These experimental observations might be accounted for by an equilibrium between species of different association degrees and accordingly of different contribution to the racemic or meso placements. This association equilibrium should be sensitive to the concentration of active species (i.e., to initiator concentration) and to the polymerization degree (i.e., to monomer conversion). Since the association degree of the propagating species is expected to decrease upon increasing monomer conversion and decreasing the initiator concentration, the observed increase in (rr) (or decrease in (mm)) with increasing monomer conversion and decreasing initiator concentration might suggest that nonassociated (or less associated) species essentially contribute to racemic placements.

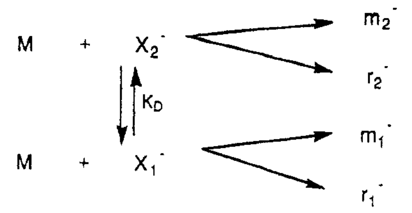
The hypothesis of an association equilibrium in PMMA$^-$Li$^+$ solutions is convincingly supported by a series of pertinent observations:

(i) The kinetics of the anionic polymerization of MMA (Li$^+$ counterion, THF, low temperature) could only be understood if an association equilibrium between associated and nonassociated ion pairs is involved.[2]

(ii) ^{13}C and ^{7}Li NMR analyses of methyl α-lithioisobutyrate (MIBLi), which foreshadows the active species of PMMA$^-$Li$^+$, have demonstrated that an equilibrium with slow interconversion between two differently aggregates species prevails in a 9/1 toluene/THF medium.[3]

(iii) The molecular weight distribution (MWD) of the PMMA samples of Figure 3 is clearly bimodal (Figure 4), which gives credit to at least two propagating species present. Moreover, both peaks gain molecular weight during monomer conversion, revealing that they are all active.

Scheme IV



From the aforementioned arguments, an equilibrium between two propagating species, i.e., associated and less (non) associated species, is a reasonable assumption. Obviously, the rate of exchange between them is slower than that of the addition of the monomer to growing species.[2,8]

On that basis, the two-state model originally proposed by Coleman and Fox[9] would account for the experimental observations reported in this work. According to Scheme IV, there is a slow interconversion between the associated active species (X_2^-) and the nonassociated (or less associated) one (X_1^-), selectively producing the meso and racemic placements, respectively. Since the monomer addition to the active centers is faster than the $X_1^- \rightleftharpoons X_2^-$ interconversion, a distribution of stereosequences in the polymer chain should occur in relation to the initiator concentration and the monomer conversion. Moreover, such a process should be inconsistent with the Bernoullian statistics.[4]

Actually, several research teams have shown that the anionic polymerization of MMA in toluene/THF mixed solvents is fairly consistent with the two-state model illustrated in Scheme IV.[7] The present work gives additional credit to that model and also indicates that these two states may correspond to the differently associated species indicated by experimental observations.

As this point, it is, however, important to state that the two-state mechanism only describes the overall distribution of stereosequences as promoted by stereoselective species. The stereochemistry of each propagating species may possibly be controlled by the *E*/*Z* mechanism[4] and/or the "penultimate" mechanism,[6] this "penultimate" mechanism assuming that the probability of a given placement depends on whether the preceding monomer diad is meso or racemic.[6]

Effects of LiCl on the Stereochemistry of the MMA Anionic Polymerization by Using DPHLi as an Initiator in a 9/1 Toluene/THF Mixture at −78 °C. The triad, tetrad, and pentad distributions in PMMA anionically prepared in the presence of various amounts of LiCl are reported in Table VI. In sharp contrast to the results in pure THF, LiCl promotes a substantial modification of the stereoregularity in 9/1 toluene/THF mixed solvent (Table VI and Figure 5). Indeed, the isotactic fraction, (mm), decreases by a factor of ca. 3 (0.06 against 0.17), and the syndiotactic one, (rr), increases by ca. 20% (from 0.58 up to 0.69), when only 1 equiv of LiCl is added to the system. Upon the addition of 2 molar equiv of LiCl, the tacticity changes further in the same direction, tending to that one observed in pure THF. When the LiCl/initiator molar ratio is increased further, no change occurs.

Furthermore, Table VI also shows that there is agreement between the experimental pentads fractions and the data calculated from the first-order Markovian statistics, at least when the LiCl/initiator ratio is ≥2. Second-order Markovian statistics, however, fits the experimental data for the system with a 1/1 LiCl/initiator ratio.

Table VI. Fraction of Pentads, Tetrads, Triads, and Diads of PMMA Prepared by Anionic Polymerization in a 9/1 Toluene/THF Mixture at −78 °C in the Presence of a Lithium Counterion and Various Amounts of LiCl and Fit of Pentads to the First-Order (1st) and Second-Order (2nd) Markovian Statistics[a]

	LiCl/I[b] = 1/1			LiCl/I = 2/1		LiCl/I = 3/1		5/1
LiCl/initiator[b]	exptl	1st	2nd	exptl	1st	exptl	1st	exptl
(mmmm)	0.04	0	0.03	0	0	0	0	
(mmmr)	0.02	0.02	0.02	0.01	0.01	0.01	0.01	
(rmmr)	0.01	0.03	0.01	0.02	0.02	0.03	0.02	
(rmrm)								
(mmrm)	0.05	0.04	0.06	0.05	0.03	0.06	0.04	
(rmrr)								
(mmrr)	0.19	0.21	0.19	0.20	0.21	0.21	0.22	
(mrrm)	0.02	0.02	0.01	0.02	0.01	0.02	0.02	
(mrrr)	0.15	0.18	0.16	0.18	0.18	0.17	0.18	
(rrr)	0.52	0.50	0.51	0.52	0.54	0.50	0.51	
(mmm)[c]	0.04							
(mmr)	0.04							
(mrm)	0.03							
(mrr)	0.19							
(rmr)	0.11							
(rrr)	0.59							
(rr)	0.69			0.73		0.72		0.72
(mr)	0.25			0.24		0.25		0.25
(mm)	0.06			0.04		0.03		0.03
(m)	0.185			0.15		0.155		0.155
(r)	0.815			0.85		0.845		0.845
ρ	1.21			1.06		1.05		1.05

[a] Initiator (I) = DPHLi, initiator concentration = 2.56×10^{-3} mol/L, monomer conversion > 80%. [b] mol/mol. [c] Calculated from eq 1.

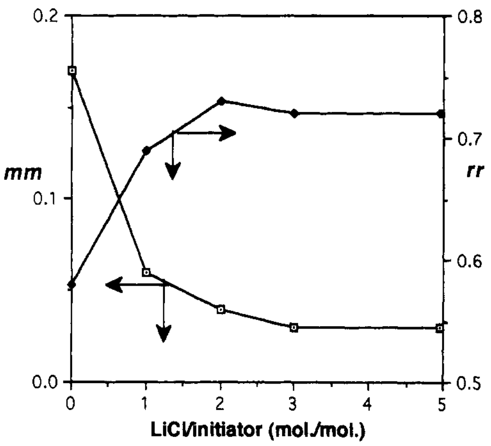


Figure 5. Effect of LiCl/initiator molar ratio on the trial fraction of PMMA anionically prepared in a 9/1 toluene/THF mixture at −78 °C in the presence of Li counterion. Initiator = DPHLi, concentration = 2.56×10^{-3} mol/L.

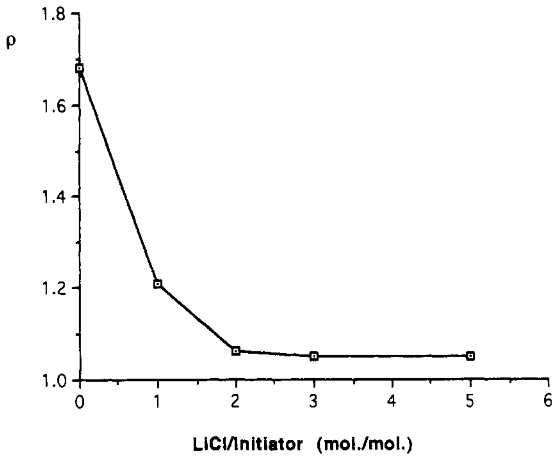


Figure 6. Effect of LiCl/initiator molar ratio on the persistence ratio, ρ, of PMMA synthesized in a 9/1 toluene/THF mixture at −78 °C in the presence of Li counterion. Initiator = DPHLi, concentration = 2.56×10^{-3} mol/L.

Finally, a change in slope of the persistence ratio, ρ, versus the LiCl/initiator molar ratio is clearly observed when a twofold molar excess of LiCl is used (Figure 6).

All together, these results clearly indicate that increasing amounts of LiCl substantially perturbs the stereochemistry of the MMA anionic polymerization in a 9/1 toluene/THF mixture in a way which strongly suggests a complex equilibrium between the growing active species and LiCl, so controlling the propagation placements.

Conversely, on top of its effect on the stereochemistry of the MMA anionic polymerization in that medium, LiCl also affects the molecular weight distribution (MWD) of the polymers (Figure 7). Indeed, in the absence of LiCl, the MWD is bimodal (Figure 4c), and the apparent polydispersity index (M_w/M_n) is ca. 2.50. Upon addition of LiCl, a unimodal distribution is observed (Figure 8), the polydispersity index decreasing as the LiCl/initiator molar ratio is increased (Figure 7). At a LiCl/initiator molar ratio ≥4, the MWD drops to ca. 1.17 with a symmetrical distribution (Figure 8b)! At this point, one may already conclude that LiCl affects not only the livingness of the anionic polymerization process as previously reported[1b] but also the stereochemistry.

A further examination of the effects of LiCl on stereochemistry and molecular weight distribution, however, reveals some differences. The considerable influence of LiCl on stereochemistry is found to be limited at ca. 2/1 LiCl/initiator ratio, whereas the beneficial effect of LiCl on the MWD appears up to ca. 4/1 LiCl/initiator molar ratio (Figure 7). Apparently, LiCl has a somewhat different effect on these two processes.

On the basis of kinetic studies, Müller has recently proposed that the association/complexation equilibria play an important role in promoting living anionic polymerization of (meth)acrylates in THF at low temperature,[2] a fact that has been confirmed by us on the basis of NMR studies of related model systems.[3] In the absence of LiCl, an association equilibrium with relatively slow interconversion dominates the behavior of the propagating PMMA$^-$Li$^+$ species. Complexation of the growing chain ends by LiCl results in the depletion of the associated species and, accordingly, in a narrow MWD.[2,3]

Assuming the aforementioned association/complexation equilibria in THF also prevail in a 9/1 toluene/THF mixture (Scheme V), the general behavior of varied MWDs

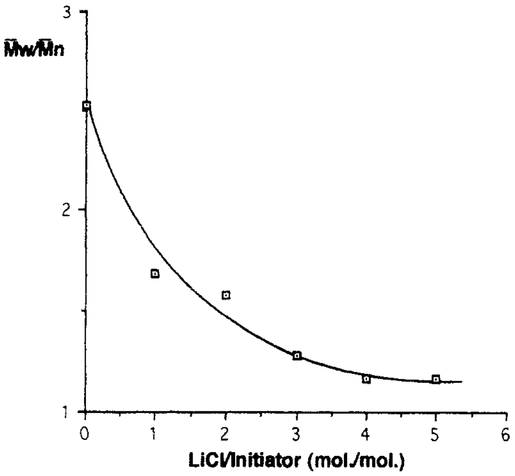


Figure 7. Effect of LiCl/initiator molar ratio on the polydispersity index ($\bar{M}_w/\bar{M}_n$) of PMMA synthesized in a 9/1 toluene/THF mixture at −78 °C in the presence of Li counterion. Initiator = DPHLi, concentration = 2.56 × 10^{-3} mol/L.

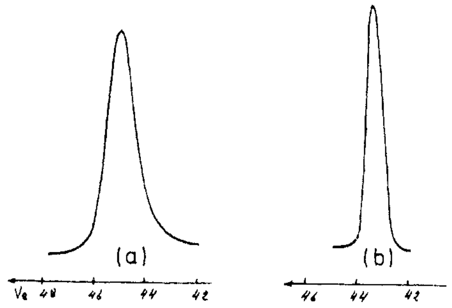


Figure 8. Size exclusion chromatograms of PMMA anionically prepared in a 9/1 toluene/THF mixture, at −78 °C at various LiCl/initiator molar ratios: (a) LiCl/I = 1, $\bar{M}_n$ = 42000, $\bar{M}_w/\bar{M}_n$ = 1.70; (b) LiCl/I = 4, $\bar{M}_n$ = 56000, $\bar{M}_w/\bar{M}_n$ = 1.15. Initiator = DPHLi, concentration = 2.56 × 10^{-3} mol/L.

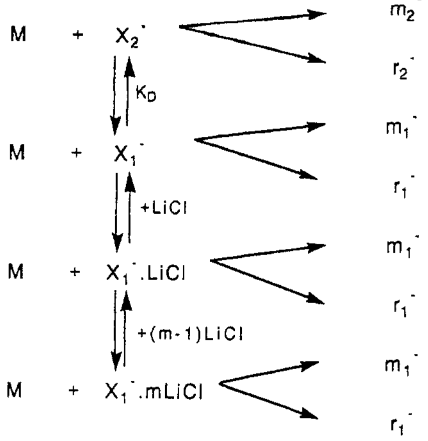
with LiCl/initiator molar ratio can be expressed as follows:

(i) At a high LiCl/initiator molar ratio (≥4/1), only the LiCl-complexed active species (X_1^-LiCl and $X_1^-\cdot m$LiCl) are present. Since the interconversion of the LiCl-complexed species is generally very fast,[2] a narrow MWD can be expected.

(ii) At a LiCl/initiator <4, the nonassociated species (X_1^-) and LiCl-complexed species (may be also associated species (X_2^-)) coexist in the system, leading to a relatively broader MWD, provided that the rate of exchange among these active species is not so fast as compared with that of monomer addition.

The fact that the global stereochemistry of polymerization remains identical when the LiCl/initiator molar ratio is decreased from 4/1 to 2/1 can only be understood if various LiCl-complexed species produce the same stereoselectivity as the LiCl-free nonassociated species, since it has been established that LiCl-free associated species affect that stereochemistry in a different way (see above). This might also give credit to the absence of associated species at LiCl/initiator molar ratios ≥ 2.

Scheme V



In conclusion, the results reported in this paper clearly indicate that LiCl not only affects the livingness of the anionic polymerization of MMA but also its stereochemistry in a 9/1 toluene/THF mixture, strongly supporting the idea that this LiCl ligand is bound to the active site throughout chain propagation (not observed in pure THF). The effects of various types of ligands on the stereochemistry of other methacrylate polymerizations in different solvents are under current investigation.

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