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Anionic Polymerization of Acrylic Monomers. 19. Effect of Various Types of Ligands Other Than Lithium Chloride on the Stereochemistry of Anionic Polymerization of Methyl Methacrylate

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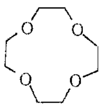
ABSTRACT: The effect of several types of ligands, i.e., 12-CE-4 (**1**), K211 (**2**), LiOtBu (**3**), and LiOEEM (**4**), on the stereochemistry of MMA anionic polymerization at −78 °C in various solvents, i.e., toluene, THF, and a 9/1 toluene/THF mixture, has been studied. Similar to the LiCl-complexed system, the stereoregularity of MMA polymerization in the presence of these additives is seemingly controlled by association/complexation equilibria among associated, nonassociated, and ligand-complexed active species. Accordingly, complexation of active species by σ-chelating ligands such as 12-CE-4 and K211 simply shifts the association equilibrium toward the formation of ligand-complexed (nonassociated) species, giving preferably syndiotactic placements (*rr*) in a 9/1 toluene/THF mixture as well as in toluene. However, the effect of a μ-type ligand, i.e., LiOtBu, seems more complicated. In THF and toluene, similar to ligand-free systems, highly syndiotactic and isotactic PMMAs are produced, respectively, implying the existence of different types of stereoselective LiOtBu-complexed species. In a 9/1 toluene/THF mixture, moreover, addition of LiOtBu gives rise to an increase in isotactic placements (*mm*) and matches the values observed in toluene. This is in striking contrast to the LiCl-added system, for which it has been tentatively proposed that a meso or racemo placement might also critically depend on the aggregation degree of the living chain in the complexed species. Nevertheless, a μ/σ dual ligand, i.e., LiOEEM, gives rise to an almost identical stereoregularity (i.e., highly syndiotactic) whatever the solvent used, well consistent with the involvement of the same type of active complex.

Introduction

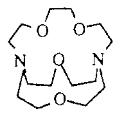
Although the coordination chemistry of enolates has been the subject of active investigation for a very long time,[1] its extension to anionic polymerization of (meth)acrylates has only received serious attention in recent years.[2] Nevertheless, several types of ligands discovered to date by us[3-5] and others[6-8] have proven to strongly coordinate with enolate-type propagating ion pairs and afford a well-controlled anionic polymerization of (meth)acrylates. That so-called "ligated" approach nowadays appears as a new powerful tool for tailoring of (meth)acrylate-based polymers.[2]

Furthermore, many efforts have also been devoted to simultaneously control the stereoregularity in the anionic (meth)acrylates polymerization hopefully by means of that same ligated approach.[9,10] This also requires a better understanding of the effect of various types of ligands on the stereochemistry of these polymerizations. In a previous paper,[11] we have reported our initial attempts directed toward that goal, including the effects of lithium chloride (LiCl) on the stereoregularity of the anionic polymerization of methyl methacrylate (MMA) in THF and in a 9/1 toluene/THF mixture at −78 °C, respectively. It has been accordingly demonstrated that the association/complexation equilibria promoted by LiCl affect not only the livingness of MMA anionic polymerization but also its stereochemistry in a 9/1 toluene/THF mixture, a phenomenon not observed in pure THF.

In this paper, we present results dealing with the stereochemistry of MMA anionic polymerization associated with a lithium counterion, in the presence of various types of ligands other than LiCl, i.e., 12-crown-4 (12-CE-4, **1**) and 211 cryptand (K211, **2**), both σ-type ligands, lithium *tert*-butoxide (LiOtBu, **3**), a μ-ligand, and lithium 2-(2-methoxyethoxy) ethoxide (LiOEEM, **4**), a dual μ/σ one, and that in various solvents, i.e., THF, a 9/1 toluene/THF mixture, and toluene. As reported elsewhere,[12-14] the complexation behavior of an active site monomeric model with these ligands has already been investigated using NMR spectroscopy. It is thus essential to know how the stereoregularity of MMA anionic polymerization relates to the structure and equilibria of these complexed ion pairs in solution.

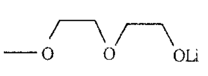


1 12-CE-4



2 K211

3 LiOtBu



4 LiOEEM

Experimental Section

Methyl methacrylate (usually 0.5 mol/L) was polymerized under moisture- and air-free conditions, using (diphenylmethyl)lithium (DPMLi) or (diphenylhexyl)lithium (DPHLi) as an initiator. Purification of monomer and solvents and polymerization techniques were described in detail elsewhere.[3]

12-Crown-4 (12-CE-4, **1**; Aldrich) was distilled over living styryllithium oligomer immediately prior to use. Cryptand 211 (K211, **2**; Merck) was used as received. Lithium *tert*-butoxide (LiOtBu, **3**) was prepared according to a literature method.[6a] Lithium 2-(2-methoxyethoxy) ethoxide (LiOEEM, **4**) was synthesized by reacting *n*-BuLi (2.3 M in hexane, Janssen) with 2-(2-methoxyethoxy)ethanol (Aldrich) in hexane at 0 °C, in the presence of a few drops of diphenylethylene as an indicator.[5]

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

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Scheme 1

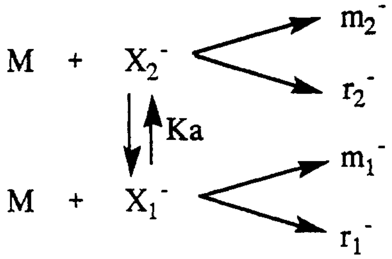


Table 1. Effect of 12-CE-4 on the Stereochemistry of MMA Anionic Polymerization Associated with a Lithium Counterion at −78 °C in Various Solvents

solvent	L/I[d]	M_n[e]	M_w/M_n[e]	*mm*	*mr*	*rr*	*m*	*r*	*ρ*
THF[a]	0	15 000	1.17	0.01	0.21	0.78	0.11	0.89	0.93
	5	13 000	1.15	0.01	0.22	0.77	0.12	0.88	0.96
(9 + 1)[a,b]	0	*f*		0.17	0.25	0.58	0.30	0.70	1.66
	5	*f*		0.07	0.23	0.70	0.19	0.81	1.34
tol[c]	0	*g*		0.88	0.09	0.03	0.93	0.07	1.45
	5	*g*		0.59	0.26	0.15	0.72	0.28	1.56

[a] Initiator = DPMLi. Concentration = 2 × 10^{-3} mol/L. [b] In a 9/1 toluene/THF mixture. [c] Initiator = DPHLi. Concentration = 2 × 10^{-3} mol/L. [d] 12-CE-4/initiator, mol/mol. [e] SEC data based on PMMA calibration. [f] Bimodal MWD. [g] Multimodal MWD.

Results and Discussion

Stereochemistry of MMA Anionic Polymerization Associated with a Lithium Counterion, in the Presence of 12-Crown-4 (12-CE-4, 1) or 211 Cryptand (K211, 2) at −78 °C. As reported previously,[11] in a 9/1 toluene/THF mixture, an association equilibrium between dimeric and monomeric active species might dominate the MMA anionic polymerization and control its stereochemistry (Scheme 1). Accordingly, a nonassociated species (X_1^-) and an associated one (X_2^-) preferably produce the racemo and meso placements, respectively. Since the complexation of active species by cation-binding ligands such as 12-CE-4 and K211 should simply shift the association equilibrium toward the formation of nonassociated species (X_1^-), the syndio-stereochemistry of the MMA anionic polymerization in the presence of these ligands should largely depend on the complexation power of the ligand.

Effect of 12-CE-4. The microtacticity of PMMA prepared in the presence of 12-CE-4 in various solvents, i.e., THF, a 9/1 toluene/THF mixture, and toluene, is listed in Table 1, which clearly shows that 12-CE-4 significantly modifies the stereochemistry of the MMA anionic polymerization initiated with DPHLi in a 9/1 toluene/THF mixture and in pure toluene but not that initiated with DPMLi in pure THF.

Accordingly, upon addition of 12-CE-4 the syndiotactic placements (*rr*) are favored at the expense of isotactic ones (*mm*) as well in a 9/1 toluene/THF mixture as in pure toluene. It is also noticeable that, in the presence of the same mole equivalents of 12-CE-4, the syndiotactic content decreases in the order toluene > 9/1 toluene/mixture > THF; i.e., increasing polarity and the solvating power of the medium results in an increase in syndiotactic placements.

Effect of K211. In sharp contrast to the above-mentioned results, data in Table 2 show that the stereoregularity of MMA anionic polymerization in the presence of K211 is independent of the solvent used, i.e., indicative of an identical single K211-complexed active species in all cases.

In addition, although K211 induces an increase in the syndiotactic fraction in pure toluene and in a 9/1 toluene/THF mixture, in THF, the addition of 2.5 mol equiv of K211 surprisingly leads to a significant decrease in the same isomer from ca. 80% to ca. 65% (Table 2). That striking phenomenon will be discussed afterward.

Table 2. Effect of K211 on the Stereochemistry of MMA Anionic Polymerization at −78 °C in Various Solvents

solvent	L/I[d]	M_n[e]	M_w/M_n[e]	*mm*	*mr*	*rr*	*m*	*r*	*ρ*
THF[a]	0	15 000	1.17	0.01	0.21	0.78	0.11	0.89	0.93
	2.5	30 000	1.01_5	0.02	0.33	0.65	0.19	0.81	0.93
(9 + 1)[a,b]	0	*f*		0.17	0.25	0.58	0.30	0.70	1.66
	2.5	31 500	1.15	0.02	0.32	0.66	0.18	0.82	0.92
tol[c]	0	*g*		0.88	0.09	0.03	0.93	0.07	1.45
	2.5	35 000	1.20	0.02	0.32	0.66	0.18	0.82	0.92

[a] Initiator, DPMLi. Concentration: 2 × 10^{-3} mol/L. [b] In 9/1 (v/v) toluene/THF mixture. [c] Initiator, DPHLi. Concentration: 2 × 10^{-3} mol/L. [d] Molar ratio of K211/initiator. [e] SEC data based on PMMA calibration. [f] Bimodal MWD. [g] Multimodal MWD.

Nevertheless, at least in a 9/1 toluene/THF mixture and pure toluene, the effect of 12-CE-4 and K211 on polymerization stereochemistry can be reasonably interpreted in terms of association/complexation equilibria,[11,15] in agreement with their complexation solvation power: K211 indeed is to date the most powerful lithium-cation-binding reagent known. Therefore, the complexation of a living end cation by this ligand might induce the same type of nonassociated species (X_1^-) in any solvent and consequently lead to an increase in the syndiotactic fraction (Scheme 1). Conversely, it has been shown that 12-CE-4 is much less powerful than K211 in complexing with propagating enolate ion pairs.[12] Indeed, addition of 12-CE-4 into coexisting tetrameric and dimeric MIBLi in THF, a model compound structurally corresponding to a living PMMA$^-$Li$^+$ end, does not completely destroy the aggregation of MIBLi and only provides for a slight increase in the population of dimeric species. It is then plausible that the 12-CE-4 free (or complexed) associated and nonassociated species might coexist during MMA anionic polymerization. In this regard, an increase in the relative amount of nonassociated species due to the presence of 12-CE-4 should depend on the polarity of the solvent, i.e., in the order 9/1 toluene/THF mixture > toluene, thereby producing more syndiotactic polymer in the same order.

In addition, it is very interesting to compare the stereochemistry of MMA anionic polymerization in the presence of 12-CE-4 and K211 in THF (Tables 1 and 2). In contrast to K211 (Table 2), addition of 12-CE-4 has no significant influence on the stereoregularity (Table 1), indicating that the 12-CE-4-complexed and -free nonassociated species display the same character in the stereoregulation process. Along the same lines, it is worth noting that complexation of MIBLi by 12-CE-4 does not modify the negative charge distribution around MIBLi carbanion, while K211 conversely induces a substantial increase in charge density at the C_α carbon of MIBLi.[12] Altogether these results might suggest a possible effect of the solvation situation around active ion pairs on the stereochemistry of the MMA anionic polymerization.

Stereochemistry of MMA Anionic Polymerization in the Presence of Lithium *tert*-Butoxide (LiOtBu) at −78 °C. In Pure THF or Pure Toluene by Using DPMLi and DPHLi as Initiator, Respectively. As illustrated in Table 3, no observable influence of LiOtBu on the stereoregularity of MMA anionic polymerization can be traced in pure THF or in pure toluene. In fact, whatever the LiOtBu/initiator ratio (up to 10/1), a highly syndiotactic PMMA (~80%) is obtained in THF, while an essentially isotactic one (~88%) is recovered in pure toluene.

At this point, it is important to point out that the lack of effectiveness of LiOtBu in pure THF and in pure toluene

Table 3. Microtacticity of PMMA Anionically Prepared in the Presence of LiOtBu at -78 °C in THF and in Toluene

solvent	L/I[a]	M_n[d]	M_w/M_n[d]	mm	mr	rr	m	r	ρ
THF[b]	0	15 000	1.17	0.01	0.21	0.78	0.115	0.885	0.97
	1/1			0.01	0.19	0.80	0.105	0.895	0.99
	10/1	13 500	1.10	0.01	0.19	0.80	0.105	0.895	0.99
tol[c]	0	e		0.88	0.09	0.03	0.925	0.075	1.54
	1/1	e		0.86	0.09	0.05	0.905	0.095	1.91
	10/1	20 500	1.35	0.87	0.09	0.04	0.915	0.085	1.73

[a] Molar ratio of LiOtBu/initiator. [b] Initiator = DPMLi. Concentration = 2×10^{-3} mol/L. [c] Initiator = DPHLi. Concentration = 2×10^{-3} mol/L. [d] SEC data based on PMMA calibration. [e] Multimodal MWD.

cannot be ascribed to the failure of LiOtBu to coordinate with the propagating chain ends. In fact, a kinetic study carried out by Müller has demonstrated that LiOtBu-complexed active species dominate the LiOtBu-added (meth)acrylates anionic polymerization, in the presence of a lithium counterion in THF.[15] This conclusion has been confirmed and extended by us in terms of the ^{13}C NMR characterization of complexation of LiOtBu to a methyl α-lithioisobutyrate (MIBLi)/THF solution: LiOtBu has a high propensity to interact with MIBLi with the formation of various μ-type mixed aggregates.[13] Furthermore, it is well-known that MMA anionic polymerization in pure toluene in the presence of a lithium counterion is a completely ill-controlled process even at low temperatures, giving very poor yields and a multimodal molecular weight distribution (MWD). By contrast, addition of LiOtBu improves the situation to the point where PMMA can be produced in practically quantitative yield and with relatively narrow MWD even at room temperature,[16,17] providing unequivocal proof for the existence of complex between LiOtBu and propagating PMMA-Li^+ in that medium. In fact, IR studies have also proven the interaction of lithiated MMA dimer with LiOtBu in benzene.[18]

The present results suggest that there exist at least two types of LiOtBu-complexed species responsible for the different stereoregularities of the MMA anionic polymerization in the presence of LiOtBu in pure THF and pure toluene, respectively. Kinetic studies developed by Müller suggest that, in MMA anionic polymerization in THF at low temperatures, the associated species (X_2^-) exists in a negligible amount and the nonassociated one (X_1^-) mainly contributes to the propagating process.[15] However, the former one is favored in toluene at low temperatures.[19] Then, it appears that the LiOtBu-complexed active species formed in pure toluene and in THF might behave similarly to the LiOtBu free associated species (X_2^-) and nonassociated species (X_1^-), respectively, in the stereoregulation process.

In a 9/1 Toluene/THF Mixture by Using DPMLi as an Initiator. The microtacticity of PMMA anionically prepared in the presence of a lithium counterion and varying amounts of LiOtBu at -78 °C in a 9/1 toluene/THF mixture is tabulated in Table 4. For comparison purposes, the data in the presence of 5 mol equiv of lithium chloride (LiCl) are also included. In contrast to the situation in pure toluene and pure THF, examination of the data shows that LiOtBu strongly affects the stereoregularity of MMA anionic polymerization in this mixed solvent (Table 4 and Figure 1). Actually, an increase in the molar ratio of LiOtBu/initiator from 0 to ca. 3 results in a rapid increase in the isotactic placements, mm, by a factor of more than 3 (58% against 17%). Conversely, the corresponding syndiotactic fraction, rr, decreases from ca. 58% to ca. 34%. When the LiOtBu/initiator molar ratio is further increased, no changes are observed (Table 4). Furthermore, Figure 2 exhibits that a discontinuity also occurs at that 3/1 ratio, when the persistence ratio, ρ (=2(m)(r)/(mr)), is plotted versus the LiOtBu/initiator ratio. These results clearly indicate that increasing the LiOtBu/initiator ratio perturbs the stereoregularity of the MMA anionic polymerization in a 9/1 toluene/THF mixture in a way which suggests a complex equilibrium between propagating ion pairs and ligand.

Table 4. Stereoregularity of MMA Anionic Polymerization Initiated with DPMLi in the Presence of Varying Amounts of LiOtBu at -78 °C in a 9/1 Toluene/THF Mixture[a]

L/I[b]	M_n[d]	M_w/M_n[d]	mm	mr	rr	m	r	ρ
0	e		0.17	0.25	0.58	0.30	0.70	1.66
0.62/1			0.20	0.25	0.55	0.33	0.67	1.77
1.25/1			0.31	0.24	0.45	0.43	0.57	2.04
2.5/1			0.47	0.19	0.34	0.56	0.44	2.59
3.0/1			0.57	0.11	0.32	0.63	0.37	4.24
6.0/1			0.58	0.11	0.31	0.63	0.37	4.24
10/1	22 000	1.20	0.57	0.11	0.32	0.63	0.37	4.24
5/1[c]	15 000	1.15	0.03	0.25	0.72	0.16	0.84	1.05

[a] Initiator concentration = 2×10^{-3} mol/L. [b] LiOtBu/initiator, mol/mol. [c] In the presence of 5 mol equiv of LiCl instead of LiOtBu.[11] [d] SEC data based on PMMA calibration. [e] Bimodal MWD.

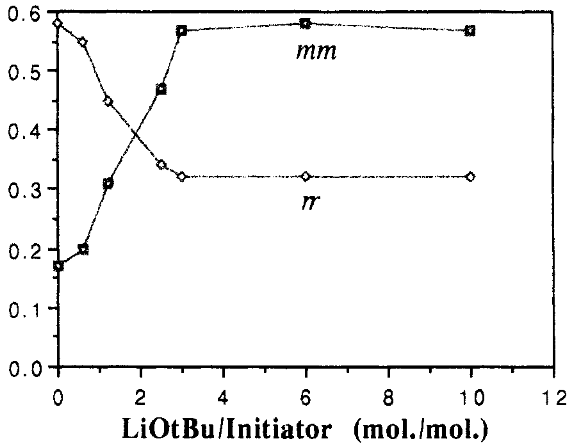


Figure 1. Effect of LiOtBu/initiator molar ratio on the triad fraction of PMMA anionically prepared in a 9/1 toluene/THF mixture at -78 °C in the presence of lithium counterion. Initiator = DPMLi. Concentration = 2×10^{-3} mol/L.

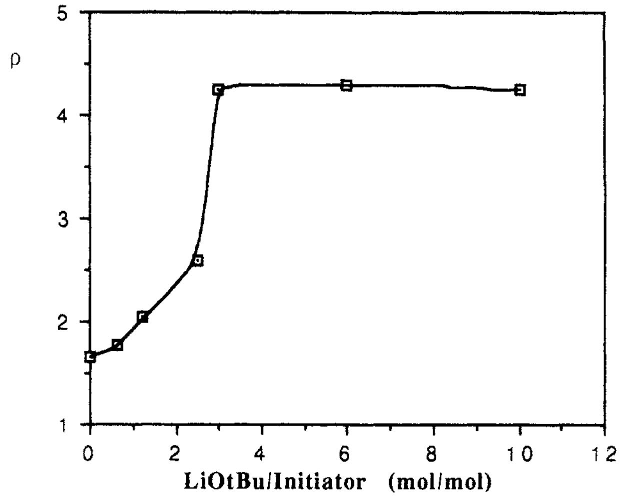


Figure 2. Effect of LiOtBu/initiator molar ratio on the persistence ratio, $\rho = 2(m)(r)/(mr)$, of PMMA synthesized in a 9/1 toluene/THF mixture at -78 °C in the presence of Li counterion. Initiator: DPMLi. Concentration: 2×10^{-3} mol/L.

Moreover, at LiOtBu/initiator ≥ ca. 3, the persistence ratio, ρ, is found to be as high as ca. 4.25 (Table 4), indicative of a highly non-Bernoullian process.[9] Although the

Table 5. Experimental and Calculated Pentad Composition of PMMA Initiated with DMPLi[a] in the Presence of 10 Mol Equiv of LiOtBu, at –78 °C, in a 9/1 Toluene/THF Mixture

	exptl[b]	Bernoullian	1st-order Markov
(*mmmm*)	0.50	0.16	0.48
(*mmmr*)	0.09	0.19	0.09
(*rmmr*)	0.00	0.05	0.00
(*rmrm*)	0.00	0.27	0.02
(*mmrm*) (*rmrr*)	0.08	0.17	0.09
(*mmrr*) (*mrrm*)	0.00	0.05	0.01
(*mrrr*)	0.08	0.09	0.08
(*rrrr*)	0.25	0.02	0.23
(*mm*)	0.57		
(*mr*)	0.11		
(*rr*)	0.32		
(*m*)	0.63		
(*r*)	0.37		
ρ	4.24		

[a] Initiator concentration = 2×10^{-3} mol/L. [b] ^{13}C NMR data at the carbonyl group.[11]

LiOtBu-free process obeys second-order Markovian statistics,[11] comparison of the observed pentads and the calculated ones for the system in the presence of 10 mol equiv of LiOtBu appears to give consistence to a first-order one (Table 5).

In striking contrast to the above results, we have previously demonstrated that upon addition of LiCl the syndiotactic placements (*rr*) are conversely favored at the expense of the isotactic ones (*mm*), for an MMA anionic polymerization carried out under the same experimental conditions (also see Table 4):[11] LiCl and LiOtBu thus affect the polymerization stereochemstry in this mixed solvent in rather different manners.

That effect of LiCl on the stereochemistry of MMA anionic polymerization in a 9/1 toluene/THF mixture could be interpreted in terms of the association/complexation equilibria controlled by associated, nonassociated, and LiCl-complexed species.[11] In the absence of LiCl, an association equilibrium between associated and nonassociated species dominates the course of the polymerization process (Scheme 1), selectively producing meso and racemo placements, respectively. Moreover, the complexation of living ends by LiCl shifts the association equilibrium toward the formation of LiCl-complexed species and accordingly results in an increase in the syndiotactic fraction,[11] as far as LiCl-complexed species afford a stereoregulation similar to that of LiCl-free nonassociated ones.

Since there are convincing evidences from kinetic studies by Müller that these association/complexation equilibria also control the MMA polymerization in the presence of LiOtBu,[11] one may reasonably assume that, similar to a LiCl-complexed system, the stereochemistry of a LiOtBu-complexed process in a 9/1 toluene/THF mixture might be as well controlled by these equilibria among associated (X_2^-), nonassociated (X_1^-), and LiOtBu-complexed species.

However, this leads to the crucial question of why LiOtBu affects the stereochemistry in a way different from LiCl. In order to answer this question, it seems of great importance to first obtain a reasonable explanation regarding the different stereochemistry of LiOtBu-complexed species in THF and in toluene.

It is well-known that LiOtBu is essentially tetrameric even in pure THF.[20] Moreover, ^{13}C NMR spectroscopy provided evidence that complexation of LiOtBu with a monomeric model for PMMA$^-$Li$^+$, i.e., MIBLi, in THF, yields various types of tetrameric mixed complexes, i.e., MIB$_x$*Li*$_4$(OtBu)$_{4-x}$ (x = 1–3).[13] As already recalled in the preceding section, nonassociated active species X_1^- mainly contributes to the propagation process in the MMA anionic polymerization in THF, whereas the associated one, say dimeric species X_2^-, most probably dominates in toluene. It then may be reasonably speculated that the LiOtBu-complexed associated active species, i.e., n(LiOtBu)·X_2^-, and LiOtBu-complexed nonassociated species, i.e., m(LiOtBu)·X_1^-, are predominantly present in THF and toluene, respectively. Similar to species X_2^- and X_1^- in the absence of LiOtBu, the LiOtBu-complexed associated species n(LiOtBu)·X_2^- might preferably produce the isotactic polymer, whereas LiOtBu-complexed nonassociated m(LiOtBu)·X_1^- would mainly give rise to racemo placements.

In that respect, the microtacticity of PMMA formed in the presence of LiOtBu in a 9/1 toluene/THF mixture might be related to the overall contribution of these two differently stereoselective active complexes. The fact that addition of LiOtBu leads to a decrease in syndiotactic placements might suggest that the stereoregularity is mainly controlled by the LiOtBu-complexed associated active species in this mixed solvent.

The same argument may apply to the above-described difference in stereoregularity observed in LiCl- and LiOtBu-complexed systems in a 9/1 toluene/THF mixture. Since LiCl can promote less aggregated species compared to LiOtBu, due to its higher solvation degree,[21] the LiCl-complexed nonassociated species may be predominantly involved in the propagation process,[11] resulting in a syndiotactic PMMA.

Thus, it may be concluded that the aggregation degree of the living chain in the complexed active species possibly plays an important role in controlling the stereochemistry in MMA anionic polymerization.

However, it might be counterargued that the highly isotactic placements in the MMA anionic polymerization in the presence of LiOtBu in toluene might originate from the interaction between the countercation and the penultimate or antepenultimate ester group, i.e., a typically "penultimate" mechanism.[22] If this were the case, addition of LiOtBu to a polymerization system in THF should induce an increase in isotactic placements as well, since it is convincingly evident from IR spectra that tBuOLi not only interacts with the lithium enolate group in a lithiated MMA dimer but also increases the extent of coordination of the penultimate ester group to the lithium counterion in THF as well as in benzene.[18] The fact that the highly syndiotactic placement in MMA polymerization in THF in the presence of LiOtBu almost remains unchanged, whatever the amount of ligand, might strongly suggest that this penultimate mechanism is less important than assumed before, when other interactions (association of living chain ends) are at play.

Stereochemistry of MMA Anionic Polymerization at –78 °C in the Presence of Lithium 2-(2-Methoxyethoxy) Ethoxide (LiOEEM). In a 9/1 Toluene/THF Mixture by Using DPMLi as an Initiator. The stereoregularity promoted under these conditions was first examined: a triad analysis of PMMA samples accordingly prepared is reported in Table 6, which clearly demonstrates the profound influence of LiOEEM in this mixed solvent. Actually, increasing the LiOEEM/initiator ratio gives rise to a considerable increase/decrease in syndiotactic (*rr*)/isotactic (*mm*) placements, respectively. In fact, when more than 3 mol equiv of LiOEEM are added to the polymerization system, the syndiotactic fraction increases up to the constant value of ca. 83%, whereas isotactic

Table 6. Microtacticity of PMMA Anionically Prepared by Using DPMLi as an Initiator and LiOEEM as a Ligand in a 9/1 Toluene/THF Mixture at −78 °C[a]

L/I[b]	M_n[c]	M_w/M_n[c]	*mm*	*mr*	*rr*	*m*	*r*	*ρ*
0	*d*		0.17	0.25	0.58	0.30	0.70	1.66
2			0.05	0.21	0.74	0.16	0.84	1.28
3			0.01	0.16	0.83	0.09	0.91	1.02
5			0.01	0.16	0.83	0.09	0.91	1.02
10	15400	1.05	0.01	0.16	0.83	0.09	0.91	1.02

[a] Initiator concentration = 2×10^{-3} mol/L. [b] LiOEEM/initiator, mol/mol. [c] SEC data based on PMMA calibration. [d] Bimodal MWD.

Table 7. Effect of LiOEEM on the Stereoregularity of MMA Anionic Polymerization at −78 °C in THF and Toluene

solvent	L/I[c]	M_n[c]	M_w/M_n[c]	*mm*	*mr*	*rr*	*m*	*r*	*ρ*
THF[a]	0	15 000	1.17	0.01	0.21	0.78	0.11	0.89	0.93
	2			0.01	0.16	0.83	0.09	0.91	1.02
	10			0.01	0.16	0.83	0.09	0.91	1.02
tol[b]	0	*d*		0.88	0.09	0.03	0.925	0.075	1.54
	2			0.10	0.21	0.69	0.205	0.795	1.55
	3			0.01	0.18	0.81	0.10	0.90	1.00
	10	12 500	1.05	0.01	0.16	0.83	0.09	0.91	1.02

[a] Initiator = DPMLi. Concentration = 2×10^{-3} mol/L. [b] Initiator = DPHLi. Concentration = 2×10^{-3} mol/L. [c] Molar ratio of LiOEEM/initiator. SEC data based on PMMA calibration. [d] Multimodal MWD.

placements practically disappear.

In addition, the persistence ratio, ρ, becomes very close to unity at LiOEEM/initiator ≥ 3 (Table 6), implying a Bernoullian process in the LiOEEM-ligated MMA anionic polymerization in a 9/1 toluene/THF mixture.

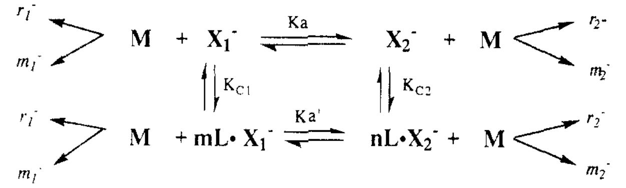
Up to this point, one may already conclude that a μ/σ dual polydentate lithium alkoxide, i.e., LiOEEM, affects the stereochemistry of MMA anionic polymerization in a 9/1 toluene/THF mixture in the same direction as LiCl[11] but different from LiOtBu (see above).

In THF and in Toluene by Using DPMLi and DPHLi as an Initiator, Respectively. Similar to LiOtBu and LiCl,[11] it appears from Table 7 that LiOEEM has no significant influence on stereoregularity in MMA anionic polymerization at −78 °C in pure THF (up to 10/1 LiOEEM/initiator molar ratio), which might also indicate that the LiOEEM-complexed active species has stereoselectivity practically similar to the LiOEEM free nonassociated one.

In sharp contrast to the results observed in pure THF, however, the data in Table 7 clearly show that LiOEEM substantially affects the stereoregularity of the MMA anionic polymerization in pure toluene at −78 °C. While, in the absence of LiOEEM, highly isotactic PMMA (*mm* ~88%) is formed, addition of that ligand leads to a substantial increase in the syndiotactic fraction, at the expense of the isotactic one. Indeed, when the LiOEEM/initiator molar ratio is increased over ca. 3/1, the microtacticity of PMMAs is surprisingly found to be the same as the one observed in pure THF and in a 9/1 toluene/THF mixture, i.e., a high syndiotactivity of ca. 83%, obviously a very different situation from that noted in the presence of a simple lithium alkoxide, i.e., LiOtBu (see above). Moreover, the stereochemistry for LiOEEM/initiator ≥ 3 ratios appears to be consistent with a Bernoullian process as indicated by $\rho \sim 1$, again similar to the situation in pure THF and in a 9/1 toluene/THF mixture.

Clearly enough, the stereoregularity of MMA anionic polymerization in the presence of ≥ 3 mol equiv of a dual μ/σ lithium alkoxide, i.e., LiOEEM, is independent of the polarity of the reaction medium within the limits of experimental error. Interestingly, such a situation has been already observed in the presence of K211, to date the most powerful lithium-cation-binding agent, and indicates the involvement of a single type of stereoselective LiOEEM-complexed active species, whichever the solvent. This is indeed in good agreement with the ^{13}C NMR results dealing with the complexation of LiOEEM and MIBLi, where only one type of μ/σ complex, i.e., 2LiOEEM·MIBLi, is observed in THF, toluene, and a 9/1 toluene/THF mixture.[14] Once again, these experimental evidences might strongly support the idea that ligand-complexed nonassociated active species play an important role in producing syndiotactic PMMA.

Scheme 2



General Discussion and Conclusions

According to the results reported above and in agreement with a previously proposed mechanism,[11] the stereoregularity of the MMA anionic polymerization in the presence of various types of ligands other than LiCl (except K211 in THF) seems to also be controlled by association/complexation equilibria among associated (X_2^-), nonassociated (X_1^-), and ligand-complexed active species. Important also, and similar to the ligand-free system,[11] ligand-complexed nonassociated active species (mL·X_1^-) and ligand-complexed associated active species (mL·X_2^-) might selectively produce the racemo and meso placements, respectively (Scheme 2).

In conclusion, the effects of various types of ligands on the stereochemistry of MMA anionic polymerization can be summarized as follows:

(i) Complexation of active species by lithium-cation-binding ligands, such as 12-CE-4 and K211, simply shifts the association equilibrium toward the formation of mL·X_1^-, resulting in syndiotactic placements in toluene and a 9/1 toluene/THF mixture.

(ii) The effect of LiOtBu strongly depends on the solvent used. Syndiotactic/isotactic PMMA are produced in THF/toluene, respectively, presumably due to the presence of active complexes mL·X_1^-/nL·X_2^-. Addition of LiOtBu in a 9/1 toluene/THF mixture induces an intermediate situation, i.e., a relative increase in isotactic placements, which might result from the predominant contribution of the LiOtBu-complexed associated active species nL·X_2^-.

(iii) Since a dual μ/σ lithium alkoxide, LiOEEM, a very strong ligand, promotes the formation of the same type of mL·X_1^--type active complex whichever the solvent, a highly syndiotactic PMMA results as well in THF as in toluene and in a 9/1 toluene/THF mixture. These results should be compared with those obtained in the presence of K211, another strong chelating ligand, the difference in the syndiotactic contents (i.e., 83 and 65%, respectively) being possibly related to a different degree of ion separation (solvation).

Once again, it is important to point out that the association/complexation equilibria model only describes the overall distribution of stereoisomers as promoted by various stereoselective active complexes. The stereochemistry of each active species is still not understood. Indeed, we are still very puzzled by the observation that K211 unexpectedly induces a significant decrease in the syndiotactic content in MMA polymerization in THF, for which actually no available mechanisms may readily accommodate. A more detailed analysis should shed more light on the intimate polymerization stereochemistry and is currently in progress.

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