Anionic Polymerization of (Meth)acrylic Monomers. 22. Anionic Polymerization of *tert*-Butyl Methacrylate in Toluene/THF Mixtures: A Preliminary Approach to the Role of Solvation/Ligation Equilibria

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ABSTRACT: Although the anionic polymerization of *tert*-butyl methacrylate (tBMA) induces a narrow and unimodal molecular weight distribution (MWD) when performed in either pure THF or pure toluene at −78 °C in the presence of a lithium counterion, that in THF/toluene mixtures, keeping other conditions unchanged, surprisingly gives rise to broad bi- and even multimodal MWD's. Moreover, with increasing polymerization temperature from −78 to 0 °C, that multimodal MWD gets narrower, atypical of termination reactions, and indeed at 0 °C, a very narrow unimodal MWD is again obtained. These results have been satisfactorily interpreted in terms of a multiple solvation equilibria mechanism: there coexist several types of THF-solvated and nonsolvated active species and the exchange among them is slow at −78 °C but fast at 0 °C compared to the monomer propagation rate, thus resulting in a multimodal MWD in the former case and a narrow one in the latter. Furthermore, this solvation mechanism also dominates the stereoregulation of the tBuMA polymerization in mixed solvent. It has indeed been demonstrated that addition of various types of ligands, i.e., lithium chloride (LiCl) and lithium *tert*-butoxide (LiOtBu) (both μ-ligands), 12-crown-4 (12CE4) and cryptand 211 (K211) (both σ-chelating ligands), and lithium 2-(2-methoxyethoxy)ethoxide (LiOE$_2$M) (a μ/σ dual type of ligand), affects the tBMA anionic polymerization in a way which can be accounted for by these so-called solvation/ligation multiple equilibria among THF-nonsolvated, THF-solvated, and ligated ion pairs. Once again, the fact that, in comparison with 12CE4 and LiOtBu, such ligands as LiOE$_2$M, K211, and LiCl can effectively promote a much narrower MWD is nicely related to their high propensity to coordinate with a lithium ester enolate and at the same time to either promote a fast-exchanging ligation equilibrium or form a single type of active complex, in good agreement with the NMR investigation of corresponding model systems as previously reported by us.

Introduction

Unlike other (meth)acrylic esters, anionic polymerization of *tert*-butyl methacrylate (tBMA) exceptionally proceeds at low rate in a living fashion under quite moderate experimental conditions. For instance, although anionic polymerization of most (meth)acrylates in nonpolar solvent, e.g., toluene, induces an ill-controlled product in terms of very limited conversion and broad multimodal molecular weight distribution (MWD), that of tBMA conversely gives rise to a quantitative yield and narrow molecular weight distribution.[1] Again, the living polymerization of most methacrylates works well only in THF at low temperatures (<−60 °C) and using highly delocalized and sterically hindered initiator.[1,2] By contrast, tBMA polymerization still displays a living character in THF even at a temperature as high as 37 °C in the presence of a lithium counterion.[2] That unusual polymerization behavior has been primarily ascribed to the significantly different steric and electronic environment of the ester carbonyl substituent.[1–4]

However, we were surprised to note that, in comparison with methyl methacrylate (MMA), much less effort has been devoted to date to an extensive investigation of tBMA anionic polymerization. Nevertheless, thanks to the recognized high stability of tBMA type of ester enolate ion pairs, that tBMA polymerization may potentially serve as a unique probe for studying the living anionic polymerization mechanism in the (meth)acrylate series, an important issue in a still not fully understood situation.

This paper aims to show an unexpected behavior in tBMA anionic polymerization in toluene/THF mixtures reminiscent of MMA behavior in the same solvents;[18] the effect of various types of ligands on that process will be simultaneously discussed. As a preliminary approach, the role of competitive solvation/ligation equilibria in that type of polymerization is accordingly addressed.

Experimental Section

Materials. tBMA from Polysciences was first dried by refluxing over CaH$_2$, distilled under reduced pressure, and stored under an inert atmosphere at −20 °C. Just before polymerization, it was treated with a 10% Et$_3$Al solution in toluene at 0 °C until a persistent yellow-green color was obtained and then again distilled under reduced pressure. Purification of solvents (toluene and THF) and ligands (lithium chloride (LiCl), 12-crown-4 (12CE4), and cryptand 211 (K211)) and preparation of initiators ((diphenylhexyl)lithium (DPHLi) and (diphenylmethyl)lithium (DPMLi)) and ligands (lithium *tert*-butoxide (LiOtBu) and lithium 2-(2-methoxyethoxy)ethoxide (LiOE$_2$M)) were described elsewhere.[5]

Polymerization was carried out in a previously flamed glass reactor under a pure nitrogen atmosphere, the monomer, solvent, ligand solution, and initiator solution being transferred by a syringe and/or capillary technique.

Characterization. Size exclusion chromatography (SEC) was carried out in THF, using a Hewlett-Packard 1037 A apparatus equipped with a refractive index detector. Poly(methyl methacrylate) standards were used for calibration.

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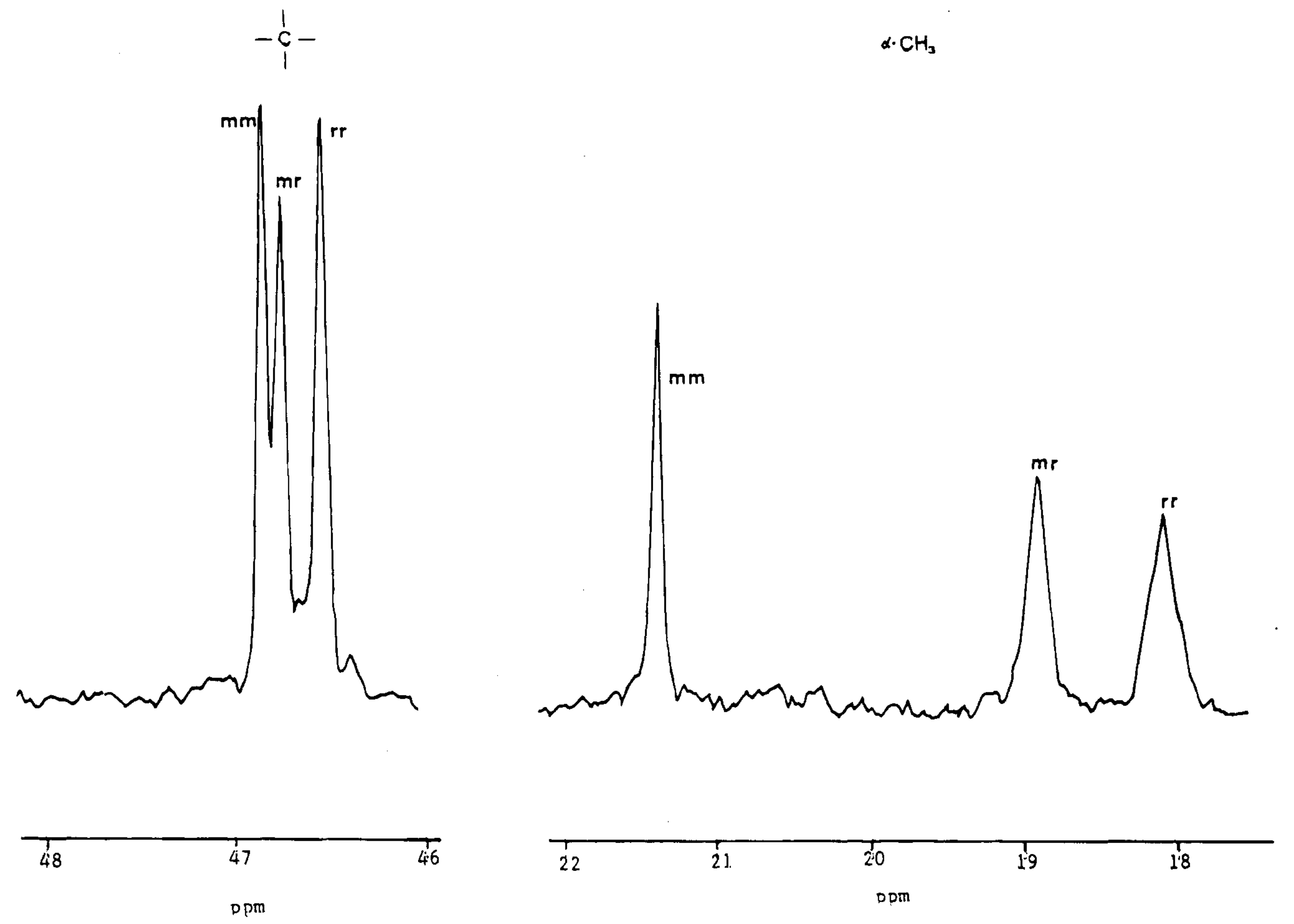


Figure 1. 100-MHz ^{13}C NMR spectra of PtBMA anionically prepared in a 9/1 toluene/THF mixture at −78 °C in the presence of a lithium counterion. Solvent: $CDCl_3$.

Table 1. Anionic Polymerization of tBMA in Various THF/Toluene Mixtures at −78 °C in the Presence of a Lithium Counterion[a]

THF (vol %)	initiator	$M_{n,SEC}$	M_w/M_n	f^b
0	DPHLi	10000	1.20	0.80
10	DPHLi	9800	2.72	0.82
10	DPHLi[c]	19500	2.68	0.83
30	DPMLi	9900	2.00	0.81
100	DPMLi	9800	1.25	0.82

[a] Initiator, 0.25×10^{-3} mol; monomer, 2 g; solvent, 50 mL; polymerization time, 2 h; yield, 100 wt %. [b] $f = M_{n,cal}/M_{n,SEC}$. [c] Initiator, 0.125×10^{-3} mol.

The ^{13}C NMR spectra were recorded at 20 °C with a Bruker AM-400 spectrometer operating at 100 MHz, using an inverse-gated proton-decoupling technique in order to perform quantitative analysis. The tacticity of PtBMA was calculated from the ^{13}C spectra of the quaternary carbon and/or of the α-methyl group with respect to the central peak of $CDCl_3$ at 77.2 ppm (Figure 1).[1b,2]

Results and Discussion

Solvent Effect on the Molecular Weight Distribution (MWD) in tBMA Anionic Polymerization in the Presence of a Lithium Counterion at −78 °C. Table 1 and Figure 2 report the characteristic molecular features of such polymerizations in different solvents, i.e., pure toluene, toluene/THF mixtures, and pure THF, using (diphenylhexyl)lithium (DPHLi) or (diphenylmethyl)lithium (DPMLi) as initiator, respectively. It is clear that the composition of the THF/toluene mixture exerts a significant influence on the livingness of the polymerization, particularly on the molecular weight distribution (MWD) of the resulting polymers.

Indeed, in pure THF, the tBuMA anionic polymerization is a well-controlled process, as evidenced by a quantitative yield, a narrow and unimodal MWD ($M_w/M_n \simeq 1.25$) (Figure 2D), and a rather good initiator efficiency ($f = 0.82$), in accordance with numerous other works.[2,4] Moreover, a similar situation is also obtained in pure toluene (Table 1), except for a small tailing on the low molecular weight side in the SEC trace of the final polymer (Figure 2A), again in agreement with previously reported data.[1b,4]

Surprisingly enough, however, for the polymerization in toluene/THF mixtures at the same temperature, i.e., −78 °C, the data summarized in Table 1 and Figure 2 reveal some striking features. First, although the yield of polymer is always quantitative and in sharp contrast to the results observed in pure THF or pure toluene (Figure 2A,D), broad and even bi- or multimodal MWD's (depending on the THF content in the medium) are now monitored in the SEC diagrams; they are of course suggestive of the coexistence of several types of propagating species not undergoing a fast exchange compared to the tBMA propagation rate.[6] Indeed, whatever their MW, all the chains corresponding to the observed multipeaks simultaneously grow to a higher molecular weight versus monomer conversion (see, for example, the case of the polymerization in a 9/1 toluene/THF mixture as illustrated in Figure 3), indicating that they all are living. Also noteworthy is that an inflection clearly occurs at ca. 10% THF by volume in the plot of the MWD's of the final raw product against THF content of the mixed solvent (Figure 4). Finally, when the medium contains > ca. 75% THF, the situation matches

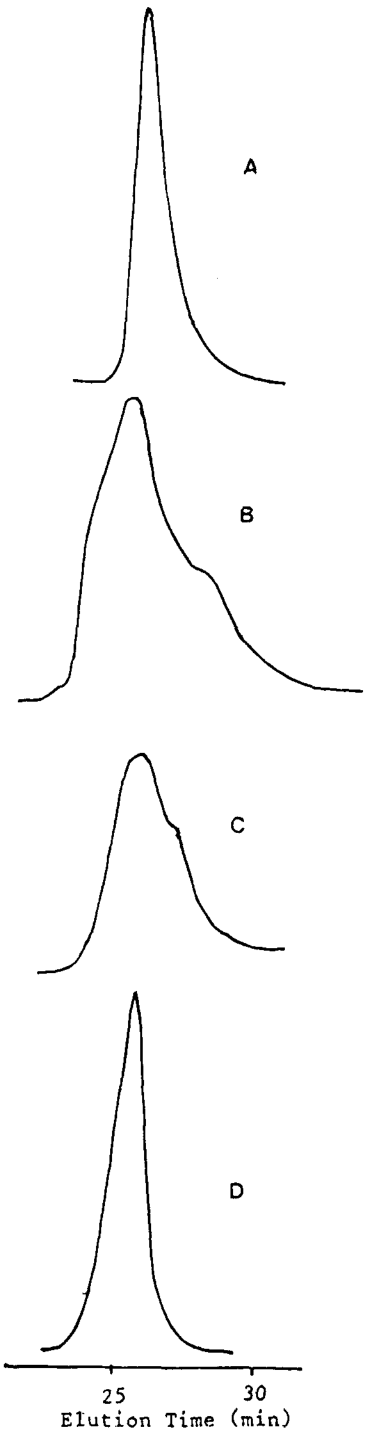


Figure 2. SEC traces of PtBMA prepared at −78 °C in different THF/toluene mixtures. Experimental conditions: see Table 1. (A) 100% toluene, M_w/M_n = 1.20; (B) 90% toluene, M_w/M_n = 2.72; (C), 70% toluene, M_w/M_n = 2.00; (D) 100% THF, M_w/M_n = 1.25.

the one obtained in pure THF (Figure 4). These results obviously provide a first unambiguous proof for the significant dependence of the MWD, characteristic of the dynamics of the polymerization process, on the solvation power of the medium.

At this point, it must be stressed that, since there is convincing evidence from kinetic data that the tBMA anionic polymerization nicely proceeds in a termination-free manner in *both* THF *and* toluene even at moderately high temperatures (also see above),[1,4] the observation of bi- and even multimodal MWD's of PtBMA synthesized in toluene/THF mixtures should definitely be accounted for by other types of mechanism(s) than termination ones.

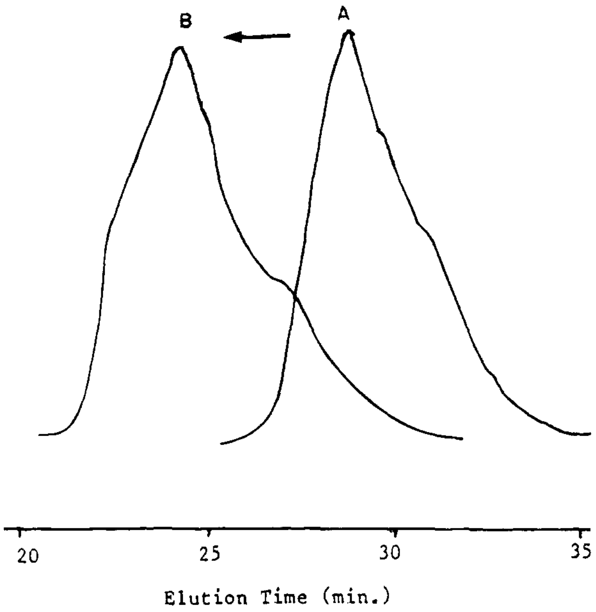


Figure 3. SEC traces of PtBMA anionically prepared in a 9/1 toluene/THF mixture at −78 °C at different conversion: (A) ca. 45%; (B) 100%. Initiator = DPHLi, initiator concentration = 5 × 10^{-3} mol/L.

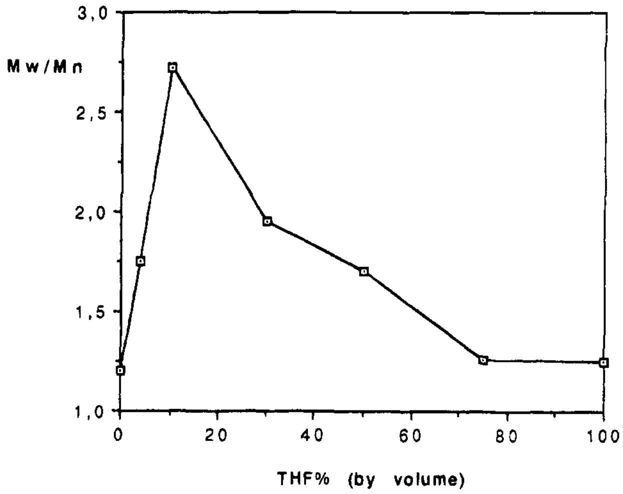
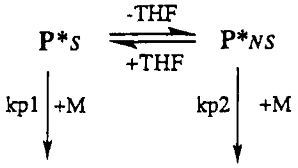


Figure 4. Dependence of the polydispersity index (M_w/M_n) of PtBMA synthesized at −78 °C on THF content in toluene/THF mixtures. Initiator = DPHLi or DPMLi, concentration = 5 × 10^{-3} mol/L.

It is worth recalling that in his kinetic studies Müller has already suggested that an "intramolecular solvation" equilibrium between several active species possibly dominates the tBMA anionic polymerization in pure toluene,[1b] whereas an association equilibrium between THF-solvated dimeric and THF-solvated monomeric living chain ends is mostly operative in pure THF.[1b,6b]

On these bases, we feel strongly justified in proposing that THF nonsolvated ($\mathbf{P}^*_{NS}$) and THF-solvated active species ($\mathbf{P}^*_s$) may reasonably coexist in tBMA anionic polymerization in toluene/THF mixtures at −78 °C. Since that polymerization has already been established to be by one order of magnitude faster in toluene than in THF,[1b] bi- and even multimodal MWD's must result,[6] provided the exchange between ($\mathbf{P}^*_{NS}$) and ($\mathbf{P}^*_S$) is slow compared to the monomer addition rate; i.e., we deal here with a solvation equilibrium mechanism (Scheme 1).

Scheme 1



It is worthwhile to recall here that a similar solvation effect on MWD has been previously reported by Erussalimsky et al.,[7] who demonstrated that isoprene anionic polymerization in cyclohexane results in a unimodal and narrow MWD, whereas addition of 0.01 molar equiv of TEMDA gives rise to a broad and even bimodal MWD. The author has attributed this effect to a coexistence of slowly exchanging TEMDA-free and -complexed active species.

Temperature Effect on the MWD of PtBMA Synthesized in Toluene/THF Mixtures. As explained above, solvation equilibria may govern the MWD of the resulting PtBMA (Scheme 1). It might then be expected that polymerization temperature exerts a profound influence on those dynamic solvation equilibria and consequently on the MWD of the polymerization. In perfect consistency with such a qualitative prediction, Figure 5 undoubtedly shows that, for quantitative tBMA polymerizations in toluene/THF mixtures, the polydispersity index (M_w/M_n) decreases with increasing polymerization temperature (down to 1.15 at 0 °C!), again strongly supporting the idea that the multimodal distribution observed at low temperatures for the same system is not due to termination reactions.

These results certainly point toward the fact that, in contrast to polymerization at low temperatures, the exchanges among different THF-solvated and nonsolvated species are becoming faster at 0 °C compared to the monomer addition rate, thus leading to a narrow MWD.[6] Obviously, this temperature effect on the MWD can well be related to the difference in activation energies for propagation and solvation processes.

However, when polymerization was carried out at a higher temperature, say 20 °C, and although the MWD is still not too broad ($M_w/M_n \sim 1.24$), a clearly visible shoulder appears to the high-MW side in the SEC trace of the resulting PtBMA sample. A similar result was also obtained by other workers,[4b] which probably implies the involvement of side reactions during polymerization at such higher temperatures.

Solvation Phenomena and Stereoregulation of tBMA Anionic Polymerization at −78 °C. To confirm such a solvation equilibria mechanism and simultaneously gain a deeper insight into solvation effects on tBMA anionic polymerization, it is obviously of great interest to further investigate how the medium polarity affects the polymerization stereochemistry. As illustrated in Figure 6, two inverse monotonous curves are obtained when the syndiotactic or isotactic contents of PtBMA anionically prepared in mixed solvents are plotted versus THF content. Accordingly, in pure toluene, tBMA anionic polymerization gives rise to an almost purely isotactic placement (*mm* = 0.99), in good agreement with previously reported data.[1b,2] However, that type of triad dramatically drops from 0.99 down to 0.29 when only 10% THF is added. Conversely, the corresponding syndiotactic one substantially increases from 0 to 0.37. A further increase in the THF content up to 50% by volume still leads to changes in tacticity in the same direction, tending to that one observed in pure THF, i.e., a moderately syndiotactic polymer (*rr* = 0.52, *rm* = 0.46, *mm* = 0.02).

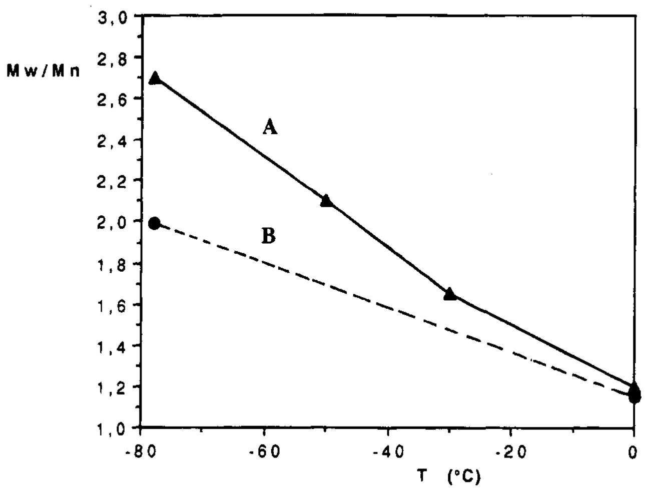


Figure 5. Temperature dependence of polydispersity index (M_w/M_n) of PtBMA synthesized in (A) 10% THF/toluene mixture and (B) 30% THF/toluene mixture. Initiator = DPHLi or DPMLi, concentration = 5 × 10^{-3} mol/L.

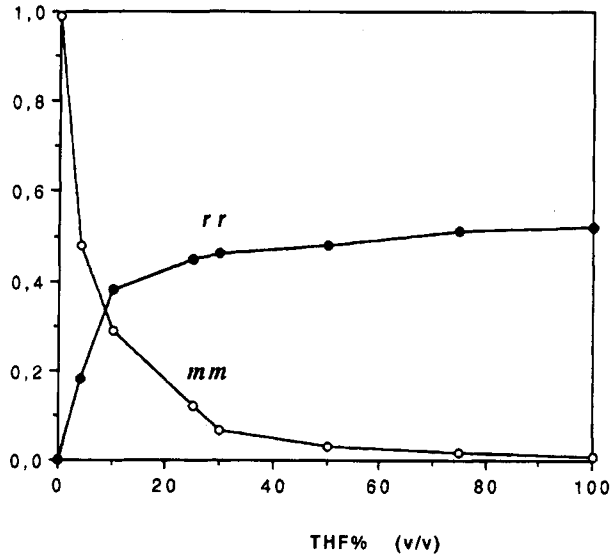


Figure 6. Effect of THF/toluene volume ratio on the triad fraction of PtBMA anionically prepared at −78 °C. Initiator = DPHLi or DPMLi, initiator concentration = 5 × 10^{-3} mol/L.

These significant observations can only be understood if the solvation equilibria mechanism described in Scheme 1 also dominates the stereoregulation of tBMA anionic polymerization, i.e., according to a typical Coleman−Fox multistate stereochemistry model:[5,9] with progressively increasing THF concentration in the system, the equilibria shift toward the formation of more and more THF-solvated active species, resulting in a stepwise increase in syndiotactic placements and a corresponding decrease in isotactic ones. In a 75% THF/toluene mixture, only THF-solvated species are probably present, thus promoting a stereoregularity similar to that in pure THF.

Suzuki has previously performed similar studies on the stereosequence distribution in PMMA anionically prepared in THF/toluene mixtures varying from 100/1 to 10/30 by volume, and a similar dependence of PMMA microtacticity on THF/toluene ratio has been observed.[10] Moreover, he concluded that the PMMA microstructure was very simply approximated by combinations of the

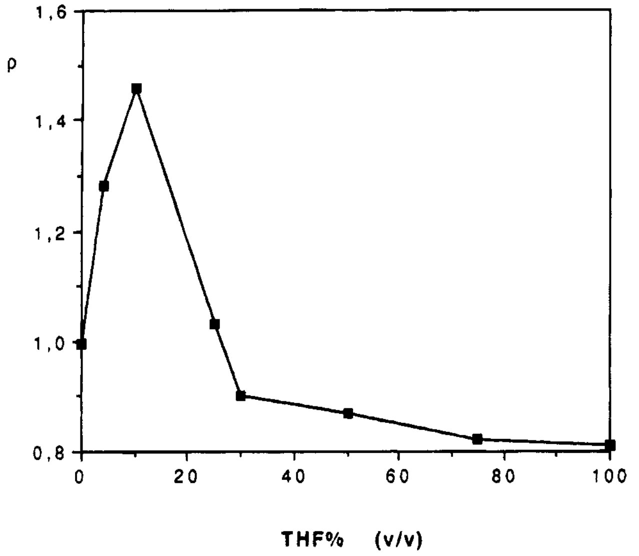


Figure 7. Effect of THF/toluene volume ratio on persistence ratio, $\varrho = (2(m)(r)/(mr))$, of PtBMA anionically prepared at −78 °C. Initiator = DPHLi or DPMLi, initiator concentration = 5 × 10^{-3} mol/L.

structures found for polymers formed in pure toluene and in THF, respectively.

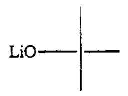
At this point, it seems essential to point out that the Coleman−Fox multistate stereochemistry model only describes the overall distribution of stereosequences as promoted by various stereoselective species. The stereochemistry of each propagating species may possibly be controlled by the *E*/*Z* mechanism[11] and/or the "penultimate" mechanism.[12] To make a quantitative description of tBMA (most probably also MMA) polymerization stereoregularity in mixed solvents, one has to take fully into account various determining factors such as the equilibrium constant of each solvation equilibrium, the propagation rate of each stereoselective species, etc. For MMA polymerization, the situation seems to be still more complex, since termination reactions often occur during the propagation in media containing <30% THF by volume even at low temperatures,[13] e.g., −78 °C.

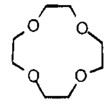
In addition to the above-described results, it is also very intriguing to observe that the persistence ratio, ϱ (=$2(m)(r)/(mr)$), goes through a maximum (ϱ = 1.46) at 10% THF content (Figure 7). Interestingly enough, the maximum MWD is exactly observed at the same THF composition (Figure 4). In view of the fact that the origin of the persistence ratio ϱ is still unclear, this relationship between ϱ and M_w/M_n remains to be elucidated.

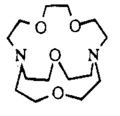
A further examination of the solvation effect on both triad fraction and MWD of the polymer formed in mixed medium, however, reveals some discrepancies. The considerable influence of THF on stereochemistry is found to be limited at ca. 50% THF content (Figure 6), whereas the beneficial effect of THF on MWD appears up to ca. 75% THF composition (Figure 4). So, the medium polarity has apparently a somewhat different effect on these two processes. Presumably, the fact that the microtacticity of the polymer remains almost identical when THF content is increased from 50 to 100% might suggest that only THF-solvated species are present and these species do produce the same stereoregularity. Assuming the interconversion rate between these THF-mediated species is critically dependent on the medium polarity, a broad MWD can be expected if the medium contains a large amount of toluene, e.g., 50% by volume.

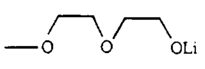
Effects of Various Types of Ligands on the MWD of tBMA Anionic Polymerization in a 9/1 Toluene/THF Mixture at −78 °C. We have recently shown that the use of suitable ligands interacting with the growing species may possibly shift the classic equilibria between different ion pairs (and/or aggregates) toward the formation of new ligation equilibria. Actually, the important role of association/complexation (ligation) equilibria in the anionic polymerization of (meth)acrylic esters has been clearly demonstrated by both kinetics investigation developed by Müller and NMR characterization of related model systems by us.[6b,14,15] It thus appeared of great importance to further demonstrate whether and how various types of ligands affect the aforementioned solvation equilibria (Scheme 1) in relation to the MWD of these polymerizations.

To achieve that purpose, three types of widely used and already well-known ligands have been accordingly considered: (1) μ-type ligands, lithium chloride (LiCl, **1**) and lithium *tert*-butoxide (LiOtBu, **2**); (2) σ-type ligands, 12-crown-4 (12-CE-4, **3**) and cryptand 211 (K211, **4**); and (3) a μ/σ dual type ligand, lithium 2-(2-methoxyethoxy)ethoxide (LiOE$_2$M, **5**).


2, LiOtBu


3, 12-CE-4


4, K211


5, LiOEEM

First, it must be mentioned that similarly to the ligand-free system, all ligated ones studied here always gave quantitative conversion. However, as clearly seen from Figure 8, ligands **1**−**5** do affect the MWD's of the resulting PtBMA quite differently.

Concerning the two σ-ligands, one may immediately see from Figure 8A that, in comparison with 12CE4, K211 has a much more beneficial influence on tBMA anionic polymerization. In fact, when the polymerization was performed in a 9/1 toluene/THF mixture at −78 °C, even in the presence of a 10-fold molar excess of 12CE4 relative to initiator, a broad MWD ($M_w/M_n \sim 1.6$) was observed (Figure 8A). By contrast, a very narrow MWD ($M_w/M_n \sim 1.08$) results upon addition of only 2 molar equiv of K211 (Figure 8A). The same influence of these two ligands on the MWD in MMA anionic polymerization in THF at −78 °C has already been reported by us[15d] and was found to well correspond to their chelating power versus lithium cations associated with the ester enolate ion pairs. Indeed, NMR investigations of related model systems have indicated that, because of the coordinative strength of the O−Li bond present in the lithium ester enolate ion pairs,[15a] 12CE4 is much less efficient than K211 (the most powerful lithium-cation-binding ligand discovered to date) in breaking such a strongly associative O−Li bond toward the formation of a single σ-active species.[15d] To account for the present results, therefore, one might reasonably assume that several types of 12CE4-complexed and -free species, probably also in a relatively slow equilibrium, may still coexist in the 12CE4-ligated system, while in the K211-ligated system either a fast exchange between various active species or more probably a single type of K211-complexed ion pair[15d] is present.

In addition, when the two μ-type ligands are considered, Figure 8B demonstrates that increasing LiCl concentration leads to a profound decrease in the MWD

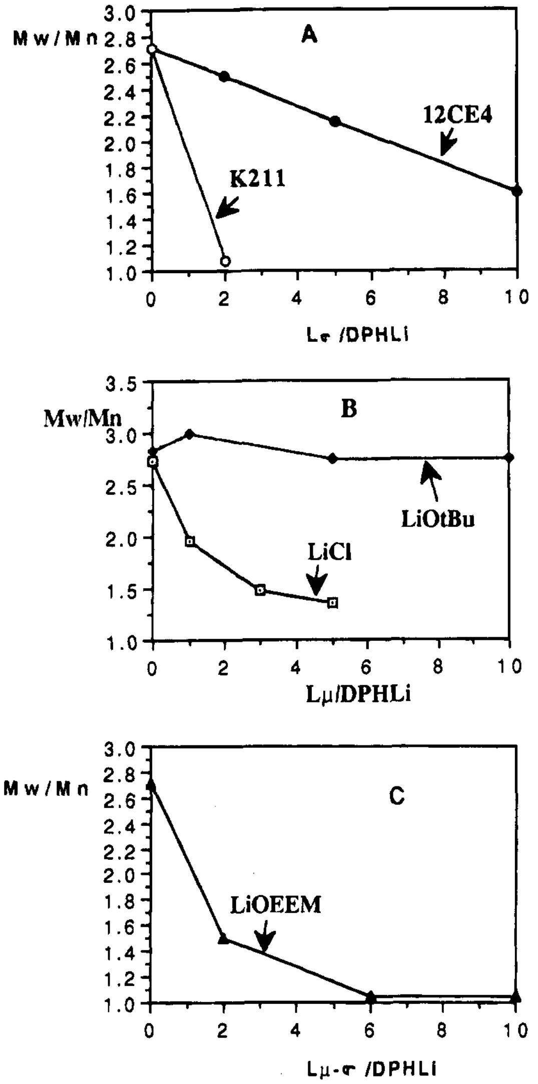


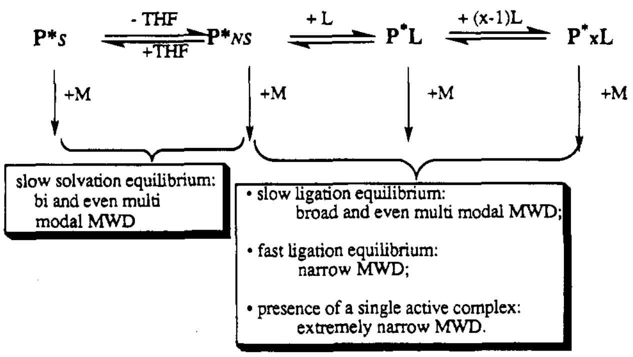
Figure 8. Effect of ligand/initiator molar ratio on the polydispersity (M_w/M_n) of PtBMA anionically prepared at −78 °C in a 9/1 toluene/THF mixture. Initiator = DPHLi, initiator concentration = 5×10^{-3} mol/L.

of the polymer to the point where a relatively narrow, unimodal and symmetrical MWD ($M_w/M_n \sim 1.35$) is obtained when 5 equiv of LiCl is added. However, addition of LiOtBu (up to 10 molar equiv) induces even broader and multimodal MWD's ($M_w/M_n \sim 3.0$) (Figure 8B).

At this point, it is necessary to stress here that there is convincing evidence that LiOtBu, similarly to LiCl, is very effective in complexing lithium ester enolates[15b,c,16] by having the electrostatic advantage of having all lithium cations in the system associated with electron-rich oxygens of the enolate species while also in close contact with the ligand ions ($tBuO^-$ or Cl^-), yielding very stable μ-complexes; the lack of effectiveness of LiOtBu in promoting a narrow MWD thus cannot be simply ascribed to the failure of LiOtBu to coordinate with the propagating species. Obviously, this is very different from the situation discussed above, where 12CE4 is not powerful enough to complex quantitatively the lithium ester enolate with the formation of a single 12CE4-ligated species (see above).

Earlier it was demonstrated by us and others that LiCl can induce fast ligation equilibria between various active species and even yield a single type of active complex in the anionic polymerization of different (meth)acrylic esters in THF and/or toluene/THF mixtures at −78 °C;[4,5,6b,15b] on the contrary, several types of complexed species do coexist in the LiOtBu-added system and the exchange between them is still slow.[6b,15c] Actually, this considerably different μ-ligation dynamics well accounts for largely different MWD's of PMMA or PtBA anionically prepared in the presence of these two μ-ligands under the same experimental conditions.[6b,14,15b,c]

Scheme 2. Schematic Illustration of the Role of Solvation/Ligation Equilibria in the Anionic Polymerization of tBuMA in Toluene/THF Mixed Solvent



One may thus conclude that the aforementioned difference in ligation dynamics of LiCl and LiOtBu might also be at the origin of completely different MWD's of PtBMA prepared in a 9/1 toluene/THF mixture at −78 °C in the presence of these two μ-ligands. It is, however, important to mention here that the observation of a not too narrow MWD ($M_w/M_n = 1.35$) in the presence of 5 molar equiv of LiCl might be partly due to a low solubility of LiCl in a 9/1 toluene/THF mixture. Nevertheless, that value is still much smaller than the ones obtained in the absence of any ligands ($M_w/M_n \sim 2.70$) and in the presence of the same molar amount of LiOtBu ($M_w/M_n \sim 3.0$).

Similarly to K211, finally, LiOE$_2$M offers the most beneficial influence on tBMA anionic polymerization in that mixed medium, as indicated by a dramatic decrease in the M_w/M_n values of the formed polymer, falling from 2.70 to 1.05 when ≥6 molar equiv of LiOE$_2$M is added (Figure 8C). In view of the fact that addition of a μ/σ dual ligand, e.g., LiOE$_2$M, can spontaneously cause a simultaneous μ and σ dual complexation with a lithium ester enolate and result in a single type of stable and bulky ligand-loose species,[15e,17] the observation of such a very narrow MWD is surely to be expected.

Altogether the results discussed above demonstrate that the solvation/ligation equilibria undoubtedly play an important role in the tBMA anionic polymerization in mixed solvents, e.g., a 9/1 toluene/THF mixture. How the thermodynamics and kinetics of the ligation process affect that polymerization can likely be expressed as in Scheme 2. Note that THF-solvated species consist of monomeric and dimeric species.

Quite importantly, as already recalled in the preceding sections, rather similar association/ligation (complexation) equilibria, originally proposed by Müller[6b] and later on confirmed and extended by us,[14,15] induce dramatic effects on the anionic polymerization of (meth)-acrylic esters, particularly on the MWD of the resulting polymer and on its stereoregularity.[6b,14,15] Interestingly enough, in both cases, i.e., anionic polymerization of (meth)acrylic esters in THF and of tBMA polymerization in THF/toluene mixed solvent, each of the ligands investigated affects the MWD in exactly the same direction, the extent of that modification being related to the formation constant of the related complexes.

In conclusion, from above-described results, tBMA anionic polymerization in THF/toluene mixed solvents is a unique model for demonstrating the role of solvation/complexation equilibria in the anionic polymerization of (meth)acrylates. Further progress should focus on the *quantitative* elucidation of these solvation/complexation equilibria in relation to the MWD and stereoregularity in tBMA anionic polymerization.

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