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MECHANISTIC ASPECTS OF 'LIGATED' ANIONIC LIVING POLYMERIZATION (LAP): THE CASE OF (METH)ACRYLIC ESTER MONOMERS

JIN-SHAN WANG*, ROBERT JÉRÔME AND PHILIPPE TEYSSIÉ†

Center for Education and Research on Macromolecules (CERM), University of Liege, Institute of Chemistry B6, Sart-Tilman, 4000 Liege, Belgium

The recently developed 'ligated' technique has proved to be very successful in promoting living anionic polymerization of (meth)acrylic ester monomers. The efficient ligands discovered to date include μ, σ and μ–σ dual types. The roles of these ligands in the control of livingness and stereoregularity of anionic polymerization of (meth)acrylates are discussed in detail. There is convincing evidences that both ligation thermodynamics (electron density redistribution and steric hindrance in the formed active complex) and kinetics (how fast and in which way ligation occurs) are very critical in promoting the livingness. Moreover, steric hindrance appears to be a determining factor maintaining the process 'living' under more demanding conditions.

INTRODUCTION

Until roughly 15 years ago, perfectly controlled polymerization of alkyl acrylates and methacrylates had been a permanent, but poorly answered challenge in polymer science. And yet, the incentives were important and many: increasing availability of the corresponding monomers (production nowadays approaching 5×10^6 tons per year); versatility of the obtained materials, including plastics, adhesives and elastomers, which may contain a number of different reactive functions; and access to higher use temperature, e.g. by increasing T_g to 130 °C or higher for poly(methyl methacrylate) (PMMA) having a syndiotactic content of at least 80%.

Several (partially) successful strategies were followed in order to gain control over the polymerization process in terms of molecular weight (MW) and MW distribution (MWD), stereochemistry and process 'livingness' (necessary for the implementation of 'tailored' molecular engineering of (meth)acrylate containing materials). They may be categorized as follows:

(i) group-transfer polymerization as proposed by Du Pont[1] (Webster *et al.*, Sogah *et al.*);
(ii) use of all-organic large and delocalized ion pairs (Reetz *et al.*,[2] Sivaram *et al.*[3]);
(iii) insertion mechanisms based on coordination complexes (Collins and Ward,[4] Inoue *et al.*,[5] Yasuda *et al.*[6]);
(iv) more recently and still not thoroughly clarified, so-called 'living' radical mechanisms (Mardare and Matyjaszewski[7]);
(v) 'ligated' anionic systems: although a time-honoured approach, studied since the 1950s, these attempts did not give practical answers until 1980s, because of a vast underestimation of the selectivity of the matching requirements between active centres and added ligands (Hatada *et al.*,[8] MR_x; Lochmann and co-workers,[9] MOR: and Teyssié and co-workers, LiCl,[10] hindered crown ethers[11] and LiOEnR[12]).

If one now considers the goals of a general, precise and practical macromolecular engineering, it should meet a number of important requirements, such as 'living', high MW homo- and copolymerization processes; compatible with 'classical' monomers such as styrenes, dienes, vinyls, oxiranes; stereoselective, particularly for PMMA (over 80% syndiotacticity); and in different solvents, preferably in hydrocarbons (and possibly avoiding THF).

If one rightly wishes to implement (co)polymeri-

* Present address: Chemistry Department, Mellon Institute, Carnegie-Mellon University, 4400 5th Avenue, Pittsburgh, PA 15213, U.S.A.
† Author for correspondence.

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zation processes where these goals would be achieved all together, one has to admit that despite their real merits, none of the first four strategies mentioned above meets that demanding challenge. That is the reason why the last aspect, which in principle appeared to be able to be answered, has been thoroughly revisited, in depth, and significantly improved to a point where the above described prospects have mostly been implemented.

The basic idea of a ligand-modified or 'ligated' anionic polymerization (LAP) is to use suitable ligand (or ligands) to interact coordinatively with a very active metal containing (usually alkali metals) initiating and/or propagating ion pairs; in that situation, these ligands fulfil a variety of functions: (i) modulation of the electron density at metal enolate ion pair and, therefore, of its stability and reactivity; (ii) provision of a steric basic barrier blocking a large enough space area around the metal-containing ion pairs, thus possibly minimizing the extent of secondary reactions; and (iii) promotion of new complexation equilibria displacing classical equilibria between different ion pairs and/or aggregates, hopefully leading to the existence of a unique active species.

The really efficient ligands discovered to date may be classified into three groups:

(i) μ-type ligands:
—metal alkoxides in Lochmann's initiator;[9]
—aluminium alkyls in Hatada's initiators;[8]
—inorganic salts, i.e. LiCl, in Teyssié's initators;[10]

(ii) σ-type ligands:
—crown ethers in Teyssié's initiators;[11]

(iii) μ/σ-type dual ligands:
—polyether metal alkoxides in Teyssié's initiators,[12] where a lithium ethoxide moiety may function as a μ-type of coordination site and a polyether component as a σ-type.

RESULTS AND DISCUSSION

Roles of ligands in the control of anionic living polymerization of (meth)acrylates

It is noteworthy that this ligated anionic living polymerization has already been very successful in producing various precisely controlled poly (meth)acrylate-based products,[13] a difficult challenge in polymer synthesis over decades.[14] However, the underlying mechanism was still not completely clear, although anionic polymerization of (meth)acrylates, ligated or not, has been investigated from the kinetic point of view mainly by Müller.[15,16] Direct investigation of the active species has only been occasionally considered,[17] owing to the problem of the unstability of living chains in solution and the complexity of UV, IR and NMR spectra for active species associated with polymer chains.

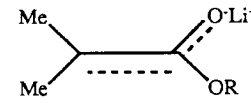
In order to overcome these difficulties, we have recently set up systematic investigations on model systems by means of multinuclear NMR spectroscopy.[18] Although it is difficult to perform a direct NMR spectroscopic investigation on 'real' 'ligated' polymerization systems (see above), the use of models has been found to be very helpful. Accordingly, three types of complexes, i.e. a μ-type of mixed complex,[19,20] a σ-type of cation-binding complex[21] and a μ/σ-type of dual mixed cation-binding complex,[22] have already been studied. The main conclusions can briefly be summarized as follows.

(1) Metal ester enolates display a delocalized character with a strong O—Mt bond,[17,23] while the strength of such an associative bond decreases with increasing size of the counter cation, leading to a more carbanionic character.[17] These results are fairly consistent with IR studies on the same systems previously carried out by Lochmann and co-workers.[24,25] Moreover, these metal enolates (particularly lithium-containing enolates) tend to form aggregated species,[17,23] and the exchange rate among differently aggregated species was generally found to be slow on the NMR time-scale.[23]

(2) The μ-type of complexation between lithium enolate and LiCl (or LiOtBu) benefits from strong spontaneous electrostatic interactions, all cations in the system being associated with enolate oxygen (and probably carbanion as well) while also in close contact with the ligand ions.[19,20] Accordingly, the self-associative O—Li bond in lithium ester enolates can be completely perturbed, resulting in a rearranged tight and highly charged delocalized μ-complex.[19,20]

(3) Because of the presence of a relatively strong O—Li bond in lithium ester enolates,[23] the various σ-type of lithium cation-binding ligands studied (i.e. DME, Glyme-3, HMPA, 12CE4 and K211) cannot induce successful σ-coordination in THF, except for K211; that situation probably leads to a coexistence of ligand-free and -added species.[21]

(4) A first NMR spectroscopic characterization[22] of complexation between a lithium ester enolate, i.e. methyl α-lithioisobutyrate (MIBLi, **1a**), and a lithium-containing μ/σ dual ligand, i.e. lithium 2-(2-methoxyethoxy)ethoxide ($LiOE_2M$), indicated that such a μ/σ dual ligand is exceptionally effective in reacting with highly aggregated lithium enolate through a 'μ-mixed/σ-binding' pathway, with formation of a bulky and relatively large charge-separated μ/σ complex.[22]



a R= CH_3,
b R= $C(CH_3)_3$

(1)

Again, it is also important to stress here that, although there appear to be some differences between models and

real living systems, documented examples have already confirmed the value of these models for a deeper understanding and a rational discussion of ion pair behaviour and polymerization process characteristics.[19-21]

In the following sections, we shall focus on the various roles of ligands in controlling the anionic living polymerization of (meth)acrylates. It is essential to know how various ligands affect the electronic structure and dynamics of the metal ester enolate ion pairs in relation to that polymerization process.

Monomer structural factors controlling the living process

It has been found that even small variations in the monomer structure (and thus in the corresponding active centre) exert a profound influence on the polymerization process.[15,16,26] In order to obtain a better insight into the 'ligation' roles, it is accordingly important first to discuss these structural factors in relation to the living polymerization process characteristics.

Ester substituent: electronic and steric factors are both crucial. There are some indications from kinetics that steric factors in the ester substituent are less important than the electronic factors in affecting the propagation rate constants (k_p)[15,16] (Table 1). Müller[16] has accordingly attributed the observed distinctly low rate constant of tBuMA polymerization to two sets of electronic influences.[16] First, the electron-donating *tert*-butyl group decreases the polarization of the monomer and hence its reactivity. Second although this *tert*-butyl group may conversely increase the charge density on the carbanion and thus its reactivity, the latter effect is partially cancelled by ion-pairing effects: the increase in charge density leads to a smaller interionic distance, which again decreases the rate constants.

Table 2 shows the ^{13}C chemical shifts of two model compounds (**1a** and **b**), which may structurally mimic the living ends of poly(methyl methacrylate) and poly(*tert*-butyl methacrylate), respectively, together with Taft's σ^* parameter,[27] which measures the electron-donating effect of the substituent. In complete contradiction to Müller's speculation, these data clearly indicate that an increase in electron-donating effect from the ester substituent (from methyl to *tert*-butyl), and whatever the counter cation, leads to a considerable decrease in the charge density at carbanion carbon but to a slight increase at the carbonyl group, as evidenced by a large downfield shift (3–7 ppm) at the α-carbon and, although small, a still detectable upfield shift (1–3 ppm) at the C(O) carbon. This might be reasonably interpreted as resulting in more charge localization at electron-rich oxyanion atom, when increasing the electron-donating effect of ester substituent, so leading to a tighter O—Li bond and subsequently to a less ionic interaction between carbanion (i.e., C-α) and lithium cation. As rightly pointed out by Muller,[16] the electronic effects of the ester substituent on kinetics are very complex and difficult to predict. Nevertheless, a considerable modification of electron density distribution around an enolate type of active centre, due to the presence of *tert*-butyl group, at least in part accounts for the special kinetic behaviour in tBuMA polymerization (cf. Table 1).

Table 1. Rate constants and activation parameters for the anionic polymerization of MMA and tBuMA in THF[a]

Compound	σ^*[b]	Parameter	Li^+	Na^+
MMA	0·00	Log A		
		k_p	100	800
tBuMA	−0·32	Log A	8·2	8·7
		k_p	6	56

[a] See Ref. 16.
[b] Taft's σ^* parameter, see Ref. 27.

Although it is also difficult at this point to generate a valuable correlation between the charge distribution around the active centre and the livingness of the polymerization, the fact that lowering the charge density at carbanion carbon may accordingly reduce the nucleophilicity of the enolate species and consequently enhance its stability might reasonably suggest that the presence of a highly electron-donating group (i.e. *tert*-butyl) should in principle minimize the extent of secondary attacks of the active centre on the monomers and/or in the so-called back-biting reactions ocurring on the growing macromolecule.

Nevertheless, the steric hindrance of the ester substituent in a methacrylic monomer and/or monomeric units in the chain apparently represents a determining parameter preventing undesirable attacks, as substantially supported by the following pertinent observations:

(i) When alkyl methacrylates were anionically polymerized in THF using LiCl-complexed simple organolithium compounds (e.g. sBuLi) as initiator (except for the tBuMA polymerization, which proceeds in a controlled manner up to at least 0 °C), terminating attack of carbonyl group by highly nucleophilic and little hindered LiCl-added sBuLi always unavoidably occurs even at −78 °C, resulting in very limited conversion and broad multimodal MWD.[28]

(ii) In sharp contrast to the 'living' process observed in the copolymerization of tBuMA–tBuA or tBuMA–MMA mixtures in THF using a LiCl-complexed initiator,[29] MMA–tBuA mixtures conversely give very poor results in terms of yield and MWD.[30] This has been well accounted for by the selective attack of a penultimate small MMA methoxy group in the copolymer chain by the less

Table 2. Carbon-13 chemical shifts[a] (δ, ppm) of 0·5 M metal isobutyrate salts in THF-d_8 at −60 °C

Compound	σ^{*b}	C(O)			C-α		
		Li[c]	Na	K	Li[c]	Na	K
Methyl α-lithioisobutyrate (**1a**)	0·00	158·9	162·4	161·6	65·4	66·7	63·3
tert-Butyl α-lithioisobutyrate (**1b**)	−0·32	157·9	159·2	158·9	72·9	69·6	70·0

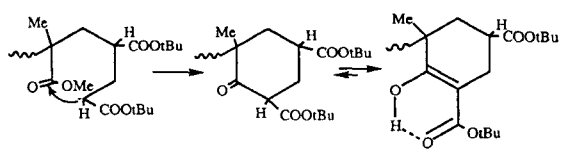
[a] Relative to high field resonance of THF-d_8, 25·3 ppm.
[b] Taft's σ^* parameter for ester substituent, see Ref. 27.
[c] Only dimeric species have been taken into account.

hindered LiCl-complexed PtBuA ion pair (i.e. a crossover back-biting termination reaction (see Scheme 1)).[30]

α-Substituent: steric factor versus electronic factor. Except for tBuA in THF at very low temperatures, when no ligands are used, the anionic polymerization of acrylate monomers always gives rise to considerable side-reactions, whichever experimental conditions used (another proof of the importance of *tert*-butyl group in promoting living polymerization). By contrast, in anionic polymerization of most alkyl methacrylates, various termination reactions can be limited to the point where a living process prevails, when certain suitable experimental conditions are accommodated.[16,26,31]

It might then at first sight seem reasonable that the presence of a α-acidic hydrogen be responsible for these ill-defined anionic polymerizations of acrylic esters. However, ^{2}H labelling experiments performed by Lochmann *et al.*[32] gave no evidence to support such a speculation. Conversely, it was found that the so-called back-biting reaction dominates the tBuA polymerization at 25 °C only after longer reaction time.[33]

Actually, the data summarized in Table 3 convincingly demonstrate that the α-hydrogen atom does not significantly perturb the living polymerization of tBuA in THF at −78 °C, even when highly nucleophilic LiCl-complexed sBuLi was used as initiator. In contrast, a completely ill-defined MMA polymerization is observed under the same experimental conditions. Up to this point, one may immediately conclude that the α-acidic hydrogen is much less important than the ester subtsituent in the control of the living (meth)acrylate polymerization process.



Scheme 1

Moreover, a further insight into the characteristic data for MMA–tBuMA and MMA–tBuA copolymerization processes (Table 4) obviously reveals that the steric hindrance at the α-position is much more influential than the electronic situation, in affecting both the reactivity of the active center towards the monomer and the livingness of the copolymerization (i.e. suppression of the so-called back biting reactions).[29]

Thermodynamics as controlled by different ligands

Coordination strength of σ-chelating ligands towards the metal–ester enolate ion pair: a key parameter in σ-ligated systems. It is well known that 12-crown-4 (12CE4) is one of the most specific σ-coordinating ligands for the lithium cation.[34]. However, ^{13}C and ^{7}Li NMR investigations on model systems indicated that[21] such a σ-ligand is still not powerful enough to destroy the self-aggregation of lithium ester enolates, nor does it have a significant influence on the charge distribution over THF-solvated lithium ester enolate: that is probably due to the presence of relatively strong O—Li associative bonds in that compound. Similar results were also obtained by Jackmann and co-workers35 and House et al.[36] in the complexation of lithium phenolates and lithium enolates with various crown ethers in polar solvents, respectively.

The lack of a sufficient coordination strength of 12CE4 and other crown ethers towards lithium ester enolates is directly reflected in their very low efficiency in promoting the anionic living polymerization of (meth)acrylates, as shown by the data reported in Table 5.

Nevertheless, the substitution of a lithium cation by a sodium cation in several crown ethers–Mt^+ complexed initiator pairs greatly improves the situation; a perfectly living polymerization of MMA can be indeed achieved even at 5 °C in toluene,[11] as long as the CEs are sterically hindered. Along the same lines, the K211–Li^+ pair was also found to work efficiently in inducing an extremely low polydispersity of living PMMA in THF at −78 °C.[21] These results paved the way for two promising approaches to a successful σ-ligation in relation to the process livingness: either enhancing the

Table 3. Anionic polymerization of MMA and tBuA in THF at −78 °C, using a 10LiCl/sBuLi initiator system

Monomer	Polymerization time (min)	Yield (wt%)	$M_{n_{cal}}$[a]	$M_{n_{SEC}}$[b]	M_w/M_nb	f[c]
MMA	90	Trace	—	—	—	—
tBuA	60	100	10000	10500	1·03	0·95

[a] $M_{n_{cal}}$ = weight of monomer (g)/concentration of initiator (mol).
[b] Based on a poly(methyl methacrylate) calibration.
[c] Initiator efficiency $f = M_{n_{cal}}/M_{n_{SEC}}$.

Table 4. Characterization data for the anionic 'random' polymerization of alkyl (meth)acrylates in THF at −78 °C[29,30]

Commoner pair (M_1–M_2)	Counter ion	Living character	r[a] M_1	r[a] M_2
MMA–tBuMA	Li^+	Yes	35[b]	0·43[b]
	Na^+	Yes	8·2[c]	0·17[c]
	10LiCl–Li^+	Yes		
MMA–tBuA	Li^+	No	0·02	9·5
	Na^+	No	0·07	7·2
	10LiCl–Li^+	No		

[a] Monomer reactivity ratio.
[b] r Values taken from Ref. 16; polymerization was carried out at −75 °C;
[c] r Values taken from Ref. 16; polymerization was carried out at −69 °C.

Table 5. Anionic polymerization of alkyl (meth)acrylates initiated with (diphenylmethyl)lithium in the presence of various crown ethers[a]

Monomer	Crown (CE)	CE : I[b]	THF : toluene (v/v)	Temperature (°C)	Time (min)	Yield (wt%)	$M_{n_{exp_3}}$ (×10^{-3})	M_w/M_n	Initiator efficiency
MMA	12-Crown-4	2 : 1	5 : 95	−78	30	72		—[c]	
	12-Crown-4	2 : 1	100 : 0	−20	60	85	64·0	1·20	0·38
	12-Crown-4	2 : 1	5 : 95	−20	30	60		—[c]	
	15-Crown-5	2 : 1	100 : 0	−20	5	95	23·0	4·50	0·55
	18-Crown-6	2 : 1	100 : 0	−20	5	90	14·0	3·50	0·45
tBuA	12-Crown-4	1 : 1	10 : 90	−20	60	100	162·5	3·50	0·14
nBuA	12-Crown-4	2 : 1	5 : 95	−78	120	12		—[c]	

[a] Initiator concentration 4×10^{-4} mol l^{-1}.
[b] Molar ratio of crown to initiator.
[c] Multimodal MWD.

coordination strength of the complexing agent versus lithium cation by using an even more powerful ligand (e.g. K211), or reducing the associative strength of the O—Mt bond in the metal enolate by increasing the size of the associated cations: it must be remembered, however, that the use of Na^+ or K^+ ion is detrimental for the aimed-at high syndiotacticity of PMMA.

It is also interesting to find that (Table 6), when n-butyl acrylate is anionically polymerized at −78 °C in the presence of various types of cryptands, all resulting characteristics (yield, efficiency and MWD) support the same conclusion: termination reactions occur to a considerable extent during the polymerization, in sharp contrast to the situation observed in the presence of $LiOtBu$[9d] or $LiOE_2M$,[12b] where a partially living or perfectly living nBuA anionic polymerization was achieved, respectively. Since cryptands (the most powerful cation-binding ligands discovered to date) often induce more charge separation between complexed cation and enolate anion, possibly with the

Table 6. Anionic polymerization of *n*-butyl acrylate (nBuA) at −78 °C using cryptand-complexed initiator system[a]

Initiator	Cryptand (molar equiv.)	Solvent	Yield (wt%)	$M_{n_{exp}}$ ($\times 10^{-3}$)	M_w/M_n	Initiator efficiency
Ph_2CHLi	K211 (2)	THF	—	—	—	—
	K211 (2)	Toluene	16	—	—	—
Ph_2CHNa	K222 (2)	THF	21	35·0	1·9	0·45
	K222 (2)	Toluene	21	23·0	1·9	0·93
Ph_2CHK	K222 (2)	THF	81	51·5	2·3	0·85
	K222 (2)	Toluene	84	36·5	2·0	0·92

[a] Initiator concentration: $2{\cdot}0 \times 10^{-4}$ mol l^{-1}.

formation of cryptand-separated ion pairs or even free ions,[37] the present results presumably suggest that these cryptand-separated or free polyacrylate type of active species might be less stable and some of them spontaneously terminate during the propagation, yielding poorer results.

Therefore, it seems most likely that the coordination strength of a σ-ligand towards the metal ester enolate ion pairs may strongly affect the degree of ion pair association, i.e. negative charge distribution around the σ-ligated complex, which in turn plays an important role in the control of the anionic polymerization of (meth)acrylates; a subtle optimization is therefore needed here.

Steric hindrance around the active complex: a determining factor for maintaining the process livingness under more demanding conditions. As noted in preceding sections, unlike the complexation between crown ethers and lithium ester enolates, μ-type ligands exhibit a high propensity to coordinate with lithium enolate ion pairs,[19,20] resulting in a tight and highly charge delocalized mixed complex. Undoubtedly, this is an important feature in stabilizing the formed active complex,[13] at the origin of living polymerizations as promoted by LiX (X = halogen, OtBu) and simple R_3Al ligands.[8a,9,10]

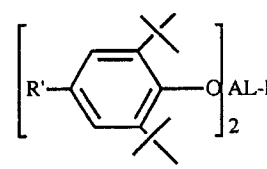
Despite a strong dependence of the complexation efficiency on the electron-withdrawing power of the ligand anion,[13b] the previously reported μ-ligated controls[8a,9,10] are usually limited to narrow experimental conditions. Typically, the use of a low polymerization temperature still appears essential to ensure the living anionic polymerization of most methacrylates and bulky acrylates.[13,38]

Moreover, whenever the steric factor becomes critical for the control of the living process, μ-type ligated systems discovered to date were found not to work really well, even at low temperatures. As a typical example illustrating this important point, it has been found that, although LiCl is very effective in promoting the perfectly living homo- and block (two directional) (co)polymerization of MMA and tBuA in THF at −78 °C,[10,39] the anionic copolymerization of MMA–tBuA mixtures under the same conditions always leads to very poor results.[30] In other words, the Cl ligand is not bulky enough to block a given space area around the μ-type complex in order to avoid the attack of the very active complex on the small methoxy group of the MMA antipenultimate unit in the polymer chain (also see above).

The same arguments are valid for explaining the inefficiency of simple inorganic salts in the anionic polymerization of acrylates other than tBuA.[13,40]

An increase in the steric hindrance around the formed stable complex, whatever its origin, brings about a significant improvement of the livingness of the polymerization, as strongly supported by numerous examples.

Hatada et al. first demonstrated that t-BuLi affords a highly syndiotactic PMMA ($rr > 90\%$) having a narrow MWD (<1·2)[8a] when the polymerization is carried out in toluene at −78 °C in the presence of trialkylaluminium. However, that ligated system is effective only at low temperatures and requires a long reaction time.[38] In this respect, Ballard et al. has recently replaced trialkylaluminium by dialkylaluminium compounds bearing a phenolate group.[8b] It was found that a controlled polymerization of MMA can be achieved at temperatures as high as 0 °C using these bulky aluminium phenolate-complexed initiators. Recently, we have demonstrated that some very bulky disubstituted monoalkyl aluminium phenolates (2) are still more effective in promoting controlled anionic polymerization of MMA even at 40 °C.[8c] Clearly, these results provide unequivocal proof for the important steric influence on the living process of a bulky phenoxy in an alkylaluminium based μ-type of ligand.



R=Me, Et, iBu
R'=H,Me,tBu

2

Along similar lines, a comparison of the effects of two crown ethers, i.e. dibenzo-18-crown-6 (DB18CE6) and 18-crown-6 (18CE6) on the MMA anionic polymerization associated with an Na^+ cation reveals that (Table 7),[41] although the electron-delocalizing effect of the benzo groups reduces the electron donor ability of the oxygen atoms [resulting in a relatively weaker Na^+-ligand interaction; see log K_f (Table 7)], DB18CE6 surprisingly gives rise to much better results than to 18CE6 (Table 7), again supporting the critical role of steric hindrance, as promoted by the former ligand in the immediate vicinity of the active species.[11]

In addition, as noted in Table 8, the importance of steric factors in 'ligated' active sites also clearly appears in the control of anionic living polymerization of primary acrylates, e.g. 2-ethylhexyl acrylate (2EtHA). Since there is convincing evidence from NMR spectroscopy that the ligands listed in Table 8 are all very effective in coordinating to lithium ester enolates with the formation of stable complexes,[19–22] the living character of 2EtHA polymerization under given conditions dramatically decreases in the sequence $LiOE_2M$ (perfectly living) > LiOtBu (partially living) > LiCl (not living), perfectly parallel to a decreasing steric barrier of the X moiety around the formed LiX–LiR complex, in the same order $ME_2O^- > tBuO^- > Cl^-$.[18]

It is also worth noting that, although LiOtBu can induce a partially living polymerization of 2EtHA owing to both the relatively higher steric hindrance of the OtBu group around the formed LiOtBu-complexed active species and that of the O-2EtH group in the monomer and polymer chain, this ligand, similarly to LiCl, does not afford any beneficial influence on the living statistical copolymerization of MMA–tBuA at −78 °C in THF (Table 9). Most likely, such a more sensitive 'living' random copolymerization requires an even much bulkier environment around PtBuA-based active species in order to avoid their vigourous nucleophilic attack towards the very sensitive small OCH_3 group (Scheme 1). Importantly, and also consistently, two sterically more hindered ligated systems, i.e. DB18CE6–Na^+ and $LiOE_2M$–Li^+, are significantly those which were found for the first time to efficiently prevent the aforementioned back-biting attacks (Scheme 1), resulting in well defined monodispersed statistical P(MMA–co-tBuA) copolymers (Table 9). Obviously, this again emphasizes the critical importance of two essential structural characteristics of both DB18CE6 and LiOE2M, giving them the capability simultaneously to coordinate with active species with the formation of single stable complexes, on the one hand, and more critically surround them with a steric barrier blocking a large enough space area, on the other (Scheme 2).

Table 7. Effect of macrocyclic crown ethers (CE, 1 mol equiv.) on MMA anionic polymerization in THF at −20 °C using (diphenylmethyl) sodium as initiator[a]

CE	log K_f[b]	Yield (wt%)	$10^{-3} M_{n,exp}$ (SEC)	M_w/M_n (SEC)	Initiator efficiency
18CE6	5·59	100	13·0	3·00	0·6
DB18CE6	4·60	100	8·0	1·05	0·97

[a] Ref. 11.

Kinetics as controlled by different ligands

From the above discussion, it is obvious that structural thermodynamics as controlled by ligands definitely governs the living polymerization process. However, in order to produce precisely defined polymers, of great importance is not only the ligation thermodynamics but also its kinetics, i.e. complex dynamics as promoted by those different ligands.

Association–ligation equilibria. Although the anionic polymerization of (meth)acrylates is often disturbed by side termination reactions, polymerization of some (meth)acrylates such as MMA and tBuA has proved to be free of side-reactions and quantitative.[13,26,32] This happens when a carefully purified monomer (i.e. on an aluminium alkyl) is polymerized with a highly delocalized and bulky initiator (e.g. diphenylhexyllithium, DPHLi) in a polar solvent (e.g. THF) at low temperature (e.g. < −60 °C).

Compared, however, with the 'ideal' living polymerization of non-polar monomers, such as styrene, the polydispersity of resulting PMMA (M_w/M_n) usually

Table 8. Anionic polymerization of 2-ethylhexyl acrylate in 9 : 1 (v/v) toluene–THF using LiX–RLi initiator system

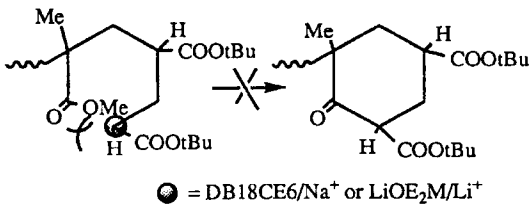
LiX/RLi (mol/mol)[a]	Steric barrier[b] of X	Temperature (°C)	Time (min)	Yield (wt%)	$M_{n,cal}$	$M_{n,SEC}$	M_w/M_n	Living character
LiCl/DPMLi (5 : 1)	▲	−78	60	25	5000	17500	2·50	No
LiOtBu/tBIBLi (3 : 1)[c]		−60	2	100	9200	16600	1·09	Partial
LiOEEM/DPMLI (10 : 1)		−78	1	100	15000	16100	1·05	Yes

[a] LiOEEM = lithium 2-(2-methoxyethoxy)ethoxide; LiOtBu = lithium *tert*-butoxide; DPMLi = diphenylmethyllithium; tBIBLi = *tert*-butyl α-lithioisobutyrate.
[b] See Ref. 18.
[c] alue taken from P. Vleck *et al.*, *Makromol. Chem., Rapid Commun.* **13**, 163 (1992).

Table 9. Anionic 'random' copolymerization of MMA–tBuA mixture[a] in THF at −78 °C using (diphenylmethyl)lithium as an initiator and in the presence of various ligands

Ligand[b]	Time (min)	Yield (wt%)	tBuA in polymer (mol%)	$M_{n_{cal}}/M_{n_{SEC}}$	M_w/M_n	Living character
—	60	6·8	87·1	0·64	2·5	No
12-CE-4	60	25·0	99·0	0·19	2·1	No
LiCl	60	18·2	95·0	0·33	2·0	No
LiOtBu	60	45·0	95·0	0·41	2·1	No
LiOEEM	3	100	42	0·91	1·15	Yes
DB18CE6[c]	10	100	42·5	0·96	1·07	Yes

[a] Molar ratio in the feed: MMA : tBuA = 58 : 42.
[b] 10 mol equiv. of ligand relative to initiator.
[c] (Diphenylmethyl)sodium was used as initiator with 2 mol equiv. of DB 18CE6.



Scheme 2

remains broad.[13,26] Moreover, a multimodal MWD may result in tBuA polymerization.[10b,13a,42]

Conversely, on addition of LiCl, the situation changes profoundly. As illustrated in Figure 1, the effect of LiCl on the MWD of PMMA and PtBuA is very pronounced. The polydispersity index, M_w/M_n, drops asymptotically (owing to complex formation) from ca 1·15 to 1·02 and from 3·50 to 1·04 for PMMA and PtBuA, respectively, when over 5 mol equiv. of LiCl with respect to the initiator are added into the system. Similar results have also been reported by Müller and co-workers.[42,43] According to these authors, addition of LiCl modifies to some extent the propagation rate of the alkyl(meth)acrylate polymerization, but not the termination rate.[42]

All these experimental data reasonably agree with a significant effect of LiCl on the initiation and propagation steps rather than on the termination step.[19,42]

Recently, Müller and co-workers have focused on the kinetics of the related polymerization systems and proposed that association–complexation equilibria dominate the anionic polymerization of MMA and tBuA.[42,43] An equilibrium between dimeric and monomeric living $PMMA^-Li^+$ or $PtBuA^-Li^+$ chains in THF should occur. However, complexation of the active centres by LiCl competes with the association of living $PMMA^-Li^+$ or $PtBuA^-Li^+$, and strongly affects kinetics and polydispersity of the living chains.

NMR investigations on model systems also support the key effect of these association–complexation equilibria in the anionic polymerization of MMA in THF, at low temperature. As shown previously,[23] there is an aggregation equilibrium between tetramer and dimer in MIBLi solutions in THF, in the absence of LiCl, and the occurrence of a slow exchange between these two species. Such dynamics are comparable to the proposal by Müller and co-workers of a slow equilibrium between dimeric and monomeric $PMMA^-Li^+$ in THF at low temperature.[42] Fast addition of monomer to living chains must then lead to a large polydisperity.[42,44] In contrast, the mixed complexation by LiCl does shift this aggregation equilibrium towards the formation of a single mixed species at LiCl/MIBLi = 1, 2 (and maybe ⩾ 3),[19] which can thus give rise to a living polymer of a very low polydispersity, i.e. close to 1.

The aforementioned role of association–ligation equilibria is further confirmed and extended by comparison of SEC data for PtBuA prepared in the presence of various types of ligands and NMR results regarding the dynamics of a complexed model compound, i.e. methyl a-lithioisobutyrate (MIBLi) combined with various ligands (Table 10).

From Table 10, it becomes clear that there is a remarkable correlation between polydispersity of the resulting polymer and dynamics of the ligated ion pairs. LiOEEM- and LiCl-complexed initiators lead to a very narrow MWD, due to a single active complex.[19,22] Although LiOtBu is very efficient in complexing enolate species with the formation of various mixed complexes,[20] a slow exchange process still occurs among these species. If they are active in propagating chains, they should be responsible for a broad MWD. Moreover, it has been demonstrated that the presence of 12-CE-4 is not powerful enough to destroy the aggregated MIBLi species, and an aggregation equilibrium still dominates in the complexed system.[21] That situation must also lead to a broad MWD, as already demonstrated in the ligand-free polymerization system.

Solvation–ligation equilibria. Recently, it has been observed by us[45] that the anionic polymerization of tert-butyl methacrylate (tBuMA) proceeds in a living

Table 10. Comparison of SEC data for PtBuA prepared in the presence of various ligands[a,b] and dynamics of MIBLi (**1a**) complexed with these ligands

Ligand (mol equiv.)	M_w/M_n (SEC)[c]	Complexed MIBLi[d]
—	3·50 (bimodal)	Slow aggregation equilibrium
12-CE-4 (10)	2·63 (bimodal)	Slow aggregation equilibrium
LiOtBu (10)	1·35	Slow mixed aggregation equilibrium
LiCl	1·04	A single mixed complex
LiOEEM (10)	1·05	A single complexed species

[a] Conditions for polymerization: temperature, −78 °C; solvent, THF; initiator, diphenylhexyllithium.
[b] Yield 100%.
[c] Calibration with a polystyrene standard.
[d] NMR results (Refs 19–23).

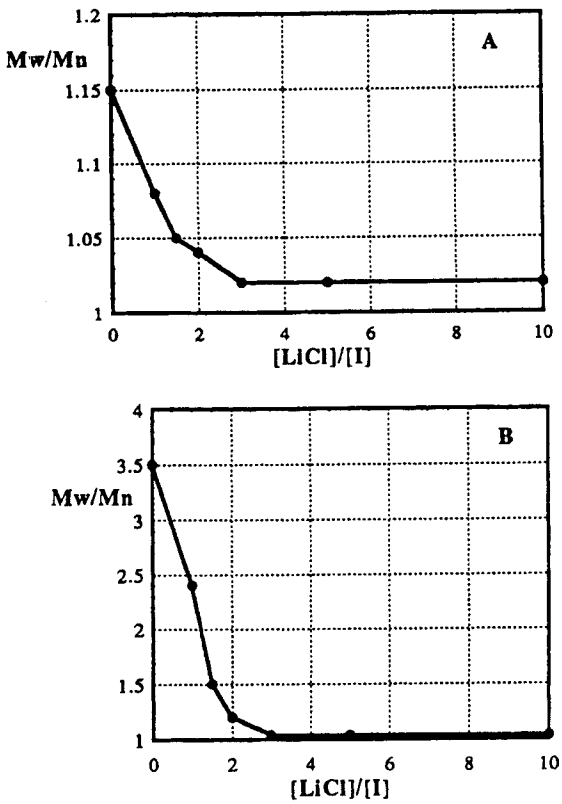


Figure 1. Polydispersity of (A) PMMA and (B) PtBuA as a function of LiCl to initiator ratio. Initiator, (diphenylmethyl) lithium (DPMLi); solvent, THF; temperature, −78 °C; Yield, 100%

fashion and induces a narrow and unimodal MWD in either pure THF or pure toluene at −78 °C in the presence of a lithium counter ion. However, in THF–toluene mixtures, keeping other conditions unchanged, surprisingly broad bi- and even multimodal MWDs were obtained. Moreover, increasing polymerization temperature from −78 °C to 0 °C promotes a narrower MWD, atypical of termination reactions; indeed at 0 °C, a very narrow unimodal MWD is again obtained. These results have been satisfactorily interpreted in terms of a solvation equilibria mechanism:[45] there coexist (several) THF-solvated and non-solvated active species, exchanging slowly at −78 °C but fast at 0 °C compared with the monomer addition rate, thus resulting in a multimodal MWD in the former case and a narrow one in the latter.

As expected, various types of ligands affect these slowly exchanging solvation equilibria in different ways characteristic of different ligation dynamics, and consequently affect also the MWD of the final polymers, as for example in the case of tBuMA anionic polymerization in a 70:30 toluene–THF mixture at −78 °C (Table 11). Similarly to the effect of these ligands on the MWD of PtBuA from anionic polymerization (see above), the results shown in Table 11 might we be accounted for by another multi-state equilibria mechanism, i.e., a solvation–ligation equilibria mechanism:[45] in comparison with 12CE4 and LiOtBu, ligands such as $LiOE_2M$, K211 and LiCl give rise to much narrower MWDs (M_w/M_n down to <1·05), in fair consistency with their high propensity to coordinate with lithium ester enolates, and to induce a fast exchanging ligation equilibrium and a single type of active complex.[19,21,22]. However, it is necessary to point out that, unlike the 12-CE-4-added system, where a broad MWD might be the consequence of a coexistence of 12-CE-4-complexed and -free active species,[21], a lack of effectiveness of LiOtBu in promoting a narrow MWD is most likely due to the involvement of several slowly exchanging LiOtBu-complexed active species.[20,45]

Role of ligation dynamics in the control of MWD. From above-described results, it is interesting to see that each ligand studied here has a similar effect on association equilibria as on solvation equilibria, in relation to the MWD of the formed polymer, suggesting

Table 11. Anionic polymerization of tBuMA in a 7:3 toluene–THF mixture at −78 °C, using (diphenylmethyl)lithium initiator and in the presence of various types of ligands[a]

Ligand	L/I[b]	Time (min)	Yield (wt%)	$M_{n_{cal}}$	$M_{n_{SEC}}$	M_w/M_n
—	—	240	100	8000	9900	2·00
LiCl	10/1	360	100	8000	8200	1·04
LiOtBu	10/1	360	100	6500	12000	2·15
12CE4	10/1	150	100	8000	9500	1·35
K211	2/1	60	100	8000	8900	1·05
LiOEEM	10/1	30	100	8500	8700	1·03

[a]Initiator concentration 5×10^{-3} mol l^{-1}.
[b]Molar ratio of ligand to initiator.

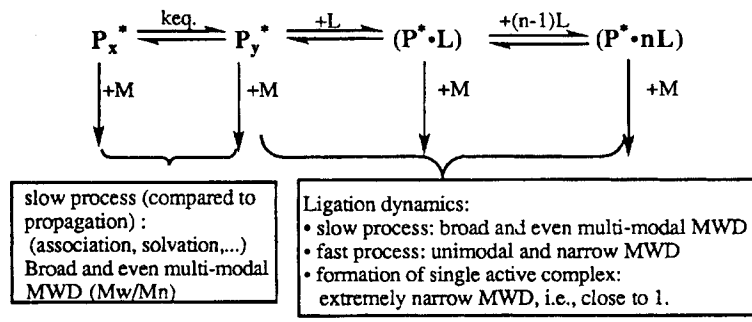
that the same original influence is at play. How the dynamics of the ligation process, whatever its origin, may affect the living anionic polymerization of (meth)acrylates is illustrated in Scheme 3. Note that the general behaviour explaining the dependence of the MWD of the resulting polymer by the dynamic equilibria between various propagating species has already been described by Szwarc.[44] The present work gives additional support to that general role in the control of our currently developed 'ligated' anionic living polymerizations of (meth)acrylates.

Stereochemistry as controlled by different ligands

Recently, much effort has also been devoted to simultaneously controlling the stereoregularity of anionic (meth)acrylate polymerization, hopefully by means of the same 'ligated' approach.[46–49] This also requires a better understanding of the effects of various types of ligands on the stereochemistry of these polymerizations. Although a sizable body of literature has resulted from such investigations,[45] the determining factors in the control of that stereoregularity are not yet fully understood.[46]

Stereochemistry of the 'ligated' anionic polymerization of MMA as controlled by Coleman–Fox multi-state mechanism. A long time ago, Coleman and Fox[51] made the assumption that the stereochemistry of a polymerization might be controlled by a multi-state dynamic equilibria mechanism in which the active living chains exist in two (or more) states being able to interconvert. On the basis of experimental observations, we recently proved that the ligation dynamics as illustrated in Scheme 3, typical of a Coleman–Fox model, apparently control both the livingness and the stereochemistry of MMA anionic polymerizations.[47,49]

Indeed, there is substantial evidence that association–ligation equilibria govern the stereoregularity of such polymerizations in THF–toluene mixtures.[47,49] The following conclusions have been reached: (i) The associated and non-associated species selectively produce the meso and racemic placements, respectively.[47] (ii) Complexation of active species by lithium cation-binding ligands, such as 12-CE-4 and K211, simply shifts the association equilibrium towards the formation of non-associated species (of course, depending on the coordinatioon power of the ligand), resulting in syndiotactic placements; (iii) The effect of a μ-type ligand strongly depends on the aggregation degree of the living polymer chains in the formed active complex. In a 9:1 toluene–THF mixture, LiCl or LiOtBu gives rise to syndiotactic or isotactic stereoregulation, matching the situation observed in pure THF or



Scheme 3

pure toluene, respectively; this is probably due to the fact that associated living chains are involved in LiOtBu-complexed species, but not in LiCl-complexed species.[19,20,47] (iv) Since a dual $\mu-\sigma$ lithium alkoxide, $LiOE_2M$, i.e. a very strong ligand, promotes the formation of the same type of non-associated $\mu-\sigma$ looser complex, whichever the solvent, a highly syndiotactic PMMA results in all cases.[49]

It is important to point out that the dynamic ligation equilibria model only describes the *overall* distribution of stereoisomers as promoted by various stereoselective active complexes. The stereochemistry of each individual propagating species, i.e. the really determining factor in the stereoregulation of the polymerization, may possibly be controlled by another type of mechanism.[47,49]

This conclusion is interestingly supported by results pertaining to the effect of LiCl on the stereochemistry of tBuMA anionic polymerization in the presence of a lithium cation. A previous study demonstrated that the solvation equilibria dominate the stereochemistry of tBuMA anionic polymerization in THF–toluene mixtures.[45] Conversely, as illustrated in Figure 2(B), addition of LiCl now leads to a progressive increase in isotactic content when tBuMA is anionically polymerized in a 9:1 toluene–THF mixture at −78 °C. This can be easily understood if solvation–ligation equilibria are at play. In contrast, as already demonstrated elsewhere,[47] under the same experimental conditions (temperature, polarity of the medium, and counter cation), LiCl affects the stereochemistry of MMA anionic polymerization in an opposite way [also see Figure 2(A)]. This provides a very clear indication that PMMA$^-$Li$^+$ and PtBuMA$^-$Li$^+$, although both complexed by the same ligand, i.e. LiCl, obviously display different stereoselective characters. The same phenomenon also emerges from a comparison of the effect of LiCl on the stereochemistry of MMA and tBuMA polymerization in pure THF at −78 °C. Although LiCl has no influence on the stereoregularity of the MMA polymerization, it does significantly affect that of the tBuMA polymerization, where the isotactic content increases in parallel with the LiCl to initiator molar ratio. Similar results have also been reported by Varshney et al.[52]

Chain-end E–Z stereoisomerism and main chain stereoregularity in the ligated anionic polymerization of MMA. Recently, Müller and co-workers have proposed that the stereochemistry of MMA anionic polymerization is mainly controlled by the E–Z stereoisomerism of the living chain end.[46,53] In comparison with the frequently used 'penultimate' mechanism,[54] this E–Z interpretation seems to offer a still preliminary but very valuable approach to the evaluation of factors controlling the behaviour of various stereoselective species.

In order to gain a better understanding of the stereochemistry of the ligated process, the chain-end E–Z

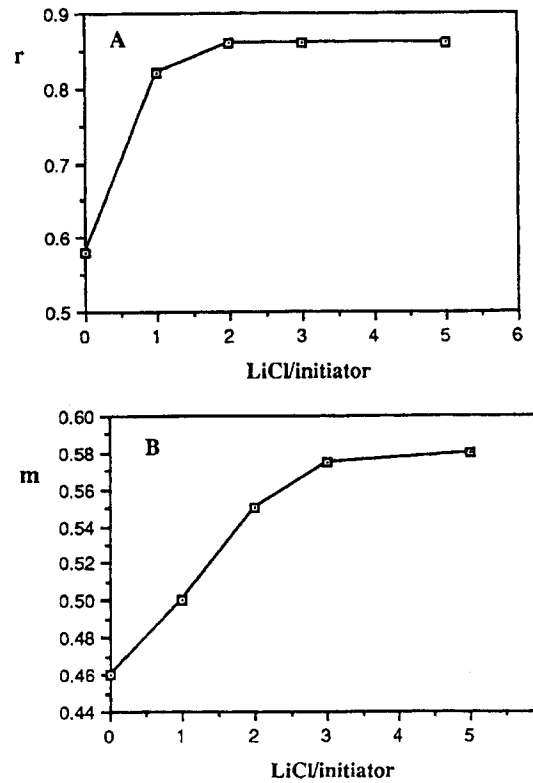


Figure 2. Effect of LiCl to initiator molar ratio on the diad fraction of (A) PMMA and (B) PtBuMA anionically prepared in a 9:1 toluene–THF mixture at −78 °C in the presence of a lithium counter ion

ratio and the main chain tacticity of living PMMA anionically prepared in the presence of various ligands, were determined from ^{13}C NMR spectroscopy of silylated PMMA, the resulting data being given in Table 12. For comparison purposes, similar data for MMA anionic polymerization associated with ligand free-Li^+ and -K^+ and K222-complexed K^+ species are also included in that Table.

From table 12, one can immediately rank the ligands studied here into three groups: (1) ligands which do not affect the chain-end Z/E ratio nor main-chain tacticity, i.e. 12CE4 (Li^+), HMPA (Li^+), and LiOtBu (Li^+): (2) ligands which affect chain-end Z/E ratio but not main-chain tacticity, i.e. LiCl (Li^+) and $LiOE_2M$ (Li^+); and (3) ligands which simultaneously affect the chain-end Z/E ratio and main-chain tacticity, i.e. K211 (Li^+) and K222 (K^+).

Although a lack of influence of 12CE4 and HMPA on both the chain-end Z/E ratio and main-chain tacticity may be accounted for by a poor coordination power towards lithium ester enolates,[21] it is still very striking that the K211–Li^+ and K222–K^+ systems afford a

Table 12. Main-chain tacticity and chain-end E/Z ratio of MMA anionic polymerization in THF at −78 °C in the presence of various ligands[a]

Counter ion	Ligand (mol equiv.)	Main-chain			Chain-end E/Z ratio: Z (%)
		rr	*mr*	*mm*	
Li^+	—	0·81	0·18	0·01	100
	HMPA (4)	0·80	0·19	0·01	100
	LiOtBu(5)	0·80	0·19	0·01	100
	LiCl (3)	0·79	0·20	0·01	88·5
	LiOEEM (5)	0·82	0·16	0·01	88·0
	12CE4 (5)	0·77	0·21	0·01	100
	K211 (2)	0·65	0·33	0·02	10
K^+[b]	—	0·38	0·56	0·05	60
	K222 (3)	0·67	0·31	0·02	10

[a]Polymerization conditions: initiator, diphenylmethyllithium; concentration, 7×10^{-3} mol l^{-1}; monomer concentration, 0·2 mol l^{-1}.
[b]Ref. 53.

living PMMA having the same chain-end E/Z ratio and the same main-chain tacticity, suggestive of the independence of the stereochemistry (both chain-end Z/E ratio and main-chain tacticity) on the counter cation associated in two different cryptated systems. This appears obviously inconsistent with a simple E–Z model such as described by Müller and Hogen-Esch,[53] saying that for E–Z ends the probabilities of producing meso/racemic placements are monotonous functions of the radius of counter ion. Since K211 and K222 are the strongest cation-binding ligands specific for Li^+ and K^+,[37] respectively, it is highly possible that they involve the same type and degree of ion association in K211–Li^+ and K222–K^+ chain ends in MMA anionic polymerization. Support for this conclusion is the fact that cryptand ligands can promote the formation of a complex in which the cation is completely encapsulated by cryptand,[55] i.e. possible formation of cryptand-separated ion pairs or even of free ions. In this regard, the present results might provide the first evidence for the important role of the ion-pairing structure rather than of cation size in the control of the stereochemistry (both chain-end Z/E ratio and main-chain tacticity) in MMA anionic polymerization, in the presence of K211–Li^+ or K222–K^+. Actually, as already mentioned above and clearly demonstrated elsewhere,[56,57] the nature of the counter cation may strongly affect the ion-pairing behaviour. In other words, the monotonous functions describing the probabilities of producing meso/racemic placements versus the counter cation radius as observed by Müller and co-workers[53] might also be inherently strongly connected with the ion pairing structure as promoted by different counter cations.

However, the effects of other three ligands, i.e. LiOtBu, LiCl and $LiOE_2M$, on the stereochemistry are even more complex. Although LiCl and $LiOE_2M$ display very different complexing behaviours versus lithium ester enolates,[19,22] both ligands have the same influence on the stereochemistry (Z/E ratio and main chain tacticity) of MMA anionic polymerization (Table 12), a fact for which no satisfactory explanation has been found. On the other hand, LiOtBu, proved to be a strong ligand, has no significant effect. A further in-depth analysis of this theoretically and practically important problem is obviously and urgently needed.

CONCLUSIONS

The significance and consequences of results and concepts presented above are rather obvious, but important enough to be highlighted here.

First, the efficiency of the 'ligated active site' approach is more than convincingly established. It allows a very fine tuningup of the reactivity of the active species, its stability and to some extent its stereoselectivity, these being the key parameters to be controlled with a view to developing a sufficiently broad and versatile macromolecular engineering.

These potentialities have been illustrated by the practical, straightforward synthesis, under convenient solvent and temperature conditions, of a wealth of promising new products: monodisperse homo-PMMA, polyacrylates and polyacrylic acid,[13] monodisperse random copolymers,[58] diblock copolymers with styrenes and dienes useful as emulsifiers and compatibilizers,[59,60] triblock[61,62] and star diblock copolymers[63] with good thermoplastic elastomer characteristics, macromonomers,[64] telechelics[65] and halatotelechelics with unexpected mesomorphic-type phase organization.[66]

Undoubtedly the same approach can also be applied, when necessary, to other monomers susceptible to nucleophilic initiation and attacks, i.e. styrenes, dienes, vinylpyridines, oxirane and cyclosiloxanes, in

combination or not with (meth)acrylates. In a still more exploratory vein, other exciting extrapolations might also be envisioned, e.g. in small molecules organic synthesis involving delicate nucleophilic mechanisms. Above all, the achievements summarized here may definitely give more confidence in the belief that coordination chemistry principles might really offer golden tools for tailoring active sites in polymerization processes, whatever their basic mechanism: coordinative, of course, but also ionic, radical or even stepwise propagation.[67]

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