

Anionic polymerization of methacrylic monomers: characterization of the propagating species

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Abstract

Ligation of the anionic species responsible for the polymerization (LAP) of alkyl(meth)acrylates has much contributed to improve polymerization control. This ligated anionic polymerization has been firstly studied by using model compounds, such as low molecular weight lithium ester enolates. Recently, effort has been devoted to the direct analysis of the species that propagate the anionic polymerization of (meth)acrylates. In addition to IR, multinuclear NMR spectroscopy has been very instrumental in the elucidation of the structure and aggregation of the active species and how these characteristic features are modified by the addition of various types of ligands. This substantial progress in the characterization of the polyalkyl(meth)acrylate anions, ligated or not, is reported in this review.

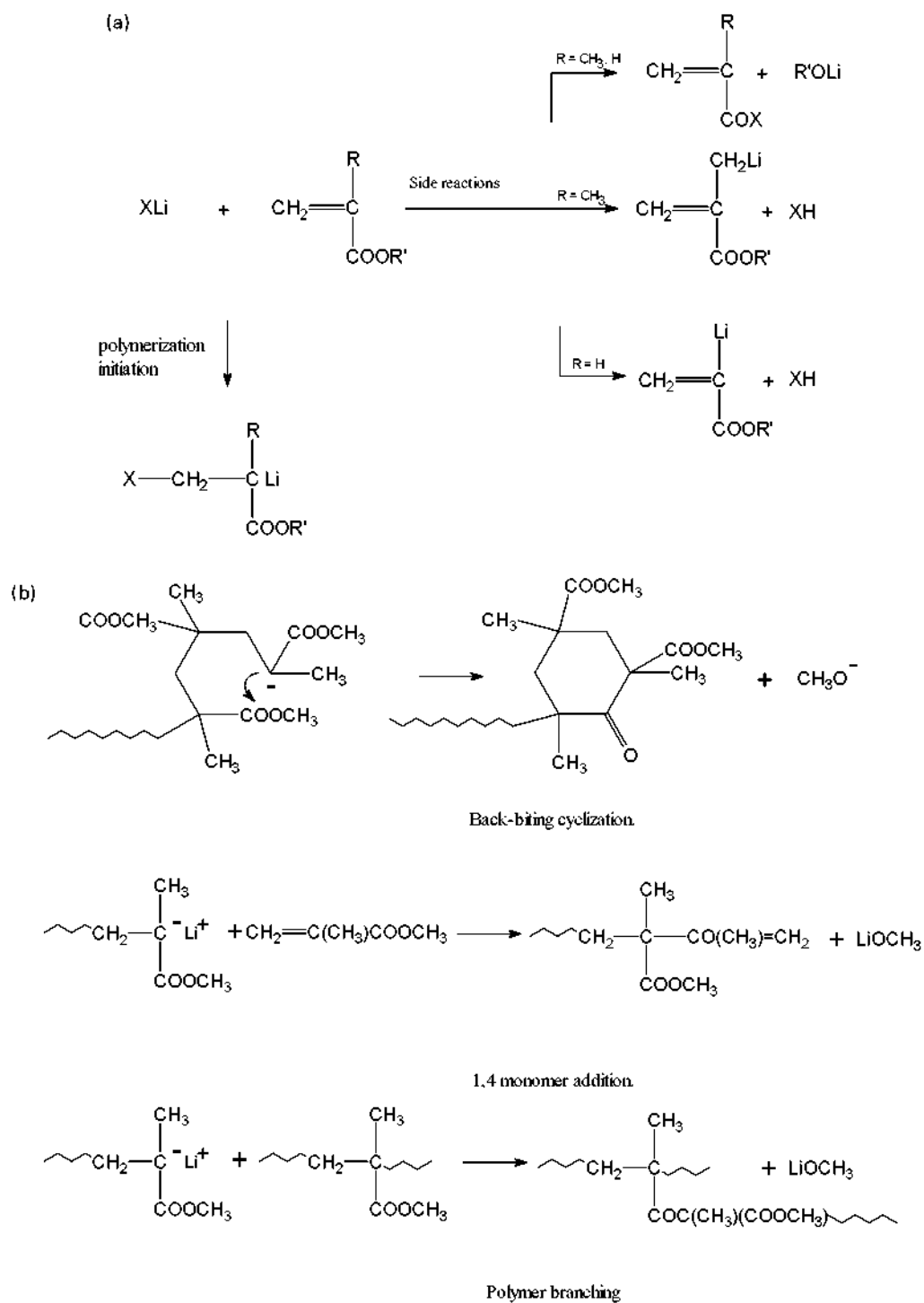
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Introduction

Although the fine control of the polymerization of alkyl (meth)acrylates has been a challenge for a long time, several successful strategies have emerged during the last few years that have imparted a high degree of livingness to this polyaddition reaction. In this respect, group transfer polymerization [1,2], metal free anionic polymerization [3], covalent living polymerization [4], controlled radical polymerization [5] and ligated anionic polymerization (LAP) [6] are worth being mentioned. Nowadays, these techniques actively contribute to the engineering of versatile products such as plastics, adhesives and elastomers containing a number of different reactive functions.

The anionic polymerization of alkyl(meth)acrylates will be the main topic of this review, particularly the structure of the active species and how this structure is modified by the addition of various types of ligands. Ligation has indeed proved to be very flexible and it is able to control precisely poly(meth)acrylate-based products [6–11]. It is worth recalling that the mechanism of anionic polymerization of apolar monomers, such as styrene [15,16] and dienes [17,18], has been thoroughly studied by a series of dedicated techniques, i.e. spectroscopy, conductimetry and kinetic analysis [15]. In contrast, very few comprehensive investigations of the anionic polymerization of polar monomers, particularly (meth)acrylates, have been reported, as result of the limited stability of the active species in solution under ambient conditions. Nevertheless, in the 1980s, very useful pieces of information were collected from kinetic analysis of the anionic polymerization of alkyl(meth)acrylate by Müller [19,20]. NMR analysis of the polymerization stereochemistry [21–24] and the study of deuterated acrylates have also contributed to the better understanding of these systems [25]. The ligated anionic polymerization (LAP) of alkyl(meth)acrylates, which has much contributed to the improvement of polymerization control, has received special attention, mainly based on the study of model compounds, such as lithium ester enolates, by IR [26] and multinuclear NMR spectroscopy [27,28]. This type of study has provided valuable information on the structure and dynamics of the growing species in the LAP of (meth)acrylates, the ultimate purpose being to understand how the molecular characteristic features of the final poly(methacrylates) (MW distribution, stereochemistry) are influenced by these species and their characteristics.

The recent progress in the direct analysis of the species propagating during the anionic polymerization of (meth)acrylates will be the topic of this review, with special emphasis on the structure of lithium ester enolate species.



Scheme 1. (a) Side reactions competing with the initiation of acrylate ($R = \text{H}$) and methacrylate ($R = \text{CH}_3$) monomers by an alkyl lithium (XLi). The same competitive reactions are also operative in the propagation step. (b) Chain termination, monomer 1,4-addition, polymer branching.

The really efficient ligands discovered to date in this field may be classified into three groups, the structure of the most representative ones being shown in Scheme 2:

1. μ -type ligands, that form polycentric bonding with the metal ester enolate: metal alkoxides [38-42], aluminum alkyls [43-45], and inorganic salts [46-49].
2. σ -type ligands, that form coordinative complexes with the metal counterion of the active species: crown ethers [50] and kryptands [51].
3. μ/σ type ligands [52-54], that form both μ - and σ -type interactions with the active species: polyether metal alkoxides, such as lithium 2-(2-methoxyethoxy) ethoxide, where the lithium ethoxide group may function as a μ -type of ligand and the polyether component as a σ -type [53,54].

Under suitable experimental conditions, e.g. initiator, solvent, temperature, it is possible to impart livingness to the polymerization of both acrylate and methacrylate monomers, and thus to implement the engineering of useful (meth)acrylate-based products, e.g. polyacrylates, polyacrylic acid [30], mono-disperse random copolymers of predictable molecular weights and low polydispersities [53,55,56], diblock copolymers with styrene and dienes having potential interfacial activity, triblock and star-shaped diblock copolymers with characteristics of thermoplastic elastomers [57,58], macromonomers [59,60], telechelics [8] and halatotelechelic polymers with mesomorphic phase organization [61].

3. Direct investigation of the lithium-ester enolate structure typical of living polyalkylmethacrylates

3.1. Preamble

In order to clarify the mechanism for the anionic polymerization of (meth)acrylates, various models have been examined, particularly lithium ester enolates or α -lithioesters designated as unimeric models [27,62,63] (1, Scheme 3). These types of compounds are the simplest models for the growth center, that have the ability to show a dramatic change of reactivity when the first, the second and the third monomer units are added [64].

Table 1

Average degree of aggregation of model enolates in benzene and THF at room temperature [69]

Enolates	Average degree of aggregation	
	Benzene	THF
$(\text{CH}_3)_2\text{CLiCO}_2\text{CH}_3$	Insoluble	3.5
$(\text{CH}_3)_2\text{CLiCO}_2\text{CH}_2\text{CH}_3$	6.6	3.5
$(\text{CH}_3)_2\text{CLiCO}_2\text{C}(\text{CH}_3)_3$	Insoluble	2.3
$(\text{CH}_3)_2\text{CCHLiCO}_2\text{CH}_3$	–	2.0
$(\text{CH}_3)_2\text{CHCO}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)\text{LiCO}_2\text{C}(\text{CH}_3)_3$	–	1.7
$(\text{CH}_3)_2\text{CLiCO}_2\text{C}(\text{CH}_3)_3 \cdot (\text{CH}_3)_3\text{OLi}$	2.8	1.8

The most reasonable explanation for this observation is the coordination of the lithium ion with the penultimate ester group of the chain, which is only feasible when the growing species contain two ester groups. The study of a dimeric model (2, Scheme 3), such as dialkyl-2-lithio-2,4,4'-trimethylglutarate, is thus most important [65,66]. Finally, it makes sense to characterize the ion pairs associated with low molecular weight living chains of poly(alkyl)methacrylates (3, Scheme 3) [67]. This review will mainly focus on the structure of the lithium ester enolate for the three types of models (1, 2, 3), that has been investigated by IR and NMR spectroscopy, conductimetry and measurements of colligative properties. Kinetic data and stereochemistry of the chain growth will also be emphasized.

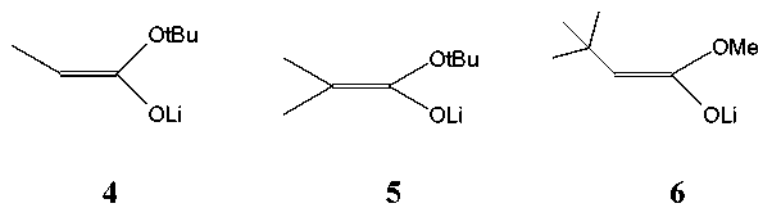
Since the structure of the ion pairs and their aggregation are intimately dependent on the solvent and the addition of ligands, the general discussion of the lithium ester enolates (1, 2, 3) will be divided into three major parts dealing with: (i) study of the models in THF; (ii) study of the ligated models in THF; and (iii) study of the models in toluene before and after ligation.

3.2. Structure of lithium ester enolates in THF

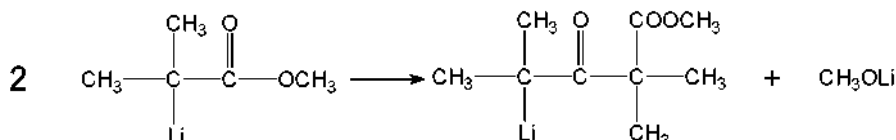
3.2.1. Unimeric model

α -lithio carboxylic esters, i.e. the simplest models for the active sites of polyalkylmethacrylate anions, were prepared by Lochmann et al. [26]. This type of compound, also recommended as an initiator for the anionic polymerization of MMA, is atopic of active research in organic chemistry. Indeed, enolates and their chemistry are of prime importance for aldol-type reactions, the synthesis of (β -lactams and Michael addition reactions. The

structure of enolate species was studied early in the 1970s by a set of experimental techniques, such as IR, NMR, RX scattering and measurements of colligative properties.



Scheme 4. Structure of the 4–6 lithium enolates.



Scheme 5. Self condensation of Li methylisobutyrate.

The analysis of α -lithio ester solutions by vapor pressure osmometry has demonstrated the propensity of these compounds to undergo aggregation [69]. As shown in Table 1, the experimental average degree of aggregation of enolates depends on the ester group and decreases as the alkyl ester group becomes bulkier.

The tendency of Li enolates to self-aggregate is confirmed by the crystalline structure observed by RX analysis, particularly in case of Li enolates derived from *tert*-butylpropionate (4), *tert*-butyl 2-methyl-propionate (5) and 3,3 dimethylbutanoate (6) (Scheme 4) [106].

Metal enolates and the neutral precursors have been analyzed by IR spectroscopy [70-72]. The characteristic absorption of the CO^-Li^+ group is observed as a single band between 1650 and 1700 cm^{-1} compared to the absorption of the $\text{C}=\text{O}$ group at ca. 1730 cm^{-1} for the parent esters. This shift to lower frequencies for the CO group as result of metallation is a way to measure the ionicity of the C-Li bond. The experimental data confirm the model of strongly polarized covalent C-Li bonds for α -lithioisobutyrate. Moreover, IR analyses have also shown that metalated esters are unstable in solution. The decomposition reaction has been studied in case of the metalated ester of isobutyric acid. γ -metalated 2,2,4-trimethyl-3-oxopentanoate is formed as result of a self-condensation reaction, at a rate which depends on the structure of the metal ester (Scheme 5).

As follow-up of ^{13}C NMR analysis of two α -lithio esters, methylisobutyrate (MiB) and ethylisobutyrate (EiB), by Bywater [27] the unimeric model for the propagation center of polymethylmethacrylate chains has been recently analyzed in THF by multinuclear NMR by Wang et al. [62] and Kriz et al. [63].

Table 2
 ^{13}C chemical shifts for lithium isobutyrate at different temperatures

Ref.	R ₁	R ₂	T(°C)	Conc. (mol/l)	Chemical shifts			
					C=O	C α	OR ₂	CH ₃
[27] ^a	Me	Me	25	–	176.8	34.3	51.3	19.2
[27]	Me	Me	–60	–	160	73.1/71.7	56.7/55.8	18.3/17.6
[62]	Me	Me	–60	0.5	160.5/158.9	73.4/72.2/65.4	56.9/56.2	18.4/18/18.9
[27]	Me	Et	–50	–	158.5/159.1	73.7/73.1	65.7/64.8	17.6/18.1
[65]	Me	<i>t</i> Bu	–40	0.1	155.9	71.9/71	28.1	18/17
[27]	Et	Me	–60	–	160/159.6	79.3/79.9	56.8/56.9	–

^a Here ^{13}C chemical shifts of the non-lithiated compounds.



Scheme 6. Isomerization equilibrium for the lithium salt of 2-methylbutyric methyl ester.

^{13}C NMR spectra for the lithium derivatives of butyric esters in THF are consistent with the structure of an ester enolate, the negative charge being delocalized on the O–C–C bond system (Table 2, entries 3 and 4) [27]. This conclusion is supported by the change in the ^{13}C NMR chemical shifts compared to the non-lithiated product (Table 2). The cation is thus expected to be next to the O atom and to assist withdrawing the negative charge from the α -position to the oxygen, decreasing accordingly the shielding of the nuclei in the α position. It is however worth noting that ^1H chemical shifts might be significantly affected by long-range shielding contributions due to neighboring solvent molecules or to conformational changes of the enolate ion. Therefore, ^{13}C chemical shifts are a much better indicator for the electron distribution at the α -position. The alkali metal enolates may exist as *cis* or *trans* isomers as shown in Scheme 6. Bywater et al. [27] studied the lithium salt of 2-methylbutyric methyl ester (M2-MiBLi) in THF by ^{13}C NMR at different temperatures. They observed two sets of signals with a constant relative intensity in the temperature range from -60°C to -20°C . If *E/Z* isomers are the origin of these signals, the isomerization should be extremely fast in the studied range of temperatures. No clear assignment for these two sets of signals has been proposed.

On the basis of the tetrameric aggregation of MiBLi and the ^{13}C NMR study by Bywater et al. [27,28], Wang et al. [62] studied further THF solutions of MiBLi by ^7Li , ^1H and ^{13}C NMR spectroscopies. Peak multiplicities in the ^7Li (Fig. 1) and ^{13}C spectra were explained by a temperature- and concentration- dependent equilibrium between tetramers and dimers as shown by Eq. (1).

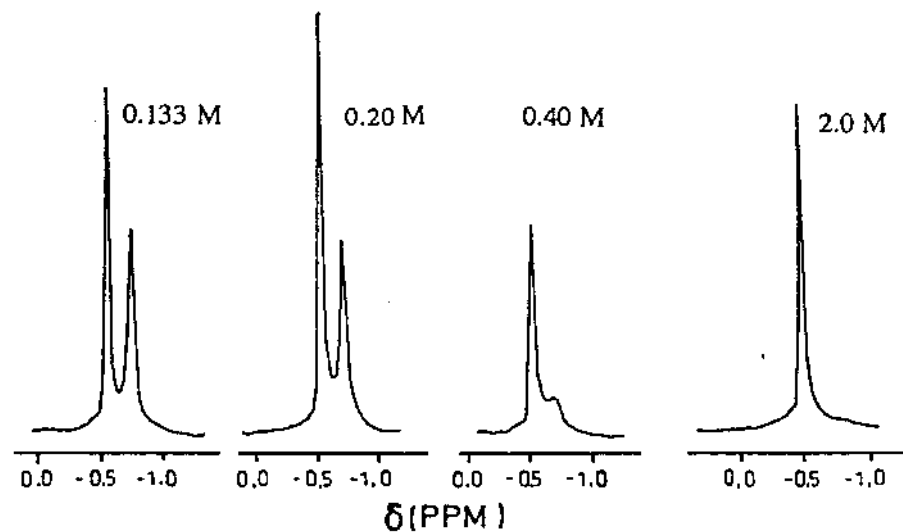


Fig. 1. ^7Li NMR of MiBLi recorded at different concentrations, in THF at 197 K.

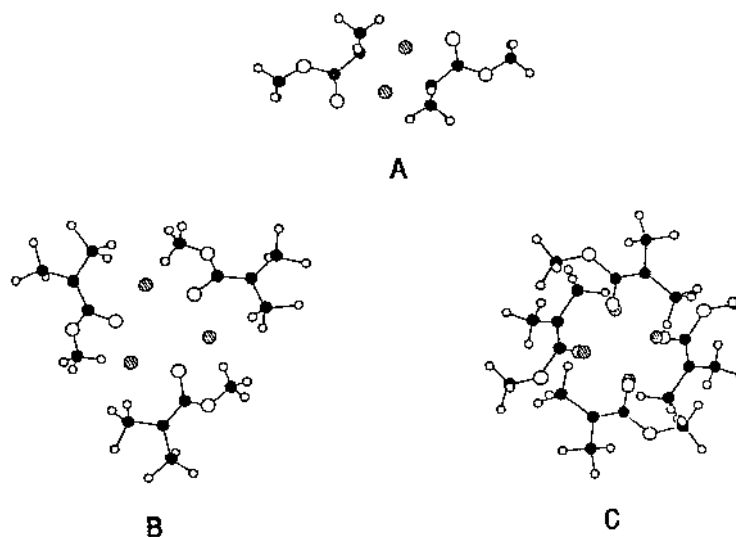
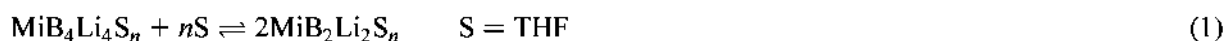


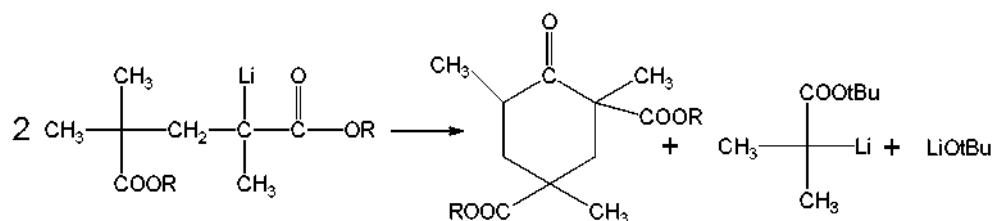
Fig. 2. Hypothetical structures for the aggregates of MiBLi: A: dimer; B: trimer; C: tetramer. Hatched symbols: lithium atoms; full symbols: carbon atoms; open symbols: oxygen atoms.

When either the temperature or the concentration is decreased, the equilibrium is shifted to the right, thus in favor of the dimer. The enthalpy change for this equilibrium was found to be -2.1 kcal/mol and $\Delta S = -13.7$ cal/mol K. The NMR data are also in agreement with Bywater's earlier results about charge delocalization in MiBLi dissolved in THF:



The actual conformation of the MiBLi molecules within the aggregates was investigated by Kriz et al. [63] on the basis of NMR chemical shifts, the heteronuclear Overhauser effect, correlation spectroscopy and relaxation data. Compared to the study by Wang et al. [62], Kriz et al. [63] observed a large variety of forms within the aggregates and a somewhat different dependence of the basic equilibria on the overall concentration and time. The exchange rate between dimers, trimers and tetramers was found to be slow compared to the propagation rate. Ab initio and semiempirical molecular orbital calculations by Dybal and Kriz [73] were in good agreement with the structures proposed for the MiBLi aggregates (Fig. 2). The calculated stabilization energy and geometry were also in line with the spectroscopic data.

tert-Butyl 2-lithioisobutyrate (tBiBLi), which is more stable than MiBLi was also investigated by Kriz [65,66] using the same methodology. A unique form was observed for tBiBLi in THF whatever be the concentration and temperature. Consistent with the relaxation data, this form is more likely a tetramer. Slow and irreversible changes above -30°C were observed and assigned to coordination of tBiBLi with the self-condensation byproducts. tBiBLi (20%) does not contribute to well-defined NMR signals, possibly because they form a partly organized pseudophase. As suggested by MNDO calculations (heat of formation and the stabilization energy), tBiBLi dimers and trimers would be somewhat more stable than tetramers. This discrepancy with the experimental observations might be due to approximations inherent with MNDO calculations that for e.g. consider molecules in vacuo.



Scheme 7. Decomposition of dimer model compounds.

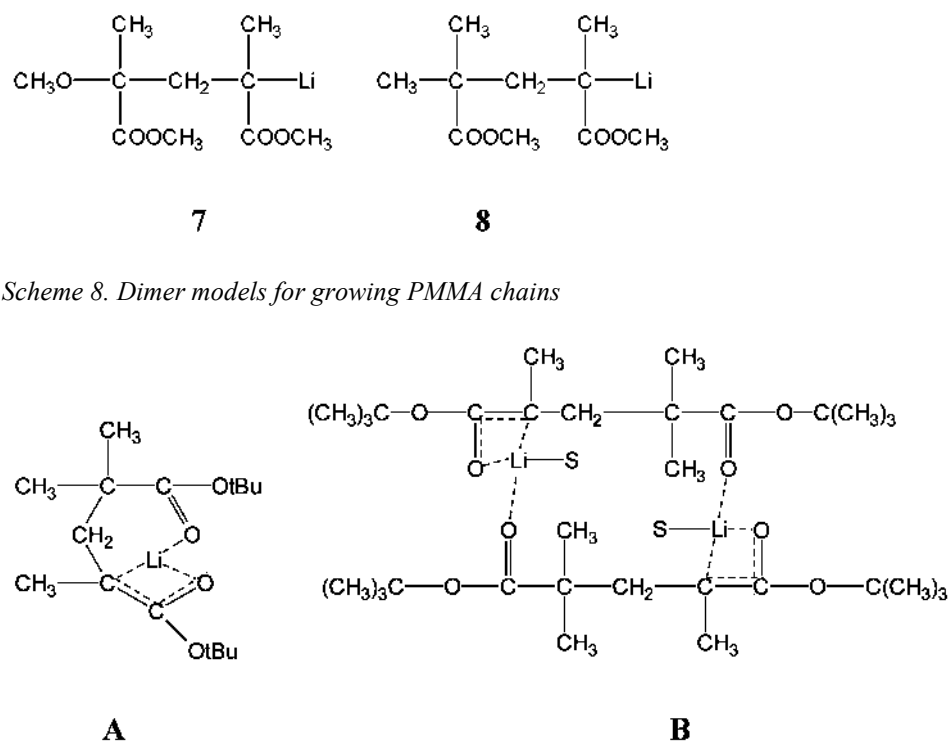
Finally, IR spectroscopy has allowed *E* and *Z* configurations to be assigned to the lithium ester enolate of lithium methyl and *tert*-butyl phenylacetates [72]. In this case, the coupling of the aromatic mode and the $\text{C}=\text{O}$ stretching vibration results in the discrimination of these two configurations. In THF, the *E* configuration is

observed for both lithium methyl and *tert*-butyl phenylacetates. The addition of HMPA promotes the *E* to *Z* isomerization.

Lithium in lithium isobutyrate thus appears to form highly polarized, i.e. semi-ionic, bonds with the negative charge delocalized over the C-C-O system. This conclusion is in fairly good agreement with previous NMR, IR and RX data [72]. The aggregation of α -lithio isobutyrate is mainly governed by the ester group and also by concentration and temperature. Consistent with the chemical behavior of these monomeric models and their close analogy with actual propagating species, it is not surprising that differences are observed between the anionic polymerizations of MMA and tBMA.

3.2.2. Dimeric model

The interest of dialkyl-2-lithio-2,4,4'-trimethylglutarate as a dimeric model can be found in the opportunity for the lithium counterion to participate to intramolecular interactions with the penultimate ester unit. Dimeric models were first prepared and studied by Lochmann et al. [26] Di-*tert*-butyl-2-lithio-2,4,4'-trimethylglutarate was prepared by the addition of tBiBLi to 1 equiv. of tBMA in THF and then purified by recrystallization from THF at low temperature. Although similarly prepared, di-methyl-2-lithio-2,4,4'-trimethylglutarate could not be purified efficiently by recrystallization. It was therefore prepared by direct metallation of dimethyl-2,4,4'-trimethylglutarate. This type of lithio ester also forms aggregates in solution as supported by molecular weight measurements. (Table 1) [69]. The IR analysis of di-*tert*-butyl-2-lithio-2,4,4'-trimethylglutarate showed that the lithium atom was interacting with the two carbon groups and not only with the α -carbonyl one [71]. Actually, the strong absorption of the ester groups of the precursor ester did not persist in the IR spectrum of the lithio ester, suggesting some interaction between the γ -ester and the α -lithioester.



Scheme 8. Dimer models for growing PMMA chains

Scheme 9. Cyclic (A) and linear structures (B) for the dimer **8** in THF.

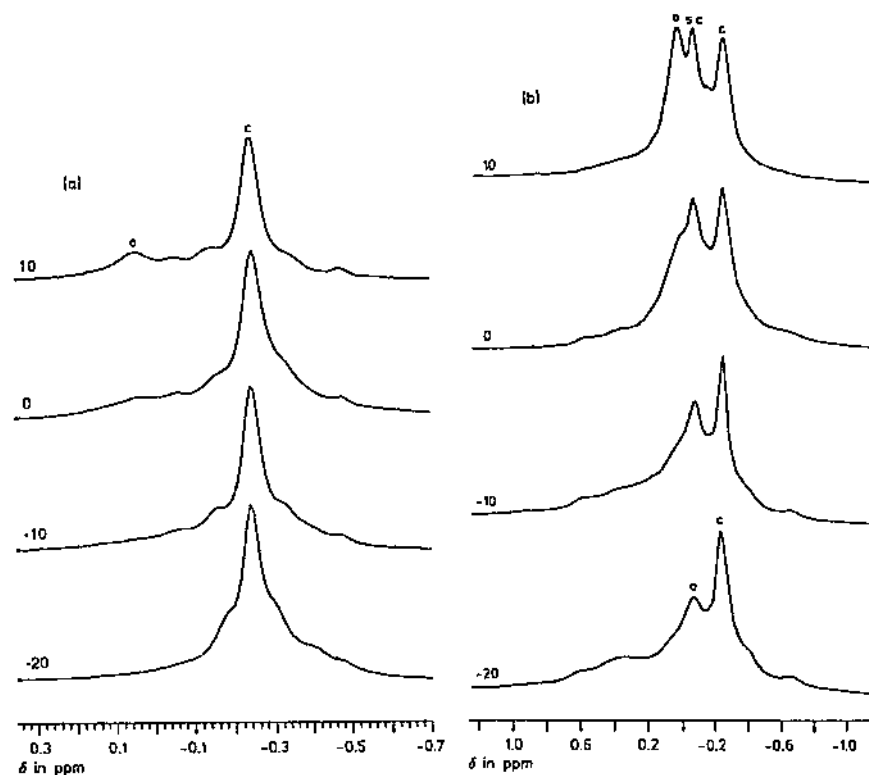
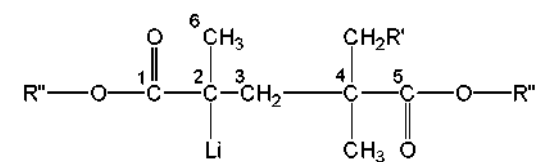


Fig. 3. ^7Li NMR spectrum for the dimer model in THF at different temperatures and concentrations: (a) 0.08 M; (b) 0.3 M. The relative importance of the linear form (O), the cyclic form (C) and byproduct (SC) is easily observed in relation to temperature at each concentration.

Table 3

^{13}C chemical shifts for dialkyl-2-lithio 2,4,4'-trimethylglutarate in THF at -20°C



Ref.	R'	R''	Chemical shifts (ppm)					
			C-1	C-2	C-3	C-4	C-5	C-6
[28]	MeO	Me	162.3	72.4	40.6	50.3	179.3	17.6
			161.2		40.6	49.1	176.9	18.2
[28]	H	Me	162.4	72.8	45.4	46.4	182.2	18.5
			161.5	74.8	44.9	43.8	178.9	17.6
[65]	H	<i>t</i> Bu	159.8	79.1	45.4	38.9	179.2	18.4
			171	71.5	42.9		179.2	

The study of the dimeric models was complicated by a self-condensation reaction occurring at a finite rate in THF even at low temperatures. This reaction was followed at room temperature by a decrease of the IR absorption at 1630 cm^{-1} characteristic of the ester enolate. Scheme 7 shows the disproportionation reaction that transforms the dimer into a cyclic ketoester, lithium *tert*-butoxide and *tert*-butyl 2-lithio isobutyrate (tBiBLi). A ^{13}C NMR study of dimers modeling the PMMA ion pair (7, 8, Scheme 8) by Bywater [28] emphasized the splitting of two signals of the main representative resonances at -20°C , particularly of the carbonyl of the penultimate unit and the α -lithio ester. Since the enolate form suffers from very restricted rotation around the C-C bond [28], the lithium counterion may be localized on either side of this planar system and thus generate diastereoisomers for the Li compound 7. This situation does not hold for dimer 8 which has no asymmetric center and cannot thus account for the two species observed by ^{13}C NMR. An explanation based on a possible

intramolecular complexation was not postulated at that time.

Kriz [65,66] analyzed further the di-*tert*-butyl-2-lithio-2,4,4'-trimethylglutarate by NMR spectroscopy and concluded that, in agreement with IR data and quantum chemical ab initio and MNDO calculations, the lithium form of this dimer has a strong tendency to form an intramolecular complex with the penultimate ester carbonyl unit. The cyclic conformation (A, Scheme 9) is thus in competition with the linear form (Scheme 9).

The cyclic and linear structures have very different ${}^6,{}^7\text{Li}$, ${}^{13}\text{C}$, ${}^1\text{H}$ NMR characteristics (relaxation time, nuclear Overhauser effect), which explains the doubling of the ${}^{13}\text{C}$ NMR signals. The linear form is actually stabilized by self-aggregation into dimeric aggregates (Scheme 9) in contrast to the cyclic form which is monomeric in THF. Since solvation is entropy-driven at low temperatures, the dimeric aggregates are more favorably formed as the temperature and concentration become higher in agreement with ${}^7\text{Li}$ NMR spectra (Fig. 3).

It is worth noting that quantum chemical calculations by ab initio self-consistent field (SCF) and Dewar's semiempirical modified neglect of differential overlap (MNDO) methods predict a stabilization energy for the intramolecular coordination of the dimeric models of ca. 33 kJ/mol [65,66].

The stabilization energy remains unchanged upon solvation by THF molecules. The lithium carrying group is predicted to be predominantly in the ester enolate form with the O–Li bond weakened by ca. 11% in agreement with the ${}^{13}\text{C}$ NMR chemical shift data (Table 3). NMR studies have also emphasized a difference in the behavior of the dimeric models for the living PMMA and PtBMA chains. Indeed, no intramolecular complexation was observed for the dimeric models of PMMA [28] by ${}^{13}\text{C}$ NMR, in contrast to strong tendency for the dimer modeling living PtBMA chains.

Table 4

Ion pair propagation rate constant for the MMA polymerization. Reprinted from Anionic polymerization: Principles and practical applications, pp. 641–684 by courtesy of Marcel Dekker, Inc. [107]

Counterion	Solvent	T (°C)	Chain end concentration (mol/L $\times 10^3$)	$k_p \pm$ (L/mol s)
Sodium	THF	— 40	—	800
		— 51	0.405	444
	Glyme ^a	— 99	0.44	31.8
		— 40	—	2550
		— 54.5	1.2	1930
Na[222]	THF	— 98	—	270
Cesium	THF	— 40	—	860
		— 64.4	0.15	374
	Glyme ^a	— 97.3	0.53	32.7
		— 40	—	2680
		— 51	0.45	1730
Lithium	THF	25	50–200	1500
		— 40	—	100
	Glyme ^a	— 46	0.78–27.2	70
		— 65	0.1–2	46
		— 40	—	16
Potassium	THF	— 40	—	750

^a 1,2-dimethoxyethane.

^b Sodium complex with heterobicyclic cryptand [222].

3.2.3. Oligomeric chains

Although molecular structure and interactions can be thoroughly studied in the case of small molecules, the monomeric and dimeric models however fail to mimic the possible interactions of the lithium counterion with the (β - and γ -placed polar groups, respectively). They also ignore the steric effect of the growing chain attached to the propagating unit. It is thus necessary to extend the study to living oligomers so as to collect pertinent information on the structure of the propagating species under the actual conditions of the anionic polymerization of the ester methacrylic monomers. Needless to say that the larger number of ester groups in the oligomeric chains will be a problem as source of termination reactions as discussed elsewhere [74]. This problem can be at least partly alleviated in studying the anionic polymerization of alkyl(meth)acrylates under controlled conditions, or even living [19,20,16]. For instance, attention has been paid to the controlled polymerization of MMA initiated by an hindered initiator or a metallated isobutyrate ester in THF at low temperature (— 78°C) [75]. This system has been investigated by direct methods, such as vibrational spectroscopy [12,13], viscosimetry [76] and conductimetry [14].

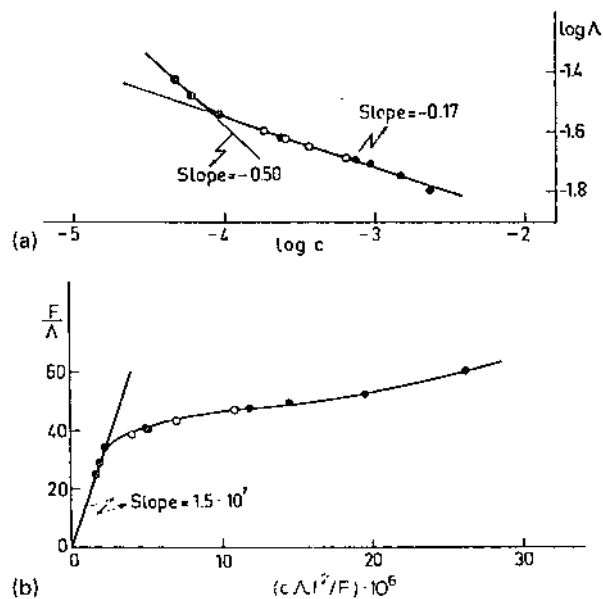


Fig. 4. (a) Log A vs. log c plot and (b) the Fuoss plot for living lithium containing poly(methylmethacrylate) in THF at -78°C .

On the basis of a kinetic study, Müller came to the conclusion that at least two species contributed to the polymerization of MMA in the presence of alkali metal counterions in THF at low temperature ($T \ll -40^{\circ}\text{C}$) [77-79,12]. That the chains ends tend to self-aggregate was supported by a decrease in the propagation rate constant, k_p , when the concentration of the active species (P^*) was increased even in the presence of common ion salts. As shown in Eq. (2), associated and non-associated ion pairs must be in equilibrium in THF. Kinetic data also indicate that the propagation rate constant of the non-aggregated species is 100-1000 times larger compared to the aggregated species [20]. In case of controlled polymerization, e.g. in THF at -100°C , polymerization is first order in monomer and the molecular weight distribution (MWD) is very narrow ($M_w/M_n = 1.2$). While the propagation rate constant, k_p , is independent of the degree of polymerization ($\text{DP} > 5$) [80], k_p strongly depends on the concentration of the living species supporting further an equilibrium between associated and non-associated ion pairs. This situation is also confirmed by the linear dependence of the apparent polymerization rate constant of MMA at 25°C on the square root of the active species concentration [64]. All these experimental observations are consistent with Eq. (2) and the associated kinetic relationships:



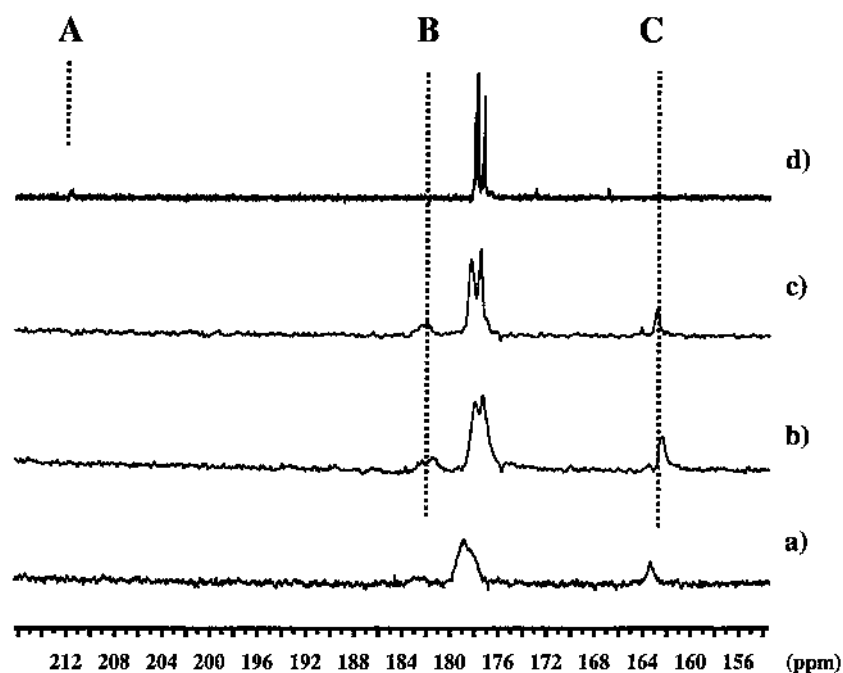


Fig. 5. ^{13}C NMR spectra of living poly(*t*BMA) initiated by diphenylhexyllithium (0.01 M) at -78°C in THF. Molecular weight of the chains ca. 3000 (*Mn*SEC, polystyrene standards). Temperature: (a) 200 K; (b) 220 K; (c) 240 K.

According to Müller [81], 50% of the ion pairs of the PMMA-type are associated at -65°C in THF. The aggregation is however less extensive in the case of PtBMA living chains, presumably because of the bulkiness of the ester group. Consistently, the dissociation constant at -65°C was calculated to be $0.75 \times 10^{-3} \text{ mol L}^{-1}$ for PMMA compared to $2 \times 10^{-3} \text{ mol L}^{-1}$ for PtBMA. Also in agreement with Eq. (2), the relative viscosities of the living PMMA chains in THF at -65°C was observed to decrease with polymer concentration [76].

In the family of the alkali metals, the ion pair propagation rate constant for MMA polymerization compares as follows: $\text{Cs} \cong \text{K} \cong \text{Na} \gg \text{Li}$ (Table 4), suggesting that the contact ion pairs are the predominant propagating species. The temperature dependence of the ion pair propagation rate constant agreed with the participation of only one type of ion pair proposed to be externally solvated contact ion pair [19].

Several experimental techniques were used in order to collect more information on the structure of the two species that coexist during the anionic polymerization of MMA.

Fowells [25] and Figueruelo [14] studied the conductivity of living PMMA chains in THF at -78°C . Fig. 4 shows the log — log dependence of the conductance of the living polymer on the solution concentration and the Fuoss plot. Although the observed increase in conductimetry with concentration must result from association phenomena, the actual structure of the associated species cannot be extracted from these preliminary results. The dissociation constant calculated from the linear part of the Fuoss plot is rather small ($K_d = 4,4 \times 10^{-10} \text{ mol}$) compared to the dissociation constant reported for polystyryllithium in THF ($K_d = 1.9 \times 10^{-7} \text{ mol}$) [89]. If the active species are basically contact ion pairs, whose counterion is not as close to the alpha carbon atom as in polystyryllithium, the model is then in accordance with a low dissociation constant.

Table 5

Effect of polymerization temperature on the PMMA and PtBMA tacticity (from Ref. [82])

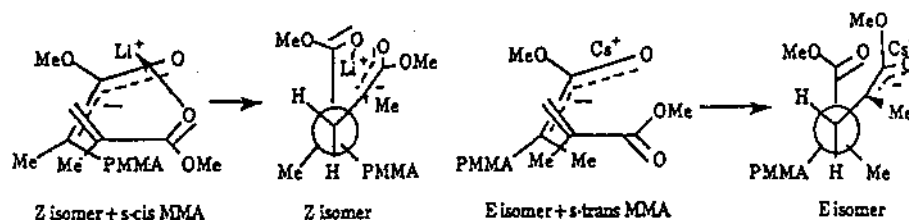
$T(^{\circ}\text{C})$	% Syndiotactic triads	% Heterotactic triads	% Isotactic triads
PMMA			
-78	81	18	1
-48	72	26	2
-20	69	28	3
0	63	33	4
PtBMA			
-78	52	48	0
0	46	50	4
25	41	49	10

Tsvetanov et al. [12] used IR spectroscopy for the analysis of the ion pairs structure. Unfortunately, the IR spectra were recorded in case of uncontrolled MMA polymerization, i.e. initiation by sBuLi in THF, at low temperature (-78°C). Actually, the main observation was the side acid-base reaction of sBuLi with the α -methyl group of MMA (see Scheme 1(a)), and an absorption at $1606\text{--}1610\text{ cm}^{-1}$ characteristic of the enolate of a ketone or ketoester, i.e. the 1,2-addition product of sBuLi or anionic growth centers to the monomer. This absorption disappears upon the addition of small quantities of ethanol. No additional IR analyses have been reported, more likely because of the inherent difficulties in recording IR spectra at low temperatures and under inert atmospheres.

Multinuclear NMR spectroscopy, mainly of carbon, proton and lithium, is a powerful technique for the quantitative analysis of the coordinative aggregation of organolithium species. However, this technique is time-consuming and requires solutions of relatively high concentration in active species which is unfavorable to the stability of the "living chains". Kriz et al. [13] have recently considered the analysis of living PMMA oligomers (PMMA-Li). Although the stability of these chains is improved by ligation with lithium *tert*-butoxide, termination reactions cannot be completely prevented from occurring (see Section 3.3.3.1). This drawback can however be overcome by substituting tBMA for MMA since tBMA can be polymerized in a living fashion under mild experimental conditions [82]. The carbonyl group of the last monomer units of living PtBMA oligomers was ^{13}C labeled so as to take advantage of ^{13}C NMR spectroscopy. Three ^{13}C NMR signals were observed in the carbonyl region (Fig. 5: A = 212 ppm, B \cong 182 ppm, C \cong 160 ppm). They were assigned to: (i) the carbonyl group of the lithium ester enolate species (C); (ii) the carbonyl of the penultimate unit (B); (iii) a keto carbonyl formed by backbiting termination (A). In contrast to the dimeric model, no intramolecular complexation of the penultimate unit by the lithium counterion was observed for these living tBMA oligomers in THF (Fig. 5). Three signals were observed by ^7Li NMR spectroscopy indicative of an aggregated species and a non-aggregated species [67].

As a whole, the experimental results indicate that the propagating PMMA and PtBMA chains are partly aggregated and that the propagating species are properly described as lithium ester enolates externally solvated by THF.

The stereochemistry of the polyaddition reaction is another source of information on the propagation mechanism. The MMA stereosequences are easily identified by ^1H NMR spectroscopy, since the $\alpha\text{-CH}_3$ protons show signals typical of iso, hetero and syndiotactic triads, and of higher *n*-ads in the case of higher stereoregularity.



Scheme 10. Monomer approach of the E/Z isomers of the propagating species.

Iso and syndiotactic diads can also be discriminated on the basis of the CH₂ signals. As a rule, the anionic polymerization of alkylmethacrylates in THF at low temperatures is predominantly syndiotactic. These syndiotactic placements however disappear in favor of heterotactic placements as the temperature is increased (Table 5) [82]. The chain tacticity is shared by syndio and heterotactic triads when *tert*-butylmethacrylate is polymerized in THF at low temperatures. That the relative importance of the heterotactic triads increases with temperature is consistent with the enthalpy-driven syndiotactic placement, which thus predominate at lower temperatures.

^{13}C -methyl iodide addition to living chains is an interesting way to study the diastereoisomer selection in the propagation reaction [83]. Four resolved ^{13}C signals are observed for the $\alpha\text{-CH}_3$ group of PMMA assigned to rr^- , rm^- , rr^+ and mm^- triads, r and m being the meso and racemo placements, respectively.

From the tetrad resolution, the probabilities of $P(r^-)$ can be known and compared to the experimental observations. The analysis of chains aged for various times at different temperatures showed that the terminal species r^- are more stable than the m^- species, and are thus responsible for the commonly observed side reactions. A possible dependence of the main chain tacticity on the E/Z stereoisomerism of the lithium ester enolate has been proposed [21,84]. The E/Z isomerism of the PMMA chain ends was indirectly observed from the parent PMMA silylated chain ends. As shown by Scheme 10, the *s-cis* and *s-trans* monomer conformation have to be considered in the transition state with respect to the anion geometry. Thus, a transition state with a *s-cis* monomer presentation will give the corresponding Z anion and the E anion will result from the *s-trans* presentation. The monomer approach will also be guided by the coordination of the alkali metal counterion with

the monomer carbonyl group in the transition state (*s-cis* in case of small size counterion, and vice-versa for Cs^+). Since the *E* and *Z* structures of the propagating species are two diastereoisomers, their reaction with the monomer should lead to the meso and racemo diads. Compared to the classical penultimate mechanism, the *E/Z* stereoisomerism concept seems to be a valuable approach for the analysis of the stereoselective species and their control. However the indirect assignment of the enolate geometry in reference to the silylated derivatives is questionable [67]. Moreover, no direct observation of these *E/Z* isomers has ever been reported, and the monomer coordination in the transition state is also unknown. Therefore, since the Li bonding to the growth center is labile, particularly in a highly solvating solvent, the *E-Z* isomerism might only be transient and have no decisive role in the polymerization mechanism.

3.3. Structure of ligated lithium-ester enolates in THF

The addition of some ligands strikingly improves the control of the anionic polymerization of (meth)acrylates, influencing decreasing polydispersity, propagation rate constants and the extent of termination reactions while changing stereochemistry.

Müller et al. [19,20] have focused on the polymerization kinetics and proposed that association/complexation equilibria dominate the anionic polymerization of methacrylates. As in the previous section, the ligation process will be discussed now in reference to the study of unimeric and dimeric models, and oligomeric chains, as well.

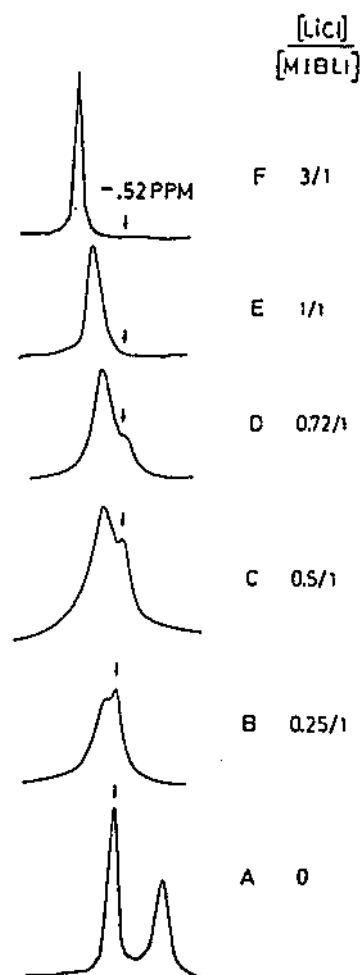
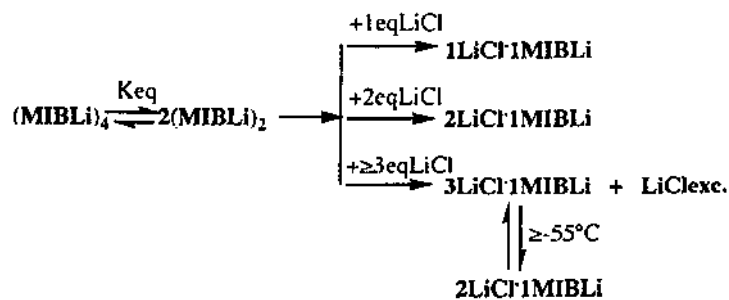
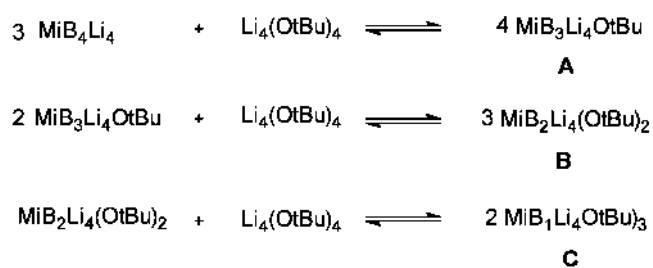


Fig. 6. ^7Li NMR spectra of MiBLi (0.133 M) added with LiCl in THF at 197 K.



Scheme 11. Ligation equilibria between MiBLi and LiCl in THF.



Scheme 12. Ligation equilibria between MiBLi and LiOtBu in THF.

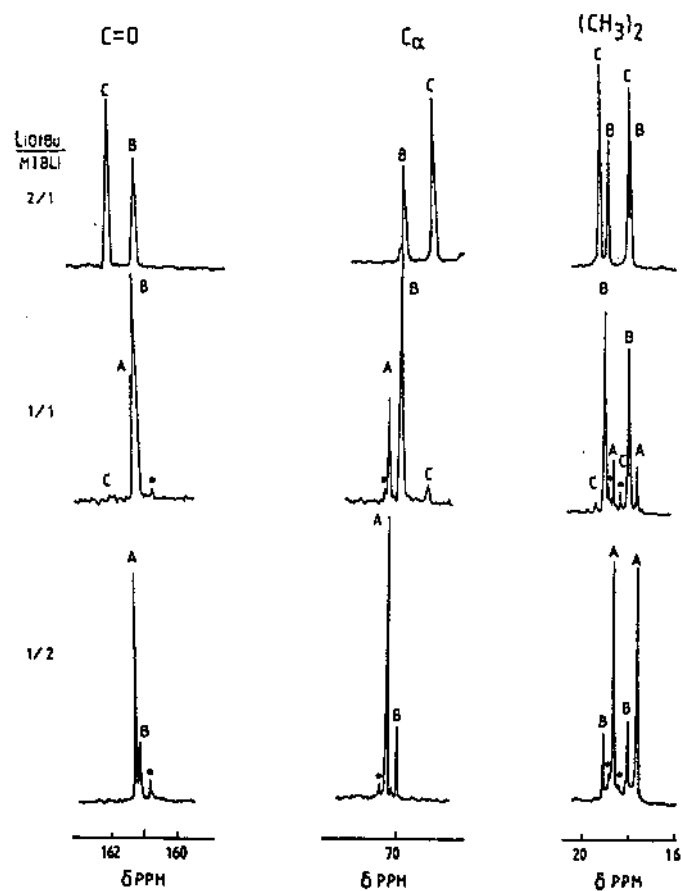


Fig. 7. Partial ^{13}C NMR spectrum for MiBLi (0.8 M) added with LiOtBu in THF at -40°C . The symbol * refers to free MiBLi species.

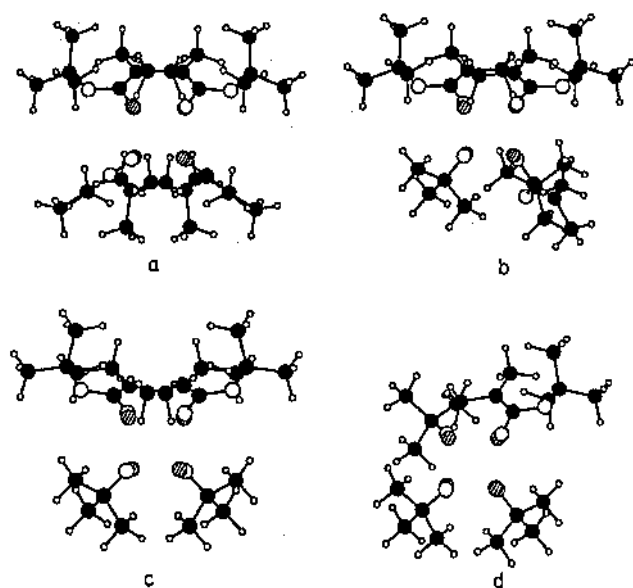


Fig. 8. Optimized geometries for the species: (a) $(tBiBLi)_4$; (b) $(tBiB)_3Li_4OtBu$ (not observed); (c) $(tBiB)_2Li_4(OtBu)_2$ and (d) $(tBiB)Li_4(OtBu)_3$.

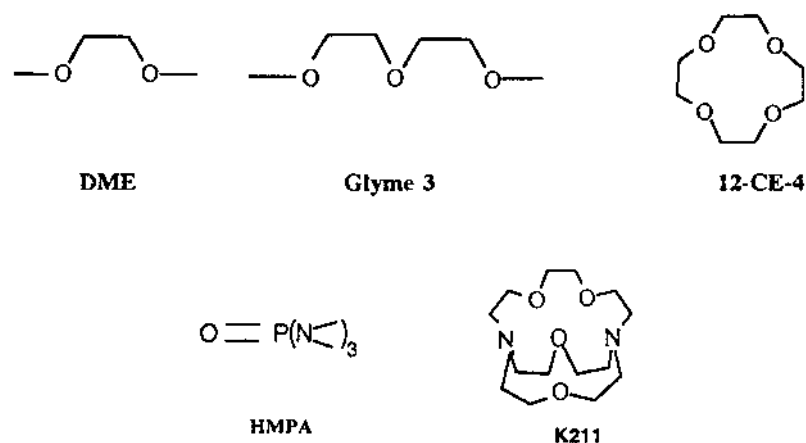
3.3.1. Ligated unimeric models

Ligation of unimeric models was mainly studied by Wang et al. [85] and Kriz et al. [86] by NMR spectroscopy, and by Lochmann who used IR spectroscopy [26].

Three types of ligands, i.e. the μ , σ and μ/σ types, were studied, as summarized in the following sections.

3.3.1.1. μ -ligands According to 7Li , ^{13}C , 1H NMR spectroscopies, ligation of the unimeric model of Li ester enolates by μ -type ligands, such as lithium chloride and lithium *tert-butoxide*, completely perturbs the self-association of these compounds in favor of tight and highly charged delocalized “ μ -complexes” [87]. As an example, Fig. 6 illustrates how the 7Li NMR spectrum of MiBLi is perturbed by the addition of LiCl. Fig. 6(A) shows the spectrum characteristic of the aggregation equilibrium between tetramers and dimers of MiBLi in THF. Upon addition of LiCl (LiCl/MiBLi = 0.5), the signal at $\delta = -0.52$ ppm assigned to the tetramer persists, whereas a new signal is observed at $\delta = -0.43$ ppm and assigned to a mixed complex between LiCl and the lithium ester enolate. This signal is shifted downfield when the LiCl/MiBLi molar ratio is increased. The ^{13}C NMR signal of the α -CH₃ group changes from $\delta = 73.5$ before ligation to $\delta = 66.5$ ppm for the mixed complex. This upfield shift is consistent with an increasing negative charge on the α carbon in the mixed complex with LiCl. Ligation equilibria have been postulated as shown in Scheme 11.

In case of ligation by LiOtBu [88,63] 7Li , ^{13}C , 1H NMR spectroscopies agree with complexation equilibria between mixed tetramers, as shown by Scheme 12. ^{13}C NMR spectra show multiple resonances for the tertiary carbon in lithium *tert-butoxide* and for the carbonyl carbon, the α -carbon and the methyl carbons of MiBLi (Fig. 7).



Scheme 13. Polyether and polyamine ligands used in LAP.

The formation rate of these complexes is inversely proportional to their stability. Indeed, the poorly stable 3/1 MiBLi/LiOtBu complex is formed immediately, whereas the complete formation of the more stable 1/3 MiBLi/LiOtBu complex requires ca. 20 h at -15°C . The temperature dependence of the ^{13}C NMR spectra indicates that the exchange between the various mixed complexes is slow on the ^{13}C NMR time scale, in contrast to LiCl complexation that leads to only one predominant LiCl complex.

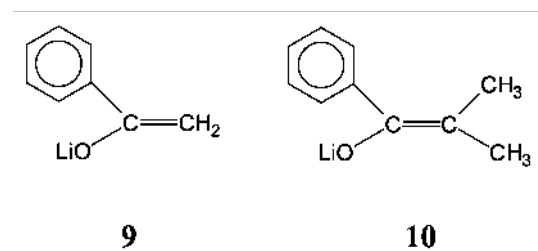
MNDO calculations are in agreement with the experimental results [63]. Indeed, these calculations predict that the stable mixed complexes must contain four molecules, namely with 3/1, 2/2 and 1/3 molar compositions. Furthermore, the stability of the aggregates is also predicted to increase with the LiOtBu content.

These NMR analysis and MNDO calculations were extended to the LiOtBu and tBiBLi pair in THF [86]. The ^7Li , ^{13}C , ^1H NMR data support that basically tetrameric complexes are formed with 2/2 and 1/3 tBiBLi/LiOtBu molar compositions. IR observations reported by Lochmann [26] confirm the interaction of LiOtBu with the unimeric model consistent with a decreased carbonyl absorption. Nevertheless, the IR spectra of the tBiBLi and tBuOLi adducts do not change very significantly with an excess of alkoxide, indicating that complexation is independent of the tBiBLi/tBuOLi molar ratio.

From the nuclear Overhauser effect, which gives information on magnetic dipolar interactions and thus on intermolecular distances, it was concluded that the ester enolate O-Li was comparable to the O-Li bond in LiOtBu. A cubic structure consisting of 4 lithium and 4 oxygen atoms has been proposed for these complexes (Fig. 8).

When lithium 3-methylpentan-3-olate is substituted for LiOtBu, the mixed complexation obtained is a much slower process, in relation to the slightly different symmetry in these two alkoxides and the higher steric hindrance in the former one [86].

Clearly, the NMR studies show that lithium ester enolates are efficiently complexed by M ligands, which leads to the formation of mixed complexes. Complexation by lithium alkoxide is deeply different from ligation by LiCl, since more than one mixed complex is formed and exchange slowly.



Scheme 14. Structure of Li enolates 9, 10.

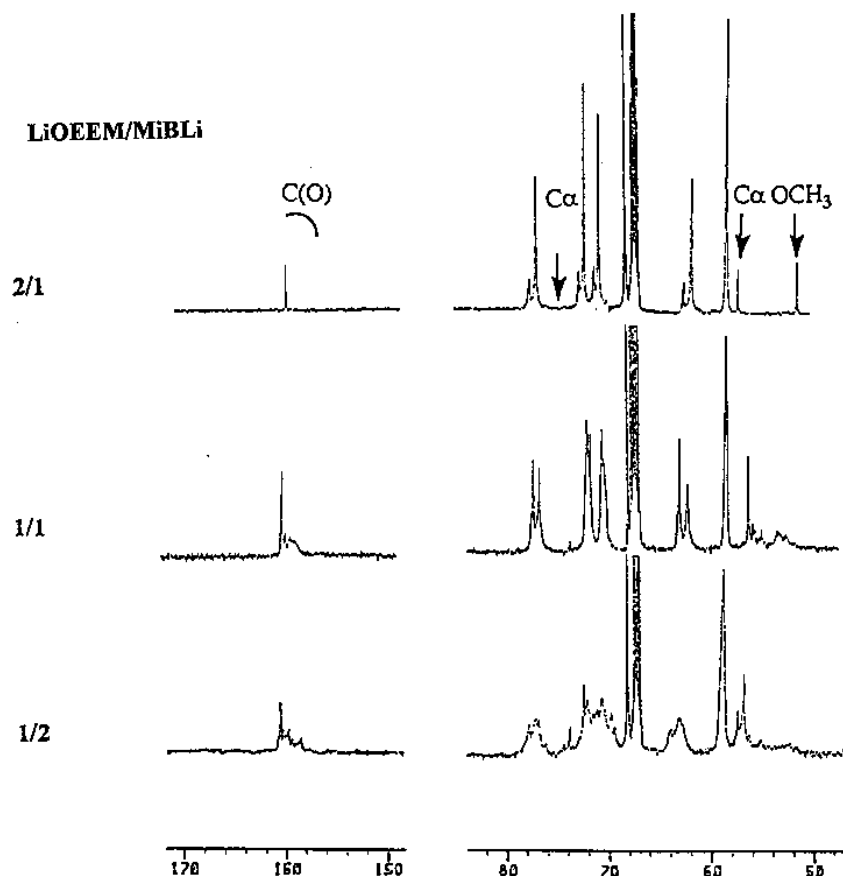


Fig. 9. Partial ^{13}C NMR spectrum for MiBLi (0.5 M) added with various amounts of LiOEEM in THF at -60°C .

3.3.1.2. σ ligands Polyethers (including crown ethers) and polyamines (including kryptands) are another type of ligands that have a very beneficial effect on the course of anionic polymerization of alkylmethacrylates. Therefore, their interaction with unimeric models has been studied in order to understand better how they modify the main characteristics of the lithium ester enolates (Scheme 13).

The effect of these ligands on the charge distribution around the carbanion of MiBLi in THF has been approached by ^{13}C NMR spectroscopy [51]. Although the O-Li bond in lithium ester enolates is rather weak and highly polarized, the σ -type ligand known for lithium cation-binding and considered in this study (Scheme 13) do not show any significant σ coordination in THF, except for K211. The ^{13}C NMR spectra are indeed quite comparable to the pattern observed for MiBLi in THF. The binding polyether ligand which is a cation stronger than THF causes a minor modification of the negative charge distribution as indicated by the minor modification in the ^{13}C chemical shift of all the carbons (ca. 0.1-0.4 ppm). Nevertheless, the addition of DME, glyme-3, 12-CE-4 and HMPA to coexisting tetrameric and dimeric MiBLi in THF shifts this equilibrium in favor of dimers as follows: DME < glyme-3 < 12-CE-4 < HMPA, thus according to increasing complexation strength between MiBLi and the ligands. This complexation is, however, not strong enough to result in the complete deaggregation of MiBLi in THF.

House et al. [91] studied the effect of DME and several crown ethers on the ^{13}C NMR spectrum of the Li enolate **9** in THF (Scheme 14). Consistently, no significant change in the chemical shifts was reported. Similar conclusions were drawn by Jackmann et al. [92] who studied the possible complexation of lithium isobutylphenone **10** (Scheme 14) in dioxolane or DME by glyme-3, 12-CE-4 and 15-CE-5.

It is remarkable that all these systems have a negative dissociation enthalpy, indicating that the solvation-assisted-dissociation process is more favorable at lower temperatures. The dissociation into smaller aggregates in coordinating solvents is accompanied by an increased Li coordination and thus favored by stronger cation-binding (solvating) reagents. Accordingly, the solvation enthalpy and the dimer formation enthalpy become more negative in the order: THF < DME < glyme-3 < 12-CE-4 which might suggest that solvent-mediated breakdown of the aggregates is entropically driven in the presence of relatively stronger lithium cation-binding ligands.

In sharp contrast, complexation of MiBLi by K211 does shift the aggregation equilibrium towards a single

monomeric K211-complexed species, which is seen in the ^{13}C NMR spectrum by ca. 13 and 5 ppm upfield shifts for the α -C resonance compared to the tetrameric and dimeric species, respectively.

3.3.1.3. σ/μ ligand Complexation of MiBLi by a short polyether capped by a lithium alkoxide group, e.g. the lithium 2-(2-methoxy ethoxy) ethoxide (LiOEEM) is a unique ligation process, since a simultaneous dual-complexation (μ/σ) of MiBLi by both the lithium alkoxide (μ -mixed complexation) and the chelating polyether component (σ -cation-binding complexation) occurs [93]. The NMR analysis of the complexation of a lithium ester enolate by a lithium containing μ/σ dual ligand (LiOEEM) has shown that this μ/σ dual ligand is exceptionally effective in forming a bulky and relatively highly charge-separated μ/σ complex. Formation of a unique mixed complex $\text{MiBLi}_3(\text{OEEM})_2$ has been proposed from ^{13}C and ^7Li NMR spectroscopies [93]. LiOEEM has a strong effect on ^{13}C NMR spectra particularly for the signals typical of the α -carbon of MiBLi. When the LiOEEM/MiBLi molar ratio is smaller than 2, the ^7Li and ^{13}C spectra are complex, and the assignment of multiresonances is quite difficult. In contrast, at a LiOEEM/MiBLi molar ratio greater or equal to 2:1, instead of two sets of resonances typical of a tetramer-dimer equilibrium in THF, a single set of ^{13}C resonances is observed consistent with a strong complexation between MiBLi and LiOEEM in THF (Fig. 9). Since the ^{13}C chemical shifts for the α -carbon and the carbonyl of MiBLi are comparable to those ones observed when MiBLi is complexed by K211, the complete deaggregation of the highly aggregated MiBLi has been proposed with formation of a mixed complex containing one MiBLi molecule for two ligands.

In conclusion, the mixed complexation of MiBLi by inorganic and organic salts is completely different from the cation complexation by polyether ligands and HMPA in THF. The mixed complexation by μ -ligands relies upon the electrostatic interactions of all the lithium cations with the MiBLi oxygen and the ligand anions (OtBu^- , Cl^-). In contrast, coordination of lithium even by powerful lithium cation-binding ligands (σ -ligand), i.e. 12-CE-4, does not extensively perturb MiBLi aggregation, except for the extremely strong K211. Finally, the σ/μ ligands are very efficient in deaggregating the original MiBLi aggregates with the formation of a unique complex.

3.3.2. Dimeric model complexed with ligands

The NMR study of the dimeric model—i.e. di-*tert*-butyl 2-lithio 2,4,4'-trimethyl glutarate—in THF has emphasized the intramolecular coordination of the lithium counterion to the γ -ester group. The question to which extent this intramolecular coordination can compete with the intermolecular coordination with ligands has been addressed by Kriz et al. [66] and Zune et al. [94].

3.3.2.1. μ ligands

3.3.2.1.1. Effect of LiOtBu ^1H , ^7Li , ^6Li and ^{13}C NMR spectroscopies have all shown that the dimeric model of the living poly(*tert*-butylmethacrylate) formed well defined aggregates with LiOtBu in THF. 2/2 and 1/3 dimer/LiOtBu aggregates dominate in a way that depends on the initial dimer and alkoxide molar ratio. According to 1D and 2D, ^1H - ^1H , ^1H - ^7Li nuclear Overhauser effects and ^1H , ^{13}C , ^7Li relaxations, three conformations (α , β , γ) can be distinguished for the dimer component in the two types of aggregates. In agreement with IR, the γ ester group of the dimer is intramolecularly coordinated by the lithium counterions in the γ form. The γ form does not exchange with the uncoordinated α , β forms on the NMR time scale. The α and β forms are two conformers that exist in the two major aggregates and have a slightly different stabilization energy. The γ form is favored by a larger molar excess of LiOtBu compared to the dimer.

MNDO calculations [66] have predicted a cubic $(\text{O-Li})_4$ for the 2/2 and 1/3 aggregates which is however distorted in the γ -form. The distorted cubic form allows one or two lithium atoms to be pulled out of the cube at the benefit of the intramolecular complexation with the γ ester group.

The stabilization of the 2/2 and 1/3 dimer/LiOtBu complexes and the effect of LiOtBu in favor of the intramolecular coordination of the γ ester group of the dimer can be explained by a cooperative system of polycentric bonds and electrostatic interactions.

3.3.2.1.2. Effect of LiCl How the model living dimer di-*tert*-butyl-2-lithio-2,4,4'-trimethylglutarate interacts with LiCl has been studied in THF- d_8 solution by ^7Li , ^6Li , ^1H , and ^{13}C (1D and 2D) NMR spectroscopies. Actually, the lithium ester enolate of di-*tert*-butyl-2-lithio-2,4,4'-trimethylglutarate forms a 1:1 complex with lithium chloride. ^1H and ^7Li NMR data suggest that the (1:1) mixed complex is in a rapid equilibrium with free LiCl, when the LiCl: lithiated dimer molar ratio is higher than 1. Measurements of ^{13}C relaxation times agree with the dimeric aggregation (i.e. $\text{Dimer}_2\text{LiCl}_2$) of the (1:1) complex, consistent with MNDO calculations [94].

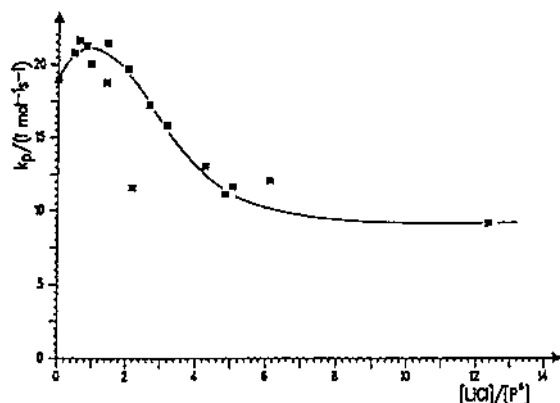


Fig. 10. Dependence of the polymerization rate constant on the molar excess of LiCl with respect to the lithiated active species in the anionic polymerization of MMA in THF at -65°C .

3.3.2.2. σ/μ ligand: effect of LiOEEM

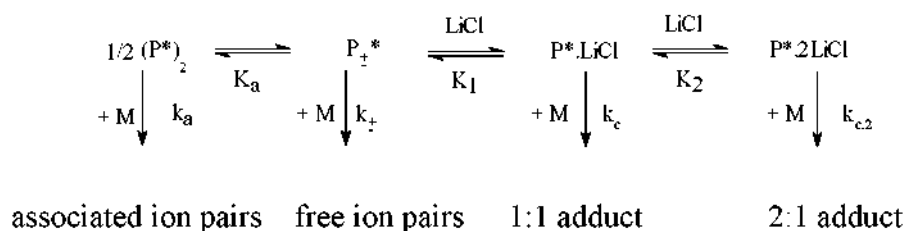
3.3.2.2.1. Effect of LiOEEM The interaction of LiOEEM with the model dimer for living *tert*-butylmethacrylate has been studied in THF at low temperatures by 1D and 2D NMR and MNDO calculations. In the presence of LiOEEM, the structure of the active site remains quite comparable to a lithium ester enolate. The ligand has actually a strong tendency to self-associate into dimeric, trimeric and tetrameric aggregates, thus in competition with mixed aggregation with the model dimer. When LiOEEM is mixed with the dimer model in THF, a metastable system is formed which requires several days at 258 K to reach equilibrium. The relative content of the complexes, such as 1:1 LiOEEM/dimer, 3:1 LiOEEM/dimer and possibly 2:1 LiOEEM/dimer, depends on the initial LiOEEM/dimer molar ratio and on the temperature and time as well. Experimental results indicate that when the molar excess LiOEEM is moderate (up to 4:1) the dimer conversion into mixed aggregates remains incomplete. So, in contrast to MiBLi, several complexes coexist when LiOEEM is mixed with the dimer model for *tert*-butylmethacrylate living chains [90].

Table 6

Effect of LiCl on the propagation rate constant for the polymerization of MMA and tBMA in THF

	k_p (L mol ⁻¹ s ⁻¹)	k_p	T. ($^{\circ}\text{C}$) (L mol ⁻¹ s ⁻¹) (5 equiv. LiCl)
MMA ^a	100	17	-40
TBMA ^b	6	0.4	-63

^a Ref. [81]. ^b Ref. [96].



Scheme 15. Complexation equilibria proposed by Müller [95].

3.3.3. Oligomer chains complexed with ligands

As a rule, when the influence of ligands on the anionic polymerization of (meth)acrylates is concerned, mainly polymerization kinetics and the molecular characteristics of the final polymers (MWD, stereochemistry, ...) have been studied. On that basis, several authors have put forward the idea that a unique active species would be formed as result of the addition of μ and μ/σ ligands.

3.3.3.1. μ ligands as additives for the anionic polymerization of alkyl (meth)acrylates

3.3.3.1.1. Effect of LiCl Müller et al. [95] have collected information on the complexation equilibrium between

free LiCl and living PMMA chains by studying the MMA polymerization kinetics for different ligand/active species molar ratios. Fig. 10 shows the plot of the propagation constant versus the LiCl/RLi ratio. The propagation rate constant is firstly increased at LiCl/RLi molar ratio smaller than 1. This is explained by a higher propagation rate for the complexed species as compared to the uncomplexed one. However, at LiCl/RLi molar ratios higher than 2, k_p decreases as the LiCl content is increased. The same observation was reported by Varshney et al. for the anionic polymerization of tBMA in presence of LiCl [96], the effect of LiCl being however more drastic in this case (Table 6). Müller et al. [97] have suggested that a 1:1 adduct would coexist with a less active 2:1 adduct (Scheme 15) [95], which has been recently debated [94].

LiCl has been reported to affect the tacticity of PtBMA. Indeed, the content of isotactic placements is increased by 10% when a threefold molar excess LiCl is added to RLi. [96] No effect is however observed in case of PMMA, which remains unexplained.

LiCl leads to a decrease in chain polydispersity when MMA and tBMA are polymerized in THF at low temperatures, and the mechanism is apparently living. The polydispersity decreases when the relative amount of LiCl is increased. From an initial value of 2, M_w/M_n is decreased down to 1.05. The same qualitative observation is reported for tBuA. In case of acrylates, however, the addition of LiCl has no favorable effect on the self-termination rate [95].

The structure of the active species complexed by LiCl has been analyzed by Zune et al. [94] Rapidly acquired ^{13}C NMR spectra have been recorded for living tBuMA oligomers initiated by DPHLi in the presence of various amounts of LiCl and terminated by a few ^{13}C -enriched monomers. The structure of the lithium ester enolate is affected by the amount of LiCl and fits an equilibrium between free lithium chloride and complexed active end-groups. A large excess of LiCl (10/1) does not change the structure of the complexed living end. The oligomers complexed with LiCl exhibit marked self-termination in THF at 273 K. Complexation of the lithium ester enolate by LiCl has also been proved by multinuclear spectroscopy.

3.3.3.1.2. Effect of LiOtBu In case of lithium alkoxide and mainly lithium *tert*-butoxide, it was firstly concluded from chain characteristics and kinetics data [97] that the complexation of the lithium ester enolate was driven by spontaneous electrostatic interactions. In contrast to LiCl, the co-existence of several LiOtBu complexed enolates was proposed [88,63]. It was however quite difficult to draw reliable conclusions since most the data available were collected under different experimental conditions. What is clear however is that the self-termination rate is significantly decreased, as shown e.g. by the kinetics of the MMA oligomerization at 23°C [64]. Consistently, LiOtBu has proved very successful in improving the anionic polymerization of tBuA which is known for its great sensitivity toward termination reactions [68].

Wang et al. studied the effects of LiOtBu on the stereochemistry of a PMMA polymerization initiated by diphenylhexyllithium in THF at -78°C [23]. No significant change in tacticity was observed in pure THF compared to the parallel decrease in polydispersity (from 1.35 to 1.10 upon addition of 10 equiv. LiOtBu). Table 7 shows the effect of ligands on the tacticity of PMMA. The experimental conditions were kept constant except for the type and quantity of these ligands employed.

Recently, Kriz et al. have analyzed the species active during the polymerization of MMA [13]. Living methylmethacrylate oligomers were prepared by mixing THF- d_8 solutions of MMA with solutions of MiBLi complexed by LiOtBu, (thus the initiator) at -70°C . The molar ratio of the three components was 2/1/3 MMA/MiBLi/LiOtBu. The final solutions were directly analyzed by multinuclear NMR techniques, keeping in mind the limited stability of the living oligomers. Therefore, only ^1H , ^{13}C INEPT and INEPT long-range and ^1H - ^1H nuclear Overhauser effect correlations were recorded for the living PMMA owing to the short accumulation times for the techniques. The first simple conclusion was that the use of a fresh mixture or an aged solution of MiBLi/tBuOLi as initiator does not change the structure of the growing chains. The ^{13}C NMR spectrum of these living systems consists of three signals in the carbonyl region (A = 212 ppm, B = 182 ppm, C = 160 ppm). Signal C has nearly the same chemical shift as the one reported for the end carbonyl in the dimer model complexed by LiOtBu. Signal B belongs to the penultimate unit consistent with a long range ^1H - ^{13}C correlation. Finally, signal A, whose intensity increases with time, is characteristic of the ketone formed by a backbiting reaction. No clear information on the enolate conformation has been provided by the nuclear Overhauser effect in the ^1H - ^{13}H 2D spectrum.

Intramolecular complexation of the lithium counterion by the penultimate unit might account for the chemical shift of the γ -carbonyl (B) at ca. 180 ppm. Nevertheless, the chemical shifts at 180 ppm were assigned to the γ carbonyl ester of the dimer model, but not in particular to the γ carbonyl ester involved in intramolecular complexation. The striking difference between the coordinated and the uncoordinated forms has to be formed in the carbonyl group of the lithium ester enolate. The resonance of this carbon is observed at 170 and 160 ppm for the intramolecularly complexed form and the linear form, respectively. In case of the living PMMA chain ends complexed by LiOtBu, no clear signal is observed for the intramolecular complexation.

Undoubtedly, a first step in the direct investigation of living chains has been cleared made by Kriz et al. [13]. The correlation of these results with the chain molecular characteristics should be the next step of this study.

Table 7

Effect of ligands on the stereochemistry expressed in triad placements for the anionic polymerization of MMA at — 78°C in THF [23]

Ligand	L/I	mm	mr	rr
	0/1	0.01	0.21	0.78
LiCl	1/1	0.01	0.21	0.78
LiCl	5/1	0.01	0.20	0.79
LiOtBu	1/1	0.01	0.19	0.80
LiOtBu	10/1	0.01	0.19	0.8
CE	5/1	0.01	0.22	0.77
K211	1.5/1	0.02	0.33	0.65
LiOEEM	2/1	0.01	0.16	0.83
LiOEEM	10/1	0.01	0.16	0.83

Table 8

Chain-end E/Z ratio for the anionic polymerization of MMA in THF at — 78°C in presence of various ligands [6]

Ligands	Chain-end E/Z ratio: Z(%)
	100
HMPA (4)	100
LiOtBu (5)	100
LiCl (3)	88.5
LiOEEM (5)	88
12CE4 (5)	100
K211 (2)	10

3.3.3.2. Effect of σ ligands Table 7 also lists the molecular characteristics of PMMA initiated by DPHLi in presence of σ ligands in THF at — 78°C. Clearly, the addition of a crown ether (12-CE-4) does not change either the chain tacticity or the polydispersity [23]. The main effect of kryptand (K211) is an increase in the syndiotactic placement and a decrease of the polydispersity down to 1.01. In agreement with independent observations 12-CE-4 is a less efficient complexing agent than K211. The crown ether is thus less complexing than THF, so that the propagating species remains unmodified as previously observed for MiBLi complexed by this σ ligand.

Müller et al. [97] have studied the kinetics of the PMMA polymerization initiated by an organolithium complexed with kryptand. Complexation results in a decrease of the polymerization rate constant, thus supporting the model of a predominant contact ion pair for the active center. The interionic distance of the ion pairs has been estimated from the dissociation constant and found to be in agreement with a close contact of the cation and the enolate carbonyl oxygen. No direct information on the structure of the propagating species has been published mainly because of the high reactivity/low stability of these species. This gap should be addressed in the future.

3.3.3.3. Effect of μ - σ ligands Finally, μ - σ ligands, e.g. LiOEEM, have also been used as additives for the anionic polymerization of MMA in THF at — 78°C [23]. The molecular characteristics of the accordingly formed PMMA are reported in Table 7. PMMA is highly syndiotactic and the syndiotactic placement increases in parallel to the relative LiOEEM content. The polymerization is very fast (100% conversion after 2 min) compared to ligation by a μ ligand. The polydispersity decreases down to 1.05 upon addition of 5 equiv. of LiOEEM.

An NMR analysis of the active species of living PtBMA oligomers has suggested for interaction between living chains and LiOEEM and thus coordination. LiOEEM is however unable to convert completely the living chains into complexed species. Traces of uncomplexed oligomers persist even in presence of 10 equiv. of LiOEEM. At least two differently growing sites coexist that impart bimodality to PtBMA. These results sharply contrast to the anionic polymerization of MMA which is basically living when LiOEEM is used as a ligand. This difference likely results from the bulkiness of the *tert*-butyl group which hinders efficient complexation.

3.3.3.4. Relationship between structure of the living chain ends and chain stereochemistry Although some

direct analysis of the complexed lithium ester enolate has been carried out, no clear correlation between the structure of the propagating species and the molecular parameters of the chains has emerged. Hogen-Esch et al. have proposed an interesting strategy for the direct analysis of the lithium ester enolate structure [84,21]. The end capture of the lithium enolate by ClSiMe_3 has been devised clearing up the origin of the stereochemistry in ligated systems [6]. The structure of the silylated enolates is reported in Table 8, as the *E/Z* stereoisomerism ratio extracted from the ^{13}C NMR spectrum of the silylated PMMA.

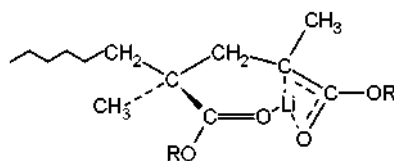
Although the influence of the ligands on the *E/Z* ratio is quite complex, three situations can be identified:

1. the ligand has no effect on the chain end *E/Z* ratio and the main-chain tacticity (12-CE-4, HMPA, LiOtBu);
2. the ligand changes the chain-end *E/Z* ratio but not the main chain tacticity (LiCl , LiOEEM);
3. the ligand has an effect on both the chain end *E/Z* ratio and the main chain tacticity (K211).

Once again, no clear conclusions can be drawn from this study. Indeed, there is no clear evidence that the *E/Z* ratio in the silylated product foreshadows that one in the enolate. Although complexation by different ligands changes the *E/Z* isomerism, no information on the approach of the monomer in the transition state can be obtained. Coordination of the ligand with the monomer may not be ignored in the stereoregulation process. Further investigation is highly desirable for drawing some correlation between the ligation process and the stereochemistry ultimately observed.

3.4. Anionic polymerization of alkylmethacrylates in toluene

Anionic polymerization of alkyl(meth)acrylate, initiated by organolithium compounds in apolar solvents, is of great interest, since this process leads to highly isotactic polymer [82]. The drastic change in stereochemistry with the solvent polarity has drawn attention as a way to approach the stereoselectivity concept. As a rule, the anionic polymerization in toluene has been essentially studied in terms of chain stereoregularity, molecular weight distribution and kinetics. Few direct investigations on the structure of the propagating chain ends have been reported in the scientific literature for living poly(-alkyl)methacrylic chains initiated by an organolithium in toluene. The unimeric model, MiBLi , is insoluble in toluene in contrast to lithium ethylisobutyrate which is soluble e.g. in benzene in which an average aggregation of 6 has been reported by Lochmann [69]. This monomeric model has been examined by NMR by Müller et al. who reported ^{13}C chemical shifts quite similar to the ones observed in pure THF [106].



Scheme 16. Intramolecular complexation.

No investigation has been reported for the dimeric model or for living chains.

Kinetic data have been collected [34] for MMA polymerization initiated by an adduct of BuLi and diphenylethylene which minimizes side reactions with MMA [20]. In spite of a broad molecular weight distribution of the formed PMMA, a linear plot of $\ln[\text{MMA}_0]/[\text{MMA}]$ versus time is observed, which indicates a constant concentration of the active species and a propagation which is first order in monomer. An independent analysis has indicated that ca. 10% initiator is consumed by attack of the ester carbonyl group with formation of MeOLi . Moreover, this amount of MeOLi increases with time which is a signature of termination reactions. Since MeOLi is known to coordinate the propagating center, some complexed active species are expected to be formed and to be more reactive than the unmodified species, thus leading to a multiplicity of propagating species and in a broadening of MWD. This partial increase in reactivity could compensate for the partial loss of growth centers and account for the observed first order kinetics.

As a rule, low molecular weight material ($M_n = 800\text{-}900$) is systematically recovered. Glusker et al. [98] have studied the MMA polymerization initiated by fluorenyllithium in toluene at -70°C . Tritiated acetic acid has been added as a terminating agent, so that radioactive low molecular weight material is recovered. The low reactivity of these oligomers is explained by the so-called pseudotermination state i.e. the formation of a cyclic intermediate that propagates only very slowly. The probability of such cyclization decreases when more than 8-10 monomer units have been polymerized.

Another complexity associated with the anionic polymerization of alkylmethacrylates in non-polar solvents, is that the polymerization livingness may depend on the initiator used, as it is the case for tBMA. Kilz et al. [99] used DPHLi and DPMLi as initiators and observed a linear dependence of $\ln[\text{tBMA}_0]/[\text{tBMA}]$ on time although the molecular weight distribution was bimodal for polytBMA initiated by DMPLi . In contrast to PMMA, PtBMA initiated by DPHLi has a very narrow molecular weight distribution (1.1). No contamination by low

molecular weight oligomers was observed, even though the molecular weight distribution was bimodal. The use of *EiBLi* and *tBiBLi* as initiators resulted in PtBMA of a broad MWD with a major trace in the low molecular weight region. The strong influence of the initiators would be related to the differences in the initial aggregation state.

Poly(tBMA) formed in toluene is highly isotactic (99%). The driving force of this remarkable selectivity is usually explained by the intramolecular coordination of the lithium counterion (Scheme 16) [25]. MNDO calculations by Dybal and Kriz [100] have recently concluded that the intramolecular coordinated form can add MMA only with an isotactic placement. The dimeric model for PMMA, i.e. di-methyl-2-lithio-2,4,4'-trimethylglutarate was used in these calculations. Pino and Sutter [101] have also reported that the syndiotactic diads are thermodynamically favored over the isotactic ones but that the difference in free energy is so small that the formation of stereoregular chains must be kinetically controlled. The kinetic control could result from the difference in the activation free energy for the two types of placements. So, a change in the activation free energy by only 1.3 kcal/mol can change the PMMA iso/syndio ratio from 50:50 to 90/10.

Fowells et al. [25] have studied the stereoregulation process in toluene. They initiated the polymerization of deuterated ethyl methacrylate by fluorenyllithium under various conditions, and analyzed polymer microstructure by ¹H NMR spectroscopy. Mainly isotactic polymers were recovered and their observations suggested that only differences in solvation lead to an isotactic placement.

In conclusion, there is a need for further thorough investigations before firm conclusions can be drawn about the polymerization mechanism of methacrylic monomers in apolar solvents. The poorly documented situation mainly results from experimental limitations in the direct analysis of the structure of lithium ester enolates. Another explanation has to be found in the high isotacticity that results in a decrease in T_g [102]. Indeed, iPMMA has no use for thermoplastic applications with a low T_g (60°C) compared to sPMMA (ca. 120°C). Furthermore, if highly isotactic PMMA is required, an anionic MMA polymerization initiated by Grignard agents is a very efficient route [103].

3.5. Ligated anionic polymerization of alkylmethacrylates in toluene

Only a few studies on LAP in toluene have been reported compared to investigations in THF. Bayard et al. [53,54] have studied the effects of LiOEEM on the MMA polymerization in toluene. The formation of highly syndiotactic PMMA is indicative of the complexation of the lithium ester enolates by the polydentate lithium alkoxide. Recently, another μ/σ ligand, i.e. lithium 2-(dimethylamino) ethoxide, was used by Fontanille et al., who polymerized MMA in toluene at a temperature as high as 70°C [52]. The addition of alkylaluminum is an efficient way to change drastically the stereoselectivity in toluene from isotactic placements to syndiotactic ones [45,104]. Müller et al. [105] have studied the effects of alkylaluminum by ¹³C NMR. The analysis of a mixture of *EiBLi* and *Et₃Al* has clearly shown the effect of the complexation on the chemical shifts. Although mixtures of solvents (THF/toluene) have been used in combination with some ligands in order to control the anionic polymerization of alkylmethacrylates, no thorough analysis of the structure of the propagating species has been undertaken under these conditions.

4. Conclusions

Although the direct analysis of the active species in the anionic polymerization of alkylmethacrylates has been scarcely reported, mainly because of the poor stability of these species substantial progress has been made in the control and the understanding of the basic mechanism of this polyaddition reaction. The structure of the species propagating during the living anionic polymerization of alkylmethacrylates has been recently elucidated by the study of model compounds using multinuclear NMR spectroscopy. The interaction of lithium isobutyrate with different types of ligands has been thoroughly studied in THF mainly by ¹H, ¹³C and ⁷Li NMR, which has extensively contributed to a better understanding of the effects of ligation on the course of the anionic polymerization. More recently, the study of a dimer model and its interaction with ligands has proved to be of great significance because of the opportunity to give evidence for the intramolecular complexation of the lithium counterion. A new approach to obtain valuable information on the structure of the growing species involved in LAP of (meth)acrylates is outlined in this review. Additional NMR investigations are however required in order to correlate the polymerization kinetics and the molecular characteristics of the polymer with the structure of the propagating species. This information is highly desirable to better understand the polymerization process in apolar solvents. Another pending question is the dependence of the polymer stereochemistry on the ligation of the active species.

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