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New Ligands for the Living Isotactic Anionic Polymerization of Methyl Methacrylate in Toluene at 0 °C. 1. Ligation of Butyllithium by Lithium Silanolates

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ABSTRACT: sBuLi and tBuLi have been combined with a new family of ligands, i.e. lithium silanolates, and used as initiators for the ligated anionic polymerization (LAP) of methyl methacrylate (MMA) in toluene at 0 °C. Compared to other known μ-ligands, the accordingly formed Bu(Me_2)SiOLi are more efficient stabilizers for the active centers. Under appropriate reaction conditions, a fast polymerization proceeds quantitatively without self-termination at 0 °C and leads to high molecular weight polymer of narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n < 1.2$) and high isotacticity (90% isotactic triads).

Introduction

Living polymerization is a concept that was originally proposed by Szwarc[1] in 1956. Nowadays, it is still the best way for the implementation of the so desirable macromolecular engineering of synthetic polymers. In case of poly(meth)acrylates, it can make a variety of materials available with a large scope of properties and potential applications. However the anionic polymerization of (meth)acrylates suffers severe limitations under the usual conditions of solvent and temperature. These problems arise from the possible nucleophilic attack of the active species on the carbonyl group of both the monomer and the polymer subunit and from the possible abstraction of the α-hydrogen atom of acrylates.

Nowadays, it is known that the reactivity of anionic species can be modulated by coordination with ligands (ligated anionic polymerization or LAP). It becomes accordingly possible to cope with the double challenge of producing high molecular weight (MW) poly(meth)-acrylates with precisely tailored chain length and chain ends, while being at the same time perfectly compatible with many other types of monomers such as vinyl aromatics, dienes, oxiranes, etc. The basic idea of that strategy is to use suitable ligands to interact coordinatively with very active metal-containing (usually alkali metals) initiating and/or propagating ion pairs. These ligands fulfill a variety of functions:[2] (i) modulation of the electron density at the metal enolate ion pair and, therefore, of its stability and reactivity; (ii) provision of a steric barrier blocking a large enough space area around the metal-containing ion pairs, thus possibly minimizing the extent of secondary reactions; (iii) promotion of new complexation equilibria displacing classical equilibria between different ion pairs and/or aggregates, hopefully leading to the formation of a single active species. The efficient ligands discovered to date may be classified into three groups: (1) μ-coordinating ligands, mainly alkali metal alkoxides,[3] aluminum alkyls,[4,5] Al phenoxides,[6,7] and LiCl;[8] (2) σ-type ligands of the crown ether type;[9] (3) μ/σ-type dual ligands as exemplified by polyether metal alkoxides,[10,11] where a lithium ethoxide moiety may function as a μ-type of coordination site and a polyether component as a σ-type. The new "μ,σ-ligated anionic initiators" are remarkably efficient in controlling "living" high MW polymerization of methacrylic and even acrylic esters, including primary ones down to butyl,[12] as well as their block or random copolymerization and end-group functionalization, at moderately low temperatures.[13] All these reactions are conducted in hydrocarbon media, which is an advantage over THF for process scaling-up. A rather high syndiotacticity (rr ∼ 80%) is maintained anytime.

The dominant syndiotacticity observed for PMMA synthesized in toluene in the presence of polydentate lithium alkoxides clearly demonstrates that the lithium is coordinatively saturated, preventing its back-coordination with the penultimate ester group of the chain. Therefore, the monomers approach in a sterically more favorable syndiotactic-like mode. It is worth recalling that PMMA chains formed in toluene at low temperature without any additive are rich in isotactic triads (mm ∼ 60%).[14−16] Under these polymerization conditions, multiple active species are commonly formed and side reactions make the molecular weight distribution (MWD) quite broad. Hatada et al.[4,5] have reported that t-C_4H_9MgBr prepared in diethyl ether causes no side reaction in the polymerization of MMA in toluene at −78 °C and forms highly isotactic polymer (mm > 95%) with rather narrow MWD ($\bar{M}_w/\bar{M}_n < 1.2$). That is the first example of the direct preparation of highly isotactic PMMA with narrow MWD, although it is limited to low temperature and does not allow the synthesis of very high molecular weight PMMA.

To our knowledge, there has been no report on a controlled anionic polymerization yielding highly isotactic PMMA of high molecular weight and narrow MWD under mild conditions. In the present paper, we wish to report on the discovery of a new class of "μ-ligated anionic initiators", which are very effective in the isotactic polymerization of MMA in toluene at 0 °C. These initiators are mixed associated species of the form $\{x\text{BuLi}, (y - x)\text{BuMe}_2\text{SiOLi}\}$.[17]

Experimental Section

Butyllithium (1.37 M solution in cyclohexane, Aldrich) and hexamethylcyclotrisiloxane (D_3) (Aldrich) were used as re-

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Table 1. Effect of the Structure of BuLi on the Polymerization of MMA in Toluene at 0 °C Using the BuLi/D$_3$ System[a]

$[RLi]_0$ (mmol)	$[RLi]_0/[D_3]_0$	ρ[b] (%)	$\bar{M}_n$ (SEC)	$\bar{M}_w/\bar{M}_n$	% microstructure iso	het	syn
tBuLi, 3.15	3.16	100	13 200	2.1	81	10	9
sBuLi, 3.42	3.13	100	21 700	1.1[c]	85	10	5
nBuLi, 3.25	3.25	~0					

[a] [MMA] = 0.50 mol·L^{-1}; polymerization time = 1 h, although the polymerization is fast, in the case of tBuLi and sBuLi (3–5 min). [b] ρ = polymer yield. [c] The SEC trace clearly shows, that the MWD is slightly bimodal.

ceived. Methyl methacrylate (MMA) (Janssen) was added with a 10 wt % AlEt$_3$ solution in hexane until a persistent yellowish color was observed and distilled before polymerization. Toluene and tetrahydrofuran (THF) were purified by refluxing over fresh sodium–benzophenone complex and distilled just prior to use. Dimethyl sulfoxide (DMSO) was distilled and stored over dry molecular sieves (4 Å grade) under a nitrogen atmosphere.

The lithium silanolate initiator system was prepared in situ in a previously flamed glass reactor under inert atmosphere, the monomer and solvent being transferred by the syringe and capillary technique.

A typical example involved introducing D$_3$ into the flask. A 5 mL aliquot of toluene and the required amount of BuLi were then transferred into the reactor by means of a glass syringe. After 20 h at 20 °C, 80 mL of toluene was added, the solution was cooled to 0 °C and 4.2 g MMA was introduced. Polymerization was performed for *t* minutes and then stopped by adding methanol. The polymers were recovered by precipitation into methanol and dried under vacuum at 70 °C for 24 h.

Size exclusion chromatography (SEC) was performed with a Hewlett-Packard 1090 apparatus equipped with 4 PLgel columns (10^5, 10^4, 10^3, and 10^2 Å) using tetrahydrofuran as eluent and a HP 1030 A refractive index detector. The flow rate was 1.0 mL/min. The number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated in reference to a polystyrene calibration.[18] Polymer chain tacticity was measured by ^{1}H NMR spectroscopy using a Bruker AM-400 spectrometer.

Results

BuMe$_2$SiOLi species (i.e. BuD$_1$Li) are formed as result of the reaction of butyllithium (BuLi) with hexamethylcyclotrisiloxane (D$_3$) in toluene at 20 °C. That reaction is well established and does not form the expected BuD$_3$Li compound because of fast redistribution reactions.[19,20] Any excess D$_3$ remains unpolymerized unless a donor solvent, such as THF, DEE, or DMSO, is added to the reaction medium. The choice of the initial $[BuLi]_0/[D_3]_0$ ratio thus dictates the actual [BuLi]/[BuD$_1$Li] ratio in the reaction medium. The strong tendency of lithium silanolates to aggregate has been noticed earlier by some authors.[21,22] It is therefore reasonable to propose that the two coexisting organolithium compounds (i.e. BuLi and BuD$_1$Li) form mixed associated species of the form {*x*BuLi, (*y* − *x*)BuD$_1$Li}.[23]

Effect of the BuLi Structure. The three isomers of BuLi, e.g., *n*-butyllithium (nBuLi), *sec*-butyllithium (sBuLi) and *tert*-butyllithium (tBuLi) have been used in order to investigate whether steric and electronic (inductive) effects associated with the structure of the BuLi and silanolate constitutive components may have an effect on the MMA polymerization. Table 1 confirms that this structural aspect has a deep influence when MMA is polymerized in toluene at 0 °C. The {*x*nBuLi, (*y* − *x*)nBuD$_1$Li}, species have no capacity to initiate the MMA polymerization, which suggests that the attack of the MMA carbonyl by nBuLi deactivates the initiator almost instantaneously. This observation also confirms that lithium silanolate is unable to initiate the MMA polymerization. In contrast to {*x*nBuLi, (*y* − *x*)nBuD$_1$Li}, the bulkier initiators {*x*sBuLi, (*y* − *x*)sBuD$_1$Li} and {*x*tBuLi, (*y* − *x*)tBuD$_1$Li} are so efficient that they form isotactic PMMA in an essentially quantitative yield. Somewhat surprisingly, the polymerization initiated by {*x*sBuLi, (*y* − *x*)sBuD$_1$Li} produces a highly isotactic PMMA of a narrow MWD. The SEC traces show however that PMMA has a slightly bimodal MWD. It is nevertheless clear from the MWD and polymer tacticity that {*x*sBuLi, (*y* − *x*)sBuD$_1$Li} provides a better control on the polymerization than the parent {*x*tBuLi, (*y* − *x*)tBuD$_1$Li} initiator.

Effect of the Initial [^{s}BuLi]$_0$/[D$_3$]$_0$ ratio (*r*). A kinetic study of the anionic polymerization of D$_3$ in THF has confirmed the strong tendency of lithium silanolates to form tetramers.[21,22] Furthermore, the colligative properties of sBuLi solutions in toluene are consistent with the tetramerization of this organolithium.[24] The following set of equilibria may accordingly be proposed for the structure of the aggregates formed by the combination of sBuLi and sBuD$_1$Li with $x \le 4$ and $y \ge 4$:

$$^3/_4\{4\text{sBuLi}\} + [(y-3)/y]\,\{y\text{sBuD}_1\text{Li}\} \rightleftharpoons \{3\text{sBuLi}, (y-3)\text{sBuD}_1\text{Li}\}$$

$$2\{3\text{sBuLi}, (y-3)\text{sBuD}_1\text{Li}\} + [(y-2)/y]\,\{y\text{sBuD}_1\text{Li}\} \rightleftharpoons 3\{2\text{sBuLi}, (y-2)\text{sBuD}_1\text{Li}\}$$

$$\{2\text{sBuLi}, (y-2)\text{sBuD}_1\text{Li}\} + \{y\text{sBuD}_1\text{Li}\} \rightleftharpoons 2\{\text{sBuLi}, (y-1)\text{sBuD}_1\text{Li}\} \quad \text{etc.}$$

Let us recall that the $[sBuLi]_0/[D_3]_0$ ratio (*r*) dictates the [sBuD$_1$Li]/[sBuLi] ratio (*R*) and thus the whole set of equilibria. Since it is worth learning how these equilibria affect the MMA polymerization, initiators of various $[sBuLi]_0/[D_3]_0$ ratios have been prepared ($2.8 \le r \le 5.9$) and tested. Table 2 shows that the monomer conversion is close to completeness and that highly isotactic PMMA is formed. The SEC traces (Figure 1) clearly show that a decrease of *r* leads to a less bimodal MWD.

For $r > 3$, the *R* molar ratio fits the equation $R = [sBuD_1Li]/[sBuLi] = [sBuD_1Li]/([sBuLi]_0 - [sBuD_1Li])$, where $[sBuD_1Li] = 3\rho'[D_3]_0$ with ρ' the yield in sBuD$_1$Li for the reaction sBuLi + D$_3$ → 3sBuD$_1$Li. The actual BuD$_1$Li and BuLi concentrations have been measured by the double titration technique commonly used for the titration of organolithium solutions mainly contaminated by LiOH.[25] For instance, $\rho' = 1$ for $r \gg 3$ and $\rho' = 0.95$ in the case of $r = 2.90$. These figures indicate that the reaction equilibrium is such that BuLi does not completely react when used with a small excess D$_3$.

Anionic Polymerization of MMA Initiated by {sBuLi, (*y* − 1)sBuD$_1$Li} in Toluene at 0 °C ($r \le 2.9$). When the $[sBuLi]_0/[D_3]_0$ ratio (*r*) is smaller than 2.9, the monomer conversion is complete and the molecular weight distribution is essentially monomodal and narrow ($\bar{M}_w/\bar{M}_n < 1.2$). These observations are consistent with only one type of living propagating species. The initiator solution would thus contain only one type of

Table 2. Effect of the Initial $[SBuLi]_0/[D_3]_0$ Ratio (r) on the Polymerization of MMA in Toluene at 0 °C Using the SBuLi/D_3 System[a]

$[sBuLi]_0$ (mmol)	r	R^b	ρ (%)	$\bar{M}_{n2}$ (%P_2), %$[P_2^-]$	$\bar{M}_{n1}{}^c$ (%P_1), %$[P_1^-]$	F^d (%)	% microstructure iso	het	syn
7.40	5.9	1.0	98	57 000 (62), 10	3900 (38), 90	1.4	86	9	5
1.23	4.3	2.2	98	250 400 (48), 11	35 000 (52), 89	2.4	78	13	9
2.05	3.7	4.4	100	177 300 (32), 7	25 100 (68), 93	4.0	85	4	11
2.88	3.5	5.6	100	141 700 (36), 7	18 300 (64), 93	5	87	9	4
3.42	3.1	23	100	225 200 (12), 1	21 700 (88), 99		85	10	5
3.56	2.9	21	100	... (~0), 0	37 000 (100), 100		93	5	2
3.29	2.8	35	100	... (~0), 0	79 000 (100), 100		92	8	1
1.64	2.8	35	100	... (~0), 0	100 000 (100), 100		91	7	2

[a] $[MMA] = 0.50\ mol{\cdot}L^{-1}$; polymerization time = 1 h except for the last two experiments ($t = 20$ min.); ρ = polymer yield. [b] Measured by titration with, and without, addition of an excess of $BrCH_2CH_2Br$. [c] $\bar{M}_w/\bar{M}_n < 1.2$. [d] $F = ([P_2^-])/([sBuLi] - (100/70)[P_1^-]) = ([P_2^-])/([sBuLi]_o - 3\rho'[D_3] - (100/70)[P_1^-])$; ρ' tends to 1 when r increasingly exceeds 3.

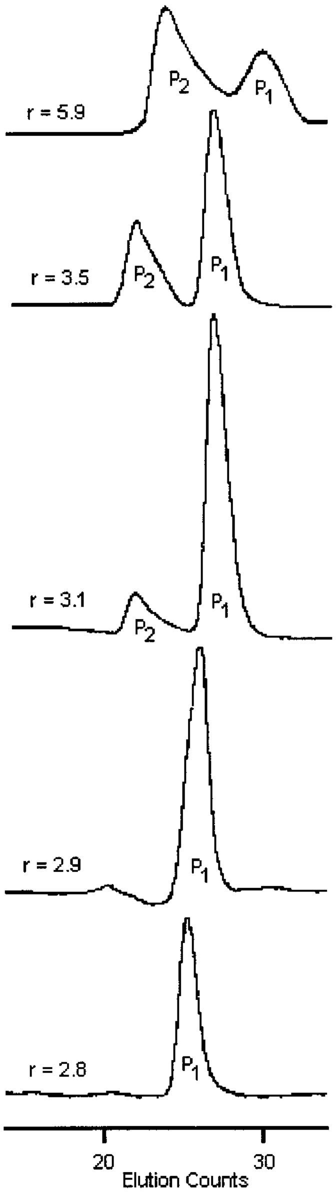

Figure 1. MWD of PMMA prepared from various $[sBuLi]_0/[D_3]_0$ ratios (r).

mixed associated species that would supposedly consist of one sBuLi molecule ligated by ($y - 1$)$sBuD_1Li$ (i.e. {sBuLi, ($y - 1$)$sBuD_1Li$}). These species are then converted into {$sBu(CH_2C(CH_3)COOCH_3)_nLi$, ($y - 1$)$sBuD_1Li$} ($P_1^-$) propagating chains.

To determine the efficiency of the {sBuLi, ($y - 1$)$sBuD_1Li$} initiator, the actual concentration of sBuLi in the initiator solution at $r = 2.9$ has been measured by the double titration method commonly used for the titration of alkyllithium solutions.[25] As a result the $[sBuD_1Li]/[sBuLi]$ ratio (R) is ca. 21 and the theoretical molecular weight (26 000) is 30% smaller than the experimental value (37 000). Therefore at least 70% {sBuLi, ($y - 1$)$sBuD_1Li$} species are available for initiation.

Monomer resumption experiments are a further evidence for the controlled polymerization of MMA initiated by the {sBuLi, ($y - 1$)BuD_1Li} species formed at $r = 2.9$. MMA is first polymerized in toluene at 0 °C, and Δt minutes later the same MMA dose is added. The size exclusion chromatogram of the final product shows two well-separated peaks, P_1 and P_3 (Figure 2b, Δt = 10 min). Since peak P_1 is quite comparable to the SEC peak for the first PMMA crop (Figures 2a), peak P_3 is characteristic of the final PMMA. It thus appears that part of the original living PMMA chains (P_1^-) have been killed before the addition of the second monomer dose. Actually, $\bar{M}_n$ of the first PMMA sample (P_1; Figure 2a) is 64 500 ($\bar{M}_w/\bar{M}_n = 1.1$) compared to 204 000 ($\bar{M}_w/\bar{M}_n = 1.1$) for the final polymer (peak P_3; Figure 2b), which indicates that ca. 40% of the originally living chains P_1^- have not contributed to the second polymerization step (i.e. $[P_3^-]/[P_1^-] \sim 0.60$). Since the MWD of the final polymer is very close to the value for the first crop, termination reactions have more likely occurred before the second polymerization starts. Therefore, the complexed P_1^- anions are either killed upon the addition of the second monomer feed or are unstable to the point where they are terminated in the time interval between the two monomer additions (Δt). In the latter case, Δt must be an experimental parameter of a critical importance. Actually, when Δt is increased from 10 to 30 min (Figure 2c), the $[P_3^-]/[P_1^-]$ ratio decreases from 0.60 to 0.30. It might thus be suggested that the loss of P_1^- anions is the result of slow reactions with impurities and/or slow self-termination reactions.

In order to clarify that situation, samples have been picked out from the reaction medium of the last experiment reported in Table 2 after different polymerization times: 3.5, 8, and 19 min (Figure 3). It appears that polymerization is quantitative after 19 min at 0 °C, and that a high molecular weight PMMA fraction becomes visible when the monomer conversion exceeds ca. 90% (i.e., $t = 3.5$ min). Therefore, the loss of P_1^- anions would result at least partly from slow inter/intramolecular termination reactions. This observation also shows that the active species (P_1^-) are stable for several minutes in toluene at 0 °C, which makes living PMMA chains of a monomodal MWD available for a period of

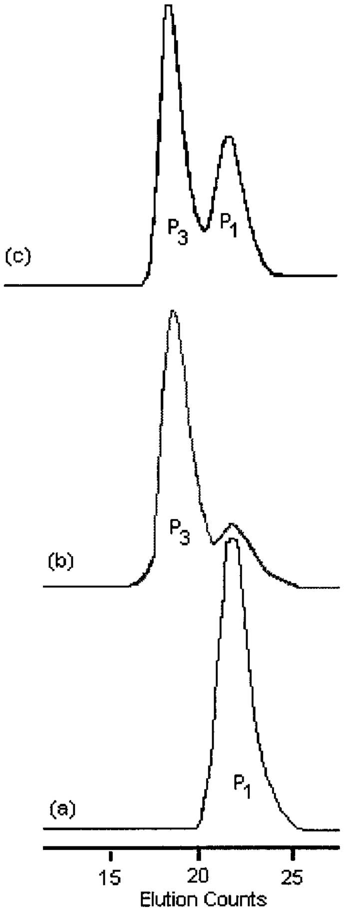

Figure 2. MMA resumption experiments in toluene at 0 °C. Conditions: $[sBuLi]_0/[D_3]_0$ ratio (r) = 2.9; $[MMA]_{\text{first dose}} = [MMA]_{\text{second dose}} = 0.41$ mol·L^{-1}; polymerization time of the first dose = Δt; polymerization time of the second dose = 40 min. Polymer yield: 100%. Key: (a) after polymerization of the first monomer dose ($[sBuLi] = [P_1^-] = 5.7 \times 10^{-5}$ mol); (b) after polymerization of the second monomer dose, $\Delta t = 10$ min ($\bar{M}_{n_1} = 64\,500$ and $\bar{M}_{n_3} = 204\,000$); (c) after polymerization of the second monomer dose, $\Delta t = 30$ min and $[sBuLi] = [P_1^-] = 8.7 \times 10^{-4}$ mol, ($\bar{M}_{n_1} = 42\,500$ and $\bar{M}_{n_3} = 115\,000$).

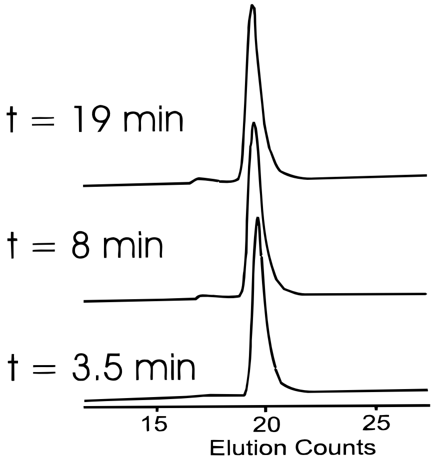

Figure 3. Size exclusion chromatograms of PMMA samples picked out from the reaction medium, after 3.5, 8, and 19 min. Experimental conditions: see last experiment in Table 2. $\bar{M}_n$ is increased from 92 000 to 100 000 when t increases from 3.5 to 19 min.

time sufficiently long for being involved in macromolecular engineering.

Anionic Polymerization of MMA Initiated by $\{x$sBuLi, $(y - x)$sBuD$_1$Li$\}$ (x = 1, 2, and 3) in Toluene at 0 °C (r > 2.9 and R < 21). The bimodal MWD observed at $r > 2.9$ (Figure 1) suggests the coexistence of at least two different propagating species. The difference in reactivity of these species can be detected at a very early stage of the polymerization reaction. When r is increased, the excess of sBuD$_1$Li with respect to the unreacted sBuLi has to decrease, so that the equilibrium has to be shifted from mixed $\{$sBuLi, $(y - 1)$sBuD$_1$Li$\}$ aggregates toward $\{$2sBuLi, $(y - 2)$sBuD$_1$Li$\}$ and $\{$3sBuLi, $(y - 3)$sBuD$_1$Li$\}$ aggregates, respectively. Although the actual structure of the active species in case of aggregates containing $(y - 2)$ and $(y - 3)$sBuD$_1$Li is unknown, they are expected to react with MMA to form $\{a[sBu(CH_2C(CH_3)COOCH_3)nLi]$, bCH_3OLi, $(y - 2)$sBuD$_1$Li$\}$ with $a + b = 2$ and $\{a[sBu(CH_2C(CH_3)COOCH_3)_nLi]$, bCH_3OLi, $(y - 3)$sBuD$_1$Li$\}$ with $a + b = 3$. CH_3OLi and isopropenyl isobutyl ketone would be formed as result of the possible reaction of sBuLi with the carbonyl group of MMA. This side reaction would also form isopropenyl isobutyl ketone, which may easily react with the propagating end to give much less active propagating species, as mentioned by Hatada et al.[32] It is worth noting that the presence of a much less active propagating species after the reaction of isopropenyl isobutyl ketone with the propagating end could not explain the bimodal distribution, since the broad MWD (P_2) which corresponds to the uncontrolled system has the highest molecular weight. Most probably, any change in the number of sBuD$_1$Li associated with the growing species would result in a difference in reactivity, the propagating species being less stable when the number of sBuD$_1$Li ligands is decreased. It is therefore proposed that $\{$sBuLi, $(y - 1)$sBuD$_1$Li$\}$ is at the origin of the low molecular weight peak (P_1) and that $\{$2sBuLi, $(y - 2)$sBuD$_1$Li$\}$ and $\{$3sBuLi, $(y - 3)$sBuD$_1$Li$\}$ lead to the high molecular weight one (P_2) as result of intermolecular termination reactions, in agreement with a much broader MWD for P_2 (>2) compared to P_1 (<1.2). An alternative explanation that the reaction of the propagating species with isopropenyl isobutyl ketone leads to much less reactive species[32] responsible for the bimodality cannot be accepted, since the chain population P_2 that appears when R is smaller than 20 is of the higher molecular weight and thus inconsistent with initiation by species of a lower reactivity.

The concentrations in the active centers $[P_1^-]$ (= $[\{sBu(CH_2C(CH_3)COOCH_3)_nLi$, $(y - 1)$sBuD$_1$Li$\}]$) and $[P_2^-]$ have been computed from data in Table 2 and reported in this table. The relative amount of $[P_1^-]$ and $[P_2^-]$ depends on r (or R), although P_1^- is by far the dominant species. Figure 4 shows that P_1^- becomes the unique active species when R exceeds 20−25. This relationship between $[P_1^-]$ and R gives additional credit to a set of equilibria between $\{$sBuLi, $(y - 1)$sBuD$_1$Li$\}$, $\{$2sBuLi, $(y - 2)$sBuD$_1$Li$\}$,$\{$3sBuLi, $(y - 3)$sBuD$_1$Li$\}$, and $\{y$sBuD$_1$Li$\}$. It is worth recalling here that the initiation efficiency of the $\{$sBuLi, $(y - 1)$sBuD$_1$Li$\}$ species has been estimated at 70%. For the sake of comparison, the initiation efficiency of the $\{$2sBuLi, $(y - 2)$sBuD$_1$Li$\}$ and $\{$3sBuLi, $(y - 3)$sBuD$_1$Li$\}$ species has been calculated as $F = ([P_2^-])/([sBuLi] - (100/70)[P_1^-])$ (Table 2). F is very small (< 5%) compared to that for the $\{$sBuLi, $(y - 1)$sBuD$_1$Li$\}$ species.

In order to demonstrate that the macroanions P_2^- are partly living in toluene at 0 °C, a monomer resumption experiment has been carried out (Figure 5). The initial

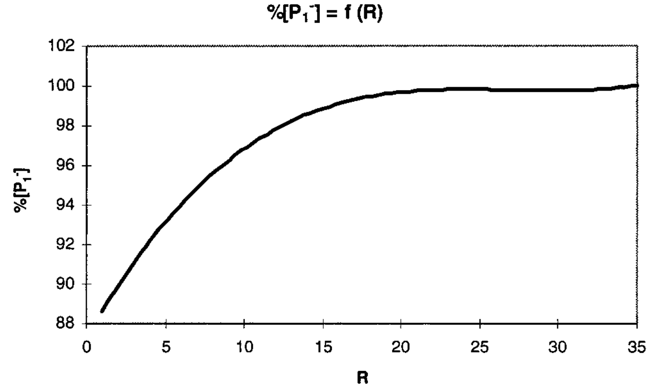

Figure 4. Dependence of the % of $[P_1^-]$ on the $[sBuD_1Li]/[sBuLi]$ ratio (*R*). (See data in Table 2.)

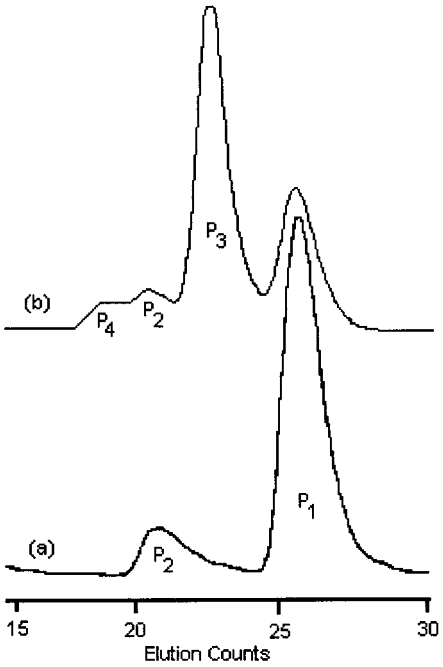

Figure 5. MMA resumption experiments in toluene at 0 °C: (a) after polymerization of the first monomer dose; (b) after polymerization of the second monomer dose. Experimental conditions: $[sBuLi]_0/[D_3]_0$ ratio (r) = 3.1; $[sBuLi]_0 = 3.56$ mmol; $[MMA]_{\text{first dose}} = [MMA]_{\text{second dose}} = 0.51$ mol·L^{-1}; polymerization time of the second dose = 1 h. Time interval between the addition of the MMA doses $\Delta t = 1$ h.

initiator solution has been prepared with $r = 3.1$ and used to polymerize a first MMA dose. Then, 1 h later, the polymerization medium contains enough active sites for the conversion of the second MMA feed to be complete. The SEC analysis of the final polymer (Figure 5b) shows four well-separated peaks, P_1, P_2, P_3, and P_4. Since the elution volumes of peaks P_1 and P_2 correspond to the volumes characteristic of the first PMMA crop (Figure 5a), peaks P_3 and P_4 are characteristic of the final PMMA. Upon polymerization of the second MMA dose, the active species have been partly shifted from peak P_1 ($\bar{M}_n = 20\,300$, $\bar{M}_w/\bar{M}_n = 1.1$) to peak P_3 ($\bar{M}_n = 93\,400$, $\bar{M}_w/\bar{M}_n = 1.1$, $f = 0.30$). The species P_2^- have also partly initiated the MMA polymerization, which indicates that they are also stabilized to some extent by the lithium silanolate in toluene at 0 °C similarly to the P_1^- species.

Effect of Polarity and Temperature of the Reaction Medium. If the ligation of the active anionic species by $sBuD_1Li$ is efficient in preventing termination reactions from occurring, strongly coordinating solvents such as THF and DMSO, should have a deleterious effect on the polymerization control. Table 3 confirms that the addition of even a limited amount of THF or DMSO to toluene has a dramatic effect on the polymerization yield, the initiator efficiency, and the PMMA isotacticity, which decrease rapidly, whereas the MWD is increased. This general observation is consistent with faster and/or more extended self-termination reactions.

An increase in the polymerization temperature up to 20 °C (Table 4) results in a monomer conversion limited at 85% and in a broader MWD. This effect is again in line with a less efficient ligation of the initiating and propagating species by $sBuD_1Li$ and then with a further loss of control on polymerization.

In contrast, when the MMA polymerization is initiated by {sBuLi, ($y - 1$)$sBuD_1Li$} in toluene at −78 °C, PMMA of a very narrow molecular distribution ($\bar{M}_w/\bar{M}_n = 1.1$) is formed with a slightly higher initiation efficiency ($f = 75\%$). A monomer resumption experiment conducted at −78 °C also confirms a better stabilization of the MMA growth centers, since they remain active for at least 90 min.

Discussion

The experimental results reported in this study show that mixed associated species of the form {xBuLi, ($y - x$)BuD_1Li} are able to prevent efficiently the nucleophilic attack of the carbonyl groups of MMA and PMMA from occurring even at 0 °C, which is a relatively high temperature for this type of polymerization. The structure of BuLi has a decisive effect, since, in contrast to {xnBuLi, ($y - x$)$nBuD_1Li$}, the PMMA polymerization initiated by the bulkier initiators {xsBuLi, ($y - x$)$sBuD_1Li$} and {xtBuLi, ($y - x$)$tBuD_1Li$} leads to isotactic polymers in a quantitative yield. The extremely low monomer conversion by {xnBuLi, ($y - x$)$nBuD_1Li$} suggests that nBuLi is very rapidly deactivated by reaction with the carbonyl group of MMA and that this reaction can be limited when a sterically hindered initiator (i.e., sBuLi or tBuLi) is used.

The polymerization initiated by sBuLi produces a highly isotactic, high molecular weight PMMA of a

Table 3. Effect of Polar Cosolvents on the MMA Polymerization Initiated by the SBuLi/D$_3$ System in Toluene at 0 °C[a]

$[sBuLi]_0$ (mmol)	$[RLi]_0/[D_3]_0$	T (°C)	cosolvent (%)	ρ (%)	$\bar{M}_n$ (SEC)	$\bar{M}_w/\bar{M}_n$	% microstructure iso	het	syn
3.56	2.9	0		100	37 200	1.1	93	5	2
3.56	2.8	0	THF (10)	23	29 300	3.1	71	17	12
3.56	3.13	0	DMSO (6)	32	18 400	2.1	7	38	55
3.29	2.8	−20	DMSO (1)	46	52 500	1.4	30	35	34

[a] [MMA] = 0.50 mol·L^{-1}; polymerization time = 1 h; ρ = polymer yield.

Table 4. Effect of Temperature (*T*) on the MMA Polymerization Initiated by the BuLi/D_3 System in Toluene[a]

RLi, $[Li]_0$ (mmol)	r	T (°C)	ρ (%)	$\bar{M}_{n1}$ (%P_1)	$\bar{M}_w/\bar{M}_n$ (P_1)	% microstructure iso	het	synd
sBuLi, 3.42	3.13	0	100	21 700[b] (88)	1.1	85	10	5
sBuLi, 3.42	3.13	20	84	13 800	*b*	90	7	3
sBuLi, 3.29	2.77	−78	100	33 100	1.1	90	6	4
sBuLi, 3.56	2.89	0	100	37 100	1.1	93	5	2
sBuLi, 3.56	2.89	20	86	36 000	1.2[c]	85	11	4
tBuLi, 4.80	3.20	20	100	12 200	2.5	83	83	10
tBuLi, 4.20	2.70	20	91	13 200	3.3	66	12	22

[a] $[MMA] = 0.50$ mol·L^{-1}, except for the third experiment where $[MMA] = 0.30$ mol·L^{-1}; polymerization time = 1 h; ρ = polymer yield. [b] The SEC trace shows a bimodal MWD ($P_1 + P_2 = 100\%$) [c] The SEC trace shows a shoulder on the high molecular weight side.

narrow MWD, and it allows a better polymerization control than tBuLi. The ^7Li NMR spectra of mixtures of trimethylsilylmethyllithium with sBuLi and tBuLi, respectively, in toluene have shown that the exchange reaction with tBuLi (containing) species was slower, and that the mixing was less random compared to sBuLi.[26,27] This suggests, in the case of tBuLi, an asymmetric distribution biased toward undissociated tBuLi species, i.e., {xtBuLi, $(y - x)$tBuD_1Li} with $x > 1$. When sBuLi is concerned, one single type of {sBuLi, $(y - 1)$sBuD_1Li} species is observed ($x = 1$) in the presence of a large excess of sBuD_1Li, i.e., for [sBuD_1Li]/[sBuLi] > 21. The very narrow MWD observed for PMMA synthesized in toluene at 0 °C indeed confirms that the mixed complexation of sBuLi by sBuD_1Li does shift the aggregation equilibrium toward the formation of a unique mixed aggregate, which is the actual initiator. Roughly 70% of the {xsBuLi, $(y - x)$sBuD_1Li} species are available for initiation. For sake of comparison, it is worth recalling that the basicity of sBuLi is so strong that, under the same experimental conditions except for the ligand, no polymerization is observed as result of deactivation of the initiator.[3] The reactivity of sBuLi is thus dramatically decreased by ligation with the parent silanolate which is known to stabilize its anion at the α-position because of an electron-withdrawing effect.[28] In contrast to {sBuLi, $(y - 1)$sBuD_1Li}, the {xsBuLi, $(y - x)$sBuD_1Li} ($x > 1$) species have a very poor initiation efficiency, indicating that the efficiency of the steric barrier around the metal-containing ion pair is rapidly lost when the number of ligands in the active mixed aggregates is decreased, in agreement with previous results for other ligands.[2] In the same vein, the addition of THF and DMSO, which are competing agents for the ligand, results in a limited monomer conversion and poor initiation efficiency. It is worth noting here that in case of the D_3 polymerization in THF, the species responsible for the controlled polymerization are proposed to be unaggregated ion pairs in equilibrium with tetrameric agregates.[21,22] This observation gives some consistency to the existence of this type of equilibrium in case of species ligated by lithium silanolates in a medium of some polarity due to the methacrylate compound. Such an equilibrium could account, at least partly, for the slow self-termination reactions of the (P_1^-) and (P_2^-) partially living chains when the polymerization is complete.

PMMA chains formed in toluene at 20 °C with tBuOLi as an additive are rich in isotactic triads (iso = 81%, het = 13%, and syn = 6%).[29] In sharp contrast to neat tBuOLi, ligation by sBuD_1Li strongly influences the stereoselectivity of the propagation reaction, since less than 10% heterotactic and syndiotactic triads are left, in favor of isotactic ones. On the basis of experimental observations, Wang et al.[2,30,31] have recently concluded that the aggregation of the living PMMA chains in complexed active species would have an important role in the stereochemistry of the MMA anionic polymerization. According to that mechanism, ligand-complexed nonassociated active species (mL, X_1^-) and ligand-complexed associated active species (mL, X_2^-) might selectively produce the racemic and meso placements, respectively. The fact that the associated species {sBu$(CH_2C(CH_3)COOCH_3)_n$Li, $(y - 1)$sBuD_1Li} selectively produce the meso placements clearly show that Wang's model is not appropriate for the present system. Most probably the presence of sBuD_1Li at the propagating center imposes stereochemical restrictions on the chain end-anion, the approach of the monomer, or both.

Conclusion

This study has shown that mixed associated species of the form {xBuLi, $(y - x)$BuD_1Li} can be used as initiators for the anionic polymerization of MMA in toluene at 0 °C. The results are at variance depending on the structure of BuLi. Polymerization initiated by {xsBuLi, $(y - x)$sBuD_1Li} leads to PMMA of a very high isotacticity, (i.e. 90%) with an usually bimodal MWD. A monomodal MWD can however be observed provided that the [sBuD_1Li]/[sBuLi] ratio is high enough ($R > 21$) and the polymerization medium is deactivated as soon as the reactions complete.

The very low polydispersity ($\bar{M}_w/\bar{M}_n = 1.1$) and the quantitative yield indicate that all the polymer chains are living at least during the polymerization time and that there exists only one type of propagating species. Roughly 70% {sBuLi, $(y - 1)$sBuD_1Li} species are available for initiation of high molecular weight chains (above 100 000). The mean lifetime of the propagating sites is long enough for block copolymers to be prepared successfully. Moreover, the silanolate stabilizers can be associated with living polyanions other than (meth)-acrylates (e.g. polystyryl, polydienyl, ...) so that the range of block copolymers made available may be increased. A detailed NMR analysis of this system has been undertaken and will be published in a forthcoming paper.

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