

# New Ligands for the Living High-Molecular-Weight Anionic (Co)Polymerization of Acrylates in Toluene at 0 °C.<sup>1,2</sup> 3. Ligation of *sec*-Butyllithium by Lithium Silanolates

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**ABSTRACT:** *sec*-Butyllithium combined with a new family of ligands, (i.e., lithium silanolates), has been used to initiate the ligated anionic polymerization of *n*-butyl acrylate (BuA) in toluene at low temperature. Compared to other  $\mu$ -ligands, *s*BuMe<sub>2</sub>SiOLi is a more efficient stabilizer of the active centers. Thus, under selectively chosen reaction conditions, the polymerization proceeds quantitatively at –40 °C, producing a high-molecular-weight polymer with narrow-molecular-weight distribution ( $\overline{M}_w/\overline{M}_n < 1.2$ ). When the copolymerization of BuA is initiated by a living {PMMALi, 5·*s*BuDLi} in toluene at –78 °C, the experimental data agree with a well-controlled block copolymerization reaction, since the final molecular-weight distribution is very narrow ( $\overline{M}_w/\overline{M}_n \leq 1.1$ ) and the polymerization efficiency very high.

## Introduction

Living polymerization, a concept first proposed by Szwarc<sup>3</sup> in 1956, is one of the best ways for controlling molecular weight and its distribution as well as the structure of the end groups. Extended to (meth)acrylates, this strategy has the potential of making a wide scale of products with diversified properties available and paving the way for new technological applications. However, this method suffers severe limitations when applied to those monomers under usual solvent and temperature conditions. The problems arise from the possible nucleophilic attack of the active species on the carbonyl groups along the chain and the possible abstraction of the acrylates  $\alpha$ -hydrogen.

It is noteworthy that the modification of classical anionic initiators by coordinating ligands (ligated anionic polymerization; LAP)<sup>4</sup> is able to answer, simultaneously, the double challenge of producing high-molecular-weight (MW) products 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, and so forth. The really efficient ligands discovered to date may be classified into three groups: (1)  $\mu$ -coordinating ligands: alkali-metal alkoxides of Lochmann,<sup>5</sup> aluminum alkyls of Hatada,<sup>6,7</sup> Al-phenoxides of Ballard<sup>8</sup> and Wang,<sup>9</sup> LiCl<sup>10</sup>, and lithium silanolates<sup>1,2</sup>; (2)  $\sigma$ -type ligands of the crown ethers type;<sup>11</sup> (3)  $\mu/\sigma$ -type dual ligands as exemplified by polyether metal alkoxides<sup>12–14</sup> where a lithium ethoxide moiety may function as a  $\mu$ -type of the coordination site bonded to a polyether fragment ( $\sigma$ -type).

With the so-called  $\mu/\sigma$ -type ligands, the anionic polymerization of (meth)acrylates has known a major turning point, when using 1,1-diphenylmethyl-1-lithium as an initiator. Indeed, syndiotactic poly(methyl methacrylate) (PMMA) can be prepared in toluene at relatively high temperatures in a living manner,<sup>15</sup> and random copolymerization of methyl methacrylate (MMA)

and *tert*-butyl acrylate is also living in THF.<sup>12,15</sup> In addition, some acrylates, such as *n*-butyl and *n*-nonyl acrylate, have been anionically polymerized in toluene/THF mixtures at –78 °C. These polymerizations allow the molecular weight to be predetermined and provide for high polymerization yields and low polydispersity.<sup>17,18</sup> On the other hand, since the polymerization of 2-ethyl hexyl acrylate (EtHA) is perfectly living at –100 °C,<sup>19</sup> block copolymerization of EtHA and MMA can be successfully carried out, whichever the addition order of the monomer.<sup>20</sup>

With the so-called  $\mu$ -type ligands, in contrast to LiCl, the stabilizing effect of which is not high enough to ensure the quantitative and “living” polymerization of acrylates in THF,<sup>21</sup> substantial improvement in the polymerization of EtHA and *n*-butyl acrylate (BuA) has been reported by Vlcek et al.<sup>22,23</sup> Indeed, the use of lithium alkyl isobutyrate ligated with lithium *tert*-butoxide or most efficiently with lithium 3-methyl pentoxide-3<sup>24</sup> as an initiator allows the polymerization of both monomers under selectively chosen reaction conditions. The polymerizations proceed quantitatively with a small extent of self-termination in a toluene/THF mixture 9/1 (v/v),<sup>25,26</sup> even at –40 and –20 °C, and produce polymers with narrow-molecular-weight distribution (MWD) ( $\overline{M}_w/\overline{M}_n = 1.2$ ).<sup>23</sup> Unfortunately, the initiator efficiency, *F*, is still very low (i.e., *F* < 60%), and when lithium alkyl isobutyrate is used as an initiator, there are critical problems in producing well-controlled poly(hydrocarbon-*b*-(meth)acrylate) copolymers.

Recently, we found a new type of  $\mu$ -ligand (i.e., lithium silanolates) and reported that mixed associated species of the form {*s*BuLi, 5·*s*BuMe<sub>2</sub>SiOLi} could be successfully used as initiators for the anionic polymerization of MMA in toluene at 0 °C.<sup>26,27</sup> This system produces a very highly isotactic PMMA with narrow MWD (i.e.,  $\overline{M}_w/\overline{M}_n < 1.2$ ), and the stabilizing effect of this new *s*BuMe<sub>2</sub>SiOLi  $\mu$ -ligand is such that roughly 70% of the *s*BuLi is available for initiation. This progress offers interesting prospects for the controlled polymerization

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**Table 1. Characteristic Data<sup>a</sup> for the Polymerization of BuA Initiated by the *s*BuLi/D<sub>3</sub> System in Toluene; Effect of the Polymerization Temperature (*T*) and the Molar Ratio *R* = [*s*BuDLi]/[*s*BuLi]**

code	( <i>s</i> BuLi) <sub>0</sub> (mmol)	<i>r</i>	<i>R</i> <sup>b</sup>	<i>T</i> (°C)	<i>t</i> (min)	$\overline{M}_{n,theor}$	$\rho$ (%)	$\overline{M}_{n_1}$ (% <i>P</i> <sub>1</sub> ) <sup>f</sup>	$\overline{M}_w/\overline{M}_n$ ( <i>P</i> <sub>1</sub> )	<i>F</i> <sup>c</sup> (%)
1	<i>s</i> BuLi 3.29	2.8	35	0	25	12 500	48	34 000	1.4	37
2	<i>s</i> BuLi 3.29	2.8	35	−20	45	27 000	90	90 000	1.4	30
3	<i>s</i> BuLi 3.29	2.8	35	−40	20	30 000	96	44 000	1.2	68
4	<i>s</i> BuLi 3.29	2.8	35	−78	30	29 000	95	29 000	1.2 <sup>d</sup>	~100
5	<i>s</i> BuLi 2.88	3.5	5.6	−78	20		100		<i>e</i>	

<sup>a</sup> [BuA] = 0.50 mol·L<sup>−1</sup>; *r* = [*s*BuLi]<sub>0</sub>/[D<sub>3</sub>]; *t* = polymerization time;  $\rho$  = polymer yield. <sup>b</sup> The actual *s*BuDLi and *s*BuLi concentrations were measured by the double titration technique commonly used for the titration of organolithium solutions mainly contaminated by LiOH.<sup>35</sup> <sup>c</sup>  $F = \overline{M}_{n_p}/\overline{M}_{n,SEC}$  = (polymer yield (g))/(mol of *s*BuLi· $\overline{M}_{n,SEC}$ ). <sup>d</sup> The SEC trace curve shows a shoulder, indicating that the polymerization mixture contains a low-molecular-weight fraction in addition to the main peak *P*<sub>1</sub>. <sup>e</sup> The SEC trace shows a multimodal MWD (see Figure 2). <sup>f</sup> *P*<sub>1</sub> = polymer chains initiated by {*s*BuLi, 5·*s*BuDLi} (at least predominantly).

of acrylates in pure toluene. Indeed, to our best knowledge, there have been no results published on the anionic polymerization of BuA and its block copolymerization with MMA, under mild conditions in pure toluene. Compared to EtHA, BuA has a higher tendency to self-termination and, consequently, requires more efficient stabilization of active species to obtain polymers with narrow MWD.<sup>27,30</sup> This monomer is thus an ideal candidate to evaluate the efficiency of the *s*BuMe<sub>2</sub>SiOLi  $\mu$ -ligand in the control of acrylates anionic polymerization. In the present work, we intend to verify whether the lithium silanolate-modified initiators are also suitable for the controlled synthesis of poly(*n*-butyl acrylate) (PBuA) and poly(MMA-*b*-BuA) diblock copolymers.

## Experimental Section

*sec*-Butyllithium (1.37 M solution in cyclohexane, Aldrich) and hexamethylcyclotrisiloxane (D<sub>3</sub>, Aldrich) were used as received. Methyl methacrylate (MMA, Janssen) and *n*-butyl acrylate (Aldrich, BuA 50/50 (v/v) solution in toluene) were added with a 10 wt % AlEt<sub>3</sub> solution in toluene until a persistent yellowish color was observed and were distilled before polymerization. Toluene was purified by refluxing over a fresh sodium–benzophenone complex and distilled just prior to use.

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

A typical example involved introducing D<sub>3</sub> into the flask. Five milliliters of toluene and *s*BuLi was 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 *T* °C, and the desired amount of (meth)acrylate was introduced. Polymerization was performed for *t* min and then stopped by the addition of methanol.

The PBuA and the poly(MMA-*b*-BuA) copolymers were recovered by precipitation into a methanol/water mixture 50/50 (v/v) and methanol, respectively, and dried under vacuum at 70 °C for 24 h.

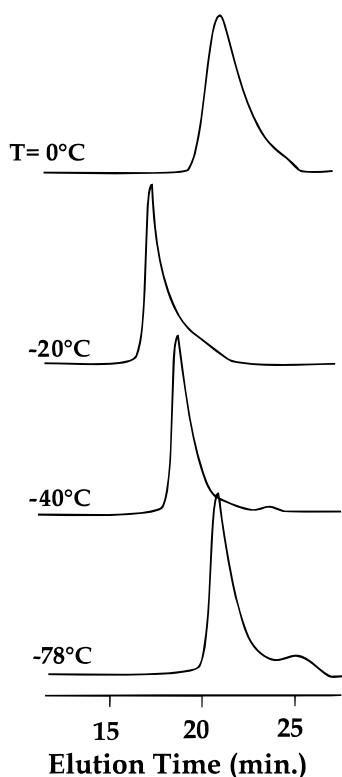
Size exclusion chromatography (SEC) was performed with a Hewlett Packard 1090 apparatus equipped with 4 PLgel columns (10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, and 10<sup>2</sup> Å) using tetrahydrofuran as the eluent and a HP 1030 A refractive index detector. The flow rate was 1.0 mL/min. The number-average molecular weight ( $\overline{M}_n$ ) and polydispersity ratio ( $\overline{M}_w/\overline{M}_n$ ) were calculated from size exclusion chromatograms on the basis of a PMMA calibration. In the case of PBuA, the Mark–Houwink–Sakurada constants valid to PMMA were used.<sup>23</sup> Polymer chain tacticity was determined by <sup>1</sup>H NMR spectroscopy using a Bruker AM-400 spectrometer.

## Results and Discussion

It is known that reaction of *s*BuLi with hexamethylcyclotrisiloxane (D<sub>3</sub>) in toluene forms *s*BuMe<sub>2</sub>SiOLi (*s*BuDLi) instead of the expected *s*BuD<sub>3</sub>Li, because of fast redistribution reactions. Excess of D<sub>3</sub> is not polymerized in the absence of activating agents.<sup>29,30</sup> Furthermore, when the [*s*BuLi]<sub>0</sub>/[D<sub>3</sub>] molar ratio (*r*) is 2.8, the in situ generated *s*BuDLi (95% yield) can form mixed associates with unreacted *s*BuLi. The <sup>7</sup>Li NMR analysis of this *s*BuLi and *s*BuDLi mixture in toluene shows that one single type of the {*s*BuLi, 5·*s*BuDLi} mixed species is formed at this high *R* = [*s*BuDLi]/[*s*BuLi] molar ratio (i.e., *R* > 21).<sup>2</sup> So, we have been interested in testing these mixed associated species {*s*BuLi, 5·*s*BuDLi} as initiators for the anionic (co)polymerization of *n*-butylacrylate (*n*BuA) and MMA in toluene.

**Effect of Temperature on the Livingness of the BuA Anionic Polymerization.** As a result of the low stability of the growing sites, the anionic polymerization of (meth)acrylates must be conducted at low temperature. As recalled in the Introduction, the most usual secondary reaction in MMA anionic polymerization (i.e., nucleophilic attack on the carbonyl groups) can be avoided by the use of {*s*BuLi, 5·*s*BuDLi} mixed species as the initiator in toluene at 0 °C.<sup>1</sup> In contrast to alkyl methacrylates, the anionic polymerization of acrylates is also perturbed by the possible abstraction of the acrylates  $\alpha$ -hydrogen. Thus, compared to MMA, the BuA polymerization should have a higher tendency to self-termination, which requires a still more efficient stabilization of the active species and a lower polymerization temperature. Indeed, Table 1 shows that, in contrast to MMA polymerization, the initiation with {*s*BuLi, 5·*s*BuDLi} promotes the BuA polymerization, although with poor monomer conversion and relatively broad MWD, if performed in toluene at 0 °C, ( $\rho$  = 48%,  $\overline{M}_w/\overline{M}_n$  = 1.4; run 1). At a temperature lower than *T* = −20 °C, the polymerization, however, proceeds almost quantitatively (runs 2–4), producing PBuA of decreasing MWDs (i.e., 1.4–1.1) and increasing *s*BuLi initiator efficiency from 30 to ~100% at −78 °C. It is worth noting that the observed initiator efficiency is higher than the one observed for MMA polymerization under the same experimental conditions (i.e., *F* = 75% at −78 °C).

The SEC curve (Figure 1) clearly shows, however, that the polymer is contaminated by a low-molecular-weight component, whose origin has to be found in the high



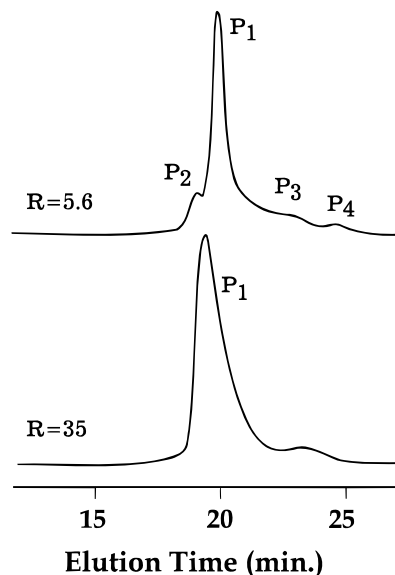
**Figure 1.** Polymerization of BuA initiated by the *s*BuLi/D<sub>3</sub> system in toluene. SEC of PBuA samples prepared at various temperatures (runs 1–4, in Table 1).

propensity of BuA to oligomerization as soon as it is purified over AlEt<sub>3</sub> and distilled.

By plotting the PBuA  $\overline{M}_n$ 's as a function of polymerization time, it appears that the polymerization is quantitative in less than 1 min at  $-78^\circ\text{C}$ .

At this point, it is worth recalling that the BuA polymerization initiated by *tert*-butyl 2-lithioisobutyrate alone, without any stabilizer, exhibits very high tendency to self-termination even at very low temperatures,<sup>31</sup> and that the initiation with a combined initiator such as *n*-butyllithium/lithium *tert*-butoxide brings the EtHA polymerization in pure toluene at  $-20^\circ\text{C}$  up to a quantitative conversion, but with a broad resulting polymer MWD<sup>32</sup> (noticed that EtHA has a lower tendency to self-termination than BuA). Thus, the very favorable effect of lithium silanolates on the BuA polymerization initiated by *s*BuLi in pure toluene allows for the preparation of PBuA of narrow MWD possibly contaminated by low-molecular-weight oligomers. Moreover, the *s*BuLi initiator efficiency is almost quantitative at  $-78^\circ\text{C}$ . This breakthrough offers interesting prospects for the synthesis of well-controlled poly(hydrocarbon-*b*-(meth)acrylate) copolymers in pure toluene.<sup>33</sup>

**Effect of the [sBuDLi]/[sBuLi] Ratio (*R*) on the Livingness of the BuA Anionic Polymerization at  $-78^\circ\text{C}$ .** As mentioned in the previous publications,<sup>1,2</sup> {*x*<sub>i</sub>·*s*BuLi, (6 - *x*)·*s*BuDLi} (*x*<sub>i</sub> ≤ 4) species coexist in equilibrium with {6·*s*BuDLi} in toluene at  $20^\circ\text{C}$ . However, when the initiator solution is prepared with a  $R = [\text{sBuDLi}]/[\text{sBuLi}]$  molar ratio higher than 21, only one type of mixed associated species (i.e., {*s*BuLi, 5·*s*BuDLi}) is observed, which leads to monomodal PMMA if the polymerization is performed at  $0^\circ\text{C}$ . Upon decreasing the  $R$  molar ratio, additional mixed species such as {2·*s*BuLi, 4·*s*BuDLi}, {3·*s*BuLi, 3·*s*BuDLi}, and {4·*s*BuLi, 2·*s*BuDLi} are formed as confirmed by <sup>7</sup>Li



**Figure 2.** Polymerization of BuA initiated by the *s*BuLi/D<sub>3</sub> system in toluene at  $-78^\circ\text{C}$ : SEC of PBuA prepared at various [sBuDLi]/[sBuLi] ratios (*R*) (runs 4 and 5, in Table 1).

NMR spectra and accordingly lead to a multimodal PMMA MWD.<sup>2</sup> It is worth recalling here that the choice of the [sBuLi]<sub>0</sub>/[D<sub>3</sub>] molar ratio (*r*) allows one to control the [sBuDLi]/[sBuLi] ratio (*R*), and thus these equilibria.

To study the dependence of the polymerization data on *R*, initiators with  $R = 35$  and  $5.6$ , respectively, were prepared and used for the polymerization of BuA in toluene at  $-78^\circ\text{C}$  (runs 4 and 5, in Table 1).

The polymerizations appear to be almost quantitative, whereas SEC analysis (Figure 2) clearly shows that a decrease in *R* (from 35 to 5.6) results in a multimodal MWD, in agreement with the coexistence of several initiating species (i.e., {*s*BuLi, 5·*s*BuDLi}, {2·*s*BuLi, 4·*s*BuDLi}, {3·*s*BuLi, 3·*s*BuDLi}, and {4·*s*BuLi, 2·*s*BuDLi}). The exact structure of the reactive centers (with 4, 3, or 2 *s*BuDLi) in the polymerization experiments cannot be stated unequivocally because temperature and concentration used in these experiments are not the same as those for the <sup>7</sup>Li NMR analysis. Nevertheless, it is reasonable to suppose that a decrease in the number of *s*BuDLi associated with the growing site is responsible for propagating species of an increased reactivity, thus increasingly prone to self-termination reactions. Moreover, it is suggested that {2·*s*BuLi, 4·*s*BuDLi} would be the dominant species at  $R = 5.6$  (see <sup>7</sup>Li NMR analysis<sup>2</sup>) so giving rise to the high-molecular-weight chains *P*<sub>1</sub>. By analogy with the MMA polymerization,<sup>1</sup> the chain population *P*<sub>2</sub> would result from an intermolecular termination reaction. The *P*<sub>3</sub> and *P*<sub>4</sub> populations of a much broader MWD (particularly *P*<sub>3</sub>) and lower molecular weight would be due to contamination of BuA by oligomers and to chains initiated by both the less abundant and less reactive {*s*BuLi, 5·*s*BuDLi} species and the more reactive and thus less stable {3·*s*BuLi, 3·*s*BuDLi} and possibly {4·*s*BuLi, 2·*s*BuDLi} species.

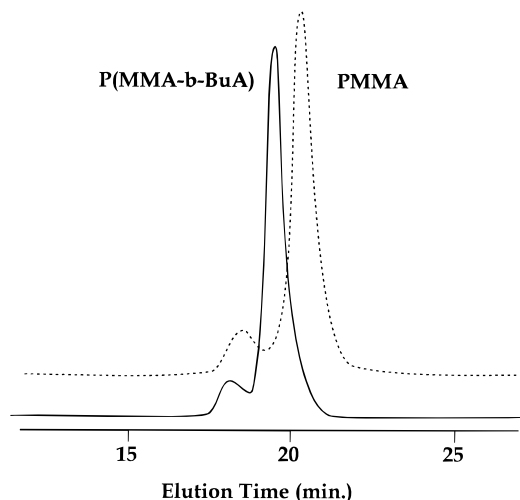
Although the PMMA MWD is monomodal (except for oligomers contaminating the monomer) when  $R = 35$ , the MWD of the *P*<sub>1</sub> population is broader than the one observed for PBuA prepared with a lower *R* ratio (Figure 2). At a high *R* ratio, only the {*s*BuLi, 5·*s*BuDLi} species would persist (see <sup>7</sup>Li NMR analysis<sup>2</sup>), but in the presence of a large excess of *s*BuDLi. Therefore,



**Table 2.** Characteristic Data<sup>a</sup> for the Copolymerization of MMA and BuA Initiated by the *s*BuLi/D<sub>3</sub> System ( $r = [sBuLi]_0/[D_3] = 2.8$ ;  $R = [sBuDLi]/[sBuLi] = 35$ ) in Toluene at  $-78\text{ }^\circ\text{C}$ 

code	( <i>s</i> BuLi) <sub>0</sub> (mmol)	(MMA) (g)	<i>t</i> <sub>1</sub> (min)	(BuA) (g)	<i>t</i> (min)	ρ (%)	$\overline{M}_n$ , MMA block	$\overline{M}_n$ , final product	$\overline{M}_w/\overline{M}_n$
6	<i>s</i> BuLi 3.29	2.5	90	1.65	60	100	33 000	59 000	1.08
7	<i>s</i> BuLi 3.29	4.2	0	1.85	60	25 <sup>b</sup>		40 800	1.16
8	<i>s</i> BuLi 3.29	2.1	0	2.0	90	50 <sup>b</sup>		29 500	1.20

<sup>a</sup> Conditions: *t*<sub>1</sub> = time interval between the two monomer additions; *t* = (MMA + BuA) polymerization time; ρ = polymer yield. <sup>b</sup> PBuA homopolymer.

**Figure 3.** Synthesis of an all-acrylic block copolymer: SEC of sample 6 in Table 2: PMMA block and poly(MMA-*b*-BuA).

the  $k_p/k_i$  ratio, where  $k_p$  and  $k_i$  are the propagation and the initiation rate constants, respectively, is expected to be different compared to the former situation ( $R = 5.6$ ), so accounting for a change in the MWD.

**Synthesis of a Fully Acrylic Block Copolymer.** When the copolymerization of BuA is initiated by living {PMMALi, 5·*s*BuDLi} chains in toluene at  $-78\text{ }^\circ\text{C}$ , the experimental data (run 6, in Table 2) indicate a living block copolymerization process: a very-narrow-molecular-weight distribution for the main peak ( $\overline{M}_w/\overline{M}_n \leq 1.1$ ), and above all the absence of any homo-PMMA in the raw copolymerization product (SEC trace, in Figure 3). In this example, two types of active species have contributed to the MMA polymerization. Indeed, when the  $[sBuLi]_0/[D_3]$  ratio is not perfectly controlled, the expected {*s*BuLi, 5·*s*BuDLi} initiator may be contaminated by the less extensively ligated, and thus more reactive, {2·*s*BuLi, 4·*s*BuDLi}. Figure 3 shows that the two populations of PMMA chains are living, since their molecular weight is increased by the addition and conversion of BuA. These results confirm the high stability of the MMA growth centers in toluene at  $-78\text{ }^\circ\text{C}$  and indicate that poly(MMA-*b*-BuA) diblock copolymers can be successfully formed.

In contrast to these results, no block copolymer is formed when the polymerization order is reversed (i.e., when MMA is initiated by living PBuA macroanions under the same experimental conditions). The present results may only be understood if the PBuA complexed anions ( $P_1^-$ ) either cannot initiate the MMA polymerization or are killed in the reaction medium during the time interval between the two monomer additions ( $\Delta t$ ). If  $P_1^-$  species are unstable, ( $\Delta t$ ) should obviously be a critical parameter for improving the experimental re-

sults. Actually, it has been observed that copolymerization of MMA and BuA mixtures under the same experimental conditions (i.e.,  $\Delta t = 0$  (runs 7 and 8)), produce a pure PBuA homopolymer. The crossover reaction between BuA and MMA does not occur, as result of reactivity ratios deeply modified by the silanolate ligation of the anionic species. So, the acrylate, which is much more reactive than MMA, is in the position of being initiated by the poorly reactive poly(MMA) anions, although the poly(BuA) anions are unable to initiate the MMA polymerization. Furthermore, when MMA is mixed with BuA, the experimental results show that the initiator efficiency *F* is decreased from  $\sim 100\%$  (run 4 in Table 1) to 50% (run 8, in Table 2). This effect of the MMA addition on *F* is the signature of a nucleophilic attack of the active species (i.e., {*s*BuLi, 5·*s*BuDLi}), on the MMA carbonyl groups, and supports the fact that the observed MMA initiator efficiency is lower than the one observed for BuA polymerization under the same experimental conditions (i.e.,  $F = 75\%$  and  $F \sim 100\%$ , respectively, at  $-78\text{ }^\circ\text{C}$ ).

## Conclusion

The above results demonstrate that mixed associated species of the form {*s*BuLi, 5·BuDLi} can be used to initiate the anionic polymerization of acrylates, such as BuA, in pure toluene at low temperatures. Indeed, the very favorable effect of lithium silanolates on the BuA polymerization provides the first example of the direct preparation of narrow MWD PBuA, using *s*BuLi as the initiator in pure toluene. Moreover, the *s*BuLi initiator efficiency is almost quantitative at  $-78\text{ }^\circ\text{C}$ . This breakthrough offers interesting prospects for the synthesis of well-controlled poly(hydrocarbon-*b*-acrylate) diblock copolymers in pure toluene.

When the copolymerization of BuA is initiated by a living {PMMALi, 5·*s*BuDLi} in toluene at  $-78\text{ }^\circ\text{C}$ , the experimental data indicate a well-controlled block copolymerization process leading to the formation of the expected poly(MMA-*b*-BuA) diblock. In contrast, no block copolymer is formed when the polymerization order is reversed (i.e., when MMA is initiated by living PBuA macroanions under the same experimental conditions). So, the reactivity ratios of the MMA/BuA pair are deeply modified by ligation of the parent anions by silanolates. The study of additional (meth)acrylate monomers is in progress in order to support this hypothesis and will be the topic of a forthcoming paper.<sup>35</sup>

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