New Ligands for the Living Isotactic Anionic Polymerization of Methyl Methacrylate in Toluene at 0 °C. 2. ^{7}Li NMR Analysis of *sec*-Butyllithium Ligated by Lithium Silanolates

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ABSTRACT: The mixed associated species {*x*sBuLi, (*y* − *x*)sBuMe$_2$SiOLi} formed by reaction of *sec*-Butyllithium (sBuLi) with octamethylcyclotetrasiloxane (Me$_2$SiO)$_4$ in toluene have been used to initiate the anionic polymerization of methyl methacrylate (MMA) in that solvent at 0 °C. The active species generated by this new type of initiator have been characterized by ^{7}Li NMR at 0 °C. The ^{7}Li NMR spectra of sBuLi and sBuMe$_2$SiOLi mixtures in toluene show that only one single type of {sBuLi, 5sBuMe$_2$SiOLi} mixed species prevails at [sBuMe$_2$SiOLi]/[sBuLi] molar ratios higher than ca. 21, as result of a large excess of {6sBuMe$_2$SiOLi} species. The ^{7}Li NMR has also concluded to the formation of {PMMALi, 5sBuMe$_2$SiOLi} species upon the addition of MMA to that initiator solution, supporting the theory that only one type of ionic species is active during the MMA conversion. These active centers are stable for at least 1 h at 0 °C as confirmed by ^{7}Li NMR.

Introduction

The anionic polymerization of (meth)acrylates suffers severe limitations when conducted under the usual conditions of solvent and temperature. These problems arise from the possible nucleophilic attack of the active species on the carbonyl groups along the chain and the acidity of the α-hydrogen in acrylates. Recently, we have reported on a way for getting rid of these side reactions, which is based on the use of mixed associated species of the form {*x*sBuLi, (*y* − *x*)sBuMe$_2$SiOLi} as efficient initiators for the anionic polymerization of methyl methacrylate (MMA) in toluene at 0 °C.[1−2] Highly isotactic poly(methyl methacrylate) (PMMA) is accordingly formed with a bimodal molecular weight distribution (MWD) which tends however to become monomodal at a high enough ligand/initiator molar ratio ($R > 21$) ($R =$ [sBuMe$_2$SiOLi]/[sBuLi]). This observation agrees with a set of equilibria between the {*x*sBuLi, (*y* − *x*)sBuMe$_2$SiOLi} species and the formation of one single type of active species complexed by sBuMe$_2$SiOLi at $R > 21$. These observations have prompted us to analyze in more detail the structure and the initiation mechanism of this new type of ligated anionic initiator.

Nuclear magnetic resonance (NMR) spectroscopy is known as one of the most useful tools for the characterization of the active species in anionic polymerization.[4] The direct investigation of the active species involved in the anionic polymerization of alkyl (meth)-acrylates has only occasionally been considered, because of the instability of the living chains in solution and the complexity of the NMR spectra of the active species associated with polymer chains.[1] To overcome these difficulties, Wang et al.[5−8] and Kriz et al. [9−11] have analyzed model systems by ^{13}C and ^{7}Li NMR spectroscopy. Although the use of models is very convenient, this strategy offers only a partial view of the actual situation. Recently, the propagating poly(*tert*-butyl methacrylate) species have been studied by ^{6}Li, ^{7}Li, and ^{13}C NMR spectroscopy and the use of ^{13}C enriched monomer.[12] At our best knowledge, living poly(methyl methacrylate) oligomers have never been studied at temperature as high as 0 °C. When ligated by lithium silanolates, living poly(methyl methacrylate) oligomers are stable in solution for the time required by the ^{7}Li NMR analysis (less than 1 h).

This paper aims at reporting on the ^{7}Li NMR characterization of mixed complexes formed by sBuLi and PMMALi oligomers with sBuMe$_2$SiOLi.

Experimental Section

sec-Butyllithium (sBuLi) (1.37 M solution in cyclohexane, Aldrich) was used as received and the concentration (1.37 M) was determined by Gilman's double titration method (purity better than 95%).[24] (Me$_2$SiO)$_4$ was used as received from Aldrich, with a high purity (99.9%) checked by GC.

MMA (Janssen) had a 10 wt % AlEt$_3$ solution in hexane added to it until a persistent yellowish color was observed and was distilled before polymerization. Toluene was purified by refluxing over fresh sodium−benzophenone complex and distilled just prior to use.

The method for preparing a moisture- and air-free organolithium solution in sealed 10-mm tubes was previously described.[5]

The initiator was prepared in a previously flamed glass reactor under inert atmosphere. The monomer and solvent were transferred by the syringe and capillary technique. In a typical example, 20 mL of toluene, 0.1 mL of (Me$_2$SiO)$_4$ (0.32 mmol), and 1 mL of sBuLi (1.37M, 1.37 mmol) ([sBuLi]/[(Me$_2$SiO)$_4$] $= r = 4.3$) were added to the reactor, and 2 mL of that solution mixed with 0.5 mL of C$_6$D$_6$ was directly injected into the NMR tube and degassed by repeated freeze−thaw cycles before the tube was sealed under vacuum. By the double titration technique of organolithium compounds (here sBuLi), the [sBuMe$_2$SiOLi]/[sBuLi] molar ratio *R* was found to be 14 when the reaction of sBuLi with (Me$_2$SiO)$_4$ was complete. After 20 h at 20 °C, the remaining initiator solution was cooled to 0 °C and 0.09 g of MMA was added. Then 2 mL of that solution plus 0.5 mL of C$_6$D$_6$ was injected into an NMR tube as described above.

The ^{7}Li NMR spectra were recorded with a Bruker AM 400 superconducting magnet system operating in the FT mode at

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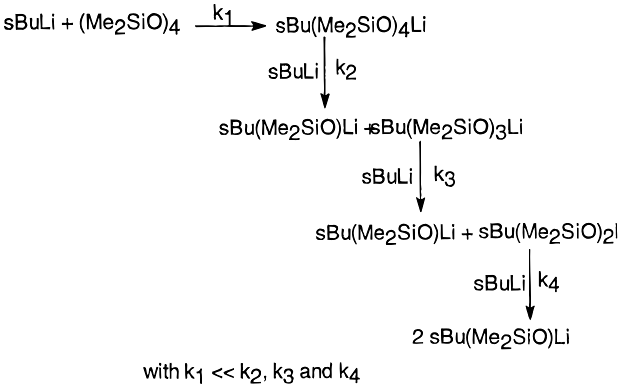
Scheme 1. Reaction of sBuLi with $(Me_2SiO)_4$[a]



[a] r is defined as the initial sBuLi/$(Me_2SiO)_4$ molar ratio, whereas R refers to the actual ligands sBuLi, i.e., $sBuMe_2SiOLi$/sBuLi molar ratio in the reaction medium.

155.5 MHz, with a deuterium lock. They were referenced to a 0.2M LiCl solution in THF-d_8.

Results and Discussion

$sBuMe_2SiOLi$ species are formed by reaction of *sec*-Butyllithium (sBuLi) with octamethylcyclotetrasiloxane ($(Me_2SiO)_4$) in toluene at 20 °C. That reaction is well established and forms almost quantitatively $sBuMe_2SiOLi$ instead of the expected $sBu(Me_2SiO)_4Li$ because of fast redistribution reactions as schematized in Scheme 1.[13,14] No polymerization of excess $(Me_2SiO)_4$ occurs until a donor solvent, such as THF and DMSO, is added.

It is worth recalling that organolithium compounds are usually observed as polyhedral aggregates, i.e., μ-complexes held together by multicenter bonds involving bridging organic groups,[15] and that cross-associated species are formed in mixtures of two different organolithium compounds.[16] It is therefore reasonable to expect that mixtures of sBuLi and $sBuMe_2SiOLi$ also contain mixed associated species of the form $\{x$sBuLi, $(y - x)sBuMe_2SiOLi\}$.[17] The actual ligand/initiator molar ratio, i.e., $R = [sBuMe_2OSiOLi]/[sBuLi]$, depends not only on the initial amounts of sBuLi and $(Me_2SiO)_4$ but also on the yield of their mutual reaction. Since the chemical shift of ^7Li NMR is sensitive to the chemical environment, this technique has been used by Brown et al. to analyze the stoichiometry of mixed complexes, such as $\{x$tBuLi, $(4 - x)Me_3SiCH_2Li\}$.[18-20] It must therefore be possible to study the composition of the mixed associated species $\{x$sBuLi, $(y - x)sBuMe_2SiOLi\}$ by analyzing the dependence of the line shape on the total concentration and the ligand/initiator molar ratio (i.e., $R = [sBuMe_2SiOLi]/[sBuLi]$). For this purpose, the progress of the reaction of sBuLi with $(Me_2SiO)_4$ in toluene at 20 °C has been traced by ^7Li NMR. The time dependence of this ^7Li NMR spectrum is shown in Figure 1 for the case of an original [sBuLi]/$[(Me_2SiO)_4]$ ratio (r) of 4.3. The NMR spectrum changes with time in agreement with the formation of the different species as shown by the reaction Scheme 1. When the reaction equilibrium is reached, the ^7Li NMR spectrum does not change anymore.

Thus, when sBuLi and $(Me_2SiO)_4$ are mixed in toluene in a molar ratio $r = 4.3$, the initial ^7Li spectrum shows one resonance at −2.47 ppm (A). Since sBuLi is known to form predominantly tetrameric aggregates in toluene,[21] resonance A must be assigned to the {4sBuLi} species. As the reaction between sBuLi and $(Me_2SiO)_4$ is going on, the R molar ratio increases until the equilibrium value of 14 is reached after 6.5 h. In the reaction course, five lithium resonances are observed at −2.67 (B), −2.83 (C), −2.98 (D), −3.09 (E), and −3.18 ppm (F). The resonance intensity of peaks A and B decreases with time, thus as the ratio R increases, and these species finally disappear. The intensity of the species C, D and E increases first, passes through a maximum and then decreases. Finally, peak F is becoming more intense until the reaction is complete. Figure 1 also shows that only a single resonance F is observed when the final R value exceeds 21 ($r < 3.4$), which corresponds mainly to a rich in $sBuMe_2SiOLi$ solution.

Although no data are available on the association of $sBuMe_2SiOLi$ in toluene at 20 °C, the strong tendency of lithium silanolates to form tetramers has been emphasized by a kinetics study of the anionic polymerization of hexamethyltricyclosiloxane conducted in THF over a concentration range of $10^{-2}-10^{-1}$ M.[22,23] Moreover, the degree of association may only increase when toluene is substitued for THF. As an example, the degree of association of tBuOLi is known to be 4 in THF[6] and 6 in toluene.[20] It is thus reasonable to assume that $sBuMe_2SiOLi$ forms hexameric species in toluene and that peak F corresponds to an hexameric $\{6sBuMe_2SiOLi\}$ species. Then, all the various possible mixed complexes (i.e., $\{x$sBuLi, $(6 - x)sBuMe_2SiOLi\}$ with $1 \leq x \leq 4$) must also exist in solution, however at concentrations that depend on the R molar ratio. Consistently, the ^7Li NMR spectrum shows that the relative amounts of the species observed (i.e., B, C, D, and E) actually change with R and that an equilibrium occurs between these four species that exchange slowly on the NMR time scale at 20 °C. This observation agrees not only with a slow intermolecular exchange among all the species but also with a rapid intramolecular exchange within each associated species, so that all the lithium atoms within each of them appear to be equivalent.[18] The fact that the spacing between peaks B, C, D, and E is quite comparable is indicative of associations of the same type, i.e., of the $\{x$sBuLi, $(y - x)sBuMe_2SiOLi\}$ type. Accordingly, the distinct ^7Li resonances B, C, D, E, and F are proposed to correspond to the $\{4sBuLi, 2sBuMe_2SiOLi\}$, $\{3sBuLi, 3sBuMe_2SiOLi\}$, $\{2sBuLi, 4sBuMe_2SiOLi\}$, $\{sBuLi, 5sBuMe_2SiOLi\}$ and $\{6sBuMe_2SiOLi\}$ species, respectively.

It can be seen that $\{sBuLi, 5sBuMe_2SiOLi\}$ and $\{6sBuMe_2SiOLi\}$ are the dominant species at $R = 21$. Then, the initiator solution contains only one type of mixed associated species, in which only one sBuLi molecule is involved. This conclusion is quite consistent with the monomodal and very narrow MWD of PMMA prepared with a R molar ratio higher than 21, in contrast to the bimodal MWD otherwise observed.[1] The bimodality of PMMA when R is smaller than 21 indicates that at least two propagating species (P_1^-) and (P_2^-) coexist.[1] The initiating species $\{sBuLi, 5sBuMe_2SiOLi\}$ leads to the lower molecular weight population P_1, whereas the $\{4sBuLi, 2sBuMe_2SiOLi\}$, $\{3sBuLi, 3sBuMe_2SiOLi\}$ and $\{2sBuLi, 4sBuMe_2SiOLi\}$ species produce the population of higher molecular weight chains P_2.

The reactivity of the anionic species (i.e., sBuLi and PMMALi) must be decreased by complexation with an increasing number of $sBuMe_2SiOLi$ ligand. Actually the very poor initiation efficiency (f) observed for the P_2^- species, (i.e., $f < 5\%$, compared to ca. 70% for {sBuLi,

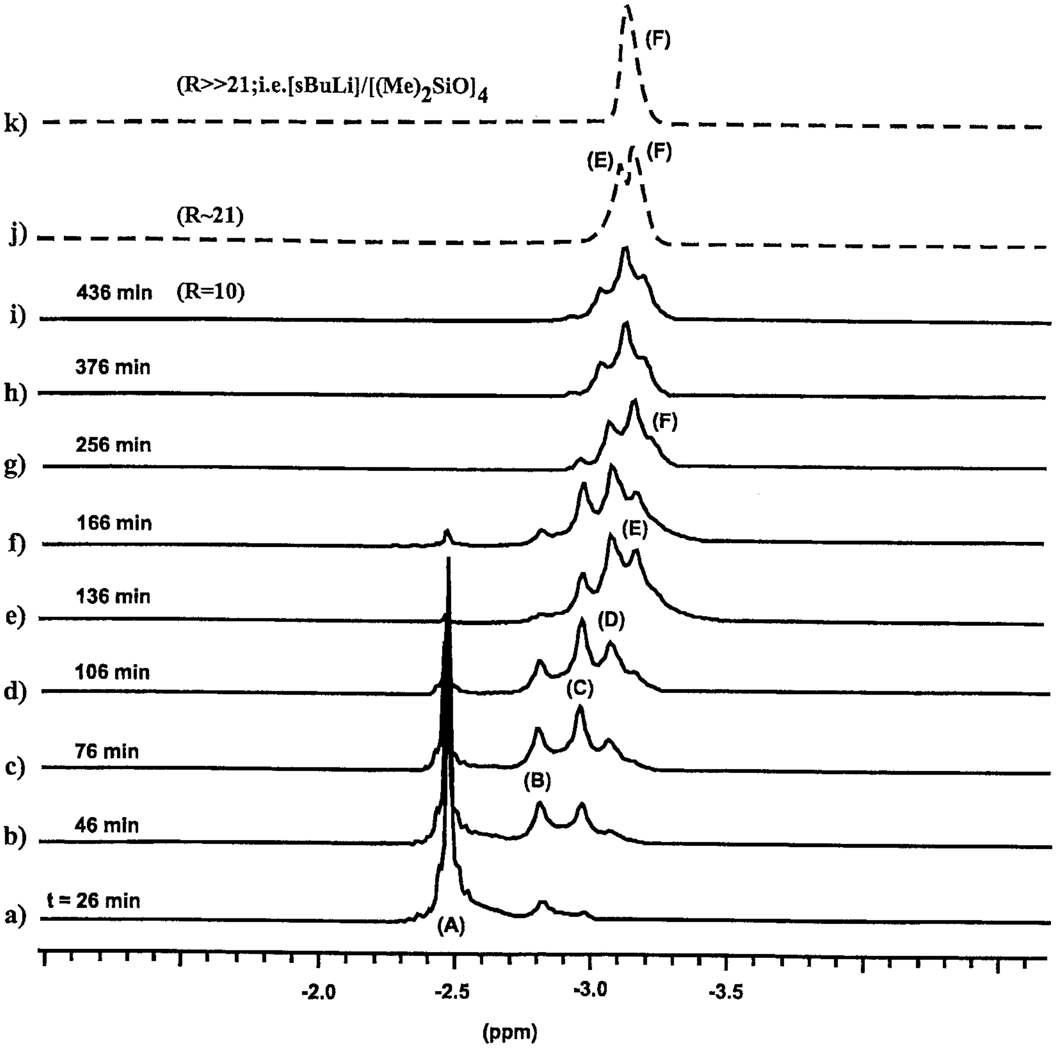


Figure 1. ^{7}Li spectrum of the reaction of sBuLi with $(Me_2SiO)_4$ in toluene at 20 °C. Time dependence: (a–i) $r = [sBuLi]/[(Me_2SiO)_4] = 4.3$; (j) $r = 3.4$; (k) $r < 3.4$ Key: A = {4sBuLi}; B = {4sBuLi, 2.sBuMe$_2$SiOLi}; C = {3sBuLi, 3sBuMe$_2$SiOLi}; D = {2sBuLi, 4sBuMe$_2$SiOLi}; E = {sBuLi, 5sBuMe$_2$SiOLi}; F = {6sBuMe$_2$SiOLi}; R = [sBuMe$_2$SiOLi]/[sBuLi].

5sBuMe$_2$SiOLi}) and the very large difference in $\bar{M}_n$'s for the P$_1$ and P$_2$ chains clearly support that hypothesis. Furthermore, when the MMA polymerization is carried out in the presence of tetrahydrofuran (THF), the polymer yield and the initiation efficiency are very poor.[1] It is worth noting here that the addition of THF to hexameric alkyllithium compounds in toluene leads to solvated tetramers even at low THF/Li molar ratios.[19] This observation has to be compared to the tetrameric aggregation of lithium silanolates in THF.[22,23] It seems thus clear from the accumulated evidences that the selective association of five sBuMe$_2$SiOLi molecules to the growth centers (P$_1$ species) is necessary to perfectly control the anionic MMA polymerization in toluene at 0 °C. The final PMMA is highly isotactic, i.e., in the range from 85% ($R = 3.13$) to 95% ($R = 2.90$).

Figure 2 shows that upon addition of MMA to an initiator solution containing {2sBuLi, 4sBuMe$_2$SiOLi}, {sBuLi, 5sBuMe$_2$SiOLi}, and {6sBuMe$_2$SiOLi} species, at 0 °C (trace a), the ^{7}Li resonances E and D, at −3.09 and −2.98 ppm, respectively, are converted into a resonance G at −3.29 ppm (trace b) which disappears after 1 week at 20 °C (trace c), whereas F remains unchanged. It is accordingly clear that the mixed associated species {sBuLi, 5sBuMe$_2$SiOLi} and {2sBuLi, 4sBuMe$_2$SiOLi} are the polymerization initiators, and that the associated species {6sBuMe$_2$SiOLi} is inert toward MMA. Since the {2sBuLi, 4sBuMe$_2$SiOLi} species have a very poor initiation efficiency at 0 °C ($f < 5\%$), the observation of ^{7}Li resonances characteristic of the mixed {2PMMALi, 4sBuMe$_2$SiOLi} species is quite a problem because of a low intensity. Similarly, byproducts such as CH$_3$OLi, resulting, e.g., from the backbiting reaction cannot be identified either. It is however reasonable to propose the formation of {CH$_3$OLi, 5sBuMe$_2$SiOLi}, {2CH$_3$OLi, 4sBuMe$_2$SiOLi}, and {3CH$_3$OLi, 3sBuMe$_2$SiOLi} species, whose resonances would be hidden by peak F. Therefore, resonance G has been assigned to the {PMMALi, 5sBuMe$_2$SiOLi} (i.e. P_1^-) species. The ^{13}C NMR analysis of oligomers has confirmed formation of a keto ester byproduct.

Conclusion

The mixed complexation of sBuLi and PMMALi by sBuMe$_2$SiOLi in toluene has been studied for the first time by ^{7}Li NMR spectroscopy. It has been shown that sBuMe$_2$SiOLi is a very efficient ligand of sBuLi, which is incrementally replaced in the original tetramers with formation of hexameric complexes, {xsBuLi, $(6 - x)$sBuMe$_2$SiOLi} ($x = 1-4$). This striking feature may nicely explain the change in MWD when PMMA is prepared from initiator solutions where the R molar

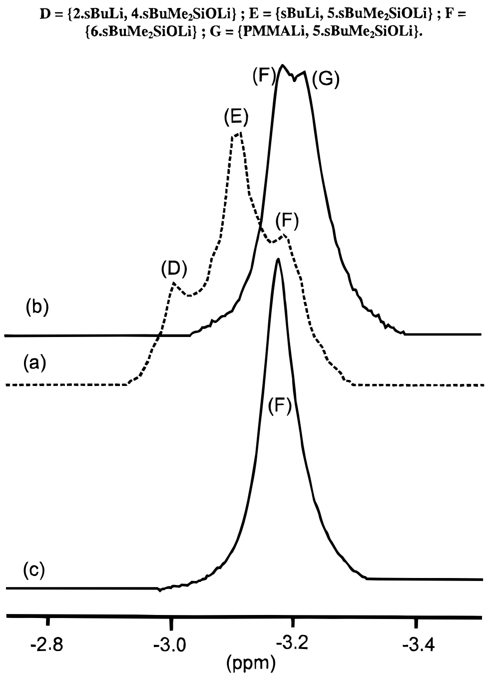


Figure 2. ^{7}Li NMR spectrum of a mixture of {*x*sBuLi, (6 − *x*)sBuMe$_2$SiOLi} where $x = 1$ and 2 (R = 14) and MMA: (a) before MMA addition; (b) after addition of MMA to the reaction medium at 0 °C (c) after addition of MMA after 1 week at 20 °C.

ratio is increased up to 21. A bimodal SEC chromatogram is consistent with two populations of differently complexed propagating species as is the case for the initiating ones. In contrast, only one single type of ligated sBuLi species is observed when *R* is higher than 21. It is also well established by ^{7}Li NMR that the aggregation equilibrium between sBuMe$_2$SiOLi and sBuLi in toluene foreshadows the structure of the propagating species attached to living PMMA chains. The NMR analysis has considerably improved the understanding of the ligation of anionic species by sBuMe$_2$SiOLi and its effect on the MMA polymerization in toluene at 0 °C.

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