# Climbing Back up the Nucleophilic Reactivity Scale. Use of Cyclosila Derivatives as Reactivity Boosters in Anionic Polymerization

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ABSTRACT: It has been well-known for a very long time that, for anionic homo-polymerization or sequential copolymerization to occur, it is mandatory that the relative nucleophilic reactivity of the initiating species be equal to or larger than the one of the (co)monomer. However, the results described in this paper demonstrate that such a classic rule can be circumvented in some cases. Indeed, it is reported for the first time that potassium trimethylsilanolate, and "living" potassium poly(ethylene oxide), both of which are unable to initiate styrene or methyl methacrylate (MMA) polymerization, can be converted from oxyanionic active ends to silyl anionic ones by reacting with cyclic disila derivatives, so allowing the homopolymerization and sequential (co)polymerization of styrene or MMA to proceed in a controlled manner.

## Introduction

Since Szwarc's and Morton's remarkable achievements in the 1950s, living anionic polymerization has been very successful from the standpoints of both basic science and commercial application,[1,2,3] particularly for the synthesis of well-defined block copolymers by sequential monomer addition.[4,5]

However, it is also known that, the order of that sequential monomer addition is extremely crucial. According to a classic rule,[6,7] for block copolymerization to occur, it is mandatory that the p$K_a$ value of the conjugate acid corresponding to the living chain end be equal to or larger than that of the second monomer. That experimental situation translates into a nucleophilic reactivity scale, dependent on p$K_a$, monomer reactivity, and growing ends associations, leading to a cascade of decreasing reactivity which cannot be reversed, in the following order: dienes ≥ styrenes > vinylpyridines > (meth)acrylates > oxiranes > siloxanes. As a typical example,[8] the polymeric oxanion formed from ethylene oxide cannot indeed initiate at all styrene polymerization. Accordingly there are very few examples showing a sequential anionic polymerization occurring, irrespective of the monomer addition order.

On the other hand it is well-known that the silicon−silicon bond is much less stable than the carbon−carbon bond (i.e. ≡Si−Si≡ 188 J·mol$^{-1}$; C−C 334 J·mol$^{-1}$).[9] Thus organosilyl anion can be obtained by ≡Si−Si≡ bond cleavage under proper basic conditions.[10] For example, in a seminal paper, Sakurai et al. has demonstrated that addition of sodium methoxide to a hexamethyldisilane/hexamethylphosphoramide (HMPA) solution at ambient temperature leads to a facile and clean cleavage of the silicon−silicon bond with quantitative formation of (trimethylsilyl)sodium and trimethylmethoxysilane ($CH_3ONa + (CH_3)_3SiSi(CH_3)_3 \rightarrow (CH_3)_3SiNa + CH_3OSi(CH_3)_3$).[11] The driving force of such a reaction is apparently the high sensitivity of the ≡Si−Si≡ bond toward nucleophilic attack and the formation of a stable trimethylmethoxysilane. The other nucleophile/solvent systems most often used to date in disilane cleavage have been: tBuOK/HMPA,[12] MeLi/HMPA,[13] KH/DME-HMPA,[14] MeOK/THF or benzene/crown ether,[15] NaH/THF/ 18-crown-6,[14] and tBuOK/THF or DME.[16]

Recently, we have revisited this ≡Si−Si≡ bond chemistry and realized that such an apparently simple reaction indeed illustrates a unique way to completely modify the nature and, still more importantly, the reactivity of metal-containing species, i.e., going from less reactive oxanions to much more reactive silyl anions, a process of "reactivity-boosting".

In particular, we were much intrigued by the possible extension of that "reactivity-boosting process" to sequential anionic polymerization. It is logical to theorize that should a ≡Si−Si≡ bond containing cyclic compound be used instead of hexamethyl disilane to properly react with living chain ends (i.e., $P_nO^-M^+$), a silyl anionic type of active end would in principle result (i.e., $P_nOSi-Si^-M^+$), possibly without forming a dead prepolymer. Since the reactivity of a silyl anion is quite comparable to the one of a corresponding carbanion,[17] a variety of monomers $M_2$ may react toward that silyl anion living end; a controlled sequential anionic polymerization might thus prevail (Figure 1), even though the reactivity of the $P_nO^-M^+$ species is lower than the one stemming from the second monomer $M_2$.

To our knowledge, the conversion of the silanolate group of a living polysiloxane into a silyl anion by using cyclodisilanes, which in principle, paves the way toward copolymers synthesis, was first indicated by Mazurek et al.[18] Nonetheless, these results were not published as a full paper.

The present report will give a preliminary answer to that challenge. It is indeed very encouraging to see how 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**I**) and 1-phenyl-1,2,2-trimethyl-1,2-disilacyclopentane (**II**) can be used as an efficient reactivity booster in styrene and MMA anionic homopolymerization, unusually initiated with potassium trimethylsilanolate, a model for a polysiloxane growing end. Finally, 1,1,2,2-tetramethyl-1,2-disila-

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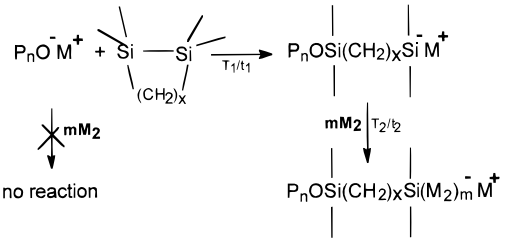


**Figure 1.** Use of cyclosila derivatives as reactivity amplifiers for the macromolecular engineering of new block copolymers: reaction scheme.

cyclopentane will also be used as an efficient reactivity promoter in a styrene sequential anionic polymerization unusually initiated with potassium poly(ethylene oxide).

## Experimental Section

Styrene (Aldrich) was dried over $CaH_2$, distilled, and stored under an inert atmosphere. Just before polymerization, it was treated with a fluorenyllithium solution and distilled. 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. Ethylene oxide (EO) was first purified with KOH and $CaH_2$ and then twice distilled over nBuLi just before use. Tetrahydrofuran (THF) was purified by refluxing over fresh sodium benzophenone, treated with a poly(styryllithium) solution, and distilled before polymerization. The HMPA was dried over $CaH_2$ and stored over molecular sieves (4 Å grade). All the experiments have been conducted under inert atmosphere in a previously flamed glass reactor. Liquid reagents have been handled with stainless capillaries and syringes.

**1,1,2,2-Tetramethyl-1,2-disilacyclopentane (I)** was prepared according to the following two-step procedure under nitrogen. 2,6-Dimethyl-2,6-dichloro-2,6-disilaheptane was synthesized[19] in 92% yield after vacuum distillation by hydrosilylation of allyldimethylchlorosilane (ABCR) with dimethylchlorosilane (ABCR) in the presence of Speier catalyst (iPrOH solution of $H_2PtCl_6$).[20] It was then converted into **I** according to Kumada et al.[21] in 88% yield; $^1$H NMR ($CDCl_3$) $\delta = 0.14$ (s, 6H), 0.68 (m, 4H), and 1.68 ppm (m, 2H). A heptane/benzene mixture was originally used as the solvent, before being replaced by cyclohexane. The reaction time was also extented from 30 h to 3 days. Due to the presence of some 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane ($^1$H NMR ($CDCl_3$) $\delta = 0.15$ (s, 6H), 0.63 (m, 4H), and 1.84 ppm (m, 2H)), the distilled material was treated with $H_2SO_4$ at low temperature, washed, neutralized, dried with $CaCl_2$, and distilled. Before polymerization, **I** was stirred under nitrogen over $CaH_2$ for 3 days and finally distilled.

**1,1,2-Trimethyl-2-phenyl-1,2-disilacyclopentane (II).** Essentially the same general procedure as for the synthesis of **I** has been applied for the synthesis of **II**. Hydrosilylation of allyldimethylchlorosilane with phenylmethylchlorosilane (ABCR) followed by vacuum distillation led to 2,6-dichloro-2-methyl-6-phenyl-2,6-disilaheptane within a 92% yield; $^1$H NMR ($CDCl_3$) $\delta = 0.43$ (s, 3H), 0.44 (s, 3H), 0.71 (s, 3H), 0.97 (m, 2H), 1.21 (m, 2H), 1.67 (m, 2H), 7.40−7.53 (m, 3H), and 7.65−7.69 ppm (m, 2H). This intermediate compound was subsequently converted into compound **II** with a 78% yield; $^1$H NMR ($CDCl_3$) $\delta = 0.26$ (s, 3H), $\delta = 0.35$ (s, 3H), $\delta = 0.54$ ppm (s, 3H), 0.81−1.22 (m, 4H), 1.84−1.94 (m, 1H), 2.0−2.1 (m, 1H), 7.45−7.47 (m, 3H), and 7.63−7.66 ppm (m, 2H). The final product was essentially free from 2,2,6,6-trimethyl-6-phenyl-1-oxa-2,6-disilacyclohexane; $^1$H NMR ($CDCl_3$) $\delta = 0.40$ (s, 3H), $\delta = 0.24$ (s, 3H), $\delta = 0.21$ ppm (s, 3H). It has been used in polymerization experiments, after drying and vacuum distillation as described for **I**.

**Hexamethyldisilane (III)** (Aldrich) was stirred under nitrogen over $CaH_2$ for 3 days and finally distilled in vacuo, before use.

**1,2-Diphenyltetramethyldisilane (IV)** (ABCR) was dried under vacuum and dissolved in HMPA.

**Potassium trimethylsilanolate** (90% technical grade chemical delivered by Aldrich) presumably contains $H_2O$, KOH, and $(CH_3)_3SiOSi(CH_3)_3$ formed by reaction of the silanolate with water. Indeed, Tatlock et al.[22] reported that when the salt is heated at 100 °C, it rapidly loses water. The loss in weight roughly corresponds to the inclusion of 1 mol of water for each mole of silanolate, but the increase in potassium content also indicates the presence of a hydroxide contaminant in the original preparation. Thus $(CH_3)_3SiOK$ is an important source of impurities which can disturb the polymerization system. Indeed direct nucleophilic attack of the ≡Si−Si≡ bond by KOH is plausible, so that part of the silacycle can be lost, which results in a limited efficiency for the envisioned polymerization reaction:

$$KOH + \equiv Si-Si\equiv \rightarrow HOSi\equiv + \equiv SiK$$

$$HOSi\equiv + \equiv SiK \rightarrow KOSi\equiv + \equiv SiH$$

$$\equiv SiH + KOH \rightarrow \equiv SiOK + H_2$$

Accordingly addition of purified $(CH_3)_3SiOK$ to $(CH_3)_3SiSi(CH_3)_3$ gave a stable silyl yellow anion in HMPA, whereas this characteristic[10] yellow color disappears very rapidly, when unpurified $(CH_3)_3SiOK$ is used. It is the reason a suitable purification technique of $(CH_3)_3SiOK$ has been developed.

$(CH_3)_3SiOK$ was thus purified according to the following two-step procedure under nitrogen. First it was heated under vacuum at 100 °C until constant weight (i.e. after 48 h and 40% weight loss; it is worth noting here that the salt sublimes slowly and with difficulty at 150 °C under high vacuum[23]). Because $(CH_3)_3SiOK$ has an appreciable solubility in THF whereas KOH is not soluble, the second step was accomplished by dissolving the residue in THF so that the hydroxide was held in suspension. The solution was then transferred by filtration, through a sintered glass funnel (No. 5) into another ampule. The THF was evaporated and the pure $(CH_3)_3SiOK$ dissolved in HMPA. The concentration of the $(CH_3)_3SiOK$/HMPA solution was determinated by titration with HCl in the presence of phenolphthaleine as indicator.

**Styrene and MMA Homopolymerization.** A typical example involved introducing the $(CH_3)_3SiOK$/HMPA solution into the reactor. The HMPA/disilane solution was then transferred into it at temperature $T_1$ and let to react under stirring for $t_1$ minutes (generation of the silyl anion). In a second step, this ≡SiK/HMPA initiator solution was added into a (1 mL) styrene (or MMA)/THF (40 mL) solution at −20 °C and the reaction mixture stirred for 2 min. The reaction was finally stopped by addition of acidified methanol, and the polymer formed recovered by precipitation in methanol.

**Sequential Polymerization of Styrene and Ethylene Oxide.** EO was added to a diphenyl methyl potassium initiator solution in a THF /HMPA mixture (98/2 v/v) at −78 °C. The temperature was then raised to 20 or 40 °C and EO was polymerized for 18 h at that temperature. An aliquot of the reaction medium was withdrawn for SEC analysis in order to determine the molecular weight of the PEO block. At the same temperature, **I** was then mixed with living $PEO^-K^+$. After the desired time $t_1$, styrene was introduced and sequential polymerization was allowed to take place for a few minutes (10 min at 20 °C or 5 min at 40 °C) at the same temperature. Copolymerization was terminated by addition of trimethylsilyl chloride.

**Characterization.** Size exclusion chromatography (SEC) was carried out in THF using a refractive index detector. Polystyrene was used as a calibration standard. $^1$H NMR spectra were recorded at 400 MHz in the FT mode on a Bruker AN 400 superconducting magnet system. IR spectra were obtained on a Perkin-Elmer 197 infrared spectrophotometer.

## Results and Discussion

### Anionic Polymerization of Styrene Using an Initiator Solution Prepared by Reaction of

**Table 1. Anionic Polymerization of Styrene Using an Initiator Solution Prepared by Reaction of $(CH_3)_3SiOK$ with 1,1,2,2-tetramethyl-1,2-disilacyclopentane (I) in a HMPA/THF Mixture[a]**

| code | [**I**]/[$(CH_3)_3SiOK$] | HMPA/THF (mL/mL) | $T_1 = T_2$ (°C) | $t_1$ (min) | $t_2$ (min) | $\rho$ (%) | $\bar{M}$n GPC | $\bar{M}_w/\bar{M}_n$ | $f$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 1.5/1.2 | 20 | | 60 | 0 | | | 0 |
| 2 | 5 | 1.5/1.2 | −20 | 120 | 15 | 100 | 29 600 | 1.7 | 12 |
| 3 | 5 | 1.5/0.7 | 0 | 17 | 6 | 88 | 32 400 | 1.7 | 10 |
| 4 | 3 | 1.5/1.2 | 20 | 165 | 15 | 93 | 19 000 | 1.6 | 18 |

[a] [$(CH_3)_3SiOK$] = 25.6 mmol; $t_1$ = mixing time of **I** and $(CH_3)_3SiOK$ at $T_1$ °C; [styrene] = 0.9 g; $t_2$ = propagation time at $T_2$ °C; $\rho$ = polymer yield; $f$ = initiator efficiency = [100 × [polymer yield]/[$(CH_3)_3SiOK$] (g/mol)]/ $\bar{M}_{n_{GPC}}$.

**Table 2. Anionic Polymerization of Styrene Using an Initiator Solution Prepared by Reaction of $(CH_3)_3SiOK$ with Disila Compounds (i.e. 1-phenyl-1,2,2-trimethyl-1,2-disilacyclopentane (II), $(CH_3)_3SiSi(CH_3)_3$ (III), and $Ph(CH_3)_2SiSi(CH_3)_2Ph$ (IV)) in HMPA[a] and Effect of the THF on the Silyl Anion Stability[b]**

| code | [$(CH_3)_3SiOK$] (mmol) | disila compounds | $T_1/t_1$ (°C/min) | method $t_1'$ (min) | $\bar{M}_n$ GPC | $\bar{M}_w/\bar{M}_n$ | $f$ (%) |
|---|---|---|---|---|---|---|---|
| 5 | 0.246 | **III** | 20/30 | C | 155 300 | 3.5 | 2 |
| 6 | 0.190 | **III** | 40/0.25 | A | 60 200 | 1.1 | 7 |
| 7 | 0.250 | **III** | 40/3.5 | A | 56 000 | *d* | 9 |
| 8 | 0.182 | **III** | 20/1230 | A | 18 700 | 1.3 | 26 |
| 9 | 0.236 | **III** | 20/1230 | B (8) | 31 200 | 1.9 | 12 |
| 10 | 0.190 | **IV** | 40/1.25 | A | 17 500 | 3.9 | 24 |
| 11 | 0.186 | **IV** | 20/ 15 | A | 53 400 | *d* | ∼10 |
| 12 | 0.261 | **IV** | 20/ 15 | B (16) | 57 700 | 1.5 | 6 |
| 13 | 0.206 | **II** | 40/0.25 and 20/5 | A | 14 900 | 1.7 | 29 |
| 14 | 0.350 | **II** | 40/0.25 and 20/5 | B (13) | 30 300 | 1.5 | 8 |

[a] The addition of $(CH_3)_3SiOK$ to the disila compound is performed in pure HMPA during $t_1$ minutes at $T_1$ °C; [$CH_3SiOK$] = [≡Si−Si≡]. [b] Key: (A) the HMPA silyl anion solution directly added in a styrene/THF mixture (1 mL/40 mL) at − 20 °C; (B) The HMPA silyl anion solution first mixed in THF (40 mL) for $t_1'$ min at 20 °C before addition of styrene (1 mL) at −20 °C; (C) 1 mL of styrene directly added into the HMPA silyl anion solution at 20 °C. [c] Propagation time = 2 min; polymer yield = 100%; $f$ = [100 × [polymer yield]/[$(CH_3)_3SiOK$] (g/mol)]/$\bar{M}_{n_{GPC}}$. [d] Multimodal.

**$(CH_3)_3SiOK$ with Disila Compounds.** Table 1 lists the results of styrene anionic polymerizations initiated with $(CH_3)_3SiOK$, in HMPA/THF mixture, modified or not with **I** at $T_1$ °C. It can be noted from this table (run 1) that without using 1,1,2,2-tetramethyl-1,2-disilacyclopentane **I** no polymer can be obtained at all, well obeying the classic rule of anionic polymerization as described in the Introduction.[6−8] However, the situation was completely changed, when ca. 5 molar equiv of **I** were first mixed with initiator $(CH_3)_3SiOK$ and allowed to react for $t_1$ min. It was also noticed that, upon addition of **I**, the initiator solution suddenly changed from colorless to yellow, characteristic[10] of silyl anions. As soon as styrene was added, a deep red color characteristic of polystyrene anions again immediately appeared, indicating that spontaneous polymerization occurred. Thus, the adduct formed was found to promote styrene polymerization in almost quantitative yield within less than 15 min. Although initiator efficiencies ($f$) are still very low, (i.e., less than 18%), and molecular weight distributions (MWD) are broad (i.e., $\bar{M}_w/\bar{M}_n \sim 1.6$), these results do provide a first convincing evidence that addition of compound **I** substantially modifies the reactivity of initiating species and promotes a quantitative styrene anionic polymerization.

Altogether these results might suggest that, in accordance with the reaction illustrated in Figure 1, addition of $(CH_3)_3SiOK$ leads to cleavage of the ≡Si−Si≡ bond in **I** yielding a new species, which can effectively initiate the styrene anionic polymerization, in good agreement with the previously reported results.[17,18]

The observed low initiator efficiency and broad MWD may be ascribed to a number of important factors. For instance, Vyazankin et al.[24] reported that the reaction of triethylsilyllithium with styrene in benzene at 20 °C gave moderate yields (23%) of the expected $(CH_3CH_2)_3SiCH_2CPhHLi$ compound. We thus believe that the stability of silyl anions in THF/HMPA mixtures, as well as the rate of conversion from $(CH_3)_3SiOK$ to potassium silyl anions, are also crucial factors in order to increase the initiator efficiency $f$.

**Stability of the Silyl Anions.** Sakurai et al.[11] demonstrated that a strongly basic (coordinating) aprotic solvent is required for the addition of sodium methoxide to hexamethyldisilane. Since the formed silyl anion ($(CH_3)_3SiNa$) is both very nucleophilic and basic, none of the commercially available solvents except HMPA, in which the silyl anion is stable for several days at room temperature, were suitable for the reaction. Accordingly addition of $(CH_3)_3SiOK$ to $(CH_3)_3SiSi(CH_3)_3$ gave a yellow silyl anion in HMPA or in HMPA/THF mixture, whereas this characteristic[10] yellow color does not appear in the absence of HMPA. It is worth noting here that the use of pure HMPA is problematic not only because it has toxic properties but also because it crystallizes at 7 °C. In addition it can be seen in Table 2 that the styrene polymerization leads to higher initiator efficiency and to lower MWD, when it is performed in a HMPA/THF mixture instead of pure HMPA (run 5).

If the potassium silyl anions are unstable in HMPA/THF solutions, the presence of THF should obviously be a critical parameter in that situation. Actually, it can be seen in Table 2 that if the addition of $(CH_3)_3SiOK$ to disila compounds **III**, **IV**, or **II**, is performed in pure HMPA, a twice higher initiator efficiency ($f$) is observed when the resulting silyl anion solutions are directly added into a styrene/THF mixture at − 20 °C (procedure A). In contrast, $f$ values are much lower when the initiator solution was first mixed in THF for $t_1'$ minutes at 20 °C before addition of styrene at −20 °C (Procedure B). This clearly indicates that potassium

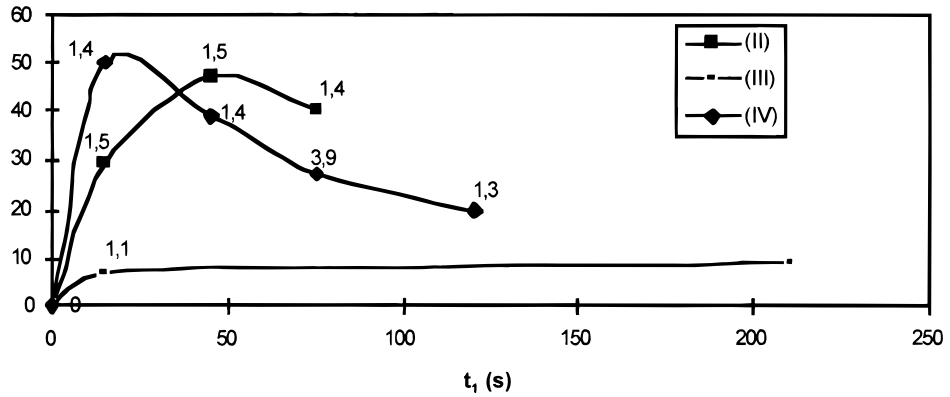


**Figure 2.** Anionic polymerization of styrene using an initiator solution prepared by reaction of $(CH_3)_3SiOK$ with disila compounds (i.e. 1-phenyl-1,2,2-trimethyl-1,2-disilacyclopentane (**II**), $(CH_3)_3SiSi(CH_3)_3$ (**III**), and $Ph(CH_3)_2SiSi(CH_3)_2Ph$ (**IV**)) in HMPA. Effect of the mixing time $t_1$ of disila compounds and $(CH_3)_3SiOK$ at 40 °C on the initiator efficiency $f$. $[CH_3SiOK] = [\equiv Si-Si\equiv]$. The HMPA silyl anion solution is directly added in a styrene/THF mixture (1 mL/40 mL) at − 20 °C; propagation time = 2 min; polymer yield = 100%; $f$ = [100 × [polymer yield]/((CH3)3SiOK) (g/mol)]/$M_n$ GPC; the $M_w/M_n$ values are written over the plots.

silyl anions are not stable in a THF/HMPA medium. Thus, keeping a very short time and a low temperature between the addition of THF and of monomer is necessary.

In fact organosilyllithium compounds cleave the THF molecule at the carbon−oxygen bond ($R_3SiLi + THF \rightarrow R_3Si(CH_2)_4OLi$).[25] However, solutions of $Ph_3SiLi$ in pure THF were found to be fairly stable over an extended period of time at room temperature (i.e., loss of 5% of active species after 20 h). However, under reflux conditions, decomposition of $Ph_3SiLi$ is rapid.[26] In all cases the rate is autoaccelerating, possibly by a catalytic effect of one of the reaction products.[27] Furthermore, HMPA could cause an apparent acceleration in the rate of cleavage.

The same studies indicate the following series of decreasing reactivity toward THF: $Ph_2MeSiLi > PhMe_2SiLi > Ph_3SiLi$.[26,27] In contrast, it can be seen, in Table 2, that the use of disila compounds containing a phenyl group (i.e. **II** and **IV**), does not really increase the potassium silyl anions stability in THF/HMPA mixtures.

It can be seen in Figure 2 that the mixing time of $(CH_3)_3SiOK$ with **II** or **III** in pure HMPA, also represents a critical parameter in controlling $f$. With increasing mixing time, from 15 and 50 s for *III* and *II* respectively, the initiator efficiency significantly decreases. These results clearly indicate that neither of the formed silyl anions is very stable in pure HMPA. However, a definite period of mixing is really necessary. It has been noted in the literature that nucleophilic reactions of the silyl anions in HMPA are often accompanied by electron-transfer processes, leading to formation of side products.[11,14,28] In addition, Hudrlik et al. mentioned that $(CH_3)_3SiLi$ reacted with $(CH_3)_3SiSi(CH_3)_3$ to give $(CH_3)_3Si(CH_3)_2SiLi$,[29] and the model reaction of 1,1,2,2-tetramethyl-1,2-disilacyclopentane with equimolar or excess amounts of trimethylsilyl anion under various conditions resulted in failure to isolate the expected 1:1 adduct, (i.e. $(CH_3)_3Si(CH_3)_2Si(CH_3)_3(CH_3)_2SiLi$).[30] Last but not least, because silicon atoms stabilize their anions at the α-position because of an electron-withdrawing effect,[31] proton abstraction (e.g. $\equiv SiK + \equiv SiCH_3 \rightarrow \equiv SiH + \equiv SiCH_2K$), may not be precluded.

**Rate of Conversion from $(CH_3)_3SiOK$ to Potassium Silyl Anions.** The fact that silyl anions are able to initiate styrene polymerization whereas $(CH_3)_3SiOK$ cannot clearly indicates that the reactivity of $(CH_3)_3SiOK$ toward the disila cyclic compound is lower than the one of the formed potassium silyl anion (i.e. $k_1 \ll k_2$ in Figure 3). Indeed, Suzuki et al.[30] have recently published that 1,1,2,2-tetramethyl-1,2-disilacyclopentane **I** and 1,2,2-trimethyl-1-phenyl-1,2-disilacyclopentane **II** were readily polymerized by using potassium trimethylsilyl anions, as initiator, and Sakurai et al. reported a $\equiv Si-Si\equiv/\equiv Si-Si\equiv$ redistribution reaction, which may involve nucleophilic attack of silyl anions on the disilanes.[32] These polymerizations were almost complete within a few hours, under conditions similar to those of our system at 20 °C. Thus, as soon as the silyl anion is generated, the polymerization of **I** or **II** may proceed, and a competing reaction of $(CH_3)_3SiOK$ and already formed silyl anions with **I** or **II** has to be considered. Accordingly the $^1H$ NMR analysis of the obtained polystyrene shows that it contains $\equiv Si-Si\equiv$ units ($\delta = 0.06$ ppm).

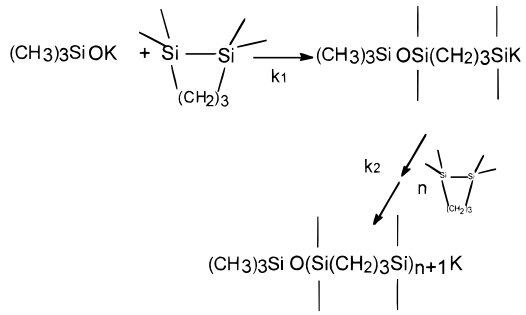


**Figure 3.** Competing reactions of $(CH_3)_3SiOK$ with the already formed silyl anion: reaction scheme, ($k_1 \ll k_2$).

If that competing reaction of $(CH_3)_3SiOK$ and already formed SiK has to be considered, the influences of both cyclic structure **II** and $[\equiv Si-Si\equiv]/[(CH_3)_3SiOK]$ molar ratio ($R$) on the $f$ value should obviously be critical parameters for improving that situation, since in any case a linear structure is not able to polymerize ($(CH_3)_3SiOK + Ph(CH_3)_2SiSi(CH_3)_2Ph \rightarrow (CH_3)_3SiOSi(CH_3)_2Ph + Ph(CH_3)_2SiK$). It can be seen in Table 3 that, when the $(CH_3)_3SiOK$ addition is carried out with **II** the $f$ value is increased by increasing the $R$ molar ratio, whereas $f$ does not significantly vary if the linear analogue (*IV*) is used. It might thus be concluded that the loss of initiator efficiency can be interpreted in such a way that the generation of silyl anions by reacting aggregated $(CH_3)_3SiOK$ with *II* is slower than the propagation of *II* with silyl anion initiating species.

**Table 3. Anionic Polymerization of Styrene Using an Initiator Solution Prepared by Reaction of $(CH_3)_3SiOK$ with Disila Compounds (i.e. 1-Phenyl-1,2,2-Trimethyl-1,2-disilacyclopentane (II) and $Ph(CH_3)_2SiSi(CH_3)_2Ph$ (IV)) in HMPA[a] and Effect of the $[(CH_3)_3SiOK]/[\equiv Si-Si\equiv]$ (*R*) Molar Ratio on the Initiator Efficiency *f***

| code | $[(CH_3)_3SiOK]$ (mmol) | ($\equiv Si-Si\equiv$) *R* | $\bar{M}_n$ GPC | $\bar{M}_w/\bar{M}_n$ | *f* (%) |
|---|---|---|---|---|---|
| 15 | 0.19 | (**IV**) 5 | 11 000 | 1.6 | 43 |
| 16 | 0.19 | (**IV**) 1 | 9 500 | 1.5 | 50 |
| 17 | 0.05 | (**II**) 3.7 | 29 000 | 1.5 | 59 |
| 18 | 0.20 | (**II**) 1 | 14 900 | 1.7 | 29 |

[a] The addition of $(CH_3)_3SiOK$ to the disila compound is performed in pure HMPA during 15 s at 40 °C; the HMPA silyl anion solution is then directly added into a styrene/THF mixture (1 mL/40 mL) at − 20 °C; propagation time = 2 min; polymer yield = 100%; *f* = initiator efficiency = [100 × [polymer yield]/[$(CH_3)_3SiOK$] (g/mol)]/$\bar{M}_{n_{GPC}}$.

It is known that increasing temperature results in partial disruption of the $[(CH_3)_3SiOK]_x$ aggregates, implying an increase in reactivity. In this way the polymerization reaction of (II) can be reduced. As expected, it can be seen in Table 2, that for short $t_1$ times, the generation of silyl anion at 40 °C leads to a higher initiator efficiency than at 20 °C.

Under comparable conditions, the phenyl derivatives (i.e. II and **IV**) lead to better initiator efficiency than the corresponding methyl ones (**III**) as is apparent in Figure 2. This can be ascribed to the fact that the phenyl group should have two effects reducing the polymerization reaction of **II** (i.e. $k_1/k_2$ is increased): on one hand it may facilitate the ring-opening reaction, and on the other hand the formed silyl anion is less reactive toward **II**. It is worth noting that polymerization of styrene (although of low initiator efficiency, $f = 2\%$) is observed in THF even in the absence of HMPA when **II** is used.

Up to this point, one may conclude that, to gain a high initiator efficiency, the experimental conditions should at least meet the following requirements: use of phenyl derivatives as disila compounds; addition of $(CH_3)_3SiOK$ to the disila compounds, in pure HMPA; addition of $(CH_3)_3SiOK$ to disila cycle at 40 °C, to minimize disilacycle polymerization; a compromise between a long enough mixing time to ensure quantitative conversion of silanolate to silyl anion, on one hand, and a limited mixing time in order to minimize possible deactivation of the resulting silyl anions on the other hand; direct addition of the initiator silyl anion solution to the styrene/THF mixture at −20 °C.

**Anionic Polymerization of MMA in HMPA/THF Mixture at −20 °C, Using an Initiator Solution Prepared by Reaction of $(CH_3)_3SiOK$ with Disila Compounds.** Table 4 lists the results of MMA polymerizations initiated with $(CH_3)_3SiOK$ modified with **II** and **IV** at 40 °C. The addition of $(CH_3)_3SiOK$ to the disila compounds was performed in pure HMPA, and the resulting silyl anion solution was directly added into the MMA/THF mixture at −20 °C. As expected the influences of both $t_1$, and $[\equiv Si-Si\equiv]/[(CH_3)_3SiOK]$ molar ratio parameters on the initiator efficiency (*f*) are quite comparable to those observed in styrene polymerization. The *f* values are however lower than those observed in the case of styrene, and polymer yields are not quantitative. The known carbonyl attack at −20 °C by the active species (toward MMA and along the PMMA chain particularly by backbiting) may explain these observations. Accordingly it has been reported in the literature that triphenylsilylpotassium adds to the carbonyl group of benzophenone[33] (potassium reagents are nevertheless less effective in addition reactions with carbonyl compounds than the corresponding lithium compounds[34]). Unfortunately, in the present case, the freezing point of HMPA prevented its addition at lower temperature.

**Anionic Sequential Polymerization of Styrene, Using an Initiator Solution Prepared by Reaction of the Poly(ethylene oxide) Macroanion with 1,1,2,2-Tetramethyl 1,2-disilacyclopentane (I).** Following the same line as demonstrated above, an attempt was also devoted to polymerization of styrene by using living poly(ethylene oxide) potassium added with compound **I**, the results of which are tabulated in Table 5. It is clear that, similar to the situation observed in the case of styrene and polymerization by $(CH_3)_3SiOK$, styrene sequential polymerization does occur. Although the reinitiating efficiency is still relatively modest, the yield is always quantitative. A typical SEC chromatogram of the crude copolymerization product (code 25) is shown in Figure 4b and compared to the elution curve of the initial PEO block (Figure 4a). The polymer on low molecular side ($P_1$) may be ascribed to unreacted homo-PEO, since its elution time is identical to the one of the initial PEO block. Quite consistently, after the sample reported in Figure 4b was extracted by water, a selective solvent for PEO, the low molecular side peak in the SEC diagram disappeared. The polymer on the high MW side ($P_2$) was found to be insoluble both in cyclohexane and water, selective solvents for homopolystyrene and homo-PEO, respectively. That indicates that this polymer is neither an admixture of two homopolymers nor one of either homopolymers; thus, it can reasonably be considered as a pure block copolymer. $^1H$ NMR and IR spectroscopy analyses of that sample further confirm that it consists of both polystyrene and PEO segments: relative contents fit the PEO and styrene feeds for an "*f*" value of 66% as obtained from integration of GPC peaks.

These results evoke another exciting potentiality of the method, i.e., the direct two-step one-pot catalytic synthesis of a poly(St-*block*-EO-*block*-St) triblock copolymer from a difunctional alkoxide initiator.

## Conclusion

The present study convincingly demonstrates that the use of a $\equiv Si-Si\equiv$-containing cyclic compound represents an efficient pathway toward modifying the nature of initiating or propagating species, allowing their reactivity boosting. These results are particularly important for tailoring of the active species, allowing a controlled sequential anionic polymerization to proceed irrespective of the monomer addition order.

Thus, it has been proven that potassium trimethylsilanolate, a model for a polysiloxane living end, and $PEO^-K^+$ are capable of polymerizing styrene and MMA, when converted into potassium silyl anion by reaction with 1,1,2-trimethyl 2-phenyl-1,2-disilacyclobutane (**II**). Thus, **II** appears as an original reactivity booster of oxyanions.

Until now, the initiation efficiency of potassium trimethylsilanolate only reaches 59% for styrene and 31% for MMA; also the molecular weight distributions of polystyrene and poly(methyl methacrylate) are still relatively broad (c.a. 1.5). Owing to both facts that the potassium silyl anions are unstable in HMPA/THF mixtures, and that **II** polymerizes, the first step of the

**Table 4. Anionic Polymerization of MMA Using an Initiator Solution Prepared by Reaction of $(CH_3)_3SiOK$ with Disila Compounds (i.e. 1-phenyl-1,2,2-trimethyl-1,2-disilacyclopentane (II), and $Ph(CH_3)_2SiSi(CH_3)_2Ph$ (IV)) in HMPA[a]**

| code | $[(CH_3)_3SiOK]$ (mmol) | (≡Si−Si≡) *R* | $t_1$ (s) | $\rho$ (%) | $\bar{M}_n$ GPC | $\bar{M}_w/\bar{M}_n$ | $f$ (%) |
|---|---|---|---|---|---|---|---|
| 19 | 0.19 | (**IV**) 1 | 75 | 82 | 18 700 | 1.4 | 17 |
| 20 | 0.19 | (**IV**) 1 | 45 | 72 | 25 700 | 1.4 | 11 |
| 21 | 0.19 | (**IV**) 5 | 15 | 40 | 4 800 | 1.2 | 33 |
| 22 | 0.14 | (**II**) 1 | 75 | 72 | 24 500 | 1.5 | 16 |
| 23 | 0.14 | (**II**) 1 | 45 | 76 | 22 000 | 1.3 | 21 |
| 24 | 0.05 | (**II**) 3.7 | 15 | 66 | 30 700 | 1.4 | 31 |

[a] The addition of $(CH_3)_3SiOK$ to the disila compound is performed in pure HMPA during $t_1$ seconds at 40 °C; the HMPA silyl anion solution is then directly added into the MMA/THF mixture (1 mL/40 mL) at − 20 °C; propagation time = 2 min; $\rho$ = polymer yield; $f$ = initiator efficiency = [100 × [polymer yield]/[$(CH_3)_3SiOK$] (g/mol)]/$\bar{M}_{n_{GPC}}$.

**Table 5. Anionic Sequential Polymerization of Styrene, Using an Initiator Solution Prepared by Reaction of the Poly(ethylene oxide) Macroanion with 1,1,2,2-tetramethyl-1,2-disilacyclopentane (I): Diblock Copolymers Synthesis[a]**

| | EO polymer | | | PEO-*block*-Pst | | |
|---|---|---|---|---|---|---|
| code | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ | $T_1/t_1$ (°C/s) | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ | $f$ (%) |
| 25 | 12 700 | 1.04 | 20/60 | 36 700 | 1.43 | 66 |
| 26 | 10 900 | 1.05 | 20/30 | 87 300 | 1.65 | 37 |
| 27 | 12 400 | 1.04 | 40/30 | 68 500 | 1.65 | 47 |

[a] Polymerization of EO, initiator, diphenyl methyl potassium, $10^{-3}$ M; [**I**]/[$PEO^-K^+$] = 5; $t_1$ = mixing time of **I** with $PEO^-K^+$ at $T_1$ °C before styrene addition; polymer yield = 100%; $f$ = initiator efficiency for sequential polymerization in terms of molecular weight ratio of block copolymer to PEO.

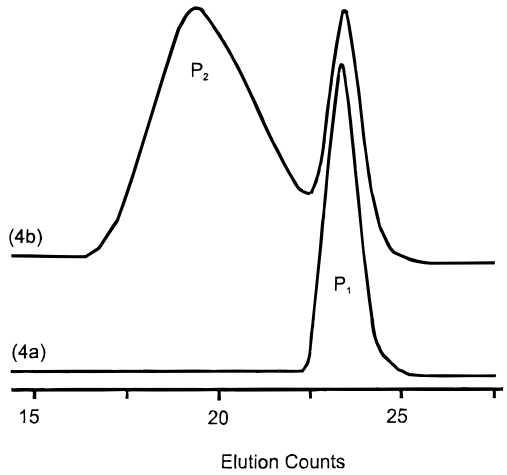


**Figure 4.** GPC trace of styrene block copolymerization using an initiator solution prepared by reaction of the poly(ethylene oxide) macroanion with 1,1,2,2-tetramethyl-1,2-disilacyclopentane (I): (a), PEO precursor; (b) reaction after adding styrene (conditions: see code 25 in Table 5).

reaction sequence is of a crucial importance for the initiation efficiency and is very sensitive to the solvent, [II]/[$(CH_3)_3SiOK$] molar ratio, temperature ($T_1$) and reaction time ($t_1$). The best results were obtained in HMPA for [**II**]/[$(CH_3)_3SiOK$ ] = 3.7, $T_1$ = 40 °C and $t_1$ = 45 s.

Although already very encouraging, these results must obviously be optimized so as to reach a complete conversion of potassium trimethylsilanolate and thus a 100% initiation efficiency for the second polymerization step. It is worth noting here that addition of potassium methoxide to the $R_3Si-SiR_3$ bond could also be performed in common aprotic organic solvents such as THF on one hand in the presence of a crown ether,[15] or on the other hand, when two or three of the R groups are phenyl ones.[16] In addition, the fact that trimethylsilylsodium anions were found to be more stable in 1,3-dimethyl-2-imidazolidinone (DMI) than in HMPA[35] suggests that DMI may be useful as a new solvent for our system. These observations illustrate an obviously promising situation that paves the way toward further optimization of the present results. Thus several analogues of the parent compounds **I** and **II** and cyclocarbosilanes have been synthesized[36] and will be scanned as alternatives for 1,1,2-trimethyl-2-phenyl-1,2-disilacyclopentane. This work in progress will be the subject of forthcoming papers.

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