Equilibrium Anionic Ring-Opening Polymerization of a Six-Membered Cyclosiloxazane

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ABSTRACT: The anionic ring-opening polymerization of heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane, initiated with organolithium compounds, has been investigated. With the addition of dimethylformamide (DMF), the polymerization is controlled. Backbiting reactions are limited and give a unique specific cyclic compound in low proportion. Thermodynamic and kinetic studies indicate that such polymerization is equilibrated. The apparent rate constants of propagation and depolymerization along with the thermodynamic parameters (enthalpy and entropy) of the polymerization have been calculated. The active species are ion pairs externally solvated by DMF in equilibrium with unreactive aggregated ion pairs.

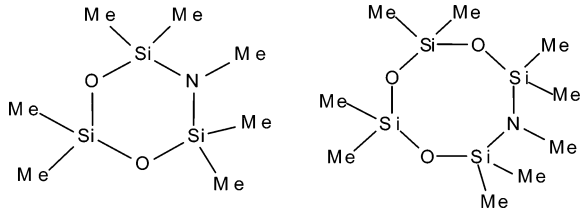
Introduction

High molar mass polysilazanes have been synthesized by ring-opening polymerization via both cationic[1,2] and anionic living process.[3−5] Structures of these polymers are similar to that of polysiloxanes, and they exhibit specific properties due to the replacement of [Si−O] bonds by [Si−N] bonds. They are semicrystalline polymers (with melting temperatures ranging from 100 to 220 °C) with higher mechanical modulus and higher thermal stability than polysiloxanes.[6,7]

Combination of the two types of enchainments (SiO and SiN bonds) is also very promising since the corresponding polymers (polysiloxazanes) exhibit intermediate properties[6] and are precursors of coating and ceramic materials such as $Si_xN_yC_zO_w$.[8,9] Polysiloxazanes have been synthesized either by copolymerization of cyclosiloxanes and cyclosilazanes[8,10] or by homopolymerization of cyclosiloxazanes.[6,11−15] Considering the second route, the different published works report that the polymerization of various cyclosiloxazanes is possible in specific conditions (in bulk at high temperature) but without any control since, besides the polymer, a large amount of various cyclic compounds is formed.[11,14,15]

Contrarily, in the present work, polysiloxazanes have been synthezized through controlled anionic ring-opening polymerization of the heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane (cyclosiloxazane **1**) (**D_2D_{NMe}**).[6] The polymerization is an equilibrium polymerization that produces polymers with a regular structure simultaneously with a very limited amount of a unique backbiting product, nonamethyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (cyclosiloxazane **2**) (**D_3D_{NMe}**) (Scheme 1).

Scheme 1. Structures of Heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane 1 (D_2D_{NMe}) and Nonamethyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane 2 (D_3D_{NMe})



Experimental Part

Reagents. Ammonium sulfate (99%), methylamine (anhydrous 98%), *n*-butyllithium (BuLi), and *tert*-butylithium (tBuLi) solutions (1.7 mol/L in pentane) are commercial products (Sigma-Aldrich) and were used as received. Dichlorosiloxanes (from ABCR, 95%) were distilled from magnesium chips under vacuum. Diethyl ether was distilled from calcium hydride. Toluene was refluxed over calcium hydride for several hours, then distilled, and dried a second time over sodium following by a vacuum distillation before use. Dimethylformamide (DMF) (Sigma-Aldrich, 99%) was distilled over KOH and stored over molecular sieves (3−4 Å). Internal standard (nonane from Sigma-Aldrich, 99%) and quenching agent (chlorovinyldimethylsilane from Sigma-Aldrich, 97%) ($Me_2ViSiCl$) were dried and stored over CaH_2 and then vacuum-distilled just before use. Benzyllithium (BzLi) was prepared by reaction of tBuLi with toluene. In a typical experiment, 1.7 mL of tBuLi was reacted with 50 mL of toluene, at 50 °C, for 72 h. The final concentration of the orange carbanionic solution was measured by UV/vis spectrophotometry ($\epsilon_\lambda = 7000$ L/(mol cm) at wavelenght $\lambda = 290$ nm in toluene) and found equal to 0.034 mol/L (>99% yield).

Monomer Synthesis. Cyclosiloxazanes were synthesized according to the literature using the reaction of dichlorosiloxanes and ammonia[6,11,16] or amines.[11,17−19] They were dried over calcium hydride, then distilled, and dried several times over sodium. They were stored under vacuum.

Synthesis of Cyclosiloxazane 1 (D_2D_{NMe}) (Scheme 1). In a typical experiment, 800 mL of diethyl ether and 79 mL of 1,5-dichlorohexamethyltrisiloxane (0.29 mol) were placed in a 2 L three-neck flask at 0 °C, under nitrogen atmosphere, and with a condenser at −30 °C. Then, 19 mL of anhydrous methylamine (0.66 mol) was slowly added into the solution until the $MeNH_3Cl$ salt formed by the reaction is completely dissolved (∼2 h). After evaporation of methylamine excess at room temperature, the solution was filtered off and diethyl ether was removed by vacuum evaporation. The resulting liquid was heated at 120 °C for 1 h with 39.6 g of ammonium sulfate (0.30 mol). Finally, D_2D_{NMe} (**1**) was removed by continuous distillation (bp = 60 °C/20 mmHg) in 60% yield (48.2 g). It was characterized by mass spectroscopy (EIMS), ^{1}H NMR, and ^{29}Si NMR. Its purity was checked by gas chromatography (≥99%). ^{1}H NMR ($CDCl_3$, δ): 0.1 (s, 12H, NSiCH_3O);

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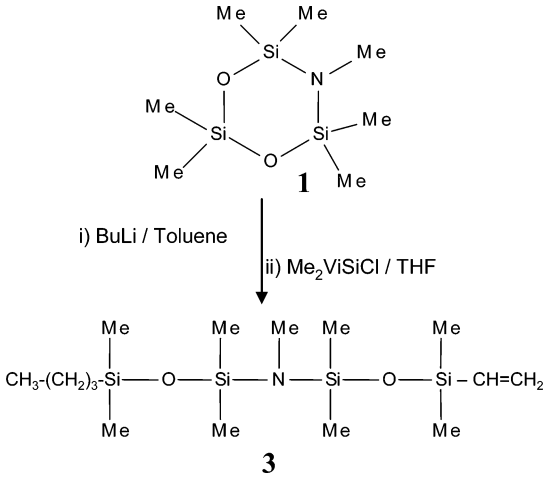
Scheme 2. Synthesis of Heptamethyl-1-butyl-7-vinyl-2,6-dioxa-4-aza-1,3,5,7-tetrasilaheptane 3 by Reaction of *n*-Butyllithium (BuLi) with Heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane 1 (D_2D_{NMe}) in Toluene and End-Capping with Methylvinyldichlorosilane ($Me_2ViSiCl$) in Tetrahydrofuran (THF)



0.11 (s, 6H, OSiCH_3O); 2.36 (s, 3H, NCH_3). ^{29}Si NMR ($CDCl_3$, δ): −2.96 (s, 2Si, NS$i$$CH_3$O); −10.78 (s, 1Si, OS$i$$CH_3$O). EIMS (*m/z*, relative intensity): 235 (M,6.6); 220 (100); 193 (35.5); 169 (4.4); *119* (4.4); 102 (10); 73 (18.8).

Synthesis of Cyclosiloxazane 2 (D_3D_{NMe}) (Scheme 1). In a typical experiment, 800 mL of diethyl ether and 100.8 mL of 1,7-dichlorooctamethyltrisiloxane (0.29 mol) were placed in a 2 L three-neck flask at 0 °C, under a nitrogen atmosphere and with a condenser at −30 °C. Then, 19 mL of anhydrous methylamine (0.66 mol) was slowly added into the solution until the $MeNH_3Cl$ salt formed by the reaction is completely dissolved (∼2 h). After evaporation of methylamine excess at room temperature, the solution was filtered off and diethyl ether was removed by vacuum evaporation. The raw resulting viscous liquid was heated for 1 h in 550 mL of refluxing toluene with 39.6 g of ammonium sulfate (0.30 mol). Then, 66.2 g of cyclosiloxazane **2** (D_3D_{NMe}) were recovered by vacuum distillation (bp = 100 °C/5 mmHg) (65% yield) and characterized by EIMS, ^{1}H NMR, and ^{29}Si NMR. Its purity checked by gas chromatography was 95%. ^{1}H NMR ($CDCl_3$, δ): 0.14 (s, 12H, NSiCH_3O); 0.15 (s, 12H, OSiCH_3O); 2.42 (s, 3H, NCH_3). ^{29}Si NMR ($CDCl_3$, δ): −2.92 (s, 2Si, NS$i$$CH_3$O); −10.20 (s, 2Si, OS$i$$CH_3$O). EIMS (*m/z*, relative intensity): 309 (M, 1); 294 (100); 278 (2); 265 (5); 191 (4); 119 (1); 73 (6); 59 (3); 45 (2).

Synthesis of Heptamethyl-1-butyl-7-vinyl-2,6-dioxa-4-aza-1,3,5,7,-tetrasilaheptane (3) (Scheme 2). In a flame-dried glass vessel, 4.7 g of D_2D_{NMe} (**1**) (0.02 mol) dissolved in 10 mL of purified toluene was reacted under vacuum with 14.1 mL of *n*-butyllithium in pentane (0.024 mol) for 1 h at 30 °C. Then, the reaction was quenched by adding 2.65 mL of $Me_2ViSiCl$ (0.022 mol) in 2 mL of THF. The solution was washed with 20 mL of hydrochloric acid solution (1 mol/L), dried over Mg_2SO_4, and evaporated. The resulting product (7.4 g) was obtained in 99% yield and was identified by GC-MS, ^{1}H NMR, and ^{29}Si NMR. ^{1}H NMR ($CDCl_3$, δ): 0.09 (s, 6H, BuSiCH_3O); 0.10 (s, 12H, NSiCH_3O); 0.11 (s, 6H, ViSiCH_3O); 0.55 (t, 2H, $C_3H_7CH_2$SiO); 0.90 (t, 3H, $CH_3(CH_2)_3$SiO); 1.3 (t, 4H, $CH_3(CH_2)_2CH_2$SiO); 2.56 (s, 3H, NCH_3); 5.7−6.3 (m, 3H, CH_2=CHSiO) (Figure 1). ^{29}Si NMR ($CDCl_3$, δ): 6.5 (s, 1Si, BuSiOSiN); −5.3 (s, 1Si, NSiOSiVi); −8.4 (s, 1Si, BuSiOSiN); −9.2 (s, 1Si, NSiOSiVi) (Figure 1). EIMS (*m/z*, relative intensity): 377 (M, 5); 362 (100); 348 (15); 336 (20); 320 (40); 306 (65); 278 (5); 264 (7); 232 (60); 220 (90); 206 (32); 193 (18); 177 (12); 147 (5); 133 (30); 119 (18); 103 (5); 85 (40); 73 (100); 59 (55); 45 (11).

Typical Polymerization Procedure. All purifications and experiments were carried out under vacuum in glass apparatus closed with Rotaflo taps. In a typical experiment, the polymerization vessel was flame-dried under vacuum and charged with 10 mL of toluene and 0.2 mL of BuLi solution in pentane (0.000 37 mol). Then, after 1 h of reaction, 4.8 g of monomer **1** (D_2D_{NMe}) (0.0205 mol), 1 mL of nonane (internal standard), and 0.95 mL of DMF (0.0123 mol) were successively introduced. After 22 h at 30 °C, the reaction gave 2 g of polymer (43% yield) (recovered by precipitation in acetonitrile and dried under vacuum), 2.7 g of residual initial monomer (56% yield), and 0.06 g of cyclosiloxazane **2** (D_3D_{NMe}) (1% yield). $\bar{M}_n$(theoretical) = 5700; $\bar{M}_n$(SEC) = 6600; molecular weight distribution (MWD) = 1.2. ^{1}H NMR ($CDCl_3$, δ): 0.09 (s, 6nH, [SiCH_3O]$_n$); 0.10 (s, 12nH, [NSiCH_3O]$_n$); 0.55 (t, 2H, $C_3H_7CH_2$SiO); 0.90 (t, 3H, $CH_3(CH_2)_3$SiO); 1.3 (t, 4H, CH_3-$(CH_2)_2CH_2$SiO); 2.56 (s, 3nH, [NCH_3]$_n$); 5.7−6.3 (m, 3H, CH_2=CHSiO) (Figure 2). ^{29}Si NMR ($CDCl_3$, δ): −9.2 (s, 1nSi, [NSiOSi]$_n$); −21.2 (s, 1nSi, [OSiO]$_n$) (Figure 3a). In experiments followed by gas chromatography, samples were withdrawn at various reaction times by pouring part of the solution into a tube under vacuum and quenching it with dimethylvinylchlorosilane.

Instrumentation and Measurements. Kinetic data were determined by gas chromatography (GC) using a Varian apparatus with thermal conductibility detection and equipped with a BP1 capillary column. The temperature program started from 50 °C (after an isothermal delay of 2 min) up to 240 °C at the rate of 10 °C/min.

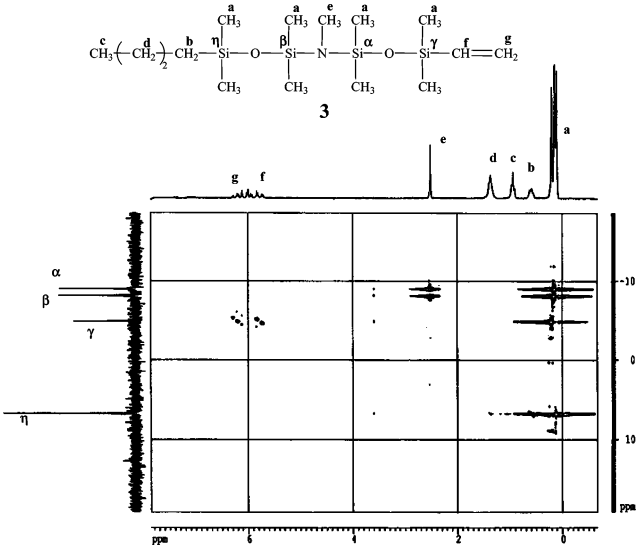


Figure 1. 2D ^{1}H−^{29}Si NMR spectrum of nonamethyl-1-butyl-7-vinyl-2,6-dioxa-4-aza-1,3,5,7-tetrasilaheptane (**3**) in $CDCl_3$.

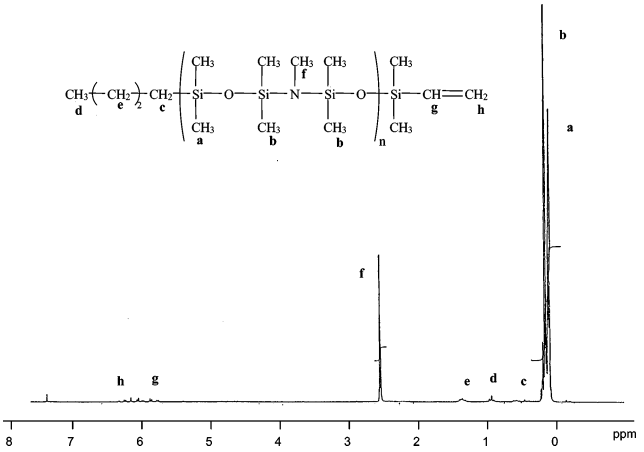


Figure 2. ^{1}H (200 MHz) NMR spectrum in $CDCl_3$ of a polysiloxazane prepared by polymerization of monomer **1**, at 30 °C, initiated by *n*-butyllithium (run 3, Table 1) and quenched by dimethylvinylchlorosilane.

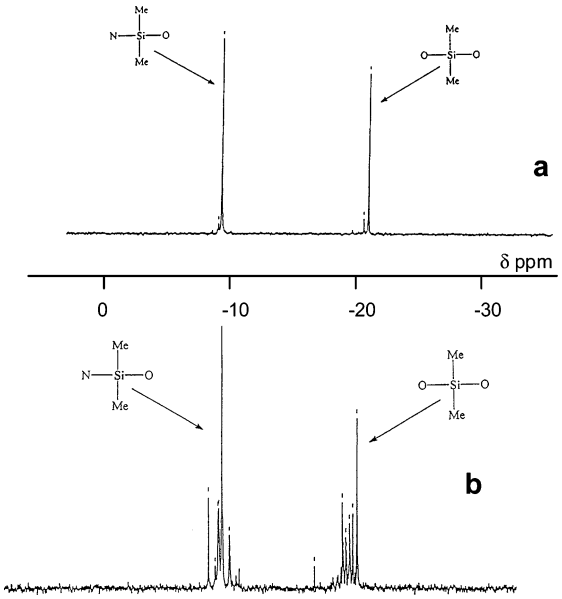


Figure 3. ^{29}Si (39.8 MHz) NMR spectra in $CDCl_3$ of polysiloxazanes prepared by polymerization of monomer **1** initiated by benzyllithium: (a) temperature of polymerization 30 °C (run 9, Table 1); δ ppm (O*Si*O) −23, (N*Si*O) −9.3. (b) temperature of polymerization 80 °C (run 12, Table 1).

The flow rate of helium was 30 mL/min. The internal standard method (with nonane) was used for determination of the monomer proportion.

Number-average molar masses ($\bar{M}_n$) and molar mass distributions (MWD) were determined by size-exclusion chromatography (SEC) on dilute polymer samples (2 mg/mL) using toluene as eluent (0.8 mL/min), at 25 °C, with a Varian 5500 apparatus equipped with three TSK columns (250 Å, 5 μm; 1500 Å, 6 μm; 10 000 Å, 9 μm), a refractive index detector (working in the range 160−800 nm) and, in some experiments, a light scattering detector (LSD) equipped with a He−Ne laser (632.8 nm, 15 mW). The refractive index increment (d*n*/d*c*) of dilute solutions of polysiloxazane (5 mg/mL) was measured, in toluene, at 25 °C, with a differential refractometer working at 632.8 nm and found equal to 0.003 mL/g. Number-average molar masses ($\bar{M}_n$) were calculated using a polystyrene calibration curve. The validity of this calibration plot (within the experimental error) was checked on several specific samples. For these samples, number-average molar masses were measured by vapor pressure osmometry ($\bar{M}_n$(SEC) = 52 000; $\bar{M}_n$(osmometry) = 49 000) or light scattering detection ($\bar{M}_n$(SEC) = 19 600 and 28 700; $\bar{M}_n$(LSD) = 18 500 and 29 100). Vapor pressure osmometry measurements were realized, in toluene, at 60 °C, on polymer solutions (1 g/100 mL) with a Gonotec Osmomat 090 apparatus equipped with cellulose membranes.

^{1}H (200 MHz), ^{13}C (50 MHz), and ^{29}Si (39.8 MHz) NMR spectra were recorded on a Bruker AC200 instrument, in $CDCl_3$, and were internally referenced using the residual protic solvent resonance relative to tetramethylsilane (δ = 0).

EI mass spectra (EIMS) were recorded on a Micromass AUTOSPEC apparatus in positive mode with a beam energy of 70 keV.

Results and Discussion

General Aspects of the Polymerization. Polymerizations of **1** were carried out, in toluene, under various experimental conditions using benzyllithium (BzLi) or *n*-butyllithium (BuLi) as initiators (Table 1). Upon addition of the monomer on to a solution of BzLi, the UV/vis absorption at 290 nm rapidily decreases (a few minutes) simultaneously with a bleaching of the solution. Then, the reaction stops and no polymer is recovered. Upon addition of dimethylformamide (DMF) the reaction restarts, and whatever the time of the polymerization, depending on temperature, initiator, and DMF concentrations, both the monomer and the polymer conversions range from 20% to 45% (Table 1). This indicates that BzLi reacts rapidly with **1** to give an active species which could not propagate the polymerization in pure toluene. In the presence of DMF, these active species can be activated and thus allow successive insertions of monomer. So, in such conditions, initiation step can easily be separated from propagation step. These has been confirmed by preparing active "seeds" which are able to initiate the polymerization in the same conditions as BzLi (Table 1, runs 6 and 7). ^{1}H NMR, ^{29}Si NMR, and EIMS analyses (Figure 1) of these "seeds" quenched by dimethylvinylchlorosilane (see Experimental Part) indicate that they are exclusively (within experimental error) siloxazanes of structure **3** (Scheme 2), resulting from the quantitative reaction of the organolithium initiator on the specific silicon atom of the [O−Si−O] bond of the monomer **1**. An analogous behavior has already been observed during the reaction of BuLi with cyclosiloxanes which gives, in the absence of any polar or complexing solvents or additives, several aggregated products resulting from ring-opening process without any polymerization.[20,21] Nevertheless, the quantitative formation of the unique compound **3** is unexpected and might result from a less hindered and/or a more electrophilic environment for the silicon atom in the [O−Si−O] bond of monomer **1** compared to that in the two others [O−Si−N] bonds. The first active species **3** might be highly aggregated (and thus unreactive) in pure toluene and less aggregated or unaggregated in presence of polar additives such as DMF (and so able to propagate).

The results presented in Table 1 also show that, in specific conditions (room temperature, short time of polymerization, and low amount of DMF), the experimental values of the number-average molar masses $\bar{M}_n$(exp) agree, within experimental error, with the theoretical ones $\bar{M}_n$(theo) calculated from the $[M]_0/[I]_0$ ratios and that the molar mass distributions (MWD) are rather narrow. Moreover, the polymers prepared in such conditions exhibit the expected regular structure coming from the same unique ring-opening process (Figure 2). Particularly, the ^{29}Si NMR spectrum shows only two types of silicon environment, thus confirming the absence of different types of monomer insertion which would give multiple ^{29}Si signals and specifically a [N−Si−N] signals around −1.9 ppm[1] (Figure 3a).

Contrarily, when the time of polymerization (Table 1, run 16) and the temperature (Table 1, runs 11 and 12) increase, $\bar{M}_n$(exp) and $\bar{M}_n$(theo) along with the monomer and polymer conversions disagree and the molar mass distribution values increase. In such conditions, GC analysis of the crude polymerization solution indicates that, besides the residual monomer and the polymer, there exists a unique product which has been characterized by GC-MS as nonamethyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane, **2** (D_3D_{NMe}). This eight-membered ring, which certainly also exists in the polymerizations carried out at 30 °C over a short period of time but in negligible amount (Figure 4), might result from a backbiting side reaction (intramolecular reaction) very usual with cyclic siloxane and siloxazane compounds.[14,22] It is also noteworthy that, in such conditions, the ^{29}Si NMR spectra of the polymers exhibit the signals of various silicon environments certainly resulting from simultaneous intermolecular redistributions of siloxazane units (randomization by chain transfer) (Figure 3b). Nevertheless, in the specific conditions used, as initiation step, the side-reaction

Table 1. Polymerizations of Monomer 1 (D_2D_{NMe}) Initiated by *n*-Butyllithium (Runs 1−3) or Benzyllithium (Runs 4−16), in Toluene, with Additions of Dimethylformamide (DMF); Temperature of Polymerization 30 °C Except Runs 11 (50 °C) and 12 (80 °C)

runs	$[M]_0$ (mol/L)	$[M]_0/[I]_0$	$[DMF]_0/[I]_0$	reaction time (h)	monomer conv[a] (%)	polymer yield[b] (%)	$\bar{M}_n$(theo)[c] (g/mol)	$\bar{M}_n$(exp)[d] (g/mol)	MWD[e]
1	2.00	50	0	1	≈1−2	0			
2	2.00	50	0	10	≈1−2	0			
3	2.05	55	33	22	44	43	5 700	6 600	1.2
4	2.05	60	50	20	40	39	5 600	6 400	1.2
5	2.05	60	50	40	45	41	6 300	7 000	1.3
6[f]	2.05	60	50	20	40	39	5 600	6 600	1.2
7[g]	2.05	60	50	20	41	39	5 800	6 300	1.2
8	2.25	205	106	3	21	20	10 100	10 200	1.1
9	2.25	205	106	20	41	40	19 700	20 100	1.2
10	2.25	205	106	44	45	39	21 700	19 600	1.3
11	2.25	205	106	44	39	36	18 800	18 000	1.5
12	2.25	205	106	44	35	30	16 900	15 600	1.5
13	2.25	511	281	4	20	18	24 000	22 500	1.2
14	2.20	511	281	8	32	30	38 400	38 000	1.2
15	2.20	511	281	45	43	38	51 600	48 500	1.3
16	2.20	511	281	97	43	35	51 600	46 500	1.5

[a] Measured by gas chromatography analysis. [b] Measured by gravimetry on precipitated polymer. [c] Theoretical number-average molar mass calculated from (monomer conversion) × 235 × ($[M]_0/[I]_0$). [d] Experimental number-average molar mass measured by size exclusion chromatography (see Experimental Part). [e] Molar mass distributions calculated from size exclusion chromatography traces. [f] Initiation by "seeds" prepared without DMF in 1 h (see Experimental Part). [g] Initiation by "seeds" prepared without DMF in 10 h (see Experimental Part).

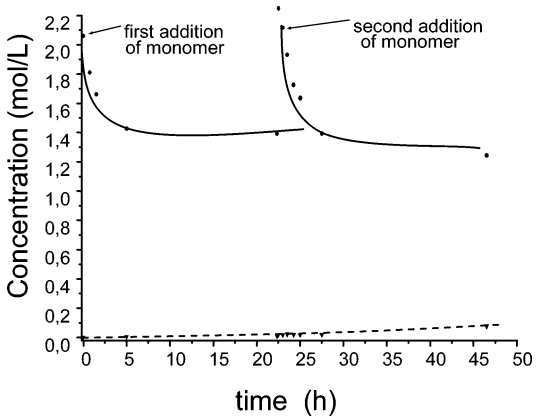


Figure 4. Variations of the concentration of monomer **1** (D_2D_{NMe}) and cyclosiloxazane **2** (D_3D_{NMe}) vs time, during a polymerization initiated by benzyllithium (BzLi), in toluene, at 30 °C with addition of dimethylformamide (DMF); $[M]_0 = 2.25$ mol/L, $[BzLi]_0 = 0.020$ mol/L, $[DMF]_0 = 1.20$ mol/L. ●: concentration of D_2D_{NMe} (**1**); ▼: concentration of D_3D_{NMe} (**2**).

process can be separated from normal propagation which allows the synthesis of polysiloxazanes with controlled architectures.

Equilibrated Polymerization. The incomplete monomer conversion whatever the experimental conditions of the polymerization can be assigned either to a termination process or to an equilibrated polymerization. As shown in Figure 4, upon a new addition of monomer **1** on an active species solution, the monomer consumption starts again with the same initial rate. This confirms that active species are stable over a long period of time (20 h) and that the polymerization of monomer **1** is equilibrated (eq 1).

$$\sim\!\!\sim M_n^* + M \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} \sim\!\!\sim M_{n+1}^* \qquad K_e = k_p/k_{-p} \tag{1}$$

Assuming that for polymers $[M_n^*] = [M_{n+1}^*]$, $K_e = 1/[M_e]$, at equilibrium:

$$\log_e(1/[M]_e) = \log_e(K_e) = -\Delta H^0_p/RT + \Delta S^0_p/R \tag{2}$$

Equilibrium monomer concentrations ($[M_e]$) were determined at various temperatures ranging from −20 to 90 °C. The plot of $\log_e(K_e)$ vs $1/T$ is linear (Figure 5), and thus the usual relation (eq 2) for equilibrium polymerization[23] is verified in the entire range of temperatures explored. The corresponding enthalpy and entropy of polymerization are $\Delta H^0_p = -4.5 \pm 0.2$ kJ/mol and $\Delta S^0_p = -18 \pm 5$ J/(mol K), and the ceiling temperature is −23 °C (with $[M_e] = 1$ mol/L). The polymerization enthalpy value of monomer **1** is lower than that reported for the analog hexamethylcyclotrisiloxane D_3 ($\Delta H^0_p = -23.4$ kJ/mol),[24] which indicates that, due to the presence of a nitrogen atom in the ring, monomer **1** is less strained than D_3. Contrarily, the polymerization entropy value of **1** is higher than that of D_3 ($\Delta S^0_p = -3$ J/(mol K)),[24] which agrees with polysiloxazane chains more rigid (less looped) than polysiloxane chains due to the replacement of a [SiO] unit by a [SiN] one.[7]

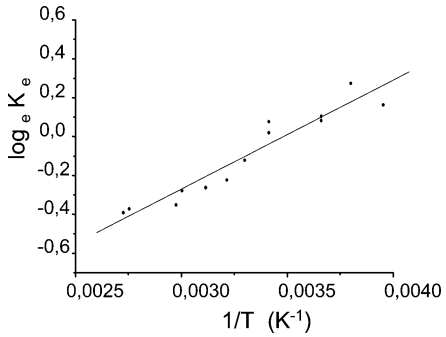


Figure 5. Variations of $\log_e K_e$ with $1/T$ for the polymerization of monomer **1** initiated by benzyllithium (BzLi), in toluene, with addition of dimethylformamide (DMF); $[M]_0 = 2.2$ mol/L, $[BzLi]_0 = 0.02$ mol/L, $[DMF]_0 = 1.2$ mol/L.

Kinetics of Polymerization. Several polymerizations of D_2D_{NMe} **1**, initiated by BzLi, were performed at 30 °C, in toluene. Since the polymerization is equilibrated, the overall rate of polymerization depends on both the propagation and the depropagation rates (eq 3). Assuming that the reaction is first-order relative to monomer concentration as usual in anionic chain polymerizations, eq 3 can be transformed in eq 4.

$$-d[M]/dt = R_p - R_{-p} = k_p(app)[M][DMF]^\beta[M_n^*]^\gamma - k_{-p}(app)[DMF]^\beta[M_n^*]^\gamma \tag{3}$$

So, with $k_p/k_{-p} = 1/[M_e]$: $-d[M]/dt = k_p(app)[DMF]^\beta[M_n^*]^\gamma$-

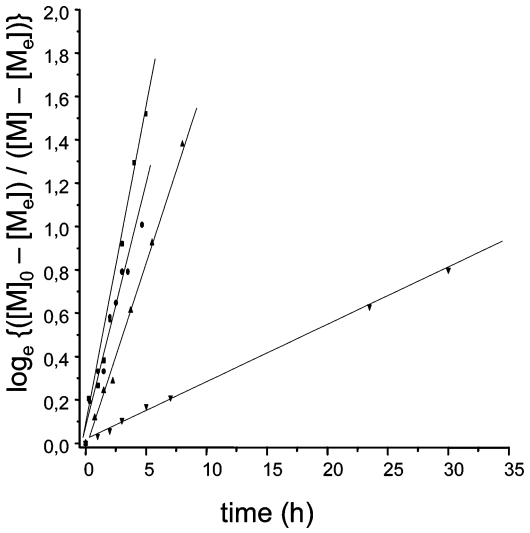


Figure 6. Variations of $\log_e(([M]_0 - [M]_e)/([M] - [M]_e))$ vs time for the polymerization of monomer **1** at 30 °C, initiated by benzyllithium (BzLi), in toluene, with dimethylformamide (DMF); $[M]_e = 1.13$ mol/L; ■: $[M]_0 = 1.98$ mol/L, $[DMF]_0 = 1.21$ mol/L, $[BzLi]_0 = 0.036$ mol/L; ●: $[M]_0 = 1.71$ mol/L, $[DMF]_0 = 1.19$ mol/L, $[BzLi]_0 = 0.038$ mol/L; ▲: $[M]_0 = 2.20$ mol/L, $[DMF]_0 = 1.21$ mol/L, $[BzLi]_0 = 0.004$ mol/L; ▼: $[M]_0 = 2.03$ mol/L, $[DMF]_0 = 0.20$ mol/L, $[BzLi]_0 = 0.040$ mol/L.

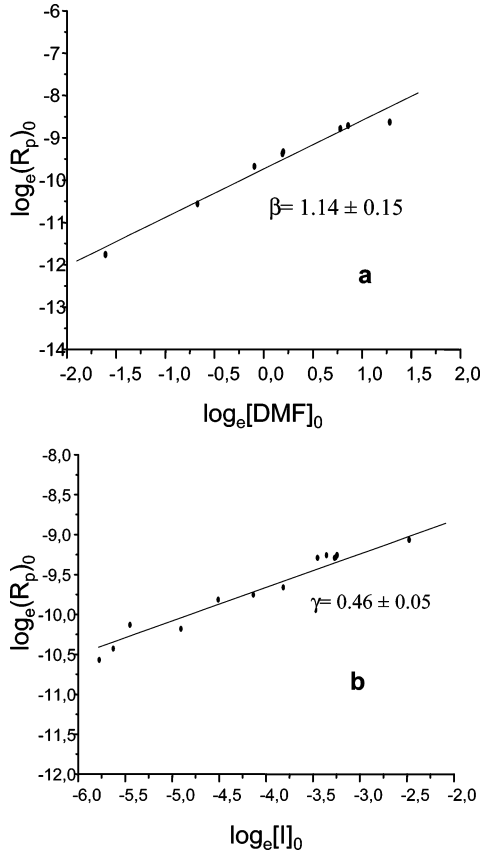


Figure 7. Variations of the initial rate of reaction $\log_e((R_p)_0)$ for the polymerization of monomer **1** in toluene at 30 °C, initiated by benzyllithium (BzLi) in the presence of dimethylformamide (DMF), vs (a) $\log_e[DMF]_0$ with $[BzLi]_0 = [I]_0 = 0.038$ mol/L and (b) $\log_e[BzLi]_0 = \log_e[I]_0$ with $[DMF]_0 = 1.20$ mol/L.

$([M] - [M]_e)$, and after integration

$$\log_e\{([M]_0 - [M]_e)/([M] - [M]_e)\} = k_p(\text{app})[DMF]^{\beta}[M_n^*]^{\gamma}t \quad (4)$$

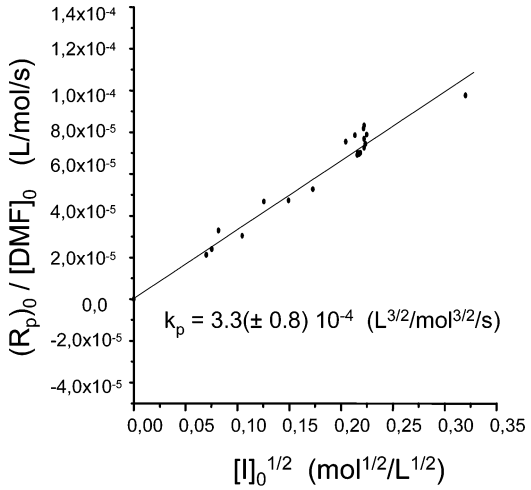


Figure 8. Variations of the initial rate of polymerization ($(R_p)_0$) vs initial concentration of benzyllithium ($[I]_0$), for the polymerization of monomer **1,** at 30 °C, initiated by benzyllithium in toluene, with addition of dimethylformamide (DMF).

$(R_p) = d(\log_e\{([M]_0 - [M]_e)/([M] - [M]_e)\})/dt = (-d[M]/dt)(1/([M] - [M]_e))$. So, $(R_p) = k_p(\text{app})[DMF]^{\beta}[M_n^*]^{\gamma} = k_p(\text{app})[DMF]^{\beta}[I]_0^{\gamma}$ assuming $[M_n^*] = [I]_0$.

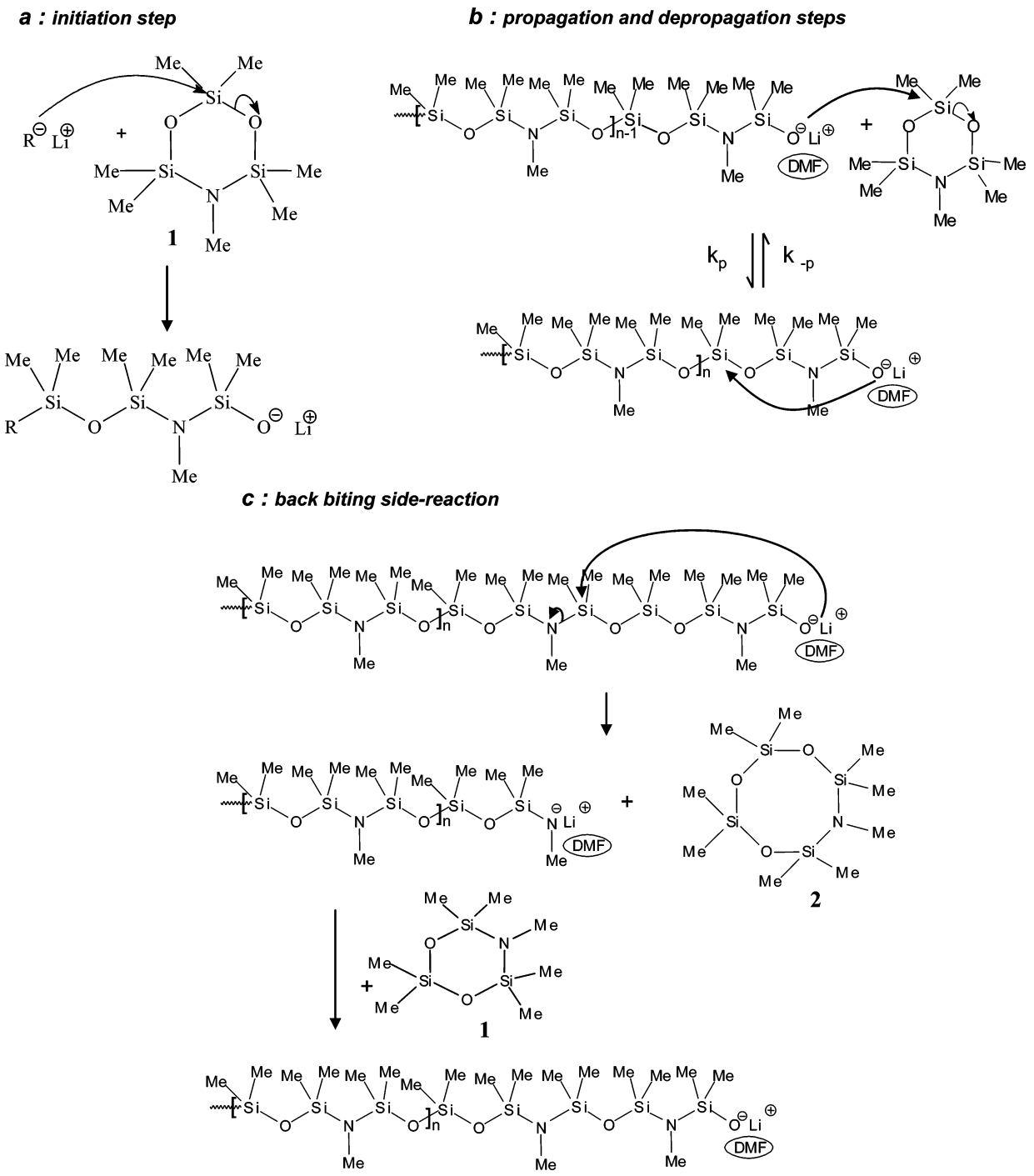
The experimental variations of $\log_e\{([M]_0 - [M]_e)/([M] - [M]_e)\}$ vs time (eq 4) are straight lines, which confirms the first order in monomer and corroborates both the fast initiation (compare to propagation and depropagation) and the stability of active centers (Figure 6). On plotting $\log_e(R_p)_0$ ($(R_p)_0$ representing the initial slope of these lines) as a function of $\log_e[I]_0$ and $\log_e[DMF]_0$ straight lines are also obtained (Figure 7). The respective slopes are $\beta = 1.1 \pm 0.1$ and $\gamma = 0.46 \pm 0.05$, which shows that, within experimental error, kinetic order relative to DMF is around 1 and that relative to active species is around 1/2. The corresponding average value of the apparent rate constant of polymerization is $k_p(\text{app}) = (3.3 \pm 0.8) \times 10^{-4}$ $\text{mol}^{3/2}/(\text{L}^{3/2}\ \text{s})$ (Figure 8).

Since initiation is fast and quantitative, the fractional value of the kinetic order relative to initiator concentration $[I]_0$ anticipates the existence of only one type of active species. Taking into account the kinetic order relative to DMF (close to 1), the high effectivity of the ion−ion interactions of silanolate anions,[22] and the facility of the Li^+ ion to be complexed by DMF, the most probable structure of these active species is that of ion pairs externally solvated by DMF, in equilibrium with inactive aggregated ion pairs, presumably dimers since the kinetic order value is around 1/2 (eq 5). Nevertheless, the treatment of kinetic data according to the method proposed by Penczeck and colleagues[25] does not agree with an aggregation number m of 2. This lets one suppose that the active species (unaggregated solvated ion pairs) concentration is not negligible (compare to aggregated ion pairs one) in the kinetic calculations and that the aggregation number is rather around 4 or more (agreement with Penczeck method is quite satisfactory within experimental error for $m = 4$).

$$(\sim\!\sim M_n^*)_m + \text{DMF} \rightleftarrows m(\sim\!\sim M_n^*, \text{DMF}) \quad (5)$$

Several depolymerizations of active polysiloxazane chains were also realized at 30 °C. Indeed, evaporating both the residual monomer and the solvents at the end of the equilibrium polymerization, polymeric active species have been isolated under vacuum. In the presence of a new addition of DMF and toluene, the depolymerization starts to give increasing amounts of monomer **1** until the equilibrium is reached ($[M_e] = 1.13$

Scheme 3. Mechanism of the Polymerization of 1 Initiated by Organolithium Compounds: (a) Initiation by Organolithium Compounds (RLi) in Toluene; (b) Propagation and Equilibrium Steps in Toluene in the Presence of Dimethylformamide (DMF); (c) Backbiting Reaction Leading to Cyclosiloxazane 2 and New Oxygen Anion Terminated Chains



mol/L at 30 °C). The corresponding apparent rate of depolymerization is $k_{-p}(\text{app}) = (2.8 \pm 0.5) \times 10^{-4}$ mol$^{5/2}$/(L$^{5/2}$ s), which is not too far, within experimental error, from the value calculated from $k_{-p} = [M_e]k_p$ with $[M_e] = 1.13$ mol/L and $k_p = (3.3 \pm 0.8) \times 10^{-4}$ mol$^{3/2}$/(L$^{3/2}$ s), which is $k_{-p}(\text{app}) = (3.7 \pm 0.8) \times 10^{-4}$ mol$^{5/2}$/(L$^{5/2}$ s).

Mechanism of Polymerization. So, the anionic polymerization of monomer **1** (D_2D_{NMe}) is a controlled process which gives, under specific conditions, poly(*N*-methyloctamethylsiloxazane) with well-defined and regular structure. With specific and controlled additions of DMF on the "seeds" obtained at the end of the quantitative initiation step (Scheme 3a), the propagation of the polymerization proceeds on ion pairs, externally complexed by DMF, in equilibrium with aggregated ion pairs. Simultaneously, intramolecular reactions of the terminal oxygen anions on to a specific silicon atom of the polymer chains give an equilibrium with monomer **1** and new chains with lower molar masses (Scheme 3b). The same type of backbiting reaction led to very few amounts of cyclosiloxazane **2** (D_3D_{NMe}) and active polymer chains terminated by a nitrogen anion (Scheme 3c). As previously reported,[10] this nitrogen anion can react with a siloxane unit of the monomer **1** to give new active oxygen anion (Scheme 3c). Usually other side reactions such as intermolecular redistributions (chain tranfer and randomization) only happen after the end of polymerization and can thus be easily avoided. This situation

is different from that reported for anionic ring-opening polymerization of hexamethylcyclotrisiloxane D_3 which gives, at equilibrium, except at very high temperature, a very low amount of initial monomer.[22] This might be related to the low polymerization enthalpy of monomer **1** compared to that of D_3.

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