

Review

# Ring-opening polymerization of nitrogen-containing cyclic organosilicon monomers<sup>1</sup>

M. Bouquey, C. Brochon, S. Bruzaud, A-F. Mingotaud, M. Schappacher, A. Soum \*

*Laboratoire de Chimie des Polymères Organiques, Unité Mixte de Recherche CNRS-ENSCP, Avenue Pey-Berland, 33402 Talence Cédex, France*

Received 12 January 1996

## Abstract

Ring-opening polymerization of nitrogen-containing cyclic organosilicon monomers such as cyclosilazanes, cyclosiloxazanes and cyclocarbosilazanes has been investigated. These monomers can be polymerized through both cationic and anionic processes. Only the latter allows high level of control of the polymer architectures. The polymers obtained exhibit promising properties, particularly higher thermal stability and mechanical resistance than polysiloxanes.

**Keywords:** Silicon; Silazanes; Siloxazanes; Carbosilazanes; Polymerization; Polysilazanes; Polysiloxazanes

## 1. Introduction

Since the first preparation of silicones [1], research on organometallic polymers (semi-inorganic polymers) has steadily grown. Most of the studies have been devoted to the synthesis of suitable polysiloxanes and evaluation of their physical properties and potential applications [2]. A new area of activity was initiated in the 1980s when polycarbosilanes were transformed into SiC fibers for the first time [3]. Since then, the number of studies on polysilanes, polycarbosilanes and polysilazanes has increased rapidly [4,5]. In addition to their potential applications as precursors to ceramic materials, these silicon-containing polymers exhibit unusual physical properties (particularly electronic, thermal and mechanical properties) which have been little investigated except in the case of polysilanes [6] and polysiloxanes [2].

The most usual methods of synthesizing silicon-based polymers involve condensations between organosilicon molecules. Generally (except for polysiloxanes and polysilanes), the resulting products from these routes

are a mixture of cyclic compounds, linear oligomers and polymers with, in some cases, a rather complicated structure and a relatively low stability towards oxidation or hydrolysis [5–8]. Therefore, until recently, these polymers have only been considered as useful ceramic precursors [8].

For a long time, development of the ring-opening polymerization of cyclic organosilicon monomers was limited to generation of high molar mass polysiloxanes because of the difficulties of synthesizing the monomers. Recently, this process was reinvestigated and it was demonstrated that under certain conditions, silicon-based polymers other than polysiloxanes (polysilanes, polysilazanes) with high molar mass and highly controlled architecture, can be obtained [9,10].

In the present review, we place the emphasis on some of our own findings that reveal the potential of the ring-opening process for making new organosilicon polymers with controlled structures. First we summarize the various routes used to synthesize three types of cyclic monomer: the cyclodisilazanes (1), cyclosiloxazanes (2) and cyclocarbosilazanes (3). Then, we discuss their behaviour in both anionic and cationic ring-opening polymerizations. Finally, we describe briefly some of the main characteristics and properties of the corresponding polymers.

\* Corresponding author.

<sup>1</sup> Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organosilicon chemistry.

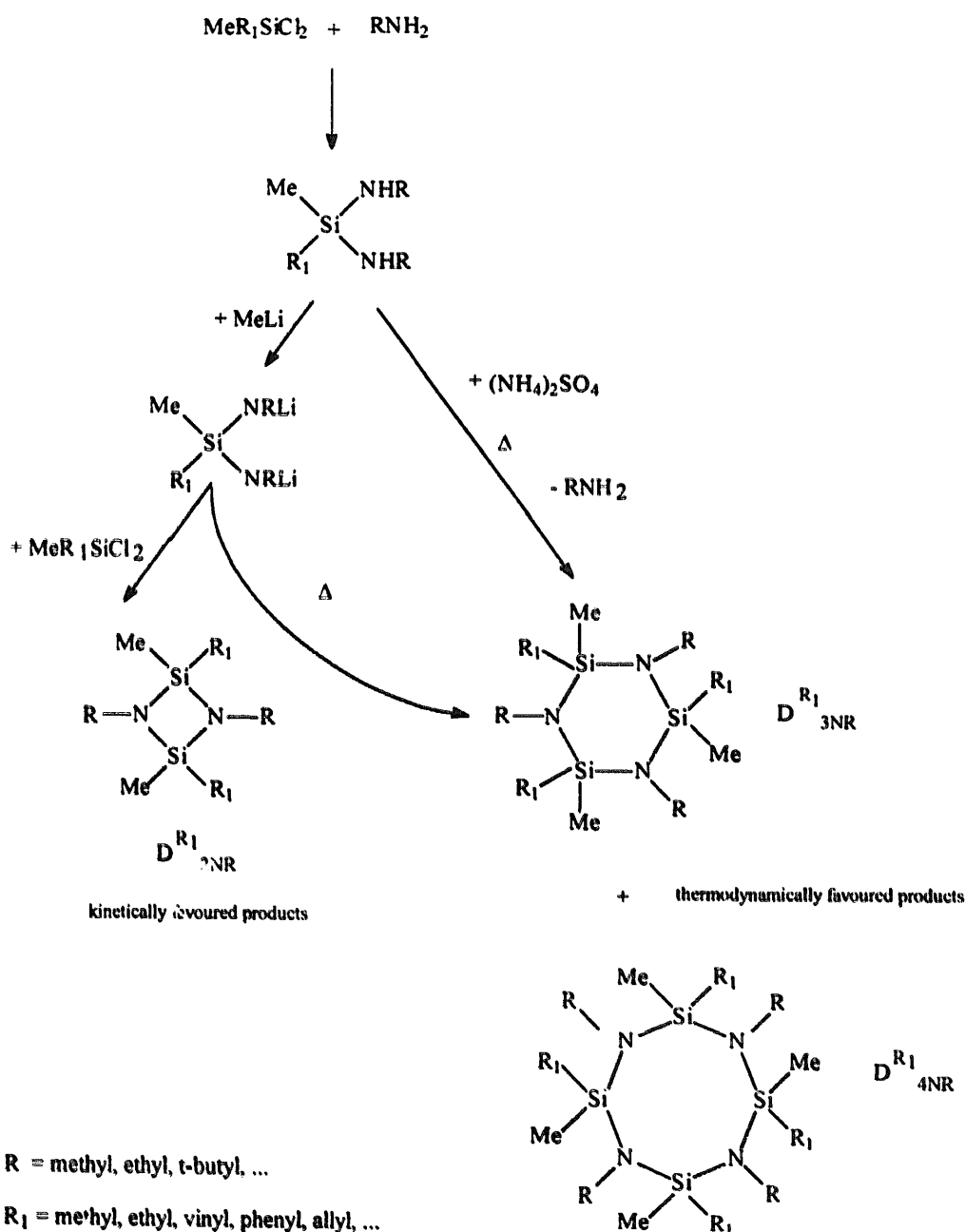
## 2. Synthesis of monomers

### 2.1. Cyclodisilazanes

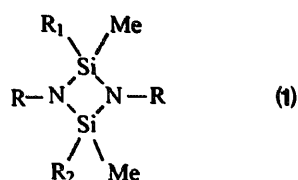
There have been several reports concerning the synthesis of cyclodisilazanes [11–13]. In these syntheses a bis(amino)silane, obtained by treating an amine with a dichlorosilane, is lithiated with RLi; the four-membered ring is then formed by treatment of the resulting dilithiumsilylamide with another appropriate dichlorosilane (Scheme 1). According to Seyferth et al. [11], after the mixture of amide and dichlorosilane in hexane has been

refluxed for 24 h, the crude product can be distilled to yield 65% of cyclodisilazane (1). In our hands such a process led to both the cyclodisilazane polymerization and formation of higher silazane rings.

Consequently, we reinvestigated the synthesis of several cyclodisilazanes in order to optimize both the selectivity and the yield of this method [14]. By controlling the three factors that favour cyclodisilazane formation, the yield of (1) is increased from 20% to 60–75% depending on the substituents on silicon; these factors are a low concentration of reagents, which facilitates intramolecular cyclization, a low temperature and a



Scheme 1. Illustration of synthesis of cyclodisilazanes as described in Refs. [11–14].



R = Methyl, Ethyl, isoPropyl, t-Butyl, Phenyl,...

R<sub>1</sub> = R<sub>2</sub> = Methyl

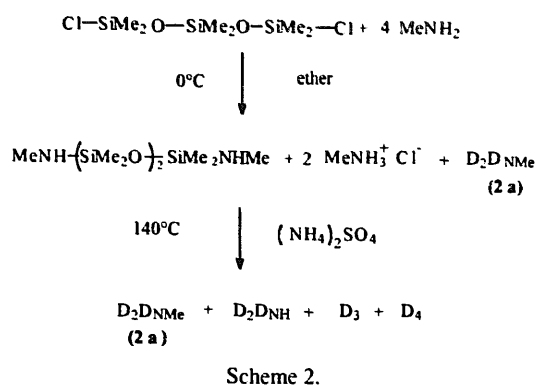
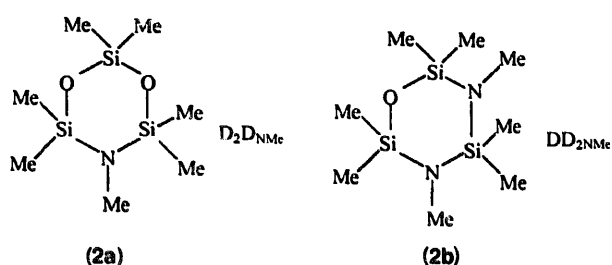
D<sub>2</sub>NR

R<sub>1</sub> = R<sub>2</sub> = Vinyl or Ethyl

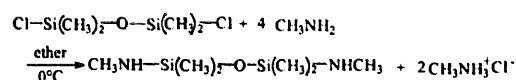
D<sup>R</sup><sub>1</sub><sub>2</sub>NR

R<sub>1</sub> = Methyl, R<sub>2</sub> = Vinyl, Allyl, Ethyl or Phenyl

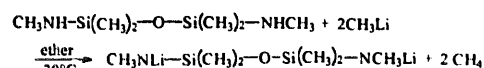
D<sup>R</sup><sub>1</sub>NR D<sub>NR</sub>



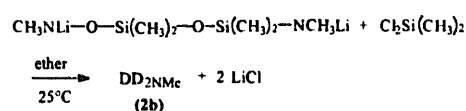
Step 1 :



Step 2 :



Step 3 :



Scheme 3.

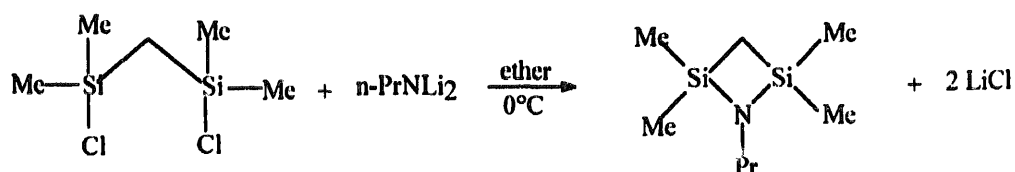
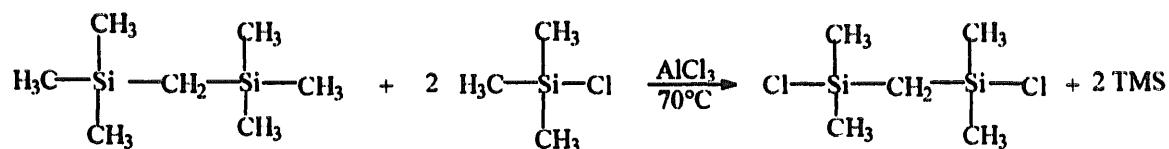
short reaction time, which minimize the formation of the thermodynamically favoured products D<sup>R</sup><sub>1</sub><sub>NR</sub> and D<sup>R</sup><sub>1</sub><sub>NR</sub> (Scheme 1).

## 2.2. Cyclosiloxazanes

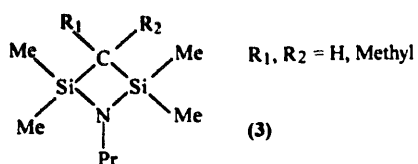
The cyclosiloxazane (2a) was synthesized by the published method [15,16] involving reaction of 1,3-dichlorohexamethyltrisiloxane with methylamine at low temperature in diethyl ether (Scheme 2). Along with the

formation of bis(methylamino)hexamethyltrisiloxane, there is partial cyclization into D<sub>2</sub>D<sub>NMe</sub>. The yield of (2a) is increased to 85% by heating the reaction mixture at 140°C for several hours in the presence of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The monomer (2a) can be recovered and purified by distillation under vacuum (b.p. = 68°C/30 mm Hg).

The cyclosiloxazane (2b) was prepared in a three-step reaction by the method used for the cyclosilazanes



Scheme 4.



(Scheme 3). The first step involves the formation of bis(methylamino)tetramethyldisiloxane by reaction of dichlorotetramethyldisiloxane with methylamine. The main product is purified by distillation under vacuum (yield, 42%; b.p. = 70°C/25 mm Hg); this is then treated with a stoichiometric amount of methyl lithium to give the corresponding dilithium amide. The reaction of the lithium salt with dimethyldichlorosilane, at room temperature, under high dilution conditions, gives (2b) (yield, 40%; b.p. = 60°C/0.1 mm Hg).

### 2.3. Cyclocarbosilazane

The cyclocarbosilazane (3) was obtained by reaction of the bis(chlorodimethylsilyl)methane [17] with the dilithium salt of *n*-propylamine [18], at low temperature under high dilution conditions in ethyl ether (Scheme 4). The monomer can be recovered and purified by distillation under vacuum (yield, 60%; b.p. = 50°C/45 mm Hg).

## 3. Ring-opening polymerizations and copolymerizations

### 3.1. Polymerization of cyclodisilazanes

Although whatever the R, R<sub>1</sub>, R<sub>2</sub> substituents, four-membered cyclodisilazanes (1) are highly strained quasi-planar rings, only those with methyl groups on the nitrogen atoms can be ionically polymerized; other *N*-alkyl or *N*-aryl cyclodisilazanes give either oligomers or undergo no reaction. The following order of reactivity for the ring-opening process has been observed: D<sub>2NMe</sub> ≫ D<sub>2NEt</sub> > D<sub>2NisoPr</sub> ≫ D<sub>2NtertBu</sub> ~ D<sub>2NPh</sub>.

Thus, the structure of the substituent on nitrogen appears to play a crucial part in the polymerization. This is not yet completely understood, since the polymerization aptitude of a monomer depends not only on its reactivity and that of active centres but also on the stability of the corresponding polymer (which is directly related to the intramolecular steric interactions in the chain). For example, with bulky groups on nitrogen atoms, the cyclodisilazane four-membered ring is stabilized [12] (i.e. less reactive) and, furthermore, the formation of linear hindered chains is highly improbable. This might account for the fact that poly(D<sub>2NtertBu</sub>) and

poly(D<sub>2NPh</sub>) cannot be formed. Moreover, although the electron releasing inductive effect of the hindered alkyl groups increases the electronic density on the nitrogen, the steric hindrance is so important that accessibility to this atom is reduced and thus the reactivity of the ring. The strong effect of the substituent on nitrogen on the ring-opening process is consistent with the localization of the charge of the active centres (which propagate the reaction) on the nitrogen atom, as has been demonstrated for both cationic and anionic polymerizations [19,20].

*N*-Methylcyclodisilazanes (4) can be polymerized by both cationic and anionic mechanisms.

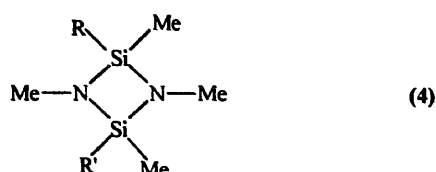
The cationic polymerization (initiated by methyl triflate, the best initiator among those tested), carried out in polar solvents at room temperature, is very fast and leads to both polymer (the highest value of  $\bar{M}_n$  reached is 30 000) and cyclic oligomers (essentially the corresponding six- and eight-membered rings). This fast and quantitative polymerization is followed by a slow and irreversible depolymerization which transforms the polymer exclusively into the six-membered ring species which appears to be the thermodynamically stable product.

Thus, synthesis of polysilazane with controlled architecture through cationic ring-opening polymerization is difficult. Moreover, owing to the presence at the end of the chain of a quaternary ammonium salt that is difficult to neutralize, the polymer is not stable over a long period of time and spontaneously depolymerizes. Although the lowering of the polymerization temperature drastically decreases the occurrence of side-reactions in the cationic mechanism, the anionic route appears more reliable for controlling the architecture of polysilazanes.

The anionic polymerizability was first reported by Seyferth et al. [11] who prepared linear oligomers ( $\bar{M}_n \approx 3000$ ) of poly(hexamethylcyclodisilazane) showing good agreement between theoretical and experimental molar masses.

In our work, various *N*-methylcyclodisilazanes (4) were polymerized in the presence of various organosodium and organolithium initiators in both polar and non-polar solvents (toluene, dioxane, THF) [20]. In all experiments the monomer conversion is quantitative and the polymerization exhibits all the characteristics of a living polymerization. In particular:

- (1) polymers with molar mass as high as 100 000 have been prepared;
- (2) the theoretical molar mass  $\bar{M}_n$  (calculated from the  $[M]_0/[I]_0$  ratios) and experimental mass are in good agreement (within the experimental error), and molar mass distributions are narrow ( $\bar{M}_w/\bar{M}_n \sim 1.1$ );
- (3) contrary to what is observed for the cationic process, there is no formation of cyclic compounds resulting from end-biting or back-biting reactions either at the beginning or during the polymerization.



R = R' = Methyl

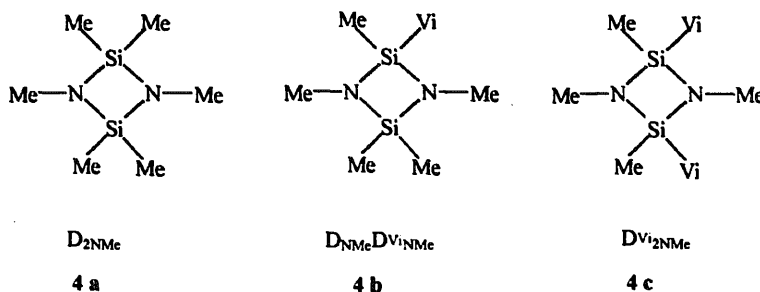
$D_{2\text{NMe}}$

R = R' = Vinyl or Ethyl

$D_{2\text{NMe}}^{\text{R}}$

R = Methyl, R' = Vinyl, Ethyl or Phenyl

$D_{\text{NMe}}^{\text{R}} D_{\text{NMe}}$



The surprising absence of intra- and intermolecular transfer reactions, a behaviour much different from that observed with cyclosiloxanes, can certainly be attributed to a lower flexibility of polysilazane than of polysiloxane chains and, overall, to the higher steric hindrance around the nitrogen than the oxygen. This is corroborated by the occurrence of side-reactions when [Si–N] and [Si–O] bonds are both involved, as in the polymerization of cyclosiloxazanes (2).

Comprehensive kinetic studies demonstrate that the rate constant of polymerization  $k_p$  increases with both the temperature of reaction and the presence of polar or complexing additives (THF, dioxane, TMEDA, ...). They also indicate that the values of  $k_p$  vary with the nature of the substituents on silicon:

$$k_p(D_{2\text{NMe}}^{\text{Vi}}) > k_p(D_{\text{NMe}}^{\text{Vi}} D_{\text{NMe}}) > k_p(D_{2\text{NMe}}) \\ > k_p(D_{\text{NMe}}^{\text{Et}} D_{\text{NMe}}) > k_p(D_{\text{NMe}}^{\text{Ph}} D_{\text{NMe}})$$

This reactivity order is difficult to explain exclusively on the basis of steric hindrance, and is certainly more strongly related to the electronic effects of the substituents. Theoretical calculations in progress on the monomer structures should be very useful in answering this question [21].

The living character of the anionic ring-opening polymerization of *N*-methyl cyclodisilazanes, which induces a high control of the polymer architectures, enables the synthesis of block and random copolymers based on both *N*-methyl silazane units (with various substituents on the silicon atom) and siloxane units. The determination of the propagation rate constant for each monomer, and the reactivity ratios in the case of ran-

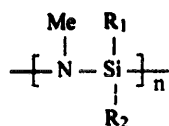
dom copolymerization, facilitates the prediction of the copolymer compositions (in random copolymers) and the length of the blocks (in block copolymers); this composition influences significantly the thermal and mechanical properties of the corresponding materials.

Block copolymerizations of various *N*-methyl cyclodisilazanes with some common vinyl monomers have also been achieved (owing to the high difference of reactivity between vinyl monomers and cyclodisilazanes, only block copolymers can be obtained). For example, block copolymers of styrene and  $D_{\text{NMe}}^{\text{Vi}} D_{\text{NMe}}$  with a well-controlled linear structure exhibit interesting phase separation behaviour.

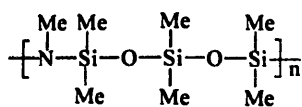
### 3.2. Polymerization of cyclosiloxazanes and cyclocarbosilazanes

Like cyclosiloxanes and cyclodisilazanes, monomers (2a) and (2b) have been polymerized by both anionic and cationic processes. However, when initiated by triflic acid (TfOH) or its methyl ester (TfOMe), the cationic polymerization is not very successful and rapidly gives a mixture of low molar mass products without any evidence of polymer formation.

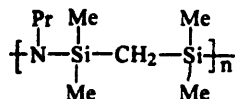
The best control of the ring-opening process has been obtained in anionic polymerization initiated by both organolithium (*n*-BuLi, BenzylLi) and organopotassium ( $\text{Me}_3\text{SiOK}$ ,  $\text{Me}_3(\text{OSiMe}_2)_4\text{OK}$ ) compounds, in the presence of polar additives (THF, DMF), at temperatures ranging from 30 to 120°C. Under these conditions, linear polymers with molar mass as high as 150 000 can be obtained. Nevertheless, formation of the polymer is



(5)



(6)

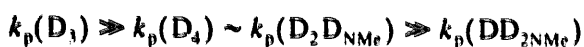


(7)

 $\text{R}_1, \text{R}_2 = \text{Me, Et, Ph, Vi}$ 

always accompanied by that of a single cyclic compound, which has been identified by GLC-MS as the corresponding eight-membered ring species. (The yield of polymer ranges from 40 to 70% depending on experimental conditions.) These results are analogous to those reported earlier by Lasocki and coworkers [22,23] for the anionic ring-opening polymerization of *N*-phenyl cyclosiloxanes.

So, the anionic ring-opening process of cyclosiloxanes appears analogous to that of cyclosiloxanes from the general point of view. The main difference appears to be in the values of the rate constants of propagation, which decrease in the order:



In contrast, at present, cyclocarbosilazane (3) can only be polymerized by the cationic mechanism, since in the presence of strong bases (i.e. organolithium initiators) there are side-reactions at the methylene group (abstraction of a proton).

The general behaviour is rather similar to that observed in cationic polymerization of cyclodisilazane (1a) but the reactivity (evaluated from the value of the rate constant  $k_p$ ) is approximately five times lower.

#### 4. Properties of polymers

NMR Spectroscopic studies ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{15}\text{N}$ ) of polymers (5), (6) and (7) demonstrate the high control of chain architecture via the ring-opening process. They confirm the expected linear structure and clearly show the absence of any branching at nitrogen or silicon or through the vinyl groups [10,24].

Polysiloxazanes (6) and polycarbosilazanes (7) are viscous liquids whereas polysilazanes (5) are either

white solids or viscous liquids, depending on the substituents on silicon.

In contrast to conventional polysilazanes, these polymers are stable in air. This is certainly due to the substitution at the nitrogen atom. For example, there is no detectable change in the molar mass or in the peak assignable to  $[\text{SiMe}_2\text{---O}]$  when the polymer is stored for several months (in the solid state or in THF solutions). Nevertheless, in the presence of strong acids (HCl, HI, ...), a breakdown of the polymer chain, with  $\text{MeNH}_2$  elimination, can slowly occur.

All the polymers exhibit a glass transition temperature  $T_g$  below ambient temperature (from  $-120^\circ\text{C}$  for (6) to  $-50^\circ\text{C}$  for (5)) and a melting temperature  $T_m$ , for the semi-crystalline polysilazanes derived from monomers (2a), (2b) and (2c), ranging from 100 to  $230^\circ\text{C}$  [24].

As previously reported, the  $[\text{Si---N}]$  bonds are more thermally stable than the  $[\text{Si---O}]$  bonds [22,23,25]. This is confirmed by TGA analyses which reveal an increase in the temperature of half-weight loss with the proportion of  $[\text{Si---N}]$  bonds on going progressively from polysiloxanes towards polysilazanes ( $50$  to  $100^\circ\text{C}$ , depending on the composition).

Insertion of  $[\text{Si---N}]$  units in  $[\text{Si---O}]$  chains also increases the value of the polymer viscosity, which shows a Newtonian behaviour across all the shear rate domain ( $\eta = 0.5 \text{ Pa s}$  for polysiloxane;  $\eta = 2 \text{ Pa s}$  for polysiloxazanes;  $\eta = 10^3 \text{ Pa s}$  for polysilazane;  $\bar{M}_n = 16\,000$ ;  $T = 25^\circ\text{C}$ ). This increase in viscosity is consistent with the increase in the storage modulus value  $E'$  at  $25^\circ\text{C}$ , which is ten times higher for polysilazanes than for polysiloxanes, and confirms the expected lower flexibility of the  $[\text{Si---N}]$  compared with the  $[\text{Si---O}]$  chains.

#### 5. Conclusions

Ring-opening polymerization of nitrogen-containing cyclic organosilicon monomers has good potential for controlling the architecture of various silicon-based polymer chains. For either homopolymerization or copolymerization, the number of  $[\text{SiR}_1\text{R}_2\text{---O}]$ ,  $[\text{Si---R}_1\text{R}_2\text{---NMe}]$  or  $[\text{SiR}_1\text{R}_2\text{---CH}_2]$  units polymerized can be controlled, thus giving a large versatile class of new silicon-based materials from polysiloxanes to polysilazanes with potential properties that have not yet been fully explored.

#### References

- [1] A. Ladenburg, *Annalen*, 164 (1872) 300.
- [2] E.G. Rochow, *Silicon and Silicones*, Springer, Berlin, 1987.
- [3] S. Yajima, Y. Hasegawa, J. Hayashi and M. Imura, *J. Mater. Sci.*, 13 (1978) 2569.

- [4] R.M. Laine, Y.D. Blum, D. Tse and R. Glaser, *Inorg. Organomet. Polym.*, ACS Symp. Ser., 360 (1988) 124.
- [5] D. Seyferth, *Inorg. Organomet. Polym.*, ACS Symp. Ser., 360 (1988) 21.
- [6] J.E. Mark, H.R. Allcock and R. West, *Inorganic Polymers*, Prentice Hall, 1992 p. 186.
- [7] B.J. Aylett, *Organomet. Chem. Rev.*, 3 (1968) 151.
- [8] C. Biran, M. Birot, J.P. Pillot and J. Dunogues, *Chem. Rev.*, 95 (1995) 1443.
- [9] M. Crypyrk, Y. Gupta and K. Matyjaszewski, *J. Am. Chem. Soc.*, 113 (1991) 1046.
- [10] E. Duguet, M. Schappacher and A. Soum, *Macromolecules*, 25 (1992) 4835.
- [11] D. Seyferth, M.J. Schwark and M.R. Stewart, *Organometallics*, 8 (1989) 1980.
- [12] W. Fink, *Angew. Chem. Int. Ed. Engl.*, 5 (1966) 760.
- [13] K.A. Andrianov and L.M. Khananashvili, *Organomet. Chem. Rev.*, 2 (1967) 141.
- [14] E. Duguet, M. Schappacher and A. Soum, *J. Organomet. Chem.*, 458 (1993) 9.
- [15] J.G. Murray and R.K. Griffith, *J. Org. Chem.*, 29 (1964) 6419.
- [16] R.L. Elliot and L.W. Breed, *Inorg. Chem.*, 4 (1969) 1455.
- [17] H. Ishikawa, M. Kumada and H. Sakurai, *J. Organomet. Chem.*, 23 (1970) 63.
- [18] M. Rivière-Baudet, P. Rivière, J. Satgé and G. Lacrampe, *J. R. Neth. Chem. Soc.*, 98 (1979) 42.
- [19] E. Duguet and M. Schappacher, A. Soum, *Polym. Int.*, 33 (1994) 129.
- [20] S. Bruzard and A. Soum, *Macromol. Chem. Phys.*, 197 (1996) in press.
- [21] H. Fournier, A. Fritsch, M.T. Rayez, J.C. Rayez and A. Soum. submitted to *J. Organomet. Chem.*
- [22] Z. Lasocki and M. Witekowa, *J. Macromol. Sci. Chem. A*, 11 (1977) 457.
- [23] Z. Lasocki, B. Dejak, J. Kulpinski, E. Lesniak, S. Piechucki and M. Witekowa, *Inorg. Organomet. Polym.*, ACS Symp. Ser., 360 (1988) 166.
- [24] A. Soum, L. Billon, M. Bouquey, S. Bruzard, E. Duguet and M. Schappacher, in J.C. Salamone (ed.) *The Polymeric Materials Encyclopedia*, 1996, p. 1891.
- [25] W. Fink, *J. Paint Technol.*, 42 (1970) 221.