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High Molar Mass Polysilazane: A New Polymer

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ABSTRACT: In this work, a study of the ionic ring-opening polymerization of cyclosilazane monomers is carried out. Various cyclosilazanes have been reacted with both anionic and cationic initiators. These reactions give either polymers or linear and cyclic oligomers, depending on the size of the ring and on the structure of both the nitrogen and the silicon substituents. Whereas cyclotrisilazanes and cyclotetrasilazanes give an equilibrated polymerization analogous to that observed with cyclosiloxanes, cyclodisilazanes with *tert*-butyl, isopropyl, or ethyl groups on the nitrogen only oligomerize. When the nitrogen substituent is a methyl group and for various silicon substituents, high molar mass polymers are obtained by both anionic and cationic processes. Moreover, the living character of the anionic polymerization is demonstrated. The polysilazanes are white crystalline polymers soluble in usual organic solvents.

Since polycarbosilanes were transformed into SiC fibers for the first time,[1] research on the synthesis of organometallic polymers, which are potential precursors to ceramic materials, has steadily grown. To give suitable ceramics in high yield, optimal precursors require several specifications:[2] high molar mass and/or branching to prevent volatilization, to reduce back-biting reactions and to facilitate the process; functional groups to make possible cross-linking just before pyrolysis; and low oxygen content to prevent crystallization of SiO_2, which reduces mechanical properties at high temperature.

In this field, polysilazanes are promising candidates as precursors to ceramics or fibers usable at very high temperature.[3,4] In the former routes to polysilazanes, much work has been done involving the ammonolysis and aminolysis of dichlorosilanes,[5,6] as well as the deamination or redistribution reactions of aminosilazanes.[7,8] The usual synthesis of polysilazanes is provided by reaction of ammonia or amines with dichlorosilanes. Generally, the resulting products are low molar mass cyclic or linear oligomers[3,4] which require further cross-linking via transamination,[9] dehydrocoupling reactions,[10] and hydrosilylation reactions.[11]

The ring-opening polymerization of cyclosilazanes is an old route to polysilazanes[9,12] which has been reinvestigated by several authors.[13-15] Particularly, Seyferth and coworkers[15] attempted to polymerize various cyclodisilazanes with alkyllithium. They only obtained low molar mass linear oligomers ($\bar{M}_n \leq 3000$).

Our interest in polysilazanes led us to study the polymerization of cyclodisilazanes. We have found that, under specific conditions, high molar mass polymers can be prepared either by anionic or by cationic ring-opening polymerization of such monomers.

Table I
Anionic Polymerizations of Cyclosilazanes Initiated by Organoalkali Salts[a]

monomer (M)	initiator (I)	[M]/[I]	time of polym, h	$\bar{M}_n$(exptl)
D_{3NMe} (**2a**)	MeLi	10	60	neither polymer nor oligomer
	t-BuLi	10	60	
	naphthalene–Na	20	60	residual monomer
$D_{2Nt\text{-}Bu}$ (**1a**)	MeLi	10	36	residual monomer
	naphthalene–Na	20	36	neither polymer nor oligomer
$D_{2Ni\text{-}Pr}$ (**1b**)	*t*-BuLi	10	60	residual monomer
	naphthalene–Na	40	17	neither polymer nor oligomer
D_{2NEt} (**1c**)	MeLi	10	20	residual monomer
	t-BuLi	10	20	oligomer
	naphthalene–Na	100	1	$\bar{M}_n \leq 2000$
D_{2NMe} (**1d**)	MeLi	10	8	4400
	t-BuLi	10	8	4200
	PhLi	10	8	4200
	naphthalene–Na	200	2	16000
	α-MeStyNa	10	4	4000

[a] Solvent, THF; temperature of polymerization, 25 °C; [M] = 1 mol·L^{-1}.

Polymerization of Cyclosilazanes

Various cyclosilazanes of general formulas **1**, **2**, and **3** were synthesized according to the method described by Fink and co-workers,[16] and their polymerization was initiated by several initiators (Tables I and II).

In anionic polymerization (Table I), contrarily to what is observed with cyclosiloxanes, cyclotrisilazanes **2a** and cyclotetrasilazanes **2b** do not polymerize (whatever the experimental conditions) whereas cyclodisilazanes **1** lead either to oligomers or to high molar mass polymers depending on the nitrogen substituent. Indeed, when cyclodisilazane monomers are $D_{2Nt\text{-}Bu}$ (**1a**), $D_{2Ni\text{-}Pr}$ (**1b**),

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Table II
Cationic Polymerizations of Cyclodisilazanes Initiated by Triflic Derivatives[a]

monomer (M)	initiator (I)	[M]/[I]	$\bar{M}_n$(exptl)
D_{3NMe} (**2a**)	CF_3SO_3Me	53	residual monomer
$D_{2Nt\text{-}Bu}$ (**1a**)	CF_3SO_3Me	53	residual monomer
$D_{2Ni\text{-}Pr}$ (**1b**)	CF_3SO_3Me	53	residual monomer
D_{2NEt} (**1c**)	CF_3SO_3Me	53	cyclic compounds with $n = 3$ and $n = 4$
D_{2NMe} (**1d**)	CF_3SO_3Me	53	16 800
		79	14 200
		192	10 100
	$CF_3SO_3SiMe_3$	141	18 000
$D^{Vi}{}_{NMe}D_{NMe}$ (**3a**)	CF_3SO_3Me	13	14 000

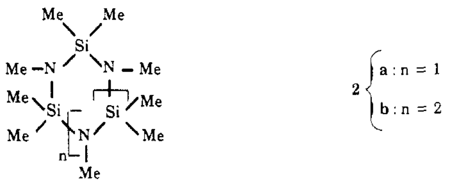
[a] Solvent, dichloroethane; [M] = 0.5 mol·L^{-1}; temperature, 30 °C; time, 30 min.

Table III
Anionic Polymerizations of N-Methylcyclodisilazanes Initiated by Organoalkali Salts[a]

monomer	[M]/[I]	$\bar{M}_n$(theor)	$\bar{M}_n$(exptl)[b]	$I = \bar{M}_w/\bar{M}_n$
$D^{Vi}{}_{NMe}D_{NMe}$ (**3a**)	100	37 200	34 000	1.1
	125	46 500	45 000	1.1
	140	52 080	48 000	1.2
	200	74 400	70 000	1.2
	250	93 000	100 000	1.3
$D^{Vi}{}_{2NMe}$ (**3b**)	95	18 700	19 000	1.3
	220	43 000	21 000	1.6[c]
	280	55 000	31 000	1.7[c]
D_{2NMe} (**1d**)	15	5 400	3 900	1.3
	32	11 000	10 900	1.3
	45	16 000	21 000	1.2
	50	17 000	16 000	1.2

[a] Solvent, THF; [M] = 1 mol·L^{-1}; temperature, −40 °C; time of polymerization, 5 min except as noted; initiator, naphthalene–sodium. [b] See Experimental Section for determination. [c] Time of polymerization, 15 min.

and D_{2NEt} (**1c**), initiation by naphthalene–sodium (characterized by the disappearance of the initiator electronic spectrum) occurs, but the reaction process stops rapidly and only oligomers and/or unpolymerized monomer are recovered (the amount of oligomers obtained decreases from **1c** to **1a**). These results agree with the observations of Seyferth.[15] Contrarily, when the nitrogen substituent of the monomer is a methyl group (D_{2NMe}) (**1d**), a fast polymerization occurs.



In cationic polymerizations initiated by either triflic acid or its ester derivatives (Table II), the same behavior is observed.

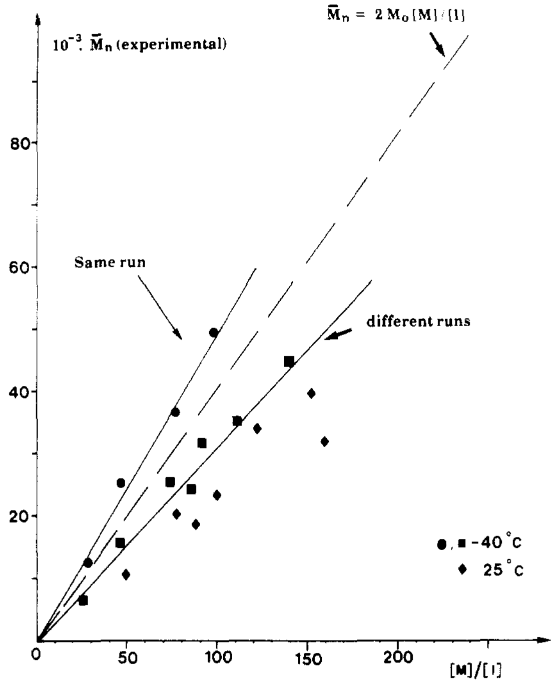


Figure 1. Variation of the experimental molar mass $\bar{M}_n$ of poly(cyclodisilazane) **4** with [M]/[I] ratio.

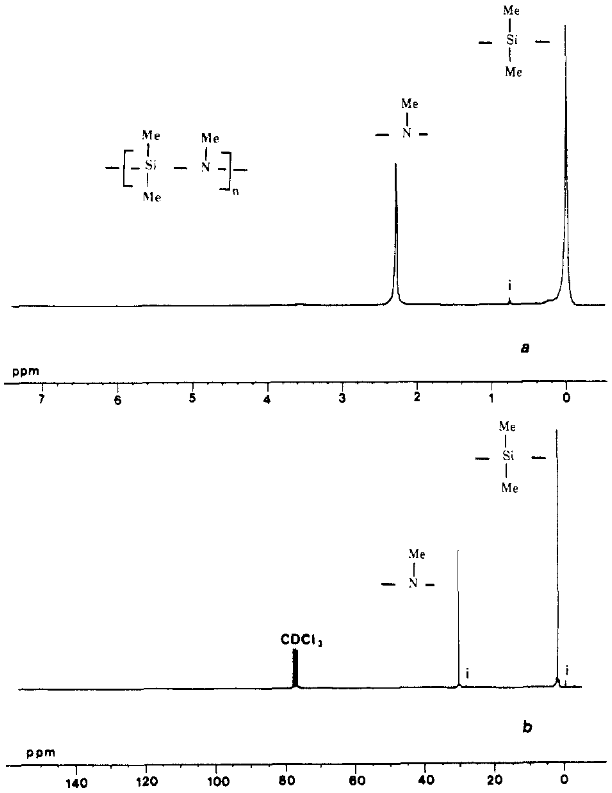


Figure 2. ^1H (250 MHz) (a) and ^{13}C (62.90 MHz) (b) NMR spectra of poly(cyclodisilazane) **5** in $CDCl_3$.

These results show that the ionic polymerization of cyclosilazanes is kinetically controlled: first, by the ring strength (which increases from monomers **2** to monomers **1**) and second, by the steric hindrance around the nitrogen atom and/or the electronic effects of the R substituent on the [Si–N] bond.

Polymerization of N-Methylcyclodisilazanes

N-Methylcyclodisilazane monomers **3** with various substituents on the silicon atoms have been anionically polymerized (Table III). Upon addition of the monomer,

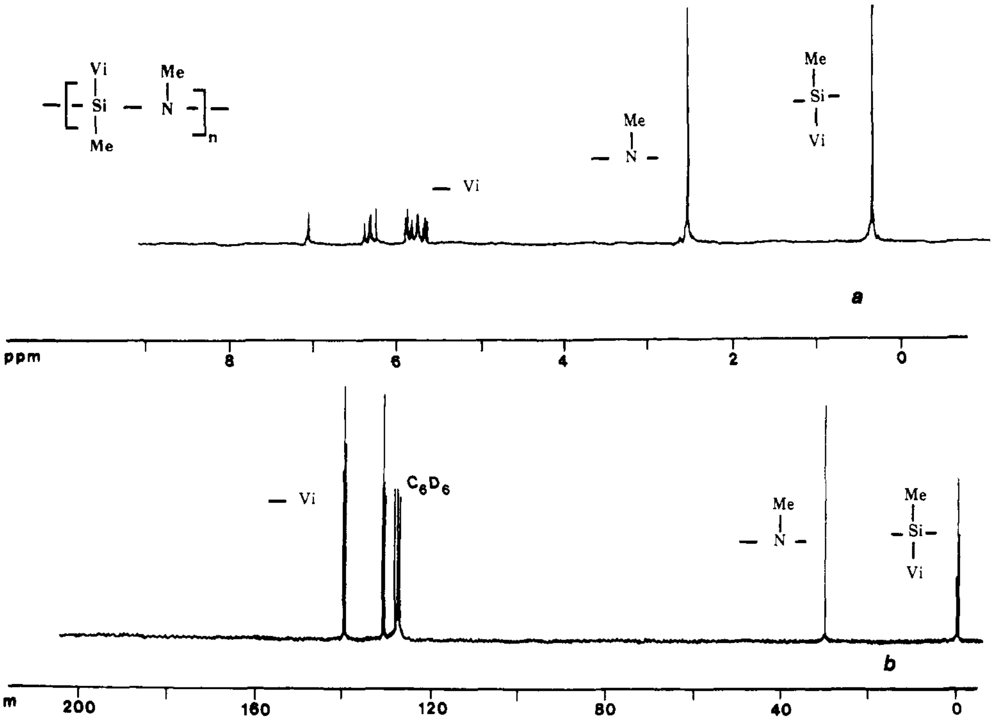


Figure 3. ^{1}H (250 MHz) (a) and ^{13}C (62.90 MHz) (b) NMR spectra of polymer 6 in CDCl$_3$.

a fast disappearance of the initiator (followed by UV spectroscopy) and an increase of the solution viscosity with time are observed. In all experiments the monomer conversion is quantitative. Several results presented in Table III are worthy of emphasis: polymers with molar masses as high as 100 000 have been prepared; the time of reaction at room temperature is short, indicating that both propagation and initiation steps are fast; theoretical molar masses $\bar{M}_n$ (calculated from the [M]/[I] ratios) and experimental ones are in relatively good agreement, within experimental error, when polymerizations are carried out at −40 °C (see Experimental Section for details on the determination of $\bar{M}_n$) (this shows that the active centers, presumably nitrogen anions, are stable at low temperature and that the polymerization occurs without significant transfer or termination reactions); the molar mass distributions $\bar{M}_w/\bar{M}_n$ (particularly that of polymers prepared at low temperature) are relatively narrow, thus corroborating the observed rapidity of the initiation step. Moreover, during the course of the reaction, there is no appearance of cyclic compounds coming from end-biting or back-biting reactions.

Figure 1 shows the variation of the experimental molar mass with the [M]/[I] ratio for successive additions of $D^{Vi}_{NMe}D_{NMe}$ monomer (**3a**) in the same run or in different runs. The linearity of this plot confirms the absence of termination reactions at low temperature and therefore the living character of the anionic polymerization of monomers such as **3**.

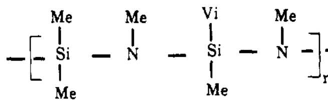
Another interesting result is that, surprisingly, as shown by the ^{1}H and ^{13}C NMR spectra of the polymers obtained (Figure 3), there is no evidence of polymerization reaction on the vinyl groups of monomers **3a** and **3b**. Moreover, our attempts to polymerize the trimethylvinylsilane in the same experimental conditions as monomers **3** did not succeed, and, besides the residual monomer, only a very small amount of organic products was recovered after several hours of reaction at room temperature.

This agrees partially with the observations of Rickle,[17] who indicated that trimethylvinylsilane only polymerizes in the absence (or at low concentration) of ethers which increase the termination rate. Also, in our case, the substitution of a methyl group by a nitrogen atom might decrease the reactivity of the vinyl group.

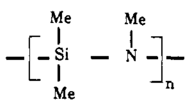
Cationic polymerizations of monomers **3a** and **1d** have also been realized (Table II). The reaction is fast, the monomer conversion is always quantitative, but, in this case, besides the polymer, cyclic compounds **2a** and **2b** (D_{3NMe} and D_{4NMe}) appear. The respective amount of each product changes with the temperature of polymerization. This indicates that both back-biting and end-biting reactions usually occur, as is observed with cyclosiloxanes.

Characterization of *N*-Methylcyclodisilazane Polymers

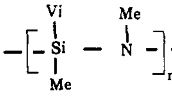
Poly[*N*-methylcyclodisilazanes] **4**–**6** are white solids soluble in usual organic solvents such as THF and CHCl$_3$. They are relatively stable to oxidation since no change in the molar mass of a polymer stored at 25 °C in THF solution (under ambient air) is observed within a week. Moreover, no peak assignable to [OSiMe$_2$O] (−22 ppm) bonds is detected in the ^{29}Si NMR spectrum of a polymer stored several months under nitrogen (Figure 4).


$-[\mathrm{Si(Me)_2}-\mathrm{N(Me)}-\mathrm{Si(Vi)(Me)}-\mathrm{N(Me)}]_n-$

4


$-[\mathrm{Si(Me)_2}-\mathrm{N(Me)}]_n-$

5


$-[\mathrm{Si(Vi)(Me)}-\mathrm{N(Me)}]_n-$

6

Except for some very small peaks assignable to impurities coming from the initial monomers, the NMR spectra (^{1}H, ^{13}C, ^{29}Si, ^{15}N) are unusually clean for polysilazanes. They corroborate the expected linear structure (Figures 2–5) and indicate the absence of significant branching,

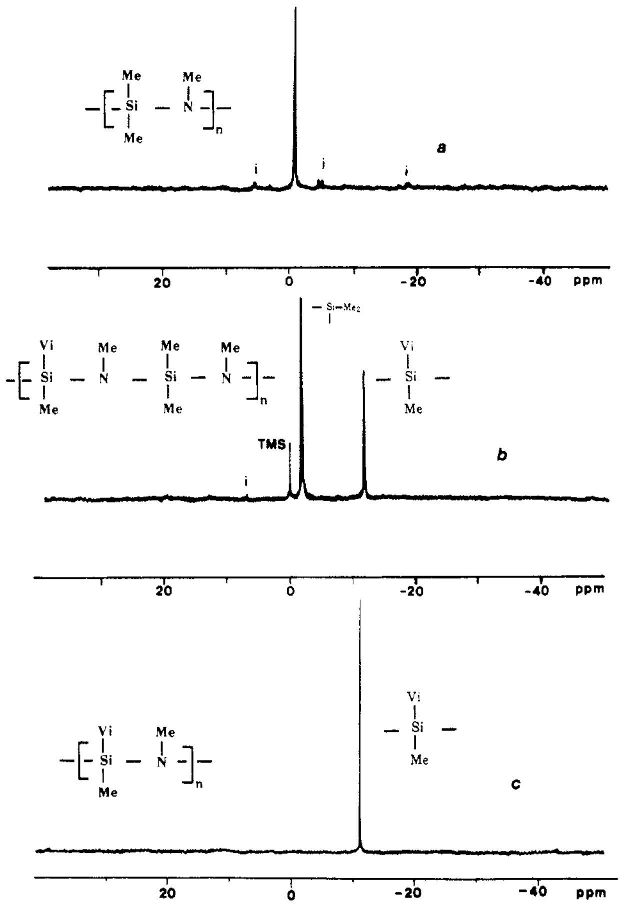


Figure 4. ^{29}Si NMR (39.8 MHz) spectra of poly(cyclodisilazanes) in $CDCl_3$: (a) polymer 5; (b) polymer 4; (c) polymer 6.

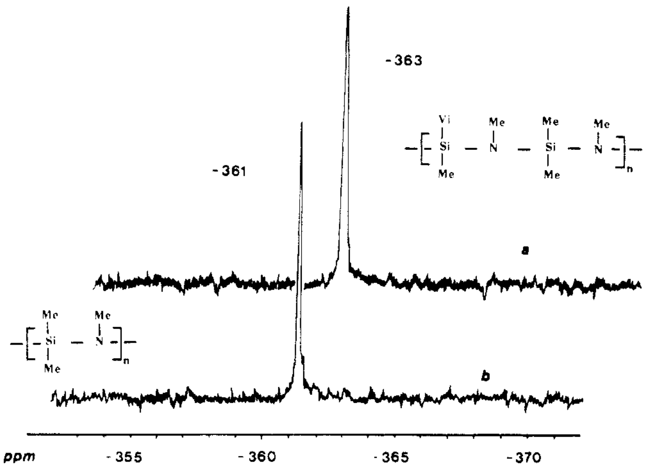


Figure 5. ^{15}N NMR (40.4 MHz) spectra of poly(cyclodisilazanes) in $CDCl_3$: (a) polymer 4; (b) polymer 5.

particularly on both the nitrogen and the silicon atoms or through the vinyl groups.

Another interesting point to note is that the ^{13}C NMR signals of both the methyl and the vinyl groups of the [SiMeVi] unit of polymer 6 are split into three lines (Figure 3). The most probable explanation is the stereosensitivity of these groups to the different configurational sequences of this polymer induced by asymmetric silicon atoms (i.e., isotactic, syndiotactic, and atactic stereosequences), as observed for polycarbosilanes.[18]

Surprisingly, DSC analyses show that all polymer samples present two endothermic transitions and a glass transition temperature (Figure 6). Upon the second and subsequent heating scans, the temperatures of the two endotherms decrease but both signals do not disappear (Figure 6c). This led us to assume that the upper transition is a melting transition and that the lower one could be attributed either to a phase transition or to the existence of smaller and more irregular crystals (lower thickness and perfection).

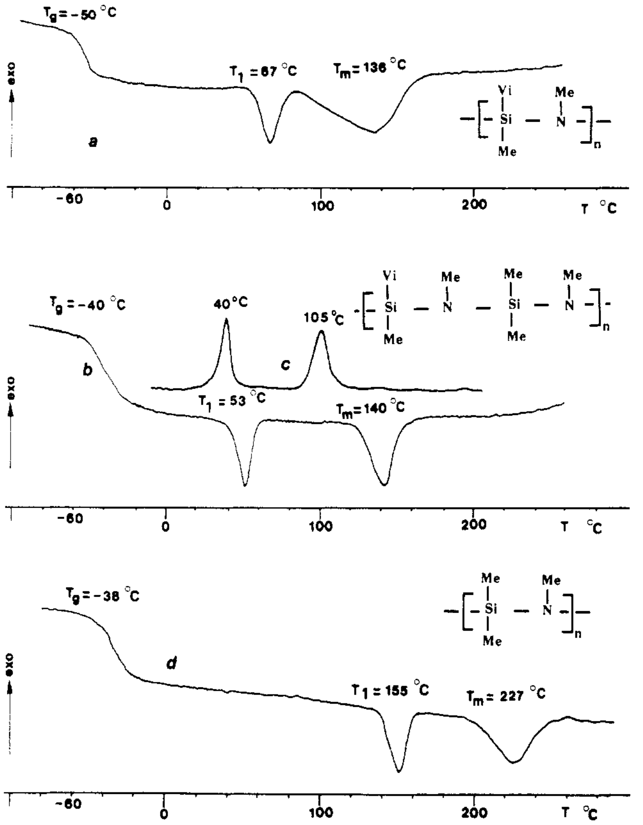


Figure 6. DSC analyses of poly(*N*-methylcyclodisilazanes) (−150 to +250 °C; 10 °C/min): (a) polymer 6; (b) polymer 4, first run (−150 to +250 °C; 10 °C/min); (c) polymer 4, second run (+200 to 0 °C; 10 °C/min); (d) polymer 5.

Nevertheless, due to the narrow distribution of the molar masses of the polymers, the most probable explanation could be the existence of a phase transition as observed for poly(dimethylsilylene)[19] and dodecamethylcyclotetrasilazane.[20] Further experiments, particularly annealing and X-ray analyses, are in progress in this field. Moreover, these transition temperatures decrease when the size of the silicon substituent increases, which led us to suppose that chain packing changes with the chain interactions.

X-ray analysis of polymer 5 (Figure 7) shows a high diffraction peak at $\theta = 6.75°$ and two small ones at $\theta = 8.83°$ and $\theta = 11.75°$. When analysis is carried out at 165 °C ($T > T_1$), the small peaks disappear whereas the high diffraction peak disappears at 250 °C ($T > T_2$). This confirms the crystalline structure of the polysilazanes synthesized and that the two transitions observed in DSC are assignable to different crystalline packings.

Preliminary experiments on the pyrolysis of networks obtained from these polysilazanes have been carried out under a nitrogen atmosphere. The ceramic yields at 1000 °C of polymer 4 cross-linked either via radical polymerization initiated by AIBN or by reaction[11] with $SiHMe_2NHMe_2SiH$ in the presence of H_2PtCl_6 are respectively around 40% and 50%.

The results presented in this paper demonstrate that, for the first time, high molar mass crystalline polysilazanes with relatively narrow molar mass distributions can be synthesized. Moreover, some of these polymers bear functional groups (i.e., vinyl) which allow further cross-linking.

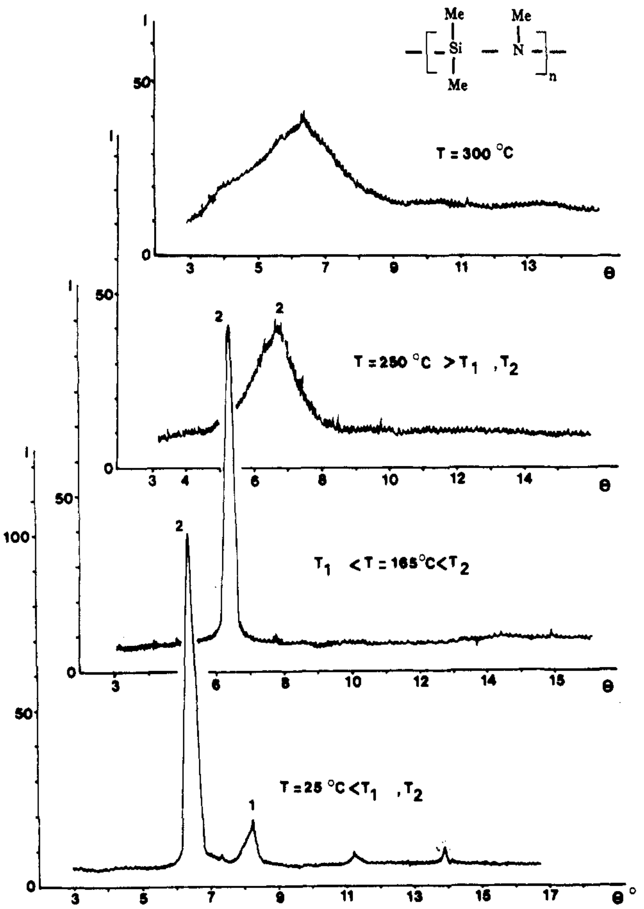


Figure 7. X-ray analysis (Cu Kα, 1.380 Å) versus temperature of powder of polymer **5**.

Further studies on the mechanism of both anionic and cationic polymerizations are in progress.

Experimental Section

Materials. Solvents, monomers, and products were purified by in vacuo distillation over drying agents (CaH_2, Na, K, etc.). Solid materials were dried and stored in vacuo. Commercial organolithium solutions were used as received.

Monomers. The monomers were synthesized according to the method of Fink[16] and were characterized by NMR (reference TMS) and mass spectrometry. Their purity was checked by gas chromatography (>95%).

D_{2NMe} (**1d**): ^{1}H NMR (250 MHz, $CDCl_3$) 0.13 (s, $SiMe_2$), 2.43 (s, NMe); ^{13}C NMR (62.90 MHz, $CDCl_3$) 0.5 ($SiMe_2$), 26.9 (NMe); ^{29}Si NMR (39.8 MHz, C_6D_6) 8.05 ($SiMe_2$).

$D^{Vi}_{NMe}D_{NMe}$ (**3a**): ^{1}H NMR (250 MHz, $CDCl_3$) 0.07, 0.09 (2 s, $SiMe_2$), 0.17 (s, Si*Me*Vi), 2.34 (s, NMe), 5.70–6.10 (m, SiMe*Vi*); ^{13}C NMR (62.90 MHz, $CDCl_3$) −2.6 (s, Si*Me*Vi), 0.3, 0.5 (2 s, $SiMe_2$), 26.7 (s, NMe), 134.1 (s, $SiCH{=}CH_2$), 138.5 (1 s, $SiCH{=}CH_2$); ^{29}Si NMR (39.8 MHz, C_6D_6) −5.56 (s, SiMeVi), 8.56 (s, $SiMe_2$).

D^{Vi}_{2NMe} (**3b**): ^{1}H NMR (250 MHz, $CDCl_3$) 0.29, 0.30 (2 s, Si*Me*Vi), 2.44 (s, NMe), 5.80–6.10 (m, SiMe*Vi*); ^{13}C NMR (62.90 MHz, $CDCl_3$) −2.4 (1 s, Si*Me*Vi), 26.8 (s, NMe), 134.6 (s, $SiCH{=}CH_2$), 138.4 (1 s, $SiCH{=}CH_2$); ^{29}Si NMR (39.8 MHz) −4.24 (1 s, SiMeVi).

Polymerizations. Polymerizations were carried out under high vacuum. Initiator concentrations were either determined by electronic spectroscopy (naphthalene–sodium) or calculated from the value of the initial commercial solutions and the amount of solvent added (organolithium compounds).

In a typical anionic experiment, naphthalene–sodium (5×10^{-4} M) was prepared by reacting in THF at room temperature during 1 h sublimed naphthalene on degassed sodium in excess. Then the green solution was filtered into the polymerization vessel and cooled to −40 °C. The monomer (0.1 M) was added with stirring by slow distillation. The reaction was stopped after 15 min by adding a small amount of methanol.

In a cationic polymerization, a solution of monomer in dichloroethane (0.2 M) was introduced in the reaction vessel by cryodistillation under vacuum. The solution was warmed to 30 °C, and then methyl triflate (4×10^{-3} M) was rapidly added with stirring. The polymerization was stopped after 5 min by adding a small amount of triethylamine.

Polymers were recovered from THF or $C_2H_4Cl_2$ solutions by precipitation in acetonitrile. SEC analysis of the residual solvent indicated the absence of significant amount of either oligomers or monomers.

Molar masses $\bar{M}_n$ were calculated from SEC analysis using polystyrene standard calibration (four-column pack: 40, 250, 1500, and 10^6 Å). In some experiments, the molar masses of the polymers were determined by vapor phase osmometry in THF at 35 °C, and their values agreed relatively well with those calculated from SEC (for example, for polymer **5**, $\bar{M}_n$ (VPO) = 3100 ± 200 and $\bar{M}_n$ (SEC) = 2800).

Anal. Calcd (% w/w) for polymer **4**: C, 41.4; H, 10.7; N, 16.2; Si, 30.2 (theoretical values: C, 41.3; H, 10.4; N, 16.1; Si, 32.2).

Anal. Calcd (% w/w) for polymer **5**: C, 45.2; H, 10.4; N, 14.2; Si, 29.2 (theoretical values: C, 45.1; H, 9.7; N, 15.0; Si, 30.2).

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