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Alkoxide initiation of anionic polymerization of masked disilenes to polysilanes

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Abstract

The polymerization of masked disilenes initiated by potassium alkoxides in the presence of cryptand[2.2.2] in benzene proceeded in a living manner, especially when using potassium (−)-menthoxide. The molecular weights of the polysilanes thus obtained were in good agreement with the calculated values. © 2000 Published by Elsevier Science S.A. All rights reserved.

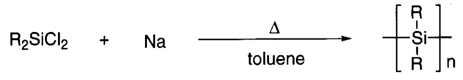
Keywords: Polysilane; Anionic polymerization; Masked disilene

1. Introduction

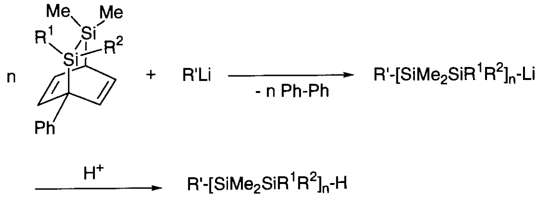
Polysilanes [1] have been widely investigated in the past decade because of their potential application in the field of materials science [2]. Polysilanes are usually prepared by the Wurtz type reductive coupling of dichlorosilanes with alkali metals (Scheme 1) [3].

Although many kinds of polysilanes have been prepared by this method [4], the structure, molecular weight, polydispersity, and terminal functionality of the polymers are usually very difficult to control [5]. Some efforts have been made to develop synthetic methods for polysilanes, such as a ring opening polymerization of cyclotetrasilanes [6] and a catalytic dehydrogenative coupling of hydrosilanes [7]. We have reported an anionic polymerization of masked disilenes (i.e. 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene derivatives) as a promising novel method for preparing well-defined polysilanes (Scheme 2) [8]. Indeed, the polymerization gave polysilanes with highly ordered structures [9] and block copolymers [10].

The anionic polymerization of masked disilenes was thought to involve polysilanyl anions. Living polymer was, however, not provided in a rigorous manner. If the polymerization is perfectly living, the degree of the polymerization should be equal to the ratio of the monomer to the initiator at the initial stage of the polymerization. However, polysilanes, prepared earlier in this series of investigations, i.e. those polymerized with a butyllithium–THF system, have much higher molecular weight than the theoretical one, because a single electron transfer (SET) process from butyllithium to the monomer occurs under these polymerization conditions [11]. The SET process inhibits the propagation to some extent and increases the molecular weight of the polymer. In order to avoid the SET process, we chose silyl anions as initiators and benzene as a solvent for the polymerization of masked disilenes. In the pres-



Scheme 1.



Scheme 2.

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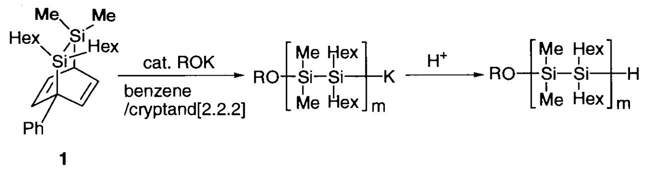

Scheme 3.

ence of suitable cryptands [12], the polymerization of masked disilenes was found to proceed in a living manner [11]. Therefore, improvement of the polymerization system is desirable for the synthesis of well-defined polysilanes in order to extend applications of the polymerization.

In the course of our studies, we have found that alkoxides [13] are good initiators for controlling the molecular weight of the polymer in the polymerization of masked disilenes. We report herein the anionic polymerization of masked disilenes initiated by alkoxides. Among the advantages of using alkoxides as initiators are their ease of preparation and the possibility to functionalize, e.g. introducing optically active groups to the polymer ends.

2. Results and discussion

2.1. Alkoxide initiation of anionic polymerization of masked disilenes

In an earlier typical example for the anionic polymerization of the masked disilenes initiated by 3 mol% of butyllithium to the monomer in THF, the molecular weight of the polysilane obtained was 140 000, while the expected value was 13 000 [9]. This indicates that the initiation is complete due to some side reactions of the initiators. In the initiation of this polymerization, the SET process from the initiator to the monomer occurred as a serious side reaction. This process caused a much higher molecular weight of the polymer than the expected value. In order to avoid the SET process, we chose a nonpolar solvent, such as benzene, for the polymerization of masked disilenes. Thus, polymerization of masked disilenes initiated by some alkoxides in benzene was examined, as shown in Scheme 3. We have used the masked disilenes **1** as the monomer since the monomer can be prepared in a highly regiospecific way [9].

The polymerization did not take place in benzene with the alkoxide anions alone. However, in the presence of suitable equimolar cryptands, the alkoxide anion initiated the polymerization in benzene solution at room temperature. The counter cations then influence the propagation process of the polymerization. For example, potassium alkoxides did initiate the masked disilenes, while the lithium and sodium alkoxides did not. Potassium *t*-butoxide, *n*-octoxide, and (−)-menthoxide were used as the initiators in the presence of cryptand[2.2.2]. Potassium *t*-butoxide and *n*-octoxide are soluble in THF, but not in nonpolar solvents such as benzene, whereas potassium (−)-menthoxide is soluble in benzene.

The results are summarized in Table 1. Here, the molecular weights of the obtained polysilanes were measured by GPC with polystyrene standards and the theoretical molecular weights were calculated on the basis of the ratio of the initiator to the monomer. Fig. 1 shows the relationships of the observed molecular weight and the monomer–initiator ratio for the polymerization initiated by some potassium alkoxides. The molecular weights of the polysilanes thus obtained were in good agreement with the calculated values within experimental errors, especially for potassium (−)-menthoxide. For example, 2.0 mol% of potassium (−)-menthoxide–cryptand[2.2.2] to the monomer gave a polymer with a molecular weight of 13 000, in good agreement with the expected molecular weight of 13 000. The rate of the polymerization was exceedingly high and the polymerization was finished within a few minutes. Yields of the polymer were generally good.

Table 1
Anionic polymerization of masked disilenes with potassium alkoxides with cryptand[2.2.2] [a] in benzene

Run	Initiator	Initiator (mol%)	Yield [b] (%)	Mn (obs.) [c]	Mn (Calc.)	Mw/Mn
1	$(CH_3)_3COK$	1.0	74	22 000	26 000	1.3
2	$(CH_3)_3COK$	2.0	79	17 000	13 000	1.3
3	$(CH_3)_3COK$	3.0	60	12 000	8600	1.4
4	$CH_3(CH_2)_7OK$	1.0	77	24 000	26 000	1.4
5	$CH_3(CH_2)_7OK$	2.0	70	15 000	13 000	1.3
6	$CH3(CH_2)_7OK$	3.0	65	11 000	8600	1.4
7	(−)-Menthoxide K	1.0	79	28 000	26 000	1.3
8	(−)-Menthoxide K	2.0	78	13 000	13 000	1.3
9	(−)-Menthoxide K	5.0	62	6500	5200	1.5

[a] An equivalent amount of cryptand to the initiator was used.

[b] After purification.

[c] GPC with polystyrene standards.

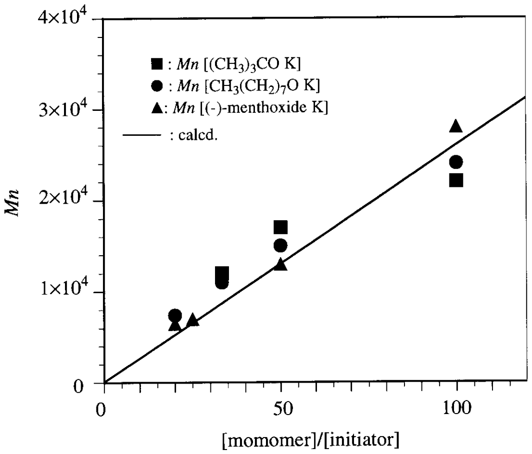

Fig. 1. Relationships of the observed molecular weight and the calculated molecular weight, on the basis of the monomer to initiator ratio for the anionic polymerization of masked disilenes in benzene initiated by various alkoxides with cryptand[2.2.2].

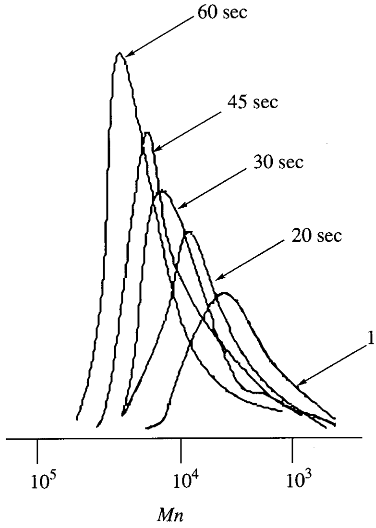

Fig. 2. GPC profiles for the propagation process of the anionic polymerization of masked disilenes in benzene initiated by the potassium (−)-menthoxide–cryptand[2.2.2] system.

Table 2
Relationship between the molecular weight and degree of monomer conversion for the polymerization initiated by 1 mol% of (−)-menthoxide–cryptand[2.2.2] in benzene

Time (s)	Conversion (%) [a]	Mn (obs.) [b]	Mn (Calc.) [c]	Mw/Mn [b]
10	28.5	7200	7400	1.4
20	32.6	10 000	8500	1.3
30	42.5	14 000	11 000	1.3
45	60	21 000	16 000	1.2
60	75	29 000	20 000	1.3

[a] Determined by GLC with *n*-dodecane as an internal standard.
[b] Determined by GPC with polystyrene standards.
[c] Calculated molecular weight.

2.2. Propagation process of the anionic polymerization of masked disilenes in benzene initiated by the potassium (−)-menthoxide–cryptand[2.2.2] system

The polymerization was monitored by GPC and the conversion of the monomer was determined by GLC. Fig. 2 shows how the GPC chromatogram changes during the course of the polymerization in benzene with potassium (−)-menthoxide–cryptand[2.2.2] as the initiator. The observed distribution of molecular weight was almost kept within a relatively narrow range during the propagation of the polymerization. The polymerization was completed within 1 min. Table 2 shows the degree of monomer conversion and molecular weights, and Fig. 3 plots the relationship. There was a linear correspondence between the molecular weight of the polymer and the monomer conversion. The experimentally determined molecular weights correlated well with the expected molecular weights, and the polydispersities consistently remained around 1.2. Thus, the polymerization can be assumed to proceed in a living manner under these conditions.

This polymerization system has some advantages because alkoxides are simple to prepare and functionalization of the polymer ends is also possible. Further work is now in progress.

3. Experimental

3.1. General procedure

^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded on a Bruker DPX 300 FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. ^{1}H and ^{13}C chemical shifts are relative to internal $CHCl_3$. A ^{29}Si chemical shift is referenced to external Me_4Si (0 ppm). GLC was

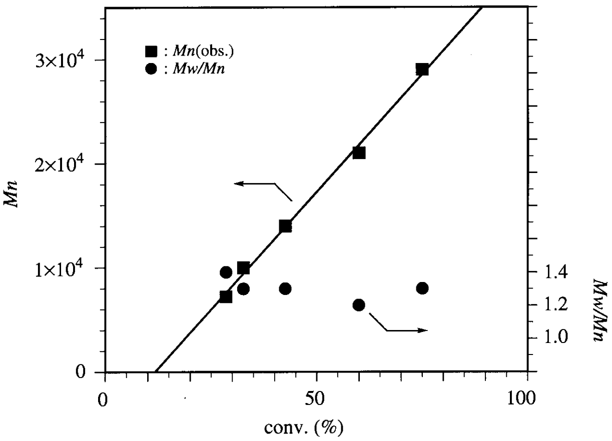

Fig. 3. Plots of molecular weight versus degree of monomer conversion for anionic polymerization in benzene initiated by the potassium (−)-menthoxide–cryptand[2.2.2] system.

recorded on a Shimadzu GC-8A. Molecular weight distributions of polymers were measured by use of a Shimadzu LC 10 HPLC equipped with PL-gel mixed-C columns calibrated with polystyrene standards. Chloroform was used as an eluent. UV spectra were recorded on a Milton Roy Spectronic 3000 array spectrometer. THF and toluene were dried and distilled from sodium–benzophenone prior to use. Potassium, potassium *t*-butoxide, *n*-octanol, (−)-menthol, and cryptand[2.2.2] were used without further purification. Hexane used for the spectroscopic measurements was of commercial UV spectral grade, and was used without further purification.

3.2. Synthesis of 1-phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (masked disilene)

1-Phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo-[2.2.2]octa-2,5-diene was synthesized as described previously [9]. Reaction of 1,2-dichloro-1,1-dihexyl-2,2-dimethyldisilane with lithium biphenyide in THF at −78°C gave the masked disilene in 62% yield. The monomer was purified by distillation and subsequently used for polymerization.

3.3. Polymerization of 1-phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene

All reactions were run under an atmosphere of argon. A typical example is as follows. The masked disilene (0.65 g, 1.58 mmol), cryptand[2.2.2] (0.013 mg, 0.035 mmol) and benzene (5 ml) were placed under dry argon in a 20-ml two-necked flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock. A toluene solution of potassium (−)-menthoxide (0.031 mmol), prepared from the reaction of potassium and (−)-menthol in toluene, was added to the solution at room temperature. The mixture was stirred for 3 min, a few drops of ethanol were then added to the mixture. After removal of the solvent, the residual mass was dissolved in benzene. Pouring the solution into methanol precipitated the polymer. A second cycle of dissolving–precipitation followed by freeze-drying gave the polymer as a white powder (315 mg, 73%). $Mn = 1.3 \times 10^4$, $MW/Mn = 1.3$, determined by GPC with polystyrene standards, $CHCl_3$ as an eluent. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.30 (brs), 0.8–1.4 (m). ^{13}C-NMR ($CDCl_3$, 75.4 MHz): δ −0.66, 13.53, 14.11, 22.83, 27.22, 31.77, 34.33. ^{29}Si-NMR ($CDCl_3$, 59 MHz): δ −36.07, −27.57. UV (hexane) $\lambda_{max} = 311$ nm ($\varepsilon_{(Si-Si\ unit)}) = 6{,}700$.

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