Stereoselective Anionic Polymerization of Amino-Substituted Masked Disilenes

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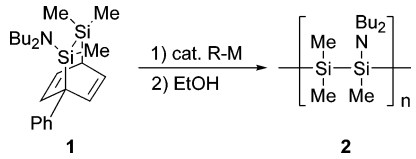
Summary: Stereoselective anionic polymerization of the amino-substituted masked disilene ***1****, 2-dibutylamino-2,3,3-trimethyl-1-phenyl-2,3-disilabicyclo[2.2.2]octa-5,7-diene, is reported. When the polymerization of* ***1*** *was initiated with silyl anions or butyllithium, it produced a highly ordered alternating polymer structure with a diad distribution where the ratio of m/r varies from ~1:3 to 1:9 depending on the metal ion in the anionic initiator and the polymerization temperature.*

Controlling the stereostructures of macromolecules is an important subject in polymer synthesis. However, polysilanes[1] with controlled stereoregularity have not been reported, because the most common synthetic method used to prepare polysilanes, the Wurtz coupling of dichlorosilanes with alkali metals, limits the potential routes.[2,3] Several reports have addressed control of stereochemistry during polymerization.[4] For example, a catalytic dehydrogenative coupling of hydrosilanes afforded polymers tentatively identified as syndiotactic,[5] but the formation of atactic polymers was subsequently confirmed by detailed NMR analysis.[6] A ring-opening polymerization of cyclotetrasilanes may also give polymers with a syndiotactic sequence.[7] Limited data have been available on stereoselective polymerization until now. Controlling polymer stereochemistry is still an important and unsolved problem in polysilane chemistry.

Scheme 1



1 **2**

Anionic polymerization of masked disilenes presents exciting opportunities for the synthesis of polysilanes with well-defined structures[8,9] and the possibility for potential control of the stereochemistry of polysilanes. Recently, we found that amino-substituted masked disilenes could be prepared and polymerized successfully to form the amino-substituted polysilane, poly[1,1,2-trimethyl-2-(dibutylamino)disilene].[10] A remarkable feature of this polymerization is that the obtained polymer has a uniform head-to-tail structure, because the monomer has no regioisomers and the polymerization process itself is highly regioselective. This makes analysis of the stereochemistry of the polymer via NMR analysis relatively straightforward. We report here the stereoselective anionic polymerization of the amino-substituted masked disilene **1**, 2-dibutylamino-2,3,3-trimethyl-1-phenyl-2,3-disilabicyclo[2.2.2]octa-5,7-diene.

The polymerizations of an amino-substituted masked disilene **1**, where the enantiomeric ratio was found to be 1.0 by HPLC analysis with an optically active chiral column (vide infra), initiated by $Ph_2MeSiLi$ or Ph_2MeSiK in THF, or by Ph_2MeSiK/cryptand[2.2.2] in benzene, were examined (Scheme 1).[10] The resulting amino-substituted polysilanes were obtained with high molecular weights ($M_n > 10^4$, Table 1). The NMR spectral pattern for the Si−Me groups provided information on the microtacticity of the amino-substituted polysilane (Figure 1). The ^1H NMR spectrum of the polymer prepared with $Ph_2MeSiLi$ in THF at room

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Table 1. Tacticity of the Anionic Polymerization of Amino-Substituted Masked Disilenes 1 Initiated with $Ph_2MeSiLi$, Ph_2MeSiK, Ph_2MeSiK/cryptand[2.2.2], and BuLi

run	initiator (mol %)	conditions: T (°C)/min/solv	yield (%)	$M_n \times 10^4$ (M_w/M_n)[a]	diad (%)[b] *m*/*r*	triad (%)[b] *mm*/*mr*/*rr*
1	$Ph_2MeSiLi$ (1)	rt/40/THF	66	2.4 (1.6)	23/77	9/23/68
2	Ph_2MeSiK (1)	rt/15/THF	68	2.1 (1.6)	27/73	11/32/57
3	Ph_2MeSiK (1)/cryptand[2.2.2] (3)	rt/3/benzene	64	1.7 (1.8)	31/69	13/38/49
4	BuLi (10)	23/60/THF	66	2.4 (1.5)	23/77	10/23/67
5		0/720/THF	40	2.1 (1.7)	22/78	11/20/69
6		−10/720/THF	89	1.5 (1.4)	20/80	9/19/72
7		−30/720/THF	89	2.6 (1.7)	18/82	7/18/75
8		−60/720/THF	66	2.1 (1.5)	11/89	6/16/78

[a] Determined by SEC (polystyrene standards, eluent: toluene). [b] Determined by ^1H NMR (600 MHz, C_6D_6).

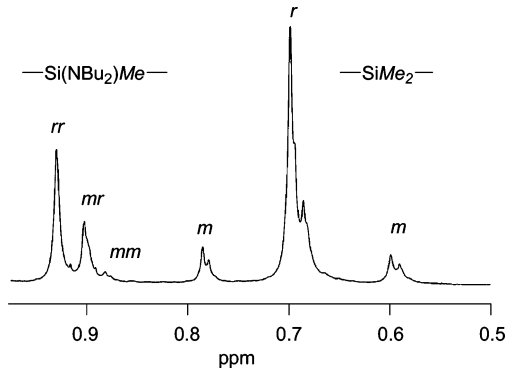

Figure 1. ^1H NMR (600 MHz) spectrum of methyl carbons in dibutylamino-substituted polysilanes obtained with $Ph_2MeSiLi$ (C_6D_6).

temperature (Table 1, run 1) showed methyl peaks of $Si(CH_3)_2$ at higher field (0.5−0.8 ppm) and Bu_2NSiCH_3 at lower field (0.85−0.95 ppm). How many signals should be observed for the polymer in ^1H and ^{13}C NMR?[11] For the dimethylsilylene unit in the monomer unit, the *meso* (*m*) structure should show two signals because each methyl group is not equivalent. In the *racemo* (*r*) structure, however, only one signal could be observed because the methyl groups are equivalent. For the (dibutylamino)methylsilylene unit, triad sequences, i.e., *mm*, *rr*, and *mr* (*rm*), are considered. The methyl groups are equivalent in the *mm* and *rr*, and only one signal could be observed in the ^1H and ^{13}C NMR. Because the methyl groups are not equivalent in the *mr* (*rm*), two signals could be observed. On the basis of this background, the ^1H and ^{13}C NMR spectra were analyzed. In the dimethylsilylene region, the spectral patterns were split because of the diad sequences, and the peaks were assigned to *r* at 0.7 ppm and *m* at 0.6 and 0.78 ppm, respectively.[12] In the (dibutylamino)-methylsilylene region, the spectral patterns also split because of the triad sequences, and the peaks were assigned to *mm*, *mr*, and *rr*, starting from the high magnetic field end. The diad and triad tacticities of the obtained polymers were estimated from the ^1H NMR spectra. Then *m*/*r* and *mm*/*mr*/*rr* were estimated to be 23/77 and 9/23/68, respectively (Table 1, run 1).

The assignment of the diad or triad sequences to these peaks is also supported by a statistical analysis. Usually, the relationship between the diad and triad contents is given by

$$(m) = (mm) + 1/2(mr) \quad (1)$$

$$(r) = (rr) + 1/2(mr) \quad (2)$$

where (*mr*) and (*rm*) are

$$(mr) \equiv (mr) + (rm) \quad (3)$$

When (*mm*) and (*mr*) were 0.9 and 0.68, (*m*) and (*r*) are calculated to be 0.21 and 79, respectively. The calculated values are in good agreement with the observed ones from the NMR analysis.[13]

Figure 2 shows the ^{13}C NMR spectra due to the methyl carbons. The peaks from −0.8 to −0.3 ppm and 0.4 to 1.1 ppm were assigned to the dimethylsilylene ($Si(CH_3)_2$)) and (dibutylamino)methylsilylene (Bu_2NSiCH_3) units, respectively, with each methyl peak split because of the microtacticity. In the dimethylsilylene region, the peaks were assigned to *r* at −0.6 ppm and *m* at −0.7 and −0.3 ppm, respectively, in diad sequences. In the (dibutylamino)methylsilylene region, the peaks were also assigned to *rr*, *mr*, and *mm* starting from the high magnetic field end. The assignment of the diad or triad sequences to these peaks is further supported by the $^1H-^{13}C$ COSY spectrum of the amino-substituted polysilane obtained with the Ph_2MeSiK/cryptand[2.2.2]. Interestingly, the spectra of the polymers obtained with $Ph_2MeSiLi$, Ph_2MeSiK, and Ph_2MeSiK/cryptand[2.2.2] show different patterns. As shown in Figure 2, the peak assigned to *mm* is not observed for the polymer obtained with $Ph_2MeSiLi$, but is observed for the polymer obtained with Ph_2MeSiK/cryptand[2.2.2]. The result indicates the polymer obtained with $Ph_2MeSiLi$ is more syndiotactic than the polymer obtained with Ph_2MeSiK/cryptand[2.2.2].

The diad and triad tacticities of the obtained polymers estimated from the ^1H NMR spectra are summarized in Table 1. The polymerization proceeded in a stereocontrolled manner; that is, the polymer obtained with $Ph_2MeSiLi$ (0.77) appears to have higher stereoregularity than that obtained with Ph_2MeSiK (0.73). The addition of cryptand[2.2.2] resulted in a low stereoselectivity (0.69). The result suggests that the coordination of the countercations to the end of the propagating polymer is important during the polymerization, giving a more highly syndiotactic polymer.

A further investigation into the effect of polymerization temperature on the tacticity during polymerization was carried out with BuLi in THF. The stereoselectivity increased gradually with a decrease in temperature

(11) For a list of diads for the dimethylsilylene unit and triad structures for the (dibutylamino)methylsilylene unit in dibutylamino-substituted polysilanes, see the Supporting Information.

(12) The limitation of peak resolution failed to estimate the higher stereoregularities.

(13) The detailed assignment of the NMR signals needs further study.

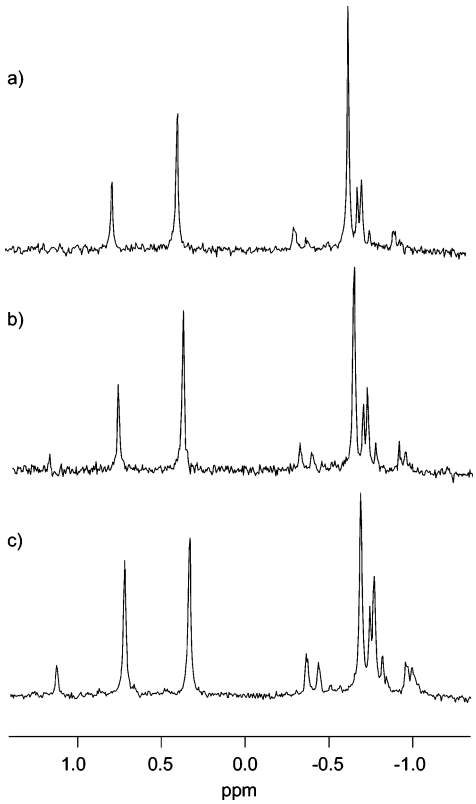

Figure 2. ^{13}C NMR spectra (150 MHz) of methyl carbons in dibutylamino-substituted polysilanes obtained with (a) $Ph_2MeSiLi$, (b) Ph_2MeSiK, and (c) Ph_2MeSiK/cryptand-[2.2.2] (C_6D_6).

during polymerization (Table 1, runs 4−8). The syndiotacticity as measured by the diad tacticity was recorded as 0.89 at −60 °C.

An important feature of this polymerization is that a highly syndiotactic polymer is produced, although the monomer is a 1:1 mixture of enantiomers. To further elucidate the polymerization mechanism, the relative consumption of each enantiomer was examined during the course of the polymerization process. Polymerization at −40 °C for 5 h was quenched by the addition of ethanol to give the polymer in 30% yield (M_n = 7500). The syndiotacticity of the resulting polymer was estimated to be 0.81 in the diad, which is almost the same as that obtained when the polymerization proceeded to completion (Table 1, run 7). The enantiomeric ratio of the remaining monomers was found to be 1.0 by HPLC analysis with an optically active chiral column.

A detailed mechanism for the polymerization process cannot yet be deduced, but the selective attack of the propagation ends on each enantiomer of the monomer **1** affecting the 1,3-interactions results in high stereoselectivity during polymerization.[14,15] This is the first example of controlling the stereochemistry of polysilanes. Further work is now in progress.

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Supporting Information Available: Experimental procedures and the detailed NMR and HPLC analyses of amino-substituted polysilanes are available (PDF). The material is available free of charge via the Internet at http://pubs.acs.org.

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