Anionic Cyclopolymerization of Bis(dimethylvinylsilyl)methane

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Cyclopolymerization is one of the effective methods for the preparation of the polymer having a cyclic structure in the main chain. Though various polymerization processes can be employed for the cyclopolymerization,[1] there have been few reports that claim quantitative yields of the polymers with narrow molecular weight distributions (MWD) via cyclopolymerization. Such a situation is due to two factors. One is the polymerization mechanism: living ionic polymerization is most suitable for obtaining polymers with narrow MWD's, whereas radical polymerization yields polymers with broad MWD's. The other is the degree of cyclization: incomplete cyclization can lead to a cross-linked polymer.

We have studied the anionic cyclopolymerization of dimethyldivinylsilane[2] and methyltrivinylsilane.[3] They have two or three vinyl groups on one silicon atom, and anionic polymerization with *sec*-butyllithium/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA) affords soluble polymers that contain six-membered and bicyclic ring units. It is characteristic of these cyclic units that two monomer units participate in their formation. In these cases some of the vinyl groups remain unreacted, and cross-linking reaction somewhat accompanies the polymerization. If the imperfect cyclization is attributable to the difficulty in the second ring closure to form the bicyclic ring structure, the monomer that is capable of forming a six-membered ring within one monomer unit would readily undergo cyclopolymerization with a high degree of cyclization. On the basis of this idea, we have attempted the anionic cyclopolymerization of bis(dimethylvinylsilyl)methane (BVSM), $(CH_2{=}CHSi(CH_3)_2)_2CH_2$ (shown in Scheme 1). Cyclopolymerization of similar monomers of the type $(CH_2{=}CHSi(CH_3)_2)_2X$ (X = O, NH, NCH_3) was recently carried out successfully with di-*tert*-butyl peroxide,[4] but BVSM was not dealt with because it cannot be radically polymerized. Among these monomers 1,3-divinylpentamethyldisilazane (X = NCH_3 in the above formula) was solely reported to give a soluble polymer anionically; however, MWD of the resulting polymer was not measured.[5]

The polymerization of BVSM was carried out with *n*-butyllithium (*n*-BuLi) in hexane at −10 °C under vacuum using breakable seal techniques. The initial concentrations of the reagents were as follows: [BVSM] = 0.1 mol/L, [*n*-BuLi] = 2×10^{-3} mol/L, [TMEDA] = 0, or 2×10^{-3} mol/L. The workup of the reaction mixture was carried out according to the previously outlined procedure.[6] When the polymerization was run in the presence of TMEDA, freeze-drying of the benzene solution gave a white powder; then it was further purified by the reprecipitation with benzene/methanol.

Scheme 1. Cyclopolymerization of BVSM

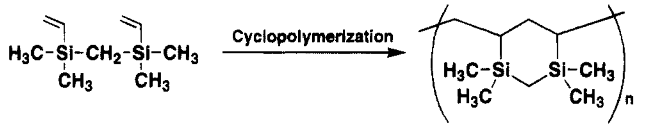

Table 1. Polymerization of BVSM[a]

entry	time, h	yield, %	$M_n/10^3$ calcd[b]	$M_n/10^3$ GPC[c]	$M_n/10^3$ VPO[d]	M_w/M_n[c]
			In the Absence of TMEDA			
1	96	2	0.19	1.0		
2	96[e]	2	0.19	1.3		
3	96[e,f]	4	0.38	2.2		
			In the Presence of TMEDA[g]			
4	6	71	6.6	7.6	6.2	1.27
5	12	93	8.6	11.1	8.6	1.28
6	48	100	9.3	12.4	10.1	1.28

[a] Solvent, hexane; temp, −10 °C; [BVSM] = 0.1 mol/L; [*n*-BuLi] = 2×10^{-3} mol/L. [b] Calculated from the monomer-to-initiator ratio and the percent polymer yield on the assumption that no cross-linking reaction takes place. [c] Determined by gel permeation chromatography calibrated with polystyrene standards. [d] Determined by vapor pressure osmometry. [e] [BVSM] = 0.5 mol/L; [*n*-BuLi] = 1×10^{-2} mol/L. [f] Temp, 40 °C. [g] [TMEDA] = [*n*-BuLi].

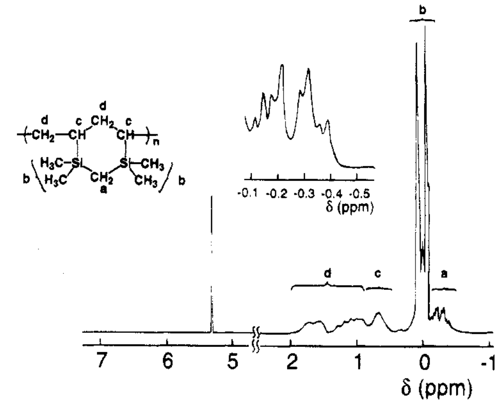

Figure 1. 200-MHz ^1H NMR spectrum in $CDCl_3$ of poly(BVSM) obtained in the polymerization with TMEDA (entry 6). CH_2Cl_2 was used as an internal standard.

The polymerization results are shown in Table 1. In no case did the resulting polymer contain a benzene-insoluble fraction. Without TMEDA the polymerization hardly proceeded even at high monomer concentration ([BVSM] = 0.5 mol/L) or high temperature (40 °C), and only an oligomer was obtained. There remained 72% of the second vinyl groups of BVSM units in the oligomer yielded in the absence of TMEDA (entry 3). When TMEDA was added to the polymerization systems, white powdery polymers were obtained in good yields. The number-average molecular weights of these polymers determined by vapor pressure osmometry were in accord with the values calculated from the monomer-to-initiator ratios and the polymer yields on the assumption that no cross-linking reaction took place. Their gel permeation chromatograms exhibited unimodal peaks though accompanied by some tailing, and MWD's were as narrow as $M_w/M_n < 1.3$.

Figure 1 shows the ^1H NMR spectrum in $CDCl_3$ of poly(BVSM) obtained in the presence of TMEDA. All signals locate between −0.4 and +2.0 ppm, and no vinyl signal can be seen around 6 ppm. The absence of vinyl groups and the agreement between the calculated and observed molecular weights of the polymer suggest that cyclopolymerization has occurred. All signals are assigned as follows provided the cyclopolymerization shown in Scheme 1 has occurred: (a) δ −0.4 to −0.1 (2H, m, $SiCH_2Si$), (b) −0.1 to +0.3 (12H, three singlets and a shoulder, $SiCH_3$), (c) 0.4−0.8 (2H, br, $SiCH$), (d) 0.8 − 2.0 (4H, br, CCH_2C). The chemical shifts of signals a and b are comparable to those of $SiCH_2Si$ (−0.28 ppm) and silylmethyl protons (0.04 ppm) of 1,1,3,3-tetramethyl-1,3-disilacyclohexane.[7]

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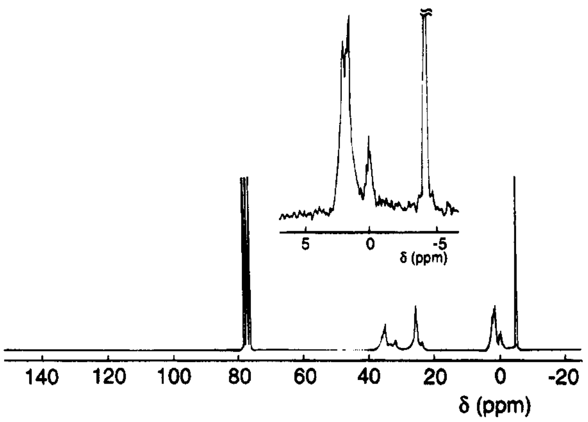

Figure 2. 50.3-MHz ^{13}C NMR spectrum in $CDCl_3$ of poly(BVSM) obtained in the polymerization with TMEDA (entry 6). $CDCl_3$ was used as an internal standard.

The six-membered ring structure is also supported by the ^{13}C NMR spectrum of this polymer shown in Figure 2. Some signals lie between −5 and +3 ppm, and they are assigned to silylmethyl carbons and the methylene carbon interposed by two Si atoms. The intense resonance at −4.3 ppm is assigned to the axial silylmethyl carbons on the six-membered ring because of its chemical shift. Saigo et al. reported that the ^{13}C NMR spectrum of poly(diallyldimethylsilane) obtained by radical cyclopolymerization exhibited only two silylmethyl carbon signals at −1.6 and −3.4 ppm.[8] Considering the stabilities of possible configurations and conformations, they concluded that the polymer was composed of 3,5-diequatorial cis-substituted silacyclohexane rings and that two silylmethyl carbon signals were assignable to equatorial and axial methyl carbons, respectively. Thus there should be only two resonances in the silylmethyl carbon region if poly(BVSM) exclusively consisted of 4,6-diequatorial cis-substituted 1,3-disilacyclohexane rings; however, the actual spectrum is more complicated. Jones et al. observed more than two silylmethyl carbon peaks in the ^{13}C NMR spectrum of poly(diallylmethylphenylsilane) and attributed them to the tacticity regarding silicon atoms,[9] but such an interpretation is not the case for poly(BVSM). Closer inspection of Figure 1 revealed that there are two sets of AB type protons between −0.4 and −0.1 ppm. When the main-chain conformation of a 4,6-cis-disubstituted 1,3-disilacyclohexane ring unit is diequatorial, two axial silylmethyl groups come to each other. On the other hand, if the main chain is a trans substituent of 1,3-disilacyclohexane and in the 4,6-diequatorial conformation, they are located at the opposite side of the ring to each other, while the ring should take the boat conformation. Hence, the trans chain configuration would coexist with the cis one.

The cyclopolymerization of BVSM hardly proceeds without TMEDA. Such a drastic effect of TMEDA is also observed in the anionic cyclopolymerization of methyltrivinylsilane.[3] Further, the addition of a large amount of triethylamine is effective for the anionic cyclopolymerization of 1,3-divinylpentamethyldisilazane.[5] The effects of amines cannot be discussed in quite the same way for all these cyclopolymerizations;[10] however, they certainly prevent cross-linking. Since amines are known to form complexes with lithium cations, the coordination of amines would play an important role in changing the reactivity of the propagating end.

In conclusion, the anionic cyclopolymerization of BVSM was accomplished with *n*-BuLi/TMEDA in hexane. The number-average molecular weight of the resulting polymer was in accord with the calculated value for the polymer without cross-linking structure. The ^{1}H and ^{13}C NMR spectra of the polymer proved that all the monomer units had formed six-membered rings. Further studies are underway to reveal the effects of various amines and initiators on the cyclopolymerization.

References and Notes

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(10) For example, in the case of methyltrivinylsilane the addition of TMEDA increases the fraction of remaining vinyl groups in the polymer, whereas the "complete" cyclopolymerization of BVSM proceeds with TMEDA.