Anionic polymerization of 2-([N,N-bistrimethylsilylaminomethyl]-1,3-butadiene and 2-(4-[N,N-bistrimethylsilylamo)nbutyl]-1,3-butadiene

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Abstract Anionic polymerization of two 1,3-butadiene derivatives containing trimethylsilyl-protected primary amino groups, 2-([N,N-bistrimethylsilylaminomethyl]-1,3-butadiene (SA1Bd) and 2-(4-[N,N-bistrimethylsilylamino)butyl]-1,3-butadiene (SA4Bd) were carried out under various conditions. When anionic polymerization of SA1Bd was attempted in cyclohexane at room temperature with using sec-BuLi as an initiator, no polymerization took place at all. Polystyrene having dienyl end group was obtained if anionic living polystyrene was used as an initiator, presumably due to the isomerization of carbanion accompanied with elimination of bistrimethylsilylamide anion. Such a side reaction was not observed in the anionic polymerization of SA4Bd. Polymer of predictable molecular weight with narrow molecular weight distributions was obtained in the polymerization in toluene. Microstructure of the resulting polymer was 86% 1,4-structure though its geometry was not clear. Block copolymer with styrene was also obtained.

Keywords 2-([N,N-bistrimethylsilylaminomethyl]-1,3-butadiene, 2-(4-[N,N-bistrimethylsilylamino)butyl]-1,3-butadiene, anionic polymerization, methylene spacer, microstructure

Introduction

It is well known that the anionic polymerization of non-functional 1,3-dienes such as 1,3-butadiene and isoprene is one of the best methods to prepare polydienes of well-characterized chain structure1–3. This method can also be applicable for the polymerization of some dieny monomers containing functional groups. Polymer of high cis-1,4- structure was obtained by the anionic polymerization of 2-(triisopropoxysilyl)-1,3-butadiene4 and 2-(N,N-dialkylaminodimethylsilyley)-1,3-butadienes5. Polydienes containing polar dialkylamide function in each monomer unit can also be obtained by the anionic polymerization of the corresponding monomer, though the microstructure is a complicated mixture6,7.

Among various types of functional groups, amine functionality is one of the most attractive one. Stadler and his coworkers have reported the anionic polymerization of various N,N-dialkylaminomethyl-1,3-butadienes8. Polydienes having various microstructures were obtained depending on the steric bulkiness of the N-alkyl substituents. These reports indicate that dialkylamino function can survive under highly basic anionic polymerization condition. On the other hand, anionic polymerization of 1,3-dienes containing protected primary amino group is very much limited. Nakahama and Hirao reported the anionic polymerization of 1,3-butadiene derivatives containing silyl-protected primary amino groups in THF at −78°C using potassium naphthalenide as an initiator9. Polymer of relatively broad molecular weight distribution (MWD) and high 3,4-structure was obtained, but detail is not clear. Since N-Si bond is reported to be stable against propagating carbanion derived from styrene10, attack of carbanion to silyl group would not to be responsible for the broadening of MWD. In addition, polymerization in non-polar solvent using lithium as counter cation would be preferable from the viewpoint of the microstructure control. In this paper, we would like to report the anionic polymerization behavior of two 1,3-butadiene derivatives containing N,N-bistrimethylsilylamino groups, 2-(N,N-bis-
trimethylsilylamonomethyl)-1,3-butadiene (SA1Bd) and 2-(4-(N,N-bistrimethylsilylamino)butyl)-1,3-butadiene (SA4Bd), where methylene spacer length between amino group and butadienyl frame are different.

**Experimental**

**Materials**

2-(N,N-Bistrimethylsilylamonomethyl)-1,3-butadiene (SA1Bd) and 2-[4(N,N-bistrimethylsilylamino)butyl]-1,3-butadiene (SA4Bd) were prepared as shown in Scheme 2. 2-Bromomethyl-1,3-butadiene was prepared from isoprene via reaction with SO₂, bromination of allylic methyl group, and thermal decomposition¹¹).

**SA1Bd**:

SA1Bd was prepared by the reaction of 2-bromomethyl-1,3-butadiene with potassium N,N-bistrimethylsilylamide in THF. In a three-neck round-bottomed flask equipped with condenser and dropping funnel, 2.2 g (55 mmol) of KH, which was rinsed with hexane to remove mineral oil prior to use, and dry THF was charged under nitrogen atmosphere. THF solution of 1,1,1,3,3,3-hexamethyldisilazane (8.94 g, 55 mmol in 10 mL THF) was added dropwise at 0℃ and stirred for 30 min at that temperature and additional 1 h at room temperature. Appropriate amount of hexane was added to the reaction mixture to precipitate inorganic salt and filtered. After usual work up, SA1Bd was isolated as colorless liquid by distillation under reduced pressure. Yield 33%, bp 40℃/3 mmHg. ¹H NMR (400 MHz, CDCl₃): δ=6.41 (dd, J=17.8, 11.2 Hz, 1H, CH₂=CH), 5.16 (s, 1H, C=CH₂), 5.14 (d, J=17.8 Hz, 1H, CH₂=CH₂), 5.10 (s, 1H, C=CH₂), 4.98 (d, 1H, J=11.2 Hz, CH₂=CH), 3.57 (s, 2H, CCH₂-N), 0.07 (s, 18H, Si-CH₃). ¹³C NMR (100 MHz, CDCl₃): δ=147.1 (C=CH₂), 137.8 (CH₂=CH), 115.9 (CH₂=CH), 111.8 (C=CH₂), 45.1 (CH₂N), 1.6 (SiCH₃).

N,N-Bistrimethylsilyl-3-bromopropylamine: In a three-neck round-bottomed flask equipped with condenser and dropping funnel, 10 g (46 mmol) of 3-bromopropylamine hydrobromide, 15.3 g (150 mmol) of dry triethylamine, and 150 mL of dichloromethane were charged under nitrogen atmosphere. Dichloromethane (25 mL) solution of trimethylsilyl chloride (11 g 100 mmol) was added dropwise in 1 h and stirred overnight. The reaction mixture was filtered to remove salt using Hyflo-supercel. The filtrate was concentrated under reduced pressure and dilute again with hexane to precipitate residual salt. It was filtered again and the filtrate was concentrated under reduced pressure. The aimed product was isolated by distillation under reduced pressure as slightly yellow colored liquid. Yield 66%, bp 43–46℃/2.5 mmHg.

**SA4Bd**:

In a three-neck round-bottomed flask equipped with condenser and dropping funnel, 2.2 g (17 mmol) of KH, which was rinsed with hexane to remove mineral oil prior to use, and dry THF was charged under nitrogen atmosphere. THF solution of 1,1,1,3,3,3-hexamethyldisilazane (8.94 g, 55 mmol in 10 mL THF) was added dropwise at 0℃ and stirred for 30 min at that temperature and additional 1 h at room temperature. Appropriate amount of hexane was added to the reaction mixture to precipitate inorganic salt and filtered. After usual work up, SA4Bd was isolated as colorless liquid by distillation under reduced pressure. Yield 3%, bp 110℃/3 mmHg. ¹H NMR (400 MHz, CDCl₃): δ=6.21 (dd, J=17.8, 11.2 Hz, 1H, CH₂=CH₂), 5.15 (s, 1H, C=CH₂), 5.13 (d, J=17.8 Hz, 1H, CH₂=CH₂), 5.09 (s, 1H, C=CH₂), 4.95 (d, 1H, J=11.2 Hz, CH₂=CH), 3.49 (s, 2H, CCH₂-N), 0.07 (s, 18H, Si-CH₃). ¹³C NMR (100 MHz, CDCl₃): δ=147.1 (C=CH₂), 137.8 (CH₂=CH), 115.9 (CH₂=CH), 111.8 (C=CH₂), 45.1 (CH₂N), 1.6 (SiCH₃).

![Scheme 2](image-url)
with condenser and dropping funnel, 1.36 g (56 mmol) of Mg and 30 ml of THF were charged under nitrogen atmosphere. The surface of Mg was activated by small amount of 1,2-dibromoethane, and then 10.0 g (37 mmol) of N,N-bistrimethylsilyl-3-bromopropylamine in 40 mL of THF solution was added dropwise at 0°C. The progress of the reaction was monitored by gas chromatography. After the reaction completed, the solution was kept stand still for a while to the magnesium dust being precipitated. Then the supernatant was transferred to another dropping funnel and added dropwise to a THF solution of 2-bromomethyl-1,3-butadiene (4.57 g, 31 mmol) containing Li2CuCl4 (0.1 M, 30 mL in THF) at 0°C. The progress of the reaction was monitored by gas chromatography. Then 20 mL of hexane was added to precipitate inorganic salt. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. Appropriate amount of diethyl ether was added to precipitate inorganic salt. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. Appropriate amount of diethyl ether and 0.1 g of LiAlH4 was added to remove residual alkyl bromide. After usual workup, aimed compound was isolated by distillation under reduced pressure. Yield 52%, bp 56–58 °C/2 mmHg. 1H NMR (400 MHz, CDCl3): δ=6.37 (dd, J=10.7, 17.5 Hz, 1H, CH=CH2), 5.19 (d, J=17.5 Hz, 1H, CH2=CH), 5.03 (d, J=10.7 Hz, 1H, CH2=CH), 4.98 (s, 1H, C=CH2), 4.85 (s, 1H, C=CH2), 2.73 (t, J=7.3 Hz, 2H, CH2N), 2.17 (t, J=6.33 Hz, 2H, CCH2CH2), 1.37–1.40 (m, 4H, CH2CH2N and CH2CH2 CH2N), 0.06 (s, 18H, SiCH3). 13C NMR (100 MHz, CDCl3): δ=146.4 (C=CH2), 139.0 (CH2=CH), 115.4 (C=CH2), 113.0 (CH2=CH), 45.5 (CH2N), 35.5 (CH2CH2N), 31.2 (CCH2), 25.6 (CCH2CH2), 2.1 (SiCH3).

Monomers thus obtained were purified by distillation under high vacuum conditions from CaH2, and diluted with cyclohexane or toluene. Anionic polymerization was carried out using breakseal method.

**Measurements**

1H and 13C NMR spectra were recorded by a JEOL JNM-AL-400 spectrometer in CDCl3. The solvent peak was used as a reference. Size exclusion chromatography (SEC) was obtained at 40°C with a TOSOH HLC-8220 instrument equipped with three polystyrene gel columns (TOSOH TSKgel HXL-4000, -3000, and -2000 (7.8 mm×30 cm)) with UV and refractive index detectors. THF was used as a carrier solvent at a flow rate of 1 mL/min. Calibration curve was made to values with standard polystyrene samples. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-ToF MS) was performed using an Bruker Daltonics Autoflex instrument in linear mode. A small amount of silver trifluoroacetate was added to enhance the sample ionization, and 2,5-dihydroxybenzoic acid was used as the matrix.

**Results and Discussion**

**Anionic polymerization of SA1Bd**

Nakahama and his coworkers have reported the anionic polymerization of SA1Bd in THF at −78°C with alkaline metal naphthalenide complex as an initiator. Although detail is not clear, conversion is not quantitative and polymer of broad molecular weight distributions was obtained9). Table 1 summarizes the anionic polymerization of SA1Bd. Upon addition of SA1Bd to sec-BuLi at 20–40°C, the color of the solution turned to pale yellow immediately. However, it faded out in 1 h and no polymeric product was obtained. Since the molar ratio of SA1Bd to initiator was set as low as 25, any protonic impurities in the monomer should not be responsible for the termination. In order to check the termination mechanism, less nucleophilic initiator, polystyryllithium was chosen as an initiator. Toluene solution of styrene was added to sec-BuLi and polymerized for 4 h at 40°C, and then cyclohexane solution of SA1Bd was added to the polymerization mixture at 40°C and allowed to react for 10 h. Upon addition of SA1Bd to polystyryllithium, orange colored solution disappeared immediately, and no actual increase of viscosity was observed. After quenching by the addition of ethanol, polymer of bimodal molecular weight distribution was

| Initiator | Monomer | M/I | Solvent | Temp. °C | Time h | Yield % | Mn×10^3 | Mw/Mn |
|-----------|---------|-----|---------|---------|--------|---------|---------|--------|
| sec-BuLi  | SA1Bd   | 3.14 | CHX     | 20      | 17     | 0       | –       | –      |
| sec-BuLi  | SA1Bd   | 3.00 | CHX     | 40      | 22     | 0       | –       | –      |
| PSi-Li+  | SA1Bd   | 3.41 | CHX/Toluene | 40      | 15     | 74      | 9.2     | 7.1    | 1.18 |
| sec-BuLi  | SA4Bd   | 3.99 | Toluene | 40      | 24     | 75      | 6.2     | 17.9   | 1.22 |
| PSi-Li+  | SA4Bd   | 2.31 | Toluene | 40      | 10     | 97      | 9.6     | 10.2   | 1.09 |

a) Mnobs=6200
obtained but the yield was much less than the theoretical value. Figure 1 show $^1$H-NMR spectrum of the polymer obtained. As can be seen, relative integrated intensity of silyl and olefinic proton signals are very weak, indicating that almost no SA1Bd was incorporated in the polymer chain.

Additional information concerning the polymer structure was provided by MALDI-ToF-MS analysis. Figure 2 shows MALDI-ToF-MS of the resulting polymer. Signals with 104 Da intervals only were observed in this region. Since the molecular weight of SA1Bd is 227, signals having 227 Da interval should present in the spectrum, if provided that block copolymerization of styrene and SA1Bd proceeds. One of the signal whose molar mass is 5026.12 is very close to the calculated value of Ag$^+$ ion adduct of 46-mer of polystyrene having $\alpha$-butyl and $\omega$-isoprenyl groups.$(m/e$ calcd=5023.02)

In our previous study, elimination of ethoxy group and introduction of isoprenyl unit was observed in the anionic polymerization of 2-ethoxymethyl-1,3-butadiene$^{13}$. If similar $S_n2'$ type reaction proceeds in the reaction between polystyryllithium and SA1Bd, polystyrene having $\omega$-isoprenyl group can be formed as illustrated in Scheme 3.

The difference in the polymerization behavior of $N,N$-dialkylaminomethyl-1,3-butadiene and SA1Bd might be explained by the difference of basicity of amide anions. It is well known that silyl group can stabilize the negative charge on the adjacent carbon atom through $\pi$-$\pi$ interaction$^{14}$. If that stabilization is possible for amide anion, $N,N$-bistrimethylsilylamide anion is more stable than dialkylamide anion. Figure 3 shows simulated isosurface
of electron density of di-tert-butylamide (Bu₂N⁻) anion and bistrimethylsilylamide ((Me₃Si)₂N⁻) anion. It is obvious that negative charge localizes on nitrogen atom in Bu₂N⁻ anion whereas it delocalized in (Me₃Si)₂N⁻ anion, indicating that the latter anion is more stable than the former anion. As a result, the latter anion can behave as good leaving group resulting in the formation of polymer with above mentioned structure.

One thing we should pay attention is that which carbon of SA1Bd is most susceptible to the nucleophilic attack of carbanion. In general, carbanion attacks olefinic carbon of the lower electron density, which can be predicted by the ¹³C NMR chemical shift of the molecule. In the case of isoprene, C4 carbon (114 ppm) is more susceptible to the nucleophilic attack of carbanion than C1 (112 ppm) in the anionic polymerization in hydrocarbon solvent with lithium counter ion, resulting in the formation of 4,1- and 4,3-structure exclusively. If this tendency is applicable to the polymerization of SA1Bd, C4 (115.9 ppm) carbon rather than C1 (111.8 ppm) should be more likely attached by initiator to form 4,1- or 4,3-anion, resulting in no isomerization and elimination of amide anion occurs. This indicates the electrophilicity of C1 is increased by the presence of good leaving group, bistrimethylsilylamino group at the appropriate position in the molecule.

Anionic polymerization of SA4Bd

If the above-mentioned isomerization of monomer structure accompanied by the elimination of bistrimethylsilylamide anion is responsible for the non-polymerizable feature of SA1Bd, length of methylene spacer between butadienyl skeleton and amino group is important. Thus anionic polymerization of SA4Bd was performed at 40°C in toluene using sec-BuLi and/or polystyryllithium as an initiator. Results of the polymerization are also summarized in Table 1.

Upon addition of SA4Bd to sec-BuLi, the reaction mixture turned to show pale yellow and it did not change till the end of polymerization. Figure 4 shows the SEC chromatogram of the resulting poly(SA4Bd). As can be seen, the polymer had bimodal molecular weight distribution though each of the peaks had relatively sharp MWD, indicating that no apparent termination reaction occurred during the propagation step. The molecular weight of the polymer estimated by SEC using polystyrene calibration was higher than that of the one based on the monomer to initiator ratio. Partial loss of carbanion might have occurred in the initial stage of polymerization, otherwise the MWD should be broad and unimodal. The second peak at the higher molecular weight side might be formed by the coupling reaction after most of the monomer was consumed. Since sec-BuLi used here was too reactive to cause side reaction, less reactive polystyryllithium was chosen as initiator. When SA4Bd was added to anionic living polystyryllithium, characteristic orange color of the anion turned to pale yellow and the color did not change till the end of the reaction. The conversion was almost quantitative. The MWD of the resulting polymer was relatively sharp and unimodal. Figure 5 shows ¹H NMR spectrum of the polymer. Both of the signals attributable to polystyrene segment and poly(SA4Bd) segments were observed, and the composition calculated from the relative integrated intensity of signals around 0 ppm and the one around 7 ppm was close to the calculated value. This indicates that initiation of SA4Bd by polystyryl anion occurred quantitatively.

Microstructure of Poly(SA4Bd)

Through the study of the diene polymerization, control and analysis of the microstructure of the polymer obtained is of considerable interest because the physical properties
of the polydienes strongly depend on the microstructure. In this study, the microstructure of poly(SA4Bd) was analyzed by 1H NMR.

Figure 6 shows the 1H NMR spectrum of poly(SA4Bd) obtained at 40°C in toluene using sec-BuLi as an initiator. In the aliphatic proton region, methylene protons adjacent to nitrogen atom were observed at 3.5 ppm, and other methylene on side chain and main chain were observed around 1.3 and 2 ppm. Signal attributable to trimethylsilyl group appeared at 0 ppm. In the olefinic proton region, two signals centered at 4.7 and 5.1 ppm attributable to methylene proton in 3,4-structure and methyne proton in 1,4-structure were clearly observed. From the relative integrated intensity of these signals, microstructure of poly(SA4Bd) obtained here was determined to be 86% 1,4- and 14% 3,4-. Unfortunately geometry of monomer unit, 1,4-E and 1,4-Z, was not able to be determined because no apparent signals assigned to each structure was observed.

Conclusion

Anionic polymerization of SA1Bd and SA4Bd was carried out in hydrocarbon solvent. Elimination of bistri-methylsilylamide anion took place in the anionic polymerization of SA1Bd via S_n2 type reaction. If allowed to react with anionic living poly styrene, poly styrene having isoprenyl end blocker was obtained. Block copolymer of narrow molecular weight distribution was obtained if SA4Bd was used as a second monomer. Microstructure of poly(SA4Bd) segment was mainly 1,4-.

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