Synthesis and Anionic Polymerizations of p-[Bis(trimethylsilyl)methyl]isopropenylbenzene

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ABSTRACT: p-[Bis(trimethylsilyl)methyl]isopropenylbenzene (BSIB) was prepared by reaction of α,p-dimethylstyrene (DMST) with lithium diisopropylamide (LDA) and trimethylsilyl chloride (TMSCl). Anionic polymerization of BSIB with *sec*-butyllithium (BuLi) or living lithium α-methylstyrene oligomers at −50 °C in THF gave polymers with the predicted molecular weights and narrow molecular weight distributions. When the temperature of the polymerization mixture was increased up to 20 °C after the monomer was almost completely consumed, the polymer formed disappeared almost completely, indicating the anionic polymerization of BSIB to be a living equilibrium system. The ceiling temperature of BSIB in the anionic polymerization was 1.2 ± 0.9 °C.

Introduction

For the last few years, we have been studying the syntheses of new organosilicon polymers and correlations between their structures and properties, particularly the gas permeability of oxygen permselective membranes and resistivity to electron beam (EB).[1] In the course of these studies, we found that p-[bis(trimethylsilyl)methyl]styrene (BSMS) showed unique characteristics as a EB resist. For example, anionic polymerization of BSMS gave a living polymer with a narrow molecular weight distribution (MWD) even at ambient temperature.[2] The polymer, however, showed an unusually high glass transition temperature (T_g = 156 °C) for a polystyrene homologue, owing to the extremely low mobility of their bulky bis(trimethylsilyl)methyl substituents.[3] It also exhibited a nega-type resist behavior against EB exposure owing to cross-linking reactions[2] and remarkably high resolution properties (the resolution parameter γ = 8.1).[4] In terms of sensitivity, however, poly (BSMS) was not so good, because their high glass transitions prevented intermolecular cross-linking reactions to some extent.

In an attempt to improve this while retaining the high-resolution properties, we designed new silicon-containing poly(α-methylstyrene) derivatives, having similar structures to that of poly(BSMS). Our idea was to create a posi-type organosilicon-containing polymers with high-resolution properties by making use of their depolymerization tendency. In this paper we describe the preparation of another new monomer from this group, p-[bis(trimethylsilyl)methyl]isopropenylbenzene (BSIB), its anionic polymerization, and some properties of the obtained polymer product.

Experimental Section

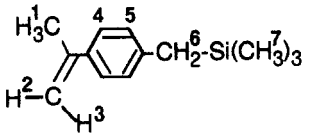
All experiments were carried out under argon atmosphere in order to eliminate oxygen and moisture.

Materials. Ethyl ether, tetrahydrofuran (THF), diisopropylamine (DPA), trimethylsilyl chloride (TMSCl), cyclohexane, 1,1-diphenylethylene (DPE), and α-methylstyrene (α-MST) were purified by conventional methods.[5] *n*-BuLi was used as a hexane solution, the concentration of which was determined by Gilman's double titration method.[6] *sec*-BuLi and *tert*-BuLi were used as cyclohexane and pentane solutions, respectively, the concentrations of which were determined by gas chromatography after quenching with DPE. α,p-Dimethylstyrene (DMST) was prepared according to the literature.[7] Purification of DMST was carried out by fractional distillation over calcium hydride under reduced pressure.

Metalation Reaction of α,p-Dimethylstyrene (DMST) with Lithium Diisopropylamide. To a stirred THF solution (24 mL) of **DPA** (2.02 g, 20 mmol), in a 100-mL round-bottomed flask, was added *n*-BuLi (6.3 mL, 10 mmol, 1.6 mol/L). After a few minutes of stirring to complete the formation of LDA, DMST (0.66 g; 5 mmol) was added via syringe. The mixture was allowed to react at 20 °C for 5 min, after which the reaction was stopped by adding carbon tetrachloride. Unreacted DMST was determined by gas chromatography (GC).

Synthesis of p-[(Trimethylsilyl)methyl]isopropenylbenzene (SIB) and p-Bis[(trimethylsilyl)methyl]isopropenylbenzene (BSIB). In a typical procedure, *n*-BuLi (560 mL, 0.9 mol, 1.6 mol/L) was added to a stirred THF solution (1140 mL) of DPA (181 g, 1.8 mol), in a 3-L round-bottomed flask equipped with a three-way stopcock and an isobaric-type dropping funnel. After a few minutes of stirring to complete formation of LDA, DMST (44 g, 0.3 mol) was added from a syringe. The color of the mixture turned pale yellow immediately, and a THF solution (270 mL) of TMSCl (60 g, 1.0 mol) was added dropwise from an isobaric-type dropping funnel over a period of 22 h at 20 °C. The resulting mixture was analyzed by GC to determine the yield of the products. SIB and BSIB thus obtained were purified from calcium hydride by fractional distillation under reduced pressure.

***p*-[(Trimethylsilyl)methyl]isopropenylbenzene, SIB**: Colorless oil; bp 82 °C (0.50 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9H, H-7), δ 2.09 (s, 2H, H-6), δ 2.15 (s, 3H, H-1), δ 5.02 (s, 1H, H-2), δ 5.36 (s, 1H, H-3), δ 6.98 (δ, 2H, $J_{5,4}$ = 8.3 Hz, H-5), δ 7.36 (d, 2H, $J_{4,5}$ = 8.3 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ −1.93 ($SiCH_3$), δ 21.75 (α-CH_3), δ 26.74 (−CH_2Si), δ 110.83 (β-vinyl C), δ 125.19 (phenyl C^2), δ 127.82 (phenyl C^3), δ 136.66 (phenyl C^1), δ 139.80 (α-vinyl C), δ 142.93 (phenyl C^4); MS (20 eV) m/z 204 (M^+), 189, 73.



***p*-Bis[(trimethylsilyl)methyl]isopropenylbenzene, BSIB**: Colorless oil; bp 93 °C (0.36 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 18H, H-7), δ 1.50 (s, 1H, H-6), δ 2.14 (s, 3H, H-1), δ 4.99 (s, 1H, H-2), δ 5.36 (s, 1H, H-3), δ 6.89 (δ, 2H, $J_{5,4}$ = 8.3 H, H-5), δ 7.32 (d, 2H, $J_{4,5}$ = 8.3 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 0.21 ($SiCH_3$), δ 21.72 (α-CH_3), δ 29.32 (-CH-Si), δ 110.50 (β-vinyl C), δ 125.08 (phenyl C^2), δ 128.50 (phenyl C^3), δ 135.78 (phenyl C^1), δ 142.53 (α-vinyl C), δ 142.76 (phenyl C^4); MS (20 eV) *m/z* 276 (M^+), 261, 188, 73.

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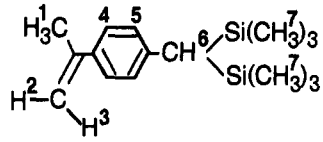


Polymerization Procedures. A typical anionic polymerization was performed in a 100-mL round-bottomed flask with a three-way stopcock. The reactor was first carefully washed with a hexane solution of BuLi, and then THF (6.6 mL), BSIB (3.1 g, 10 mmol), and *sec*-BuLi (0.28 mL; 0.50 mmol; 1.77 mol/L) were added via a syringe at −78 °C. The color of the mixture turned brownish red immediately. The reaction was allowed to continue for 20 min, before a small amount of methanol was added to quench it. The resulting mixture was analyzed by gel permeation chromatography (GPC) to determine the conversion of BSIB and then poured into a large excess of methanol. The precipitate was purified by 3-fold successive reprecipitations from THF solution. The polymer obtained was freeze-dried with benzene to remove the solvents employed.

Measurements. A Hewlett-Packard 5890 Series II GC was used (column: glass capillary column DB-1 0.25 $\mu m\phi \times 30$ m). GC/MS spectra were obtained by using the Hewlett-Packard 5890 Series II, equipped with a 5971A mass selective detector. GPC measurements were performed on a Shimadzu LC 6A liquid chromatography with a RID-6A IR detector and TSK-Gel G4000H8 + G3000H8 + G2500H8 columns. ^1H and ^{13}C NMR spectra (^1H, 399.65 MHz; ^{13}C, 100.53 MHz) were measured on a JEOL EX400 spectrometer using $CDCl_3$ as a solvent at room temperature. Chemical shifts relative to $CHCl_3$ (^1H, $\delta = 7.26$) and $CDCl_3$ (^{13}C, $\delta = 77.0$) were employed. Differential scanning calorimetry (DSC) was performed on a Mettler TA 4000 scanning calorimeter calibrated with indium standard. Molecular orbital (MO) calculations were carried out by using the AM1 method.[8] A modified version of the QCPE-MOPAC program[9] was employed for full geometry optimization.

Results and Discussion

Synthesis of Organosilicon-Containing α-Methylstyrene Derivatives. We reported earlier that LDA induces metalation of *p*-methylstyrene (MST) to form *p*-vinylbenzyllithium (VBL) without any side reactions.[10] By utilizing VBL as an intermediate for synthesis of new monomers, several kinds of other organosilicon-containing styrene monomers were synthesized.[11] If this reaction can be applied to DMST instead of MST, new organosilicon-containing monomers having an α-methylstyrene skeleton can be synthesized.

With this in mind, we examined if metalation reaction of DMST by LDA proceeds also without any side reaction. When DMST was added to a THF solution containing LDA and DPA, the color of the observed mixture turned pale yellow immediately, and when small amount of methanol was added, it diminished, indicating a carbanion formation. To verify this, the reaction mixture was quenched with TMSCl and analyzed by gas chromatography. The results obtained are shown in Figure 1. As an electrophile, TMSCl tends to react with LDA, and a peak appearing around 6.4 min was assigned to the coupling product of TMSCl and LDA: $[(CH_3)_2CH]_2NSi(CH_3)_3$ by GC/MS analysis. The peak appearing raound 10.4 min was also found to originate from the product of the reaction between TMSCl and LDA: $[(CH_3)_2CH]_2NSi(CH_3)_2CH_2Si(CH_3)_3$, by GC/MS analysis, obtained by a metalation of $[(CH_3)_2CH]_2NSi(CH_3)_3$ by LDA followed by a reaction with TMSCl. Peaks appearing around 11.4 and 13.3 min (products A and B) can be assigned to mono- and bis-trimethylsilylated DMST, respectively, by GC/MS analysis. Thus, formation of trimethylsilylated DMST can be a proof that DMST was metalated by LDA.

To determine position of trimethylsilyl groups in the silylated DMST, ^1H NMR measurements were carried out

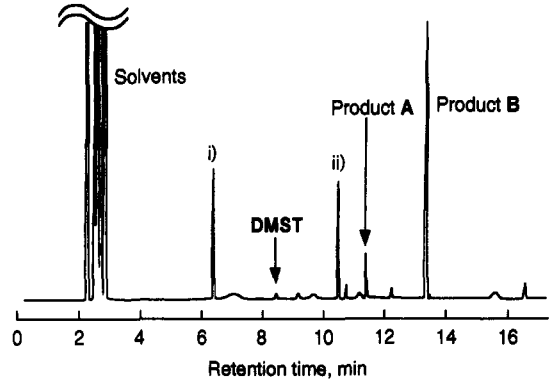


Figure 1. GC of the products from the reaction of DMST and TMSCl in the presence of LDA. $[[DMST]_0 = 0.15$ mol/L; $[LDA]_0 = [DPA]_0 = 0.45$ mol/L; $[TMSCl]_0 = 2.5$ mol/L. Column: DB-1 (30 m); temp, 80 − 220 °C (initial hold time 5 min, final hold time 7 min, rate 30 °C/min), injection temp, 260 °C, detector temp, 260 °C.] From GC/MS analysis, signals i and ii were assigned to $[(CH_3)_2CH]_2NSi(CH_3)_3$ and $[(CH_3)_2CH]_2NSi(CH_3)_2CH_2Si(CH_3)_3$, respectively.

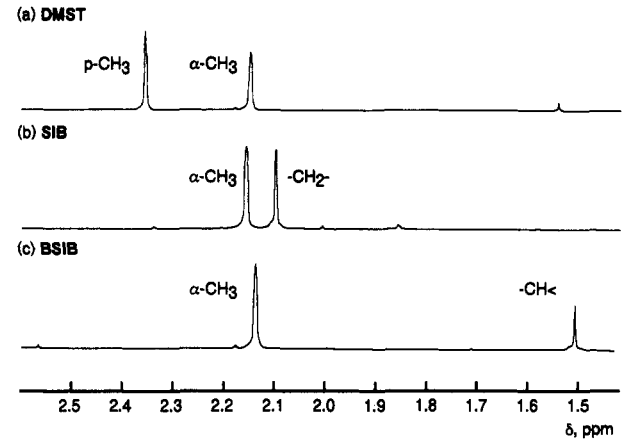
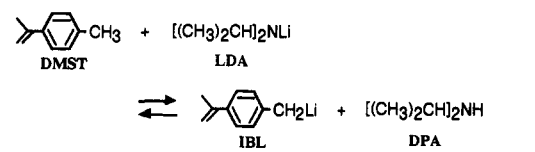


Figure 2. ^1H NMR spectra of (a) DMST, (b) SIB, (c) BSIB. The 1.4–2.6-ppm regions relative to chloroform (7.26 ppm) were shown.

after purifications of the products by fractional distillations under reduced pressure. Using α-methylstyrene and *p*-methylstyrene as the reference standards, assignments for the signals of DMST indicate α- and *p*-methyl protons for the peaks appearing at 2.15 and 2.35 ppm, respectively (Figure 2a). In the ^1H NMR spectra of mono-trimethylsilylated DMST, the α-methyl protons peaks remained at 2.15 ppm and *p*-methyl protons peak disappeared, but a new methylene signal appeared around 2.09 ppm, assignable to (trimethylsilyl)methyl protons adjacent to the phenyl ring by using *p*-[(trimethylsilyl)methyl]styrene as a reference compound (Figure 2b).[12] From these results, it was concluded that metalation of DMST by LDA proceeded at the *p*-methyl position as shown in eq 1.



Metalated DMST [(isopropenylbenzyl)lithium, IBL] reacted with TMSCl to form mono-trimethylsilylated DMST [*p*-[(trimethylsilyl)methyl]isopropenylbenzene, SIB, eq 2].

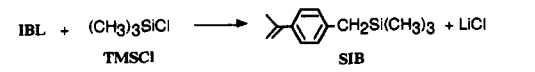
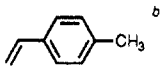
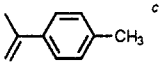
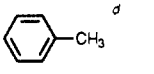
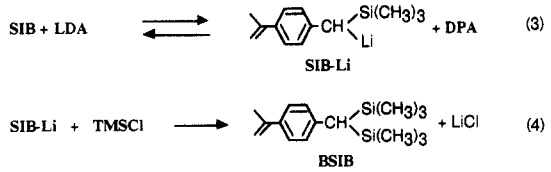


Table 1. Equilibrium Constants for Metalation Reactions of DMST, MST, and Toluene by Lithium Diisopropylamide (LDA)[a]

	10^2K
 [b]	54
 [c]	9.3
 [d]	~0.0

[a] Solvent THF; reaction temperature, 20 °C. [b] $[MST]_0 = [LDA]_0 = [DPA]_0 = 0.1$ mol/L. [c] $[DMST]_0 = 0.25$ mol/L; $[LDA]_0 = [DPA]_0 = 0.5$ mol/L. [d] $[Toluene]_0 = 0.25$ mol/L; $[LDA]_0 = [DPA]_0 = 0.5$ mol/L.

The bis-trimethylsilylated DMST showed a methine signal at 1.50 ppm (in addition to α-methyl protons at 2.14 ppm), indicating that two trimethylsilyl groups were bonded to the benzylic carbon (BSIB) (Figure 2c). The formation of BSIB can be explained by a reaction between TMSCl and lithiated SIB which was formed by LDA shown in eqs 3 and 4.



To get more information about the metalation reaction of DMST, the equilibrium constant of eq 1 was determined and compared to that of MST and toluene (Table 1). In contrast to the reaction between MST and LDA ($K_{MST} = 5.4 \times 10^{-1}$ at 20 °C in THF[10]), the equilibrium constant for the reaction of DMST and LDA was smaller ($K_{DMST} = 9.3 \times 10^{-2}$ under the same reaction conditions) and the metalation of toluene was not detected under the same reaction condition (run 3 in Table 1). The lower equilibrium constant for the metalation reaction of DMST than that of MST may result from the lower stability of carbanion, IBL, as compared to VBL, because of less extended conjugation of the phenyl π-system with the isopropenyl group than that with the vinyl group, due to steric hindrance of the methyl group in the isopropenyl substituent. Actually, an AM 1 calculation showed that a twist angle[13] between the phenyl plane and the isopropenyl plane in DMST was not 0° but 37.9°, indicating lower contribution of the isopropenyl group in the conjugation with the phenyl system. From the equilibrium constant obtained, the mole ratio of [DMST]/[LiDMST] should be 0.138/0.012 (mol/L) for the metalation reaction carried out under the initial concentration of $[DMST]_0/[LDA]_0/[DPA]_0 = 0.15/0.45/0.45$ (mol/L) in THF at 20 °C.

However, as we reported previously,[10] the rate of the reaction of TMSCl with LDA was much lower than with the carbanion, so that if TMSCl is added into the reaction system containing lithiated DMST and LDA slowly enough, the yield would be expected to increase. Therefore, we maintained the concentration of TMSCl as low as possible, because a small amount of TMSCl can react preferentially with lithiated DMST, and subsequently, lithiated DMST was added to maintain the equilibrium system. In this way, BSIB was obtained in 82% yield even when $[DMST]_0/[LDA]_0/[DPA]_0/[TMSCl]_0 = 0.15/0.45/0.45/2.5$ (mol/L) in THF at 20 °C, if TMSCl was slowly added over a period of 22 h.

Anionic Polymerization of BSIB. To investigate polymerizability of this organosilicon-containing α-methylstyrene derivative, anionic polymerization was carried out, and the results obtained are summarized in Table 2. *n*-BuLi was found to be a good initiator to form a polymer with a narrow molecular weight distribution (MWD) at −50 °C in THF. The molecular weight of that polymer was, however, much higher than expected from the monomer/initiator ratio. Contrary to *n*-BuLi, *sec*-BuLi gave the polymer with the expected molecular weight and narrow MWD. These results indicated that aggregation of *n*-BuLi in THF slowed down initiation with respect to the rate of propagation from free ion species.[14] Actually, living lithium α-methylstyrene oligomer, which is also known to exist monomeric species in THF, gave the polymer almost quantitatively with the expected molecular weight and narrow MWD. In the case of *tert*-BuLi as an initiator, the polymerization showed the similar tendency to that of *n*-BuLi although the initiator efficiency was slightly higher than that of *n*-BuLi. Gordon and his coworkers reported that a rate of anionic polymerization of styrene in THF followed the order *sec*-BuLi > *tert*-BuLi ≫ *n*-BuLi.[14b] From the computational studies, they reported that lower reactivity of *tert*-BuLi relative to *sec*-BuLi was due to the difference in activation energies of the initiation reactions, but not to aggregation of *tert*-BuLi. The BSIB polymerization with *tert*-BuLi, however, cannot be explained by the difference in activation energies, because high activation energy usually induces broadening of the MWD. The present polymerization system with *tert*-BuLi strongly indicates two different initiator species (monomeric and aggregates) as in an *n*-BuLi system although the aggregates may not be a tightly bounded. Initiation by 1,1-diphenylhexyllithium gave no polymer even at −50 °C, probably due to higher stability of diphenylmethyl carbanion relative to that of the potential propagating BSIB carbanion. Therefore, anionic polymerization of BSIB gave a polymer with narrow MWD at −50 °C in THF although initiation efficiency was strongly

Table 2. Anionic Polymerizations of BSIB[a]

initiator	T, °C	t, h	conversion,[b] %	$\bar{M}_n \times 10^{-3}$ calcd[c]	$\bar{M}_n \times 10^{-3}$ measured	$\bar{M}_w/\bar{M}_n$[b]	initiator efficiency,[d] %
n-BuLi	−50	4	93.4	5.2	58[b]	1.20	9.0
sec-BuLi	−50	1	93.4	5.2	5.7[e]	1.18	91.2
tert-BuLi	−50	4	93.5	5.2	40[b]	1.23	13.0
living lithium oligo(α-methylstyrene)	−40	1	94.5	5.7	5.6[e]	1.24	102.6
(1,1-diphenylhexyl)lithium	−50	13	0.0				0.0

[a] $[M]_0 = 1.0$ mol/L; $[I]_0 = 0.05$ mol/L; solvent, THF. [b] Determined by GPC. [c] Calculated by the following equation: M_n(calcd) = {(MW of BSIB × $[BSIB]_0$ × conversion}/(100 × $[initiator]_0$) + MW of initiator. [d] Calculated by following equation: initiator efficiency (%) = 100 × M_n(calcd)/M_n(measured). [e] Determined by ^1H NMR. Phenyl protons and methyl protons of *sec*-butyl moiety at the polymer chain end were used for calculation. (*sec*-BuLi was used to prepare living lithium oligo(α-methylstyrene).)

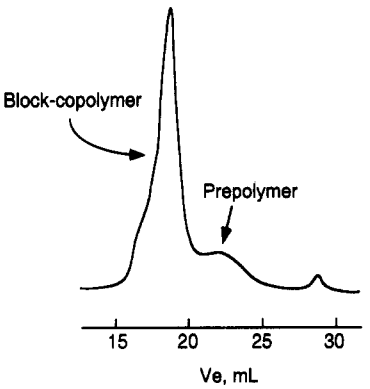


Figure 3. GPC of the reaction mixture from copolymerization of BSIB with styrene.

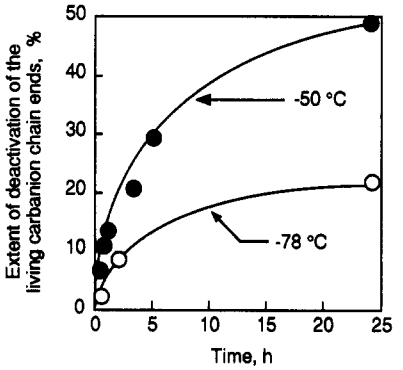


Figure 4. Stability of the living chain ends of poly(BSIB) in THF at −50 (●) and at −78 °C (○). $[\text{Living end}]_0$ = 0.05 mol/L.

affected by the structure of initiator.

As BSIB was a novel monomer, thermodynamics of this polymerization were investigated. After the polymerization had been run for 24 h at −50 °C (more than 93% of the monomer was consumed within 5 min under the following conditions: $[\text{BSIB}]_0/[\textit{sec}\text{-BuLi}]_0$ = 1.0/0.05 (mol/L); THF), the temperature was raised to 20 °C. GPC measurement showed that 48.7% of the polymer resisted depolymerization, indicating certain deactivation of the carbanion active centers. To verify this observation, a block copolymerization with styrene was carried out. Figure 3 shows GPC of the polymerization mixture after styrene was added to a prepolymer solution prepared under the same condition as above. As can be seen from this figure, 56% of the prepolymer remained unreacted, indicating that more than one half of the poly(BSIB) carbanion deactivated after 24 h at −50 °C in THF. It should be noted that the carbanions of the living poly(α-methylstyrene) chain end were stable under the same reaction conditions.[15] The instability of poly(BSIB) carbanions may be explained by an electron-donating character of the *p*-bis[(trimethylsilyl)methyl] substituent toward the benzylic systems. Figure 4 shows the extent of deactivation of the carbanion chain ends at −50 and −78 °C as a function of time. At −50 °C, 6.6% of the chain ends was deactivated after about 5 min. With increasing reaction time, this increased to 50% after 24 h at −50 °C. At −78 °C, less than 2.3% of the carbanions was deactivated within 20 min of the reaction. To evaluate the rate of deactivation, the first-order plots were constructed using the data of Figure 4. In THF, an unstable alkyllithium such as *n*-BuLi is known to react with the solvent to form (vinyloxy)lithium at ambient temperature.[16] If the similar reaction can be assumed for the deactivation of poly(BSIB) carbanion in THF, the first-order plots should be straight, because of a large excess of THF. However, the first-order plots for

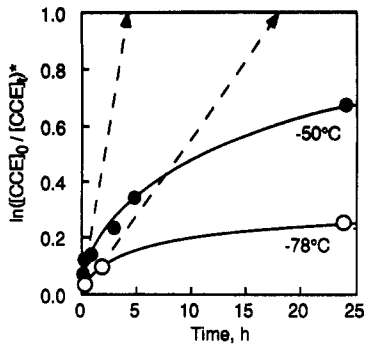


Figure 5. First-order plots for the deactivation reaction of the poly(BSIB) chain ends. (Condition as in Figure 4. The asterisk (*) CCE denotes "carbanion chain end".)

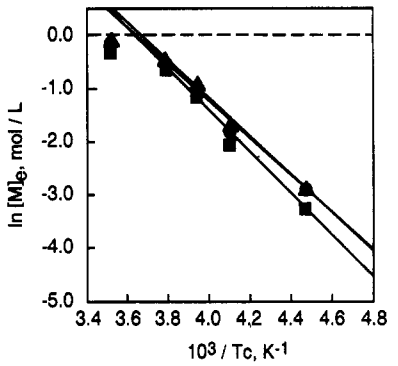


Figure 6. Plots of the equilibrium monomer concentration, $[M]_e$, *vs* $1/T$. $[M]_e$ values were determined by GC (■), GPC (●), and ^{1}H NMR (▲).

the deactivation reaction showed a gradual decrease of the rate of deactivation (Figure 5), suggesting that this rate was affected by stabilization of the carbanions by surrounding alkoxide groups liberated from the side reactions.[17]

To get further information on thermodynamic data including the ceiling temperature, the equilibrium monomer concentrations ($[M]_e$) were determined at a different temperature by using GC, GPC, and ^{1}H NMR. Figure 6 shows plots of $\ln[M]_e$ vs $1/T$ thus obtained. Regardless of different analytic methods used, the obtained data agreed well with each other within the experimental error and showed good linearities. From the straight lines shown in the figure, the ceiling temperature (T_c) for the anionic polymerization of BSIB in THF ($[M]_e$ = 1.0 mol/L) was estimated to be 1.2 ± 0.9 °C. By using eq 5,[18] $\Delta H°$ and $\Delta S°$ were determined to be −30.3 ± 1.6 kJ mol^{-1} and −110.2 ± 5.7 J mol^{-1} K^{-1}, respectively; very similar to those for α-methylstyrene (T_c = 5.7 °C, $\Delta H°$ = −33.5 kJ mol^{-1}, $\Delta S°$ = −120.2 J mol^{-1} K^{-1}).[15]

$$\ln[M]_e = \Delta H°/RT - \Delta S°/R \qquad (5)$$

Stereoregularity of Poly(BSIB) Formed by Anionic Polymerization. We reported previously that anionic polymerization of *p*-bis[(trimethylsilyl)methyl]styrene in apolar solvents gave higher stereoregular polymer probably due to steric effect of the bulky substituent.[19]

^{13}C NMR Spectra of poly(BSIB) showed only one signal assignable to phenyl C^1 at 143 ppm (Figure 7b), indicating fairly high stereoregularity. In addition to this, the main-chain methylene group signal was also a sharp singlet, which supports the above consideration.

Thermal Properties of Poly(BSIB). Similar to the situation earlier found for other Si-containing poly(methylstyrene) derivatives,[3] the polymers synthesized in

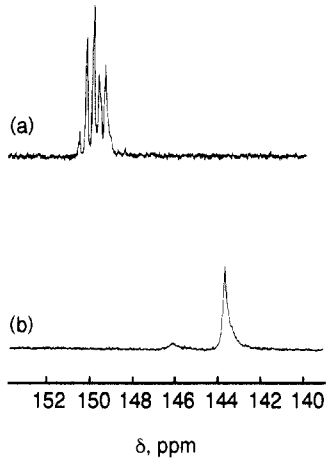


Figure 7. ^{13}C NMR spectra of C^1 of poly(α-methylstyrene) and poly(BSIB).

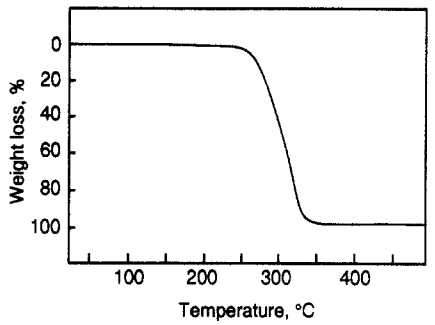


Figure 8. Thermal gravimetric analysis (TGA) curve of poly(BSIB). (Sample weight 7 mg; heating rate 20 °C/min from 30 to 500 °C under argon atmosphere.)

this study showed that the T_g values of the polymers depended on the relative content of the Si-substituents. Thus, one or two trimethylsilyl group(s) in poly(DMST), gave T_g values of 132 and 224 °C, respectively. Therefore, poly(BSIB) was found to have one of the highest glass transition temperatures among polystyrene homologues.

Figure 8 shows TGA curve of poly(BSIB) in an argon atmosphere. It can be seen from this figure that the weight loss onset was around 250 °C and that the polymer was annihilated completely at about 350 °C.

Conclusion

The novel Si-containing α-methylstyrene derivative (BSIB) was synthesized in 83% yield by reaction of DMST with LDA and TMSCl. The anionic polymerizations of BSIB using *sec*-BuLi and living lithium α-methylstyrene oligomer as initiators proceeded homogeneously to give polymers with controlled molecular weights and narrow molecular weight distributions. The ceiling temperature for this anionic polymerization in THF was 1.2 ± 0.9 °C, slightly lower than that for α-methylstyrene. Other thermodynamic data for this polymerization were, $\Delta H° = -30.3 \pm 1.6$ kJ mol^{-1} and $\Delta S° = -110.2 \pm 5.7$ J mol^{-1} K^{-1}. The obtained polymer was highly stereoregular with an extremely high glass transition temperature, owing to its bulky para substituents. It is expected that such silicon-containing polymers with high T_g and depolymerization tendency can be promising candidates for positive electron-beam resist materials.

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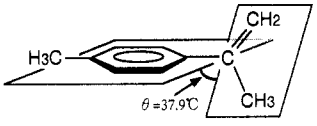
References and Notes

(1) Nagasaki, Y. Silicon-containing Monomers and Polymers. In *Polymers for Emerging Technologies*; Arshady, R., Ed.; American Chemical Society: Washington, DC, 1994 (in press).
(2) Kato, N.; Nagasaki, Y.; Kato, M. *Polym. Adv. Technol.* **1990**, *1*, 341.
(3) Kato, N.; Takeda, K.; Nagasaki, Y.; Kato, M. *Ind. Eng. Chem. Res.* **1994**, *33*, 417.
(4) Kato, N.; Suruga, T.; Takeda, K.; Nagasaki, Y.; Kato, M. *J. Photopolym. Sci. Technol.* **1992**, *5*, 585.
(5) Perrin, D. D.; Armarego, W. L. F.; Moor, F. W. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, 1980.
(6) (a) Gilman, H.; Langham, W.; Moor, F. W. *J. Am. Chem. Soc.* **1941**, *62*, 2327. (b) Gilman, H.; Haubeim, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515.
(7) Yuki, H.; Otsu, K. *Kougyoukagakuzasshi* **1967**, *70*, 123.
(8) Dewar, M. J. S.; Zoebische, E. G.; Healy, E. F.; Stwart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(9) MOPAC version 4.01, supplied from J. J. P. Stwart, Frank J. Seiler Research Lab., U.S. Air Force Academy, Colorado Springs, CO 80840, and implemented on HITAC M680 by T. Hirano and T. Tominaga.
(10) Nagasaki, Y.; Tsuruta, T. *Makromol. Chem.* **1986**, *187*, 1583.
(11) For reviews, see: Nagasaki, Y.; Tsuruta, T. *New Polym. Mater.* **1991**, *2*, 357.
(12) Nagasaki, Y.; Tsuruta, T. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 437.
(13) A twist angle (θ) between the phenyl plane and the isopropenyl plane was defined as follows:



(14) (a) Waiter, B.; William, R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371. (b) Ogle, C. H.; Wang, X. L.; Johnson, H. C., IV; Strickler, F. H.; Gordon, B., III. *Polymer Preprints (ACS)* **1993**, *34*, 336.
(15) Worsfold, D. J.; Bywater, S. *J. Polym. Sci.* **1957**, *26*, 299.
(16) Jung, M. E.; Blum, R. B. *Tetrahedron Lett.* **1977**, 3791.
(17) Müller et al. reported that *tert*-butoxylithium suppressed a deactivation rate in an anionic polymerization of acrylate. (Janata, M.; Lochmann, L.; Vlcek, P.; Dybal, J.; Müller, A. H. E. *Makromol. Chem.* **1992**, *193*, 10.1.)
(18) McCormick, H. W. *J. Polym. Sci.* **1957**, *25*, 488.
(19) Kato, N.; Nagasaki, Y.; Kato, M. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 569.