# Polymaleimides Bearing a Readily Hydrolyzable Side Group: Synthesis and Polymerization of N-Trialkylsilylmaleimides and Characterization of the Polymers

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ABSTRACT: Three N-trialkylsilylmaleimides (RSiMI), i.e., N-(trimethylsilyl)maleimide (MSiMI), N-(tert-butyldimethylsilyl)maleimide (BSiMI), and N-(dimethylthexylsilyl)maleimide (TSiMI) were prepared by reactions of maleimide or silver maleimide with a respective trialkylsilylchloride. These RSiMIs were polymerized in bulk or in benzene with a radical initiator to give high molecular weight polymers ($[\eta] = 0.12$—$1.35\,\mathrm{dl\,g^{-1}}$). Anionic polymerization was also performed with s-butyllithium in tetrahydrofuran at $-78°C$. The resulting polymaleimides bearing N-silyl substituents were soluble in many organic solvents including benzene, tetrahydrofuran, dioxane, and chloroform. They showed excellent thermal stability. The glass transition temperatures were determined to be 261, 216, and 204°C for poly(MSiMI), poly(BSiMI), and poly(TSiMI), respectively, by differential scanning calorimetry. The onset temperatures of decomposition of the polymers were 328—335°C by thermogravimetric analysis in nitrogen. Poly(RSiMI)s were quantitatively converted into polymaleimide by hydrolysis.
 KEY WORDS Polymaleimide / N-Trialkylsilylmaleimide / Radical Polymerization / Anionic Polymerization / Thermal Stability / Hydrolysis /

Polymaleimide derivatives have been recently advanced as a new vinyl polymer with merits of facility of polymer production (high polymerization reactivity of the monomers) and excellent thermal stability. In previous papers,[1-7] we reported the radical polymerization of N-alkyl-substituted maleimides and N-(alkyl-substituted phenyl)maleimides and some properties of the resulting polymers. These polymaleimides have excellent thermal stabilities, i.e., high glass transition temperatures ($T_g$) and decomposition temperatures. They consist of a substituted polymethylene structure as well as polymers from other 1,2-disubstituted ethylenes such as dialkyl fumarates.[8,9]

In recent years, many silyl-containing polymers have been prepared and applicated to a wide variety of fields,[10-19] e.g., material separation, lithographic photoresists, electron-conductive polymers, and composites with ceramics. On the other hand, several trialkylsilyl groups are popularly used as a protective group of various functional groups in organic synthesis because of convenience of protection and deprotection.[20,21] The protection of functional groups in some vinyl monomers has been intensively developed by Nakahama and coworkers to synthesize functional polymers with a well-defined structure by living anionic polymerization.[22]

However, there is no report on polymerization of maleimide of which N–H group is protected by trialkylsilyl group i.e., N-trialkylsilylmaleimides (RSiMI), except our preliminary results of preparation and polymerization of RSiMIs.[23] In this paper, the preparation and radical and anionic polymerizations of N-(trimethylsilyl)maleimide (MSiMI), N-(tert-butyldimethylsilyl)maleimide (BSiMI), and N-
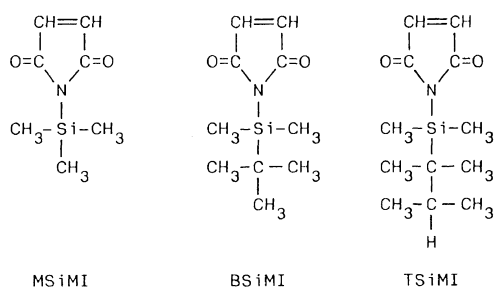
Scheme 1.

(dimethylthexylsilyl)maleimide (TSiMI) as shwon in Scheme 1, and thermal stability and hydrolysis of the resulting polymers are described.

## EXPERIMENTAL

### Monomers

To synthesize MSiMI, maleimide (25 g, 0.26 mol) was reacted with trimethylsilylchloride (65 ml, 0.52 mol) in the presence of triethylamine (36 ml, 0.26 mol) in benzene (300 ml) with reflux for 5 h. MSiMI obtained was purified by column chromatography on alumina with benzene as an eluent, followed by distillation under a reduced pressure: Colorless liquid, yield 33.6 g (77%), bp 75°C (5 mmHg). IR (neat) 3100, 2950, 2900, 1700, 1590, 1330, 1250, 1135, 1070, 995, 845, 760, 700, and 625 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz), $\delta$ 6.67 (s, 2H, CH=) and 0.42 ppm (s, 9H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 100 MHz), $\delta$ 176.2 (C=O), 136.2 (C=C), and $-0.5$ ppm (CH$_3$).

BSiMI was prepared from maleimide (8.2 g, 0.084 mol) and tert-butylsilylchloride (14 g, 0.093 mol) in the presence of triethylamine (14 ml, 0.10 mol) in benzene (200 ml) with reflux for 10 h. BSiMI was recrystallized from benzene after passed through alumina with benzene: White crystal, yield 7.4 g (41%), mp 72°C. IR (KBr) 3100, 2950, 2850, 1695, 1595, 1470, 1340, 1255, 1140, 1085, 1005, 860, 830, 790, and 705 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz), $\delta$ 6.69 (s, 2H, CH=), 0.93 (s, 9H,
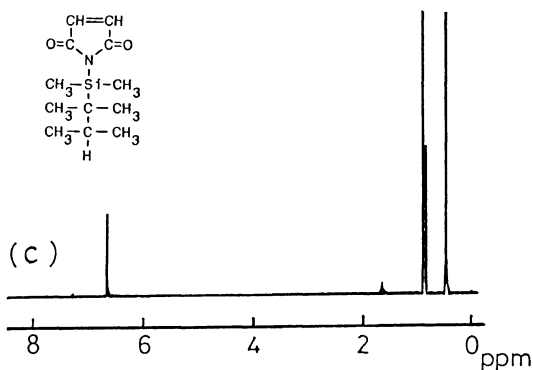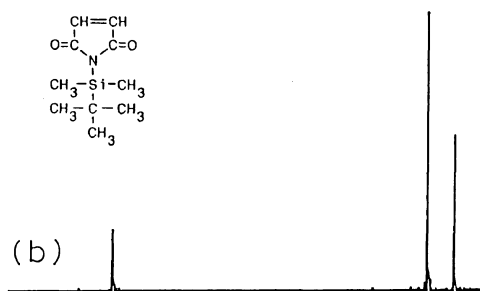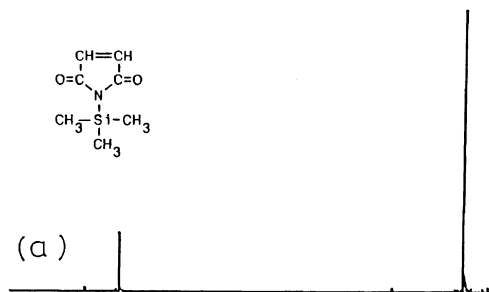


Figure 1. $^1$H NMR spectra of (a) MSiMI, (b) BSiMI, and (c) TSiMI in CDCl$_3$.

C(CH$_3$)$_3$), and 0.44 ppm (s, 6H, Si(CH$_3$)$_2$); $^{13}$C NMR (CDCl$_3$, 100 MHz), $\delta$ 176.4 (C=O), 136.1 (C=C), 26.1 (C(CH$_3$)$_3$), 18.8 (C(CH$_3$)$_3$), and $-4.7$ ppm (Si(CH$_3$)$_2$).

BSiMI was also obtained by an alternative reaction of silver maleimide[24] (5 g, 0.033 mol) and tert-butyldimethylsilylchloride (6.8 g, 0.033 mol) in benzene (50 ml) with reflux for 3 h: Yield 4.8 g (69%), mp 72°C.

TSiMI was synthesized from silver maleimide similarly to BSiMI by the latter method:
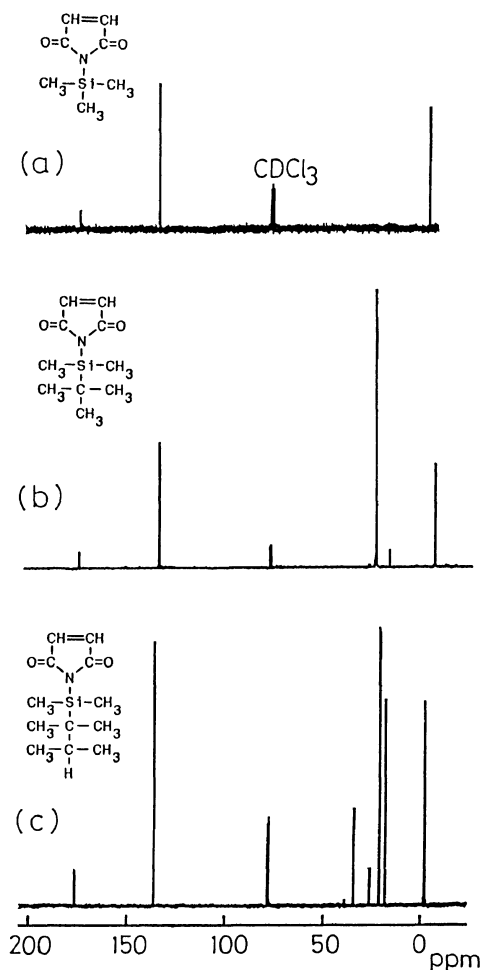
**Figure 2.** $^{13}$C NMR spectra of (a) MSiMI, (b) BSiMI, and (c) TSiMI in CDCl$_3$.



**Figure 3.** IR spectra of (a) MSiMI, (b) BSiMI, and (c) TSiMI.

White crystal, yield 54%, mp 42°C. IR (KBr) 3050, 2910, 1685, 1615, 1580, 1455, 1305, 1240, 1115, 1065, 985, 845, 800, 770, and 690 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz), $\delta$ 6.67 (s, 2H, CH=), 1.65 (sept, $J$=6.7 Hz, 1H, CH), 0.91 (s, 6H, C(CH$_3$)$_2$), 0.87 (d, $J$=6.7 Hz, 6H, CH(CH$_3$)$_2$), and 0.48 ppm (s, 6H, Si(CH$_3$)$_2$); $^{13}$C NMR (CDCl$_3$, 100 MHz), $\delta$ 176.5 (C=O), 136.2 (C=C), 34.0 (CH), 26.0 (SiC(CH$_3$)$_2$), 20.9 (C(CH$_3$)$_2$), 18.4 (C(CH$_3$)$_2$), and −2.2 ppm (Si(CH$_3$)$_2$).

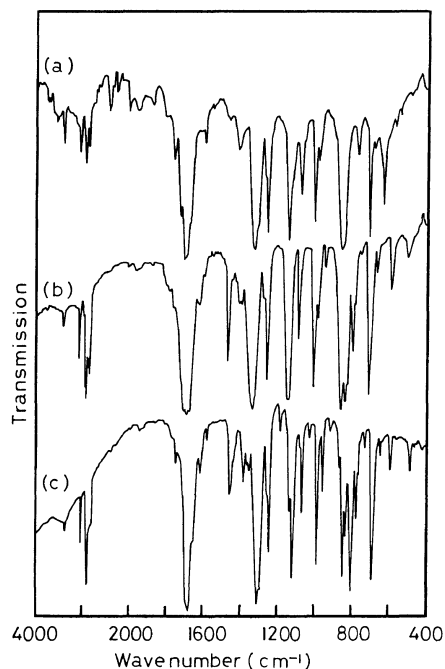$^1$H and $^{13}$C NMR and IR spectra of RSiMIs obtained are shown in Figures 1—3, respec-

tively.

*N-tert*-Butylmaleimide (tBMI) was prepared as the method described previously[3]: bp 54°C (3.5 mmHg). IR (neat) 2980, 1710, 1600, 1380, 1240, 1170, 1015, 865, 725, and 620 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 60 MHz), $\delta$ 6.55 (s, 2H, CH=) and 1.55 ppm (s, 9H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 15 MHz), $\delta$ 171.1 (C=O), 133.3 (C=C), 56.2 (C(CH$_3$)$_3$), and 28.1 ppm (CH$_3$).

### Other Reagents

2,2'-Azobisisobutyronitrile (AIBN) and 1,1'-azobiscyclohexanecarbonitrile (ACN) as an initiator were recrystallized from methanol. Solvents and other reagents were used after purification by ordinary methods.

### Polymerization Procedures

Radical polymerization was carried out in benzene or bulk in the presence of AIBN or ACN in a sealed glass tube. After a given time, a polymerization mixture was poured into a

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large amount of methanol or hexane to precipitate a polymer, which was filtered, washed with methanol or hexane, and then dried *in vacuo* at room temperature.

Anionic polymerization was performed with *s*-butyllithium (sBuLi) in tetrahydrofuran (THF) at $-78°C$. Transfer of materials was carried out by use of a Y-shaped tube and a hypodermic syringe in a nitrogen atmosphere. Polymerization was stopped with a small amount of methanol containing hydrochloric acid, and then the polymerization mixture was poured into a large amount of methanol. The polymer was filtered and dried.

## Measurements

$^1H$ and $^{13}C$ NMR spectra were recorded on Hitachi R-24B (60 MHz) or JEOL GX-400 (400 MHz) spectrometers with deuterochloroform and deuterodimethyl sulfoxide (DMSO-$d_6$) as a solvent. Infrared spectra were recorded on a JASCO A-202 spectrometer. Intrinsic viscosity ($[\eta]$) of polymers was determined in benzene or *N,N*-dimethylformamide (DMF) at 30°C by using an Ubbelohde viscometer. Differential scanning calorimetry (DSC) was performed with a scanning rate of $20°C \, min^{-1}$ by use of a Seiko DSC-200. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream with a heating rate of $10°C \, min^{-1}$ by use of a Seiko TG-200.

## RESULTS AND DISCUSSION

### Radical Polymerization

Radical polymerization of RSiMIs was carried out in benzene or bulk in the presence of a radical initiator. The results are summarized in Table I. Polymerizations of all RSiMIs proceeded homogeneously and gave high molecular weight polymers. Bulk polymerization yielded higher molecular weight poly-(RSiMI)s, *i.e.*, $[\eta] = 1.35$ and $0.84 \, dl \, g^{-1}$ for poly(MSiMI) and poly(BSiMI), respectively, as expected. When the polymerization reactivity was compared, steric bulkiness of the *N*-substituents of RSiMI seemed to be significant on reactivity, *i.e.*, the yields and $[\eta]$ of poly(RSiMI)s in the polymerization in benzene with AIBN at 60°C for 5 h were as follows: the polymer yields were 62.1, 60.5, and 28.0%, and $[\eta]$ was 0.40, 0.35, and $0.12 \, dl \, g^{-1}$ for poly(MSiMI), poly(BSiMI), and poly(TSiMI), respectively.

The effect of the *N*-substituents of polymerization rates ($R_p$) of RSiMIs was further examined. Time-conversion relationships are depicted in Figure 4, where the results of *N-tert*-butylmaleimide (tBMI) are also included for comparison. It is clear that all RSiMIs have smaller slopes of the lines in the figure, *i.e.*, lower $R_p$ than that of tBMI, and the order of $R_p$ is as follows: tBMI > BSiMI ≳

**Table I.** Radical and anionic polymerizations of RSiMIs

| Monomer | Initiator | Solvent | Temp. | Time | Yield | $[\eta]$[a] |
|---|---|---|---|---|---|---|
| mol l$^{-1}$ | mmol l$^{-1}$ | | °C | h | % | dl g$^{-1}$ |
| MSiMI (1.0) | AIBN (5) | Benzene | 60 | 5 | 62.1 | 0.40[b] |
| MSiMI (bulk) | AIBN (5) | None | 60 | 5 | 33.4 | 1.35[b] |
| MSiMI (1.3) | sBuLi (54) | THF | −78 | 3 | 0 | — |
| BSiMI (1.0) | AIBN (5) | Benzene | 60 | 5 | 60.5 | 0.35 |
| BSiMI (bulk) | ACN[c] | None | 80 | 5 | 39.7 | 0.84 |
| BSiMI (0.17) | sBuLi (16) | THF | −78 | 1 | 34.7 | 0.35[b] |
| TSiMI (1.0) | AIBN (5) | Benzene | 60 | 5 | 28.0 | 0.12 |

[a] In benzene at 30°C.
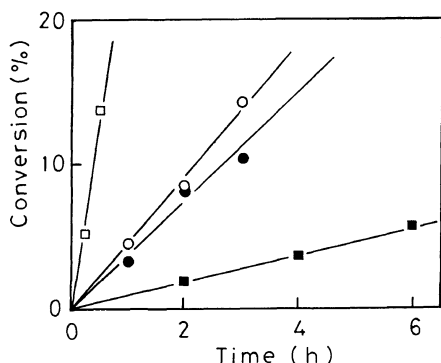[b] In DMF at 30°C, determined as poly(MI) after hydrolysis.
[c] 0.1 mol%.

**Figure 4.** Time–conversion relationships for radical polymerization of RSiMIs with AIBN ($1 \times 10^{-3}\,mol\,l^{-1}$) in benzene at 60°C: (●) [MSiMI] = 1.42 mol l$^{-1}$; (○) [BSiMI] = 1.50 mol l$^{-1}$; (■) [TSiMI] = 1.50 mol l$^{-1}$; (□) [tBMI] = 1.42 mol l$^{-1}$.
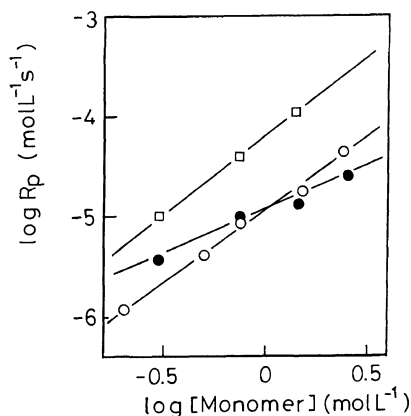


**Figure 5.** Dependence of the monomer concentration on $R_p$ for radical polymerization of RSiMI with AIBN ($1 \times 10^{-3}\,mol\,l^{-1}$) in benzene at 60°C: (●) MSiMI; (○) BSiMI; (□) tBMI.

MSiMI > TSiMI. A similar decrease in polymerization reactivity by introduction of bulky N-substituents has also been reported in the case of polymerization of N-tert-alkylmaleimides.[4]

In Figure 5, monomer concentration dependence on $R_p$ for MSiMI, BSiMI, and tBMI is shown. In the whole range of monomer concentrations examined, MSiMI and BSiMI showed lower $R_p$ than that of tBMI. The reason for the less reactivity of RSiMIs is not clear, but the difference in an electronic structure of

the monomers might not be negligible as well as steric hindrance. When the chemical shifts of the C=C bond in NMR spectra were compared, the resonance of MSiMI was observed at a lower magnetic field than tBMI in spite of resemble structures, i.e., $\delta$ 136.2 and 6.67 for MSiMI and $\delta$ 133.3 and 6.55 for tBMI in the $^{13}$C and $^{1}$H NMR spectra, respectively. The slopes of the lines in Figure 5 represent a kinetic order with respect to the monomer concentration in polymerization, being larger than unity; i.e., the slopes were 1.43 and 1.54 for BSiMI and tBMI, respectively. On the other hand, the order of MSiMI was almost unity. Since viscosity of polymerization media affects termination rates to enlarge the apparent kinetic order,[25–27] a correction with viscosity of the polymerization systems in this work was attempted. However, the reaction orders were 1.27 and 1.50 for BSiMI and tBMI, respectively, indicating that factors other than viscosity should be considered. Similar high reaction orders with respect to the monomer concentration have been reported for other maleimide derivatives,[28–31] but the real reason has not been clarified yet at the present time. We are now continuing kinetic studies on N-substituted maleimides including RSiMI by means of electron spin resonance spectroscopy.

### Anionic Polymerization

Anionic polymerization of maleimide derivatives has already been reported by several workers.[32–38] In this work, anionic polymerization of RSiMI was carried out with sBuLi as an initiator in THF at −78°C. BSiMI was found to give a high molecular weight polymer ($[\eta] = 0.35\,dl\,g^{-1}$), whereas MSiMI did not give any polymer. It is considered that the high nucleophilicity of the s-butyl anion induces predominantly a side reaction, presumably an attack to the N–Si bond of MSiMI. In the case of BSiMI, a bulky tert-butyl group on Si is likely to obstruct such a reaction by steric hindrance.[39] Hirao et al. reported[40–42]

**Table II.** Solubility of poly(RSiMI)s[a]

| Solvent | Poly(MSiMI) | Poly(BSiMI) | Poly(TSiMI) | Poly(MI) |
|---------|-------------|-------------|-------------|----------|
| Hexane | i | sw | sw | i |
| Benzene | s | s | s | i |
| THF | s | s | s | i |
| CHCl$_3$ | s | s | s | i |
| Acetone | — | sw | i | i |
| Dioxane | s | s | s | i |
| DMF | — | s | sw | s |
| DMSO | — | s | sw | s |
| Methanol | — | i | i | i |

[a] s, soluble; sw, swelling; i, insoluble.



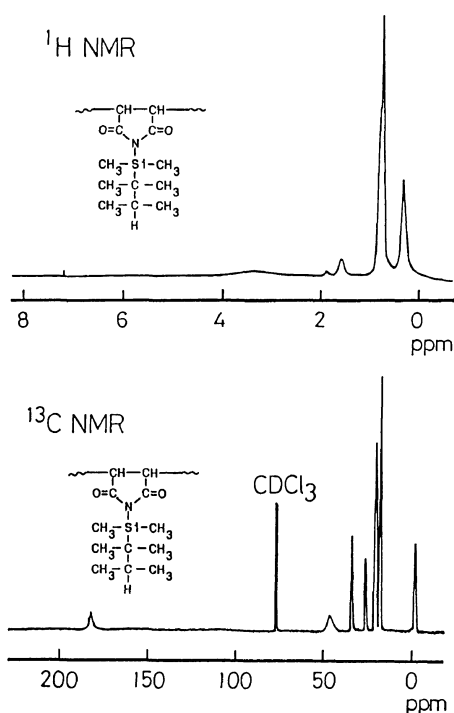**Figure 6.** $^1$H and $^{13}$C NMR spectra of poly(TSiMI) in CDCl$_3$.

the anionic polymerization of *p*-hydroxystyrene derivatives bearing trialkylsilyl groups as a protect of the hydroxy group. They found that a *tert*-butyldimethylsilyl group was superior as a protected group to give a high molecular weight polymer, whereas trimethylsilyl-substituted one did not polymerize.

## Characterization of the Polymers

All poly(RSiMI)s are colorless powders and soluble in THF, benzene, chloroform, and dioxane, as shown in Table II. Poly(BSiMI) is also soluble in DMSO and DMF, and swelling in hexane and acetone. Poly(MSiMI) is liable to be hydrolyzed in protic solvents, leading to precipitation of the polymer as mentioned later. Transparent thin-films were obtained by casting of the solution of poly(RSiMI)s, but were considerably brittle.

$^1$H and $^{13}$C NMR spectra of poly(TSiMI) are shown in Figure 6. In these spectra, absorption due to the carbon-to-carbon double bond of the monomer at $\delta$ 6.67 and 136.2 ppm are absent, and broad peaks due to the methine proton and carbon were observed at *ca.* $\delta$ 3.5 and 45 ppm, respectively. Similar results were also observed for other poly(RSiMI)s. In IR spectra of poly(RSiMI)s (Figures 9(a) and 11(a)), absorption due to stretching vibration of the C=C bond of the monomer around 1590 cm$^{-1}$ disappeared on polymerization. These results indicate the formation of a substituted polymethylene *via* an opening of the double bond of RSiMIs.

## Thermal Stability of the Polymers

The thermal properties of poly(RSiMI)s were examined. From DSC curves in Figure 7, it is clear that these poly(RSiMI)s have high $T_g$: 261, 216, and 204°C for poly(MSiMI), poly(BSiMI), and poly(TSiMI), respectively.

From the TGA thermograms as shown in Figure 8, the initial and maximum decomposition temperatures ($T_{init}$ and $T_{max}$) were determined. The results are summarized in Table III with the results for other poly($N$-substituted maleimide)s. $T_{init}$ and $T_{max}$ for poly(RSiMI)s are 328—335°C and 380—396°C, respectively, independent the structures of the $N$-substituents. This indicates that poly(RSiMI)s are thermally stable as well as poly($N$-alkylmaleimide)s reported previously,[1] although they are rather iniferior to poly($N$-phenylmaleimide) (poly(PhMI)) or its alkyl-substituted derivatives[2] and polymaleimide (poly(MI)).[4] Poly(tBMI) bearing a tertiary alkyl group as an $N$-substituent shows lower thermal stability because of the two-step decomposition accompanying quantitative elimination from the side-chain,[4] but it was confirmed that poly(RSiMI)s decompose via a one-step mechanism without olefin elimination from the side chain.

## Hydrolysis of the Polymers

Figure 9 shows IR spectra of poly(MSiMI) recovered under various conditions. When hexane was used as a precipitant for polym-
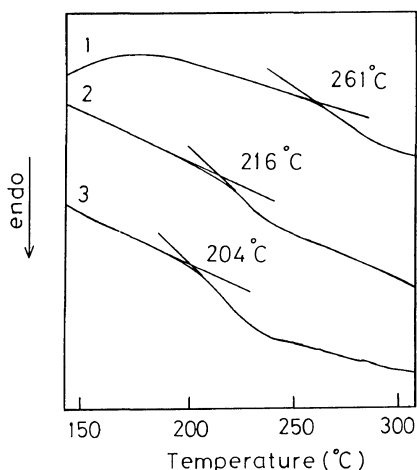
**Figure 7.** DSC traces of poly(RSiMI)s with a heating rate of 20°C min$^{-1}$: (1) poly(MSiMI); (2) poly(BSiMI); (3) poly(TSiMI).
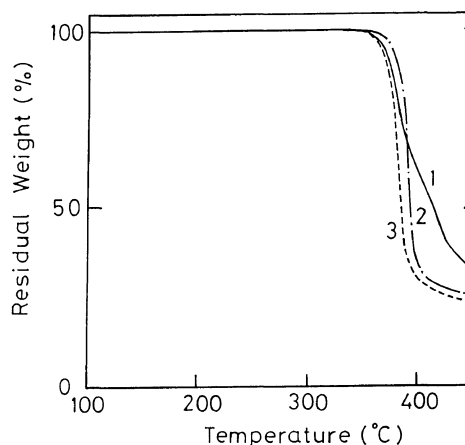
**Figure 8.** TGA curves of poly(RSiMI)s in a nitrogen stream with a heating rate of 10°C min$^{-1}$: (1) poly(MSiMI); (2) poly(BSiMI); (3) poly(TSiMI).

**Table III.** Thermal properties of poly(RSiMI)s

| Polymer | $N$-Substituent | $T_g{}^a$ °C | $T_{init}{}^b$ °C | $T_{max}{}^b$ °C |
|---------|-----------------|--------------|-------------------|------------------|
| Poly(MSiMI) | $Si(CH_3)_3$ | 261 | 328 | 380 |
| Poly(BSiMI) | $Si(CH_3)_2C(CH_3)_3$ | 216 | 335 | 396 |
| Poly(TSiMI) | $Si(CH_3)_2C(CH_3)_2CH(CH_3)_2$ | 204 | 329 | 385 |
| Poly(tBMI) | $C(CH_3)_3$ | —$^c$ | 281 | 328, 432$^d$ |
| Poly(MI) | H | —$^c$ | 380 | 426 |
| Poly(PhMI) | Phenyl | —$^c$ | 364 | 422 |

$^a$ By DSC; Heating rate of 20°C min$^{-1}$.
$^b$ By TGA in a nitrogen stream; Heating rate of 10°C min$^{-1}$.
$^c$ Not detected below $T_{init}$.
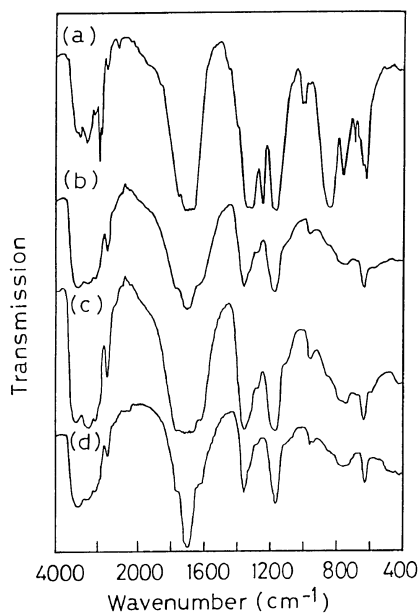$^d$ Decomposed via a two-step reaction.[4]

**Figure 9.** IR spectra of poly(MSiMI): (a) precipitated with hexane; (b) precipitated with methanol; (c) hydrolyzed quantitatively with HCl in dioxane; (d) authentic poly(MI).



**Figure 10.** $^1$H and $^{13}$C NMR spectra of poly(MI) derived from poly(MSiMI) by hydrolysis in dioxane with HCl at room temperature (Figure 9(c)). Solvent, DMSO-$d_6$.

erization of MSiMI, the resulting polymer was isolated as poly(MSiMI). This was confirmed by observation of absorption on the basis of Si(CH$_3$)$_3$ at 1260, 845, and 760 cm$^{-1}$ (Figure 9(a)), where the former is due to a symmetrical deformation of methyl groups, and the latter two absorptions are stretchings of a silyl-methyl bond. A similar conclusion was also obtained by NMR spectroscopy and solubility. On the other hand, when methanol was used as the precipitant, the spectrum of the polymer recovered was consistent with that of authentic poly(MI) (Figures 9(b) and (d)). But it was insoluble in DMF, whereas poly(MI) was soluble in DMF, suggesting that hydrolysis proceeded incompletely in methanol as a precipitant. The quantitative hydrolysis of poly(MSiMI) was accomplished in dioxane containing HCl (0.2 mol l$^{-1}$) at room temperature after several minutes to give a DMF-soluble polymer (Figure 9(c)), and confirmed by $^1$H and $^{13}$C NMR spectra of the hydrolyzed polymer in Figure 10.
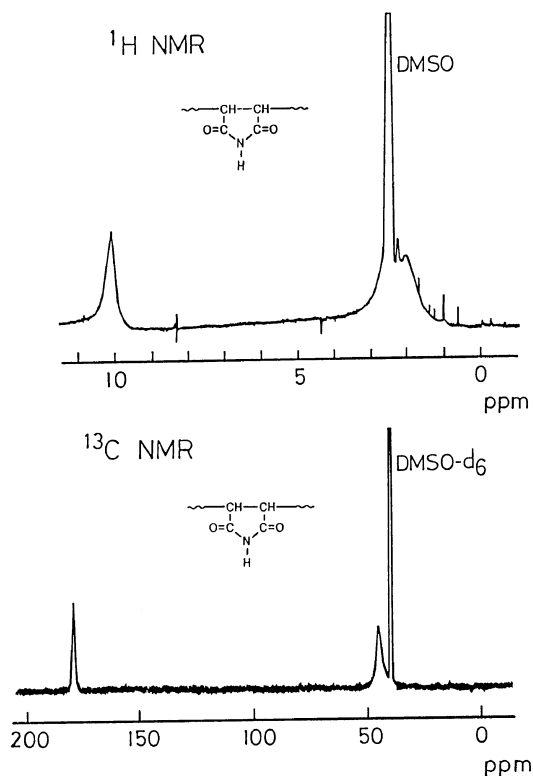
Poly(BSiMI) and poly(TSiMI) showed some resistance to such acid hydrolysis. When methanol was used as a precipitant, the resulting polymers were isolated as poly-(BSiMI) and poly(TSiMI), as shown in the NMR spectra in Figure 6. Absorption on the basis of Si(CH$_3$)$_2$ at around 1250 and 800 cm$^{-1}$ was also detected in the IR spectra (Figure 11(a)), being different from the case of poly(MSiMI). Furthermore, hydrolysis proceeded rather hardly in dioxane solution of poly(BSiMI) with HCl (0.2 mol l$^{-1}$) after 20 h at room temperature, and reflux of the solution resulted in the formation of a partially hydrolyzed polymer (Figure 11(b)), insoluble in both benzene and DMF. Hydrolysis was performed completely under the following conditions. HCl (1 mol l$^{-1}$) in dioxane with reflux

**Table IV.** Hydrolysis of poly(RSiMI)s[a]

| Conditions | Poly(MSiMI) | Poly(BSiMI) | Poly(TSiMI) |
|---|---|---|---|
| HCl (0.2 mol l$^{-1}$)/Dioxane/r.t./20 h | Q ( <0.5 h) | P | H |
| HCl (1 mol l$^{-1}$)/Dioxane/reflux/5 h | — | Q | P (24 h) |
| Bu$_4$NF (0.2 mol l$^{-1}$)/THF/r.t./1 h | — | Q | Q |

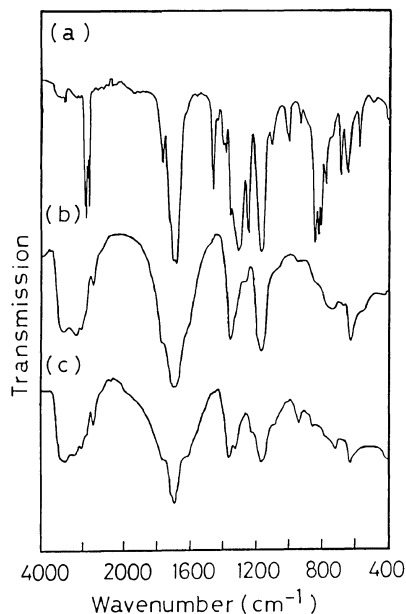[a] Q, quantitatively; P, partially; H, hardly hydrolyzed.



**Figure 11.** IR spectra of poly(BSiMI): (a) precipitated with methanol; (b) refluxed with HCl in dioxane; (c) reacted with Bu$_4$NF in THF.

for 5 h (Figure 11(b)) or tetrabutylammonium fluoride (Bu$_4$NF) (0.2 mol l$^{-1}$) in THF at room temperature for 1 h (Figure 11(c)). Quantitative deprotection was also confirmed by NMR spectroscopy, giving similar spectra to those in Figure 10. The introduction of the bulkier thexyl group gave a more resistant polymer. Hydrolysis of poly(TSiMI) was performed completely by reaction with Bu$_4$NF similarly to poly(BSiMI), but reflux in the dioxane solution of poly(TSiMI) with HCl (1 mol l$^{-1}$) for 24 h resulted in a partially hydrolyzed polymer, which was insoluble in both benzene and DMF.

The results of hydrolysis of poly(RSiMI)s with HCl or Bu$_4$NF are summarized in Table IV. It is concluded that the resistance to hydrolysis of poly(RSiMI)s depends on the steric bulkiness of the alkyl groups in the N-substituents.

## CONCLUSION

RSiMIs were prepared readily from maleimide (or via silver maleimide) with trialkylsilylchlorides. Radical and anionic polymerization of RSiMIs gave high molecular weight polymers soluble in organic solvents such as benzene, THF, and chloroform. These poly(RSiMI)s have excellent thermal stability, i.e., high glass transition temperatures and onset temperatures of decomposition. The hydrolysis of poly(RSiMI)s leads to quantitative formation of polymaleimide under mild conditions for the trimethylsilyl derivative, and more severe conditions for deprotection of the bulkier groups.

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