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Synthesis and Characterization of Poly(*N*-trialkylsilylmaleimide)s through Radical and Anionic Polymerizations

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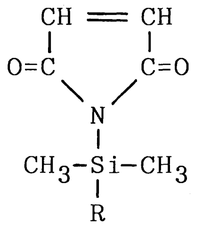
N-Trialkylsilylmaleimides bearing trimethylsilyl, *t*-butyldimethylsilyl and dimethylthexylsilyl groups as *N*-substituents were prepared and polymerized with a radical or anionic initiator. It was revealed that the resulting polymers had a high molecular weight, and showed excellent thermal stability. These polymers were readily converted to polymaleimide by acid hydrolysis.

Recently, polymaleimide derivatives have attracted great attentions on account of their excellent thermal stability. We have reported on the radical polymerization of *N*-alkyl-substituted maleimides and *N*-(alkyl-substituted phenyl)maleimides and on the thermal properties of the resulting polymers,1-4) in the series of study on synthesis and characterization of poly(substituted methylene) from 1,2-disubstituted ethylene monomers.5)

In general, trialkylsilyl groups are widely used as a protective group of various functional groups in organic chemistry because of its convenience of protection and deprotection.6) The protection of the functional groups in some vinyl monomers has been intensively developed by Nakahama et al. to synthesize structure-controlled functional polymers by living anionic polymerization.7) However, no polymerization of maleimides of which N-H group is protected by a trialkylsilyl group, i.e., *N*-trialkylsilylmaleimides has been ever reported. We took a great interest in the polymerization behavior of such silyl-containing maleimides and properties of the resulting polymers. It is also expected that such protection and deprotection method is useful as a route for synthesis of high molecular weight polymaleimide (poly(MI)). It has been reported that *N*-unsubstituted maleimide proceeds radical polymerization and the resulting poly(MI) does not melt below its decomposition temperature,8) but no high molecular weight poly(MI) has been obtained.9) In our previous paper,3) it was reported that relatively high molecular weight poly(MI) was prepared by thermolysis of poly(*N*-*t*-alkylmaleimide)s, i.e. quantitative olefin elimination from the *N*-alkyl substituents, but the decrease in the molecular weight could not be avoided in the reaction at high temperature such as 280-320 °C.

In this study, *N*-(trimethylsilyl)maleimide (**1**) and *N*-(*t*-butyldimethylsilyl)maleimide (**2**) and *N*-dimethylthexylsilyl)maleimide (**3**) were prepared10) and polymerized, and the polymers obtained were characterized on hydrolysis as well as thermal analysis.



R = CH_3 (**1**)
$C(CH_3)_3$ (**2**)
$C(CH_3)_2CH(CH_3)_2$ (**3**)

Radical polymerization of these maleimides was carried out in benzene or in bulk in the presence of 2,2'-azobisisobutyronitrile (AIBN) or 1,1'-azobiscyclohexane-1-carbonitrile (ACN) as an initiator in a sealed glass tube with or without UV irradiation. The resulting polymers were isolated with hexane for poly(**1**) or methanol for poly(**2**) and poly(**3**) as a precipitant. The results of polymerization are summarized in Table 1. The polymerizations of these monomers were found to proceed easily as well as other *N*-alkylmaleimides.1) The measurement of intrinsic viscosity of the resulting polymers has revealed that the polymers have considerably high molecular weight, e.g., [η] = 0.40 and 0.35 dLg^{-1} for poly(**1**) and poly(**2**), respectively, from polymerization in benzene, and [η] = 1.35-1.67 dLg^{-1} from bulk polymerization of **1**. **2** shows high polymerization reactivity as well as **1**, but it has been found that the yield and [η] of the polymer from **3** bearing the bulkiest *N*-substituent decrease. A similar effect of the substituents has been also observed for polymerization of *N*-*t*-alkylmaleimides. Anionic polymerization with *s*-butyllithium (sBuLi) as an anionic catalyst was also attempted in THF at -78 C. As a result, **2** was found to give a high molecular weight polymer ([η] = 0.35 dLg^{-1}) as shown in Table 1, whereas **1** 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 **1**.7) In the case of **2**, the bulky *t*-butyl group on Si is likely to obstruct such a reaction by steric hindrance.

The silyl-containing polymaleimides obtained are colorless powder and soluble in benzene, chloroform, THF and dioxane, and insoluble in methanol. In the IR spectra of the polymers, the absorption of the C-C double bond of the monomers at 1595 cm^{-1} disappeared, indicating the formation of poly(substituted methylene) via an opening of the double bond. Similar results

Table 1. Results for Polymerization of *N*-Trialkylsilylmaleimides

Monomer	Initiator	Solvent	Temp	Time	Yield	$[\eta]^{a)}$
mol L^{-1}	mmol L^{-1}		°C	h	%	dL g^{-1}
1(1.0)	AIBN(5)	Benzene	60	5	62.1	(0.40)
1(bulk)	AIBN(5)	None	60	5	33.4	(1.35)
1(bulk)	AIBN(5)	None	30	138	18.1	(1.67)
1(1.0)	AIBN(50)	Benzene	30(*hv*)	20	64.3	(0.58)
1(1.3)	sBuLi(54)	THF	-78	3	0	-
2(1.0)	AIBN(5)	Benzene	60	5	60.5	0.35
2(bulk)	ACN(5)	None	80	5	39.7	0.84
2(0.17)	sBuLi(16)	THF	-78	1	34.7	(0.35)
3(1.0)	AIBN(5)	Benzene	60	5	28.0	0.12

a) In benzene at 30 °C. The values in parentheses indicate those in DMF at 30 °C after derived into poly(MI) by hydrolysis.

were also observed by NMR spectroscopy.

The thermal stability of these polymaleimides was examined. From DSC measurement, the glass transition temperatures were determined to be 261, 216, and 204 °C for poly(1), poly(2), and poly(3), respectively. Thermogravimetric analysis was also carried out in a nitrogen stream with a heating rate of 10 °Cmin^{-1}. The initial and maximum decomposition temperatures were 328-335 and 380-396 °C for these silyl-containing polymaleimides, respectively. These results indicate that these polymers are thermally stable as well as other poly(*N*-substituted maleimide)s.[1,2]

Poly(1) was readily hydrolyzed to give poly(MI) as expected. When methanol containing water was used as a precipitant for polymerization of 1, the IR spectrum of the polymer recovered was consistent with that of authentic poly(MI). The quantitative hydrolysis of poly(1) was readily accomplished in dioxane containing HCl(0.2 molL^{-1}) at room temperature after several minutes. Poly(MI) is soluble in DMF and DMSO, and insoluble in benzene, THF, and chloroform. It has been found that poly(MI) is also much thermally stable, i.e., it does not show any transition peaks in the DSC thermogram below its decomposition temperature, and the initial and maximum decomposition temperatures are 388 and 426 °C, respectively.[3]

On the other hand, poly(2) and poly(3) showed resistance to an acidic hydrolysis, e.g., no change was observed in dioxane solution of poly(2) with HCl (0.2 molL^{-1}) after 20 h at room temperature. The reflux of the solution resulted in a formation of partly hydrolyzed polymer, which was insoluble in both benzene and DMF. The hydrolysis was performed completely under the following conditions; HCl (1 molL^{-1}) in dioxane with reflux for 5 h or tetrabutylammonium fluoride (0.1 $\mathrm{molL^{-1}}$) in THF at room temperature for 5 h.

Further investigations on polymerizations and some applications of the resulting polymers are now in progress.

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10) **1** was prepared from maleimide and trimethylsilylchloride in the presence of triethylamine in benzene with reflux for 5 h, followed by column chromatography and distillation under a reduced pressure; Yield 77%, bp 75 °C(5 mmHg); ^{13}C NMR($CDCl_3$)δ176.2(C=O), 136.2(C=C), -0.5(CH_3); ^{1}H NMR($CDCl_3$)δ6.67(s, 2H, CH=), 0.42(s, 9H, CH_3). **2** was prepared similarly with reflux for 10 h and recrystallized from benzene; Yield 41%, mp 72 °C. **2** was also obtained by the reaction of silver maleimide[11] with *t*-butyldimethylsilylchloride in benzene with reflux for 3 h; Yield 69%, mp 72 °C; ^{13}C NMR($CDCl_3$)δ176.4(C=O), 136.1(C=C), 26.1($C(\underline{C}H_3)_3$), 18.8($\underline{C}(CH_3)_3$), -4.7($Si(CH_3)_2$); ^{1}H NMR($CDCl_3$)δ6.69(s, 2H, CH=), 0.93(s, 9H, $C(CH_3)_3$), 0.44(s, 6H, $Si(CH_3)_2$). **3** was prepared by the latter method; Yield 54%, mp 42 °C. ^{13}C NMR($CDCl_3$)δ176.5(C=O), 136.2(C=C), 34.0 (CH), 26.0($-\overset{|}{\underset{|}{C}}-$), 20.9 and 18.4($C(\underline{C}H_3)_2$), -2.2($Si(CH_3)_2$); ^{1}H NMR($CDCl_3$) δ 6.67(s, 2H, CH=), 1.65(sept, J = 6.7 Hz, 1H, CH), 0.91(s, 6H, $C(\underline{C}H_3)_2$), 0.87(d, J = 6.7 Hz, 6H, $CH(\underline{C}H_3)_2$), 0.48(s, 6H, $Si(CH_3)_2$).

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