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Synthesis and Reactions of a Polymer Bearing Allylsilane Structure by Radical Ring-Opening Polymerization of a Vinylcyclopropane

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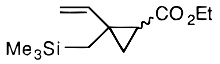
Introduction. Ring-opening polymerization can introduce functional groups into the main chain of the polymer that cannot be attained by vinyl polymerization. Ring-opening polymerization affords a wide range of products, many of which have found important industrial application such as Nylon 6. The chemistry of ring-opening polymerization has been developed by inventions of new cyclic monomers and catalysts. Many cyclic monomers undergo cationic, anionic, and coordination ring-opening polymerizations, while there are some monomers that undergo radical ring-opening polymerization. Most of these radically polymerizable cyclic monomers undergo vinyl polymerization without ring-opening as well as ring-opening polymerization; however, vinylcyclopropanes have been reported to undergo complete ring-opening polymerization.[1] In the course of the study of the radical ring-opening polymerization of vinylcyclopropanes, we have explored poly(silyl enol ether)s via radical ring-opening polymerization and their conversion to polyketones.[2] Meanwhile, allylsilane derivatives are useful synthetic intermediates that react with various electrophiles. Radical ring-opening polymerizations of vinylcyclopropanes may be appropriate to introduce allylsilane structure into the polymer main chain. Polymers bearing allylsilane structure are expected as reactive polymers to convert the functional polymers. In this paper, synthesis of a novel polymer bearing an allylsilane structure by radical ring-opening polymerization of 1-(ethoxycarbonyl)-2-[(trimethylsilyl)methyl]-2-vinylcyclopropane (**1**) and its polymer reaction are disclosed.



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Results and Discussion. Monomer **1** was prepared by the coupling reaction of 2-[(trimethylsilyl)methyl]-butadiene and ethyl diazoacetate[3] in the presence of copper acetylacetonate as a catalyst.[4] 2-[(Trimethylsilyl)methyl]butadiene was prepared by the coupling reaction of chloroprene and [(trimethylsilyl)methyl]-magnesium chloride according to the reported method (Scheme 1).[5] The coupling reaction proceeded at the double bond substituted by the (trimethylsilyl)methyl group, probably due to the electron-donating character of the substituent.[6] From the capillary GC analysis, monomer **1** was confirmed to consist of two isomers whose GC area % ratio was 49:51. The isomers could be separated by preparative HPLC.[7] The configurations of the isomers were analyzed by ^{1}H NMR using the nuclear Overhauser enhancement (NOE) technique.[8]

Scheme 1

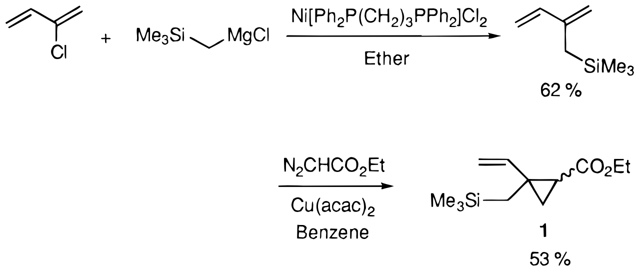


Table 1. Radical Polymerization of 1[a]

run	init[b]	temp (°C)	conv[c] (%)	yield[d] (%)	$\bar{M}_n$[f]	$\bar{M}_w/\bar{M}_n$[c]	olefin content[e] (%)
1	AIBN	60	46	38	7200	2.19	86
2	BPO	80	45	36	3800	2.25	65
3	DTBP	120	62	47	4500	3.32	53

[a] Conditions: monomer 3 mmol, polymerization time 40 h. [b] Initiator 5 mol % *vs* monomer. AIBN, 2,2′-azobis(isobutyronitrile); BPO, benzoyl peroxide; DTBP, di-*tert*-butyl peroxide. [c] Estimated by GPC (based on polystyrene standard samples). [d] Isolate by HPLC. [e] Estimated by ^{1}H NMR.

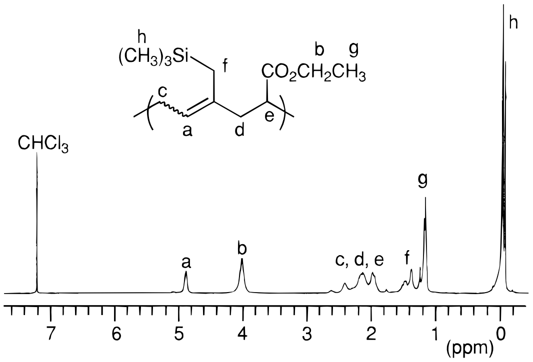
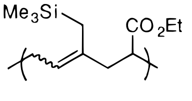


Figure 1. ^{1}H NMR spectrum (solvent $CDCl_3$, 400 MHz) of poly(**1**) (run 1 in Table 1).

Radical polymerization of **1** was carried out in the presence of an appropriate radical initiator (5 mol %) in a degassed sealed tube for 40 h. The polymer formed was isolated by preparative HPLC. Colorless transparent liquid polymers, which were soluble in common organic solvents such as *n*-hexane, methanol, dichloromethane, chloroform, and THF were obtained. The conditions and results are summarized in Table 1. The conversion of **1** was higher in polymerization at 120 °C (run 3) than those at 60 and 80 °C (runs 1 and 2). Single modal GPC curves were observed in any polymers. The molecular weight of the polymer obtained at 60 °C (run 1) was higher than those obtained at 80 and 120 °C (runs 2 and 3).

The structure of poly(**1**) was examined by ^{1}H and ^{13}C NMR spectra. It was confirmed that no cyclopropane ring was incorporated into the polymer, as evidenced by the absence of signals in the field higher than 1 ppm in the ^{1}H NMR spectrum (Figure 1). The main structure of the polymer might consist of 1,5-ring-opened unit **2**, as previously reported in the radical polymerization of 1,1-disubstituted-2-vinylcyclopropanes.[1] Since no



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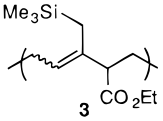

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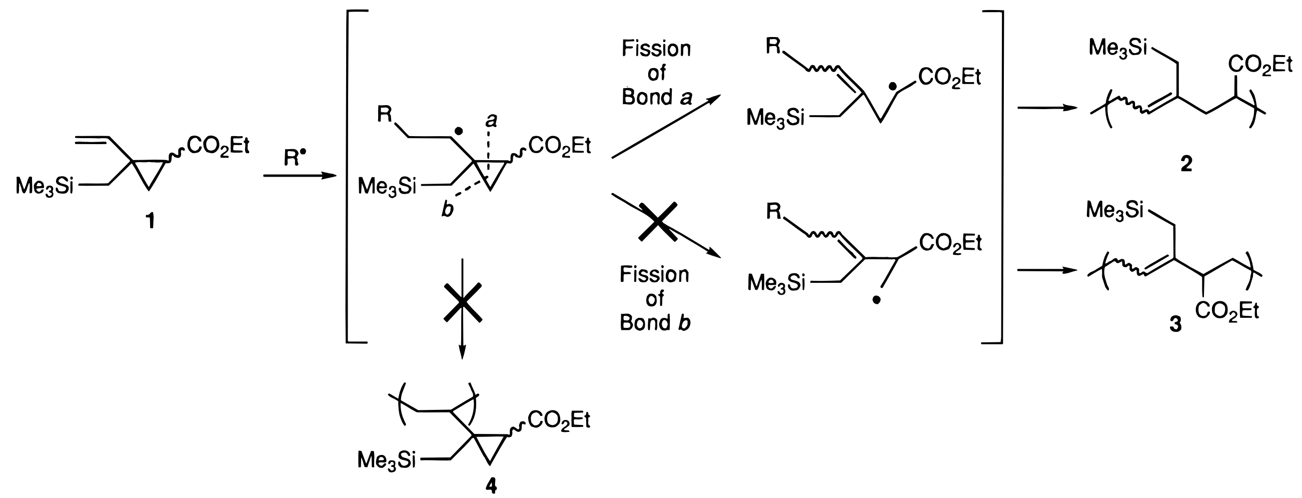
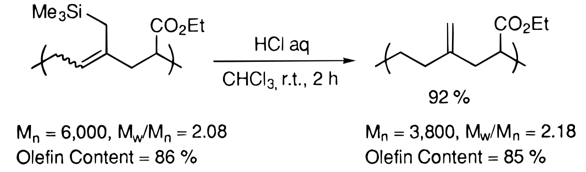
Scheme 2



Scheme 3



signal was observed at 3 ppm assignable to a methine proton α to the ester and olefin moieties, unit **3** was not contained in the polymer. The ^{13}C NMR spectrum was very consistent with the structure as determined by the ^{1}H NMR spectrum.

In the ^{1}H NMR spectrum of poly(**1**), the integration ratio of the olefin proton (Figure 1, a) to the methylene proton of the ester group (Figure 1, b) was smaller than that expected from 1,5-ring-opened unit **2** (1:2). In the ^{13}C NMR spectrum, unassignable signals were observed at 26.4 and 35.2 ppm. These signals appear to be derived from a unit which has no olefin moiety. Since the polymers were soluble in ordinary organic solvents and showed unimodal GPC curves, the disappearance of the olefin moiety might not be caused by intermolecular reactions such as cross-linking but by an intramolecular reaction similar to that reported in the radical polymerization of vinylcyclopropanes.[9] The glass transition temperature (T_g) and 10% weight loss temperature under nitrogen of poly(**1**) (run 1 in Table 1) were 4 and 323 °C, respectively.

A plausible mechanism of the polymerization of **1** is shown in Scheme 2. The 1,5-ring-opened unit **2** is formed through selective cleavage of a C−C bond containing the carbon substituted by the ester group. The electron-withdrawing ester group of **1** should contribute to this selectivity.[9] Vinyl-polymerized unit **4** was not contained in the polymer, probably due to the large rate of rearrangement of a cyclopropylmethyl radical to a 3-butenyl radical.[10]

As described above, allylsilanes are useful intermediates in organic synthesis. Therefore, polymers having the allylsilane structure are expected to be reactive polymers. Allylsilanes can be easily hydrolyzed to afford the corresponding olefins.[11] Hydrolysis of poly(**1**) by 12 M aqueous hydrochloric acid was carried out to obtain a polymer having an exomethylene group (Scheme 3). In the ^{1}H NMR spectrum of the polymer obtained by the hydrolysis of poly(**1**), the signal assignable to the olefin proton at 4.90 ppm observed in the ^{1}H NMR spectrum of poly(**1**) completely disappeared, and a signal assignable to exomethylene protons at 4.70 ppm appeared, which indicated the quantitative conversion of the allyl silane structure. $\bar{M}_n$ of the polymer changed from 6000 to 3800 during the polymer reaction, which well agreed with the decrease of molecular weight of the monomer unit. The hydrolysis did not proceed with 3 M aqueous hydrochloric acid.

Scheme 4

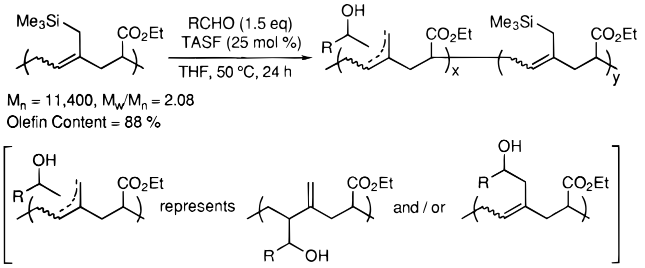


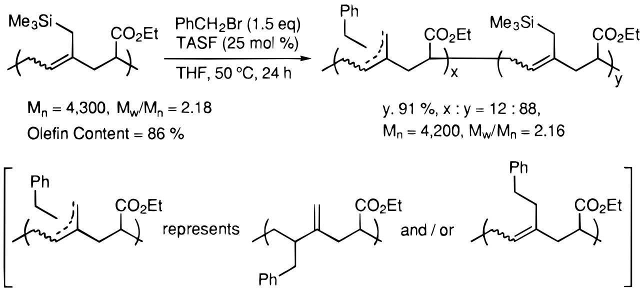
Table 2. Reactions of Poly(1) with Aldehydes[a]

run	R	yield[b] (%)	x:y[c] (mol %)	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
1	Ph	99	17:83	12400	2.47
2[e]	Ph	97	24:76	4200[f]	3.18[f]
3	4-MeOC$_6$H$_4$	96	9:91	9600	2.75
4	4-ClC$_6$H$_4$	100	24:76	4500	3.46
5	PhCH$_2$CH$_2$	89	4:96	10700	2.41

[a] Conditions: aldehyde 1.5 equiv, TASF 25 mol %, solvent THF (poly(**1**) 0.14 M), 50 °C, 24 h. [b] Isolated by HPLC. [c] Estimated by ^{1}H NMR. [d] Estimated by GPC (based on polystyrene standard samples). [e] Poly(**1**): $\bar{M}_n$ 6000, $\bar{M}_w/\bar{M}_n$ 2.08, olefin content 86%. [f] After desilylation by HCl(aq).

Next, the reaction of poly(**1**) with aldehydes was examined. The polymer reactions in the presence of a Lewis acid such as titanium(IV) chloride or aluminum chloride as a catalyst were not satisfactory and afforded only cross-linked polymers. Meanwhile, the polymer reactions with aldehydes using tris(dimethylamino)sulfur trimethylsilyl difluoride (TASF) as a catalyst proceeded without gelation to afford the expected polymers (Scheme 4). The results are summarized in Table 2. The incorporation ratio of the aldehyde into the polymer was estimated by the integration ratio of the signals of aromatic protons and methylene protons of the ethoxycarbonyl group in the ^{1}H NMR spectrum. The ease of incorporation of the aldehydes was in the following order: p-ClC$_6$H$_4$CHO (24%) > C$_6$H$_5$CHO (17%) > p-MeOC$_6$H$_4$CHO (9%) > hydrocinnamaldehyde (4%). Electron-withdrawing substituents of benzaldehyde increased the reactivity. The lower incorporation ratio of

Scheme 5



hydrocinnamaldehyde than those of aromatic aldehydes might be due to an aldol reaction. The low incorporation ratio of the aldehydes (24−4%) might be caused by the decrease of reactivity of the allylsilane moiety due to the electron-withdrawing ethoxycarbonyl group. The polymer effect could be another reason for the low incorporation ratio because the polymer of lower molecular weight showed a higher incorporation ratio of benzaldehyde than the polymer of higher molecular weight (runs 1 and 2).

Finally, reaction of poly(**1**) with benzyl bromide in the presence of TASF as a catalyst was examined to find that the reaction of poly(**1**) with higher molecular weight ($\bar{M}_n$ = 11 400) did not proceed, but the reaction of the polymer with lower molecular weight ($\bar{M}_n$ = 4 300) afforded the corresponding polymer in a 12% incorporation ratio (Scheme 5). The incorporation ratio was determined by the integration ratio of the signals of aromatic protons and methylene protons of the ethoxycarbonyl group in the ^{1}H NMR spectrum. Polymer reactions of poly(**1**) with acid chlorides and epoxides did not proceed.

In summary, synthesis and radical polymerization of a novel vinylcyclopropane having a (trimethylsilyl)methyl group, 1-(ethoxycarbonyl)-2-[(trimethylsilyl)methyl]-2-vinylcyclopropane (**1**), and the reactions of the obtained polymers were examined. Poly(**1**) was determined to consist of a 1,5-ring-opened unit and a unit without having an olefin moiety. Poly(**1**) was hydrolyzed by aqueous hydrochloric acid in quantitative conversion and reacted with aldehydes and benzyl bromide to afford the corresponding polymers. Thus, it could be demonstrated that the radical ring-opening polymerization of **1** was a novel and excellent method to obtain a polymer bearing an allylsilane structure as a reactive group.

Supporting Information Available: Procedures of hydrolysis of poly(**1**), reaction of poly(**1**) with benzaldehyde, and reaction of poly(**1**) with benzyl bromide and figures giving NMR spectra [figure S1, ^{1}H NMR and differential NOE ^{1}H NMR spectra (solvent $CDCl_3$, 400 MHz) of **1(syn)**; Figure S2, ^{1}H NMR and differential NOE ^{1}H NMR spectra (solvent $CDCl_3$, 400 MHz) of **1(anti)**; Figure S3, ^{13}C NMR spectrum (solvent $CDCl_3$, 100 MHz) of poly(**1**) (run 1 in Table 1); Figure S4, ^{1}H NMR spectrum (solvent $CDCl_3$, 400 MHz) of the polymer obtained by the hydrolysis of poly(**1**) with aqueous hydrochloric acid; Figure S5, ^{1}H NMR spectrum (solvent $CDCl_3$, 400 MHz) of the polymer obtained by the reaction of poly(**1**) with benzaldehyde (run 2 in Table 2); Figure S6, ^{1}H NMR spectrum (solvent $CDCl_3$, 400 MHz) of the polymer obtained by the reaction of poly(**1**) with benzyl bromide. Ordering information for these 7 pages is given on any current masthead page.

References and Notes

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(4) **1** was prepared as follows. To a solution of 2-[(trimethylsilyl)methyl]butadiene (7.01 g, 50.0 mmol) and copper(II) acetylacetonate [$Cu(acac)_2$] in benzene (15 mL) was added a solution of ethyl diazoacetate (5.70 g, 50.0 mmol) in benzene (50 mL) with benzene refluxing for 4 h. Benzene was distilled off from the mixture, and ether (70 mL) was added. The precipitated $Cu(acac)_2$ was filtrated off, and the filtrate was evaporated. The residue was distilled under reduced pressure to yield a colorless oil; yield 6.02 g (53%), bp 67.0−58.0 °C/0.68 mmHg. **1(syn)**: ^{1}H NMR δ ($CDCl_3$) 5.72 (dd, J = 16.7 and 10.9, 1 H, $=CH-$), 4.92 (d, J = 16.7 Hz, 1 H, $=CH_2$ (trans)), 4.91 (d, J = 10.9, 1 H, $=CH_2$ (cis)), 4.08−4.12 (m, 2 H, $-CO_2CH_2-$), 1.61 (dd, J = 8.1 and 6.1 Hz, 1 H, $-CH<$ of cyclopropane), 0.94−1.25 (m, 7 H), −0.02 (s, 9 H, $-Si(CH_3)_3$) ppm; ^{13}C NMR δ ($CDCl_3$) 171.9, 143.6, 112.2, 60.3, 31.0, 28.7, 20.5, 16.7, 14.4, −0.2 ppm. **1(anti)**: ^{1}H NMR δ ($CDCl_3$) 5.80 (dd, J = 17.3 and 10.9 Hz, 1 H, $=CH-$), 5.06 (d, J = 17.3 Hz, 1 H, $=CH_2$ (trans)), 5.07 (d, J = 10.9 Hz, 1 H, $=CH_2$ (cis)), 4.07 (q, J = 7.0 Hz, 2 H, $-CH_2-$), 1.68 (dd, J = 7.9 and 4.9 Hz, 1 H, $-CH<$ of cyclopropane), 1.47 (t, J = 4.9 Hz, 1 H, (Z)-CH_2- of cyclopropane), 1.20 (t, J = 7.0 Hz, 3 H, $-CH_3$), 1.09 (d, J = 15.0 Hz, 1 H, $SiCH_2-$), 1.01 (dd, J = 7.9 and 4.9 Hz, 1 H, (E)-CH_2- of cyclopropane), 0.69 (d, J = 15.0 Hz, 1 H, $SiCH_2-$), −0.01 (s, 9 H, $-Si(CH_3)_3$) ppm; ^{13}C NMR δ ($CDCl_3$) 171.3, 138.2, 115.2, 60.2, 30.9, 30.5, 25.8, 21.7, 14.4, 0.04 ppm. IR (**1(syn)** and **1(anti)**, neat): 2955, 2901, 1726, 1637, 1400, 1381, 1249, 1174, 845 cm^{-1}. Calcd for $C_{12}H_{22}SiO_2$: C, 63.67; H, 9.80. Found: C, 63.36; H, 9.60.

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(7) An unknown compound (9% by GC) was contaminated in **1**. The unknown compound could not be isolated by preparative HPLC. Since the monomer mixture was distilled with a very narrow bp range, the GC retention times of **1(syn)**, **1(anti)**, and the unknown compound were very close together, and the elemental analysis of the monomer mixture was well consistent with **1**, this unknown compound may be 1-(ethoxycarbonyl)-2-[1-(trimethylsilyl)methyl]propenyl]cyclopropane formed by the coupling reaction of ethyl diazoacetate and 2-[(trimethylsilyl)methyl]butadiene at the double bond which was not substituted by the (trimethylsilyl)methyl group.

(8) 4.18 and 0.87% NOE effects were observed for the signals assigned to the olefin protons when the methine proton α to the ester carbonyl group of the syn isomer was irradiated. Meanwhile, 2.40 and 6.15% NOE effects were observed for the signals assigned to the methylene protons α to the trimethylsilyl group of the anti isomer when the methine proton α to the ester carbonyl group of the anti isomer was irradiated.

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