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Synthesis and properties of polynorbornenes bearing oligomeric siloxane pendant groups

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ABSTRACT

The ring-opening metathesis polymerization (ROMP) of norbornene derivatives **1**–**5** bearing oligomeric siloxane pendant groups was carried out with Grubbs 1st and 2nd generation, and Grubbs–Hoveyda ruthenium (Ru) catalysts. Monomer **1** gave high-molecular-weight polymers (M_n ca. 27 000–180 000) in high yields (80–100%). Monomers **2**–**5** also polymerized with Ru carbene catalysts to give high-molecular-weight polymers (M_n ca. 34 000–240 000) in high yields (66–100%). The onset temperatures of weight loss (T_0) of the polymers were 180–250 °C. The glass transition temperatures (T_gs) of poly(**1**) and poly(**2**) bearing branched siloxane linkages were near or higher than room temperature (27 and 101 °C). Meanwhile, the T_gs of poly(**3**)–poly(**5**) bearing linear siloxane linkages were much lower (−115 to −23 °C), and decreased with increasing length of the siloxane linkages. Poly(**1**) and poly(**2**) were hydrogenated completely, which was confirmed by ^{1}H NMR spectroscopy. The free-standing membranes of poly(**1**) and poly(**2**) showed high gas permeability; especially poly(**2**) is the most permeable to various gases among ROMP–polynorbornene derivatives reported so far.

1. Introduction

Olefin metathesis reaction is one of the most useful and efficient methods in organic and polymer syntheses due to the formation of new carbon–carbon double bonds. Titanium, tantalum, molybdenum, tungsten, and ruthenium catalysts are well known for olefin metathesis reactions [1]. However, transition metal catalysts of groups 4–6 are readily deactivated under air and moisture and by polar functional groups in substrates and solvents. On the other hand, catalysts based on ruthenium (Ru), a late transition metal of group 8, can be handled in air and used for substrates having polar functional groups and/or in polar and protic solvents including water [2]. These advantages allow a wide variety of applications of Ru catalysts.

Ru carbene catalysts show high activity for olefin metathesis, and they are widely applied not only to organic reactions such as ring-closing metathesis (RCM), cross-metathesis (CM), and ring-opening cross-metathesis (ROCM) but also to polymer syntheses including ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization [3]. In particular, cycloolefins with large ring strain readily polymerize with Ru carbene catalysts, and their living polymerization has been achieved by using suitable Ru catalysts [4]. There are few limitations about the kind of substituents in the monomer in the Ru-catalyzed polymerization of norbornenes due to excellent functional group tolerance of the catalysts.

The siloxane (Si–O–Si) linkage is characterized by unique properties such as high flexibility and high thermal stability. Thus, siloxane-containing polymers have been gathering attentions as interesting functional and high-performance polymers, especially with respect to their excellent thermal properties and applications to gas and liquid separation membranes [5]. Poly(dimethylsiloxane) is a rubbery polymer whose glass transition temperature (T_g) is about −125 °C, and it displays high gas permeability ($PO_2 = 800$ barrers) [6]. Various polymers carrying dimethylsiloxane polymeric and/or oligomeric moieties have also been developed [7]. Polystyrenes with several trimethylsiloxy groups are more gas-permeable than are polystyrene and poly{(*p*-trimethylsilyl)styrene} because gas molecules easily diffuse in the former membranes due to the high local mobility of siloxane linkage (e.g., poly[*p*-{bis(trimethylsiloxy)methylsilyl}styrene]: $PO_2 = 72$ barrers, $PO_2/PN_2 = 2.8$; polystyrene: $PO_2 = 1$ barrer, $PO_2/PN_2 = 5.5$; poly{*p*-(trimethylsilyl)styrene}: $PO_2 = 14$ barrers, $PO_2/PN_2 = 3.4$) [8]. The gas permeation properties of polynorbornene derivatives have been studied [9]. Polynorbornenes bearing trimethylsilyl or trifluoromethyl groups are more gas-permeable than the unsubstituted counterparts, but their permeability coefficients are not very large compared to those of the other gas-permeable

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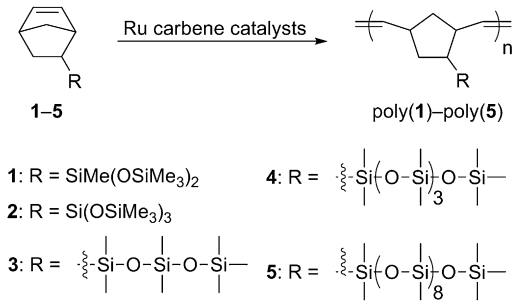


Scheme 1. Polymerization of **1**–**5**.

polymers [10]. Although several examples of polynorbornene carrying siloxane pendant groups have been reported [11], gas permeation properties of these polymers have not been investigated so far.

This paper deals with the synthesis of polynorbornene derivatives poly(**1**)–poly(**5**) bearing dimethylsiloxane oligomeric pendant groups via ROMP (Scheme 1), along with the hydrogenation of poly(**1**) and poly(**2**). It also investigates the thermal properties and gas permeation properties of the formed polymers.

2. Experimental section

2.1. Instrumentation

The molecular weights of polymers were estimated by gel permeation chromatography (THF as eluent, Showa Denko Shodex KF-805L × 3 polystyrene calibration). ^{1}H NMR (400 MHz) spectra were measured in $CDCl_3$ on a JEOL EX-400 spectrometer. Chemical shifts (δ) for ^{1}H and ^{13}C NMR were referenced to the resonances of the internal solvent and shown relative to tetramethylsilane (TMS). Gas permeability coefficients of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C. Thermogravimetric analyses (TGA) were conducted in air with a Shimadzu TGA-50 thermal analyzer. Differential scanning calorimetric (DSC) analyses were performed using a Perkin–Elmer PYRIS Diamond DSC under a nitrogen atmosphere at scanning rates of 100, 120, 140, 160, and 180 °C/min. Glass transition temperatures extrapolated to the scanning rate of 0 °C/min were calculated by using the following equation (φ: scanning rate, C: constant value, E: activation energy, R: gas constant, and T_g: glass transition temperature) [12].

$$\ln \frac{\varphi}{T_g^2} = C - \frac{E}{RT_g}$$

2.2. Materials

Grubbs 2nd generation and Grubbs–Hoveyda catalysts were donated by Materia (USA) and used without further purification. Grubbs 1st generation catalyst was purchased from Aldrich. 5-{$SiMe(OSiMe_3)_2$}norbornene [**1**: purity 99% (by GC); bp 108 °C/2 mm Hg], 5-$Si(OSiMe_3)_3$norbornene [**2**: purity 90% (by GC); bp 140–143 °C/15 mm Hg], 5-($SiMe_2OSiMe_2OSiMe_3$)norbornene [**3**: purity 98% (by GC); bp 94–96 °C/3 mm Hg], 5-{$SiMe_2(OSiMe_2)_3$-$OSiMe_3$}norbornene [**4**: purity 97% (by GC); bp 128–130 °C/3 mm Hg], and 5-{$SiMe_2(OSiMe_2)_8OSiMe_3$}norbornene [**5**: purity 88% (by GC)] were offered by Shin-etsu chemical Co., Ltd. (Japan). Toluene and THF used as solvents for polymerization were distilled by the standard procedures before use.

2.3. Polymerization

Unless otherwise specified, polymerizations were carried out in an argon atmosphere. A detailed procedure of polymerization is as follows: a monomer solution was prepared in a Schlenk tube with a three-way stopcock by mixing monomer **1** (1.9 g, 6.0 mmol) and toluene (50 mL), and another Schlenk tube was charged with Grubbs 2nd generation catalyst (5.0 mg, 6.0 μmol) and toluene (10 mL). Polymerization was initiated by adding the catalyst solution to the monomer solution, and continued at 40 °C for 20 min. Then the reaction was quenched by adding ethyl vinyl ether (0.5 mL, 9.2 mmol), and stirred for 15 min. The polymerization mixture was poured into a large amount of methanol, and the polymer precipitated was filtered and dried under vacuum to constant weight. The yield was determined by gravimetry.

2.4. Hydrogenation of polymers

A ROMP polymer (2.0 mmol) was dissolved in xylene (50 mL) in an autoclave. To this solution, *p*-toluenesulfonhydrazide, a hydrogenation agent (2.79 g, 15 mmol; 7.5 equiv to the monomer unit of the polymer), and a trace amount of 2,6-di-*tert*-butyl-4-methylphenol (inhibitor) was added. The solution of polymer and hydrogenation agent was degassed thrice via a freeze-pump-thaw cycle and sealed, and then stirred at 120 °C for 12 h. A hydrogenated polymer was obtained by precipitating with methanol. The polymer was filtered and dried under vacuum to constant weight, whose yield was determined by gravimetry.

2.5. Spectroscopic data of the polymers

2.5.1. Poly(*1*)

^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 5.6–4.9 (br, 2H, –CH=CH–), 3.1–0.6 (br, 7H, $–CH_2–$ and –CH–), 0.3–0.0 (br, 21H, $–CH_3$). IR (cm^{-1}, KBr): 2998, 2894, 1651, 1610, 1415, 1254, 1178, 1128, 1014, 889, 879, 704.

2.5.2. Poly(*2*)

^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 5.7–4.9 (br, 2H, –CH=CH–), 3.2–0.7 (br, 7H, $–CH_2–$ and –CH–), 0.4–0.0 (br, 27H, $–CH_3$). IR (cm^{-1}, KBr): 2962, 2900, 1654, 1449, 1414, 1255, 1064, 969, 757, 687.

2.5.3. Poly(*3*)

^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 5.5–5.0 (br, 2H, –CH=CH–), 3.2–0.8 (br, 7H, $–CH_2–$ and –CH–), 0.3–0.0 (br, 21H, $–CH_3$). IR (cm^{-1}, KBr): 2974, 2894, 1650, 1446, 1412, 1254, 1138, 1085, 873, 730, 689.

2.5.4. Poly(*4*)

^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 5.6–5.0 (br, 2H, –CH=CH–), 3.2–0.7 (br, 7H, $–CH_2–$ and –CH–), 0.4–0.0 (br, 33H, $–CH_3$). IR (cm^{-1}, KBr): 2961, 2901, 1656, 1448, 1413, 1260, 1084, 1060, 842, 777, 683.

2.5.5. Poly(*5*)

^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 5.6–5.0 (br, 2H, –CH=CH–), 3.2–0.8 (br, 7H, $–CH_2–$ and –CH–), 0.5–0.0 (br, 63H, $–CH_3$). IR (cm^{-1}, KBr): 2962, 2902, 1652, 1445, 1413, 1260, 1091, 1030, 840, 797, 699, 687.

2.5.6. Poly(*1H*)

^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 2.4–0.5 (br, 11H, $–CH_2–$ and –CH–), 0.4–0.0 (br, 21H, $–CH_3$). IR (cm^{-1}, KBr): 2958, 2862, 1453, 1414, 1050, 845, 757, 687, 593.

2.5.7. *Poly(**2H**)*

^{1}H NMR (400 MHz, δ in ppm, CDCl$_3$): 2.2–0.5 (br, 11H, –CH$_2$– and –CH–), 0.2–0.0 (br, 27H, –CH$_3$). IR (cm^{-1}, KBr): 2958, 2862, 1452, 1414, 1060, 843, 756, 685, 592.

2.6. *Membrane fabrication*

Membranes (thickness ca. 50–80 μm) of poly(**1**), poly(**2**) and poly(**2H**) were fabricated by casting toluene solutions of the polymers (concentration ca. 1.0–2.0 wt%) onto a flat-bottomed Petri dish. The Petri dish was covered with a glass vessel to slow solvent evaporation (ca. 3–5 days).

2.7. *Gas diffusivity and solubility of polymer membranes*

The gas permeability coefficients (P) were calculated from the slopes of time–pressure curves in the steady state where Fick's law holds [13]. The diffusion coefficients (D) were determined by the time lag method using the following equation:

$$D = l^2/6\theta$$

where l is the membrane thickness and θ is the time lag, which is given by the intercept of the asymptotic line of the time–pressure curve to the time axis. The solubility coefficients (S) were calculated by using the equation $S = P/D$.

3. Results and discussion

3.1. *Polymerization*

The polymerization of monomer **1** with Grubbs 1st generation, 2nd generation, and Grubbs–Hoveyda catalysts shown in Chart 1 was examined in toluene and THF (Table 1). Polymers were obtained almost quantitatively under all the conditions examined. The polymers formed by the polymerization with Grubbs 2nd generation (runs 3 and 4) and Grubbs–Hoveyda catalysts (runs 5 and 6) possessed rather broad molecular weight distributions (MWDs), suggesting the proceeding of intra- and inter-macromolecular metathesis reactions. The number–average molecular weight (M_n) of the polymer obtained by the polymerization with Grubbs–Hoveyda catalyst in toluene (run 5) was the lowest and the MWD was the broadest. The high activity of Grubbs–Hoveyda catalyst probably should have caused a side reaction and/or a backbiting reaction under these conditions.

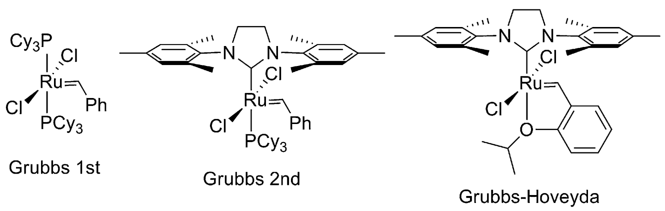


Chart 1. Ruthenium catalysts.

Table 1
Polymerization of monomer **1** with various Ru carbene catalysts.[a]

Run	Catalyst	Solvent	Polymer[b]		
			Yield, %	M_n[c]	M_w/M_n[c]
1	Grubbs 1st	Toluene	96	114 300	2.74
2	Grubbs 1st	THF	92	126 900	2.40
3	Grubbs 2nd	Toluene	96	123 300	3.96
4	Grubbs 2nd	THF	91	146 600	5.09
5	Grubbs–Hoveyda	Toluene	100	27 400	7.32
6	Grubbs–Hoveyda	THF	99	183 200	5.46

[a] At 40 °C for 2.5 h; $[M]_0 = 0.20$ M, [Ru] = 1.0 mM.
[b] Methanol-insoluble part.
[c] Measured by GPC (THF, PSt).

Table 2
Polymerization of monomer **1** with Grubbs 2nd generation catalyst.[a]

Run	$[M]_0$, M	[Ru], mM	Polymer[b]		
			Yield, %	M_n[c]	M_w/M_n[c]
1	0.10	0.50	100	–[d]	–[d]
2	0.10	0.20	100	–[d]	–[d]
3	0.10	0.10	100	–[d]	–[d]
4	0.050	0.50	80	–[d]	–[d]
5	0.050	0.20	95	124 300	4.99
6	0.050	0.10	99	110 800	6.54
7	0.050	0.050	100	169 000	5.76

[a] In toluene at 40 °C for 20 min.
[b] Methanol-insoluble part.
[c] Measured by GPC (THF, PSt).
[d] Insoluble in common organic solvents.

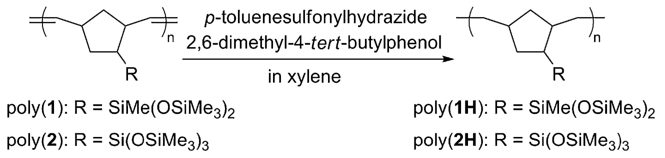
The effects of monomer and catalyst concentrations on the polymerization were examined at 40 °C (Table 2). Poly(**1**) formed by the polymerization at $[M]_0 = 0.10$ M was insoluble in common organic solvents (runs 1–3), presumably because the M_n was very high. The decrease of $[M]_0$ to 0.050 M resulted in the formation of soluble polymers when [Ru] was 0.20 mM and lower. The monomer/catalyst ratio hardly affected the M_n of the formed polymers, while the MWD was broad, indicating that the polymerization of monomer **1** did not proceed in a living fashion. In general, the living polymerization of norbornene derivatives can be achieved at low temperature (e.g., −20 °C) due to their high polymerizability based on large ring strains, and the Grubbs–Hoveyda catalyst does not show high initiation efficiency. These facts seem to be responsible for the non-living character of the present polymerization.

Table 3 shows the results of polymerization of monomers **2**–**5** using Grubbs 1st and 2nd generation catalysts. Monomer **2** gave a polymer insoluble in common organic solvents with Grubbs 2nd generation and Grubbs–Hoveyda catalysts. On the other hand, Grubbs 1st generation catalyst provided poly(**2**) with a high-molecular weight ($M_n = 240\ 000$) and good solubility in CHCl$_3$, CH$_2$Cl$_2$, toluene, and THF. Solvent-soluble poly(**3**) could not be obtained with any catalyst, although soluble oligomers (M_n <5000) formed by the polymerization at a very low catalyst concentration (0.050 mM). Grubbs 1st generation catalyst produced only oligomers from monomer **4**, while Grubbs 2nd generation catalyst gave transparent viscous rubbery poly(**4**). Monomer **5** afforded a polymer with a narrow MWD by using Grubbs 2nd generation catalyst, although it gave no polymer with Grubbs 1st generation catalyst. The polymerizability of monomers decreased with the increment of the length of the oligomeric pendant groups, which is attributed to the fact that the longer

Table 3
Polymerization of monomers **2**–**5**.[a]

Monomer	Catalyst	Polymer[b]		
		Yield, %	M_n[c]	M_w/M_n[c]
2	Grubbs 1st	95	240 000	2.51
3	Grubbs 1st	99	–[d]	–[d]
4	Grubbs 2nd	100	142 000	4.00
5	Grubbs 2nd	66	33 600	1.64

[a] In toluene at 30 °C for 15 min; $[M]_0 = 0.050$ M, [Ru] = 0.50 mM.
[b] Methanol-insoluble part.
[c] Measured by GPC (THF, PSt).
[d] Insoluble in common organic solvents.



Scheme 2. Hydrogenation of poly(**1**) and poly(**2**).

siloxane group prevents the olefin from coordinating to the ruthenium center.

It has been reported that the catalytic activities of Grubbs 2nd catalyst generation and Grubbs–Hoveyda catalysts are almost the same as each other, while that of Grubbs 1st generation is lower [14]. As mentioned above, the formation of solvent-insoluble polynorbornene and its derivatives is most probably attributable to their high-molecular weights. It is likely that the formation of high-molecular-weight polymers is caused by the use of too active catalysts. Considering these facts, the results described above imply that the polymerizability of monomer **3** is the highest, followed by **2**, **4**, and **5**. The reactivity of monomer **1** seems to be almost the same as that of **2**. The monomer reactivity is explicable in terms of both the number of siloxane linkages and the steric effect of the substituent. It is important to choose a catalyst suitable for an individual norbornene monomer to obtain a solvent-soluble polymer in a high yield. Monomers **1**–**5** possessing siloxane linkages did not polymerize with WCl_6–Ph_4Sn and $MoCl_5$–Ph_4Sn catalyst systems.

3.2. Hydrogenation of poly(*1*) and poly(*2*)

The hydrogenation of poly(**1**) and poly(**2**) was carried out with *p*-toluenesulfonhydrazide in xylene at 120 °C (Scheme 2). After the reaction for 12 h, hydrogenated poly(**1H**) and poly(**2H**) were isolated by precipitation with methanol. Poly(**1**) and poly(**2**) showed ^1H NMR signals assignable to *cis* and *trans* olefinic protons at 5.0–5.7 ppm, while poly(**1H**) and poly(**2H**) showed almost no signal in this region (Fig. 1), indicating that both poly(**1**) and poly(**2**) were hydrogenated nearly quantitatively. The molecular weights of the hydrogenated polymers scarcely decreased compared to those of the starting polymers [poly(**1**): $M_n = 253\,800$; poly(**1H**): $M_n = 245\,300$; poly(**2**): $M_n = 392\,900$; poly(**2H**): $M_n = 337\,000$]. The cleavage of main chain during the hydrogenation reaction is negligible.

3.3. Thermal properties

The thermal stability of the formed polymers was examined by TGA in air (Fig. 2). The onset temperatures of weight loss (T_0) for all the polymers were 180–250 °C, and ashes composed of silica remained when the polymers were heated in air above 600 °C in all cases.

The glass transition temperatures (T_gs) determined by DSC are shown in Table 4. Although no transition point was observed at a scanning rate of 10 °C/min, the increase of rate up to 100 °C/min and above resulted in clear appearance of the T_g peaks [15]. The DSC curves at a heating rate of 180 °C/min are depicted in Fig. 3. The T_g values were calculated as described in Experimental section. Poly(**1**) having two branched trimethylsiloxy groups showed a T_g at 27 °C, while poly(**2**) with three trimethylsiloxyl groups showed it at a much higher temperature (101 °C). The T_g values of poly(**3**), poly(**4**), and poly(**5**) having linear oligo(dimethylsiloxane) moieties were lower (−23, −89, and −115 °C) than those of poly(**1**) and poly(**2**). The T_g decreased with increasing length of the oligomeric pendant group, and poly(**5**) bearing decamers of dimethylsiloxane showed almost the same T_g (−115 °C) as that of poly(dimethylsiloxane) (PDMS). The incorporation of linear siloxane pendant groups led to lower T_g than that of polynorbornene (PNB; $T_g = 39$ °C). Polymers having spherical and/or branched siloxane linkages showed higher T_g values than those of the polymers with linear ones, which is attributable to much higher flexibility of the side groups of the latter polymers. The T_g values of poly(**1H**) and poly(**2H**) were lower than those of precursors [poly(**1**) and poly(**2**)], presumably because the disappearance of double bonds along the polymer backbone led to the enhancement of flexibility.

3.4. Gas permeation properties

The free-standing membranes of poly(**1**), poly(**2**), and poly(**2H**) could be fabricated by casting from polymer solutions, while the

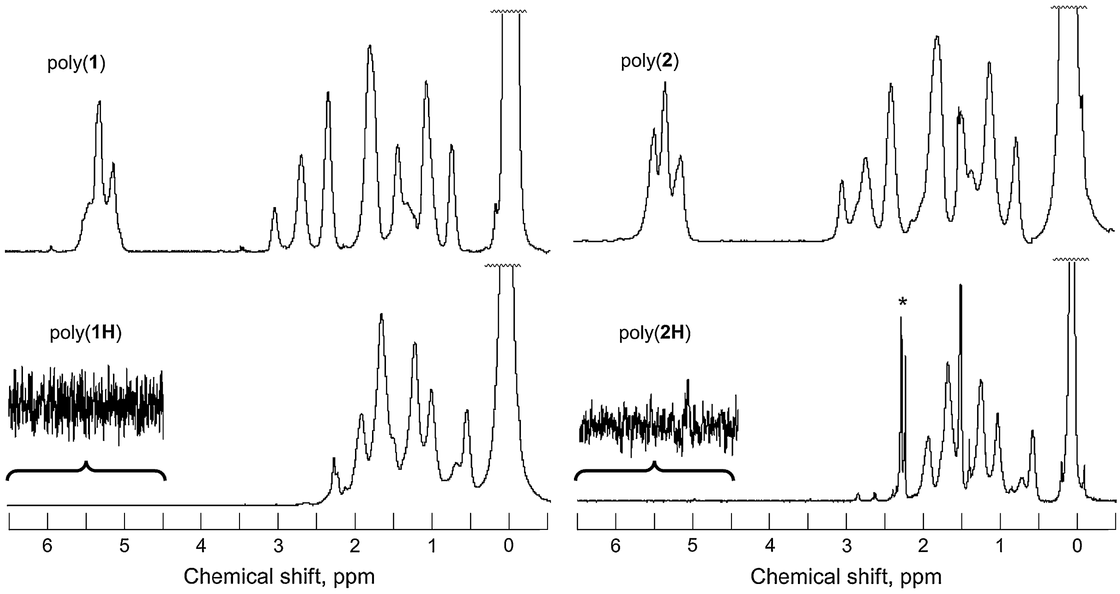


Fig. 1. ^1H NMR spectra of poly(**1**), poly(**2**), poly(**1H**), and poly(**2H**) measured in $CDCl_3$. Asterisk indicates methyl proton signals of xylene.

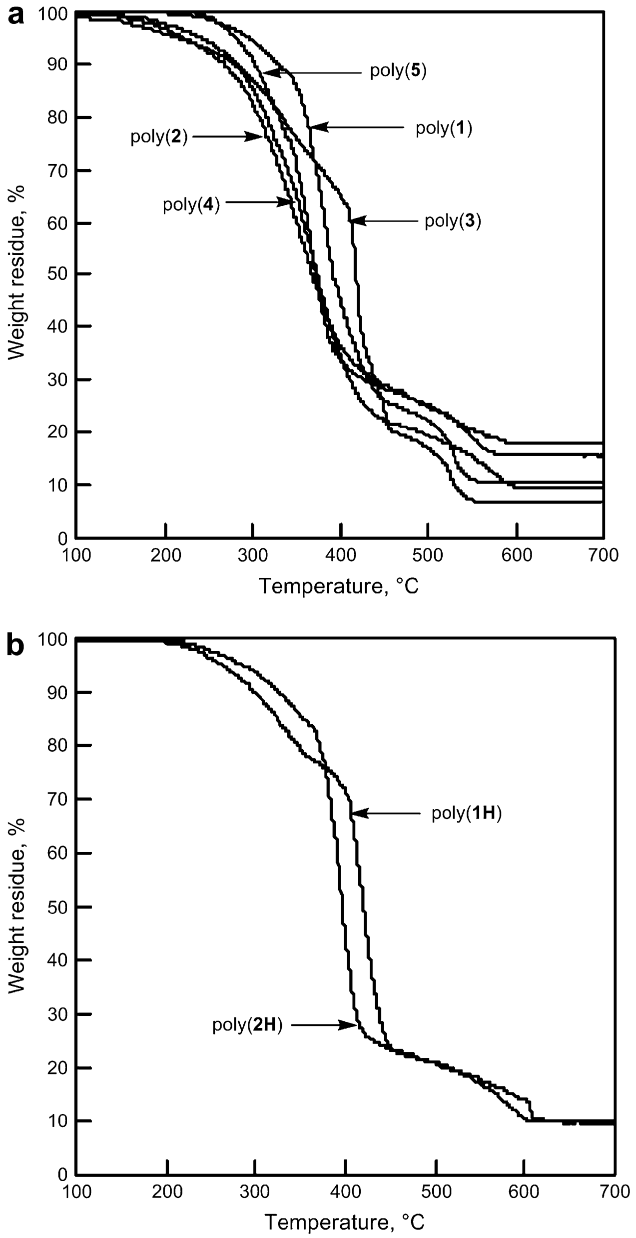


Fig. 2. TGA curves of (a) poly(**1**)–poly(**5**) and (b) poly(**1H**) and poly(**2H**) (in air, heating rate 10 °C/min).

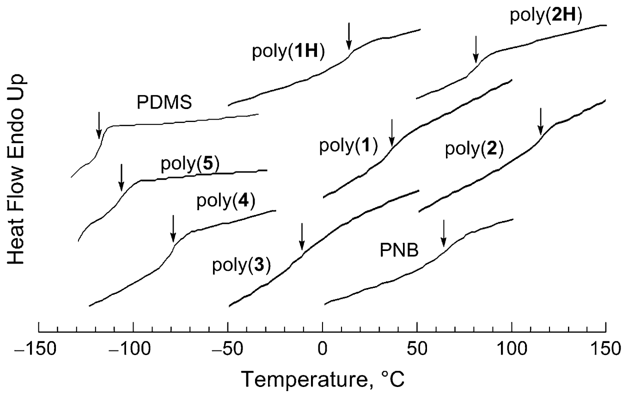


Fig. 3. DSC curves of poly(**1**)–poly(**5**), poly(**1H**), poly(**2H**), PDMS, and PNB (in N_2, heating rate 180 °C/min).

Table 5
Gas permeability coefficients (P) of poly(**1**), poly(**2**), poly(**2H**) and related ROMP polymers at 25 °C.[a]

Polymer	P[a]						PO_2/PN_2
	He	H_2	O_2	N_2	CO_2	CH_4	
Poly(**1**)	150	230	99	30	430	87	3.3
Poly(**2**)	290	430	290	93	910	260	3.1
Poly(**2H**)	200	320	160	55	610	160	2.9
PNB[b]	–	21	2.8	1.5	15	2.5	1.9
PTMSNB[c]	–	140	30	7.2	89	8.5	4.2
PFMNB[b]	–	170	50	17	200	13	2.9
PDSNB[c]	240	375	95	25	445	45	3.8

[a] In the unit of barrer (1 barrer = 1×10^{-10} cm^3 (STP) cm/(cm^2 s cm Hg)).
[b] Data from Ref. [9c].
[c] Data from Ref. [9a].

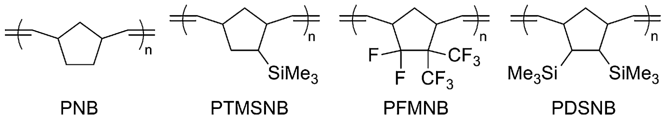


Chart 2. Polynorbornene and its derivatives based on ROMP.

membranes of poly(**3**)–poly(**5**) and poly(**1H**) could not because the T_g values of these polymers were lower than room temperature. Table 5 lists the gas permeation properties of the polymer membranes in this study, along with those of polynorbornene derivatives shown in Chart 2 for comparison. The oxygen permeability coefficient (PO_2) of unsubstituted polynorbornene (PNB) is no more than 2.8 barrers, whereas PTMSNB having trimethylsilyl groups showed a PO_2 value almost 10 times higher [9a]. The most oxygen-permeable ROMP-based polynorbornene derivative reported so far is bis(trimethylsilyl)-substituted polynorbornene (PDSNB, $PO_2 = 95$ barrers) [9a]. The polymers in the present study showed higher gas permeability, and especially the PO_2 of poly(**2**) reached 290 barrers, which is attributable to the presence of two or three trimethylsilyl groups. The gas permeability of poly(**2H**) was lower than that of poly(**2**) as a result of decrease of both main-chain rigidity and affinity to gases after hydrogenation.

Table 6 shows the solubility and diffusion coefficients (S and D) of poly(**1**) and poly(**2**) along with some polynorbornene derivatives for carbon dioxide and methane gases. The S values of both poly(**1**) and poly(**2**) were lower than those of trimethylsilyl or trifluoromethyl-containing polymers (PTMSNB, PFMNB, and PDSNB); especially, the S value of poly(**1**) for methane gas is approximately one-tenth of that of PFMNB. On the other hand, the D values of the present polymers were approximately 10 and 30–100 times larger than those of the reported ones for carbon dioxide and methane,

Table 4
Glass transition temperatures (T_g) of the polymers.

	T_g,[a] °C		T_g,[a] °C
Poly(**1**)	27	Poly(**1H**)	–12
Poly(**2**)	101	Poly(**2H**)	62
Poly(**3**)	–23	PNB	39
Poly(**4**)	–89	PDMS	–126
Poly(**5**)	–115		

[a] Determined by DSC.

Table 6
Gas solubility and diffusion coefficients (*S* and *D*) at 25 °C.

	$S \times 10^{2}$[a]		$D \times 10^{7}$[b]	
	CO_2	CH_4	CO_2	CH_4
Poly(**1**)	1.0	0.33	42	26
Poly(**2**)	1.7	0.65	53	39
PNB[c]	0.96	0.87	1.6	0.36
PTMSNB[d]	5.0	0.78	3.3	1.4
PFMNB[c]	24	3.9	0.84	0.33
PDSNB[d]	8.5	2.6	4.0	1.3

[a] In the units of cm^3 (STP) cm^{-3} cm/Hg.
[b] In the units of $cm^2\ s^{-1}$.
[c] Data from Ref. [9c].
[d] Data from Ref. [9a].

respectively. This suggests that the incorporation of siloxane moieties having large local mobility leads to enhanced gas permeability due to high diffusivity of gases in polymer membranes.

4. Conclusions

The ROMP of norbornene derivatives bearing branched or linear oligomeric dimethylsiloxane pendant groups was carried out with Grubbs 1st and 2nd generation Grubbs–Hoveyda catalysts. Monomer **1** having two branched siloxane linkages polymerized quantitatively. The monomer/catalyst ratio hardly affected the molecular weight and MWD of the formed polymer, indicating the non-living nature of the polymerization of **1**. Monomers **2**–**5** gave polymers in high yields. Poly(**1**) and poly(**2**) were quantitatively hydrogenated using *p*-toluenesulfonhydrazide keeping the molecular weights. All the polymers exhibited moderate thermal stability ($T_0 = 180$–$250\ ^\circ C$). The T_g decreased with increasing length of the pendant siloxane groups. The oxygen permeability coefficient of poly(**2**) was 290 barrers, which is the largest among the ROMP–polynorbornene derivatives reported so far. This is attributable to the large local mobility of the siloxane pendant groups.

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