Polynorbornenes with Oligodimethylsiloxanyl Substituents for Selectively Oxygen Permeable Membrane Material

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ABSTRACT: 2-Oligodimethylsiloxanyl substituted 5-norbornene-2-carbonitriles and carboxylates were synthesized from 5-norbornene-2-carbonitrile and methyl 5-norbornene-2-carboxylate by metalation at the 2-position followed by reaction with monochloro functionalized oligodimethylsiloxane. Polymers were obtained by the ring-opening polymerization of the monomers by a metathesis catalyst. Permeation of oxygen through the polymer films was highly selective over nitrogen. The diffusion coefficient was shown to play the principal role in the permeation.

KEY WORDS Norbornene / Oligosiloxane / Oxygen Permeation / Permselectivity / Membrane / Molecular Design / Diffusion Coefficient /

One basic idea for obtaining a highly gas permeable membrane material is to use semirigid backbone polymers with bulky substituents which cannot pack densely. An example of such a polymer is poly(1-trimethylsilylpropyne), reported by Higashimura, which has conjugated double bonds along with the polymer backbone and bulky trimethylsilyl groups as substituents. This polymer was reported to show the highest P_{O_2} among the organic polymers, although relaxation was seen by heat treatment.^{1,2}

We have proposed three basic principles for the molecular design of selectively oxygen permeable membrane materials.

1) To synthesize a polymer by the combination of highly gas permeable oligodimethylsiloxane and highly permselective polymer of relatively high glass transition temperature (T_g) (usually by the introduction of oligodimethylsiloxanyl groups as side chains

to backbone polymer of relatively high T_g), and to take the balance between permeability and permselectivity,

2) To give self-supporting property to polydimethylsiloxane (PDMS) by introducing it in a block or graft copolymer with hard segment, and

3) To use high oxygen solubility coefficient (S_{O_2}) at the surface of the surface-modified polymer membrane with surface active PDMS graft copolymer.

An example of the molecular design according to the principle 1), we showed that poly(*p*-pentamethyldisiloxanylstyrene) (PS2) is a well balanced polymer between permeability, permselectivity, and film forming properties. It was also elucidated that the high permeability coefficient (P_{O_2}) was brought about by the remarkable increase in the diffusion coefficient of oxygen (D_{O_2}) through the polymer film by the introduction of oligodimethylsiloxanyl

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substituents.³⁻¹⁰ Examples of the design according to principle 3) are that both P_{O_2} and the separation factor (P_{O_2}/N_{O_2}) increased in surface-modified polymers with a surface active graft copolymer as an additive.¹¹⁻¹³ The simultaneous enhancement in permeability and permselectivity was attributed to the selective solubilization of oxygen over nitrogen into PDMS domain at the surface of surface-modified film of the base polymers. We also reported an example of the design according to principle 2). Alternative copolymer of styrene type PDMS macromer and 7,7,8,8-tetracyanoquinodimethane (even containing 70% of PDMS component) is a solid self-supporting polymer and showed considerably good P_{O_2} .¹⁴

Poly(5-norbornene-2-carbonitrile) is a polymer of semi-rigid backbone having an alternating cyclopentane ring and double bond along the backbone, and it shows good permselectivity and film forming property although the permeability coefficient is low. In order to improve the permeability of the norbornene polymer and to have balance between permeability and permselectivity, it will be effective to introduce oligodimethylsiloxanyl side chains into the semi-rigid polymer backbone according to the principle 1).

EXPERIMENTAL

Synthesis of Monomers

Monomers in this study were synthesized according to Scheme 1. The general procedure of the synthesis is given.

5-Norbornene-2-carbonitrile (NN) (2.94 g,

24.7 mmol) or methyl 5-norbornene-2-carboxylate (NE) (3.76 g, 24.7 mmol) was metalated with lithium diisopropylamide (LDA) (28.1 mmol) in tetrahydrofuran (THF) (30 ml) at -78°C and then alkylated (NNR series, R=ethyl, propyl, butyl; and NNMn series, R=CH₂Si(CH₃)₃CH₂Si(CH₃)₂OSi(CH₃)₃), or silylated (NNn series, $n=1-3$; NNSi2; NEN series, $n=1,2$) by haloalkane (37.8 mmol) or chlorosilane (39.5 mmol) derivatives.

¹H NMR spectra were recorded at 60 MHz in CCl₄ and the chemical shifts are given as δ values in ppm from TMS. The protons in norbornene ring are numbered as shown in Scheme 1.

2-Ethyl-5-norbornene-2-carbonitrile (NNEt). Ethyl bromide was used as an alkylating agent. bp 65°C (1.4 mmHg). 65.8% Yield. Chemical shifts: 1.06 (t, 3H, $J=6.0$ Hz, CH₃), 1.20–1.92 (m, 6H, overlapped signals of CH₂, H₂, H₃, H₇, H₈), 2.69–3.03 (m, 2H, H₁, H₄), 6.09–6.36 (m, 2H, H₅, H₆).

2-Propyl-5-norbornene-2-carbonitrile (NNPr). Propyl chloride was used as an alkylating agent. bp 78.5°C (2.4 mmHg). 58.2% Yield. Chemical shifts: 1.01 (m, 3H, CH₃), 1.21–1.94 (m, 8H, overlapped signals of CH₂H₂, H₂, H₃, H₇, H₈), 2.64–3.10 (m, 2H, H₁, H₄), 6.04–6.34 (m, 2H, H₅, H₆).

2-Butyl-5-norbornene-2-carbonitrile (NNBu). Butyl chloride was used as an alkylating agent. bp 63.5°C (0.19 mmHg). 72.7% Yield. Chemical shifts: 0.71–1.77 (m, 13H, overlapped signals of CH₃CH₂CH₂CH₂, H₂, H₃, H₇, H₈), 2.63–3.09 (m, 2H, H₁, H₄), 6.04–6.37 (m, 2H, H₅, H₆).

2-Trimethylsilyl-5-norbornene-2-carbonitrile

Scheme 1. Synthesis of monomers.

(NN1). Trimethylsilyl chloride was used as a silylating agent. bp 61–65°C (0.33 mmHg). 75.5% Yield. Chemical shifts: 0.14 (s, 9H, SiCH₃), 1.12–1.30 (m, 2H, H₂, H₃), 1.39 (q, 1H, $J_1=2.0$ Hz, $J_2=12.0$ Hz, H₈), 1.91 (q, 1H, $J_1=3.8$ Hz, $J_2=12.0$ Hz, H₇), 2.86–3.11 (m, 2H, H₁, H₄), 6.07–6.44 (m, 2H, H₅, H₆).

2-Pentamethyldisiloxanyl-5-norbornene-2-carbonitrile (NN2). Pentamethylchlorosiloxane was used as a silylating agent. bp 91°C (0.45 mmHg). 57.0% Yield. Chemical shifts: 0.11 (s, 9H, Si(CH₃)₃), 0.25, 0.30 (two s, 6H, Si(CH₃)₂), 0.99–1.38 (m, 2H, H₂, H₃), 1.36 (q, 1H, $J_1=2.4$ Hz, $J_2=12.0$ Hz, H₈), 2.02 (q, 1H, $J_1=3.4$ Hz, $J_2=12.0$ Hz, H₇), 2.82–3.22 (m, 2H, H₁, H₄), 6.04–6.44 (m, 2H, H₅, H₆).

2-(Heptamethyltrisiloxan-1-yl)-5-norbornene-2-carbonitrile (NN3). Heptamethyl-1-chlorotrisiloxane was used as a silylating agent. bp 78.0–83.5°C (0.03 mmHg). 41.5% Yield. Chemical shifts: 0.03 (s, 6H, OSi(CH₃)₂O), 0.07 (s, 9H, Si(CH₃)₃), 0.29, 0.30 (two s, 6H, CSi(CH₃)₂), 1.18–1.45 (m, 2H, H₂, H₃), 1.36 (q, 1H, $J_1=2.6$ Hz, $J_2=11.8$ Hz, H₈), 2.04 (q, 1H, $J_1=3.4$ Hz, $J_2=11.8$ Hz, H₇), 2.89–3.16 (m, 2H, H₁, H₄), 6.07–6.47 (m, 2H, H₅, H₆).

2-Trimethylsilylmethyl-5-norbornene-2-carbonitrile (NNM1). Trimethylsilylmethyl chloride was used as an alkylating agent. bp 71.0°C (0.19 mmHg). 63.5% Yield. Chemical shifts: 0.14 (s, 9H, SiCH₃), 1.10 (s, 2H, CH₂), 1.40–1.62 (m, 2H, H₂, H₃), 1.60–1.82 (m, 2H, H₇, H₈), 2.79, 2.92 (two s, 2H, H₁, H₄), 6.08–6.40 (m, 2H, H₅, H₆).

2-Pentamethyldisiloxanylmethyl-5-norbornene-2-carbonitrile (NNM2). Pentamethyldisiloxanylmethyl chloride was used as an alkylating agent. bp 88.5–95.0°C (0.17 mmHg). 87.0% Yield. Chemical shifts: 0.07 (s, 9H, Si(CH₃)₃), 0.20 (s, 6H, CSi(CH₃)₂), 1.07 (s, 2H, CH₂), 1.41–1.59 (m, 2H, H₂, H₃), 1.59–1.84 (m, 2H, H₇, H₈), 2.70–3.05 (m, 2H, H₁, H₄), 6.13–6.37 (m, 2H, H₅, H₆).

2-Pentamethyldisilanyl-5-norbornene-2-carbonitrile (NNSi2). Pentamethylchlorodi-

silane¹⁵ was used as a silylating agent. bp 103–104°C (0.90 mmHg). 44.8% Yield. Chemical shifts: 0.16 (s, 9H, Si(CH₃)₃), 0.23, 0.26 (two s, 6H, CSi(CH₃)₂), 1.18–1.38 (m, 2H, H₂, H₃), 1.46 (q, 1H, $J_1=2.0$ Hz, $J_2=11.6$ Hz, H₈), 1.94 (q, 1H, $J_1=3.0$ Hz, $J_2=11.6$ Hz, H₇), 2.91–3.16 (m, 2H, H₁, H₄), 6.17–6.50 (m, 2H, H₅, H₆).

Ester derivatives of norbornene could be synthesized similarly.

Methyl 2-Trimethylsilyl-5-norbornene-2-carboxylate (NE1). bp 86.0°C (6.0 mmHg). 62.0% Yield. Chemical shifts: 0.16, 0.19 (two s, 9H, SiCH₃), 1.37 (m, 2H, H₂, H₃), 1.64 (m, 1H, H₈), 2.05, 2.29 (two m, 1H, H₇), 2.90 (m, 1H, H₄), 3.19, 3.32 (two m, 1H, H₁), 3.44, 3.48 (two s, 3H, CH₃), 6.00 (m, 2H, H₅, H₆).

Methyl 2-Pentamethyldisiloxanyl-5-norbornene-2-carboxylate (NE2). bp 41.0°C (0.01 mmHg). 53.5% Yield. Chemical shifts: 0.12 (m, 15H, SiCH₃), 1.40 (m, 2H, H₂, H₃), 1.85 (m, 1H, H₈), 2.10, 2.34 (two m, 1H, H₇), 2.92 (m, 1H, H₄), 3.34 (m, 1H, H₁), 3.50, 3.54 (two s, 3H, CH₃), 6.01 (m, 2H, H₅, H₆).

Polymerizations were carried out in degassed chlorobenzene using metathesis catalyst system Al(iso-butyl)₃-WCl₆-1-octene.^{16–18} Polymers were isolated and purified by reprecipitation from THF, CHCl₃, or dimethylformamide into methanol.

Glass transition temperatures (T_g 's) or polymers were estimated by a SEIKO Instruments DSC model DSC 100.

Films were prepared by casting a 5–8% THF or chloroform solution of a polymer on clean slide glass. The formed films were detached from the glass by immersion in water, and dried under vacuum for 48 h at 25°C. The films were conditioned at 60°C for 24 h. The permeability and diffusion coefficients were estimated for supplied air by measuring the amount of the gas permeated maintaining the upstream pressure at 1 atm and the downstream as zero on a Yanagimoto gas chromatographic gas permeability apparatus Model GTR-20 at 25°C. A detailed method of

the measurement is given in ref 3 and 5. The solubility coefficients were calculated from the permeability and diffusion coefficients.

$$q = DSp_1A(t - \theta)/l \quad (1)$$

where D and S are respectively diffusion and solubility coefficients, p_1 is partial pressure of the permeate at the upstream side (pressure of downstream side is approximated to be 0), l is the thickness of the film, t is time, and θ is time lag in permeation. The diffusion coefficient was estimated by

$$D = l^2/6\theta \quad (2)$$

The permeation coefficient is defined by

$$P = DS \quad (3)$$

By measuring q , p_1 , A , l , and θ , P , and D

were estimated by the least-squares methods, and S was calculated from P and D .¹⁹⁻²¹

Selectivity in permeation is defined by

$$\alpha = P_{O_2}/P_{N_2} \quad (4)$$

RESULTS AND DISCUSSION

Polymerization

All the monomers could be obtained in reasonable yield. The monomers seem to be isomeric mixtures (see NMR assignments in experimental part). The results of polymerization are shown in Table I.

The polymers have molecular weights in the order of 10^4 – 10^5 , estimated by GPC correlating to standard polystyrene, and are solid. In case of nitrile monomers, the yield of the alkyl

Table I. Polymerization of norbornene monomers^a

No.	Monomer (M)		M: W: Al: Oc ^b	Time	Yield	GPC ^c		
	mol l ⁻¹					molar ratio	h	%
1	NN ^d	4.09	240/1/3.3/0	3.5	85.0			
2	NNEt	0.77	113/1/3.0/0	20	9.7	12.9	7.9	1.63
3		1.39	50/1/3.0/0	54	21.3	5.55	2.48	2.24
4		0.93	24/1/3.0/0	14	34.9	2.98	1.35	2.21
5	NNPr	0.83	21/1/3.0/0	14	43.6	16.9	5.83	2.90
6	NNBu	0.88	23/1/3.0/0	14	74.7	33.2	11.5	2.89
7	NN1 ^d	2.36	150/1/3.0/0	17	23.8	19.3	6.36	3.04
8		0.39	57/1/3.0/0.5	20	13.9	12.0	4.85	2.48
9	NN2	4.11	200/1/3.0/0	88	3.4	—	—	— ^e
10		0.35	52/1/3.0/0.5	45.5	37.7	57.6	20.2	2.86
11	NN3	0.78	58/1/3.0/0.5	572	11.7	—	—	— ^e
12	NNM1	1.48	177/1/3.7/0	2	16.5	10.6	4.37	2.43
13		0.36	52/1/3.0/0.5	20	36.6	45.0	12.9	3.50
14	NNM2 ^f	0.71	54/1/3.0/0.7	1032	10.8	—	—	—
15	NNSi2	0.33	52/1/3.0/0.5	66	6.1	34.8	6.69	5.20
16	NE	0.56	60/1/3.3/0	15.2	88.2	29.0	15.5	1.87
17	NE1	0.65	57/1/3.0/0	0.07	42.5 ^g	44.1	23.3	1.90
18	NE2	0.56	49/1/3.0/0	0.07	46.5 ^g	23.0	13.3	1.73

^a In chlorobenzene at 80°C using WCl_6 -Al(iso-butyl)₃-1-octene as the initiator.

^b M: monomer, W: WCl_6 , Oc: 1-Octene.

^c Estimated correlating to standard polystyrene.

^d Using triethylaluminum at 70°C.

^e Polymer was insoluble in THF, $CHCl_3$ or DMF.

^f In toluene.

^g The silyl substituents were cleaved in the purification procedure, and the polymers were identical with polyNE. See discussion in the text.

substituted polymers seemed to depend on the ratio of monomer to WCl_6 and the molecular weight tended to decrease by increasing the amount of WCl_6 maintaining the monomer concentration constant (No. 2—4). However, a definite relation was not observed between the yield and molecular weight of the polymer of 2-oligodimethylsiloxanyl substituted norbornene. The presence of 1-octene did not necessarily reduce the molecular weight of the formed polymer (No. 12, 13). Further confirmation of the role of 1-octene seems necessary. Introduction of oligodimethylsiloxanyl substituents reduced the reactivity of nitrile monomers considerably with increasing length of the substituents (No. 10, 11). The monomers having the oligodimethylsiloxanyl substituents separated from norbornene system by methylene spacer showed only low reactivity in polymerization (No. 14). The reason for this is not clear at present. The ester monomers showed much higher reactivity in polymerization (No. 16—18); however, it was found that oligosiloxanyl substituents were cleaved very easily after the polymerization in the purification step in methanol eventually leading to poly(methyl 5-norbornene-2-carboxylate) (PNE). This results in the low yields of PNE1 and PNE2.

In order to make it easy to understand the following discussions, the abbreviations and structures of the polymers are shown.

The PNN series have the following basic structures.

PNN: $n=1$, $R=H$; PNNMe: $n=1$, $R=\text{methyl}$; PNNEt: $n=1$, $R=\text{ethyl}$; PNNPr: $n=1$, $R=\text{propyl}$; PNNBu: $n=1$, $R=\text{butyl}$; PNN1: $n=1$, $R=\text{trimethylsilyl}$; PNN2: $n=2$, $R=\text{trimethylsilyl}$; PNN3: $n=3$, $R=\text{trimethylsilyl}$; PNNM1:

$n=1$, $R=\text{trimethylsilylmethyl}$; PNNM2:

$n=1$, $R=\text{pentamethyldisloxanymethyl}$;

PNNSi2: $n=1$, $R=\text{pentamethyldisilyl}$.

PNE stands for an analogous series in which the nitrile group is replaced by carbomethoxyl group. However, in this article, PNE was used to denote poly(methyl 5-norbornene-2-carboxylate).

Glass Transition Temperature

Glass transition temperatures of the polymers are summarized in Table II.

The glass transition temperature of the polymer once increases by the introduction of bulky trimethylsilyl group (No. 7) and decreases about 70°C by inserting the methylene group between trimethylsilyl group and norbornene ring (No. 13), and further decreases $50\text{--}100^\circ\text{C}$ by the introduction of siloxane linkage into the substituents (No. 10, 11, 14). Introduction of methyl substituents at 2-position increases the glass transition temperature of the polymer (No. 19). Longer alkyl substituents reduce the glass transition temperature, but the effect is not as remarkable as that in case of the siloxanyl substituents (No. 2, 5, 6). Bulky trimethylsilyl groups will increase the friction between polymer backbones in their motion, hence resulting in the higher glass transition temperature. Introduction of flexible siloxane linkages in side chains reduces the friction and results in lower glass transition temperature. Methyl and longer alkyl groups have similar effects with those of trimethylsilyl and oligodimethylsiloxanyl groups, respectively; however the lower flexibility of alkyl chain compared with oligodimethylsiloxanyl chain had smaller effects than oligodimethylsiloxanyl chains in reducing the glass transition temperature. Although these trends are quite similar to that of polystyrene with *p*-oligodimethylsiloxanyl or alkyl substituents, norbornene polymers showed better film forming properties than the styrene type polymer with siloxane or alkyl side chains of the same length, and could be cast into thin film (*ca.*

Table II. Glass transition temperature and oxygen permeation behavior of norbornene polymers

No.	Polymer	T_g K	P_{O_2} ^a	P_{N_2} ^a	P_{O_2}/P_{N_2}	D_{O_2} ^b	D_{N_2} ^b	S_{O_2} ^c	S_{N_2} ^c
1	PPN	413	0.53	0.084	6.3	0.70	0.21	0.75	0.39
19	PNNMe	438 ¹⁶	—	—	—	—	—	—	—
2	PNNEt	407	1.7	0.32	5.2	1.51	0.62	1.12	0.52
5	PNNPr	381	2.0	0.39	5.0	1.01	0.50	1.94	0.78
6	PNNBu	360	2.4	0.52	4.6	1.81	0.95	1.33	0.54
7	PNN1	484	7.6	1.66	4.6	1.68	0.79	4.50	2.10
10	PNN2	361	15.3	3.54	4.4	6.54	4.01	2.34	0.88
11	PNN3	320	—	—	—	—	—	—	—
13	PNNM1	401	11.2	2.67	4.2	1.73	1.33	6.46	2.00
14	PNNM2	341	—	—	—	—	—	—	—
15	PNNSi2	393	4.4	0.97	4.6	1.23	0.96	3.60	1.01
16	PNE	338	0.83	0.19	4.4	0.57	0.25	1.46	0.76
20	PSt	373	1.2	0.22	5.5	0.56	0.20	2.20	1.10
21	PEtSt	300 ^d	—	—	—	—	—	—	—
22	PBuSt	279	6.7	2.1	3.2	6.7	—	1.0	—
23	PS1	409	14.0	4.4	3.2	—	—	—	—
24	PS2	309	40.0	13.0	3.0	18.0	11.0	2.2	1.3
25	PDMS	—	352	185	1.9	189	123	1.9	1.5
26	PDMS ^e	—	489	222	2.2	120	85	4.1	2.7

^a In $10^{-10} \text{ cm}^3 \text{ (STP)} \cdot \text{cm cm}^{-2} \cdot \text{s} \cdot \text{cmHg unit}$.^b In $10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ unit}$.^c In $10^{-3} \text{ cm}^3 \text{ (STP)} \text{ cm}^{-3} \cdot \text{cmHg unit}$.^d Taken from Polymer Handbook.^e Values for 10% cross-linked polymer at 0°C. PSt, polystyrene; PEtSt, poly(*p*-ethylstyrene); PBuSt, poly(*p*-butylstyrene); PS1, poly(*p*-trimethylsilylstyrene); PS2, poly(*p*-pentamethyldisiloxanylstyrene); PDMS, polydimethylsiloxane.

5—100 μm thick).

Introduction of oligodimethylsiloxanyl groups as side chains to back bone poly(5-norbornene-2-carbonitrile) which has high glass transition temperature was found effective to give the polymer film forming property.

Oxygen Permeation Behavior

The oxygen permeation behavior is also shown in Table II.

It can be seen that the permeability coefficients increased by the introduction of alkyl or oligodimethylsiloxanyl substituents at the 2-position of poly(5-norbornene-2-carbonitrile). Such increase in permeability coefficients is similar to that seen in the case of introduction of *n*-butyl or pentamethyldisiloxanyl groups at the *p*-position of polystyrene (No. 20—24).^{4,5,9,10} In order to obtain a little more

insight into the mechanism of permeation, the permeability coefficient was divided into diffusion and solubility coefficients according to eq 3 as a first approximation although the T_g of the polymer is considerably higher than 25°C.

The increase of permeability coefficients in case of poly(*p*-*n*-butylstyrene) or poly(*p*-*n*-pentamethyldisiloxanyl)styrene was elucidated to be brought about by the increase in the diffusion coefficient in permeation.³⁻¹⁰ This seems to be also true with poly NN2 which has disiloxane linkage in the 2-substituents. Compared with this, the increase in permeability coefficients of 2-trimethylsilyl, 2-trimethylsilylmethyl or 2-alkyl substituted norbornene polymers seems to be brought about by increase in both the diffusion and apparent solubility coefficients. The bulky substituents,

specially trimethylsilyl group, together with the higher T_g of the norbornene polymers compared with the styrene polymers may make it difficult for the polymer backbones to pack densely, resulting in wide gaps between polymer backbones or the formation of microvoids. Dual mode sorption may have occurred in the polymers resulting in the apparently higher role of the solubility coefficient and accordingly higher permeability coefficients of gases through the polymer film compared with poly (5-norbornene-2-carbonitrile) itself in permeation under the conditions studied. Asakawa and Nakagawa reported the unusually high role of the solubility and diffusion coefficients in the permeation of inert gases through the poly(1-trimethylsilyl-propyne) film being at glassy state.^{22,23} Bulky trimethylsilyl groups of this polymer and the rigid polymer backbone would make it difficult for the polymer backbone to pack densely. Permeation may have occurred between wide gaps of polymer backbones resulting in the high role of the diffusion and solubility of the gas in permeation. It is necessary to carry out sorption experiments and study the effects of the pressure of gas on permeability coefficient in order to precisely understand the mechanism.

By the introduction of pentamethyldisiloxanyl groups at 2-position, the role of diffusion coefficient increased remarkably, and the permeability became controlled principally by the diffusion coefficient as was in the case of polystyrene with pentamethyldisiloxanyl substituents; however, the role of the diffusion coefficient in norbornene polymers seems lower compared with that in the case of polystyrene. Recently, we found that the change in permeability through *p*-oligodimethylsiloxanyl substituted polystyrene film can be correlated to the flexibility of the substituents and the mobility of the substituents which could be estimated by the spin-lattice relaxation time of the trimethylsilyl carbon in the substituent.¹⁰⁾ A similar study showed reveal the exact role of

the oligodimethylsiloxanyl side chains in norbornene polymer systems. In either case, the introduction of flexible oligodimethylsiloxanyl groups as side chains to polymer back bone with high glass transition temperature was found quite effective increase the permeability of gases through the polymer by increasing the diffusion coefficient.

In case of trimethylsilyl or trimethylsilylmethyl substituted norbornene (polyNN1 and polyNNM1), which does not have siloxane linkage in the substituents, the substituents are less mobile than pentamethyldisiloxanyl substituents, which will result in higher T_g and a lower permeability coefficient of the polymer. Further research is needed to clarify permeation through norbornene polymers.

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