



Short communication

Synthesis and oxygen permeability of novel graft copolymers consisting of a polyphenylacetylene backbone and long oligosiloxane grafts from phenylacetylene-type macromonomers



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HIGHLIGHTS

- Acetylene-type oligosiloxane macromonomers were synthesized and copolymerized.
- Novel graft copolymers of polyacetylene and oligosiloxane were synthesized.
- The copolymers with high content of oligosiloxane formed self-standing membranes.
- Oxygen permeation performance of the graft copolymers were better than polysiloxane.

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ABSTRACT

Novel graft copolymers consisting of rigid poly(substituted acetylene) as a main chain and flexible linear oligodimethylsiloxane (ODMS) as grafts have been synthesized from well-defined macromonomers which were synthesized by living polymerization. The length and the content of ODMS in these graft copolymers have been controlled. The graft copolymers had high molecular weights, good solubility, and good membrane forming ability. Surprisingly the graft copolymers containing the linear ODMSs of more than 80% still had good membrane forming ability. In addition, more surprisingly both permeabilities (P_{O_2}) and permselectivities (P_{O_2}/P_{N_2}) for some of the graft copolymers having higher content of ODMS were higher than those for cross-linked PDMS.

1. Introduction

Gas permselective membranes are very interesting from the viewpoint of fundamental science such as polymer chemistry and membrane science, and practical application such as purification of gas resources and removal of exhaust gases. For materials as gas permselective membranes, there are generally two requirements, that is, good membrane strength and good performance (i.e., high permeability and high selectivity) [1,2]. Although many gas permselective membranes have been reported [3–5], rigid polymers tended to give brittle and low permeable membranes, and flexible polymers tended to give waxy (weak) and low permselective membranes. In other words, some trade-off relationships have been often seen [3–5]. Among several kinds of materials as gas permselective membranes, polymer materials have

some advantages because we can precisely and freely design their molecular structures and they can easily form very thin membranes.

Linear polydimethylsiloxane (PDMS) has a very flexible main chain and therefore does not form self-supporting membranes. Therefore, usually cross-linking was applied to yield flexible and strong PDMS membranes. Cross-linked PDMS membranes show the highest oxygen permeability (P_{O_2}) among commercially available polymers. However, their permselectivities (P_{O_2}/P_{N_2}) were the lowest, and the permeabilities were much lower than those for some ultrahigh permeable polymers [5,6]. Therefore, these defects of PDMS membranes should be improved.

One of the authors successfully synthesized polystyrene-graft-poly-siloxane before [7–9]. However, their self-membrane forming ability was still poor. To improve this defect, we designed more rigid

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polyphenylacetylene instead of polystyrene as the main chain in this study.

Poly (substituted acetylene)s (poly A) also form good membranes showing good performances as oxygen permeation membranes [10–12]. The good properties seem to be due to their rigidity of the main chain. Therefore, to improve the disadvantages of PDMS as oxygen permeation membranes, we designed to combine rigid poly A and flexible PDMS in this study.

There are mainly four kinds of two-component polymers; blend polymers (physical blending), random copolymers, block copolymers, and graft copolymers. Preparation of flexible membranes from some of the blend polymers of PDMS and poly A may be difficult because of their immiscibility. In the case of the random copolymers, since they have no long oligodimethylsiloxane (ODMS) sequences, the original merit (high permeability) of PDMS must disappear. On the other hand, because the block copolymers and graft copolymers can contain long ODMS sequences, they can maintain the original high permeability of PDMS. The graft copolymers and AB block copolymers consisting of polysiloxane and poly(substituted acetylene) (poly A) seem to show similar properties. However, the controlled synthesis of the block copolymers is difficult and actually has not been reported. Therefore we selected the graft copolymers [13,14] whose chemical structures can be precisely controlled by macromonomer method using living polymerization.

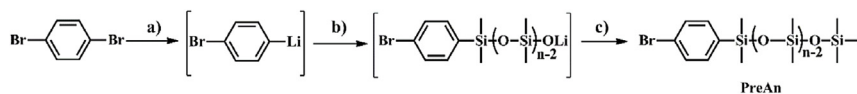
In order to synthesis well-defined graft copolymers consisting of poly A and PDMS, we selected macromonomer method [8]. It contains two steps (Scheme 1) as follows: step 1) synthesis of well-defined acetylene-type ODMS macromonomers, step 2) copolymerization of the macromonomer with an acetylene comonomer (A1 in Chart 1). By this method, the two important structures affecting their oxygen permeation performances, that is, the length of ODMS and the content of ODMS in the copolymers, can be controlled precisely. We previously reported oxygen permeability of comb-shaped polymers by homopolymerization of disiloxanylphenylacetylene monomer (A2 in Chart 1) [9]. In this case, the oxygen permeability was low because of low content of ODMS although the permselectivity was higher.

In this study, to improve performance as oxygen permselective membranes of PDMS, new graft copolymers, where the length of ODMS (n) and the content of ODMS (Si %) were controlled, were synthesized by copolymerization of well-defined macromonomers containing various lengths of ODMS. The macromonomers were synthesized by living polymerization. As a result we realized improvement of oxygen permeation performances of PDMS, that is, both permeability (P_{O_2}) and permselectivity (P_{O_2}/P_{N_2}) have been enhanced. We discuss the relationships between the chemical structures such as n and Si% and the performance.

2. Results and discussion

New acetylene-type oligodimethylsiloxane macromonomers (An) have been synthesized using two-step reaction as shown in Scheme 1 (for the detail conditions, see the supporting information). At the first

Step 1



Step 2

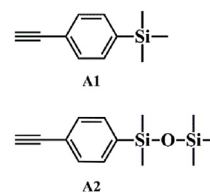
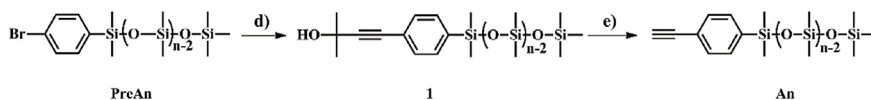


Chart 1. Chemical structures of A1 and A2. Synthesized in our previous report [9].

Table 1

Synthesis of prepolymers (PreAn) of acetylene-type oligodimethylsiloxane macromonomers (An) by living polymerization (Step 1).

No.	Feed [D ₃]/[initiator]	Prepolymers(PreAn)				
		$n_{\text{calc.}}^a$	Yield (%)	NMR		GPC ^d
				n^b	$M_n (\times 10^3)^c$	M_w/M_n
1	40	121	87.6	111	8.46	1.12
2	18	55	76.6	75	4.10	1.18
3	13	40	75.8	46	3.58	1.19
4	10	31	79.2	32	2.54	1.18
5	6.0	19	83.5	21	1.73	1.19

^a $n_{\text{calc.}} = \{[D_3]/[\text{initiator}]\} \times 3 + 1$.

^b $n = \{[\text{peak area for } (\text{Si}(\text{CH}_3)_2\text{O})]/[\text{peak area for PhH}]\} \times 4/6$.

^c $M_n = n \times 74 (= \text{MW of } (\text{Si}(\text{CH}_3)_2\text{O})) + 190 (= \text{MW of the other part in An})$.

^d By GPC correlating polystyrene standard (eluent: THF).

step, we synthesized prepolymers (preAn) having a linear oligosiloxane whose length are controlled by living ring opening polymerization of cyclohexamethyltrisiloxane (D₃). Table 1 shows the results of the first step. The calculated values (n_{calc}) from $[D_3]/[\text{initiator}]$ in the feed are almost consistent with the experimental ones (n) determined from ¹H NMR. In other words, the lengths (n) were controlled. In addition the molecular distributions (M_w/M_n) are quite narrow. Therefore, living polymerization has been achieved in this system.

At the second step, we converted the terminal group from the bromo substituent in preAn to the terminal triple bond in An via the protected triple bond by two polymer reactions (Scheme 1, d) and e). The final functionalities (f) of the terminal triple bond in An were almost 1.0 as shown in Table 2. Therefore, these polymer reactions successfully proceeded. In addition, since the M_n values of An measured by VPO are almost consistent with the experimental values (n) from ¹H NMR, An macromonomers have been successfully synthesized by the two-step method shown in Scheme 1. By this method, An's having various lengths (n = 18–110) of an linear oligodimethylsiloxane (ODMS) chain were obtained.

The desired graft copolymers (copoly(An/A1)) consisting of a rigid polyphenylacetylene backbone and flexible long oligosiloxane grafts were synthesized by copolymerization of An with A1 using a rhodium catalyst (Scheme 2, for the detail condition, see the supporting

Scheme 1. Synthetic route to acetylene-type oligodimethylsiloxane (ODMS) macromonomers (An).

Step 1 (synthesis of prepolymer(PreAn) by living polymerization of D₃): a) C₄H₉Li, ether; b) hexamethylcyclotrisiloxane (D₃), THF; c) trimethylchlorosilane;

Step 2 (synthesis of macromonomer (An) by polymer reactions): d) 2-methyl-3-butyn-2-ol, PPh₃, CuI, Pd(PPh₃)₂Cl₂, triethylamine; e) NaH, toluene.

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