Polymer 54 (2013) 2231–2234

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymer communication

Excellent oxygen permselectivity of fluorine-containing poly(trimethylsilyldiphenylacetylene)s prepared by direct alkylation of perfluorodecyl groups in membrane state

Takashi Sato [a], Naoki Yoshida [b], Akihiro Ishida [b], Masahiro Teraguchi [b,c], Toshiki Aoki [b,c,*], Takashi Kaneko [b,c]

[a] Tsukuba Research Laboratory, Sumitomo Chemical Co. Ltd., Kitahara 6, Tsukuba 300-3294, Japan
[b] Graduate School of Science and Technology and Department of Chemistry and Chemical Engineering, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan
[c] Center for Transdisciplinary Research, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan

ARTICLE INFO

Article history:
Received 6 December 2012
Received in revised form
7 February 2013
Accepted 4 March 2013
Available online 13 March 2013

Keywords:
Oxygen permselectivity
Fluorine-containing polymer
Membrane

ABSTRACT

Two poly(trimethylsilyldiphenylacetylene) membranes containing different contents of fluorine-containing groups were prepared by direct perfluorodecylation of poly(trimethylsilyldiphenylacetylene) (**poly 1**) in the membrane state using different ratios of (perfluorodecyl)phenyliodonium triflates to the phenyl groups in the polymer. The resulting perfluorodecylated poly(trimethylsilyldiphenylacetylene) (**poly 2a** and **poly 2b**) membranes were self-standing and tough. The two membranes showed better performance in oxygen permselectivity compared with all the membranes reported by many researchers. The performance ($PO_2 > 10^3$ barrer and $\alpha = PO_2/PN_2 = 2.9$) of the **poly 2a** membrane having a lower content of the fluorine groups located on the upper boundary line reported by Robeson in 2008. The **poly 2b** membrane having a higher content of the fluorine groups was one of the polymers having the highest PO_2 values ($PO_2 > 10^4$ barrer) in all the polymers reported.

1. Introduction

Many polymer membranes have been studied for gas separation in academic and industrial fields on the past three decades [1–14]. Among them, a family of poly(disubstituted acetylene)s was one of the most important materials for polymer membranes because of their good self-membrane forming ability and very high gas permeability [15]. Poly(1-(trimethylsilyl)-1-propyne) (**PTMSP**) (Chart 1) [16] discovered by Prof. Masuda is a polymer material that has one of the highest gas permeability coefficients($>10^4$ barrer) in the all polymers reported and has been widely investigated by many researchers [17–31]. **PTMSP** has been modified to enhance its performance but most of the trials ended in failure because modification was difficult with maintaining the original advantage. On the other hand, poly(1-(4-trimethylsilylphenyl)-2-phenylacetylene) (**Poly 1**) [32] (Chart 1) having relatively high oxygen permeability($>10^3$ barrer) is easy to modify chemically because it contains two phenyl rings. For example, we previously reported gas and enantiomer.

Permeability of **poly 1** was improved by the desilylation in the membrane state [33,34]. The polymer reactions in the membrane state we reported and called "reaction in membrane state (RIM)" were very useful to obtain good materials as separation membranes [33–36], because the reactions were quantitative and modified polymer membranes maintaining self-standing property were able to be easily obtained even if the target polymers could not be obtained by polymerization of the corresponding monomers due to their low polymerizabilities and the membranes could not be fabricated from the polymer due to their low solubilities [33–36]. In particular, the RIM method is thought to be suitable for fluorine-containing polymers because fluorine-containing polymers tend to be insoluble and show bad processability.

In general, it is known that fluorine-containing compounds show high affinity to oxygen, and therefore, modifications of polymer membranes by fluorine-containing compounds and groups has been reported [37–47]. For example, the oxygen permeability as well as permselectivity have been improved by the introduction of perfluoroalkyl groups due to the increase of the oxygen diffusion and solubility coefficients [44]. We also reported that perfluoroalkyloxysilyl poly(phenylacetylene) membranes had

* Corresponding author. Graduate School of Science and Technology and Department of Chemistry and Chemical Engineering, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan.
E-mail address: toshaoki@eng.niigata-u.ac.jp (T. Aoki).

0032-3861/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2013.03.008

higher oxygen permeability and permselectivity than the corresponding alkylsilyl ones [45].

As described above, the RIM method is promising to obtain good fluorine-containing polymer membranes and **poly 1** is suitable polymer as a starting polymer membrane. However, the introduction of fluorine-containing groups to **poly 1** by polymer reactions in the membrane state has not been reported. Here, we propose introduction of perfluoroalkyl groups to the **poly 1** membrane through the polymer reaction using (perfluoroalkyl) phenyliodonium triflates (FITS) [48]. FITS is an effective reagent for the introduction of perfluoroalkyl groups to aromatic compounds because it is highly reactive electrophilic perfluoroalkylation agents. In this communication, we report that two novel fluorine-containing poly(trimethylsilyldiphenylacetylene)s (**poly 2a** and **poly 2b**) membranes were successfully prepared by RIM using FITS, and their extremely good performance as oxygen permselective membrane materials.

2. Experimental section

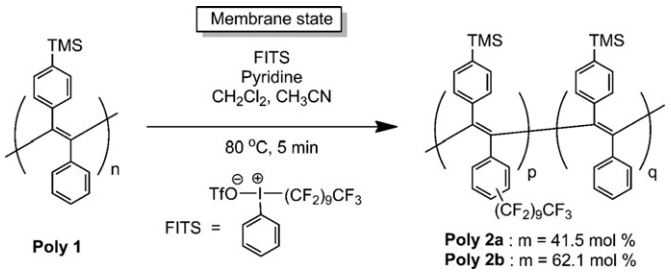
Poly 2a membrane was prepared by the following procedure (Scheme 1): **Poly 1** membrane (35.5 mg, 0.143 mmol) prepared by polymerization of **1** was gently immersed to the solution of FITS(124 mg, 0.143 mmol) and pyridine(13.9 μL, 0.172 mmol) in chloroform (2 mL) and acetonitrile (1.3 *m*L) at 80 °C for 5 min. The crude **poly 2a** membrane was washed by being immersed in methanol at room temperature for 1 day and dried at room temperature in *vacuo* for 1 day to a constant weight. The content of the repeating units having the fluorine group (m (mol%) in Scheme 1) was determined from the elemental analysis (For the detail see the Supporting information). **Poly 2b** membrane was also prepared by the same procedure and condition using **poly 1** membrane (27.8 mg, 0.111 mmol), FITS (484 mg, 0.555 mmol), and pyridine (44.8 μL, 0.555 mmol) in chloroform (10 mL) and acetonitrile (6.7 mL). For details of determination of fractional free volume (FFV) and oxygen and nitrogen permeability coefficients (PO_2 and PN_2) and oxygen/nitrogen permselectivity coefficient ($\alpha = PO_2/PN_2$), see the Supporting information.

Poly 2a membrane: IR (KBr, cm^{-1}) : 3056 (C–H), 2959 (Ph–H), 1246 (Si–C), 1218 (C–F), 1152 (C–F), 838 (Si–CH_3), 690 (Ph–H). Thickness: 24–37 μm. Elemental analysis : C, 55.61; H, 4.26; F, 35.61. m = 41.5 mol%.

Poly 2b membrane: IR (KBr, cm^{-1}) : 3068 (C–H), 2960 (Ph–H), 1246 (Si–C), 1245 (Si–C), 1218 (C–F), 1152 (C–F), 838 (Si–CH_3), 692 (Ph–H). Thickness: 65–135 μm. Elemental analysis: C, 48.88; H, 3.21; F, 43.34. m = 62.1 mol%.

3. Results and discussion

The introduction of perfluorodecyl groups to **poly 2** membranes was confirmed by IR spectroscopy (Fig. 1) because they were



Scheme 1. Synthesis of **poly 2** by direct perfluorodecylation of **poly 1** with FITS reagent in membrane state. (m (mol%) = p/(p + q) × 100).

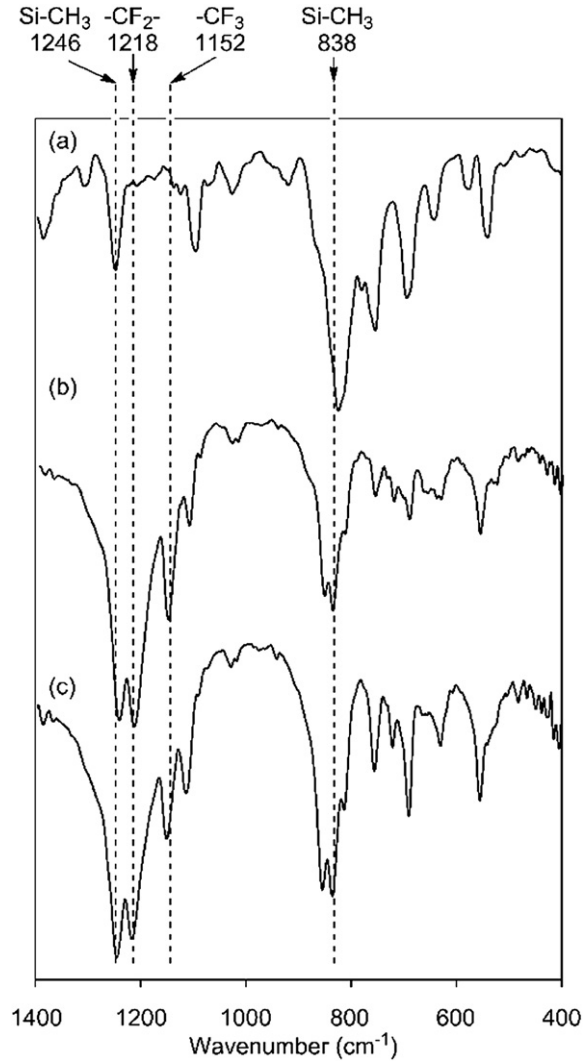


Fig. 1. IR spectra of membranes of **poly 1** (a), **poly 2a** (b), and **poly 2b** (c).

insoluble in general NMR solvents. Both **poly 2a** and **poly 2b** membranes showed the peaks at 1218 and 1152 cm^{-1} assigned to the perfluorodecyl groups. Since the IR of poly 2a,b (Fig. 1) has no S=O peaks at 1035 cm^{-1}, complete removal of the FITS reagent was confirmed. The contents of the perfluorodecyl groups of **poly 2a** and **poly 2b**, *i.e.*, the compositions of the repeating units.

Having the fluorine group(m = p/(p + q) x 100 in Scheme 1: mol%) were calculated from the elemental analysis (**poly 2a** : m = 41.5 mol%,

Table 1
Synthesis of **poly 2** by direct perfluorodecylation of **poly 1** with FITS reagent in membrane state.[a]

Run	Sample	[FITS]/[Phenyl ring]	Content of perfluorodecylated monomer unit (m: mol %)[b]	Contact angle[c] (o)	FFV[d]
1	Poly 1	0.0	0.0	110	0.260
2	**Poly 2a**	1.00	41.5	126	0.353
3	**Poly 2b**	5.00	62.1	135	0.370

[a] For 5 min at 80 °C.
[b] By elemental analysis. m = p/(p + q) × 100.
[c] Using water droplet.
[d] Calculated from : FFV = $(v_{sp}-v_0)/v_{sp} \simeq (v_{sp}-1.3v_W)/v_{sp}$. For the detail, see the Supporting information.