

Novel poly(diphenylacetylene)s with both alkyl and silyl groups as gas permeable membranes: Synthesis, desilylation, and gas permeability

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ABSTRACT

Diphenylacetylenes having a dimethyloctylsilyl group and an alkyl group at *para* positions [$\text{Me}_2n\text{-C}_8\text{H}_{17}\text{SiC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{R}$; R = H (**1a**), *i*-Pr (**1b**), *t*-Bu (**1c**), *n*-Bu (**1d**)] and having only an alkyl group [$\text{PhC}\equiv\text{CC}_6\text{H}_4\text{R}$; R = *i*-Pr (**1B**), *t*-Bu (**1C**)] were synthesized and then polymerized with $\text{TaCl}_5/n\text{-Bu}_4\text{Sn}$ catalyst to provide the corresponding poly(diphenylacetylene)s (**2a**, **2b**, **2c**, **2d**, **2B**, and **2C**). The formed polymers afforded tough free-standing membranes by casting from toluene solutions. Desilylation reaction of Si-containing membranes (**2a–d**) was carried out with trifluoroacetic acid to give the desilylated membranes (**3a–d**). The permeability of these membranes to O_2 , N_2 , and CO_2 were determined. All the Si-containing membranes exhibited almost the same gas permeability. The desilylation of Si-containing membranes of **2a–c** resulted in large increase of gas permeability. No apparent increasing of gas permeability was observed in the desilylation of **2d**. To clarify the effects of desilylation, CO_2 diffusivity ($D(\text{CO}_2)$), CO_2 solubility ($S(\text{CO}_2)$), and fractional free volume (FFV) of the polymer membranes were investigated. The $S(\text{CO}_2)$ values of desilylated membranes were much larger than that of Si-containing counterparts. The $D(\text{CO}_2)$ and FFV of membranes of **2a–c** increased through desilylation. The desilylated membrane of **3d** had small $D(\text{CO}_2)$ value and almost the same FFV compared with **2d**. Further, the comparison of the permeability between three types of membranes with the same chemical structure revealed that the microvoids were not generated by the desilylation of membranes of poly(diphenylacetylene)s containing alkyl groups.

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1. Introduction

Polyacetylenes with bulky spherical substituents show extremely high gas permeability. This is because both their stiff main chain composed of alternating double bonds and the steric repulsion of the bulky substituents make membranes sparse [1]. Therefore, poly(substituted acetylene)s are promising materials for gas separation membranes. A variety of poly(substituted acetylene)s have been synthesized so far, and the gas permeability of their membranes has been investigated [1–3]. Since a polymer membrane is usually prepared by casting its solution, the membrane of a solvent-insoluble polymer is not prepared directly by solution-casting. However, several membranes of insoluble poly(substituted acetylene)s have been prepared by an indirect method, namely desilylation of solvent-soluble membrane containing silyl groups [4]. In the desilylation reaction of polymer membrane, it has been predicted that the spaces occupied by silyl groups are maintained in some level as microvoids because the

mobility of polymer chain is restrained in a solid state [4–9]. However, the details about the effect of desilylation in a solid state upon gas permeability have not been known yet.

In the previous paper [10], we investigated the desilylation of membranes of poly(diphenylacetylene)s containing both trimethylsilyl and linear alkyl groups, and reported that additional microvoids in their membranes were not generated through desilylation. Linear alkyl groups are flexible pendant chains, and thus they are unsuitable to maintain a microvoid. However, poly(diphenylacetylene)s having both trimethylsilyl and branched alkyl groups such as *t*-butyl groups were insoluble in any solvents, and their membranes could not be prepared. Therefore, the effect of the branched alkyl groups versus the linear alkyl groups remains unknown. In order to solve the problem of insolubility, dimethyloctylsilyl groups were introduced to poly(diphenylacetylene)s instead of trimethylsilyl groups. This enabled us to investigate the effect of desilylation on gas permeability of poly(diphenylacetylene)s having branched alkyl groups for the first time.

In this paper, the desilylation of membranes of poly(diphenylacetylene)s having dimethyloctylsilyl and various alkyl groups, which contain linear and branched alkyl groups, at *para* position of phenyl groups was performed. The effect of

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desilylation on gas permeability was investigated in detail. The desilylated polymers in this study dissolve in common solvents, and the polymer membranes with the same chemical structure could be prepared by three different routes (Scheme 1). First method is the desilylation of Si-containing membranes, and second is solvent-casting method using the desilylated polymers. Final route is solvent-casting method using polymers synthesized directly by the polymerization of monomers without silyl group. The comparison of the permeability between such three types of membranes can reveal the effect of desilylation of the membrane on gas permeability. The membranes which were prepared by desilylation in a solid state exhibited the same or low permeability compared with the other two types of membranes without silyl group. This indicates that the microvoids were not generated by the desilylation of the membranes.

2. Experimental

2.1. Measurements

The molecular weights and polydispersity ratios of polymers were estimated by gel permeation chromatography (tetrahydrofuran (THF) as eluent, polystyrene calibration) at 40 °C on a Shimadzu LC-10AD chromatograph equipped with three polystyrene gel columns (Shodex KF-802.5 × 1 and A-80M × 2) and a Shimadzu RID-6A refractive index detector. IR spectra were recorded on a Nicolet MAGNA 560 spectrometer. NMR spectra were obtained on a Jeol LA-500 spectrometer. Elemental analyses of monomers were performed at the Microanalytical Center of Kyoto University.

Gas permeability coefficients of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C under 1 atm upstream pressure. The permeability coefficient

P expressed in barrer unit (1 barrer = 10^{-10} cm³(STP) cm cm⁻² s⁻¹ cm Hg⁻¹) was calculated from the slope of the steady-state line. The D value was determined by the time lag method using the following equation:

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

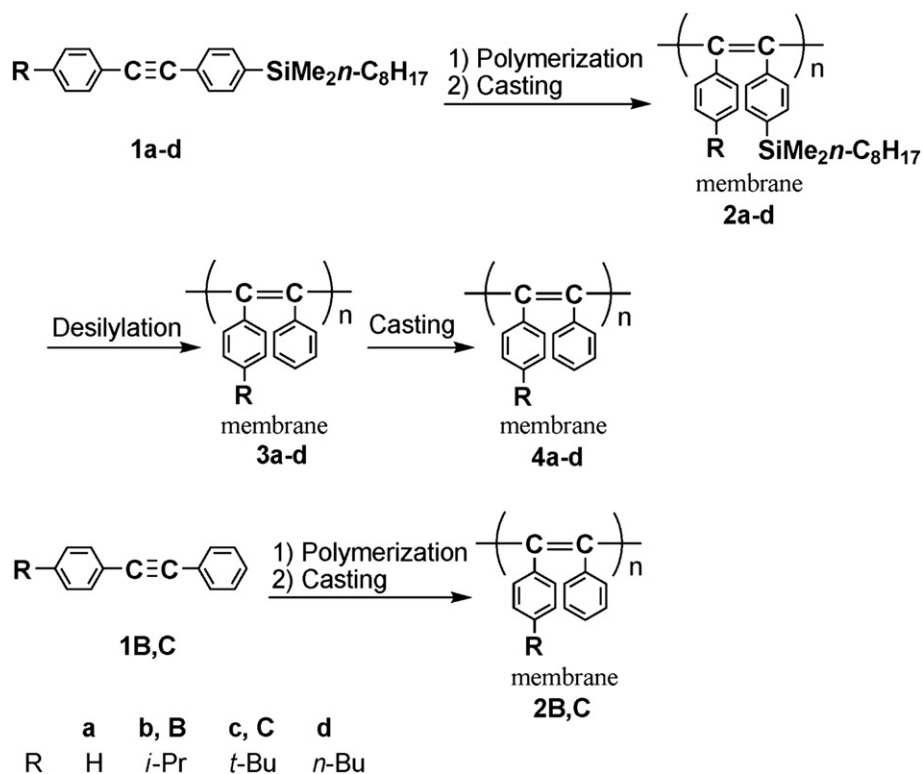
here, l is the membrane thickness and θ is the time lag, which is given by the intercept of the asymptotic line of time-pressure curve to the time axis. The S value was calculated by using equation $S = P/D$.

2.2. Materials

Toluene as polymerization solvent was purified by distillation over calcium hydride. TaCl₅ as main catalyst was commercially supplied by Aldrich and used without further purification, while *n*-Bu₄Sn as cocatalyst was purified by distillation. Phenylacetylene, *p*-iodo-*i*-propylbenzene, *p*-*t*-butyliodobenzene, *p*-*n*-butyliodobenzene and common organic solvents were commercially obtained and used without further purification. *p*-Dimethyloctylsilylphenylacetylene were synthesized referring to the literature [11]. 1-(*p*-Dimethyloctylsilyl)phenyl-2-phenylacetylene (**1a**), 1-(*p*-*i*-propyl)phenyl-2-phenylacetylene (**1B**), and 1-(*p*-*t*-butyl)phenyl-2-phenylacetylene (**1C**) were synthesized according to the literatures [5,12]. Synthesis and properties of poly[1-(*p*-*n*-butyl)phenyl-2-phenylacetylene] (**2D**) have been reported in our previous paper [10], and the data of **2D** were used in this study to compared with **3d**.

2.3. Monomer synthesis

Monomers were synthesized according to Scheme 2 with reference to the literature [13]. The synthesis procedures and analytical data of monomers are as follows.



Scheme 1. Synthesis of polymers and preparation of polymer membranes.

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