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Poly(diphenylacetylene) Membranes with High Gas Permeability and Remarkable Chiral Memory

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The design and synthesis of novel functional polymers are essential to materials science, membrane science, and so forth. For instance, the development of efficient polymers as separation membranes will play a crucial role in the fields of energy-saving and the environment.[1] In general, the membranes of polyacetylenes with bulky substituents possess many molecular-scale voids owing to both the stiff main chain and the steric repulsion of substituents, and consequently, gases and liquids readily permeate these membranes.[2] Poly[1-(trimethylsilyl)-1-propyne] was synthesized for the first time in 1983, and it proved to have the highest oxygen permeability among all the synthetic polymers.[3] This finding stimulated many membrane scientists to study the behavior and mechanism of gas permeation through this polymer.[4]

Poly(diphenylacetylene) (**1**) is, thermally, the most stable substituted polyacetylene, but it is insoluble in any solvent, and hence it is impossible to fabricate a membrane from it by solution casting[5a] (Scheme 1). When relatively bulky substituents are introduced onto the para or meta position of diphenylacetylene, the resulting polymers become soluble. For instance, poly[1-phenyl-2-*p*-(trimethylsilyl)phenylacetylene] (**2a**) obtained with $TaCl_5-n\text{-}Bu_4Sn$ catalyst is soluble in common solvents such as toluene and chloroform and possesses high molecular weight ($>1 \times 10^6$).[5b] This polymer is membrane-forming by solution-casting and exhibits a fairly high gas permeability. Furthermore, poly[(−)-1-*p*-[dimethyl(10-pinanyl)silyl]phenyl-2-phenylacetylene] (**2b**), a poly(diphenylacetylene) having optically active silyl substituents, displays strong CD signals due to the helical main chain structure.[5c] This polymer shows enantioselectivity in the permeation of racemic tryptophan to permeate the (*R*)-enantiomer faster than the (*S*)-isomer.

It is known that aryltrimethylsilanes undergo scission of the aryl−Si bond in the presence of proton acids.[6] Thus, if desilylation of the membrane of **2a** is achieved, molecular-scale voids are generated in the space where the trimethylsilyl groups were present, which will hopefully endow the polymer with high gas permeability. It is also expected that the resulting polymer membrane will have both high thermal stability and insolubility in organic solvents like the conventional **1**. In the present paper, we report the preparation of poly(diphenylacetylene) membranes (**3a**, **3b**) through desilylation of membranes of **2a** and **2b** and on the high gas permeability and the highly retained chiral memory of the resulting polymer membranes.

Desilylation of membranes of **2a**[5b] was explored by using four proton acids, i.e., trifluoromethanesulfonic acid, sulfuric acid, trifluoroacetic acid, and acetic acid. Desilylation proceeded smoothly in the presence of the first three acids, whereas the reaction was extremely sluggish with acetic acid. Trifluoroacetic acid was the most useful among the proton acids examined, because it dissolves in organic solvents, shows adequate catalytic activity, and can be easily removed owing to its low boiling point (72 °C).[7]

The membrane of **2a** showed the expected decrease of weight and shrank somewhat upon desilylation.[8] It was confirmed by the IR spectra of the membranes before and after reaction that desilylation proceeded to completion (Figure 1). Thus, the absorptions at 1250 ($\delta_{s,SiC-H}$), 1119, 855 ($\nu_{as,Si-CH_3}$), and 812 cm^{-1} ($\nu_{s,Si-CH_3}$) completely disappeared in the IR spectrum of the **3a** membrane, which agreed well with that of **1**, the poly(diphenylacetylene) obtained directly by polymerization. **2a** was soluble in common organic solvents such as toluene and chloroform, whereas **3a** was insoluble in any solvents. This is consistent with the insolubility of **1**. No weight loss was observed below 450 °C in the thermogravimetric analyses of **2a** in air. The onset temperature of **3a** was even higher (480 °C) and close to that of **1**. When **2a** was heated above 700 °C in air, a residue due to SiO_2 remained, whereas no residue was detected in **3a**. This also confirms that the silyl groups were completely removed.

The oxygen permeability coefficient (P_{O_2}) of **3a** at 25 °C was 6000 barrers and ca. 4 times as large as that of **2a** (1550 barrers[9]). The increase of oxygen permeability is attributed to the formation of molecular-scale voids by desilylation. The permeability coefficients to other gases were as follows (25 °C; barrers): He, 3100; N_2, 4700; CO_2, 9000; CH_4, 3700. These values are all larger than the values for **2a**[5b] (He, 1000; N_2, 520; CO_2, 4700; CH_4, 1500).

The construction of controlled secondary structures of polymers has attracted much attention in recent years, a typical example of which is one-handed helical polymers.[11] The preparation of one-handed helical polymers has usually been achieved by one of the following methods: (i) polymerization of optically active monomers, (ii) polymerization of prochiral monomers by using optically active catalysts or initiators, and (iii) chirality induction by interaction between achiral polymers and chiral additives.

It has been revealed that **2b,** which is obtained by the polymerization of a diphenylacetylene having an optically active *p*-(dimethylpinanylsilyl) group, exhibits a large optical rotation and intense CD signals in the UV−vis region corresponding to the backbone $\pi-\pi^*$ transition.[5c] These findings indicate that the main chain of **2b** probably assumes a helical conformation with a large excess helix sense. Thus, it is very interesting to examine whether polymer **3b** obtained by the desilylation of the membrane of **2b** maintains the helical conformation of the main chain. The membrane (thickness 0.89 μm) of **2b** was prepared by casting a toluene solution of the polymer onto a quartz plate, and desilylation was carried out under the same conditions as for **2a** (Scheme 1). The completion of the reaction was confirmed by the IR spectrum (Figure 1).

Quite interestingly, the resultant polymer (thickness 0.65 μm), **3b**, showed a specific rotation ($[\alpha]_D$ +5590°) even larger than the value ($[\alpha]_D$ +2380°) of **2b** and intense CD signals comparable to those of **2b** in the

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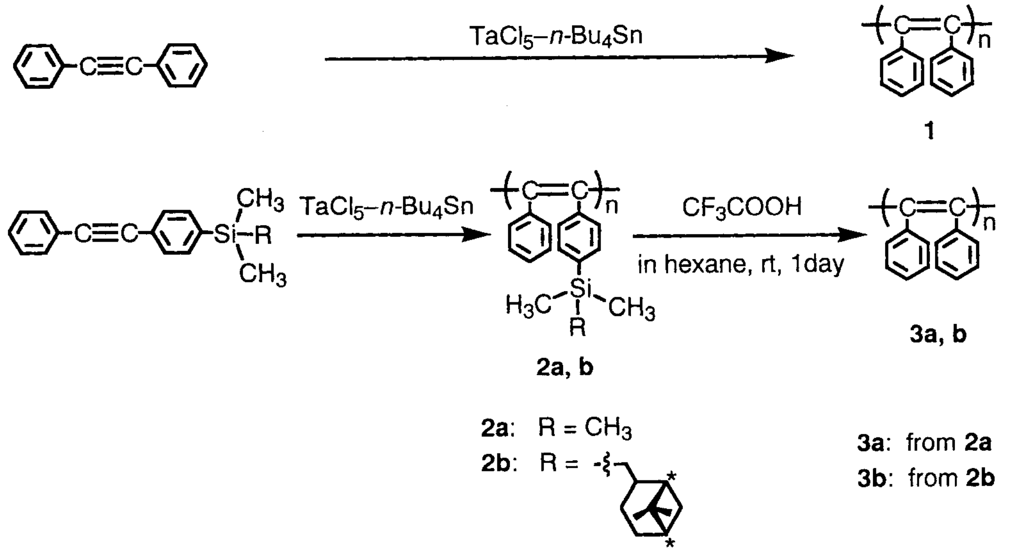
Scheme 1



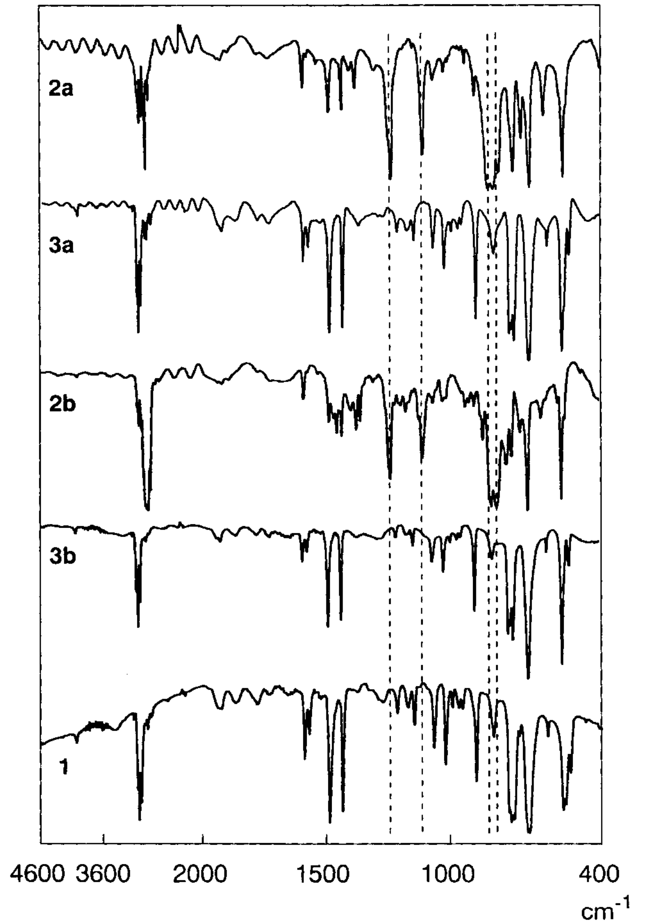


Figure 1. IR spectra of **1**–**3** (**1**: KBr pellet; **2**, **3**: film).

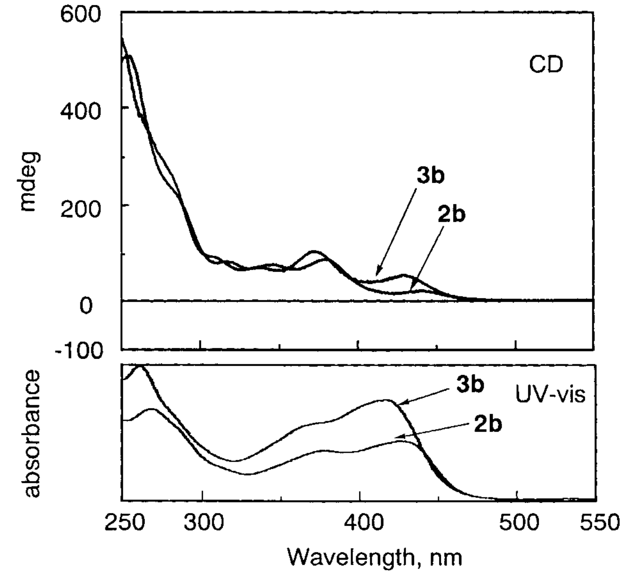


Figure 2. CD and UV–vis absorption spectra of **2b** and **3b** (film).

350–450 nm region[12] (Figure 2). The large $[\alpha]_D$ value and CD signals of **3b** compared to those of **2b** should be partly due to the shrinkage of the membrane upon desilylation. These results indicate that **3b** retains practically the same one-handed helical conformation in the main chain as in **2b.** In other words, the main chain of **3b** can exist in a sufficiently stable helical conformation with a large excess helix sense in the solid state irrespective of the absence of any chiral pendant group. To our knowledge, this is a new category of chiral memory apart from molecular imprinting, etc.[13] Owing to its helical structure, insolubility to organic solvents, and thermal stability, **3b** is expected to find applications as membranes and chromatographic materials for chiral separation and recognition.

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(7) A typical procedure of the desilylation reaction is as follows: A polymer membrane was immersed in a mixture of hexane/trifluoroacetic acid (volume ratio 1:1) at room temperature for 24 h; the orange membrane gradually turned green. To neutralize the remaining acid in the polymer matrix, the membrane was then immersed in a mixture of hexane/triethylamine (volume ratio 1:1) at room temperature for 5 h. The membrane color changed from green to dark orange. Finally, the membrane was immersed in methanol for a few hours to remove residual impurities, washed with methanol, and dried to constant weight at room temperature for 10 h.

(8) For instance, the weight, thickness, and diameter of a **2a** membrane changed from 37.3 mg, 41 μm, and 38 mm to 26.8 mg, 38 μm, and 33 mm, respectively, after desilylation. The observed weight agrees well with the theoretical value (26.6 mg) for the quantitative desilylation reaction.

(9) The present value of 1550 barrers was obtained after methanol conditioning of the membrane; this value is larger than the previously reported value of 1100 barrers measured without methanol conditioning.[5b] It is known that the conditioning of substituted polyacetylene membranes with nonsolvents increases gas permeability.[10]

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