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Preparation and properties of polytolan membranes bearing *p*-hydroxyl groups

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Abstract

The polymerization of a novel monomer *p*-(*t*-butyldimethylsiloxy)tolan (**1**) with $TaCl_5$–n-Bu_4Sn provided a high molecular weight polymer (poly(**1**)), whose M_w reached 4.0×10^6. The poly(**1**) membrane was prepared by the casting method, and converted into poly[(*p*-hydroxy)tolan] (poly(**2**)) with a mixture of trifluoroacetic acid/water. Whereas poly(**1**) dissolved in low polarity solvents such as toluene and chloroform, poly(**2**) was practically insoluble in any solvents, although it partly dissolved in methanol and ethanol. The onset weight loss temperatures of poly(**1**) and poly(**2**) in air were 320 and 360 °C, respectively, indicating fair thermal stability among substituted polyacetylenes. The oxygen permeability coefficients (P_{O_2}) of poly(**1**) was 150 barrers, which is relatively small among polytolan derivatives, while that of poly(**2**) was 8.0 barrers and smaller owing to the presence of polar hydroxyl groups.

Keywords: Polytolan; Membrane; Hydroxyl group

1. Introduction

Separation membrane technology is expected to play an important role in the fields of energy conservation and environmental engineering [1–3]. One polymer class, which has shown promise in these two fields, is substituted polyacetylenes, particularly those examples possessing bulky substituents. These polymers exhibit useful properties including air stability, good solubility, easy film formation and high gas permeability [4–6]. The extremely high gas permeability of certain such polymers has attracted much attention [7,8], where high gas permeability is attributed to the presence of many molecular-scale voids resulting from the stiff main chain and bulky spherical substituents. Among these substituted polyacetylenes, polytolans [poly(diphenylacetylenes)] with bulky ring substituents are especially interesting since they possess excellent thermal stability and high gas permeability [9,10], as illustrated by poly[*p*-(trimethylsilyl)tolan] which exhibits an onset temperature of weight loss in air at 450 °C and an oxygen permeability coefficient (P_{O_2}) at 25 °C of 1550 barrers [11,12].

Polytolan is difficult to work with, since it is insoluble and infusible and hence cannot be fabricated into a membrane by a direct method [13]. Consequently, forming precursor polymers is necessary, and recently, we succeeded in the preparation of a polytolan membrane by the desilylation of poly[*p*-(trimethylsilyl)tolan] membrane [14]. Desilylation of the polymer enhances the oxygen permeability of the membrane by a factor of 4, with the value increasing from 1550 to 6000 barrers. Furthermore, polytolan membranes can be applied to the separation of organic mixtures, given the insolubility of the membrane itself [15].

Ta and Nb catalysts, which are effective for polymerization of disubstituted acetylenes, are inactivated by polar substituents such as hydroxyl and carboxyl groups, and hence disubstituted acetylenes with hydroxyl groups cannot be polymerized directly. A possible approach to obviate this problem would be to polymerize disubstituted acetylene

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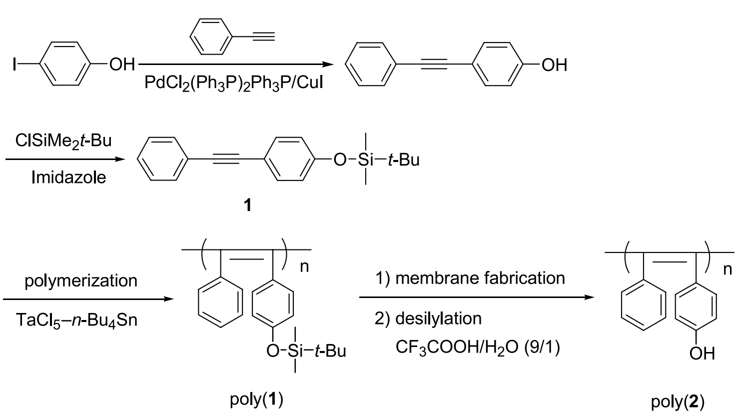

Scheme 1. Synthesis of polytolan bearing hydroxyl groups.

monomers possessing protected hydroxyl groups [16,17] and then deprotect the polymers that form. No examples of the synthesis of hydroxyl containing polytolans have been reported, polymers that would be interesting as separation membranes, since the hydroxyl group would render them polar. Thus, we invoke protection/deprotection methodology in the preparation of hydroxyl polytolan membranes.

In the present communication, we report the polymerization of a novel monomer *p*-(*t*-butyldimethylsiloxy)tolan (**1**) (Scheme 1), the preparation of a membrane comprised of the resultant polymer (poly(**1**)), and the conversion of poly(**1**) to poly[(*p*-hydroxy)tolan] (poly(**2**)) by desilylation. The gas permeability and other properties of poly(**1**) and poly(**2**) also are described.

2. Experimental

The synthesis of **1a** is composed of two steps (Scheme 1). As the first step [18–20], a 500 ml three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar, and flushed with dry nitrogen. *p*-Iodophenol (25 g, 110 mmol), phenylacetylene (12 g, 110 mmol), dichlorobis(triphenylphosphine)palladium (0.80 g, 1.1 mmol), triphenylphosphine (1.2 g, 4.6 mmol), cuprous iodide (1.3 g, 6.8 mmol), and trietylamine (300 ml) were placed in the flask. The reaction mixture was stirred at room temperature for 2 h. After the triethylamine in the reaction mixture was evaporated, diethyl ether (300 ml) was added, and then the insoluble salt was filtered off. The solution was washed with 1 N hydrochloric acid and then with water. The ethereal solution was dried over anhydrous sodium sulfate followed by rotary evaporation of ether. Purification of the crude product by flash column chromatography (eluent: hexane/ethyl acetate =9/1) provided the desired product (14 g, 61%) as white solid. As the second step [21], a 500 ml three-necked flask was equipped with a dropping funnel and a magnetic stirring bar, and flushed with nitrogen. (*p*-Hydroxy)tolan (13 g, 65 mmol), imidazole (13 g, 200 mmol), and *N*,*N*-dimethylformamide (100 ml) were placed in the flask. Then, a solution of *t*-butyldimethylchlorosilane (5.3 g, 90 mmol) in *N*,*N*-dimethylformamide (80 ml) was added dropwise at 0 °C for 30 min, and then the reaction mixture was stirred for an additional 10 h at room temperature. After diethyl ether (100 ml) was added, the solution was washed with water and then with 1 N aq. sodium hydroxide. The ethereal solution was dried over anhydrous sodium sulfate, and then concentrated at reduced pressure. The crude product was purified by flash column chromatography (eluent: hexane) to provide the desired product (new compound; 13.3 g, 67%) as colorless liquid. Purity: >99% (^{1}H NMR). IR (KBr): 2957, 1603, 1260, 916, 855, 812, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.67 (d, 2H, Ar), 7.57 (d, 2H, Ar), 7.37–7.47 (m, 3H, Ar), 6.93 (d, 2H, Ar), 1.13 (s, 9H), 0.33 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 155.9, 133.0, 131.4, 128.3, 127.9, 123.5, 120.2, 116.0 (each s, Ar), 89.4, 88.2 (each s, C≡C), 25.6 (s, CH_3), 18.2, −4.5 (each s, Si–C). Anal. Calcd for $C_{20}H_{24}OSi$: C, 77.9; H, 7.8. Found: C, 78.0; H, 7.9.

The polymerization of monomer **1** was accomplished

Table 1
Polymerization of **1** by $TaCl_5$–*n*-Bu_4Sn

Run	$[M]_0$ (M)	Polymer[a]		
		Yield (%)	$M_w/(10^3)$ [b]	$M_n/(10^3)$ [b]
1	0.10	61	4000	330
2	0.050	54	2400	200

In toluene at 80 °C for 24 h; $[TaCl_5]=20$ mM, [*n*-Bu_4Sn] $=40$ mM.

[a] Toluene-soluble and methanol-insoluble product.

[b] Measured by GPC.

Table 2
Gas permeability coefficients (P)

	P (barrer)						
	H_2	He	O_2	N_2	CO_2	CH_4	P_{O_2}/P_{N_2}
Poly(**1**)[a]	330	170	160	50	810	160	3.2
Poly(**2**)[b]	56	38	8.0	2.3	110	2.3	3.5

Measured at 25 °C.

[a] The sample was conditioned with methanol before measurement.

[b] The sample was conditioned with hexane before measurement.

using a 1:2 mixture of $TaCl_5$ and n-Bu_4Sn as catalyst in toluene solution at 80 °C (Table 1). The polymerization conditions were as follows: 24 h, $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM. The formed polymers were isolated by precipitation into a large amount of methanol, and the polymer yields were determined by gravimetry. The molecular weights of the polymers were estimated by gel permeation chromatography ($CHCl_3$ as eluent, polystyrene calibration).

Poly(**1**) (using the run 2 sample in Table 1) was converted into a membrane, which then was transformed into a durable membrane via desilylation using a mixture of trifluoroacetic acid/water. A detailed method of desilylation of membranes is as follows: the membrane of polymer was immersed in a mixture of trifluoroacetic acid and water (vol. ratio 9:1) at room temperature for 24 h. To neutralize the remaining acid in the polymer matrix, the membrane was then immersed in aqueous sodium carbonate solution at room temperature for 24 h, and then dried in air at room temperature. Finally, the membrane was immersed in hexane for 24 h to remove residual impurities and dried to constant weight at room temperature for 24 h. Complete desilylation was confirmed by IR spectroscopy (no absorptions were seen at 1250 ($\delta_{s,\ Si\text{–}CH}$), 855 ($\nu_{as,\ Si\text{–}CH_3}$), and 812 cm^{-1} ($\nu_{s,\ Si\text{–}CH_3}$), which had been observed in poly(**1**)). Desilylation also was confirmed by measuring the weight of the membrane before and after desilylation, thereby verifying loss of the silyl group (e.g. poly(**1**): 53.6 mg, poly(**2**): measured weight 33.5 mg, calculated weight: 33.5 mg).

3. Results and discussion

This chemistry yields a very high molecular weight polymer ($M_w = 4.0 \times 10^6$) at an initial monomer concentration, $[M]_0$, of 0.10 M; somewhat lower molecular weights result ($M_w = 2.4 \times 10^6$) when $[M]_0$ is lowered to 0.05 M. Molecular weight distributions of both polymers were quite broad ($M_w/M_n = 10.0$–15.0) (Table 1).

While poly(**1**) dissolves in common organic solvents such as toluene, chloroform and tetrahydrofuran (THF) and partly in hexane and cyclohexane, it does not dissolve in N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, and lower molecular weight alcohols. These solubility properties are similar to those of other polytolan derivatives [9,10]. In contrast, poly(**2**) was insoluble in common organic solvents including toluene, chloroform, THF, DMF and DMSO although it partly dissolved in methanol and ethanol. This significant variation in solubility behavior is important and is reflective of the incorporation of hydroxyl groups in polytolan. Onset weight loss temperatures for poly(**1**) and poly(**2**) in air were 320 and 360 °C, respectively, indicating relatively high thermal stability among substituted polyacetylenes [4–6]. The λ_{max} and ε_{max} values of poly(**1**) in chloroform solution ($c = 1.27 \times 10^{-4}$ mol/l) were 429 nm and 5400 $M^{-1}cm^{-1}$, respectively, which resemble those of other polytolan derivatives; e.g. $\lambda_{max} = 430$ nm, $\varepsilon_{max} = 5000$ $M^{-1}cm^{-1}$ in poly[p-(trimethylsilyl)tolan] [11,12].

The permeability coefficients (P) of the poly(**1**) membrane to various gases were measured at 25 °C after conditioning the membrane by immersing in methanol for 24 h and drying to constant weight at room temperature for another 24 h (Table 2). The P_{O_2} value of poly(**1**) was 160 barrers, which is a relatively small value for polytolan derivatives. Furthermore, the permeability of poly(**1**) to other gases was also relatively low. The gas permeability of poly(**2**) was examined at 25 °C after the membrane was immersed in hexane (rather than methanol) for 24 h, as it was partly soluble in methanol. The gas permeability coefficients of poly(**2**) were smaller than those of poly(**1**). The polymers bearing hydroxyl groups such as poly(vinyl alcohol) generally show very low gas permeability and are known as gas barrier membranes [22–25]. The relatively high gas permeability of poly(**2**) among hydroxyl group-bearing polymers suggests a fairly sparse structure as seen in many substituted polyacetylenes.

This new class of polar polytolan membranes offers new opportunities in membrane preparation. Consequently the synthesis and characterization of various polytolans possessing hydroxy groups is in progress.

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