Polymer Communication

Synthesis of rodlike polysiloxane containing polyol moieties derived from glucose with regularly controlled higher-ordered structure

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Abstract

A rodlike polysiloxane (**3**) containing polyol moieties derived from the sugar has been synthesized by reaction of an amine-functionalized rodlike polysiloxane (**1**) with gluconolactone (**2**) in the presence of triethylamine in DMF. Formation of **3** was estimated by the IR and ^{1}H NMR measurements. The functionality of **2** to the amino groups in **1** was ca. 75%, based on the ^{1}H NMR spectrum of the product. The XRD profile of **3** showed three peaks for a typical hexagonal phase, and the d-value of (100) peak of **3** was larger than that of **1**, indicating the regularly controlled higher-ordered structure of **3**.
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1. Introduction

The synthesis of polymers having sugar-residues, so-called 'glycopolymers', has widely been investigated because of their possible applications for biological functions [1]. So far, a number of such glycopolymers have been synthesized, which are composed of various organic polymer backbones combined with a variety of sugar-residues [2–7]. For example, lactose-containing polystyrene and polypeptide were prepared as the useful culture substrate of hepatocytes with asialoglycoprotein receptors [8]. However, it is difficult for these glycopolymers to keep the three-dimensional arrays of the sugar-residues because of a flexible nature of the common polymer backbones. It has been pointed out that the relative spatial compatibility of sugar-residues is important for molecular recognition in addition to their structural compatibility [9]. Controlling the three-dimensional arrays of sugar-residues in the glycopolymers would give the

relative spatial compatibility, leading to recognition of specific cell receptors. To control them, some studies have previously been made on the synthesis of glycopolymers with controlled higher-ordered structures by employing the organic rigid polymer backbones, such as polyisocyanide [10], polyacetylene [11], and poly(*p*-phenylene ethynylene) [12].

Inorganic polymers such as polysiloxanes have a number of interesting properties, e.g. high oxygen permeability, high temperature stability, low toxicity, and biocompatibility. These properties had inspired to construct new and unique materials by combining with sugar-residues or related moieties. Although some examples for preparation of sugar-polysiloxane hybrid materials have been reported [13–16], their higher-ordered structures are not controlled well. If sugar-containing polysiloxanes with regular higher-ordered structures are available, they can be expected to have a significant potential for biological functions.

Recently rodlike polysiloxanes were synthesized [17,18], and their rigidness would have advantage in controlling the higher-ordered structures. These materials were prepared by sol–gel reaction of organoalkoxysilanes containing amino groups in strong acid aqueous solutions. These polysiloxanes have rodlike structures existing the reactive amino groups on the surface, and construct hexagonal phases in

solid state. In our recent research interest concerning control of the three-dimensional arrays of the sugar-residues in glycopolymers, we have employed rodlike polysiloxane (**1**) to prepare sugar-containing inorganic polymer, i.e. inorganic glycopolymer, having the regular higher-ordered structure. We now report the synthesis of a polysiloxane (**3**) containing polyol moieties derived from glucose with regularly controlled higher-ordered structure by reaction of **1** with gluconolactone (**2**); **2** is commercially available compounds prepared by oxidation of glucose. This study is a first step for development of inorganic glycopolymers controlling the three-dimensional arrays of sugar-residues.

2. Experimental

2.1. Materials

The rodlike polysiloxane **1** was prepared according to the literature procedure [17]. *N,N*-Dimethylformamide (DMF) was purified by distillation. Other reagents were used as received.

2.2. Synthesis of 3

A typical experimental procedure was as follows. To a suspension of **1** (0.147 g, 1.0 mmol unit) in DMF (2.5 mL) was successively added triethylamine (0.15 mL, 1.1 mmol) and a solution of **2** (0.891 g, 5.0 mmol) in DMF (10 mL) with vigorously stirring at 80 °C under argon. After the mixture was stirred further at that temperature for 13 h, the obtained product was isolated by filtration, washed with DMF and acetone, and then dried under reduced pressure at 40 °C to yield 0.191 g of the yellow-powdered **3**. ^{1}H NMR (600 MHz, D$_2$O): δ 4.38–4.26 (1H, br, –C(=O)C*H*–), δ 4.16–4.05 (1H, br, –C(=O)CH(OH)C*H*–), δ 3.88–3.60 (4H, br, –C*H*(OH)C*H*(OH)C*H*$_2$–), δ 3.41–3.10 and 3.06–2.91 (2H, br, –NC*H*$_2$–), δ 1.88–1.45 (2H, br, –NCH$_2$C*H*$_2$CH$_2$Si–), δ 0.94–0.47 (2H, br, –C*H*$_2$Si–).

2.3. Measurements

The IR spectra were recorded using a SHIMADZU FTIR-8400 spectrometer. The ^{1}H NMR spectra (600 MHz) were recorded using a JEOL ECA600 spectrometer. The gel permeation chromatographic (GPC) analyses were performed by using a TOSOH CCPD with RI detector under the following conditions: Shodex GF-310 column with water as the eluent at a flow rate of 0.5 mL/min. The calibration curve was obtained using pullulan standards. The XRD measurements were conducted at a scanning speed of $2\theta = 0.2°$/min using a RINT 1200 (Rigaku Co., Ltd) diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm).

3. Result and discussion

We employed **2** for the reaction with **1**, because the sugar lactones like **2** react with the amino groups without protection of the hydroxy groups. An introduction of **2** to **1** was performed by heating in the presence of triethylamine in DMF (Scheme 1). The reaction proceeded heterogeneously, which would be favorable for progress of the reaction with keeping the higher-ordered structure. After the mixture was cooled to room temperature, the obtained product was collected by filtration, washed with DMF and acetone, and dried under reduced pressure at 40 °C to yield a yellow powder. The obtained product **3** was soluble in water and dimethyl sulfoxide (DMSO), but insoluble in typical organic solvents such as methanol, acetone, chloroform, and *n*-hexane. The structure of **3** was characterized by the IR and ^{1}H NMR spectra, as well as the X-ray diffraction (XRD) measurement.

The IR spectrum of the product showed absorptions at 1150 and 1050 cm^{-1} attributed to the Si–O bond of the polysiloxane, an absorption at 1080 cm^{-1} assigned to the C–O bond of the incorporating moiety, and an absorption at 1650 cm^{-1} due to the C=O bond of the amide group. These data supported the structure **3** of the product.

The ^{1}H NMR spectrum in D$_2$O of the product in Fig. 1 shows both signals due to **1** and **2**. Furthermore, a methylene signal **c** neighboring the amide group is appeared. These results indicate that the product has the structure **3** connecting **1** with **2** by the covalent bonds. However, methylene signals **b′** and **c′** are also appeared, indicating existence of the unreacted amino groups. The functionality of **2** to **1** was calculated to be ca. 75% based on the integrated ratio of the signal **c** to the signals **a** and **a′**. At higher temperature like 100 °C, the water-insoluble product was obtained. Although the reason of the insolubility is not yet clear, **2** or the moieties from **2** may be denatured by heating at that temperature.

The molecular weights (M_ns) of **3** and **1** were evaluated by GPC analyses with water as the eluent. The GPC peak of **3** was shifted to the range of higher molecular weight compared to that of **1**. The M_n values of **3** and **1** estimated using pullulan standards were 21,200 g/mol ($M_w/M_n = 1.33$) and 10,300 g/mol ($M_w/M_n = 1.41$), respectively.

For the XRD measurements, films of the products on glasses were prepared by drying aqueous solutions of the products spread on flat glass substrates. The XRD profile of
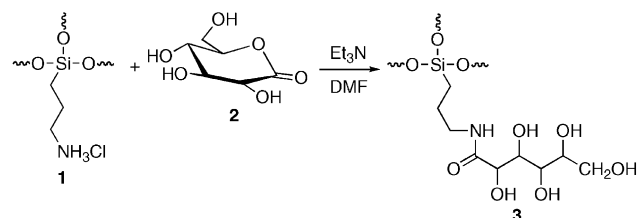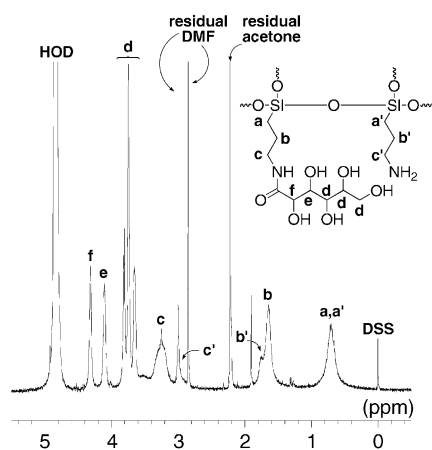
Scheme 1.

Fig. 1. ^{1}H NMR spectrum of **3** in D$_2$O. Chemical shifts were referenced to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) (δ 0.0 ppm).

Fig. 2. XRD patterns of **1** (a) and **3** (b).

3 showed three peaks with the *d*-value ratio of $1 : 1/\sqrt{3} : 1/2$ assigned to the (100), (110) and (200) peaks, respectively, indicating that the product has a hexagonal phase (Fig. 2). Additionally, the *d*-value of the (100) peak of **3** ($d=$ 1.76 nm) was larger than that of **1** ($d=1.41$ nm). This indicates that the hexagonal phase was maintained in spite of the increase in the *d*-value by introduction of **2** to **1**. However, the diffraction peaks of **3** are weaker and broader than that of **1** probably due to the less regularity of the higher-ordered structure. The surface of **3** is probably occupied by the incorporating polyol moieties, which decrease a stacking regularity due to their relative flexible nature.

A small amount of the low molecular weight compound was obtained in the solution of **3** in water, confirmed by the GPC analysis. The compound was probably formed by the hydrolysis of the siloxane bond of **3** due to the basic condition of the solution by existence of amino groups of **3**. The detailed studies on the stability and hydrolytic properties of **3** are now in progress.

In conclusion, we have synthesized the rodlike polysiloxane (**3**) having polyol moieties derived from glucose by reaction of **2** with **1**. This material has the regularly controlled higher-ordered structure of the hexagonal phase. The present reaction method will be applied to provide new inorganic glycopolymers with control of the three-dimensional arrays of the sugar-residues by employing various sugar lactones in the future. A series of these inorganic glycopo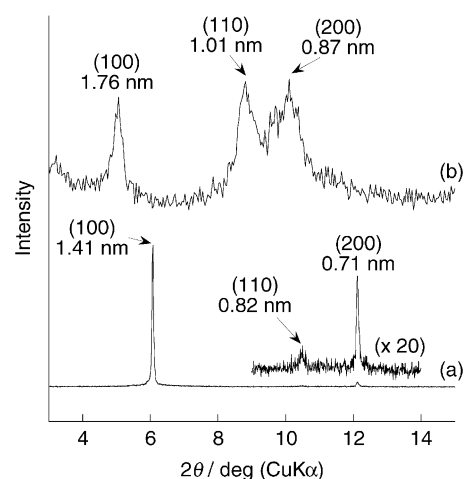lymers can be expected for the applications to the recognition of specific cell receptors due to such control of the three-dimensional arrays of sugar-residues.

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