Preparation of Monolayer of Poly(γ-benzyl-L-glutamate) by Chemical Reaction on a Silicon Crystal Surface

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Poly(γ-benzyl-L-glutamate) (PBLG) reacts with a silane coupling agent on a silicon crystal surface to form a molecular oriented film; the reaction yield was determined to be 77% by X-ray photoelectron spectroscopy and the orientation of PBLG molecules attached to the substrate was interpreted based on the attenuated total reflection spectrum.

Recently, organized molecular films have been widely investigated for utilization of the anisotropic character of the molecules in the films.[1] However, to obtain a wide variety of functional molecules in these films, a new method is required that stabilizes the orientation of organic molecules in a wide temperature range. In our previous paper,[2] we proposed a new method which organized molecules on a substrate surface by chemical reaction, and demonstrated a new technique for determining the reaction yield of lithocholic acid with an amino silane coupling agent on a Si surface by the use of X-ray photoelectron spectroscopy (XPS).[2] We call this method of preparing organized films chemical reaction alignment (CRA). The CRA method is applicable to various rigid organic molecules and can be expected to control the molecular orientation easily. On the other hand, there have been few reports concerning the reaction between organic molecules and silane coupling agents connected to a substrate surface. The XPS technique described in our earlier report is a useful way to observe the reaction of organic molecules with a surface functional group. In this paper, we report on the application of the CRA method to the preparation of monolayer films consisting of a rigid polymer molecule. We also discuss a quantitative analysis of bond formation between the polymer end group and a silane coupling agent attached to a Si surface by the use of XPS. Further, the orientation of polymer molecules on the Si surface is also discussed based on the polarized attenuated total reflection (ATR) spectrum.

PBLG was selected as the CRA molecule. This polymer takes an α-helical structure which gives it rigidity and has different functional groups, a carboxy group and an amino group, at individual terminal positions of the main chain.[3] These features make it suitable for use as a model polymer in the CRA method. Mercaptopropyltrimethoxysilane and Si crystal (100) surface were selected as the silane coupling agent and substrate, respectively. The Si surface was treated with an aqueous solution of pH 1 HCl before reaction with the silane coupling agent because the density of OH groups on a Si surface was reported to increase to 5.0 OH groups nm^{-2} after treatment with a strong acid.[4] Generally, OH groups on a Si surface are believed to react with a silane coupling agent, although there is no quantitative proof of it. According to the typical method, the Si surface was treated with the silane coupling agents in an acidic water solution of pH 4 at 5 wt% concentration for 24 h.[†] The substrate was then treated with PBLG as follows.[‡] PBLG (1 g) was dissolved in methylene chloride (100 ml) with an excess of DCC (dicyclohexylcarbodiimide, 1 g) at 0 °C. The Si substrates treated with the silane coupling agent were immersed in the solution very gently, and

left for a week at room temperature. Then the substrates were washed with methylene chloride and acetone repeatedly.

Although there are many reports on the treatment of a Si surface with a silane coupling agent,[5] the reaction of a silane coupling agent on a Si surface with organic molecules, especially as regards the polymer end group, has hardly been analysed. Therefore, we tried first to determine quantitatively the reaction yield of the mercaptosilane coupling agent with PBLG by XPS.[§] To examine the region close to the surface, the photoelectron detection angle was set to 5°. As shown in Fig. 1(a), the S$_{2p}$ peak of the XPS spectrum before the
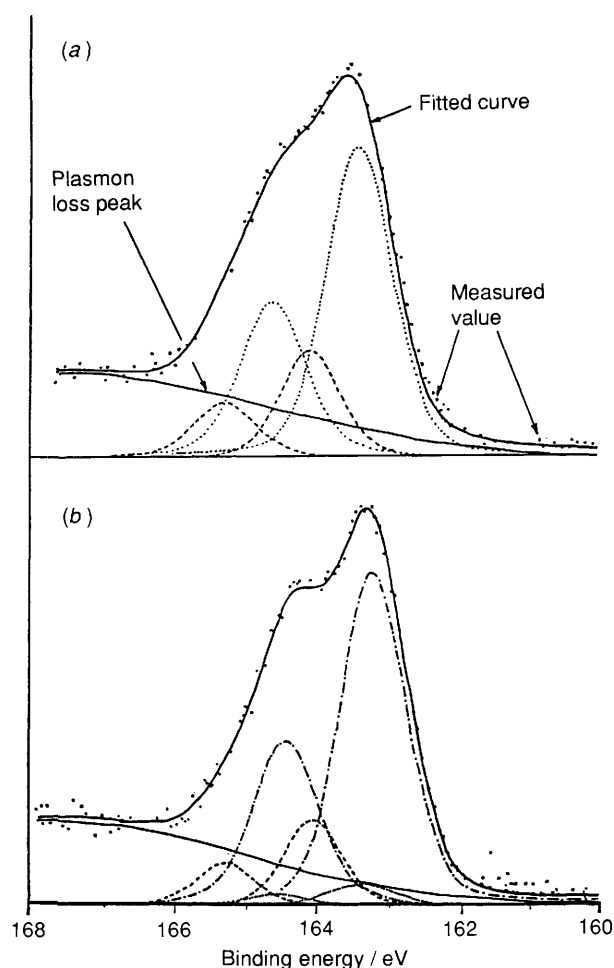

Fig. 1 S$_{2p}$ peak of XPS spectra. (a) Before reaction with PBLG and (b) after reaction with PBLG. Photoelectron detection angle is 5°. S$_{2p}$ peak is deconvoluted to (a) two pairs of peaks and (b) three pairs of peaks, respectively.
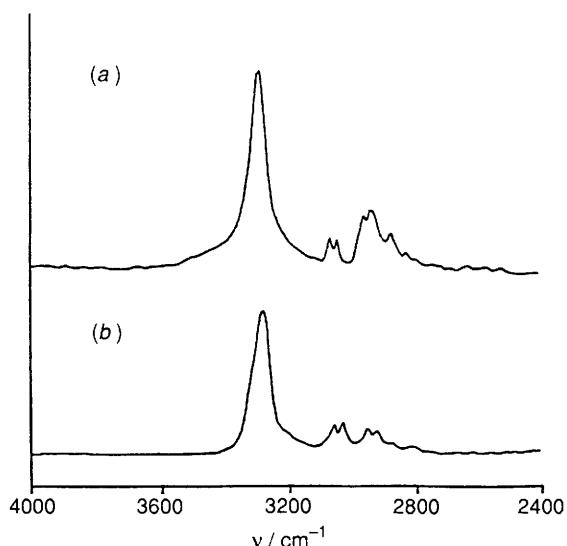

Fig. 2 FTIR–ATR spectra of (a) PBLG–CRA film and (b) PBLG cast film
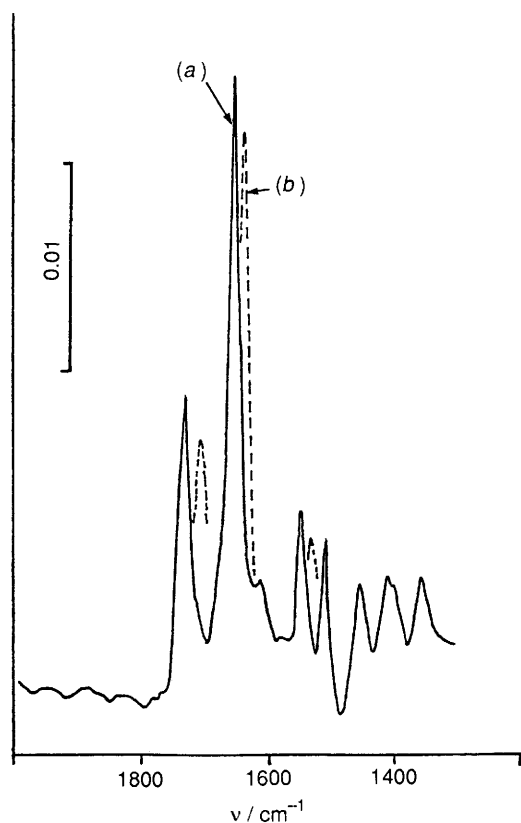
Fig. 3 FTIR–ATR spectra of PBLG–CRA film with (a) p-polarized radiation and (b) s-polarized light

Fig. 4 SEM image of PBLG–CRA film. SEM image was taken with Au coating at 1.5 kV accelerating voltage. Scale bar indicates 100 nm length. The white balls are dust.

Table 1 Deconvolution of S_{2p} peaks (a) before and (b) after reaction with PBLG. The ratio of 2p1/2 (upper row) : 2p3/2 (lower row) is fixed as 1 : 2

Pair of peaks	Position/ eV	FWHM/ eV	Constituent of sulfur states(%)	Assignment
(a)	165.3	1.0	13	Thiol–silanol
	164.1	1.0		
	164.6	1.1	87	Free thiol
	163.4	1.1		
(b)	165.3	1.0	18	Thiol–silanol
	164.1	1.0		
	164.6	1.1	5	Free thiol
	163.4	1.1		
	164.5	1.1	77	Thioester
	163.2	1.1		

reaction with PBLG was deconvoluted to two pairs of peaks. These are thought to be the free thiol peaks (······) and the peaks of thiol interacting with the Si surface (- - -), respectively. After the reaction with PBLG, the S_{2p} peak was deconvoluted to three pairs of peaks assigned to the free thiol peaks (······), the peaks of thiol interacting with the Si surface (- - -) and the thioester peaks generated by the reaction with carboxy end groups of PBLG molecules (-·-·), respectively, as shown in Fig. 1(b). The thioester peaks appeared in the lower binding energy region because of the electrical environmental change from thiol group to thioester group. By deconvoluting the S_{2p} peak, the reaction yield was determined to be 77%.
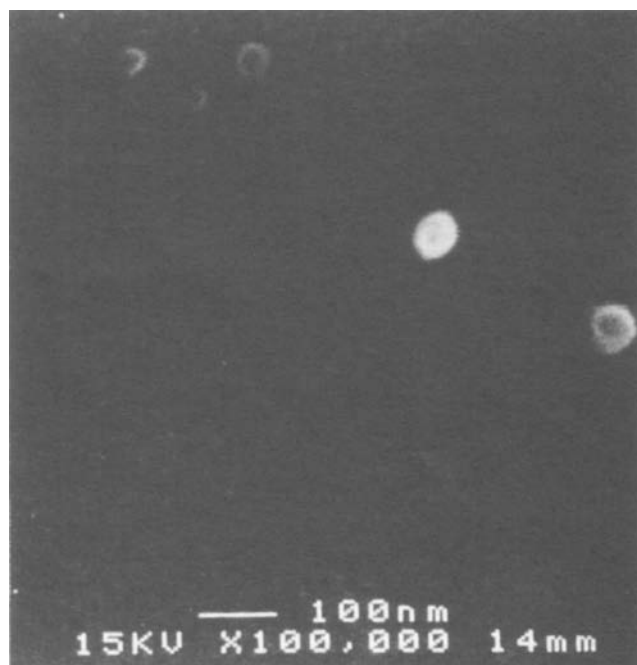
Next, in order to investigate the orientation of PBLG molecules in the CRA film, the IR spectrum was measured in ATR mode with eight reflections.¶ As shown in Fig. 2, the relative intensity of ν_{C-H} (alkyl) to ν_{C-H} (phenyl) was quite different between the CRA film [Fig. 2(a)] and a PBLG cast film [Fig. 2(b)]. This result suggests that PBLG molecules have a particular orientation in the CRA film. Both p-polarized and s-polarized ATR spectra of the PBLG–CRA film are shown in Fig. 3. According to Sagiv's method,[6] the tilt angle from surface normal of PBLG molecule axis was

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¶ The IR spectra were recorded with a Bio-Rad FTS-60A/896 FTIR spectrometer equipped with an MCT detector. The number of corrected interferograms was 256 with a resolution of 4 cm⁻¹. The ATR spectra were a result of the subtraction of the curves measured with the clean Si prism from those measured after CRA treatment.

estimated to be about 57° from the relative ratio of amide band I (*p*-polarized) to amide band I (*s*-polarized). We do not consider this angle to be a magic angle because of the difference in the v_{C-H} region between the CRA film and the PBLG cast film described above.

Fig. 4 shows a scanning electron microscope (SEM) image of the PBLG–CRA film. The film surface is approximately smooth with few irregularities.[1] This result suggests that the CRA method produces almost homogeneous films even in the case of polymer molecules.

We concluded that a bond-forming reaction between thiol groups immobilized on a silicon surface and carboxy end groups of PBLG was successfully accomplished, and the reaction yield was determined to be 77% by XPS. The tilt angle of the PBLG molecular axis in the CRA film was estimated from a polarized ATR spectrum to be about 57°. It is well known that the longer molecular axis of PBLG in a Langmuir–Blodgett (LB) film is parallel to the substrate (germanium) and oriented to the substrate dipping direction.[7] Accordingly, this is the first case in which the molecular axis of PBLG is not parallel to the substrate and it is expected that the PBLG–CRA film has different properties from the LB film. We are now making an effort to use this PBLG–CRA film as

an orienting interface of liquid crystals, as one example of its application.

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