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Drastic Variation of Optical Intensity due to Phase Transition of Multibilayers Immobilized on a Plastic Optical Fiber

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A multibilayer-coated plastic optical fiber was prepared by solvent casting of the polyion complex composed of dioctadecylammonium bromide and sodium poly(styrenesulfonate). When a He-Ne laser light was passed through the fiber, the modified optical fiber exhibited a steep change in the optical intensity at the crystal-to-liquid crystal phase transition temperature (45 °C) of the bilayer component, resulting from the drastic change of refractive index of the bilayer phase.

Optical fibers have received much attention in terms of their applicability to chemical sensors because either light absorption or fluorescence of chemical indicators can be remotely monitored on a real-time basis. In such sensor devices, however, optical fibers play simply the role of an optical waveguide to deliver and transport signals except for the use of an optical fiber itself as the sensor part for humidity measurements.[1,2)]

In this paper, we describe the detectability of phase transition of multibilayer-coated plastic optical fibers based on an optical signal measurement. Polyion complexation of bilayer membranes facilitates their use as organic thin films in various media because the complexed membranes are insoluble in water but still retain bilayer characteristics similar to those of aqueous bilayer dispersions.[3-6)] We employed dioctadecyldimethylammonium bromide($2C_{18}N^+$) and sodium poly(styrene sulfonate)(PSS) as a bilayer-forming amphiphile and a ployanion, respectively. A polyion complex($2C_{18}N^+/PSS^-$) was prepared according to the manner reported previously.[3)] The sensor part was prepared as follows. The plastic optical fiber(LB500, Asahi Chemical Industry Co., LTD.) used in this study consists of the core(refractive index=1.49) with a diameter of 500 μm and the cladding(refractive index=1.41) with a thickness of 10 μm. A small part of the cladding was skinned off and the bared optical fiber, with a 5 cm long core section, was then immersed in a tetrachloromethane solution of the polyion complex, $2C_{18}N^+/PSS^-$ (4 mg/mL) for a few mins and dried overnight at room temperature. Then the fiber was immersed in a hot water(60 °C) and aged for 60 min, so that the polyion complex immobilized on the core of the fiber reconstructs a well-developed bilayer structure. In fact, the differential scanning calorimetry (DSC) for $2C_{18}N^+/PSS^-$ cast films in water gave a single endothermic peak at 45 °C (T_c), due to crystal to liquid-crystal phase transition of the bilayer structure when the films were treated with a hot water. The peak-top temperature also corresponds to that of water-dispersed bilayers of $2C_{18}N^+2C_1Br^-$ (45 °C).[7)] Figure 1 shows the experimental arrangement for detecting the thermal behaviors of multibilayer-coated plastic optical fiber.

The modified plastic optical fiber thus obtained was placed in a thermostated water bath. A He-Ne laser light with a wavelength of 633 nm was focused onto one end of the optical fiber. Laser light passing through the fiber was picked up by a photodiode. Finally, the signal was amplified by a lock-in amplifier and was plotted out by a chart recorder.

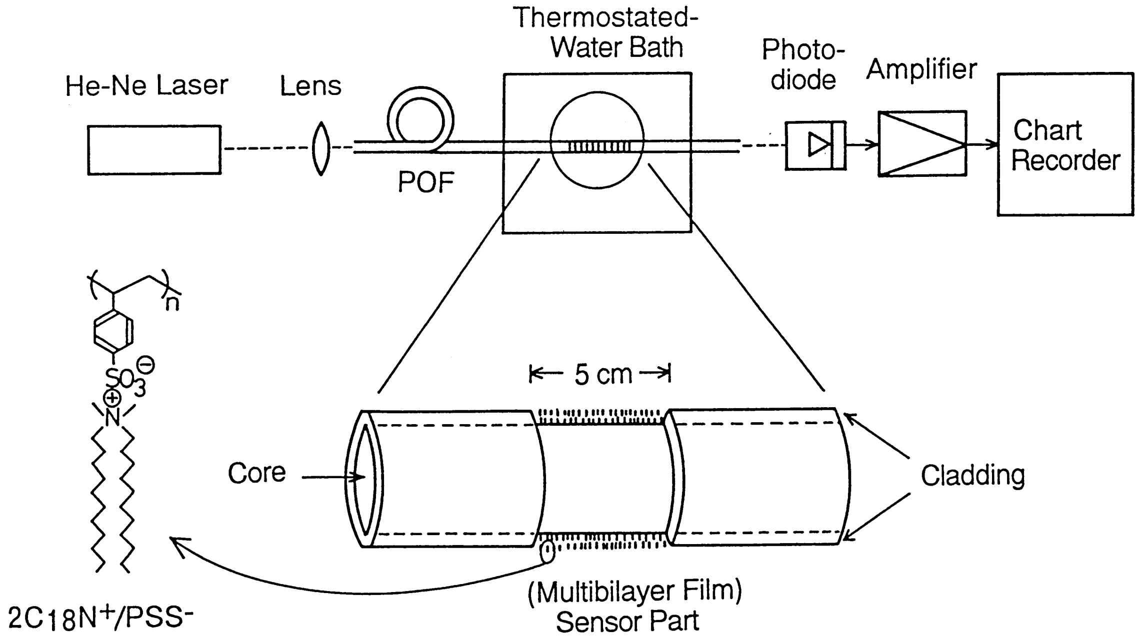

Fig. 1. Schematic diagram of the experimental arrangement.

Figure 2(A) shows the temperature dependence of optical intensity for the $2C_{18}N^+/PSS^-$-modified optical fiber. The optical intensity exhibited a remarkable temperature dependence. Blow 45 °C, the fiber showed low optical intensity, but at close to 45 °C this increased drastically. In the cooling process, a drastic decrease in optical intensity was also observed at around 45 °C, whereas there was only slight hysteresis in the higher temperature region. In order to confirm whether such a drastic change of optical intensity is ascribable to the phase transition of immobilized-multibilayers on the optical fiber, two other optical fibers modified by $2C_{14}$-de-$2C_2N^+/PSS^-$[8] and $2C_{18}$-de-C_2N^+/PSS^-,[8] which had a phase transition temperature (DSC) at 29 °C and 58 °C, respectively, were prepared, and their temperature dependence of optical intensity was estimated according to the same manner as mentioned above. $2C_{14}$-de-C_2N^+/PSS^- or $2C_{18}$-de-C_2N^+/PSS^--modified optical fiber gave a similar optical intensity-temperature profile to that of $2C_{18}N^+/PSS^-$-modified fiber and the steep change in optical intensity took place at a temperature corresponds exactly to T_c of each fiber. These results clearly demonstrate that such a drastic change in optical intensity passed through the multibilayer-coated optical fibers is due to the phase transition of bilayer phases immobilized on the core of fibers. It is expected that the optical intensity change with temperature will be derived from a variation of the refractive index of multibilayer films. Thus, we measured the refractive index for wet multibilayer-films.

Figure 2(B) displays the temperature dependence of the refractive index for $2C_{18}N^+/PSS^-$ cast film with a thickness of about 10 μm. The $2C_{18}N^+/PSS^-$ film was prepared by solvent casting and aged in a hot water. Then, the wet film was set at a refractometer (Shimadzu Abbe Refractometer) and its refractive index was measured at various temperatures. Elevating temperature, the refractive index gradually decreases, and then a steep decrease is observed at a temperature region of 40-50 °C which corresponds to the phase transition temperature of $2C_{18}N^+/PSS^-$ film and also to the temperature of an optical intensity transition of the modified optical fiber. This strongly suggests that the crystal-to-liquid crystal phase transition causes a refractive index change of the bilayer film which results in the drastic variation in optical intensity through the bilayer-coated fiber. When the bilayer film is in crystalline state (below T_C), the magnitude of optical intensity is relatively lower than that in liquid crystalline state, reflecting that light passing through the fiber might be absorbed into the bilayer film coated on the core due to the higher refractive index (1.52-1.50) of the crystalline bilayer phase as a cladding compared with that of the core (1.49). In contrast, in liquid crystalline state (above T_C) such a light absorption into the bilayer phase might be suppressed owing to a lowering of refractive index.

Figure 3 shows the optical intensity changes of the modified optical fiber, responding to the temperature. The optical intensity rapidly increased after immersing the fiber in a hot water (54 °C > T_C), and reverted to the original value on immersing the fiber in a cold water (19 °C < T_C). Repeated cycling of the fiber between different temperatures showed reproducibility, indicating good stability of the multibilayer film coated on the optical fiber.

In conclusion, we have found remarkable phase transition temperature dependence of the optical intensity for the multibilayer-coated optical fiber which results from the drastic change of refractive indexes of bilayer phases. This is the first example of transduction of the fundamental bilayer characteristics to optical signals.

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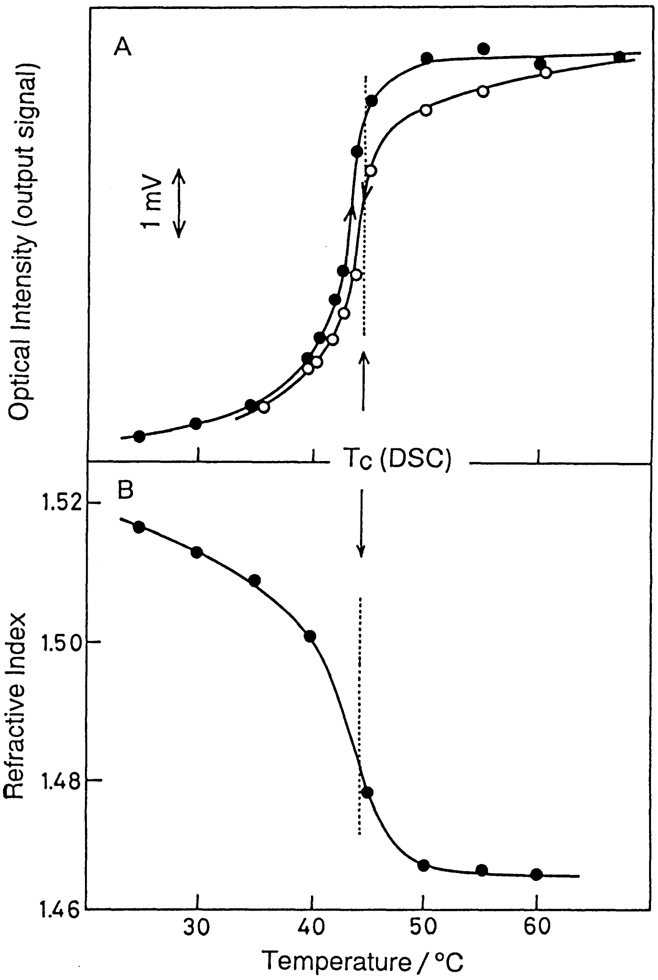

Fig. 2. Temperature dependences of the optical intensity (A) and the refractive index (B) for the multibilayer-coated optical fiber and the multibilayer cast film, respectively

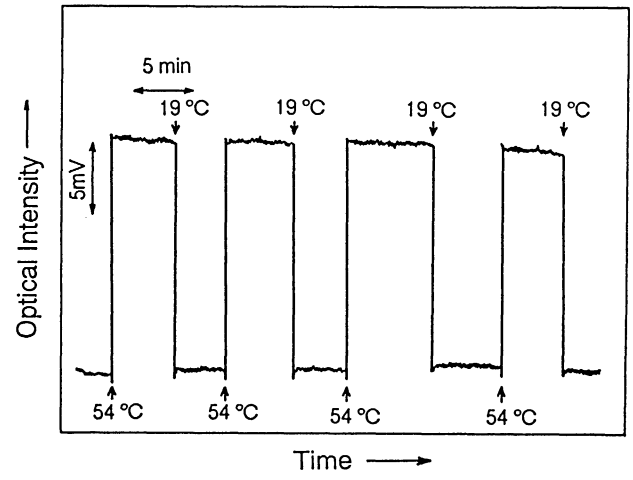

Fig. 3. Reversible optical intensity change of the multibilayer-coated optical fiber responding to temperature.

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8) $2C_{14}$-de-C_2N^+ and $2C_{18}$-de-C_2N^+ denote *O,O'*-ditetradecanoyl-*N*-((α-trimethylammonio)acetyl) diethanolamine and *O,O'*-dioctadecyl-*N*-((α-trimethylammonio)acetyl) diethanolamine, respectively. Both amphiphiles were prepared according to the literature.9)

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