pH-Responsive Plastic Optical Fibres Modified with Polyion Complexed Multibilayers Containing a Poly(methacrylic acid) Segment

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Plastic optical fibres modified with a triblock polyion complexed multibilayer containing a poly(methacrylic acid) segment gave a pH-induced optical signal change, resulting from the alternation in refractive index, derived from the conformational transition of the polymer segment.

It has been found that the water-insoluble multibilayer (PSS–**1**)-coated plastic optical fibre (POF) shows a marked dependence of the optical signal on phase transition temperature, resulting from the drastic change of refractive indices of the bilayer phase.[1] In the present paper, we report that POFs coated with polyion complexed multibilayers such as $S_nM_mS_n$–**1** (Fig. 1) show reversible optical signal changes responding to pH. The optical signal changes correspond to variations in the refractive index of the membrane matrices coating the fibre, and are caused by a conformational change of poly(methacrylic acid) (PMAA) segments with pH.

The triblock polyanion ($S_{10}M_{49}S_{10}$)[2] and polyion complexes ($S_{10}M_{49}S_{10}$–**1**[2] and PSS–**1**[1,3]) were prepared according to the manner reported previously. The POF (LB 500, Asahi Chemical Industry Co., Ltd) used in this study consists of a core (refractive index = 1.49) with a diameter of 500 μm and a cladding (refractive index = 1.41) with a thickness of 10 μm.

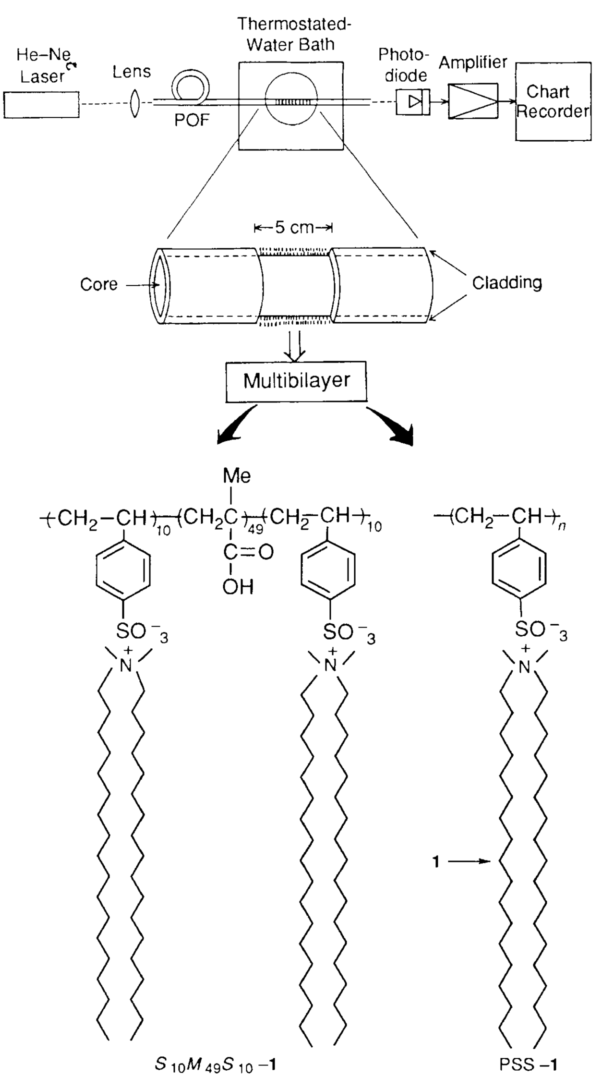

Fig. 1 Schematic diagram of the experimental arrangement and structures of the polyion complexes

The modified POF† was placed in a thermostated water bath as shown in Fig. 1. He–Ne laser light with a wavelength of 633 nm was focused onto one end of the POF. Laser light passing through the fibre was picked up by a photodiode, and the output signal was amplified and plotted. Fig. 2 shows the temperature dependence of the optical signal for the $S_{10}M_{49}S_{10}$–**1**-coated POF in pure water (pH 6.2). The $S_{10}M_{29}S_{10}$–**1** cast film in water gave a crystal to liquid crystal phase transition temperature of 42 °C (T_c) on the basis of a differential scanning calorimetry (DSC) measurement. Below 42 °C, the fibre showed low optical signal intensity, but close to 45 °C the signal intensity increased drastically. This result implies that the change in optical signal stems from the phase transition of the bilayer phase immobilized on the core. Fig. 2 also includes data for the refractive index of the $S_{10}M_{49}S_{10}$–**1** cast film.‡ As the temperature is raised the refractive index gradually decreases, and then a steep decrease is observed at the temperature region of 40–45 °C which corresponds to the T_c (DSC) of the film and also to the temperature of an optical signal transition of the modified POF.

Fig. 3 displays the pH dependence of the optical signals for $S_{10}M_{49}S_{10}$–**1** and PSS–**1**-coated POF at a temperature of 54 °C (above T_c). The PSS–**1**-coated POF showed no pH dependence of the optical signal, as expected. On the other hand, the optical signal for the $S_{10}M_{49}S_{10}$–**1**-coated POF exhibited a marked pH dependence. A steep increase in the optical signal was clearly observed at a value between pH 5 and 7. Thomas *et al.*[4] demonstrated on the basis of fluorescence-probing that a pyrene-labelled PMAA showed a conformational transition

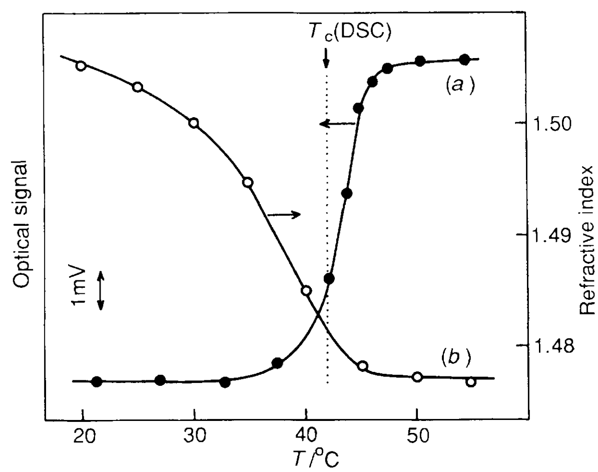

Fig. 2 Temperature dependences of the optical signal (*a*) and the refractive index (*b*) for the $S_{10}M_{49}S_{10}$–**1**-coated POF and the multibilayer cast film, respectively, at pH 6.2

† A small part of the cladding was skinned off and the bare optical fibre, with a 5 cm long core section, was then immersed in a CCl_4 solution of the polyion complexes (4 mg ml^{-1}) for a few minutes and dried overnight at room temperature.

‡ The $S_{10}M_{49}S_{10}$–**1**-film was prepared by solvent casting and aged in hot water. The wet film was then placed in a refractometer (Shimadzu, Abbe Refractometer) and its refractive index was measured at various temperatures.

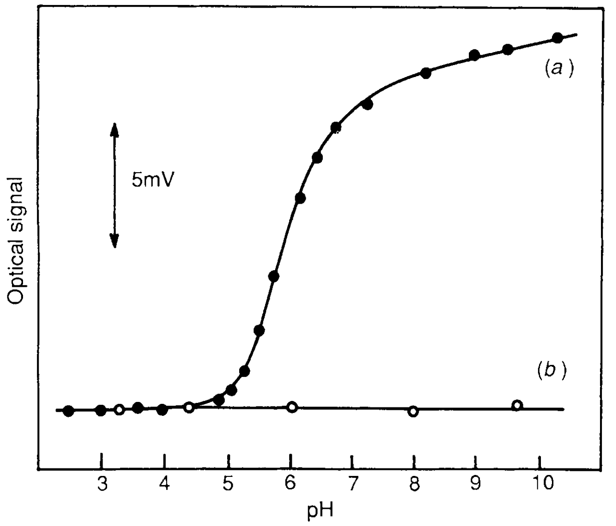

Fig. 3 pH Dependences of the optical signals for the $S_{10}M_{49}S_{10}$–**1**-coated POF (*a*) and the PSS–**1**-coated POF (*b*) at a temperature of 54 °C (above T_c)

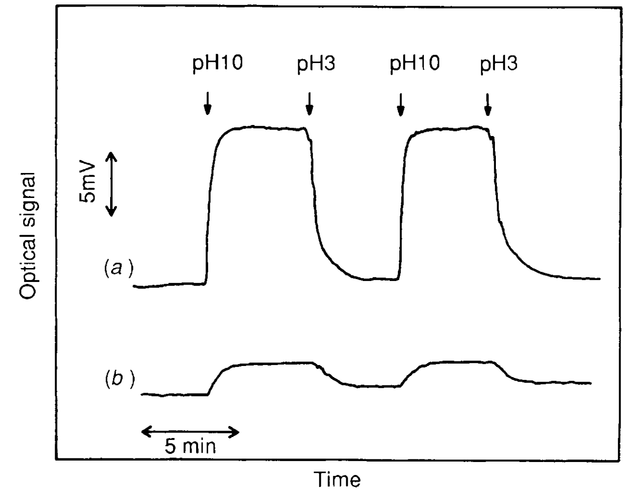

Fig. 4 Reversible optical signal change of the $S_{10}M_{49}S_{10}$–**1**-coated POF responding to pH at temperatures of 54 °C (above T_c) (*a*) and 23 °C (below T_c) (*b*)

in the same pH region. At this pH, therefore, the conformation of the PMAA segment in the polyion complex immobilized on POF might be changed from the hypercoiled form to the expanded one, and this transition induced the refractive index change of the bilayer phase. Fig. 4 shows the optical signal variations for $S_{10}M_{49}S_{10}$–**1**-coated POF by varying pH at 54 °C ($>T_c$). The optical signal immediately increased after the addition of alkaline solution (pH 10), and reverted to the original value by addition of acidic solution (pH 3), showing that the conformational change of the PMAA segments occurs reversibly in the polyion complexed multibilayer.

It must be emphasized that the experiments on the pH-responsiveness are conducted at a temperature above T_c. Below T_c (in the crystalline state), the optical signal change was considerably suppressed compared with that in the liquid crystalline state, although a slight change in optical signal upon pH alternation was obviously observed as shown in Fig. 4. This difference in the extent of optical signal change is considered to be due to the differences in facility of conformational change of the PMAA segments and/or of diffusion of H^+ or OH^- through the membrane matrices between the tight crystalline state and the fluid liquid crystalline state.

In conclusion, the modified POF provides reversible optical signal changes sensitive to pH. This phenomenon was attained owing to a combination of the conformational property of the polymer and the change of the membrane physical state (refractive index), which was induced by the conformational transition of the polymer.

Received, 19th November 1990; Com. 0/05181K

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