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# Synthesis of Ultra-thin Films of Poly(vinylenebenzothiazole) at Air/Water Interface

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Ultra-thin films of poly(vinylenebenzothiazole) (PVBT) were formed at the air/water interface. The resulting PVBT thin films had a repeatable and finely controllable thickness; the per layer thickness of PVBT multilayers was 36 Å. The films remained fairly stable when subjected to heat treatment up to 200 °C. They also had good solvent resistance.

Aromatic polymers are known for their outstanding thermal stability, solvent resistance, and optical properties. However, they have severe processing problems due to the lack of soluble and processable polymers. Recent developments in this field are the synthesis of ultra-thin films using the Langmuir-Blodgett (LB) technique. In order to make stable multilayers, two approaches using polymers have been proposed. One is to form monolayers or multilayers having polymerizable functional groups and then to bring about polymerization by treatments such as heating, UV or γ-ray irradiation.1-4) The other is to form monolayers of amphiphilic polymers and to deposit then onto substrates by the LB method.5-7) These thin films have a great potential for use in electronic and optical devices. Our interest has been focused on the possibility of obtaining aromatic polymer films directly at the air/water interface. By doing so, we avoid the problem that aromatic polymers, due to their poor solubility, cannot be spread on the water surface. In previous reports, we described the synthesis of aromatic polyazomethine,8) polybenzimidazole,9,10) polybenzoxazole11) and polybenzothiazole12) at the air/water interface. These aromatic high temperature polymers are generally synthesized in bulk by heating at high temperature or in polyphosphoric acid under more severe conditions.13-15) In this report, we describe the synthesis of poly(vinylenebenzothiazole) (PVBT) thin films at the air/water interface, and investigation of their properties.

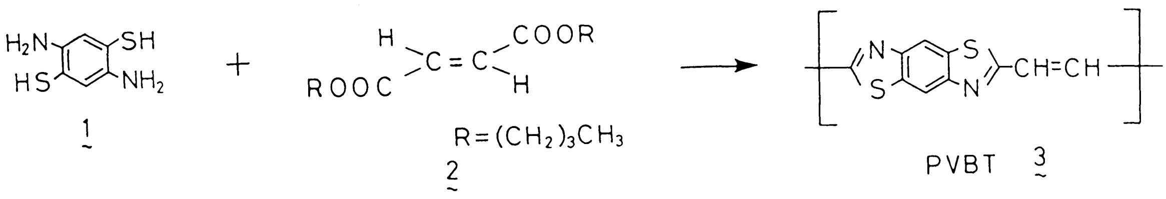

Fig.1. Synthetic route for poly(vinylenebenzothiazole).

Figure 1 shows the reaction scheme for the synthesis of PVBT 3 films. After the deposition of the surface films, the resulting multilayer is treated by heating in order to complete the reaction in air (180 °C, 15 min). Fumaric acid di-n-butyl ester 2 in benzene ($1.94\times10^{-2}$ $mol\cdot dm^{-3}$) was spread onto an acidic aqueous solution of 2,5-diamino-1,4-benzenedithiol 1 ($2.85\times10^{-5}$ $mol\cdot dm^{-3}$) until further monolayer solution could not be spread and remained as lens. The polymerization proceeded at the air/water interface even at room temperature. The films formed at the air/water interface were built up by a horizontal lifting method16) or a vertical dipping method.17) In the former case, a "Teflon" sheet mask was placed over the water surface after the reaction. The mask was made with holes to match the substrate on which the film was to be deposited. The substrate, held horizontally, was lowered through the mask to touch the film-cover surface. Further, we tried to deposit the surface films by means of the vertical dipping method of LB technique using a conventional LB trough. But the films could not be deposited because of the friction between the surface films and the walls of the trough. Therefore, we modified the trough, that is, set "Teflon" seals, which could be moved with a pressure bar, along the walls of trough for the prevention of friction. Deposition of the surface films at the air/water interface was carried out by drawing only in the upward direction; the transfer ratio constant was almost 1.

To follow the speed of formation, the surface films were transferred to the quartz plates at prescribed times and were measured by UV-vis spectroscopy. The spectra in Fig. 2 show that polycondensation reached an equilibrium after 24 hours. We also compared the chemical structure of the surface films with that of authentic benzothiazole polymers prepared from a number of carboxylic reactants which were reported by Hergenrother et al.13,14) The structure of the film was confirmed by FT-IR. In the transmission FT-IR spectrum of multilayers (50 layers) deposited on calcium fluoride plate, typical absorptions were observed due to converted thiazole ring, in addition to the vinyl absorption. However, no major changes were

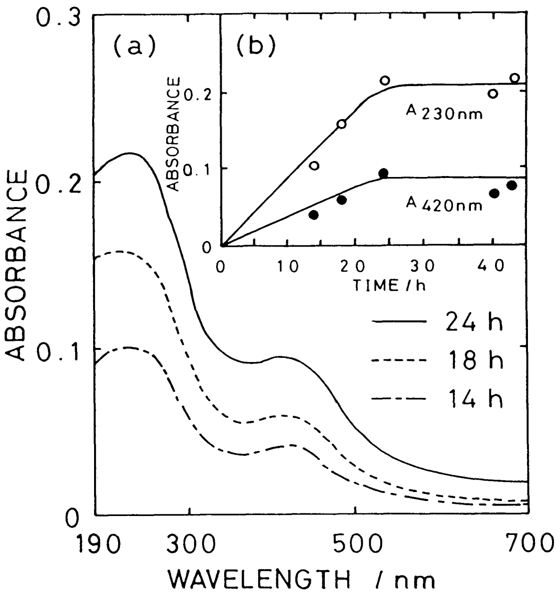

Fig.2. (a)Change in electric spectra of built-up films (5 layers) as a function of reaction time at the air / water interface; (b)Absorbance at 230 nm and 420 nm of built-up films as a function of reaction time.

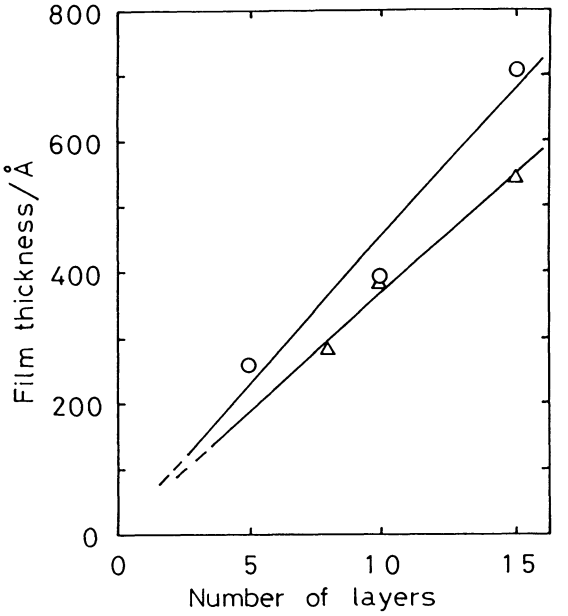

Fig.3. Thickness of before (○) and after (△) heating films as a function of the number of layers.

seen in the infrared spectrum after the heating. So, we concluded that the PVBT films were prepared at the air/water interface as illustrated in Fig. 1 at the air/water interface and that the reaction was driven further to completion by heating. Figure 3 shows the relationship between the number of layers and the thickness as determined by tali-step method of the multilayers prepared by the vertical dipping method. The film thickness was proportional to the number of layers. The per-layer thickness of the multilayers before and after heating was 45 Å and 36 Å, respectively (Table 1). We thought that the decrease in the film thickness accompanied by heating was due to increased packing between the monolayers or to the removal of impurities. PVBT films had a good sovent resistance and were insoluble in organic solvents such as N,N-dimethylformamide or N,N-dimethylacetamide and only slightly soluble even in conc. sulfuric acid. The UV-vis spectra of the PVBT films didn't change with heating at 200 °C, which indicated the resulting films had a good thermal stability. We also evaluated the non-linear optical properties, and successfully measured the third-order optical non-linear susceptibility, $\chi^{(3)}$, of PVBT thin films. Table 1 summarizes the values of $\chi^{(3)}$ before and after heating. The estimated $\chi^{(3)}$

Table 1. The per-layer thickness and $\chi^{(3)}$ values of the multilayers

| Sample | Thickness / Å | $\chi^{(3)}$/ esu |
|---|---|---|
| Before heating | 45 | $2.2 \times 10^{-12}$ |
| After heating | 36 | $1.3 \times 10^{-12}$ |

value before heating was as same as after heating. It is suggested that the films formed at the air/water surface had π-conjugated chains as well as the case of films after heating.

We successfully prepared the PVBT thin films by the novel and simple method. These films had a repeatable and finely controllable thickness in addition to the good thermal stability and solvent resistance.

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