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Preparation of Highly Oriented Poly(p-phenylenevinylene) Thin Film by Using Langmuir-Blodgett Technique

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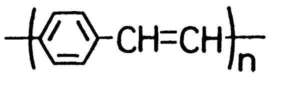
Precursor polyelectrolyte of poly(p-phenylenevinylene) with bilayer-forming amphiphile as counterion forms a stable monolayer at the air-water interface. The monolayers could be transferred on substrates by Langmuir-Blodgett (LB) technique. A poly(p-phenylenevinylene) LB film could be obtained from heat treatment of the precursor LB film. Planar orientation of π-conjugated phenylenevinylene sequences was exhibited in the LB films.

Preparation of main-chain conjugated polymers by the solid state thermal reaction of processible precursor polymers is one of the most promising methods to obtain dense and tough polymer films with developed -conjugated structures. However, it is difficult to obtain polymers with ideally extended π-conjugated system by this method; the polymer chains include many conformational defects because π-conjugated chains are caused to develop from disordered precursor polymers, which have random coil conformations, in solid states.1)

Elongation of precursor films during thermal elimination reactions has been the only way to extend coiled chains and diminish conformational defects. This letter provides an utterly new way to loosen coiled precursor polymer chains and introduce orderliness in precursor polymers. The new method brings about π-conjugated polymers with diminished conformational defects.

Poly(p-phenylenevinylene) (1, PPV) films were prepared by the thermal elimination of sulfonium group from the polyelectrolyte precursor 2 films.2,3) As solid precursor films are obtained by casting from the aqueous polyelectrolyte, the polymer chains are regarded as three-dimensional, somewhat expanded coils in the



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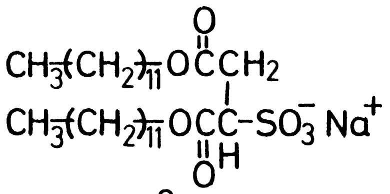

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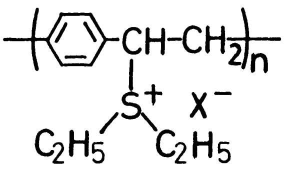

2 : $X^- = Br^-$

4 : X^-=anionic part of 3

films. If counter Br anions are replaced with large anionic amphiphiles 3, the precursor chains will take more expanded coils. It is also anticipated that the precursor chains assume ordered forms owing to the self-organization of the amphiphile 3.[4] Moreover, one can force the chains to be oriented in a two-dimensional plane, when the sulfonium polyelectrolyte precursor - cationic amphiphile complexes (from now on, we call them precursor complexes) are caused to form a monolayer at the air-water interface. Therefore, Langmuir-Blodgett (LB) films obtained from the complex monolayer are expected to possess much more ordered aggregated structures than that of simple cast films of sulfonium salt precursor 2.

Kakimoto and his coworkers reported the preparation of ultra-thin aromatic polyimide films using the LB technique.[5] They obtained the polyimide films from multilayers of a polyamic acid - alkylamine complex. Referring to their procedure, we prepared the LB films of the precursor complex and converted them to PPV films with heat treatment.

PPV precursor polymer 2 was prepared according to the method of Ref.2. Bilayer-forming amphiphile 3 purchased from Sogo Pharmaceutical Co. was used without further purification. An aqueous solution of precursor polymer was added dropwise to an aqueous solution 3. The precursor complex precipitated, and the precipitates were filtered and washed with deionized water. The precursor complex was soluble in chloroform. The precursor monolayer was spread on deionized water (18 Mohm, from Millipore Milli-Q system) from the chloroform solution. Then, the surface pressure - area isotherms were measured at 10 °C with a Wilhelmy type film balance (Kyowa Kaimen Kagaku Co. HBM-AP).

The surface pressure - area isotherm of the precursor complex monolayer is shown in Fig.1. In the same figure, the isotherm of amphiphile 3 was also shown. The limiting area of the precursor complex monolayer was 79 $\mathrm{\AA}^2$, which was larger by 14 $\mathrm{\AA}^2$ than that of the amphiphile 3. It is indicated that the precursor complex forms a more expanded monolayer than that of amphiphile 3.

The preparation of the LB films was accomplished at a surface pressure of 20 mN m^{-1} at 10 °C by using conventional Langmuir-Blodgett technique. The dipping rate is 1 cm/min. More than 60 monolayers could be transferred on fused quartz substrates which were made hydrophobic by the 5 layers deposition of cadmium arachidate. The transfer ratio was nearly unity at both up- and down-stroke.

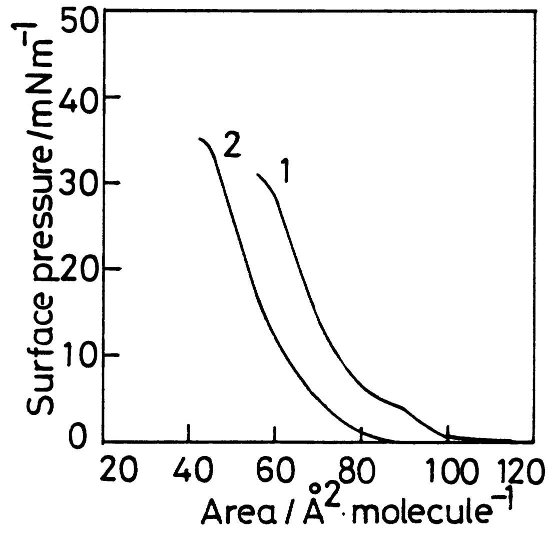

Fig.1. Surface pressure - area isotherms of the precursor polymer-amphiphile complex 4 (line 1) and amphiphile 3 (line 2).

Finally, the LB films were heated at 300 °C for 1 h in vacuo (ca. 10^{-2} Torr). The absorption spectra of the LB film before and after the heat-treatment are depicted in Fig.2. A strong absorption appeared in visible region after the heat-treatment, demonstrating the formation of π-conjugated system (PPV structure) in the LB film. Then, the LB films with the PPV structure were obtained.

It should be noted that the absorption peak wavelength (450 nm) of the PPV LB film is

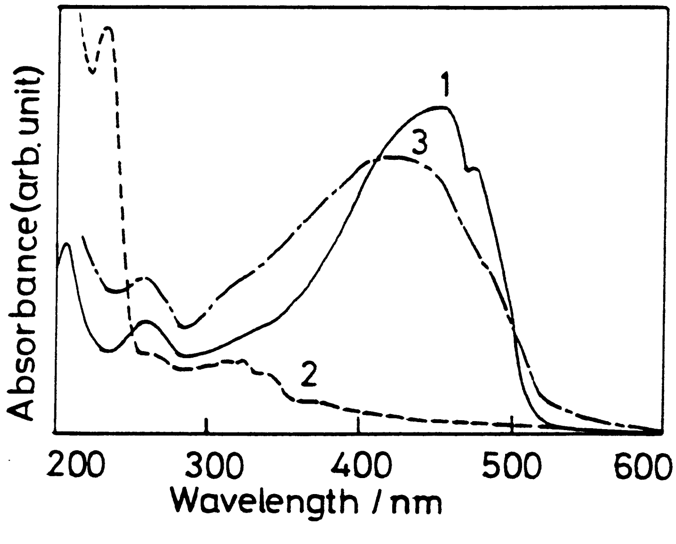

Fig.2. Absorption spectra of the PPV LB film (line 1), the precursor LB film (line 2) and a conventional cast film of PPV (line 3).

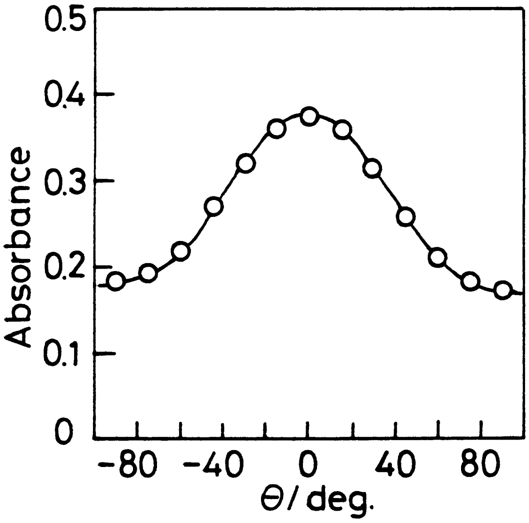

Fig.3. The angular dependence of absorbance at peak wavelength for the PPV LB film; θ is the angle between polarization vector of polarized light and the dipping direction.

about 30 nm longer than that of the conventional PPV film obtained from the cast film of polyelectrolyte 2. This result clearly indicates that the extension of π-conjugation length was realized in the LB films. As we expected, two-dimensionally extended chains in the monolayer brought about the decrease of conformational defects.

The orientation of PPV chains in the films was examined by the measurement of UV-visible spectra with polarized light. The angular dependence of absorbance at 450 nm due to π-conjugated system is shown in Fig.3, where Θ is an angle between the dipping direction and the polarization vector of light which is incident at normal to the film plane. Absorbance of the light with polarized vector parallel to the dipping direction is about twice larger than that of a polarized light perpendicular to the dipping direction. This result shows that PPV chains are highly oriented along the dipping direction.

Further, planar orientation of PPV chains in the film plane was demonstrated from the linear dichroism of the PPV LB films in visible region: dichroic ratio Ap/As decreased from 2.1 to 1.2, when the incident angle of polarized light increased from 0° to 45° (where Ap and As are absorbances of p- and s-polarized light at 450 nm, respectively and the axis of p-polarization coincides with the dipping direction).

Conclusively, it should be stressed that the linear and rigid PPV chains are highly oriented in our LB films: the PPV chains possess uniaxial orientation along the dipping direction and planar orientation in the film plane.

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