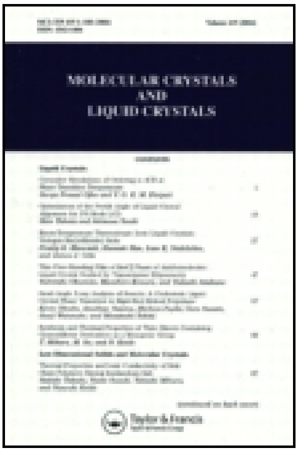

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LANGMUIR-BLODGETT FILMS OF POLYBENZOTHIAZOLE PREPARED BY PRECURSOR METHOD

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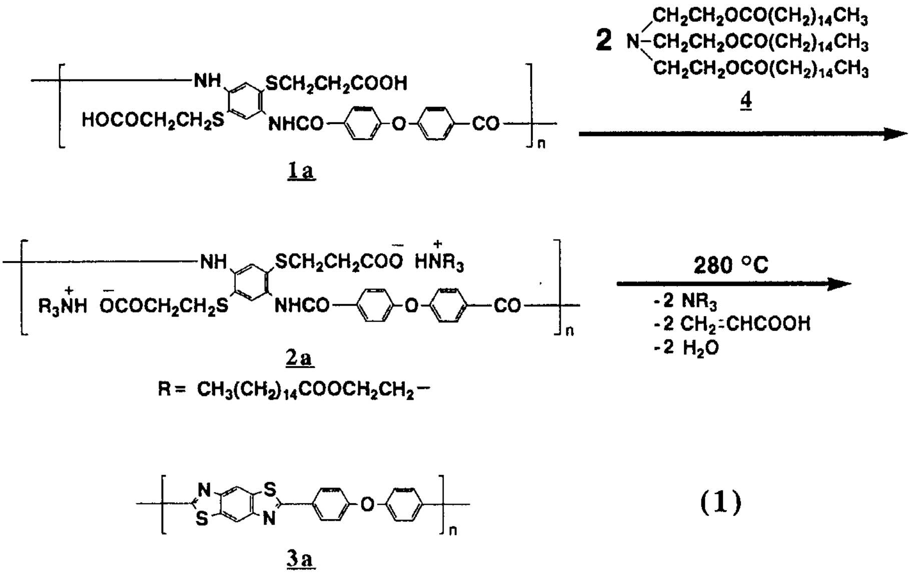
Abstract Polyamide with side chain carboxylic acid 1a, which was the precursor polymer for polybenzothiazole, was mixed to obtain the precursor salt polymer 2a with the three armed tertiary amine in a mixture of benzene and N,N-dimethylacetamide (1:1). The solution was spread onto the water surface to prepare the L film of 2a. The LB film of 2a, which was successfully obtained with the Y type deposition, was converted to the LB film of polybenzothiazole (PBT) 3a by heating at 280 °C with removal of the tertiary amine. The FTIR and UV-Vis absorption spectra, and the elemental analysis obtained by XPS proved the chemical structure of the PBT LB film. The measurement of SAXS indicated the thickness of the precursor LB films was 2.9 nm, where the results of the ellipsometry were 2.8 and 0.34 nm for the precursor and PBT LB films, respectively.

INTRODUCTION

We have reported the "Precursor Method" for the preparation of the non-amphiphilic and insoluble polymeric Langmuir-Blodgett (LB) films. This technique consists of the preparation of the amphiphilic and soluble precursor polymeric LB films, and the subsequent treatment to obtain the final LB films. The LB films of polyimides and poly(p-phenylenevinylene) have been successfully prepared by the precursor method.[1-5] The most characteristic of this class of LB films is that they have no long alkyl chain between the layers of the LB films.

Ogata et al. reported the preparation of thin films of polybenzothiazoles, which are known the thermally stable aromatic polymers, by the polycondensation of amphiphilic dipentyl terephtalaldimine with water soluble 2,5-diamino-1,4-benzenedithiol dihydrochloride on the air/water interface.[6] The deposited film, however, had larger thickness compared with the expected monomolecular film.

We have developed a new preparative method of PBT via aromatic precursor polyamides, whose thiol function was modified with acrylic acid. In this paper, novel LB films of PBT are prepared by the "Precursor Method" using the precursor polyamide having carboxylic acid as the side chain group.



(1)

EXPERIMENTAL

A spreading solution for the Langmuir (L) film was prepared just before its use by the following procedure. Polyamide 1a, which had carboxylic acid as the side chain group, dissolved in a mixture of benzene and N,N-dimethylacetamide (DMAc) (1:1) at a concentration of 1 mmol/L was mixed with double amount of three armed tertiary amine 4 in the same solvent system at the same concentration. The obtained mixture was further diluted with the same solvent system to the concentration of 6.7 x 10^{-2} mmol/L.

The surface pressure-area (π-A) isotherm was measured under a continuous compression of the monolayer using a San-Esu FSD-20 computer-controlled film balance. The temperature of the water subphase was kept constant at 20 °C. Deposition of the L film was performed by a NLE NL-LB240S-MWC trough, where the dipping speed of the substrate was kept constant at 10 and 15 mm/min for the upward and downward strokes, respectively. FT-IR spectra of the LB films were measured by a JEOL JIR-MICRO 6000 spectrophotometer. UV-Vis spectroscopy was performed by a Otsuka Electronic MCPD-1000 apparatus. X-ray photoelectron spectroscopy (XPS) and small-angle X-ray scattering (SAXS) were recorded by a ULVAC PHI-5500MT and a Rigaku RU-200, respectively. Thickness of the LB films was measured by using a NIIC EL-101 ellipsometer.

RESULTS AND DISCUSSION

Precursor polymer 2a was prepared by simply mixing polyamide 1a with three armed tertiary long alkyl amine 4, consisted of the backbone of the hydrophilic polyamide salt and the hydrophobic three armed long alkyl chain as shown in Eq.(1). The usual LB technique was applied to prepare the LB film of 2a. The π-A curve of 2a (Figure 1) suggested the solid phase composed of the long alkyl chain, judging from the steep increase at the condensed phase after the phase transition phenomenon. The deposition of the L film of 2a was successfully carried out to form the Y-type LB film.

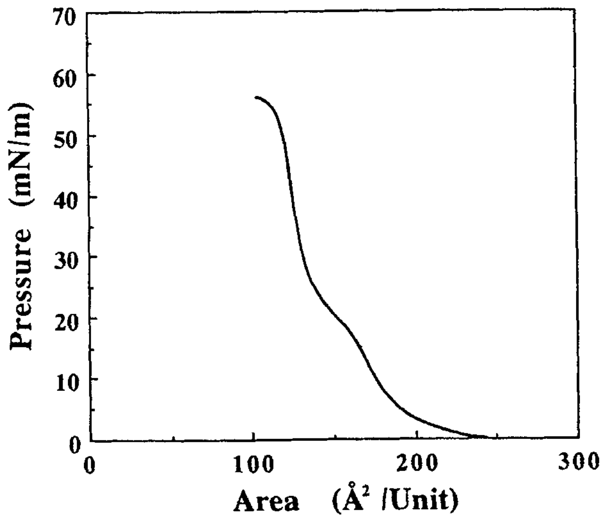


Fig.1. Surface pressure-area isotherm of 2a

The LB film of 2a was converted to the LB film of 3a by heat treatment at a high temperature. In the thermogravimetry (TG) curve shown in Figure 2, polyamide 1a lost 26 % of its weight by heating up to 350 °C. The weight loss value agreed fairly well with the calculated one of 33 % that was based on the elimination of acrylic acid and water to convert 1a to PBT 3a. Judging from the TG curve, the precursor LB film was heated at 280 °C to obtain the LB film of 3a.

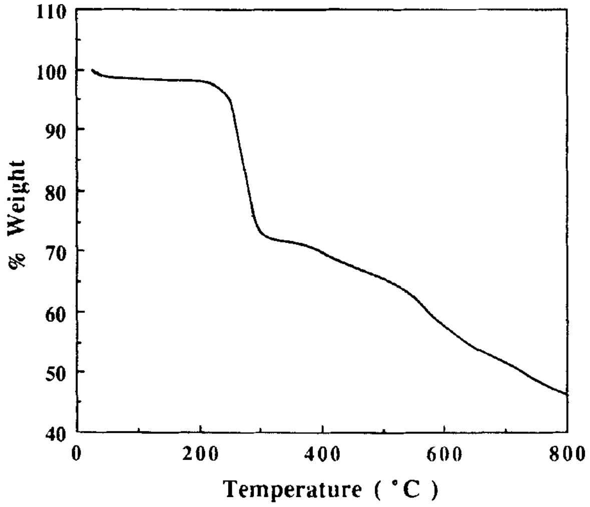


Fig.2. TG curve of 1a

The transmission FTIR spectra before and after heat treatment of the LB film of 2a are shown in Figure 3. The disappearance of absorption bands of the tertiary amine 4, which are methylene absorptions at 2850 and 2915 cm^{-1} and a carbonyl absorption at 1730 cm^{-1}, indicated that the long alkyl amine was eliminated from the precursor LB film by the heat treatment. Furthermore, the absorption of amide carbonyl on the backbone of 2a at 1660 cm^{-1} diminished, whereas new absorption bands belonging to polybenzothiazole at 1490 and 1400 cm^{-1} appeared. These results indicated that the chemical structure of the precursor polymer 2a was converted to PBT 3a with elimination of tertiary amine 4. The UV-Vis absorption spectra depicted in Figure 4 exhibited that the conversion from the precursor LB film to the PBT LB film caused the drastic spectral change because of growing the π conjugation system, which was extended by cyclization to PBT. The results of the elemental analysis performed by XPS are shown in Table 1. The observed values of all atoms were in agreement with the theoretical ones in the both cases of the precursor and PBT LB films.

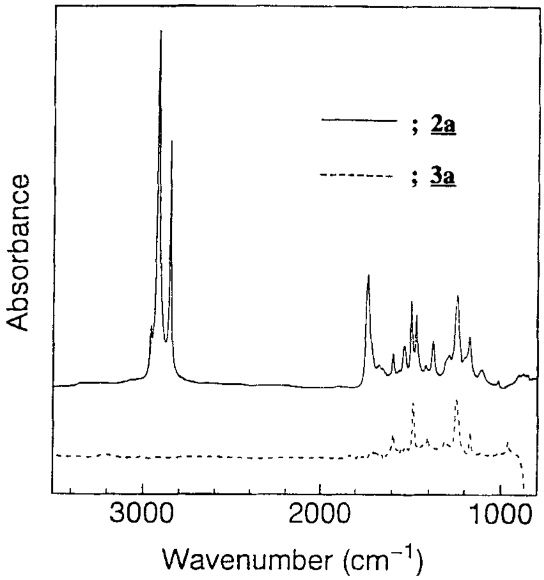


Fig.3. Transmission FT-IR spectra of LB films of 2a and 3a

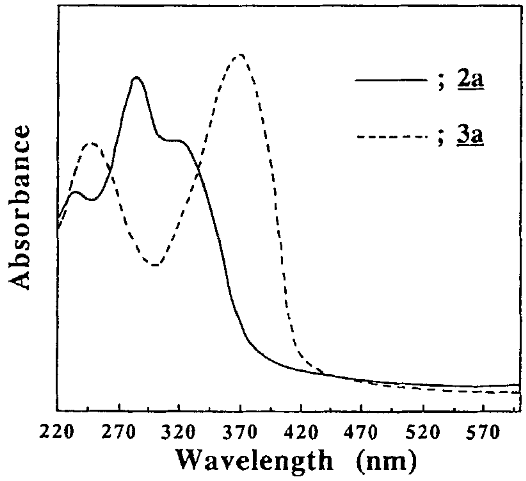


Fig.4. UV-Vis spectra of LB films of 2a and 3a

Table I. XPS results of LB films of 2a and 3a

	Precursor 2a $(C_{134}H_{232}N_4O_{19}S_2)_n$		PBT 3a $(C_{20}H_{10}N_2OS_2)_n$	
	LB film	Calculated	LB film	Calculated
C (%)	96.0	95.7	88.7	83.3
N (%)	2.84	2.86	5.93	8.33
S (%)	1.15	1.43	5.41	8.33

As shown in Figure 5, the LB film of the precursor polymer 2a showed one diffraction peak in SAXS. The periodicity of the electron density in the LB films was estimated to be 5.8 nm. Because the precursor film had the Y-type structure, the film thickness per layer of the precursor LB films was calculated to be 2.9 nm. Figure 6 showed the thickness of the LB films of 2a and 3a as a function of the number of layers measured by the ellipsometry. From the slope of the line, the thickness per layer of these LB films were estimated to be 2.8 nm and 0.34 nm, respectively. For the precursor LB film, the ellipsometric measurement was in good agreement with the result from the SAXS.

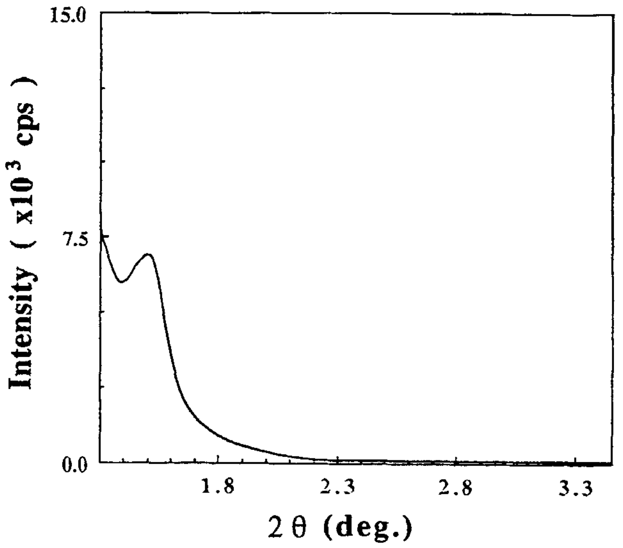


Fig.5. X ray diffraction of LB film of 2a

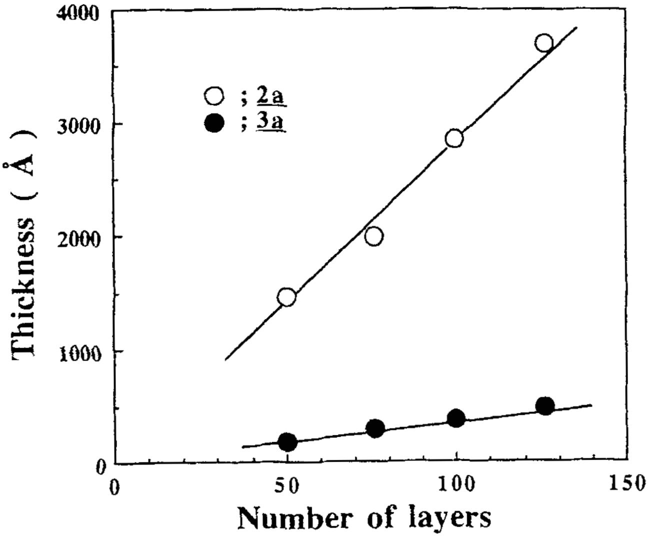


Fig.6. Thickness of LB films of 2a and 3a as a function of the number of layers

In conclusion, the LB film of PBT was successfully prepared via the new precursor amphiphilic polymer, which had the salt structure derived from the polyamide-acid and the three armed tertiary long alkyl amine. Since the obtained PBT LB film has the high π conjugation system with no long alkyl chain, it is expected that the LB film possesses the third order nonlinear optical property with highly thermal stability.

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