

Preparation of a Conducting Ultrathin Multilayer Film of Poly(*p*-phenylene vinylene) using a Langmuir–Blodgett Technique

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An electrically conducting Langmuir–Blodgett (LB) film of poly(*p*-phenylene vinylene) (**4**) with no alkyl spacer chains has been prepared for the first time by the deposition of a LB film of poly(sulphonium salt) (**2b**) ($X = C_9H_{17}CO_2$) on an appropriate plate, followed by thermal conversion.

The Langmuir–Blodgett (LB) technique is accepted as a method for the preparation of ultrathin ordered multilayer films of organic molecules.¹ Electrically conducting LB films are one of the most fascinating targets in this field. Despite several attempts, the monomeric and polymeric conducting LB films^{2–5} obtained so far have been anisotropic owing to the presence of insulating alkyl chains between the layers. Thus, their conductivities were between 10^{-2} – 10 S cm^{-1} (in-plane) and 10^{-11} – 10^{-14} S cm^{-1} (normal). In this com-

munication, we report the first preparation of a poly(*p*-phenylene vinylene) (PPV) LB film with no alkyl spacer chains, which was expected to be more isotropic in nature. PPV is a well known conducting polymer which has been synthesized by thermal conversion of the precursor poly(sulphonium salts) (**2**).^{6,7} On the other hand, polyimide LB films without alkyl spacer chains have been prepared *via* precursor polyamic acid long-alkyl amine salts LB films.^{8,9,10} A similar 'polyion precursor method' was applied to the

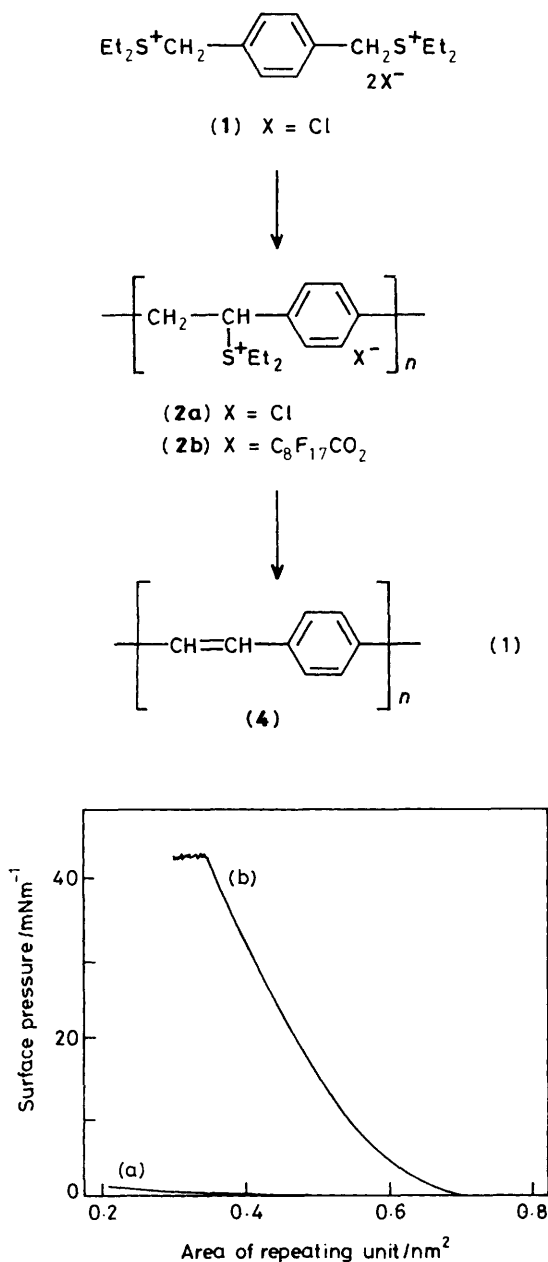


Figure 1. Surface pressure–area isotherm for poly(sulphonium salt) (2b). The isotherm was measured on deionized water at 20 °C with a compression speed of 3.2 mm s⁻¹ using a Wilhelmy film balance, where the trough was 500 mm long and 150 mm wide (SAN-ESU FSD-20). (a) Solution of (2a) alone and (b) mixed solution of (2a) and (3).

present PPV LB film formation shown in equation (1). A LB film of poly(sulphonium salt) (2b) with long-chain perfluoroalkyl substituents was chosen as the precursor.

An aqueous solution of poly(sulphonium salt) (2a) (X = Cl), which is a precursor polymer for PPV (4), was readily obtained from α, α' -bis(diethylsulphonium) *p*-xylylene dichloride (1) in aqueous alkaline media.^{6,7,11} The concentration of (2a) was adjusted from *ca.* 20 to 2 mM by dilution with ethanol and then to 1 mM with 1,1-trichloroethane. The resulting solution of (2a) was mixed with the same volume of a 1 mM solution of sodium perfluorononanoate (3) in ethanol–

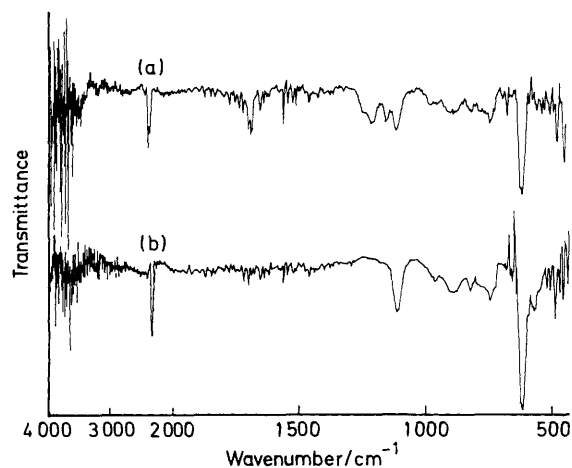


Figure 2. Transmission F.t.-i.r. spectra of LB films of (a) poly(sulphonium salt) (2b) and (b) PPV (4) deposited (800 layers) on a silicon wafer.

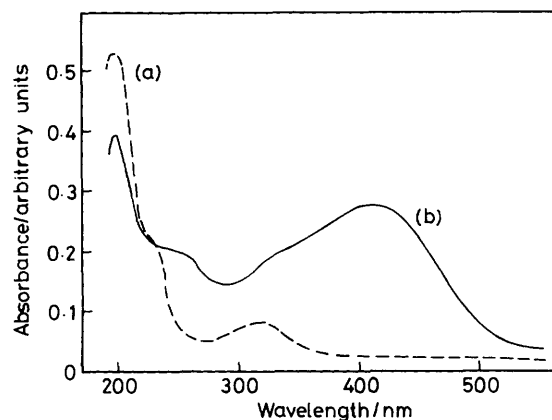


Figure 3. U.v. spectra of LB films of (a) poly(sulphonium salt) (2b) and (b) PPV (4) deposited (100 layers) on a quartz plate.

1,1,1-trichloroethane (1:1 by volume). This means that an equimolar amount of perfluorononanoate and sulphonium groups are present in the solution. The mixed solution was spread on distilled deionized water to measure the surface pressure–area isotherm (π -*A* curve), which is shown in Figure 1 (curve b). The curve rose steeply and the collapse pressure reached over 40 mN m⁻¹. In contrast, a stable monolayer film did not form from the solution of (2a) without (3) (curve a). The extrapolated value of the steepest region of curve b to $\pi = 0$ is 0.56 nm², which agrees with the corresponding calculated surface area where the repeating unit of (2) lies flat on the water surface.

The monolayer film prepared from the mixed solution of (2a) and (3) at the air/water interface was successively deposited using the LB technique onto glass and quartz plates through Y-type deposition and a silicon wafer through Z-type deposition at a surface pressure of 25 mN m⁻¹, where the transfer ratios were 0.96–1.00. The transmission Fourier transform (F.t.)-i.r. spectrum of the multilayer film deposited on silicon wafer is shown in Figure 2a. The absorptions at about 1 100, 1 600, and 800 cm⁻¹ are assigned to the C–F bond,

carbonyl group, and *p*-phenylene structure, respectively, and the structure of the deposited film was thus confirmed to be poly(sulphonium salt) (**2b**) ($X = C_8F_{17}CO_2$). The monolayer thickness of the multilayer film of (**2b**) was 1.0 nm, determined by ellipsometry.

Figure 2b shows the i.r. spectrum of the multilayer film of (**2b**) after heat treatment at 200 °C for 2 h under reduced pressure (*ca.* 1 Torr).^{6,7} The disappearance of absorptions around 1100 and 1600 cm^{-1} indicated the removal of perfluorononanoic acid spacer groups. Figure 3 shows (a) the u.v. spectrum of the multilayer film of (**2b**) and (b) that after heat treatment. A very strong and broad absorption appeared around 420 nm in spectrum (b), suggesting that the poly(sulphonium salt) was converted into PPV.¹² Thus the multilayer film of PPV (**4**) was successfully prepared by heat treatment of the multilayer film of poly(sulphonium salt) (**2b**) with elimination of diethyl sulphide and perfluorononanoic acid.

The surface of the multilayer film of (**2b**) was flat and smooth with no cracks and voids as observed by scanning electron microscopy (SEM). These characteristics remained unchanged after thermal conversion to the PPV multilayer film. The monolayer thickness of the multilayer film of (**4**) determined by ellipsometry, was 0.34 nm, which compares reasonably with the value of 0.4 nm for a polyimide LB film.⁹

The electrical conductivity of the present PPV LB film (300 layers) doped with SO_3 was 0.5 $S\ cm^{-1}$ (in-plane) and 4×10^{-6} $S\ cm^{-1}$ (normal). Although PPV LB film still had an anisotropic conductive nature, the conductivity for the normal

direction was much larger than those of conventional conductive LB films, and was in the semiconductor range.

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