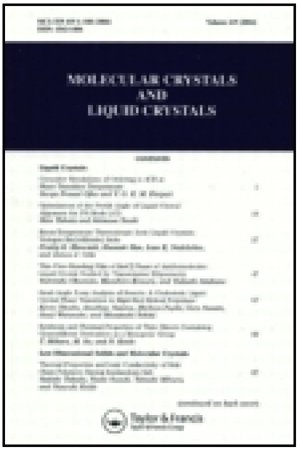

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Lyotropic Poly(n-Anilino-1-Alkanesulfonate)s for an Alignment Membrane

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LYOTROPIC POLY(N-ANILINO-1-ALKANESULFONATE)S FOR AN ALIGNMENT MEMBRANE

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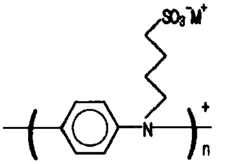
Abstract Conductive polymer films of poly(aniline N-butylsulfonate)s, PANBuS, was investigated to prepare alignment layers for liquid crystals. Alignment of nematic liquid crystals, E7 was found to be effective when a liquid crystal cell was fabricated with either sheared or rubbed PANBuS films. Rubbing strength had little influence on the orientation of E7 as evidenced by insignificant change in the tilt angle. Tilt angle of E7 was dependent on the processing method of PANBuS and higher tilt angle was obtained with the sheared PANBuS layer.

INTRODUCTION

Conductive liquid crystalline polymers are a new class of materials that are characterized by the combination of self-assembling properties and electrical conductivity. However, synthesis and characterization of these polymers have been limited because conducting polymers are unstable, intractable, and infusible in general. Few successful examples are poly(phenylene-2,5-thiophene) with different alkyl side chains,[1] and self doped-polythiophene and polypyrrole derivatives.[2] Another example is acid doped polyaniline, which can be dissolved and processed in its conducting form by doping with funtionalized protonic acid such as camphor sulfonic acid.[3]

In our previous paper we have reported the synthesis and characterization of poly(aniline N-alkylsulfonate)s, where alkyls are propyl, butyl, and pentyl. These self-doped polyaniline derivatives, in which the dopants are covalently bonded to the side chains,[4] showed excellent redox stability and lyotropic phase behavior.[5] These self-doped polyanilines are most challenging materials to prepare conductive alignment layers by virtue of electrical conductivity and lyotropic processibility. In particular, processing from an ordered polymer phase is capable of imparting a high degree of chain alignment and greatly enhanced mechanical, electrical, and optical properties.

In this presentation we report the lyotropic processing of poly(aniline N-butylsulfonate)s, PANBuS, and application potential as a conductive alignment layer.



PANBuS

EXPERIMENTS

Materials

Liquid crystal molecule, E7 (BDH Chemical Ltd., Poole, U.K.) was used as received. 4-Anilino-1-butanesulfonic acid and its sodium salt were synthesized from the reaction of aniline with 1,4-butane sultone as described before.[5] Electrochemical polymerization was carried out through a constant current method (8 mA) using a 0.025 M solution of 4-anilino-1-butanesulfonic acid sodium salt in acetonitrile containing 0.1 M $NaClO_4$ and 8 % aq-$HClO_4$. The resultant electrochemically synthesized PANBuS (EPANBuS) showed d.c. conductivity of 6×10^{-5} S/cm. Chemically synthesized PANBuS (CPANBuS) was obtained as follows: Aniline N-butylsulfonate (1 g) was dissolved into 10 % HCl-aqueous solution and then chilled with ice bath. To this solution was slowly added aqueous solution of ammonium persulfate (1g) and then the mixture was stirred at 0 °C. After 6 h of stirring, low molecular weight product (Mw $\leq$ 3500) was removed using dialysis technique. Dark green powder with a conductivity of 5×10^{-6} S/cm was obtained upon solvent evaporation.

Preparation of PANBuS coated films for conductive alignment layer.

Alignment layers were prepared by either shearing of a viscous lyotropic solution or rubbing of a PANBuS film prepared by spin-coating method. The lyotropic solution was prepared using a solution of PANBuS in EtOH/Water (10/90 v/v) followed by slow evaporation of the solvent. The lyotropic phase was then sheared in one direction and the resultant film was air-dried at r.t. for 30 min and then dried in a vacuum oven at 40 °C for 2 h. A solution (3 or 5 wt.%) of PANBuS in EtOH/Water (10/90 v/v) was spin-coated on a freshly cleaned glass substrate at 600 rpm for 20 s and then at 3000 rpm for 40 sec. The isotropic polymer layers were air-dried at r.t. for 30 min and then dried in a vacuum oven at 40 °C for 2 h. Unidirectional rubbing was performed with a rubbing machine that is consisted of a rubbing cylinder covered with a cotton velvet rubbing cloth. Rubbing strength (RS) of the sample was determined according to the Equation 1,[6]

$$\textit{Rubbing Strength (RS)} = N\,L\left(\frac{2\,\pi\,r\,n}{60\,V} + 1\right) \tag{1}$$

where N is the cumulative number of rubbings (3 ~ 5), L is the contact length of the rubbing pile (3mm), r is the radius of the rubbing wheel (275 mm), n is the rotation speed of the cylinder (654 or 1163 rpm), V is the velocity of the substrate stage (30 mm/s).

Preparation of liquid crystal cells.

Liquid crystal (LC) cells were fabricated with two PANBuS coated glass plates spaced with 50 μm polyimide film. Either rubbed or sheared PANBuS film with thickness of ~100 nm was used as alignment layers, in which the rubbing directions or sheared directions were anti parallel. Liquid crystals were introduced into the cell by capillary action. The cell was heated up to 65 °C, at which liquid crystals undergo complete isotropication. Nematic-to-isotropic transition was observed at 58.6 °C upon cooling. The cell was then cooled to r.t. with a cooling rate of 0.2 °C/min. All LC cells were similarly isotropicated before measurement

Measurements.

Tilt angles were evaluated by analyzing angular dependence of transmitted light (T) through an LC cell with a rotation angle of θ, according to the crystal rotation method.[7] Optical bench was consist of a polarizer and an analyzer, photo detector (silicon type), amplifier (OP07DP), AD/DA converter (DATA TRANSLATION DT01-EZ), stepping motor and driver (Parker Compumotor SX). Tilt angle θ_T was calculated from the symmetry angle (ψ) in the plot of T vs θ according to the approximation by Birecki[8]:

$\sin\theta_T = \sin^{-1}[\sin\psi / (n_e + n_o)]$, where, n_e and n_o are the extraordinary and ordinary refractive indices, respectively, of the liquid crystal (for E7, $n_e = 1.7464$ and $n_o = 1.5211$).

RESULT AND DISCUSSION

Aqueous solutions containing 50 wt % of PANBuS were birefringent under crossed polarized light. The optical textures observed from PANBuS were bilateral focal conic entities,[5] being similar to the optical textures of a smectic phase. Such a lyotropic phase behavior was also found from the solution of PANBuS in a mixture of ethanol and water. These lyotropic solutions of PANBuS could be cast onto a glass substrate and oriented by shearing the viscous surface in one direction. Removal of the solvent from the sheared PANBuS film resulted in highly ordered film with d.c. conductivity of 2 X 10^{-3} S/cm. The orientation of the polymer chains was observed by a cross-polarized microscope and was stable up to 170 °C. The sheared surface showed characteristic peaks of 2θ at 7.6, 12,13, and ~16 - 20° in XRD.

Nematic liquid crystals were effectively aligned between the PANBuS surfaces as determined by an orthoscopic observation by microscope. In order to examine this alignment property of PANBuS layer in detail, we carried out tilt angle measurement using an LC cell fabricated with either sheared or rubbed PANBuS alignment layers. A homogeneous, defect free alignment of liquid crystal molecules which were sandwiched between the treated (rubbed or sheared) PANBuS layers was observed by orthoscopic measurements. This indicates that rubbing or shearing of PANBuS layers leads to good orientation of the polymer, which can induce homogeneous alignment of the liquid crystal. Without rubbing or shearing treatment, the PANBuS layer induced poor alignment of liquid crystals with many defects. Furthermore, angular profile plotted against transmittance of the rotating sample with untreated PANBuS layer did not show symmetric angle.

FIGURE 1 shows angular dependence of transmittance of a monitoring He-Ne laser beam through an E7 LC cell fabricated with rubbed CPANBuS layers. The characteristic symmetric angle was obtained at 1.18 °, from which the tilt angle was determined as 0.36°. Slightly higher tilt angles (0.46 °) could be obtained by using

EPANBuS layers rubbed with RS of 574, as summarized in TABLE I. It is noteworthy that tilt angle of 0.46 for E7 with the PANBuS film rubbed with RS = 574 was not much affected by the increase in the rubbing strength (RS = 1005). This result indicates that rubbing process induce immediate orientation of polymer chains on the surface of the film, not very deep inside the film. In order to induce higher molecular alignment on PANBuS layer, we have prepared alignment layer from lyotropic solution.

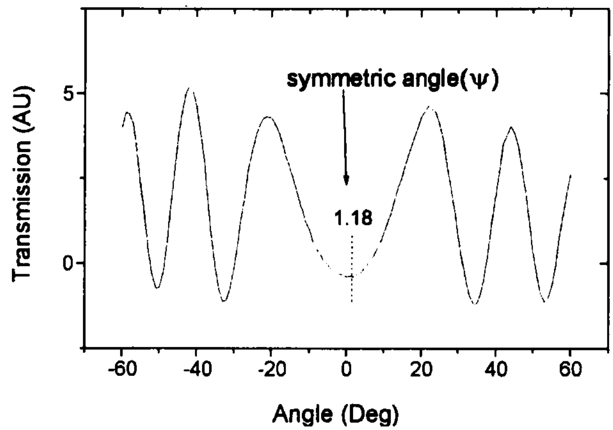


FIGURE 1. Angular dependence of transmittance in the E7 cell.

Interestingly, tilt angles were varied from 0.4 to 0.9 depending on the processing method of PANBuS solution. The cell fabricated with sheared PANBuS layer showed higher tilt angle (0.9) than with rubbed PANBuS layers (0.36 ~ 0.48). This result strongly suggests that shearing of the lyotropic solution may induce effective orientation of the pre-oriented PANBuS chains, to increase physicochemical interactions between liquid crystal and the oriented surface. On the other hands, rubbing the isotropic PANBuS surface do not induce effective alignment of polymer chains, because penetration depth of rubbing process is less than 20 Å, in general. Such a small penetration depth can not induce molecular reorientaion in deeper layer and alignment of liquid crystalline molecules may not be effective compared to the sheared layer processed from the pre-aligned solution. One of the problem associated with shearing method, however, is that it can not be applied to a large area display without defect formation. Therefore it seemed important to develop lyotropic processing method for higher tilt angle.

TABLE I. Effect of film preparation method on tilt angle

Sample	Processing	Tilt Angle (deg)
EPS1	sheared	0.90
EPS6	as spin-coated	Not available[a]
CPR3	rubbed[b]	0.36
EPR5	rubbed[b]	0.46
EPR6	rubbed[c]	0.48

[a] Asymmetric curve in the plot of T vs θ. [b]Rubbed with RS of 574 mm.
[c]Rubbed with RS of 1005 mm.

The liquid crystal alignment on the conductive PANBuS layer was stable for a prolonged time. The tilt angles of liquid crystals with PANBuS were lower than that on insulating inorganic surfaces or polyimide surfaces (typically higher than 2).[9] Such a low tilt angle may arise from the polar ionic property of PANBuS surface having sulfonate anionic group and cationic imino-quinone group in the polymer backbone. Further improvements of processing method and modification of polymer structure are in progress.

In conclusion, liquid crystal alignment layer with conductivity of 2×10^{-3} S/cm was prepared from a solution of poly(aniline N-butylsulfonate)s by shearing or rubbing method. The PANBuS layer was successfully applied to an LC cell containing E7. Orientation of liquid crystals was dependent on the processing method of PANBuS solution and the tilt angle of E7 was higher with the sheared PANBuS layers than with the rubbed layers.

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