Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 26 May 2010

To cite this article: Nobutaka Tanigaki, Claire Heck & Toshiko Mizokuro (2009): Oriented Thin Films of Polyaniline by Friction Transfer Method, Molecular Crystals and Liquid Crystals, 505:1, 80/[318]-86/[324]

To link to this article: http://dx.doi.org/10.1080/15421400902942169

Mol. Cryst. Liq. Cryst., Vol. 505, pp. 80/[318]–86/[324], 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902942169

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Oriented Thin Films of Polyaniline by Friction Transfer Method

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Oriented thin films of polyaniline (emeraldine base) were prepared by the friction transfer method by rubbing solid polyaniline against a glass substrate to form a thin coating film on the substrate. Characterization by polarized ultraviolet-visible-near infrared spectra showed the dichroic property of the films, suggesting that the polyaniline was oriented on the glass substrate. Hydrochloric acid treatment transformed the film into emeraldine salt without loss of orientation. Moreover, the oriented film of emeraldine base could be recovered by aqueous ammonia treatment of the emeraldine salt. The oriented film could also be doped with camphorsulfonic acid.

Keywords: doping; polarized light: molecular alignment; polyaniline; thin films

INTRODUCTION

Conducting polymers have been studied intensively because of their excellent optical and electrical properties. Polyaniline is one of the most important conducting polymers because it has a great range of applications, such as transparent electrode [1], solar cell [2], battery, capacitor, sensor, memory, actuator, electrochromic display [3] and so on. For device application the thin film fabrication is a very important process. In the case of polyaniline, films can be obtained by means of conventional methods like solution casting and *in-situ* polymerization [4]. On the other hand, we have been applying the friction transfer method, which is a solvent free technique, to fabricate oriented thin

The authors wish to thank to Dr. Kenji Kamada (AIST) for his kind help with the spectral measurements.

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films of various conjugated-polymers [5,6]. In this work we report the use of this friction transfer method as a simple way to fabricate oriented polyaniline thin films.

EXPERIMENTAL

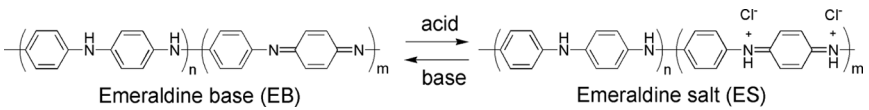
Polyanilines [emeraldine base (EB) with molecular weight (MW), 5,000, 50,000, and 300,000, purchased from Sigma-Aldrich company], were used without any further purification. Emeraldine salt (ES) (hydrochloride) was synthesized by the common procedures [7]. Glass slides were used as substrates after they were washed in an ethanolic alkaline solution and treated by UV-ozone. The friction transfer was carried out as follows [5,6]: A polymer block, which was produced by compressing polymer powder, was slid on the substrate at controlled temperature, pressure, and sliding speed, forming a polymer film onto the substrate's surface. Various films were produced varying the substrate's temperature in a range between ambient temperature and 250°C with typical pressure and sliding speed fixed at around 2.1 MPa and 1 m/min, respectively. Typical film size was about 1 cm × 1 cm. The polyaniline films were characterized by optical absorption spectroscopy using a Shimadzu UV-3150 spectrophotometer. Polarized spectra were measured with a Glan-Taylor polarizing prism.

RESULTS AND DISCUSSION

Preparation of EB Oriented Films

Polyaniline is roughly classified in two forms: EB form (undoped and insulator) and ES form (doped and conductive) (Scheme1).

First the EB form was studied to determine the appropriate friction transfer condition to produce oriented EB films. Figures 1 and 2 show the polarized optical micrographs and the polarized absorption spectra of an EB (MW: 50,000) film prepared at 180°C. The photographs were taken under the crossed Nicol condition with the angle between the friction direction and the polarizer direction being 45° (left photo) and 0° (right photo), respectively. The right photograph is completely



SCHEME 1 Two forms of Polyaniline: Emeraldine base (EB) and emeraldine salt (ES).

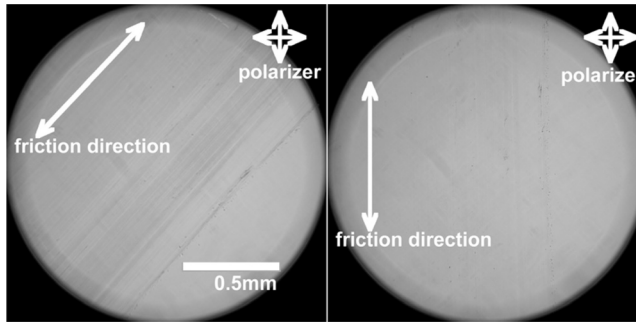


FIGURE 1 Polarized optical micrographs of a friction-transferred EB film (MW:50,000) (prepared at 180°C) under the crossed Nicol condition with the reflection mode.

dark indicating that polyaniline molecules oriented homogeneously in the same direction in the whole film. In Figure 2 strong absorption peaks can be seen around 330 and 620 nm, which are typical features for the EB samples [8]. These peaks show dichroism, especially the band intensity at 620 nm where the intensity of the peak for parallel polarization is about 3 times larger than that for orthogonal polarization. This shows that the EB molecular chains are aligned in the friction direction. The dichroic ratio was larger than that of reported for a stretched film obtained from polarized reflectance [9]. The

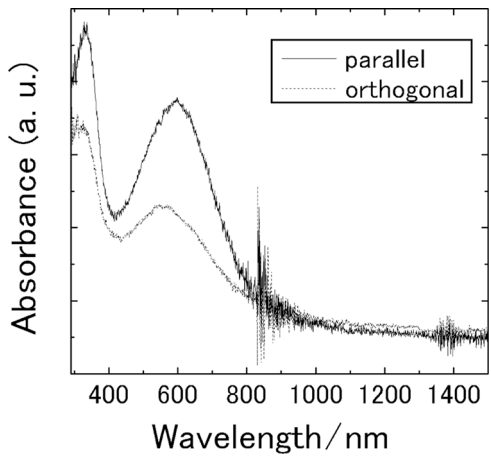


FIGURE 2 Polarized absorption spectra of a friction-transferred EB film (MW:50,000) (prepared at 180°C). The spectra were measure with light parallel (solid line) and orthogonal (dashed line) to the friction direction.

thickness of these friction-transferred films was about 2 nm estimated by absorbance with reference to that of spin-coated films.

We prepared friction-transferred films of EB with MW = 50,000 at various substrate temperatures. EB films could be deposited on glass substrates at temperatures from ambient temperature to 250°C. However, films produced at temperatures below 100°C were not uniform, while those obtained at temperatures higher than 200°C had a very small orientation. The best orientation was obtained for films produced at temperatures between 100 and 200°C. Figure 3 shows absorbance and dichroic ratios of the EB films fabricated at various temperatures, where absorbance values are those of non-polarized spectra around 630 nm, and the dichroic ratios were defined by A_{para}/A_{ortho} (A_{para}, A_{ortho} were respectively calculated from the integrated values of the parallel and orthogonal polarized absorption spectra). In Figure 3 one can see that the dichroic ratios are about 2.5 for the films prepared at temperatures between 100 and 200°C.

The friction transfer of EB with MW = 5,000 and MW = 300,000 were also examined. The EB with the low molecular weight (MW = 5,000) could not be deposited uniformly, while friction-transferred films of EB with MW = 300,000 were very uniform and highly oriented. For these higher molecular weight samples, the dichroic ratios of the films prepared between 100 and 200°C varied between 3 and 5. The reproducibility in preparation of oriented films was good when the surfaces of the substrate and the polymer block were very clean.

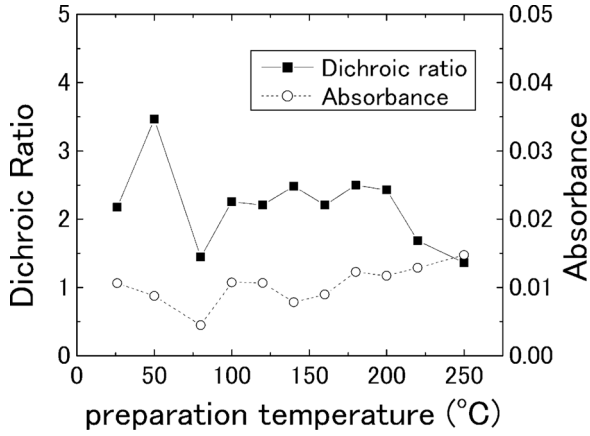


FIGURE 3 Preparation temperature dependence of absorbance (circle) and dichroic ratio (square) of spectra of the friction transferred EB (MW:50,000) films.

Moreover, similar results were obtained when the glass substrates were substituted by silicon wafers and indium tin oxide (ITO) coated glass.

We were not able to prepare oriented films from ES form of polyaniline. This ES form is doped with chloride ion so that the polymer chain and the dopant were ionized, and both have an electrical charge. This gives rise to stronger molecular interaction in ES form when compared to the EB form of polyaniline, which could explain the difficulty to deposit the ES form.

Doping of the Friction-Transferred Films

The oriented EB films were doped with hydrochloric acid (HCl) by immersing the friction-transferred EB film in 1 N aqueous HCl for 1 minute and then washing it in distilled water. Figure 4a shows the polarized spectra of an oriented polyaniline film after HCl treatment. The peak around 600 nm is diminished and a broad band appears near the infrared (NIR) region. The NIR band shows dichroism, which suggests that the film became the ES form without loosing its orientation. The HCl-doping process was accomplished within 1 minute, but even when the treatment time was longer, no clear changes were observed.

An alkaline treatment converted the ES films into the EB form, i.e., when the ES film was treated with 1 N aqueous ammonium hydroxide

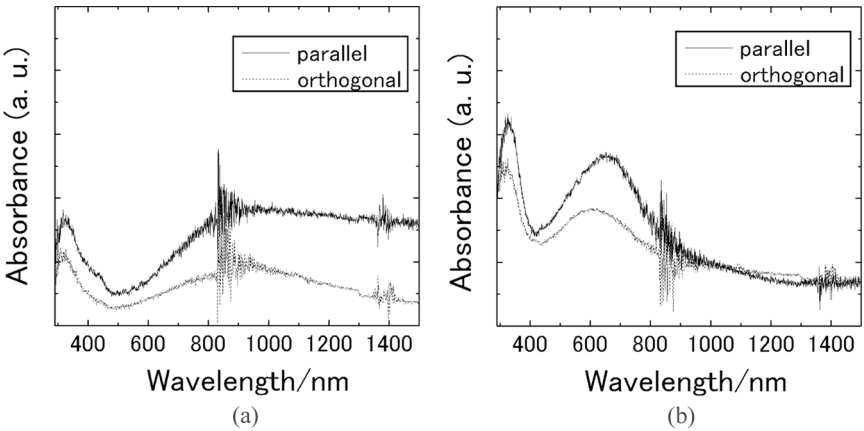


FIGURE 4 Polarized absorption spectra of a friction-transferred film (MW: 50,000 prepared at 180°C) after treatment with 1 N HCl for 1 minute (a), and in addition with a treatment of 1 N NH_4OH treatment for 1 minute (b). The scale of the vertical axis is the same as Figure 2.

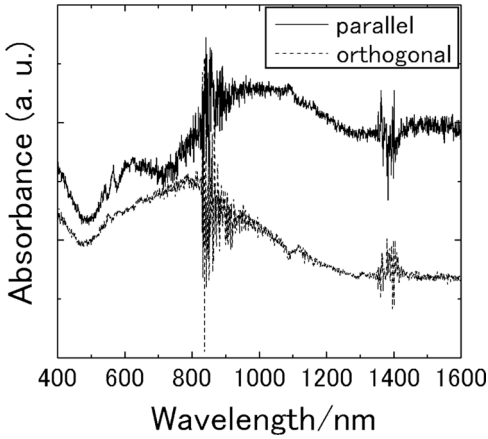


FIGURE 5 Polarized absorption spectra of a friction-transferred film (MW:50,000 prepared at 180°C) after treated with 10 wt% CSA aqueous solution for 30 minutes.

for 1 minute followed by washing in distilled water, the EB film was recovered (Figure 4b). Absorbance decreased in comparison with that of the original EB film probably due to some exfoliation, but the recovered EB films kept its orientation.

Polyaniline can be doped with some organic acids. Here, the camphorsulfonic acid (CSA) was doped into the friction-transferred EB films by immersing the oriented EB films in 10 wt% *d, l*-CSA aqueous solution for 30 minutes and then washing it in distilled water. Figure 5 shows polarized absorption spectra of the CSA-doped polyaniline film where the broad absorption at 800–1200 nm is polarized. This band was observed to decrease while the EB absorption peak at 600 nm remained the same with shorter treatment of CSA. The CSA-doping is usually a longer time process than HCl-doping process because of the larger CSA molecular size.

CONCLUSION

Oriented films of polyaniline (EB form) were successfully prepared by the friction transfer method. These EB oriented films were changed to the ES form, without loosing their orientation, by means of aqueous HCl treatment. The friction-transferred polyaniline films were very thin, and oriented, and could be doped with acids. Therefore, these films can be applied in the organic electronics field, for example as the device's interface layer between an organic film and an inorganic electrode [10].

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