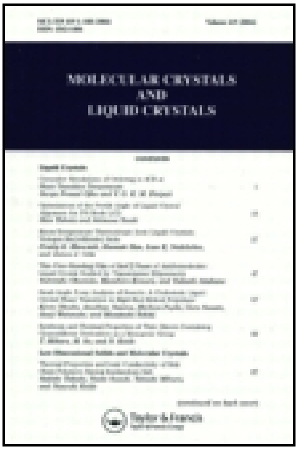

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A Photoluminescent LB Film of a Polyurethane with Cyanostilbene Side Group

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A Photoluminescent LB Film of a Polyurethane with Cyanostilbene Side Group

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The dependence of photoluminescent property on the molecular orientation in polymeric thin films was investigated using spin-coated and LB films. A polyurethane (PU-CN) was prepared from condensation polymerization of a cyanostilbene diol and 2,4-toluene diisocyanate. The PU-CN monolayer was characterized by surface pressure-area isotherms and Brewster angle microscopy. Additional UV-Vis absorption peak was observed at 350 nm in the LB film. A blue shift was found in the PL emission of the LB film when compared with that of the spin-coated film. The cyanostilbene side groups were supposed to stack partly together as J-aggregate in the LB film.

Keywords: polyurethane; photoluminescence, LB film, spin-coated film, molecular orientation

INTRODUCTION

The optoelectronic properties of organic compounds are considerably dependent on the molecular orientation in the thin films. Langmuir-Blodgett (LB) technique provides one of the featured ultrathin films with nm-sized film thickness and ordered molecular structure. The LB films of polythiophenes, poly(phenylenevinylene)s, and organic dyes have been investigated to

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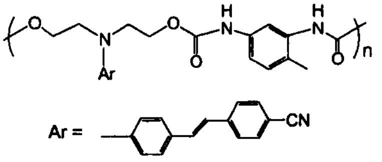
understand the optoelectronic properties in the state of ordered molecular films[1-4]. We report herein the dependence of photoluminescent (PL) property on molecular orientation in thin films of a newly synthesized polyurethane (PU-CN) with cyanostilbene group. Two kinds of fabrication techniques, such as spin-coated and LB methods, were applied to differentiate the molecular orientation in the thin films. The PU-CN monolayer was characterized by surface pressure-area isotherms and Brewster angle microscopy. The chemical structure of the films was determined by UV-Vis and FT-IR spectroscopy.

EXPERIMENTAL

The employed polyurethane (PU-CN) was prepared from condensation polymerization of a cyanostilbene diol and 2,4-toluene diisocyanate. A cyanostilbene diol was synthesized by Wittig reaction of 4-[N,N-bis(2-hydroxyethyl)amino] benzaldehyde with 4-cyanobenzyltriphenyl phosphonium chloride.



PU-CN

A film balance system NLE-LB200-MWC (Nippon Laser and Electronics) was used for measuring surface pressure as a function of molecular area and for LB transfer of monolayer by the vertical mode (trough surface size, 80x585 mm^2). BAM images were obtained from Mini BAM (Nanofilm Technologie GmbH). PL spectra were obtained by fluorophotometer (Hitachi-F 4500).

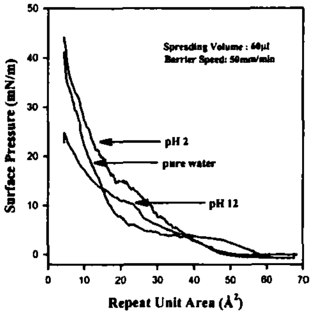


FIGURE 1 Surface pressure-area isotherms of PU-CN.

RESULTS AND DISCUSSION

A chloroform solution of PU-CN was spread on water subphases with different pH. When the subphase has low or high pH, slightly expanded area of the polymer repeat unit on the monolayer was produced (Fig. 1). The surface pressure-area isotherms showed high monolayer stability up to 40 mN/m. The monolayer images by Brewster angle microscopy indicated island structures as-spread state, the separated islands became coalesced to uniform monolayers by monolayer compression. The monolayers were transferred on calcium fluoride or quartz crystal plates as Y type.

The chemical structures of the LB films were determined from FT-IR and UV-Vis spectra. Fig. 2 shows UV-Vis absorption and PL emission spectra of the LB film. Specifically, additional UV-Vis absorption peak, which was not found in spin-coated film, was observed at 350 nm in the LB film. In the case of spin-coated film, only the peak at 400 nm was observed. The PL emission spectra of PU-CN were also different between the spin-coated film and the LB film. A blue shift was also found in the PL emission of LB film

(λ_{max} at 400 nm) when compared with spin-coated film (λ_{max} at 510 nm). The blue shift of λ_{max} in UV-Vis and PL spectra was supposed owing to the J-aggregate in LB film. However, the appearance of the absorption peak at 400 nm still in the UV-Vis spectra of LB film means that the cyanostilbene chromophores are not totally ordered as J-aggregate. As a conclusion, we could demonstrate the PL dependence on the molecular orientation in a polyurethane thin film by comparison of the spin-coated film with the LB film.

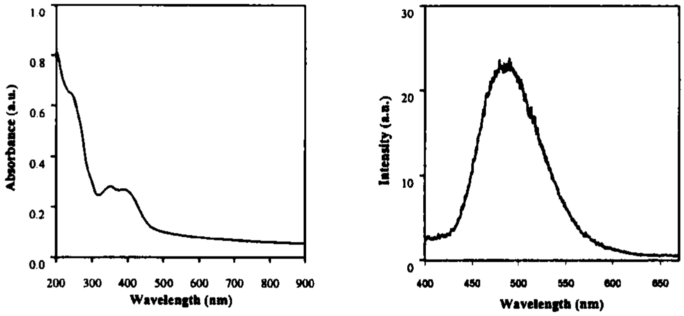


FIGURE 2 UV-Vis absorption (left) and PL emission (right) spectra of PU-CN LB film.

Acknowledgments

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