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### Fabrication, Characterization and Optical Properties of Epitaxially Grown Oligomer/polymer Double Layers

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## Fabrication, Characterization and Optical Properties of Epitaxially Grown Oligomer/polymer Double Layers

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Oligomeric dimethylsilane (ODMS) and 1,6-di-(p-methoxy-styryl)benzene (DSB-1) grew epitaxially on the friction-transferred polydimethylsilane (PDMS) and poly(p-phenylenevinylene) (PPV) layers. The ODMS/PDMS and DSB-1/PPV double layers indicated the remarkable anisotropic feature in absorption and emission properties.

**Keywords:** oligomer, polymer, double layer, epitaxy, optical properties

### INTRODUCTION

Thin films of polymers with one-dimensional conjugation system along their main chain have been attracted much interest as materials for electronics and opto-electronics. However, it is difficult to prepare such polymer films from solution and vapor because of their insolubility and infusibility. Recently, the friction transfer method has much studied as a kind of preparation method of oriented thin film of insoluble polymers. We have reported the fabrication and characterization of thin film of insoluble polymers such as poly(tetrafluoroethylene), polydimethylsilane (PDMS) and poly(p-phenylenevinylene) (PPV). These polymer films formed uniaxially-oriented thin layers.

In this study, oligomeric dimethylsilane and 1,6-di-(p-methoxy-styryl)benzene (DSB-1: one of trimers of PPV) were vapor-deposited on

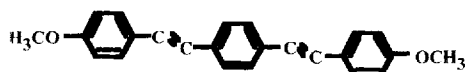


FIGURE 1 Molecular structure of DSB-1.

a corresponding friction-transferred polymer layer. Structure and optical properties of oligomer/polymer double layers were investigated.

## EXPERIMENTAL

PDMS and oligomeric dimethylsilane (ODMS: average molecular weight  $\approx 2,000$ ) were purchased from Nippon Soda Co., Ltd. and Wako Chemicals Co., Ltd., respectively. PPV and DSB-1 (Fig.1) were synthesized according to the literatures[1]. Thin layers of PDMS and PPV used as a substrate were formed by friction transfer method on a fused silica glass plate. The thickness of a friction-transferred polymer layer was about 10–15 nm. ODMS and DSB-1 were deposited onto the friction-transferred PDMS and PPV layers in a vacuum of  $1 \times 10^{-3}$  Pa. The structure and optical properties of the films were investigated by electron microscopy (TEM) and UV-VIS and fluorescence spectroscopy.

## RESULTS AND DISCUSSION

Figure 2 shows the transmission electron micrographs and the electron diffraction (ED) patterns of the PDMS and PPV films. The films indicate a row-like structure which covers the glass surface almost completely. The ED patterns of the polymer films show the similar fiber diagrams, suggesting that the films were oriented and crystalline. The reflection spots can be indexed as shown in the figures with their crystal parameters[2,3]. The chain axes of the PDMS and PPV macromolecules,

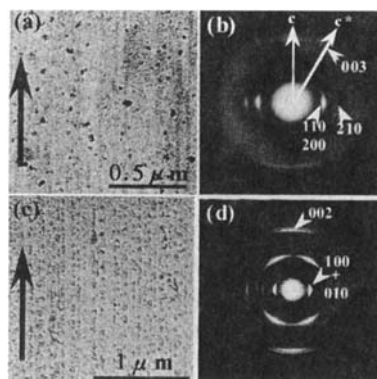


FIGURE 2 TEM and ED patterns of friction-transferred PDMS(a,b) and PPV(c,d) layers. Arrow indicates the friction direction.

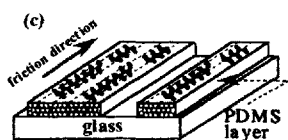
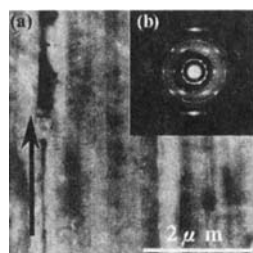


FIGURE 3 TEM(a) and ED pattern (b) of ODMS/PDMS double layer and schematic model of molecular orientation (c).

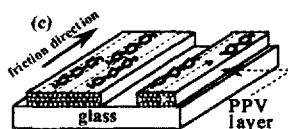
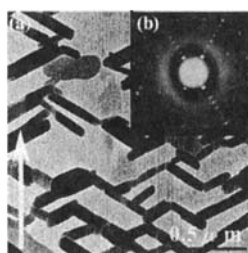


FIGURE 4 TEM(a) and ED pattern (b) of DSB-1/PPV double layer and schematic model of molecular orientation (c).

corresponding to the *c* axes of their crystals, orient uniaxially along the friction direction.

Figure 3(a) and (b) shows the electron micrograph and the ED pattern of the ODMS/PDMS double layer. No distinct structure is observed in the ODMS/PDMS double layer. However, it is noteworthy that the electron diffraction pattern of the double layer changes from arc to spots. This indicates that the deposited ODMS molecules take the same orientation as well as the PDMS layer. The ODMS molecules lie parallel to the PDMS surface and grow epitaxially, as shown in Fig. 3(c). DSB-1 forms rectangular crystals growing along two directions crossing at  $120^\circ$  on a friction-transferred PPV layer, as shown in Fig. 4(a). The bisectional direction of crossing angles of these crystals corresponds to the friction direction of PPV. The ED pattern of the DSB-1/PPV double layer indicates the superposition of the reflection spots from the deposited DSB-1 crystals and those from the PPV layer used as the substrates. From the crystallographic consideration, it is found that the *c*-axis of DSB-1 crystal makes an angle of  $60^\circ$  to the polymer axis of PPV. The schematic representation of the orientation overgrowth of DSB-1 on the PPV surface is shown in Fig. 4(c).

The UV absorption spectra of the friction-transferred PDMS layer

showed the maximum peaks at 340nm and the dichroic ratio of absorption intensity ( $I_{//} / I_{\perp}$ ) was about 13. Figure 5 shows the polarized absorption and emission spectra of the ODMS/ PDMS double layer. The absorption peak of the deposited ODMS film blue-shifts to 304nm due to its low molecular weight. The ODMS/ PDMS double layer indicates the remarkable dichroism in optical properties. The dichroic ratios calculated directly from the peak heights of absorption and emission intensity are about 40 and 9, respectively. It is known that the transition moment of the lowest singlet exciton associated with  $\sigma - \sigma^*$  band-gap is parallel to the transplanar Si backbone. Therefore, the Si main chains both in friction-transferred PDMS layer and ODMS/ PDMS double layer are found to align in the sliding direction. The PPV layer has an absorption around

450 nm and the deposited DSB-1 film shows an absorption peak at 340nm, as shown in Fig.6. These bands are assigned to the exciton band with the  $\pi - \pi^*$  transition in PPV and DSB-1 molecules. The friction-transferred PPV layer and DSB-1/PPV double layer also indicate the remarkable anisotropic feature in absorption and emission properties.

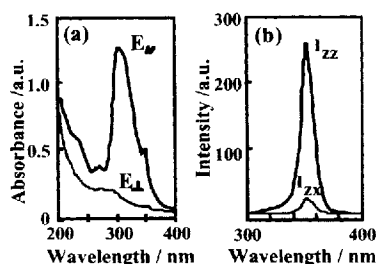


FIGURE 5 Polarized absorption (a) and emission spectra (b) of the ODMS/ PDMS double layer.

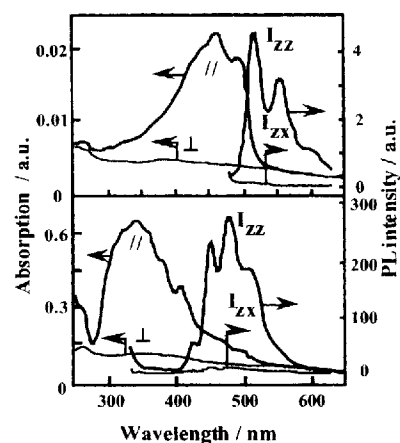


FIGURE 6 Polarized absorption (a) and emission spectra (b) of the DSB-1/ PPV double layer.

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