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Nobutaka Tanigaki [a], Yukiko Iwase [a], Akira Kaito [a], Yuji Okada [b], Naohiro Yamahira [b] & Kiyoshi Yase [a]

[a] National Institute of Materials and Chemical Research, AIST, MITI Tsukuba, Ibaraki, 305-8565, Japan

[b] Carl Zeiss Co. Ltd., Shinjuku-ku, Tokya, 160-0003, Japan

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NOBUTAKA TANIGAKI[a], YUKIKO IWASE[a], AKIRA KAITO[a], YUJI OKADA[b], NAOHIRO YAMAHIRA[b] and KIYOSHI YASE[a]

[a]*National Institute of Materials and Chemical Research, AIST, MITI Tsukuba, Ibaraki 305-8565, Japan and* [b]*Carl Zeiss Co. Ltd., Shinjuku-ku, Tokya 160-0003, Japan*

Oriented thin films of poly(diphenylsilane) were prepared by the friction transfer technique. It was found that the film properties depended strongly upon the preparation temperature. Oriented films exhibited purple polarized photoluminescence. Electron diffraction pattern of the oriented PDPhS exhibited that the conformation of the polymer in crystalline state should not be all-*trans* structure.

Keyword: polysilane; oriented thin film; polarized light; structure

INTRODUCTION

Polysilanes are the hopeful materials for opto-electronic devices. The electronic properties of polysilanes are due to the σ-conjugation along the molecular chain, so that the orientation of the molecular chains is very important in controlling the opto-electronic properties. We have investigated highly oriented thin films of insoluble polysilanes which were prepared by the friction transfer method[1-3]. Highly oriented films of poly(dialkylsilane)s emitted strongly polarized photoluminescence in the ultraviolet region. Poly(diarylsilane)s emitted visible lights and were applied to electroluminescent devices[4,5]. In this work, we prepared oriented thin films of insoluble poly(diphenylsilane) (PDPhS).

EXPERIMENTALS

PDPhS was synthesized by Wurtz coupling of diphenyldichlorosilane with sodium in toluene. Because PDPhS was insoluble, oligomers could be eliminated by extraction with boiling toluene. Oriented thin films of PDPhS were made by friction transfer technique[3]. Electron diffraction was measured with a Zeiss CEM902 transmission electron microscope.

RESULTS AND DISCUSSION

Preparation Temperature Dependence

Oriented thin films of PDPhS could be prepared by the friction transfer technique. The properties of the PDPhS films were strongly dependent upon the substrate temperature during the preparation. The polarized ultraviolet-visible (UV) spectra of PDPhS films prepared at various temperatures are shown in Figure 1. The strong absorption around 380nm might be assigned to be an exciton band of σ-σ^* transition. It showed a parallel dichroism, namely, the light with the electric vector parallel to the friction direction was more strongly

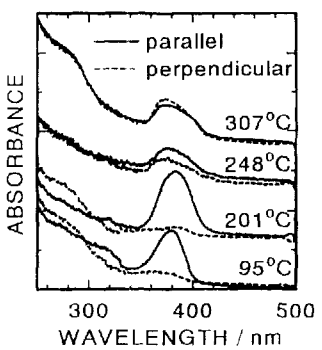

FIGURE 1 Polarized UV spectra of PDPhS films prepared at various temperatures.

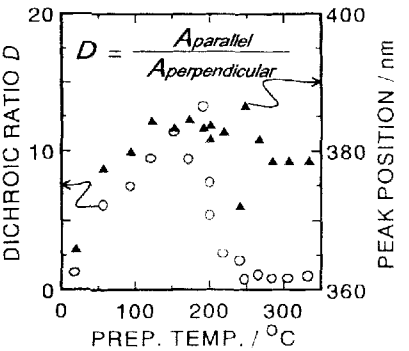

FIGURE 2 Temperature dependence of dichroic ratios and peak maxima.

absorbed than the light with perpendicular polarization. It suggested that the polymer chains were aligned to the friction direction. Figure 2 shows absorption maxima and dichroic ratios of the polarized spectra plotted against the preparation temperatures. In the range of 150-200°C, highly oriented thin films were obtained. The film prepared at about 200°C had the absorption band with the longest wavelength.

Polarized Photoluminescence

The PDPhS film had purple photoluminescence (PL). Figure 3 shows the polarized PL spectra of PDPhS prepared at 200°C with the used geometry, in which the sliding direction is labeled z, and the transverse direction x. The PL intensity measured with a polarizer along the i-axis (excitation) and an analyzer along the j-axis (emission) is denoted by I_{ij} (i, j = x, z). Four components, I_{zz}, I_{zx}, I_{xz} and I_{xx}, were measured. When the oriented film was excited at 370nm, the I_{zz} component was dominant. However, the I_{xz} was stronger than other components at the 270nm excitation. The π–electron systems of the phenyl substituent are mainly excited at

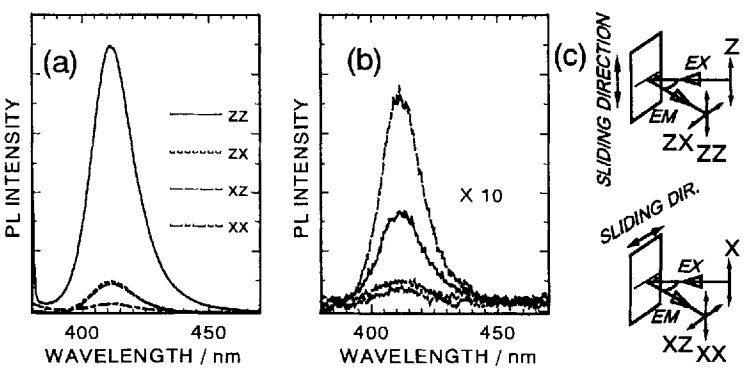

FIGURE 3 Polarized PL spectra of PDPhS: (a) excited at 370nm, (b) excited at 270nm and (c) optical geometry.

270nm , and then the excited energy should be transferred from the phenyl rings to the main chain. As the transition moment of the π–π^* excitation is perpendicular to the main chain and that of the σ–σ^* emission is parallel polarized, the intensity I_{XZ} was higher than the other components. Although the film was excited by non-polarized light, the polarized light parallel to the sliding direction was emitted.

Electron Diffraction

To explore the structure of PDPhS, we measured electron diffraction of the oriented thin films (Figure 4). The diffraction pattern was composed of a set of crystalline reflections and a set of diffuse reflections from an oriented amorphous portion, suggesting the coexistence of the two phases in the solid state. The sharp meridional reflection was observed at the third layer. The fiber period was 1.0nm. It revealed that the backbone of PDPhS in crystalline state should not be conformations already known, such as *trans*-zigzag or 7/3 helix. More detail analysis is progressing to determine the fine structure of PDPhS.

FIGURE 4 Electron diffraction pattern of PDPhS.

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