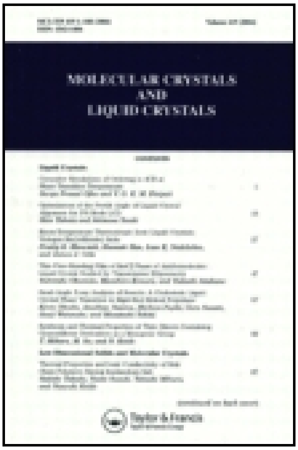

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Epitaxial Growth of Polysilanes on Friction-Transferred Poly(Dimethylsilylene) Film

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Version of record first published: 24 Sep 2006

To cite this article: Nobutaka Tanigaki, Yuji Yoshida, Kiyoshi Yase Akira Kaito & Hiroko Kyotani (1997): Epitaxial Growth of Polysilanes on Friction-Transferred Poly(Dimethylsilylene) Film, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 294:1, 39-42

To link to this article: http://dx.doi.org/10.1080/10587259708032243

Mol. Cryst. Liq. Cryst., 1997, Vol. 294, pp. 39–42
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EPITAXIAL GROWTH OF POLYSILANES ON FRICTION-TRANSFERRED POLY(DIMETHYLSILYLENE) FILM

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Abstract Highly oriented poly(dimethylsilylene) films, which were prepared by friction-transfer technique, have an ability of orienting soluble polysilanes. Solution-cast films of polysilanes on the friction-transferred film were oriented. The oriented films were characterized by polarized ultraviolet absorption spectroscopy. Several soluble polysilanes were examined and then poly(di-*n*-hexylsilylene) and poly(methyl-*n*-propylsilylene) had higher orientation. Their main chains were arranged along the main chains of the poly(dimethylsilylene).

INTRODUCTION

The polysilane has high potential as opto-electronic devices. Such electronic properties are caused by delocalization of σ-electrons along the Si-backbone. Therefore, it is important to align the molecular chain of polysilanes. Recently, we have prepared highly oriented films of poly(dimethylsilylene) (PDMS)[1, 2] and other polysilanes[3] by the friction-transfer technique. However, as the friction-transferred films were not uniform, they were not appropriate for electronic devices.

It was reported that a friction-transferred PTFE film could be employed in orienting other molecules.[4] Some soluble polysilanes can be arranged by casting on the PTFE film.[5, 6] In this work, we examined whether the polysilanes can be oriented epitaxially on the friction-transferred PDMS film.

EXPERIMENTAL

PDMS was purchased from Nippon Soda Co., Ltd. Poly(di-*n*-hexylsilylene) (PDHS), poly(methyl-*n*-propylsilylene) (PMPrS), poly(di-*n*-butylsilylene) (PDBS), and poly(methylphenylsilylene) (PMPhS) were synthesized by conventional Wurtz coupling from dialkyl dichlorosilanes. In this work, they were used after low molecular weight fractions were eliminated by reprecipitation.

The friction-transfer was performed as follows. The PDMS pellet, which was made by compressing the powder, was slid onto the smooth substrate, such as a quartz plate, whose temperature was controlled at 210-235℃, and then the oriented film was formed on the substrate surface. The oriented films of soluble polysilanes were prepared by solution-casting and spin-coating on the PDMS films. Toluene, chloroform and *n*-hexane were used as solvent.

The morphology of the oriented films were observed by a polarized optical microscope. The orientation of the films were evaluated by the polarized ultraviolet absorption spectroscopy. The spectra were measured using a Shimadzu MPS2000 spectrophotometer with a Gran-Thompson polarizing prism.

RESULTS AND DISCUSSION

Putting the polysilane solution onto the friction-transferred PDMS film and evaporating the solvent gave us an oriented polysilane film. The morphology of the polysilane films on the PDMS film were different from those of the film casted on the quartz plate without PDMS. Figure 1 shows the polarized optical micrograph of PDHS/PDMS film spin-coated from *n*-hexane solution under the crossed Nicol condition. In the area of the PDHS film without PDMS, unoriented crystals are observed. By contrast, the all area of the films on PDMS changed alternately between bright and dark. It suggests that the film was uniaxially oriented.

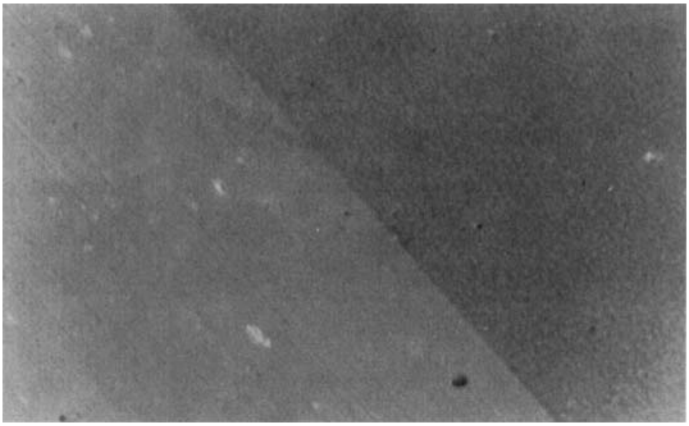

FIGURE 1. A polarized light micrograph of PDHS/PDMS film. The lower left part of the photograph shows PDHS on the friction-transferred PDMS, while the upper right part shows unoriented PDHS on quartz substrate.

Figures 2 (a) and (b) show polarized UV spectra of the friction-transferred PDMS film and the PDHS film casted on the PDMS substrate. The difference spectrum between (a) and (b) is shown in (c), which exhibits the spectrum of only the PDHS film. The transition moment of the absorption of polysilanes is known to be parallel to the main chain direction.[6] The spectra of (a) and (c) have the same dichroic character. It suggests the PDHS main chain aligned along the PDMS molecular chain direction.

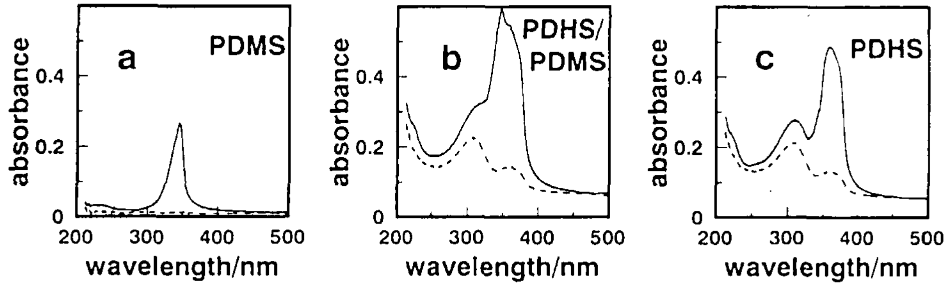

FIGURE 2. Polarized UV spectra of PDHS/PDMS film. The spectra were measured with the light polarized parallel (solid line) to the friction direction and perpendicular (dashed line). (a)PDMS, (b)PDHS/PDMS and (c)the difference between (a) and (b).

Figures 3 (a)-(c) show the difference spectra between the spectrum of PDMS and that of the cast film of PMPrS, PDBS and PMPhS, respectively. The PMPrS/PDMS was highly oriented, but PDBS/PDMS is poorly oriented. PMPhS was moderately oriented. These results were considered at standpoint of the polysilane structure. The conformation of the main chains of PDHS and PMPrS is all-*trans*, which is same to that of PDMS. The fiber periods (the cell dimensions of *c*-axis) of these polysilane crystals were the same value (about 0.4nm). It is considered that the PDHS and PMPrS crystallites were epitaxially grown along the *c*-axis of PDMS. On the other hand, PDBS has 7/3 helical structure (*c* =1.4nm). Because of large mismatching, PDBS crystallites could not be epitaxially grown on the PDMS. This consideration is not applied to PMPhS yet, because the structure of PMPhS has not been known.

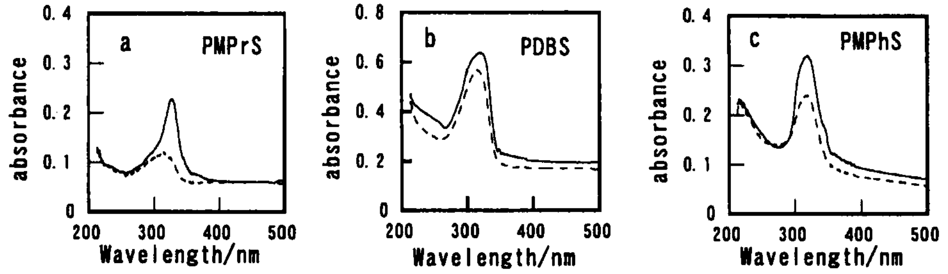

FIGURE 3. Difference between polarized UV spectra of polysilanes/PDMS films and that of PDMS substrate are shown. (a)PMPrS/PDMS, (b)PDBS/PDMS and (c) PMPhS/PDMS.

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