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Highly oriented films of poly(dimethylsilylene) by friction deposition

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Highly oriented films of poly(dimethylsilylene) on smooth substrates such as glass and quartz plates were prepared by the friction deposition technique. The structure of the oriented film was characterized by polarized optical microscopy, transmission electron microscopy and polarized ultraviolet absorption spectroscopy. The polymer backbone in the film was parallel to the sliding direction. The orientation was confirmed to be dependent on the temperature of substrates during deposition.

(Keywords: poly(dimethylsilylene); friction deposition; orientation)

Introduction

Polysilanes are very attractive materials because of their unusual electronic and optical properties[1]. They are expected to be used for new electronic devices. Their unusual electronic properties have been considered to be caused by the delocalized σ electrons in the Si–Si catenated backbone. Many researchers have attempted to control the structure of polysilanes by various materialization techniques, such as elongation[2–5], rubbing[6,7], Langmuir–Blodgett technique[8–10], and vapour deposition[11,12]. Oriented polysilanes would be important not only in the investigation of anisotropy of electronic properties but also in the application of their properties. We provide a very convenient technique for orienting the polysilanes.

It is well known that when some polymers, such as polyethylene and poly(tetrafluoroethylene) (PTFE), are rubbed against a clean surface, highly oriented thin films are deposited onto the surface (friction transfer)[13,14]. Recently, Wittmann and co-workers investigated friction-deposited thin layers of PTFE and other polymers[15–18]. They found that the surface has the ability to induce oriented growth of small organics and polymers[15,18]. It is very interesting that highly oriented films could be prepared in the solid state from solid materials by the friction deposition technique. We attempted to orient an untractable polymer by applying the friction deposition technique. We have already had a successful result in its application to poly(*p*-phenylene)[19].

Poly(dimethylsilylene) (PDMS) is known to be the simplest polysilane. Because PDMS is difficult to dissolve in any solvents and cannot melt, its structural study has been delayed compared with the other polysilanes, which have longer alkyl side chains. Recently, Lovinger *et al.*[5] prepared a PDMS oriented film, which was cast from boiling α-chloronaphthalene and stretched with polymer substrate at 200°C. They investigated the structure of PDMS and solid-state phase transition. It was reported that the main chain of PDMS has an all-*trans* conformation, and that it has two phase transitions at 160 and 220°C. They also prepared the single crystal of PDMS[5,20].

In this study, we prepared a highly oriented film of PDMS and characterized it by polarized optical microscopy, transmission electron microscopy (TEM) and polarized ultraviolet (u.v.) absorption spectroscopy.

Experimental

Preparation of PDMS oriented films. The PDMS powder used in this study was obtained from Nippon Soda Co., Ltd. Glass slides and quartz plates were used as the substrates. The PDMS powder was compressed into a disc with about 235 MPa pressure under vacuum. The PDMS disc was slid onto the smooth substrate, whose temperature was controlled while applying a pressure. The temperatures of the substrates during deposition were varied from ambient temperature to 235°C.

Measurements. Transmission electron micrographs were taken using a Hitachi H-9000 with an acceleration voltage of 300 kV. The specimen for TEM observation was covered with carbon for reinforcement, separated from the substrate on a water surface by using dilute hydrofluoric acid, and scooped up onto an electron microscopic grid. Polarized u.v. spectra were measured by a Shimadzu MPS2000 spectrophotometer with a Glan-Thompson polarizing prism. The u.v. spectra were obtained with the transmission mode.

Results and discussion

We could obtain oriented films of PDMS by a more convenient method than those previously reported. Thin oriented films of PDMS on quartz substrate could be obtained at all temperatures from 20 to 235°C. The temperature range was divided into three regions in terms of the continuity of films. Deposition below about 150°C is difficult. The significant non-uniformity of the obtained films could be seen even with the naked eye. The free surface looked dark and the polymer film looked light in the polarized optical micrographs (*Figures 1a* and *b*). At moderate temperature, from 150 to 210°C, better films

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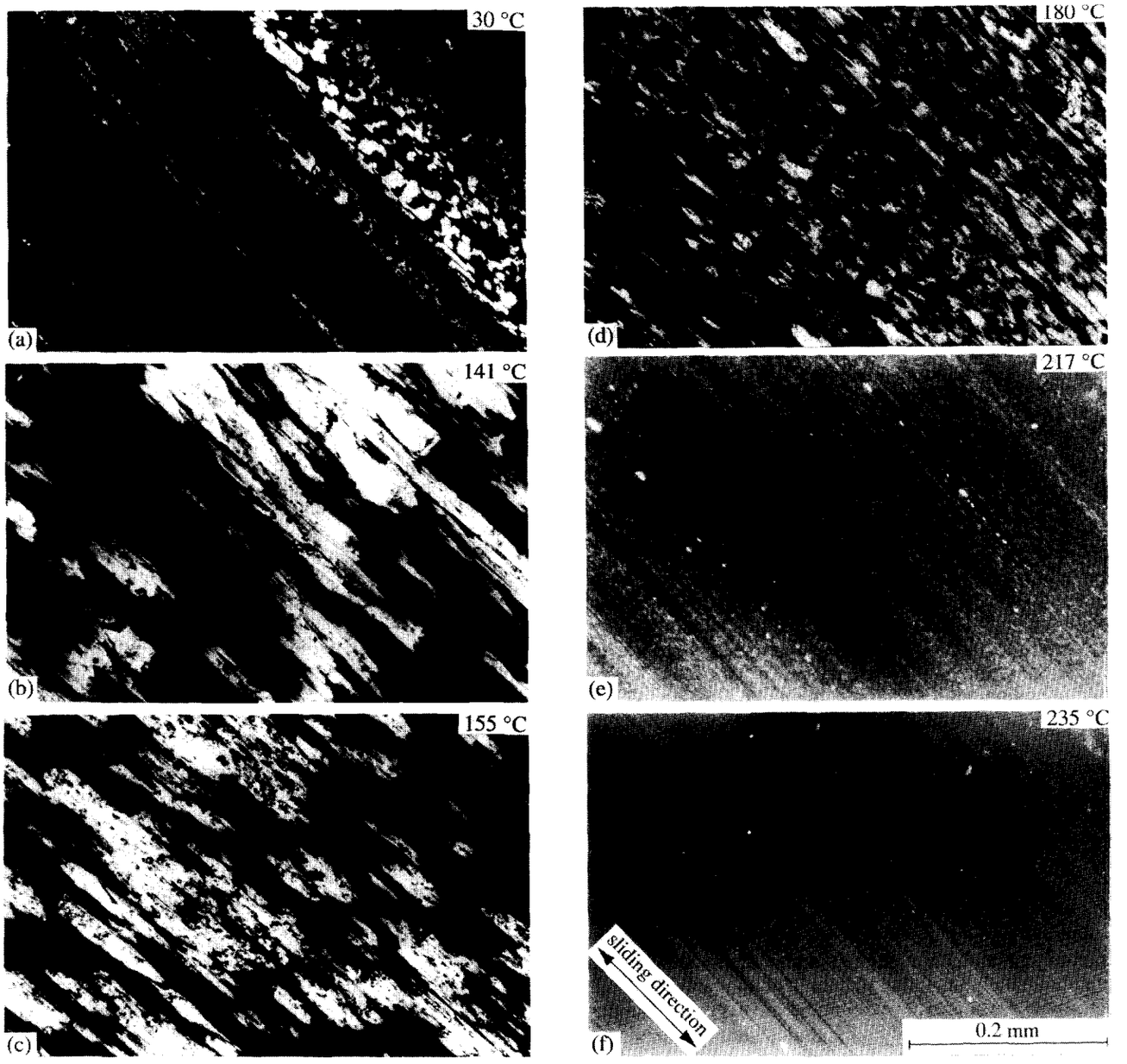

Figure 1 Polarized optical micrographs of PDMS thin films friction-deposited on quartz substrate at (a) 30°C, (b) 141°C, (c) 155°C, (d) 180°C, (e) 217°C and (f) 235°C

could be obtained than at lower temperature. These films were not very uniform and were discontinuous, as viewed by an optical microscope (*Figures 1c* and *d*). At higher temperature, above about 210°C, uniform films of PDMS could be obtained (*Figures 1e* and *f*). The variation in continuity of films and the difficulty of deposition were related to the difference in the degree of orientation of the films evaluated by polarized u.v. spectra, as mentioned later. Observations by polarized microscope of all of these films revealed the orientation of PDMS.

TEM was used to observe the morphology and structure of the oriented films. A transmission electron micrograph and an electron diffraction pattern of the PDMS thin film are shown in *Figure 2*. No distinct structure was observed in the micrograph of friction-deposited PDMS film, while the friction-deposited PTFE film showed some grooves along the sliding direction[15,16]. However, electron diffraction of the film showed a fibre diagram, suggesting that the film was oriented and crystalline. The backbone of the polymer was found to align parallel to the sliding direction. The fibre period suggested that the backbone conformation was all-*trans* in the oriented film.

In order to evaluate the orientation of the films, we measured polarized u.v. absorption spectra of the oriented films on quartz substrates. *Figure 3* shows the polarized u.v. spectra of the PDMS films, which were prepared on the substrates at various temperatures. The polysilanes, including PDMS, have a u.v. absorption band at 300–350 nm arising from σ–σ^* transition, and the polarized u.v. spectra have been used for evaluating the orientation of polysilanes[4,6 10,12]. Tachibana *et al.*[6,7]

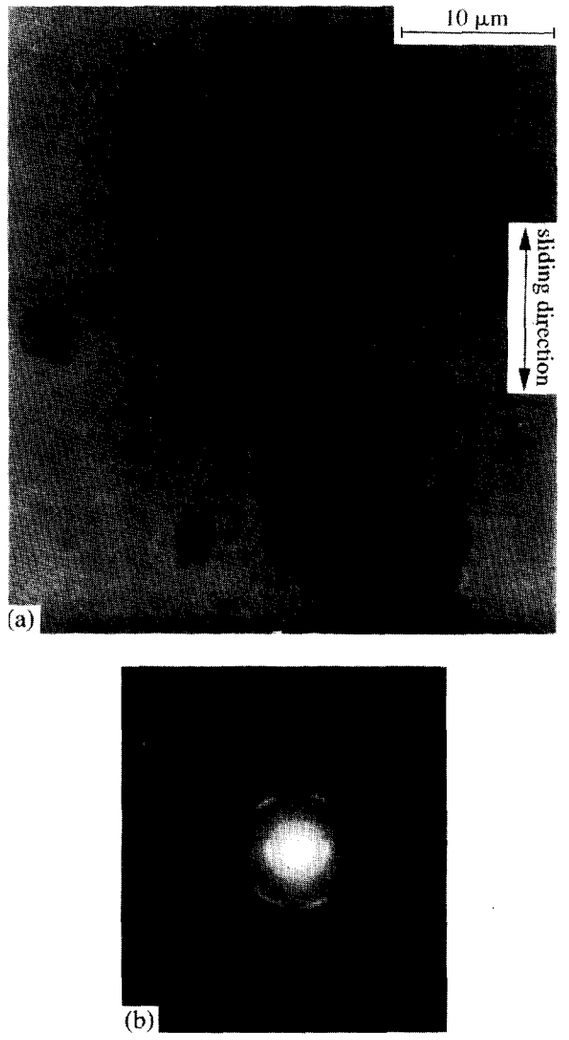

Figure 2 (a) Transmission electron micrograph; and (b) electron diffraction pattern of a PDMS film

Table 1 Features of friction-deposited PDMS films depending on substrate temperature

Temperature range (°C)	Appearance	Dichroic ratio	Peak position (nm)	Peak width (nm)
20–150	non-uniform	1.4–4.5	335–343	29–44
150–210	medium	11.3–11.5	344–346	23–24
210–235	uniform	∞	345–346	14–18

studied the anisotropy of the optical absorption of oriented poly(di-*n*-hexylsilylene), and they concluded from their experimental results and theoretical consideration that the transition moment of the lowest singlet exciton, associated with the σ–σ^* band-gap, lay along the *trans* planar Si backbone chain. Surprisingly, the friction-deposited PDMS films on quartz substrates at relatively high temperature, above about 210°C, were extremely oriented. The PDMS films showed very strong absorption at 345 nm for light polarized parallel to the sliding direction, while no absorption could be observed in the direction normal to it. The orientation of the PDMS film

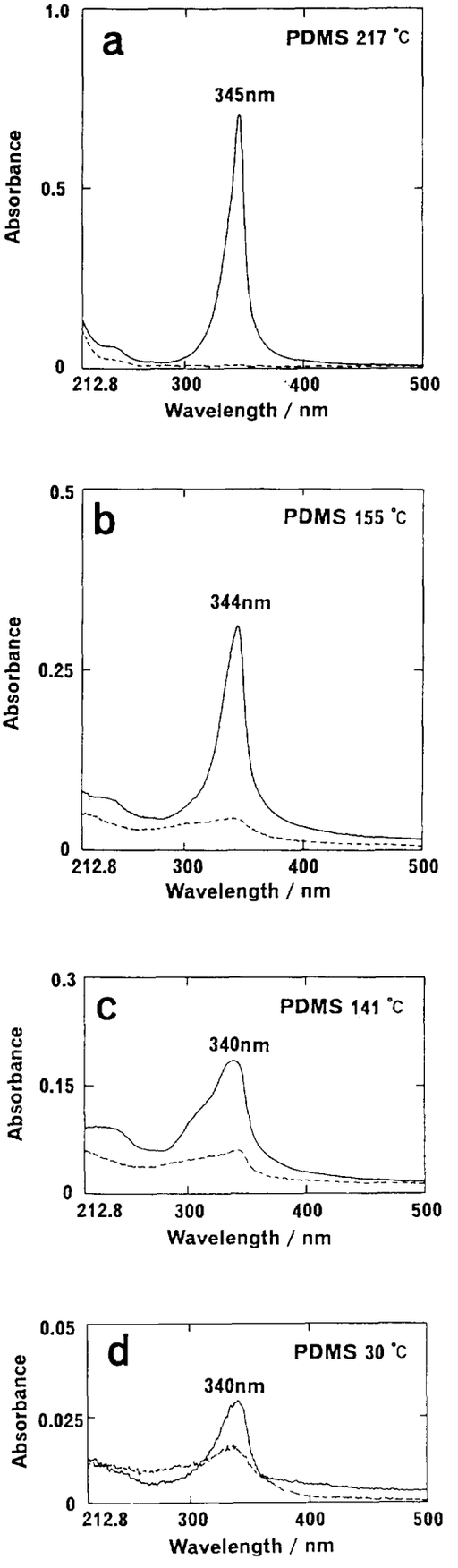

Figure 3 Polarized u.v. spectra of PDMS films on quartz substrates prepared at (a) 217 °C, (b) 155 °C, (c) 141 °C and (d) 30 °C

was dependent on the substrate temperature during deposition of the film. The higher the temperature, the higher the degree of orientation that could be obtained. In addition, the absorption peak was sharper and the wavelength at the absorption peak was slightly longer at the higher deposition temperature. *Table 1* briefly summarizes features of PDMS films and dependence of substrate temperature, which was obtained by u.v. measurement and microscopic observation.

Conclusion

We prepared highly oriented film of PDMS on a smooth substrate by the friction deposition technique. This method is very convenient and makes it possible to obtain oriented specimens from untractable polymers. Polarized u.v. spectroscopy and TEM observation confirmed that the PDMS chain aligned parallel to the sliding direction. The degree of orientation of the film was dependent upon the temperature of the substrate during deposition. A very highly oriented PDMS film could be obtained when it was deposited at more than 210 C.

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