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

Photocontrol of Poly(dihexylsilane) Chain Organization using a Photochromic Monolayer

K. Fukuda [a], T. Seki [a] & K. Ichimura [a]

[a] Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

Version of record first published: 24 Sep 2006

To cite this article: K. Fukuda, T. Seki & K. Ichimura (2000): Photocontrol of Poly(dihexylsilane) Chain Organization using a Photochromic Monolayer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 137-142

To link to this article: http://dx.doi.org/10.1080/10587250008023908

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 137-142
Reprints available directly from the publisher
Photocopying permitted by license only

Photocontrol of Poly(dihexylsilane) Chain Organization using a Photochromic Monolayer

K. FUKUDA, T. SEKI and K. ICHIMURA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226–8503, Japan

The in-plane orientation of a polysilane film on photochromic monolayer was controlled by irradiation with linearly polarized visible light. The polymer backbone was aligned in the perpendicular direction to the polarization plane of actinic light. In this photoprocess, the orientational order could be controlled by the light exposure dose.

Keywords: azobenzene; orientation; poly(dihexylsilane); photocontrol

INTRODUCTION

Control of polymer chain orientation in thin films is of technological importance since it is directly connected to physical properties, such as electrical, optical, and mechanical characteristics. Our recent interest has been directed to surface-mediated photochemical control of polymer main chain, which is anticipated to provide new opportunities in the polymer processing technology. Illumination of linearly polarized light (LPL) to surface polymer films involving the azobenzene (Az) units leads to induction of orientational anisotropy.[1] Attempts have been made to transfer this molecular information to the contacting polymer chains.

In this work, we used poly(dihexylsilane) (PDHS) as the polymeric material because the UV-vis absorption spectra of PDHS favorably provide us the information on both conformational and orientational state of the backbone due to the delocalization of σ-electron in the Si main chain. Our preliminary results show that the molecular orientation of the Az monolayer generated by LPL can be utilized for control of PDHS chain orientation.[2] This paper describes some detailed exploration on this new photoprocess.

EXPERIMENTAL

The chemical structures of materials and a schematic representation of the system are shown in FIGURE 1. A photochromic monolayer of Az-containing amphiphilic polymer (6Az10-PVA) was first transferred onto a quartz plate by the Langmuir-Blodgett (LB) method. The photochromic monolayer was irradiated with non-polarized UV

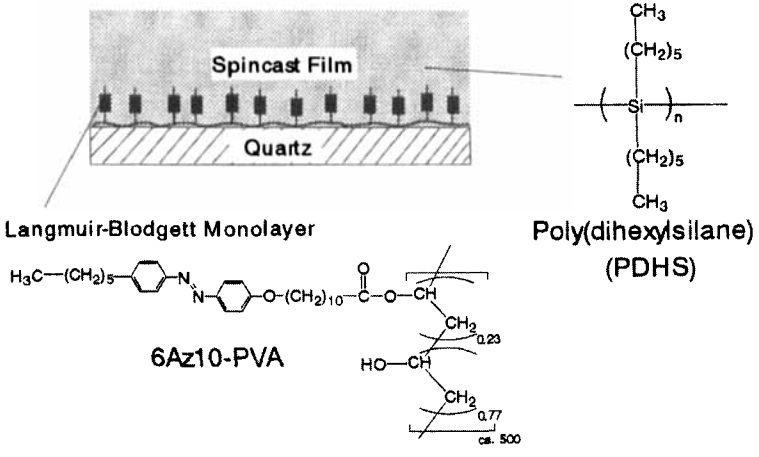

FIGURE 1 Schematic representation of PDHS spincast film on a photochromic azobenzene-containing monolayer.

light to enrich the cis photoisomer content and then with linearly polarized visible light. Subsequently, the spincast film of PDHS on the Az monolayer was obtained from a hexane solution (1 wt %).

UV-vis absorption spectra were taken on a Hewlett-Packard 8452A. For polarized spectra, a Glan-Thomson-type prism mounted on a rotatory holder was placed in front of the specimen. The light irradiation was performed with a 150 W Hg-Xe lamp (San-ei UV Supercure-230S) combined with optical filters for wavelength selection.

RESULTS AND DISCUSSION

Orientational control of PDHS chain

Like thermotropic liquid crystals[3-5] and chromonic dye aggregates,[6] the in-plane orientation of the PDHS main chain can be controlled by application of LPL. In this experiment, the Az monolayer was first irradiated with LPL. Exposure of polarized visible light to Az monolayer gave the alignment of Az moiety in perpendicular direction to the polarization plane of actinic light. Subsequently, PDHS spincast film was prepared on this pre-irradiated Az monolayer.

Before crystallization, the PDHS film had no optical anisotropy. In contrast, after sufficient crystallization at room temperature for a week, the PDHS film exhibited a highly in-plane anisotropic nature (FIGURE 2). The polarized absorption spectra revealed that the Si main chain is aligned perpendicular to the polarization plane of the irradiating light. This orientational direction agrees with that of Az monolayer. This fact indicates that the orientational information possessed by the Az monolayer is transferred to the PDHS films.

The orientational order of PDHS film was further enhanced

upon annealing. The order parameter, S [= (R-1)/(R+2), where R = Abs(90°)/Abs(0°)], evaluated for the ordered phase was 0.38 before annealing. The PDHS film was annealed at 100 °C for 3 h. The annealing procedure gave the complete transition to the conformationally disordered phase. In this case, the PDHS chain orientation was highly retained (S = 0.63). Subsequent cooling of this sample to room temperature gave an enhanced orientational order (S = 0.54) and higher crystallinity.

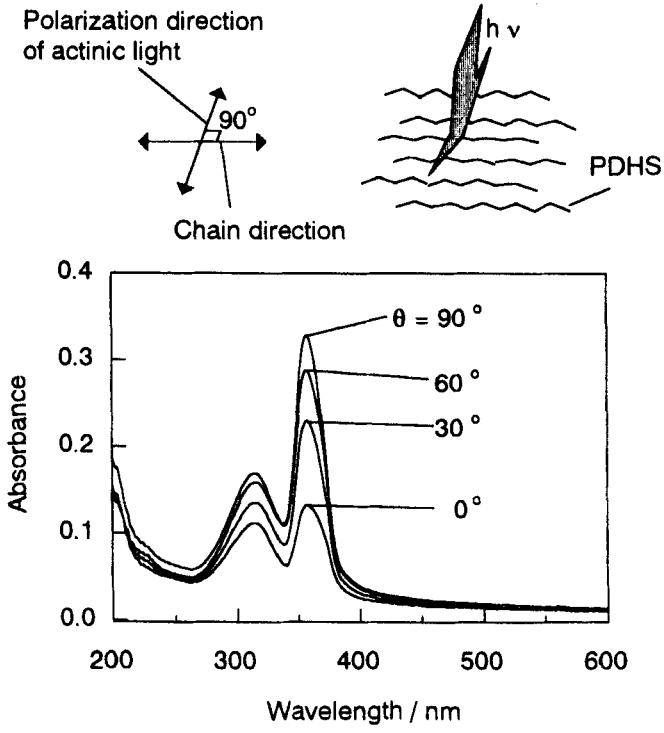

FIGURE 2 Polarized UV-visible spectra of PDHS film crystallized on the azobenzene monolayer irradiated with linearly polarized visible light. Probe beam was set at angle θ relative to the polarization direction of actinic light.

Effect of exposure energy to Az monolayer

The same procedure was achieved with changing the exposure energy to Az monolayer. FIGURE 3 shows the dichroic ratio (DR [= (R-1)/(R+1)]) of LPL-irradiated Az monolayer, and orientational order parameter (S) induced in PDHS films as a function of exposure energy. With increasing exposure energy, the anisotropy of Az monolayer became substantially greater. The order parameter of PDHS films moderately followed the orientational order of the Az monolayer. As the anisotropy of Az monolayers became larger, the order parameter of PDHS films increased accordingly. In these manners, the orientational order of PDHS chain could be controlled by the exposure dose of the LPL.

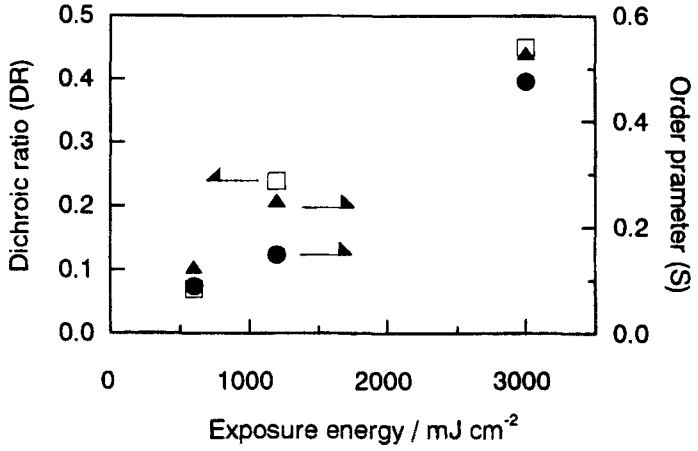

FIGURE 3 Dichroic ratio of Az monolayers (□) and order parameter of PDHS films after first (●) and second crystallization (▲) as a function of exposure energy. The film thickness of PDHS was 40 nm.

In the polymer films, the orienting behavior (orientational order parameter) may be affected by other factors such as molecular weight and film thickness. Further investigation is now underway for elucidation of such details.

Acknowledgements

We thank Drs. S. Morino, M. Nakagawa, and K. Arimitsu for technical assistance. This work was in part supported by the Grant-in-Aid Scientific Research on Priority Areas, "Molecular Synchronization for Design of New Materials System (No. 404/11167230)," from The Ministry of Education, Science, Sports and Culture Japan.

References

[1] T. Todorov, L. Nikolova, N. Tomova, *Appl. Opt.* **23,** 4309 (1984).
[2] T. Seki, K. Fukuda, K. Ichimura, *Langmuir* **15,** 5098 (1999).
[3] W. M. Gibbons, P. J. Shannon, S.-T. Sun, B. J. Swetlin, *Nature* **351,** 49 (1991).
[4] Y. Kawanishi, T. Tamaki, M. Sakuragi, T. Seki, Y. Suzuki, K. Ichimura, *Langmuir* **8,** 2601 (1992).
[5] M. Schadt, K. Schmitt, V. Kozinkov, V. Chigrinov, *Jpn. J. Appl. Phys.* **31,** 2155 (1992).
[6] K. Ichimura, M. Momose, K. Kudo, H. Akiyama, N. Ishizuki, *Langmuir* **11,** 2341 (1995).