

Structural Design of Azobenzene Monolayer for Orientational Control of Polysilane Chain

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The main chain orientation of poly(dihexylsilane) (PDHS) films on a photochromic monolayer was controlled by irradiation with linearly polarized visible light. PDHS chain aligned perpendicularly to the polarization plane of actinic light. The effect of tail length (alkyl chain) of azobenzene (Az) units and the packing density of Az units were studied to estimate the optimal design of the Az monolayer. The highest orientational order of PDHS was obtained for the Az monolayer having octyl tail at a lateral density of ca. 0.4 nm² per Az unit.

Key words: polysilane, azobenzene, orientational control, linearly polarized light

1. INTRODUCTION

Control of polymer chain in thin film is important in several technological applications because physical properties of the polymer depend on the orientation and conformation¹⁾. Polymer chain orientation of thin film is in general controlled by mechanical procedures such as rubbing²⁾, stretching³⁾, friction transfer⁴⁾ and Langmuir-Blodgett technique⁵⁻⁷⁾. The epitaxial process from oriented surfaces can be also used to control polymer chain. However, such method is far limited to inactive surfaces of inorganic crystals⁸⁾ or polymer surfaces⁸⁾⁻¹⁰⁾ modified mechanically by stretching, rubbing, and friction deposition at a macroscopic scale.

Our recent interest has been directed to surface-mediated photochemical control of polymer main chain since it allows active micro-patterned control which can be hardly achieved by mechanical procedures. Irradiation with linearly polarized light (LPL) to polymer films involving azobenzene (Az) units leads to orientational anisotropy of the Az moiety as a result of repeated photoisomerization¹¹⁾. The Az is aligned in perpendicular to the polarization plane of the actinic light. From the point of views, we examined the possibility of active epitaxial photocontrol of polymer chain using photochromic monolayer. Here, we used poly(dihexylsilane) (PDHS) as polymeric material because the UV-vis absorption spectra of PDHS provides information on both conformational state and orientational direction of the main chain.

Our preliminary result showed that the photocontrol of PDHS chain orientation can be performed by photochromic reaction of the surface monolayer^{12), 13)}. The Az monolayer was first exposed

to LPL and then PDHS was spin-casted on the pre-irradiated Az monolayer, resulting in surface-induced orientational anisotropy. In this work, we examined the effect of tail length (alkyl chain) of Az units and the packing density of Az units to estimate the optimal design of the Az monolayer in this process.

2. EXPERIMENTAL

The chemical structures of the materials and a schematic representation of the system are shown in Fig. 1. A mAz10-PVA (m = 2, 4, 6, 7, 8, and 10) monolayer was formed on a trough (LAUDA, FW-II) filled with pure water (Milli-Q) at 20 °C by spreading a chloroform solution (1 x 10⁻³ mol dm⁻³) which was pre-irradiated with UV light (365 nm) for 5 min. This monolayer was transferred onto a quartz substrate at a constant pressure, which provides a target molecular area, by the standard vertical dipping method (transfer ratio was ca.0.9±0.5). The deposited monolayer was stored in the dark over four days under dry atmosphere, which allowed a complete thermal conversion to the trans form of Az.

The mAz10-PVA film was then irradiated with non-polarized 365 nm light (0.3 J cm⁻²) to enrich the cis-Az content and successively with linearly polarized 436 nm light (3.0 J cm⁻²). Films of PDHS (Mw = 2.3 x 10⁴, Mw / Mn = 2.7) were prepared by spincoating from a hexane solution on the top of the monolayer. The thickness of the films were 45±3 nm. The PDHS films were kept in the dark at room temperature for two days, annealed at 100 °C for 1h, and then cooled down to room temperature. The light irradiation was performed with a 150 W Hg-Xe lamp (San-ei UV supercure-230S)

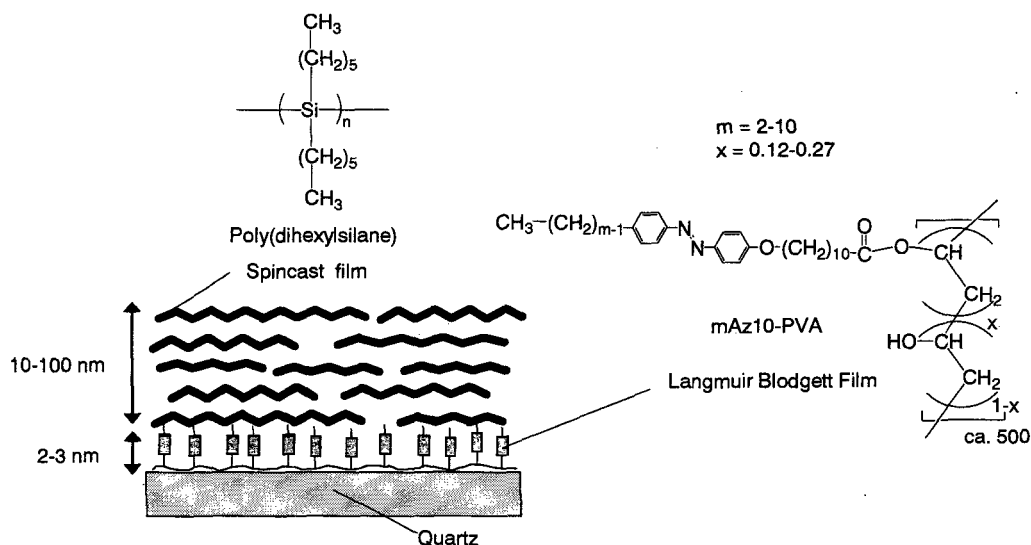


Fig. 1. Schematic representation of the system in this work. A spincast film of PDHS is placed on a photochromic azobenzene-containing LB monolayer.

combined with optical filters for wavelength selection (Toshiba optical filters UV-35 / UV-D36A for 365 nm illumination, and Y-44 / V-42 for 436 nm illumination).

UV-visible absorption spectra were taken on a Hewlett Packard diode array spectrometer.

3. RESULTS AND DISCUSSION

3.1 PDHS CHAIN ORIENTATION BY LPL

Figure 2 shows the polarized absorption spectra of PDHS film on the pre-irradiated Az monolayer under different conditions. The PDHS film had no optical anisotropy before crystallization (Fig. 2, a). In contrast, the film exhibited a high in-plane anisotropy after sufficient crystallization (2 days) at room temperature (Fig. 2 b). The polarized absorption spectra revealed that the Si main chain is aligned perpendicularly to the polarization plane of the actinic light. The orientational direction is in agreement with that of Az moiety. This fact indicates that the epitaxial crystallization of PDHS main chain was achieved on the anisotropic Az monolayer.

The orientational order of PDHS film was further enhanced upon annealing. The order parameter, S [$= (R-1)/(R+2)$, where $R = \text{Abs}(90^\circ)/\text{Abs}(0^\circ)$], evaluated for the ordered phase was 0.38 before annealing. After annealing at 100 °C for 3 h, the intensity of the peak around 316 nm, which corresponds to disordered phase, increased and the peak around 360 nm disappeared¹⁴. The annealing procedure gave a complete transition to the conformationally disordered phase. In this case, the PDHS chain orientation was retained at the high level ($S = 0.63$). Subsequent cooling of this sample to room

temperature maintained the orientational order ($S = 0.54$) and gave higher crystallinity. Lovinger et al reported that the lateral packing correlation of the disordered part was improved with heating³. Our results also confirm that the reorientation of PDHS main chain was achieved on annealing procedure.

3.2 THE EFFECT OF PACKING DENSITY

The 6Az10-PVA monolayers were prepared at various occupying areas (A_{oc}) ranging from 0.30 to 1.20 nm² per Az unit by the Langmuir-Blodgett method¹⁵. The behavior of polysilane main chain orientation was investigated using these precisely area-controlled Az monolayers. Figure 3 shows the dichroic ratio (DR) of Az monolayers and the order parameter (S) of PDHS films on the Az monolayers as a function of A_{oc} . As shown, the photoinduced orientational order in the Az monolayer was strongly dependent on A_{oc} . When the packing density of Az was ca. 0.4 nm², the photoinduced orientational order of Az monolayer became maximum value. With decreasing A_{oc} , λ_{max} ($\pi-\pi^*$ long axis) of 6Az10-PVA deposited film showed blue shifts. These results indicate that smaller A_{oc} promotes the formation of a side-by-side aggregation (H-aggregation). Therefore, the photoinduced anisotropy can be related to the formation of H-aggregation of Az moieties. However, under the most densely packed condition, a decrease in the orientational order was observed. The DR values at $A_{oc} = 0.4$ and $0.3 \text{ nm}^2 \text{ Az}^{-1}$ were 0.42 and 0.35, respectively. Probably, such a decrease in the DR arises from reduced motional freedom of Az moieties restricted in a densely packed state. The same tendency was also observed for the dependence of tail

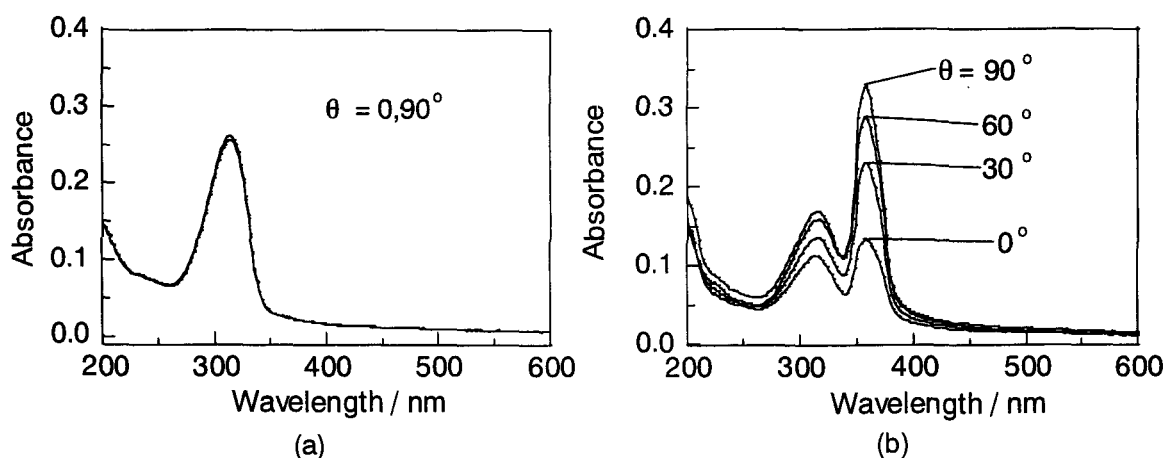


Fig. 2. Polarized absorption spectra of the PDHS film on the pre-irradiated 6Az10-PVA monolayer ($r = 0.23$). The spectra were taken as-spincasting (a) and after sufficient crystallization (b).

length (see next section).

The profile of the order parameter of PDHS films (S) on these Az monolayers almost exactly followed the DR of Az monolayers. These results indicated that the in-plane orientational order of Az critically governs the orientational order of the PDHS film. In other words,

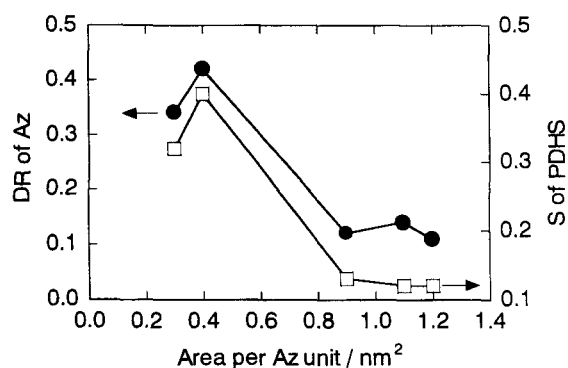


Fig. 3. The DR of 6Az10-PVA monolayers ($r = 0.23$) and the S of PDHS films on the Az monolayers as a function of A_{oc} .

the information of LPL inscribed to the Az monolayer is precisely transferred onto the polymer chain orientation.

3.3 THE EFFECT OF TAIL LENGTH

Since the Az monolayer is anchored to the hydrophilic substrate surface via the polar PVA backbone, PDHS should interact directly with the outermost tail part of the Az moiety. In this context, spincast PDHS films were prepared on the Az monolayers having varied tail length. In this series of experiments, the A_{oc} was fixed at ca. 0.40 nm^2 .

Figure 4 shows the DR of the Az monolayers and the order parameter (S) of PDHS film as a function of tail length. As obviously shown, the photoinduced anisotropy of Az monolayers showed maximum value for the Az monolayer having an octyl tail.

Here, the magnitude of the DR changing with the tail length could be related to the shift of λ_{max} . The monolayers providing larger DR gave λ_{max} at shorter wavelength. Thus, the larger in-plane anisotropy was obtained for the films providing the side-by-side Az aggregation, implying that the molecular cooperatively among the Az side chains plays an important role.

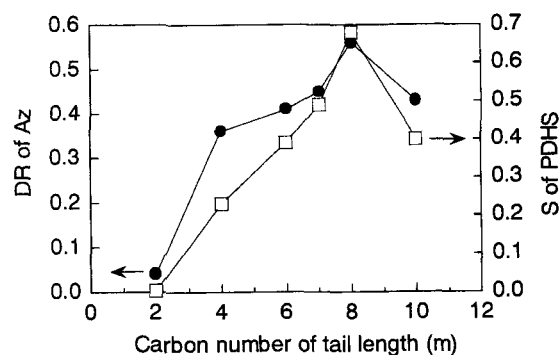


Fig. 4. The DR of Az monolayers and the S of PDHS films on the Az monolayers as a function of tail length.

The orientational order parameter of PDHS was also enhanced in a parallel fashion with the change in the DR of the Az monolayer. It is obvious that the change in the tail length influenced the packing state of Az, and the most profitable results were obtained for 8Az10-PVA monolayer.

4. CONCLUSIONS

In this work, efforts were made to optimize the design of Az monolayers. The largest orientational order of PDHS was obtained at lateral Az density of 0.4 nm². The effect of tail length showed that the octyl tail led to the most efficient orientational control. We anticipate that other types of polymer chains can also be orientated by light using such Az monolayers. The knowledge obtained here should pave effective ways in the extensions of this research.

5. REFERENCES

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