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Phototriggered Mass Migration Consorted with Surface Dewetting in Thin Films of a Liquid Crystalline Azobenzene-containing Dendrimer

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ABSTRACT: A dendritic molecule of poly(propylene imine) whose periphery is modified with photoresponsive mesogenic azobenzene units was synthesized. This compound exhibited highly ordered smectic B or smectic A layer structure orienting parallel to the substrate in the film state. When this film of 90 nm thickness on a hydrophilic substrate was exposed to UV (365 nm) light, the initial flat film morphology started to form holes followed by a drastic transformation to form separated dome structure of micrometer levels. Upon continuous UV light irradiation, the domain height increased and reached to a level of ca. 8-fold higher than that of the initial thickness, which can be correlated with the disordering of layer structures as revealed by grazing angle incidence X-ray diffraction measurements. This phototriggered dewetting behavior depended on the film thickness. The thinner film resulted in local migrations to form the smaller and more homogeneous domes. The dewetting was observed below a threshold thickness of 100 nm. By UV light irradiation through a photomask, phototriggered migration at micrometer distances also occurred. By the combination of phototriggered migration and concerted dewetting, characteristic hierarchical morphologies were formed, depending on the initial film thickness. This work proposes a new possibility to control and design the dewetting processes of thin films using the dendritic material.

1. INTRODUCTION

Various types of molecular architectures are available in liquid crystalline (LC) polymers.^{1,2} Among them LC dendrimers have been attracted great attention to elucidate effects of the highly and regularly branched chain topology on the aggregation states and LC nature.¹⁻⁴ Due to their well-defined chemical architecture, introduction of photoresponsive and photoreactive units have also been a subject of great interest.^{2,5} Dendrimers possessing photochromic azobenzene (Az) unit(s) have already been extensively explored. The Az unit can be

introduced to interior⁶⁻¹¹ or exterior^{9,12-21} of the dendritic skeleton. For LC studies, the exterior type (peripherally modified) dendrimers are mostly investigated.

On the other hand, since the discovery in 1995,^{22,23} the phenomenon of photoinduced mass migration in Az-containing polymer films, leading to the surface relief formation, has been a

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major stream of research for both chemists and physicists. At the early stage of research, the systems are mostly limited to amorphous Az-containing polymer films,^{22–26} however, recent activities have been rapidly accumulating new knowledge, expanding to other types of materials including amorphous low-molecular-mass compounds^{27,28} and the surface of molecular crystals.²⁹

In regard to photoinduced mass migration of dendiritic materials, several investigations have been reported for various types of branching architecture. Archut et al.¹⁴ first reported the surface grating formation of thin films of dendritic molecules containing Az units in the periphery by holographic irradiation with laser beam. They found that the dendrimer generation and attached position of Az influence the photoinduced migration. Gharagozloo-Hubmann et al.³⁰ discussed the effect of main chain branching (linear or star-branched polymers of different number of arms) on the surface relief grating formation. In this case, little effect was admitted for the extent of main chain branching. Galgano et al.³¹ explored a series of Az-containing polyester possessing dendrons in the side chain. The generation of the dendrons affected the mass migration behavior. As the relating process, photoinduced optical anisotropy (photoorientation of Az) by irradiation with linearly polarized light was also investigated for Az-containing dendrimers by Bobrovsky et al.,^{20,21} and block copolymers containing a dendritic Az block by del Barrio et al.³

Our work has been focusing onto LC Az-polymer materials that show highly sensitive phototriggered mass migrating systems.^{33–38} The mass migration is completed at uncommonly small dose levels (<100 mJ cm⁻²), which is 3 orders of magnitude smaller than those required for conventional amorphous polymer films. Here the Az unit providing a long lifetime of cis-isomer is employed, and thus the photoirradiation with UV (365 nm) light leads to the smectic LC to isotropic phase transition.^{35–37} The mass transport in the LC polymers occurs at boundary areas between the smectic LC and isotropic phases. Probably, the disparity in the viscosity and surface tension at the boundaries promote the mass transfer. Basically such migrating motions are explained as a thermally driven self-assembly process of the LC materials.

To date, such phototriggered mass migrations of LC materials have been achieved only for linear polymers.³³⁻³⁷ We expected that the dendritic scaffold of constituting material in the thin film would exhibit some characteristic effects in phototriggered migrating behavior, because it has been pointed out that the dendritic topology eliminates chain entanglement and interlacing with the neighboring molecules.^{39,40} Yonetake et al.41 synthesized and evaluated the LC properties of poly(propylene imine) dendrimers peripherally modified with cyanobiphenyl mesogens. The Az dendrimer employed in the present study adopts the identical scaffold of this dendrimer with the second generation (G2) (16 mesogens). The chemical structure of this molecule is indicated in Scheme 1 (AzD6). In thin films of this dendritic molecule, we found the UV (365 nm) light irradiation induces both dewetting⁴² and mass migration on a hydrophilic substrate under proper conditions. We report herein a new aspect of phototriggered mass transport consorted with photoinduced surface dewetting to form hierarchical surface morphologies by single patterned irradiation. With regard to photoinduced surface dewetting, Cristofolini et al.43 reported a thickness dependent photoinduced dewetting on a hydrophobic surface using linear Azcontaining polyacrylate Langmuir-Blodgett films. This work





proposes a new possibility to engineer morphologies in thin films through the phototriggered mass migration and surface dewetting by employing the dendritic scaffold.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(propylene imine) dendrimer (G2) was purchased from Aldrich and used as received. Other reagents and solvents were obtained commercially. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl just before use.

4-(4'-Hexylphenylazo)phenol. To a solution of hexylaniline (7.3 mL, 37 mmol) and concentrated hydrochloric acid (20 mdm³), aqueous solution (25 mdm³) and NaNO₂ (4.2 g, 62 mmol) was added to the resulting a blue solution. Aqueous solution (25 mL) and NaOH (3.0 g, 21 mmol) and phenol (8.2 g, 37 mmol) were then added. Into this solution, concentrated hydrogen chloride was added dropwise until the solution became acidic. After stirring for 3 h at 10 $^{\circ}$ C, the resulting precipitate was filtered, washed with water, and dissolved in diethyl ether (100 m dm³). The etheral solution was washed with water, dried over anhydrous MgSO4, and concentrated under reduced pressure. The residue was recrystallized from hexane to give a brown powder. Yield: 4.6 g (16.4 mol, 44.2%). ¹H NMR (CDCl₃, 270 MHz): δ (ppm) = 6.63-7.88 (s, 8H, ArH), 5.0 (1H, OH), 2.55 (t, 2H, PhCH2), 1.29–1.62 (m, 8H, CH₂), 0.96 (t, 3H, AlkylCH₃). IR (KBr): ν (cm⁻¹) = 1465 (Ph), 1589 (Ph), 2854 (CH₂), 2954 (CH₂), 3409 (OH).

6-[4-(4-Hexylphenylazo)phenoxy]hexanol. A solution containing 4-(4'-hexylphenylazo)phenol (5.5 g, 20 mmol), 6-bromo-1-hexanol (3.1 mdm³, 20 mmol), and KOH (1.1 g, 20 mmol) in ethanol (30 mdm³) was stirred under reflux for 12 h under nitrogen. The solvent was evaporated, and the residue extracted with diethyl ether. The organic layer was washed with water, dried over anhydrous MgSO₄ and concentrated. The resulting solid was recrystallized from hexane to give a glossy yellow crystal. Yield: 4.32 g (11 mmol, 57.9%) ¹H NMR (CDCl3, 270 MHz): δ (ppm) = 0.96 (t, 3H, alkyl CH₃), 1.29- 1.71 (m, 16H, CH₂), 2.55 (t, 2H, PhCH₂), 3.65 (2H, CH₂OH), 4.0 (2H, OCH₂), 6.97–7.88 (s, 8H, ArH). IR (KBr): ν (cm⁻¹) = 1249 (Ph– O–), 1465 (Ph), 1604 (Ph), 2854 (CH₂), 2931 (CH₂), 3262 (OH), 3332 (OH).



Figure 1. Characterizations of AzD6 and its film: (a) DSC profiles, (b) POM image at room temperature, (c) X-ray diffraction patterns for a bulk sample at various temperatures, (d) GI-XRD 2D pattern taken on a imaging plate, and (e) molecular conformation model of AzD6 in a thin film. The picture is drawn as a fully extended state.

4-(6-Acryloxyhexyloxy)-4'-hexylazobenzene. To a solution containing 6-[4-(4-hexylphenylazo)-phenoxy]-hexanol (5.4 g, 14 mmol) and triethylamine in 2-butanone, a solution of acryloyl chloride (1.2 mdm³, 14 mmol) in 2-butanone (20 mdm³) was added dropwise at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was concentrated and extracted with diethyl ether. The organic layer was washed with water, dried over anhydrous MgSO4 and concentrated under reduced pressure. The residue was recrystallized from hexane to give a yellow powder. Yield: 4.0 g (9.2 mol, 65%). ¹H NMR(CDCl3, 270 MHz): δ (ppm) = 0.96 (t, 3H, alkyl CH₃), 1.29-1.71 (m, 16H, CH₂), 2.55 (t, 2H, PhCH₂), 4.15 (t, 2H, COOCH₂), 3.94 (t, 2H, PhOCH₂), 5.83 (dd, 1H, =CH), 6.13(dd, 1H, =CH₂= CH-), 6.41 (dd, 1H, =CH), 6.67-7.88 (s, 8H, ArH). IR (KBr): ν (cm⁻¹) = 840 (C=C), 1010 (C-O-C) 1211 (Ph-O-), 1465 (Ph), 1604 (Ph), 1720 (C=O), 2861 (CH₂), 2931 (CH2). Anal. Calcd for C₂₇H₃₆N₂O₃: C, 74.28; H, 8.31; N, 6.42. Found: C, 74.48; H, 8.62; N, 6.35.

Az Dendrimer (AzD6). Synthesis of the Az dendrimer was undertaken in a similar manner as described previously.⁴¹ Into a solution of poly(propylenimine) dendrimer (G2) (0.039 g, 0.51 mmol) in THF (5 mdm³), a solution of 4-(6-acryloxyhexyloxy)-4'hexylazobenzene (4.9 g, 11.2 mmol) in THF (5.0 mdm³) was added. The resulting solution was stirred at 45 °C for 2 week under nitrogen and then poured into 500 mdm3 of hexane. The precipitate was collected by filtration, and the obtained powder was purified by reprecipitation by pouring THF solution into hexane. Yield 3.90 g (0. 50 mol, 98.8%) ¹H NMR (CDCl₃, 270 MHz): δ (ppm) = 0.96 (t, 48H, alkyl CH₃), 1.29-1.71 (m, 304H, CH₂), 2.35 (t, 32H, CH₂C= O), 2.36 (t, 52H, CH₂-N), 2.55 (t, 32H, CH₂Ph), 2.75 (m, 32H, CH₂CH₂C=O), 3.94 (t, 32H, PhCH₂O), 4.08 (t, 32H, COOCH₂), 6.97–7.88 (s, 128H, ArH). IR (KBr): ν (cm⁻¹) = 840 (C=C), 1010 (C-O-C) 1249 (Ph-O-), 1465 (Ph), 1604 (Ph), 1735 (C=O), 2854 (CH₂), 2931 (CH₂). Anal, Calcd. for C₄₇₂H₆₇₂N₄₆O₄₈: C, 73.07; H, 8.73; N, 8.30. Found: C, 71.54; H, 9.50; N, 8.47.

Poly[4-(6-methacryloxyhexyloxy)-4'-pentylazobenzene] (**PAZMA**). 4-(6-Methacryloxyhexyloxy)-4'-pentylazobenzene and its polymerized material (M_n = 7400) was synthesized by atom transfer radical polymerization in a similar manner as described previously.^{44,45}

2.2. Methods. Measurements. Optical textures of the samples were examined using the polarizing optical microscope (POM) equipped with a hot stage (Linkam Co. TH-600RMS) under nitrogen. Transmission X-ray diffraction (XRD) experiments were carried out by a MiroMax007 diffractometer (Rigaku Denki Co. Ltd.) operated at 40 kV and 20 mA. Cu K α X-ray beams monochromatized with a confocal mirror were shone onto the specimen through a pinhole collimator of 0.2 mm in diameter. The imaging plate $\tilde{R}\text{-}A\tilde{XIS}\ IV^{+2}$ system was utilized as an X-ray detector at a camera length of 150 mm. Grazing incidence angle X-ray diffraction (GI-XRD) measurements were operated with a FR-E X-ray diffractometer (Rigaku Corp.) detected by a R-AXIS IV two-dimensional detector using the imaging plate Rigaku Corp.). The incident angles of X-ray beam to the films were set at 0.18-0.22° by using pulse controllers ATS-C310-EM and ALV-300-HM (Chuo Precession Industrial). 0.3-mm collimated Cu K α radiation was used as X-ray beam and camera length was set at 300 mm. Differential scanning calorimeter (DSC) was carried out on a DSC Q20 MO-DSC-UV under helium purging gas (0.11 MPa) at a heating/cooling rate of 2 °C min⁻¹. The morphology of all films was observed by an atomic force microscope (Nanopics 2100, Seiko instruments) using the damping mode. Original film thickness was also obtained using the same AFM instrument by creating and measuring a scratch on the film. UV-vis absorption spectra were taken on an Agilent 8453 diode array spectrometer.

Film Preparation. Quartz substrates were first immersed in a KOH-methanol mixture for several days, washed with deionized water several times and finally cleaned by ultrasonic treatment for 15 min while immersing in deionized water. The contact angle for water was below 10° . Films were formed on the hydrophilic quartz substrates from chloroform solutions of AzD6 by spin-coating method. The spinning speed was 3000 rpm. All procedures were carried out at room temperature. The initial thickness was obtained under AFM by scratching method for all samples. All films were prepared on hydrophilic substrates. Freshly prepared films are subjected to light irradiation experiments.

Light Irradiation. Light irradiation was performed with a Xe–Hg UV lamp, (Sanei-200S) made by San-ei Electric through a combination of optical filters to select 365 nm line at room

temperature. Unless stated otherwise, nonpolarized light was used. Incident light intensity was adjusted to 5 mW cm⁻². The photomask used for SRG formation of all the samples was a stipe patterned photo mask with a line and space pattern of 10 μ m width.

3. RESULTS AND DISCUSSION

3.1. Structural Characterizations of AzD6. Figure 1a depicts DSC profiles of AzD6 on the heating and cooling processes. A glass transition temperature was observed at -5° C in the heating scan and additional two endothermal peak was observed at 34 °C ($\Delta H = 0.26 \text{ J g}^{-1}$) and 85 °C ($\Delta H = 12.0 \text{ J g}^{-1}$). T_g was observed at nearly the same temperature as for a dendrimer possessing cyanobiphenyl mesogens in the periphery.⁴¹ Below 85 °C, a POM observation exhibited a birefringent character of smectic liquid crystalline phase as indicated by a focal conic fan texture (Figure 1b). Above 85 °C, this compound became isotropic to give a dark field in the POM observation. In the cooling process, the peaks were observed at slightly lowered temperatures by ca. 1 °C. In this way, the thermal transitions showed only a very small hysteresis effect.

X-ray diffraction 2θ profiles obtained with transmission beam along the radial direction at various temperatures were displayed in Figure 1c. In the small angle region, a sharp diffraction peak at $2\theta = 2.60^{\circ}$ (layer spacing, d = 3.4 nm) was observed up to 80 °C, showing the existence of a smectic layer structure. This intense peak corresponds to the second order diffraction (n = 2) because a less intense peak assignable to n =1 (d = 6.7 nm) was observed in the smaller angle region. This layer spacing of 6.7 nm is comparable to the length when each half of the dendrimer is stretched as shown in Figure 1e (7.8 nm). The smaller value of the actual layer spacing should show the involvement of gauche conformations with some interdigitation between the terminal substituent of hexyl group of aggregated Az units. Thus, the POM observation and X-ray analysis imply the formation of a smectic B or A phase. The diffraction peak in the wide angle region below 30 °C became sharper, indicative of formation of a more ordered packing structure, most likely the smectic B phase.⁴⁶ XRD measurements in the wider angle region showed that the mesogen-to-mesogen distance is 0.43 nm, which well coincides with that for the homologous dendrimer with cyanobiphenyl mesogens (0.45 nm).⁴¹

GI-XRD was performed for the film (film thickness = 200 nm) to elucidate the orientation of smectic layer structure in the trans-Az form (d). Clear diffraction spots attributed to the half length of smectic layer (d/2 = 3.5 nm) was observed only in the out-of-plane direction in the imaging plate, showing the formation of highly ordered multilayered layer structure orienting parallel to the substrate surface. The existence of duplicated spots is due to a superposition of diffracted beams on the film and substrate surfaces. The layer spacing was slightly increased in the thin film state, which suggests that a more stretched conformation is adopted in the thin film state.

Figure 2 shows UV-visible absorption spectra of AzD6 in chloroform (dash-dotted line), and of a spincast film with 30 nm thickness before (solid line) and after (dash line) UV exposure. The absorption peak of the π - π * long-axis transition of Az in chloroform was positioned at 360 nm, while that of the spincast film exhibited a large hyprochromic shift to 320 nm. This fact indicates that the Az units form a strong side-by-side aggregation in the spincast thin film. The π - π * long-axis transition of Az around 340 nm was considerably small



Figure 2. UV-visible absorption spectra of AzD6 taken in chloroform solution (dashed line), as-cast film of 30 nm thickness (dotted line) and after UV irradiation (solid line).

compared to that of the $\pi - \pi^*$ transition of phenyl (244 nm) band. The ratio of $A_{\pi - \pi^*}(Az)/A_{\pi - \pi^*}(phenyl)$ in the spin-cast film was ca. 0.4. This spectral feature indicates that the trans-Az units are oriented mostly perpendicular to their substrate plane as observed for linear polymer systems.^{35,37,47} After UV irradiation to the film, the $n - \pi^*$ transition around 450 nm band became distinct due to the photoisomerization to the cisform. The absorbance of $\pi - \pi^*$ band also became larger, which is ascribed to the orientational randomization of Az. After UV irradiation, the film became slightly opaque, which is reflected by an uprise in the baseline particularly at shorter wavelengths. The increased light scattering is ascribed to a surface dewetting of the film as mentioned in more detail later.

In all aspects of structural characterizations, the AzD6 thin film adopts highly ordered layer structure orienting parallel to the substrate surface, Az mesogens directing normal to the surface. Such packing and orientation feature is very similar to that observed for relating linear polymers hitherto investigated.^{34–37}

3.2. Photoinduced Dewetting. On the basis of the structural feature of AzD6 film, highly sensitive mass migrations upon patterned light irradiation were anticipated to take place.^{34–38} The massive migration actually occurred, however we noticed that unexpected surface morphologies were obtained consequently. The resulting surface morphologies did not reflect simply the photomask patterns, but finer sub structures within the photopatterning experiments, photoirradiation with uniform 365 nm light without a photomask was conducted.

Figure 3 shows optical microscopic observations of film morphology of thin films (initial thickness = ca. 20 nm) of AzD6 (molecular mass = 7753) (b) and a linear polymer of almost identical molecular mass (**PAzMA**, $M_{\rm p}$ = ca. 7400) (a) on a hydrophilic surface after irradiation with UV light at 500 mJ cm^{-2} . The film of the linear polymer exhibited no morphological change (a). By contrast, for the dendritic compound of AzD6, the film showed marked morphological change (b). Together with the observed morphology by AFM (c), the morphological change can be recognized as the surface dewetting providing a number of separated domains of a few micrometers. We assume that this marked difference arise from the chain topology. It is likely that the reduced interchain interactions for AzD6 effectively lower the film viscosity. The thermophysical properties should be also taken into account. Unfortunately, we were not able to correctly determine the $T_{\rm g}$ of PAzMA due to a lack of enough accuracy in the DSC



Figure 3. Optical microscopic images of films (initial thickness =20 nm) after irradiation with UV light of **PAzMA** (a) and **AzD6** (b), and topographical AFM image of AzD6 (c).

measurement. However, the comparisons of the two materials should make sense because they possess almost identical side Az mesogenic groups with essentially the same molecular mass. The photoinduced dewetting behavior was examined for a AzD6 film (thickness = 50 nm) both on a clean hydrophilic quartz surface and a hydrophobic quartz surface modified by exposure to a vapor of 1,1,1,3,3,3-hexamethyldisilazane for 3 days (contact angle of water = 92°). With the hydrophobic surface, this dendrimer film exhibited no dewetting behavior upon UV light irradiation. Thus, the present work will be focused on the explorations with the hydrophilic surfaces.

Figure 4 shows the topographical AFM images ($100 \ \mu m \times 100 \ \mu m$) observed in the photoinduced dewetting process of an **AzD6** films with initial thickness of 90 nm. Without UV irradiation, the film was highly flat and did not show any morphological change at least for a month at room temperature. Upon UV irradiation, the film exhibited drastic morphological changes. The initial highly flat state (0 mJ

 cm^{-2}) started to exhibit dewetting at 150 mJ cm^{-2} . At this stage, holes of $3-5 \ \mu m$ diameter with the film depth were formed. At 175 mJ cm⁻² irradiation, the holes grew to ca. 10 μ m diameter and started to coalesce with each other. At the same time the film became highly corrugated. Around 200 mJ cm^{-2} , the continuous film became separated and the morphology was characterized by formation of separated dome structures (see AFM image of 225 mJ cm^{-2}). The domes possessed round bottoms of diameters of several micrometers and this basal bottom did not virtually changed in shape upon further irradiation. Interestingly, the prolonged irradiation led to significant growth of dome height. When UV dose reached 400 mJ cm⁻², the average height of domes reached 770 nm, which corresponds, to our surprise, to ca. 8fold of the initial thickness. At this stage, the height growth ceased and the morphology and the height of domes remained unchanged even at further energy dose up to 600 mJ cm^{-2} . The shape change of the domes displayed a characteristic tendency. At earlier stages, most of the domes possessed a flat top (see AFM image at 225 mJ cm⁻²). Along with UV irradiation, the flat tops were mostly lost and characterized by a smooth droplet structure (see AFM image at 400 mJ cm^{-2}). The flat top should reflect that the domes are constituted with smectic layers orienting parallel to the substrate. In Figure 5, the average height difference in the AFM profiles is plotted against the light energy dose. As obviously indicated, the profile exhibited a sigmoidal shape, suggesting that the height growth proceeds in a highly cooperative manner. The starting point of the height growth around 170–180 mJ cm⁻² corresponds to the change in the morphological feature from the initial hole formation to the successive dome growth. The extent of surface dewetting is time dependent in general. Thus the data shown in Figures 4 and 5 are expected to be changed by the time required for the experimental procedures. However, we obtained reproducible results as far as the irradiation time is adjusted. This fact means that the pure motions in the dark are negligible at room temperature in the time scale of experimental procedures within a few hours, and that plotting versus irradiation dose in Figure 5 instead of irradiation time makes sense. It is further deduced that the dewetting motions are effectively driven only by light. The molecular motion of repeated back and forth isomerization of Az during the UV irradiation or local molecular heating via radiationless relaxation could activate the motions.

The smectic layer structure of an AzD6 film with 200 nm thickness at each stage of UV irradiation was evaluated by GI-XRD measurements. Figure 6a shows changes in the 2D profile taken by the imaging plate with increase in the UV irradiation dose. Initially a strong diffraction at $2\theta = 2.6^{\circ} (d/2 = 3.5 \text{ nm})$ was observed in the out-of-plane direction. The intensity of this diffraction peak reduced along with UV irradiation without changing the diffraction spot position, indicating that disordering of the layer structure proceeded with retention of the spacing length. The diffraction intensity at the peak was monitored and plotted in Figure 6b. The peak intensity immediately reduced after the initiation of UV irradiation up to ca. 150 mJ cm⁻². Beyond this stage, the peak intensity decreased gradually in the range 200-800 mJ cm⁻². At 800 mJ cm^{-2} , the peak intensity became considerably weakened but not fully diminished.

These GI-XRD data can be correlated with the photodinduced dewetting and dome formation processes shown in Figures 4 and 5. At the earlier stage less than ca. 200 mJ cm⁻²



Figure 4. Topographical AFM images of AzD6 film (initial thickness =90 nm) after irradiation with UV light at different periods (intensity 5 mW cm^{-2}). The irradiated energy doses are indicated on the top in the each figure.

irradiation, the dewetting behavior can be characterized by formation of holes and their growth in the 2D plane directions. After this threshold amount of irradiation, the film is separated to form domes and successive 3D growth (height increase) proceeds. Judging from the GI-XRD data, the dome formation becomes predominant after considerable disordering of the layer structure at ca. 200 mJ cm⁻² (corresponding to one tenth of the initial peak intensity in the profile of Figure 6) is involved. Most probably, the viscosity is highly lowered around this threshold stage. A loose layer structure is still involved at later stages, as shown by the retention of the X-ray diffraction spot. We assume that the tendency to form piled-up layer structure is responsible for the height growth. As will be stated later, the film of 200 nm subjected to GI-XRD measurements did not exhibit dewetting. This thicker film was used for a requirement to obtain higher quality data. Nevertheless, we consider that the comparisons of the morphology feature with the X-ray data is meaningful because sufficient photon doses are provided to induce the trans-to-cis photoisomerization of Az for both films of 90 and 200 nm thicknesses used for AFM and X-ray measurements, respectively.

Irradiation with linearly polarized UV light was further attempted to perform angular selective excitation in an expectation to induce an anisotropic dewetting. In this procedure, however, the anisotropic irradiation was not reflected in the shape of the dome structure. During the UV-induced dewetting, the irradiated film may become sufficiently fluid and did not exhibit a directional photofluidization.⁴⁸



Figure 5. Average height differences in AFM images of **AzD6** film (initial thickness = 90 nm) as a function of UV irradiation dose. The height difference was evaluated based on the images in Figure 4.



Figure 6. GI-XRD images on imaging plates at different period of UV irradiation dose (upper), and changes in the diffraction peak intensity corresponding to d/2 = 3.5 nm with UV irradiation dose (lower) for a **AzD6** film with 200 nm thickness.

The surface dewetting behavior of polymer thin films is essentially dependent on the film thickness. $^{43,49-51}$ Therefore, UV irradiation was performed onto AzD6 films with various thicknesses ranging from 20 to 100 nm. Figure 7 depicts topographical AFM images observed after 225-250 mJ cm⁻² irradiation. In thinner films of 20 or 50 nm thickness, the dewetting migration proceeded in local regions, resulting in a relatively dense and uniform distribution of small domes. A film with 20 nm thickness provided most dense and uniform sized domes with a few μ m diameters. For thicker film the domain becomes larger with the size feature more distributed, which is well recognized for a film with 90 nm thickness. When the thickness became more than 100 nm, the dewetting hardly occurred any more as shown in the left image of the 100 nm film (denoted as 'typical image'). Instead, some protrusions of several μ m diameter were observed on the film surface. This type of protrusions were also observed for thinner films in flat regions at the earlier hole formation stage (see Figure 4, 150 mJ cm⁻²). The formation of 3D protrusions may be related to UVinduced expanding behaviors of the Az-containing molecular film as has been observed for Langmuir-Blodgett films of amphiphilic Az-cotaining polymers.^{52,53} However, precise understanding for the origin of protrusions requires further investigation. In any event, the difference in morphological features observed for 90 and 100 nm films was drastic. In occasional cases, a separated dewetted part depicted as "occasional image" were observed, which were characterized by a large (>10 μ m diameter) dewetted dent with a film portion left in the center. In the films thicker than 110 nm, no dewetted areas were admitted. Thus, the thickness of 100 nm was the threshold between the stable wetting and photoinduced dewetting.

Such thickness dependent photoinduced dewetting is qualitatively in good agreement with the observations by Cristofolini et al.⁴³ using Langmuir–Blodgett multilayers on a hydrophobic surface with varied layer numbers. They reported that a 4 monolayered film (8-9 nm thickness) provided fine local dewetted structures resulting from submicrometer migrations, whereas a 24 monolayered (ca. 50 nm thickness) one showed a macroscopic dewettng transferring some tens of micrometer distances. The difference has been discussed by the dimensionality on the dewetting process. Dewetting behavior of the thicker film is based on the three-dimensional spinodal decomposition,⁴⁹ and in contrast, the thinner film cannot undergo such process and thus two-dimensional aggregation proceeds to form local particles. However, there remain some ambiguities on the wetting behavior. They observed photodinduced dewetting for linear polymers with $M_{\rm n} = 12000$ despite that we did not observed photoinduced dewetting for our linear polymer of **PAzMA** ($M_n = 7400$). We assume that a difference in the liquid crystal phase at room temperature leads to this discrepancy. The linear polymer employed by Cristofolini et al. adopt a nematic phase, while our linear polymer shows a smectic phase. The viscosity should differ significantly between them and this may critically influence the migrating flow motions. Furthermore, the surface energies of the substrate are different. They employed a hydrophobic surface in the observation of the dewetting, whereas we used hydrophilic surfaces. Further study is required for precise understandings.

3.3. Mass migration with Patterned Irradiation. As the next step, a series of AzD6 films with varied thicknesses were prepared and exposed to patterned UV light using a photomask instead of uniform irradiation at room temperature. The UV irradiation was performed at 5 mW cm⁻² equally for 50 s for each film. Figure 8 shows the topographical AFM images after the patterned irradiation (line and space pattern with 10 μ m width in typical cases) under the conditions stated above.

As shown in Figure 8, the morphologies after UV irradiation exhibited various aspects depending on the film thickness. In thinner films, hierarchical structures in which fine domes are embedded in the mass transport patterns of the photomask were observed upon a simple UV irradiation. When the film is initially a thin film of 15 nm thickness, the irradiated regions indicated hierarchical fine dewetted domes with the largest number. The average diameter of the dewetting domains was the smallest ranging from 1 to 3 μ m. For a film with thickness of 20–30 nm, the dome in the irradiated regions became larger and typically recognized as formation of hierarchical doublecolumned domes in a photoirradiated line. Here, the average domain diameter increased to $3-5 \ \mu m$. For a thicker film of 30-40 nm thickness, distorted column structure was observed. When the film thickness reached 40-60 nm, the dome pattern showed another typical structure constituted with an ordered



Figure 7. Topographical AFM images of AzD6 films of varied initial thickness after a constant dose of uniform UV irradiation ($225-250 \text{ mJ cm}^{-2}$). The initial film thickness is indicated at the top left for each figure.

single column dome lines. The average domain diameter increased to $5-8 \mu m$. As expected, when the film thickness reached 100 nm, the hierarchical morphology disappeared, and partial dent was observed in the bulged lined regions. For a film with 120 nm thickness, no additional morphology was admitted, which can be regarded as the "ordinary" relief formation simply reflecting the mask pattern.

Our approach to observe dewetting behavior in photomask line patterns is analogous with the strategy conducted on a chemically patterned surface using self-assembled monolayers by Sehgal et al.⁵⁴ They observed the dewetting behavior of polystyrene thin film in patterned narrow stripes. Depending on the chemically patterned stripes, the dewetted droplets polystyrene can be arranged in double or single line column. In their system, the confinement is achieved by chemical patterning by imprinting on the substrate surface, and in our case the film material itself is spatially transformed to exert confined dewetting by patterned irradiation.

The number of domes at 1000 μ m² area were counted and plotted as a function of film thickness in Figure 9. As the film thickness decreased, the number of dewetted domes increased in a nonlinear manner. The figure involves data counted for dewetted films after a uniform UV irradiation (closed circles) and in a 10 μ m line patterned UV irradiation (open circles). The thickness dependence qualitatively agreed in both cases, however, the number became apparently smaller for the line patterned films. This should be the consequence of increased thickness in the UV irradiated regions due to the mass migration.

3.4. On the Tendency To Form a 3D Structure. The marked tendency to increase the film thickness of AzD6 in the dewetted domes (Figure 7, 20-90 nm thickness) and also the formation of protrusions in flat film surface (Figure 7, 100 nm) upon UV irradiation is worth noting. We assume that the dendritic core architecture with the defined mass will isolate molecules with each other in the smectic layers without forming interlacing or entanglement. This situation would apt to pull out the isolated dendrimers from the smectic layer to form 3D structuring. As far as the Az unit is kept in the trans-form in the dark, the cast films did not show the surface morphology change. Thus, UV irradiation can reduce the intermolecular interaction considerably due to the involvement of cis-Az isomers. Considering the data of GI-XRD measurements (Figure 6), even at prolonged irradiation conditions, a full photoinduced transition to the isotropic phase does not take place but the disordered layer structure is still maintained during the UV irradiation. We assume that the highly fluid disordered layer structure is a requisite to form 3D morphological growth upon UV irradiation. Systematic investigations with other types of Az dendrimers changing the core generation and spacer length between the Az mesogenic unit to the core and precise evaluations of the viscoelastic properties should be helpful to gain more insights into these processes. Work along such directions is in progress.

4. CONCLUSIONS

This work proposed UV light-triggered dewetting of thin films of a dendritic LC molecule in which the 16 mesogenic Az units



Figure 8. Topographical AFM images of AzD6 films of varied initial thickness after a patterned UV irradiation through a photomask at 250 mJ cm⁻². The initial film thickness is indicated at the top left for each figure.



Figure 9. Number of formed domes as a function of initial film thickness after UV irradiation at 250 mJ cm^{-2} . The domes are counted for samples with uniform (closed) and line-and-space patterned (open) irradiation.

are attached in the periphery of the branched poly-(propylamine) core (G2). With this dendritic material, unexpected phototriggered dewetting with uniform UV irradiation and dome-shaped hierarchical morphologies are formed with simple patterned UV irradiation in thinner films less than 100 nm. We assume at the moment that such characteristic migrating motions are characteristically formed for smectic LC films comprising of dendritic molecules. The hierarchical structure is generated by the combination of mass transport and surface dewetting. The dome size and density on the surface is largely dependent on the initial film thickness. In the patterned irradiation, thickness control will provide single or "quasi" double column along the irradiatied line in a 10 μ m irradiated line. We expect that after an optimization of the experimental conditions, one can generate precisely the number of arrayed columns simply by changing the film thickness. For thicker films above the threshold thickness, the patterned film shows the "ordinary" relief structure which simply reflects the photopatterns. Controlling the dewetting process of thin polymer films is of great technological significance. For this purpose, "directed dewetting" has been extensively investigated by manipulating the substrate surface such as rubbing,^{55,56} chemical,^{54,57} or topographical^{50,51,57,58} patterning. In such a framework, this work proposes a new directing method of film dewetting on an unmodified uniform substrate surface using pattered irradiation.

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Notes

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