

Photoinduced Self-Structured Surface Pattern on a Molecular Azo Glass Film: Structure—Property Relationship and Wavelength Correlation

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Supporting Information

ABSTRACT: In this study, three series of star-shaped molecular azo glasses were synthesized, and self-structured surface pattern formation on the azo compound films was studied by laser irradiation at different wavelengths. The molecular azo glasses were synthesized from three core precursors (Tr-AN, Tr-35AN, Tr-H35AN), which were prepared by ring-opening reactions between 1,3,5-triglycidyl isocyanurate and corresponding aniline derivatives. The star-shaped azo compounds were obtained through azo-coupling reactions between the core precursors and diazonium salts of 4-chloroaniline, 4-aminobenzonitrile,



and 4-nitroaniline, respectively. By using the two-step reaction scheme, three series of azo compounds with different structures were obtained. The core precursors and azo compounds were characterized by using ¹H NMR, FT-IR, UV—vis, mass spectrometry, and thermal analyses. The self-structured surface pattern formation on films of the azo compounds was studied by irradiating the azo compound films with a normal-incident laser beam at different wavelengths (488, 532, and 589 nm). The results show that the photoinduced surface pattern formation behavior is closely related to the structure of the azo compounds, excitation wavelength, and light polarization conditions. The absorption band position of the $\pi - \pi^*$ transition is mainly determined by the electron-withdrawing groups on the azo chromophores. When the excitation wavelength is between λ_{max} and the band tail at the longer wavelength side, the self-structured surface pattern formation for certain excitation wavelengths. Increasing molecular interaction also shows an effect of restraining the surface pattern formation. The irradiations with linearly and circularly polarized light cause significant differences in the alignment manner of the pillarlike structures and their saturated height.

INTRODUCTION

Photoinduced surface pattern formation of azo polymers (polymers containing azobenzene and its derivatives) has attracted considerable attention in recent years.¹⁻⁴ Photoinduced surface-relief-grating (SRG) formation on azo polymer films has been intensively investigated since it was first reported by Natansohn et al. and Tripathy et al. in 1995.^{5,6} The study shows that when exposed to the interfering laser beams, SRGs can be formed on the azo polymer films at a temperature well below the glass transition temperatures (T_g) of the polymers. The sinusoid surface patterns, which are stable at temperatures below the T_{σ} values of the polymers, can be erased by heating samples to a temperature above their $T_{\rm g}$ values. The surface patterns are also erasable by light irradiation below the T_{g} values, such as by irradiation with a uniform circularly polarized laser beam.^{1,6} Photoinduced SRG formation has been observed for different types of polymers, such as side-chain azo polymers, main-chain azo polymers, and hyperbranched azo polymers, among others. $^{\rm 1-7}$ This novel processing method has been used for applications in data storage, optical device fabrication, and surface modification.^{8–13} The reversible nature suggests that the SRG formation is a

physical process related to photoinduced mass transport. The mechanism of SRG formation has been investigated to understand the general nature of the process. SRG formation has been attributed to isomerization-driven free volume expansion in the bulk,¹⁴ the force based on the dipolar interaction with the optically induced electric field gradient,¹⁵ a translational wormlike diffusion caused by the photoisomerization of the azobenzene chromophores,¹⁶ a mean-field force caused by the molecule alignment,¹⁷ and a photomechanical effect occurring in thin films.¹⁸

Recently, another unusual photoinduced surface pattern formation behavior has been reported by Hubert et al.^{19,20} Instead of irradiation with the interfering laser beams to inscribe SRGs, the submicrometer hexagonal patterns on the azo polymer films were induced by irradiation with a uniform laser beam at normal incidence.¹⁹ The patterns are characterized by regularly spaced pillarlike structures with a saturated height of about 100 nm. This effect is known as spontaneous surface pattern formation through light irradiation.¹⁹ The phenomenon is somehow reminiscent of

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the laser-induced periodic surface structure (LIPSS), the formation of parallel ripple structures on polymer surfaces induced by irradiation with a single beam of an excimer laser or a Nd:YAG pulsed laser.^{21–24} The LIPSS can be observed for many polymers without a specific requirement for structures and has been explained by models based on electromagnetic field theory such as the surface-scattered wave model.^{25,26} The pattern formation on azo polymer films makes a clear distinction with the LIPSS by the self-structured characteristics and lower light intensity used in the writing process. The influences of the laser intensity, irradiation time, and wavelength have been studied to understand the self-structured pattern formation on azo polymer films.^{20,27} The possible application of this effect in highly efficient data storage has been demonstrated.²⁸ However, in contrast to the extensive study of SRGs by using different azo polymers, the selfstructured surface pattern formation has been studied only for a poly(methyl methacrylate)-based copolymer (DR1MA/MMA 35/65), among a few others.^{20,28}

Molecular glass is a new type of glassy material based on welldesigned low-molecular-weight organic compounds.^{29,30} The amorphous molecular material shows thermodynamic stability and glass-transition behavior similar to those of an amorphous polymer. On the other hand, it possesses well-defined structures and better reproducible properties in comparison with polymers. Thin solid films with a smooth surface can be feasibly prepared from an amorphous molecular material by spin-coating. It has been reported that SRGs can be inscribed on molecular azo glass films with a higher formation rate compared to those observed for azo polymers.³¹⁻³⁴ Very recently, it has been reported that complex periodic superstructures can be formed on films of small-molecule-based photochromic materials upon irradiation of high interferential illumination.³⁵ The formed superstructures show a large amplitude, which is even larger than the initial film thickness. In a previous paper, we have reported that a photoinduced self-structured surface pattern can be induced on films of a star-shaped molecular azo glass.³⁶ Because of the well-defined structures, molecular azo glasses can be a desirable type of material for studying the influence of the molecular structures and light irradiation conditions on the self-structured surface pattern formation. However, to our knowledge, a report concerning a systematic study in this area is still lacking in the literature.

In this work, three series of star-shaped molecular azo glasses with different molecular structures were synthesized. Using the amorphous molecular materials, the self-structured surface pattern formation was studied by irradiating films of the materials with a laser beam at three different wavelengths (488, 532, and 589 nm). The influences of the molecular structures and light irradiation conditions on the surface pattern formation behavior were investigated in detail.

EXPERIMENTAL SECTION

Materials. 3,5-Dimethylaniline, bromoethane, 2-chloroethanol, 4-chloro aniline, 4-aminobenzonitrile, 4-nitroaniline, and 1,3,5-triglycidyl isocyanurate were purchased from Alfa Aesar. All the other materials, reagents, and solvents were commercially available products, which were used as received without further purification.

Characterization. Infrared spectra were determined using a Nicolet 560-IR FT-IR spectrophotometer by incorporating samples in KBr disks. ¹H NMR spectra were recorded using a JEOL JNM-ECA600 NMR spectrometer. Mass spectra were determined by an Agilent 6300 ion trap LC/MS system. Thermal analyses of the compounds were

carried out using TA Instruments DSC 2920 and TGA 2050 systems with a heating rate of 10 °C/min in a nitrogen atmosphere. UV–vis absorption spectra were recorded on a Perkin-Elmer Lamba Bio-40 spectrophotometer.

N-Ethyl-3,5-dimethylaniline. 3,5-Dimethylaniline (12.1 g, 0.1 mol) and bromoethane (10.9 g, 0.1 mol) were dissolved in THF to form a homogeneous solution. Anhydrous potassium carbonate (15.2 g, 0.11 mol) and a small amount of potassium iodide were added to the solution. The reaction was carried out at 40 °C for 6 h under the protection of nitrogen gas. After the reaction, the mixture was filtrated and the solvent in the filtrate was removed by rotary evaporation. The residue was purified by column chromatography using a mixture of ethyl acetate and petroleum ether (v/v = 1/12) as the eluent. The final product was obtained as a yellow liquid. Yield: 49%. MS: m/z [M]⁺ 149.19, calcd 149.12. ¹H NMR (DMSO-*d*₆): δ (ppm) 1.13 (m, 3H), 2.12 (s, 6H), 2.97 (m, 2H), 5.24 (br, 1H), 6.15 (s, 3H).

2-((3,5-Dimethylphenyl)amino)ethanol. This compound was synthesized by the reaction between 3,5-dimethylaniline (12.1 g, 0.1 mol) and 2-chloroethanol (8.06 g, 0.1 mol) via a procedure similar to that for preparing *N*-ethyl-3,5-dimethylaniline with a reaction temperature of 90 °C and a reaction time of 8 h. Yield: 53%. MS: m/z [M]⁺ 164.96, calcd 165.12. ¹H NMR (DMSO-*d*₆): δ (ppm) 2.13 (s, 6H), 3.06 (m, 2H), 3.54 (m, 2H), 4.63 (m, 1H), 5.18 (br, 1H), 6.17 (s, 1H), 6.19 (s, 2H).

Core Precursors Tr-AN, Tr-35AN, and Tr-H35AN. The core precursor Tr-AN was synthesized by a method reported previously.³⁶ In the reaction, 1,3,5-triglycidyl isocyanurate (2.97 g, 0.01 mol) and *N*-methylaniline (4.28 g, 0.04 mol) were mixed and slowly heated in the reactor. After the solid was melted, the mixture was continuously stirred and kept at 110 °C for 8 h. The product was dissolved in THF (50 mL) and then precipitated with petroleum ether. The solid was collected by filtration and dried in a vacuum oven at 70 °C for 24 h. The crude product was further purified by column chromatography (CH₂Cl₂, the first component). The core precursors Tr-35AN and Tr-H35AN were synthesized by reaction of 1,3,5-triglycidyl isocyanurate with *N*-ethyl-3,5-dimethylaniline and 2-((3,5-dimethylphenyl)amino)ethanol via a procedure similar to that for preparing Tr-AN. The analytical result for Tr-AN has been reported before,³⁶ and analytical results for Tr-35AN and Tr-H35AN are given below.

Data for *Tr*-35AN. Yield: 83%. MS: m/z [M]⁺ 744.52, calcd 744.46. ¹H NMR (DMSO-*d*₆): δ (ppm) 1.03 (m, 3H), 2.15 (s, 6H), 3.15 (m, 1H), 3.30 (m, 2H), 3.38 (m, 1H), 3.71 (m, 1H), 3.90 (m, 1H), 4.04 (m, 1H), 4.89 (d, 1H), 6.19 (s, 1H), 6.25 (s, 2H).

Data for Tr-H35AN. Yield: 85%. MS: m/z [M]⁺ 792.34, calcd 792.44. ¹H NMR (DMSO- d_6): δ (ppm) 2.14 (s, 6H), 3.20 (m, 1H), 3.33 (m, 1H), 3.42–3.53 (m, 5H), 3.71 (m, 1H), 3.90 (m, 1H), 4.08 (m, 1H), 4.67 (m, 1H), 4.99 (d, 1H), 6.20 (s, 1H), 6.26 (s, 2H).

Azo Compounds Tr-AZ-Cl, Tr-AZ-CN, Tr-AZ-NT, Tr-35AZ-Cl, Tr-35AZ-CN, Tr-35AZ-NT, Tr-H35AZ-Cl, Tr-H35AZ-CN, and Tr-H35AZ-NT. The azo compounds were synthesized by azo-coupling reactions.³⁶ The synthesis of Tr-AZ-Cl is given here as a typical example. 4-Chloroaniline (0.64 g, 5 mmol) was mixed with sulfuric acid (0.5 mL) and glacial acetic acid (12 mL). Diazonium salt was prepared by slowly adding an aqueous solution of sodium nitrite (0.4 g, 5.78 mmol, in 1 mL of water) to the 4-chloroaniline solution. The mixture was stirred at 5 °C for 5 min and then added dropwise to a solution of Tr-AN (0.618 g, 1 mmol) in N,N-dimethylformamide (DMF; 60 mL). The solution was stirred at 0 °C for 8 h and then poured into plenty of water. The precipitate collected by filtration was dissolved in THF, and it was again precipitated with petroleum ether. The final product was vacuum-dried at 70 °C for 24 h. The azo compounds Tr-AZ-CN and Tr-AZ-NT were synthesized by the azo-coupling reactions between Tr-AN and diazonium salts of 4-aminobenzonitrile and 4-nitroaniline via a procedure similar to that for preparing Tr-AZ-Cl. The azo compounds Tr-35AZ-Cl, Tr-35AZ-CN, Tr-35AZ-NT, Tr-H35AZ-Cl, Tr-H35AZ-CN, and Tr-H35AZ-NT were synthesized by the azo-coupling reactions of Tr-35AN

and Tr-H35AN with the diazonium salts of 4-chloroaniline, 4-aminobenzonitrile, and 4-nitroaniline, respectively, via a procedure similar to that for preparing Tr-AZ-Cl. Analytical results for Tr-AZ-CN and Tr-AZ-NT have been given before.³⁶ Analytical results for the other newly synthesized azo compounds are given below.

Data for Tr-AZ-Cl. Yield: 87%. DSC: $T_g = 98$ °C. MS: $m/z \text{ [M]}^+$ 1032.59, calcd 1032.31. ¹H NMR (DMSO- d_6): δ (ppm) 3.11 (s, 3H), 3.34 (m, 1H), 3.69 (m, 1H), 3.78 (m, 1H), 3.96 (m, 1H), 4.16 (m, 1H), 5.17 (d, 1H), 6.84 (d, 2H), 7.55 (d, 2H), 7.75 (m, 4H). IR (KBr, cm⁻¹): 3350, 2954, 2908, 1693, 1601, 1514, 1460, 1417, 1375, 1313, 1242, 1209, 1142, 1086, 1009, 949, 835, 760, 544.

Data for Tr-35AZ-Cl. Yield: 88%. DSC: $T_g = 92$ °C. MS: $m/z \text{ [M]}^+$ 1158.51, calcd 1158.45. ¹H NMR (DMSO- d_6): δ (ppm) 1.11 (m, 3H), 2.47 (s, 6H), 3.30 (m, 1H), 3.50–3.55 (m, 3H), 3.80 (m, 1H), 3.99 (m, 1H), 4.15 (m, 1H), 5.10 (d, 1H), 6.47 (s, 2H), 7.53 (d, 2H), 7.66 (d, 2H). IR (KBr, cm⁻¹): 3444, 2966, 2920, 1695, 1599, 1495, 1462, 1416, 1371, 1344, 1286, 1124, 1088, 835, 766, 521.

Data for Tr-35AZ-CN. Yield: 87%. DSC: $T_g = 123$ °C. MS: $m/z \text{ [M]}^+$ 1131.63, calcd 1131.56. ¹H NMR (DMSO- d_6): δ (ppm) 1.12 (m, 3H), 2.50 (s, 6H), 3.31 (m, 1H), 3.50–3.57 (m, 3H), 3.80 (m, 1H), 4.00 (m, 1H), 4.15 (m, 1H), 5.13 (d, 1H), 6.50 (s, 2H), 7.76 (d, 2H), 7.90 (d, 2H). IR (KBr, cm⁻¹): 3481, 2968, 2922, 2224, 1693, 1597, 1498, 1462, 1367, 1344, 1309, 1286, 1273, 1176, 1142, 1122, 1076, 987, 845, 766, 553.

Data for Tr-35AZ-NT. Yield: 84%. DSC: $T_g = 122$ °C. MS: $m/z [M]^+$ 1191.61, calcd 1191.53. ¹H NMR (DMSO- d_6): δ (ppm) 1.11 (m, 3H), 2.51 (s, 6H), 3.34 (m, 1H), 3.54–3.62 (m, 3H), 3.82 (m, 1H), 3.99 (m, 1H), 4.16 (m, 1H), 5.16 (d, 1H), 6.52 (s, 2H), 7.78 (d, 2H), 8.28 (d, 2H). IR (KBr, cm⁻¹): 3521, 2968, 2920, 1695, 1601, 1514, 1462, 1335, 1271, 1174, 1144, 1124, 1105, 987, 858, 766.

Data for Tr-H35AZ-Cl. Yield: 85%. DSC: $T_g = 103 \text{ °C. MS: }m/z \text{ [M]}^+$ 1206.45, calcd 1206.44. ¹H NMR (DMSO- d_6): δ (ppm) 2.47 (s, 6H), 3.34 (m, 1H), 3.51–3.63 (m, 5H), 3.79 (m, 1H), 3.97 (m, 1H), 4.18 (m, 1H), 4.79 (m, 1H), 5.16 (d, 1H), 6.49 (s, 2H), 7.51 (d, 2H), 7.66 (d, 2H). IR (KBr, cm⁻¹): 3284, 2956, 2918, 1693, 1597, 1462, 1348, 1273, 1163, 1088, 1034, 1007, 985, 835, 766, 521.

Data for Tr-H35AZ-CN. Yield: 86%. DSC: $T_g = 125$ °C. MS: m/z [M]⁺ 1179.55, calcd 1179.54. ¹H NMR (DMSO- d_6): δ (ppm) 2.50 (s, 6H), 3.38 (m, 1H), 3.54–3.63 (m, 5H), 3.67 (m, 1H), 3.80 (m, 1H), 3.99 (m, 1H), 4.19 (m, 1H), 4.82 (m, 1H), 5.18 (d, 1H), 6.53 (s, 2H), 7.77 (d, 2H), 7.90 (d, 2H). IR (KBr, cm⁻¹): 3377, 2956, 2918, 2225, 1693, 1597, 1464, 1350, 1271, 1171, 1142, 1099, 1045, 982, 843, 766, 553.

Data for Tr-H35AZ-NT. Yield: 82%. DSC: $T_g = 133 \text{ °C. MS: } m/z \text{ [M]}^+$ 1239.57, calcd 1239.51. ¹H NMR (DMSO-*d*₆): δ (ppm) 2.52 (s, 6H), 3.40 (m, 1H), 3.57–3.63 (m, 5H), 3.71 (m, 1H), 3.80 (m, 1H), 3.99 (m, 1H), 4.20 (m, 1H), 4.83 (m, 1H), 5.20 (d, 1H), 6.55 (s, 2H), 7.80 (d, 2H), 8.28 (d, 2H). IR (KBr, cm⁻¹): 3311, 2956, 2918, 1693, 1601, 1514, 1464, 1335, 1269, 1167, 1144, 1103, 982, 856, 756, 690.

Film Preparation. Solid films of the azo compounds with smooth surfaces were prepared by spin-coating. The homogeneous solutions of the azo compounds were obtained by dissolving a suitable amount of the azo compounds in DMF. After being filtered through 0.45 μ m membranes, the solutions were spin-coated onto clean glass slides. The film thicknesses were controlled to be in a range from 400 to 600 nm by adjusting the solution concentrations and the spinning speed. The films obtained from the spin-coating were dried at 60 °C under vacuum for 48 h before use.

Laser Light Irradiation. A linearly or circularly polarized beam from an Ar^+ laser (488 nm) and diode-pumped frequency-doubled solid-state lasers (532 and 589 nm) was used as the excitation light. The laser beam with proper intensity was obtained after being spatially filtered, expanded, and collimated. The laser beam (typically with an intensity of 200 mW/cm²) was perpendicularly incident to the film surfaces for a

proper time period (typically 30 min). After the light irradiation, the surfaces of the films were examined by using an atomic force microscope (Nanoscope IIIa) in the tapping mode.

RESULTS AND DISCUSSION

Nine star-shaped azo compounds (Tr-AZ-Cl, Tr-AZ-CN, Tr-AZ-NT, Tr-35AZ-Cl, Tr-35AZ-CN, Tr-35AZ-NT, Tr-H35AZ-Cl, Tr-H35AZ-CN, and Tr-H35AZ-NT) were used to study the photoinduced self-structured surface pattern formation. The synthetic route and chemical structure of all azo compounds are given in Scheme 1. Among them, Tr-AZ-CN and Tr-AZ-NT have been synthesized and reported in our previous paper.³⁶ For these two azo compounds, the formation of the self-structured surface patterns was only observed on the Tr-AZ-CN film upon irradiation with the laser beam at 532 nm.³⁶ In the current study, the newly synthesized molecular azo glasses together with Tr-AZ-CN and Tr-AZ-NT were used to study the structureproperty relationship of the photoinduced surface pattern formation. The correlation with the excitation wavelength was studied upon irradiation with the laser beams at three different wavelengths.

Synthesis and Characterization. The synthetic route of the azo compounds includes the preparation of star-shaped core precursors and the azo-coupling reactions of the precursors (Scheme 1). N-Ethyl-3,5-dimethylaniline and 2-((3,5-dimethylphenyl)amino)ethanol were synthesized through the nucleophilic substitution of 3,5-dimethylaniline with bromoethane and 2-chloroethanol, respectively. Three star-shaped core precursors (Tr-AN, Tr-35AN, Tr-H35AN) were synthesized through the ring-opening reactions of 1,3,5-triglycidyl isocyanurate (TGIC) with the aniline derivatives N-methylaniline, N-ethyl-3,5-dimethylaniline, and 2-((3,5-dimethylphenyl)amino)ethanol, respectively. Each series of azo compounds was obtained by introducing three types of azo chromophores through the azocoupling reactions of the core precursor with the corresponding diazonium salts in DMF. The chemical structure and abbreviated names of the azo compounds are shown in Scheme 1. The first two parts of the names specify the azo compounds obtained from the core precursors Tr-AN, Tr-35AN, and Tr-H35AN, and the last part makes the distinction of the electron-withdrawing groups on the azo chromophores. The series of azo compounds based on Tr-35AN contain 3,5-dimethyl substituents on the azobenzene moieties, which is different from those obtained from Tr-AN. The series of azo compounds obtained from Tr-H35AN bear an extra hydroxyl on the ethyl group compared with the azo compounds obtained from Tr-35AN. The structures of the azo compounds were confirmed by ¹H NMR, FT-IR, UV-vis, and mass spectrometry.

All three series of the star-shaped azo compounds obtained from Tr-AN, Tr-35AN, and Tr-H35AN show typical behavior of the amorphous materials. The glass transition temperatures (T_g) and decomposition temperatures (T_d) of the star-shaped azo compounds obtained from thermal analyses are given in Table 1. The T_g values of the azo compounds are significantly higher than those of the corresponding core precursors because of the existence of the azo chromophores. On the other hand, compared with the corresponding core precursors, the T_d values of the azo compounds are reduced due to the lower thermal stability of the azo bonds. The azo compounds were easily dissolved in polar organic solvents such as tetrahydrofuran (THF), DMF, and N,N-dimethylacetamide (DMAc). Solid thin films with smooth

Scheme 1. Synthetic Route of the Star-Shaped Azo Compounds



surfaces could be obtained through spin-coating by using the azo compound solutions.

Figure 1 gives UV—vis absorption spectra of the spin-coated films of the three series of azo compounds. The spectra exhibit typical characteristics of the pseudo-stilbene-type azo chromophores, where the absorption bands corresponding to the $\pi-\pi^*$ transition appear in the visible spectrum region. The λ_{max} values of the $\pi-\pi^*$ transition for the azo compounds (both spin-coated films and DMF solutions) are listed in Table 1. The λ_{max} values of the azo compounds are strongly affected by the electron-withdrawing groups on the azo chromophores. As the electron-withdrawing ability increases, the λ_{max} values increase in the order of chloro, cyano, and nitro substituents. The λ_{max} values of the azo compounds in DMF solutions show significant red shifts compared with those of spin-coated films, which can be attributed to the strong solvatochromic effect of DMF.

Molecular Azo Glasses with a Chloro Electron-Withdrawing Group. When irradiated at different wavelengths, the molecular azo glasses with different λ_{max} values show distinct pattern formation behavior. As λ_{max} values are mainly determined by the electron-withdrawing groups on the azo chromophores, the behavior of the photoinduced self-structured pattern formation will be discussed separately for each type of electronwithdrawing group. This section gives the results of three starshaped azo compounds with chloro as the electron-withdrawing group on the azo chromophores. The results were obtained by irradiating the solid films with a uniform normal-incident laser beam (200 mW/cm²) at three different wavelengths (488, 532, and 589 nm).

Figure 2 shows typical AFM images of the photoinduced surface patterns formed on the Tr-AZ-Cl film upon laser irradiation at 488 nm for 30 min. After the irradiation, the film surfaces show regularly spaced pillars with some localized hexagonal arrangement. Obvious differences can be seen for the surface patterns formed after irradiations of linearly and circularly polarized laser beams with the same light intensity and irradiation time. Upon irradiation with linearly polarized light, the alignment of the localized hexagonal pattern shows correlation with the polarization direction (Figure 2a,b), which is confirmed by the two-dimensional Fourier transform (2D-FT) of the AFM image (Figure 2c). The period of the regularly spaced pillars is 450 \pm 15 nm, which is obtained along $\pm 60^{\circ}$ with respect to the light polarization direction. The pattern formed by the circularly polarized light irradiation does not show the alignment correlation (Figure 2d,e). The 2D-FT analysis of the AFM image verifies the 2D isotropic alignment of the pillars (Figure 2f).

 Table 1. Thermal and Spectral Parameters of the Star-Shaped

 Azo Compounds

	$T_{\rm g}$	$T_{\rm d}$	λ_{\max} (nm)	λ_{\max} (nm)
compound	$(^{\circ}C)$	$(^{\circ}C)$	(DMF solution)	(spin-coated film)
Tr-AN	38	310		
Tr-AZ-Cl	98	268	430	409
Tr-AZ-CN	120	277	463	424
Tr-AZ-NT	116	250	494	454
Tr-35AN	43	286		
Tr-35AZ-Cl	92	255	424	404
Tr-35AZ-CN	123	247	451	433
Tr-35AZ-NT	122	237	490	463
Tr-H35AN	55	313		
Tr-H35AZ-Cl	103	263	423	399
Tr-H35AZ-CN	125	240	450	425
Tr-H35AZ-NT	133	233	487	453

The saturated height and period of the surface patterns for Tr-AZ-Cl and other molecular azo glasses with chloro electronwithdrawing groups are summarized in Table 2. For Tr-AZ-Cl, the saturated amplitude of the surface patterns is 59 \pm 11 nm for irradiation with linearly polarized light. Meanwhile, the saturated amplitude of the surface patterns induced by circularly polarized light is 85 \pm 15 nm. The above observations of the influence of light polarization on self-structured surface pattern formation are consistent with those reported for DR1MA/MMA 35/65 and molecular azo glass.^{19,36}

With irradiation with a linearly polarized laser beam at 532 nm under similar conditions, a self-structured surface pattern was also observed to form on the Tr-AZ-Cl film. The period of the regularly spaced pillars formed on the Tr-AZ-Cl film is 490 \pm 20 nm along the directions of $\pm 60^\circ$ with respect to the polarization direction. The saturated amplitude of the surface patterns is 35 \pm 8 nm, which is smaller than that obtained by irradiation with the 488 nm laser beam. When the film of Tr-AZ-Cl was irradiated with the linearly polarized laser beam (200 mW/cm²) at 589 nm for 30 min, no self-structured surface pattern formation could be observed.

Figure 3 shows the patterns formed on the films of Tr-35AZ-Cl after irradiation with the linearly polarized laser beam (200 mW/cm^2) at 488 nm for 30 min. Similar to Tr-AZ-Cl, surface pattern formation can be observed on the film of Tr-35AZ-Cl (Figure 3a,b). The saturated amplitude of the pillarlike structures for the Tr-35AZ-Cl film is only 12 \pm 3 nm, which is much smaller than that of Tr-AZ-Cl when irradiated with the 488 nm light. The smaller saturated amplitude can be attributed to the steric hindrance of the bulky 3,5-dimethyl groups and the inhibition of the trans-cis-trans isomerization of the adjacent azo bond. The space period of the pillars is 455 ± 15 nm. For comparison, the film of Tr-35AZ-Cl was also irradiated with the linearly polarized laser beam (200 mW/cm^2) at 532 nm for 30 min. The self-structured surface pattern forms on the film of Tr-35AZ-Cl with a saturated amplitude of 42 \pm 9 nm, which is even slightly higher than that of Tr-AZ-Cl when irradiated with 532 nm light. The possible reason why there is no obvious steric hindrance after irradiation with 532 nm light is given in the Discussion by considering the different photoisomerization pathways of the azo chromophores. The space period of the pillarlike structures is 490 \pm 20 nm. When the film of Tr-35AZ-Cl was irradiated with the



Figure 1. UV-vis spectra of the molecular azo compounds as spincoated films: (a) azo compounds obtained from Tr-AN; (b) azo compounds obtained from Tr-35AN; (c) azo compounds obtained from Tr-H35AN.

linearly polarized laser beam (200 mW/cm^2) at 589 nm for 30 min, no self-structured surface pattern formation could be observed.

For the Tr-H35AZ-Cl film, no obvious self-structured surface pattern formation was observed after irradiation with 488 nm light under the same conditions. Only shallow irregular fluctuations with an amplitude of less than 6 nm appeared on the surface (Figure 3c,d). Even after irradiation with the laser beam with a much higher intensity and for a longer irradiation time (400 mW/cm^2) 60 min), no regular self-structured surface patterns could be seen on the Tr-H35AZ-Cl film. The main difference between Tr-35AZ-Cl and Tr-H35AZ-Cl is the extra hydroxyl on the ethyl group. This observation indicates that the extra hydroxyl groups in the Tr-H35AZ-Cl structure can further inhibit the surface pattern formation. This can be attributed to the strong intermolecular interaction through hydrogen bonding of the hydroxyl groups. Similarly, when the films of Tr-H35AZ-Cl were irradiated with the linearly polarized laser beam (200 mW/cm^2) at 532 nm for 30 min, no self-structured surface pattern formation could be observed on the film. Like Tr-AZ-Cl and Tr-35AZ-Cl, after irradiation at 589 nm with the linearly polarized laser beam (200 mW/cm²) for 30 min, no self-structured surface pattern formation could be observed for the Tr-H35AZ-Cl film. In these cases, the irradiation wavelength is much longer than the λ_{\max} values of the $\pi - \pi^*$ transition bands and even away from the absorption band tails at the longer wavelength side (Figure 1).



Figure 2. Typical AFM images $(10 \,\mu m \times 10 \,\mu m)$ and 2D-FT images of the photoinduced surface patterns formed on Tr-AZ-Cl films upon irradiation with a normal-incident laser beam at 488 nm and different polarizations: (a) linearly polarized, 2D view; (b) linearly polarized, 3D view; (c) linearly polarized, 2D-FT image; (d) circularly polarized, 2D view; (e) circularly polarized, 3D view; (f) circularly polarized, 2D-FT image. The light intensity was 200 mW/cm², and the irradiation time was 30 min.

Table 2.	Saturated Amplitude and Space Period of the Surface Patterns on the Molecular Azo Glasses with Chloro as the Ele	ectron-
Withdra	ring Group Obtained under Different Light Irradiation Conditions	

azo compound	wavelength (nm)	intensity (mW/cm^2)	time (min)	state of polarization	amplitude (nm)	period (nm)
Tr-AZ-Cl	488	200	30	linearly	59 ± 11	450 ± 15
Tr-AZ-Cl	488	200	30	circularly	85 ± 15	
Tr-AZ-Cl	532	200	30	linearly	35 ± 8	490 ± 20
Tr-35AZ-Cl	488	200	30	linearly	12 ± 3	455 ± 15
Tr-35AZ-Cl	532	200	30	linearly	42 ± 9	490 ± 20
Tr-H35AZ-Cl	488	200	30	linearly		
Tr-H35AZ-Cl	488	400	60	linearly		
Tr-H35AZ-Cl	532	200	30	linearly		

Molecular Azo Glasses with a Cyano Electron-Withdrawing Group. For the azo compounds with cyano as the electronwithdrawing group, the photoinduced self-structured surface pattern formation was studied by the same method. The saturated heights and periods of the surface patterns for the molecular azo glasses are summarized in Table 3. When the films of Tr-AZ-CN, Tr-35AZ-CN, and Tr-H35AZ-CN were irradiated with the linearly polarized laser beam (200 mW/cm²) at 488 nm for 30 min, the surface pattern could only be observed to form on the film of Tr-AZ-CN with a saturated amplitude of the surface patterns of 20 \pm 4 nm and a space period of 420 \pm 15 nm.

With irradiation with the laser beam (200 mW/cm^2) at 532 nm, the self-structured surface patterns can be efficiently induced on films of Tr-AZ-CN as reported by us before.³⁶ Compared with Tr-AZ-CN, the surface pattern formation on the film of Tr-35AZ-CN is less efficient upon irradiation with 532 nm light under the same conditions. Figure 4 shows AFM images of the photoinduced surface patterns formed on the Tr-35AZ-CN film upon laser irradiation (200 mW/cm²) at 532 nm for 30 min. The irradiations with the linearly and circularly

polarized laser beams also show different influences on the pattern formation. With irradiation with the linearly polarized laser, the alignment of the localized hexagonal pattern shows correlation with the polarization direction (Figure 4a–c). The saturated amplitude of the surface pattern is 25 ± 4 nm with a space period of 470 ± 20 nm. Upon irradiation with the circularly polarized laser, the pattern does not show the alignment correlation (Figure 4d–f). The saturated amplitude of the surface patterns is 85 ± 18 nm, which is significantly higher than the case for linearly polarized light irradiation. For Tr-35AZ-CN, the saturated amplitude of the surface patterns is obviously smaller than that of Tr-AZ-CN, especially for the film irradiated with the linearly polarized laser.

When the film of Tr-H35AZ-CN was irradiated with the linearly polarized laser beam at 532 nm (200 mW/cm², 30 min), no self-structured surface pattern formation could be observed. However, when the Tr-H35AZ-CN film was irradiated at 532 nm with a much higher intensity (400 mW/cm², 30 min), self-structured surface pattern formation was observed. The pillarlike structures show a saturated amplitude of 50 ± 10 nm with a space



Figure 3. AFM images ($10 \ \mu m \times 10 \ \mu m$) of the photoinduced surface patterns formed on Tr-35AZ-Cl and Tr-H35AZ-Cl films upon irradiation at 488 nm: (a) Tr-35AZ-Cl, 2D view; (b) Tr-35AZ-Cl, 3D view; (c) Tr-H35AZ-Cl, 2D view; (d) Tr-H35AZ-Cl, 3D view. The light intensity was 200 mW/cm², and the irradiation time was 30 min.

Table 3. Saturated Amplitude and Space Period of the Surface Patterns on the Molecular Azo Glasses with Cyano as the Electron-Withdrawing Group Obtained under Different Light Irradiation Conditions

azo compound	wavelength (nm)	intensity (mW/cm^2)	time (min)	state of polarization	amplitude (nm)	period (nm)
Tr-AZ-CN	488	200	30	linearly	20 ± 4	420 ± 15
Tr-AZ-CN ³⁶	532	200	15	linearly	80	440 ± 20
Tr-AZ-CN ³⁶	532	200	15	circularly	120	
Tr-35AZ-CN	488	200	30	linearly		
Tr-35AZ-CN	532	200	30	linearly	25 ± 4	470 ± 20
Tr-35AZ-CN	532	200	30	circularly	85 ± 18	
Tr-H35AZ-CN	488	200	30	linearly		
Tr-H35AZ-CN	532	200	30	linearly		
Tr-H35AZ-CN	532	400	30	linearly	50 ± 10	490 ± 20

period of 490 \pm 20 nm. When films of Tr-AZ-CN, Tr-35AZ-CN, and Tr-H35AZ-CN were irradiated at 589 nm with the linearly polarized laser beam (200 mW/cm²) for 30 min, no self-structured surface pattern formation could be observed, which is similar to the cases for Tr-AZ-Cl, Tr-35AZ-Cl, and Tr-H35AZ-Cl. This can also be attributed to the very weak absorption at the irradiation wavelength as shown in Figure 1.

Molecular Azo Glasses with a Nitro Electron-Withdrawing Group. Tr-AZ-NT, Tr-35AZ-NT, and Tr-H35AZ-NT bear strong electron-withdrawing nitro groups on the azo chromophores. Due to the strong electron-withdrawing effect, the molecular azo glasses possess significantly larger λ_{max} values for the $\pi - \pi^*$ transition. Therefore, the molecular azo glasses show strong absorption for light with wavelengths of 488 and 532 nm and have some absorption even for the 589 nm light. However, different from the above-mentioned azo compounds, these three molecular azo glasses did not show the ability to form a surface pattern when irradiated with the linearly polarized laser beam (200 mW/cm^2) at 488, 532, and 589 nm for 30 min. The possible reason for this observation is given in the Discussion.

Dynamic Process of Pattern Formation. As discussed above, Tr-AZ-Cl exhibits the typical self-structured surface pattern formation behavior when irradiated with 488 nm light. Therefore, the molecular azo glass was used to study the dynamic process of pattern formation. Figures 5 and 6 reveal the gradual pattern formation processes on Tr-AZ-Cl films when irradiated with linearly and circularly polarized laser beams at 488 nm for different time periods. By closely examining the AFM images given in Figure 5, it can be seen that, after irradiation with the linearly polarized laser for 30 min, the pillarlike structures obviously merge in two directions about $\pm 60^{\circ}$ to the light polarization direction. On the contrary, no such deformation is observed after irradiation with the circularly polarized laser for the same time. The pattern formation seems to be in a more



Figure 4. Typical AFM images (10 μ m × 10 μ m) and 2D-FT images of the photoinduced surface patterns formed on Tr-35AZ-CN films upon irradiation with a normal-incident laser beam at 532 nm and different polarizations: (a) linearly polarized, 2D view; (b) linearly polarized, 3D view; (c) linearly polarized, 2D-FT image; (d) circularly polarized, 2D view; (e) circularly polarized, 3D view; (f) circularly polarized, 2D-FT image. The light intensity was 200 mW/cm², and the irradiation time was 30 min.



Figure 5. AFM images $(10 \,\mu\text{m} \times 10 \,\mu\text{m})$ of the photoinduced surface patterns on Tr-AZ-Cl films upon irradiation for different times. The incident laser beam (488 nm, 200 mW/cm²) was linearly polarized. The irradiation time was (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 30 min, and (f) 40 min.

complicated and random manner. This observation further verifies that the light polarization condition can cause the obvious difference in the pattern formation and surface deformation manner. Figure 7 gives the corresponding relationship between the modulation amplitude and irradiation time. It can be seen that, after a slow initial stage, the self-structured pattern formation exhibits a rapid increase in the first 15 min. After that, the pattern growth rate is obviously slowed. With irradiation with the circularly polarized laser beam, the self-structured pattern formation reaches the saturated level in about 20 min. With irradiation with the linearly polarized laser beam, the amplitude still gradually increases after 20 min and becomes saturated in 30-40 min.

Discussion. The above results indicate that self-structured surface pattern formation is a process closely related to the molecular structure and excitation wavelength. The structural factors studied here include the type of electron-withdrawing groups, the 3, 5-dimethyl substitution, and the extra hydroxyl group. The influence of the light wavelength is also correlated with some of the structural factors. All these factors and correlation are discussed below.

The electron-withdrawing groups on the azo chromophores show a significant influence on the surface pattern formation. Tr-AZ-Cl, Tr-35AZ-Cl, Tr-AZ-CN, and Tr-35AZ-CN, which contain chloro and cyano as the electron-withdrawing groups, show the ability to form self-structured surface patterns when irradiated with light at the proper wavelengths (488 and 532 nm).



Figure 6. AFM images $(10 \ \mu\text{m} \times 10 \ \mu\text{m})$ of the photoinduced surface patterns on Tr-AZ-Cl films upon irradiation for different times. The incident laser beam (488 nm, 200 mW/cm²) was circularly polarized. The irradiation time was (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 30 min, and (f) 40 min.



Figure 7. Amplitude of the surface patterns formed on a Tr-AZ-Cl film as a function of the irradiation time upon irradiation with linearly and circularly polarized laser beams. The wavelength of the laser beams was 488 nm, and the light intensity was 200 mW/cm².

For the molecular azo glasses bearing cyano as the electronwithdrawing group, the λ_{\max} values of the $\pi - \pi^*$ transition are red-shifted about 30 nm compared with those of the molecular azo glasses bearing a chloro group. Therefore, the molecular azo glasses show distinct efficiencies in response to the different excitation wavelengths. When the irradiation time is the same, the amplitude of the pillarlike structures can be used to characterize the relative efficiency of pattern formation. For Tr-AZ-Cl, self-structured surface pattern formation is more efficiently induced by irradiation with 488 nm light. On the other hand, pattern formation on the Tr-AZ-CN and Tr-35AZ-CN films is more efficiently induced by irradiation with 532 nm light. Comparing this observation with the UV-vis spectra of the compounds (Figure 1), it can be inferred that when the excitation wavelength is between the λ_{\max} of the $\pi - \pi^*$ transition and the absorption band tail at the longer wavelength side, light irradiation can cause surface pattern formation more efficiently. A similar influence of the excitation wavelength on the SRG formation efficiency has been reported before. $^{37-39}$ It has been indicated that the trans-cis photoisomerization efficiency depends on the competition between excitation $(\pi - \pi^* \text{ or } n - \pi^*)$ transition) and relaxation.³⁹ The trans-cis isomerization yield of the $n-\pi^*$ excitation is higher than that of the $\pi-\pi^*$ excitation. Therefore, under conditions of adequate excitation at a wavelength

between the λ_{max} of the trans $\pi - \pi^*$ transition and the λ_{max} of the cis $n - \pi^*$ transition, the rate of SRG formation is increased at a longer laser excitation wavelength. For the surface pattern formation studied here, the correlation with the excitation wavelength could also be attributed to the different trans—cis isomerization efficiencies connected to the excitation at the absorption band positions. Tr-35AZ-Cl might not be a true exception to this rule, although it does form the surface pattern more efficiently when irradiated with 532 nm light than with 488 nm light. The possible reason for this phenomenon is given below by considering the substitution effect.

The 3,5-dimethyl substitution on the azo chromophores shows more complicated influences on self-structured surface pattern formation. In most cases, the 3,5-dimethyl substitution on the azo chromophores obstructs the self-structured surface pattern formation, which results in a lower saturated amplitude. This can be seen for Tr-35AZ-Cl irradiated with 488 nm light and Tr-35AZ-CN irradiated with 488 and 532 nm light. This effect can be attributed to the steric hindrance of the dimethyl substitution to the trans-cis isomerization of azo chromophores through the rotation mechanism (the twist around the C—N=N—C dihedral angle).^{3,40} As mentioned above, upon irradiation with 532 nm light, the amplitude of the pillarlike structures on the Tr-35AZ-Cl film is similar to that of Tr-AZ-Cl. The 3,5-dimethyl substitution does not show obvious inhibition of pattern formation. A possible explanation is that irradiation at this wavelength could mainly cause $n-\pi^*$ transition and the trans-cis isomerization might go through the inversion pathway (the inversion of one or both of the CNN angles through a linear transition state).^{3,40} In this case, the dimethyl substitution could not show the steric hindrance to the photoinduced trans-cis isomerization of the azo chromophores. Considering the model based on competition between excitation and relaxation,³⁹ if the λ_{\max} values of both trans $n-\pi^*$ transition and cis $n-\pi^*$ transition are closer to 532 nm, irradiation at this wavelength can cause efficient trans-cis isomerization. For this reason, Tr-35AZ-Cl is more efficient at forming the surface pattern when irradiated with 532 nm light compared with 488 nm light.

Intermolecular interaction shows obvious obstruction to the surface pattern formation. This can be seen for the molecular azo glasses obtained from Tr-H35AN, which bear an extra hydroxyl

on the ethyl group. After irradiation with the light (200 mW/cm^2) , no pattern formation is observed for this series of azo compounds, which can be attributed to the hydrogen bonds between the molecules. This inference is partially supported by the observation that self-structured surface patterns could be induced on the Tr-H35AZ-CN film when irradiated with a much higher intensity light (400 mW/cm²). For molecular azo glasses containing nitro substituents on the azo chromophore, no selfstructured surface patterns can be induced by irradiation at the three wavelengths. The dipole moment of the azo chromophore bearing nitro as the electron-withdrawing group is significantly larger than that of the azo chromophore bearing cyano as the electron-withdrawing group (9.1 D vs 6.4 D).³⁹ It has been reported that the strong dipolar interaction exists between the 4-amino-4'-nitroazobenzene moieties of the side-chain azo polymer.⁴¹ It is believed that the inhibition of the surface pattern formation could be attributed to the strong dipole-dipole interaction between the 4-amino-4'-nitroazobenzene moieties. On the other hand, it cannot be ruled out that, for Tr-AZ-NT, Tr-35AZ-NT, and Tr-H35AZ-NT, the λ_{\max} values of the cis n $-\pi^*$ transitions are located at even longer wavelength positions. In this case, the lower trans-cis isomerization efficiency could also result in the failure to form the self-structured surface pattern.

The structure-property relationship and correlation with the wavelength discussed above can shed some new light on the mechanism of self-structured surface pattern formation. First, the above results suggest that the photoinduced trans-cis isomerization plays a critical role in the pattern formation process. One point of direct evidence is that irradiation with 589 nm light cannot cause pattern formation, which is away from the absorption bands and unable to cause trans-cis isomerization. Second, the driving force for pattern formation is quite weak, which can be significantly obstructed by the noncovalent molecular interaction. Third, the difference with the LIPSS can also be seen from the relationship between the excitation wavelength and the space periods of the surface patterns. For the LIPSS, the ripple spacing is approximately equal to the vacuum wavelength at normal incidence.^{25,26} Although the space periods reported here show correlation with the light wavelengths, they are always smaller than the light wavelengths (Tables 2 and 3).

CONCLUSIONS

Three series of molecular azo glasses were prepared and used for studying photoinduced surface pattern formation when irradiated with laser beams at three different excitation wavelengths. The self-structured surface patterns formed on the starshaped azo compound films show close correlation with the type of azo chormophores and light irradiation conditions. Upon light irradiation with the same intensity (200 mW/cm²), efficient surface pattern formation can be observed on the Tr-AZ-Cl, Tr-35AZ-Cl, Tr-AZ-CN, and Tr-35AZ-CN films. Irradiation with linearly and circularly polarized light shows significant differences in the alignment manner of the pillarlike structures and their saturated height. When the excitation wavelength is between the λ_{\max} of the $\pi - \pi^*$ transition and the band tail at the longer wavelength side, the self-structured surface pattern can be more efficiently induced by irradiation. In most cases, the 3,5-dimethyl substitution on azo chromophores shows an effect of inhibiting surface pattern formation for certain excitation wavelengths. The exception to this rule could be attributed to the different pathways of photoinduced trans-cis isomerization. The driving force

for pattern formation is quite weak, which can be obviously restrained by the noncovalent molecular interaction.

ASSOCIATED CONTENT

Supporting Information. More characterization results of the core precursors and star-shaped azo compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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