Macromolecules

Self-Structured Surface Patterns on Epoxy-Based Azo Polymer Films Induced by Laser Light Irradiation

Xiaolin Wang, Jianjun Yin, and Xiaogong Wang*

Department of Chemical Engineering, Laboratory for Advanced Materials, Tsinghua University, Beijing 100084, P. R. China

Supporting Information

ABSTRACT: In this study, two series of epoxy-based azo polymers with high chromophore density were synthesized and self-structured surface pattern formation on the polymer films was studied by laser light irradiation under different conditions. To synthesize the azo polymers, two epoxy-based precursor polymers (PEP-AN and PEP-35AN) were prepared by step polymerizations of *N*,*N*-di(epoxypropyl)aniline and *N*, N-di(epoxypropyl)-3,5-dimethylaniline with aniline and 3,5dimethylaniline, respectively. The azo polymers were obtained



through postpolymerization azo-coupling reactions between the precursor polymers and diazonium salts of 4-chloroaniline, 4-aminobenzonitrile, 4-nitroaniline, and 2-methyl-4-nitroaniline. The epoxy-based precursor polymers and azo polymers were characterized by using ¹H NMR, FT-IR, UV-vis, and DSC analyses. The self-structured surface pattern formation on films of the two series of azo polymers was studied by irradiating the polymer films with a normal-incident laser beam at two different wavelengths (488 and 532 nm). The results show that the photoinduced surface pattern formation is closely related with the structure of azo chormophores, excitation wavelength, and light polarization condition. The efficient excitation wavelength is closely related with the absorption band position, which is mainly determined by the electron-withdrawing groups on the azo chromophores. The methyl substituents on the azo chromophores can enhance the photoinduced surface pattern formation ability in some cases. For comparison, the surface-relief-grating (SRG) formation was studied by irradiating the polymer films with interfering laser light. The SRG formation rate is also dependent on the azo chromophore structure and wavelength of the incident laser light. The self-structured surface pattern formation needs a higher energy input and shows stricter wavelength requirement compared with those of the SRG formation. These observations could lead to the deeper understanding of the mechanism of the self-structured surface pattern formation and development of materials with better performance.

INTRODUCTION

Azobenzene and its derivatives have been widely used as dyestuffs and pigments for a long time owing to their colorful nature.^{1,2} In recent years, these chromophoric structures have been intensively explored as functional groups for developing photoresponsive polymers, whose structure and property variations can be triggered by the photoinduced trans-cis isomerization of the azo groups.^{3,4} Polymers containing azobenzene and its derivatives (azo polymer for short) have been synthesized through various molecular engineering approaches and investigated for the unique properties. 5^{-7} Azo polymers can show some very interesting photoresponsive properties such as phase transition,⁸ chromophore orientation,⁹ surface-relief-grating (SRG) formation,^{10,11} and deformation of thin films.^{12–15} Polymers with such properties are currently being expected for the applications in areas such as data-storage, optical switching, sensors and actuators.

Photoinduced SRG formation on azo polymer films has attracted considerable attention since it was first reported in 1995.^{10,11} Upon irradiation with interfering laser beams, SRGs can be formed on azo polymer films at a temperature well below the glass transition temperatures (T_{gs}) of the polymers.^{5,6,10,11}

The SRGs are stable below the T_{g} s of the polymers and can be erased by heating samples to a temperature above their T_{g} s or by irradiation with a uniform circularly polarized laser beam below the $T_{\rm g}$ s. Photoinduced SRG formation has been observed for hostguest systems, side-chain azo polymers, main-chain azo polymers, and hyperbranched azo polymers among others.^{5,6,10,11,16,17} The surface modulation has been attributed to the mass-transport induced by the light field as a result of the trans-cis isomerization of azo chromophores. Although different models and theories have been proposed to explain this interesting photoresponsive property, the mechanism of SRG formation has not been fully understood until now.^{18–26} This unique function of azo polymers has been used for optical device fabrication and surface modulations. $^{27-32}$

Recent research uncovers another unusual photoresponsive behavior of azo polymer films when irradiated with a uniform laser beam.^{33,34} The observations reveal that submicrometer hexagonal patterns on the azo polymer films can be induced by

Received:	April 11, 2011
Revised:	May 20, 2011
Published:	August 10, 2011

Scheme 1. Synthetic Route of the Epoxy-Based Azo Polymers



irradiation with the uniform laser beam at normal incidence.³³ The patterns are characterized by regularly spaced pillar-like structures with saturated height about 100 nm. This effect has been known as the spontaneous surface pattern formation through light irradiation.³³ The self-structured characteristics of the pattern formation makes a clear distinction between this effect and the formation of parallel ripple structures on polymer surfaces induced by irradiation with a single beam of excimer laser or Nd:YAG pulsed laser.^{35–39} The latter has been known as laser-induced periodic surface structure (LIPSS) and explained by the models based on electromagnetic field theory such as the surface-scattered wave model.^{40,41} In order to understand the self-structured pattern formation on azo polymer film, the influences of laser intensity, irradiation time, and wavelength have been studied in detail.^{34,42} The possible application of this effect in high efficient data-storage has been demonstrated.^{43,44} However, in contrast to the extensive study of SRGs for different azo polymers, the self-structured surface pattern formation has been observed only for a poly(methyl methacrylate)-based copolymer (DR1MA/MMA 35/65) among few others.^{32,43,44} To our knowledge, a deep understanding of the relationship between polymer structures and this unique photoresponsive behavior of azo polymers has not been reached at this moment.

In this work, two series of epoxy-based azo polymers bearing push—pull type azo chromophores with high density were synthesized. Epoxy-based azo polymers have been synthesized and studied for the nonlinear optical properties and SRG formation for years.^{11,45–47} However, no self-structured pattern formation has been observed for those epoxy-based azo polymers under the single laser beam irradiation. In order to enhance the light irradiation effect, the epoxy-based azo polymers developed in this study were prepared to bear high density of azo

chromophores with different structures. The photoinduced surface pattern formation was studied by irradiating the azo polymer films with a single laser beam at 488 and 532 nm. For comparison, the SRG formation on the azo polymer films were studied by irradiation with interfering laser beams at the wavelengths. The correlation of the surface pattern formation with polymer structures was investigated for the processes. The experimental methods and Results and Discussion will be presented in the following sections in detail.

EXPERIMENTAL SECTION

Materials. Aniline, 3,5-dimethylaniline, 4-chloroaniline, 4-aminobenzonitrile, 4-nitroaniline, and 2-methyl-4-nitroaniline were purchased from Alfa Aesar. The other materials, reagents and solvents were commercial products and 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 Agilent 6300 Ion Trap LC/MS Systems. Molecular weights and molecular weight distributions were determined by using a gel permeation chromatography (GPC) apparatus at room temperature with THF as the eluent (1 mL min⁻¹). The instrument was equipped with a refractive index (RI) detector (Wyatt Optilab rEX) and fitted with a PLgel 5 µm mixed-D column. The molecular weights and distributions were obtained by calibration with linear polystyrene standards. Thermal phase transitions of the polymers were determined using TA Instruments DSC 2920 with a heating rate of 10 °C/min in nitrogen atmosphere. UV-vis absorption spectra were recorded on a Perkin-Elmer Lamba Bio-40 spectrophotometer. The surface images of the photoinduced surface patterns and surface-relief-gratings were monitored using an atomic force microscope (AFM, Nanoscope IIIa) in the tapping mode.

Table 1. T_{gs} of the Epoxy-Based Azo Polymers

	$T_{ m g}$ s (°C) o	$T_{\rm g}$ s (°C) of azo polymers	
Х	PEP-AZ-X	PEP-35AZ-X	
-Cl	160	150	
-CN		150	
-NT		152	
-mNT	156	149	

N,*N*-Di(epoxypropyl)aniline. Silica gel catalyzed ring-opening method was used to prepare this compound.⁴⁸ It was carried out by adding silica gel (0.93 g, 100–200 mesh) into a homogeneous mixture of aniline (9.3 g, 0.1 mol) and 2-(chloromethyl)oxirane (37 g, 0.4 mol), and reacting at 40 °C for 5 h. After the reaction, the mixture was filtrated and added dropwise into petroleum ether to precipitate the white powder. The dried powder without purification was dissolved in a solution of THF (100 mL) and KOH (15 g). The solution was stirred at room temperature for 3 h and filtrated. The THF was removed by rotary evaporation and the residue was purified by column chromatography using a mixture of ethyl acetate and petroleum ether (v/v = 1:10) as eluent. The final product was obtained as a yellow liquid. Yield: 54%. MS: m/z [M]⁺, 204.97; calcd, 205.11. ¹H NMR (DMSO-*d*₆), δ (ppm): 2.57 (m, 2H), 2.73 (m, 2H), 3.11 (m, 2H), 3.38 (m, 2H), 3.66 (m, 2H), 6.65 (d, 1H), 6.83 (d, 2H), 7.17 (m, 2H).

N,N-Di(epoxypropyl)-3,5-dimethylaniline. It was synthesized by the reaction between 3,5-dimethylaniline (12.1 g, 0.1 mol) and 2-(chloromethyl)oxirane (37 g, 0.4 mol) via a procedure similar to that used for preparing *N*,*N*-di(epoxypropyl)aniline. The final product was obtained as a yellow liquid. Yield: 47%. MS: m/z [M]⁺, 233.04; calcd, 233.14. ¹H NMR (DMSO- d_6), δ (ppm): 2.19 (s, 6H), 2.56 (m, 2H), 2.72 (m, 2H), 3.09 (m, 2H), 3.39 (m, 2H), 3.61 (m, 2H), 6.30 (s, 1H), 6.45 (s, 2H).

PEP-AN. Aniline (1.86 g, 20 mmol) and *N*,*N*-di(epoxypropyl)aniline (4.1 g, 20 mmol) were homogeneously mixed and stirred at 110 °C for 10 h under nitrogen protection. The crude product as a slightly yellow solid was dissolved in THF and added dropwise into a mixture of ethanol and petroleum ether (v/v = 1:3) to obtain a sticky precipitate. The precipitate was collected by removing the liquid and was dried in a vacuum oven at 60 °C for 48 h to get product. Yield: 31%. DSC: *T*_g 87 °C. GPC: *M*_n = 5000; MWD = 1.56. ¹H NMR (DMSO-*d*₆), δ (ppm): 3.25 (1H), 3.40 (1H), 3.45 (1H), 3.60 (1H), 4.03 (1H), 5.28 (1H), 6.49 (1H), 6.60 (2H), 6.99 (2H). IR (KBr, cm⁻¹): 3307, 2870, 1599, 1504, 1346, 1232, 1194, 1117, 1034, 991, 858, 746, 692, 509.

PEP-35AN. PEP-35AN was synthesized from the reaction between 3,5-dimethylaniline (2.42 g, 20 mmol) and *N*,*N*-di(epoxypropyl)-3,5-dimethylaniline (4.66 g, 20 mmol) through a similar procedure for preparing PEP-AN. The polymerization was carried out at 110 °C for 3 h. Yield: 27%. DSC: T_g 80 °C. GPC: M_n = 2400; MWD = 1.48. ¹H NMR (DMSO- d_6), δ (ppm): 1.96 (6H), 3.18 (1H), 3.37 (1H), 3.39 (1H), 3.60 (1H), 4.03 (1H), 5.30 (1H), 6.12 (2H), 6.17 (1H). IR (KBr, cm⁻¹): 3334, 2916, 1601, 1481, 1360, 1196, 1124, 1038, 989, 816, 692.

PEP-AZ-Cl. 4-Chloroaniline (0.64 g, 5 mmol) was dissolved in a homogeneous mixture of glacial acetic acid (6 mL), propionic acid (3 mL) and sulfuric acid (98%, 0.7 mL). Diazonium salt was prepared by adding an aqueous solution of sodium nitrite (0.38 g, 5.5 mmol in 1 mL of water) dropwise into the 4-chloroaniline solution. The mixture was stirred at 5 °C for 5 min and then added dropwise into a solution of PEP-AN (0.6 g, 4 mmol) in DMF (100 mL) at 0 °C. The solution was stirred at 0 °C for 12 h and then added dropwise into plenty of water. The precipitate collected by filtration was dried and then dissolved in THF, filtrated and precipitated with abundant petroleum ether. The product was collected by filtration and dried in a vacuum oven at 60 °C for 48 h.



Figure 1. UV-vis spectra of the epoxy-based azo polymers as spincoated films: (a) azo polymers obtained from PEP-AN; (b) azo polymers obtained from PEP-35AN.

Table 2. λ_{max} of the Epoxy-Based Azo Polymers

	λ_{max} (nm) (DMF solutions/spin-coated films)	
Х	PEP-AZ-X	PEP-35AZ-X
-Cl	427/401	416/394
-CN	454/440	440/424
-NT	488/459	471/445
-mNT	485/453	472/448

Yield: 85%. DSC: T_g 160 °C. ¹H NMR (DMSO- d_6), δ (ppm): 3.56 (2H), 3.78 (2H), 4.21 (1H), 5.46 (1H), 6.91 (2H), 7.47 (2H), 7.67 (4H). IR (KBr, cm⁻¹): 3313, 2902, 1599, 1510, 1477, 1390, 1360, 1313, 1232, 1155, 1142, 1086, 1009, 835, 542.

Other azo polymers were synthesized via a similar procedure as the PEP-AZ-Cl synthesis. PEP-AZ-CN, PEP-AZ-NT, and PEP-AZ-mNT were synthesized by azo-coupling reactions between PEP-AN and diazonium salts of 4-aminobenzonitrile, 4-nitroaniline, and 2-methyl-4-nitroaniline, respectively. PEP-35AZ-Cl, PEP-35AZ-CN, PEP-35AZ-NT, and PEP-35AZ-mNT were synthesized through the azo-coupling reactions between PEP-35AN and diazonium salt of 4-chloroaniline, 4-aminobenzonitrile, 4-nitroaniline, and 2-methyl-4-nitroaniline, respectively. Analytical results of these polymers are given below.



Figure 2. Typical AFM images $(10 \,\mu\text{m} \times 10 \,\mu\text{m})$ and their two-dimensional Fourier transform (2D-FT) images of the photoinduced surface patterns formed on PEP-AZ-Cl films upon irradiation with incident laser light 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 intensity of the laser light was 200 mW/cm² and the irradiation time was 30 min.

 Table 3. Spatial Periods of the Self-Structured Surface Patterns Formed by Irradiation with 488 and 532 nm Laser Light^a

	period (nm) (488 nm/532 nm)		
Х	PEP-AZ-X	PEP-35AZ-X	
-Cl	$440 \pm 10/$	$450 \pm 15/495 \pm 15$	
-CN	$400 \pm 10/495 \pm 15$	$405 \pm 15/500 \pm 15$	
-mNT	$/460 \pm 15$	/	
^{<i>a</i>} . The AFM images of the patterns are given in Figures 2–6.			

PEP-AZ-CN. Yield: 84%. DSC: no obvious glass transition. ¹H NMR (DMSO- d_6), δ (ppm): 3.60 (2H), 3.81 (2H), 4.22 (1H), 5.49 (1H), 6.96 (2H), 7.74 (4H), 7.86 (2H). IR (KBr, cm⁻¹): 3363, 2904,

2225, 1597, 1510, 1443, 1419, 1387, 1313, 1243, 1159, 1138, 845, 823, 559.

PEP-AZ-NT. Yield: 81%. DSC: no obvious glass transition. ¹H NMR (DMSO- d_6), δ (ppm): 3.60 (2H), 3.82 (2H), 4.24 (1H), 5.51 (1H), 6.96 (2H), 7.78 (4H), 8.20 (2H). IR (KBr, cm⁻¹): 3342, 2914, 1601, 1514, 1443, 1421, 1389, 1336, 1234, 1140, 1103, 858, 823, 754, 688, 538.

PEP-AZ-mNT. Yield: 81%. DSC: T_g 156 °C. ¹H NMR (DMSO- d_6), δ (ppm): 2.51 (3H), 3.62 (2H), 3.80 (2H), 4.24 (1H), 5.50 (1H), 6.94 (2H), 7.45 (1H), 7.72 (2H), 7.96 (1H), 8.04 (1H). IR (KBr, cm⁻¹): 3346, 2920, 1599, 1514, 1443, 1419, 1389, 1338, 1259, 1236, 1146, 1117, 1084, 931, 823, 796, 752.

PEP-35AZ-CI. Yield: 83%. DSC: T_g 150 °C. ¹H NMR (DMSO- d_6), δ (ppm): 2.34 (6H), 3.43 (1H), 3.56 (1H), 3.75 (2H), 4.18 (1H), 5.47 (1H), 6.50 (2H), 7.46 (2H), 7.62 (2H). IR (KBr, cm⁻¹): 3311, 2956, 2916, 1599, 1481, 1356, 1271, 1169, 1111, 1088, 1009, 980, 833, 519.



Figure 3. AFM images ($10 \,\mu m \times 10 \,\mu m$) of the photoinduced surface patterns formed on PEP-35AZ-Cl film upon irradiation at (a) 488 and (b) 532 nm. The intensity of the laser light was 200 mW/cm², and the irradiation time was 30 min.

PEP-35AZ-CN. Yield: 81%. DSC: T_g 150 °C. ¹H NMR (DMSO- d_6), δ (ppm): 2.38 (6H), 3.50 (2H), 3.80 (2H), 4.20 (1H), 5.48 (1H), 6.52 (2H), 7.74 (2H), 7.84 (2H). IR (KBr, cm⁻¹): 3446, 2956, 2918, 2224, 1655, 1597, 1493, 1431, 1356, 1269, 1174, 1144, 1111, 978, 843, 553.

PEP-35AZ-NT. Yield: 78%. DSC: T_g 152 °C. ¹H NMR (DMSO- d_6), δ (ppm): 2.40 (6H), 3.59 (2H), 3.85 (2H), 4.24 (1H), 5.50 (1H), 6.55 (2H), 7.79 (2H), 8.26 (2H). IR (KBr, cm⁻¹): 3417, 2956, 2918, 1601, 1514, 1495, 1431, 1336, 1269, 1171, 1144, 1103, 980, 858, 756, 688.

PEP-35AZ-mNT. Yield: 80%. DSC: T_g 149 °C. ¹H NMR (DMSOd₆), δ (ppm): 2.30–2.57 (9H), 3.60 (2H), 3.82 (2H), 4.22 (1H), 5.51 (1H), 6.49 (2H), 7.42 (1H), 7.96 (2H). IR (KBr, cm⁻¹): 3419, 2956, 2918, 1601, 1516, 1495, 1423, 1336, 1259, 1190, 1163, 1113, 1086, 980, 926, 835, 808, 754.

Film Preparation. Solid films of the azo polymers with smooth surfaces were prepared by spin-coating. The homogeneous solutions of the polymers were obtained by dissolving a suitable amount of the polymers in *N*,*N*-dimethylformamide (DMF). The solutions filtered through 0.45 μ m membranes 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 Irradiation. A linearly or circularly polarized beam from an Ar^+ laser (488 nm) and diode-pumped frequency doubled solid state

laser (532 nm) was used as the light source. The laser beam with proper intensity was obtained after being spatially filtered, expanded, and collimated. For inducing the self-structured surface patterns, the laser beam (typically with intensity of 200 mW/cm²) was incident perpendicularly to the film surfaces. Surface-relief-grating (SRG) inscription was carried out by the experimental setup similar to those reported before.^{10,11} A linearly polarized laser beam with different wavelengths (488 nm, 532 nm) was used as the light source. The *p*-polarized laser beam, obtained after being spatially filtered, expanded, and collimated, was adjusted to the intensity of 100 mW/cm². The writing beam was split by a mirror in order that one-half of the beam reflected onto the film surface was coincident with the other half beam which is directly incident onto the film to form an interference pattern. The formation of SRGs was probed with a low power He–Ne laser beam at 632.8 nm by measuring the diffraction efficiency of the first-order diffracted beam in a real time mode.

RESULTS AND DISCUSSION

The two series of epoxy-based polymers with high chromophore density were synthesized through the postpolymerization azo-coupling reactions of the two precursor polymers (Scheme 1). In order to obtain the azo polymers with the high chromophore density, the precursor polymers were prepared to contain aniline moieties in the high density. The postfunctionalization scheme was adopted to yield the polymers with the high degree of functionalization and avoid possible side-reactions of the azo chromophores in the polymerization process.^{45–47} The degree of polymerization (DP) of the azo polymers in each series was the same because they were obtained from the same-batch of the precursor polymers, which could avoid possible influence of DP on the properties in the following study. The self-structured surface patterns and SRGs were induced by irradiating the spincoated solid films of the polymers with the laser light at two different wavelengths. The surface patterns formed in the processes were characterized by AFM and the results were obtained to understand the influences of the chromophoric structures and light irradiation conditions on the pattern formation behavior.

1. Polymer Synthesis and Characterization. The precursor polymers were synthesized through step polymerization of the monomers as shown in Scheme 1, where PEP-AN and PEP-35AN were obtained by reactions of N, N-di(epoxypropyl)aniline (2a) with aniline and N,N-di(epoxypropyl) -3,5-dimethylaniline (2b) with 3,5-dimethylaniline, respectively. The precursor polymers possess the high density of aniline moieties compared with the precursor polymer obtained from the reaction between aniline and bisphenol A diglycidyl ether (BADGE), which was typically used in previous study.^{11,45,47} The polymerization temperature was controlled to be 110 °C to avoid the possible side reaction between the hydroxyl groups generated by ring-opening reaction and the unreacted epoxide rings.⁴⁵ Low molecular weight oligomers, which were mainly cyclic oligomers, were removed by dissolving and precipitation.⁴⁹ The numberaverage molecular weights (M_n) of PEP-AN and PEP-35AN are 5000 and 2400 with the polydispersity indexes of 1.56 and 1.48, which were determined by GPC. The polymers show good solubility in polar solvents such as tetrahydrofuran (THF), N, N-dimethylformamide (DMF), and N,N-dimethylacetamide (DMAc). The precursor polymers were functionalized by introducing four types of azo chromophores through the postpolymerization azo-coupling reactions in DMF. The chemical structure and abbreviated names of the azo polymers are shown in Scheme 1. The first two parts of the names specify the azo



Figure 4. AFM images $(10 \ \mu m \times 10 \ \mu m)$ of the photoinduced surface patterns formed on PEP-AZ-CN and PEP-35AZ-CN films upon irradiation at 488 and 532 nm: (a) PEP-AZ-CN, 488 nm; (b) PEP-AZ-CN, 532 nm; (c) PEP-35AZ-CN, 488 nm; (d) PEP-35AZ-CN, 532 nm. The intensity of the laser light was 200 mW/cm². The irradiation time with the 488 nm laser was 30 min and the irradiation time with the 532 nm laser was 15 min.

polymers obtained from the precursor polymers PEP-AN or PEP-35AN and the last part makes the distinctions of the substituents on the azo chromophores.

The precursor and azo polymers were characterized by ¹H NMR and other spectral analyses. The results are given in the Experimental Section and the Supporting Information (Figure S1–S6). The ¹H NMR spectrum of precursor polymer PEP-AN shows the resonance signals of the aniline moieties at 6.49, 6.99, and 6.60 ppm (Figure S1, Supporting Information), which are attributed to the protons at para, meta, and ortho positions of the amino group. In the ¹H NMR spectrum of precursor polymer PEP-35AN (Figure S1, Supporting Information), the resonance signals of the 3,5-dimethylaniline moieties appear at 6.17 and 6.12 ppm attributed to the protons at *para* and *ortho* positions of the amino group, and at 1.96 ppm attributed to the protons of the methyl groups. After the postpolymerization azo-coupling reactions, where excess amount of diazonium salts (molar ratios to aniline moieties of the precursor polymers) was used, the ¹H NMR spectra show the changes described below. The resonance signals corresponding to the protons at para positions of the aniline moieties (6.49 ppm in PEP-AN and 6.17 ppm in PEP-35AN) completely disappear (Figure S2 and S3, Supporting Information). It indicates that the azo-coupling reaction occurs at the *para* positions with the degree of functionalization (DF) close to 100%. The signals of other protons in aniline residues (ortho and meta to the amino group in PEP-AN; ortho to the

amino group in PEP-35AN) shift to relative lower magnetic field. These spectral changes are attributed to the introduction of the electron-withdrawing groups and the increase of the conjugation length after forming the azo bonds. Moreover, additional resonance signals corresponding to the newly introduced benzenoid protons appear at the even lower magnetic field. The high DFs can also be confirmed by the ratios of the integration areas for the protons on the azo chromophores. The high efficiency of the postpolymerization azo-coupling reactions is consistent with those reported before.^{45–47} From the ¹H NMR and other analytical results, it can be concluded that the epoxy-based azo polymers with the high chromophore density were successfully synthesized.

2. Thermal and Spectral Properties. The epoxy-based precursor polymers and most of the azo polymers show typical phase transition behavior of an amorphous polymer. The glass transition temperatures ($T_{\rm g}$ s) of PEP-AN and PEP-35AN are 87 and 80 °C determined by DSC (Figure S7 and S8, in the Supporting Information). Because of the existence of the azo chromophores, the $T_{\rm g}$ s of the azo polymers are significantly higher than those of the corresponding precursor polymers, which were determined by DSC and are given in Table 1. However, no obvious glass transition can be observed for PEP-AZ-CN and PEP-AZ-NT, which is different from the other azo polymers. This observation can be rationalized by considering the high chromophore density in the polymers and strong dipole—dipole interaction for these



Figure 5. AFM images $(10 \,\mu\text{m} \times 10 \,\mu\text{m})$ of the surface morphology of four azo polymers containing chromophoric nitro groups upon irradiation at 532 nm: (a) PEP-AZ-NT; (b) PEP-AZ-mNT; (c) PEP-3SAZ-NT; (d) PEP-3SAZ-mNT. The incident laser light was linearly polarized. The intensity of the laser light was 300 mW/cm² and the irradiation time was 40 min.

two type azo chromophores. The strong interaction between the chromophores can inhibit the thermal-induced movement of the segments. Compared with cyano and nitro groups, chloro is a relatively weaker electron-withdrawing group and weakly conjugated with the aromatic ring. PEP-AZ-mNT bears a methyl group on the azo chromophore, which will prevents the chromophores to aggregate to each other. Therefore, the intermolecular interaction is weaker in PEP-AZ-Cl and PEP-AZ-mNT, which show the obvious glass transition. For the series of azo polymers obtained from PEP-35AN, all of them show typical glass transition behavior. It can be attributed to the 3,5-dimethyl substituents on the azo chromophores, which also barricade the tight packing of the chromophores. Compared with the epoxybased azo polymers reported before, 45-47 the azo polymers with high chromophore density prepared in this work show higher T_{gs} because of the high chromophore density.

Figure 1 gives the UV-vis absorption spectra of spin-coated films of the azo polymers. The spectra show typical characteristics of the pseudostilbene type azo chromophores, where the absorption bands corresponding to the $\pi - \pi^*$ transition appear in visible spectrum region. The λ_{max} s of the azo polymers in DMF solutions and the spin-coated films are compared in Table 2. The λ_{max} s of the azo polymers are strongly affected by the electron-withdrawing groups on the azo chromophores. As the electron-withdrawing ability increases, the λ_{max} show significant red-shift from the top to bottom in the table. The λ_{max} s of the azo polymers in DMF solutions show red-shifts compared with those of spin-coated films, which can be attributed to the strong solvatochromic effect of DMF. When compared between the two series of polymers with same electronwithdrawing groups, the λ_{max} of the azo polymers obtained from PEP-35AN show blue-shift compared with those of the corresponding polymers obtained from PEP-AN. It can be reasonably attributed to the steric hindrance of the 3,5-methyl substituents, where the planar configuration is crowded for the groups in the excited states.

3. Photoinduced Self-Structured Surface Pattern Formation. The self-structured surface pattern formation was investigated by irradiating the spin-coated films of the azo polymers with the uniform laser single beam at 488 and 532 nm under the normal incidence condition. Figure 2 shows typical AFM images of the photoinduced surface patterns formed on the PEP-AZ-Cl films after the irradiation with the laser light at 488 nm with the intensity of 200 mW/cm² for 30 min. After the irradiation, the film surfaces show regularly spaced pillars with periods correlated with the light wavelengths (Table 3), and localized hexagonal arrangement of the pillars can be recognized. Obvious differences can be seen for the surface patterns formed after irradiation with linearly and circularly polarized laser lights with the same irradiation time and light intensity. When irradiated with the linearly polarized light, the alignment of the localized hexagonal pattern shows correlation with the polarization direction, which can be seen from the two-dimensional Fourier transform (2D-FT) images (Figure 2c). The period of the regularly spaced pillars is 440 \pm 10 nm, which were obtained along \pm 60° with respect to the polarization direction. The pattern formed after the circularly polarized light irradiation does not show the orientational correlation (Figure 2, parts d and e). The 2D-FT analysis indicates the 2D isotropic alignment of the pillars (Figure 2f). The saturated amplitude of the surface patterns is 56 ± 8 nm for irradiation with the linearly polarized light. The saturated amplitude of the surface patterns induced by the circularly polarized light is 71 \pm 14 nm. The above observations of the influence of light polarization on self-structured surface pattern formation is consistent with those reported for DR1MA/MMA 35/ 65 and molecular azo glass.^{33,34,50} When irradiated with 532 nm laser light under similar conditions, no self-structured surface pattern formation was observed for PEP-AZ-Cl film.

Figure 3 shows the patterns formed on the films of PEP-35AZ-Cl after irradiated with linearly polarized laser light at 488 and 532 nm with the intensity of 200 mW/cm² for 30 min. Similar surface pattern formation as PEP-AZ-Cl can be observed. The saturated amplitudes of the pillar-like structures for the PEP-35AZ-Cl films are 36 ± 8 nm and 58 ± 8 nm for the 488 and 532 nm light irradiation. When irradiated with 488 nm light, PEP-35AZ-Cl shows the smaller surface modulation compared with that of PEP-AZ-Cl, which could be attributed to the steric hindrance of the bulky 3,5-dimethyl groups and its inhibition to



Figure 6. AFM images $(10 \,\mu\text{m} \times 10 \,\mu\text{m})$ of the photoinduced surface patterns on PEP-35AZ-CN films upon the irradiation with 532 nm laser light for different time. The intensity of the laser light was 200 mW/cm². The irradiation time was (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 30 min, (f) 40 min.



Figure 7. Amplitude of the surface patterns formed on PEP-35AZ-CN film as a function of irradiation time, irradiated with linearly polarized laser light. The wavelength of the laser light was 532 nm and the intensity of the laser light was 200 mW/cm^2 .

the trans-cis-trans isomerization of the adjacent azo bond. However, when irradiated with 532 nm laser light, the selfstructured surface patterns can be observed for PEP-35AZ-Cl film, which is contrast to the case of PEP-AZ-Cl. The periods of the ordered structures show obvious correlation with the light wavelengths, which are 450 ± 15 nm and 495 ± 15 nm for the irradiation with the 488 and 532 nm laser light.

Figure 4 shows typical AFM images of the self-structured patterns formed on PEP-AZ-CN and PEP-35AZ-CN films upon

irradiation with laser light at both 488 and 532 nm with the intensity of 200 mW/cm². The irradiation time was 30 and 15 min for the 488 and 532 nm illuminations, respectively. The surface patterns show similar characteristics as described above for PEP-AZ-Cl and PEP-35AZ-Cl, where the surface patterns comprise regularly spaced pillars with the period determined by the light wavelength. The space periods for PEP-AZ-CN are 400 \pm 10 and 495 \pm 15 nm when irradiated with 488 and 532 nm laser light (Figure 4a and 4b); correspondingly the periods are 405 ± 15 and 500 ± 15 nm for PEP-35AZ-CN (Figure 4, parts c and d. The saturated amplitude of the surface structures is also closely related with the light wavelength for both polymers. After the irradiation at 488 nm, the saturated heights of the pillars are 19 \pm 3 nm and 15 \pm 3 for PEP-AZ-CN and PEP-35AZ-CN films (Figure 4, parts a and c). After the irradiation with 532 nm laser light with the same intensity and time, the saturated heights of the pillars can reach 55 \pm 10 and 47 \pm 9 nm for PEP-AZ-CN and PEP-35AZ-CN (Figure 4, parts b and d).

The four polymers containing nitro group as the electronwithdrawing group were studied by the similar method. When irradiated with linearly or circularly polarized laser light at 488 nm, no surface pattern formation can be seen for films of PEP-AZ-NT, PEP-35AZ-NT, PEP-AZ-mNT, and PEP-35AZmNT even with the higher light intensity and longer irradiation time (300 mW/cm², 40 min). When irradiated with the laser light at 532 nm, the self-structured surface pattern formation can only be observed for film of PEP-AZ-mNT. Figure 5 shows AFM images of the surface morphology of the azo polymer films after irradiation with laser light at 532 nm (300 mW/cm², 40 min). The surface pattern is only observed on the film of PEP-AZ-mNT (Figure Sb) with the saturated amplitude of 69 \pm 14 nm and



Figure 8. Typical AFM images $(10 \,\mu\text{m} \times 10 \,\mu\text{m})$ of the surface relief grating formed on PEP-35AZ-CN and PEP-AZ-NT films with irradiation of the 488 nm laser light: (a) PEP-35AZ-CN, 2D-view; (b) PEP-35AZ-CN, 3D-view; (c) PEP-AZ-NT, 2D-view; (d) PEP-AZ-NT, 3D-view; The intensity of the incident laser light was 100 mW/cm² and the irradiation time was 600 s.

space period of 460 ± 15 nm. In this case, the methyl substitution on the benzene ring bearing the nitro group plays a role to promote the pattern formation.

Figure 6 shows the pattern formation on PEP-35AZ-CN film at different times when irradiated with linearly polarized 532 nm laser light. Figure 7 gives the corresponding relationship between the modulation amplitude and the irradiation time. It can be seen that the self-structured pattern formation undergoes a gradually developing process and is saturated in about 20 min. Careful observation can reveal another interesting characteristic of the self-structured surface pattern related with the light polarization conditions. After the irradiation with linearly polarized laser light for long time (such as longer than 20 min), the pillars obviously deformed in two directions that are about $\pm 60^{\circ}$ to the polarization direction. This characteristic can also be recognized for other azo polymers (Figure 2-5). However, no such deformation is observed after the irradiation with circularly polarized laser light, where the deformation seems to be around some incomplete circles (Figure 2d).

4. Photoinduced Surface-Relief-Gratings. For comparison, the surface-relief-grating (SRG) formation on the azo polymer films was also studied by irradiating the spin-coated films with the 488 and 532 nm laser light. SGRs were inscribed by exposing the films to interference pattern formed by two *p*-polarized laser beams with the intensity of 100 mW/cm². Upon the light irradiation, SRG formations can be observed on the films of all

kinds of azo polymers. Figure 8 shows some representative AFM images of the SRG formed on the films of PEP-35AZ-CN and PEP-AZ-NT when irradiated with the incident laser light at 488 nm for 600 s. The SRGs formed on azo polymer films appear as regularly spaced sinusoidal surface structures, which are similar to many previous reports.^{10,11,18–25} The first order diffraction efficiency of the SRGs was used to describe the inscription rate of the SRG formation. Figure 9 gives the first order diffraction efficiency of the SRG as a function of time in the process of SRG inscription on the films of the azo polymers. Parts a and b of Figure 9 show the curves for the azo polymers obtained from PEP-AN when irradiated with 488 and 532 nm laser light. Parts c and d of Figure 9 give similar results for azo polymers obtained from PEP-35AN.

The SRG formation rates show a correlation with the type of electron-withdrawing groups, methyl substitution and excitation wavelength. PEP-AZ-Cl and PEP-35AZ-Cl, bearing chloro group as the electron-withdrawing group, show relative fast SRG formation rate when irradiated with 488 nm light (Figure 9, parts a and c). However, when irradiated with 532 nm light, the SRG formation rates become very low (Figure 9, parts b and d), where the excitation wavelength is near the tail of the absorption bands of the polymers (Figure 1). In this case, PEP-AZ-CN and PEP-35AZ-CN, bearing cyano as the electron-withdrawing group, show the fastest SRG formation rates in the series (Figure 9, parts b and d). The azo polymers bearing nitro as



Figure 9. First order diffraction efficiency of the SRG as a function of time in the course of SRG inscription on the films of the epoxy-based azo polymers with incident laser light at 488 and 532 nm: (a) azo polymers obtained from PEP-AN, 488 nm; (b) azo polymers obtained from PEP-AN, 532 nm; (c) azo polymers obtained from PEP-35AN, 488 nm; (d) azo polymers obtained from PEP-35AN, 532 nm.

the electron-withdrawing group (PEP-AZ-NT, PEP-AZ-mNT, PEP-35AZ-NT, and PEP-35AZ-mNT) show relatively low SRG formation rate. The 3,5-methyl substituents at the benzene ring show a significant effect to inhibit or retard the SRG formation for most of the azo polymers. However, as exceptions, the 3,5-methyl substitution almost show no effect on the SRG formation rate for azo polymers bearing cyano as the electron-withdrawing group (PEP-AZ-CN and PEP-35AZ-CN) no matter irradiated with 488 or 532 nm light. PEP-AZ-mNT shows a lower SRG formation rate compared with PEP-AZ-NT, owning to the steric hindrance of methyl group *ortho* to the azo bond.

5. Discussion. Above results indicates some unique characteristics related with the self-structured surface pattern formation. First, for the epoxy-based azo polymers, the self-structured surface pattern formation can only be observed for those with high chromophore density as prepared in this study. In order to confirm this point, the light irradiation experiment was also carried out on the epoxy-based azo polymers with lower chromophore densities, which were synthesized from a precursor polymer obtained through the step polymerization of bisphenol A diglycidyl ether (BADGE) and aniline.⁴⁷ The polymers contain the same types of azo chromophores as reported in this article. The chemical structure of the two azo polymers (BP-AZ-CN and BP-AZ-NT) is given in Figure S9 (in the Supporting Information).

Figure S10 (Supporting Information) shows AFM images of the epoxy-based azo polymers after the laser light irradiation under the typical pattern-formation conditions. No self-structured patterns can be observed on the films of BP-AZ-CN and BP-AZ-NT. On the other hand, although the SRG formation rate is dependent on the azo chromophore density, SRG formation can be observed for epoxy-based azo polymers with a very low chromophore density.⁴⁷ Second, the self-structured surface pattern formation shows reliance on the excitation wavelength, which is similar to SRG formation, but the exact correlation with the wavelength is different in some ways. The SRG formation rates of PEP-AZ-Cl and PEP-35AZ-Cl are much larger when irradiated with 488 nm light compared with 532 nm light (Figure 9). It is consistent with previous reports that when the excitation wavelength is between the λ_{max} and the band tail at longer wavelength side, the SRG formation rate is the largest.^{47,51} On the contrary, PEP-35AZ-Cl shows ability to form selfstructured surface pattern in a efficient way when irradiated with 532 nm laser light (Figure 3). For self-structured surface pattern formation, the heights of self-structured surface structures for PEP-AZ-CN and PEP-35AZ-CN are much larger when irradiated with 532 nm light compared with the cases irradiated with 488 nm light (Figure 4). No obvious dependence on the two wavelengths has been observed for SRG formation of these two

polymers. Third, in most cases, the methyl substitution shows effect to inhibit or retard the SRG formation. However, for the self-structured surface pattern formation, the promotion effect of the methyl substitution can be observed for PEP-35AZ-Cl and PEP-AZ-mNT when irradiated with 532 nm laser light.

The exact mechanism of the self-structured surface pattern formation is still unclear to us at this stage. The laser-induced periodic surface structure (LIPSS), i.e., the formation of parallel ripple structures on polymer surfaces induced by irradiation with a single beam of excimer laser or Nd:YAG pulsed laser, has been partially explained by the models based on electromagnetic field theory.^{40,41} The models suggest that one or several Fourier components of the random surface disturbance scatter light from the incident beam nearly along the surface. The interference of the diffracted wave with the incident beam then gives rise optical interference fringes that reinforce the initial disturbance in a positive feedback way to cause the temperature distribution on the surface. The well-organized structures of the surface patterns reported here are quite distinct from parallel ripple structures of LIPSS. The light intensity used here is much lower than those typically used to produce LIPSS. Moreover, one common characteristic of LIPSS is that when the laser beam is normally incident, the period of ripples is nearly equal to the incident wavelength.^{40,41} The periods of the self-structured surface patterns also show some correlations with the incident wavelengths. But the period is obviously smaller than the incident wavelength. Especially, when there is strong absorbance for the incident light, the period is further deviated to the smaller values, such as PEP-AZ-CN and PEP35-AZ-CN irradiated with the laser light at 488 nm, PEP-AZ-mNT at 532 nm (Table 3). Very recently, a model based on the Fick diffusion was proposed for the molecular motion induced by the light in the pattern formation process.⁴² However, unique characteristics of the self-structured surface pattern formation, reported in this article and other previous literature, cannot be explained by the theories.

Previous reports indicate that the SRG formation is closely related with the photoisomerization of azo chromophores.^{18–25} The results obtained in this study strongly suggest that the self-structured surface pattern formation also has a close correlation with the excitation manner and photoisomerization pathway of the azo chromophores. The observations reported here can lead to better understanding of this interesting photoinduced phenomenon in its correlation with the chromophoric structures. However, to elucidate its mechanism at molecular level will require further theoretical and experimental investigations in the future.

CONCLUSIONS

Two series of epoxy-based azo polymers with high chromophore density were prepared by postpolymerization azo-coupling reaction. The laser light irradiation study shows that the photoinduced self-structured surface patterns can be formed on the polymer films, which shows closely correlation with the type of azo chormophore and light irradiation condition. Upon the irradiation of the normally incident 488 nm laser light (200 mW/ cm² for 30 min), the self-structured surface patterns can be formed on films of PEP-AZ-Cl, PEP-35AZ-Cl, PEP-AZ-CN, and PEP-35AZ-CN. When irradiated with the 532 nm laser light under similar condition, the self-structured surface patterns can be formed on films of PEP-35AZ-Cl, PEP-AZ-CN, PEP-35AZ-CN and PEP-AZ-mNT. The photoinduced surface pattern formation also shows reliance on the high chromophore density of the epoxy-based azo polymers, which are distinct from the epoxy-based azo polymers reported before.

ASSOCIATED CONTENT

Supporting Information. Synthesis of the anilines, ¹H NMR spectra of epoxide monomers, ¹H NMR spectra, IR spectra, and DSC diagrams of epoxy-based precursor polymers and azo polymers, and the chemical structure and AFM images of the two epoxy-based azo polymers (BP-AZ-CN and BP-AZ-NT). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wxg-dce@mail.tsinghua.edu.cn.

ACKNOWLEDGMENT

Financial support from the NSFC under Projects 91027024 and 50873054 is gratefully acknowledged.

REFERENCES

(1) Zollinger, H. Azo and diazo chemistry: aliphatic and aromatic compounds; Interscience Publishers: New York, 1961.

(2) Zollinger, H. Color chemistry: synthesis, properties, and applications of organic dyes and pigments, 2nd rev. ed.; VCH: Weinheim, Germany, 1991.

(3) Kumar, G. S.; Neckers, D. C. Chem. Rev. **1989**, 89 (8), 1915–1925.

(4) Xie, S.; Natansohn, A.; Rochon, P. Chem. Mater. 1993, 5 (4), 403-411.

(5) Delaire, J. A.; Nakatani, K. Chem. Rev. 2000, 100 (5), 1817–1845.

(6) Natansohn, A.; Rochon, P. Chem. Rev 2002, 102 (11), 4139-4175.

(7) Ikeda, T.; Mamiya, J.; Yu, Y. L. Angew. Chem. Int. Ed. 2007, 46 (4), 506–528.

(8) Ikeda, T.; Horiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. P. *Macromolecules* **1990**, *23* (1), 42–48.

(9) Todorov, T.; Nikolova, L.; Tomova, N. *Appl. Opt.* **1984**, *23* (23), 4309–4312.

(10) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66* (2), 136–138.

(11) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. Appl. Phys. Lett. **1995**, 66 (10), 1166–1168.

(12) Finkelmann, H.; Nishikawa, E.; Pereira, G. G.; Warner, M. *Phys. Rev. Lett.* **2001**, *8701* (1), 015501(4pp).

(13) Li, M. H.; Keller, P.; Li, B.; Wang, X. G.; Brunet, M. *Adv. Mater.* **2003**, *15* (7–8), 569–572.

(14) Yu, Y. L.; Nakano, M.; Ikeda, T. Nature 2003, 425 (6954), 145-145.

(15) Camacho-Lopez, M.; Finkelmann, H.; Palffy-Muhoray, P.; Shelley, M. Nat. Mater. 2004, 3 (5), 307–310.

(16) Viswanathan, N. K.; Kim, D. Y.; Bian, S. P.; Williams, J.; Liu, W.; Li, L.; Samuelson, L.; Kumar, J.; Tripathy, S. K. *J. Mater. Chem.* **1999**, *9* (9), 1941–1955.

(17) Che, P. C.; He, Y. N.; Wang, X. G. Macromolecules 2005, 38 (21), 8657–8663.

(18) Barrett, C. J.; Natansohn, A. L.; Rochon, P. L. J. Phys. Chem. 1996, 100 (21), 8836-8842.

(19) Barrett, C. J.; Rochon, P. L.; Natansohn, A. L. J. Chem. Phys. 1998, 109 (4), 1505–1516.

- (20) Kumar, J.; Li, L.; Jiang, X. L.; Kim, D. Y.; Lee, T. S.; Tripathy, S. Appl. Phys. Lett. **1998**, 72 (17), 2096–2098.
- (21) Bian, S. P.; Williams, J. M.; Kim, D. Y.; Li, L.; Balasubramanian, S.; Kumar, J.; Tripathy, S. K. J. Appl. Phys. **1999**, 86 (8), 4498–4508.
- (22) Lefin, P.; Fiorini, C.; Nunzi, J. M. Pure Appl. Opt. **1998**, 7 (1), 71–82.
- (23) Pedersen, T. G.; Johansen, P. M.; Holme, N. C. R.; Ramanujam, P. S.; Hvilsted, S. *Phys. Rev. Lett.* **1998**, *80* (1), 89–92.
- (24) Tanchak, O. M.; Barrett, C. J. Macromolecules 2005, 38 (25), 10566–10570.
- (25) Yager, K. G.; Tanchak, O. M.; Godbout, C.; Fritzsche, H.; Barrett, C. J. *Macromolecules* **2006**, *39* (26), 9311–9319.
- (26) Yager, K. G.; Barrett, C. J. Macromolecules 2006, 39 (26), 9320-9326.
- (27) Perschke, A.; Fuhrmann, T. Adv. Mater. 2002, 14 (11), 841–843.
- (28) Kim, M. J.; Kumar, J.; Kim, D. Y. Adv. Mater. 2003, 15 (23), 2005–2008.
- (29) Li, Y. B.; He, Y. N.; Tong, X. L.; Wang, X. G. J. Am. Chem. Soc. **2005**, 127 (8), 2402–2403.
- (30) Liu, B.; He, Y. N.; Wang, X. G. Langmuir 2006, 22 (24), 10233-10237.
- (31) Guo, M. C.; Xu, Z. D.; Wang, X. G. Langmuir 2008, 24 (6), 2740–2745.
- (32) Goldenberg, L. M.; Gritsai, Y.; Kulikovska, O.; Stumpe, J. *Opt. Lett.* **2008**, 33 (12), 1309–1311.
- (33) Hubert, C.; Fiorini-Debuisschert, C.; Maurin, I.; Nunzi, J. M.; Raimond, P. *Adv. Mater.* **2002**, *14* (10), 729–732.
- (34) Hubert, C.; Fiorini-Debuisschert, C.; Rocha, L.; Raimond, P.; Nunzi, J. M. J. Opt. Soc. Am. B-Opt. Phys. **200**7, 24 (8), 1839–1846.
- (35) Bolle, M.; Lazare, S.; Leblanc, M.; Wilmes, A. Appl. Phys. Lett. **1992**, 60 (6), 674–676.
 - (36) Bolle, M.; Lazare, S. J. Appl. Phys. 1993, 73 (7), 3516-3524.
- (37) Hiraoka, H.; Sendova, M. Appl. Phys. Lett. **1994**, 64 (5), 563–565.
- (38) Ivanov, M.; Rochon, P. Appl. Phys. Lett. 2004, 84 (22), 4511-4513.
- (39) Tsutsumi, N.; Fujihara, A. Appl. Phys. Lett. 2004, 85 (20), 4582-4584.
- (40) Sipe, J. E.; Young, J. F.; Preston, J. S.; Vandriel, H. M. *Phys. Rev.* B **1983**, 27 (2), 1141–1154.
- (41) Zhou, G. S.; Fauchet, P. N.; Siegman, A. E. *Phys. Rev. B* **1982**, *26* (10), 5366–5382.
- (42) Leblond, H.; Barille, R.; Ahmadi-Kandjani, S.; Nunzi, J. M.; Ortyl, E.; Kucharski, S. J. Phys. B. At. Mol. Opt. Phys. 2009, 42, 205401.
- (43) Ahmadi-Kandjani, S.; Barille, R.; Dabos-Seignon, S.; Nunzi, J. M.; Ortyl, E.; Kucharski, S. *Opt. Lett.* **2005**, *30* (15), 1986–1988.
- (44) Ahmadi-Kandjani, S.; Barille, R.; Dabos-Seignon, S.; Nunzi, J. M.; Ortyl, E.; Kucharski, S. *Mol. Cryst. Lig. Cryst.* **2006**, 446, 99–109.
- (45) Wang, X. G.; Kumar, J.; Tripathy, S. K.; Li, L.; Chen, J. I.; Marturunkakul, S. E. *Macromolecules* **1997**, 30 (2), 219–225.
- (46) Wang, X. G.; Balasubramanian, S.; Kumar, J.; Tripathy, S. K.; Li, L. Chem. Mater. **1998**, *10* (6), 1546–1553.
- (47) He, Y. N.; Wang, X. G.; Zhou, Q. X. Polymer **2002**, 43 (26), 7325–7333.
- (48) Chakraborti, A. K.; Rudrawar, S.; Kondaskar, A. Org. Biomol. Chem. 2004, 2 (9), 1277–1280.
- (49) Klee, J. E.; Flammersheim, H. J. Macromol. Chem. Phys. 2002, 203 (1), 100–108.
- (50) Yin, J. J.; Ye, G.; Wang, X. G. Langmuir 2010, 26 (9), 6755-6761.
- (51) Kim, M. J.; Lee, J. D.; Chun, C.; Kim, D. Y.; Higuchi, S.; Nakayama, T. *Macromol. Chem. Phys.* **2007**, 208 (16), 1753–1763.