Azobenzene-Containing Supramolecular Side-Chain Polymer Films for Laser-Induced Surface Relief Gratings

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In this article, we describe the fabrication of azobenzene-containing supramolecular side-chain polymer films based on hydrogen bonds, on which surface relief gratings can be laser-induced. The supramolecular polymer side-chain is formed by attaching different azobenzene-type compounds to poly(4-vinylpyridine) through hydrogen bonding, thus allowing for tuning the content and kind of the azobenzene derivatives easily and avoiding the tedious synthetic work. It is found that such an azobenzene-containing supramolecular side-chain polymer can form nice films by the spin-coating method for surface relief gratings, and moreover, a large surface modulation depth of 312 nm can be observed. We anticipate that this research provides a type of materials for surface relief gratings. In closing, we have provided a new approach for fabricating surface relief gratings employing hydrogen-bonded supramolecular side-chain azo polymers.

Introduction

Azobenzene-containing polymers are fascinating materials because of efficient photoisomerization and photoinduced anisotropy of the azobenzene groups. The incorporation of azo chromophores into the polymers based on covalent bonds or noncovalent bonds can introduce structural diversity and processible ability into the functional materials. Laser-induced surface relief gratings (SRGs) on azobenzene polymer films, first reported by Natansohn et al. and Tripathy et al. in 1995,[1] has aroused considerable attention since then.[2] The large-scale polymer chains migration leads to the formation of SRGs, which are stable below the glass-transition temperature of the polymers. Polymers with such properties have shown potential applications in areas such as optical information storage, optical switching devices, holographic gratings, and so on. It has also been demonstrated that SRGs can be photoinduced on amphiphilic liquid-crystalline azobenzene-containing diblock copolymer or hyperbranched azobenzene-containing polymer films.[3] Recently, Moore et al. studied the azobenzene functionalized polymers via ring-opening metathesis polymerization, and SRGs were inscribed on such polymer films.[4] To avoid the tedious synthesis of azobenzene-containing polymers, the method of doping normal polymers with azobenzene-type compounds has been introduced for the photofabrication of SRGs.[5] The doping method allows for the easy variation of the content and type of the azobenzenes. However, as there is no specific interaction between the polymer and dopants in the mixing systems, the azo compounds can be molecularly dispersed in the system only when the doping concentration is low. As a result, the saturated modulation depth is usually low for the mixing systems.

We wondered whether the concept of supramolecular polymers could be applied in doping systems for the realization of incorporating azo chromophores to polymeric chains and creating a large modulation depth. Supramolecular polymers as introduced first by Lehn can be built on the basis of different intermolecular interactions, including coordination bond, hydrogen bond, $\pi-\pi$ interaction, and so on.[6,7] Usually, supramolecular polymers are classified into two classes: main chain and side chain. Kato and Fréchet et al. reported a hydrogen-bonded supramolecular side-chain

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polymer, which exhibits a stable liquid-crystalline phase.[8−10] Several supramolecular azo polymers were reported for the research of supramolecular liquid crystalline based on hydrogen bonding.[11−12] Ikkala et al. described the fabrication of supramolecular polymeric materials with multiple length scales employing noncovalent bond.[13] Knoll et al. employed the electrostatic interactions to stabilize orientational order in novel materials for second-order nonlinear optics.[14] Tripathy et al. studied the formation of the SRGs on self-assembled polyion/dye composite films.[15] Seki et al. developed an approach using a binary system of a polymer containing azobenzene in the side chain and 4′-pentyl-4-cyanobiphenyl for the SRGs.[16] We synthesized an azobenzene-containing building block for fabricating supramolecular main-chain polymer films based on multiple hydrogen bonds and showed that SRGs could be laser-induced on such azobenzene-containing supramolecular main-chain polymer films.[17] However, SRGs are not deep enough for the azobenzene-containing supramolecular main-chain polymer films. In this paper, we describe the fabrication of azobenzene-containing supramolecular side-chain polymer films based on hydrogen bonds and hope that the supramolecular side-chain polymer allows for easy tuning of the content and variety of the azobenzene moietyies. In addition, a nice film with deep SRGs is anticipated.

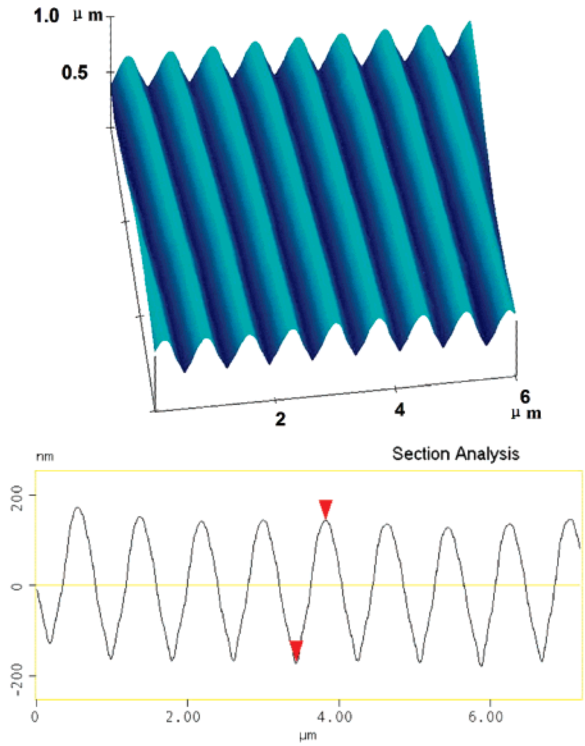
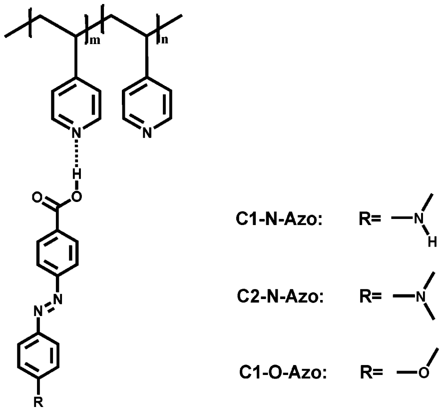


Figure 1. AFM image of the surface relief gratings formed on azobenzene-containing supramolecular side-chain polymer film and the section analysis.

Scheme 1. Proposed Azobenzene-Containing Supramolecular Side-Chain Polymer and Chemical Structure of Azobenzene Derivatives Used



Results and Discussion

Preparation and Characterization of Surface Relief Gratings. The azobenzene-containing side-chain supramolecular polymer was formed by attaching several azobenzene-type compounds to poly(4-vinylpyridine) (P4VP) through hydrogen bonding (see Scheme 1). In the process, suitable amounts of azobenzene derivatives and P4VP were dissolved in *N*,*N*-dimethylformamide (DMF) to obtain the mixed solutions. The azobenzene-containing supramolecular side-chain polymer films were prepared by spin-coating the mixed solutions at 500−2500 rpm onto the clear glass slides and were dried at 70 °C under a vacuum for 24 h. By changing the content and the kind of azobenzene derivatives bearing strong or weak electron-releasing moieties, we can easily prepare a series of azobenzene-containing supramolecular side-chain polymer films with optical-quality surfaces without tedious synthetic work.

We have found, interestingly, that the above prepared azobenzene-containing supramolecular side-chain polymer films can be used for SRGs with a surface modulation depth as large as 312 nm, as shown in Figure 1. The experimental setup for SRG fabrication was similar to those reported before.[1] An Ar$^+$ laser beam at 488 nm with an intensity of 80 mW/cm^2 was used as the light source. SRGs were optically inscribed on the films with *p*-polarized interfering laser beams, where the Ar$^+$ laser beam was split by a mirror and the reflected half-beam coincided with the other half on the film surfaces. Atomic force microscope (AFM) observation indicated that sinusoidal surface relief structures with regular spaces were fabricated on the surfaces of azobenzene-

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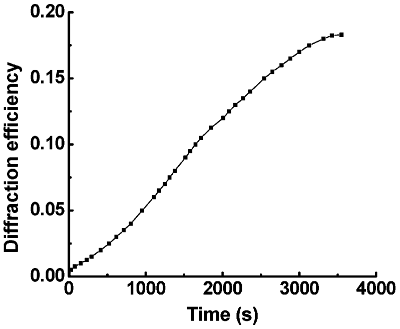

Figure 2. Diffraction efficiency of SRGs inscribed on the azobenzene-containing supramolecular side-chain polymer film as a function of time.

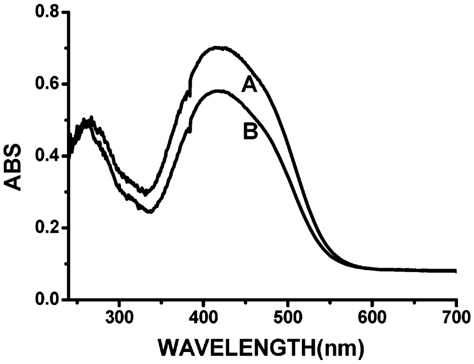

Figure 3. UV−vis spectra of the azobenzene-containing supramolecular polymer film measured after irradiation with a linearly polarized Ar$^+$ laser beam for 20 min: (A) perpendicular to the polarization direction of the laser beam; (B) parallel to the polarization direction of the laser beam.

containing supramolecular side-chain polymer films. For the azobenzene-containing supramolecular side-chain polymer films with 1:1 P4VP:4′-carboxy-4-(methylamino)azobenzene (C1-N-Azo) molar ratios, AFM section analysis shows that the surface modulation depth is about 312 nm, and the grating spacing is about 728 nm after irradiation for 1 h at room temperature. The modulation depth depends on the irradiation time, and the spatial period can be adjusted by the angle θ between the two interfering beams and the wavelength λ of the writing beams.

The process of grating formation can be probed by measuring the first-order diffraction efficiency of the SRGs during the optical inscription. In our experiments, the diffraction efficiency was in situ recorded in transmission mode with an unpolarized low-power He−Ne laser beam at 633 nm as described in the literature.[1b] Figure 2 shows the diffraction efficiency as a function of irradiation time for the azobenzene-containing supramolecular side-chain polymer films. The diffraction efficiency increases with increasing irradiation time and reaches a saturated value of 18% at 3600 s.

Photoinduced Dichroism. To study the orientation of azobenzene in the resulting gratings, we employed a polarized UV−vis spectroscopy. After the film with a 1:1 P4VP:C1-N-Azo molar ratio was exposed to the linearly polarized Ar$^+$ laser beam for 20 min, significant dichroism was observed. As shown in Figure 3, the absorbance in the direction parallel to the polarization of the laser beam is clearly smaller than that in the direction perpendicular to the polarization of the laser beam. This result indicates that the preferential orientation of the azobenzene chromophores is perpendicular to the electric vector of the laser beam. The orientation order parameter S can be estimated from the dichroic ratio $S = (A_\perp - A_\parallel)/(A_\perp + 2A_\parallel)$, where $A_\perp$ and $A_\parallel$ are the maximum absorbance in directions perpendicular and parallel to the polarization, respectively.[18] The orientation order parameter S of this azobenzene-containing supramolecular side-chain polymer films is estimated to be 0.065 at the photostationary state.

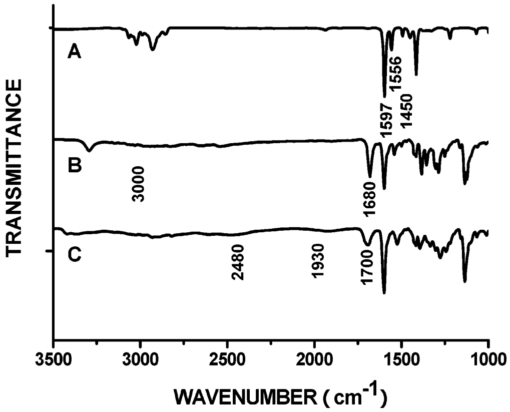

Figure 4. FT-IR transmission spectrum of the films of (A) pure P4VP, (B) pure C1-N-Azo, and (C) mixed 1:1 P4VP:C1-N-Azo on CaF2 plates.

Confirmation of the Hydrogen Bond in the Supramolecular Polymer Films. The existence of the hydrogen bond in the azobenzene-containing supramolecular side-chain polymer films was confirmed by FT-IR.[1919] Figure 4 shows the IR spectra of the casting films of P4VP, C1-N-Azo, and a 1:1 mixture of P4VP and C1-N-Azo on CaF$_2$ plates. The absorption peaks at 1597, 1556, and 1450 cm^{-1} in Figure 4A can be assigned to the ring vibration of pyridine of P4VP. The broad absorption band around 3000 cm^{-1} and the absorption appearing at 1680 cm^{-1} in Figure 4B indicate that the carboxyl group in pure C1-N-Azo is not in a free but in an associated state. As shown in Figure 4C, a C═O stretching vibration appeared at 1700 cm^{-1} indicates that the carbonyl group is in a less associated state than that in pure C1-N-Azo. Moreover, a O−H stretching vibration appeared at 2480 and 1930 cm^{-1} shows that the hydroxyl group forms stronger hydrogen bonds than those in pure C1-N-Azo. Therefore, the above results confirm that hydrogen bonds are formed between P4VP and C1-N-Azo. It should be noted that there is almost no change in position of the absorption peaks from 1600 to 1300 cm^{-1} comparing plots A and C in Figure 4. This result implies that the carboxyl group of C1-N-Azo in the film as well as the pyridine group of P4VP are not ionized, thus excluding the possibility that azobenzene-containing supramolecular side-chain polymer is not assembled via electrostatic attraction but hydrogen bonding.

Aggregation of Azobenzene in the Supramolecular Polymer Films. UV−vis spectroscopy indicates that C1-N-Azo

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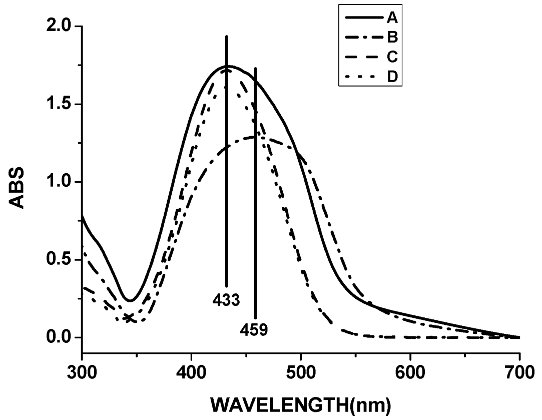

Figure 5. UV spectra of the films of (A) 1:1 P4VP:C1-N-Azo (film), (B) C1-N-Azo (film), (C) C1-N-Azo/DMF (solution), and (D) 1:1 P4VP:C1-N-Azo/DMF (solution).

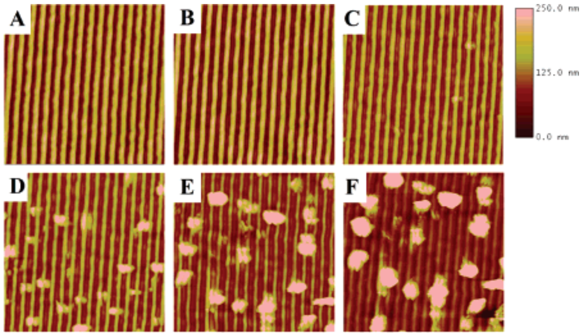

Figure 6. AFM images showing the surface profiles change of surface relief gratings formed on azobenzene-containing supramolecular polymer films of C1-N-Azo (50%) at various temperatures: (A) 60, (B) 90, (C) 120, (D) 130, (E) 140, and (F) 150 °C (the image size is 10 × 10 μm^2 in each case and each image was recorded in the height mode).

is dispersed well when attached to P4VP by hydrogen bonding. As shown in Figure 5, the maximum absorption of pure C1-N-Azo in the DMF solution (Figure 5C) appears at 433 nm, corresponding to the $\pi-\pi^*$ transition. It red-shifts to 459 nm, however, when it is in the film (Figure 5B). This red shift could be attributed to J-aggregation that involves head-to-tail stacking of C1-N-Azo in the film. Notably, both the mixture of P4VP and C1-N-Azo in DMF solution (D) and their film (A) show a maximum absorption around 433 nm. The fact that the maximum absorption of C1-N-Azo in the film is very similar to its solution indicates that there is no serious aggregation of C1-N-Azo in the supramolecular film.

Thermal Stability of the Surface Relief Gratings. To test whether the surface relief grating based on such hydrogen-bonding supramolecular polymers can withstand high temperature, we observed the change of the surface profiles on increasing the temperature of the substrate by temperature-dependent AFM. Figure 6 shows the AFM images of the SRGs at different temperatures. It is found that the surface modulation depth at 90 °C is the same as that observed at room temperature indicated by AFM section analysis, and it keeps good stability until 120 °C. The SRGs begin to be erased at that point and are evidently removed by 150 °C. Therefore, the supramolecular polymer film has demonstrated a good thermal stability, though it is formed on the basis of hydrogen bonds.

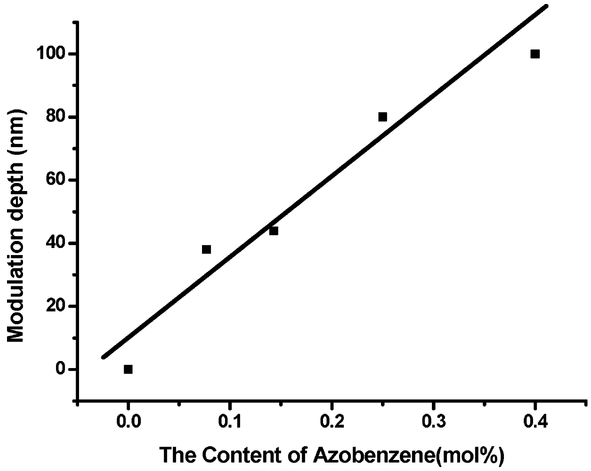

Figure 7. Dependence of the modulation depth of the surface relief gratings on the azobenzene content in the supramolecular polymer films.

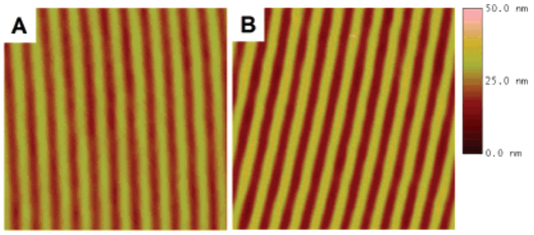

Figure 8. AFM images of the surface relief gratings formed on azobenzene-containing supramolecular polymer films of (A) C1-O-Azo (25%) and (B) C2-N-Azo (4%).

Control of the Content and Kind of the Azobenzene Derivatives. One of the advantages of this azobenzene-containing supramolecular side-chain polymer for fabricating the SRGS is that tedious synthesis of azobenzene-containing polymer can be avoided and the content of azobenzene is easily adjusted by changing the mixing ratio. The influence of azobenzene content on the modulation depth of SRGs is shown in Figure 7. A general trend is clearly seen: the modulation depth of the SRGs increases linearly with increasing the C1-N-Azo content in the range studied. In other words, one can obtain SRGs with desired modulation depth by controlling the molar ratio between azobenzene and P4VP.

It should be pointed out that the type of electron donors on azobenzene derivatives can influence the formation of SRGs. Our previous results have shown that the rates of SRG formation significantly depend on the types of the electron-withdrawing groups in the para-positions of the azobenzene units.[3a,20] Herein, by using different azobenzene derivatives to mix with P4VP, we obtained a series of azobenzene-containing supramolecular side-chain polymers. After inscribing with the *p*-polarized interfering laser beams for 1000 s, a series of SRGs with different modulation depth were obtained. As shown in Figure 8, for 4′-Carboxy-4-(methoxy)-azobenzene (C1-O-Azo) bearing a weak electron-releasing moiety, the modulation depth is just about 10 nm even at a high content of 25%. But for C1-N-Azo bearing a stronger electron-releasing moiety than C1-O-Azo, the modulation depth will reach 80 nm. And the depth of the SRGs based

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on 4′-carboxy-4-(dimethylamino)azobenzene (C2-N-Azo) could be 20 nm at a content of 4%, which is higher than that of C1-N-Azo by about 10 nm under the same condition. However, C2-N-Azo cannot be used to obtain better SRGs because of its poor solubility. These results indicate that the kind of azo chromophores in the supramolecualr polymers also plays a key role in the SRG-forming process: the strong electron-releasing azobenzene derivative can form SRGs with high modulation depth.

Conclusions

In summary, we have provided a new approach for fabricating surface relief gratings employing a hydrogen-bonded supramolecular side-chain azo polymer. Using such azobenzene-containing supramolecular side-chain polymer films, we can observe large surface modulation depth of 312 nm. Because the SRGs are formed on the basis of the large-scale migration of polymer chains driven by photoisomerization, the interaction between the polymer and azobenzene side chains should be a key factor. The large modulation depth indicates that the hydrogen bond is strong enough to ensure a kind of force transfer for migration of the polymers. It is anticipated that this line of research may open new avenues for optical information storage, all-optical switching, diffractive optical elements, and nonlinear optical devices.

Experimental Section

General Method. A commercial multimode Nanoscope IV AFM was used to investigate the surface profiles of the resulting gratings. UV−vis spectra were performed on a Lambda Bio 40 spectrometer equipped with a polarizer. Infrared spectra were run on a Bruker IFS 66v/s spectrophotometer. The field-emission scanning electron microscope (FE-SEM) images were obtained with Sirion 200 scanning electron microscope (FEI). ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a JEOL JNM-ECA300 (300 MHz) spectrometer. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane. Thermal properties were performed by TGA 2050 and DSC 2910 (TA instruments). The heating rate was 20 °C/min for TGA measurements and 10 °C /min for the DSC measurements.

Materials. Poly(4-vinylpyridine) ($M_w = 60\,000$) was purchased from Aldrich. Other chemicals were purchased from Beijing Chemical Reagents Company.

4′-Carboxy-4-(methylamino)azobenzene. A solution of $NaNO_2$ (4.14 g, 60 mmol) in 60 mL of H_2O was added dropwise to a cooled solution of 4-aminobenzoic acid (8.23 g, 60 mmol) in 16.5 mL of concentrated HCl along with 120 mL of H_2O at 0−5 °C. The solution was then stirred for another 30 min. After dropwise addition of *N*-methylaniline (6.54 mL, 60 mmol), the mixture was stirred for 2 h. (Red-orange precipitate was filtered off.) Filtrate was diluted with water. After 24 h, a red-violet precipitate was filtered off and recrystallized from 1:1 H_2O:C_2H_5OH. ^{1}H NMR (DMSO-d_6): δ 2.79 (s, 3H, CH_3N), 6.68 (d, 2H, ArH), 7.77 (d, 2H, ArH), 7.81 (d, 2H, ArH), 8.06 (d, 2H, ArH).

4′-Carboxy-4-(dimethylamino)azobenzene. A solution of $NaNO_2$ (4.14 g, 60 mmol) in 60 mL of H_2O was added dropwise to a cooled solution of 4-aminobenzoic acid (8.23 g, 60 mmol) in 24 mL of concentrated HCl at 0−5 °C. The solution was then stirred for another 30 min and added to *N*,*N*-dimethylaniline (8.3 mL) in 600 mL of H_2O (pH 6). The mixture was stirred for 2 h. Dark red precipitate was filtered off and recrystallized from 1:1 H_2O:C_2H_5OH. ^{1}H NMR (DMSO-d_6): δ 3.06 (s, 6H, $(CH_3)_2N$), 6.82 (d, 2H, ArH), 7.80 (d, 2H, ArH), 7.83 (d, 2H, ArH), 8.07 (d, 2H, ArH).

4′-Carboxy-4-(hydroxy)azobenzene. A solution of $NaNO_2$ (4.14 g, 60 mmol) in 60 mL of H_2O was added dropwise to a cooled solution of 4-aminobenzoic acid (8.23 g, 60 mmol) in 24 mL of concentrated HCl at 0−5 °C. The solution was then stirred for another 30 min and added to sodium phenolate (7.31 g, 63 mmol) in 600 mL of H_2O (pH 9). The mixture was stirred for 2 h and acidified with 2 M HCl aq. Orange precipitate was filtered off and recrystallized from 1:1 H_2O:C_2H_5OH. ^{1}H NMR (DMSO-d_6): δ 6.95 (d, 2H, ArH), 7.82 (d, 2H, ArH), 7.87 (d, 2H, ArH), 8.10 (d, 2H, ArH).

4′-Carboxy-4-(methoxy)azobenzene. 4′-Carboxy-4-(hydroxy)-azobenzene (10 mmol; 2.42 g) was dissolved in 100 mL of ethanol. Ten milliliters of NaOH aq (2.5 M) was then added. After the solution was stirred for 0.5 h at room temperature, 1 mL of iodomethane (15 mmol) was added. The mixture was stirred for over night at 70 °C. After the mixture was cooled, 20 mL of 2 M HCl aq was added. Orange precipitate was filtered off and recrystallized from 1:1 H_2O:C_2H_5OH. ^{1}H NMR (DMSO-d_6): δ 3.85 (s, 3H, $-CH_3$), 7.12 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.91 (d, 2H, ArH), 8.10 (d, 2H, ArH).

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Supporting Information Available: TGA and DSC of the resulting azobenzene-containing supramolecular side-chain polymer; SEM images of the SRGs and original NMR data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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