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Photoresponsive Behaviors of Azobenzene Functionalized 2-Arm, 3-Arm, and 4-Arm Telomers: A Comparative Study

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Azobenzene functionalized 2-arm, 3-arm, and 4-arm telomers were synthesized according to the synthetic process described earlier. Here we report their photoresponsive behaviors to elucidate the effects of number of arms of star azotelomers on their photoresponsive behaviors. Photoisomerization behaviors of star azotelomer films were investigated. Surface relief gratings were inscribed on spin-coated azotelomer films by irradiating interference pattern of Ar+ laser at 488 nm. Diffraction efficiencies of azotelomers were found to increase with an increase in number of arms. The formation of surface relief gratings (SRG) was observed with atomic force microscopy (AFM) and optical polarized microscopy.

Keywords: Azopolymer, photoisomerization, star polymer, surface relief gratings

Q2 1. Introduction

Recently star shaped polymers have been of interest due to their inherent properties such as reduced viscosity, good solubility, low glass transition temperature and fast response to external stimuli [1,2]. Star polymers possess more compact structure than the analogous linear structure because of high segment density. Recently we reported the synthesis of azobenzene functionalized 2-arm, 3-arm, and 4-arm telomers by free radical telomerization of 6-(4-(4′-Methoxyphenylazo)-phenoxy]hexylmethacrylate), MAB6Mc using di-, tri-, and tetra-functional chain transfer agents in presence of AIBN as initiator [3].

The incorporation of azobenzene moiety in star-shaped telomers could significantly widen their potential applications in optical information storage, optical switching devices, diffractive optical elements, and other areas [3–12]. Since the discovery of unusual light driven polymer mass transport on azopolymer films, a variety of applications have already been realized. Photoinduced formation of surface relief gratings (SRGs) on azopolymer films is among the most interesting effects found in recent years [13–15]. By irradiation of an interference pattern of coherent Ar+ laser beams, SRGs can be formed on azopolymer films in a single-step process at a temperature well below their glass transition temperatures. Since the phenomenon was first reported, the mechanism responsible for SRG formation has been actively investigated. It has been confirmed by experiments that the origin of SRG formation at low or medium light intensity is neither a thermally driven process nor ablation in the irradiation regions [16,17]. Repetitive *trans*-*cis* photoisomerization cycles conduct to a fast birefringence process where photochromes orient perpendicularly to the impinging light polarization plane. Such a fast process is followed by slower migration of photochromes from the lighted to the dark regions to form SRG. But the actual mechanism is still debated. This study is aimed at an investigation of photoresponsive behaviors of azobenzene-functionalized 2-arm, 3-arm, and 4-arm telomers to reveal the effects of number of arms on their photoresponsive properties.

2. Experimental

6-(4-(4′-Methoxyphenylazo)phenoxy]hexylmethacrylate), MAB6Mc was synthesized in good yield and purity according to the synthetic method described elsewhere and was used to synthesize star azotelomers by free radical telomerization using multifunctional chain transfer agents in presence of AIBN as initiator [3]. Telomer films were prepared by spin coating their solutions on glass substrates. Thickness of telomer films was controlled by varying the concentration of telomer solution in THF and speed of coating. UV-Vis spectra of telomer films were recorded by a Shimadzu spectrophotometer. Reversible *trans*-*cis* photoisomerization of azotelomers was studied by irradiating UV and visible light on spin-coated azotelomer films respectively. SRGs were

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inscribed on azotelomer films by irradiating interference pattern of Ar+ laser (488 nm) beams. Diffraction efficiencies of the gratings were monitored by measuring the intensity of first order diffracted beams by He-Ne laser (633 nm).

3. Results and Discussions

In our previous article we reported that molecular weight of linear and star telomers depend on the amount of telogen introduced in telomerization. Thus molecular weights of linear and star telomers can be controlled very easily. In this study 2-arm, 3-arm, and 4-arm telomers of almost equal molecular weights were synthesized so that the effect of number of arms can be observed very easily. Figure 1 shows typical schematic structures of star shaped azotelomers synthesized by free radical telomerization of MAB6Mc using multifunctional chain transfer agents. Molecular weights of telomers were determined by GPC. The characterization of 2-arm, 3-arm, and 4-arm telomers are stated in Table 1. Molecular weights of azotelomers are almost similar. Viscosity and glass transition temperatures of star azotelomers were found to decrease with an increase in number of arms. It is assumed that this may be due to lack of entanglement with increasing number of arms of star azotelomers.

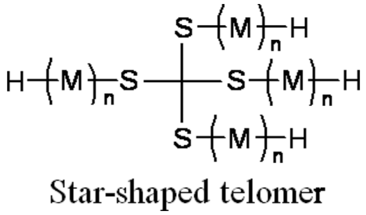


Fig. 1. Schematic structure of star azotelomers; M is the azobenzene functionalized monomer (MAB6Mc).

Table 1. Characterization of 2-Arm, 3-Arm, and 4-Arm telomer

Telomer	Mn	Viscosity, cP	Thermal phase transition behaviors
2-arm	8700	1.10	G 76 S 90 N130 I
3-arm	8700	1.08	G 72 S 86 N125 I
4-arm	8500	0.85	G 60 S 81 N122 I

G: Glassy, S: Smectic, N: Nematic, I: Isotropic. Viscosity was measured with 0.08 g/mL solution in THF at 25°C.

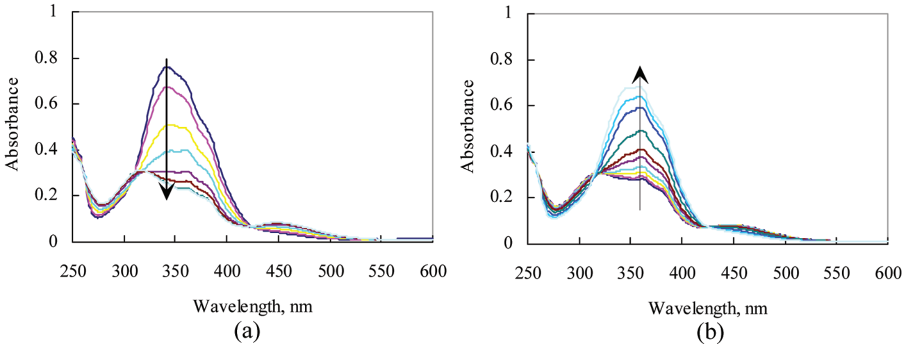
3.1 Photoisomerization Behaviors of Star Azotelomers

Photoisomerization properties of azotelomer films was studied by irradiating UV and visible light. Azotelomer films were prepared by spin-coating of their solutions in THF onto cleaned glass slides. The spin-coated films were air dried at room temperature. For comparative studies, film thicknesses of azotelomers were controlled to be almost the same. The thickness of the films were measured to be about 200–400 nm.

Figure 2 shows the changes in absorption spectra of 3-arm telomer film by UV and visible light irradiation. The UV/visible absorption spectra are characterized by a strong π-π^* transition of *trans*- azobenzene moiety at 359 nm and a weak absorption at 450 nm, which originates from n-π^* transition. Upon UV light irradiation absorbance at 359 nm decreased due to *trans→cis* photoisomerization and absorbance at 450 nm increased a little due to *cis→trans* photoisomerization. By visible light irradiation (435 nm) a reverse situation was observed. Thus UV light irradiation (366 nm) generates a photostationary state with a high amount of *cis*-isomer and the visible light irradiation (435 nm) generates a *trans*-isomer rich photostationary state. The subsequent *cis→trans* isomerization by visible light irradiation rebuilt the initial state completely, which demonstrates the reversibility of the reaction. The UV/Visible absorption spectra of 2-arm and 4-arm telomers also exhibited almost similar reversible photoisomerization behaviors.

3.2 Fabrication of Surface Relief Gratings

It is evident from Figure 2 that telomer film has a little absorbance at around 488 nm. This makes it possible to record holographic gratings by repeated *trans→cis→trans* photoisomerization in telomer films upon exposure to an interference pattern of Ar+ laser at 488 nm. Figure 3 shows the optical setup of instruments for inscription of SRG on star-shaped azotelomer films. Circularly polarized Ar+ laser at 488 nm was used as writing beam and He-Ne laser at 633 nm was used as reading beam. Moderate power (100 mW/cm^2) was used for inscription of SRG to avoid possible



(a) (b)

Fig. 2. Photoisomerization of 3-arm telomer films by UV (a) and visible light irradiation (b).

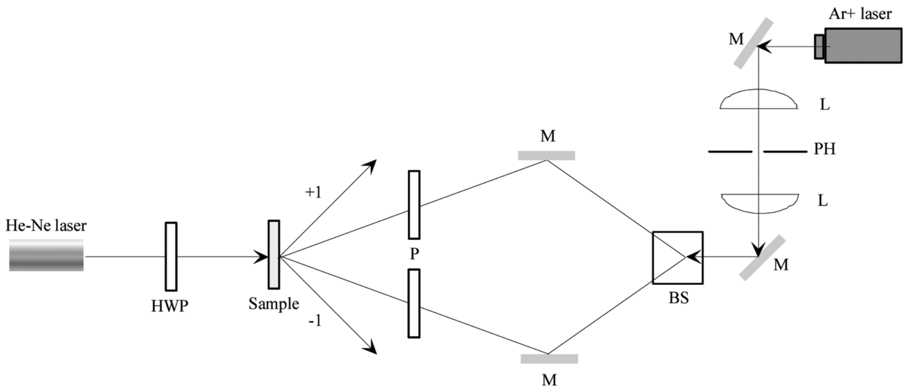


Fig. 3. Instrumental setup for SRG inscription on azotelomer films. M- Mirror, L- Lens, PH- Pinhole, BS- Beam splitter, P- Polarizer, HWP- Half wave plate.

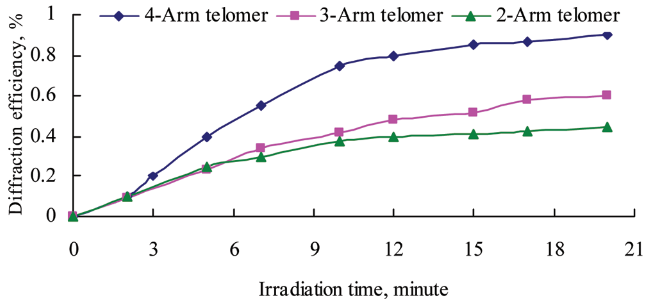


Fig. 4. Diffraction efficiencies of 2-arm, 3-arm, and 4-arm azotelomer films as a function of irradiation time.

side effects caused by high intensity laser irradiation. The laser power was controlled to be the same for each experiment. Grating formation was confirmed by monitoring the intensity of the first order diffraction beam. Diffraction efficiency was measured by the following equation:

$$\eta = \mathrm{I}_1/\mathrm{I}_0,$$

where I_1 is the intensity of first order diffraction beam and I_0 is the intensity of transmitted beam through the film without the writing beams.

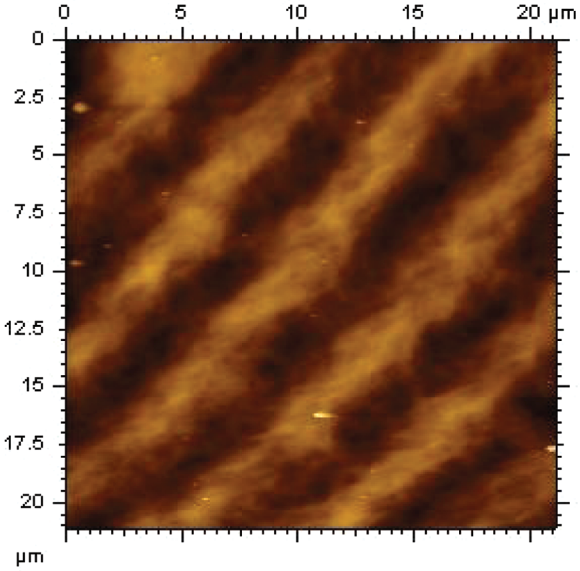


Fig. 5. AFM image of 3-arm azotelomer film after irradiating interference pattern of Ar+ laser for 30 min.

The formation of SRG was studied for the spin-coated thin films of 2-arm, 3-arm, and 4-arm azotelomers. Figure 4 shows diffraction efficiency of star-shaped azotelomers as a function of irradiation time. Diffraction efficiencies increased with an increase in irradiation time. 4-arm telomer showed the highest diffraction efficiency, while 3-arm telomer showed higher diffraction efficiency compared to 2-arm telomer. The results reveal that diffraction efficiency of star-shaped telomers increased with an increase in number of arms. It is assumed that this may be due to the lower glass transition temperature, lower viscosity and lack of entanglement. Irradiation at $\lambda_{\max}$ could accelerate *trans→cis→trans* photoisomerization circles and increase the inscription rates. The photoinduced dynamic process has been found to depend on the polarization state and intensity of the interfering beams, the thickness of the films, and the molecular weight of polymers.

Formation of SRGs on azotelomer films can be observed by AFM and optical polarized microscopy. Figure 5 exhibits the atomic force microscopic image of 3-arm azotelomer film after irradiation of two interfering beams of Ar+ laser for 30 min. It reveals that a regularly spaced sinusoidal pattern was seen in the AFM image. The spacing of the gratings was found to be 2.5 µm. But the grating formed on azotelomer film was not smooth. The stability of SRG formed on azotelomer films were studied by placing the sample under dark at room temperature. The gratings were found to be very stable at room temperature. Thus azotelomers synthesized in this study could be potential candidates for various photonic applications.

4. Conclusion

2-arm, 3-arm, and 4-arm telomers were synthesized by free radical telomerization of MAB6Mc with di-, tri-, and tetra-functional chain transfer agents in presence of AIBN as initiator. All azotelomers synthesized in this study showed reversible photoisomerization by irradiation of UV and visible light. Surface relief gratings were fabricated on azotelomer films by irradiating interference pattern of Ar+ laser and were characterized by measuring first order diffraction efficiency. It was observed that diffraction efficiency of star-shaped azotelomers were found to be increased with an increase in number of arms due to their lower viscosity and lower glass transition temperature which originates from lack of entanglement. Thus, the number of arms of star azotelomers largely influences their photoresponsive behaviors.

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