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Notes

A Photoactive Polymer with Azobenzene Chromophore in the Side Chains

Liming Ding and Thomas P. Russell*

Department of Polymer Science & Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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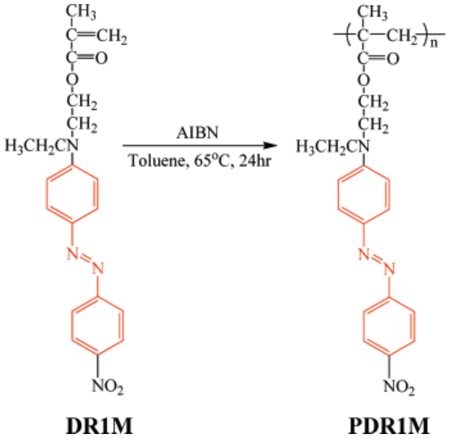
Introduction

Azobenzene and its derivatives can be transformed between the generally more stable *trans* form and the less stable *cis* form upon exposure to UV or visible light. The composition of the photostationary state depends on irradiation wavelength and temperature.[1] The *trans* isomer has no dipole moment while the *cis* isomer has a dipole moment of 3.0 D. Polymers containing azobenzene chromophores (azo-polymers) show nonlinear optical properties and light-induced dichroism and birefringence. Photoinduced motions in azo-polymer films can lead to the formation of surface relief gratings (SRG).[2] Owing to their photoactivity, azo-polymers can be used in photomechanical systems,[3] photoswitches, holographic data storage devices, and micropatterning.[6] Ikeda et al.[3a] reported that a free-standing film of a liquid-crystal network containing the azobenzene chromophore can be repeatedly and precisely bent along any chosen direction by using linearly polarized light. This photomechanical function results from a photoselective volume contraction accompanying the *trans*-to-*cis* photoisomerization. Hoffman et al.[4] developed a photoswitch based on azo-polymers that serve as molecular antennae and actuators to reversibly turn the enzymatic activity on and off in response to a distinct light wavelength. Berg et al.[5] designed novel photoactive oligomers, diamino acid-N$^{\alpha}$-substituted oligo-peptides (DNOs), in which azobenzene side chains were linked to a peptide-like backbone. The holographic gratings of the oligomer films with large first-order diffraction efficiencies (up to 80%) could be written and erased optically. Seki et al.[6a] reported a new optical 3-D alignment of nanocylinders in a diblock copolymer film consisting of liquid-crystalline photoresponsive azo-block and poly(ethylene oxide) block by applying photoinduced mass migration. Natansohn and Rochon et al.[7] studied the photoinduced birefringence and thermal *cis*−*trans* isomerization in poly(disperse red 1 methacrylate) (PDR1M). In this Note, we will present a detailed photophysical study of monomer DR1M and polymer PDR1M (Scheme 1). The effects of UV irradiation on absorption, fluorescence quantum yield, contact angle, hydrodynamic radius, and thin film thickness were investigated and discussed.

Results and Discussion

Scheme 1. Synthesis of PDR1M



PDR1M was synthesized in a manner similar to that of PDR1A (poly(disperse red 1 acrylate)), as reported by Natansohn et al.[8] Polymerization of the monomer DR1M was performed in dry toluene with 2.1 mol % AIBN as the initiator. The reaction solution was stirred at 65 °C for 24 h. The solid product was dissolved in THF and then precipitated in methanol. The precipitate was washed with methanol repeatedly to ensure removal of unreacted DR1M. The ^{1}H NMR spectrum of PDR1M in THF-d_8 is shown in Figure S1 (Supporting Information). M_n, M_w, and PD of PDR1M are 9700, 13 700, and 1.41, respectively. TGA and DSC curves of PDR1M are shown in Figure 1. TGA result indicates that the thermal decomposition of PDR1M in nitrogen occurs in two major steps—one at 284 °C and the other at 430 °C—suggesting a two-staged decomposition process. At 255 °C, PDR1M has only a 5% weight loss, indicating its good thermal stability. The second heating scan of PDR1M displays a glass transition temperature of ~105.6 °C. The DSC curve from the first heating scan was not smooth, which might be due to the thermal history of the polymer sample.

In solution, DR1M shows two absorption bands at 283 and 475 nm originating from the $\pi-\pi^*$ electronic transition of azobenzene chromophore (Figure S2). The 475 nm band might obscure the lowest spin-allowed n$-\pi^*$ transition whose energy is less sensitive to substituent effects.[9] The low-energy bands in the absorption spectra of PDR1M show blue shifts of ~10 nm compared with those in the absorption spectra of DR1M/THF solution with same concentration. In monomer solutions, azobenzene chromophores can easily $\pi-\pi$ stack, while in PDR1M solutions the movement of azobenzene units is restricted. The decrease in $\pi-\pi$ stacking also causes a blue shift in the PL spectra of PDR1M solutions in comparison to monomer solutions (Figure S3). It is interesting to note that the high-energy vibronic band ($S_{10} \rightarrow S_{00}$ transition) intensifies in the PL spectrum of PDR1M which might be due to the confinement of exciton migration. With increasing solution concentration, the PL spectra for DR1M/THF and PDR1M/THF solutions display a red shift of 10 nm which results from excimer emission.

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* To whom correspondence should be addressed: Tel 413-545-2680; Fax 413-577-1510; e-mail Russell@mail.pse.umass.edu.

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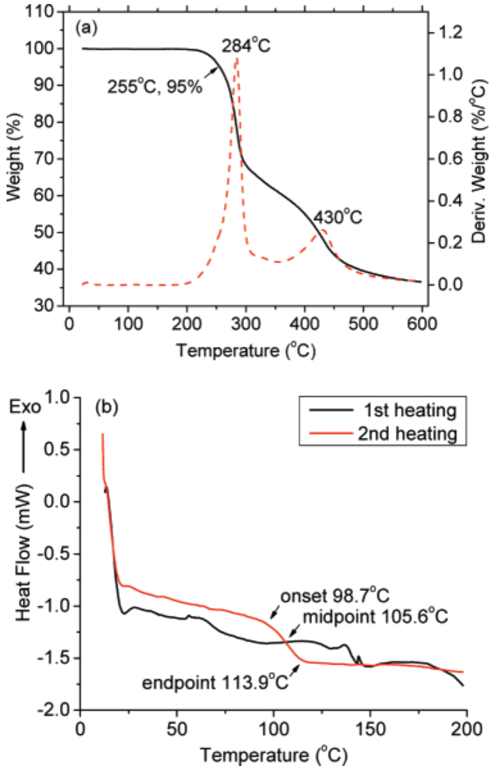

Figure 1. Thermograms of PDR1M: (a) TGA; (b) DSC.

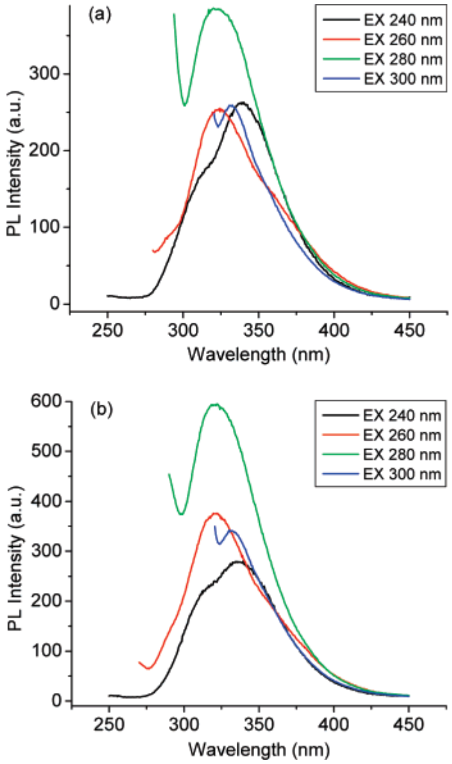

Figure 2. PL spectra of 10^{-5} mg/mL DR1M/THF (a) and PDR1M/THF (b) solution under different excitation wavelengths.

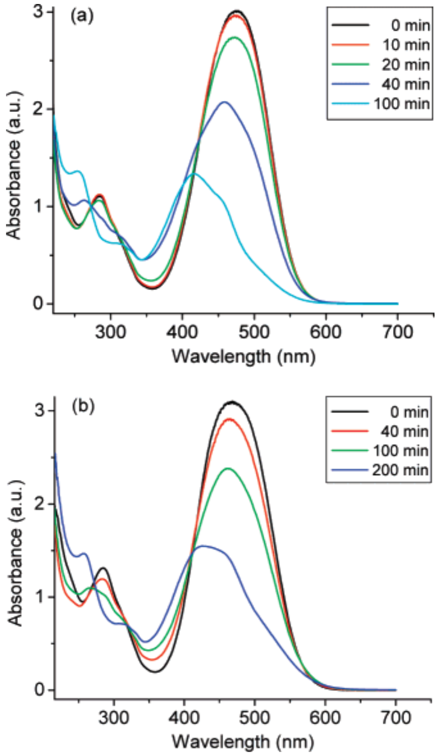

Figure 3. Effect of UV irradiation on the absorption spectra of 0.04 mg/mL DR1M/THF (a) and PDR1M/THF (b) solution.

To understand the effect of excitation energy on the fluorescence spectra, PL spectra of 10^{-5} mg/mL DR1M/THF and PDR1M/THF solution under different excitation wavelengths were studied (Figure 2). Under 240, 260, 280, and 300 nm excitation wavelengths, PL spectra of a 10^{-5} mg/mL DR1M/THF solution show peaks at 339, 324, 322, and 332 nm, respectively. Increasing the excitation wavelength from 240 to 280 nm, the PL spectra show a continuous blue shift, which might be due to the increasing *trans*-to-*cis* photoisomerization at these wavelengths. It has been suggested that *cis*-azobenzene molecules obtained from the transformation of the planar *trans* form have a globular geometry with the phenyl rings twisted perpendicular to the plane determined by C−N=N−C.[10] So the π-electron delocalization and conjugation are better in *trans*-azobenzene, where a bathochromic shift can be expected. A hypsochromic shift should be seen in the *cis* form. Increasing the content of the *cis* form may cause a blue shift in the PL spectra. It is interesting to note that the PL spectrum under 300 nm excitation wavelength does not follow the blue-shift trend. However, currently its mechanism is not clear. Under 240, 260, 280, and 300 nm excitation wavelengths, PL spectra of 10^{-5} mg/mL PDR1M/THF solution show peaks at 336, 321, 320, and 331 nm, respectively. A similar behavior was seen in the PDR1M/THF solution.

Films with different thickness were prepared from 10 mg/mL PDR1M/THF solutions by using different spin-coating speeds. With increasing film thickness, the absorption spectra show a red shift of 32 nm (Figure S4) which is due to the increasing azobenzene chromophore stacking and the extended π-electron conjugation. The PL spectra of PDR1M films show a peak at ~360 nm (Figure S5). Compared with PDR1M solution (10^{-5} mg/mL), there is a red shift of 24 nm, which results from an excimer emission in the solid films. The emission from PDR1M films is very weak compared with that from solution. This might be due to the significant intersystem crossing between the excited singlet state and the excited triplet state, the nonradiative relaxation,[11] and the exciton−exciton annihilation in the azo-polymer films.

Figure 3 shows the effect of UV irradiation on the absorption spectra of DR1M/THF and PDR1M/THF solutions. After sufficient irradiation, the low-energy $\pi-\pi^*$ transition displays a blue shift (40−60 nm), indicating *trans* → *cis* photoisomerization. It is interesting to note that the high-energy band of the *trans* isomer splits into two bands at 255 and 315 nm.

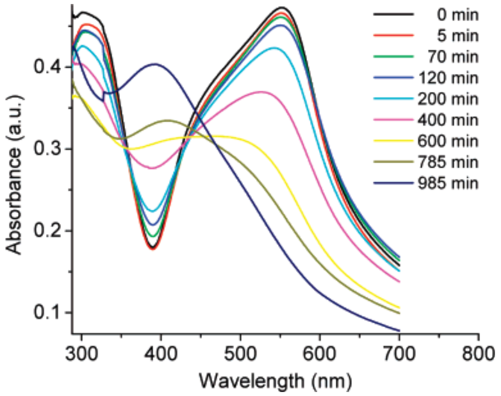

Figure 4. Effect of UV irradiation on the absorption spectra of 100 nm PDR1M film.

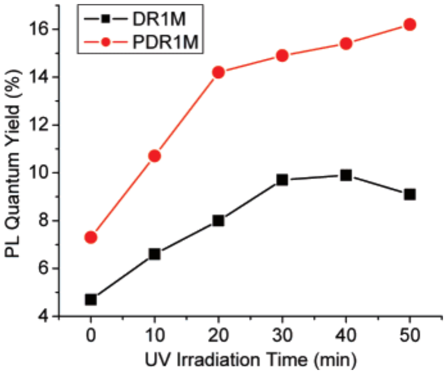

Figure 5. Effect of UV irradiation on the PL quantum yields of DR1M/THF and PDR1M/THF solutions.

Because of the spatial hindrance in the polymer, the azo-chromophore in PDR1M is not as active as that in the monomer DR1M. The effect of UV irradiation on the absorption of the film was also investigated (Figure 4). A very large blue shift of about 160 nm was observed for PDR1M film. Photoisomerization in the solid state takes longer than in solution. Two basic mechanisms are suggested for the azo molecule isomerization. One is N═N bond rotation, and the other is N−C bond inversion. In solid films, since segmental mobility is reduced and the bond rotation requires substantially more local free volume, the photoisomerization is much more difficult.

PDR1M/THF solutions show a higher PL quantum yield (7.3%) than that of the monomer solutions (4.7%). The exciton migration in PDR1M is confined, so exciton−exciton annihilation is reduced, which is favorable for efficient radiative decay of excitons, thereby improving the photoluminescence efficiency. Figure 5 indicates that proper UV irradiation (40−50 min) can increase the PL quantum yield of the azo-containing monomer and polymer solutions to maximum values of 9.9% and 16.2%, respectively. The photoisomerization dilutes the *trans* chromophore which is very easy to form PL-inefficient excimer. This result provides an interesting approach for improving the PL quantum yields of azobenzene-containing photoactive polymers.

Nonplanar *cis*-azobenzene has a dipole moment. After UV irradiation, the polarity of the PDR1M film surface should increase, which should improve the wettability of the film surface. The effect of UV irradiation on the water contact angle of PDR1M film is shown in Table 1. After 3 h UV irradiation, the advancing water contact angle θ_A decreases almost 10°, indicating an improvement in the wettability. GPC results indicate that the M_n of PDR1M increased 2% after 6 h UV irradiation, suggesting that the hydrodynamic radius of PDR1M in THF increased because of the *trans* → *cis* photoisomerization. The nonplanar *cis* form simply occupies more space.

Table 1. Effect of UV Irradiation on the Water Contact Angle of PDR1M Film

UV irradiation time (h)	contact angle (θ_A/θ_R) (deg)
0	100.1/11.2
3	90.3/10.5
11	89.9/8.6

The effect of UV irradiation on film thickness was investigated. After 3, 7, and 9 h UV irradiation, the thickness of PDR1M spin-coated films increased 2.6, 3.6, and 9.3%, respectively. The *trans* → *cis* photoisomerization requires bond rotation which causes side-chain movement and may lead to motion along the polymer backbone giving rise to film expansion. The photoexpansion is expected to be very sensitive to light intensity,[12] temperature, humidity, chemical environment, and thermal history.

In summary, the photophysical properties of an azo-polymer and its monomer were investigated. The decrease of $\pi-\pi$ stacking in PDR1M solution causes a blue shift in the absorption and PL spectra compared to that of the monomer solution. The high-energy vibronic band ($S_{10} \rightarrow S_{00}$ transition) is intensified in the PL spectrum of PDR1M which can be attributed to the restriction of exciton migration. Increasing the excitation wavelength from 240 to 280 nm causes a continuous blue shift in the PL spectrum, which might be due to the increasing *trans* → *cis* photoisomerization at these wavelengths. After sufficient UV irradiation, the low-energy $\pi-\pi^*$ transition displays a remarkable blue shift (40−60 nm), indicating a *trans* → *cis* photoisomerization. The high-energy band of *trans* isomer splits into two bands at 255 and 315 nm. Because of the spatial hindrance in the polymer, the azo-chromophore in PDR1M is not as active as that in monomer DR1M. In solid films, since segmental mobility is reduced and the bond rotation requires substantially more local free volume, the photoisomerization is much more difficult than that in solution. The exciton migration in PDR1M is confined, so exciton−exciton annihilation is reduced, which is favorable for efficient radiative decay of the excitons. Proper UV irradiation (40−50 min) can increase the PL quantum yields of the azo-containing monomer and polymer solutions. Photoisomerization can be used to tune the wettability and thickness of polymer films.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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