Spiropyran Dimer Toward Photo-Switchable Molecular Machine

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Spiropyrans are a class of photochromic compounds whose molecular structure is alterable upon exposure to UV/visible light or changes in temperature.[1,2] Two typical forms are a colorless spiro (Sp) form and a colored merocyanine (MC) form. The polar MC form exists as a zwitterion in polar solution and has more complicated isomers based on the cis−trans isomerization of the conjugated bonds such as TTC (trans-transoid-cis), CTC, CTT, and TTT. Furthermore, the planar MC structure tends to associate into stacking structures called J-aggregates and H-aggregates by ionic interaction.[1] A number of attempts to incorporate spiropyran molecules into polymer systems have been reported. Photochromism studies of spiropyrans in polymer matrices,[3] liquid crystal polymers containing spiropyran as mesophases,[4] and spiropyran-grafted dextran,[5] pullulan,[6] polydimethylsiloxane,[7] and other synthetic polymers[8] have recently been undertaken. However, no work has been reported regarding single polymer behavior utilizing the structural changes of spiropyran by controlling its shape, orientation, and environment.

We are particularly interested in remarkable changes in polarity and structure (especially planarity) between Sp and MC forms of spiropyran. To effectively utilize these properties, we have designed a functional polymer attached to a newly developed spiropyran dimer (BIPSD), as illustrated in Figure 1. This photo-switchable polymer has great potential for site recognition of specific biomolecules and as a sensor of organic/inorganic compounds. The polar face of the MC form strongly attracts ionic species, which can be released through visible light irradiation upon transformation into the nonpolar Sp form. The aggregates of this BIPSD−polymer are attractive, because MC-to-Sp conversion destroys the planarity of the molecules, which disallows maintenance of the self-assembling structure. This paper reports a preparation of BIPSD and preliminary results of its photochromic study.

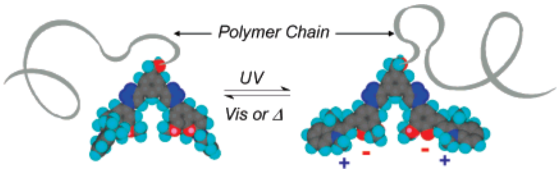

Figure 1. Schematics of photochromism of the BIPSD−polymer conjugate.

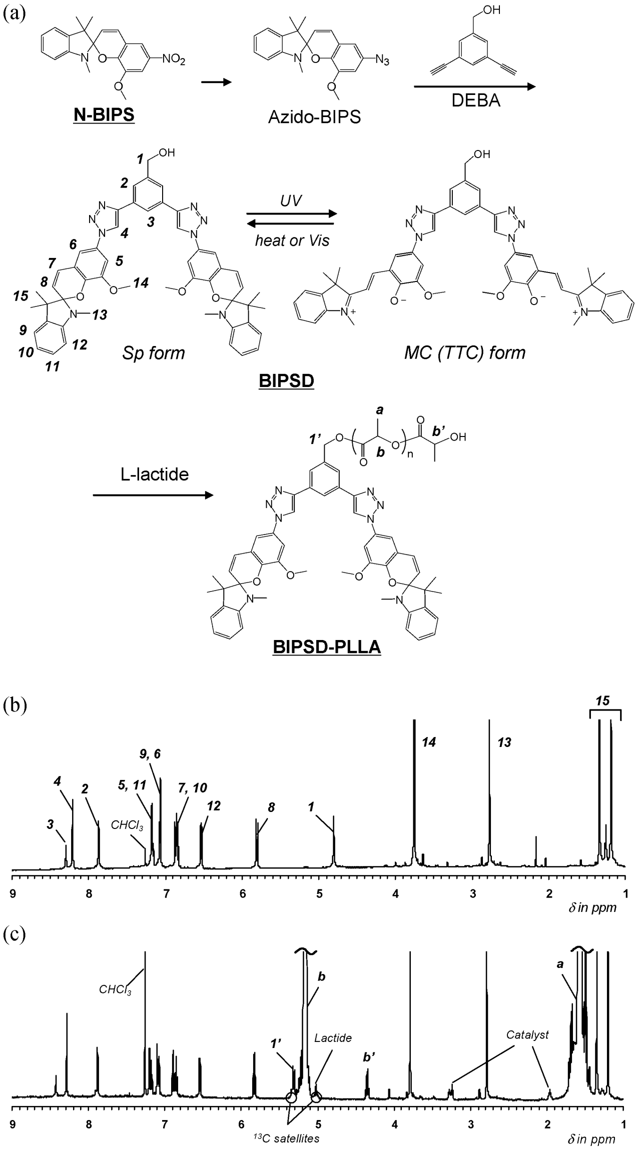

Figure 2. (a) Synthesis scheme and ^{1}H NMR spectra of (b) BIPSD and (c) BIPSD-PLLA (500 MHz, in $CDCl_3$).

The synthetic route of BIPSD and typical polymer conjugate are summarized in Figure 2a. 8-Methoxy-6-nitro-1′,3′,3′-trimethylspiro(2*H*-1-benzopyran-2,2′-indoline), N-BIPS, was used as a starting material. The nitro group was reduced to an amine under acidic conditions followed by

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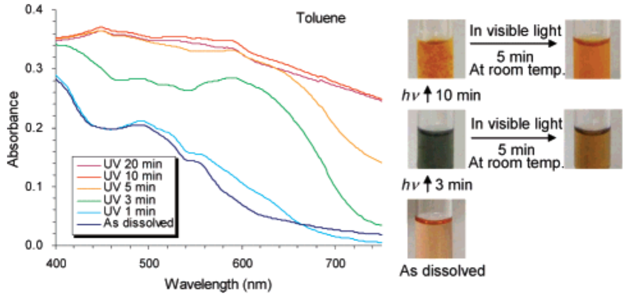

Figure 3. UV−vis absorption spectra and typical color changes of BIPSD in toluene before and after UV irradiation.

neutralization. Azido-BIPS was obtained via a diazonium salt intermediate. 3,5-Diethynylbenzylalcohol (DEBA) was prepared from 3,5-dibromobenzylalcohol coupled with trimethylsilylacetylene by the Sonogashira reaction, followed by deprotection. The click reaction between azido-BIPS and DEBA was carried out using a conventional catalyst.[9] After purification, the dark purple solid, BIPSD, was isolated. BIPSD was identified by various NMR techniques. The accurate assignments of proton and carbon resonances were established by performing 2D NMR (TOCSY, ROESY, HMQC, and HMBC) measurements (see Figures S1−S5 in the Supporting Information). All proton resonances in Figure 2b appear in exact intensities and are correlated to other spiropyrans found in the literature.[10] The BIPSD−polymer conjugates were also successfully prepared. Monomethoxy-PEG, $M_W = 2000$, was tosylated and then reacted with BIPSD. The BIPSD−PEG, a pale red solid, was characterized by ^{1}H NMR. Another system with poly(L-lactide), BIPSD−PLLA ($M_W = 850-3500$), was prepared by ring-opening polymerization of L-lactide initiated from the hydroxy group of BIPSD using an organic catalyst recently developed by Hedrick et al.[11] We found that the ordinary ring-opening catalysts, e.g., Sn(Oct)$_2$, did not initiate polymerization in the presence of BIPSD, because of the capturing of metallic catalysts into BIPSD. Figure 2c shows a typical ^{1}H NMR spectrum of BIPSD−PLLA. Shifting of the benzyl peak (1) of BIPSD from 4.8 to 5.3 ppm proves BIPSD−PLLA conjugation.

The photochromism study of the spiropyran dimer, BIPSD, was carried out using a medium-pressure mercury lamp equipped with a Pyrex water-cooling jacket without filters. The BIPSD toluene solution was a pale orange color, changing to blue-green after 3 min of UV irradiation, as shown in Figure 3. The dramatic color change correlated with the increase in absorption ($\lambda_{max} = 590$ nm), indicating the transformation from Sp to the MC form.[12] This color quickly bleached under the room light at room temperature. The absorption spectrum after 5 min of sample irradiation increased the baseline due to the appearance of insoluble precipitates. After 10 min of UV irradiation, a distinctly turbid solution was produced, with orange precipitates congregating in the bottom of the test tube. In relatively nonpolar solvents such as toluene, the MC form of BIPSD was less stable and began to aggregate after 3 min of UV irradiation. Similar absorption data in various solvents (dichloromethane, acetone, ethanol) were obtained. We observed that more polar solvents produce insoluble aggregates more slowly (see Figures S6 and S7 of the Supporting Information). In any solvent, the MC form of BIPSD was produced by quick UV irradiation, and the MC color then disappeared along with the appearance of precipitates by long-term UV irradiation.

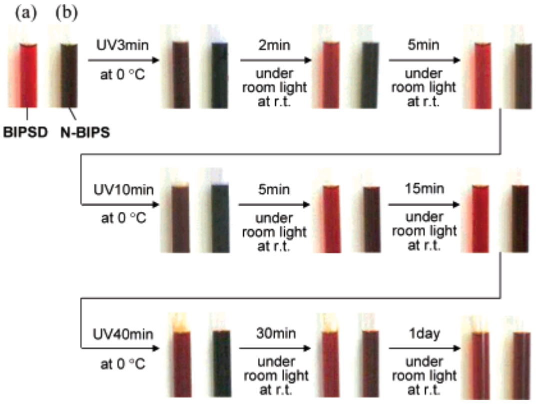

Figure 4. Color changes of (a) BIPSD and (b) N-BIPS by UV irradiation in acetone-d_6.

To compare the photochromism properties of BIPSD to that of the starting spiropyran N-BIPS, we dissolved each compound in acetone-d_6. The BIPSD and N-BIPS solutions are transparent and colored light red and dark brown, respectively. The color changes produced by repeating UV irradiation are shown in Figure 4. The dimer, BIPSD (left sample (a) in all photos), showed dramatic coloration when observed in toluene. The light red color turned to dark purple-brown under UV light, which immediately faded in ambient conditions, returning to the original color within 5 min. A similar color change occurred after 10 min of UV irradiation; however, after over-irradiation for 40 min, a slight color change was noted with a significant amount of insoluble orange precipitates. Note that these precipitates produced from BIPSD slowly disappeared at ambient conditions, and the original color was restored after a week. The N-BIPS in acetone-d_6 (right sample (b) in all photos) also showed instant color changes; however, after over-irradiation for 40 min, the solution subsequently turned red under room light and temperature. Unlike BIPSD, over-irradiated N-BIPS solution did not return to the original color.

NMR spectroscopy has contributed significantly to the mechanistic understanding of photochromism.[2,13] Low-temperature (−20 °C) ^{1}H NMR measurements of UV-irradiated BIPSD and N-BIPS were performed in various solvents. Typical results in acetone-d_6 corresponding to the samples in Figure 4 are shown in Figure 5. The NMR spectra of BIPSD immediately after UV irradiation for 3, 10, and 40 min (a) revealed that there was no difference in their spectra from the original solution, despite the obvious color change

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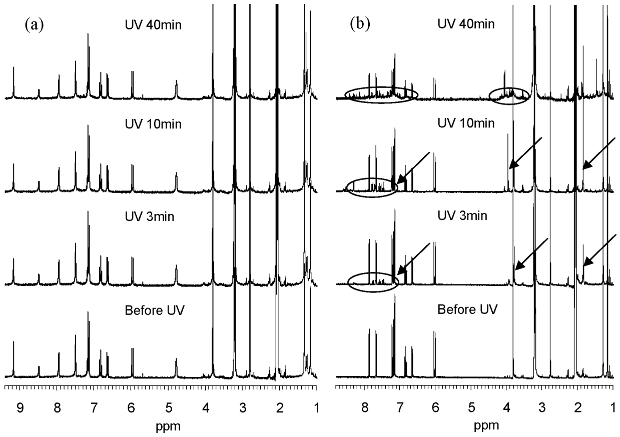

Figure 5. ^{1}H NMR spectra of (a) BIPSD and (b) N-BIPS in acetone-d_6 at −20 °C before and after UV irradiation for 3, 10, and 40 min, which correspond to the sample in Figure 4. The color of each sample did not change between the before and after NMR measurements.

and the increase in absorbance near 550 nm by UV−vis spectroscopy. In contrast, UV irradiated N-BIPS (b) showed small resonances in addition to the original Sp form in the spectrum before UV irradiation. A part of the two methyl groups of N-BIPS at 1.1 and 1.3 ppm shifted to one peak at 1.8 ppm in the MC form after 3 min of UV exposure and increased in intensity after 10 min of irradiation. The N−CH$_3$ peak at 2.8 ppm showed a significant shift to ~4 ppm in the MC form, showing a variation based on the cis−trans isomerization. Many complex doublets and triplets appeared downfield (>7 ppm) after UV irradiation. The dependence of MC resonance shifts on irradiation time suggests the transformation between CTT/TTT and CTC/TTC forms and into aggregation forms.

The results of BIPSD suggest that the MC form has been produced but is insoluble in acetone-d_6, because the solution maintains a dark MC color even after NMR measurements at low temperature. The MC form is completely reversible with a soluble Sp form. The BIPSD aggregates by over-irradiation are suggested to be in a stacking structure of the MC form, which also returns to the Sp form at a much slower rate and different conditions than in the MC form. NMR analyses in CDCl$_3$ showed similar photochromism results at −13 °C (see Figure S8 in the Supporting Information). Interestingly, in polar DMSO-d_6, both BIPSD and N-BIPS showed no structural change or coloration by UV (see Figure S9 in the Supporting Information).

The typical photochromism result of the polymer, BIPSD−PLLA, in dichloromethane is shown in Figure 6. When UV exposure time was increased, the absorbance at 570 nm slowly increased initially, and the absorbance at 490 nm then increased slowly but significantly. The color change occurred moderately for BIPSD−PLLA and was similar to that for BIPSD: from pale orange to bluish orange (corresponds to 570 nm) and finally to an orange solution. BIPSD−PLLA did not produce precipitation over UV irradiation for 120 min. This result suggests that the BIPSD molecule in the polymer maintains its photochromism from Sp to MC and its aggregates; however, the polymer chain slows BIPSD photochromism. Inhibition of precipitation of the insoluble MC form and its aggregates indicates formation of a self-assembly structure in a good solvent of PLLA chain. The BIPSD−PEG conjugate showed similar color changes in dichloromethane.

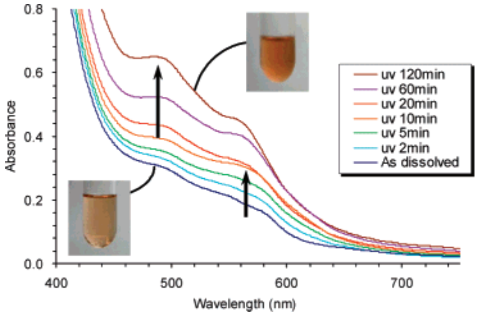

Figure 6. UV−vis absorption spectra and typical color changes of BIPSD−PLLA in CH$_2$Cl$_2$ before and after UV irradiation.

In summary, a novel spiropyran dimer BIPSD and BIPSD−polymer conjugates have been successfully prepared. The photochromism studies of BIPSD using UV light, UV−vis spectroscopy, and low-temperature ^{1}H NMR revealed unique properties of reversible coloration and aggregation by strong interaction of the MC form. A similar transformation was observed for BIPSD−PLLA but was much slower than BIPSD. These results suggest that BIPSD−polymer systems possess great potential as controlled molecular machines in sensing and delivery systems.

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Supporting Information Available: Details of synthesis, 2D NMR spectra, and photochromism data of BIPSD in various solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

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