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Photophysical Properties of Perdeuterated *trans*-Stilbene Grafted Polystyrene

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Introduction

Under UV irradiation stilbene undergoes an isomerization between cis and trans isomers both in the excited singlet state (S^1) and in the triplet state (T^1). Studies on the trans−cis photoisomerization of perhydro- and perdeuteriostilbene in benzene indicated that perdeuteration does not affect cis−trans decay ratios of stilbene S^1 and T^1 states. Loss of triplet excitation through interaction with *trans*-stilbene ground states does not occur.[1] The cis-to-trans isomerization is realized by a rotation around the C═C double bond via two possible mechanisms. The hula-twist (HT) mechanism involves simultaneous rotation of a double bond and an adjacent single bond and is postulated to reduce the volume requirements associated with a 90° torsional relaxation (the one bond twist, OBT). Photoisomerization studies of *cis*-1-(2-naphthyl)-2-phenylethene in methylcyclohexane at 77 K argue against a HT process,[2] whereas the photochemical cis−trans isomerization of free stilbene molecules follows an HT pathway.[3] The cis isomer can undergo either a cis-to-trans isomerization or cyclization to form dihydrophenanthrene. The dihydrophenanthrene can be further oxidized to give phenanthrene or be reverted to the starting cis isomer.[4] Photoisomerization of stilbene dendrimers takes place within the lifetime of the excited singlet state even though the molecular weight of the dendrimer can be 6500.[5] When exposed to irradiation, a concentrated solution of stilbene oxalyl amide cis isomer turned into a gel. This photoinduced gelation was due to a rapid cis → trans isomerization followed by a self-assembly of the trans molecules.[6] Photoisomerization is a very important reaction for some physiological processes. For example, photoisomerization of the retinal chromophore in rhodopsin is the primary step in vision for our eyes. Rhodopsin consists of the 11-*cis*-retinal prosthetic group covalently bound to a protein called opsin. The absorption of light results in the cis-to-trans isomerization of 11-*cis*-retinal to form a red-absorbing photoproduct, bathorhodopsin. The ultrafast (200 fs), 11-cis to all-trans isomerization of the retinal chromophore is regarded as a key step for energy storage/transduction in rhodopsin.[7]

Tran-Cong et al.[8] studied the phase separation of a blend of *trans*-stilbene-labeled polystyrene (PSS) and poly(vinyl methyl ether) (PVME) driven by photoisomerization. The microstructure of polymer chains can be continuously altered via a trans-to-cis isomerization under UV irradiation. Since the cis form of stilbene has a propeller-like conformation that is much bulkier than the planar trans form, it is expected that the packing between PVME and PSS chains in the blend becomes worse upon photoisomerization, thus leading to a decrease in miscibility. It was shown that polymeric materials with novel morphologies can be obtained by coupling photochemical reactions with phase separation.[9] Here, we synthesized a perdeuterated *trans*-stilbene grafted polystyrene (SgPS) (see Scheme 1). The photophysical properties of this perdeuterated photoactive polymer were studied by considering the effect of chromophore concentration, solvent polarity, excitation energy, chromophore aggregation, and UV irradiation time.

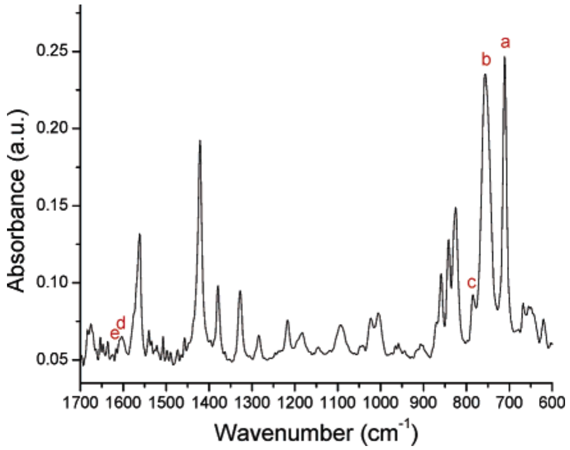

Figure 1. IR spectrum of SgPS. Marked peaks: a, 711 cm^{-1}; b, 756 cm^{-1}; c, 785 cm^{-1}; d, 1604 cm^{-1}; e, 1617 cm^{-1}.

Results and Discussion

The synthetic procedure for the preparation of perdeuterated SgPS is shown in Scheme 1. ^{13}C NMR results indicate that stilbene substituted vinyl units occupy 88 mol %. ^{13}C NMR spectrum of SgPS in 1,1,2,2-tetrachloroethane-d_2 is shown in Figure S1 (see Supporting Information). Figure 1 shows the IR spectrum of SgPS. The marked peaks at 711, 756, 785, 1604, and 1617 cm^{-1} can be attributed to C−D out-of-plane bending (*trans*-stilbene), phenyl out-of-plane vibration (*trans*-stilbene), phenyl out-of-plane vibration (*cis*-stilbene), C═C stretching (*trans*-stilbene), and C═C stretching (*cis*-stilbene), respectively. Spectral peak analysis via Lorentzian fitting gives a *trans*-stilbene content of ∼96%.

Figure S2 shows the absorption spectra of SgPS/THF solutions. With dilution, the absorption spectra of the solutions display well-resolved vibronic structures. The four bands at 290, 301, 315, and 332 nm correspond to $S_{00} \rightarrow S_{13}$, $S_{00} \rightarrow S_{12}$, $S_{00} \rightarrow S_{11}$, and $S_{00} \rightarrow S_{10}$ transitions, respectively. The concentration dependence of the photoluminescence (PL) spectra for SgPS/chloroform solution is shown in Figure 2. With increasing stilbene chromophore concentration, the PL spectra show a red shift and a broadening, which is due to excimer formation. At 3.3×10^{-3} mg/mL, the PL spectrum exhibits three bands at 348, 366, and 382 nm, which correspond to the $S_{10} \rightarrow S_{00}$, $S_{10} \rightarrow S_{01}$, and $S_{10} \rightarrow S_{02}$ transitions, respectively. At 3.3×10^{-2} mg/mL, a very broad band appears with maximum at 401 nm, suggesting strong excimer emission. It is very interesting to note that at higher concentrations the solution PL spectra exhibit only one band at around 382 nm. With increasing concentration, the chromophores in the solution undergo a disorder-to-order transition. At low concentrations (3.3×10^{-2} mg/mL), the emission from single dispersed stilbene chromophore (monomer emission) competes with the emission from excimer which results from polymer chain entanglement; thus, two corresponding emission bands are seen. At high concentrations (1.7×10^{-1} mg/mL), both monomer emission and excimer emission are very

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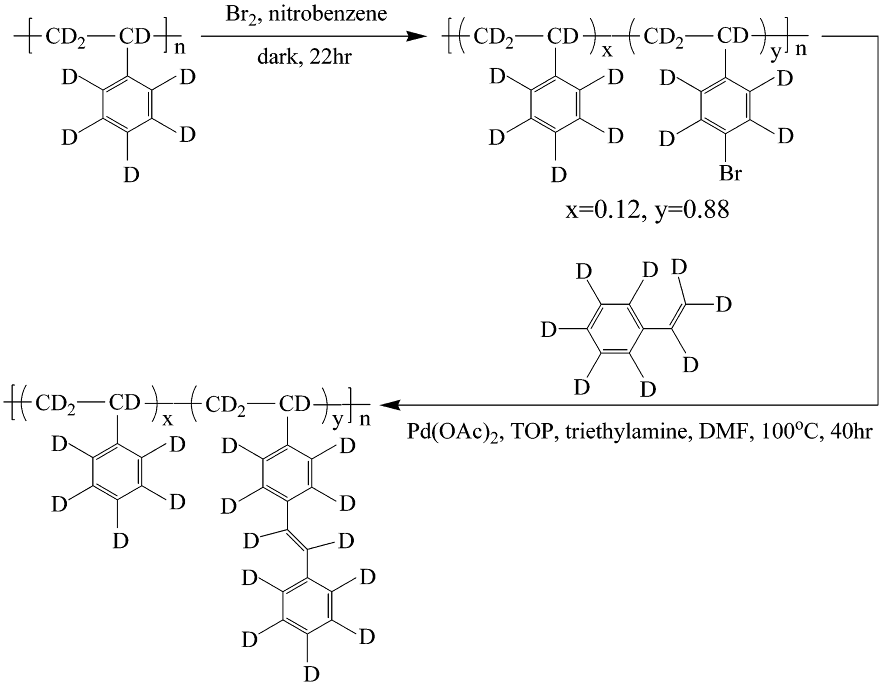
Scheme 1. Synthesis of *trans*-Stilbene Grafted Polystyrene (SgPS)



strong; they overlap with each other and display only one strong emission band, similar to the PL spectrum of a film, even though there is a large red shift of 36 nm in the film.

To understand the effect of solvent polarity on the solution PL, we compared the emission spectra of SgPS in five solvents (7.6×10^{-4} mg/mL), and the results are summarized in Figure 3. The order of polarity for the solvents is benzene < *o*-xylene < THF < chloroform < DMF.[10] In polar solvents, the PL spectra display resolvable vibronic bands. In the PL spectra of THF and chloroform solutions, $S_{10} \rightarrow S_{00}$, $S_{10} \rightarrow S_{01}$, and $S_{10} \rightarrow S_{02}$ transitions are clearly seen. As the solvent polarity increases, $S_{10} \rightarrow S_{01}$ and $S_{10} \rightarrow S_{02}$ bands show red shifts, and the relative intensity of the $S_{10} \rightarrow S_{02}$ band increases. In DMF, the 374 nm band becomes the most intense emission band. This band is a combination of excimer emission and the $S_{10} \rightarrow S_{02}$ band. The light-emitting polymer studied here is a nonpolar molecule, its solubility in polar solvents is not as good as in nonpolar solvents, and the molecular conformation in polar solvent is not expanded. Therefore, in polar solvents, the intramolecular interaction between the stilbene chromophore units are stronger, leading to more excimer emission.

Figure 4 shows the effect of excitation energy on the PL spectra of 0.15 mg/mL SgPS/chloroform solution. The emission spectra obtained by using five excitation wavelengths (340, 320, 300, 280, and 260 nm) were compared. Generally, the solution PL spectra of light-emitting polymers correlate with excitation wavelength where the high-energy excitation leads to a blue-shifted emission or an intensification of the high-energy band.[11] It is noted that stilbene isomerizes from the trans to cis form under UV irradiation of 300−400 nm. The cis form can revert to the trans form under UV light of 254 nm.[12] In the PL measurements, SgPS can undergo an isomerization under UV light, and the configurational change of stilbene chromophore will, of course, change the band-gap of the material, providing

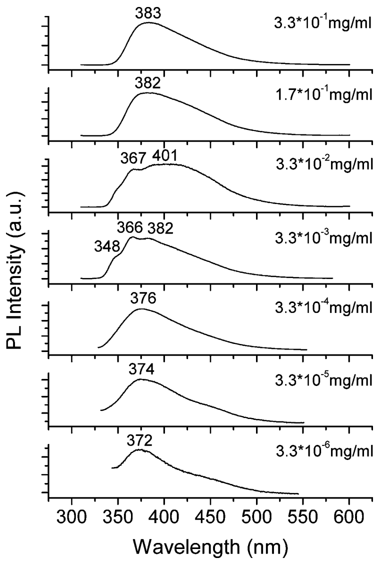


Figure 2. Concentration dependence of PL spectra for SgPS/chloroform solution. Excitation wavelength 300 nm.

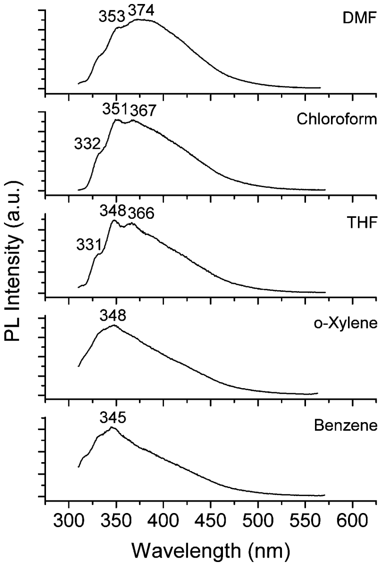


Figure 3. Solvent polarity effect on PL spectra of 7.6×10^{-4} mg/mL solution. Excitation wavelength 300 nm.

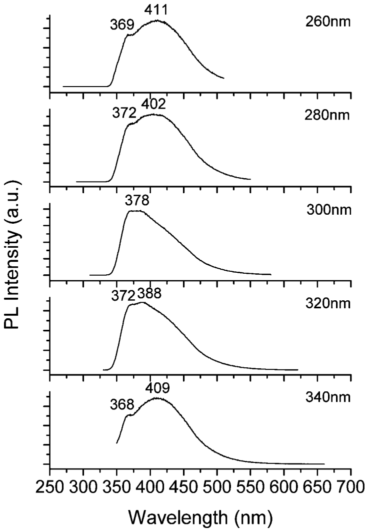


Figure 4. Excitation energy dependence of PL spectra for 0.15 mg/mL SgPS/chloroform solution.

another factor to influence the emission properties. Under 340 nm excitation, the PL spectrum shows two bands at 368 and 409 nm, corresponding to monomer emission and excimer emission, respectively. The excimer results from the interaction between one excited stilbene unit and another unexcited stilbene unit. As the excitation wavelength decreases from 340 to 300 nm (excitation energy increasing), the emission shows a remarkable blue shift. This phenomenon can be attributed to the excitation energy increase. The photoisomerization of *trans*-stilbene to *cis*-stilbene can increase the chromophore band-gap and decrease the *trans*-stilbene*−*trans*-stilbene excimer formation (* denotes the excited state), which also contributes to the blue shift of PL. With short wavelength excitation (280 and 260 nm), the 4% *cis*-stilbene in SgPS can isomerize to *trans*-stilbene, which decreases the band-gap of the chromophore, also favoring excimer formation. In the PL spectra, 402 and 411 nm bands result from excimer emission. Compared with that of the 0.15 mg/mL solution, the emission spectra of the 1.43 mg/mL solution display only one band (see Figure S3), which is the combination of a monomer emission and an excimer emission, as discussed before. As the excitation wavelength decreases from 340 to 280 nm, the PL spectra is blue-shifted from 401 to 387 nm, indicating a stronger correlation between the excitation energy and emission. Under 260 nm photoexcitation, *cis*-stilbene is transformed to the trans form (chromophore band-gap being decreased), causing a red shift in the PL. The PL spectrum resulting from 260 nm photoexcitation is broader than that from the 280 nm excitation due to greater excimer formation.

Chromophore aggregation in solution was studied by gradually adding a nonsolvent, methanol, to the 3 mL SgPS/chloroform solution (1.43 mg/mL) and then measuring the emission spectra. The results are shown in Figure 5. Upon adding a small amount of methanol, the conformation of SgPS polymer in the solution is changed, where the swollen polymer chains begin to collapse, causing the stilbene chromophore units to get closer, thus leading to excimer formation and a red shift in the PL. With large amounts of added methanol, the polymer precipitates and the emission spectra are similar to that of solid state.

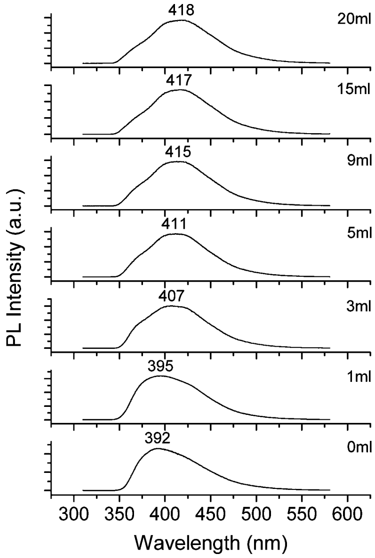


Figure 5. PL spectra of 1.43 mg/mL SgPS/chloroform solution (3 mL) upon adding nonsolvent methanol.

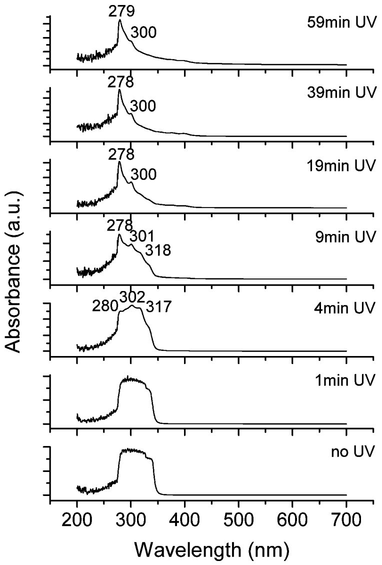


Figure 6. Effect of UV irradiation on absorption of 0.15 mg/mL SgPS/benzene solution.

In this work, 302 nm UV light was used for the photoisomerization of SgPS. Figure 6 shows the effect of UV irradiation on the absorption of 0.15 mg/mL SgPS/benzene solution. Without UV irradiation, the absorption spectrum shows a broad band, which is due to a high concentration of the *trans*-stilbene chromophore. After 4 min UV irradiation, the spectrum shows resolved vibrational structures with five bands. The bands at 290, 302, 317, and 334 nm correspond to $S_{00} \rightarrow S_{13}$, $S_{00} \rightarrow S_{12}$, $S_{00} \rightarrow S_{11}$, and $S_{00} \rightarrow S_{10}$ transitions, respectively, which come from *trans*-stilbene. As the irradiation time is increased, the intensities of these bands decrease, suggesting more *trans*-stilbene is transformed into *cis*-stilbene. The band at 280 nm shifts to 278 nm and its relative intensity continues to increase, which can be attributed to the absorption of *cis*-stilbene. Figure S4 shows the effect of irradiation time on the absorption of the 0.15 mg/mL SgPS/*o*-xylene solution. After 4 min irradiation, a new band at 286 nm appears, which can be attributed to *cis*-stilbene. Figure S5 shows the effect of irradiation time on absorption of 0.15 mg/mL SgPS/DMF solution. After 9 min irradiation, two new bands at 270 and 279 nm are observed, corresponding to the $S_{00} \rightarrow S_{11}$ and $S_{00} \rightarrow S_{10}$ transitions of *cis*-stilbene, respectively.

It is proposed that *trans*-stilbene possesses a near-planar structure while *cis*-stilbene is nonplanar.[13] So the π-electron delocalization and conjugation are better in *trans*-stilbene, where

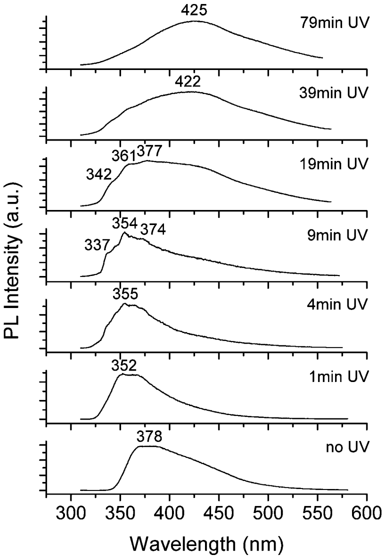


Figure 7. Effect of UV irradiation on PL of 0.15 mg/mL SgPS/chloroform solution.

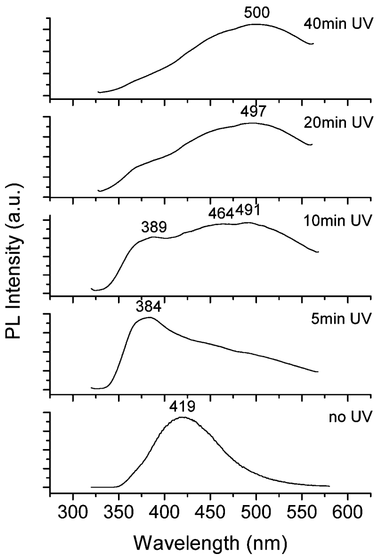


Figure 8. Effect of UV irradiation on film PL.

a bathochromic shift can be expected. A hypsochromic shift should be seen in the cis form. Figure 7 shows the effect of UV irradiation (302 nm) on emission spectra of 0.15 mg/mL SgPS/chloroform solution. Without UV irradiation, the emission spectrum displays a band centered at 378 nm. After several minutes of UV irradiation, the emission spectra show more than a 20 nm blue shift, which is due to the trans-to-cis isomerization. After 9 min of irradiation, the PL spectrum displays well-resolved vibronic structures with three bands at 337, 354, and 374 nm. The 337 and 354 nm bands can be attributed to *cis*-stilbene and the 374 nm band to *trans*-stilbene. As the sample solution continues to be irradiated, the PL spectra show a large red shift and are broadened. This can be attributed to the further photochemical reaction of *cis*-stilbene, which produces dihydrophenanthrene and, finally, phenanthrene. The final PL spectrum displays only one band at 425 nm, which can be assigned to the emission of the phenanthrene chromophore. The UV irradiation of a 1.43 mg/mL solution shows similar effects (see Figure S6).

Figure 8 shows the effect of UV irradiation on the emission spectra of a SgPS film. The PL spectrum of SgPS film without UV irradiation displays a peak at 419 nm basically resulting from the trans form. After 5 min irradiation, the emission shows a large blue shift of 35 nm, which is due to the formation of the high-band-gap *cis*-stilbene chromophore. After 10 min irradiation, two broad bands peaked at 464 and 491 nm appear, corresponding to the emissions of phenanthrene and its excimer. With increasing irradiation time, more low-band-gap phenanthrene chromophores are produced, leading to the domination of the excimer emission at ~500 nm. It should be noted here that the formation of tetraphenylcyclobutanes by irradiation as a product of the [2 + 2] cyclization reaction may interfere with the production of phenanthrene, which was indicated previously by Maeda et al.[4f] Some interesting studies on the absorption and fluorescence of phenanthrene can be found in ref 14.

Conclusions

We have synthesized a perdeuterated *trans*-stilbene grafted polystyrene. The effect of chromophore concentration, solvent polarity, excitation energy, chromophore aggregation, and UV irradiation on photophysical properties of this photoactive material was systematically investigated. In polar solvents, the polymer exhibits a red-shifted emission. The photoexcitation of the stilbene chromophore was affected by the photoisomerization process which introduces two chromophores to the system: a low-band-gap trans form and a high-band-gap cis form. The photoluminescence consists of contributions from the two light-emitting isomers. Chromophore aggregation leads to excimer formation and red-shifts the PL spectra significantly. By using UV irradiation, we can obtain well-resolved solution absorption spectra in which absorption of trans form and cis form can be easily determined. PL studies indicate that this *trans*-stilbene grafted polystyrene is very photochemically reactive under UV irradiation, and the final product of the photochemical reaction emits blue-green light in the solid state.

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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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