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Enhanced Bistability of a Photochromic Microparticle in Condensed Medium

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Display technologies rely on stimuli-responsive species that are interchangeable between a noncolored and a colored form.[1] This modulation can be induced by application of heat (thermochromic),[2] electron injection (electrochromic),[3] or radiation (photochromic).[4] The choice of stimulus to be applied defines the device architecture and the components required for their manufacture.[5] As examples, thermochromic materials require thermally resistant components and electrochromic displays require conducting electrodes to transfer electronic energy to the materials, whereas photochromic compounds rely on light at specific wavelength(s) to initiate the color change.

The spiropyran (SP)−merocyanine (MC) molecular switch serves as a model photochromic system.[6] Upon excitation in the UV region (ca. 350 nm), the spiro-carbon−oxygen bond ruptures, forming an intensely colored molecule due to extended π-conjugation. Irradiation in the visible region (ca. 550 nm) or thermal reversion converts the open MC form back to the closed SP. Thermal reversion, a first-order process, occurs over a wide range of temperatures. It is this reversion process that restricts its general incorporation into modern displays. Various attempts have been made to inhibit this process, including protonation of the MC−phenoxide moiety,[7] intramolecular bidentate metal ion chelation,[8] and synthetic modification of the SP with dinitro groups,[9] crown-ether moieties,[10] or a 7-trifluoromethylquinoline group.[11]

The SP−MC system has been well-studied in solution,[12] but very little research has been performed in the solid state. Recent research in this area has focused on SP-functionalized surfaces: Au electrodes,[13] polymer nanoparticles,[14] Au nanoparticles,[15] and CdSe/ZnS nanocrystals.[16] Previous studies have incorporated this molecular switch into the hydrophobic cavities of polymer nanoparticles, in order to enhance the fluorescence properties of the open MC form.[14] In this case, restriction of the molecule imposed by the polymer bead isolates the molecules from nonradiative decay pathways. Increased fluorescence quantum yield can also be attributed to the reduced flexibility of the MC isomer, minimizing the nonradiative relaxation mechanism through

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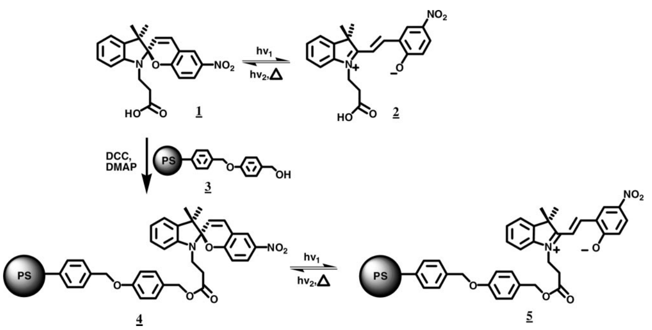
Scheme 1



internal motions of the excited MC form. Another example includes derivatization of colloidal silica particles with SP-modified poly(methylmethacrylate) via atom transfer radical polymerization (ATRP).[17] Colloidal behavior of these particles was examined and it was found that stable suspensions were formed in toluene but UV irradiation to the open MC form caused rapid aggregation and sedimentation.

The need to carry out experimental work on solid-state properties of this system is based on modern displays having moved away from solution-based technologies to solid-state optoelectronic devices. To the best of our knowledge, no work has specifically examined the kinetics of thermal reversion MC → SP in a condensed media environment under STP. From an application perspective, the bistability of this system remains a crucial barrier to successful integration of these systems into technological devices. Herein, we report our first findings utilizing attachment of an SP to the cross-linked polystyrene Wang Resin with the aim of inhibiting the thermal reversion process and enhancing bistability of this system in condensed medium.

SP (**1**) was used in this study to take advantage of the carboxylic acid group functioning as a linker to the solid support. A polystyrene Wang Resin (WR),[18] **3**, was chosen as the solid support because of the reactive hydroxymethyl groups that are generally used for solid-phase organic synthesis (1.0% cross-linked, ~1.0 mmol (OH) g^{-1}). Particle sizes for the resin beads were 50 μm. SP **1** was prepared as previously published.[19] Preparation of **4** was effected via DCC/DMAP coupling of **1** with the Wang resin, **3** (Scheme 1). FT-IR spectroscopy was used to verify the formation of **4**, with a concomitant shift of the C=O stretch vibration from 1709.8 to 1733.1 cm^{-1} (see the Supporting Information, Figure 1S). ^{1}H-magic angle spinning NMR spectroscopy (^{1}H-MAS) was further used to characterize these photochromic particles by quantifying the amount of **1** that reacted with available OH sites on the resin. Following a previously reported method,[20] our calculations showed that ~35% of the WR hydroxymethyl end groups contained SP substituents (Figure 1). This new photochromic particle will act as a model system for current and continuing studies in the solid state.

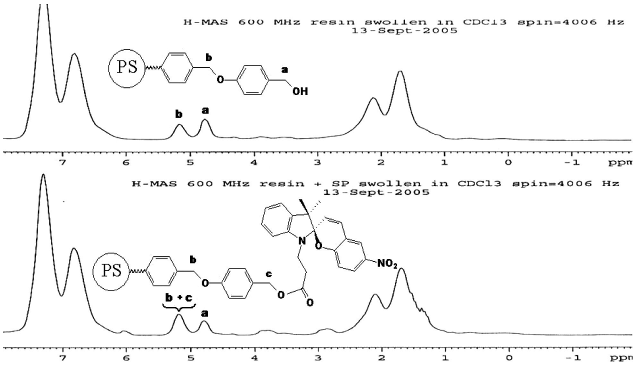


Figure 1. ^{1}H-MAS spectra before and after SP functionalization of the WR.

Scheme 1 displays the reversible photoinduced processes of the free SP $\rightleftharpoons$ MC (**1** $\rightleftharpoons$ **2**), and of the photochromic particle (**4** $\rightleftharpoons$ **5**). We have compared the thermal reversion rates of **2** and **5** upon irradiation of **1** (90 s) and **4** (300 s) in a nonpolar condensed medium, using a Spectroline CX series ultraviolet fluorescence analysis cabinet equipped with a Spectroline XX-15N UV lamp (dual 15 W, 365 nm). The base solvent was toluene and the solution viscosity was increased by adding a thickener to create a medium that formed a stable suspension of the photochromic beads and allowed monitoring of the spontaneous thermal reversion rate. Polystyrene was used for this purpose and the viscosity range chosen was 1−12 cS, to encompass the viscosity of the suspended **4**. Because the physical and chemical properties of this molecular switch are highly dependent on solvent, Reichardt's dye[21a] (2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenoxide) was used to ensure that there were no changes in the polarity of the system. Although there are many methods of expressing solvent polarity,[21] there is a relationship between $E_T(30)$ and k_{obs} for the thermal reversion of **2** → **1**.[22] Solvent polarity was determined by monitoring λ_{max} of this zwitterionic dye in each solution; E_T values remained invariant within the viscosity range chosen.

As a control, **1** was suspended in each of the viscous mixtures prepared, and following irradiation, the reversion rate constant and half-life were monitored spectrophotometrically. It was found that the kinetics of thermal reversion **2** → **1** showed a negligible decrease in $t_{1/2}$ as the viscosity of the medium increased (10.6 s (1 cS) → 7.58 s (12 cS)), see the Supporting Information, Table 1S.

The photochromic microbeads, **4**, were swollen in viscous toluene and satisfactorily suspended in a solution of 11 cS viscosity. The absorption spectrum of **4** (λ_{max} = 356 nm) was monitored to ensure a stable suspension; no sedimentation was observed during a 1 h time period. Irradiation of these samples produced **5**, which thermally reverted to **4** following a first-order decay process. A marked difference was seen in the reversion half-life of the open MC isomer following attachment to the cross-linked polymer support: $t_{1/2}$ for the suspended particles **5** in viscous toluene was

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Table 1. Results for the Rate Constant and Half-Life of Free MC and Attached to WR, in Viscous Toluene (10 cS)

sample	k_{obs} (s^{-1})	$t_{1/2}$ (s)
2 → **1**	7.43×10^{-2}	9
5 → **4**	3.22×10^{-3}	215

almost 24-fold that of the free MC in the nonpolar viscous solution. The calculated $t_{1/2}$ for **5**, 215 s (k_{obs} 3.22×10^{-3} s^{-1}), compared to the control experiment of **2** → **1** at 11 cS where $t_{1/2}$ is 9 s (k_{obs} 7.43×10^{-2} s^{-1}; Table 1).

This effect on $t_{1/2}$ is a direct consequence of immobilizing the MC onto a surface that will restrict the preferred geometry for subsequent ring-closure. In nonpolar media, the mechanism for ring-closure is rotation about the central single bond, followed by electrocyclic ring-closure. Because there is rotation involved, increased sterics would be expected to impose restrictions, manifesting in reduced k_{obs} of thermal reversion. In addition to sterics, the environment of the merocyanine in solution (**2**) and immobilized on the resin (**5**) are different. This is evidenced by the hypsochromic shift in λ_{max} of the merocyanine, from 604 nm (**2**) to 588 nm (**5**) in nonpolar condensed medium. Generally, for solvatochromic merocyanines, this shift represents a change in the polarity of the media. However, it has already been demonstrated that the E_T (30) values remain unchanged throughout the viscosity range examined in this study (see the Supporting Information, Table 1S). This shift in λ_{max} of **2** suggests a change in stabilization of the more polar transition-state in ring closure of the quinoidal MC form. In the nonpolar microparticle, the surroundings of the activated complex are restricted, i.e., its stabilization through reorientation cannot occur and hence the increase in energy required for excitation is observable by a decrease in λ_{max}.

Comparison of the photostability between the solution and condensed medium was effected through standard cycling experiments. It was found that the photostability of the solid supported MC isomer is superior to that of the free MC in solution by over 4-fold. Pimienta et al. have previously noted that the resultant products of photodegradation serve to catalyze the thermal reversion process.[23] Following immobilization of the photochromic dye within the resin, these products, once formed, should be inhibited from accelerating the thermal ring-closing reaction, as is evidenced by the results.

To further investigate the physical properties of the photochromic microparticle following SP functionalization, we performed TGA (Figure 2) and DSC studies on **3**−**5** to determine the decomposition (T_d) and glass-transition (T_g) temperatures, respectively. Results are given in Table 2. The TGA graphs show a shoulder for both **4** and **5**. Taking this shoulder as the onset of decomposition, it can be seen that the T_d values follow the order **3**, **4**, **5**, or 309, 267, and 260 °C, respectively. This order could result from formation of radicals at the double bond of the SP and quinoidal MC at such high temperatures that initiate the destruction of the microenvironment of the polymer resin, before the rest of the bead follows suit and decomposes into its constituent parts. The merocyanine would be expected to exist in the quinoidal form because the microparticle is composed of PS, a nonpolar material, and the majority of the immobilized photochromes are internal in a nonpolar environment. However, it is clearly shown that functionalizing a polymer bead with a photochromic molecule decreases the thermal decomposition temperature, T_d. Results of DSC experiments show no change in T_g values.

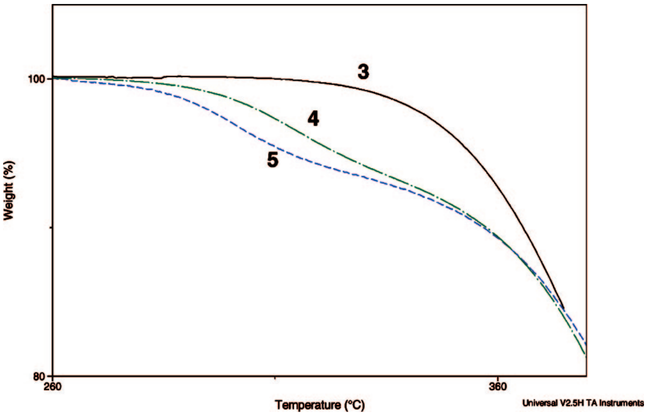

Figure 2. TGA graphs of **3**, **4**, and **5**.

Table 2. Decomposition Temperatures of 3, 4, and 5, and the Respective Glass-Transition Temperature of the Polymer Systems (values in parentheses represent the first shoulder in the TGA spectra)

system	T_d (°C)	T_g (°C)
3	309	111
4	(267) 335	113
5	(260) 323	110

Immobilization of the photochromic spiropyran dye into commercially available cross-linked polystyrene has been found to greatly increase the thermal and photochemical stability of the quinoidal MC isomer suspended in nonpolar viscous medium. Though further solid-state studies are underway, results described herein indicate the ease of preparation and viability of using resin-incorporated spiropyrans toward optoelectronic applications.

We have shown how incorporation of a photochromic spiropyran molecule into a cross-linked polystyrene resin suspended in viscous toluene, can be exploited to enhance the thermal bistability (↑ $t_{1/2}$) and photostability (↑ cycling) of an otherwise unstable colored MC form. It is also shown, according to T_d values of the WR and substituted WR, that the properties of the host particle can be modified through incorporation of a photochromic molecule. Further work is ongoing to examine the effect of N-substituents on spiropyran and spirooxazine molecules on kinetic behavior in viscous media over a range of polarities. These molecular switches are currently being adsorbed onto colloidal particles of TiO_2 and SiO_2, with a view to preparing annealed thin films of the metal oxides and observing the kinetic behavior therein. For display purposes, solid-state properties must be known. Utilizing particles suspended in viscous media may act as a bridge toward evaluating the kinetics of switching photochromic particles in condensed or solid media.

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Supporting Information Available: Synthesis of **4**, preparation of viscous media, procedure for kinetics of thermal reversion and IR spectra of **1** and **4** (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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