

Supporting information

Photochromic materials with tunable color and mechanical flexibility

Hyun-Kwan Yang, Evren A. Özçam, Kirill Efimenko and Jan Genzer

Department of Chemical & Biomolecular Engineering, North Carolina State University
Raleigh, NC 27965-7905, USA

Figure S1 depicts the UV/Vis spectra of spiropyran (SP)-doped poly(vinylmethyl siloxane) (PVMS) networks prepared by mixing (solid lines) and impregnation (dotted lines) methods. See experimental section in the paper for the description of the two preparation techniques. The solid and dashed lines represent UV/Vis spectra measured on samples before and after UV irradiation. From the data in **Figure S1** it is obvious that the SP molecules is in the closed (solid lines) and open (dotted lines) form before and after UV exposure, respectively. Depending on the processing conditions the amount of SP in the samples prepared by the impregnation method ranges from ≈ 40 to $\approx 80\%$ of the concentration present in the specimen prepared by mixing.

In **Figure S2** we present the photographs of SP-doped PVMS, PVMS-OH and PVMS-COOH networks after UV irradiation for 1 minute followed by relaxation in visible light for various times. The right portion of the figure depicts the corresponding UV/Vis spectra for the same samples. As evident from the data, the ME open form (dominant in the PVMS and PVMS-OH specimens) relaxes faster than the MEH form (present in the PVMS-COOH sample).

The effect of UV and UVO on SP stability was studied by NMR before and after each treatment. **Figure S3** presents NMR data for bare SP (black) and SP treated with UV (red lines) and UVO (blue lines) for 20 and 42.5 mins. [^1H NMR (300 MHz, CDCl_3) δ 1.19 (3H, s, 3- CH_3), 1.29 (3H, s, 3- CH_3), 2.74 (3H, s, N- CH_3), 5.88 (1H, d, vinyl H), 6.55-7.26 (6 H, m, ArH, vinyl H), 8.0-8.1 (2H, m, ArH)]. By comparing the spectra, there does not seem to be any damage to SP due either to the UV or UVO treatment. The variable intensity of the peaks located at 7.24 and 1.56 can be ignored because they correspond to CDCl_3 and water, respectively.

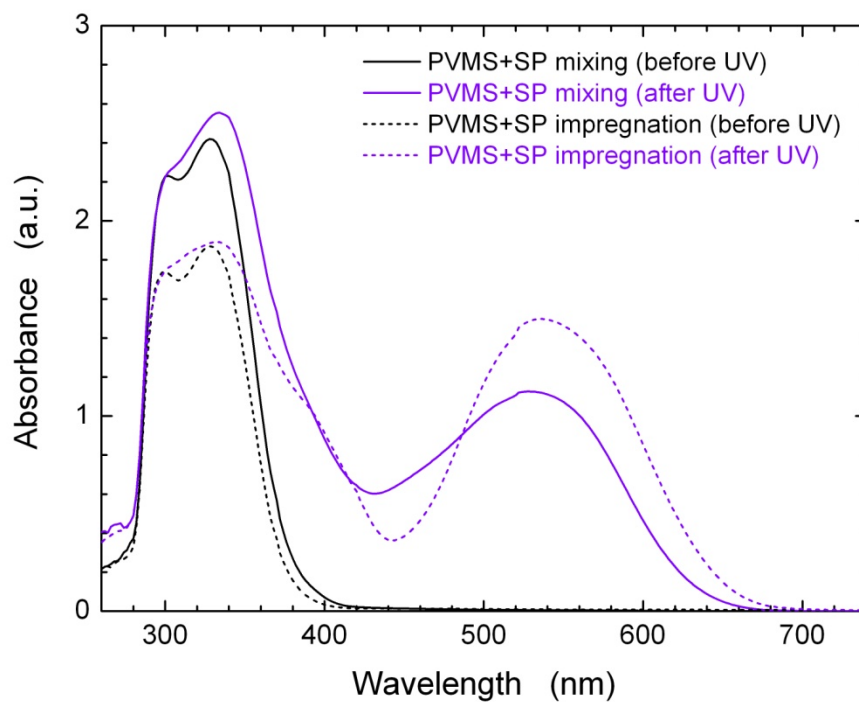


Figure S1 UV/Vis spectra collected from SP-doped PVMS networks prepared by the mixing (solid lines) and impregnation (dotted lines) methodologies. The black and purple lines represent the spectra of the closed and open forms of SP collected before and after UV irradiation, respectively.

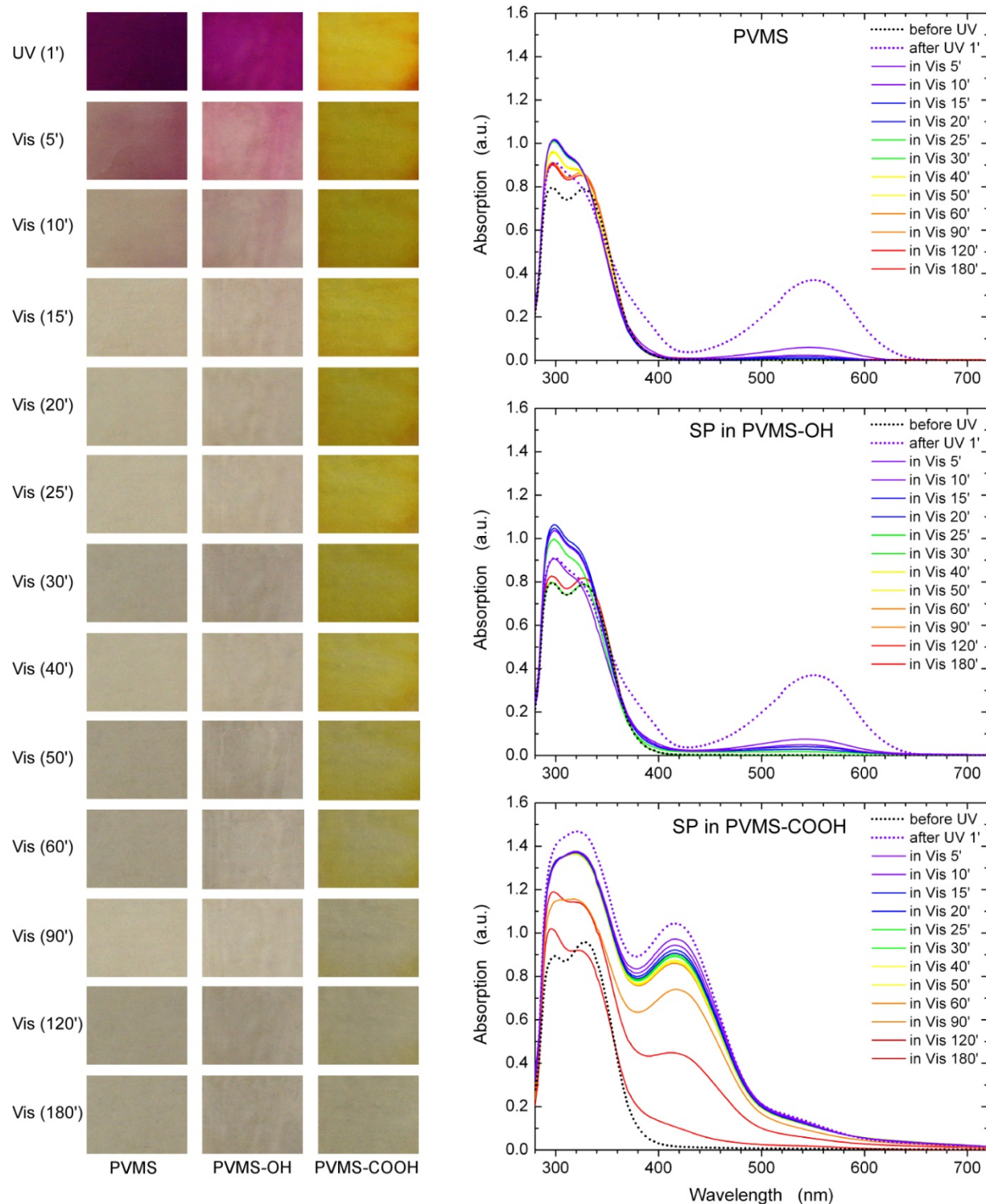


Figure S2 (left) Photographs of samples containing SP-doped PVMS networks before and after modification with $-OH$ and $-COOH$ based thiols. (right) corresponding UV/Vis spectra collected from SP-doped PVMS (top), PVMS-OH (middle) and PVMS-COOH (bottom) networks after UV irradiation for 1 minute and various relaxation times in visible light.

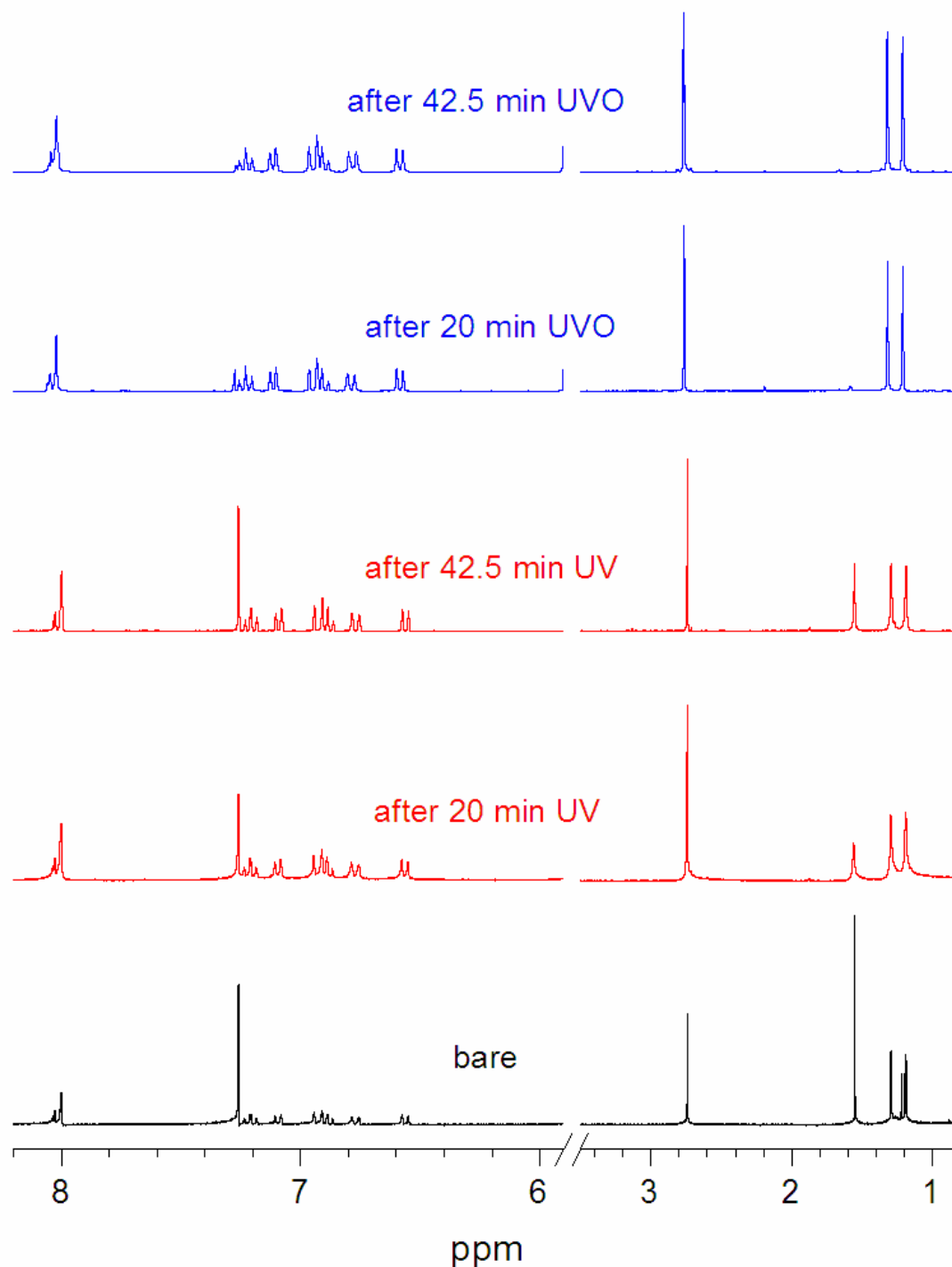


Figure S3 NMR of parent SP (black), after UV irradiation for 20 and 42.5 mins (red) and after UVO treatment for 20 and 42.5 mins (blue). The UV irradiation was carried out with a low pressure Hg pen-Ray 5.5 Watt UV lamp (Ultra-Violet Product, Upland, CA) with a primary output at 254 nm; the areal power density was 1.16 mW/cm² for the UV source-sample distance used in the irradiation experiments. The UVO treatment was carried out in a commercial UVO chamber (Jelight Company, Inc., Model 42); the power of the UV lamp was ≈ 8 mW/cm².