Supporting Information for

Polydiacetylene/Silica Nanocomposites with Tunable Mesostructure and Thermochromatism from Diacetylenic Assembling Molecules

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Synthesis and Characterization of bridged silsesquioxanes

Diacetylenic acids (or diol) were filtered using the membrane with the pore diameter of 20 nm to remove any PDA present prior to use. The purified monomer (2.8mmol) was then dissolved in THF (20 mL, anhydrous) under a nitrogen atmosphere in a schlenk tube. γ-Isocyanatopropyltriethoxysilane (equal molar number to the COOH or OH groups) was slowly added at room temperature. The resultant solution was refluxed for 24 h and then cooled to room temperature. Evaporation of the solution produced colorless viscous liquid (S1) or solid (S2, 3, 4, 5). The overall yield was about 90%, and the purity was high based on Nuclear Magnetic Resonance and Fourier transform infrared analysis.

S1: FTIR ($CHCl_3$): $\tilde{\nu}$=1569(δ_{NH}), 1640 (ν_{CO}), 3422 cm^{-1} (ν_{NH}); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ =0.59 (t, 4 H; CH_2Si), 1.20 (t, 9 H; CH_3), 1.57 (qt, 4 H; CH_2), 3.11 (m, 4 H; NCH_2), 3.70 (qd, 12 H; OCH_2), 5.15 (m, 2 H; NH); ^{13}C NMR (400 MHz, $CDCl_3$): δ=7.8(CH_2Si), 18.4 (CH_3), 23.3 (CH_2), 43.7 (CH_2N), 58.5 (CH_2O), 77.2 ($C\equiv C$), 155.5 ppm (CO).

S2: FTIR ($CHCl_3$): $\tilde{\nu}$=1568 (δ_{NH}), 1644 (ν_{CO}), 3440 cm^{-1} (ν_{NH}); ^1H NMR (500 MHz, $CDCl_3$, TMS): δ =0.59 (t, 4 H; CH_2Si), 1.19 (t, 9 H; CH_3), 1.57 (qt, 4 H; CH_2), 3.11 (m, 4 H; NCH_2), 3.70 (qd, 12 H; OCH_2), 5.10 (m, 2 H; NH); ^{13}C NMR (500 MHz, $CDCl_3$): δ=7.9 (CH_2Si), 18.5 (CH_3), 23.0 (CH_2), 42.0 (CH_2N), 58.5 (CH_2O), 77.2 ($C\equiv C$), 155.0 ppm (CO).

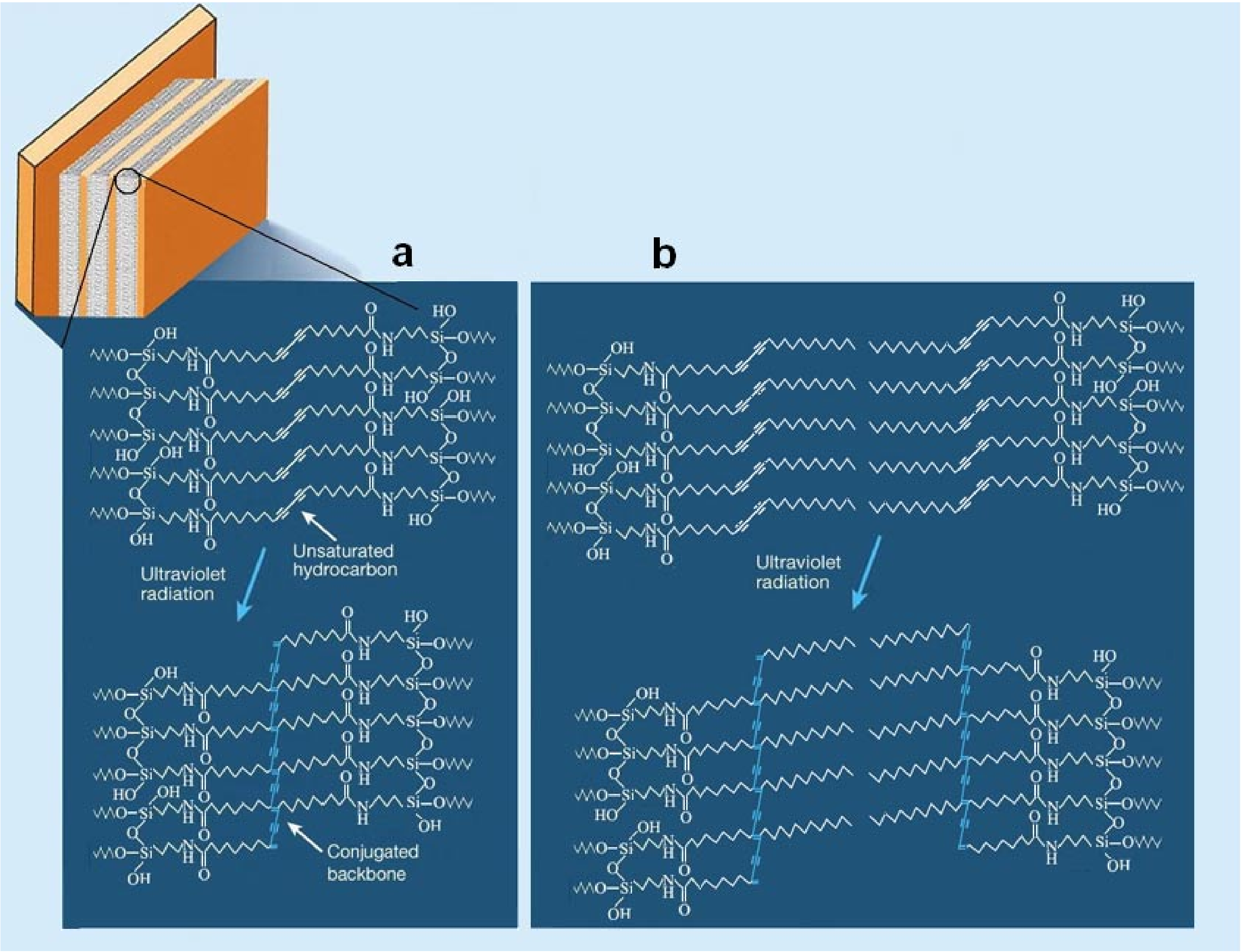
S3: FTIR ($CHCl_3$): $\tilde{\nu}$=1558 (δ_{NH}), 1645 (ν_{CO}), 3403 cm^{-1} (ν_{NH}); ^1H NMR (500 MHz, $CDCl_3$, TMS): δ =0.62 (t, 4 H; CH_2Si), 1.21 (t, 9 H; CH_3, 3.10 (m, 4 H; NCH_2), 3.73 (qd, 12 H; OCH_2), 5.12 (m, 2 H; NH); ^{13}C NMR (500 MHz, $CDCl_3$): δ=7.9 (CH_2Si), 18.2 (CH_3), 23.3 (CH_2), 43.2 (CH_2N), 58.5 (CH_2O), 77.0 ($C\equiv C$), 155.2 ppm (CO).

S4: FTIR ($CHCl_3$): $\tilde{\nu}$=1556 (δ_{NH}), 1645 (ν_{CO}), 3418 cm^{-1} (ν_{NH}); ^1H NMR (500 MHz, $CDCl_3$, TMS): δ =0.61 (t, 4 H; CH_2Si), 1.23 (t, 9 H; CH_3, 3.10 (m, 4 H; NCH_2), 3.77 (qd, 12 H; OCH_2), 5.15 (m, 2 H; NH); ^{13}C NMR (500 MHz, $CDCl_3$): δ=7.7 (CH_2Si), 18.4 (CH_3), 23.2 (CH_2), 43.3 (CH_2N), 58.8 (CH_2O), 77.5 ($C\equiv C$), 155.4 ppm (CO).

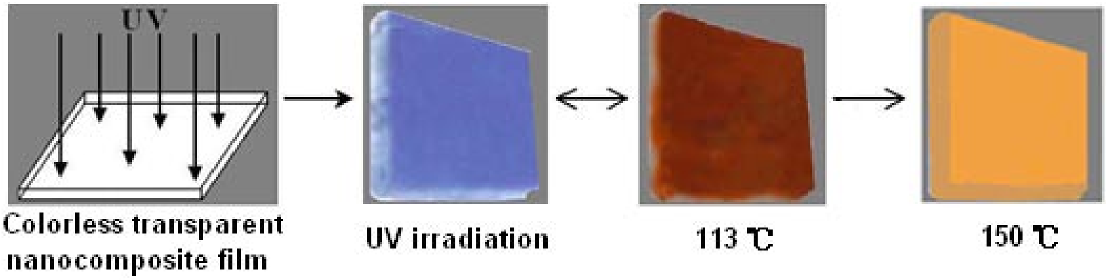
S5: FTIR ($CHCl_3$): $\tilde{\nu}$=1561 (δ_{NH}), 1643 (ν_{CO}), 3404 cm^{-1} (ν_{NH}); ^1H NMR (500 MHz, $CDCl_3$, TMS): δ =0.60 (t, 4 H; CH_2Si), 1.20 (t, 9 H; CH_3, 3.11 (m, 4 H; NCH_2), 3.70 (qd, 12 H; OCH_2), 5.15 (m, 2 H; NH); ^{13}C NMR (500 MHz, $CDCl_3$): δ=7.9 (CH_2Si), 18.5 (CH_3), 23.0 (CH_2), 43.5 (CH_2N), 58.6 (CH_2O), 77.2 ($C\equiv C$), 155.0 ppm (CO).

Preparation of Diacetylene/silica and PDA/silica nanocomposites

The bridged silsesquioxanes (0.17 mmol) were dissolved in THF (1.5 mL). A solution of HCl (0.1 M, 1.0mL) was added and the mixture was stirred at room temperature for ~1 days. Thin colorless DA/silica nanocomposite films were prepared by casting the resultant solution on the glass substrate followed by very slow evaporation. Polymerization of diacetylenic units to the blue form was done by UV exposure at 254 nm for times ranging from 10 min to 2 h. Subsequent transformation to the red form was accomplished by heating at ~90 °C for times ranging from 30 s to 2 min.



Scheme 1. Polymerization of S2 (a) and S5 (b).



Scheme 2. Schematic and photographs of PDA/silica films with different colors for the thermochromatic process.

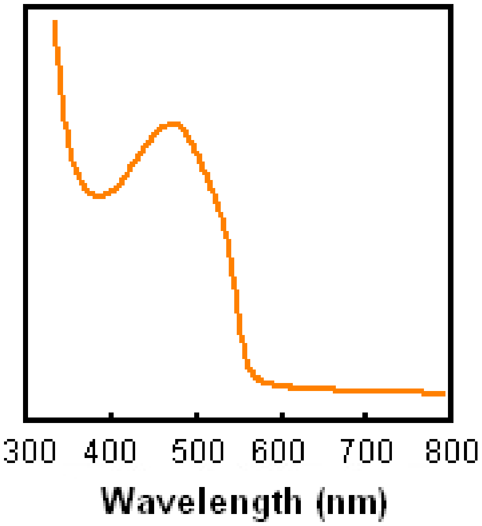


Figure 1. Typical UV-vis spectrum of orange PDA/silica films.

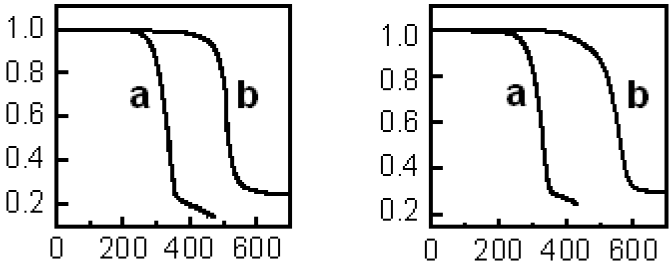


Figure 2. Thermogravimetric analysis (TGA) of pure PDA and PDA/silica nanocomposites derived from the precursor S2 (left) and S5 (right), respectively. a. PDA from the diacetylenic precursor; b. PDA/silica nanocomposite.

The chemical structures of the bridged silsesquioxanes were examined using the FTIR (Thermo Nicolet Nexus ^{TM} 670) and NMR (GE Omega PSG500 500 MHz). The mesostructure was characterized with X-ray diffraction (XRD) scans obtained with a Phillips Xpert X-ray diffractometer (Cu Kα radiation at λ=0.1542 nm). The chemical structures of the nanocomposites were examined using a Beckman^{TM} DU 640B Ultraviolet-visible (UV-vis) spectrophotometer. The transmission electron microscopy (TEM) images were taken using a JEOL 2010 microscope operated at 120 kV.

Reference (5)

Y. F. Lu, Y. Yang, A. Sellinger, M. Lu, J. Huang, H. Fan, R. Haddad, G. Lopez, A. R. Burns, D. Y. Sasaki, J. Shelnutt, C. J. Brinker, *Nature* **2001**, 410, 913-917.