Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information

Shape Memory Polymers with Built-In Threshold Temperature Sensors

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Materials. **C18-RG** was prepared as described before (M. Kinami, B. R. Crenshaw and C. Weder, *Chem. Mater.* **2006**, *18*, 946). Polycyclooctene (Vestenamer 8012® with a high *trans* content of 80%) was purchased from Degussa Corporation. Dicumyl peroxide (DCP) (> 98% purity) was obtained from Aldrich. These materials were used as received.

Film Preparation. PCO pellets were dried in vacuo at 45 °C overnight prior to processing. Binary blends of PCO and DCP were prepared by feeding the appropriate amount of crosslinker (1.25% w/w with respect to the polymer) and 4 g of dry polymer into a recycling, co-rotating twin-screw mini-extruder (DACA Instruments), mixing for 5 min at 80 °C, and subsequent extrusion. Films with a thickness of 0.4 mm were prepared by compression-molding the blend at 180 °C between Teflon

films in a Carver press for 30 min under a load of 10,000 lbs. After removal from the hot press, the fully cured samples were cooled to RT.

Cross-linked PCO films were swollen in THF overnight and then transferred into a solution of **C18-RG** in THF at 50 °C for 2 h. Films were removed and dried overnight at RT, rinsed with THF, and dried overnight again to create phase-separated PCO/**C18-RG** blends.

Instrumentation. Temperature dependent photoluminescence (PL) spectra were acquired on an Ocean Optics ACD1000-USB spectrometer (λ_{ex} = 377 nm, emission spectra are uncorrected) through the use of a Y-shaped optical fiber in conjunction with a hot stage. Steady-state spectra of the pristine films and of films annealed for 1 min at 100 °C were taken by placing the films on a glass slide on a Gel Instrumente AG hotstage with a TC2 temperature controller. In-situ controlled temperature runs were done using a HCS402 hot stage (Instec Inc.) equipped with a liquid nitrogen LN_2-P cooling accessory for accurate temperature control during heating and cooling runs. The samples were sandwiched between two glass coverslips and heated to 100 °C at 10°C/min, held for 1 min, cooled to -20 °C at a specified rate, held for 1 min, heated to 100 °C at a specified rate and held for 1 min. Spectra were collected during the cooling and second heating steps.

Differential scanning calorimetry (DSC) experiments were conducted under N_2 atmosphere on a TA Instruments Q100. The samples were heated at a rate of 10 °C/min from -90 to 100 °C and were then cooled to -90 °C at a cooling rate of 10 °C/min. Subsequently, a second heating run to 100 °C at the same rate of 10 ^{o} C/min was performed. The observed melting temperature (T_m) of each cross-linked PCO sample was determined from the second heating curve. The melting temperatures and heats-of-fusion were evaluated from the peak and the areas of maxima of the appropriate endotherms.

A dynamic mechanical analyzer (TA-DMA Q800) was used to explore and analyze one-way shape memory behavior. Samples were cut into rectangular strips with dimensions of 0.4 × 2.0 × 15.0 mm. Each PCO or PCO/**C18-RG** strip was placed in tension between a fixed and movable clamp. One-way shape memory behavior was characterized using a four-step program that begins at elevated temperature ($T > T_m$). (1) *Deformation:* the sample was elongated by increasing the applied load from 0 to 0.48 N (600 kPa) at a rate of 0.05 N/min and at T = 75 °C. (2) *Fixing:* the sample was then cooled at 2 °C/min to a temperature (5 °C) below T_c under constant load - this step was found to fix the temporary shape quite completely. (3) *Unloading:* the load was removed at a constant rate of 0.1 N/min, revealing the quality of fixing through the resulting final strain. (4) *Recovery:* Finally, heat-induced recovery toward the original length was examined by heating to 75 °C at a rate of 2 °C/min. The cycle of steps 1-4 was repeated. The furnace door was programmed to open after each step and pictures were taken under 365 nm UV light.

The sample used in Figure 6 was made by heating a rod of 1.5 mg/mL PCO/**C18-RG** to 80 °C, twisting it into a spiral, and fixing at room temperature. Recovery to the permanent shape (rod) occurred upon immersing the temporary shape (spiral) into silicon oil at 75 °C.

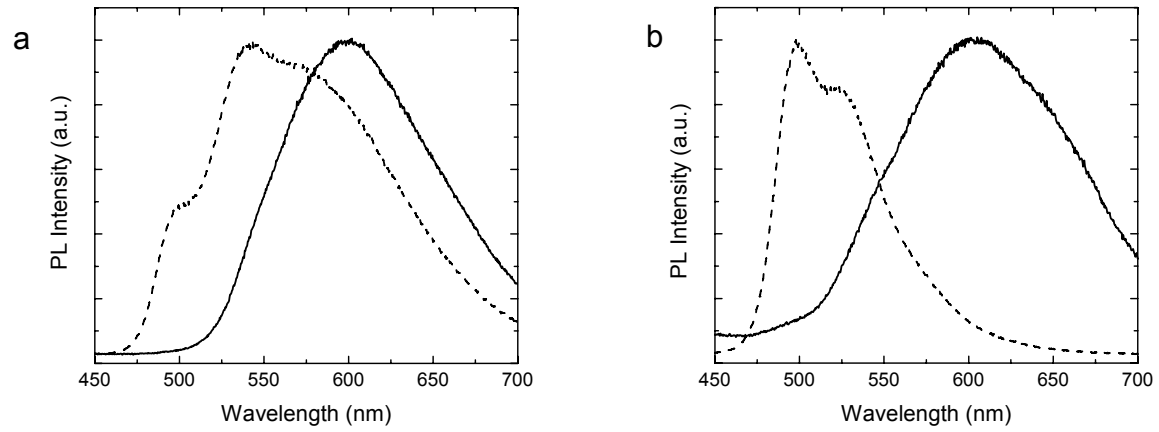

Figure S1. Normalized PL emission spectra of an initially phase-separated (a) 1.5 mg/mL and (b) 0.5 mg/mL PCO/**C18-RG** blend film at 25 °C (solid line) and after annealing for 1 min at 100 °C (dashed line).

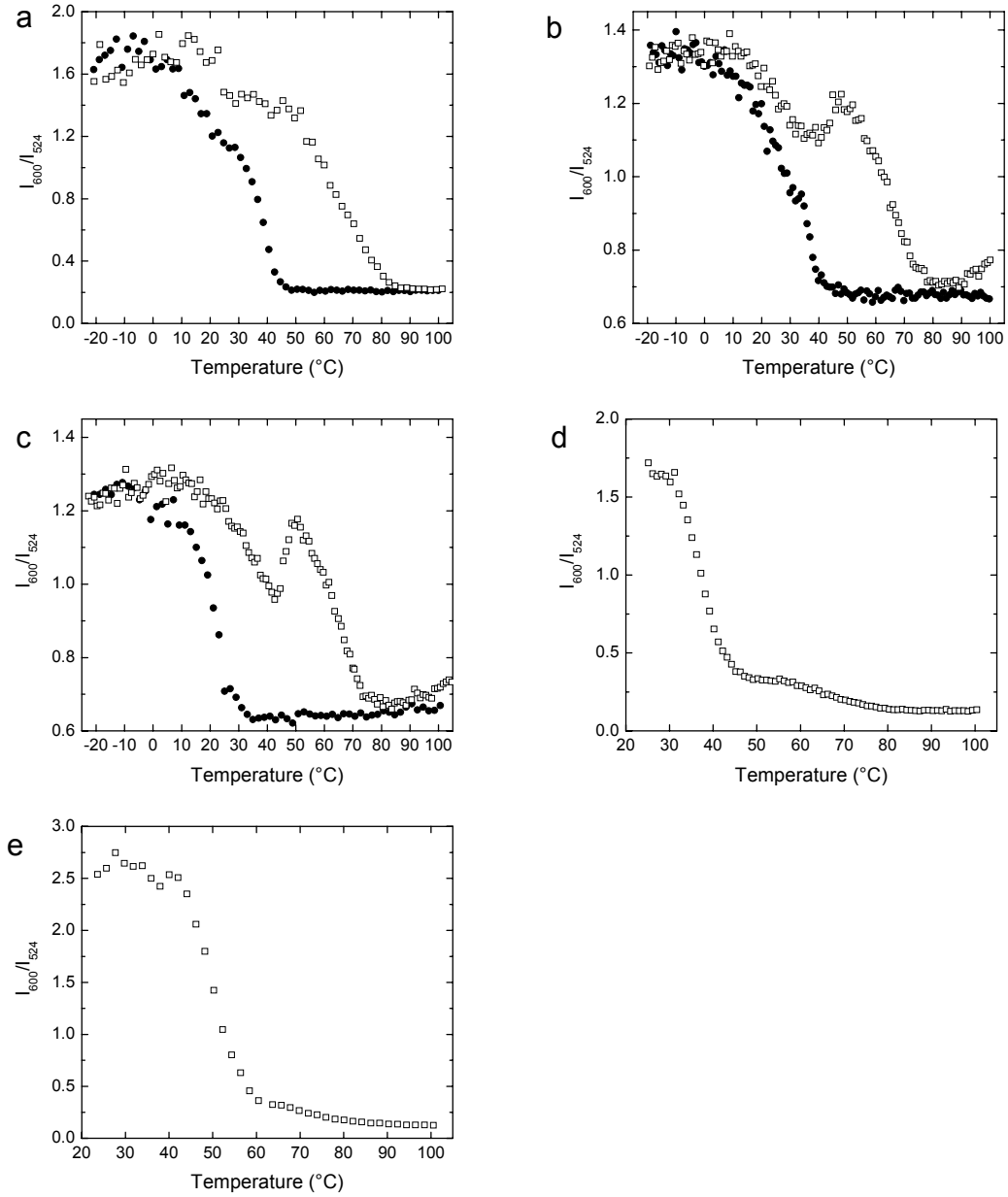

Figure S2. Color change (expressed as I_{600}/I_{524}, see manuscript) extracted from the spectra of (a) 0.5 mg/mL or (b,c) 0.1 mg/mL PCO/**C18-RG** blend films cooled (closed circles) and heated (open squares) as a function of temperature. The cooling and heating rates were (a) 10 °C/min cooling and heating, (b) 1 °C/min cooling and heating, and (c) 10 °C/min cooling and 1 °C/min heating. PL spectra of a 0.1 mg/mL PCO/**C18-RG** blend film heated at (d) 1 °C/min and (e) 10 °C/min as a function of temperature.

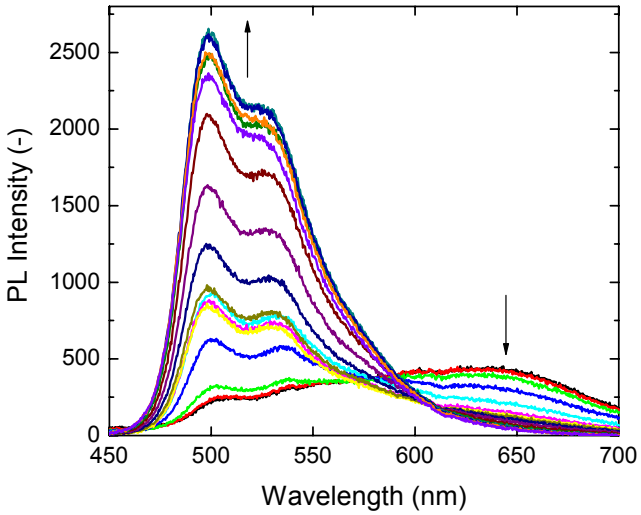

Figure S3. PL emission spectra of an initially phase-separated 0.1 mg/mL PCO/**C18-RG** blend film during heating from 25 °C to 100 °C at 1 °C/min. Spectra shown were collected every 5 °C.

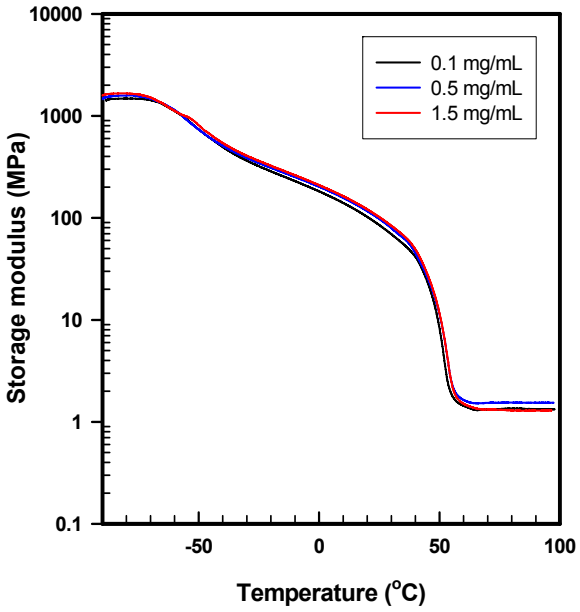

Figure S4. Storage modulus (E') vs. temperature for PCO/**C18-RG** blends. E' was recorded at a heating rate of 3 °C/min with a frequency of 1 Hz.

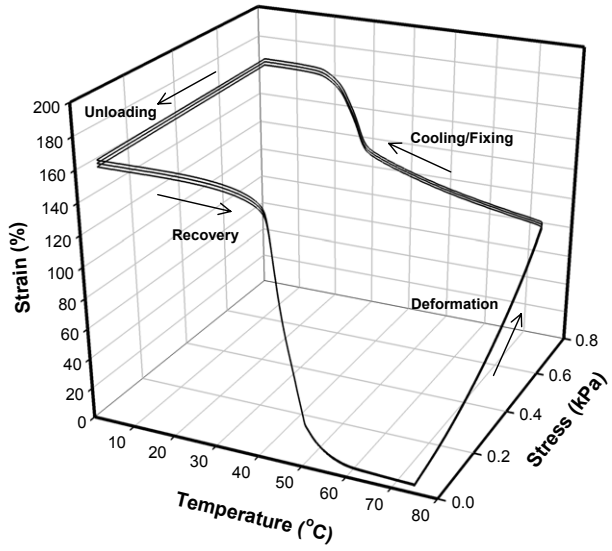

Figure S5. One-way shape memory cycles for a 0.1 mg/mL PCO/**C18-RG** sample. The asterick indicates the beginning of the experiment. The material is elongated by increasing stress at 75 °C (i). Cooling (ii) and removing the stress (iii) yields a temporary "fixed" strain that can be recovered to the original strain upon heating (iv).