Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information: Leveraging the gel-to-sol transition of physically crosslinked thermoresponsive polymer hydrogels to enable cold triggered reactions

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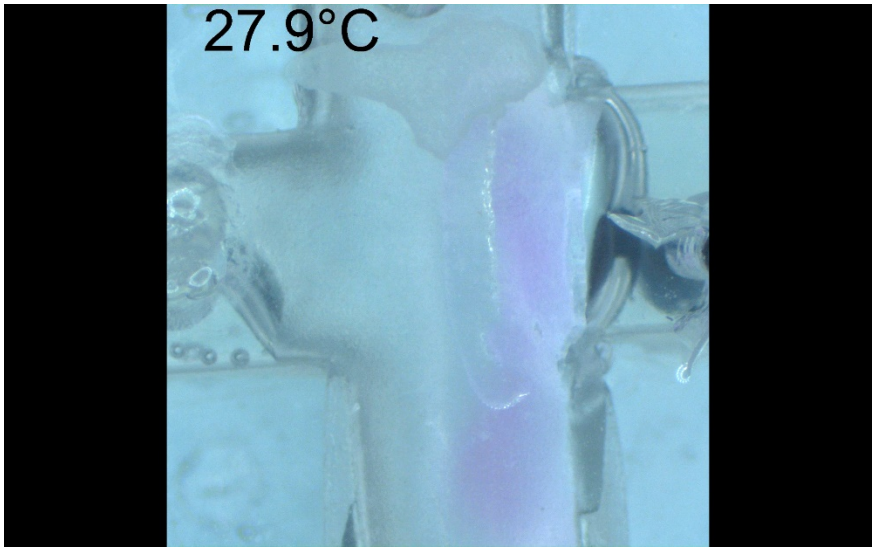


Movie S1. Discrete reagent-laden hydrogels shown undergoing gel-to-sol transition and flowing into each other (with their reactive payloads) upon cooling. The solution point of the "first-flowing gel" (on the left) is 33±1°C. Movie is sped up by a factor of 25.

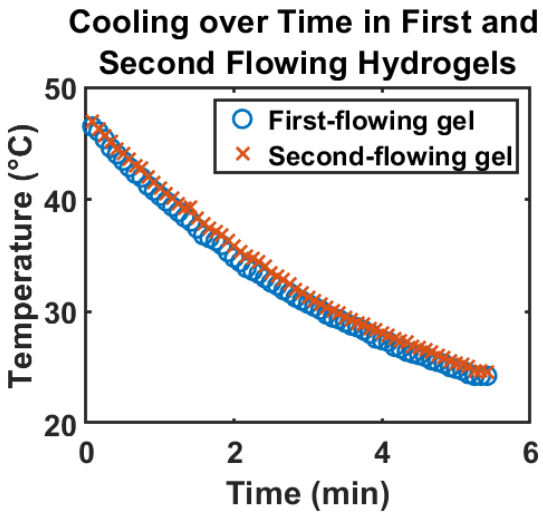


Fig. S1. Cooling curve measured in first-flowing gel vs. cooling curve measured in second-flowing gel. The curves remain within ~1°C of each other.

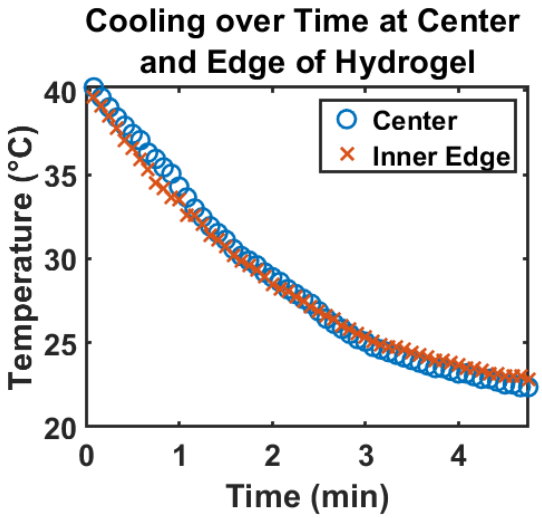


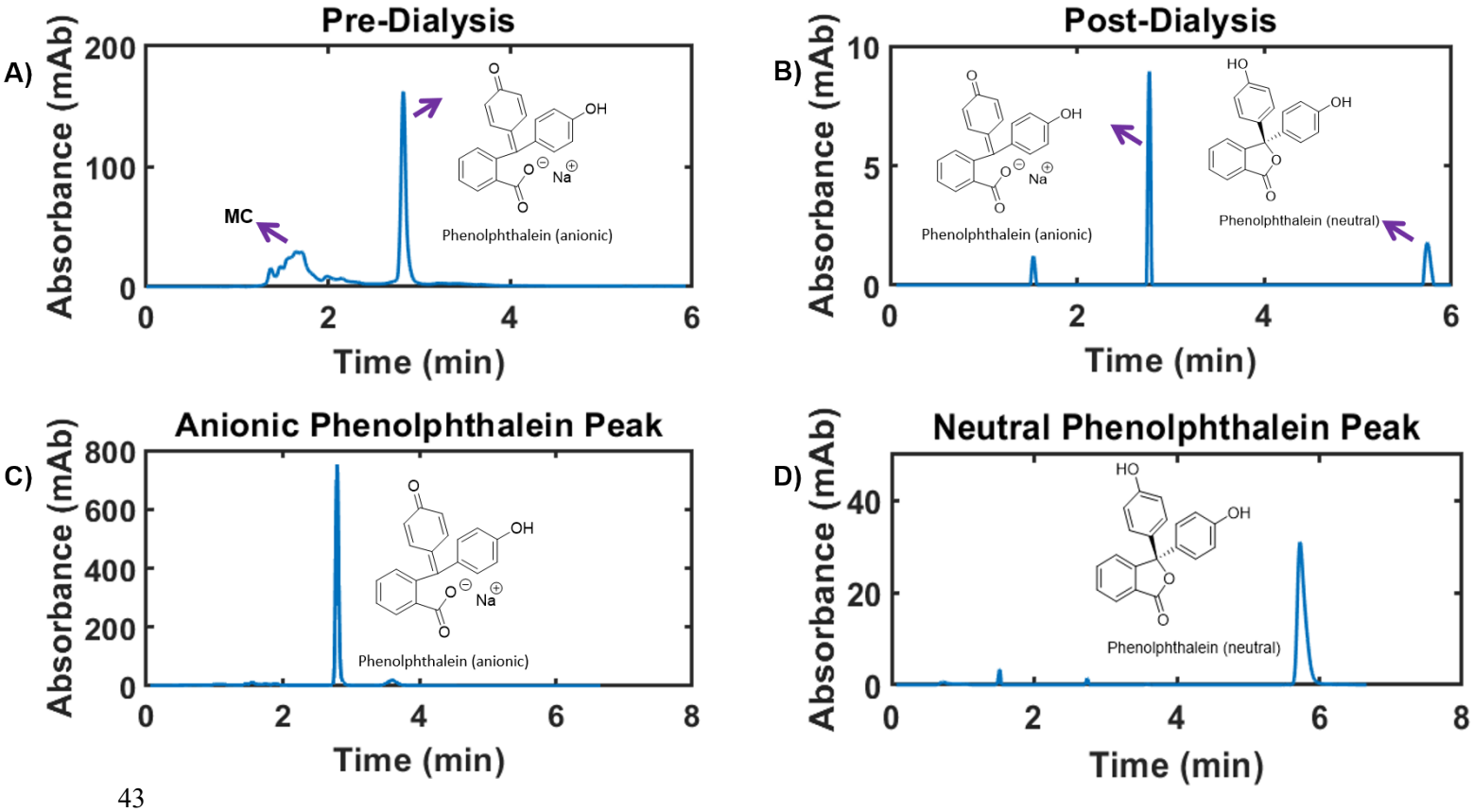
Fig. S2. Cooling curves measured at center and inner extremity of a single hydrogel's long axis. The curves remain within ~1°C of each other.

Extraction of reaction products for analysis

We separated reaction products from methylcellulose (MC) using dialysis, then characterized the results of this dialysis using HPLC (high-performance liquid chromatography). Specifically, we loaded 3 ml of MC containing anionic phenolphthalein (post reaction with NaOH) into 3.5kDa dialysis tubing and left said tubing in 60 ml of DI water for 18 hours with gentle stirring. Samples drawn from the original product-laden MC and from outside the dialysis tubing after 18 hours were then analyzed with HPLC.

An Agilent 1200 series high-performance liquid chromatography (HPLC) system was used to analyze products. 20 µL of sample was injected into an Agilent ZORBAX Eclipse Plus C18 column of 150 mm length with an internal diameter of 4.6 mm and 3.5 µm fused silica particles, protected by a ZORBAX Eclipse Plus-C18 analytical guard column (4.6x12.5mm 5-micron) at a flow rate of 1 mL/min (linear gradient of 40 % v/v acetonitrile in water for 35 min, gradually rising to 100 % (v/v) acetonitrile in water at 35 min). This concentration was kept constant until 40 min when the gradient was decreased to 40 % (v/v) acetonitrile in water at 42 min. The products were identified by using Agilent 1200 Series multiple wavelength detectors SL at 280 nm.

HPLC chromatograms of the pre-dialysis sample display two retention peaks. The peak at around 1.8 min is for the MC and at around 3 min is for the anionic phenolphthalein (as the pH of the medium is ~9) (Fig. S3A). The post dialysis sample was taken from the DI water in the beaker. In the post-dialysis chromatogram, the peak around 3 min is for the anionic phenolphthalein and 6 min for neutral phenolphthalein (as pH decreases due to dilution when phenolphthalein exits the dialysis membrane into the large volume of the DI water) and trace amount of MC at 1.8 min (Fig S3B). The reference HPLC chromatograms of anionic (Fig. S3C) and neutral phenolphthalein (Fig. S3D) samples show peaks at 3 min and 6 min, respectively. The peak intensity of the post dialysis sample was low as it was more dilute (20 times) compared to the pre-dialysis sample.



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44 Fig. S3. HPLC chromatograms for product-laden MC before dialysis (A), dialysis well after 18 hours of
45 dialysis (B), and anionic (C) and neutral (D) phenolphthalein.