

Supporting/Supplementary information

Experimental Details. All DNP and EPR measurements were performed at a commercial 9.7 GHz Bruker EPR spectrometer at an operating magnetic field of $B_0=0.345$ T ($\nu(^1\text{H})=14.7$ MHz). The CW EPR spectra were detected with a critically coupled ENDOR probehead. For the NMR detection the ENDOR probe was externally tuned and matched to the operating NMR frequency. The DNP effect was measured in dependence of the irradiated microwave (mw) power and the temperature which ranged from 5°C to 55°C (cf. $T_C=63^\circ\text{C}$). CW EPR spectra were recorded for all temperatures. The temperature was adjusted with a closed-cycle cryostat. The continuous mw irradiation time on the EPR center line was kept as short as possible (ranging from 3 times T_1 of water in hydrogels ≤ 1 s) to minimize heating effects. The spin-label concentration of the SL-Hydrogels in the swollen/soaked state could be determined by CW EPR calibration measurements with the reference radical TEMPOL (data not shown). For the 5 % and the 15 % labeling degree we found a final spin-label concentration of ~ 1 and ~ 6.8 mM, respectively.

Materials. Methacrylic acid (MAA, 99%, Aldrich) was distilled prior to use. N,N-Ethylmethacrylamide (EMAAM) and 4-Methacryloyloxybenzophenone (MABP) were prepared according to reported procedures [1,2]. Dioxane was distilled over CaH_2 and dried over a molecular sieve (4 Å). 2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Acros) was recrystallized from methanol. Triethylamine (NEt_3 , 99.5%, Fluka), pentafluorophenyltrifluoroacetate (PFTFA, 98%, Aldrich) and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (Amino-TEMPO, 97%, Acros) were used as received. Distilled water was further purified by a MilliQ System (Millipore) to achieve a resistivity of 18.2 M Ω cm.

Thermoresponsive Polymer. Statistical terpolymers based on EMAAM (3 g, 26.5 mmol) admixed with small amounts of MAA and MABP were obtained via free radical polymerization initiated by AIBN (20 mg, 0.12 mmol). The reaction took place in 20 mL dioxane at 60 °C for 24 h under exclusion of air and moisture. The polymers were precipitated in 200 mL diethyl ether and purified by re-precipitation from ethanol into diethyl ether. They were freeze-dried from water in vacuo. The yield was around 90 %.

$^1\text{H-NMR}$ (250 MHz, d^4 -MeOH): δ / ppm = 0.9-1.2 (m, $-\text{CH}_3$, MAA, MABP, $-\text{CH}_2\text{CH}_3$ EMAAM), 1.5-1.9 (m, CH_2 backbone), 2.2-3.7 (m, CH backbone, $-\text{CH}_2\text{CH}_3$, $-\text{Me}$, EMAAM), 6.8-8.0 (m, C-H_{arom}).

The molecular weight and the polydispersity index (M_w/M_n) were determined by gel permeation chromatography with dimethylformamide as mobile phase. The measurement was conducted at 60°C, PMMA served as internal standard. The monomer composition and the molecular weight distribution of the synthesized polymers are summarized in **Table S1**.

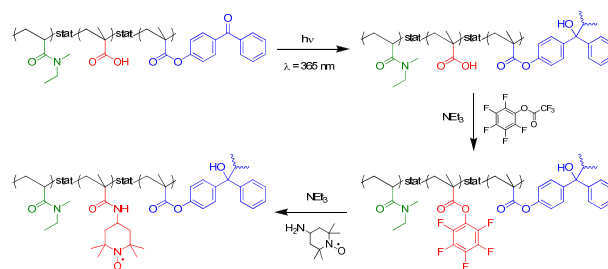
Spin-Labeling and Sample Preparation. 15 wt% polymer solutions in ethanol were drop-cast on hexamethyldisilazane modified glass slides and dried over night in vacuo at 40°C to achieve polymeric films in the range of 10 – 15 μm . The polymer

was crosslinked and tethered to the substrate by UV irradiation (6.82 J/cm²) with a Stratagene UV Stratalinker with a peak wavelength of 365 nm. The carboxylic acid groups of the resulting gels were converted to active ester units with a two-fold excess of PFTFA and NEt_3 in dichloromethane (DMC). After washing the gels with DMC twice, they were reacted with a two-fold excess of 4-amino-TEMPO and NEt_3 in DMC to achieve the spin-labeled material. The synthetic route is described in **Scheme S1**. In order to remove unreacted nitroxide molecules, the gels were subjected to dialysis (Spectra/Por 3 Dialysis Membrane, MWCO = 3500 gmol⁻¹) in ethanol for one week. The solvent was removed in vacuo and the spin-labeled gel was abraded with a scalpel, filled into EPR sample canules (i.d. 0.8 mm) and swollen with deionized water. Excess water not bound to the hydrogel was removed.

Table S1 Properties of the Synthesized Polymers

	monomer composition [mol%]			M_w [gmol ⁻¹] ^a	M_w/M_n ^a	Yield [%]
	EMAAM m	MAA	MA BP			
P5	94	5	1	49600	3.1	89
P15	84	15	1	28000	4.2	92

^a determined by GPC at 60°C in DMF



Scheme S1 Synthetic Route to the Spin-labeled Hydrogel

References

- 1 K. J. Shea, G. J. Stoddard, D. M. Shavelle, F. Wakui, R.M. Choate, *Macromolecules*, 1990, **23**, 4497.
- 2 R. Toomey, D. Freidank, J. R uhe, *Macromolecules*, 2004, **37**, 882.