Peculiar Nanocomposite Hydrogel with Controllable Multiple Thermosensitivity: Double Phase Transition and Ternary Stable States

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Supplementary Information for Chemical Communications

Experimental

Materials: *N*-isopropylacrylamide (NIPAAm) (99 %, Acros Co., Belgium), Laponite XLS (Clay-S) (Rockwood Co., U.S., 92.32 wt% $Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$, 7.68 wt% $Na_4P_2O_7$), *N,N'*-methylenebisacrylamide (NMBA), potassium persulfate(KPS), and *N,N,N',N'*-tetramethyldiamine (TEMED) (Shanghai Chemical Reagent, Analytic Reagent), polyethylene glycol (M_w = 400, 1000, 2000, 4000, 6000, Shanghai Chemicals Co., China). All reagents were used as received. All solutions used in experiments were prepared in deionized water.

Preparation of clay/PNIPAAm/PEG nanocomposite hydrogels: Hydrogels were prepared using initial solutions consisting of monomer (NIPAAm), crosslinker (Clay-S or NMBA), polyethylene glycol (PEG), initiator (KPS), and accelerator (TEMED). In all cases, the water/initiator ratio, and the volume of accelerator were fixed at 1000/1 (w/w), and 24 μL, respectively. First, a transparent aqueous solution consisting of water (28 mL), clay (3 g) or NMBA(0.03 g), NIPAAm(3 g), and PEG(0.5-4 g) was prepared. Then, the accelerator (TEMED, 24 μL) and the aqueous solution of initiator (KPS 0.03 g in water 2 mL) were subsequently added to the former solution with stirring at 0 ^oC. Next, free-radical polymerization was carried out at 5 ^oC for 48 h.

Measurements of Transparency: Transparency of the gels synthesized in a quartz cell (10 mm×10 mm×40 mm) was measured using a UV/VIS spectrophotometer (UV 1901, Puxi Co. China). The temperature of the quartz cell was regulated electrically. Transparency at 600 nm was recorded after 30 min at every temperature.

Irreversibility of Phase Transition: Transparency of gel samples synthesized in quartz cells was measured until it became stable at three different temperatures (15 ^oC, 23 ^oC, 26 ^oC).

Transparency Change during Polymerization: The reaction solution was contained in a quartz tube with a cap, which was regulated at 5 ^oC. Transparency was recorded continuously during polymerization.

Table S1. Compositions of all samples

Gels	Clay/g	NMBA/g	NIPAAm/g	PEG		H_2O/	KPS/	TEMED/
				M_w	Weight/g	mL	g	μL
S10N10	3	/	3	/	/	30	0.03	24
S10N10P1-0.5	3	/	3	1000	0.5	30	0.03	24
S10N10P2-0.5	3	/	3	2000	0.5	30	0.03	24
S10N10P4-0.5	3	/	3	4000	0.5	30	0.03	24
S10N10P6-0.5	3	/	3	6000	0.5	30	0.03	24
S10N10P6-1	3	/	3	6000	1.0	30	0.03	24
S10N10P6-2	3	/	3	6000	2.0	30	0.03	24
S10N10P6-4	3	/	3	6000	4.0	30	0.03	24
S10P6-4	3	/	/	6000	4.0	30	/	/
LR-N10P6-4	/	/	3	6000	4.0	30	0.03	24
OR-N10P6-4	/	0.03	3	6000	4.0	30	0.03	24