

**Fig. 1** The hydrodynamic radii ( $R_h$ ) of the P(NIPAM-AA) microgels in pH3.5 water ( $\Box$ ) and the corresponding P(NIPAM-PBA) microgels in 0.050M pH8.5 PBS ( $\odot$ ) as a function of temperature. Scattering angle = 90°.

## **Experimental Details**

**Materials** and Apparatus: N-Isopropylacrylamide (NIPAM), N,N'-methylenebis(acrylamide) (BIS), acrylic acid (AA), acrylamide (AAm), 3-aminophenylboronic hemisulfate acid (APBA), N-(3-dimethylaminopropyl)-N'-ethyl-carbodiimide hydrochloride (EDC), and 2,2-diethoxyacetophenone (DEAP) were purchased from Aldrich or ACROS. NIPAM was purified by recrystallization from a hexane/acetone mixture and dried in a vacuum. AA was distilled under reduced pressure. Reflective spectra were measured with the incident light normal to the PCCA film using a fiber spectrometer (Avantes AvaSpec-2048). Hydrodynamic radii (R<sub>h</sub>) of the microgel particles were measured on a Brookhaven 90Plus particle size analyzer. UV-vis spectra were measured on a TU-1810PC UV-Vis spectrophotometer (Purkinje General, China).

**Synthesis of P(NIPAM-AA) microgels**: NIPAM (1.000 g, 8.8 mmol), AA (0.287 g, 4.0 mmol), BIS (0.030 g, 0.2 mmol), and sodium dodecyl sulfate (0.039 g) were dissolved in water (95 mL). The solution was transferred to a three-necked round-bottom flask equipped with a condenser and a nitrogen inlet and heated to 70 °C under a gentle stream of nitrogen. After 1 h, 0.06 M ammonium persulfate (5 mL) was added to initiate the reaction. The reaction was allowed to proceed for 4 h. The resultant microgels were purified by dialysis against water for 1 week.

**Synthesis of P(NIPAM-PBA) microgels**: Purified P(NIPAM-AA) microgel suspension (5 mL) was added to a mixture solution of APBA (0.233 g, 1.25 mmol) and EDC (0.239 g, 1.25 mmol) in water (45 mL) at 0 °C. After 4 h, the product was purified by dialysis against water for 2 days.

**Preparation of P(NIPAM-AA) microgel PCCA**: Concentrated P(NIPAM-AA) microgels (2g), AAm (0.1g, 1.4 mmol), BIS (0.005 g, 0.032 mmol) and 10 wt% DEAP solution in DMSO (7.7  $\mu$ L) were mixed and put between two parallel quartz plates separated by a Parafilm spacer. After fully crystallized, it was exposed to UV light (365 nm) for 1 h. The resulting PCCA film was washed extensively in DI water.

**Preparation of P(NIPAM-PBA) microgel PCCA**: The P(NIPAM-AA) microgel PCCA was treated with a mixture solution of APBA (0.466g) and EDC (0.478g) in

water (90 mL) at 0°C for 4 h. The resulting PCCA film was washed extensively in DI water.