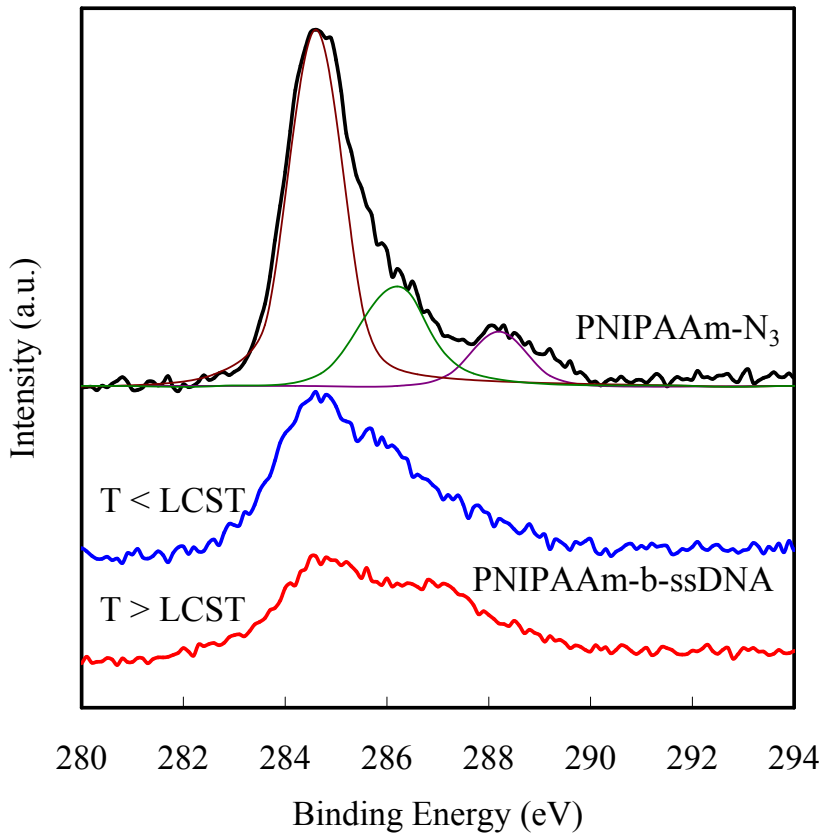
Supplemental information

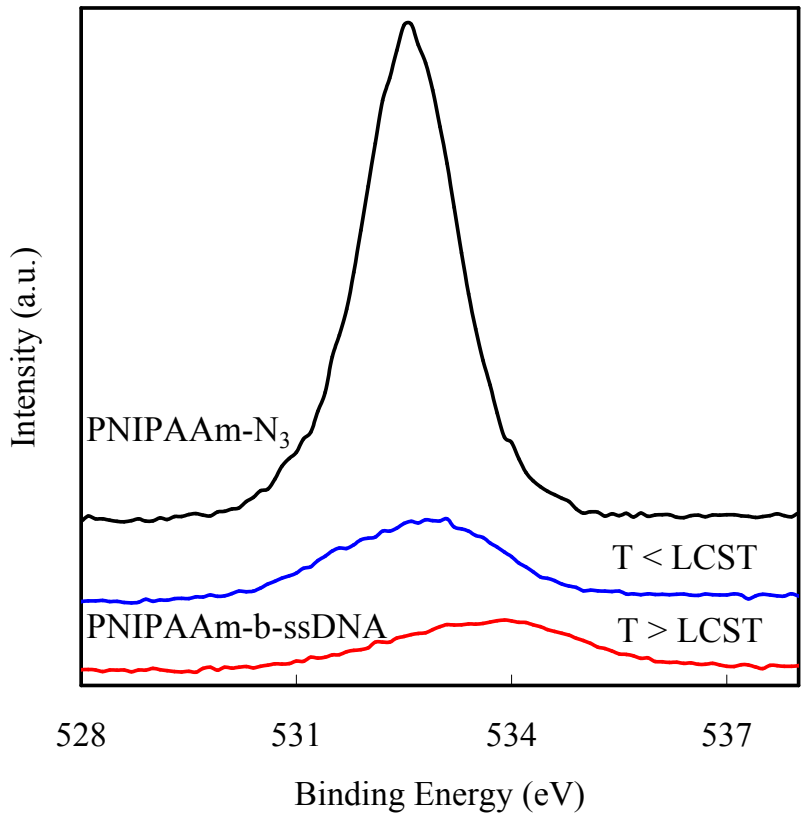
From the high-resolution C 1s spectra in Figure S1a, we determined an oxygen:nitrogen:carbon molar ratio for PNIPAAm-N_3 of 12.1:12.9:75.5, consistent with the expected ratio of 12.5:12.5:75.0 for PNIPAAm. These values were obtained after curve-fitting using of the signals with binding energies (BEs) of 284.6, 286.2, and 288.2 eV, attributable to C–C/H, C–N, and C=O chemical bonding environments, respectively. The BE for the C=O groups was slightly higher than that previously reported [1]; thus, the BE for the C=O groups of PNIPAAm increased slightly after azido-terminating the surface. In addition, the peak area ratios of C–N and C=O to C–C/H were both significantly greater for the PNIPAAm-*b*-ssDNA brush surface, consistent with ssDNA grafting [2]. Furthermore, we heated the PNIPAAm-*b*-ssDNA surface at a temperature above its LCST to investigate the HB between its PNIPAAm and ssDNA units. A peak with a BE of 287.1 eV appeared for the PNIPAAm-*b*-ssDNA brush surface above its LCST, presumably representing the BE of the C=O groups of the ssDNA. These results suggest that the BMHBs between PNIPAAm and ssDNA weakened as a result of increased intramolecular HB of PNIPAAm at temperatures above the LCST; this phenomenon led to the ssDNA segments being driven up to the surface. Figure S1b presents the corresponding high-resolution O 1s spectra. For PNIPAAm-N_3, one peak was centered at 532.5 eV in the O 1s region, attributable to C=O bonding. At a temperature below the LCST, this peak shifted to

532.9 eV after grafting the ssDNA onto the PNIPAAm-N_3; above the LCST of the PNIPAAm-b-ssDNA copolymer brushes, it shifted further to 533.9 eV. The survey spectrum of the bromo-PNIPAAm brushes featured a Br 3d peak at 70 eV and a Br (3p) peak at 188 eV, along with the other peaks [3, 4]. The bromine atoms were converted to azido groups through substitution with NaN_3 in DMF. This transformation was clearly evident in the high-resolution N 1s XPS scan (Figure S1c), which we curve fitted using the peaks with BEs of 400.2, 403.8, and 401.6 eV. We attribute the major peak at 401.6 eV to the CNH units of PNIPAAm. The spectrum features a minor characteristic double peak structure for the azido groups at 400.2 and 403.8 eV, with a BE split of 3.6 eV [5]. The peak areas were in a ratio of 2.6:1, as expected for an azide structure (an internal nitrogen atom surrounded by two nitrogen atoms). The less-intense peak at 404.2 eV represented the electron-deficient nitrogen atom of the azido groups [6]. Figure S1d presents corresponding high-resolution P 2p spectra. The P 2p peak at 133.8 eV also shifted to 135.2 eV upon heating the PNIPAAm-b-ssDNA copolymer to a temperature above its LCST. Whereas the BE shifts for the O 1s peaks were small (□1.0 eV), those of the P 2p peaks were relatively large (□1.4 eV). Larger BE shifts have also been observed in the P 2p spectra of pure DNA monolayers, suggesting that the ssDNA segments interacted with the PNIPAAm units through the phosphate atoms in the nucleic acid bases.

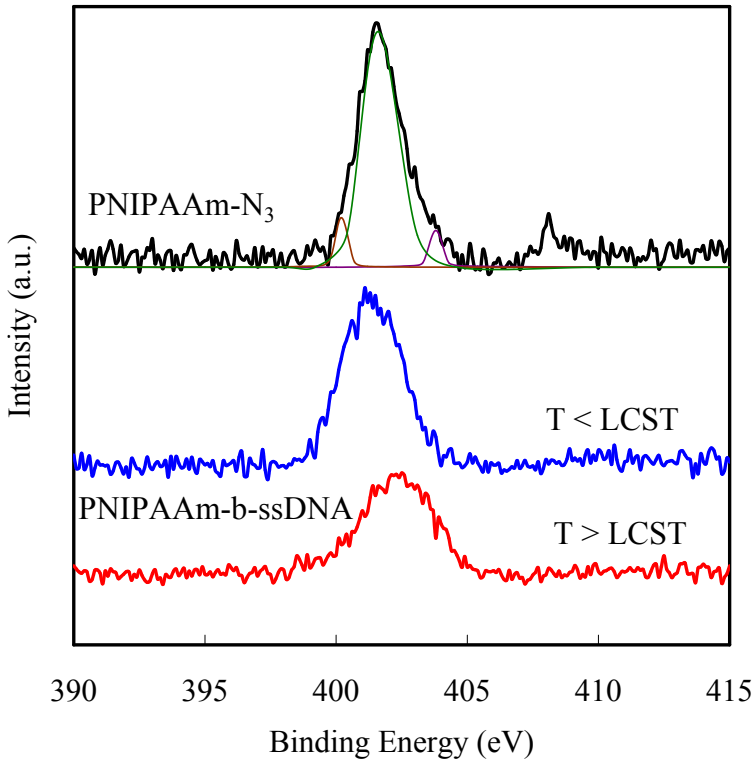
(a)


Intensity (a.u.)
PNIPAAm-N3
T < LCST
PNIPAAm-b-ssDNA
T > LCST
280
282
284
286
288
290
292
294
Binding Energy (eV)

(b)


Intensity (a.u.)
PNIPAAm-N3
T < LCST
PNIPAAm-b-ssDNA
T > LCST
528
531
534
537
Binding Energy (eV)

(c)



(d)

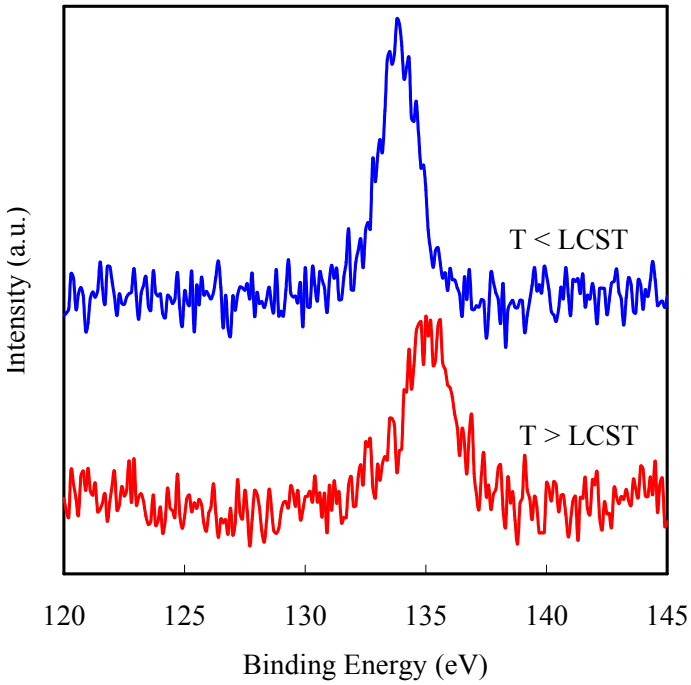


Figure S1 High-resolution (a) C 1s, (b) O 1s, and (c) N 1s core level XPS spectra of PNIPAAm-N3 and PNIPAAm-b-ssDNA polymer brushes grafted onto Au surfaces for 20 h and (d) P 2p core level XPS spectra of PNIPAAm-b-ssDNA polymer brushes, all recorded at temperatures below and above the LCST.

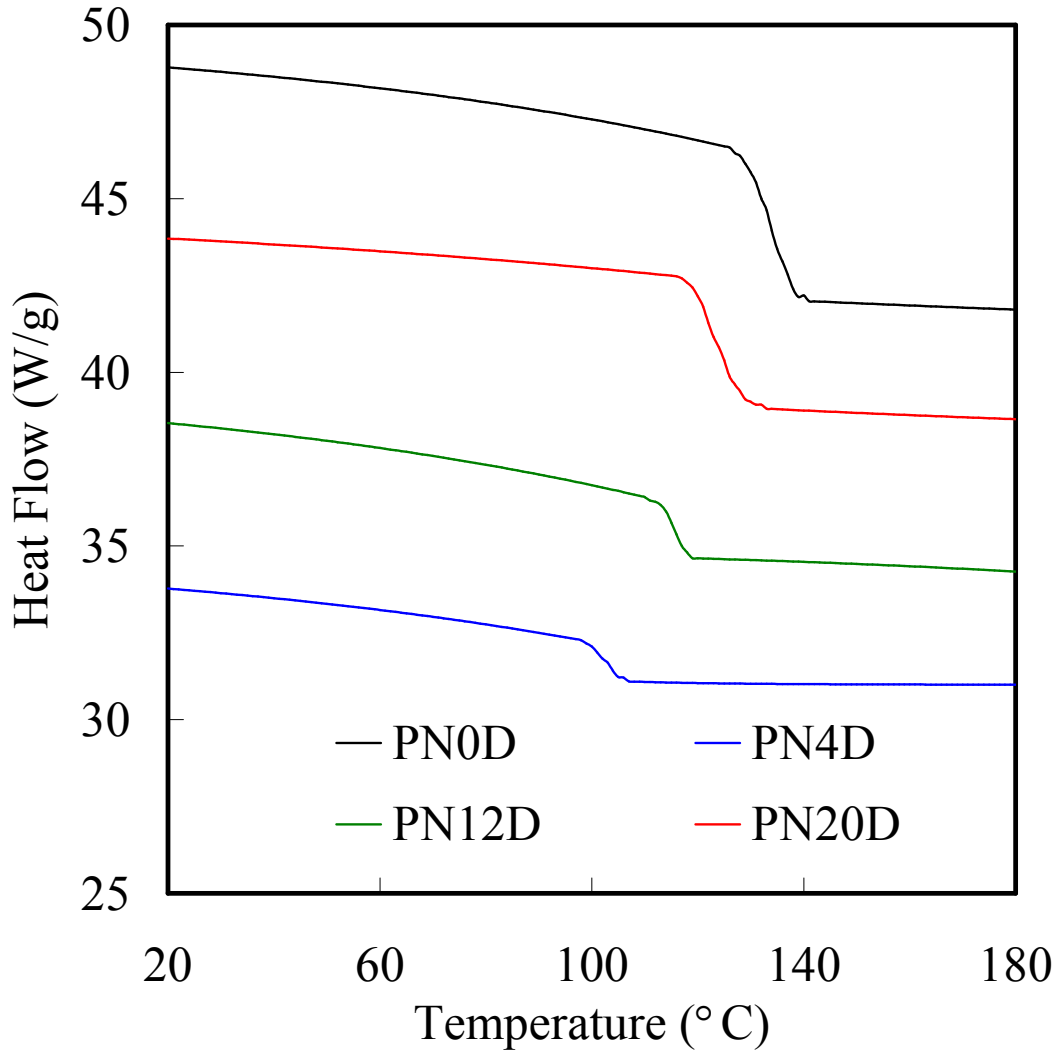
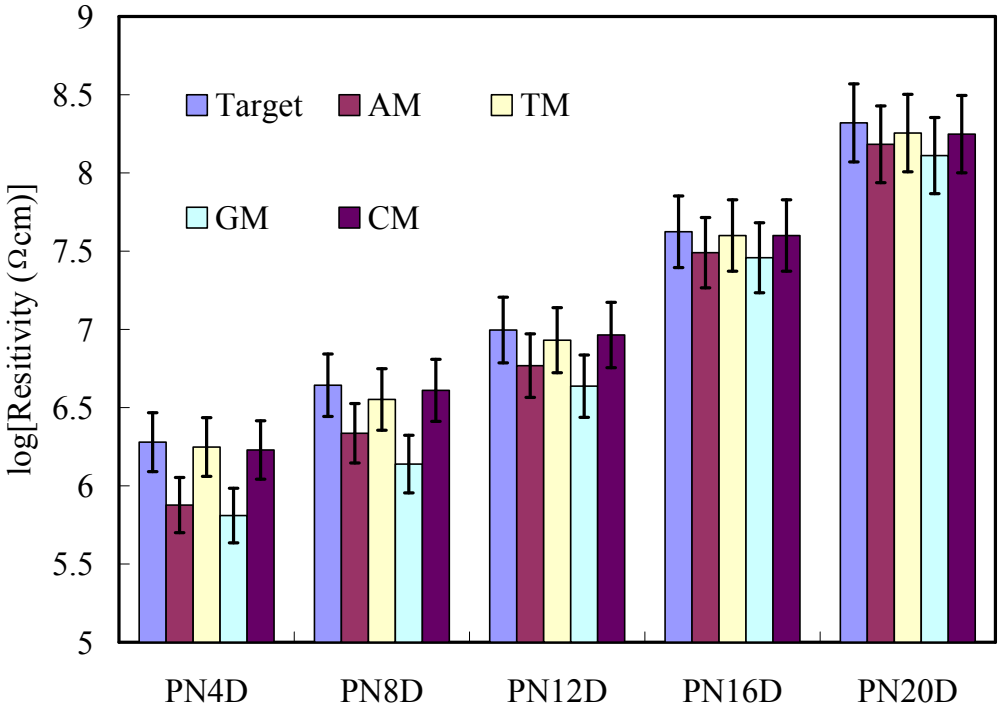


Figure S2 DSC curves of PN0D, PN4D, PN12D and PN20D, respectively.

(a)



(b)

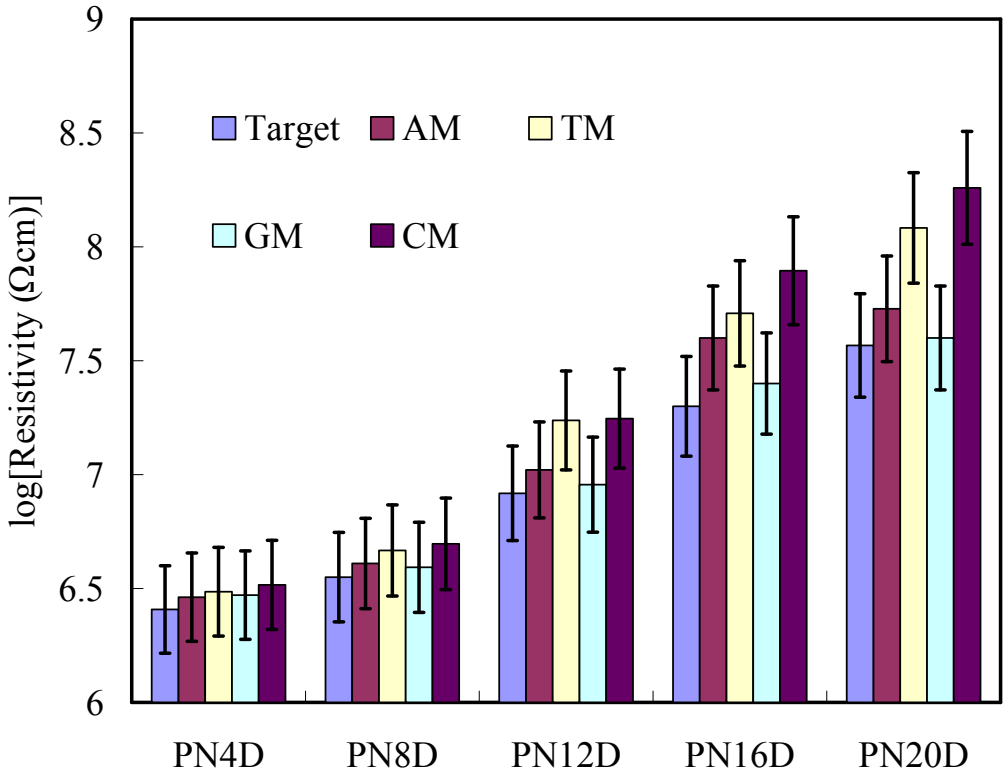


Figure S3 : Resistivities of PNIPAAm-b-ssDNA copolymer brushes (logarithm scale) after hybridization with the target, AM, TM, GM, and CM at 0.5 pg/nL at (a) 25 and (b) 80 °C.

Reference

[1] Q. Yu, Y. Zhang, H. Chen, F. Zhou, Z. Wu, H. Huang, J.L. Brash, Protein adsorption and cell adhesion/detachment behavior on dual-responsive silicon surfaces modified with poly(N-isopropylacrylamide)-block-polystyrene copolymer, Langmuir 26 (2010) 8582–8588.

[2] C. Lee, P. Gong, G.M. Harbers, D.W. Grainger, D.G. Castner, L.J. Gamble, Surface coverage and structure of mixed DNA/alkylthiol monolayers on gold: Characterization by XPS, NEXAFS, and fluorescence intensity measurements, Anal. Chem. 78 (2006) 3316–3325.

[3] J. Chen, J. Li, Synthesis of tethered poly-(N-isopropyl-acrylamide) for detection of breast cancer recurrence DNA, J. Colloid Interface Sci. 358 (2011) 454–461.

[4] J. Chen, J. Wang, C. Cheng, J. Chang, Reversibly thermoswitchable two-dimensional periodic gratings prepared from tethered poly(N-isopropylacrylamide) on silicon surfaces, ACS Appl. Mater. Interfaces 5 (2013) 2959–2966.

[5] S.S. Balamurugan, E. Soto-Cantu, R. Cueto, P.S. Russo. Preparation of organosoluble silica-polypeptide particles by “click” chemistry, Macromolecules 43 (2010) 62–70.

[6] S. Prakash, T.M. Long, J.C. Selby, J.S. Moore, M.A. Shannon. “Click” modification of silica surfaces and glass microfluidic channels, Anal. Chem. 79 (2007) 1661–1667.