Electronic Supplementary Information (ESI) for:

Reversible Sol-Gel Transitions of Aqueous Dispersions of Silica Nanoparticles Grafted with

Diblock Copolymer Brushes Composed of a Thermosensitive Inner Block and a Charged

Outer Block

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Cleavage of Polymer Brushes from Hairy Silica NPs Using HF. The following is the procedure for the cleavage of PDEGMMA-*b*-P(DEGMMA-*co*-DMAEMA) diblock copolymer brushes from BHP-3 hairy NPs. A similar procedure was used to cleave PDEGMMA brushes from HHP. PDEGMMA-*b*-P(DEGMMA-*co*-DMAEMA) brush-grafted silica NPs (BHP-3, 10.1 mg) were dispersed in THF (5 mL) in a Teflon tube. Hydrofluoric acid (HF, 48 ~ 51 % aqueous solution, 0.5 mL) was then added to the dispersion, and the mixture was stirred overnight. After the excess HF was neutralized using a saturated aqueous solution of $Ca(OH)_2$, the cleaved polymer from hairy NPs was extracted with methylene chloride at 35 °C. The free polymer and the cleaved polymer were analyzed back-to-back using a PL-GPC 50 Plus, an integrated GPC/SEC system from Polymer Laboratories, Inc. with a differential refractive index detector, one PSS GRAL guard column (50 × 8 mm, Polymer Standards Service-USA, Inc.), and two PSS GRAL linear columns (each 300 × 8 mm, molecular weight range from 500 to 1,000,000 according to Polymer Standards Service-USA, Inc.) at ambient conditions. DMF was the carrier

solvent with a flow rate of 1.0 mL/min. Narrow-disperse polystyrene standards (Polymer Laboratories, Inc.) were used for calibration.
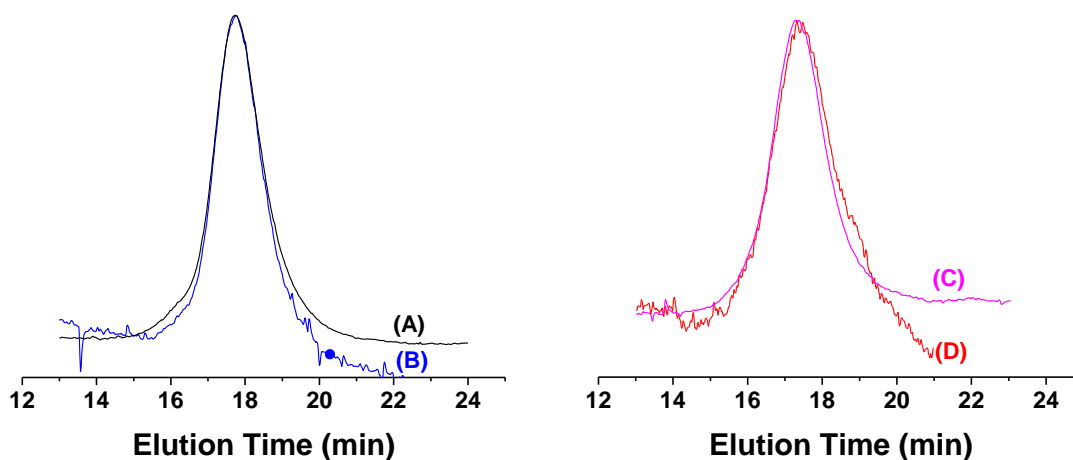

Figure S1. Size exclusion chromatography (SEC) traces of (A) the free PDEGMMA formed in the synthesis of PDEGMMA brush-grafted silica nanoparticles (HHP), (B) the PDEGMMA brush cleaved from HHP, (C) the free diblock copolymer PDEGMMA-*b*-P(DEGMMA-*co*-DMAEMA) (BCP-3) formed in the synthesis of diblock copolymer brush-grafted silica NPs (BHP-3), and (D) the polymer cleaved from hairy NPs BHP-3. The SEC analysis was performed using a PL-GPC 50 Plus with DMF as the carrier solvent.

Calculation of Degree of Polymerization (DP) of PDEGMMA Formed in Synthesis of PDEGMMA Brush-Grafted, 17 nm Silica Nanoparticles (HHP). The DP of PDEGMMA formed in the synthesis of HHP was calculated using monomer conversion, as determined by ^{1}H NMR spectroscopy, and TGA data of hairy NPs and initiator NPs.

The TGA curve of the initiator NPs was shifted vertically so that the weight retentions of initiator NPs and HHP at 100 °C were identical. (The difference in weight retentions of initiator NPs and HHP at 100 °C is believed to come from the absorbed moisture despite drying under high vacuum.) The corrected weight retention of the initiator NPs at 800 °C is 89.90 %. The ratio

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of the silica residue to the volatile portion at 800 °C is 100 : 11.23 for initiator NPs and 100 : 338.60 for HHP. As the mass of the initiator NPs used in the polymerization was 1.057 g, the total mass of the grafted polymer is [(338.60 − 11.23)/(100 + 11.23)] × 1.057 g = 3.111 g. Because the mass of DEGMMA used in the polymerization was 20.074 g and the monomer conversion was 29.84 %, the total mass of polymer, both free and grafted polymer, is 5.990 g. Thus, the mass of free polymer is 2.879 g. Using the ratio of free to bound polymer and the amount of free initiator used (29.7 mg, 152.3 µmol), the surface initiator that successfully initiated polymerization was found to be 164.6 µmol. Therefore, as the sum of the free initiator and the surface initiator is 316.9 µmol and the amount of monomer added was 106.7 mmol, the monomer-to-initiator ratio was calculated to be 337 : 1. Thus, the DP of PDEGMMA is 101.

Calculation of Grafting Density of PDEGMMA Brushes Grafted on 17 nm Silica Nanoparticles (HHP). For the calculation of grafting density of PDEGMMA brushes, assuming that the silica NPs are spherical and the density is 2.07 g/cm^3, the mass of a single NP with a diameter of 17 nm is 5.32×10^{-18} g. Therefore, the amount of the grafted PDEGMMA on one silica NP is 1.74×10^{-17} g. The molecular weight of PDEGMMA calculated from DP is 19010 g/mol. Thus, the number of the grafted PDEGMMA chains on one silica NP is (1.74×10^{-17} g/19010 g/mol) $\times 6.022 \times 10^{23}$ = 551 chains. The surface area of one bare silica NP is πD^2 = 908 nm^2. Therefore, the grafting density of PDEGMMA brushes on silica NPs is 0.61 chains/nm^2.

Calculation of the DP of PDEGMMA-*b*-P(DEGMMA-*co*-DMAEMA). To determine the total monomer conversion in the synthesis of the second block, the small sample removed for ^{1}H NMR spectroscopy analysis immediately after the addition of DMAEMA was designated as $t = 0$ min for this phase of the polymerization. The sum of the integrals of the two vinyl peaks at 6.15 and 6.13 ppm was compared against the $t = 0$ sample, using the summed integrals of all -COO

CH_2- peaks (from 4.35 to 4.00 ppm), which was a constant through the polymerization, as internal reference. In this way, a conversion was obtained regarding only the polymerization of the second block. To calculate the new monomer-to-initiator ratio, it must be recalled that a significant portion of the polymerization mixture (27.25 wt %) had been removed, and the amounts of DEGMMA and both free and bound initiator must be recalculated accordingly: mmol DEGMMA = 106.7 mmol × (1 − 0.2725) × (1 − 0.2984) = 54.46 mmol, where 0.2984 corresponds to the fraction of monomer having already been polymerized (monomer conversion), and mmol initiator = (free initiator + bound initiator) = 316.9 μmol × (1 − 0.2725) = 230.5 μmol. Therefore, the ratio of monomer-to-initiator is (54.46 mmol DEGMMA + 59.23 mmol DMAEMA)/230.5 μmol initiator = 493 : 1. In the case of BCP-1, the monomer conversion for the second block was 8.6 %, making the DP of the second block 0.086 × 493 = 42 units and the total DP = 101 + 42 = 143. To calculate the number of DMAEMA units (n_{DMAEMA}), the molar percentage of DMAEMA units was obtained from the ^{1}H NMR analysis of the free polymer by comparing the integral of the peak at 2.56 ppm (-CH_2N(CH$_3$)$_2$ from DMAEMA units) to the integral of the peak at 3.38 ppm (-OCH_3 from DEGMMA units). The molar content of DMAEMA units in BCP-1 was found to be 12.1 %. Therefore, n_{DMAEMA} = 143 × 0.121 = 17, making the composition of the second block 17 DMAEMA units and 25 DEGMMA units. The DPs and the values of n_{DMAEMA} and n_{DEGMMA} units in the second block of BCP-2 and BCP-3 were calculated using the same method.

Calculation of Grafting Density of Diblock Copolymer Brushes. The grafting densities of PDEGMMA-*b*-P(DEGMMA-*co*-DMAEMA) brushes in BHP-1, -2, and -3 were calculated using the same method as for that of PDEGMMA brushes.

Quaternization of PDEGMMA-*b*-P(DEGMMA-*co*-DMAEMA) (BCP-3) Using CH₃I. A control quaternization experiment using free diblock copolymer BCP-3 was performed under the similar conditions as for BHP-3 to further confirm that the quaternization of DMAEMA units with iodomethane went to completion. BCP-3 (190.3 mg, 0.2394 mmol DMAEMA units) were added to a 25 mL two-necked flask and dissolved in dry THF (10 mL) under an N_2 atmosphere. The flask was then completely wrapped in aluminum foil, preventing any exposure to light. Iodomethane (1.953 g, 13.76 mmol) was added to the solution, which was then stirred at ambient temperature for 90 min. All volatile portions were removed under vacuum and the polymer residue was characterized using ^{1}H NMR spectroscopy. As shown in Figure S2, the reaction was complete after 90 min.
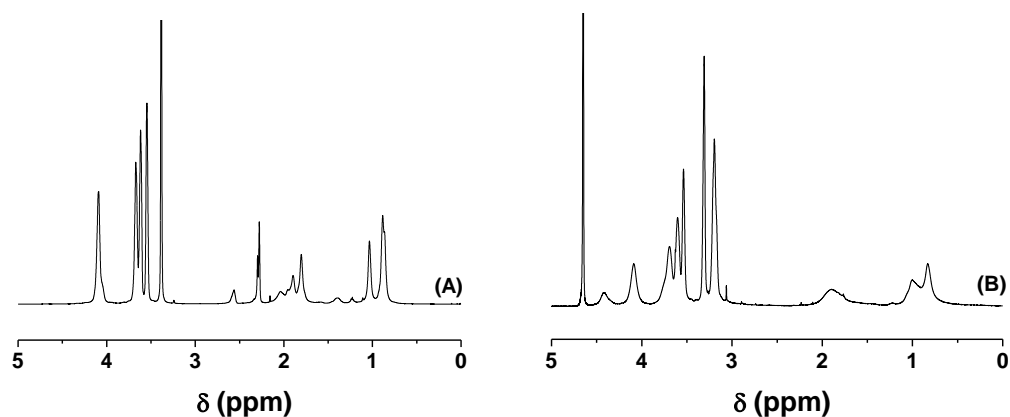

Figure S2. ^{1}H NMR spectra of free diblock copolymer BCP-3 PDEGMMA-*b*-P(DEGMMA-*co*-DMAEMA) before (A) and after (B) quaternization with iodomethane for 90 min.
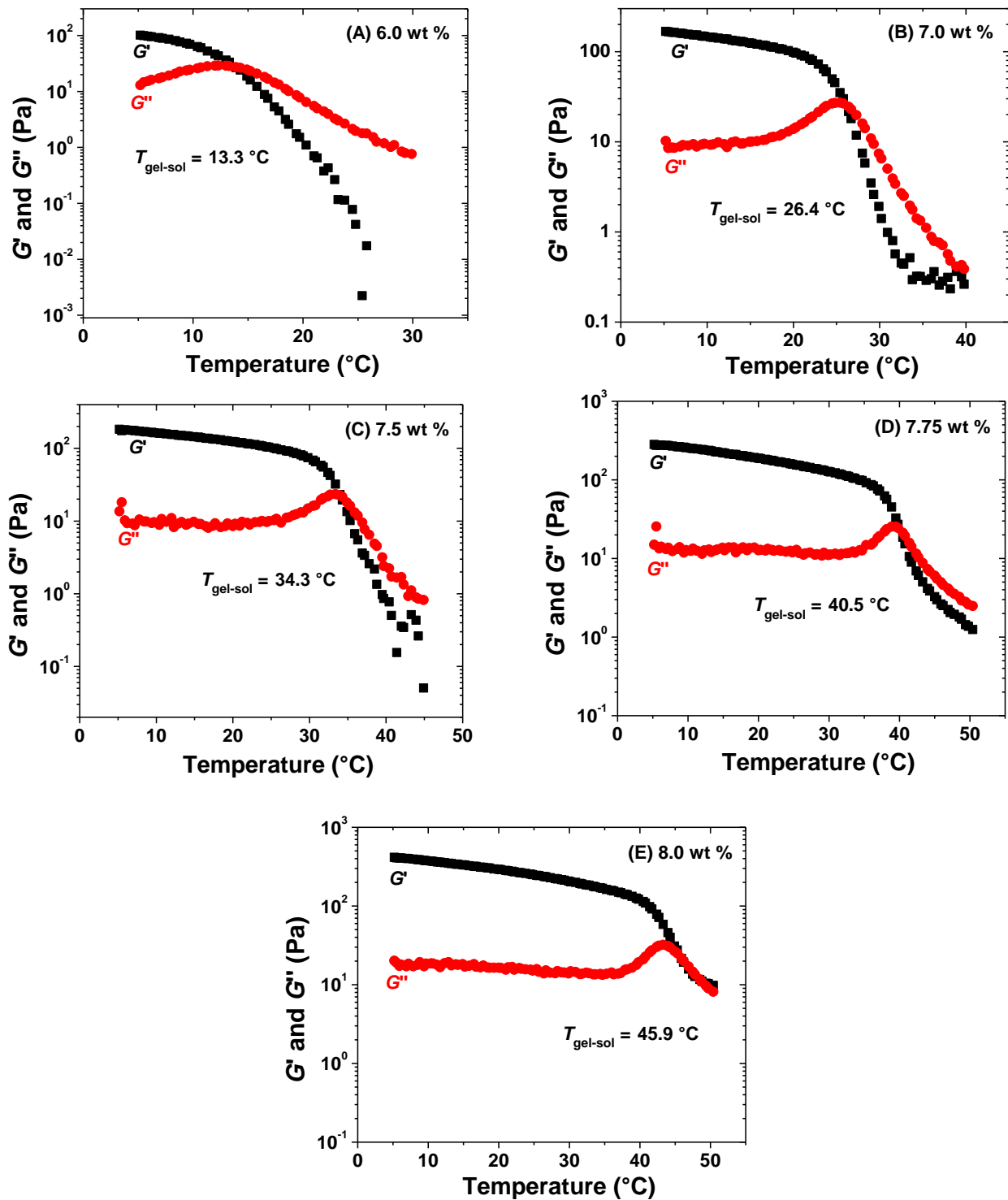
Figure S3. Plots of dynamic storage modulus G' (black square) and loss modulus G'' (red circle) of aqueous dispersions of BHP-1-Q at various concentrations versus temperature. The data were collected from oscillatory shear experiments performed in heating ramps by using a frequency of 1 Hz, a strain amplitude of 1.0 %, and a heating rate of 3 °C/min.
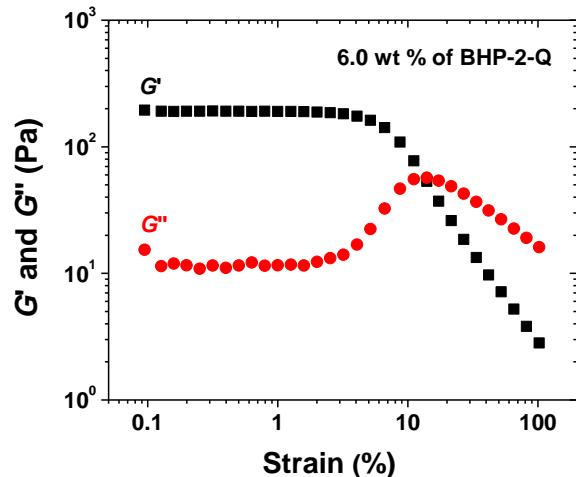
Figure S4. A strain sweep performed on the 6.0 wt % aqueous dispersion of BHP-2-Q at 5 °C using a frequency of 1 Hz.
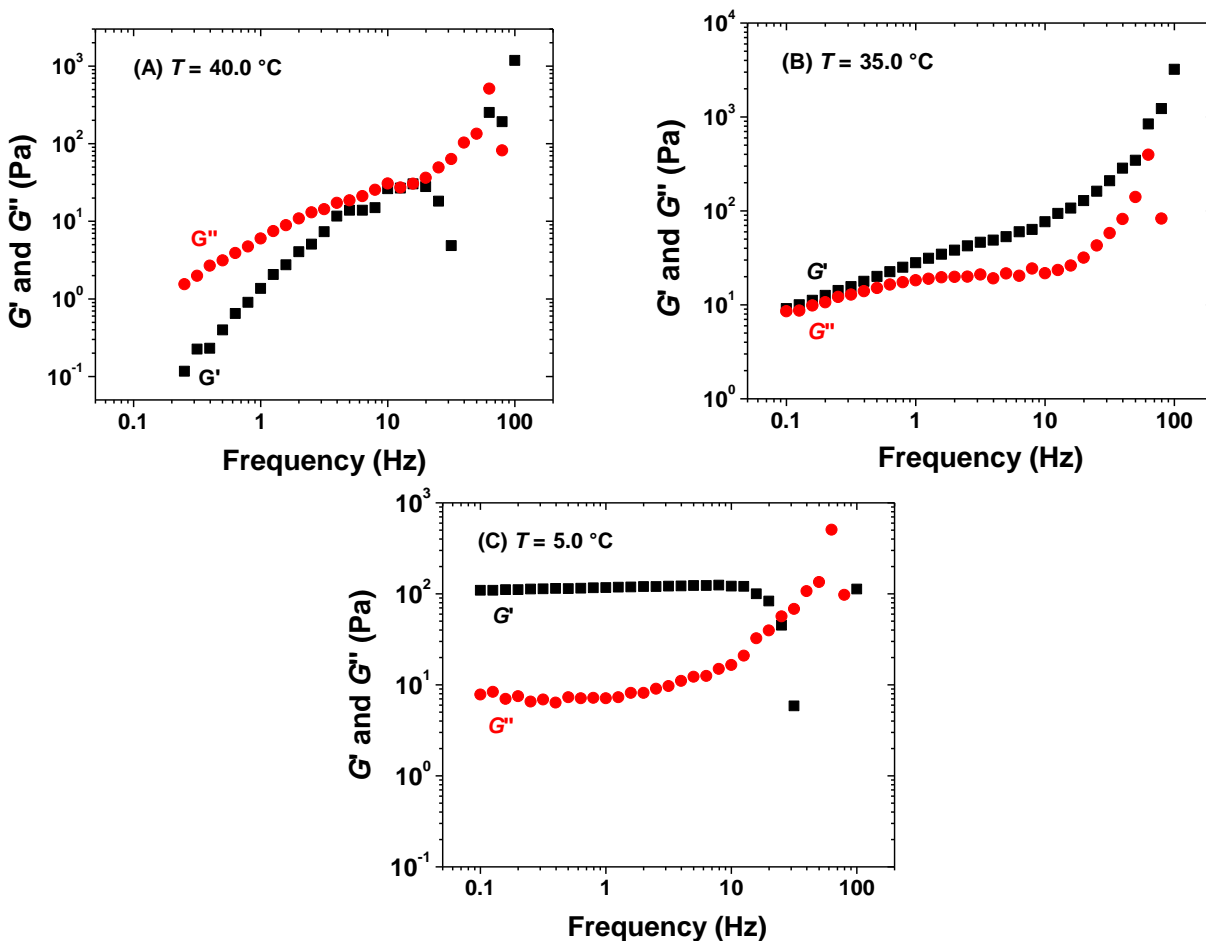

Figure S5. Plots of dynamic storage modulus G' and loss modulus G'' of a 6.0 wt % aqueous dispersion of BHP-2-Q versus frequency at (A) 40 °C, (B) 35 °C, and (C) 5 °C with a constant strain amplitude of 1.0 %.
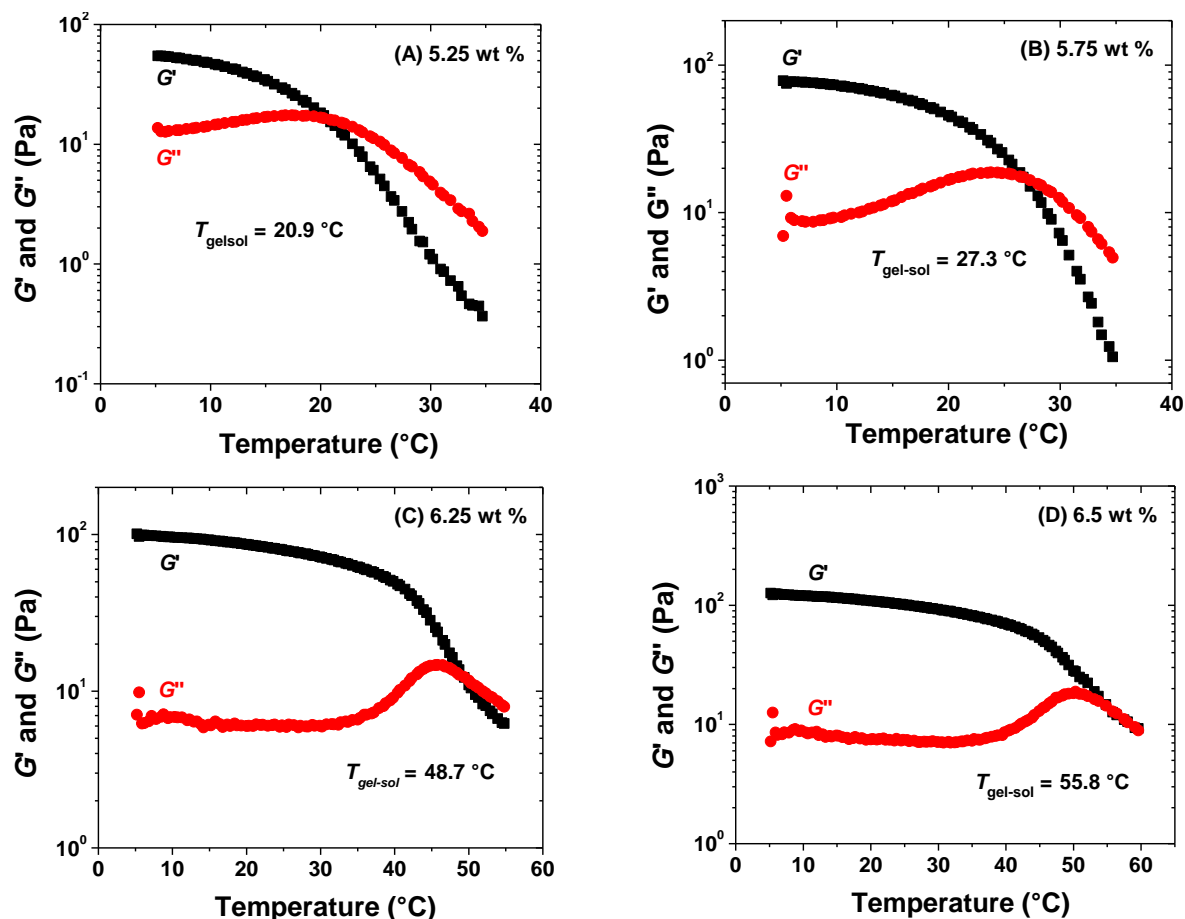
Figure S6. Plots of dynamic storage modulus G' (black square) and loss modulus G'' (red circle) of aqueous dispersions of BHP-2-Q at various concentrations versus temperature. The data were collected from oscillatory shear experiments performed in heating ramps by using a frequency of 1 Hz, a strain amplitude of 1.0 %, and a heating rate of 3 °C/min.
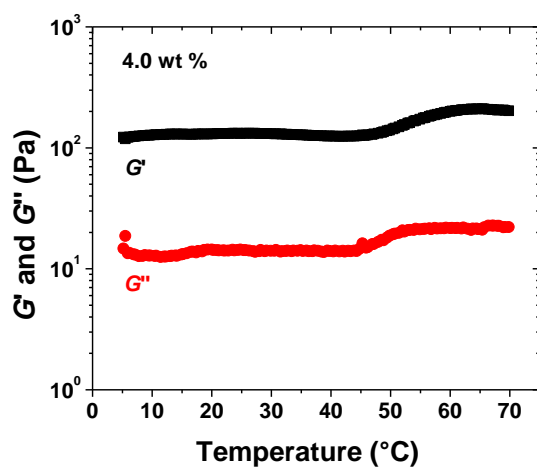

Figure S7. Plot of dynamic storage modulus G' (black square) and loss modulus G''' (red circle) of a 4.0 wt% aqueous dispersion of BHP-3-Q. The data were collected from an oscillatory shear experiment performed in a heating ramp by using a frequency of 1 Hz, a strain amplitude of 1.0 %, and a heating rate of 3 °C/min.