

Hybrid micellar network hydrogels of thermosensitive ABA triblock copolymer and polymer brush-grafted nanoparticles: Effect of LCST transition of polymer brushes on gel property

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ABSTRACT

This article presents a study of the effect of LCST transition of polymer brushes on properties of hybrid micellar network hydrogels of a thermosensitive ABA triblock copolymer and polymer brush-grafted nanoparticles (hairy NPs) with NPs initially residing outside the core of micelles. Four batches of thermosensitive polymer brush-grafted, 20 nm silica NPs with different lower critical solution temperatures (LCSTs) and a thermosensitive ABA triblock copolymer composed of a poly(ethylene oxide) central block and thermosensitive outer blocks (ABA-N) were prepared. The LCSTs of hairy NPs were significantly higher than the critical micellization temperature of ABA-N, resulting in the NPs being initially located outside the core of micelles. The effects of LCST transition of hairy NPs and NP-to-polymer mass ratio on properties of hybrid micellar hydrogels of ABA-N with a concentration of 10 wt% and hairy NPs were investigated by rheological measurements. For all hybrid hydrogels studied in this work, the dynamic storage modulus G' exhibited a sharp increase on top of a plateau that was forming in the heating ramp at a temperature corresponding to the LCST transition of hairy NPs. This phenomenon was caused by the collapse of the brushes on NPs triggering the absorption of thermosensitive outer blocks of ABA-N molecules in the dangling and loop forms and the reorganization of the 3-D gel network structure, which increased the density of bridging chains and thus the G' . This explanation was supported by the results from fluorescence resonance energy transfer studies. The maximum values of G' ($G'_{\max}$) of the gels containing higher LCST hairy NPs were noticeably lower compared with the gels with lower LCST hairy NPs and the gel with no NPs. The $G'_{\max}$ of all hybrid hydrogels decreased gradually with the increase of the NP-to-polymer ratio.

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1. Introduction

Thermosensitive block copolymer micellar hydrogels have great potential in a variety of applications, including controlled or triggered release of drugs and tissue engineering [1–6]. Unlike chemically crosslinked hydrogels, these polymer gels can undergo in situ thermally-induced, reversible sol–gel transitions, making it possible to use syringe and needle to administer the gel systems; the aqueous polymer solution can be loaded into a syringe as a liquid, which turns into a gel after the injection due to the temperature changes. The intriguing sol–gel transition and the accompanied property change have motivated a tremendous

amount of research activities, both basic and application-oriented [1–15]. For example, Jeong et al. developed injectable drug delivery systems using poly(ethylene oxide) (PEO)-based reversible block copolymer hydrogels [15].

Incorporating inorganic or metallic nanoparticles (NPs) into stimuli-responsive hydrophilic block copolymer hydrogels can greatly increase the gels' functions, because NPs exhibit unique mechanical, optical, magnetic, or electronic properties that are usually not associated with responsive organic polymers [16–18]. A synergistic combination of two vastly different components could yield properties that might not be possible with either only block copolymers or NPs [19–35]. There have been many reports in the literature on hybrid micellar hydrogels of stimuli-responsive block copolymers and NPs. Earlier examples include those reported by Pozzo and Walker [27–29]; in their work, hydrophilic silica NPs were added into the aqueous solution of PEO-*b*-poly(propylene

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oxide)-*b*-PEO triblock copolymers (PEO-*b*-PPO-*b*-PEO, i.e., Pluronics) and were partitioned into the interstitial space, forming cocrystals with micelles. Qin et al. reported ferrogels by using PEO-*b*-PPO-*b*-PEO to encapsulate magnetic NPs and dispersing them into moderately concentrated aqueous solutions of a Pluronic at low temperatures [33]. Upon heating, the mixtures underwent gelation with NPs residing in the core of micelles. The hybrid hydrogels were used as matrices for sustained release of a hydrophobic drug, and they showed that the release profile can be modulated with a static magnetic field. Reinicke et al. showed that aqueous solutions of hybrid micelles of ABC triblock copolymers and maghemite NPs, formed via the electrostatic interaction between the charged NPs and the oppositely charged block of the triblock copolymer, exhibited reversible gelation upon magnetic inductive heating using an AC magnetic field [35].

We have been particularly interested in hybrid micellar hydrogels of thermosensitive ABA triblock copolymers and polymer brush-grafted NPs (hairy NPs). In a previous work [36], we studied the effect of NP's locations, either inside or outside the core of micelles, on properties of hydrogels of a thermosensitive ABA triblock copolymer (ABA-D) and hairy NPs. A method was devised to control the location of NPs in the gels. When the LCST of hairy NPs ($LCST_{NP}$) was about the same as that of the thermosensitive outer blocks ($LCST_{ABA}$), the NPs (named as NP-D) resided in the core of micelles upon heating from below the $LCST_{NP}$. When the $LCST_{NP}$ was much higher than the $LCST_{ABA}$, the NPs were excluded from the core of micelles. The NPs with a higher LCST were poly(methoxytri(ethylene glycol) methacrylate) (PEGMMA)-grafted silica NPs (NP-T). We found that the dynamic storage modulus G' of the hydrogels containing NP-D exhibited little change with increasing the NP-to-polymer mass ratio (up to 50: 100). In contrast, the G' of the gels with NP-T in the interstitial space dropped significantly with the increase of NP-to-polymer ratio. In addition, for the gels containing NP-T, we observed a noticeable increase in G' in the heating ramps around the LCST transition of hairy NPs. This observation motivated the present work; we further studied the effect of incorporating various thermosensitive hairy NPs with LCSTs greater than the $LCST_{ABA}$ on properties of resultant hybrid hydrogels.

A thermosensitive ABA triblock copolymer (ABA-N) was prepared by atom transfer radical polymerization (ATRP) of a mixture of methoxydi(ethylene glycol) methacrylate (DEGMMA), ethoxydi(ethylene glycol) methacrylate (DEGEMA), and RhBMA (Scheme 1) from a difunctional PEO macroinitiator with a molecular weight of 20 kDa [36]. The critical micellization temperature (CMT) of ABA-N in water was 13 °C, measured by dynamic light scattering (DLS). Four hairy NP samples with LCSTs of 29, 34, 44, and 51 °C were made by surface-initiated ATRP from initiator-functionalized, 20 nm silica NPs using either pure monomers or mixtures of DEGMMA, TEGMMA, and methoxytetra(ethylene glycol) methacrylate (TrEGMMA). The cloud points of homopolymers of DEGEMA, DEGMMA, TEGMMA, and TrEGMMA in water are 4, 26, 52 and

68 °C, respectively [37–42]. A very small amount of NBDMA was incorporated into the brushes; NBDMA and RhBMA form a pair for fluorescence resonance energy transfer (FRET) [43,44]. The effects of LCSTs of hairy NPs on gel properties were studied by rheometry. We found that all hybrid hydrogels exhibited a sharp increase in G' at temperatures corresponding to the LCST transitions of hairy NPs. However, the effects of NPs with lower and higher LCSTs are different.

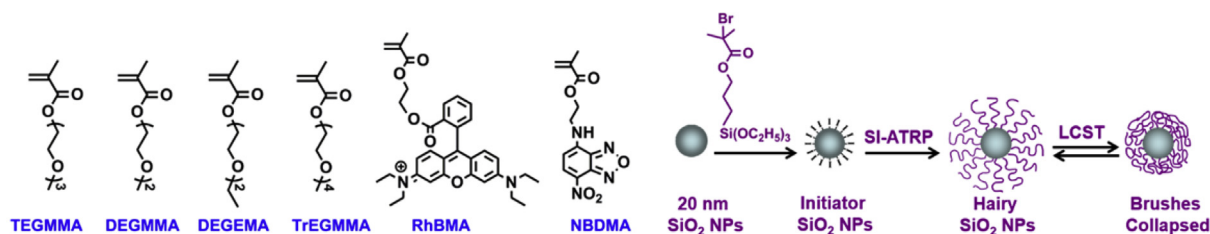
2. Experimental section

2.1. Materials

Triethoxysilane (95%) was purchased from Acros and used as received. MIBK-ST, a dispersion of silica NPs in methyl isobutyl ketone (30–31 wt % SiO_2) with an average size of 10–15 nm (according to the manufacturer), was obtained from Nissan Chemical. The platinum–divinyltetramethyldisiloxane complex in xylene with a Pt concentration of 2.1–2.4% was purchased from Gelest, Inc. CuBr (98%, Aldrich) was purified via a procedure described previously.¹¹ *N,N,N',N',N''*-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), ethyl 2-bromoisobutyrate (EBiB, 98%, Aldrich), and di(ethylene glycol) methyl ether methacrylate (DEGMMA, 97%, TCI) were each stirred with CaH_2 and distilled under reduced pressure. Di(ethylene glycol) ethyl ether methacrylate (DEGEMA), tri(ethylene glycol) methyl ether methacrylate (TEGMMA), and tetra(ethylene glycol) methyl ether methacrylate (TrEGMMA) were made via the reactions of methacryloyl chloride (95%, Acros) with di(ethylene glycol) monoethyl ether (>99.0%, TCI), tri(ethylene glycol) monomethyl ether, and tetra(ethylene glycol) monomethyl ether, respectively, in dry CH_2Cl_2 in the presence of triethylamine (99%, Acros) [37–39]. Their molecular structures were confirmed by ^1H NMR spectroscopy. The synthesis of allyl 2-bromo-2-methylpropionate, 4-(2-methacryloyloxyethylamino)-7-nitro-2,1,3-benzoxadiazole (NBDMA), and the Rhodamine B-containing methacrylate (RhBMA) was reported in the literature [36,45]. The PEO macroinitiator, Br–PEO–Br, was prepared by reacting PEO (HO–PEO–OH, 20 kDa, Aldrich) with 2-bromoisobutyryl bromide [36]. All other chemical reagents were purchased from either Aldrich or Fisher/Acros and used without further purification.

2.2. General characterization

NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer and the residual solvent proton signal was used as the internal standard. Size exclusion chromatography (SEC) of the free polymers formed in the synthesis of hairy NPs (NP-29, -34, and -51) was carried out at room temperature using PL-GPC 20 (Polymer Laboratories, Inc.) with a refractive index detector, one PLgel 5 μm guard column (50 $\times$ 7.5 mm), and two PLgel 5 μm mixed-C columns (each 300 $\times$ 7.5 mm, linear range of molecular



Scheme 1. Molecular structures of monomers used in this work and scheme for the synthesis of hairy nanoparticles by surface-initiated atom transfer radical polymerization (SI-ATRP).

weight from 200 to 2,000,000 Da). THF was used as the solvent and the flow rate was 1.0 mL/min. Narrow-disperse polystyrene standards were used to calibrate the system. The data were processed using Cirrus™ GPC/SEC software (Polymer Laboratories, Inc.). The molecular weights and polydispersity indexes (PDI) of ABA-N and the free polymer formed in the synthesis of NP-44 were determined using PL-GPC 50 Plus (Polymer Laboratories, Inc.) consisting of 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). The carrier solvent is *N,N*-dimethylformamide (DMF) containing 50 mM LiBr, and the flow rate was 1.0 mL/min. The system was calibrated by polystyrene standards, and the data were processed with Cirrus™ GPC/SEC software. Thermogravimetric analysis (TGA) was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C using TA Q-series Q50. The NPs were dried at 45 °C in vacuum for >5 h prior to analysis.

2.3. Synthesis of thermosensitive ABA triblock copolymer *P*(DEGMMA-*co*-DEGEMA-*co*-RhBMA)-*b*-PEO-*b*-*P*(DEGMMA-*co*-DEGEMA-*co*-RhBMA) (ABA-N)

ABA-N was synthesized by ATRP of a mixture of DEGMMA, DEGEMA, and RhBMA with a molar ratio of 1.00: 1.48: 0.0014 from the PEO difunctional initiator Br-PEO-Br via a procedure similar to that for the synthesis of ABA-D described in a previous publication [36]. SEC analysis using PL-GPC 50 Plus with DMF-LiBr as the carrier solvent showed that the $M_{n,SEC}$ was 92.6 kDa and the PDI was 1.20, relative to polystyrene standards. From the ^1H NMR spectrum of ABA-N, the numbers of DEGMMA and DEGEMA monomer units were calculated to be 238 and 324, respectively [46].

2.4. Synthesis of thermosensitive polymer brush-grafted silica nanoparticles

Silica NPs (MIBK-ST, Nissan Chemical) were surface-functionalized with 3-(triethoxysilyl)propyl 2-bromo-2-methylpropanoate, prepared by hydrosilylation of allyl 2-bromo-2-methylpropanoate with triethoxysilane as reported previously [36,41]. The initiator-functionalized NPs were then dispersed in DMF to form an NP dispersion with a concentration of 15.5 wt%, which was determined by gravimetric analysis. Four thermoresponsive polymer brush-grafted, 20 nm silica NP samples with different thermosensitive properties were synthesized by surface-initiated ATRP from the same batch of initiator NPs. Shown below is the procedure for the synthesis of *P*(DEGMMA-*co*-TEGMMA-*co*-NBDMA) brush-grafted silica NPs with a LCST transition of 29 °C (NP-29).

CuBr (19.7 mg, 137 μmol), CuBr₂ (5.6 mg, 25.0 μmol), the dispersion of the ATRP initiator-functionalized NPs in DMF with a concentration of 15.5 wt% (2.703 g of solution, corresponding to 419 mg of initiator NPs), and DMF (19.83 g) were added into a two-necked flask. The mixture was sonicated in an ultrasonic water bath to form a homogeneous dispersion. DEGMMA (2.839 g, 15.1 mmol), TEGMMA (1.506 g, 6.49 mmol), NBDMA (11.7 mg, 4.0×10^{-2} mmol), and ethyl 2-bromoisobutyrate (29.5 mg, 151 μmol) were then added into the flask. After the mixture was degassed by three freeze–pump–thaw cycles, PMDETA (32.6 mg, 188 μmol) was injected into the flask at the thawing point of the frozen mixture by using a microsyringe. The flask was then placed in an oil bath with a preset temperature of 45 °C, and the progress of the polymerization was monitored by ^1H NMR spectroscopy analysis. After 2 h and 55 min, the flask was taken out from the oil bath and opened to air, and an aliquot was withdrawn immediately for ^1H NMR

spectroscopy analysis to determine the monomer conversion. The mixture was diluted with THF (20 mL), and the polymer-grafted NPs were isolated by ultracentrifugation at 35 k rpm for 40 min. The NPs were then dispersed in THF and separated again by centrifugation. This dispersion–centrifugation washing process was repeated for a total of 5 times. The supernatant liquid from the first cycle was passed through a column of silica gel (bottom)/activated basic aluminum oxide (top) (2/1, v/v) to remove the copper catalyst. The free polymer was precipitated in a mixture of hexanes and diethyl ether (3:1, v/v), re-dissolved in CH₂Cl₂ and precipitated again. The precipitation–dissolution process was repeated for additional two times. The purified free copolymer, *P*(DEGMMA-*co*-TEGMMA-*co*-NBDMA), was dried under high vacuum for 6 h, and then analyzed by SEC (PL-GPC 20) relative to polystyrene standards. The values of $M_{n,SEC}$ and PDI were 10.4 k and 1.20, respectively. The monomer conversion was 36.9%, determined by ^1H NMR spectroscopy analysis. The degree of polymerization (DP) of the polymer was 42, which was calculated from the monomer conversion and the ratio of the monomer-to-the sum of surface initiator and free initiator as detailed in our previous report [36]. The chemical composition of *P*(DEGMMA-*co*-TEGMMA-*co*-NBDMA) was determined from the ^1H NMR spectrum of the purified free copolymer, and the numbers of DEGMMA and TEGMMA units were 28 and 14, respectively.

The aqueous dispersion of NP-29 was prepared by dialysis, detailed below. NP-29, isolated by ultracentrifugation from the THF dispersion, was fully dispersed in DMF (10 g) using an ultrasonic water bath. Ethanol (2 mL) and water (2 mL) were then added dropwise into the hairy NP dispersion under the stirring condition. The resultant NP dispersion was dialyzed against water in an ice/water bath using a regenerated cellulose tubular dialysis membrane with a nominal MWCO of 3500. The ice/water bath-cooled water was changed frequently to ensure that DMF and ethanol were completely removed. The concentration of NP-29 in the final aqueous dispersion was 17.36 mg/g, which was determined by gravimetric analysis as for the dispersion of initiator NPs in DMF.

Other thermosensitive hairy NP samples (NP-34, NP-44, and NP-51) were prepared via similar procedures. A small amount of NBDMA was incorporated in all hairy NP samples. NP-34 was synthesized by SI-ATRP of a mixture of DEGMMA and TEGMMA with a molar ratio of 1: 2.32. The concentration of NP-34 in the final aqueous dispersion was 14.72 mg/g. NP-44 and -51 were PTEGMMA and *P*(TEGMMA-*co*-TrEGMMA) brush-grafted silica NPs, respectively. NP-51 was prepared by ATRP of a mixture of TEGMMA and TrEGMMA with a molar ratio of 1: 1. The concentrations of NP-44 and -51 in the final dispersions were 5.43 and 6.85 mg/g, respectively.

2.5. DLS studies of LCST transitions of thermosensitive hairy NPs and ABA-N in water

DLS studies of thermosensitive properties of hairy NPs and thermally induced micellization of ABA-N in dilute aqueous solutions were performed on a Brookhaven Instruments BI-200SM goniometer equipped with a PCI BI-9000AT digital correlator, a temperature controller, and a solid-state laser (model 25-LHP-928-249, $\lambda = 633$ nm) at a scattering angle of 90°. The NP concentrations of aqueous dispersions of thermosensitive hairy NPs employed in the DLS studies were 1.0 mg/g, and the polymer concentration in the aqueous solution of ABA-N was 0.2 mg/g. The samples were filtered using Millipore hydrophilic PTFE filters (0.2 μm pore size), and the DLS tubes were sealed with PE stoppers. The temperature was gradually increased, and at each chosen temperature, the sample was equilibrated for 20 min before the measurements were taken.

2.6. Fluorescence spectroscopy study of aqueous mixtures of thermosensitive hairy NPs and ABA-N

For fluorescence measurements, aqueous solutions containing only thermosensitive hairy NPs, only ABA-N, and both hairy NPs and ABA-N were prepared. The following is a description of the detailed procedure for NP-29. Other samples were prepared via similar procedures. A 0.208 mg/g aqueous solution of ABA-N, a 0.010 mg/g aqueous dispersion of NP-29, and an aqueous mixture of ABA-N with a concentration of 0.208 mg/g and NP-29 with a concentration of 0.010 mg/g were prepared. All samples were sonicated in an ultrasonic ice/water bath for 15 min and stirred in an ice/water bath for 3 h. The solutions were then placed in an Isotemp and were equilibrated at the set temperature for 20 min. The samples were used for fluorescence spectroscopy measurements, which were done in ~2 min. The samples were then heated in the Isotemp at an interval of 5 °C and equilibrated at each temperature for 20 min, followed by fluorescence measurements. All fluorescence studies were performed on a Perkin Elmer LS 55 luminescence spectrometer. The slit widths were set at 10 nm for both excitation and emission with a scan speed of 100 nm/min. The fluorescence emission spectra were recorded from 500 to 700 nm, with the excitation wavelength set at 480 nm.

2.7. Rheology studies of aqueous mixtures of ABA-N and thermosensitive hairy NPs

Described below is the preparation of aqueous mixtures of ABA-N and NP-29. Other samples with different NP-to-ABA-N mass ratios for rheological measurements were prepared via similar procedures. ABA-N was dried thoroughly in a 100 mL flask in vacuum and weighed (1.184 g). Water (10.597 g) was then added, and the mixture was stored in a refrigerator (4 °C) overnight and then sonicated in an ultrasonic ice/water bath to ensure that ABA-N was fully dissolved to form a homogeneous solution with a polymer concentration of 10 wt%. A small portion of the sample was used for rheological measurements to study the thermally induced sol–gel transition. For the aqueous mixtures of ABA-N and hairy NPs, the polymer concentration was defined as $[\text{polymer mass}/(\text{polymer mass} + \text{water mass})] \times 100\%$. To prepare the aqueous mixture of ABA-N and NP-29 with a polymer concentration of 10 wt% and a NP-to-polymer weight ratio of 30: 100, an aqueous dispersion of NP-29 with a concentration of 17.36 mg/g (stored in a refrigerator, 3.828 g, corresponding to 66.5 mg of NP-29) was added into the aqueous solution of ABA-N with a concentration of 10 wt% (2.215 g). To maintain the polymer concentration at 10 wt%, a gentle air stream was used to evaporate water until the calculated weight of the sample was reached. A Teflon tape was used to seal the capped sample tightly and then the mixture was sonicated in an ultrasonic ice/water bath for 15 min. After the rheological measurement, a calculated amount of NP-29 was added into the sample to increase the NP-to-polymer mass ratio to 40: 100, and again a calculated amount of water was evaporated to maintain the polymer concentration at 10 wt %.

Rheological experiments were performed on a rheometer from TA Instruments (Model TA AR 2000ex). A cone–plate geometry with a cone diameter of 20 mm and an angle of 2° (truncation 52 μm) was employed, and the temperature was controlled by the bottom Peltier plate. For each rheological measurement, 90 μL of the sample was loaded onto the plate by a micropipet. To minimize water loss at elevated temperatures, the solvent trap was filled with water and covered with the solvent trap cover. Dynamic storage modulus G' and loss modulus G'' of a sample at various temperatures were measured by oscillatory shear experiments performed at a fixed frequency of 1 Hz in a heating ramp at a heating rate of

3 °C/min. The strain amplitude used in all dynamic viscoelastic measurements was $\gamma = 1.0\%$. Note that for micellar hydrogels of this type of thermosensitive ABA triblock copolymers, our previous dynamic strain sweep experiments showed that the gels typically exhibited a linear response up to ~15% [11]. For each rheological study, three measurements were taken and the average value was used.

3. Results

3.1. Synthesis and thermoresponsive properties of ABA triblock copolymer $P(\text{DEGMMA-co-DEGEMA-co-RhBMA})\text{-}b\text{-PEO-}b\text{-}P(\text{DEGMMA-co-DEGEMA-co-RhBMA})$ (ABA-N) and thermosensitive hairy NPs with various LCST transitions

This work was intended to study the effect of LCST transition of thermosensitive hairy NPs on properties of hybrid micellar hydrogels of a thermosensitive ABA triblock copolymer and hairy NPs with the NPs initially located in the interstitial space among micellar cores. The hairy NPs were designed to exhibit LCST transitions at temperatures significantly higher than the CMT of the thermosensitive ABA triblock copolymer. We previously reported the synthesis of a thermosensitive ABA triblock copolymer (ABA-D) exhibiting a CMT of 14 °C in water [36]. Following the same procedure, we made a new ABA triblock copolymer (ABA-N) by ATRP of a mixture of DEGMMA, DEGEMA, and RhBMA with a molar ratio of 1.00: 1.48: 0.0014 from a difunctional PEO macroinitiator with a molecular weight of 20,000 Da. A very small amount of RhBMA was incorporated into the thermosensitive outer blocks for fluorescence resonance energy transfer (FRET) study of the mixtures of ABA-N and hairy NPs. SEC analysis using DMF-LiBr as carrier solvent showed that the $M_{n,SEC}$ was 92.6 kDa and the PDI was 1.20 relative to polystyrene standards, which indicated that the polymerization was well controlled. From the ^1H NMR spectrum, the numbers of DEGMMA and DEGEMA monomer units in ABA-N were calculated to be 238 and 324; the molar ratio of two monomers in the copolymer was close to the feed ratio. The CMT of ABA-N in water at a concentration of 0.2 mg/g, measured by DLS, was 13 °C [46], consistent with what we expected.

Four thermosensitive hairy NP samples with different thermoresponsive properties (Table 1) were synthesized by surface-initiated ATRP from the same batch of ATRP initiator-functionalized silica NPs. NP-29 and -34 were made by using DEGMMA and TEGMMA with different feed ratios in the polymerization mixtures. NP-44 was PTEGMMA brush-grafted silica NPs, and NP-51 was prepared by SI-ATRP of TEGMMA and TrEGMMA with a molar ratio of 1: 1. A free initiator, ethyl 2-bromoisobutyrate, was added, and the polymerizations were monitored by ^1H NMR spectroscopy analysis. After desired monomer conversions were reached, the polymerizations were stopped and the NPs were separated by ultracentrifugation. The hairy NPs were washed by five dispersion–ultracentrifugation cycles to remove untethered polymers. The PDIs of all free polymers were <1.25, indicating that the polymerizations were controlled. The hairy NPs were characterized by thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). From the TEM micrographs of hairy NPs, the average size of silica core NPs was found to be 20 nm. On the basis of the TGA data, DP of the polymer, average size of silica core NPs, and the assumption that the molecular weight and the PDI of the grafted polymer are the same as those of the free polymer, the grafting densities of four hairy NP samples were calculated [36,47]; they were in the range of 0.38–0.43 chains/nm². The characterization data of four hairy NP samples and the corresponding free polymers are summarized in Table 1.

The thermoresponsive properties of four hairy NP samples in

Table 1

Characterization data for four hairy nanoparticle samples with different thermoresponsive properties and the corresponding free polymers.

Sample	$M_{n,SEC}$ (Da), PDI ^a	DP ^b	σ^f (chains/nm ²)	LCST _{onset} (°C) ^g	LCST _{end} (°C) ^g	LCST _{mid} (°C) ^g
NP-29	10.4 k, 1.20	42 (28, 14) ^c	0.42	25	32	29
NP-34	9.2 k, 1.24	36 (11, 25) ^d	0.43	30	38	34
NP-44	15.1 k, 1.22	60	0.38	40	48	44
NP-51	11.6 k, 1.20	46 (22, 24) ^e	0.40	45	56	51

^a $M_{n,SEC}$ and PDI were number average molecular weight and polydispersity index of the free polymer measured by size exclusion chromatography (SEC) relative to polystyrene standards.^b DP: degree of polymerization.^c The DP of P(DEGMMA-co-TEGMMA-co-NBDMA) was 42, and the numbers of DEGMMA and TEGMMA monomer units were 28 and 14, respectively.^d The DP of P(DEGMMA-co-TEGMMA-co-NBDMA) was 36, and the numbers of DEGMMA and TEGMMA units were 11 and 25, respectively.^e The DP of P(TEGMMA-co-TrEGMMA-co-NBDMA) was 46, and the numbers of TEGMMA and TrEGMMA monomer units were 22 and 24, respectively.^f σ : grafting density.^g LCST_{onset}, LCST_{end}, and LCST_{mid} were onset temperature, end temperature, and middle point of the LCST transition determined by DLS study.

dilute aqueous solutions were studied by DLS [46]. Consistent with our previous reports [36,39], the LCST transitions of the brushes grafted on NPs were broader than those of the corresponding free polymers in water. The onset temperature (LCST_{onset}), end temperature (LCST_{end}), and middle point (LCST_{mid}) of the LCST transition of each sample were measured and are summarized in Table 1. From NP-29, to -34, to -44, and -51, the LCST_{onset} increased from 25, to 30, to 40, and 45 °C, and the LCST_{mid} changed from 29, to 34, to 44, and 51 °C. Note that all these temperatures are significantly higher than the CMT (13 °C) of ABA-N. Thus, if aqueous mixtures of ABA-N and hairy NPs are gradually heated from ~0 °C to above the CMT, the hairy NPs would be located outside the micellar core [36,48]. This allows us to study how the LCST transition of hairy NPs affect the properties of hybrid hydrogels of ABA-N and hairy NPs with NPs initially residing outside the core of micelles.

3.2. Rheological study of aqueous mixtures of ABA-N and NP-29 with a polymer concentration of 10 wt% and various NP-to-polymer mass ratios

We first made a 10 wt% aqueous solution of ABA-N, which as expected exhibited a sol–gel transition upon heating from ~0° in an ice/water to room temperature. Fig. 1A shows the dynamic storage modulus G' and loss modulus G'' as a function of temperature obtained from a heating ramp experiment performed by using a constant frequency of 1 Hz, a strain amplitude of 1%, and a heating rate of 3 °C/min. At 14 °C and below, the values of G' and G'' were small, indicative of the liquid state of the sample. With temperature going up, both G' and G'' increased significantly. The crossover of the two curves, at which $G' = G''$, occurred at 17.0 °C, which is commonly taken as the sol–gel transition temperature ($T_{sol-gel}$) [11,49]. Above the $T_{sol-gel}$, G' quickly leveled off and G'' gradually decreased; this is a typical behavior of an elastic physical hydrogel.

To study the effect of incorporating NP-29 into the thermosensitive micellar hydrogel of ABA-N, the aqueous dispersion of NP-29 was added into the aforementioned 10 wt% aqueous solution of ABA-N. The concentration of ABA-N, defined as [(polymer mass)/(polymer mass + water mass)] × 100%, was maintained at 10 wt % by evaporating a calculated amount of water from the sample. The mass ratio of NP-29 to ABA-N was gradually increased from 30: 100 to 40: 100, to 50: 100, to 60: 100, and 70: 100. For each mass ratio, three rheological measurements were taken using the same conditions as for the pure ABA sample. Representative rheological curves are presented in Fig. 1; the other two heating ramps are included in the Supplementary Data [46].

By looking through Fig. 1B–F, one can find that there was little change in $T_{sol-gel}$ with the increase of NP-to-polymer mass ratio, which indicates that the presence of NP-29 did not affect the ability of ABA-N to form a 3-dimensional network in water, even when the

NP-to-polymer ratio reached 70: 100. However, several new features were observed from the rheological curves for aqueous mixtures of ABA-N and NP-29 compared with that of the 10 wt% aqueous solution of ABA-N (Fig. 1A). To better appreciate the effect of adding NP-29 into the 10 wt% aqueous solution of ABA-N, we re-plotted G' versus temperature for all six samples on a linear scale (Fig. 2). (i) With the increase of temperature from 17 to 29 °C, for all hybrid samples, G' increased gradually and a plateau was forming just like that for the 10 wt% solution of ABA-N. Most notably, when the temperature reached ~29 °C, G' exhibited a sharp increase for all aqueous mixtures of ABA-N and NP-29. This transition temperature coincided with the LCST transition of NP-29, which was in the range of 25–32 °C with the middle point at 29 °C. For the mixture with the NP-to-ABA mass ratio of 30: 100, the G' increased dramatically upon further heating and at 47.4 °C reached 1800 Pa, which is almost the same as the maximum value of G' (G'_{max}) of the sample without NPs (1878 Pa). Note that at 47.4 °C the G' value was even greater than that of the pure ABA sample. This is totally different from the hybrid hydrogels of ABA-D and NP-D that we reported previously [36], where NP-D, having a LCST essentially same as the CMT of ABA-D, resided in the core of micelles and little change in G' was observed compared with the pure ABA sample. The behavior of NP-29 was similar to our previous observation for NP-T [36], the hairy NPs with a LCST significantly higher than the CMT of ABA-D; the hybrid samples of ABA-D and NP-T exhibited a noticeable increase in G' at a temperature around the LCST of NP-T. We believe this observation is caused by the thermally induced collapse of polymer brushes on NPs.

(ii) While the G' of the sample containing no hairy NPs exhibited a slight drop at temperatures above 60 °C (Fig. 2), a more dramatic decrease was observed for all mixed samples, with the lowest G' values at ~60 °C in the range of 40–125 Pa. In addition, the decrease occurred at lower temperatures, e.g., ~47.4 °C for the sample with a NP-to-polymer mass ratio of 30: 100, and there was a general trend that the onset temperature shifted to the lower temperature side with the increase of the NP content. (iii) The G'_{max} decreased gradually with the increase of the NP-to-polymer ratio, with the average G'_{max} value of three measurements dropping from 1879 Pa for the NP-to-polymer mass ratio of 0: 100 to 1266 Pa for the ratio of 70: 100. Apparently, the hydrogel became weaker when more NPs were added into the system.

3.3. Rheological study of aqueous mixtures of ABA-N and NP-34, -44, and -51 with a polymer concentration of 10 wt% and various NP-to-polymer mass ratios

The gel properties of hybrid samples of ABA-N and NP-34, -44, and -51 with a polymer concentration of 10 wt% and various NP-to-polymer mass ratios were also studied by rheological

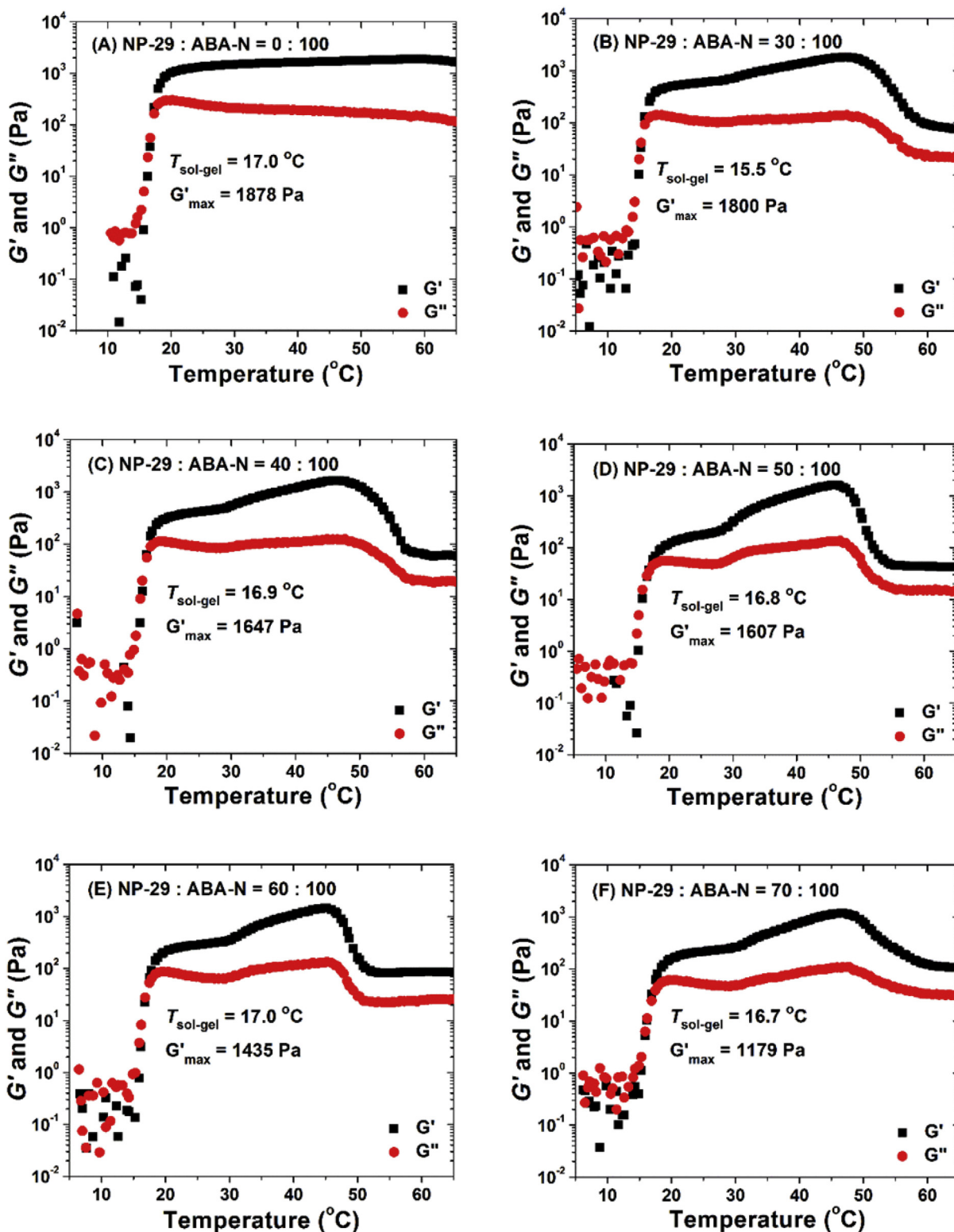


Fig. 1. Plots of dynamic storage modulus G' and loss modulus G'' of aqueous mixtures of ABA-N with a concentration of 10 wt % and NP-29 with various NP-to-polymer mass ratios versus temperature. The rheological data were collected from heating ramp experiments performed by using a frequency of 1 Hz, a strain amplitude of 1%, and a heating rate of 3 °C/min.

measurements using the same conditions. Again, for each mass ratio, three rheological measurements were taken. Fig. 3 shows the representative plots of G' versus temperature for various NP-to-polymer mass ratios for NP-34, -44, and -51. The original heating

ramps can be found in the [Supplementary Data](#) [46].

As can be seen from Fig. 3, for all three thermosensitive hairy NP samples, the G' exhibited a characteristic, sharp increase on top of a plateau at a critical temperature, as for NP-29. The critical

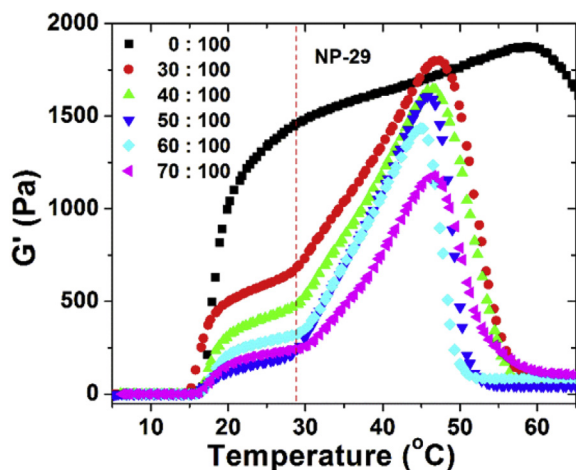


Fig. 2. Plots of dynamic storage modulus G' versus temperature for aqueous mixtures of ABA-N and NP-29 with different mass ratios. The data were replotted from Fig. 1.

temperatures for NP-34, -44, and -51 were 32, 40, and 45 °C, respectively, which corresponded to their LCST transitions. For NP-34, the onset temperature for the sharp increase of G' is between the $LCST_{onset}$ (30 °C) and $LCST_{mid}$ (34 °C), while for NP-44 and NP-

51, the critical temperatures from rheological curves appeared to be the same as the onset temperatures of their LCST transitions in water (40 and 45 °C, respectively). It should be emphasized here that the LCST transitions of thermosensitive hairy NPs were determined by DLS studies of hairy NPs in dilute aqueous solutions with a concentration of 1.0 mg/mL. Much like the cloud point of a thermosensitive polymer in water [50], the LCST transition of thermosensitive hairy NPs in the hybrid samples could be affected by many factors such as NP concentration and the presence of ABA-N. For NP-44, the sharp increase of G' occurred at a temperature essentially the same as that we previously observed for hybrid hydrogels of ABA-D and NP-T [36]. Note that NP-44 and NP-T both were PEGMMA brush-grafted NPs. The shift in the onset temperature for G' to increase sharply can be better appreciated from Fig. 4, where G' was plotted against temperature for the aqueous mixtures of ABA-N and four thermosensitive hairy NPs with a mass ratio of 30: 100.

From Figs. 3 and 4, one can find that the G'_{max} of the hybrid hydrogel of NP-34 and ABA-N at a mass ratio of 30: 100 is comparable to that of the 10 wt% solution of ABA-N, which is similar to the observation for NP-29. In contrast, for hybrid hydrogels of ABA and NP-44 and NP-51, the G'_{max} values are significantly lower. It appears that the incorporation of NPs with a higher LCST results in weaker micellar hydrogels. Same as NP-29, G' exhibited a large drop at elevated temperatures for all three hairy NP samples, and

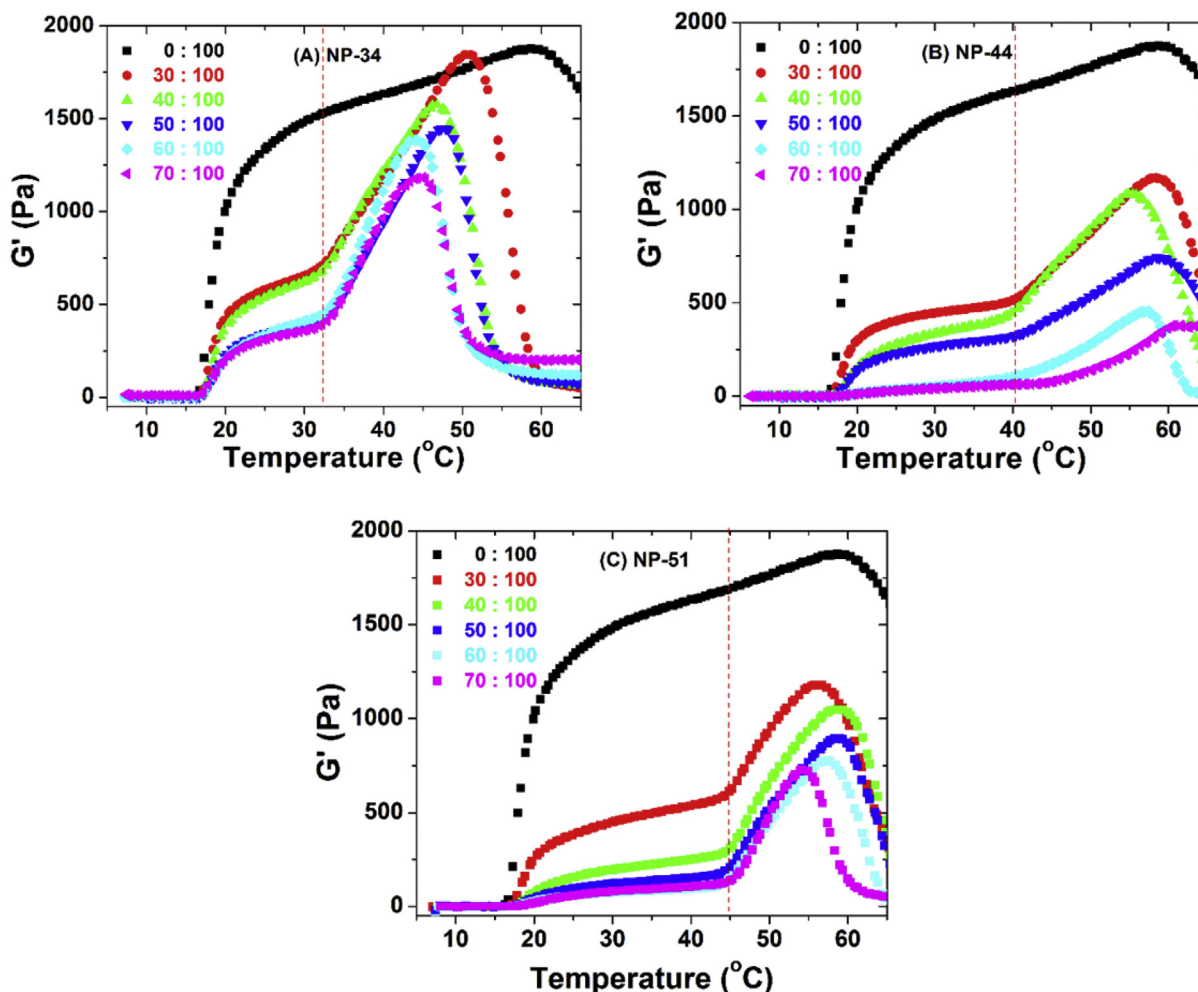


Fig. 3. Representative plots of dynamic storage modulus G' versus temperature for aqueous mixtures of ABA-N and (A) NP-34, and (B) NP-44, and (C) NP-51 with various NP-to-ABA-N mass ratios. The data were replotted from one of the three heating ramps for each mass ratio that can be found in the [Supplementary Data](#).

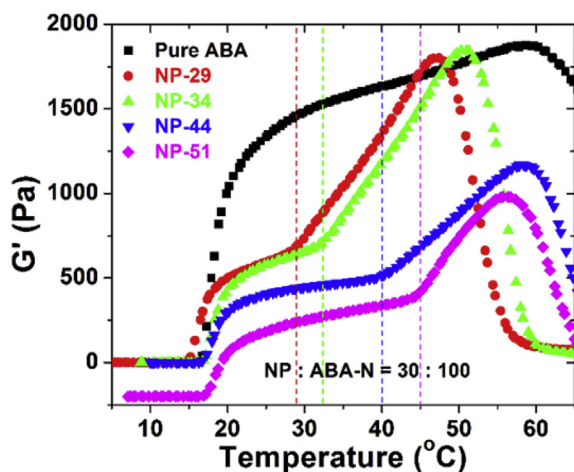


Fig. 4. Plots of dynamic storage modulus G' of aqueous mixtures of ABA-N and four thermosensitive hairy NPs with different LCSTs at a NP-to-polymer mass ratio of 30:100 as a function of temperature. The rheological data were from Figs. 2 and 3. For the sake of clarity, the G' vs T curve for ABA-N and NP-51 was vertically shifted by -200 Pa.

the extent of decrease was significantly higher than that of the 10 wt% sample of ABA-N without any hairy NPs. In addition, there was a general trend that the $G'_{\max}$ decreased with the increase of NP-to-polymer mass ratio (Fig. 3).

3.4. Comparison of hybrid micellar hydrogels of four hairy NP samples

Although the hybrid hydrogels of ABA-N with four hairy NP samples share some common features such as the sharp increase of G' at the LCST of hairy NPs and the large drop of G' at elevated temperatures, there are differences. Fig. 5 shows the plots of average $G'_{\max}$ of three rheological measurements versus the NP-to-polymer mass ratio. For comparison, we also included the data from the previous publication for hybrid hydrogels of ABA-D and NP-D (with a LCST $\approx$ the CMT of ABA-D) and ABA-D and NP-T (with a

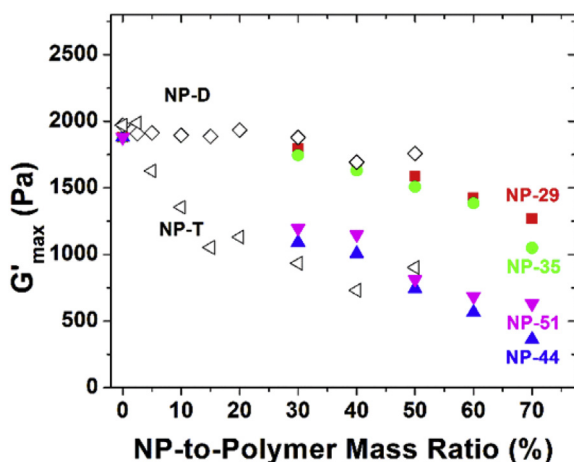
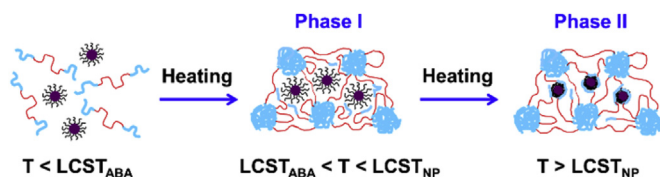


Fig. 5. Effect of NP-to-polymer mass ratio on $G'_{\max}$ of hybrid micellar hydrogels of thermoresponsive hairy NPs and ABA-N with a polymer concentration of 10 wt %. The values of $G'_{\max}$ are the averages of three rheological measurements. NP-29 (red solid square); NP-35 (green solid circle); NP-44 (blue upward pointing solid triangle); NP-51 (magenta downward pointing solid triangle); NP-D (black empty diamond); NP-T (black left-pointing empty triangle). The data for NP-D and NP-T are from Ref. 36 and used here for comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

LCST higher than the CMT of ABA-D by nearly 30°C) [36]. For NP-29 and -34, the decrease of $G'_{\max}$ with the increase of NP-to-polymer ratio is small, with the largest drop observed at a ratio of 70:100. At mass ratios of 30–50%, the G' values for both NP-29 and -34 are more in line with those of hybrid hydrogels of ABA-D and NP-D. It should be noted that for the hybrid hydrogels of ABA-D and NP-D, there was no dramatic increase in G' on the plateau of G' vs. T , similar to that of the pure ABA sample. For NP-44 and -51, the G' values were significantly lower (by > 500 Pa), even at a NP-to-polymer ratio of 30:100 (Fig. 5), which further corroborated our previous results for hybrid micellar hydrogels of ABA-D and NP-T [36].

4. Discussion

It is clear from the results presented above that for hybrid micellar hydrogels of thermosensitive ABA triblock copolymers and hairy NPs with NPs residing initially outside the micellar core, the LCST transition of hairy NPs has a significant effect on gel property. In particular, a sharp increase of G' on top of a plateau in the heating ramp was observed at a temperature corresponding to the LCST transition of the incorporated thermosensitive hairy NPs. Interestingly, for all four thermosensitive hairy NP samples, the G' values right before the sharp increase were much smaller than that of the hydrogel formed from the 10 wt% aqueous solution of ABA-N at the same temperature. According to the trend, if there was no sharp increase in G' at the LCST of hairy NPs, the $G'_{\max}$ would be significantly smaller than that of the hydrogel of the 10 wt% solution of pure ABA-N. The G' of a transient physically crosslinked hydrogel is known to be a measure of the number density of effective gel network strands and can be described by $G' = \nu k_B T$, where ν is the number density of elastically active/bridging polymer chains per unit volume, k_B is Boltzmann constant, and T is the absolute temperature [11,51,52]. This observation suggests that the incorporation of thermosensitive hairy NPs with LCST transitions higher than the CMT of the ABA triblock copolymer affected the formation of the 3-D network in a negative way (Phase I in Scheme 2), likely by increasing the fraction of loops (both thermosensitive outer blocks of an ABA triblock copolymer molecule are located in the same micellar core) assuming the number of dangling polymer chains is only a function of temperature. The loops and dangling polymer chains do not sustain the mechanical stress applied to the network and thus do not contribute the modulus of micellar hydrogels [2,11]. These observations are different from the hybrid micellar gels of ABA-D and NP-D, where the addition of NPs with a LCST $\approx$ the CMT of ABA-D resulted in a negligible effect on the gel strength, presumably because of the incorporation of NPs into the network's nodes [36]. For all four hairy NP samples, there was a general trend that the $G'_{\max}$ decreased with the increase of the NP-to-polymer mass ratio, which meant that incorporating more NPs into the system affected the formation of the network to a greater extent. It can be imagined that the presence of a sufficient amount of such thermosensitive hairy NPs in the gel could increase the



Scheme 2. Schematic illustration of formation of 3-D network by ABA-N in the presence of hairy NPs and reorganization of network structure upon heating above the LCST transition temperature of hairy NPs.

stretching of the bridging PEO blocks; the formation of loops thus could become entropically more favorable compared with the bridging chains among micelles. Apparently, adding more NPs would disrupt the network formation to a greater extent. As a result, a network with a lower density of bridging chains and thus lower G' values is formed.

The sharp increase in G' is believed to be caused by the collapse of polymer brushes in hairy NPs, which triggered reorganization of the 3-D network to achieve the lowest energy (Phase II in Scheme 2). This reorganization likely involves the conversion of entropically unfavorable polymer loops into bridging chains as well as the adsorption of dangling thermosensitive blocks of the ABA triblock copolymer, resulting in an increase in the density of elastically active polymer chains and thus G' values. Interestingly, for NP-29 and -34, the $G'_{\max}$ values at lower NP-to-polymer mass ratios were comparable to that of the gel with no hairy NPs, while for NP-44 and -51, the $G'_{\max}$ values were significantly lower. We speculate that this might be a result of the lower LCST transition temperatures of NP-29 and -34, at which the reorganization of the polymer networks is energetically and kinetically easier compared with NP-44 and -51. Note that the LCST of hairy NPs was determined by the chemical structure/composition of the grafted polymer brushes on NPs; the longer the oligo(ethylene glycol) side chain, the higher the LCST. The trend that $G'_{\max}$ decreased with the increase of NP-to-polymer mass ratio reflected the fact that the network became increasingly weaker with the number of NPs in the system increasing, despite that the LCST transition of hairy NPs triggered reorganization of polymer chains in the system.

To estimate the change in the fraction of bridging polymer chains before and after the LCST transition of hairy NPs, we took hybrid hydrogels with a NP-to-ABA-N mass ratio of 30: 100 as an example and calculated the maximum possible moduli at the onset temperature for G' to begin to increase sharply and the temperature at which $G'_{\max}$ occurred using $G' = \nu k_B T$. We assumed that all hybrid samples have a density of 1.0 g/mL and every polymer chain is elastically active. The calculated G' values and the fractions of bridging polymer chains are shown in Table 2. Clearly, for every hybrid hydrogel, there is a dramatic increase in the fraction of bridging polymer chains at the temperature of $G'_{\max}$ compared with that at the onset temperature. For example, the fraction of bridging polymer chains for ABA-N/NP-29 was 35% at 29 °C but increased to 88% at 47 °C. Apparently, the LCST transition of hairy NPs triggered reorganization of the 3-D network structure and increased the crosslinking density as discussed earlier.

Another feature is the dramatic decrease of G' at elevated temperatures, which reflects the breakdown of the network structure. Although a slight decrease in G' was also seen for the 10 wt% solution of pure ABA-N, the decrease of G' occurred at lower temperatures and to a greater extent for hybrid micellar hydrogels. We believe that this is caused by the thermally induced shrinking of the bridging PEO blocks and the less uniform network because of the presence of thermosensitive hairy NPs. It is known that water

becomes an increasingly poor solvent for PEO upon heating, and thus the bridging PEO block underwent shrinking at elevated temperatures [11], making the formation of polymer loops become entropically comparable with or even more favorable than the formation of bridging chains among micellar cores. Consequently, the fraction of bridging PEO blocks, and thus the G' , decreases upon further heating. In addition, the 3-D networks of hybrid micellar hydrogels was formed via two steps (Scheme 2); the network was less uniform and had more defects, caused by the reorganization of the network and adsorption of dangling chains, compared with the gel formed by the 10 wt% aqueous solution of ABA-N. This can also be seen from the general trend for all four thermosensitive hairy NP samples that the temperature for $G'_{\max}$ shifted to the lower temperature side, though there are some exceptions, particularly for NP-44 (Fig. 3B). We speculate that the exceptions from the general trend might be related to the preparation of samples and the rheological measurements. At this point, we cannot provide an explanation for the observation that the breakdown of hydrogels containing NP-44 and -51 took place at higher temperatures than NP-29 and -34 (Fig. 4). It should be noted here that the grafting densities of four hairy NP samples were very similar to each other (0.42 chains/nm² for NP-29, 0.43 chains/nm² for NP-34, 0.38 chains/nm² for NP-44, and 0.40 chains/nm² for NP-51). Thus, the effect of the grafting density difference on gel property in our study should be negligible. Nevertheless, the grafting density of hairy NPs could affect the LCST transition of polymer brushes and thus the properties of hybrid hydrogels.

To experimentally elucidate the origin of the sharp increase of G' in the heating ramps shown in Figs. 2–4 and confirm our hypothesis that it is caused by the LCST transitions of hairy NPs, we conducted fluorescence resonance energy transfer (FRET) studies for four dilute aqueous mixtures of ABA-N and hairy NPs at various temperatures. Note that a fluorescent dye NBD-containing monomer, NBDMA, was incorporated into the polymer brushes of all four hairy NP samples and Rhodamine B-containing monomer RhBMA was copolymerized into the thermosensitive outer blocks of ABA-N. NBDMA and RhBMA are a FRET pair; NBDMA and Rhodamine B emit at 521 and 575 nm, respectively, upon excitation with 480 nm light [46]. We previously employed FRET to study the spatial location of thermosensitive hairy NPs in aqueous solutions of a thermosensitive ABA triblock copolymer [36]. Here four aqueous mixtures of ABA-N and hairy NPs with polymer concentrations of ~0.21 mg/g and NP concentrations of ~0.010 mg/g were prepared, and the fluorescence emission spectra with an excitation wavelength of 480 nm were recorded at various temperatures. All four samples exhibited two peaks with one maximum at ~521 nm, which is attributed to the emission of NBDMA, and another at 575 nm, which is from RhBMA. If NBDMA and RhBMA are in close proximity (within 1–10 nm), FRET would occur [43], resulting in a decrease in the fluorescence emission intensity at 521 nm and an increase in the intensity at 575 nm. To quantify the FRET data [46], we plot the intensity ratio of the peaks at 521 and 575 nm ($I_{521/575}$)

Table 2
Calculated fractions of bridging polymer chains at certain temperatures for hybrid hydrogels of ABA-N and four hairy NP samples with a NP-to-ABA mass ratio of 30: 100.

Sample	ABA-N/NP-29		ABA-N/NP-34		ABA-N/NP-44		ABA-N/NP-51	
	T_{onset}	T at $G'_{\max}$	T_{onset}	T at $G'_{\max}$	T_{onset}	T at $G'_{\max}$	T_{onset}	T at $G'_{\max}$
Temperature	29 °C	47 °C	32 °C	51 °C	40 °C	58 °C	45 °C	56 °C
G'_{calc} (Pa) ^a	1930	2045	1949	2070	2000	2115	2032	2102
G'_{expt} (Pa) ^b	685	1800	699	1845	514	1168	584	1179
Fraction of Bridging Chains ^c	35%	88%	36%	89%	26%	55%	29%	56%

^a G'_{calc} is the calculated maximum modulus at T_{onset} or T of $G'_{\max}$ based on $G' = \nu k_B T$.

^b G'_{expt} values at T_{onset} and T for $G'_{\max}$ are from Fig. 4.

^c The fraction of bridging chains at a particular temperature is calculated from the ratio of G'_{expt} to G'_{calc} .

against temperature for four mixtures, as shown in Fig. 6.

As can be seen from Fig. 6, with increasing temperature, a sharp decrease in I_{521}/I_{575} was observed for all four aqueous mixtures, suggesting that the FRET occurred to a much greater extent. The onset temperatures for the sharp decrease of I_{521}/I_{575} were 23, 30, 40, and 45 °C for the solutions containing NP-29, -34, -44, and -51, respectively. Except the first one, which was 2 °C lower than the $LCST_{onset}$ of NP-29 and 6 °C lower than the critical temperature for the sharp increase of G' , the other three onset temperatures are essentially the same as those observed in the rheology studies. Note that similar fast decreases were observed for I_{521} from the plots of I_{521} vs T [46]. Apparently, when the temperature reached the LCST of hairy NPs, the brushes collapsed and absorbed the thermosensitive outer blocks of ABA-N, resulting in a closer proximity of NBDMA and RhBMA and thus a more substantial FRET. This supports our hypothesis that the LCST transition of hairy NPs triggered absorption of thermosensitive blocks of ABA-N and reorganization of the network structure in the hybrid micellar hydrogels. Note that below the LCST of hairy NPs, the I_{521}/I_{575} ratio also decreased with increasing temperature but at a slower pace than that at the LCST. This is because with the increase of temperature, water becomes an increasingly poor solvent for the PEO-type thermosensitive water-soluble polymers, which undergo shrinking, though small, even when the temperature is still below the LCST [53]. Thus, there is an increasing interaction between the ABA-N micelles and hairy NPs, resulting in FRET to some extent and consequently a decrease in

I_{521}/I_{575} .

5. Conclusions

A thermosensitive ABA triblock copolymer with a CMT of 13 °C and four thermoresponsive hairy NPs with LCSTs of 29, 34, 44, and 51 °C in water were prepared for study of the effect of LCST transition of hairy NPs on properties of hybrid micellar hydrogels of the triblock copolymer and hairy NPs with NPs located initially outside the core of micelles. We found from rheological measurements that for all hairy NPs, a sharp increase in G' occurred on top of the plateau at a temperature around the LCST transition of hairy NPs for aqueous solutions with a polymer concentration of 10 wt% and NP-to-ABA-N mass ratios from 30: 100 to 70: 100. This phenomenon was caused by the collapse of hairy NPs, which triggered the reorganization of the 3-D gel network nanostructure with the absorption of thermosensitive outer blocks of ABA-N molecules in the dangling, loop, or stretched bridging forms. This was supported by the results from the FRET experiments where upon heating a sharp decrease of I_{521}/I_{575} of aqueous solutions of ABA-N and hairy NPs was observed at a temperature corresponding to the LCST of hairy NPs. In addition, the G'_{max} decreased with the increase of NP-to-ABA-N mass ratio, but the effects were different for hairy NPs with different LCSTs. The G'_{max} values of the hydrogels containing NP-29 and -34 at lower NP-to-polymer mass ratios were comparable to that of the gel with no hairy NPs, while for NP-44 and -51,

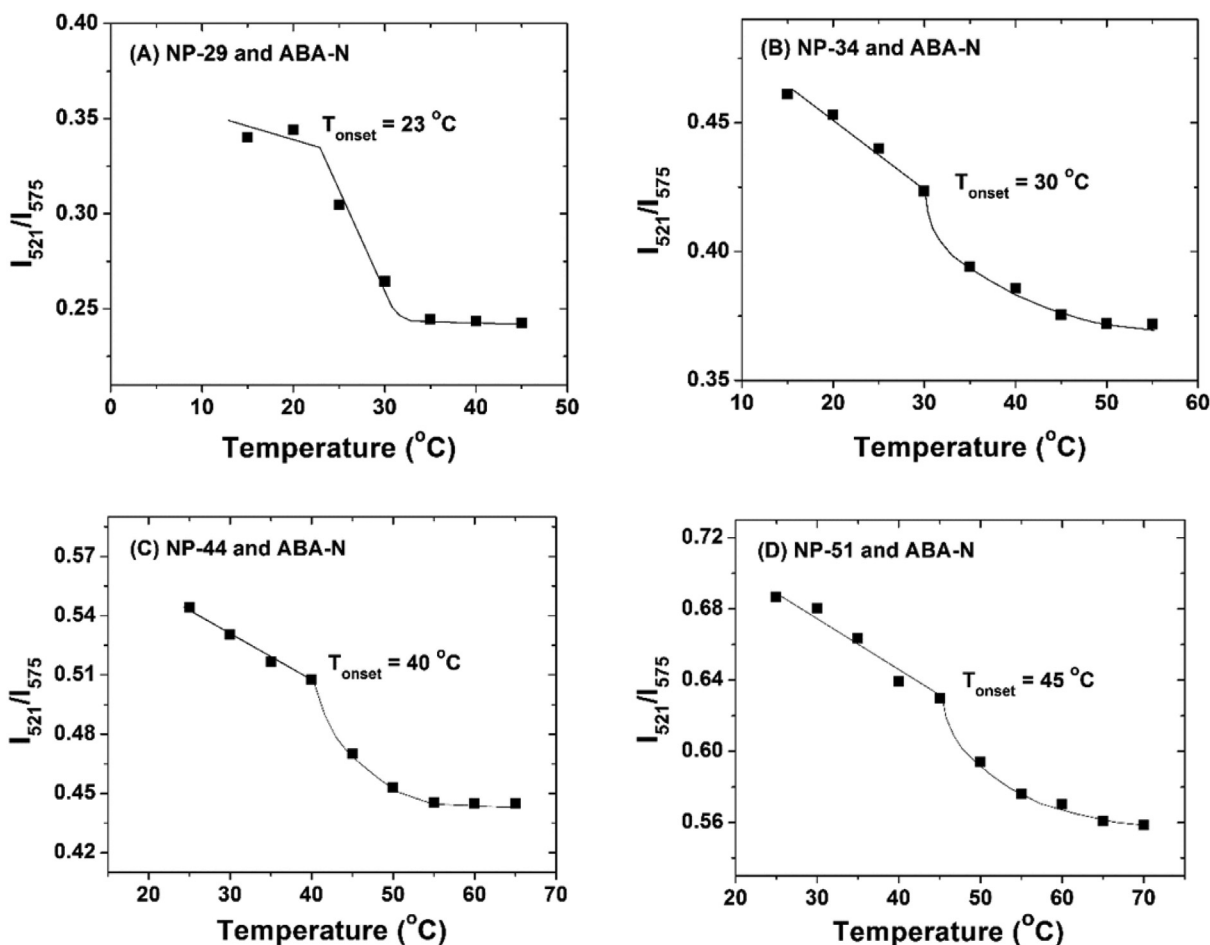


Fig. 6. Plot of the intensity ratio of the emission peaks at 521 nm and 575 nm (I_{521}/I_{575}) versus temperature for an aqueous mixture of (A) ABA-N (concentration: 0.208 mg/g) and NP-29 (conc.: 0.010 mg/g), (B) ABA-N (conc.: 0.208 mg/g) and NP-34 (conc.: 0.011 mg/g), (C) ABA-N (conc.: 0.206 mg/g) and NP-44 (conc.: 0.010 mg/g), and (D) ABA-N (conc.: 0.205 mg/g) and NP-51 (conc.: 0.013 mg/g).

the $G'_{\max}$ values were significantly lower. Hydrogels have been widely used in biomedical applications, and it has been shown that hydrogel stiffness has a significant effect on cell behavior, e.g., cell growth and differentiation [54]. The hybrid hydrogels reported here might be useful in studying the effect of mechanical properties of hydrogels on cell behavior because the moduli of these hybrid gels can be easily tuned.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2015.11.050>.

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