



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., Pluronic) 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) (PTEGMMA)-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.

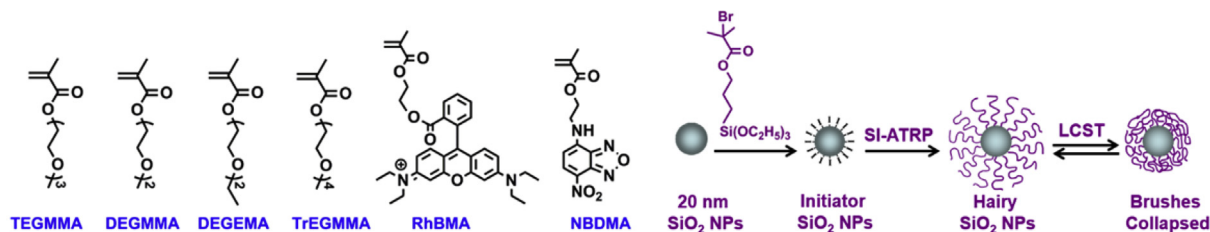
2. Experimental section

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).

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