



Design of stimuli-responsive nanoparticles with optoelectronic cores by post-assembly cross-linking and self-assembly of functionalized block copolymers



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ABSTRACT

Temperature- and pH-sensitive nanoparticles having optoelectronic cores were synthesized by post-assembly cross-linking reaction of a block copolymer composed of poly(*N*-vinyl amine) and poly(*N*-isopropylacrylamide), which was prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization. The self-assembly of the block copolymer in a selective solvent, followed by the site-selective cross-linking of poly(vinyl amine) segment with anthracene and thiophene dialdehydes, afforded stable and uniform core cross-linked nanoparticles having pH-sensitive imine linkages. As comparisons, the poly(vinyl amine) segment in the block copolymer was modified selectively with monoaldehyde derivatives to yield anthracene- and thiophene-functionalized block copolymers, which can form self-assembled micelles with optoelectronic cores in aqueous solutions. Temperature-dependent morphological changes and optical properties of the core cross-linked nanoparticles and the functionalized block copolymers were compared in selective and non-selective solvents, which were characterized by DLS, UV–vis, fluorescence, and CV measurements. The core cross-linked nanoparticles also exhibited pH-triggered disintegration. To the best of our knowledge, this is the first report on the comparison of two series of stimuli-responsive nanoparticles, in which the optoelectronic cores are formed by post-assembly cross-linking reaction with the dialdehyde derivatives and self-assembly of the functionalized block copolymers prepared with the monoaldehyde derivatives.

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1. Introduction

Temperature- and pH-sensitive polymers and gels have been the subject of continuing interest in academic researches as well as in important technologies, because of their characteristic stimuli-responsive behaviors [1–5]. Block copolymers with optoelectronic, fluorescent, and π -conjugated segments and their abilities to self-assemble into hierarchical structures are another central concept deriving developments in various scientific fields [6–10]. In particular, much interest has been recently devoted to thermoresponsive block copolymers having temperature-dependent fluorescence emission [11–13], as promising candidates for

diverse bio- and optoelectronic applications such as imaging, diagnostics, sensors, and smart optical systems. In view of the microenvironment complexity in these applications, it is desired to manipulate external stimuli-responsive optoelectronic properties, such as stimuli-triggered activation/deactivation of specific emitting fluorophores, and spatial location and distribution of fluorescent and optoelectronic units in three-dimensional assembled structures under various environments.

In recent years, growing attention has been paid to polymeric nanoparticles composed of chromophore and conjugated polymer, due to increasing interest in numerous fields [14,15], such as optoelectronics [16–18] and biological imaging and sensing [19–24]. Attractive features of these polymeric nanoparticles involve high specific surface area, good processibility, characteristic optoelectronic properties and energy transfer [14,25–27], which can be tuned by the chemical structures, compositions, sizes, topologies, and spatial assembly of individual constituents and their interfaces.

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The outermost surface, which is generally organic shell, determines the chemical properties of such materials and their interaction with the environment, whereas their physical and optoelectronic properties are mainly governed by chromophore/conjugated polymer cores as well as surrounding organic layer. Several methods, such as self-assembly of block/graft copolymers [22,24,28] and emulsion polymerization [21,23], have been employed for the production of chromophore- and conjugated polymer-based nanoparticles with water-soluble and thermoresponsive shells [19–24]. Other intriguing subclasses of such responsive polymers are hydrogel nanoparticles and microgels consisted of poly(*N*-isopropylacrylamide), poly(NIPAM), and optoelectronic units, such as thiophene and anthracene [29,30].

For practical applications of the self-assembled nanostructures derived from block copolymers, the fixation and fabrication of self-assembled structures have progressively become important, particularly polymeric micelles through covalent cross-linking in either the core or shell domains [31–33]. A variety of methodologies has been developed for the cross-linking and/or functionalization/decoration of polymeric micelles [31–34]. Recently, we have developed an efficient strategy for the preparation of cross-linked core-shell nanoparticles with π -conjugated core components, in which Suzuki coupling reaction was conducted between the cross-linkable (di)bromide groups in block copolymers and various diboronic acid compounds, following the formation of micelles [35–37]. Similarly, rylene bisimide-based nanoparticles with cross-linked core and thermoresponsive shell were synthesized by a single-step imidization of poly(vinyl amine)-based block copolymer, which was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization, with rylene dianhydride derivatives [38]. In these systems, in-situ Suzuki coupling reaction and imidization were employed for the formation of the cross-linked cores in polymeric micelles in selective solvents, where the non-soluble part having reactive site self-assembles to form core and the soluble part forms the solvated shell.

In this study, we focused on core-cross linking reactions of primary amine groups in the poly(vinyl amine)-based block copolymer with dialdehyde derivatives (Scheme 1), owing to the structural diversity of aldehyde compounds and pH-triggered dissociation property of the resulting imine bonds. Reaction of primary amine groups with aldehyde derivatives has been frequently employed as an efficient route to incorporate functional groups and cross-linking units into various polymers [39–49]. For example, Armes et al. reported the synthesis of a statistical copolymer by addition of conventional poly(vinyl amine) with 2-thiophenecarboxyaldehyde and its application for the production of primary amine functionalized polypyrrole particles [40]. McCormick et al. demonstrated RAFT synthesis of α -methoxy poly(ethylene oxide)-*b*-poly(*N*-(3-aminopropyl)methacrylamide)-*b*-poly(NIPAM), and the primary amine groups in the middle segment of the triblock copolymer were cross-linked with terephthalaldehyde to generate shell cross-linked micelles with cleavable imine linkages [41]. Other examples involve the synthesis of biotinylated copolymers by the conjugation of aldehyde-functionalized biotin to poly(poly(ethylene glycol) methacrylate-*co*-methacryloyl hydrazide) [42] and formation of core cross-linked micelles by the formation of an imine linkage by mixing amino and aldehyde modified α -methoxy poly(ethylene oxide)-*b*-poly(aspartamide)s [43]. Because imine bond is stable at physiological pH and hydrolyzes under acidic conditions, the imine has been extensively investigated in biomedical fields, particularly for pH-triggered controlled release systems [39,41–44].

In the present work, we report the synthesis of stimuli-responsive nanoparticles with cross-linked optoelectronic cores by post-assembly cross-linking reaction of poly(vinyl amine)-based

block copolymer with dialdehyde derivatives, including 2,5-thiophenedicarboxyaldehyde and anthracene-9,10-dicarboxyaldehyde (Scheme 1b). Poly(vinyl amine)-based block copolymer with thermoresponsive poly(NIPAM) segment, which was synthesized by RAFT polymerization, was employed in this study, because of high primary amine content in the poly(vinyl amine) segment and diverse modification possibilities [50,51]. In this system, the formyl groups on the dialdehyde derivatives react with the primary amine groups of the block copolymer to afford imine bonds, resulting in the formation of the core cross-linked nanoparticles. Different from our previous works using Suzuki coupling reaction and imidization [35–38], the imine bond used in this study exhibits pH-triggered dissociation, which affords characteristic pH- and temperature-responsive properties. As comparisons, the poly(vinyl amine) segment in the block copolymer was modified with monoaldehyde derivatives to yield anthracene- and thiophene-functionalized block copolymers (Scheme 1a), which can form self-assembled micelles with optoelectronic cores in a selective solvent. The process can be recognized as self-assembly of the functionalized block copolymers.

Our approach to the design of tunable nanoparticles is focused on the creation of spherical core-shell nanoparticles, in which thermoresponsive shell can significantly influence the optoelectronic properties of the nanoparticles with and without fixation of the cores. The post-assembly cross-linking reaction was employed for the synthesis of the nanoparticles with fixed cores, whereas the self-assembly of the thiophene- and anthracene-functionalized block copolymers led to the formation of the nanoparticles without fixed cores (Scheme 1). The functionalized block copolymers were synthesized by the reaction of poly(vinyl amine)-based block copolymer with monoaldehyde derivatives, 2-thiophenecarboxyaldehyde and 9-anthracenecarboxyaldehyde (Scheme 1a). In the cases, the reactions were conducted in THF/H₂O mixed solvent, where the reaction proceeded homogeneously. In contrast, the preparation of the core cross-linked nanoparticles was carried out by a single-step reaction of poly(vinyl amine)-*b*-poly(NIPAM) and dialdehyde derivatives in THF, in which the block copolymer can form micelles consisting of a core of poly(vinyl amine) covered with a shell of poly(NIPAM) segment (Scheme 1b). These systems have several advantages: firstly no addition of catalyst was employed during the imine formation, secondary three-dimensional structure, their stability, and optoelectronic property can be manipulated by adjusting the structures of mono- and dialdehyde derivatives and reaction conditions, and finally thermoresponsive and pH-responsive properties can be tuned by the circumstance of poly(NIPAM) chains and the acid-cleavable imine linkage. The understanding of the relationship between the core cross-linked nanoparticles and corresponding block copolymers in terms of the optoelectronic properties, specific interactions, and assembled structures under various environments will allow us to develop new smart nanomaterials with characteristic optoelectronic properties as well as three-dimensional structured systems caused by the self-assembly.

2. Experimental section

2.1. Materials

Poly(vinyl amine)-containing block copolymer, poly(vinyl amine)-*b*-poly(NIPAM), was synthesized by RAFT polymerization of NIPAM using dithiocarbamate-terminated poly(*N*-vinylphthalimide) macro-chain transfer agent, followed by the deprotection. A detailed description of the synthetic procedure can be found in earlier publications [38,52,53]. The synthetic method afforded the block copolymer with a pre-determined chain length

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