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Communication

Quadruple thermo-photo-redox-responsive random copolypeptide nanogel and hydrogel

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Graphical Abstract

Quadruple thermo-photo-redox-responsive random copolypeptide nanogel and hydrogel

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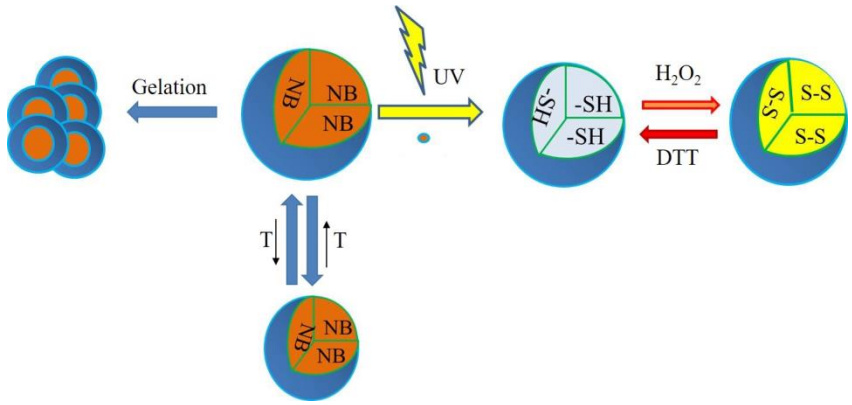

Quadruple stimuli-responsive random copolypeptide of poly(methoxydiethyleneglycol-*L*-glutamate)-*co*-poly(*S*-(*o*-nitrobenzyl)-L-cysteine) was synthesized by ring-opening copolymerization, simultaneously presenting thermo-photo-redox-responsive self-assembly behavior and forming nanogel and hydrogel in water.

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ABSTRACT
A series of random copolypeptides of poly(methoxy-diethylene glycol–L-glutamate)-co-poly(S-(o-nitrobenzyl)-L-cysteine)was synthesized by ring-open copolymerization of methoxydiethylene glycol-L-glutamate-N-carboxyanhydride (EG_2-Glu-NCA) and S-(o-nitrobenzyl)-L-cysteine-N-carboxyanhydride (NBC-NCA) in dried dimethylformamide solution, which presents quadruple thermo-photo-redox responsive self-assembly behavior and forms the related nanogel and hydrogel in water

Keywords: Random copolypeptide Quadruple stimuli Photoresponsive Redox Thermosensitive Nanogel Supramolecular hydrogel

In the past decades, various stimulus-responsive polymeric nanostructures (*e.g.*, micelles, vesicles, nanogel) and hydrogels are receiving great attention in biomedical applications [1-3]. Owing to excellent biocompatibility, biodegradability, and easy-to-access modification and functionalization, synthetic polypeptides and their copolymers have been widely used for engineering stimulus-responsive soft materials [4]. These polypeptide-based biomaterials hold great potentials in drug, protein, DNA or siRNA delivery systems, anti-microbial treatments, and tissue engineering scaffolds [4-8].

In the case of thermosensitive polypeptide, Li *et al.* systematically investigated the thermosensitive phase behavior and the conformation transition of poly(methoxydiethylene glycol-*L*-glutamate) and other poly(*L*-glutamate)s with long methoxyethylene glycol segment [9, 10]. Chen *et al.* synthesized the thermosensitive oligo(ethylene glycol)-derived poly(*L*-glutamate) by using a click grafting method [11]. We found that star-shaped poly(methoxydiethylene glycol-*L*-glutamate) without other hydrophobic segments or terminal groups could form thermosensitive hydrogel *via* the micellar aggregation mechanism [12]. As for the photosensitive polypeptides and copolymers, the spiropyran-containing block copolymer poly(*L*-glutamic acid)-b-poly(ethylene oxide) (PEO) can

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