首届致远学术节
学生科研成果展示

Photosensitive Poly(o-nitrobenzyloxycarbonyl-L-lysine)-bPEO Polypeptide Copolymers: Synthesis, Multiple Self-Assembly Behaviors, and the Photo/pH-Thermo-Sensitive Hydrogels

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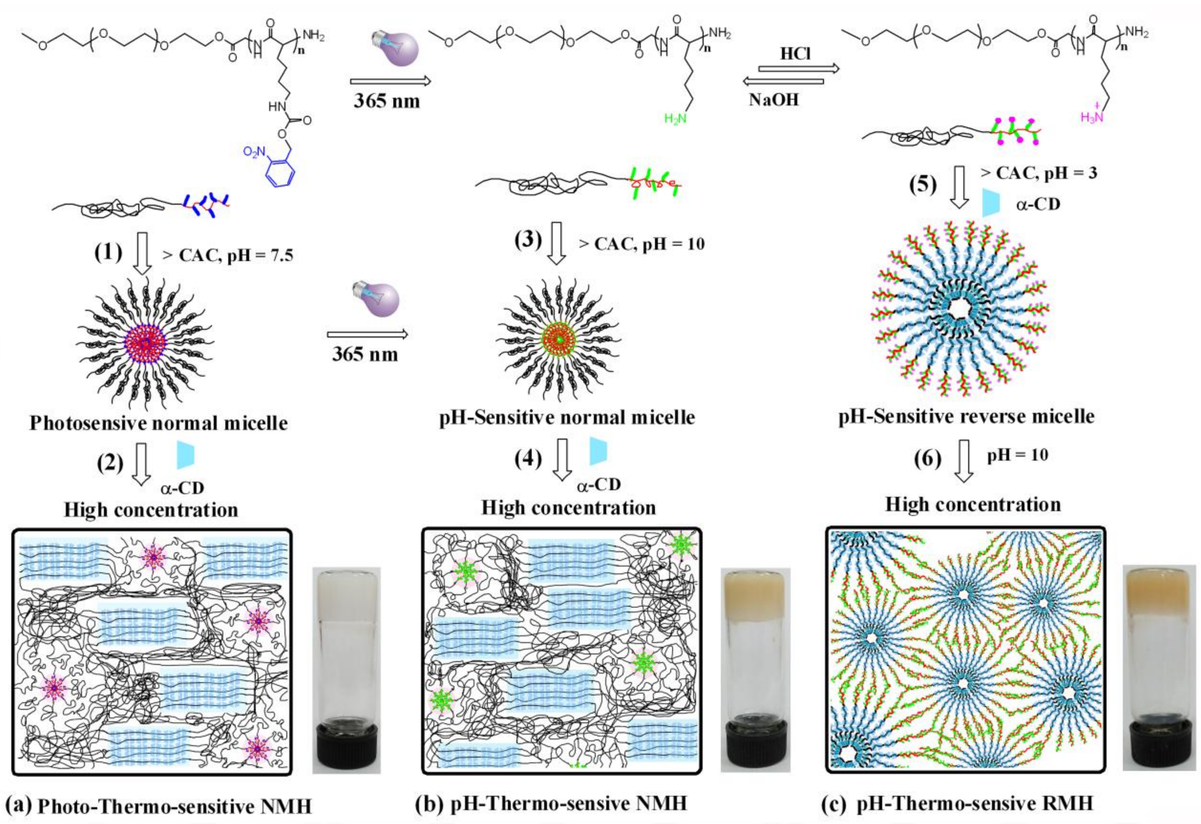
Introduction

- Owing to their good biocompatibility, multiple stimuliresponse and three-dimensional networks mimicking the extracellular matrix, **supramolecular hydrogels** are being extensively investigated for use as drug/gene/protein delivery systems, injectable tissue engineering scaffolds,and smart actuators.
- **Light** is becoming a practical tool to tune the physical and biological properties of polymers and hydrogels in a spatiotemporal manner,however ,the fabrication of photoresponsive polypeptide-based hydrogels with stronger and tunable mechanical properties is still challenging.
- To **enhance the mechanical properties** and **endow the photosensitivity** of the polypeptide hydrogels we have for the first time synthesized a photosensitive poly(onitrobenzyloxycarbonyl-L-lysine)-b-poly(ethylene glycol) (PNBLb-PEO) block copolymer and fabricated three kinds of dualsensitive (i.e., photo/pH-thermo) polypeptide normal and reverse micellar hydrogels via the physical cross-linking of micelles.

Scheme



Scheme 1 Schematic illustration of the proposed structures and gelation process of supramolecular hydrogels: (a) photo-thermo-sensitive NMH; (b) pH-thermo-sensitive NMH; (c) pH-thermo-sensitive RMH. Conditions: (1) and (3) normal micelles, and (5) the reverse micelles; (2) and (4) normal micellar hydrogels (NMH), and (6) the reverse micellar hydrogel (RMH).

Conclusion

A series of photosensitive PNBL-b-PEO block copolymers were synthesized successfully, which exhibited fast photocleavage and photosensitive self-assembly behaviors in methanol and in aqueous solutions. Using the self-assembled polypeptide normal micelles or the reverse micelles as the cross-linking units, three kinds of supramolecular photo/pH-thermo-sensitive polypeptide normal and reverse micellar hydrogels were easily fabricated at a low copolymer concentration of 1–2 wt% with different α-CD concentrations of 4.2–14.4 wt%, in which the multiple self-assembly and hydrogelation behaviors were studied thoroughly. Importantly, these dualstimuli-sensitive polypeptide hydrogels have a higher storage modulus of 10–105 kPa, while the mechanical modulus can be further tuned by varying the UV-irradiation time, the amount of α-CD added, and the copolymer concentration.

Characterization

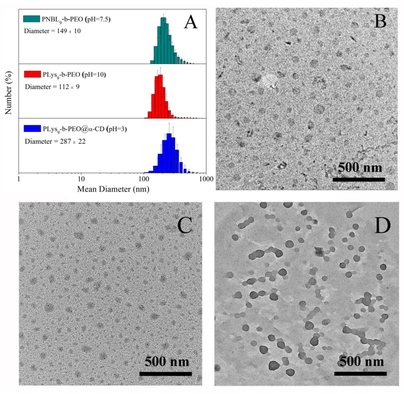


Figure 1. DLS data (A) and TEM for micelles of $PNBL_9$-b-PEO (B), $PLys_9$-bPEO (C) and $PLys_9$-b-PEO@α-CD (D)

Thermo-sensitive

Table 1. The parameters for the polypeptide micellar hydrogels.

Hydrogel	Copolymer	C_{poly} (wt%)	$C_{\alpha\text{-CD}}$ (wt%)	$R_{\alpha\text{-CD}}$	pH	T_{gel} (°C)
H1	$PNBL_9$-b-PEO	1.0	4.2	0.6	7.5	56.9
H2	$PNBL_9$-b-PEO	1.0	5.6	0.8	7.5	64.7
H2’	$PNBL_9$-b-PEO	2.0	11.2	0.8	7.5	84.5
H3	$PNBL_9$-b-PEO	1.0	7.0	1.0	7.5	68.0
H4	$PNBL_9$-b-PEO	1.0	5.6	0.8	3.0	63.3
H5	$PLys_9$-b-PEO	1.0	7.2	0.8	10.0	63.8
H5’	$PLys_9$-b-PEO	2.0	14.4	0.8	10.0	71.2
H6	$PLys_9$-b-PEO	1.0	7.2	0.8	3.0→10.0	53.6
H6’	$PLys_9$-b-PEO	2.0	14.4	0.8	3.0→10.0	65.9

Photo-sensitive

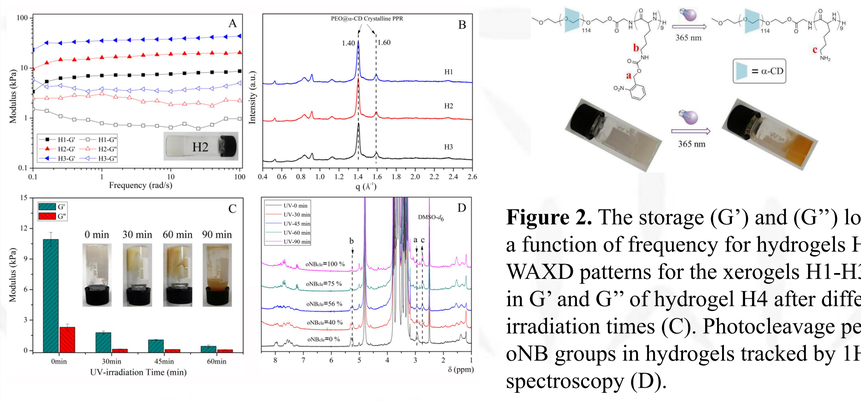


Figure 2. The storage (G’) and (G’’) loss modulus as a function of frequency for hydrogels H1-H3 (A). WAXD patterns for the xerogels H1-H3 (B). Changes in G’ and G’’ of hydrogel H4 after different UV-irradiation times (C). Photocleavage percentage of oNB groups in hydrogels tracked by 1H NMR spectroscopy (D).

pH-sensitive

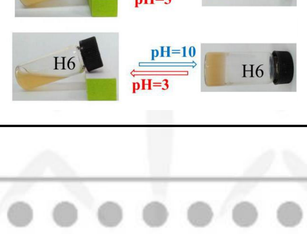


Figure 3. The gel–sol transition occurs when the pH changes in the htdrogel H5/H6.

Reference:
1.Li P, Zhang J, Dong C M. *Polymer Chemistry,* 2017, 8(45): 7033-7043.

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