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Supporting Information

Injectable Thermogel Constructed From Self-Assembled Polyurethane Micelle Networks For 3D Cell Culture and Wound Treatment

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Characterization of Ly−PEG segments（LP）.

The structures and compositions of LP analyzed by ^{1}HNMR and their ^{1}HNMR results are presented in Figure S2. The sharp peak at 3.66 ppm is attributed to the methine protons on the PEG block (-CH_2CH_2O-). The chemical shifts of Lysine tertiary carbon (-CH-COO) and PEG methoxy proton (-OCH_3) are 3.27 ppm and 3.15 ppm, respectively, indicating that the multifunctional chain extender has been successfully synthesized. [1-2]

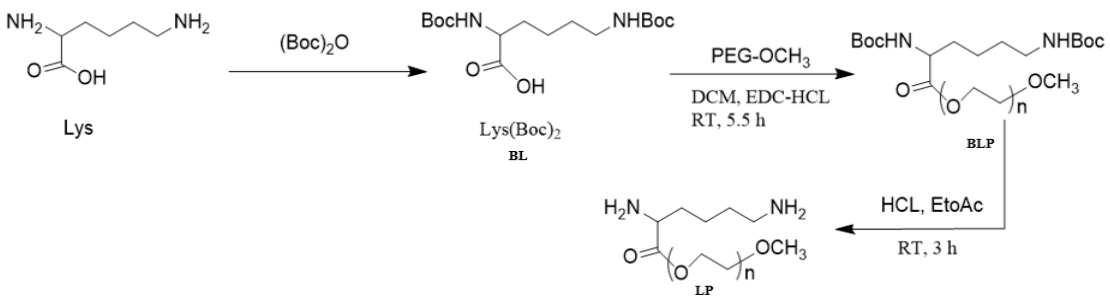


Fig. S 1 Synthesis of LP.

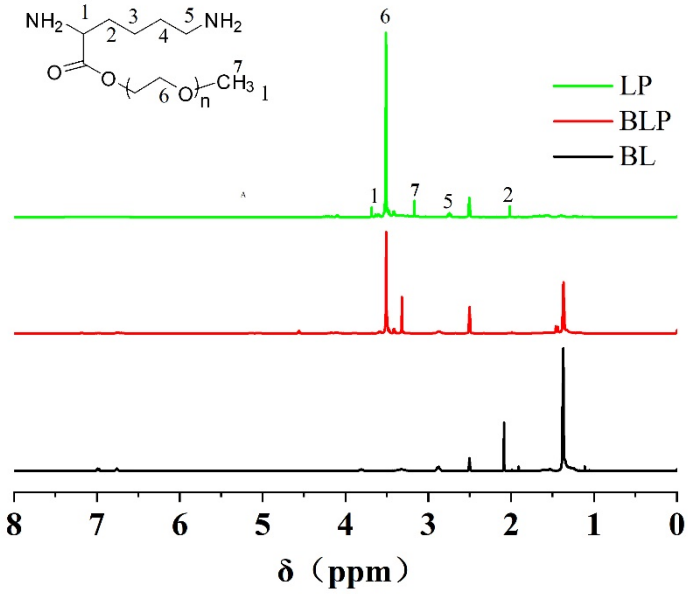
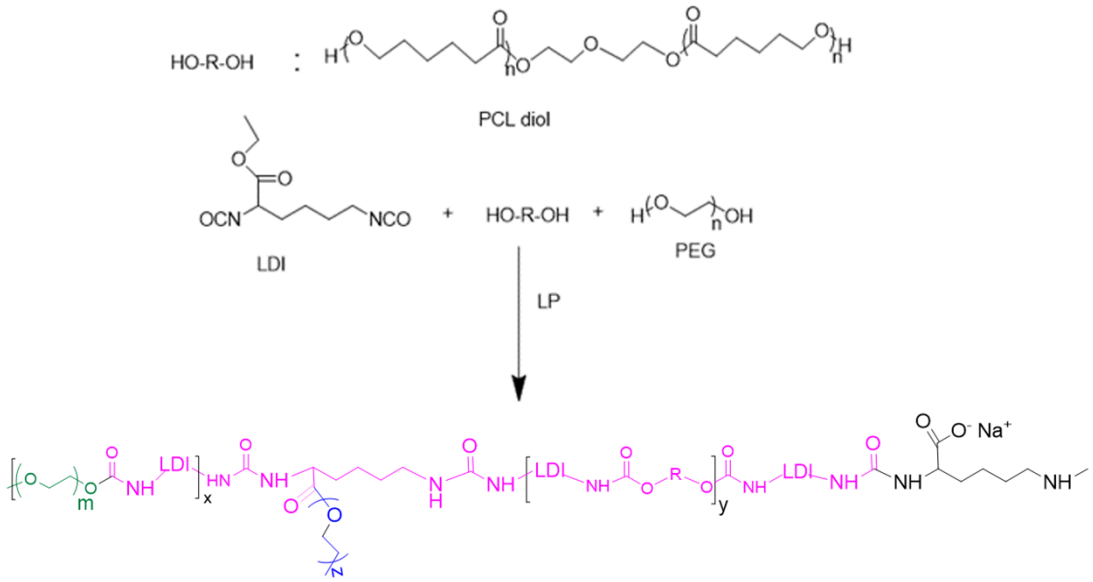


Fig. S 2 ^{1}H NMR spectrum of LP.

Synthesis of PUxPy.

PUxPy containing polyurethane emulsion was synthesized by a two-step process: PEG and PCL were added to a three-neck flask. Under nitrogen protection, dehydrate for 2 h at 90 °C under reduced pressure. The reaction was catalyzed by adding LDI and reacted for 2 h at 80 °C. To reduce viscosity, the LP was dissolved with a small amount of DMAc at 40 °C. Then, it was added to the three-neck flask, and the chain was extended at 40 °C for 1.5 h. After

dilution with a small amount of acetone, the pre-polymer was pour into lysine solution emulsified with high-speed stirring, and add NaOH to maintain pH 8-9, and then stir at low speed for 30 min to defoam. Finally, the solid content of the water emulsion is about 20-30%. The infrared spectra of various WPUs were shown in Figure S4.



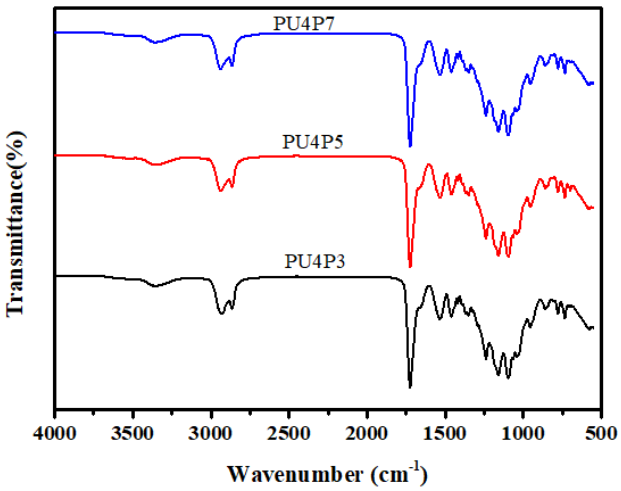


Fig. S 3 Synthesis procedure of WPU.

Fig. S 4 The infrared spectra analysis of various WPUs.

Table S1 The assignment of the FTIR investigations of WPU.

Wavenumber(cm^{-1})	Assignment
3315	H-bond υ(NH)
2930	$\upsilon_a(CH_2)$
2864	$\upsilon_s(CH_2)$
1723	Free υ(C=O) urethane amide I
1533	H-bond υ(C-N) + δ(N-H)
1460	free υ(C-N) + δ(N-H)
1238	υ(C-N) +δ(N-H)
1094	free υ(C-O-C)

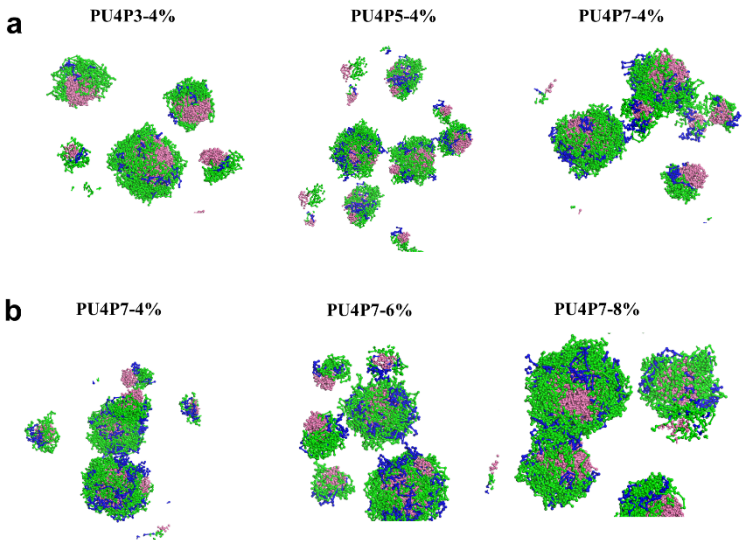


Fig. S 5 DPD simulations of the self-assembly of WPU emulsion. (a)self-assembly behavior of WPU with varying PEG side chain length, (b) self-assembly behavior of WPU with varying polymer concentration.

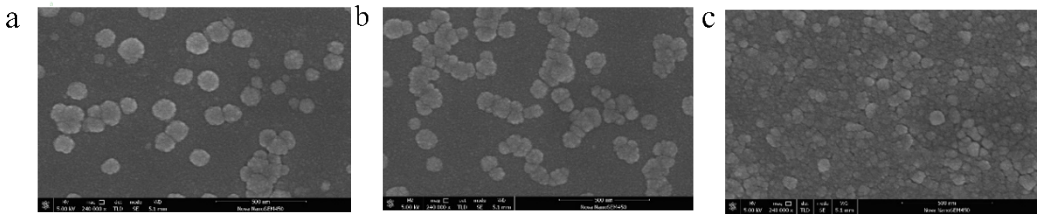


Fig. S 6 The SEM photographs of PU4P7 emulsion particles. (a) concentration of 0.01 wt% at 25 ℃, (b) concentration of 0.01 wt% at 37 ℃, (C) concentration of 1.0 wt% at 37 ℃.

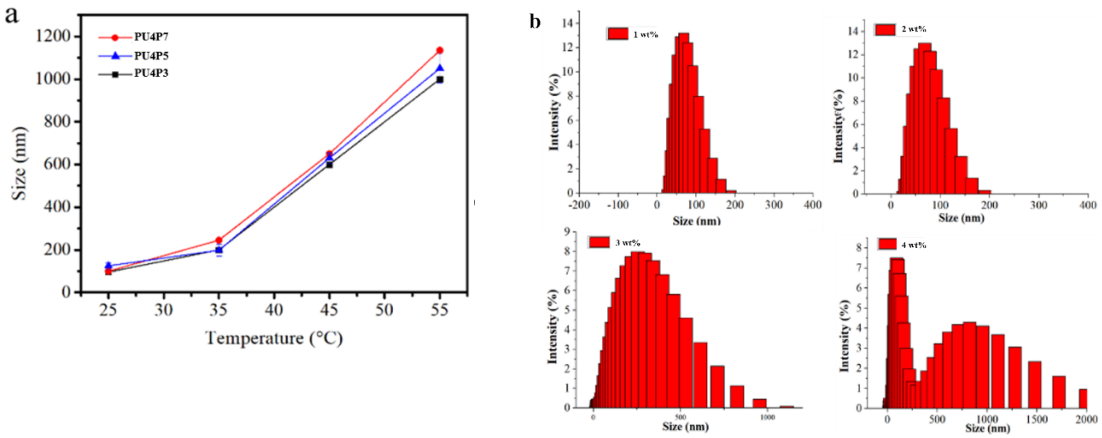


Fig. S 7 The size statistics of PU4Py （y=3,5,7）emulsion particles. (a) Average size vs temperature for the DLS test, (b) size distribution of PU4P7 emulsion at different concentrations at 37 ℃.

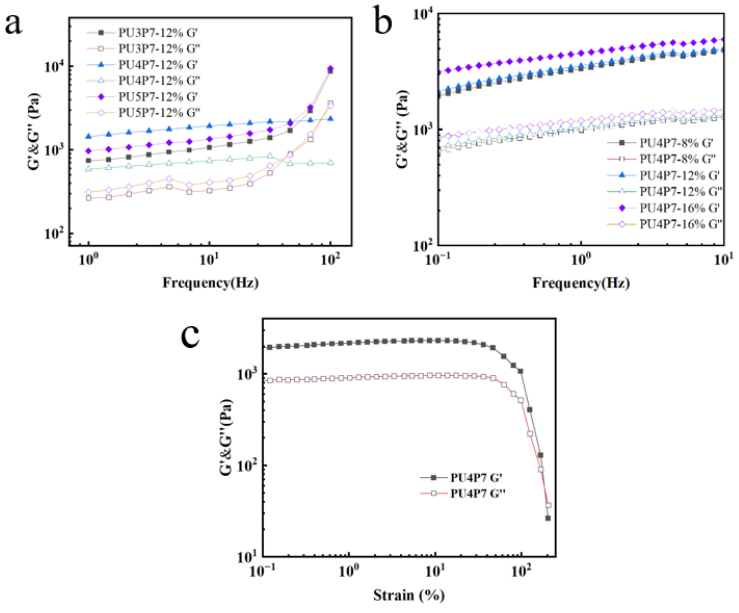


Fig. S 8 (a) PUxP7 (x=3,4,5) Hydrogel scanning was conducted within the frequency range, (b) hydrogel scanning was performed under different solid contents ranging from 8% to 16%, (c) PU4P7 hydrogel scanning was performed under strain levels ranging from 0.1% to 200% .

Table S 2 Composition and Molecular Weights Polyurethanes with Various Amounts of LP.

Sample	Size (nm)	PDI
PU4P3	106	0.267
PU4P5	120	0.236
PU4P7	136	0.235

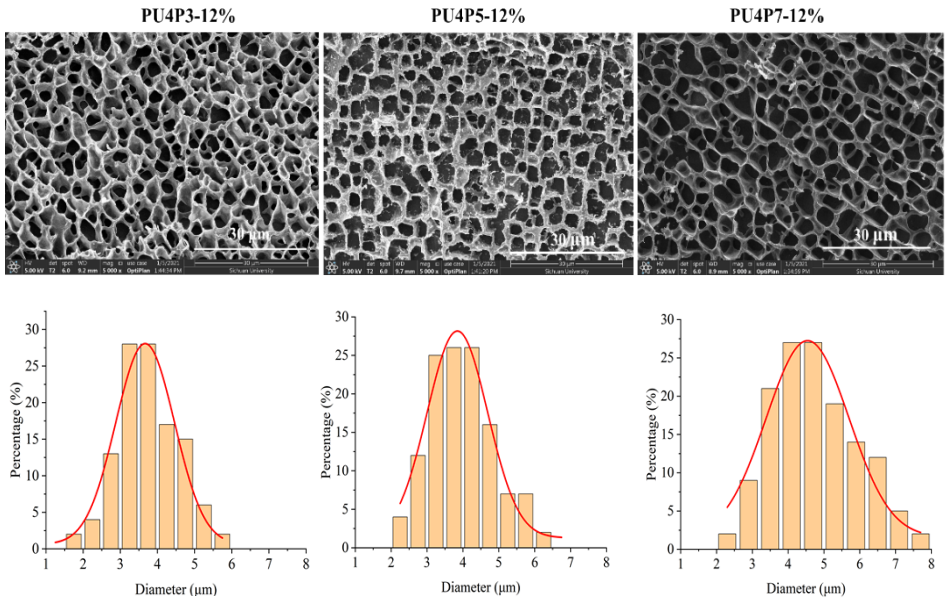


Fig. S 9 Pore size distribution of PU4Py-12% hydrogels.

Table S3 molar ratio of different polyurethane emulsions.

PUxPy	PEG/ %	LP / g·mol^{-1}
PU3P3	30	350
PU3P5	30	550
PU3P7	30	750
PU4P3	40	350

PU4P5	40	550
PU4P7	40	750
PU5P3	50	350
PU5P5	50	550
PU5P7	50	750

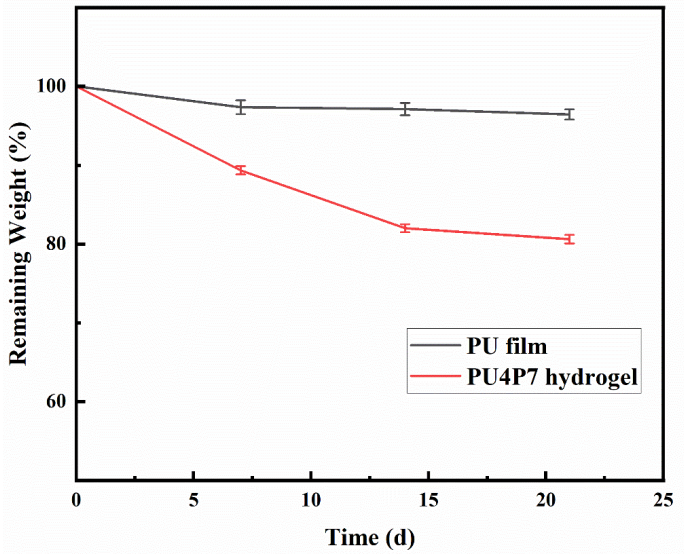


Fig. S 10 Degradation curves of PU film and PU4P7 hydrogels in PBS buffer.

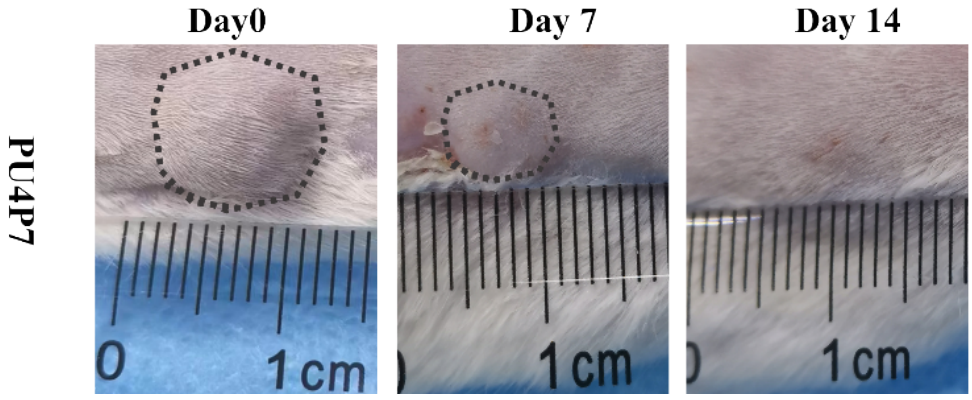


Fig. S 11 Subcutaneous degradation of PU4P7 hydrogels in rats.

REFERENCE

[1] K. Wu, X. Chen, S. Gu, S. Cui, X. Yang, L. Yu, J. Ding, *Macromolecules* 2021, 54, 7421.

[2] S. M. Hashemnejad, A. Z. M. Badruddoza, B. Zarket, C. R. Castaneda, P. S. Doyle, Nature Communications 2019, 10,2749.