Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

A thermo-/pH-Responsive Hydrogel (PNIPAM-PDMA-PAA) with Diverse Nanostructures and Gel behaviors as a General Drug Carrier for Drug Release

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Table S1 Molecular parameters of polymers synthesized in this study

	M_n, NMR[a](g·mol^{-1})	**M_n, GPC[b](g·mol^{-1})**	**PDI[c](M_w/M_n)**
PNIPAM macro-CTA	11992	12413	1.13
PNIPAM-b-PDMA	72858	73874	1.18
PNIPAM-b-PDMA-b-PtBA	82855	84127	1.20
PNIPAM-b-PDMA-b-PAA	78262	79494	1.23

[a]The molecular weight by ^{1}HNMR analysis. [b]The number-average weight by GPC analysis. [c]The PDI or the M_w/M_n values determined by GPC analysis.

Table S2 The PDI of NDB and NDA triblock copolymer with different temperature.

T/℃	**PDI**		
	NDB, pH=7	**NDA, pH=2**	**NDA, pH=8**
25	0.196	0.347	0.86
30	0.202	0.236	0.82
35	0.204	0.237	0.798
40	0.188	0.218	0.595
45	0.329	0.199	0.627
50	0.249	0.193	0.192
60	0.245	0.177	0.272
70	0.240	0.172	0.289

(a) NDB triblock copolymer; (b) NDA triblock copolymer at different pH, (b_1) pH=2; (b_2) pH=8.

Table S3 The PDI of NDA triblock copolymer with different pH at 25℃.

pH	**PDI**
2	0.347
4	0.457
6	0.610
8	0.860

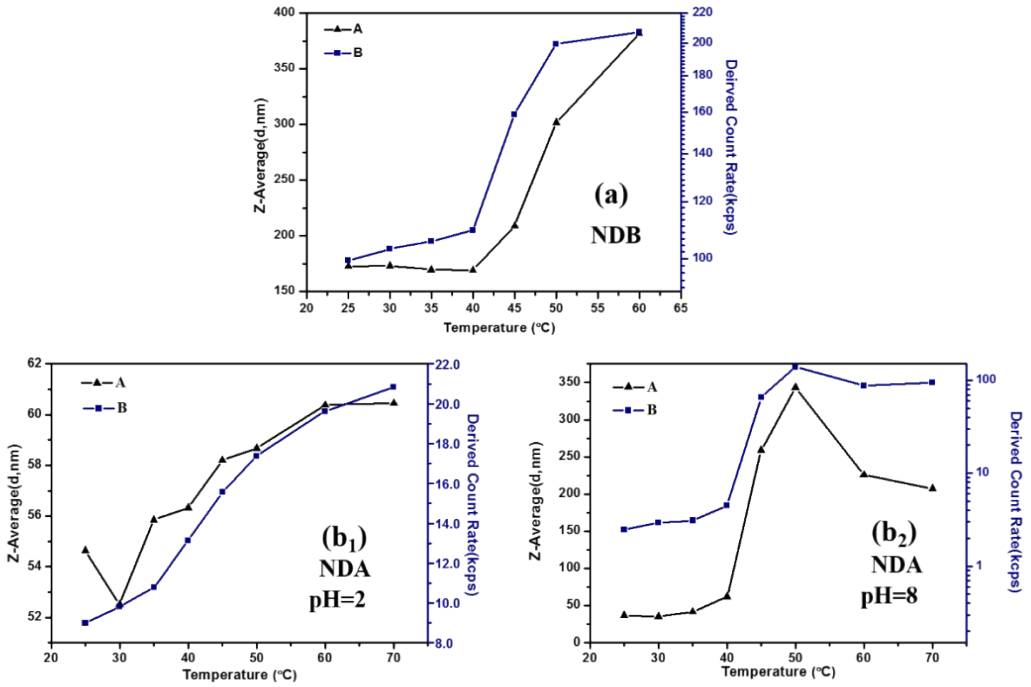

Fig. S1 The Z-average diameter (line A) and light scattering intensity (line B) at different temperature, 0.5 wt% : (a)NDB triblock copolymer at pH=7; (b) NDA triblock copolymer at pH=2 or pH=8.

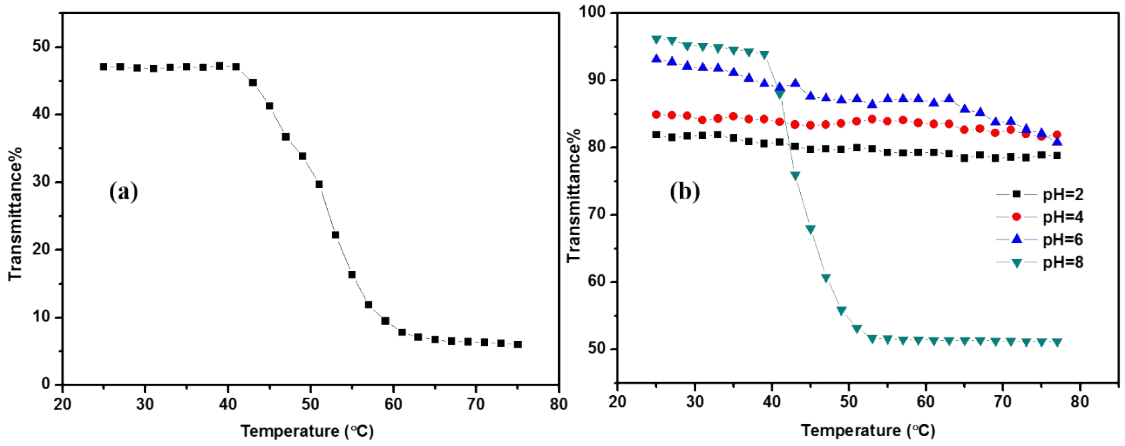

Fig. S2 Temperature dependence of the transmittance of NDB (a) and NDA (b) triblock copolymer, 0.5 wt%.

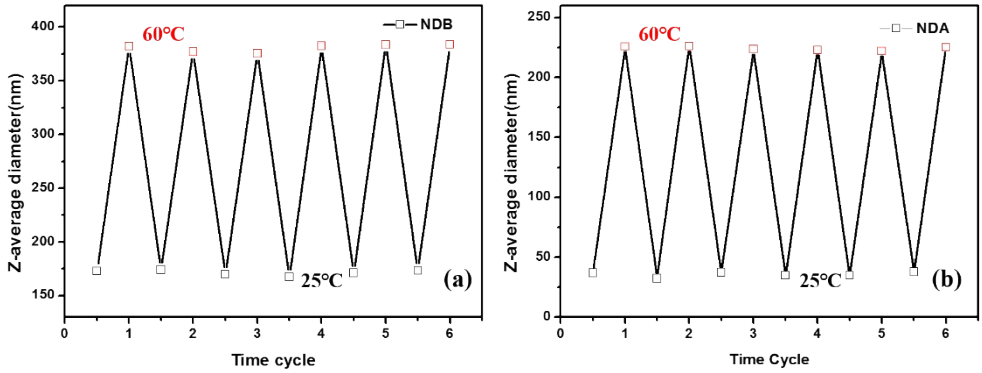

Fig. S3 The reversible change profile of Z-average diameter under heating and cooling. (a) NDB copolymer at 0.5 wt%; (b) NDA copolymer at 0.5 wt%, pH=8.

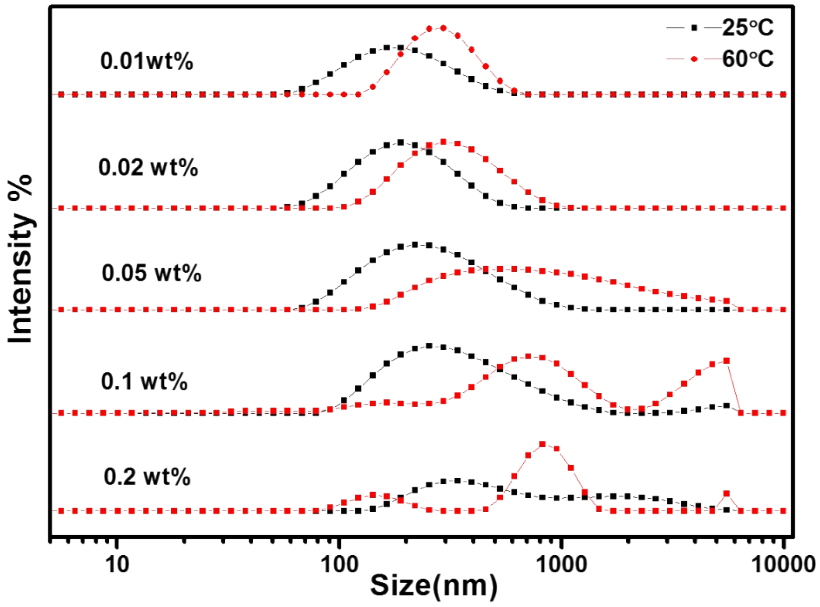

Fig. S4 Intensity distribution of NDB as the concentration increases at 25℃ and 60℃.

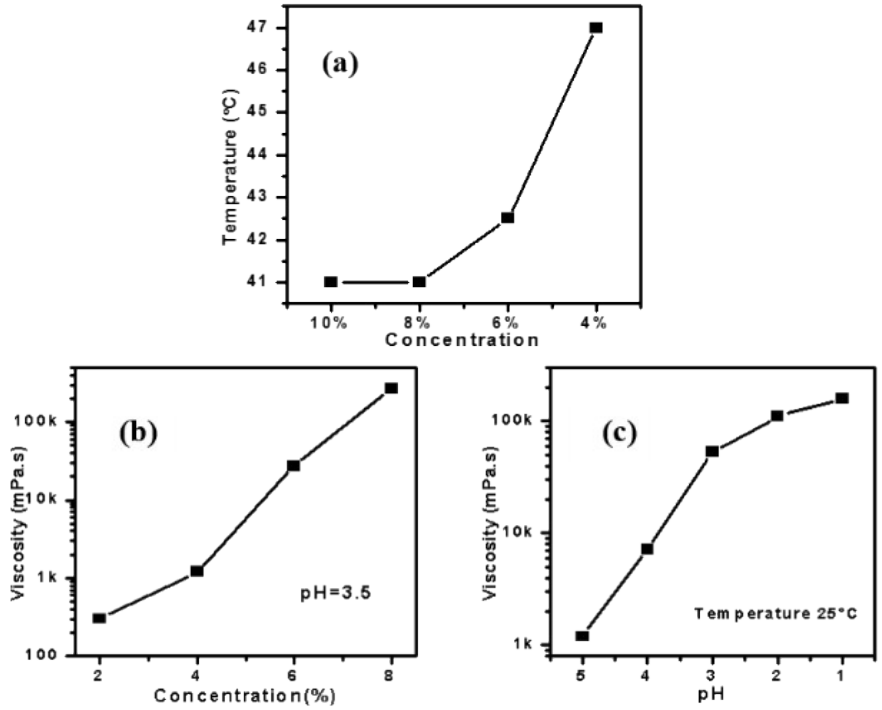

Fig. S5 (a) The LCST of NDB depends on concentration; Viscosity curve of NDA: (b) The viscosity depends on concentration at same temperature, pH=3.5; (c) The viscosity depends on pH at same temperature, 7 wt%.

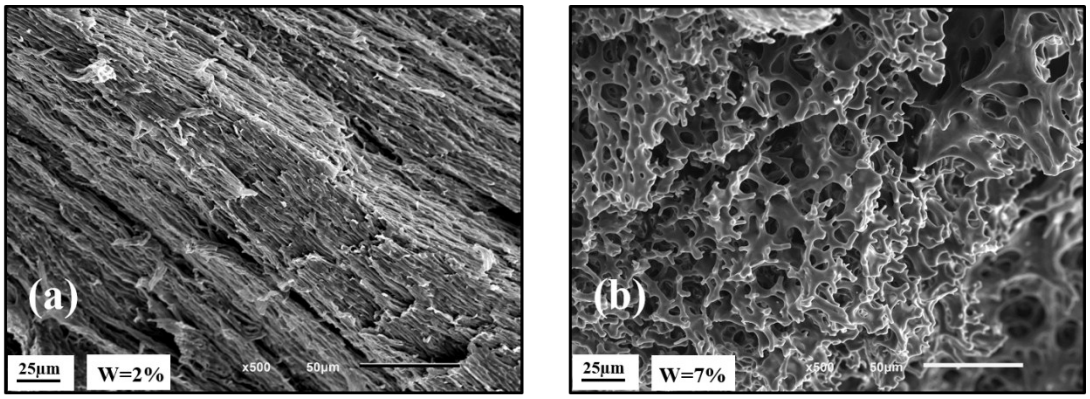

Fig. S6 SEM images of gelation behavior at 2 wt% and 7 wt%, respectively. All tests are in NDA aqueous solutions of pH=2 at 25℃

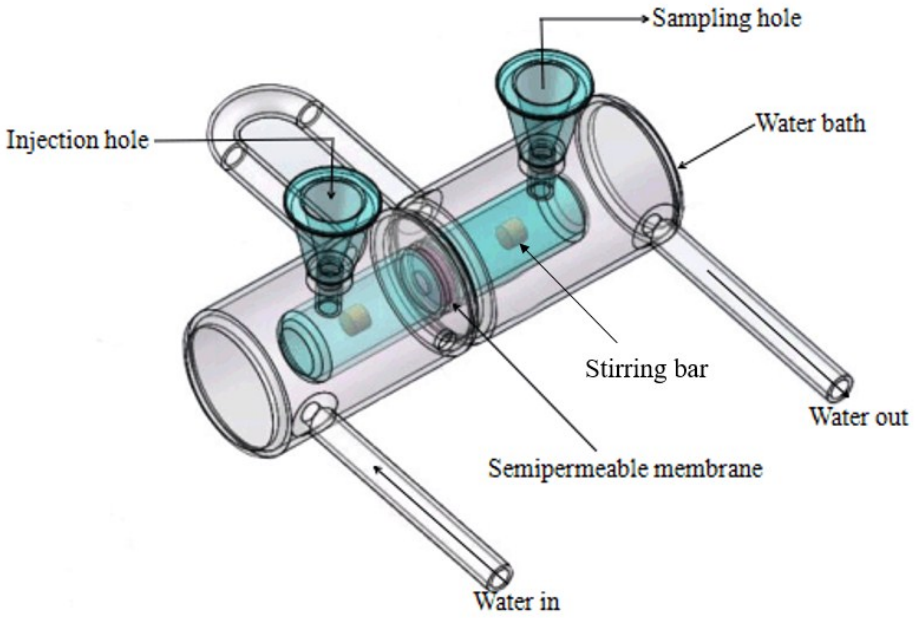

Fig. S7 Schematic diagram of the device used for drug release test.

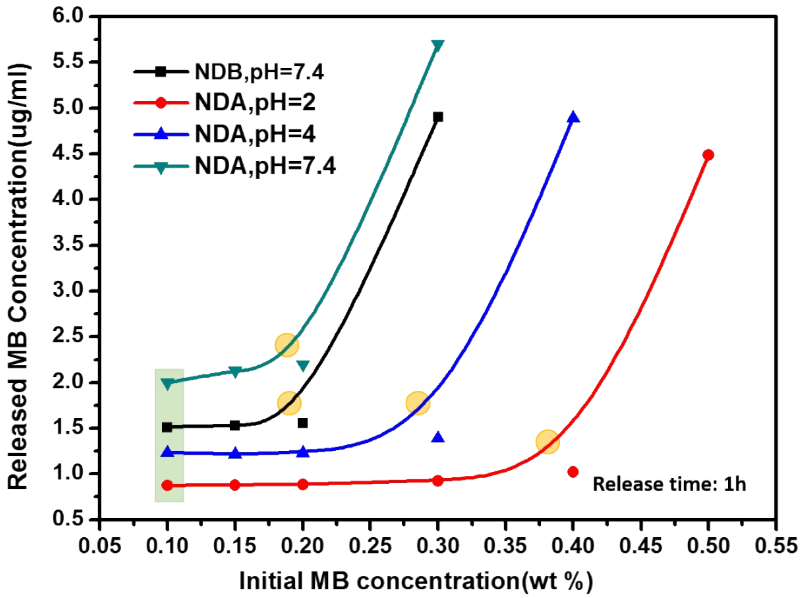

Fig. S8 The released drug concentration under different initial MB concentration after 1h. Yellow circle represents the mutational site of initial MB concentration. NDB and NDA concentration= 7wt% ; T=37℃.

Fig. S8 shows the capacity of gel to encapsulate the drug. At low MB initial concentration (0.15 wt%), there are a few and no obvious changes of released concentration after 1h in any system. When the drug concentration in the initial drug delivery system increases, the 0.2 wt%, 0.3 wt%, 4 wt% correspond to the mutational site of initial MB concentration of NDB and NDA (pH=7.4) , NDA (pH =4) and NDA (pH =2) system, respectively. These phenomenon are due to the different cross-linking degree in NDB or NDA hydrogel. However, it is necessary to choose the minimum optimal concentration of MB to ensure the comparability in the drug release experiment, namely the state of NDA (pH=7.4, 40℃). Even so, in order to ensure a more effective drug delivery effect, the drug concentration in the experiment was slightly less than the optimal value. Therefore, the 0.1 wt% initial MB concentration was selected in the drug release system to ensure all the MB have entered the hydrogel networks and without free MB in the system.

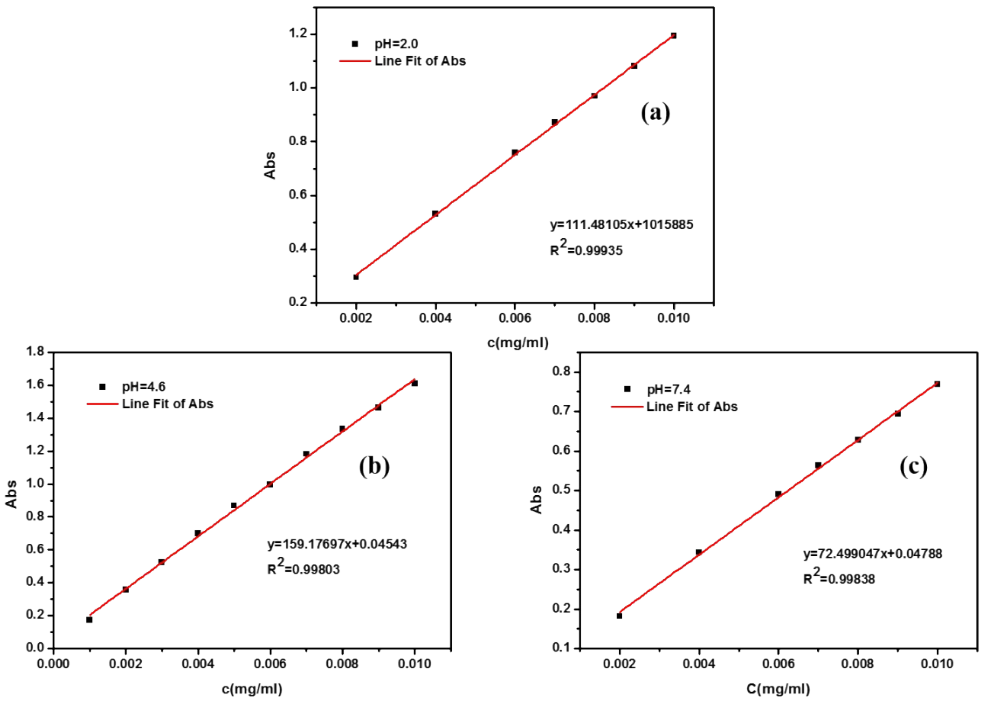

Fig. S9 Standard curve of MB in PBS buffer solution: (a) pH=2.0; (b) pH=4.6; (c) pH=7.4.