Supporting Information

A pH and UCST thermo-responsive tri-block copolymer (PAA-b-PDMA-b-P(AM-co-AN)) with micellization and gelatinization in aqueous media for drug release

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Table S1 Molecular parameters of polymers synthesized in this study

Samples	Mn, NMR[a] (g mol$^{-1)}$	Mn, GPC [b] (g mol$^{-1)}$	PDI[c] (Mw/Mn)
PtBA macro-RAFT	15380	15734	1.23
PtBA-b-PDMA macro-RAFT	52355	53864	1.49
PtBA-b-PDMA-b-P(AM-co-AN)	65667	67152	1.66
PAA-b-PDMA-b-P(AM-co-AN)	58934	61001	1.67

a The molecular weight by 1HNMR analysis. b The number-average weight by GPC analysis. c The PDI (for molecular weight distribution) or the Mw/Mn values determined by GPC analysis.

Table S2The PDI of ADAA triblock copolymer with different temperature

(The PDI was for diameter distribution)

Temperature(℃)	PDI	
	ADAA(pH=3)	ADAA(pH=7)
25	0.293	0.649
30	0.287	0.28
35	0.269	0.353
40	0.283	0.335
45	0.271	0.386
50	0.252	0.404
55	0.25	0.301
60	0.231	0.277
65	0.232	0.32
70	0.221	0.24

Table S3 The PDI of ADAA triblock copolymer with different pH

(The PDI was for diameter distribution)

pH	PDI	
	ADAA(T=25℃)	ADAA(T=50℃)
2	0.284	0.409
3	0.293	0.252
4.5	0.292	0.244
6	0.259	0.302
7	0.649	0.404
8.5	0.607	0.508
11	0.375	0.438

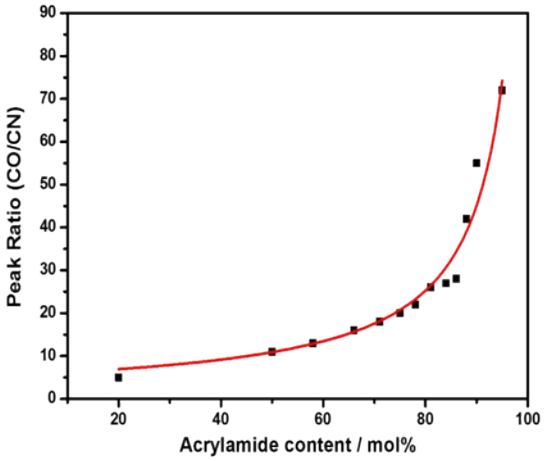

Figure S1 Calibration curve obtained by plotting the integral ratio of the CO absorption band to the CN band

Calculation method of polymer polymerization degree and molecular weight

The formula for calculating the degree of polymerization is:

$$D_P = \frac{S_{x+1} n_x}{S_x n_{x+1}} \quad (1)$$

In the formula, x represents the block number of the block copolymer, if x=0, it represents the homopolymer. Dp represents the ratio of the x+1 block to the x block polymer, if x=0, it represents the degree of polymerization of the polymer. And sx, nx represent the peak area of the characteristic H chemical shift peak and the number of characteristic H of the x block, respectively. As the molecular chain of the polymer increases, the nuclear magnetic signal of the remaining CTA becomes weaker and weaker. Therefore, when calculating the degree of polymerization of other block units, the relative degree of polymerization can be obtained by comparing the characteristic H peak area ratio before and after the block and using the formula. Thus, the final polymer is obtained.

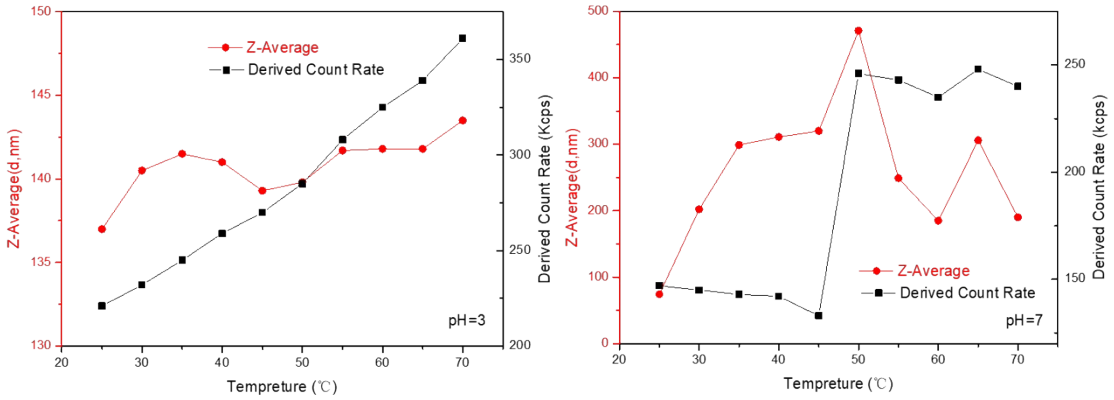

Figure S2 The Z-average diameter and light scattering intensity at different temperature, 0.5 wt% : ADAA triblock copolymer at pH=3 or pH=7.

As shown in Figure S2, in the case of strong acidity, when the pH is less than the pKa of PAA, the

protonated PAA combining with PAM to form a hydrogen bond or the hydrogen bonding force inside PAA cause ADAA to aggregate (in this case, PAA as the core, PDMA as the link chain, P(AM-co -AN) as the core). And the effect of such hydrogen bonding is so strong that the temperature has a small positive effect on the change of its particle size (the particle size has a tendency to increase slightly, and the average particle size increases from 137nm to 143.8nm), but the overall structure is relatively stable. Among them, the increase in particle size with temperature is mainly due to the fact that P (AM-co-AN) breaks by itself, and the polymer and water molecules form a strong force. When the pH is increased to 7, the hydrogen bond of the ionized PAA breaks, and then generates a hydrogen bond with the water molecule to become a hydrophilic chain (in this case, P(AM-co-AN) as the core , PDMA-PAA as the shell). At this time, temperature has a huge impact on the microstructure of ADAA. As the temperature rises, P(AM-co-AN) gradually becomes hydrophilic, ADAA gradually becomes loose from tight, and the particle size begins to increase. Until P(AM-co-AN) is completely hydrophilic, and the particle size begins to decrease.

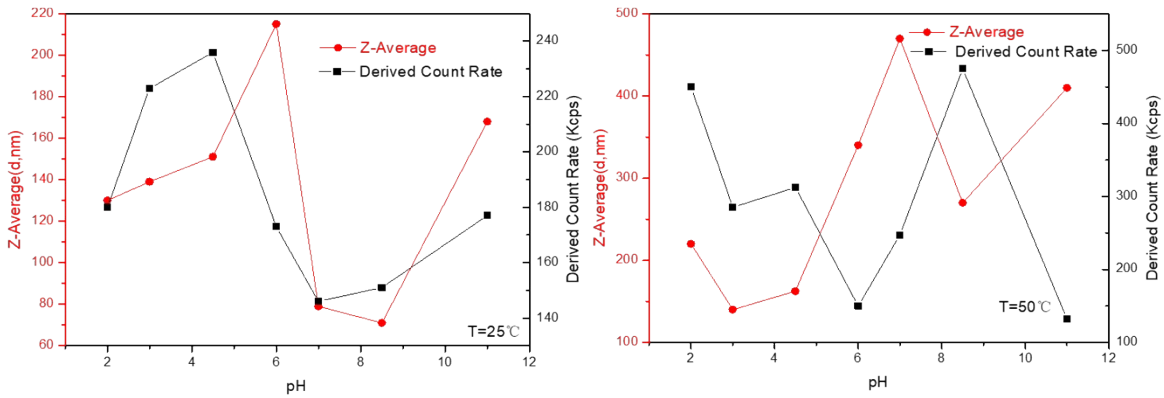

Figure S3 The Z-average diameter and light scattering intensity at different pH, 0.5 wt% : ADAA triblock copolymer at T=25℃ or T=50℃.

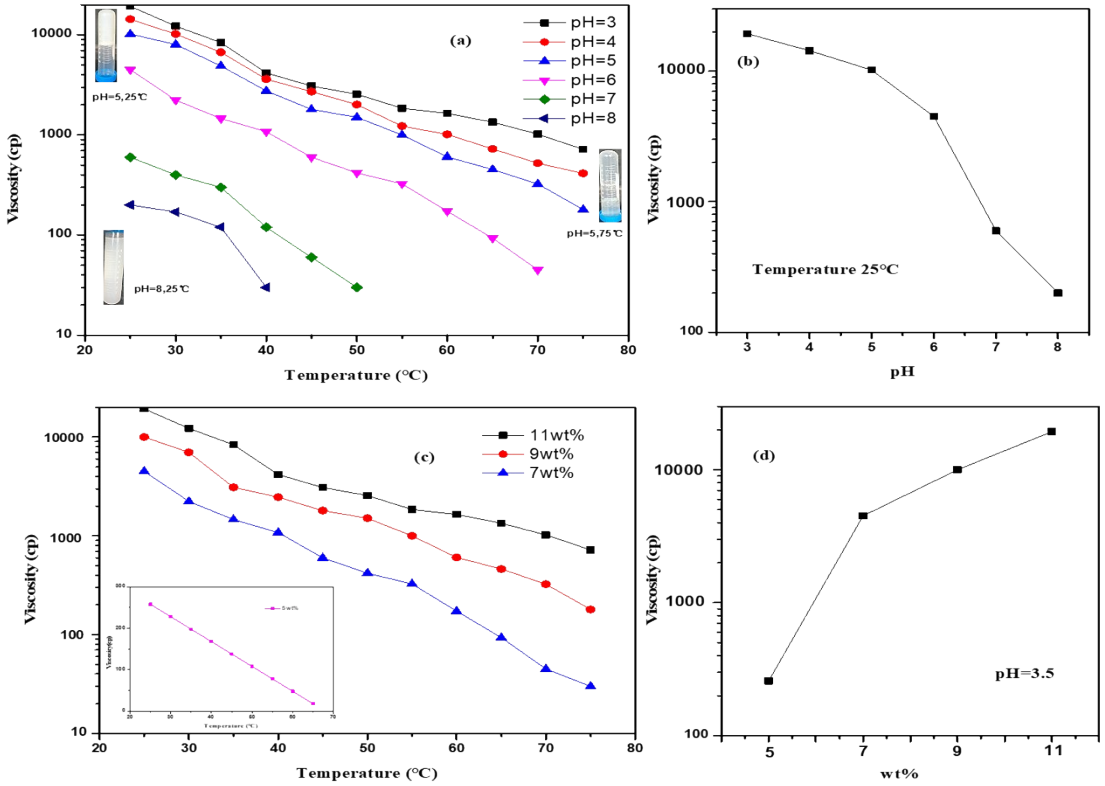

Figure. S4 (a)Viscosity curves of ADAA system depend on temprerature with different pH aqueous solution.(b)The first gradient equilibrium viscosity versus pH,wt%=10%.(c)Viscosity curves of ADAA system depend on temperature with different copolymer concentrations in an aqueous solution.(d)The viscosity depend on concentration of the ADAA system at the same temperature,pH=3.5.

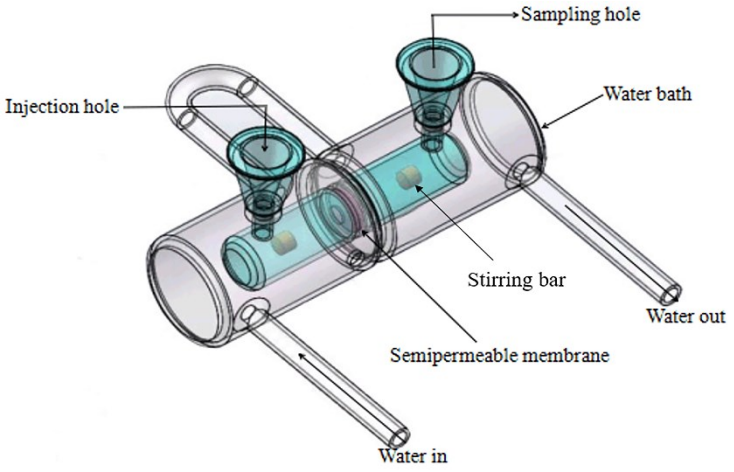

Figure. S5 Schematic diagram of the device used for drug release test

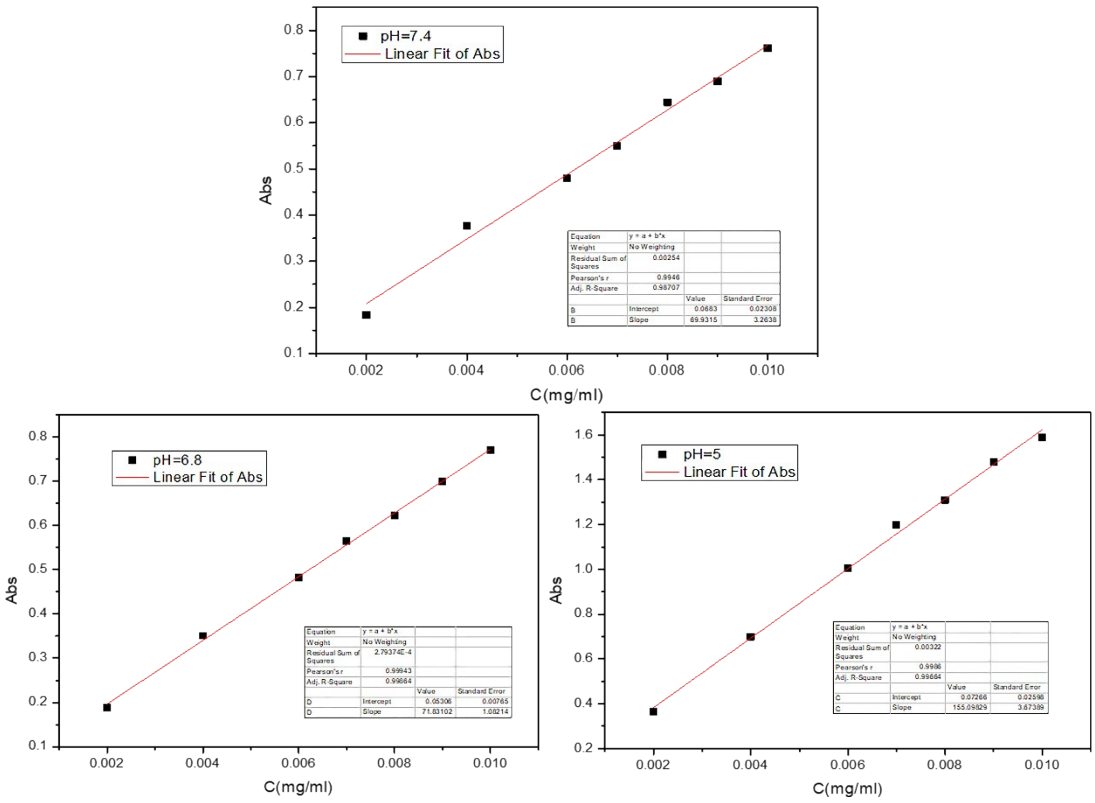

Figure. S6 Standard curve of MB in PBS buffer solution: (a) pH=7.4; (b) pH=6.8; (c) pH=5.