Supporting Information

A hyperbranched amphiphilic acetal polymer for pH-sensitive drug delivery

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Fig. S1 ¹H-NMR spectra of PEG2000-Br macroinitiaor.



Fig. S2 ¹H NMR spectra of di(2-acy-loyloxy ethoxy)-[4-methoxy-phenyl]methane) (ACD) monomer.



Scheme S1. Synthesis of PEG-b-pACDs by a modified DE-ATRP.

 $\begin{array}{l} \text{Branch} & \text{ratio} \\ \text{Branch} & \text{ratio} \\ \hline integrals of h \\ \hline integrals of g \end{array} * ACD\% (Eq. S1) \\ \end{array} \\ \begin{array}{l} \overset{\text{Branched ACD units}}{=} * ACD\% \\ = (1 - \frac{Linear ACD units}{All ACD units}) * ACD\% \\ = (1 - \frac{Linear ACD$



Fig. S3 Gel permeation chromatograms of the polymers after purification (P₁: M_n=15360, PDI=1.67; P₂: M_n=22060, PDI=2.93; P₃: M_n=24190, PDI=4.32).



Scheme S2. Cleavage of the branching units to small fragments in acidic condition.



Fig. S4 Gel permeation chromatograms of polymer before and after pH response for 48 hrs.



Fig. S5 ¹H-NMR spectra of polymer before and after 48 hrs core cross-linking.



Fig. S6 DOX mean fluorescence intensity of Hela cells incubated free DOX and DOX-loaded micelles for 0.5, 3 and 6 hrs, respectively (DOX concentration = 2 μ g/mL). Data represented as the mean \pm SD (n = 3,*p < 0.001).