Supporting Information

A hyperbranched amphiphilic acetal polymer for pH-sensitive drug delivery

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Fig. S1 $^1$H-NMR spectra of PEG2000-Br macroinitiaor.
Fig. S2 $^1$H NMR spectra of di(2-acyloyloxy ethoxy)-[4-methoxy-phenyl]methane) (ACD) monomer.
Scheme S1. Synthesis of PEG-b-pACDs by a modified DE-ATRP.

[I]:[M]:[CuCl$_2$]:[PMDETA]:
[AA]=1:20:0.5:0.5:0.2 in butanone at 50 °C
Branch ratio \( \frac{\text{Branched ACD units}}{\text{All ACD units}} \)* ACD% = \( \frac{\text{Linear ACD units}}{\text{All ACD units}} \) * ACD% = (1- \( \frac{\text{integrals of } h}{\text{integrals of } g} \)) * ACD% (Eq. S1)

Fig. S3 Gel permeation chromatograms of the polymers after purification (\( P_1 \): \( M_n=15360 \), PDI=1.67; \( P_2 \): \( M_n=22060 \), PDI=2.93; \( P_3 \): \( M_n=24190 \), 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 $^1$H-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 μg/mL). Data represented as the mean ± SD (n = 3, *p < 0.001).