Supporting Information

Block and random copolymers bearing cholic acid and oligo(ethylene glycol) pendant groups: Aggregation, thermosensitivity and drug loading

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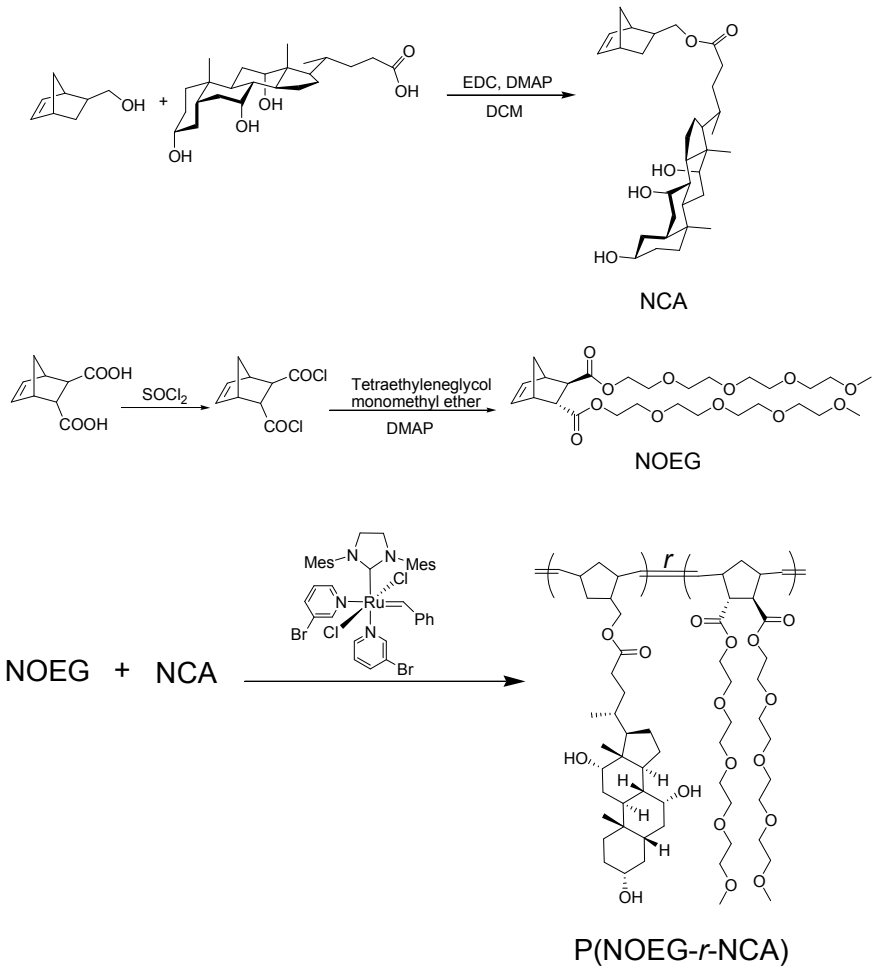

Figure S1. Synthetic scheme for the norbornene monomers NCA and NOEG and the random copolymers.

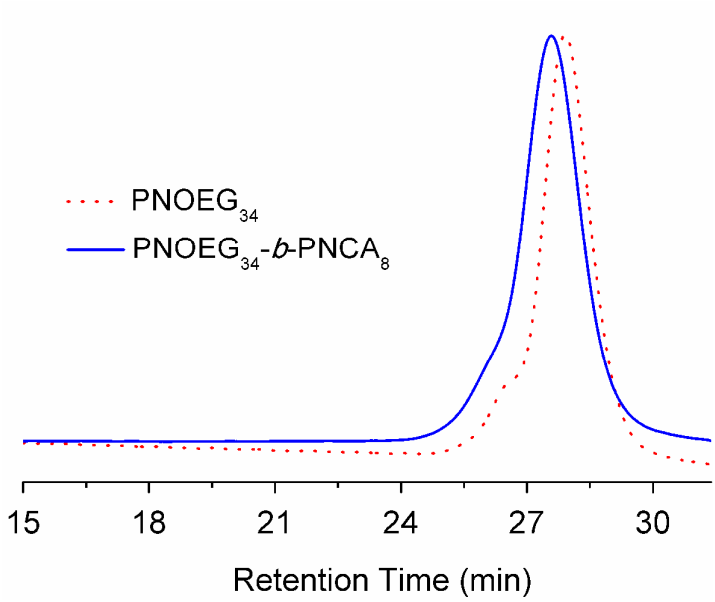

Figure S2. SEC traces of homopolymer $PNOEG_{34}$ and block copolymer $PNOEG_{34}$-*b*-$PNCA_8$. DMF was used as the mobile phase with a flow rate of 1.0 mL/min at 50 °C and with PMMA standards.

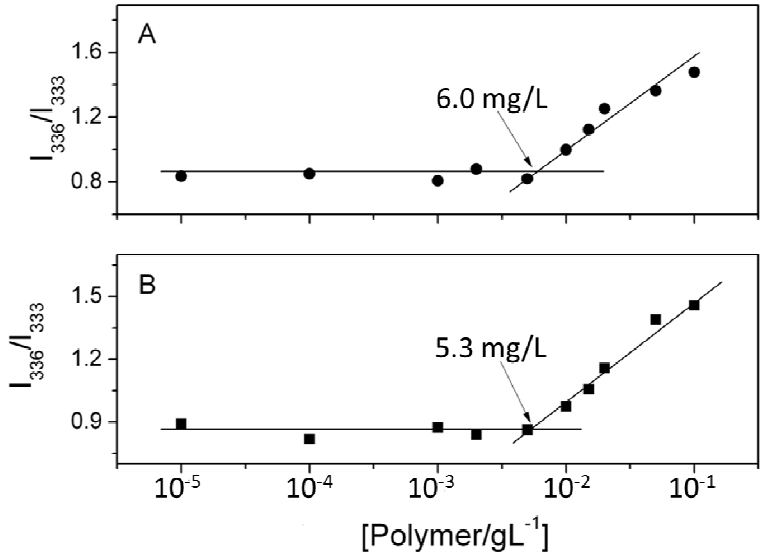

Figure S3. Plot of intensity ratios (I_{336}/I_{333}) as a function of copolymer concentrations (A) $P(NOEG\text{-}r\text{-}NCA)_{4:1}$ and (B) $PNOEG_{34}$-*b*-$PNCA_8$. Excitation spectra of pyrene were recorded on an FLS-900 (Edinburgh Instruments, UK) fluorescence spectrophotometer equipped with Xe-900 lamp ranging from 300 to 360 nm with a fixed emission at 390 nm. The extremely close CMC values of block and random copolymers suggest that the structural difference has no significant effect on the formation of micelles.

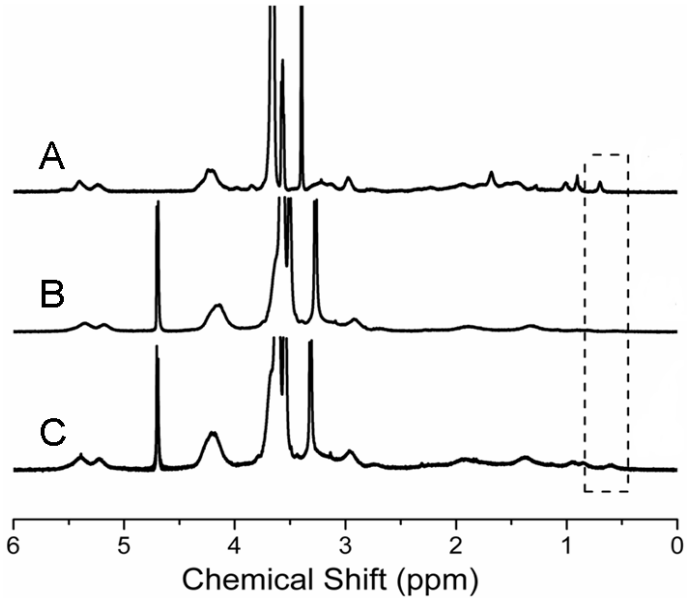

Figure S4. ^{1}H NMR spectra of typical block and random copolymers: (A) $PNOEG_{34}$-*b*-$PNCA_8$ in $CDCl_3$, (B) $PNOEG_{34}$-*b*-$PNCA_8$ in D_2O and (C) P(NOEG-*r*-NCA)$_{4:1}$ in D_2O. The disappearance of signal from methyl group on cholic acid (B, dashed rectangle) in water indicates the copolymers are capable of forming micelles with a hydrophobic cholic acid core surrounded by a hydrophilic PEG shell. The signal from methyl group on cholic acid (C, dashed rectangle) is still visible indicates the shell of micelles formed by random copolymers is thinner than that of block copolymers.

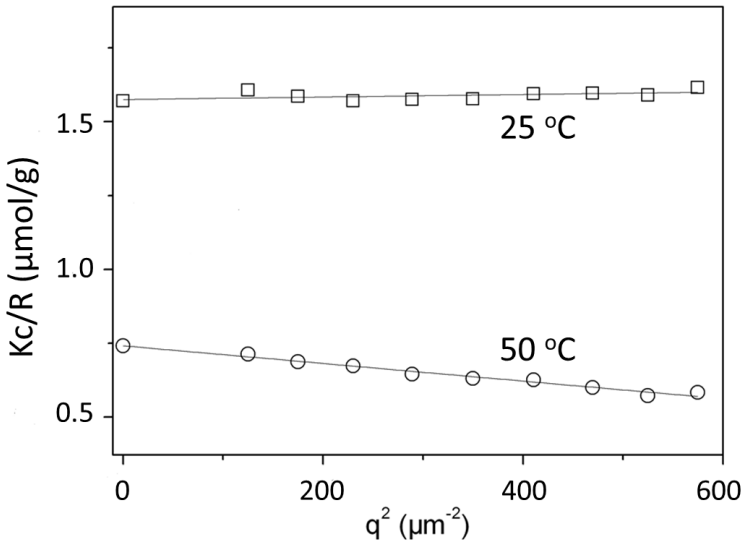

Figure S5. The static light scattering (SLS) experiments for P(NOEG-*r*-NCA)$_{4:1}$ (2.0 g/L) in water were conducted on a CGS-3 compact goniometer (ALV GmbH) equipped with an ALV-5000 multi tau digital real time correlator at 25 and 50 °C. Since the aggregation is expected to be concentration dependent, the weight-average molecular weight of the aggregates, M_w could not be measured using a concentration series. We have therefore made the approximation that the relatively low concentration (c) of 2 g/L is in the region where c → 0. In the low-q region, this approximation holds [*J. Chem. Phys.* **1948**, 16, 1099-1116;

Adv. Polym. Sci. **2006**, 195, 101-176]. M_w of micelles was obtained from angular dependence of light scattering by the use of the equation below; it increased from ca. 6.37×10^5 to 1.35×10^6 g/mol as temperature was raised from 25 to 50 ºC.

$$\frac{Kc}{R_w(q)} \approx \frac{1}{M_w}\left(1 + \frac{1}{3}R_g^2 q^2\right)$$

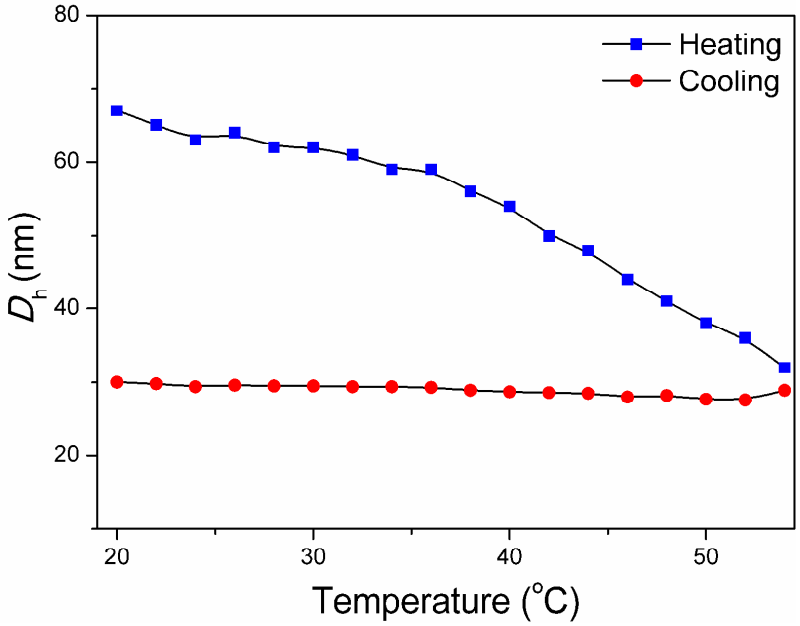

Figure S6. Hydrodynamic diameter of polymer aggregates formed by $PNOEG_{34}$-*b*-$PNCA_8$ in aqueous solutions as a function of temperature (2.0 g/L), indicating the shrinkage of the micelles formed by block copolymer is non-reversible under this condition.