Core-Crosslinked Micelles Made of Diblock Glycopolymers Bearing Dopamine and Cholic Acid Pendants

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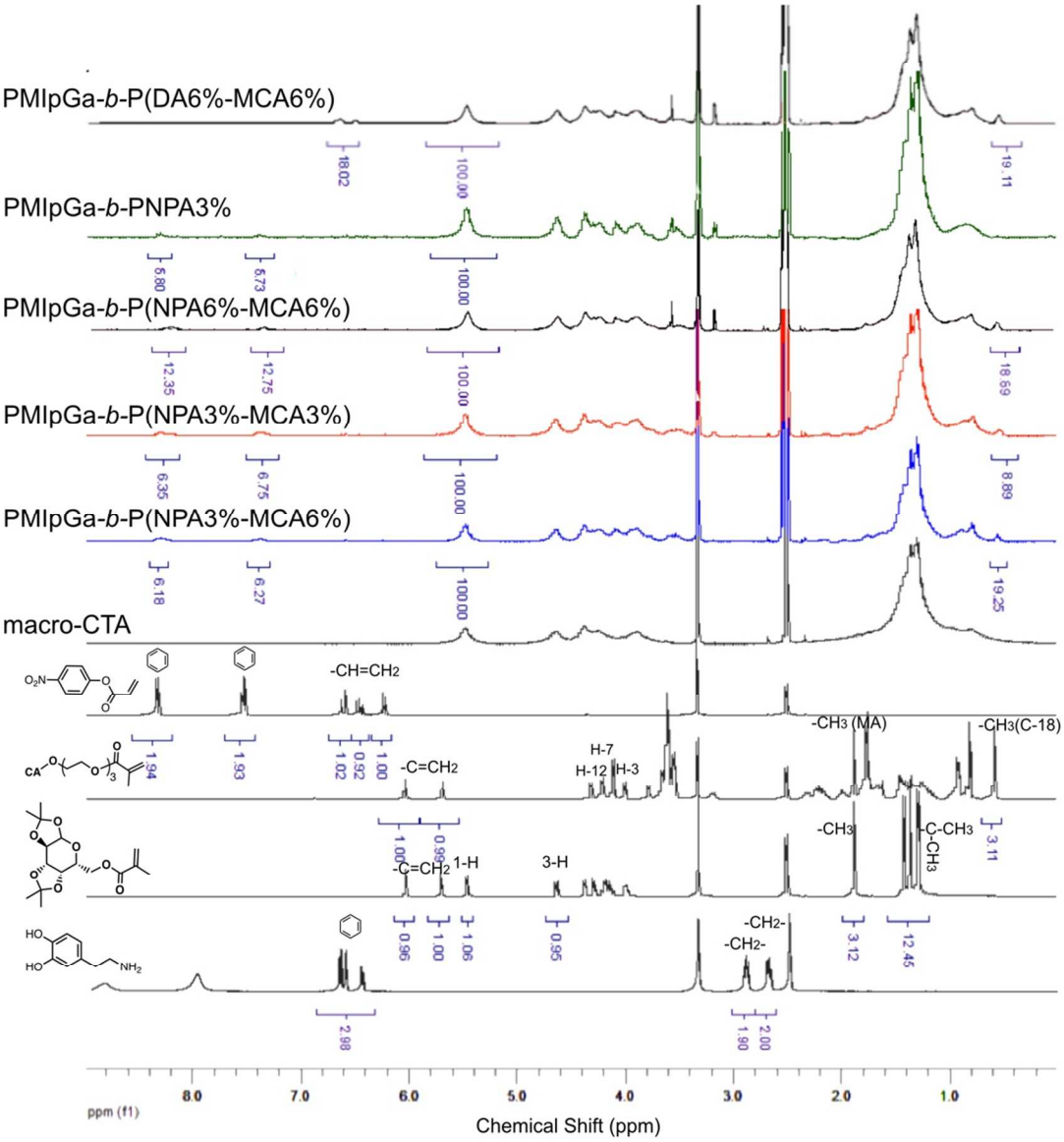

Fig. S1. ^{1}H NMR spectra of the monomers and the copolymers in DMSO-d_6. The peak at 5.53 ppm is attributed to the proton attached to the anomeric carbon in the sugar ring. The peaks at 8.30 and 7.38 ppm are from the benzene ring of the NPA. The signal at 0.63 ppm is assigned to the methylene group of cholic acid. After dopamine substitution, ^{1}H NMR spectra of copolymer PMIpGa-b-P(DA3%-MCA6%) show the dopamine peaks at 6.90-6.50 ppm and the disappearance of the active ester peaks at 8.30 and 7.38 ppm. The dopamine substitution is almost quantitative as estimated from the integration of the ^{1}H NMR signals. The molar percentage of DA and MCA can be calculated from the integration ratios of the peaks at δ = 6.90-6.50 ppm and 0.63 ppm. The

spectrum confirms that the H-3, H-7 and H-12 protons of cholic acid remained unchanged in the MCA monomer.

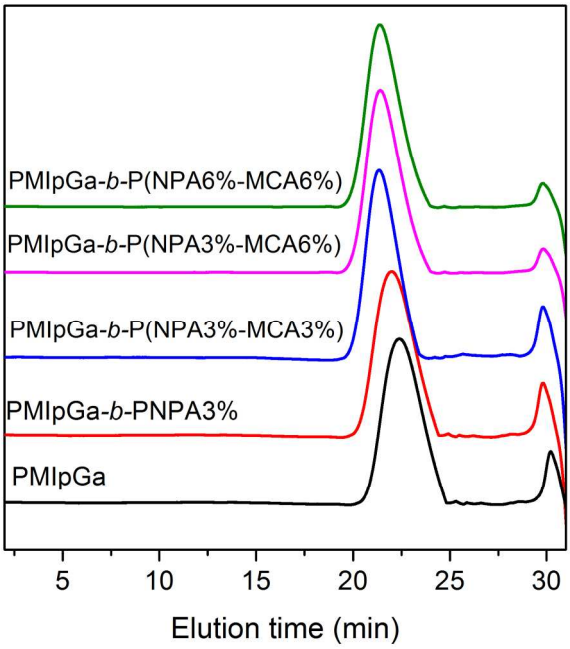

Fig. S2. GPC elution traces of the macro-CTA (PMIpGa) and the copolymers, all protected with the isopropylidene (Ip) group to keep them soluble in THF.

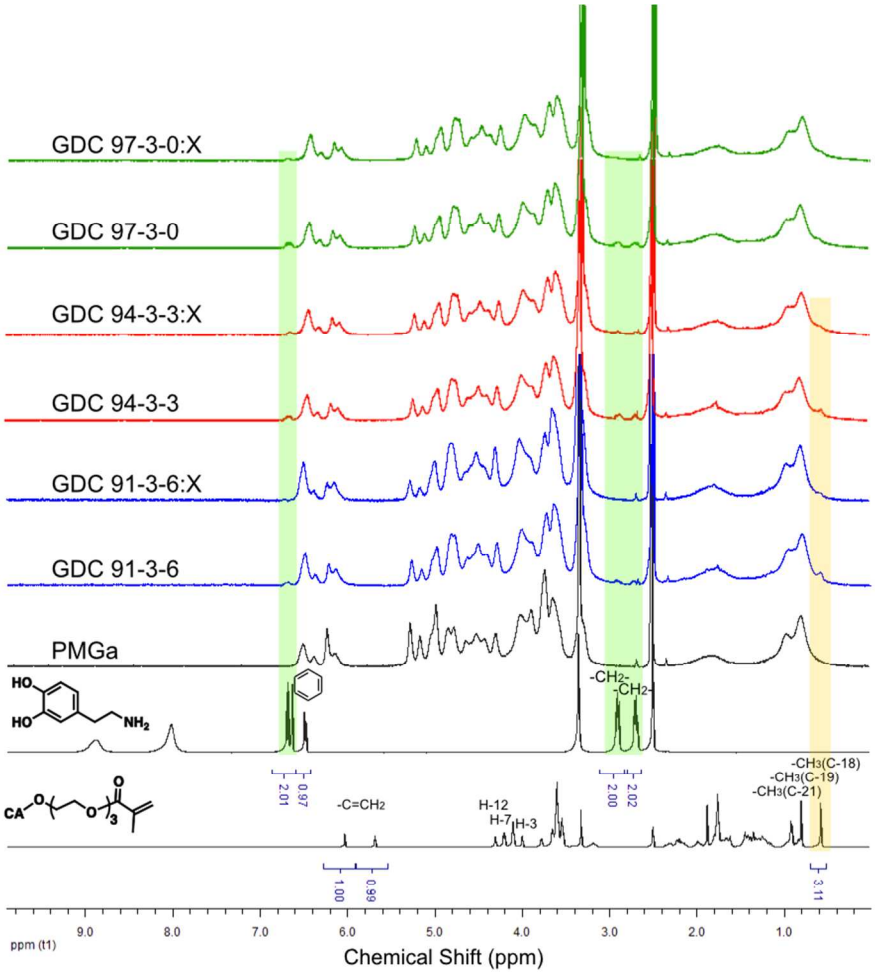

Fig. S3. ^{1}H NMR spectra of the copolymers and the cross-linked micelles (X) in DMSO-d_6. The ^{1}H signals of the small molecules are indicated in the spectra. The disappearance of selected ^{1}H signals upon crosslinking is shown in the shaded areas.

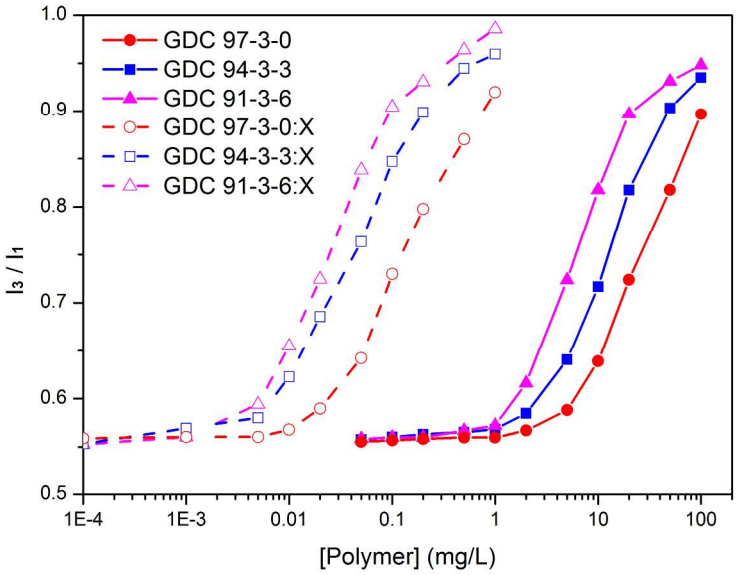

Fig. S4. Variation of the I_3/I_1 ratio of the pyrene fluorescence spectra as a function of polymer concentration for the polymer-water mixtures of 3 different GDC copolymers before and after crosslinking (X).