Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

to

Supracolloidal Chains of Patchy Micelles in Water

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Synthesis of PEO macro-CTA

PEO-OH, PEO-CPB as well as the RAFT agent itself were characterized by ^{1}H-NMR spectroscopy in deuterated chloroform. See Figure S1 for the spectra along with the peak assignments of the compounds. Upon comparison of the monoethoxy PEO-OH and PEO-CBP spectra, we can observe the disappearance of the PEO-OH signal at 2.6 ppm (corresponding to the proton of the alcoholic group), while a signal at 2.0 ppm (corresponding to the methyl group of the CBAP compound located adjacent to the dithioester and nitrile functionality) emerges. This suggests, that the PEO-OH polymers had been succesfully end-capped with the CBPA. SEC investigations on the product revealed a dispersity of 1.08 with Polystyrene standards using THF as eluent. The main peaks form as well as the retention time of 28.5 min is very similar to the SEC measurement of the monoethoxy PEG-OH compound, which is anticipated as there is barely any change in the molecular weight.

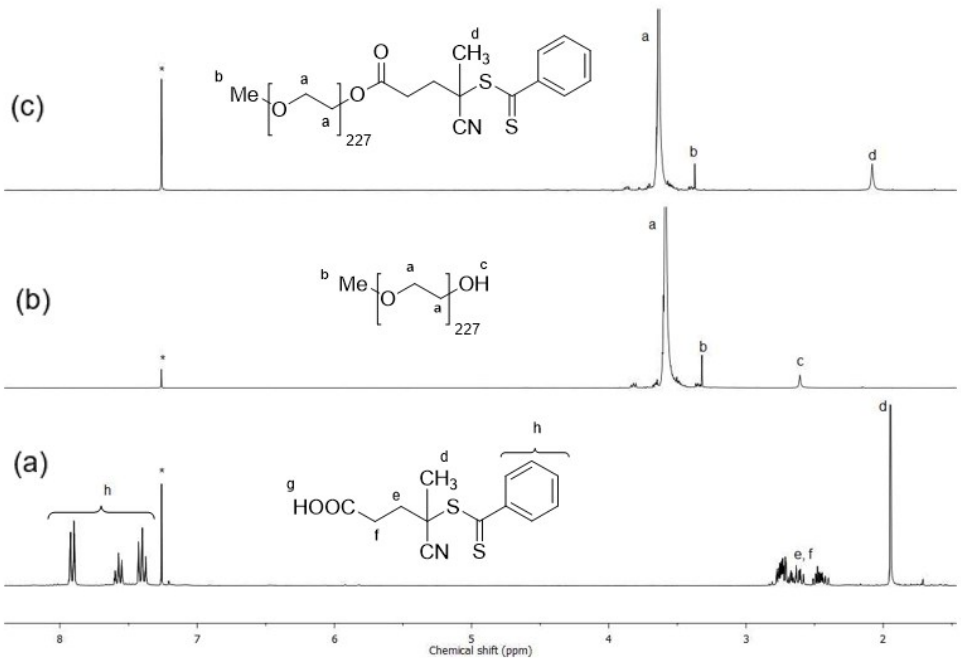

Fig. S1. ^{1}H NMR spectra of a) 4-cyano-4-(thiobenzoylthio)pentanoic acid, b) PEO-OH and c) PEO-CBP. All spectra were recorded in $CDCl_3$.

Table S1. Conditions of polymerization for ABC Triblock Copolymers and its precursors

Polymer	mCTA	Monomer	Solvent	Temp [°C]	Time [h]
PEO_{227}-*b*-PS_{334}	PEO-CTA	St	-	70	4
PEO_{227}-*b*-PS_{102}	PEO-CTA	St	-	70	2
PEO_{227}-*b*-PS_{334}-*b*-$P2VP_{32}$	PEO-*b*-PS-CTA	2VP	DMF	80	48
PEO_{227}-*b*-PS_{102}-*b*-$P2VP_{39}$	PEO-*b*-PS-CTA	2VP	DMF	80	48
PEO_{227}-*b*-PS_{334}-*b*-$P2VP_{227}$	PEO-*b*-PS-CTA	2VP	DMF	90	40

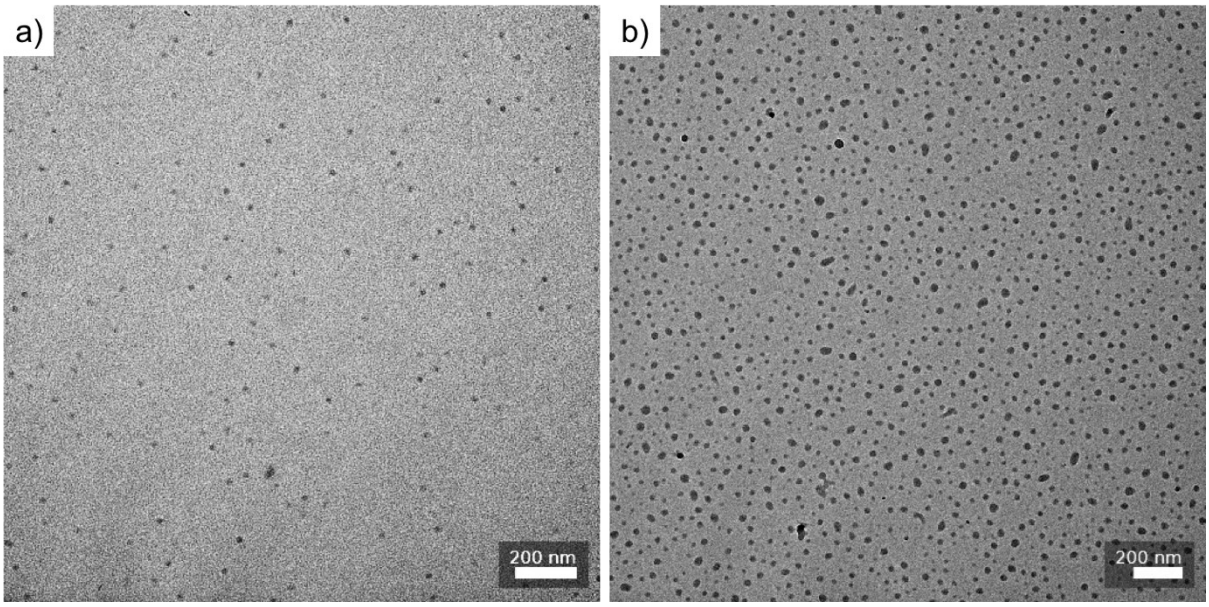

Fig. S2: TEM of patchy sperical micelles after dialysis from THF into acetone/IPA (v/v 4/1) for a) EOSV2 and b) EOSV3.

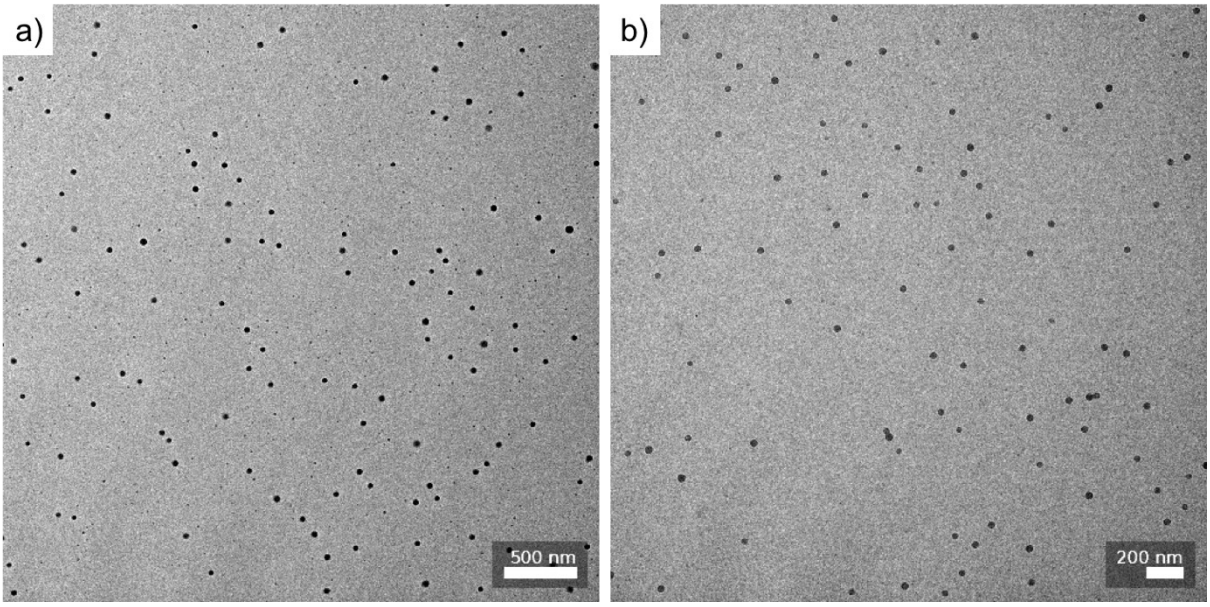

Fig. S3: TEM of patchy sperical micelles of EOSV3 after dialysis from acetone/IPA (v/v 4/1) into water pH 2 before a) and after heat treatment b).

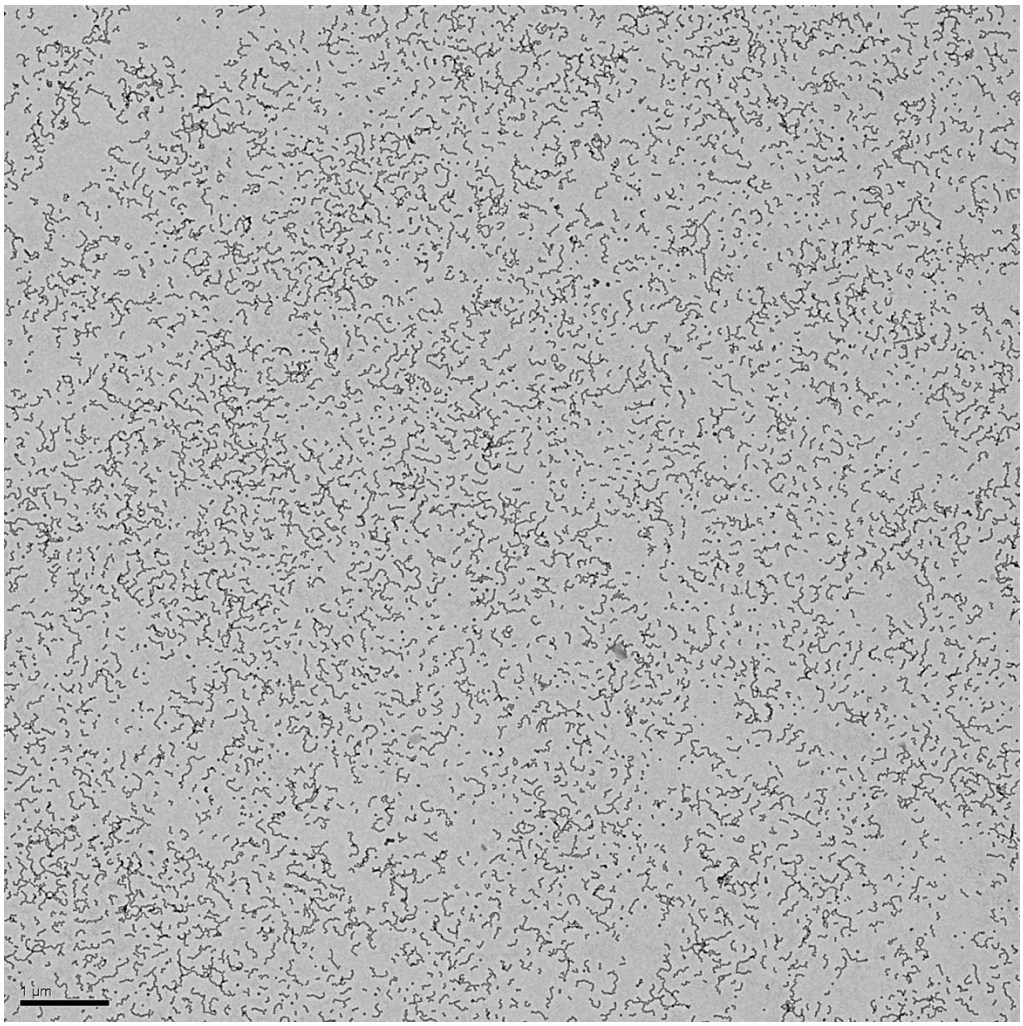

Fig. S4: TEM of EOSV1 dialysed first from THF to acetone/IPA (v/v 4/1) followed by dialysis into milliq water. The chains result from heating at 70°C for 24h.

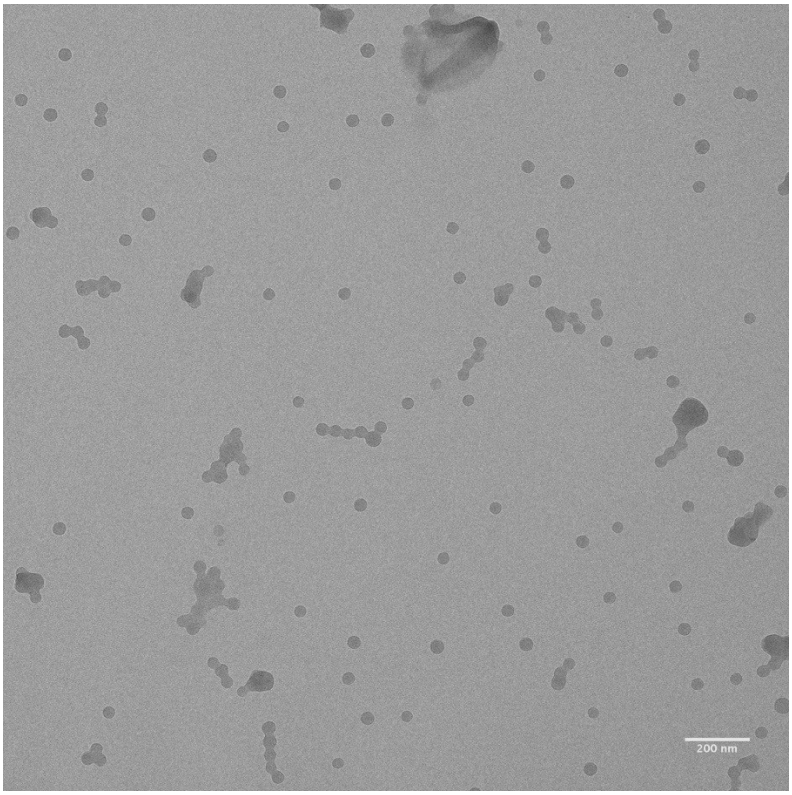

Fig. S5: TEM of EOSV3 dialysed first from THF to acetone/IPA (v/v 4/1) followed by dialysis into milliq water. The clusters result from heating at 70°C for 24h.