Supplementary Material (ESI) for Journal of Materials Chemistry
This journal is (c) The Royal Society of Chemistry 2010

Semiconductor amphiphilic blockcopolymers for hybrid donor-acceptor nanocomposites

Johannes C. Brendel, Hubertus Burchardt, Mukundan Thelakkat

Applied Functional Polymers, Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany

Electronic Supplementary Information (ESI)

Experimental section

Materials and characterization

1H NMR spectra were recorded in chloroform on a Bruker Avance 250 spectrometer at 300 MHz. The spectra were calibrated according to solvent signals. Size exclusion chromatography (SEC) measurements were carried out in THF using a UV detector from Waters and a mixed-C PL-Gel (PL) column. Polystyrene was used as external standard and 1,2-dichlorobenzene as an internal standard for calibration. Matrix-assisted laser desorption ionization spectroscopy with time-of-flight detection mass spectroscopy (MALDI-TOF MS) measurements were performed on a Bruker Reflex I using *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) with silver trifluoroacetate (AgTFA) as matrix and a mixture of 1000:1 (matrix:polymer). The laser intensity was set to around 20%. The reflection mode was calibrated with a fullerite mixture from Sigma-Aldrich (CAS 131159-39-2).

Octadecylphosphonic acid (98%, ABCR) was recrystallized from toluene prior to use. All other reagents were purchased from Sigma-Aldrich or ABCR and used as received. Neopentyl styrene sulfonate (NeoSS) was prepared according to known procedures. (ref Neo).

Synthesis of Bis(4-methoxyphenyl)-4'-vinylphenylamine (DMTPA)

Sodium tert-butoxide (5.04 g, 52.4 mmol), Palladium(II) acetate (0.094 g, 0.420 mmol), 4-Bromoanisole (7.90 ml, 62.9 mmol) and 4-Vinylaniline (2.5 g, 20.98 mmol) were dissolved in Toluene (80 ml) and degassed with an Argon stream for 30 min. Tri-tert-butylphosphine (0.424 g, 2.098 mmol) was added and the reaction was stirred for 12 h at 100°C. The reaction mixture was filtered through Alox B and washed with Aceton. The organic layer was concentrated using a rotary evaporator. The crude product was purified by column chromatography with toluene. After evaporation of the solvent the oil was added to degased hexane and storred at 4°C for crystallization as a white solid (4 g, 72%);

^{1}H-NMR (300 MHz, CD_2Cl_2): δ 7.26 (d, $J = 8.6$ Hz, 2H), 7.07 (d, $J = 9.0$ Hz, 4H), 6.83-6.92 (m, 6H), 6.67 (dd, $J = 17.6$ Hz, $J = 10.9$ Hz, 1H), 5.62 (dd, $J = 17.6$ Hz, $J = 0.8$ Hz, 1H), 5.12 (dd, $J = 10.9$ Hz, $J = 0.8$ Hz, 1H), 3.81 (s, 6H); MS (*m/z*, M+) 331 (57.3).

Synthesis of PNeoSS homopolymer

Under Argon, NeoSS (2 g, 7.86 mmol), 2-cyanopropan-2-yl benzodithioate (23.2 mg, 0.11 mmol) and 2,2'-Azobisisobutyronitrile (3.4 mg, 0.021 mmol) were added to a 5 mL schlenk flask and dissolved in 2 ml Anisole. The reaction mixture was degassed by three freeze-thaw cycles and the reaction was started in an oil bath at 80°C. The reaction was stopped after 18 h by immersing the flask into an ice bath. For purification the reaction mixture was diluted with few chloroform and added to hexane for precipitation of the polymer. The solid polymer was filtered off and dissolved again in a small amount of chloroform. After the second precipitation in hexane no further monomer could be detected by NMR. M_w (SEC) = 12900 g/mol, PDI = 1.06; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.93-7.46 (m, -O-SO_2-$C_3\mathit{H_2}$=C_3H_2-, 2H), 7.00-6.36 (m, -SO_3-C_3H_2=$C_3\mathit{H_2}$-, 2H), 3.92-3.60 (m, -O-$C\mathit{H_2}$-$C(CH_3)_3$, 2H), 2.22-1.70 (m, -$CH_2C\mathit{H}$-C_6H_4-SO_3-, 1H), 1.69-1.04 (m, -$C\mathit{H_2}CH$-C_6H_4-SO_3-, 2H), 1.02-0.76 (m, -OCH_2-$C(C\mathit{H_3})_3$, 9H).

Synthesis of PDMTPA(1)

Under Argon, DMTPA (2 g, 6.03 mmol), 2-cyanopropan-2-yl benzodithioate (26.7 mg, 0.12 mmol) and 2,2'-Azobisisobutyronitrile (4.0 mg, 0.024 mmol) were added to a 5 mL schlenk flask and dissolved in 2 ml Anisole. The reaction mixture was degassed by three freeze-thaw cycles and the reaction was started in an oil bath at 60°C. The reaction was stopped after 22 h by immersing the flask into an ice bath. For purification the reaction mixture was diluted with few THF and added to hexane for precipitation of the polymer. The solid polymer was filtered off and dissolved again in a small amount of THF. After the second precipitation in hexane no further monomer could be detected by NMR. M_w (SEC) = 3510 g/mol, PDI = 1.09; ^{1}H-NMR (300 MHz, C_6D_6): δ 7.23-6.50 (m, CH_3-O-$C_6\mathit{H_4}$-N-, -CH_2CH-$C_6\mathit{H_4}$-N-, 12H), 3.45-3.17 (m, $C\mathit{H_3}$-O-C_6H_4-N-), 6H), 2.78-2.23 (m, -$CH_2C\mathit{H}$-C_6H_4-N-, 1H), 2.07-1.59 (m, -$C\mathit{H_2}CH$-C_6H_4-N-, 2H).

Synthesis of PDMTPA(2)

The same procedure as for PMDTPA(1) was used except the temperature was raised to 80°C and the polymerization was stopped after 4 h. M_w (SEC) = 6440 g/mol, PDI = 1.12.

Synthesis of PDMTPA(3)

Here the temperature was 100°C and the polymerization was stopped after 1 h. M_w (SEC) = 5510 g/mol, PDI = 1.11.

Synthesis of PDMTPA(4)

To lower the polarity of the surrounding medium benzene was used as solvent and the temperature was kept at 60°C. The polymerization was stopped after 22 h. M_w (SEC) = 4840 g/mol, PDI = 1.07.

Synthesis of PNeoSS-*b*-PDMTPA

Under Argon, PNeoSS (0.25 g), DMTPA (0.55 g, 1.66 mmol) and 2,2'-Azobisisobutyronitrile (0.5 mg, 0.003 mmol) were added to a 5 mL schlenk flask and dissolved in 1.6 ml Anisole. The reaction mixture was degassed by three freeze-thaw cycles and the reaction was started in an oil bath at 80°C. The reaction was stopped after 6 h by immersing the flask into an ice bath. For purification the reaction mixture was diluted with few THF and added to hexane for precipitation of the polymer. The solid polymer was filtered off and dissolved again in a small amount of THF. After the second precipitation in hexane no further monomer could be detected by NMR.
M_w (SEC) = 23560 g/mol, PDI = 2.60; ^{1}H-NMR (300 MHz, C_6D_6): δ 7.93-7.46 (m, -O-SO_2-C_3H_2=C_3H_2-, 2H), 7.23-6.50 (m, CH_3-O-C_6H_4-N-, -CH_2CH-C_6H_4-N-, -SO_3-C_3H_2=C_3H_2-, 14H), 4.15-3.69 (m, -SO_2-O-CH_2-C$(CH_3)_3$, 2H), 3.45-3.17 (m, CH_3-O-C_6H_4-N-), 6H), 2.78-2.23 (m, -CH_2CH-C_6H_4-, 1H), 2.07-1.59 (m, -CH_2CH-C_6H_4-, 2H), 1.04-0.63 (m, -OCH_2-C$(CH_3)_3$, 9H).

Synthesis of PDMTPA(1-4)-*b*-PNeoSS

All polymerizations were carried out under equal conditions. Therefore the ratio of macro-CTA/NeoSS/AIBN was kept at 1/100/0.4. A representative synthesis proceeded as follows. Under Argon, PDMTPA(1) (0.2 g), NeoSS (0.85 g, 3.33 mmol) and 2,2'-Azobisisobutyronitrile (1.1 mg, 0.007 mmol) were added to a 5 mL schlenk flask and dissolved in 1 ml Anisole. The reaction mixture was degassed by three freeze-thaw cycles and the reaction was started in an oil bath at 80°C. The reaction was stopped after 22 h by immersing the flask into an ice bath. For purification the reaction mixture was diluted with few THF and added to hexane for precipitation of the polymer. The solid polymer was filtered off and dissolved again in a small amount of THF. After the second precipitation in hexane no further monomer could be detected by NMR.

PDMTPA(1)-*b*-PNeoSS: M_w (SEC) = 6220 g/mol, PDI = 1.30;
PDMTPA(2)-*b*-PNeoSS: M_w (SEC) = 11100 g/mol, PDI = 1.28;
PDMTPA(3)-*b*-PNeoSS: M_w (SEC) = 11790 g/mol, PDI = 1.34;
PDMTPA(4)-*b*-PNeoSS: M_w (SEC) = 15860 g/mol, PDI = 1.37;
^{1}H-NMR (300 MHz, C_6D_6): δ 7.93-7.46 (m, -O-SO_2-C_3H_2=C_3H_2-, 2H), 7.23-6.50 (m, CH_3-O-C_6H_4-N-, -CH_2CH-C_6H_4-N-, -SO_3-C_3H_2=C_3H_2-, 14H), 4.15-3.69 (m, -SO_2-O-CH_2-C$(CH_3)_3$, 2H), 3.45-3.17 (m, CH_3-O-C_6H_4-N-), 6H), 2.78-2.23 (m, -CH_2CH-C_6H_4-, 1H), 2.07-1.59 (m, -CH_2CH-C_6H_4-, 2H), 1.04-0.63 (m, -OCH_2-C$(CH_3)_3$, 9H).

Deprotection of the sulfonate group

PDMTPA(4)-*b*-PNeoSS (0.1 g) was dissolved in DMF (7 ml) and degassed by an argon stream for 30 min. After addition of a 1M tetrabutylammonium hydroxide solution in methanol (3 ml, 4.65 mmol) the mixture was stirred for 2.5 h at 150°C. To remove the methanol and the resulting neopentanol a destillation bridge was attached to the flask. After cooling to room temperature, methanol was added dropwise to induce the micelle formation. This dispersion was dialyzed first against methanol and secondly against purified water.

^{1}H-NMR (300 MHz, C_6D_6): δ 7.80-7.08 (m, $\text{-O-SO}_2\text{-C}_3H_2\text{=C}_3\text{H}_2\text{-}$, 2H), 6.99-5.94 (m, $\text{CH}_3\text{-O-C}_6H_4\text{-N-}$, $\text{-CH}_2\text{CH-C}_6H_4\text{-N-}$, $\text{-SO}_3\text{-C}_3\text{H}_2\text{=C}_3H_2\text{-}$, 14H), 3.89-3.34 (m, $\text{C}H_3\text{-O-C}_6\text{H}_4\text{-N-}$), 6H), 3.29-2.88 (m, $\text{+N(-C}H_2\text{-CH}_2\text{-CH}_2\text{-CH}_3)_4$, 8H), 1.97-1.34 (m, $\text{-CH}_2\text{C}H\text{-C}_6\text{H}_4\text{-}$, $\text{-C}H_2\text{CH-C}_6\text{H}_4\text{-}$, 1H), 1.66-1.39 (m, $\text{+N(-CH}_2\text{-C}H_2\text{-CH}_2\text{-CH}_3)_4$, 8H), 1.36-1.13 (m, $\text{+N(-CH}_2\text{-CH}_2\text{-C}H_2\text{-CH}_3)_4$, 8H), 0.96-0.80 (m, $\text{+N(-CH}_2\text{-CH}_2\text{-CH}_2\text{-C}H_3)_4$, 12H).

Synthesis of CdSe nanorods

The CdSe particles were prepared according to published procedures with slight modifications. (ref cdse) cadmium oxide (0.205 g, 1.60 mmol), tri-n-octylphosphine oxide (3.00 g, 7.76 mmol), octadecylphosphonic acid (0.97 g, 2.91 mmol) and methylphosphonic acid (0.03 g, 0.29 mmol) were loaded into a schlenk flask and then heated to 320°C under argon until all the cadmium oxide reacted to give a transparent solution. The solution was kept at 320°C for 10 min and then it was cooled to room temperature under argon flow. After aging for at least 48 h, the mixture was directly used without further purification. Selenium (0.06 g, 0.80 mmol) was stirred in tri-n-octylphosphine (1.48 g, 4.00 mmol) over night to obtain the injection solution. This solution was injected to the Cd solution at 320°C. The crystals were allowed to grow for 8 min at 300°C, after which the heating bath was removed and the mixture was allowed to cool down to room temperature. Chloroform (5 ml) was added into the flask at ~50°C and the nanorods were precipitated out by addition of methanol (10-15 ml). For purification the CdSe nanorods were separated by centrifugation and decantation and then dissolved in chloroform. This procedure was repeated several times to remove the residual ligands.

For the ligand exchange, the cadmium selenide nanoparticles (0.20 g) were dispersed in DCM (100 ml) and poured into a schlenk flask. Aminoethanethiol hydrochloride (6 g, 52.8 mmol) was added and the dispersion was degassed with an argon stream for 30 min. For exchange of the phosphonic acid ligands the mixture was refluxed for 20 h. For precipitation of the particles Ethanol (100 ml) was added to the hot solution and the mixture was refluxed for another hour. For purification the particles were dispersed in methanol and centrifuged five times to remove the residual ligands. Finally the particles were dried, redispersed in water solution and filtered through a 0.2 µm Nylon filter to remove larger aggregates.

Blockcopolymerization starting from PNeoSS as macro-CTA

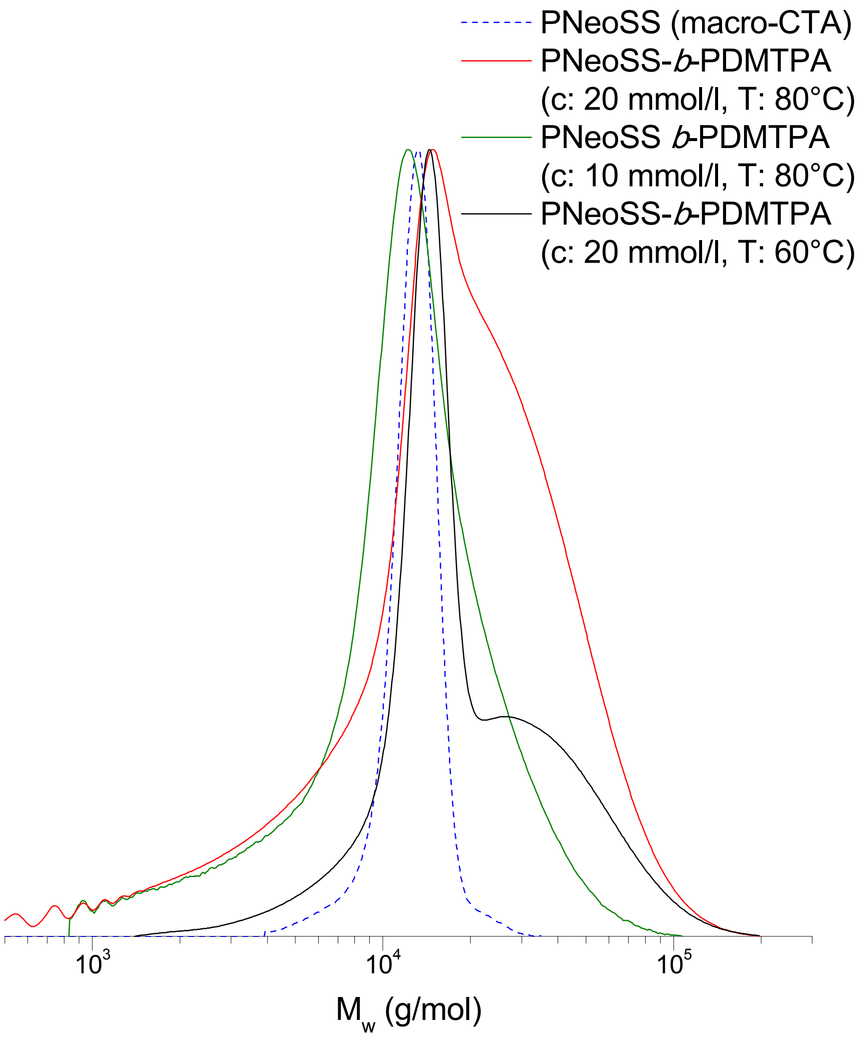

Fig. S1 GPC traces of the resulting blockcopolymers starting from PNeoSS. The dashed line presents the macro-CTA. The reaction ratios macro-CTA/DMTPA/AIBN were kept at 1/100/0.4. The temperature and concentration were varied according to the values given in the plot.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) measurements of the macro-CTAs PDMTPA(1), PDMTPA(2), PDMTPA(3) and PDMTPA(4)

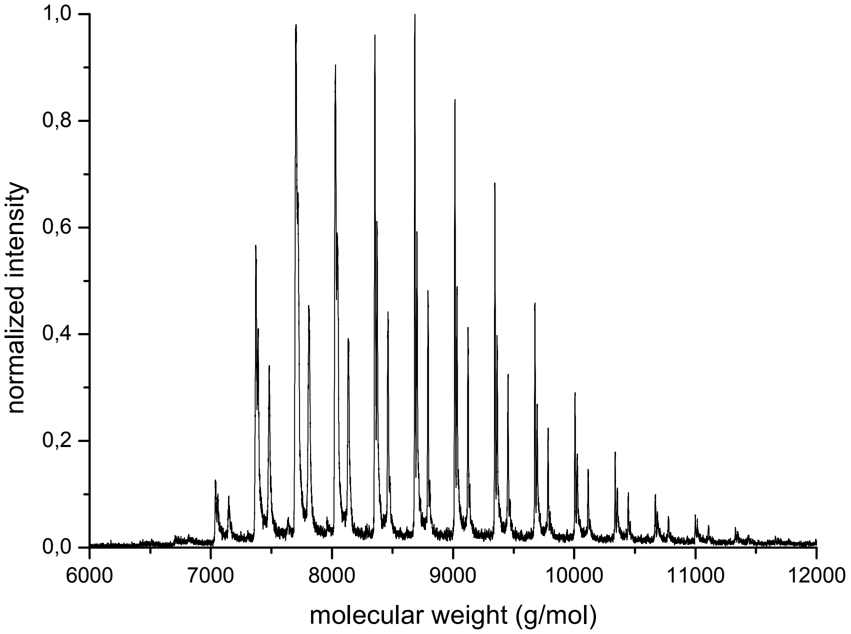

Fig. S2 MALDI spectrum of PDMTPA(1).

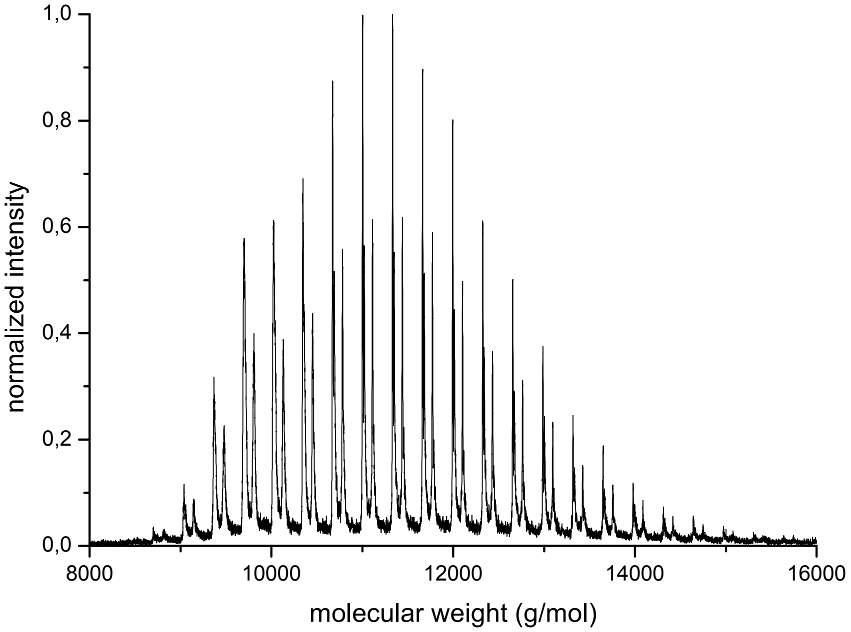

Fig. S3 MALDI spectrum of PDMTPA(2).

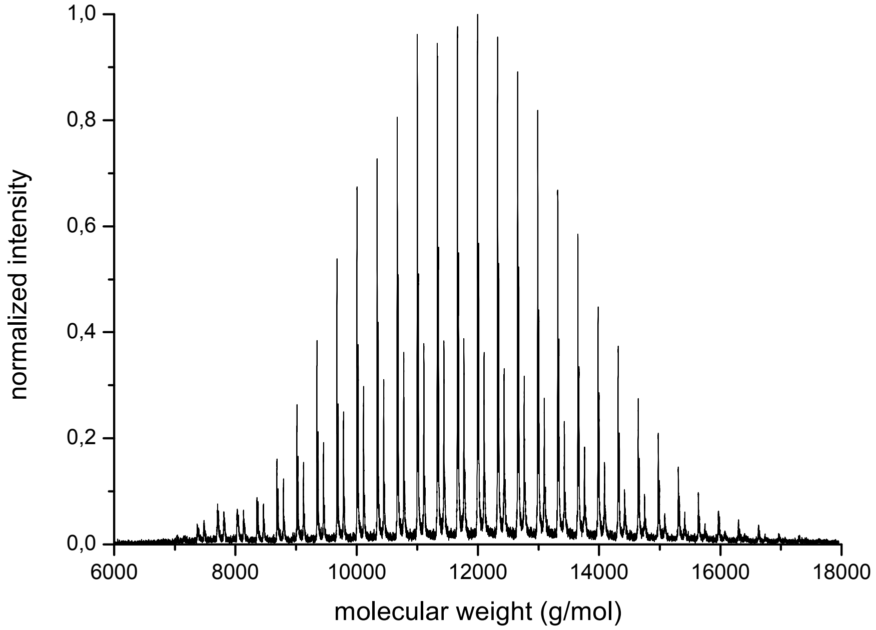

Fig. S4 MALDI spectrum of PDMTPA(3).

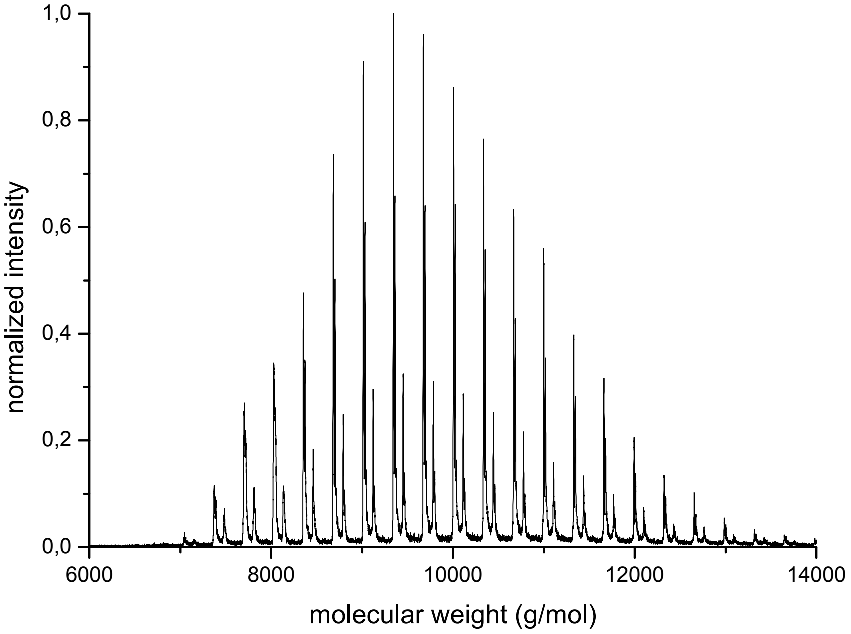

Fig. S5 MALDI spectrum of PDMTPA(4).

Self-initiation test of the DMTPA monomer

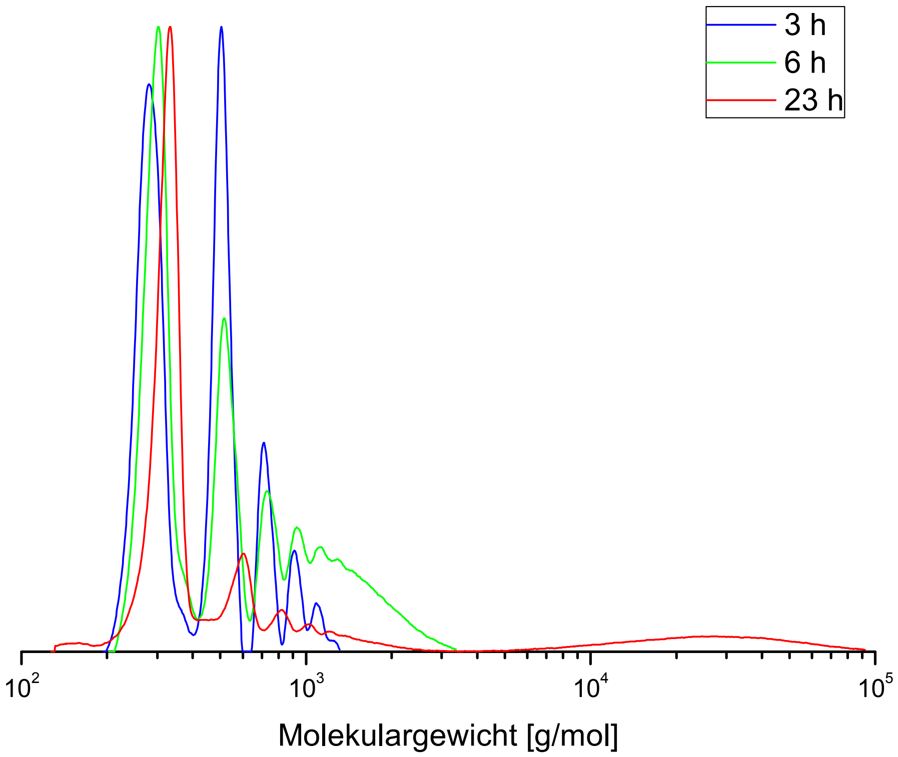

Fig. S6 GPC traces of samples taken from a polymerization of DMTPA without AIBN initiator.

Deprotection of sulfonate groups

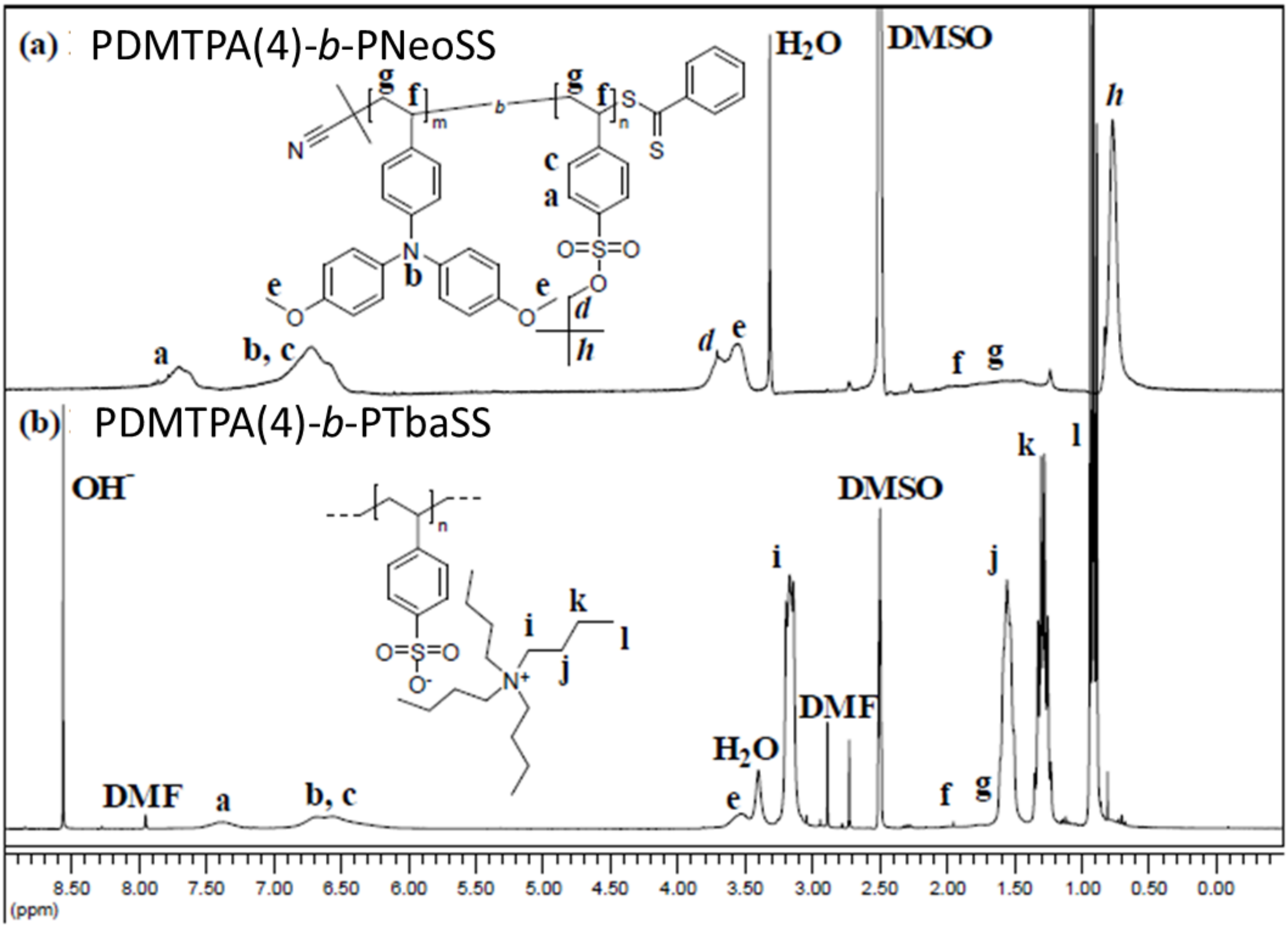

Fig. S7 NMR-spectra of the blockcopolymer PDMTPA(4)-*b*-PNeoSS and the deprotected polymer PDMTPA(4)-*b*-PTbaSS.

TEM of the CdSe nanoparticles

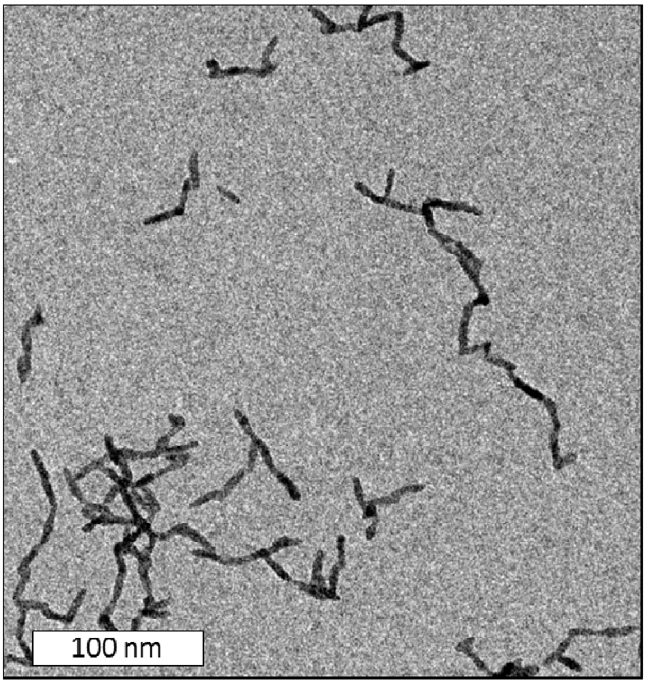

Fig. S8 Transmission electron micrograph of the prepared CdSe nanoparticles