Supplementary Material (ESI) for Soft Matter

Supporting Information

Well-Defined Star Shaped Polymer-Fullerene Hybrids via *Click* Chemistry

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Experimental Section

Materials

Structure **1** (see main manuscript),[1] 2-hydroxyethyl-2'-bromopropionate,[2] 4,4'-azobis(4-cyanopentanol) (ACP),[3] 4-cyano-1-hydroxypent-4-yl dithiobenzoate (RAFT ACP)[4] and *S*-1-dodecyl-*S'*-(α, α'-dimethyl-α''-propargylacetate)[5] were synthesized according to literature procedures. Styrene (Aldrich) was passed through a column of basic alumina and stored at -19 °C. 2,2'-azobis(isobutyronitrile) (AIBN, Sigma-Aldrich) was recrystallized twice from methanol before use and stored at -19 °C. Copper (I) bromide (Fluka) was purified by sequential washing with sulphurous acid, acetic acid and ethanol, followed by drying under reduced pressure. Copper (II) sulfate pentahydrate (Aldrich), *N,N'*-dicyclohexylcarbodiimide (DCC, Aldrich), 4-dimethylaminopyridine (DMAP, Aldrich), poly(ethylene glyol) monomethyl ether 2000 (Aldrich), hexylamine (99 %, Aldrich), sodium ascorbate (Acros), 4-pentynoic acid (95 %, Aldrich), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, Merck), and triphenylphosphine (Ph_3P, 99 %, Aldrich) were used as received.

Measurements

The structures of the synthesized compounds were confirmed by ^{1}H-NMR spectroscopy using a Bruker AM 500 spectrometer at 500 MHz for hydrogen nuclei. All samples were dissolved in $CDCl_3$. The δ-scale is referenced to tetramethylsilane (δ = 0.00 ppm) as internal standard.

GPC measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5µm bead-size guard column (50 x 7.5 mm) followed by three PLgel 5µm MixedC columns (300 x 7.5 mm) and a differential refractive index detector using *N,N'*- dimethylacetamide (DMAc) with 0.3 wt% LiBr as the eluent at 50 °C with a flow rate of 1.0 mL·min^{-1}. The GPC system was calibrated against linear poly(styrene) standards with molecular weights ranging from 160 to $6\cdot10^6$ g·mol^{-1}.

UV/Vis spectroscopy was performed using a Cary 300 Bio UV/Vis Photospectrometer (Varian). Absorption was measured in dichloromethane solution from 200 nm to 800 nm with a resolution of 1 nm in a 10 mm UV cuvette. Cloud points were measured on the same apparatus. Aqueous solutions of PNIPAM (3 mg·mL^{-1}) were heated at 0.5 °C·min^{-1}. Both the temperature, as determined by the internal temperature probe, and the transmittance of the aqueous solutions were monitored at a wavelength of 700 nm.

Synthesis

ATRP of styrene: Copper (I) bromide was added to a dried Schlenk tube and sealed under nitrogen. Into another Schlenk tube was added styrene and PMDETA. The resulting monomer solution was then deoxygenated by three freeze-pump-thaw cycles and subsequently transferred to the copper (I) bromide via cannula. The tube was sealed under a nitrogen atmosphere and placed in a thermostatic oil bath set to 110 °C. 2-hydroxyethyl-2'-bromopropionate was then added via syringe. The initial ratio of [styrene]:[initiator]:[CuBr]:[PMDETA] was 2100:1:1:1. The polymerization was stopped by cooling the mixture in an ice bath and exposure to oxygen. The mixture was then diluted with the addition of THF and passed through a column of neutral alumina to remove the copper catalyst. Hydroxy-functionalized poly(styrene) PS-OH was obtained as a white powder after two-fold precipitation in cold methanol. GPC (DMAc): M_n = 12 200 g·mol^{-1}, *PDI* = 1.19.

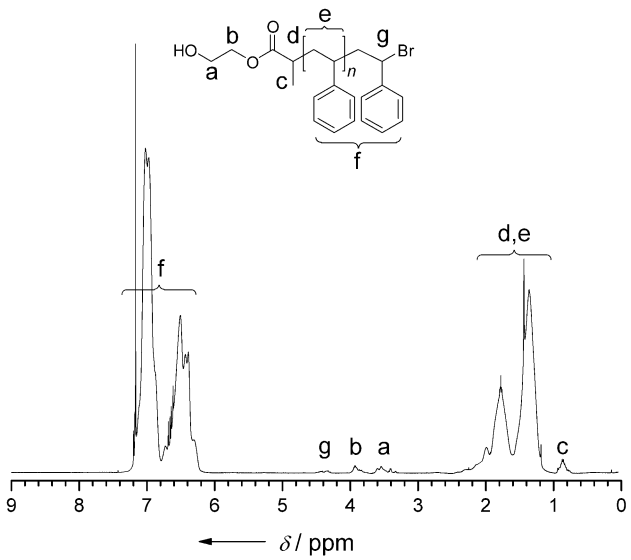

Fig S1. ^{1}H-NMR spectrum of PS-OH synthesized by ATRP.

RAFT Polymerization of styrene: A mixture of styrene, 4,4'-azobis(4-cyanopentanol), 4-cyano-1-hydroxypent-4-yl dithiobenzoate and 4,4'-azobis(4-cyanopentanol) was prepared with ratios of [styrene]:[RAFT ACP]:[ACP] = 440:1:0.17. The mixture was deoxygenated by purging with nitrogen for 40 min. The mixture was then placed in a thermostatic oil bath set to 65 °C. After 24 hr, the polymerization was stopped by chilling in an ice bath and exposure to oxygen. Hydroxy-functionalized poly(styrene) PS-OH was obtained as a pink powder by two-fold precipitation in cold methanol. GPC (DMAc): M_n = 4200 g·mol^{-1}, *PDI* = 1.06.

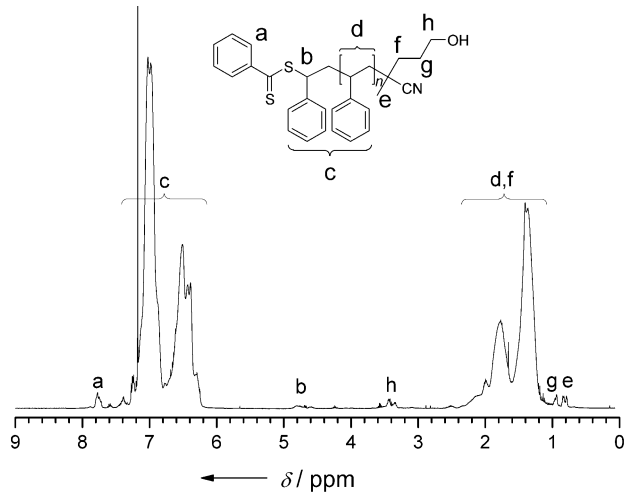

Fig S2. ^{1}H-NMR spectrum of PS-OH synthesized by RAFT polymerization.

RAFT Polymerization of *N*-isopropylacylamide (5): A solution of *N*-isopropylacrylamide (NIPAM), *S*-1-dodecyl-*S'*-(*α, α'*-dimethyl-*α''*-propargylacetate) (DDPA) and AIBN in 1,4-dioxane (29 mL) was prepared with the following composition: [NIPAM]:[DDPA]:[AIBN] = 50:1:0.05. The mixture was deoxygenated by purging with nitrogen for 40 min and then placed in a thermostatic oil bath set to 70 °C. After 100 min, the polymerization was stopped by cooling the mixture in an ice bath and exposure to oxygen. Alkyne-functionalized PNIPAM **5** was obtained as a yellow powder after two-fold precipitation in cold diethyl ether. GPC (DMAc): M_n = 10 500 g·mol^{-1}, *PDI* = 1.10.

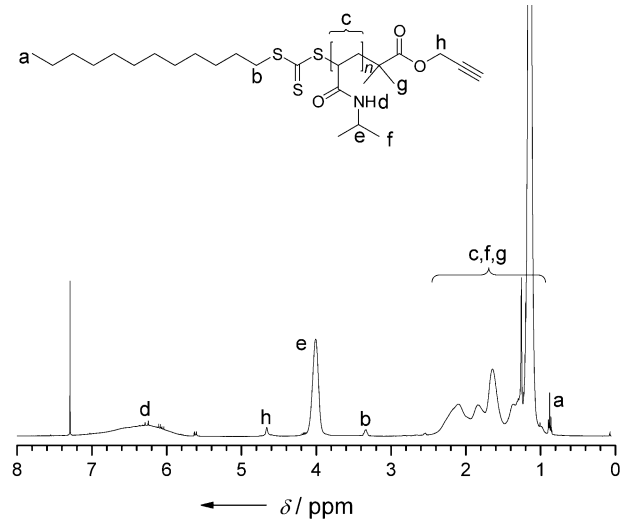

Fig S3. ^{1}H-NMR spectrum of PNIPAM **5**.

Synthesis of Alkyne Functionalized PEG (2): Poly(ethylene glycol) monomethyl ether (2.0 g, 1.0 mmol), 4-pentynoic acid (294 mg, 3.0 mmol) and DMAP (24.4 mg, 0.2 mmol) were dissolved in dichloromethane (15 mL). The resulting mixture was cooled to 0 °C and a solution of DCC (619 mg, 3.0 mmol) in dichloromethane (5 mL) was added dropwise. After the addition, the stirred mixture was allowed to warm to room temperature and allowed to continue stirring at this temperature for 20 hr. The formed precipitate was removed by filtration and the polymer was recovered from the filtrate by two-fold precipitation in cold diethyl ether. Yield: 1.91 g, 91 %. GPC (DMAc): M_n = 2010 g·mol^{-1}, *PDI* = 1.04.

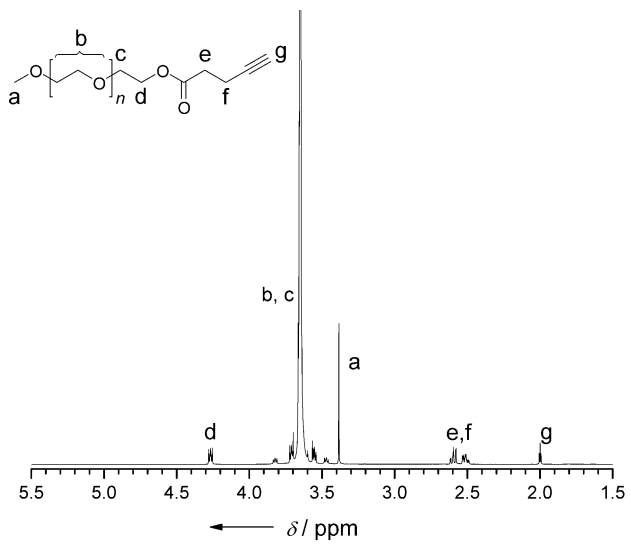

Fig S4. ^{1}H-NMR spectrum of PEG **2**.

Synthesis of alkyne terminated PS (3,4): PS-OH prepared by ATRP or RAFT (0.2 mmol), 4-pentynoic acid (58.8 mg, 0.6 mmol) and DMAP (4.9 mg, 0.04 mmol) were dissolved in dichloromethane (15 mL). The resulting mixture was cooled to 0 °C and a solution of DCC (124 mg, 0.6 mmol) in dichloromethane (5 mL) was added dropwise. After the addition, the stirred mixture was allowed to warm to room temperature and allowed to continue stirring at this temperature for 20 hr. The formed precipitate was removed by filtration and the polymer was recovered from the filtrate by two-fold precipitation in cold methanol.

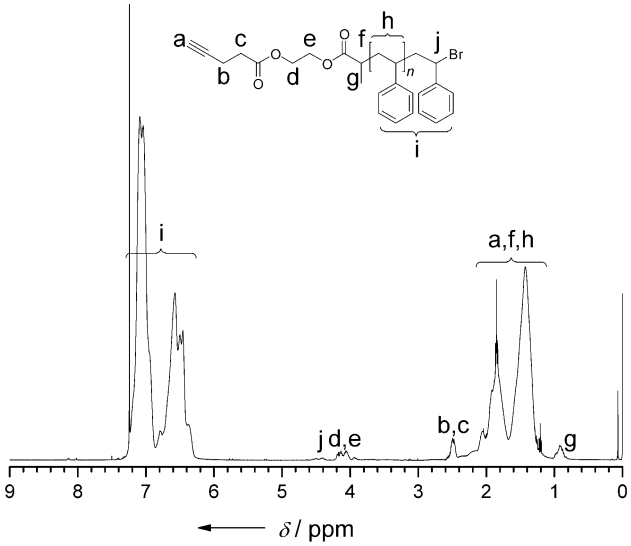

Fig S5. ^{1}H-NMR spectrum of PS**3**.

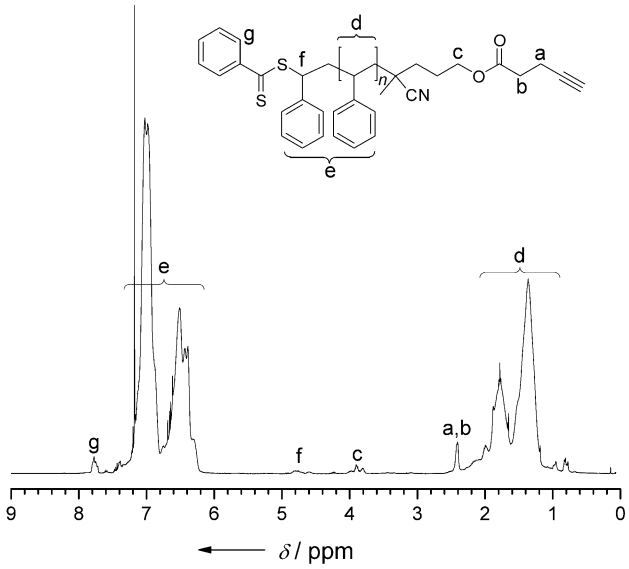

Fig S6. ^{1}H-NMR spectrum of PS **4**.

Click Reactions (Typical Procedure): Hexakisazido fullerene derivative **1** (5.0 mg, 1.27 mmol), alkyne terminated polymer (6 equiv.), copper (II) sulfate pentahydrate (18 equiv.) and sodium ascorbate (18 equiv.) were dissolved in DMF (1.0 mL). The resulting mixture was stirred at room temperature for 24 h before the copper catalyst was removed by passage through a short column of neutral alumina. The solvent was removed under reduced pressure and the residue directly analyzed by GPC and ^{1}H-NMR spectroscopy.

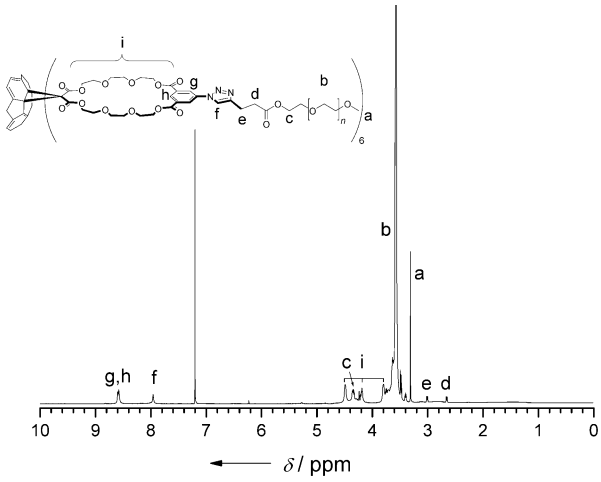

Fig S7. ^{1}H-NMR spectrum of PEG_6 **6**.

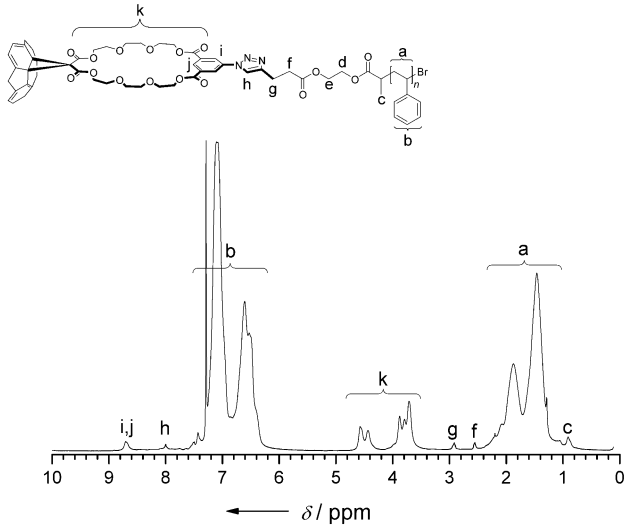

Fig S8. ^{1}H-NMR spectrum of PS_6 **7**.

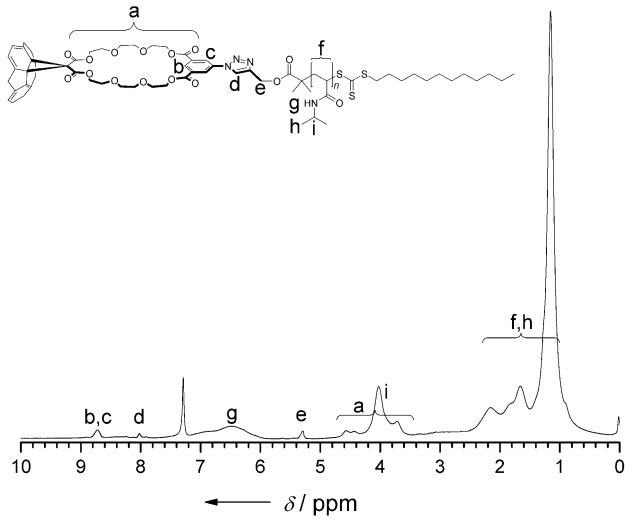

Fig S10. ^{1}H-NMR spectrum of $PNIPAM_6$ **9**.

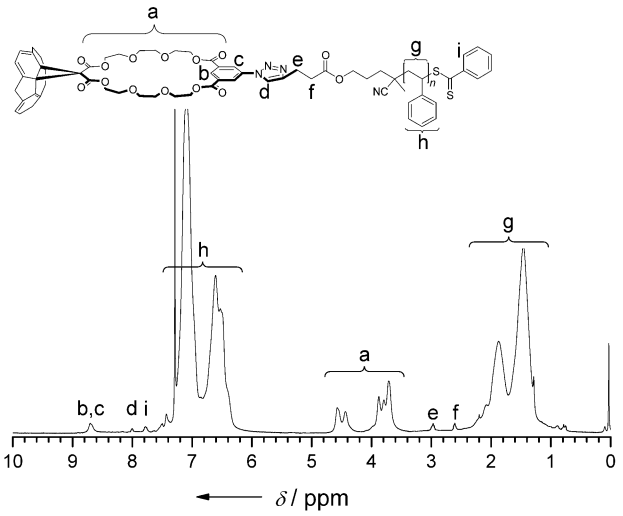

Fig S9. ^{1}H-NMR spectrum of PS_6 **8**.

Aminolysis of $PNIPAM_6$ 9: Under a nitrogen atmosphere, the star-shaped click product $PNIPAM_6$ **9** (20 mg, $3.27 \cdot 10^{-4}$ mmol) was dissolved in DMF (1.0 mL) in the presence of hexylamine and triphenylphosphine ([$PNIPAM_6$ **9**]:[hexylamine]:[Ph_3P] = 1:10:1). The resulting mixture was allowed to stir at room temperature for 5 h. Thiol terminated $PNIPAM_6$ **10** was obtained by precipitation in cold diethyl ether and drying under reduced pressure. GPC (DMAc): M_n = 41 700 g·mol^{-1}, *PDI* = 1.11.

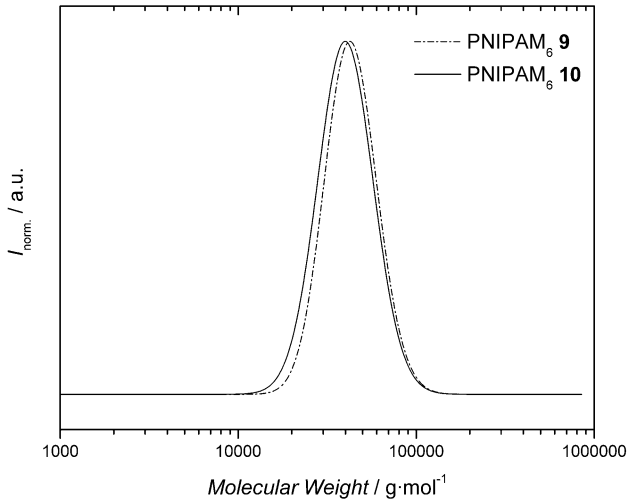

Fig S11. Molecular weight distribution of $PNIPAM_6$ **9** in comparison to that of the aminolysis product $PNIPAM_6$ **10**.

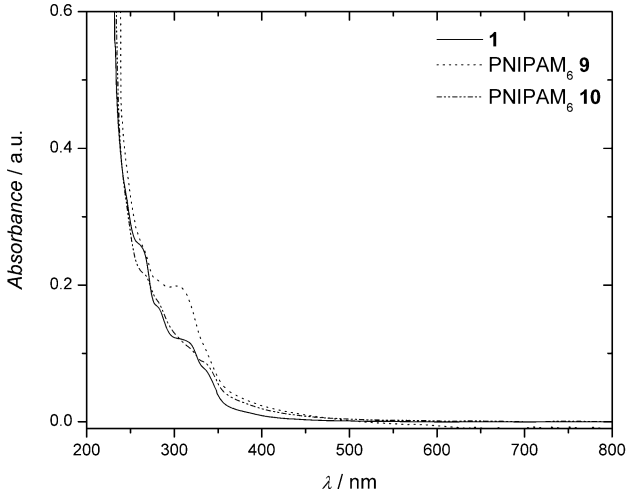

Fig S12. UV/Vis spectra of $PNIPAM_6$ **9** in comparison to the precursor **1** and the aminolysis product $PNIPAM_6$ **10**.

Discussion

Figure 3 in the main manuscript shows the optical transmittance of a 3 mg mL^{-1} aqueous solution of the modified $PNIPAM_6$ **10** at various temperatures, measured at a wavelength of 700 nm. At ambient temperature, the aqueous $PNIPAM_6$ **10** exhibits an optical transmittance of ~ 50 %. Existing reports on the thermoresponsive behaviour of linear PNIPAM-fullerene conjugates describe reduced optical transmittance of aqueous solutions of such structures (~50–70 %) at ambient temperature.[6,7] This has been ascribed to characterisics such as the colour of the solution and the formation of self-assembled aggregates due to the high hydrophobicity of the fullerene component. A similar phenomenon is observed in the case of the presently investigated star conjugates. Figure 3 also shows the optical transmittance behaviour of an aqueous solution (3 mg mL^{-1}) of the precursor PNIPAM **5** under conditions of varying temperature. For comparison, the LCST of the respective solutions was taken to be the temperature at which onset of the phase transition took place. As such, the LCST of the precursor PNIPAM **5** is observed to be 28 °C. This low value with respect to the generally reported 32 °C can be attributed to increased hydrophobic interactions resutling from the presence of the dodecyl end group. By comparison, the LCST of the star-shaped $PNIPAM_6$ **10** was determined to be 26.8 °C, an observation which is consistent with previous reports on the reduction in LCST values for branched PNIPAM.[8,9]

An additional important observation is the broad phase transition behaviour of the $PNIPAM_6$ **10** (~10 °C) with respect to the very sharp transition of PNIPAM **5**. Such broadening has been discussed from a theoretical perspective by Zhulina *et al.*[10] for polymer chains attached to surfaces. Schild *et al.*[11] has also reported such a phenomenon for highly polydisperse PNIPAM (*PDI* = 2.3-6.9), which can be explained by the fact that the LCST of this polymer in aqueous solution is influenced by the molecular weight of the chains, thus the broadening effect results from the contribution of chains with wide-varying molecular weight. The PNIPAM used in the present investigation, however, is of narrow *PDI*, thus the broadening effect is presumed to be caused by the anchoring of the PNIPAM chains to the highly hydrophobic fullerene core.

References

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