Supporting Information

Facile synthesis and versatile topological transformation of monocleavable symmetric starlike terpolymers

Xiao Jiang, Meijing Zhang, Shixian Li, Wei Shao, and Youliang Zhao*

Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China.

Experimental

Materials

All solvents, monomers, and other chemicals were purchased from Sigma-Aldrich unless otherwise stated. ε-Caprolactone (CL, 99%) and bis(2-hydroxyethyl) disulfide (Alfa Aesar, 90%) were distilled from calcium hydride under reduced pressure. N,N-Dimethylaminoethyl methacrylate (DMA, 99%) and tert-butyl acrylate (tBA, 98%) were passed through a basic alumina column to remove the inhibitor before use. N-Isopropylacrylamide (NIPAM, 97%) was recrystallized twice from mixtures of hexane and toluene. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Monomethoxy poly(ethylene glycol) with $M_n = 750$ g/mol (MPEG, Fluka) was dried by azeotropic distillation in the presence of toluene. Vinylbenzyl-terminated PEG (St-PEG), $^1$ N-(2-hydroxyethyl) maleimide (HEMI), $^2$ 2-(2-cyanopropyl) dithiobenzoate (CPDB), $^3$ 4-cyanopentanoic acid dithiobenzoate (4-CPDB) $^4$ and symmetric disulfide-linked difunctional RAFT agent S-CPDB $^5$ were synthesized and purified according to literature procedures. N,N'-Dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. DL-dithiothreitol (DTT, 99%,
Merck) and doxorubicin hydrochloride (> 99%, Zhejiang Hisun Pharmaceutical Co, Ltd.) were used as received. Dichloromethane (DCM) and dioxane were dried and distilled over CaH₂. Tetrahydrofuran (THF) and toluene were distilled over sodium and benzophenone and stored under nitrogen. N,N-Dimethylformamide (DMF) was dried over MgSO₄ and distilled under reduced pressure before use.

**Characterization**

The gel permeation chromatography (GPC) systems were used to determine molecular weight and polydispersity (PDI) of the resultant polymers. GPC was conducted in THF at 35 °C with a flow rate of 1 mL/min. Three TSK-GEL H-type columns (pore size 15, 30 and 200 Å, with molecular weight range of 0–1000, 0–20000 and 0-400000 g/mol, respectively) with 5 μm bead size were used. Detection consisted of a RI detector (Optilab rEX) and a multi-angle (14-145°) laser light scattering (MALLS) detector (DAWN HELLOS) with the He-Ne light wave length at 658.0 nm. The refractive index increment dn/dc for samples were measured off-line by Optilab rEX refractive index detector (λ = 658 nm) at 25 °C using a series of different concentration solutions. Data were collected and processed by use of ASTRA software from Wyatt Technology, and molecular weights were determined by the triple detection method. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Varian spectrometer at 25 °C using CDCl₃ or DMSO-d₆ as a solvent. Fourier Transform Infrared (FT-IR) spectra were recorded on a Perkin-Elmer 2000 spectrometer using KBr discs.

**Synthesis of Poly(St-PEG-alt-HEMI) (PSH) Starlike Polymer by RAFT Copolymerization of St-PEG with HEMI**

RAFT copolymerization was conducted in dioxane using AIBN as a primary radical source and S-CPDB as a difunctional CTA. In a typical polymerization (run 1 of Table 1), HEMI (1.41 g, 10.0 mmol), St-PEG (8.67 g, 10.0 mmol), S-CPDB (0.677 g, 1.0 mmol) and AIBN (33.0 mg, 0.20 mmol) were added to a glass tube with a magnetic stirring bar, and dioxane was added until the total volume was 28.5 mL. The tube was sealed with a rubber septum, and the contents were flushed with
nitrogen for 15 min. The tube was subsequently immersed into an oil bath preheated to 70 °C. After 18 h, the polymerization was quenched by putting the tube into an ice-water bath. After precipitating into a large amount of methanol and diethyl ether mixtures three times, 6.60 g (58.8% conversion) of starlike copolymer PSH was obtained. Molecular weight and polydispersity (PDI) determined by GPC-MALLS were $M_{n,GPC} = 6600$ and PDI = 1.08. The degree of polymerization (DP) of comonomer units was determined to be DP$_{St-PEG} = 5.8$ and DP$_{HEMI} = 6.0$ by $^1$H NMR.

$^1$H NMR (CDCl$_3$): $\delta$ 6.2-8.5 (PhH of terminal PhC(=S)S and ArH of St-PEG unit), 4.52 (ArCH$_2$ of St-PEG unit), 4.37 (CH$_2$O), 3.88 (CH$_2$OH of HEMI unit), 3.65 (CH$_2$CH$_2$O of St-PEG unit and CH$_2$N of HEMI unit), 3.38 (CHCH of HEMI unit and CH$_3$O of St-PEG unit, and CH$_2$ and CH$_2$ of St-PEG unit). IR (KBr): 3451, 2869, 1770, 1736, 1701, 1635, 1550, 1513, 1453, 1398, 1351, 1300, 1251, 1102, 1043, 950, 766, 692 cm$^{-1}$.

Synthesis of (PEG)$_{2m}$(PM)$_2$ Starlike Copolymers by RAFT Chain Extension Polymerization

In a typical run, PSH (0.64 g, 0.10 mmol), DMA (1.89 g, 12.0 mmol) and AIBN (3.3 mg, 0.02 mmol) were added to a glass tube with a magnetic stirring bar, and dioxane was added until the total volume was 15.0 mL. The tube was sealed with a rubber septum, and the contents were flushed with nitrogen for 15 min. The tube was subsequently immersed into an oil bath preheated to 80 °C. After 20 h, the polymerization was quenched by putting the tube into an ice-water bath. After precipitating into a large amount of cold hexane three times, 2.03 g (73.6% conversion) of (PEG)$_{2m}$(PDMA)$_2$ starlike copolymer was obtained. Molecular weight and polydispersity determined by GPC-MALLS were $M_{n,GPC} = 20800$ and PDI = 1.10. (PEG)$_{2m}$(PNIPAM)$_2$ and (PEG)$_{2m}$(PtBA)$_2$ stars were synthesized and purified according to similar procedures.

(PEG)$_{2m}$(PDMA)$_2$: $^1$H NMR (CDCl$_3$): $\delta$ 6.2-8.2 (PhH of terminal PhC(=S)S and ArH of St-PEG unit), 4.52 (broad, ArCH$_2$ of St-PEG unit and CH$_2$O), 4.07 (CH$_2$O of PDMA), 3.88 (CH$_2$OH of HEMI unit), 3.65 (CH$_2$CH$_2$O of St-PEG unit and CH$_2$N of HEMI unit), 3.38 (CHCH of HEMI unit and CH$_3$O of St-PEG unit, and CH$_2$ and CH$_2$ of St-PEG unit, and CH$_2$ and CH$_3$ of PDMA). IR (KBr): 3448, 2949, 2866, 2822, 2769, 1730, 1701,
1509, 1459, 1400, 1353, 1272, 1148, 1101, 1042, 1016, 954, 851, 779, 748 cm\(^{-1}\).

\((\text{PEG})_{2m}^\circledR (\text{PNIPAM})_2\): \(^1\)H NMR (CDCl\(_3\)): \(\delta 6.0-8.2\) (PhH of terminal PhC(=S)S, ArH of St-PEG unit and NH of PNIPAM), 4.52 (ArCH\(_2\) of St-PEG unit), 4.36 (CH\(_2\)O), 4.01 (CH of PNIPAM), 3.88 (CH\(_2\)OH of HEMI unit), 3.65 (CH\(_2\)CH\(_2\)O of St-PEG unit and CH\(_2\)N of HEMI unit), 3.38 (CHCH of HEMI unit and CH\(_3\)O of St-PEG unit), 2.91 (CH\(_2\)SSCH\(_2\)), 0.5-2.8 (CH\(_2\)CH\(_2\)COO, CCH\(_3\), CH and CH\(_2\) of St-PEG unit, and CH, CH\(_2\) and CH\(_3\) of PNIPAM). IR (KBr): 3527, 3278, 3066, 2973, 2867, 1772, 1702, 1654, 1541, 1458, 1386, 1366, 1252, 1172, 1104, 951, 842 cm\(^{-1}\).

\((\text{PEG})_{2m}^\circledR (\text{PrBA})_2\): \(^1\)H NMR (CDCl\(_3\)): \(\delta 6.0-8.2\) (PhH of terminal PhC(=S)S and ArH of St-PEG unit), 4.52 (ArCH\(_2\) of St-PEG unit), 4.36 (CH\(_2\)O), 3.88 (CH\(_2\)OH of HEMI unit), 3.65 (CH\(_2\)CH\(_2\)O of St-PEG unit and CH\(_2\)N of HEMI unit), 3.38 (CHCH of HEMI unit and CH\(_3\)O of St-PEG unit), 2.91 (CH\(_2\)SSCH\(_2\)), 0.5-2.8 (CH\(_2\)CH\(_2\)COO, CCH\(_3\), CH and CH\(_2\) of St-PEG unit, and CH, CH\(_2\) and CH\(_3\) of PrBA). IR (KBr): 3438, 2929, 2933, 2872, 1729, 1701, 1480, 1459, 1394, 1369, 1258, 1152, 1095, 1032, 951, 846, 752 cm\(^{-1}\).

**Synthesis of (PEG)\(_{2m}^\circledR (\text{PCL})_2n(\text{PM})_2\) Starlike Terpolymers by CL Polymerization**

To a Schlenk tube were added (PEG)\(_{2m}^\circledR (\text{PDMA})_2\) (0.63 g, 0.18 mmol of -OH), CL (1.03 g, 9.0 mmol), Sn(Oct)\(_2\) (14.6 mg, 0.036 mmol) and a magnetic stir bar under nitrogen, and then dry toluene was added until the total volume was 18.0 mL. After three freeze-vacuum-thaw cycles, the tube was immersed into an oil bath at 110 °C to perform polymerization. After 20 h, the polymerization was quenched by putting the tube into an ice-water bath. The crude product was precipitated into cold hexane, and the precipitation processes from THF to hexane were repeated twice. After drying at 40 °C under vacuum, 1.35 g (69.9% conversion) of (PEG)\(_{2m}^\circledR (\text{PCL})_2n(\text{PDMA})_2\) starlike terpolymer was obtained. Molecular weight and polydispersity determined by GPC-MALLS were \(M_n,\text{GPC} = 44900\) and PDI = 1.12. Other starlike terpolymers were synthesized and purified according to similar procedures using (PEG)\(_{2m}^\circledR (\text{PM})_2\) as macroinitiators.

\((\text{PEG})_{2m}^\circledR (\text{PCL})_2n(\text{PDMA})_2\): \(^1\)H NMR (CDCl\(_3\)): \(\delta 6.2-8.2\) (PhH of terminal PhC(=S)S and ArH of St-PEG unit), 4.5 (broad, ArCH\(_2\) of St-PEG unit and CH\(_2\)O), 4.07 (CH\(_2\)O of PCL and CH\(_2\)O of PCL) cm\(^{-1}\).
PDMA), 3.65 (CH₂CH₂O of St-PEG unit and CH₂N of HEMI unit), 3.38 (CHCH of HEMI unit and CH₃O of St-PEG unit), 0.6-3.0 (CH₂CH₂COO, CH₂SSCH₂, CCH₃, CH and CH₂ of St-PEG unit, CH₂ and CH₃ of PDMA, and CH₂CH₂CH₂CH₂CO of PCL). IR (KBr): 3448, 2948, 2864, 2822, 2771, 1732, 1465, 1392, 1357, 1274, 1237, 1158, 1100, 1041, 1016, 957, 852, 748 cm⁻¹.

(PEG)₂m(PCL)₂n(PNIPAM)₂: ¹H NMR (CDCl₃): δ 6.0-8.2 (PhH of terminal PhC(=S)S and ArH of St-PEG unit), 4.5 (broad, ArCH₂ of St-PEG unit and CH₂O), 4.06 (CH₂O of PCL and CH of PNIPAM), 3.65 (CH₂CH₂O of St-PEG unit and CH₂N of HEMI unit), 3.38 (CHCH of HEMI unit and CH₃O of St-PEG unit), 0.5-3.0 (CH₂CH₂COO, CH₂SSCH₂, CCH₃, CH and CH₂ of St-PEG unit, CH, CH₂ and CH₃ of PNIPAM, and CH₂CH₂CH₂CH₂CO of PCL). IR (KBr): 3358, 3066, 2940, 2868, 1735, 1649, 1545, 1459, 1389, 1366, 1237, 1167, 1104, 957, 842, 738 cm⁻¹.

(PEG)₂m(PCL)₂n(PtBA)₂: ¹H NMR (CDCl₃): δ 6.0-8.2 (PhH of terminal PhC(=S)S and ArH of St-PEG unit), 4.5 (broad, ArCH₂ of St-PEG unit and CH₂O), 4.06 (CH₂O of PCL), 3.65 (CH₂CH₂O of St-PEG unit and CH₂N of HEMI unit), 3.38 (CHCH of HEMI unit and CH₃O of St-PEG unit), 0.5-3.0 (CH₂CH₂COO, CH₂SSCH₂, CCH₃, CH and CH₂ of St-PEG unit, CH, CH₂ and CH₃ of PtBA, and CH₂CH₂CH₂CH₂CO of PCL). IR (KBr): 3448, 2943, 2867, 1732, 1459, 1420, 1394, 1368, 1247, 1157, 1103, 1044, 961, 846, 733 cm⁻¹.

Hydrolysis of (PEG)₂m(PCL)₂n(PtBA)₂ Star

In a typical run, to a solution of 300 mg of (PEG)₂m(PCL)₂n(PtBA)₂ star polymer in DCM (20 mL) was added 0.30 mL of trifluoroacetic acid (TFA). The solution was stirred at room temperature for 15 h, concentrated, and precipitated into hexane twice. After vacuum drying, (PEG)₂m(PCL)₂n(PAA)₂ star was obtained as light pink powders.

¹H NMR (CDCl₃): δ 6.0-8.2 (PhH of terminal PhC(=S)S and ArH of St-PEG unit), 4.36 (ArCH₂ of St-PEG unit, CH₂O and terminal CH₂OH of PCL), 4.06 (CH₂O of PCL), 3.65 (CH₂CH₂O of St-PEG unit and CH₂N of HEMI unit), 3.38 (CHCH of HEMI unit and CH₃O of St-PEG unit), 0.5-3.0 (CH₂CH₂COO, CH₂SSCH₂, CCH₃, CH and CH₂ of St-PEG unit, CH and CH₂ of PAA, and CH₂CH₂CH₂CH₂CO of PCL).
\(^1\)H NMR (DMSO-\(d_6\)): \(\delta\) 12.2 (broad, COOH of PAA), 6.0-8.2 (PhH of terminal PhC(=S)S and ArH of St-PEG unit), 4.37 (ArCH\(_2\) of St-PEG unit, CH\(_2\)O and terminal CH\(_2\)OH of PCL), 3.98 (CH\(_2\)O of PCL), 3.50 (CH\(_2\)CH\(_2\)O of St-PEG unit and CH\(_2\)N of HEMI unit), 2.77 (CH\(_2\)SSCH\(_2\)), 0.6-2.4 (CH\(_2\)CH\(_2\)COO, CCH\(_3\), CH and CH\(_2\) of St-PEG unit, CH and CH\(_2\) of PAA, and CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CO of PCL).

**Cleavage of Disulfide-Linked (PEG)\(_2m\)(PCL)\(_2n\)(PrBA)\(_2\) Star**

Dried (PEG)\(_2m\)(PCL)\(_2n\)(PrBA)\(_2\) star polymer (100 mg) was dissolved in 10 mL of THF under nitrogen, and 5-fold excess of Bu\(_3\)P was added to the solution at ambient temperature. The mixture was stirred overnight, diluted with THF and subjected to GPC analysis. Molecular weight and polydispersity of degraded (PEG)\(_m\)(PCL)\(_n\)PrBA star determined by GPC-MALLS were \(M_n = 23500\), PDI = 1.11.

**Aminolysis to Obtain Telechelic Dithiol-Functionalized Stars and Reversible Conversion Between Comblike-Linear Multiblock Copolymer and Cleaved (PEG)\(_m\)(PCL)\(_n\)PM Star via Redox Reactions**

In a typical run, a solution of 10-fold excess of hydrazine in THF was added dropwise to 5 mL of THF solution with 100 mg of (PEG)\(_2m\)(PCL)\(_2n\)(PrBA)\(_2\) star under nitrogen, and the mixture was further stirred at room temperature for 1 h. After concentration, dithiol-functionalized (PEG)\(_2m\)(PCL)\(_2n\)(PrBA)\(_2\) star was obtained as white powders.

The dithiol-functionalized (PEG)\(_2m\)(PCL)\(_2n\)(PrBA)\(_2\) star was dissolved in 5 mL of THF, and 5-fold excess of Bu\(_3\)P was added. The mixture was stirred at ambient temperature for 20 h, and 0.5 mL of polymer solution was drawn and subjected to GPC analysis after dilution. The residual solution was concentrated and precipitated into hexane, and 85 mg of cleaved (PEG)\(_m\)(PCL)\(_n\)PrBA star was obtained. GPC-MALLS: \(M_n = 23200\), PDI = 1.10.

To a round flask were added 80 mg of dithiol-functionalized (PEG)\(_m\)(PCL)\(_n\)PrBA star, 50 mg of FeCl\(_3\) and 2.0 mL of DMF, and the mixture was stirred at 60 °C for 40 h to perform thiol-thiol coupling reaction. After concentration, precipitation into hexane and vacuum drying,
disulfide-linked \([(\text{PEG})_m(\text{PCL})_nP\text{BA})_o\] multiblock copolymer was obtained. GPC-MALLS: $M_n = 150400$, PDI = 1.77.

In cycle II, the reversible coupling and cleavage of thiol-disulfide moieties were performed according to the above-mentioned procedures. The multiblock copolymer obtained in first cycle was converted into degraded dithiol-functionalized \([(\text{PEG})_m(\text{PCL})_nP\text{BA})_p\] in the presence of 5-fold excess of $\text{Bu}_3\text{P}$, which was further oxidized to form \([(\text{PEG})_m(\text{PCL})_nP\text{BA})_p\] comblike-linear multiblock copolymer ($M_n = 124700$, PDI = 1.80).

References


Table S1. Synthesis of starlike PSH with PEG arms by RAFT copolymerization of St-PEG and HEMI mediated by S-CPDB (run 1) and PSH-(PM)$_2$ (M = DMA, NIPAM and tBA) miktoarm stars via a subsequent chain extension polymerization (runs 2-4)$^a$

<table>
<thead>
<tr>
<th>run</th>
<th>CTA</th>
<th>M</th>
<th>C%$^b$</th>
<th>$M_{n,th}^c$</th>
<th>$M_{n,GPC}^d$</th>
<th>$M_{w,GPC}^d$</th>
<th>PDI$^d$</th>
<th>$M_{n,NMR}^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S-CPDB</td>
<td>St-PEG/HEMI</td>
<td>58.8</td>
<td>6450</td>
<td>6600</td>
<td>7140</td>
<td>1.08</td>
<td>6390</td>
</tr>
<tr>
<td>2</td>
<td>PSH</td>
<td>DMA</td>
<td>73.6</td>
<td>20300</td>
<td>20800</td>
<td>22900</td>
<td>1.10</td>
<td>19900</td>
</tr>
<tr>
<td>3</td>
<td>PSH</td>
<td>NIPAM</td>
<td>70.5</td>
<td>16000</td>
<td>17200</td>
<td>19200</td>
<td>1.12</td>
<td>15700</td>
</tr>
<tr>
<td>4</td>
<td>PSH</td>
<td>tBA</td>
<td>78.2</td>
<td>18400</td>
<td>19600</td>
<td>21300</td>
<td>1.09</td>
<td>18700</td>
</tr>
</tbody>
</table>

$^a$ Polymerization conditions: [St-PEG]$_0$:[HEMI]$_0$:[S-CPDB]$_0$:[AIBN]$_0$ = 10:10:1:0.2, [St-PEG]$_0$ = 0.35 mol/L, in dioxane at 70 °C for 18 h (run 1); [M]$_0$:[PSH]$_0$:[AIBN]$_0$ = 120:1:0.2, [M]$_0$ = 0.60 mol/L, in dioxane (runs 2 and 3) or toluene (run 4) at 80 °C for 20 h. $^b$ Monomer conversion determined by gravimetry. $^c$ Theoretically calculated molecular weight. $^d$ Molecular weight and polydispersity determined by GPC-MALLS. $^e$ Molecular weight determined by $^1$H NMR.

Table S2. Synthesis of (PEG)$_{2m}$(PCL)$_{2n}$(PM)$_2$ starlike terpolymers by ring-opening polymerization of CL using hydroxyl-functionalized miktoarm stars as macroinitiators$^a$

<table>
<thead>
<tr>
<th>run</th>
<th>Initiator</th>
<th>C%$^b$</th>
<th>$M_{n,th}^c$</th>
<th>$M_{n,GPC}^d$</th>
<th>$M_{w,GPC}^d$</th>
<th>PDI$^d$</th>
<th>$M_{n,NMR}^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(PEG)$_{2m}$(PDMA)$_2$</td>
<td>56.4</td>
<td>39200</td>
<td>39600</td>
<td>46800</td>
<td>1.18</td>
<td>38600</td>
</tr>
<tr>
<td>2</td>
<td>(PEG)$_{2m}$(PNIPAM)$_2$</td>
<td>55.2</td>
<td>34600</td>
<td>35700</td>
<td>41500</td>
<td>1.16</td>
<td>33800</td>
</tr>
<tr>
<td>3</td>
<td>(PEG)$_{2m}$(PrBA)$_2$</td>
<td>69.9</td>
<td>42800</td>
<td>44900</td>
<td>50400</td>
<td>1.12</td>
<td>44200</td>
</tr>
</tbody>
</table>

$^a$ Polymerization conditions: [CL]$_0$:[OH]$_0$:[Sn(Oct)$_2$]$_0$ = 50:1:0.2, [CL]$_0$ = 0.50 mol/L, in toluene at 110 °C for 20 h. $^b$ Monomer conversion determined by gravimetry. $^c$ Theoretically calculated molecular weight. $^d$ Molecular weight and polydispersity determined by GPC-MALLS. $^e$ Molecular weight determined by $^1$H NMR.
Figure S1. $^1$H NMR spectrum of (PEG)$_{2m}$(PDMA)$_2$ star.

Figure S2. $^1$H NMR spectrum of (PEG)$_{2m}$(PNIPAM)$_2$ star.
Figure S3. $^1$H NMR spectrum of (PEG)$_{2m}$(PCL)$_{2n}$(PDMA)$_2$ star.

Figure S4. $^1$H NMR spectrum of (PEG)$_{2m}$(PCL)$_{2n}$(PNIPAM)$_2$ star.
Figure S5. $^1$H NMR spectra of (PEG)$_{2n}$(PCL)$_{2n}$(PAA)$_2$ starlike terpolymer in DMSO-$d_6$ (a) and CDCl$_3$ (b).

Figure S6. GPC traces (normalized weight distribution) of (PEG)$_{2m}$(PCL)$_{2n}$(PrBA)$_2$ star (a, $M_{n,GPC}$ = 44900, PDI = 1.12), cleaved dithiol-functionalized (PEG)$_m$(PCL)$_n$PrBA stars (first cycle, b, $M_{n,GPC}$ = 23200, PDI = 1.10; second cycle, d, $M_{n,GPC}$ = 23000, PDI = 1.22), and disulfide-linked comblike-linear multiblock copolymers (first cycle, c, $M_{n,GPC}$ = 150400, PDI = 1.77; second cycle, e, $M_{n,GPC}$ = 124700, PDI = 1.80) obtained by redox reactions.
Figure S7. IR spectra of PSH (a), (PEG)$_{2m}$(PDMA)$_2$ (b), (PEG)$_{2m}$(PNIPAM)$_2$ (c), (PEG)$_{2m}$(PrBA)$_2$ (d), (PEG)$_{2m}$(PCL)$_{2n}$(PDMA)$_2$ (e), (PEG)$_{2m}$(PCL)$_{2n}$(PNIPAM)$_2$ (f), and (PEG)$_{2m}$(CPL)$_{2n}$(PrBA)$_2$ (g) starlike polymers.