Polymer Chemistry

ARTICLE

Janus Long-Chain Hyperbranched Copolymer of PSt and POEGMA from Self-Assembly Mediated Click Reaction

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Self-assembly mediated synthesis was successfully adopted in the preparation of Janus long-chain hyperbranched copolymer composed of polystyrene (PSt) and poly[oligo(ethylene glycol) methacrylate] (POEGMA) half-dendrons. Firstly, seesaw macromonomers with one alkynyl group at the chain center and one azido group at each chain end, [alkynyl-(PSt-N$_3$)$_2$ and alkynyl-(POEGMA-N$_3$)$_2$], were prepared through atom transfer radical polymerization and used to produce their own long-chain hyperbranched homopolymers (lhb-PSt and lhb-POEGMA) through click reaction, followed by the conversion of azido end-groups into amino end-groups. Meanwhile, one hetero four-arm copolymer of μ-PSt$_2$-POEGMA$_2$ with four azido end-groups was obtained by the sequential click reaction of alkynyl-(PSt-Br)$_2$ and alkynyl-(POEGMA-Br)$_2$ with α, ω-diazido tetra(ethylene glycol) and the conversion of bromo groups into azido groups. Finally, with the help of self-assembly in different selective solvents, lhb-POEGMA and lhb-PSt were linked alternately onto μ-PSt$_2$-POEGMA$_2$ through click chemistry, resulting in Janus long-chain hyperbranched copolymer [μ-(lhb-POEGMA)(lhb-PSt)]. The different analytical techniques confirmed the successful preparation of μ-(lhb-POEGMA)(lhb-PSt) and its different precursors. The self-assembly behavior of different amphiphilic copolymers was investigated by TEM, DLS and DSC. The variation of contact angle of μ-(lhb-POEGMA)(lhb-PSt) with the casting solvent was correlated to its self-assembly behavior in selective solvents.

Introduction

Highly branched polymers like hyperbranched and dendritic polymers have been widely studied due to their structural characteristics and wide applications.[1-5] In the last decade, amphiphilic hyperbranched and dendritic copolymers have received more and more research attention due to the unique self-assembly behaviours and potential utilities. Most reported examples came from core/shell-like copolymers with dendritic or hyperbranched polymers as the core and linear grafting chains as the shell.[6-12] As for long-chain hyperbranched copolymers composed of two branched segmental components, Hutching's group firstly synthesized HyperBlocks copolymers from AB$_2$ macromonomers of polystyrene-polyisoprene-polystyrene triblock copolymer and studied the microphase separation behavior.[13,14] Wu's group prepared amphiphilic hyperbranched copolymer of polystyrene (PSt) and poly(acrylic acid) from click copolymerization of two seesaw macromonomers of PSt and poly(t-butyl acrylate), and studied the self-assembly in a selective solvent and the gelation

behaviour.[15] However, such hybrid amphiphilic hyperbranched copolymers have uniform distribution of two components over the whole macromolecules.

Janus hyperbranched and dendritic copolymers have two opposite half-dendrons made up of each component and are amphiphilic in nature. From amphiphilic block/graft copolymers to Janus micelles and particles,[16,17] such asymmetrical substances not only possess special surfacial/interfacial properties, but also self-assemble into the aggregates with different morphologies. Thus, Janus hyperbranched and dendritic copolymers have come into the research sight. Up to now, almost all Janus hyperbranched and dendritic copolymers are constituted of two disparate wedges but not two different bulks.[2,18-20] A series of Janus dendrimers have been prepared and their self-assembly behaviours into complex architectures and dendrimesomes reported by Percec et al.[21,22] Deschenaux et al. also reported Janus dendritic liquid crystals with fullerene as the core.[23] The dendronized diblock copolymers reported by Fiset and Morin also have Janus features.[24] As far as known by us, Janus long-chain hyperbranched copolymers have not been reported previously. The most related example was done by Smuel and Ramakrishnan, where amphiphilic hyperbranched polyester with C$_{22}$-alkyl terminal groups and poly(ethylene glycol) terminal chains self-adapted into Janus hybramer.[25]

Self-assembly is the intrinsic aptitude of amphiphilic copolymers while self-assembly mediated synthesis strategy can feedback the preparation of polymers with various

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structures. Wu et al. has developed Self-assembly Mediated Polypolymerization to obtain effectively multiblock copolymers.[26] Taking advantage of dynamic equilibrium between the self-assembled micelles and unimers of responsive block copolymer, Liu et al. succeeded in preparing a cyclic block copolymer under high concentration (10 g/L^{-1}).[27] The previous reports have opened a gate for polymer chemistry, i.e. macromolecular synthesis mediated by self-assembly of polymeric precursors. In this paper, we further extend this strategy to obtain Janus long-chain hyperbranched copolymer composed of PSt and poly[oligo(ethylene glycol) methacrylate] (POEGMA) via self-assembly mediated click chemistry, as illustrated in Scheme 1. As well, their self-assembly in selective solvents was investigated to confirm the Janus structure.
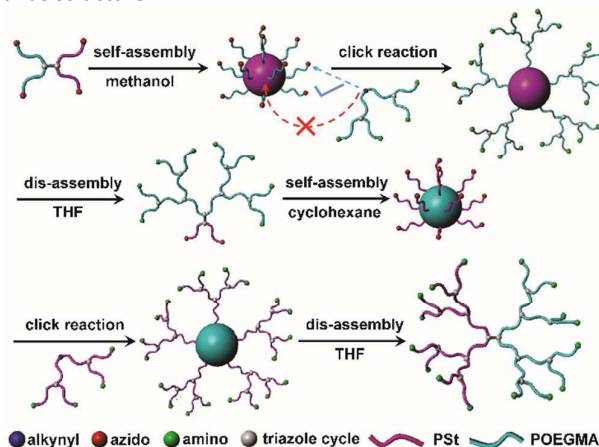

Scheme 1. Schematic of Janus long-chain hyperbranched copolymer through self-assembly mediated synthesis

Experimental

Materials

Styrene (St, Sinopharm, 97%) was passed through a basic alumina column to remove inhibitor and distilled under reduced pressure. Seesaw macromonomer of PSt having one alkynyl group at the chain centre and one azido group at each chain end [alkynyl-(PSt-N$_3$)$_2$] ($M_{n,GPC}$ = 5000, M_w/M_n = 1.07) was synthesized according to our previous literature (Scheme 2).[28, 29] OEGMA (M_n= 475 g/mol, Sigma-Aldrich) was passed through a neutral alumina column to remove the inhibitor. Propargyl 2,2-bis((2'-bromo-2'-methylpropanoyloxy)-methyl)propanoate (PBMPMP) used as ATRP initiator of OEGMA was prepared in our laboratory.[30] CuBr (Sinopharm) was purified as follows. After crude CuBr was reduced by 0.01 M Na$_2$SO$_3$ aqueous solution, the solid was filtered and washed with 1 wt% HBr aqueous solution. Finally, pure CuBr was obtained by washing with acetic acid and alcohol. Wang resin with alkynyl groups and Merrifield resin with azido groups were prepared according to the literatures.[31, 32] THF was refluxed over CaH$_2$ for 6 h, dried with sodium/benzophenone and distilled before use. DMF was firstly dried with anhydrous magnesium sulphate and then distilled under reduced

pressure prior to use. Triethylamine was stirred with KOH for 12 h at room temperature, refluxed with toluene-4-sulfonyl-chloride and distillated before use., N, N, N', N'', N''-Pentamethyl-diethylenetriamine and 2-bromoisobutyryl bromide from Sigma-Aldrich, 2,2'-bipyridine (bpy), propargyl alcohol, propargyl bromide, sodium azide and tetra(ethylene glycol) (TEG) from Sinopharm, N,N-dimethyl 4-amidopyridine (DMAP), dicyclohexyl carbodiimide (DCC), 2-bromoisobutyryl bromide (Aladdin), p-toluenesulfonic acid monohydrate (PTSA), 2,2-dimethoxypropane (DMP, 99%) and triphenylphosphine (PPh$_3$) from Aladdin as well other analytic grade reagents (Sinopharm) were used as received.
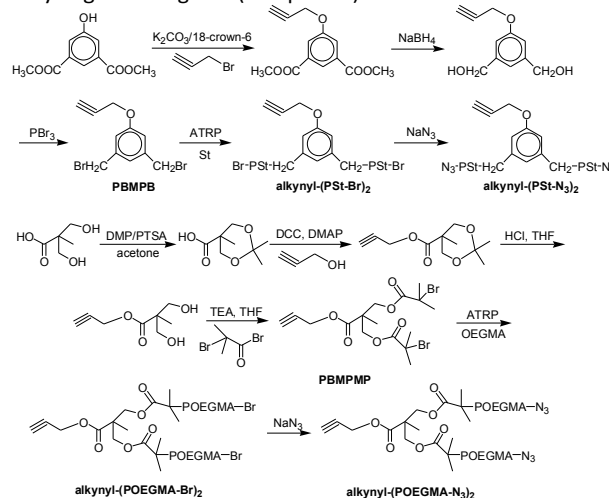
**Scheme 2.** Synthesis of seesaw macromonomers and their precursors

Synthesis of seesaw macromonomer of alkynyl-(POEGMA-N$_3$)$_2$

POEGMA with one alkynyl group at the chain centre and one bromo group at each chain end [alkynyl-(POEGMA-Br)$_2$] was prepared through atom transfer radical polymerization (ATRP) of OEGMA with PBMPMP as the initiator (Scheme 2). Thus, OEGMA (9.0 g, 0.2 mol), PBMPMP (130 mg, 0.3 mmol), CuBr (87 mg, 0.6 mmol), bpy (280 mg, 1.8 mmol) and isopropoanol (8.0 mL) were charged into in a 20-mL glass tube. The tube was degassed by three freeze-pump-thaw cycles and sealed under vacuum. The polymerization was carried out at room temperature for 4 h before it was quenched in ice bath. The resulted mixture was diluted with THF and passed through a neutral alumina column to remove copper salt. Alkynyl-(POEGMA-Br)$_2$ (4.5 g, $M_{n,GPC}$ = 12.3 k, $M_{n,NMR}$ = 15 k, M_w/M_n = 1.21) was obtained by three precipitations with THF/hexane and dryness under vacuum overnight at room temperature.

POEGMA seesaw macromonomers with one alkynyl group at the chain centre and one azido groups at each chain end [alkynyl-(POEGMA-N$_3$)$_2$] was prepared through the conversion of bromo group into azido group. Thus, alkynyl-(POEGMA-Br)$_2$ (3.8 g, 0.25 mmol), DMF (30 mL) and NaN$_3$ (0.325 g, 5 mmol) were added into a 100-mL round-bottom flask. The mixture stood at room temperature for 36 h while stirring. After the removal of most solvent under reduced pressure, the remaining mixture was diluted with CH$_2$Cl$_2$, passed through a

neutral alumina column, and then precipitated into excess hexane. After being dried under vacuum at room temperature overnight, alkynyl-(POEGMA-N$_3$)$_2$ was obtained (yield: 92 %).

Synthesis of four-arm star copolymer of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$

Four-armed star copolymers with one azido group at each end of two PSt blocks and two POEGMA blocks [μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$] was prepared through the successive linkage of alkynyl-(PSt-Br)$_2$ and alkynyl-(POEGMA-Br)$_2$ onto α, ω-diazido tetra(ethylene glycol) and the conversion of bromo groups into azido groups, as illustrated in Scheme 3.
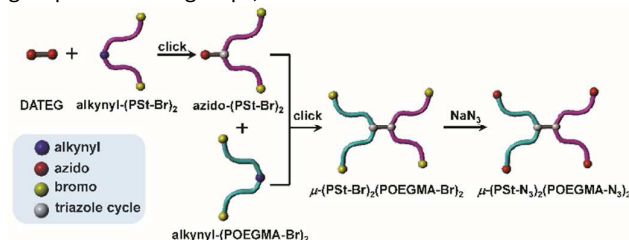
Scheme 3. Schematic synthesis of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$

Synthesis of α, ω-diazido tetra(ethylene glycol) (DATEG)

DATEG was synthesized according to the literature.[33] TEG (10.0 g, 51 mmol), THF (50 mL) and triethylamine (10.0 g, 99 mmol) were placed in a 250-mL round-bottom flask and cooled to 0 °C. Methanesulfonyl chloride (13.0 g, 110 mmol) was added dropwise over 30 min. The reaction mixture was gradually warmed to room temperature and stirred overnight. Then, the mixture was diluted with NaHCO$_3$ (2.0 g) aqueous solution (100 mL) and sodium azide (10.0 g, 154 mmol) was added. After the distillation removal of THF, the reaction mixture was refluxed overnight. After cooling, the reaction mixture was extracted with chloroform (5 × 60 mL). The combined organic phase was dried over anhydrous MgSO$_4$, filtered, and evaporated to give pale-brown oil. The crude product was chromatographed in silica column with CHCl$_3$/MeOH (40:1 in volume) as the eluent to give pure DATEG (yield: 8.9 g, 71.5 %). ^{1}H-NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 3.62-3.71 (br, 12H, CH$_2$–O), 3.40 (t, 4H, CH$_2$–N$_3$).

Synthesis of azido-(PSt-Br)$_2$

Alkynyl-(PSt-Br)$_2$ (1.0 g, M_n= 5.0 k, 0.2 mmol), DATEG (1.0 g, 4 mmol), CuBr (29 mg, 0.2 mmol), PMDETA (34 mg, 0.2 mmol) and DMF (3.0 mL) were charged in a 10-mL glass tube equipped with a stirring bar. The tube was degassed by three freeze-pump-thaw cycles and sealed under vacuum. Then, the reaction stood at 40 °C for 1 h before it was quenched in ice bath. The resulted mixture was thinned with THF and passed through a neutral alumina column to remove copper salt. PSt with a central azido group and two bromo end-groups [azido-(PSt-Br)$_2$] (yield: 0.9 g) was obtained by two precipitations and dryness under vacuum overnight at room temperature.

Synthesis of four-armed copolymer of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$

Azido-(PSt-Br)$_2$ (0.50 g, M_n = 5 k, 0.1 mmol), alkynyl-(POEGMA-Br)$_2$ (1.0 g, $M_{n,NMR}$ = 15 k, 0.07 mmol), CuBr (12 mg, 0.08 mmol), PMDETA (17 mg, 0.1 mmol) and DMF (5 mL) were added in a 10-mL glass tube equipped with a stirring bar. The tube was

degassed by three freeze-pump-thaw cycles and sealed under vacuum. Then, the reaction stood at 40 °C for 1.5 h. Subsequently, Wang Resin (0.2 g) and CuBr (4 mg, 0.025 mmol) were added in the tube. After the reaction under vacuum at 40 °C for 2 h, the mixture was quenched in ice bath and diluted with THF. Thus, the thinned mixture was passed through a column of neutral alumina. Pure four-armed star copolymer with four bromo end-groups [μ-(PSt-Br)$_2$(POEGMA-Br)$_2$] (yield: 1.1 g) was obtained through two precipitations with THF/hexane and dryness overnight under vacuum at room temperature. The conversion of bromo groups into azido groups was performed through a similar procedure to that of alkynyl-(POEGMA-Br)$_2$, leading to the formation of four-arm star copolymer with four azido groups [μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$] (yield: 90 %).

Synthesis of long-chain hyperbranched polymers with amino terminal groups

Synthesis of long-chain hyperbranched POEGMA with amino terminal groups

A 20-mL glass tube equipped with a stirring bar was charged with alkynyl-(POEGMA-N$_3$)$_2$ (3.0 g, $M_{n,NMR}$ = 15 k, 0.2 mmol), PMDETA (34 mg, 0.2 mmol), CuBr (28 mg, 0.2 mmol) and DMF (10 mL). The tube was degassed by three freeze-pump-thaw cycles and sealed under vacuum. After the tube was placed in an oil bath thermosetted at 40 °C for 1 h, the click reaction was quenched by lowering the temperature in ice bath and the glass tube was opened. Then, the resulted mixture diluted with THF was passed through a neutral alumina column to remove copper salt. Long-chain hyperbranched POEGMA with azido terminal groups (*lhb*-POEGMA-N$_3$) (yield: 2.7 g, $M_{w,GPC}$ = 46 k) was obtained by two THF/hexane precipitations and dryness under vacuum overnight at 30 °C.

To convert azido groups into amino groups, *lhb*-POEGMA-N$_3$ (2.7 g), PPh$_3$ (0.52 g, 2 mmol) and dried THF (30 mL) were added into a 100-mL round-bottom flask equipped with a stirring bar. The reaction mixture was stirred at room temperature for 24 h, and H$_2$O (0.036 g, 2 mmol) was added. After additional 12 h, *lhb*-POEGMA with amino terminal groups (*lhb*-POEGMA-NH$_2$) (yield: 2.2 g) was obtained by two THF/hexane precipitations and dryness under vacuum overnight at 30 °C.

Synthesis of long-chain hyperbranched PSt with amino terminal groups

Click polymerization of alkynyl-(PSt-N$_3$)$_2$ (1.0 g, M_n = 5 k) with PMDETA (34 mg) and CuBr (28 mg) as the catalytic system was carried out in DMF (10 mL) at 40 °C for 2 h. Long-chain hyperbranched PSt with azido terminal groups (*lhb*-PSt-N$_3$, $M_{w,GPC}$ = 42 k) was obtained at 80 % yield. The polymer purification was carried out by THF/CH$_3$OH precipitation. The conversion of azido groups into amino groups was done as the above procedure and *lhb*-PSt with amino terminal groups (*lhb*-PSt-NH$_2$) (yield: 85 %) was obtained.

Synthesis of Janus μ-(*lhb*-POEGMA)(*lhb*-PSt) through self-assembly mediated click reaction

This synthesis was completed through two successive click reactions in two different selective solvents, as illustrated in Scheme 1.

Self-assembly mediated click reaction of lhb-POEGMA-NH₂ with μ-(PSt-N₃)₂(POEGMA-N₃)₂ in methanol

μ-(PSt-N₃)₂(POEGMA-N₃)₂ (0.3 g) was dissolved in THF (4.0 mL) to form a real solution. After that, methanol (26.0 mL) was added dropwise into the solution through a syringe pump under vigorous stirring over 1 h. The obtained micelle dispersion was dialyzed against CH₃OH at room temperature for 6 h using a dialysis bag with cut-off molecular weight of 3000 to remove THF. Afterwards, a glass tube equipped with a stirring bar was charged with *lhb*-POEGMA-NH₂ (1.5 g, $M_{w,GPC}$ = 46 k), sodium ascorbate (40 mg, 0.2 mmol), CuSO₄·5H₂O (25 mg, 0.1 mmol) and μ-(PSt-N₃)₂(POEGMA-N₃)₂ micelle dispersion in methanol (10 mg/mL, 30 mL). The tube was degassed by three freeze-pump-thaw cycles and sealed under vacuum. After the tube was kept in an oil bath thermosetted at 40 °C for 12 h, Merrifield resin with azido groups (0.2 g) and CuSO₄·5H₂O (10 mg, 0.04 mmol) was added into the reaction mixture. After additional 6 h, the click reaction was quenched by lowering the temperature in ice bath and the glass tube was opened. The diluted mixture with THF was passed through a neutral alumina column to remove copper salt. After two THF/hexane precipitations, the product was further washed with hot cyclohexane (60 °C). The pure product of *lhb*-POEGMA-NH₂ blocked with two PSt segments at one conjunction, μ-*lhb*-(POEGMA-NH₂)(PSt-N₃)₂, was obtained (yield: 1.6 g) by the evaporation removal of solvents and dryness under vacuum overnight at 30 °C.

Self-assembly mediated click reaction of lhb-PSt-NH₂ with μ-lhb-(POEGMA-NH₂)(PSt-N₃)₂ in cyclohexane/THF

Through a syringe pump, the solution of μ-*lhb*-(POEGMA-NH₂)(PSt-N₃)₂ (0.5 g) in THF (7.0 mL) was added into hot cyclohexane (35.0 mL) at 60 °C under vigorous stirring over 1 h. The obtained micelle dispersion was stirred for another 8 h. Afterwards, a glass tube equipped with a stirring bar was charged with *lhb*-PSt-NH₂ (0.5 g, $M_{n,GPC}$ = 22 k), PMDETA (17 mg, 0.1 mmol), CuBr (14 mg, 0.1 mmol) and the micelle dispersion of μ-*lhb*-(POEGMA-NH₂)(PSt-N₃)₂ (5 mg/mL, 40 mL) in cyclohexane/THF (v/v = 5). The tube was degassed by three freeze-pump-thaw cycles and sealed under vacuum. After the tube was kept in an oil bath thermosetted at 40 °C for 12 h, Merrifield resin with azido groups (0.2 g) and CuBr (6 mg, 0.04 mmol) was added. The reaction stood for additional 6 h and was quenched by cooling in ice bath. The mixture diluted with THF was passed through a neutral alumina column to remove copper salt. After two THF/hexane precipitations, the crude product was further washed alternatively with CH₃OH and hot cyclohexane for three times. The pure product of Janus long-chain hyperbranched copolymer [μ-(*lhb*-PSt-NH₂)(*lhb*-POEGMA-NH₂)] was obtained (yield: 0.9 g) by the evaporation removal of solvents and dryness under vacuum overnight at 30 °C.

Structure Characterizations

Proton nuclear magnetic resonance (^{1}H-NMR, 300 MHz) spectra were recorded on a Bruker DRX-300 NMR instrument at room temperature with tetramethylsilane and CDCl₃ as the internal standard and the solvent, respectively. Fourier transform infrared spectra (FTIR) were recorded on a Bruker VECTOR-22 IR spectrometer in KBr pellets. Number-averaged molecular weight and molecular weight distribution were determined at 30 °C on a Waters 150C GPC equipped with Styragel columns (10³, 10⁴ and 10⁵ Å) and a Waters 2414 refractive index detector. THF was used as eluent at a flow rate of 1 mL/min. Narrowly distributed PSt standards were used in the calibration of molecular weight.

Morphology observation by transmission electron microscopy

Transmission electron microscopy (TEM) observations were conducted on a Philips CM 120 electron microscope at an acceleration voltage of 100 kV. The sample for TEM observation was prepared by placing a 10 μL micelle dispersion on copper grids successively coated with thin films of Formvar and carbon. No staining was required.

Differential scanning calometry (DSC) study

DSC measurements were performed on a TA-Q2000 DSC (TA Instruments) under a nitrogen atmosphere and bout 5 mg of each sample were used. The sample was heated from room temperature to 180 ˚C, held for 5 min to remove thermal history, cooled to -120 ˚C at a rate of 10 ˚C·min⁻¹, held at -120 ˚C for 5 min. Then, the sample was heated from -120 to 160 ˚C at a heating rate of 10 ˚C·min⁻¹. The heat flow curves were analyzed to determine the glass transition temperatures (T_g) using the Universal Analysis 2000 software (TA Instruments).

Laser Light Scattering (LLS) Study

A commercial spectrometer (ALV/DLS/SLS-5022F) equipped with multi-τ digital time correlation (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser (λ_0= 632 nm) as the light source was used. The incident beam was vertically polarized with respect to the scattering plane. In dynamic LLS (DLS), Laplace inversion of each measured intensity–intensity time correlation function $G^{(2)}(q,t)$ in the self-beating mode can lead to a line-width distribution $G(\Gamma)$, where q is the scattering vector. For dilute solutions, Γ is related to the translational diffusion coefficient D by $(\Gamma/q^2)_{q\to0,C\to0} \to D$, so that $G(\Gamma)$ can be converted into a hydrodynamic radius distribution $f(R_h)$ via the Stokes–Einstein equation, $R_h = (k_BT/6\pi\eta_0)/D$, where k_B, T and η_0 are Boltzmann constant, absolute temperature and solvent viscosity, respectively. The time correlation functions were analysed by CONTIN analysis.

Contact angle Measurement

Contact angle to water (CA_w) or oil (CA_o) was determined on polymer films with a Contact Angle Meter (SL200B, Solon Tech). Polymer films were prepared by depositing polymer solution in THF, polymer micelle dispersions in methanol and cyclohexane onto clean glass slices. The solvents were removed by evaporation at room temperature for THF and methanol, or at 40 °C for cyclohexane. A droplet of water or oil (*n*-hexadecane) (2 μl) was dropped onto the films from the auxiliary syringe. The droplet shape on the films was cameraed

and the data were analysed with Software CAST 2.0. Three measurements on each of three films for different samples were averaged as the final results.

Results and discussion

The synthesis procedure for Janus long-chain hyperbranched copolymer composed of *lhb*-PSt and *lhb*-POEGMA dedrons includes three main stages (Scheme 1~3): 1) the preparation of four-armed star copolymer with four azido terminal groups [μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$]; 2) the preparation of *lhb*-PSt and *lhb*-POEGMA via azido-alkynyl click polymerization of seesaw macromonomers, and the conversion of terminal azido group into amino groups; 3) the sequential anchoring of *lhb*-POEGMA and *lhb*-PSt onto μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ in two different selective solvents.

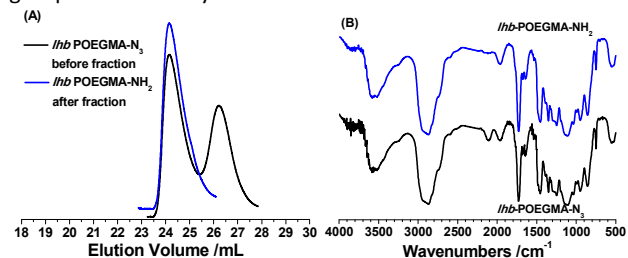### Preparation of *lhb*-PSt-NH$_2$ and *lhb*-POEGMA-NH$_2$

In our previous reports, long-chain hyperbranched PSt with azido terminal groups [*lhb*-PSt-N$_3$] have been successfully obtained.[25, 26] Herein, narrowly distributed alkynyl-(PSt-N$_3$)$_2$ with $M_{n,GPC}$ = 5.0 k was used as the macromonomer and the click polymerization only lasted for a short duration to sustain sufficient alkynyl focal groups for the following anchoring onto μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$. Figure 1A shows GPC diagrams of the so-produced *lhb*-PSt-N$_3$. The peak with the lower elution volume is attributed by the cyclized alkynyl-(PSt-N$_3$)$_2$, which can be easily removed by the dissolution fraction as done before.[26] Thus, the purified *lhb*-PSt-N$_3$ without cyclized macromonomer has apparent weight-averaged molecular weight ($M_{w,GPC}$) of 42 k and M_w/M_n of 2.11, as seen in Figure 1A. Figure 1B shows FTIR spectra of long-chain hyperbranched PSt before and after the terminal group conversion, where the characteristic absorbance of azido group at 2100 cm^{-1} disappears completely for *lhb*-PSt-NH$_2$. Unfortunately, ^{1}H-NMR analysis failed in offering the detail about the presence of alkynyl group in *lhb*-PSt as did for alkynyl-(PSt-N$_3$)$_2$ (Figure S1), because of quite little alkynyl groups in *lhb*-PSt. However, as evidenced in our previous work,[26] click polymerization of alkynyl-(PSt-N$_3$)$_2$ lasted up to 7 d, leading to the continuous growth of *lhb*-PSt. Thus, two-hour duration herein would ensure the existence of alkynyl groups in the obtained sample.
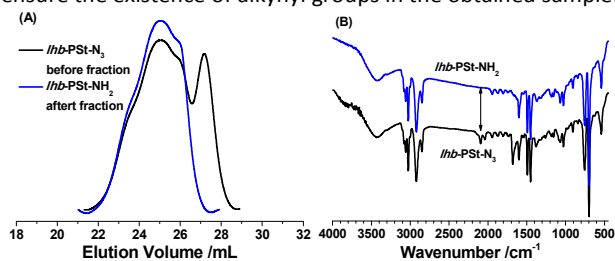
Figure 1. (A) GPC diagrams of *lhb*-PSt-N$_3$ before and *lhb*-PSt-NH$_2$ after dissolution fraction; (B) FTIR spectra of *lhb*-PSt-N$_3$ and *lhb*-PSt-NH$_2$

Through the similar route, *lhb*-POEGMA-NH$_2$ was obtained from narrowly distributed alkynyl-(POEGMA-N$_3$)$_2$ ($M_{n,NMR}$ = 15

k, M_w/M_n = 1.21, Figure S2). Since click polymerization of alkynyl-(POEGMA-N$_3$)$_2$ lasted for only 1 h, GPC diagram (Figure 2A) of *lhb*-POEGMA-N$_3$ exhibits bimodal distribution of molecular weight. Two peaks with higher and lower elution volume corresponds to macromonomers and hyperbranched polymers, respectively. With careful dissolution fraction with ethyl ether, pure *lhb*-POEGMA-N$_3$ without macromonomer has been obtained ($M_{w,GPC}$ = 46 k, M_w/M_n = 1.48). Figure 2B shows FTIR spectra of *lhb*-POEGMA before and after end-group conversion, indicating the disappearance of azido absorbance in *lhb*-POEGMA-NH$_2$. Since the carbon atom next to bromo or azido group has no proton, it is difficult to identify the end-group conversion by NMR.

Figure 2. (A): GPC diagrams of *lhb*-POEGMA-N$_3$ before and *lhb*-POEGMA-NH$_2$ after dissolution fraction; (B): FTIR spectra of *lhb*-POEGMA-N$_3$ and *lhb*-POEGMA-NH$_2$

### Preparation of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$

Four-arm block copolymer having azido terminal groups [μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$] was used as the centre to avoid bulky hindrance during uniting both hyperbranched polymers together. To obtain μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ with well-defined structure, the synthesis procedure was optimized, including the linkage sequence of alkynyl-(POEGMA-Br)$_2$ and alkynyl-(PSt-Br)$_2$ onto DATEG, reactant ratio and purification for each linkage.

Firstly, alkynyl-(PSt-Br)$_2$ was reacted with excess DATEG to obtain azido-(PSt-Br)$_2$ through azide-alkyne 1,3-cycloaddition click reaction. The unreacted DATEG was removed by the precipitation purification with THF/methanol, which was confirmed by GPC analysis. Figure 3A shows that azido-(PSt-Br)$_2$ has almost the same GPC diagram as alkynyl-(PSt-Br)$_2$. Figure 3B compares ^{1}H-NMR spectra of two seesaw-type PSt samples, focusing on the characteristic signals. Azido-(PSt-Br)$_2$ has the signal of methine proton next to bromo group (H_b at 4.52 ppm) and those of different methylene protons from DATEG (3.3~4.3 ppm). The methylene protons from propargyl group changes its chemical shift from 4.50 ppm [H_a of alkynyl-(PSt-Br)$_2$] to 5.07 ppm [$H_{a'}$ of azido-(PSt-Br)$_2$] due to the formation of electron-withdrawing triazole group. Integral height ratio of $H_{a'}$: H_b : H_c is roughly 1 : 1 : 8. Those results suggests the successful couping between alkynyl-(PSt-Br)$_2$ and DATEG.

Secondly, azido-(PSt-Br)$_2$ was coupled with alkynyl-(POEGMA-Br)$_2$ in DMF. Since the polarity of DMF may cause alkynyl-alkynyl Glaser coupling reaction of alkynyl-(POEGMA-Br)$_2$,[34,35] azido-(PSt-Br)$_2$ should be excess. Wang Resin with alkynyl

groups was used to remove the residual azido-(PSt-Br)$_2$. After that, bromo groups at all four block ends were converted into azido groups through the reaction with sodium azide in DMF, and μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ was obtained. In Figure 3A, GPC curve of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ moves to lower elution volume compared with its two precursors and is symmetrically narrow without shoulder peak, suggesting that the product would have increasing molecular weight and narrow distribution. Table 1 summarizes the molecular weight characterization of different polymers by GPC measurement.

^{1}H-NMR spectrum of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ is compared with those of azido-(PSt-Br)$_2$ and alkynyl-(POEGMA-Br)$_2$ in Figure 3C. The four-arm star copolymer exhibits the main signals from both PSt and POEGMA units, such as phenyl protons (6.3~7.4 ppm) and EG protons (3.69 ppm and 4.10 ppm), indicating the existence of PSt and PEGMA blocks in the product. Since the signal of methine proton next azido group of PSt block end is overlapped by that of methylene protons from $-$COOCH_2- in POEGMA blocks, FTIR other than ^{1}H-NMR was used to confirm the conversion of end groups. As shown in Figure 3D, besides the characteristic absorbance signals from PSt and POEGMA blocks, such as C-H stretching vibration of phenyl ring at 3025 cm^{-1}, C=O stretching vibration of ester bond at 1670 cm^{-1} and C-C bending vibration of phenyl ring at 698 cm^{-1}, that for azido group is clearly observed at 2200 cm^{-1}.
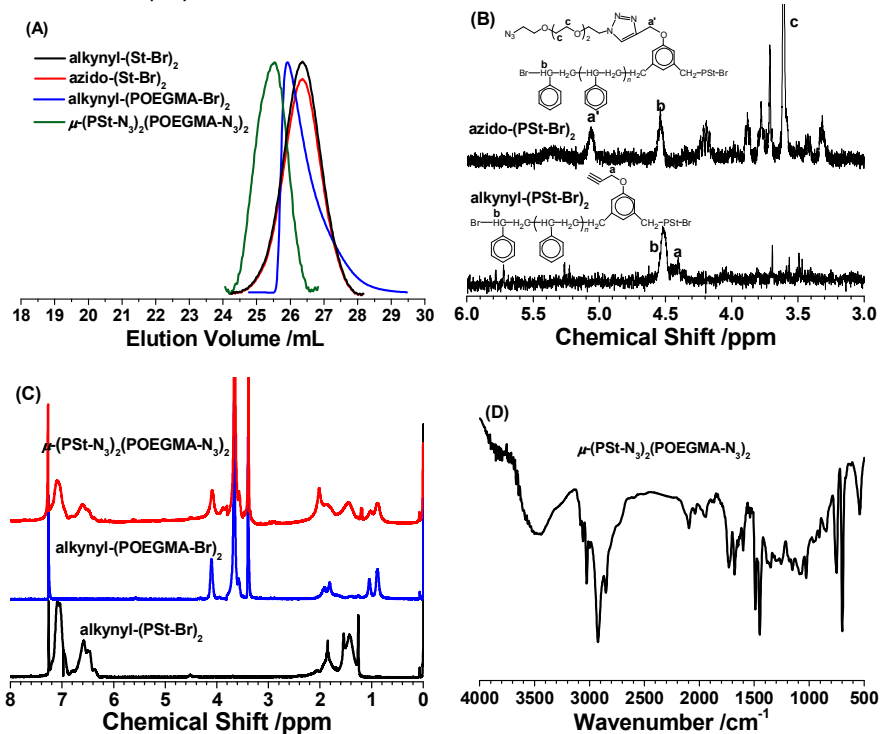
Figure 3. (A) GPC diagrams of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ and its precursors; (B) ^{1}H-NMR comparison of alkynyl-(PSt-Br)$_2$ and azido-(PSt-Br)$_2$; (C) ^{1}H-NMR spectra comparison of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ with its precursors; (D) FTIR spectra of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$

Table 1 GPC characterization of different polymers

sample	M_n (k)	M_w (k)	M_w/M_n
alkynyl-(PSt-N$_3$)$_2$	5.0	5.5	1.10
alkynyl-(POEGMA-N$_3$)$_2$	12	15	1.25
μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$	15	17	1.30
lhb-POEGMA	22	46	1.48
lhb-PSt	20	42	2.11
μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$	27	50	1.85

Studying self-assembly of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$

Because methanol is a good solvent to POEGMA but a non-solvent to PSt, μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ self-assembles into the core-shell micelles in methanol. TEM image (Figure 4A) suggests the spherical morphology of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ assemblies in methanol. Figure 4B shows the hydrodynamic radius (R_h) distribution with an average value of 50 nm in the solvated state, being a little higher TEM result in the dried state. To distinguish the core/shell composition of the obtained micelles, contact angle to water (CA_w) was measured on the polymer films prepared by casting the micelle dispersion in methanol onto glass slice. As revealed by camera imaging (Figure S3), CA_w from methanol is fairly low (39.8°), indicating the high hydrophilicity of such films. The films of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ were also separately obtained with cyclohexane and THF as the casting solvent. CA_w from cyclohexane and THF was determined to be 89.5° and 51.0°, respectively. The variation of CA_w with casting solvent reflects the core/shell composition.
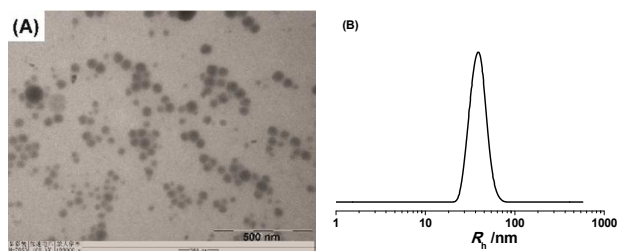
Figure 4. TEM image (A) and hydrodynamic radius distribution (B) of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ (methanol, 25 °C, $C_{polymer}$ = 10 mg/mL)

Since the μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ micelle in methanol have POEGMA shell and PSt core, the resultant film should have POEGMA continuous phase and be the highest hydrophilic. Cyclohexane is a good solvent to PSt and a non-solvent to POEGMA. Thus, the μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ micelle in cyclohexane should have the inversed core-shell structure, leading to the highest CA_w of the obtained film to water. In THF, μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ is molecularly dissolved and the obtained film is uniform in the composition, resulting in the moderate value of hydrophilicity. This water-angle measurement suggests that one component of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ could be buried in the micelle core with proper solvent, prohibiting its azido end-groups from click reaction with the coming chemicals.

**Synthesis of Janus μ-(*lhb*-POEGMA)(*lhb*-PSt) through self-assembly mediated click reaction Materials**

Coupling lhb-(POEGMA-NH$_2$) with μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ in methanol

To make sure that *lhb*-POEGMA having one focal alkynyl group was selectively linked to POEGMA arms of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ through click chemistry, methanol was used as the reaction medium. In such a solution, PSt blocks of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ was entrapped in the micelle cores and the azido end-groups of PSt block had hardly the opportunity to stretch out of the micelles, while the azido end-groups of POEGMA block were exposed completely. Thus, *lhb*-POEGMA was exclusively linked onto POEGMA terminal azido groups of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ to result in hyperbranched-block copolymer with two components joined at one centre, i.e. μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$. Figure 5A demonstrates GPC diagrams of those three polymers and the results are listed in Table 1. Obviously, the elution volume of μ-(PSt-N$_3$)$_2$(*lhb*-POEGMA) is lower than that of *lhb*-POEGMA and μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$, indicating the successful anchoring of *lhb*-POEGMA onto μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ core. At the same time, GPC trace of μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$ is not symmetrical. The proposed reason is that poly-dispersed *lhb*-POEGMA would have the different coupling ability dependent on overall molecular weight and amino groups at the *lhb*-POEGMA ends might induce the adsorption retarding effect in GPC measurement.
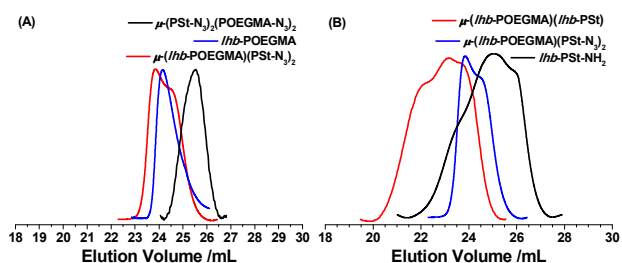
Figure 5. GPC monitoring the formation of μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$ (A) and μ-(*lhb*-POEGMA)(*lhb*-PSt) (B)

The self-assembly of μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$ in the selective solvent of cyclohexane was also investigated by TEM and DLS. While TEM image (Figure 6A) demonstrates the spherical morphology of the micelles, DLS analysis offers R_h of 71 nm. Those results suggest the formation of multi-molecule aggregates of μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$ in this selective solvent. It can be observed that the hydrodynamic radius distribution of μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$ micelles in cyclohexane is broader than that of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ in methanol. The probable reason is that *lhb*-POEGMA with relatively broad molecular weight distribution was introduced. Camera images for contact angle measurement on μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$ films casted from different solvents are shown in Figure S4 and the results are summarized in Table S1. With cyclohexane as casting solvent, μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$ film has the lowest contact angle to oil (CA_o) and the highest CA_w, suggesting that PSt blocks should be the shell of μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$ micelles in cyclohexane.
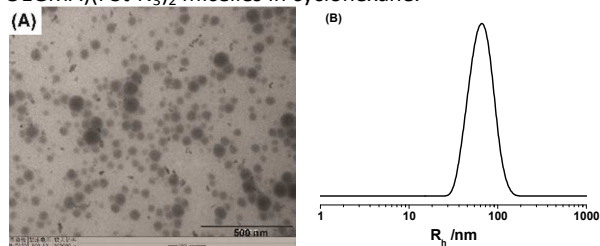
Figure 6. TEM image (A) and hydrodynamic radius distribution (B) of μ-(*lhb*-POEGMA)(PSt)$_2$ (cyclohexane, 40 °C, $C_{polymer}$ = 10 mg/mL)

Coupling lhb-(PSt-NH$_2$) with μ-(lhb-POEGMA)(PSt-N$_3$)$_2$ in cyclohexane/THF

At last, anchoring *lhb*-(PSt-NH$_2$) onto μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$ was performed in the mixture of cyclohexane/THF (5:1, v/v). Small portion of THF was introduced into cyclohexane to accelerate azide-alkyne click reaction. Figure 5B shows GPC diagrams of μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$, *lhb*-(PSt-NH$_2$) and Janus hyperbranched copolymer [μ-(*lhb*-POEGMA)(*lhb*-PSt)] and the results are listed in Table 1. Although GPC diagram of Janus hyperbranched copolymer is not symmetrical, its elution volume is obvious lower than that of both *lhb*-(PSt-NH$_2$) and μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$, indicating the successful linkage of *lhb*-PSt onto μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$.

Figure 7A collects ^{1}H-NMR spectra of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$, μ-(*lhb*-POEGMA)(PSt-N$_3$)$_2$ and μ-(*lhb*-POEGMA)(*lhb*-PSt). The signals at ~6.7 ppm (a) and ~4.1 ppm (b) are assigned to the two meso-protons of phenyl group from St and methylene protons next to oxycarbonyl group from OEGMA, respectively. From the integration ratio of H_a to H_b, it could be deduced that St content in three copolymers varies sequentially from 1:1, then 1:6, to 1:1, roughly being consistent with theoretical values from the amount of charged reactants and the yields. As well, the methyl signal at 0.95 ppm (from methacrylate) exhibits the similar variation.

The successful synthesis of μ-(*lhb*-POEGMA)(*lhb*-PSt) was also supported by DSC analysis. As shown in Figure 7B, both macromonomer of alkynyl-(PSt-Br)$_2$ and alkynyl-(POEGMA-Br)$_2$ has its individual glass transition temperature (T_g) of 99.8 ˚C and -62.9 ˚C, respectively. Moreover, crystalline and melting signals are observed in alkynyl-(POEGMA-Br)$_2$ thermogram. As for μ-(*lhb*-POEGMA)(*lhb*-PSt), two glass transition regions are distinguished, indicating the existence of two polymer components. However, T_g of POEGMA component increases to -57.5 ˚C and that of PSt component decreases to 80.8 ˚C, because the two components in the micro-phase separation system would interfere with each other, which also weakens heavily the crystalline and melting signals of OEG segments, as illustrated in the lowest diagram in Figure 7B.
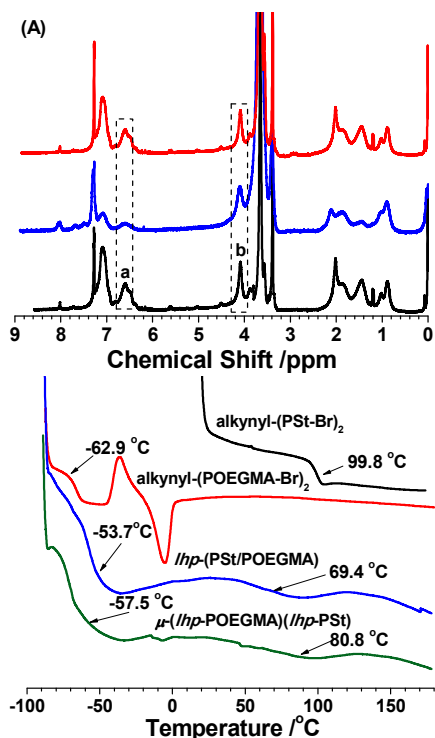
Figure 7. (A) ^{1}H-NMR spectra of μ-(*lhb*-POEGMA)(*lhb*-PSt) (upper) and its ancestors of μ-(*lhb*-POEGMA)(PSt-N$_3$) (middle) and μ-(POEGMA-N$_3$)(PSt-N$_3$) (lower) ; (B) DSC diagrams of μ-(*lhb*-POEGMA)(*lhb*-PSt) and its counterparts

To confirm Janus feature of μ-(*lhb*-POEGMA)(*lhb*-PSt), we further prepared another hybrid hyperbranched copolymer by simultaneous click reaction of alkynyl-(PSt-N$_3$)$_2$ and alkynyl-(POEGMA-N$_3$)$_2$, named as *lhb*-(PSt/POEGMA). This kind of hybrid hyperbranched copolymer has closer contact between two components, leading to the further increase of $T_{g,POEGMA}$ (-53.7 ˚C), the further decrease of $T_{g,PSt}$ (69.4 ˚C) and the disappearance of the crystalline and melting signals of OEG segments.

The formation of Janus architecture for μ-(*lhb*-POEGMA)(*lhb*-PSt) is also suggested by DLS study at the polymer concentrations of 10 and 0.1 mg/mL. Three solvents of THF, methanol and cyclohexane/THF mixture (v/v = 5) were used and different temperature was chosen to ensure the selectivity of solvent (THF: 25 °C, methanol: 40 °C, cyclohexane/THF: 60 °C). At the both concentrations, the hydrodynamic radius distributions of μ-(*lhp*-POEGMA)(*lhp*-PSt) are quite similar in different solvents. Figure 8 demonstrates them at 10 mg/mL. Since μ-(*lhp*-POEGMA)(*lhp*-PSt) is totally dissolved in THF, its R_h is certainly low (18 nm) at both polymer concentrations. In the selective solvents, self-assembly of μ-(*lhb*-POEGMA)(*lhb*-PSt) would occur to form multi-molecule aggregates as the previous μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ did. However, only unimer micelles of μ-(*lhb*-POEGMA)(*lhb*-PSt) were observed in methanol and cyclohexane/THF. Bulky half-dendrons of *lhb*-POEGMA and *lhb*-PSt would inhibit the multi-molecule aggregation and unimer micelles might be formed in selective solvents for μ-(*lhb*-POEGMA)(*lhb*-PSt). Moreover, since the dense contraction of core component, the value of R_h is 12 and 10 nm in methanol and cyclohexane/THF, respectively.
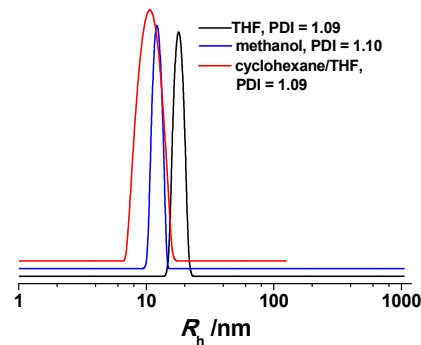
Figure 8. R_h distribution of μ-(*lhb*-POEGMA)(*lhb*-PSt) in different solvents ($C_{polymer}$ = 10 mg/mL)

Additionally, the hydrophilicity of μ-(*lhb*-POEGMA)(*lhb*-PSt) film can also be tuned with casting solvent (Figure S5), indicating the allocation of two components in the unimer micelles is correlated with self-assembly behaviour.

Conclusions

Janus hyperbranched copolymers were successfully achieved by self-assembly mediated click chemistry. Firstly, with α, ω-diazido tetra(ethylene glycol) as the conjoint core, four-arm star copolymer of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ was synthesized

by sequential click coupling alkynyl-(PSt-Br)$_2$ and alkynyl-(POEGMA-Br)$_2$, followed with the conversion of terminal bromo groups into azido groups. Then, long-chain hyperbranched polymers of *lhb*-PSt and *lhb*-POEGMA with a focal alkynyl group were synthesized within short duration through click polymerizations of alkynyl-(PSt-N$_3$)$_2$ and alkynyl-(POEGMA-N$_3$)$_2$ and their terminal azido groups were reduced to amino groups. Afterwards, in two different selective solvents, *lhb*-POEGMA and *lhb*-St was consecutively linked onto the core copolymers of μ-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$, during which self-assembled micelles ensured that only one components of amphiphilic copolymers could be linked with coming hyperbranched polymers. Therefore, long-chain hyperbranched copolymers, μ-(*lhb*-POEGMA)(*lhb*-PSt), was obtained. DSC comparison between μ-(*lhb*-POEGMA)(*lhb*-PSt) and *lhb*-POEGMA/PSt with uniform composition suggested asymmetrical distribution of POEGMA and PSt components. DLS results demonstrated the formation of unimer micelles in both selective solvents to POEGMA and PSt components. With other analytical techniques of NMR and contact angle measurement, it can be announced that Janus long-chain hyperbranched copolymers of μ-(*lhb*-POEGMA)(*lhb*-PSt) has been successfully obtained.

Acknowledgements

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Graphical Abstract

Janus Long-Chain Hyperbranched Copolymer of PSt and POEGMA from Self-Assembly Mediated Click Reaction

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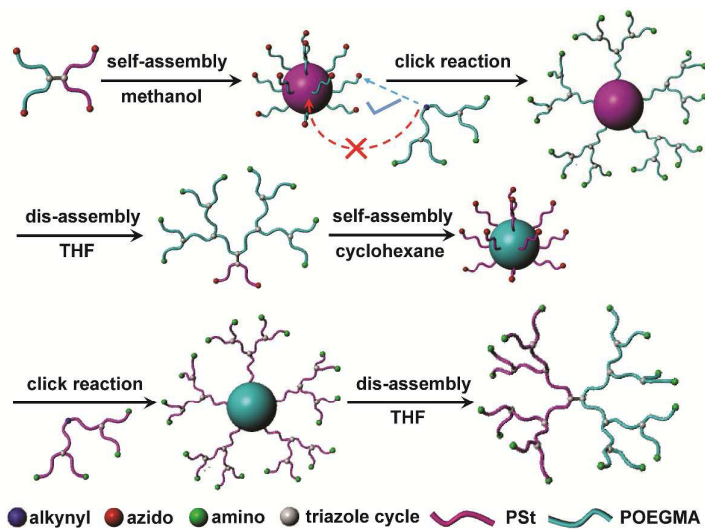
Janus hyperbranched POEGMA/PSt copolymer with long sub-chains was prepared through self-assembly mediated click reaction in selective solvents.