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Water-Soluble and Clickable Segmented Hyperbranched Polymers for Multifunctionalization and Novel Architecture Construction

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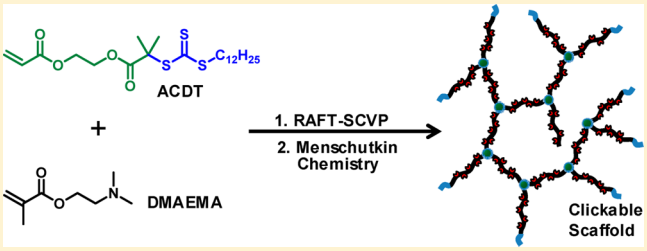
Supporting Information

ABSTRACT: A series of novel and narrowly polydispersed regular chain-segmented hyperbranched poly(tertiary amino methacrylate)s (HPTAM)s with hydrophilic core and hydrophobic shell were synthesized via the combination of self-condensing vinyl copolymerization (SCVCP) and reversible addition−fragmentation chain transfer (RAFT) methodology. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) and 2-((2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoyl)oxy)-ethyl acrylate (ACDT) at various molar feed ratios (γ, [DMAEMA]:[ACDT]) were chosen as monomers for linear segment formation of the structure. The copolymerization kinetics revealed that during the polymerization the real-time γ value kept almost constant and was consistent with the initial feed ratio. So HPTAMs possesses regular linear chains between every two neighboring branching units, which closely resemble HyperMacs in structure. Fast click-like Menschutkin reaction (i.e., quaternarization) of the segmented hyperbranched polymers with propargyl bromide and 2-azidoethyl 2-bromoacetate readily afforded water-soluble and clickable poly(propargyl quaternary ammonium methacrylate) (HPPrAM) and poly(azide quaternary ammonium methacrylate) (HPAzAM), respectively. Through Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAC), the HPPrAMs were functionalized with 1-azidododecane and 2-azidoethyl 2-bromoisobutyrate, giving birth to amphiphilic hyperbranched polyelectrolytes (or hyperbranched surfactants) and hyperbranched ATRP macroinitiators, respectively. The HPAzAMs were efficiently decorated with monoalkynyl poly(ethylene glycol) (PEG-Alk) via CuAAC, generating dendritic polymer brushes, a novel architecture reported for the first time. In addition, core-functionazlied star-shaped HPPrAM-*star*-poly(*tert*-butyl acrylate) was synthesized by RAFT copolymerization and Menschutkin reaction.



INTRODUCTION

Segmented hyperbranched polymers (SHPs, long-chain hyperbranched polymers) are receiving broad interests due to their unique topological structures and chemical/physical properties.[1] Three main methods have been developed to synthesize SHPs: (1) $A_2 + B_3$ approach,[2,3] (2) macromonomer AB_2 approach (HyperMacs),[4,5] and (3) self-condensing vinyl polymerization (SCVP) approach.[6−10] In vein of the $A_2 + B_3$ approach, Long and co-workers reported the preparation and structure−property behaviors of segmented hyperbranched poly(urethane urea) elastomer, poly(ether ester)s, poly(ether urethane)s, and polysulfone ionomers by polycondensation of an A_2 chain and a B_3 monomer.[2] They also synthesized poly(caprolactone) containing segmented hyperbranched poly(ester urethane)s via A_2 with oligomeric B_3 polymerization.[3] By varying the feed ratio of A_2 to B_3 in a reasonable extent, the degree of branching (DB) could effectively be controlled, but gelation remains to be an unavoidable problem that limits the availability of this approach. Alternatively, Hutchings and co-workers synthesized SHPs by polycondensation of AB_2 macromonomers, which were also defined as HyperMacs.[4] A few types of HyperMacs have been successfully prepared, such as polystyrene, polybutadiene, polybutadine-*co*-polystyrene, poly(methyl methacrylate), polynorbonene, poly(dimethylacrylamide)-*co*-polystyrene, poly(*tert*-butyl acrylate), and polystyrene-*co*-polyisoprene-*co*-polystyrene.[5] This macromonomer strategy possesses the undoubted advantage of offering the linear segments with precise molecular weights, however, to some extent, limited by the tedious synthesis of telechelic macromonomers. SCVP[11] has also been extended to readily prepare hyperbranched copolymers from vinyl monomers via copolymerization based on atom transfer radical polymerization (ATRP)[6,12] or reversible addition−fragmentation chain transfer (RAFT) process.[7−10,13] However, it is difficult to achieve segment regularity due to the reactivity difference between inimer (or chain-transfer monomer, CTM) and comonomer. Therefore, to simply and controllablly synthesize regular SHPs structures still remains a challenge.

On the other hand, few SHPs with functional groups at their linear segments have been reported so far, making the postfunctionalization of SHPs an unexplored research area. Moreover, to extend the applicability of SHPs, it is quite

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necessary to realize water solubility. Herein, we designed a new CTM and successfully used it to conduct RAFT copolymerization with 2-(dimethylamino)ethyl methacrylate (DMAEMA) via SCVP (RAFT-SCVP), affording regular chain-segmented hyperbranched poly(tertiary amino methacrylate)s (HPTAM)s of uniform linear chains hung with tertiary amino group at every repeat unit. The principle of our strategy is stepwise radical polymerization of vinyl monomers in the presence of CTMs. Further modification of HPTAMs with alkynyl or azido bromide via Menschutkin reaction[14] endowed them with desired chain-clickable structures and water solubility simultaneously. Such multifunctional SHPs promise wide applications in many fields such as antibacterial, drug delivery, gene transfection, phase-transfer agent, and versatile platform for novel architecture and functionality design.

EXPERIMENTAL SECTION

Materials. Monoalkynyl poly(ethylene glycol) (PEG-Alk) (M_n = 350) were prepared according to previous reports.[15] 2-Hydroxyethyl acrylate (HEA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), *tert*-butyl acrylate (*t*BA), CuBr (98%) and 2,2′-azobis(isobutyronitrile) (AIBN) were purchased from Aldrich. HEA, DMAEMA, and *t*BA were passed through a column of basic alumina to remove the stabilizing agents before use. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA, 98%) was purchased from Alfa Aesar. Propargyl bromide was purchased from Aladdin Chemical Co. China. Triethylamine (TEA), dimethylformamide (DMF), 1,4-dioxane, chloroform, dichloromethane, and other organic solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. and dried over CaH_2 before use.

Instruments. Gel permeation chromatography (GPC) was recorded on Perkin-Elmer HP 1100, using THF as eluent at a flow rate of 1 mL/min, RI-WAT 150 CVt+ as detector, and linear polystyrene as calibration at 40 °C. Light scattering data were recorded through Viscotek/Malvern GPC system consisting of a GPCMax autoinjector fitted to a TDA 305 triple detector array (differential RI, right angle light scattering (RALS), low angle static light scattering (LALS), and four-capillary differential viscometer detectors) using LiBr/DMF (0.02 mol/L) as eluent at a flow rate of 0.7 mL/min and linear poly(methyl methacrylate) as calibration at 50 °C. ^{1}H NMR (300 MHz) spectroscopy was carried out on a Varian Mercury plus 300 NMR spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. ^{13}C NMR (125 MHz) measurements were carried out on an Avance III 500 NMR spectrometer. Fourier transform infrared (FTIR) spectra were recorded on a PE Paragon 1000 spectrometer (film or KBr disk). Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan LCQ Mat LC/MS mass spectrometer system operating in a positive ion mode. Intrinsic viscosity of the polymer solution in THF was measured by a Ubbelohde viscometer at 30 °C.

Synthesis of (*s*)-1-Doceyl-(*s*)-(α,α′-dimethyl-α″-acidic acid) Trithiocarbonate, DDMAT. DDMAT was prepared according to the procedure reported in previous literature.[16] 1-Dodecanethiol (37.3 g, 0.184 mol), acetone (107 g, 1.84 mol), and Aliquat 336 (2.99 g, 7.37 mmol) were mixed in a 250 mL flask and then cooled to 10 °C. Sodium hydroxide aqueous solution (50 wt %) (15.5 g, 0.193 mol) was added dropwise. After the reaction mixture was stirred for 30 min at 10 °C, a mixture of carbon disulfide (14.0 g, 0.18 mol) and acetone (18.6 g, 0.32 mol) was added dropwise for another 20 min and stirred for another 10 min. Then chloroform (32.8 g, 0.28 mol) was added at once followed by dropwise addition of 50 wt % of sodium hydroxide aqueous solution (73.7 g, 0.922 mol). The reaction mixture was stirred overnight, and then 300 mL of water was added followed by dropwise addition of concentrated HCl aqueous solution (50 mL) to acidify the mixture until pH ≈ 2. The solid components were collected by filtration and then redispersed into 2-propanol (300 mL) with vigorous stirring. The undissolved solids were filtered off, and the filtrate was concentrated to dryness. The obtained solid was recrystallized from petroleum ether (60−90 °C) to generate 55.2 g of yellow crystal solid. ^{1}H NMR (300 MHz, $CDCl_3$): 3.32−3.26 (t, 2H, CH_2CH_2S), 1.72 (s, 6H, $COC(CH_3)_2S$), 1.64−1.70 (m, 2H, $CH_2CH_2CH_2S$), 1.25−1.45 (m, 20H, $CH_3(CH_2)10CH_2$), 0.85−0.90 (t, 3H, CH_3CH_2).

Synthesis of 2-((2-(((Dodecylthio)carbonothioyl)thio)-2-methylpropanoyl)oxy)ethyl Acrylate, ACDT. DDMAT (5.8 g, 16.0 mmol) and dry dichloromethane (58 mL) were charged to a 150 mL two-neck flask sealed with rubber septum and connected with a reflux condensor on top of which an oil bubbler was fitted. The flask was cooled in an ice−water bath and into which a dichloromethane (5 mL) solution of thionyl chloride (1.682 mL) was added dropwise through a syringe with vigorous stirring. Then, the flask was placed in an oil bath thermostated at 45 °C. After reacting for 1.5 h, dichloromethane and excess thionyl chloride were evaporated by vacuum distillation to afford acyl chloride as an orange liquid.

The as-prepared liquid was redissolved in dry dichloromethane (30 mL), and the solution was cooled to 0 °C. To this solution, a mixture of dry triethylamine (1.62 g, 16.0 mmol), HEA (2.34 g, 20.0 mmol), and dichloromethane (8 mL) was added dropwise. The reaction was stirred overnight. Then, the reaction solution were washed in sequence with 1 M HCl (50 mL) and saturated NaCl solution and dried over $MgSO_4$. After filtration, the volatiles were removed by a rotary evaporator. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (25:1) to give ACDT as an orange viscous liquid (6.81 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.37−6.44, 6.06−6.16, and 5.81−5.86 (m, 3H, CH_2CHCO), 4.31−4.39 (m, 4H, $COO(CH_2)_2OCO$), 3.25 (t, 2H, $SCH_2(CH_2)_{10}CH_3$), 1.69 (s, 6H, $COC(CH_3)_2S$), 1.20−1.41 (m, 20H, $CH_3(CH_2)_{10}CH_2$), 0.88 (t, 3H, CH_3CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): 220.7, 172.7, 165.7, 131.1, 128.3, 63.6, 62.0, 55.9, 37.1, 32.1, 29.6, 25.5, 22.8, 14.2. ESI-MS: product + NH^{4+}, 480.1 Da; calculated 480.2 Da.

Synthesis of Core−Shell Hyperbranched Poly(tertiary amino methacrylate) (HPTAM) by RAFT Copolymerization of ACDT with DMAEMA. In a typical polymerization, ACDT (0.3 g, 0.65 mmol), DMAEMA (0.5 g, 3.18 mmol), AIBN (1.8 mg, 0.01 mmol), and 1,4-dioxane (0.5 mL) were mixed in a 10 mL round-bottom flask sealed with a rubber stopper. After the solution was bubbled with N_2 for 15 min, the reaction system was placed into a 75 °C thermostatic oil bath. After stirring for 24 h, the polymerization was quenched by quick immersion of the reaction flask into liquid nitrogen and then subjected to GPC measurement (M_n: 13 400; PDI: 1.77). The solution was then diluted with chloroform (2 mL) and poured into a large amount of cold hexane (−10 °C). The precipitates were collected and dried in vacuo at 40 °C overnight to afford HPTAM (0.656 g) with a yield of 82%. ^{1}H NMR (300 MHz, $CDCl_3$): 4.20 ($COO(CH_2)_2OCO$, HEA unit), 4.06 ($COOCH_2CH_2N(CH_3)_2$, DMAEMA unit), 3.32 ($SCH_2(CH_2)_{10}CH_3$, docecyl chain), 2.56 ($CH_2CH_2N(CH_3)_2$, DMAEMA unit), 2.27 ($N(CH_3)_2$, DMAEMA unit), 1.68 ($COC(CH_3)_2$, DDMAT unit), 1.25 ($CH_3(CH_2)_{10}CH_2$, docecyl chain), 0.86 ($CH_2C(CH_3)(COO(CH_2)_2N(CH_3)_2$, DDMAT chain). ^{13}C NMR (125 MHz, $CDCl_3$): 220.7, 177.6, 170.5, 63.0, 57.4, 52.0, 45.9, 44.9, 41.7, 37.7, 32.1, 29.7, 28.0, 25.5−16.8, 22.9, 14.3.

Synthesis of Core−Shell Hyperbranched Poly(propargyl quaternary ammonium methacrylate), HPPrAM, by Reacting HPTAM with Propargyl Bromide. Typically, 0.5 g of HPTAM (γ = 5:1) was dissolved in a mixture of DMF (10 mL) and chloroform (4 mL) in a 25 mL round-bottom flask jacketed with aluminum foil and sealed with a rubber septum. Then, propargyl bromide (0.5 g, 4.23 mmol) was injected dropwise into the flask through a syringe. After the reaction was stirred at 30 °C for 24 h, the solution was poured into ethyl ether. The crude products were then redissolved in methanol and precipitated out from ethyl ether for removal of DMF and excess propargyl bromide. Drying in vacuo at 30 °C overnight afforded HPPrAM (0.70 g) as light yellow transparent solid with a yield of 94.0%.

Click Modification of HPPrAM via Alkyne−Azide Cycloaddition. HPPrAM (0.1 g), 1-azidododecane (0.14 g), methanol (1 mL), DMF (2 mL), and CuBr (5 mg) were mixed in a 25 mL round-bottom flask sealed with a rubber septum. After N_2 was purged into the flask to eliminate O_2 for 15 min, PMDETA (7.3 μL) was then

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injected through an airtight microsyringe. The reaction was stirred at 40 °C for 30 min. Then, the rubber septum was taken off to let O_2 quench the catalyst. The reaction solution was poured into ethyl ether to give the precipitates. The crude products were dissolved in methanol and precipitated into ether again for further purification. After dried in vacuo overnight, 0.93 g of products was obtained at conversion rate up to 100% determined from ^{1}H NMR spectrum.

In another modification experiments, 0.13 g of 2-azidoethyl 2-bromoisobutyrate was used following the same procedure with conversion rate near 100% determined from the FTIR spectrum and ^{1}H NMR spectrum.

Synthesis of Core−Shell Hyperbranched Poly(azide quaternary ammonium methacrylate), HPAzAM, by Reacting HPTAM with 2-Azidoethyl 2-Bromoacetate. 2-Azidoethyl 2-bromoacetate was prepared from bromoacetyl bromide and 2-azidoethanol in the presence of a bulk amine, *N*,*N*-diisopropylethylamine, in order to reduce the side reaction between amine and bromoacetyl groups. Freshly distilled bromoacetyl bromide (20 g, 100 mmol) and dried CH_2Cl_2 (80 mL) were mixed in a 250 mL round-bottom flask in an ice−water bath. A CH_2Cl_2 (50 mL) solution containing 2-azidoethanol (10.44 g, 120 mmol) and *N*,*N*-diisopropylethylamine (12.9 g, 100 mmol) was added dropwise to the flask with vigorous stirring for 2 h. The reaction was carried out in an ice−water bath for 4 h and then at ambient temperature for 20 h. The precipitates were filtered off, and the filtrate was washed in sequence with 1 M HCl, 1 M NaOH, and saturated NaCl aqueous solution. The organic phase was separated and dried over $MgSO_4$. After removal of CH_2Cl_2 via rotary evaporation, the residual was distilled under reduced pressure to afford 2-azidoethyl 2-bromoacetate (18.8 g, 90.5%) as a colorless liquid.

HPTAM (0.45 g, γ = 5:1) was mixed with 10 mL of DMF and 3 mL of chloroform in a 25 mL round-bottom flask coated with aluminum foil. Then, 0.79 g of 2-azidoethyl 2-bromoacetate was added to the flask. The reaction was stirred at room temperature until the methyl proton signal was totally shifted in the ^{1}H NMR spectrum. Then, ethyl ether was added to the solution to precipitate out the products. The crude products were then dissolved in methanol and precipitated into ethyl ether for further purification. Drying in vacuo at room temperature overnight gave 0.75 g of HPAzAM as light yellow transparent solid with a yield of 91%.

Click Modification of HPAzAM via Alkyne−Azide Cycloaddition with PEG-Alk. PEG-Alk (M_n = 350) was prepared following the procedure reported previously by our group.[15] 0.04 g of HPAzAM, 0.11 g of PEG-Alk, and 8 mg CuBr were added to a 25 mL round-bottom flask charged with 1 mL of DMF. The flask was then sealed with a rubber stopper and bubbled with N_2 for 15 min. 11.6 μL of PMDETA was injected into the flask through an airtight syringe. The reaction was carried out at 40 °C until the N_3 brand at 2100 cm^{-1} dissappeared in the FTIR spectrum. Then, the polymer was precipitated out from 9 mL of ethyl ether and dried in vacuo at room temperature overnight to give a 0.072 g of the product at 85% yielding rate and conversion rate near 100% determined from the ^{1}H NMR (300 MHz, $CDCl_3$) spectrum and FTIR spectrum.

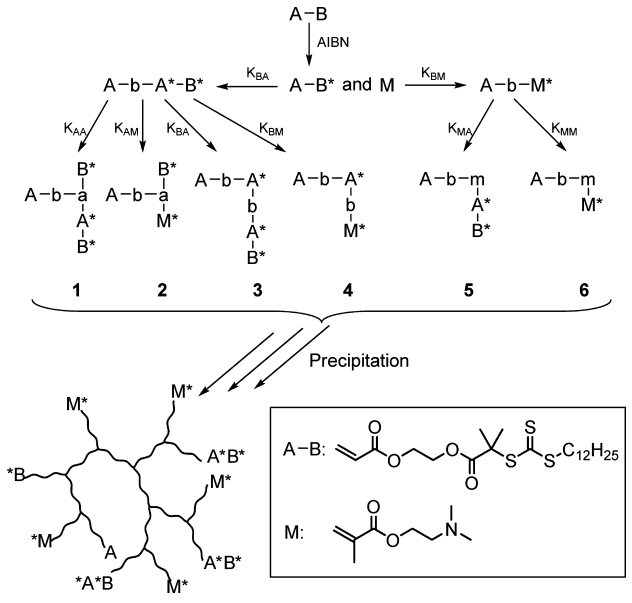
Synthesis of Star-Shaped Poly(*tert*-butyl acrylate) with HPTAM as the Macro-CTA Core, HPTAM-*star*-P*t*BA. To a 10 mL round-bottom flask, 143 mg of HPTAM, 147 mg of *t*BA, 0.94 mg of AIBN, and 1 mL of toluene were added, and N_2 was purged for 15 min. Then, the flask was placed in an oil bath thermostated at 70 °C for 3−5 h. Air was then purged to stop the polymerization. The polymer solution was poured into 10 mL of cold methanol/water (3/1) mixture (−5 to 0 °C). The precipitates were collected and dried in vacuo at ambient temperature overnight. The GPC measurements revealed that HPTAM-*star*-P*t*BA at 5 h had a PDI of 1.73 and a M_n of 19 100. ^{1}H NMR (300 MHz, $CDCl_3$): 4.19 ($COOCH_2CH_2OCO$, HEA unit), 3.32 ($SCH_2(CH_2)_{10}CH_3$, dodecyl chain), 1.43 ($COOC(CH_3)_3$, methyl proton at tBA unit), 1.24 ($SCH_2(CH_2)_{10}CH_3$, dodecyl chain), 0.88 (CH_3, polymer chain/dodecyl chain unit).

Synthesis of HPPrAM-*star*-P*t*BA by Quaternizing HPTAM-*star*-P*t*BA with Propargyl Bromide. 81 mg of HPTAM-star-P*t*BA, 0.11 g of propargyl bromide, 2 mL of DMF, and 0.67 mL of chloroform were charged to a 20 mL round-bottom flask coated with aluminum foil. After stirring for 48 h at room temperature, the solution was mixed with 10 mL of ethyl ether, and the precipitates were collected and dried in vacuo overnight to give 56 mg of HPPrAM-*co*-P*t*BA. ^{1}H NMR (300 MHz, $CDCl_3$): 4.82 ($NCH_2C{\equiv}CH$/$COOCH_2CH_2N$, propargyl unit/DMAEMA unit), 4.46 ($COOCH_2CH_2OCO$, HEA unit), 4.134 ($NCH_2C{\equiv}CH$/CH_2CH_2N, propargyl unit/DMAEMA unit), 3.34 ($N(CH_3)_2(CH_2C{\equiv}CH)$, DMAEMA unit), 1.38 ($C(CH_3)_3$, tBA unit), 1.22 ($SCH_2(CH_2)_{10}CH_3$, dodecyl chain), 0.84 ($CH_3$, polymer chain/dodecyl chain unit).

RESULTS AND DISCUSSION

Molecular Design and Reaction Mechanism. This article aims to synthesize water-soluble and chain-clickable regular SHPs with high molecular weight and low polydispersity for tailoring novel architecture and functionality via a controllable RAFT-SCVP strategy. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) is chosen as the monomer because the dimethylamino moiety could be used to introduce clickable groups via highly efficient and mild Menschutkin reaction. The CTM, 2-((2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoyl)oxy)ethyl acrylate (ACDT), is synthesized by esterification between 2-hydroxyethyl acrylate (HEA) and chain-transfer agent, (*s*)-1-doceyl-(*s*)-(α,α'-dimethyl-α''-acidic acid) trithiocarbonate (DDMAT). The reaction steps and initiating mechanism are illustrated in Scheme 1. The free

Scheme 1. Synthetic Mechanism for Segmented Hyperbranched Polymers via Self-Condensing RAFT Copolymerization (RAFT-SCVP)[a]



[a]"A" means the acrylic group of ACDT, "B" the trithiocarbonyl group of ACDT, "M" DMAEMA monomer, "a" the reacted A, "b" the reacted B, and "*" the radical site generated by the fragmentation of the trithiocarbonyl group.

radicals generated by the thermolysis of AIBN are first captured by the trithiocarbonyl part of CTM (A−B) to form A−B*. Then A−B* attaches onto the double bonds of CTM (A−B) and DMAEMA (M) at rate constants of K_{BA} and K_{BM} forming species A-*b*-A*−B* and A-*b*-M*, respectively. Subsequently, A-*b*-A*−B* couples A−B and M to form species **1**−**4** with rate constants of K_{AA}, K_{AM}, K_{BA}, and K_{BM}; A-*b*-M* couples A−B and M to form species **5** and **6** with rate constants of K_{MA} and K_{MM}. Further chain extension would result in SHPs at the

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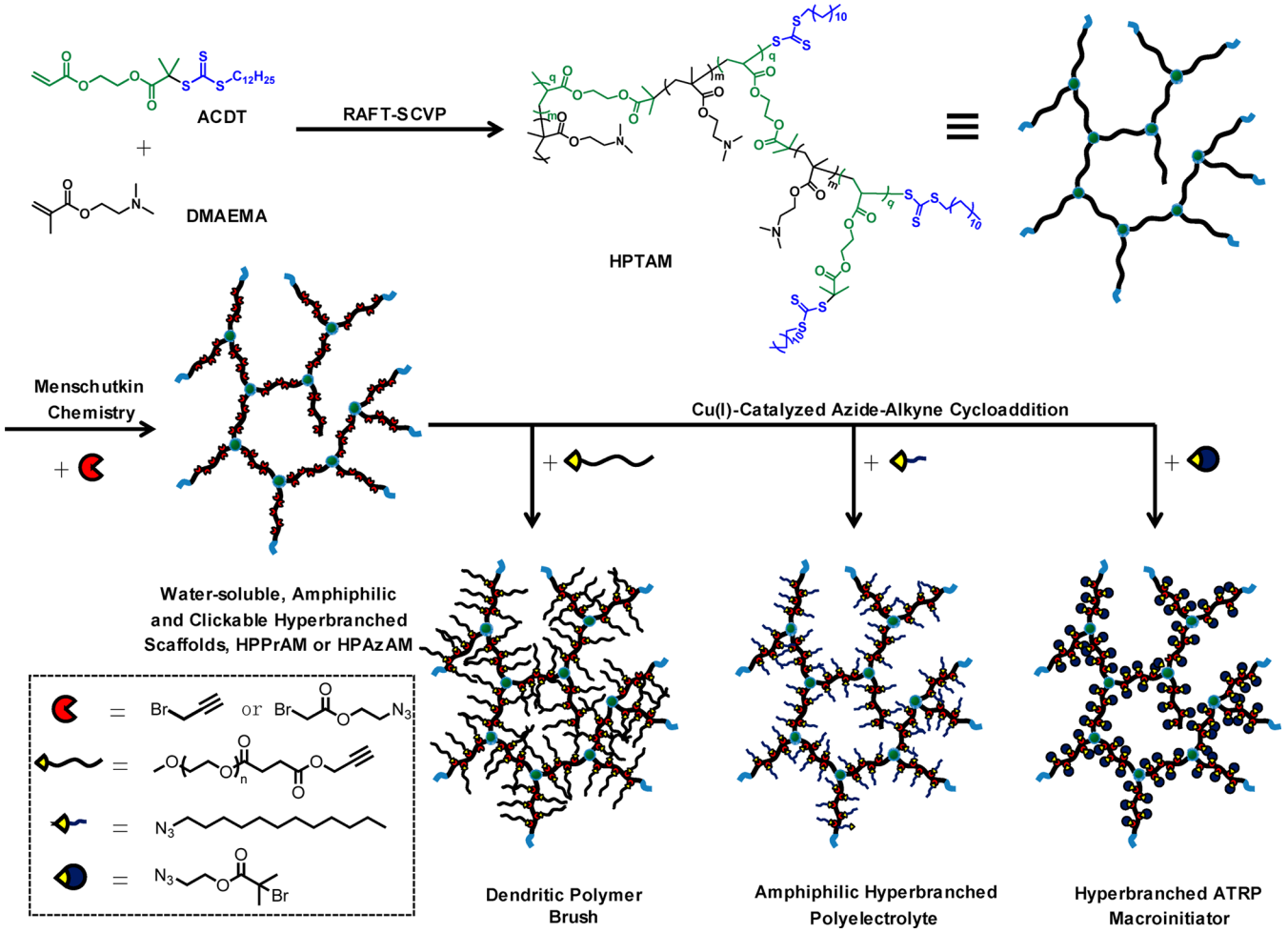
Scheme 2. Synthesis of HPTAMs and Subsequent Functionalization through Menschutkin Chemistry and Cu(I)-Catalyzed Azide−Alkyne Cycloaddition Click Chemistry



polymerization rate as depicted in eqs 1 and 2 (where M represents molar concentration of DMAEMA and D denotes molar concentration of double bonds of DMAEMA and ACDT).[17]

$$\frac{dM}{dt} = -M(K_{AM}A^* + K_{BM}B^* + K_{MM}M^*) \quad (1)$$

$$\frac{dD}{dt} = -A(K_{AA}A^* + K_{BA}B^* + K_{MA}M^*) \quad (2)$$

For an ideal compatibility of DMAEMA and ACDT in RAFT copolymerization, the six constant rates are relatively close, so that the ratio of dM/dt to dD/dt depends more on the monomer concentration in the mixture than on the constant rates. If so, at every reaction time point, the ratio of consumed DMAEMA to CTM should be close to the feed ratio γ, forming regularly segmented chains with repeat unit of "m" (Scheme 2). In our system, we have proved that the "m" remained relatively constant and near to the feed ratio γ during copolymerization. Then the polymers are reacted with bromo compounds (propargyl bromide or 2-azidoethyl 2-bromoacetate) via Menschutkin reaction, producing water-soluble SHPs with abundant clickable alkyne or azide sites. Based on the clickable platform of SHPs, a series of complex topological macromolecules are designed and synthesized.

Synthesis of Chain-Transfer Monomer (CTM). DDMAT was first converted into acyl chloride by reaction with thionyl chloride and then reacted with 2-hydroxyethyl acrylate (HEA) in the presence of triethylamine (TEA) to afford 2-((2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoyl)oxy)-ethyl acrylate (ACDT) as an orange viscous liquid in high yield. In the ^{1}H NMR spectrum of ACDT (Figure 1a), the signals emerged at 4.31−4.39 ppm are assigned to the ethylene protons, implying the formation of ester bond. The proton signals of the acrylic group appear at 6.37−5.86 ppm, while the terminal methyl proton signal originally belonging to DDMAT is observed at 0.88 ppm, and the ratio of their integrations is 1:1. In the ^{13}C NMR spectrum of ACDT, the carbon signal of trithiocarbonyl group is seen at 220.7 ppm, and other carbon signals are also clearly classified as depicted in Figure 1b.

Synthesis of HPTAMs via RAFT-SCVP of ACDT and DMAEMA. Scheme 2 shows the copolymerization protocol. ACDT, DMAEMA, AIBN initiator, and 1,4-dioxane at designed feed ratios were mixed in a round-bottom flask and heated at 75 °C under N_2 for a given time span. The viscous reaction system was then diluted with chloroform and poured into cold hexane (around −10 °C). The yields were generally above 92%, implying the high efficiency of our polymerizations. The structures of the resulting HPTAMs were characterized by ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectrum (Figure 1c), the resonance signal of the dimethylamino group, labeled

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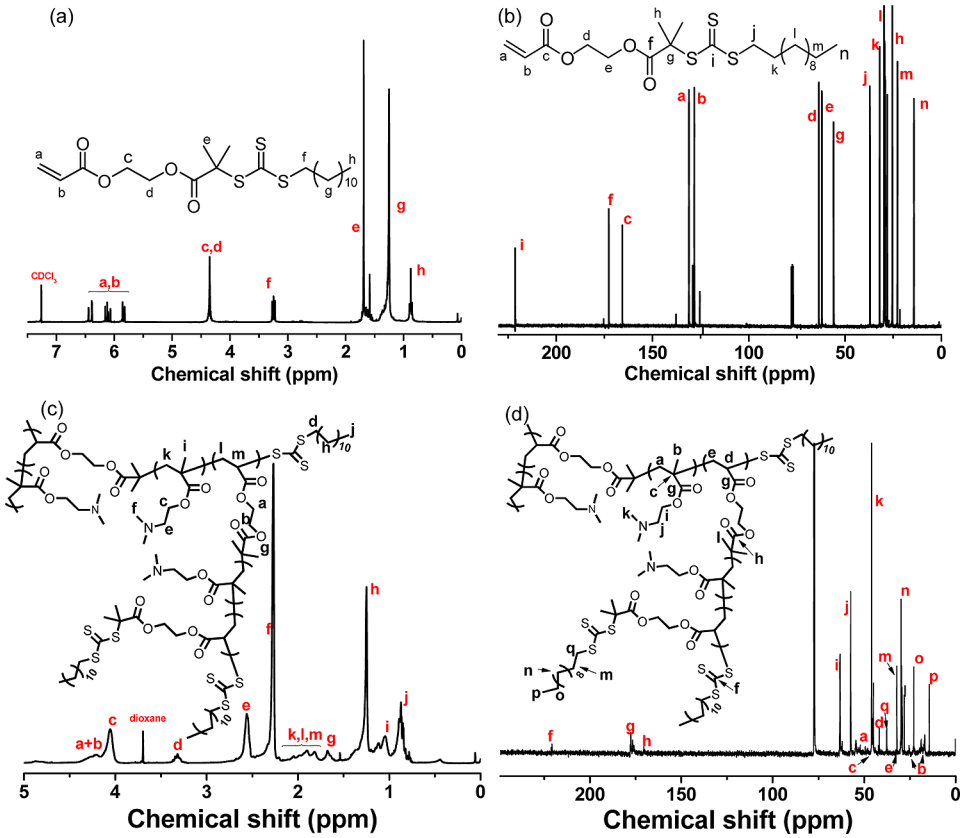

Figure 1. (a) ^{1}H NMR spectrum of ACDT in $CDCl_3$. (b) ^{13}C NMR spectrum of ACDT in $CDCl_3$. (c) ^{1}H NMR spectrum of HPTAM (feed ratio = 5:1) in $CDCl_3$. (d) ^{13}C NMR spectrum of HPTAM in $CDCl_3$.

as "f", is observed at 2.27 ppm, the signals of dodecyl chain at 1.25 and 0.86 ppm, and the proton signals of the polymer backbone at 2.1−1.7 ppm. No proton signals existed between 5.0 and 6.5 ppm which belonged to the acrylic groups of DMAEMA and ACDT, indicating the complete elimination of monomer from the polymer matrix and high conversion of ACDT. The compositions of HPTAMs (γ = 5:1, 15:1, 30:1) are determined by comparing the integration value of the proton signal labeled as "f" with those values of the signals labeled as "a, b, and d". The molar ratios of copolymerized DMAEMA to copolymerized ACDT in the HPTAMs were calculated as 4.68, 13.7, and 29.3, respectively, being quite closed to the feed ratios (γ = 5:1, 15:1, 30:1). This result is consistent with the high yields of polymers and high conversions of DMAEMA and CTM, promising high molecular weights. In the ^{13}C NMR spectrum (Figure 1d), the trithiocarbonyl carbon signal still locates at 220.7 ppm, implying that the as-prepared HPTAMs still could undergo further RAFT polymerization to form star-shaped structures. Unfortunately, owing to the overlapping of typical peaks, it is difficult to calculate DBs of the polymers.

The relative molecular weights and polydispersity indices (PDIs) of HPTAMs were determined by means of gel permeation chromatography (GPC) (Table 1). Generally, HPTAMs possess relatively high M_ns (generally above 11 000) and relatively low PDIs (1.71−2.64). The investigation on the influence of monomer concentration in 1,4-dioxane varying from bulk to 1 M was conducted at γ = 30:1. Increasing the monomer concentration, both molecular weights and PDIs increased. This is likely because higher monomer concentration favors the chain extension, and thus increases molecular weights, whereas the movement of radicals became less free,

Table 1. Synthesis of HPTAMs via Self-Condensing RAFT Copolymerization of ACDT (M_1) and DMAEMA (M_2)

code	$[M_2]:[M_1]$	conc^a (M)	time (h)	M_n ^{b}	M_w ^{b}	M_p ^{b}	PDI^b
1	30:1	bulk	24	28 600	75 400	50 700	2.64
2	30:1	10	24	25 200	37 700	61 000	1.83
3	30:1	5	24	22 100	50 900	42 400	2.30
4	30:1	2.5	24	22 700	47 600	46 400	2.09
5	30:1	1.5	24	11 500	20 000	19 800	1.73
6	30:1	1	24	8000	14 200	14 300	1.77
7	100:1	5	24	21 800	36 200	33 100	1.66
8	50:1	5	24	40 200	76 200	85 573	1.89
9	15:1	5	24	16 500	27 300	26 100	1.65
10	5:1	5	24	14 900	24 500	26 600	1.64

^{a}Feed concentration of DMAEMA. ^{b}Number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), peak value of M_n (M_p), and polydispersity index (PDI) determined by GPC.

causing difficulty for chain transfer agent in capturing radicals and resulting in broader PDIs. This fact is in accordance with another RAFT-based hyperbranched system reported by Mori and co-workers that higher concentration of monomers enhanced the occurrence of gelation, leading to higher molecular weight and broader PDI.[18] At a constant feed concentration of ACDT, experiments with gradient γs were conducted, and a series of SHPs with high molecular weights and relatively narrow PDIs were obtained (Table 1).

Considering the possible system errors in characterizing molecular weights by means of GPC introduced by the hyperbranched structures and the high polarity of dimethyla-

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mino groups, we adopted the differential RI/right angle light scattering (RALS)/low angle static light scattering (LALS) triple detector to possibly explore the real molecular weights of the SHPs. The corresponding results of representative polymer samples at different feed ratios (i.e., code 2, code 8, code 9, and code 10) are displayed in Table 2 and Figure 2. Monomodal

Table 2. Synthesis of HPTAMs via Self-Condensing RAFT Copolymerization of ACDT (M_1) and DMAEMA (M_2)

code	$[M_2]$:$[M_1]$	M_n[a]	M_w[a]	M_p[a]	PDI[a]	$[\eta]$ (dmL/g)[b]
10	5:1	31 500	52 200	40 000	1.65	10.15
9	15:1	43 100	100 800	58 022	2.34	13.75
2	30:1	96 300	279 900	236 900	2.90	30.71
8	50:1	99 700	184 600	157 000	1.85	19.27

[a]Number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), peak value of M_n (M_p), and polydispersity index (PDI) determined by Viscotek TDA305 with laser-light scattering detector. [b]Intrinsic viscosity.

traces of the molecular weight in Figure 2a indicated the relatively narrow M_n dispersions of the chain-segmented hyperbranched polymers compared with most hyperbranched polymers made from AB_2 methodolygy. The weight-averaged molecular weights (M_ws) increased from 52.2 to 184.6 kDa as the feed ratio expanded from 5:1 to 50:1 (Table 2), which means that the real molecular weight of HPTAMs are probably even larger than the results from conventional GPC characterizations. Compared with previous reports on hyperbranched structures via the RAFT-SCVP method which were characterized by similar light scattering triple detectors, molecular weights of the HPTAM series also are apparently much larger.[8] Moreover, the M_ws of sample code 2 is apparently larger than M_ws of sample code 8 in Table 2, which is against the result in Table 1. This disagreement of data from the same sample collected by conventional GPC, and the light scattering technique also indicated the unsuitability of using conventional GPC to characterize actual molecular weights of chain branched structures, since difference in hydrodynamic volumes makes the linear standards could hardly calibrate the hyperbranched strucutres. Besides, it is worth noting that Larson and co-workers have recently reported on the combination of temperature gradient interaction chromatography (TGIC) and rheological measurement for more accurate characterization of molecular weight of polymers with long chain branching fraction, and Hutchings et al. have also reported on the TGIC's better sensitivity to structural heterogeneity over the conventional GPC techniques.[19] In addition, intrinsic viscosities, $[\eta]$s, of the four samples characterized by Ubbelohde viscometer are listed in Table 2. The $[\eta]$ value regularly arises with increasing of M_ws. Especially, the relatively small $[\eta]$ values indicate the nature of hyperbranched structures.

Kinetic Study of RAFT-SCVP Polymerization. To investigate the evolution of components and structures during the RAFT-SCVP, kinetic study on polymerization (γ = 5:1) was performed by sampling at given time points for ^{1}H NMR and GPC characterizations. In the ^{1}H NMR spectra of kinetic samples (Figure 3b), the resonance signals of acrylic group of ACDT appeared at 6.4, 6.1, and 5.8 ppm, and the signal of methacrylic group of DMAEMA at 6.1 and 5.5 gradually became weaker and broader as polymerization proceeded, indicating the transformation of acryloyl groups into polymerized terminal acryloyl groups of HPTAMs. The conversions of DMAEMA, ACDT, and the total vinyl group (denoted as C_{M1}, C_{M2}, and C_M, respectively) were calculated from the integrations of these peaks and listed in Table 3. In 14 h, C_{M1} and C_{M2} reached ~98.3% and ~92.4%, respectively. Significantly, the ratio of C_{M1} to C_{M2} was relatively constant (~1), implying that DMAEMA and ACDT formed the branched structures in a ratio of ~5, identical to the feed ratio γ, during the whole polymerization (Figure 3d). Hence, the resulting HPTAM regularly has 5 repeat DMAEMA units between each two neighboring branching points.

Kinetic GPC results and curves were depicted in Table 3 and Figure 3a, respectively. In the initial 20 min, no peak of polymer or oligomers was detected, implying that an induction period existed during this time. After 40 min, oligomers gradually formed with M_n of ~2500 g/mol. With increasing polymerization time, molecular weights grew larger as indicated appearance of elution peaks at earlier retention time. From 5 to 14 h, approximate Gaussian distributions of GPC curves were observed, and all of PDIs are in the range of 1.2−1.7 (<1.8). Notably, though the molecular weight data of this kinetics are collected by conventional GPC, it might still be referential in vertical comparison of the same kind of polymers with different copolymerization time.

To probe the possible step-growth polymerization mechanism of RAFT-SCVP, we investigated the evolution of M_n as a

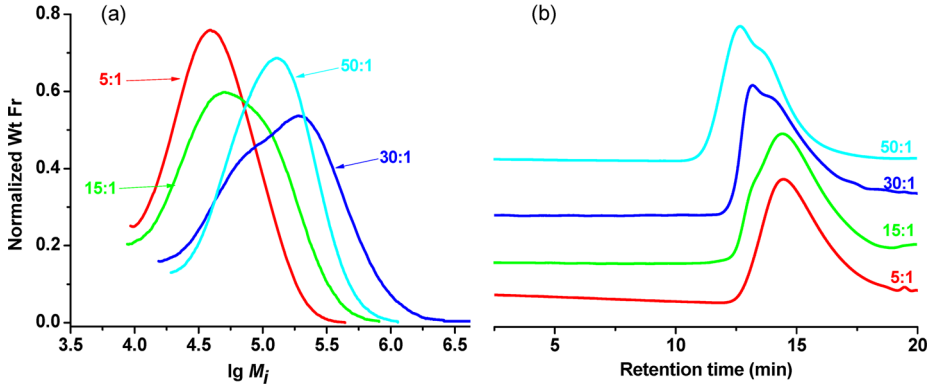

Figure 2. (a) Molecular weight dispersion traces obtained from RI/RALS//LALS triple detector at feed ratios of 50:1, 30:1, 15:1, and 5:1 corresponding to code 8, 2, 9, and 10 in Tables 1 and 2. (b) Conventional GPC traces of HPTAM at feed ratios of 50:1, 30:1, 15:1, and 5:1 corresponding to code 8, 2, 9, and 10 in Tables 1 and 2.

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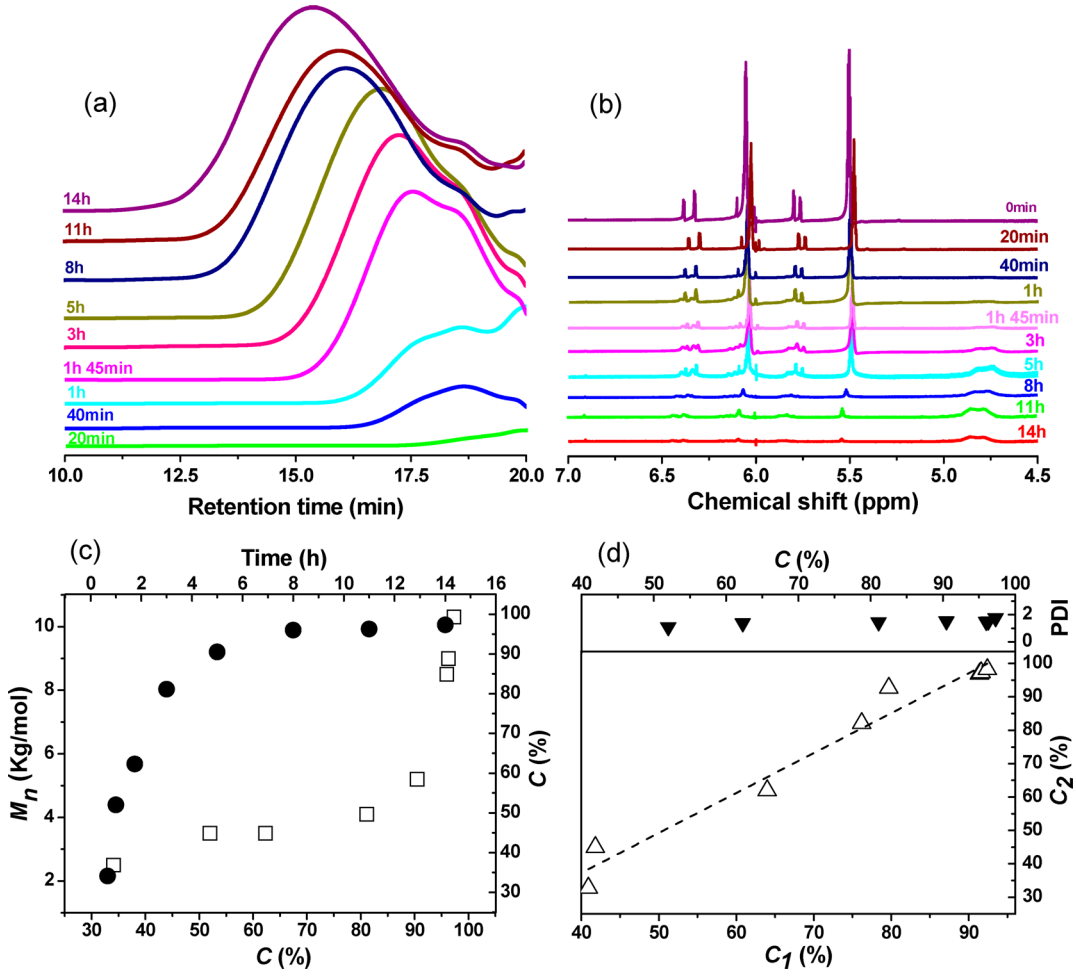

Figure 3. (a) GPC traces of HPTAM (γ = 5:1) collected at different polymerization time points for kinetic study. (b) ^{1}H NMR spectra of double bond signals collected at different polymerization points points for kinetic study. (c) Hollow square: dependence of M_n on total vinyl group conversion C. Filled circle: dependence of total vinyl group conversion C on polymerization time. (d) Hollow regular triangle: dependence of DMAEMA conversion C_2 on ACDT conversion C_1 during copolymerization. Filled inverse triangle: dependence of PDI on total vinyl group conversion C. Dashed line denotes the fitted linear line. See Table 3 for detailed reaction conditions.

Table 3. Kinetics Study of HPTAMs via Self-Condensing RAFT Copolymerization of ACDT (M_1) and DMAEMA (M_2)[a]

code	t (h)	C_{M1} (%)[b]	C_{M2} (%)[b]	C (%)[c]	M_n[d]	M_p[d]	PDI[d]	m[e]
K-1	0	N/A	N/A	N/A	N/A	N/A	N/A	N/A
K-2	0.33	N/A	N/A	N/A	N/A	N/A	N/A	N/A
K-3	0.67	40.9	32.8	34.1	2500	2600	1.25	4.01
K-4	1	41.8	45.0	52.0	3500	4300	1.10	5.38
K-5	1.75	64.0	62.0	62.3	3500	5100	1.39	4.84
K-6	3	76.2	82.1	81.1	4100	6000	1.46	5.39
K-7	5	79.7	92.7	90.5	5200	7300	1.53	5.82
K-8	8	91.4	96.9	96.0	8500	11200	1.49	5.30
K-9	11	91.6	97.3	96.3	9000	12100	1.51	5.21
K-10	14	92.4	98.3	97.3	10300	16000	1.77	5.32

[a]Polymerization conditions: [DMAEMA]:[ACDT]:[AIBN] = 150:30:1, [DMAEMA] = 6.5 M. [b]Conversions of M1 (C_{M1}) and M2 (C_{M2}) determined by ^{1}H NMR analysis. [c]Total conversion of double bonds (C), calculated by $C = (C_{M1} + 5C_{M2})/6$. [d]Number-averaged molecular weight (M_n), peak value of M_n (M_p), and polydispersity index (PDI) determined by GPC. [e]Unit ratio of DMAEMA to ACDT in polymers, calculated from ^{1}H NMR results and C_{M1} and C_{M2}.

function of total vinyl group conversion and the evolution of conversion rate as a function of copolymerizing time (Figure 1c). During the starting period (30 min−3 h), the conversion increased very fast and reached up to 81.1%, but M_n of HPTAM slowly increased to 4100 g/mol; after 3 h, the conversion increase was in a slow pace, but the molecular weight sharply increased. It took 11 h for the conversion rate of total vinyl groups to reach 100% while the M_n exponentially expanded to 10 300. This phenomenon is in full accordance with the polycondensation nature of SCVP that in the early stage monomers are condensed into oligomers with high conversion, and then the oligomers further polycondensed into

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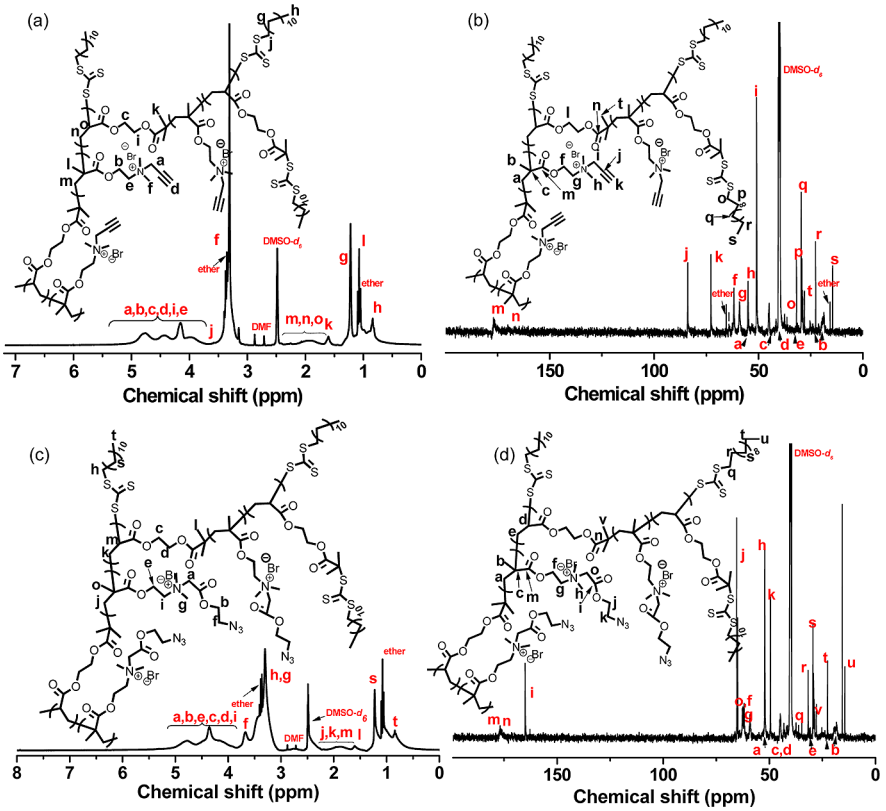

Figure 4. (a) ^{1}H NMR spectrum of HPPrAM in DMSO-d_6. (b) ^{13}C NMR spectrum of HPPrAM in DMSO-d_6. (c) ^{1}H NMR spectrum of HPAzAM in DMSO-d_6. (d) ^{13}C NMR spectrum of HPAzAM in DMSO-d_6.

macromolecules with the slow increase of conversion. Such a radical-initiating step-growth mechanism of RAFT-SCVP is also shared by the well-known SCVP-ATRP method.[17]

Menschutkin Reaction and Subsequent Click Functionalization. To render the SHPs with water solubility and abundant functional groups, especially clickable groups, highly efficient Menschutkin reaction was employed to functionalize the dimethylamino groups of the as-prepared HPTAMs (Scheme 2). The reaction can easily convert tertiary amines into quaternary ammonium salts in the presence of alkyl halides and help enhancing the polarity of HPs.

In order to explore the feasibility and the reaction conditions for Menschutkin reaction of HPTAM, a series of model compounds, including 2-(dimethylamino)ethyl methacrylate (DMAEMA), tetramethylethylenediamine (EDTA), and pentamethyldiethylenetriamine (PMDETA), were reacted with propargyl bromide in different kinds of solvents (Table S1) and characterized by ^{1}H NMR analysis. In aprotic solvents with high polarity such as DMF and DMSO, the reaction proceeded to completion quite fast (<1 h) at room temperature, while in other solvents, only partially quaternized products were acquired because of the precipitation of intermediates due to the high polarity of quaternary ammonium. In addition, the products could be easily purified by pouring the DMF or DMSO solution into low polar solvents, like acetone and ethyl ether. Accordingly, this Menschutkin reaction of high efficiency, mild condition, and absence of byproduct, though limited by the solubility of products in lower polar solvents, shares some common features with "click" chemistry and is a desirable click-like synthetic method for polymer postmodification.[20] The ^{1}H and ^{13}C NMR spectra of model compounds were presented in Figures S1−S3. The proton signal of the dimethylamino group at 2.4 ppm was replaced by a new one ascribed to the dimethylammonium group at 3.2 ppm. The proton signals of propargyl group appeared at 4.2−4.8 ppm.[21]

Likewise, clickable propargyl groups were introduced to HPTAMs via Menschutkin click reaction, affording HPPrAM. The ^{1}H NMR spectrum of HPPrAM showed that the proton signal of the HPTAM's dimethylamino group at 2.27 ppm completely disappeared, while a new signal ascribed to the HPPrAM's dimethylammonium group emerged at 3.37 ppm (Figure 4a). The introduced propargyl groups were detected as proton signals at 4.15 and 4.8 ppm and carbon signals at 50.8, 72.8, and 83.9 ppm (Figure 4b). These NMR analyses proved 100% conversion of dimethylamino groups into propargylammonium, which matches the "click" nature of Menschutkin reaction in polymer functionalization. The as-prepared HPPrAM became insoluble in chloroform and soluble in water (Table 4), indicating that the polarity was greatly enhanced due to the formation of quaternary ammonium groups. Notably, the existence of enough amount of hydrophobic chains served as solubilizing corona is responsible for 100% conversion, since it helps to retard overpolarization of the product to circumvent precipitation, guaranteeing homogeneous reaction during the whole Menschutkin click process.

The introduction of dense propargyl groups onto the SHPs affords a versatile platform for tailoring their structures and functions via Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAC) click chemistry. First, 1-azidododecane was employed to convert water-soluble HPPrAMs into amphiphilic hyperbranched polyelectrolytes (or hyperbranched surfactants). The products can be easily purified by repeated precipitation into ethyl ether. The newly emerged proton signal at 8.7 ppm was indicative of the formed triazole rings (Figure 5a). The

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Table 4. Solubility of Different Hyperbranched Structures in Selected Solvents[a]

polymer	H_2O	DMF	$CHCl_3$
HPTAM	×	√	√
HPPrAM	√	√	×
HPPrAM-N_3C_{12}[b]	√	√	√
HPPrAM-N_3Br[c]	√	√	×
HPAzAM	√	√	×
HPAzAM-PEG[d]	√	√	√
HPTAM-*star*-P*t*BA	×	√	√
HPPrAM-*star*-P*t*BA	√	√	×

[a] √ denotes soluble; × denotes insoluble. [b] HPPrAM clicked with 1-azidododecane. [c] HPPrAM clicked with 2-azidoethyl 2-bromoisobutyrate. [d] HPAzAM clicked with PEG-Alk.

characteristic absorption band of alkyne groups at 2128 cm^{-1} in the FTIR spectrum disappeared after the reaction (Figure 5d), implying the high efficiency of CuAAC. Because lots of hydrophobic dodecyl chains were installed on the linear segments of HPPrAMs, the obtained hyperbranched polyelectrolytes become well soluble again in $CHCl_3$ (Table 4). In another try, HPPrAMs were functionalized with ATRP initiator, 2-azidoethyl 2-bromoisobutyrate, affording hyperbranched ATRP macroinitiators whose structures were also demonstrated by ^1H NMR and FTIR characterizations (Figure 5b,d). The hyperbranched ATRP macroinitiators can be used to undergo ATRP polymerization to generate dendritic polymer brushes via the "grafting from" strategy, which is in progress and will be reported elsewhere.

Apart from alkynyl platform, the azide conuterpart is also designed and synthesized through Menschutkin click reaction between HPTAMs and 2-azidoethyl 2-bromoacetate to afford HPAzAMs. In the FTIR spectrum (Figure 5d), a strong absorption band of azido groups appeared at 2110 cm^{-1}. In the ^1H NMR spectrum of HPAzAM (Figure 4c), the signal of the *N*-methyl groups shifted from 2.2 to 3.3 ppm, indicating the complete transformation of tertiary amines into quaternary ammonium salts. Figure 4d shows the ^{13}C NMR spectrum of HPAzAM. The carbon signal at 52.1 ppm was assigned to the methyl carbon connected to the nitrogen atom, and the signals at 64.9 and 49.5 ppm represented the two ethylene carbons next to the azido group. Similarly, the HPAzAM was highly soluble in water and DMF and insoluble in $CHCl_3$ (Table 4). These results declared the successful preparation of HPAzAM.

To demonstrate the vitality of azido groups linked on HPAzAM, we conducted CuAAC between HPAzAM and monoalkyne PEG (PEG-Alk, M_n = 350) via the "grafting to" strategy to prepare dendritic polymer brushes. In the ^1H NMR spectrum of the dendritic polymer brush (Figure 5c), the characteristic protons of PEG repeat unit were observed as a peak at 3.6 ppm. As shown by real-time FTIR spectroscopy, the click reaction finished in 3 min with the complete disappearance of the strong band of azide groups at 2110 cm^{-1}, validating the rapidness and high efficiency of CuAAC.

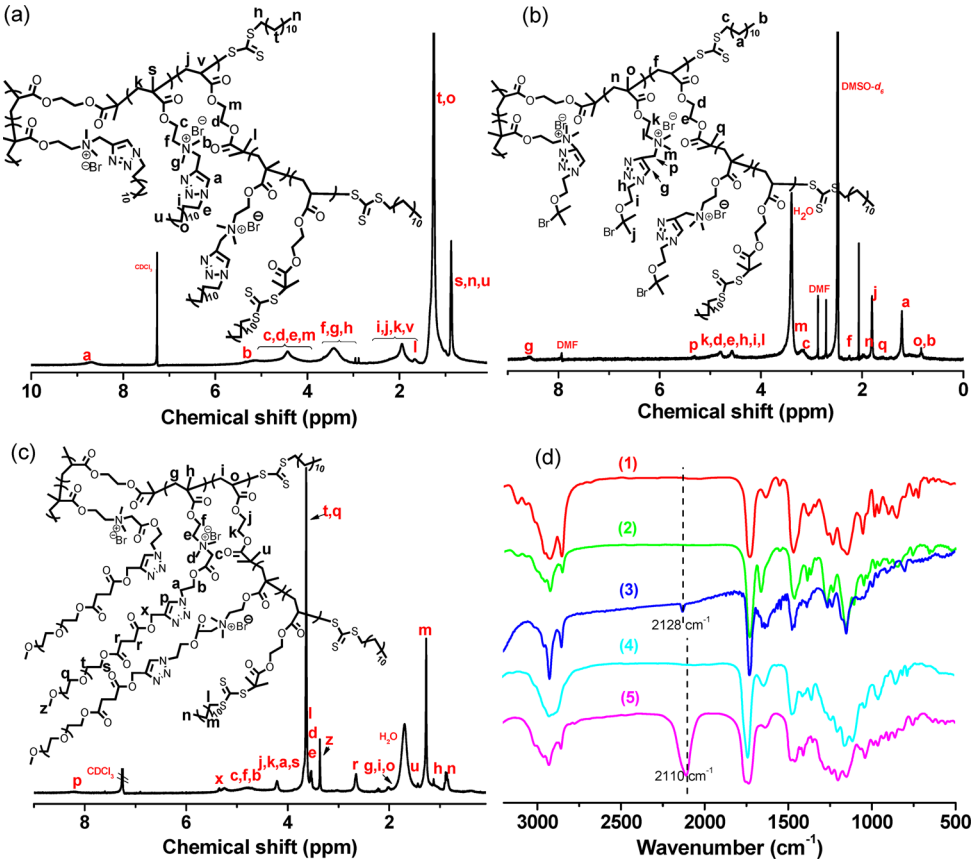

Figure 5. (a) ^1H NMR spectrum of HPPrAM modified with 1-azidododecane in $CDCl_3$. (b) ^1H NMR spectrum of HPPrAM functionalized with 2-azidoethyl 2-bromoisobutyrate in DMSO-d_6. (c) ^1H NMR spectrum of HPAzAM decorated with PEG-Alk in $CDCl_3$. (d) FTIR spectra of (1) HPPrAM modified with 1-azidododecane, (2) HPPrAM functionalized with 2-azidoethyl 2-bromoisobutyrate, (3) HPPrAM, (4) HPAzAM decorated with PEG-Alk, and (5) HPAzAM.

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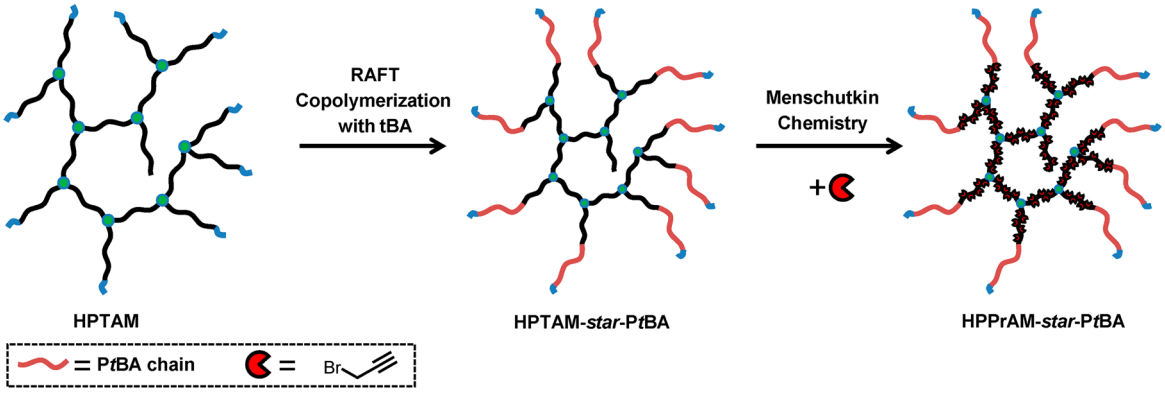
Scheme 3. Synthesis of Star-Shaped HPPrAM-*star*-P*t*BA via RAFT Copolymerization and Menschutkin Reaction



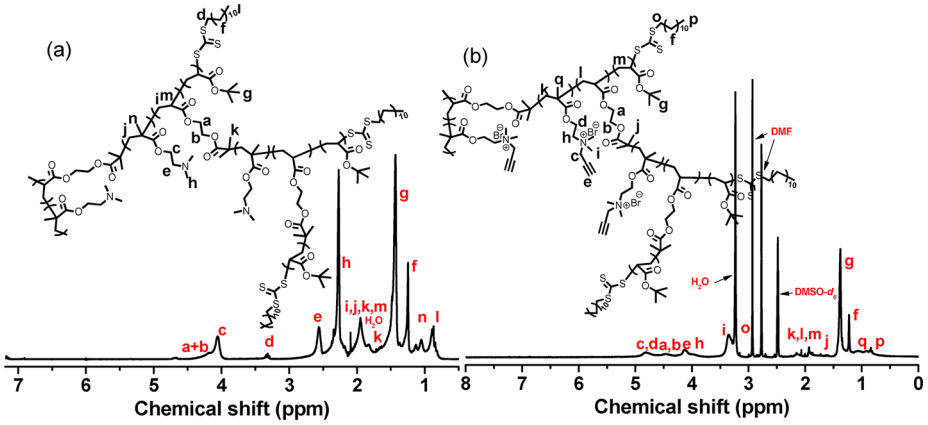


Figure 6. (a) ^{1}H NMR spectrum of HPTAM-*star*-P*t*BA in $CDCl_3$. (b) ^{1}H NMR spectrum of HPPrAM-*star*-P*t*BA in DMSO-d_6.

The introduction of PEG chains made the dendritic polymer brush soluble again in $CHCl_3$ (Table 4). All of these facts pronounce the versatility of clickable SHPs as a stretched-dendritic platform for multifunctionalization and novel architecture construction.

Star-Shaped Core−Shell Triblock Copolymer and Subsequent Efficient Menschutkin Reaction. In addition to scaffolds of our clickable SHPs, their functionalization at the corona was realized as well. The carbon signal of the trithiocarbonate groups of HPTAM was found at 220.7 ppm, implying that the HPTAM could serve as macro-CTA for further RAFT polymerization to form core−shell star polymers.[7] Experimentally, *tert*-butyl acrylate monomer and HPTAM in toluene was polymerized at 70 °C for 3−5 h in the presence of AIBN to afford HPTAM-*star*-P*t*BA (Scheme 3). In the ^{1}H NMR spectrum (Figure 6a), the characteristic signal of methyl groups of P*t*BA chains appeared at 1.43 ppm. The M_n increased from 6600 to 10 700 at 3 h and to 19 100 at 5 h, while the PDI still kept narrow (Table 5). Subsequently, HPTAM-*star*-P*t*BA was also modified with propargyl bromide via Menschutkin reaction, forming amphiphilic core−shell HPPrAM-*star*-P*t*BA. As a result, the signal at 2.27 ppm disappeared with the emergence of new signal at 3.35 ppm (Figure 6b), indicating that all of the tertiary amino groups had been transformed into quaternary ammonium groups.

CONCLUSIONS

HPTAMs with regularly linear chains in structure were successfully synthesized through self-condensing RAFT copolymerization (RAFT-SCVP) between ACDT (chain transfer

Table 5. Synthesis of HPTAM-*star*-P*t*BA via RAFT Copolymerization with *tert*-Butyl Acrylate[a]

polymer	time (h)	M_n[b]	M_w[b]	M_p[b]	PDI[b]	C_{tBA}[c] (%)
HPTAM		6 600	11 300	9 400	1.71	
HPTAM-*star*-P*t*BA	3	10 700	16 600	16 200	1.54	18.1
HPTAM-*star*-P*t*BA	5	19 100	33 000	29 100	1.73	58.3

[a]Condition: [thiocarbonate group]:[*t*BA]:[AIBN] = 20:200:1, [*t*BA] = 1 M. [b]Number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), peak value of M_n (M_p), and polydispersity index (PDI) determined by determined by GPC. [c]Conversion of *tert*-butyl acrylate determined from ^{1}H NMR analysis.

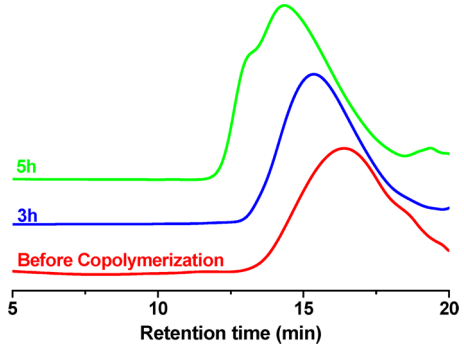


Figure 7. GPC traces of HPTAM (γ = 5:1) and HPTAM-*star*-P*t*BAs obtained via polymerization for 3 and 5 h.

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monomer, CTM) and DMAEMA at different feed ratios ranging from 100 to 5. The relatively low PDIs of HPTAM and high molecular weights demonstrate the practicability of this methodology. Kinetics study of the copolymerization proved the similar reactivity between CTM and monomer and that the polymerization rate of DMAEMA monomer to CTM is close to the initial feed ratio (γ, [DMAEMA]:[ACDT]), therefore confirming the regular SHP structures of HPTAMs. Based on the subsequent synthetic strategy (i.e., Menschutkin chemistry and CuAAC), evolution of HPTAMs into water-soluble and chain clickable hyperbranched scaffolds (HPPrAM and HPAzAM) for multifunctionalization and novel architecture building was realized. HPPrAM was modified with azide-containing long-chain alkane and ATRP initiator, affording amphiphilic hyperbranched polyelectrolyte (or hyperbranched surfactant) and hyperbranched ATRP macroinitiator, respectively; HPAzAM was clicked with PEG chains to form a novel structure, dendritic polymer brush. These water-soluble, amphiphilic, and azide/alkyne-containing SHPs, HPPrAM, and HPAzAM promise wide range of practical applications. The realization of multifunctional segmented hyperbranched polymers opens a new avenue for design and synthesis of novel materials and complex macromolecules.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section and results about NMR spectra and solubilities of the model compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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