Synthesis and Characterization of Hyperbranched Poly(ether amide)s with Thermoresponsive Property and Unexpected Strong Blue Photoluminescence

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ABSTRACT: A facile and efficient strategy for the syntheses of novel hyperbranched poly(ether amide)s (HPEA) from multihydroxyl primary amines and (meth)acryloyl chloride has been developed. The chemical structures of the HPEAs were confirmed by IR and NMR spectra. Analyses of SEC (size exclusion chromatography) and viscosity characterizations revealed the highly branched structures of the polymers obtained. The resultant hyperbranched polymers contain abundant hydroxyl groups. The thermoresponsive property was obtained from in situ surface modification of abundant OH end groups with *N*-isopropylacrylamide (NIPAAm). The study on temperature-dependent characteristics has revealed that NIPAAm-*g*-HPEA exhibits an adjustable lower critical solution temperature (LCST) of about 34−42 °C depending on the grafting degree. More interestingly, the work provided an interesting phenomenon where the HPEA backbones exhibited strong blue photoluminescence.

Introduction

Dendrimers and hyperbranched polymers, together classified as dendritic polymers, have attracted tremendous interest due to their three-dimensional globular architecture and unique properties, such as low viscosity, good solubility, and high functionality.[1] The procedures for the syntheses of structure-perfect dendrimers are usually multistep and time-consuming, which currently limits their practical use. In comparison with dendrimers, their imperfect analogues hyperbranched polymers can be prepared more conveniently and more cost-effectively from AB_n-type ($n \geq 2$) monomers via one-pot procedure.[2] Therefore, hyperbranched polymers have received attention as alternatives to dendrimers for emerging applications in areas such as polymer modifier,[3] molecular encapsulation and drug delivery,[4] and catalyst.[5] In the past decade, various types of hyperbranched polymers have been prepared by diverse synthetic strategies, such as self-polycondensation,[6] ring-opening polymerization,[7] self-condensation vinyl polymerization,[8] atom transfer radical polymerization,[9] and reversible addition−fragmentation chain transfer polymerization (RAFT).[10]

Michael addition reaction has recently gained widespread attention as a polymer synthesis strategy for tailored architectures, benefiting from mild reaction conditions, high functional group tolerance, a large number of polymerizable monomers as well as high conversions and favorable reaction rates.[11] Significant developments in synthetic methodologies of Michael addition polymerization beginning with the early use of specifically designed AB_n-type monomers[12] to the more recent use of $A_2 + B_3$ type monomers,[13] and variants thereof that exploit differential reactivities, such as $A_2 + BB'_2$,[14,15] have led to the synthesis of a wide range of hyperbranched structures. As an example, Liu, Pan, and their co-workers developed an approach to obtain hyperbranched poly(amino ester)s, by the Michael addition polymerization of diacrylate (A_2) or triacrylate (A_3) with 1-(2-aminoethyl)piperazine (BB'_2).[15a,b] However, up to now, only limited families of hyperbranched polymers have been prepared via the methods mentioned above. Our recent efforts have also focused on the facile synthesis of more types of novel hyperbranched polymers.[16] We developed a novel straightforward strategy for synthesis of hyperbranched poly(ether amide) (HPEA) via Michael addition polymerization from the commercially available multihydroxyl secondary amines and (meth)-acryloyl chloride.[16b] In this work, we extend the strategy to new monomers multihydroxyl primary amines.

Many efforts have been made to provide functionalities to dendritic polymers to elevate their usefulness and find new applications. Thermoresponsive polymers, which undergo a sharp coil−globule transition and phase separation at a lower critical solution temperature (LCST), are the most popular stimulus-responsive polymers and widely investigated for biomedical and biotechnological applications.[17] Combining the advantages of dendritic and thermoresponsive polymer are highly attractive for the production of functional or intelligent materials. In general, there are two major effective strategies to access the thermoresponsive dendritic polymers. One of them utilizes the incorporation of thermoresponsive polymers, such as poly(*N*-substituted acrylamide), onto the surface of a dendrimer or hyperbranched polymer.[18] Previously, Kimura et al. prepared the poly(propylenimine) (PPI) dendrimer having poly(*N*-isopropylacrylamide) (PNIPAAm) arms as a temperature sensitive host for catalysts.[18a] Recently, Liu and co-workers prepared thermosensitive dendritic copolymers with PNIPAAm as the arms and commercial hyperbranched polyester as the cores by RAFT polymerizations.[18d,e] The other strategy involves the attachment of some specific functional groups to the periphery of the dendritic polymers. Kono et al. reported that the introduction of isobutyramide groups or *N*-isopropylamide (NIPAAm) groups, which are common structural units in the linear thermosensitive polymer, to the chain ends of poly(amido amine) or PPI dendrimers could exhibit a sharp LCST.[19]

The mechanism of thermoresponsive property of the two strategies is different. In former case, the temperature sensitivity

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was given to the dendrimer by conjugation of the temperature-sensitive poly(*N*-substituted acrylamide) with the dendrimer. Their LCST properties were only contributed by their fundamental composition of the thermoresponsive linear polymer. In contrast, for the later case, the *N*-substituted amide-terminated dendrimer itself could achieve temperature-sensitive water solubility by balance of hydrophilicity and hydrophobicity.[19a] However, the reports on the later thermosensitive polymers based on hyperbranched polymers were relatively scarce. Only very recently, Chen et al. compared the LCST properties of hyperbranched polyethylenimines bearing terminal isobutyramide units with those of analogous dendrimers and linear systems.[20]

In this contribution, we described a facile synthetic method to access hyperbranched poly(ether amide) via Michael addition polymerization. Apart from demonstrating the utility of this simple approach, we have attempted to provide hyperbranched polymers with thermosensitive properties via in situ end group modification with NIPAAm groups. The LCST can be readily adjusted by the grafting degree of NIPAAm groups near the biological temperature. More interestingly, the work provided an interesting phenomenon that the hyperbranched poly(ether amide) backbones exhibited strong blue photoluminescence, which enables its new potential application.

Experimental Section

Materials. 2-Amino-2-methyl-1,3-propanediol (AMPO), tris(hydroxymethyl)aminomethane (THAM) and *N*-isopropylacrylamide were purchased from ACROS and used as received. 2,2-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Dimethyl sulfoxide (DMSO) was dried over calcium hydride (CaH_2) and distilled under reduced pressure. Acetonitrile was distilled over P_2O_5 after refluxing until colorless. *N*,*N*-Dimethylformamide (DMF) was distilled over calcium hydride after refluxing for 12 h under reduced pressure. Triethylamine (Et_3N) was distilled over calcium hydride after refluxing for 12 h. Distilled deionized water was prepared from Millpore Filtration System (Millpore, US). Acryloyl chloride (AC), methacryloyl chloride (MAC), potassium *tert*-butoxide (*t*-BuOK), triphenylphosphine (Ph_3P), *p*-quinone, and other reagents were used as received.

Characterization. ^1H NMR spectra were recorded on a Bruker AV 300 MHz spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent. ^{13}C NMR spectra were recorded on a Varian Unity 400 spectrometer operating at 100.0 MHz. The quantitative ^{13}C NMR spectra were conducted against with NOE (nuclear Overhauser enhancements) effects by inverse gated decoupling and with a pulse interval of 10.5 s to allow complete recovery of all carbons. At least 5000 acquisitions were collected for each spectrum. ESI−MS was measured by LCQ ion trap instrument (Finnigan MAT, San Jose, CA) with an electrospray source in positive ion mode. Electrospray voltage was 5.0 kV, and capillary temperature was set as 260 °C. Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) on a Perkin-Elmer Pyris 1 DSC with the heating/cooling rates of 10 °C/min, and taken as the midpoint of the inflection tangent, upon the third or subsequent heating scan. Thermogravimetric analytic (TGA) measurements were performed with a Perkin-Elmer Pyris 1 thermogravimetric analyzer with a heating rate of 20 °C/min in nitrogen. The inherent viscosities were measured with an automatic Ubbelohde viscometer thermostatted at 25 °C in a DMF solution.

The molecular weight and molecular weight distribution were determined by size exclusion chromatography/multiangle laser light scattering (SEC−MALLS). The SEC system consists of a Waters 515 pump, two Waters Ultrahydrogel columns, a Wyatt Optilab DSP differential refractometer detector, and a Wyatt DAWN EOS multiangle laser light scattering detector. An aqueous solution of 0.1 M $NaNO_3$ was used as the mobile phase at 1.0 mL/min flow rate at 35 °C. The refractive index increment d*n*/d*c* was determined with Wyatt Optilab DSP differential refractometer at 690 nm. Data analysis was performed with Astra 4.90 software (Wyatt Technology). Turbidity measurements of aqueous solutions of NIPAAM-terminated HPEAs were carried out on a Shimadzu UV-3600 spectrophotometer equipped with a peltier temperature control accessory. The transmittance of visible light ($\lambda = 500$ nm) was recorded as a function of temperature from 20 to 70 °C. Solutions of the polymers were prepared in distilled deionized water with the same concentration of 1% w/v and were stirred at room temperature until all polymers were dissolved. The heating rate of sample cells was adjusted at 1.0 K/min, data pitch in 5 s. The LCST was taken as the initial break points in the resulting transmittance versus temperature curve. Excitation spectra and emission spectra were obtained on a Perkin-Elmer LS 50B luminescence spectrometer with xenon discharge lamp excitation. Measurements were made from 1% w/v aqueous solutions, using quartz glass cuvettes with a 10 mm path length. Temperature was kept constant at 25 ± 1 °C throughout measurement. Fluorescence quantum yields were estimated with quinine sulfate in 0.1 N H_2SO_4 as the reference ($\Phi_F = 0.546$); the experimental error is estimated to be ±2.5%.

Model Reaction of Synthesis of Monomers. *2-Acryloylamino-2-methyl-propan-1,3-diol (**M1**).* **M1** was prepared according to the modified published literature.[21] Acryloyl chloride (1.81 g, 20 mmol) was added in drops under nitrogen atmosphere into a cold suspension of AMPO (2.10 g, 20 mmol) and triethylamine (8.3 mL, 60 mmol) in acetonitrile (200 mL). The reaction was allowed to proceed under stirring at 0 °C for 6 h. The suspension was heated to 60 °C and filtered while hot to remove the insoluble hydrochloride salt. The filtrate was concentrated to 20 mL followed by stored at room temperature, then the white crystal was formed and isolated by filtration (2.70 g). Yield: 90%. Mp: 83.8 °C.^1H NMR (DMSO-d_6): δ 7.35 (1H, s, CONH), 6.23 (1H, dd, J = 10.1, 17.0 Hz, CH_2=CH), 5.93 (1H, dd, J = 2.2, 17.0 Hz, *trans* CHH=CH), 5.42 (1H, dd, J = 2.2, 10.1 Hz, *cis* CHH=CH), 4.71 (2H, t, J = 5.7, OH), 3.39 (4H, dt, CCH_2OH), 1.05 (3H, s, CCH_3). ^{13}C NMR (DMSO-d_6): δ 165.7, 133.4, 125.6, 64.6, 59.5, 19.5. IR ν_{max}/cm^{-1}: 3359, 3264, 1648, 1613, 1560, 1083, 996. ESI−MS: found 182.08 $(M + Na)^+$ (calcd 182.17).

*2-Methacryloylamino-2-methyl-propan-1,3-diol (**M2**).* The synthesis procedure was similar to that of **M1**. Yield: 93%. Mp: 108.6 °C. ^1H NMR (DMSO-d_6): δ 6.83 (1H, s, CON*H*), 5.59 (1H, s, *trans* CH*H*=CCH_3), 5.30 (1H, s, *cis* CH*H*=CCH_3), 4.82 (2H, t, J = 5.7, OH), 3.48 (4H, dt, CCH_2OH), 1.84 (3H, s, CH_2=CCH_3), 1.18 (3H, s, CCH_3). ^{13}C NMR (DMSO-d_6): δ 169.0, 141.4, 119.8, 64.6, 59.4, 19.4, 19.0. IR ν_{max}/cm^{-1}: 3303, 3257, 1653, 1610, 1560, 1055, 930. ESI−MS: found 196.09 $(M + Na)^+$ (calcd 196.20).

*N-(Tris(hydroxymethyl)methyl)acrylamide (**M3**).* The synthesis procedure was similar to that of **M1**. Yield: 90%. Mp: 138.1 °C. ^1H NMR (DMSO-d_6): δ 7.41 (1H, s, CON*H*), 6.33 (1H, dd, J = 10.1, 15.9 Hz, CH_2=C*H*), 6.01 (1H, dd, J = 2.1, 15.9 Hz, *trans* CH*H*=CH), 5.61 (1H, dd, J = 2.1, 10.1 Hz, *cis* CH*H*=CH), 4.65−4.85 (3H, br, OH), 3.53 (6H, s, CH_2OH). ^{13}C NMR (DMSO-d_6): δ 164.4, 131.2, 124.1, 61.5, 59.5. IR ν_{max}/cm^{-1}: 3432, 3274, 1651, 1608, 1556, 1056, 967. ESI−MS: found 198.07 $(M + Na)^+$ (calcd 198.18).

*2-Methacryloylamino-2-hydroxymethyl-propan-1,3-diol (**M4**).* The synthesis procedure was similar to that of **M1**. Yield: 95%. Mp: 87.2 °C. ^1H NMR (DMSO-d_6): δ 6.73 (1H, s, CON*H*), 5.59 (1H, s, *trans* CH_2=CCH_3), 5.30 (1H, s, *cis* CH_2=CCH_3), 4.65−4.85 (3H, br, OH), 3.53 (6H, d, J = 3 Hz, CH_2OH), 1.81 (3H, s, CH_2=CCH_3). ^{13}C NMR (DMSO-d_6): δ 167.4, 139.2, 118.3, 60.9, 59.4, 17.4. IR ν_{max}/cm^{-1}: 3335, 3264, 1650, 1608, 1521, 1030, 995. ESI−MS: found 212.09 $(M + Na)^+$ (calcd 212.21).

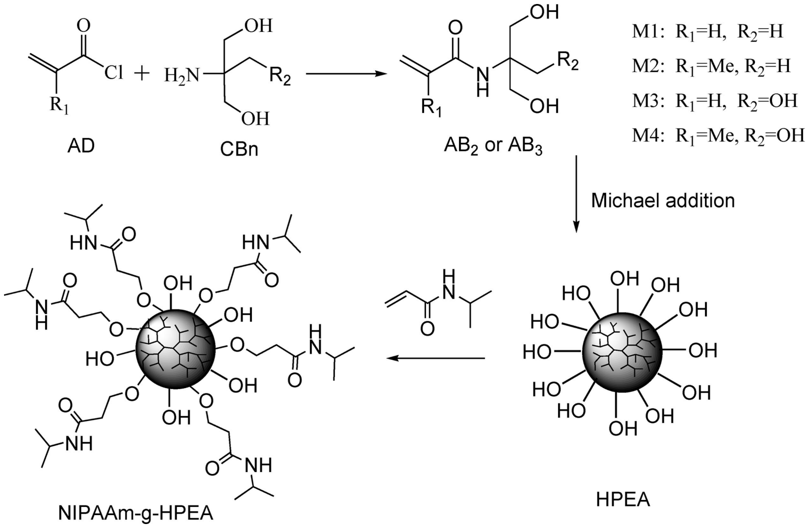
Polymerization Procedure. Take the polymer at Table 1, run 1 as an example. Typical polymerization procedure is as follows. A solution comprising **M1** (3.0 g, 19 mmol), *t*-BuOK (0.11 g, 0.95 mmol), *p*-quinone (0.015 g, 5‰ w/w), and DMSO (5 mL) was added to a Schlenk polymerization tube. The tube was degassed three times by the usual freezing and thawing technique in vacuo, flushed with nitrogen, and then sealed off. The polymerization was conducted under stirring at 60 °C for 48 h. The purification of the polymer was done via precipitation from DMSO solution by adding excess acetone three times. The product collected by filtration was

Table 1. Reaction Conditions and Polymerization Results of various Monomers[a]

run	monomer[b]	initiator	$\overline{M}_{w,LS}$[c] (kDa)	PDI	η_{inh}[d] (dL/g)	DB[e]	T_g (°C)	$T_d^{10\%}$ (°C)[f]
1	**1**	*t*-BuOK	21.3	3.41	0.157	0.62	15.5	338
2	**1**	Ph_3P	18.7	3.67	0.140	0.65	13.6	332
3	**2**	*t*-BuOK	7.6	1.97	0.115	0.54	−10.2	278
4	**2**	Ph_3P	5.3	1.88	0.106	0.58	−12.5	264
5	**3**	*t*-BuOK	16.6	2.53	0.135	0.50	20.6	315
6	**3**	Ph_3P	14.6	2.47	0.126	0.53	21.1	308
7	**4**	*t*-BuOK	5.4	1.51	0.095	0.47	−4.6	285
8	**4**	Ph_3P	4.8	1.58	0.084	0.44	−7.7	276

[a] All of the polymerizations were carried out at DMSO at 60 °C for 48 h. [b] The monomer concentration [M] = 25 wt %. [c] Calculated based on absolute measurement using a light scattering detector. [d] Measured at 25 °C with a concentration of 0.5 g/dL in DMF with an Ubbelohde viscometer. [e] The average value calculated by ^{13}C and ^{1}H NMR spectrum. [f] The temperature at which a 10% weight loss occurred at TGA measurements with a heating rate of 20 °C/min in nitrogen.

Scheme 1. Synthetic and Functionalized Strategy for Hyperbranched Poly(ether amide)s



dried under vacuum at 50 °C for 24 h. The resultant polymers exhibited as yellow honey-like oil or viscous rubber depending on the value of molecular weight.

Hyperbranched Poly(AC-AMPO), ***HP1***. FTIR (cm^{-1}, KBr): 3550−3250 (OH, NH), 1741 ($CH_2O\mathit{CO}$), 1661, 1560, 1466 ($NH\mathit{CO}$). ^{1}H NMR (DMSO-d_6): δ 7.53, 7.37, 7.25 ($N\mathit{H}CO$), 5.0−4.5 (broad, OH), 3.55, 3.42, 3.21 ($C\mathit{H_2}O$), 2.63, 2.31, 2.14 ($C\mathit{H_2}CONH$), 1.15, 1.07 ($C\mathit{H_3}$). ^{13}C NMR (DMSO-d_6): δ 174.6, 173.4, 171.6 ($NHCO$), 78.0, 77.1, 74.2, 69.2, 64.6 ($\mathit{C}H_2O$), 59.4, 58.7, 57.8 ($\mathit{C}(CH_2OH)_n(CH_2O)_{2-n}CH_3$), 38.4, 37.5, 37.2 ($\mathit{C}H_2CONH$), 19.6, 19.4, 19.3 ($\mathit{C}H_3$).

Hyperbranched Poly(MAC-AMPO), ***HP2***. FTIR (cm^{-1}, KBr): 3510−3250 (OH, NH), 1736 ($CH_2O\mathit{CO}$), 1655, 1560, 1459 ($NH\mathit{CO}$). ^{1}H NMR (DMSO-d_6): δ 7.68, 7.25, 7.20 ($N\mathit{H}CO$), 5.59, 5.30 (minor, $C\mathit{H_2}{=}CCH_3$), 5.0−4.7 (broad, OH), 3.54, 3.45, 3.17 ($C\mathit{H_2}O$), 2.79, 2.63 ($C\mathit{H}(CH_3)CONH$), 1.83 (minor, $CH_2{=}CC\mathit{H_3}$), 1.55 ($CH(C\mathit{H_3})CONH$), 1.05−0.59 ($C(CH_2OH)_n(CH_2O)_{2-n}C\mathit{H_3}$). ^{13}C NMR (DMSO-d_6): δ 178.7, 172.4, 168.8 ($NH\mathit{C}O$), 79.2, 78.3, 78.0, 70.7, 70.4 ($\mathit{C}H_2O$), 59.7, 59.0, 58.1 ($\mathit{C}(CH_2OH)_n(CH_2O)_{2-n}CH_3$), 43.8, 42.9, 42.7 ($\mathit{C}H(CH_3)CONH$), 19.5, 19.3, 18.9 ($C(CH_2OH)_n(CH_2O)_{2-n}\mathit{C}H_3$), 13.8 ($CH(\mathit{C}H_3)CONH$).

Hyperbranched Poly(AC-THAM), ***HP3***. IR (cm^{-1}, KBr): 3510−3250 (OH, NH), 1738 ($CH_2O\mathit{CO}$), 1659, 1536, 1463 ($NH\mathit{CO}$). ^{1}H NMR (D_2O): δ 6.21, 6.11, 5.59 (minor, $C\mathit{H_2}{=}C\mathit{H}$), 3.70−3.20 (group, $C\mathit{H_2}O$), 2.25 ($C\mathit{H_2}CONH$). ^{13}C NMR (D_2O): δ 174.4, 174.1, 173.8 ($NH\mathit{C}O$), 130.2 ($CH_2{=}\mathit{C}H$), 126.8 ($\mathit{C}H_2{=}CH$), 72.1($C(\mathit{C}H_2OCH_2)_n$), 68.2, 67.0, 66.6, 65.6 ($C(\mathit{C}H_2OH)_{3-n}$), 63.8, 63.6, 63.5 ($O\mathit{C}H_2CH_2CO$), 60.0, 59.2, 58.8, 58.4, 57.9 ($\mathit{C}(CH_2O)_n(CH_2OH)_{3-n}$), 37.3, 36.6, 36.2 ($OCH_2\mathit{C}H_2CO$).

Hyperbranched Poly(MAC-THAM), ***HP4***. FTIR (cm^{-1}, KBr): 3510−3000 (OH, NH), 1725 ($CH_2O\mathit{CO}$), 1644, 1573, 1462 ($NH\mathit{CO}$). ^{1}H NMR (D_2O): δ 5.51, 5.28 (minor, $C\mathit{H_2}{=}CCH_3$), 3.90−3.48 (group, $C\mathit{H_2}O$), 2.78−2.48 ($C\mathit{H}(CH_3)CONH$), 2.05 (minor, $CH_2{=}CC\mathit{H_3}$), 1.45, 1.23, 1.07 ($CH(C\mathit{H_3})CONH$). ^{13}C NMR (D_2O): δ 176.1, 175.8, 175.5 ($NH\mathit{CO}$), 77.6 ($O\mathit{C}H_2CH(CH_3)$-$CONH$), 72.4 ($C(\mathit{C}H_2OCH_2)_n$), 67.9, 66.5, 64.8 ($C(\mathit{C}H_2OH)_{3-n}$), 60.3, 59.5, 58.7, 58.1 ($\mathit{C}(CH_2O)_n(CH_2OH)_{3-n}$), 43.6, 42.7, 42.5 ($OCH_2\mathit{C}H(CH_3)CONH$), 13.8 ($OCH_2CH(\mathit{C}H_3)CONH$).

Graft of *N*-Isopropylacrylamide to Hyperbranched Poly(ether amide). After Michael addition polymerization was completed, graft of NIPAAm was performed in situ. The predetermined amount of NIPAAm and *t*-BuOK (5 wt ‰ of NIPAAm) were introduced into the solution polymerization system under nitrogen atmosphere, and then the temperature was raised to 80 °C. After reacting for 2 days, the solution was precipitated into excess diethyl ether, and the NIPAAm-grafted polymer was collected and purified by reprecipitation from a THF solution into diethyl ether three times. The resultant polymer was dried at 50 °C under vacuum for 24 h to give a highly viscous liquid.

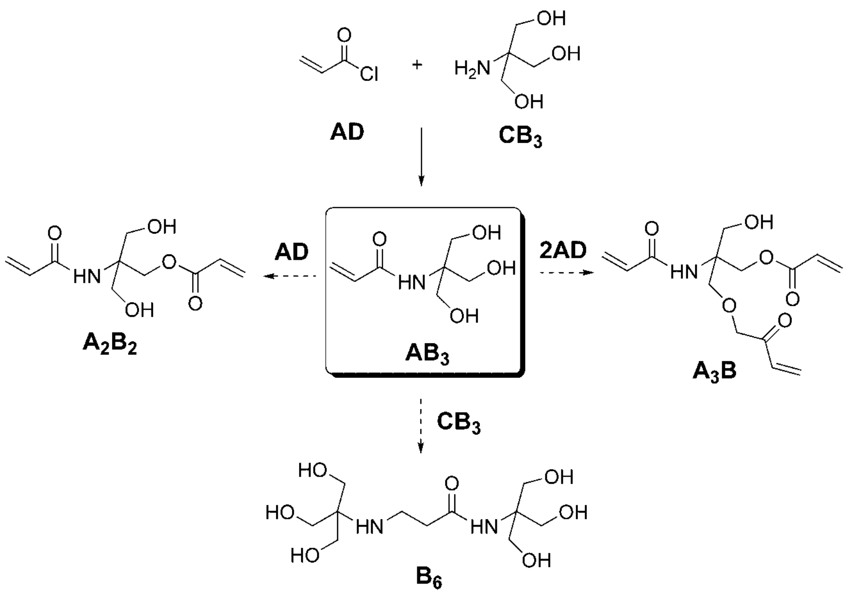
Results and Discussion

1. Molecular Design and Syntheses of Hyperbranched Poly(ether amide)s.

According to previous work,[16b] it is reasonable to access HPEA from commercially available AD type monomer, double bond and acryloyl chloride group, and CB_n ($n = 2, 3$) type monomer, primary amine with two or three hydroxyls. As shown in Scheme 1, amine will react faster with (meth)acryloyl chloride than hydroxyls on account of the sufficient reactivity difference between amine and hydroxyl functionality to selectively form amide-derived AB_n type monomers, and then the monomers are subjected to Michael addition polymerization to produce HPEAs.

First, effective strategy which allowed high yield of AB_n monomer is explored. Take the reaction of THAM with AC for an example, possible products are shown in Scheme 2. Compound AB_3 is the targeted molecule. The byproducts A_2B_2, and A_3B

Scheme 2. Possible Products of the Reaction between AC and AMPO



containing two or three double bonds, will make the reaction system unstable and easily lead to gel even at room temperature. THAM was reacted with equimolar AC at various temperatures in acetonitrile, and the reaction was monitored by FTIR spectra. As shown in Figure 1, for the reaction above 20 °C, the products contain ester (absorbance peak around 1735 cm^{-1}) only for 1 h, while at 0 °C, only amide can be produced even for longer reaction time (over 6 h). The phenomenon is due to the fact that at low temperature, the reactivity difference between amine and hydroxyl groups to acryloyl chloride was enlarged, which favored the dominant formation of AB_3 type monomer. Thus, at the initial stage of acylate reaction, the reaction temperature was kept 0 °C, in order to inhibit cross-linking when hyperbranched polymers formed. The yields of these monomers were about or above 90%. The structure of **M1−4** was confirmed by^{1}H NMR, IR spectra, and elemental analysis.

Since the nucleophilicity of oxygen is lower than that of nitrogen, Michael addition of hydroxyl group to electrophilic double bond usually remains challenge.[12d,22] To improve the reaction rate and get polymer with moderate high molecular weight, hereby, Lewis bases such as *t*-BuOK, and Ph_3P were used as the catalyst. Michael addition polymerization was conducted at 60 °C in DMSO. To make sure this reaction proceeding as expected, FTIR and ^{1}H NMR experiments were carried out. As shown in Figure 2, the C=C absorption at 1612 cm^{-1} disappears and a new absorption band at 1115 cm^{-1} attributed to asymmetrical stretching vibration of C−O−C appears, which is the only characteristic of ether in FTIR. As also reflected in Figure 3, the peaks at the range of 5.4−6.4 ppm ascribed to double bond were markedly weakened. Compared with the proton signals of the **M1**, the peaks of the corresponding polymers **HP1** are broader and absent from fine structures due to complicated repeat units. Moreover, the signals of the amide protons split into three groups of proton signals, corresponding with three different subunits resulted from branched architecture. It will be discussed in more details in the following section. Likewise, Figure 4 presents the ^{1}H NMR spectrum of **HP3** in D_2O. Judging from the significantly weakened double bond, the polymerization has also occurred. The multiple signals of the methylene protons near oxygen atom were overlapped and not distinguishable from each other in

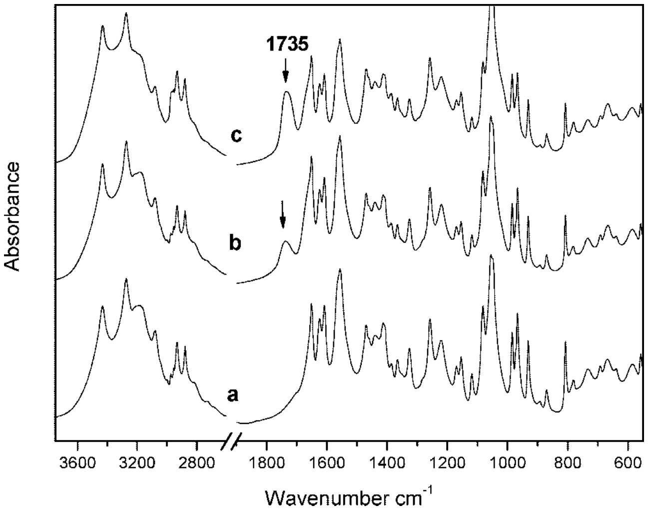


Figure 1. FTIR spectra of the products of AC reacting with THAM for 6 h at (a) 0, (b) 20, and (c) 40 °C, respectively. The peak at 1735 cm^{-1} indicated the formation of ester byproducts.

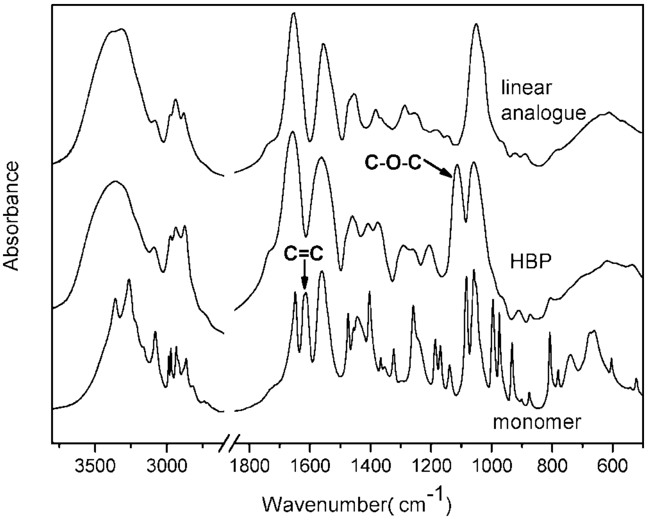


Figure 2. FTIR spectra of **M1**, **HP1**, and its linear analogue (from bottom to top). The disappearance at 1612 cm^{-1} indicated the polymerization of double bond. The presence of a peak at 1115 cm^{-1} indicated the formation of ether.

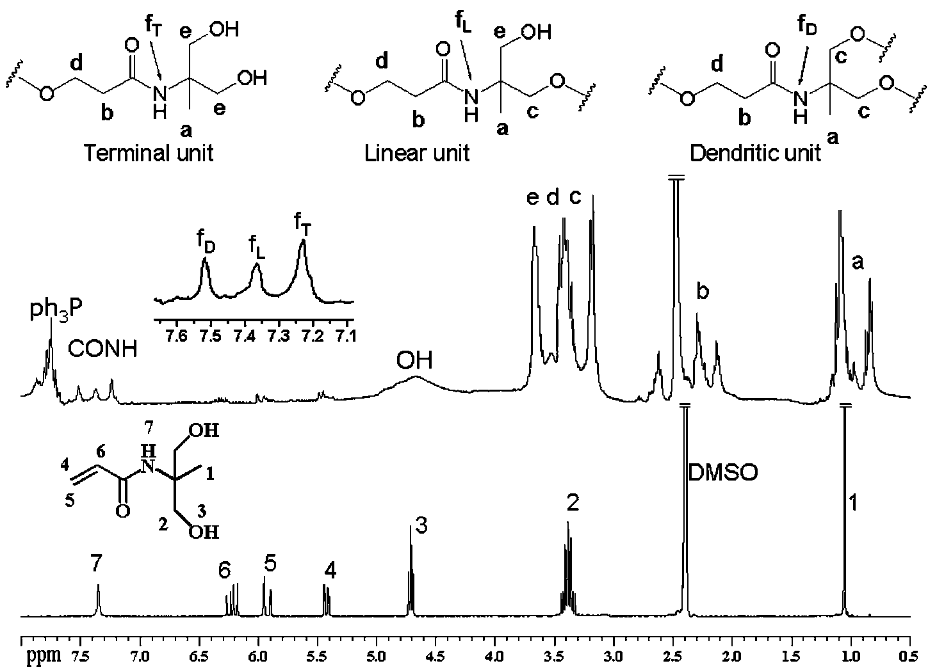


Figure 3. ^{1}H NMR spectra of **M1** and **HP1**.

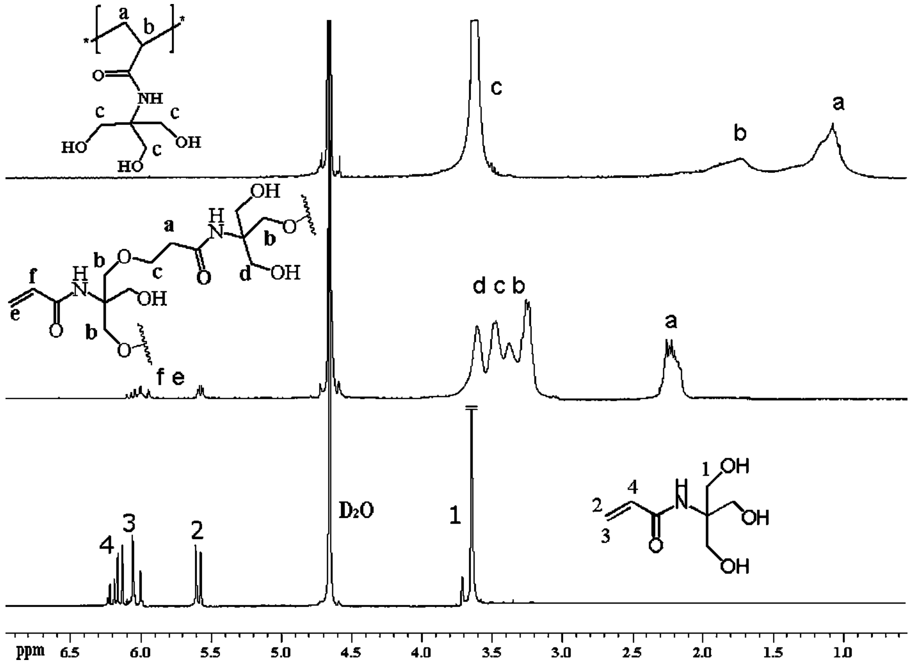


Figure 4. ^{1}H NMR spectra of **M3**, **HP3**, and its linear analogue.

Figure 4, indicating complex microenvironments were resulted from various architectures in polymer.

To avoid the possibility of radical polymerization of acrylamide monomer at elevated temperature, the *p*-quinone was employed as free radical inhibitor to prevent radical polymerization. To further confirm the resultant polymer was the product of Michael addition, linear polymer from radical polymerization initiated by AIBN was employed for comparison. From the FTIR spectrum in Figure 2, we can found the biggest characteristic for linear polymer is the absence of the absorption band at 1115 cm^{-1} assigned to ether groups. Furthermore, at ^{1}H NMR spectrum in Figure 4, the linear product presented the signals of backbone protons at high field (1−2 ppm). This result demonstrated that the polymers **HP1**−**HP4** were exactly the product from Michael addition, as expected.

2. Evolution of Molecular Weight and its Monomer and Catalyst Effect. Since SEC allows the evolution of molecular weight and branch architecture to be conveniently characterized,[23] close monitor of the Michael addition polymerization by SEC at various stages was explored. Figure 5 showed the development of SEC traces of the **HP1** system with polymerization time. At the initial 10 h, the curve showed narrow and symmetrical distribution, after then the peak was shifted to shorter retention time accompanying the lost of monomodal nature, and finally exhibit broad and multimodal distributions. The SEC curve remained unchanged after 48 h, thus we consider the polymerization was finished completely in the period of 48 h. The multimodal appearance of SEC profiles indicates different components with different branching generations in hyperbranched polymers.[10a,b] The molecular

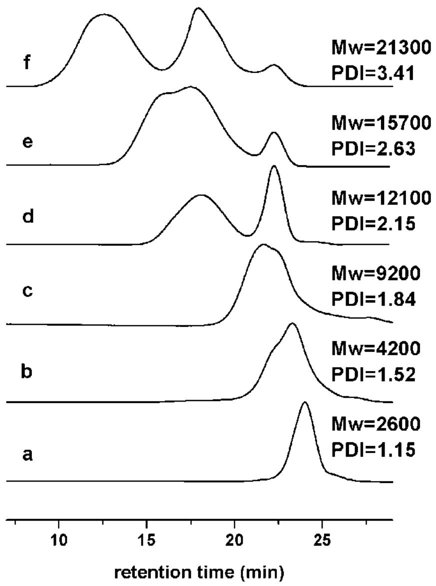


Figure 5. SEC elution profiles of **HP1** at different polymerization times: (a) 10, (b) 20, (c) 28, (d) 34, (e) 42, and (f) 48 h.

weight of the resultant polymers increased with the evolution of the polymerization, suggesting that the Michael addition was step-growth polymerization.

It is already established that conventional SEC measurement has only limited suitability for hyperbranched polymers and usually underestimates the true molecular weight, since SEC is essentially based on hydrodynamic volume, as hyperbranched polymers are expected to have smaller hydrodynamic volumes than their linear analogues, resulting in longer retention times in SEC and thus leading to apparently lower molecular weight values.[6b,10,16] To resolve this problem, in the present work, SEC coupled with multiangle laser light scattering detector (SEC−MALLS) was used to yield absolute molecular weight, regardless of the architecture of the macromolecule.[23] The molecular weights of the resultant polymerizations from various monomers with different initiators were summarized in Table 1. It is noteworthy that for **HP2** and **HP4**, the molecular weight was significantly lower than that of **HP1** and **HP3**. The reason is attributable to the electronic effect of methyl substitution at the double bond.

In Michael addition, the reactivity of an acceptor toward nucleophilic attack is directly correlated with the electron-withdrawing tendency of the group linked to the double bond. The commonly accepted explanation for this correlation is based on the ability of the electron-withdrawing group to stabilize the negative charge formed on the carbon adjacent to the site of nucleophilic attack.[24] As a result, the reactivity of the acceptor will decrease if the substituent is electron rich, such as methyl at the double bond in **M2** and **M4**. Also, the catalyst employed considerably affects the Michael addition polymerization. The molecular weights of the resulting hyperbranched polymers are at the sequence of *t*-BuOK > Ph_3P, in consistent with the sequence of base strength.

3. Branched Structure and Thermal Properties. The degree of branching (DB) is one of the most important molecular parameters of hyperbranched polymers because it characterizes the difference in molecular structure from their linear analogue. NMR is a powerful tool for determining the DB value.[25] In some cases, the DB can be determined by ^{1}H NMR spectroscopy. As described in Figure 3, there are three structural subunits for the hyperbranched polymers from potential AB_2 type monomers, dendritic units (D), linear units (L), and terminal units (T). The definition of DB put forward by Fréchet and his colleague[26] is the ratio of the sum of dendritic and terminal units versus the amount of total units ($DB = (D + T)/(D + T + L)$), where D, T, and L stand for the amounts of the dentritic, terminal, and linear units, respectively. Fortunately, the signals of amide protons display three splitting peak at 7.53, 7.37, and 7.25, with an integration ratio of 1.00:1.25:1.47, respectively. The amide protons are identified on the basis of chemical shift and assignments of related compounds. Therefore, the DB of **HP1** (Table 1 run 2) was determined to be 0.66 calculated from the integration of proton attributed to each unit with Fréchet's DB definition.

To obtain further confidence in the result from ^{1}H NMR spectra, the ^{13}C NMR experiments of **HP1** were also conducted (Figure 6). The signal peaks in the ^{13}C NMR spectra of the polymers were assigned on the basis of the NMR signals of corresponding monomers. Distortionless enhancement by polarization transfer 135 (DEPT-135) experiment was explored to assist in the ^{13}C NMR group assignment. It yields multiplicity assignments for the various resonances, i.e., whether the carbon is primary, secondary, tertiary, or quaternary.[27] The positive

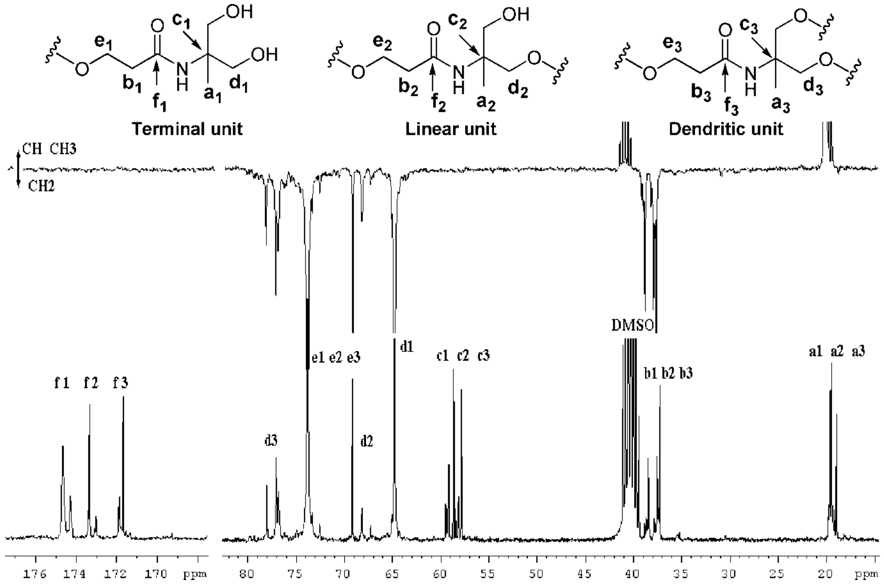


Figure 6. ^{13}C NMR spectra of **HP1** in DMSO: (1) inverse-gated decoupling spectrum; (2) DEPT-135 spectrum, the CH and CH_3 resonances are above the baseline and the CH_2 resonances are directed below the baseline.

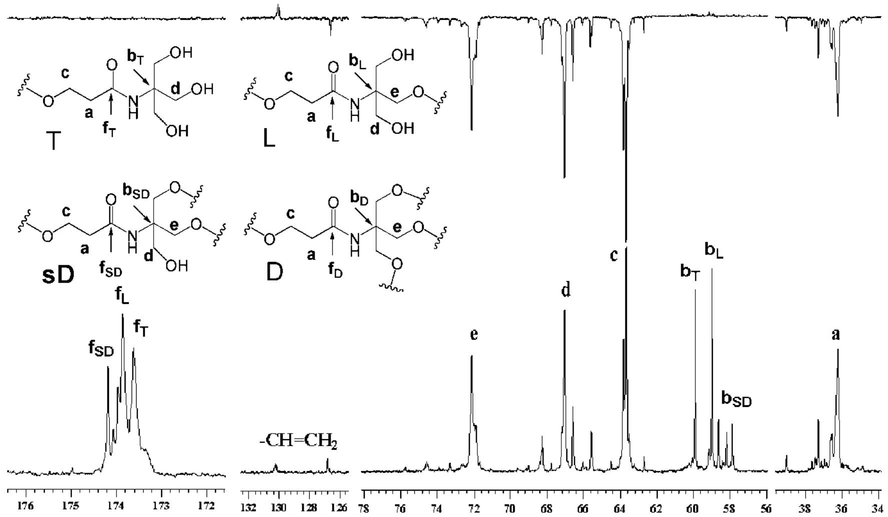


Figure 7. ^{13}C NMR spectra of **HP3** in D_2O: (1) inverse-gated decoupling spectrum; (2) DEPT-135 spectrum, the CH and CH_3 resonances are above the baseline and the CH_2 resonances are directed below the baseline.

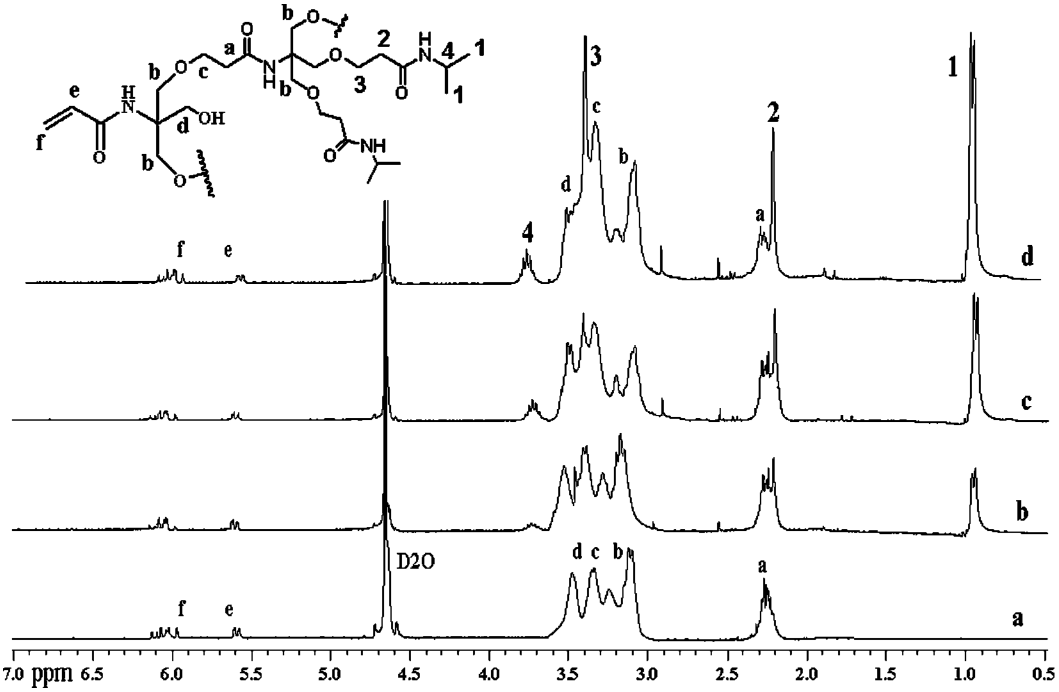


Figure 8. ^{1}H NMR spectra of NIPAAm-*g*-HP3 with a NIPAAm grafting degree of (a) 0%, (b) 13%, (c) 45%, and (d) 78%.

resonances for methyl and methine carbons are readily distinguished from the negative resonances of methylene carbons, while the quaternary carbons are not found in DEPT-135 spectroscopy. Comparing ^{13}C NMR with DEPT-135 spectrum, it was found that two groups of signals (c_1, c_2, c_3 and f_1, f_2, f_3) assigned to the quartenary carbons disappeared in the ^{13}C DEPT-135 NMR spectrum. The DB study was greatly facilitated by the observation that the ^{13}C NMR resonance for the quartenary carbon of amide repeating units is very sensitive to the chemical environment. According to the chemical environment of the subunits, similar to the case of the paper reported,[16b,c,28] the signal peaks $\mathbf{f_1}$, $\mathbf{f_2}$, $\mathbf{f_3}$ at 174.6, 173.4, and 171.6 ppm should be attributed to the carboxyl carbons of the terminal, linear and dendritic fraction, respectively. The DB of **HP1** (Table 1 run 2) was 0.64 calculated from the integrations of the peak $\mathbf{f_1}$, $\mathbf{f_2}$, $\mathbf{f_3}$ using the Fréchet's equation mentioned above, quite close to that from ^{1}H NMR (0.66). To be consistent, the DB values of polymer listed in Table 1 are the average value of the two values obtained from ^{1}H NMR and ^{13}C NMR.

The quantitive ^{13}C NMR and DEPT-135 spectra of **HP3** (Table 1 run 5) were also shown in Figure 7. In contrast to the polymer prepared from AB_2 monomers, the hyperbranched polymers prepared from AB_3 monomers possibly have four structural subunits, terminal units (T), linear units (L), semi-dendritic (sD), and perfect dendritic (D). Frey and co-workers have derived an expression for DB in the hyperbranched polymers from AB_3 monomers.[29] Similar to the case of the **HP1**, quartenary carbon of amide displayed triple peaks. Dendritic units were not observed, which may be due to the fact that the hindrance of the molecular chain restrains the third hydroxyl group from reacting with semidendritic units to form dendritic units. Therefore, the DB of **HP3** was 0.50 calculated with Frey's DB definition. Likewise, the DBs of other resultant polymers calculated with the same method were also listed in Table 1.

Hyperbranched polymers are well-known to exhibit unusual solution behavior, such as inherent viscosity are remarkably low because of the compact character of the branched structure lead to the lack of chain entanglements and low hydrodynamic equivalent sphere.[30] Viscosity behavior of the resulting polymers was studied to support the formation of hyperbranched structure in the synthetic procedure. As seen from the data in Table 1, all the hyperbranched polymers exhibited relatively low inherent viscosity (0.08−0.16 dL/g). The resulted HPEAs possess abundant OH terminal groups, accordingly, they have good solubility in high polar solvents such as water, ethanol, methanol, DMF, and DMSO.

Thermal properties of the hyperbranched polymers were evaluated by DSC and TGA measurements. The results of DSC and TGA measurements are also listed in Table 1. The polymers exhibited glass transition temperatures (T_g) at a range of −12.5 to +21.1 °C, which indicates that the polymer is in the rubber-like viscous state at room temperature. The lower T_g of the polymers **HP2** and **HP4** in comparison with other polymers can be attributed to their smaller molecular weights. No melting and crystallization peaks were observed, indicating their amorphous state, which is typical for highly branched polymers. TGA analysis showed that the 10% weight-loss temperatures ($T_d^{10\%}$) were higher than 260 °C, some of them even up to 330 °C, demonstrating the reasonable thermal stability of these polymers.

4. In Situ End-Capped with *N*-Isopropylacrylamide and Their Thermoresponsive Characteristics. Surface modification of hyperbranched polymers is one important strategy for improving their properties and finding new applications. The resultant HPEAs contained a large number of "tunable" hydroxyl groups. Those groups can be used to modify their properties via surface modification. Herein, NIPAAm was added and grafted to the terminal hydroxyl groups via Michael addition reaction in situ.

Take **HP3** as an example, compared with the ^{1}H NMR spectrum of HPEA precursor (Figure 8a), the new broad signal at 1.07 ppm (**peak 1** in Figure 8b−d) originated from the methyl protons of NIPAAm moieties was the strong evidence of the successful attachment of NIPAAm groups to the HPEA. Besides, the solubility of the resultant polymer has been modified. For instance, the original HPEA is not soluble in THF, but the NIPAAm-grafted hyperbranched poly(ether amide) (NIPAAm-*g*-HPEA) can easily resolve in THF. NIPAAm grafting degree, i.e., the molar ratio of the NIPAAm unit to the hydroxyl groups of HPEA was determined using ^{1}H NMR. The number of hydroxyl groups per repeating unit was generally assumed as two,[31] since the AB_3 type of monomer applied in the preparation of HPEA. Therefore, the grafting degree of NIPAAm groups was calculated from the ^{1}H NMR spectra by dividing the average integration values of **peak 2** by two times of **peak a**. Unfortunately, because of the slight overlapping of **peak a** with **peak 2**, it is difficult to precisely determine the grafting degree of NIPAAm groups. Herein, we use **peak 1** to give a rough integration of **peak 2**. NIPAAm grafting degree in NIPAAm-*g*-HPEA was determined using following equation, where I_l and I_{2+a} are the integral intensities of **peak 1** and the peak group from 2.15 to 2.35 ppm in Figure 8, respectively.

$$\text{NIPAAm grafting degree} = \frac{I_2}{2I_a} = \frac{I_1/3}{2 \times (I_{2+a} - I_1/3)}$$

Although the accuracy of the values was indeed lower, we believe it can sufficiently reflect the tendency. The NIPAAm grafting degree could be changed through adjusting the feeding molar ratio of NIPAAm to the OH groups of HPEA. For example, NIPAAm-*g*-HPEA with a NIPAAm grafting degree of 13%, 45%, and 78% (Figure 8b−d) were obtained with the feeding molar ratio of NIPAAm to the OH groups of HPEA to be 20%, 80%, and 150%, respectively. The conversion of NIPAAm was 65%, 56%, and 52%, respectively. The low conversion of NIPAAm indicated the low addition reactivity of NIPAAm to OH groups.

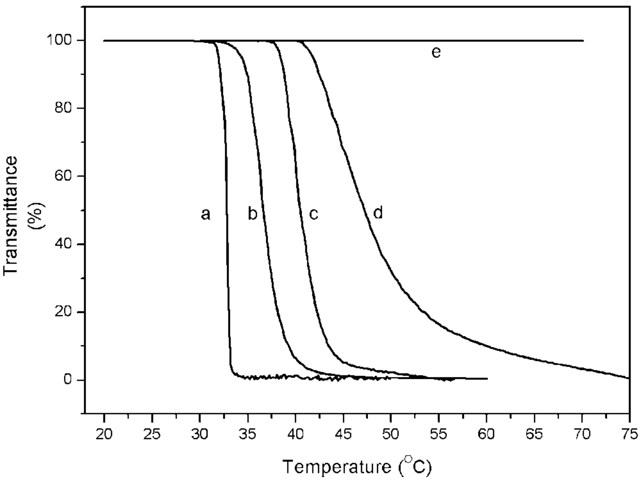


Figure 9. Temperature dependence of the transmittance of 1% w/v aqueous solution of (a) linear PNIPAAm, (b) NIPAAm-*g*-HP3 with a NIPAAm grafting degree of 78%, (c) 45%, (d) 27%, and (e) 13%.

The NIPAAm-*g*-HPEAs are highly soluble in water under low-temperature conditions. Interestingly, the transparent aqueous solutions of the hyperbranched polymers become opaque at a specific temperature as the temperature is increased and become transparent again when the temperature decreases. Moreover, the reversible phase transition occurs repeatedly. Indeed, no change in the transmittance was observed for the solutions of the unmodified hyperbranched polymer over the experimental temperature range. Therefore, it is considered that the introduction of NIPAAm group to the surface of hyperbranched polymer could successfully produce a thermo-sensitive material as expected. Figure 9 represents the LCST of the 1.0 wt % aqueous neutral solution of NIPAAm-*g*-HPEA as a function of the NIPAAm grafting degree. Linear PNIPAAm, which has a LCST in water at 32 °C was used as a comparison. PNIPAAm exhibited a sharp decrease in transmittance at 32 °C, which indicates that this polymer underwent conformational transition from a hydrated coil to a dehydrated globule at this temperature. Similarly, solutions of NIPAAm-terminated HPEA showed a sharp decrease in turbidity at a certain temperature. As can be seen, the transmittance decreases drastically in response to a minute change of the temperature around the LCST, indicating the highly sensitive phase separation. Moreover, the LCST can be tuned via adjustment of the NIPAAm grafting degree. A lower NIPAAm grafting degree results in a higher LCST. Figure 10c shows that the LCST of NIPAAm-*g*-HPEA is elevated to 38.8 and 42.4 °C when the NIPAAm grafting degree is reduced to 45% and 27%, respectively. However, the curve transition of the NIPAAm-*g*-HPEA was not as sharp as that of linear PNIPAAm (Figure 9a) and NIPAAm-*g*-dendrimer in the literature,[19] especially of the one with low NIPAAm grafting degree (Figure 9d). It is likely because the shell formed by the terminal NIPAAm groups in HPEA was not as dense as dendrimer, due to the structure irregularity of the hyperbranched polymer. Besides, a further decrease of the NIPAAm grafting degree to 13% leads to loss of thermal response. This is due to the increased hydrophilic nature of the backbone. Note here that the HPEA backbone is hydrophilic as indicated by their good solubility in water. As addressed in introduction, the nature of the temperature sensitivity of the *N*-substituted amide-terminated dendrimer was the appropriate balance of hydrophilic and hydrophobic moieties.[19a] In nature, the hydroxyl groups on the surface of HPEA are hydrophilic. When NIPAAm was grafted onto the HPEA surface, the number of hydroxyl groups would decrease, and it then resulted in the increase of hydrophobicity and LCST.

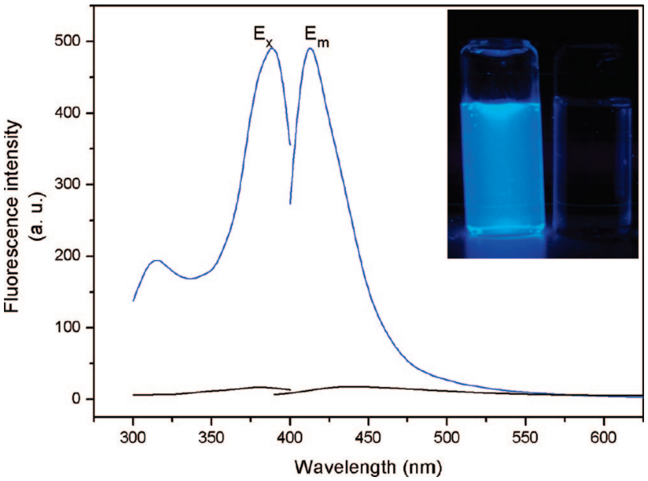


Figure 10. Fluorescence excitation and emission spectra of **HP3** (up) and its linear analogue (bottom). Insert: An illumination photograph of **HP3** (left) and linear analogue (right). The aqueous solution was excited by a 4.5-W UV lamp.

5. Intrinsic Blue Fluorescence Property. As a curiosum, we observed strong blue photoluminescence from the resultant hyperbranched poly(ether amide)s without any treatment or functionalization. Figure 10 shows the fluorescence excitation and emission spectra of **HP1** and its linear analogue. The **HP1** has the emission band at 423 nm with the excited band at 388 nm. On the contrary, the linear polymer failed to exhibit any fluorescence. From the classical viewpoint, the fluorescent signal from HPEA is rather surprising, since there are no functional groups that would be expected as conventional fluorophores. The interesting phenomenon has already been observed by some groups.[32] For example, Bard and co-workers reported the commercial poly (amido amine) dendrimers (PAMAM) to show blue photoluminescence ($E_m = 450$ nm) after simple treatment with $(NH_4)_2S_2O_8$, and suspected that the phenomenon was related to oxidation.[32a] Afterward, the strong fluorescence emission from G4 NH_2-terminated PAMAM dendrimer upon adjusting the pH value was reported by Imae's group, and it was attributed to that chemical reaction of functional groups along dendrimer branches took place under acidic conditions to form new fluorescent chemical species.[32b] However, the new fluorescence-emitting moiety with structure unidentified has not been separated and evidenced yet. Very recently, Liu etc. reported hyperbranched poly(amino ester)s could also emit blue photoluminescence ($E_m = 460$ nm) without oxidation and protonation, and assumed a coexistence of tertiary amines/carbonyl groups in the core was one of the key structural factors in inducing fluorescence.[32c] However, the fluorescence mechanism remains unresolved.

We speculated that the fluorescence property of HPEA was in close relationship with its unique three-dimensional architecture. It has been generally established that hyperbranched polymers are highly cascade polymers with three-dimensional globular architecture. Because of the unique topological structure, H-bonding between amide hydrogens and carbonylic oxygen atoms of neighboring branches is easily formed, an important phenomenon also seen in protein folding.[33] Furthermore, a protic solvent like H_2O can act also as a hydrogen donor for the interior oxygen atoms of ether, and thus the molecular conformation and array are stabilized by the H-bondings. Due to the constrained geometric freedom and relatively rigid structure, dendritic polymers exhibit an intrinsic fluorescent behavior rather than radiationless transition, such as vibrational relaxation,[34] which happened at flexible linear polymers.

We measured the fluorescence emission intensity of the hyperbranched polymers with different molecular weights. To make sure the same concentration of functional groups, the samples were prepared at the same weight concentration 1% in water. Figure 11 shows that the hyperbranched polymers with different molecular weights have the same emission bands at about 425 nm, suggesting the same fluorophore exists. On the other hand, the relative intensity of fluorescence increases with increasing molecular weight, resulting from the enhanced rigidity of molecular architecture. It is considered that the overall shape of the dendritic macromolecule exhibits a structural change from a very flexible, domed, and loose structure at low molecular weights to a rigid, dense, spheroid-like topology at high molecular weights.[35] Furthermore, the **HP1** gave the highest fluorescence quantum yields of 23%, much lower than that of PAMAM dendrimer (58%), also demonstrating that the rigidity of molecular architecture played an important role in the fluorescence.

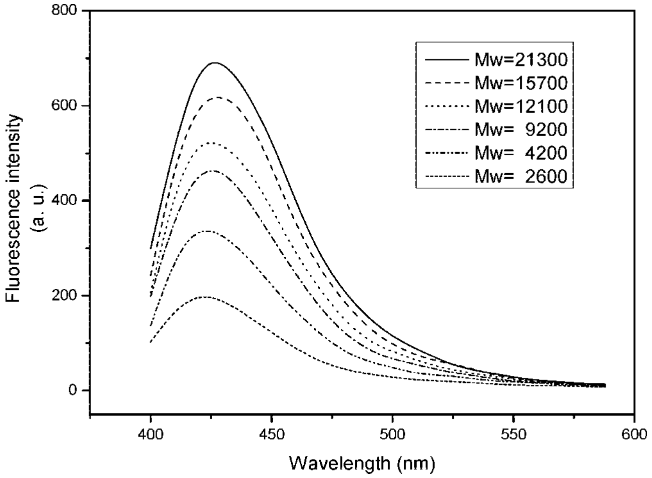


Figure 11. Molecular weight dependence of fluorescence intensity of **HP3** (excitation at 380 nm, 1% w/v aqueous solutions).

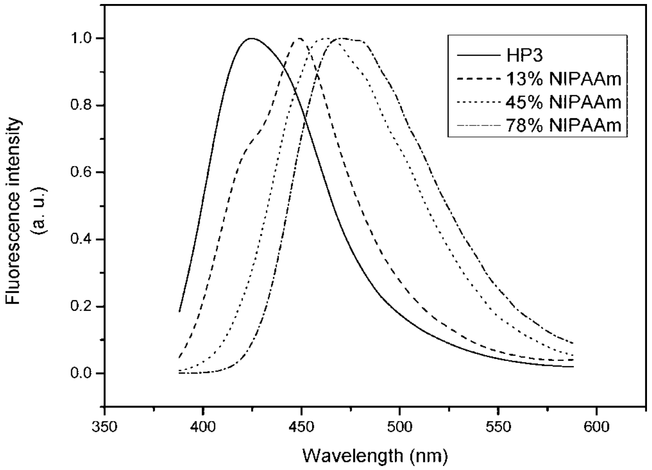


Figure 12. NIPAAm grafting degree dependence of fluorescence intensity of **HP3** (excitation at 380 nm, 1% w/v aqueous solutions).

Moreover, the NIPAAm-terminated hyperbranched poly(ether amide)s still remain the striking fluorescence property. Interestingly, a red-shift in emission occurred with the increase of the grafting degree (Figure 12), which was first found. We speculate that the shift of emission band would be corrected with the change of topology structure of the hyperbranched polymers, since the grafting of NIPAAm groups influences the hydrophilicity/hydrophobicity ratio and thus leads to the change of molecular shape in water. Also, these data make the existence of an impurity in the studied samples or the generation of fluorophore through oxidation improbable. Even though the exact nature of photoluminescence of the hyperbranched poly(ether amide)s is still under further investigation, it is apparent that the fluorescence emitted by HPEA enables its wide potential applications. Significantly, when HPEA is utilized as prospective carriers in drug and gene delivery, the need for fluorescent tagging in probing transport with its attendant problems can be avoided.

Conclusions

We report a facile and one-pot synthesis of water-soluble hyperbranched poly(ether amide)s from widely commercialized monomers (meth)acryloyl chloride and multihydroxyl primary amines via Michael addition polymerization. In this study, we demonstrated that the attachment of NIPAAm groups to the chain ends of the hyperbranched polymer give them a temperature-sensitive water solubility. The attachment of NIPAAm groups to abundant end-groups of the hyperbranched polymer renders them temperature-sensitive functionality. Importantly, the LCST of resultant polymers can be feasibly tuned by varying the grafting degree of NIPAAm around biological temperature. Reducing the degree of substitution by NIPAAm groups can effectively increase the LCST; however, the transition curves of light transmittance versus temperature would become less sharp. Interestingly, strong intrinsic blue fluorescence of the hyperbranched polymers both with and without NIPAAm surface was observed. It is expected that the novel hyperbranched polymer can be used as potential intelligent biomaterial in biotechnology and drug delivery applications.

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