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Preparation of epoxy-ended hyperbranched polymers with precisely controllable degree of branching by thiol-ene Michael addition

Daohong Zhang,[1] Yimei Wang,[1] Zhicai Xu,[1] Juan Cheng,[1] Sufang Chen,[2] Junheng Zhang,[1] Menghe Miao[3]

[1]Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, South-central University for Nationalities, Wuhan, Hubei Province, 430074, China
[2]Key Laboratory for Green Chemical Process of Ministry of Education, Wuhan Institute of Technology, Wuhan, Hubei, 430073, China
[3]CSIRO Manufacturing, PO Box 21, Belmont, Victoria, 3216, Australia
Correspondence to: D. Zhang (E-mail: zhangdh27@163.com)

ABSTRACT: Epoxy-ended hyperbranched polymers (EHPs) have a wide range of applications due to their outstanding performances. Because their microstructures are not positively identified, it is very difficult to ascertain the reinforcing and toughening mechanisms of EHPs and their interface interaction with other matrixes. Controllable synthesis of EHPs with precise degree of branching (DB) remains to be a major challenge. Here, a method for preparing novel nitrogen-phosphor skeleton epoxy-ended hyperbranched polymers (NPEHP) with controllable DB by a thiol-ene Michael addition between thiol-ended hyperbranched polymers (NPHSH) and glycidyl methacrylate have been firstly reported. NPHSH is synthesized by an esterification between hydroxyl-ended hyperbranched polymers (NPHOH) and 3-mercaptopropionic acid. NPHOH is prepared by a thiol-ene Michael addition between methacrylate group of a monomer and thiol group of linear monomer (AB) and/or branched monomer (AB₂). The molar ratio between the AB and AB₂ monomers controls the DB of the products. The ^{1}H NMR spectra analysis of NPHOH shows that their experimentally determined DBs are very close to their theoretical values, indicating good controllability of their DBs. The narrow molecular weight distributions of NPHOH, NPHSH, and NPEHP suggest high efficiency of the thiol-ene Michael addition. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44277.

INTRODUCTION

Hyperbranched polymers (HBPs) are receiving increasing attention because they are simple to be synthesized and have high degree of functionality, and unique material properties.[1] Compared with linear polymers, HBPs have lower viscosity and better solubility due to their abundant functional groups and globular shape.[1,2] HBPs also have promising applications. Despite of these remarkable progresses in synthetic methods and material characterization, precise control of the degree of branching (DB) of HBPs is still a challenge. As an important class of HBPs, epoxy-ended hyperbranched polymers (EHPs)[3] can be used as rheology modifiers, processing aids and, more recently, as multifunctional additive for reinforcing and toughening diglycidyl ether of bisphenol-A (DGEBA).

Considerable efforts[4] have been devoted to exploring novel manufacturing methods and designing new chemical structures of EHPs. Five types of synthetic approaches have been reported:

1. Etherification reaction between hydroxyl groups of hydroxyl-ended HBPs and epichlorohydrin,[5,6] is derived from a similar reaction between bisphenol-A and epichlorohydrin.
2. Esterification reaction between carboxyl groups of hydroxyl-ended HBPs and epichlorohydrin,[7,8] is similar to the synthesis of traditional glycidyl ester epoxy resins. Both esterification[7–9] and etherification[5,6] routes for preparing EHPs were integrated into a grafting method[6–8,10–17] in which epoxy group grafts on hyperbranched polymers (HBPs) using epichlorohydrin. This requires tedious processes[18–20] and large

Additional Supporting Information may be found in the online version of this article.
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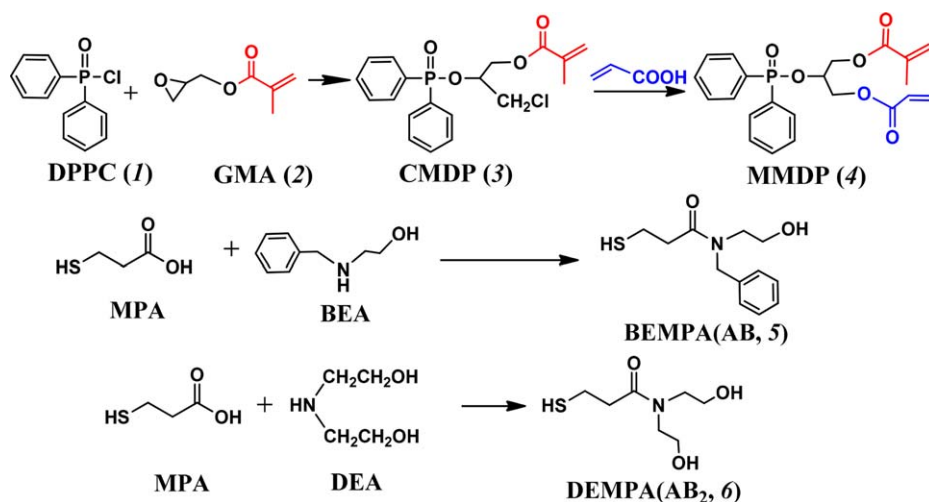
Scheme 1. Synthesis scheme of monomers. [Color figure can be viewed at wileyonlinelibrary.com.]

quantities of organic solvents[9] during reaction, and water is also used to wash and remove the byproduct from NaCl.[6,7,14–22]

3. Proton transfer polymerization[18–20] or atom transfer radical polymerization (ATRP)[21,22] is also used to prepare EHPs, based on the repetitive addition of monomer to growing radicals generated from dormant alkyl halides by a reversible redox process, which is catalyzed by a transition metal complex.[21] This involves a tedious and complicated preparation process of epoxy monomers because of water washing and organic solvent separation.

4. Hydrosilylation[23,24] reaction between the double bond of an allyl-ended hyperbranched organic silicone and the —Si—H group of glycidyl ether monomer can produces EHPs. Although hydrosilylation eliminates the environmental pollution of water washing and organic solvent extraction, the multistep reactions and expensive platinum catalyst used in the preparation of EHPs hinder its upscaling and industrial application.

5. Thiol-ene reaction (Michael addition and coupling) is a novel synthetic method of EHPs.[25,26] This is a reaction between the thiol group in mercaptopropionate and the epoxy group in glycidyl methacrylate or allylglycidyl ether.

The thiol-ene Michael addition has some beneficial properties[27–29] of click reaction, including high yield, harmless byproducts and high selectivity. The thiol-ene click reaction simplifies product isolation and opens an avenue for synthesizing EHPs by taking advantage of its simple synthetic condition[30] without organic solvent. Another important advantage of the thiol-ene click reaction is that the resultant epoxy resins have excellent stability due to the absence of hydroxyl group, leading to a much simpler synthetic process than the traditional chromatographic column separation synthesis of hydroxyl-free EHPs.

Besides these progresses on synthetic methods, and application in reinforcing and toughening DGEBA, controllable synthesis of EHPs with different degree of branching (DB) remains to be a major challenge. In this article, we report a facile synthetic
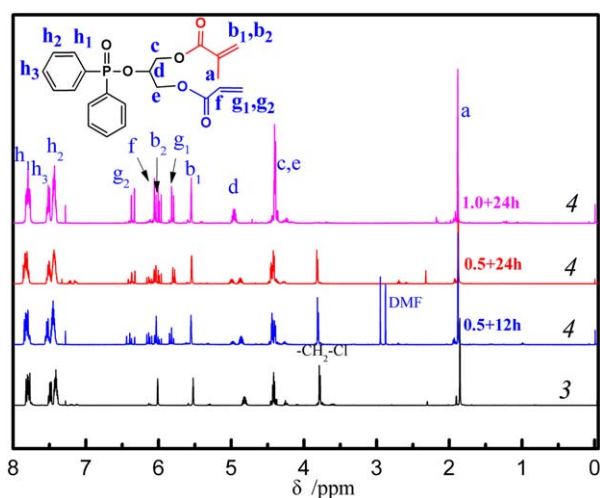

Figure 1. ^{1}H NMR spectra of **3** and **4** at various reaction conditions. [Color figure can be viewed at wileyonlinelibrary.com.]
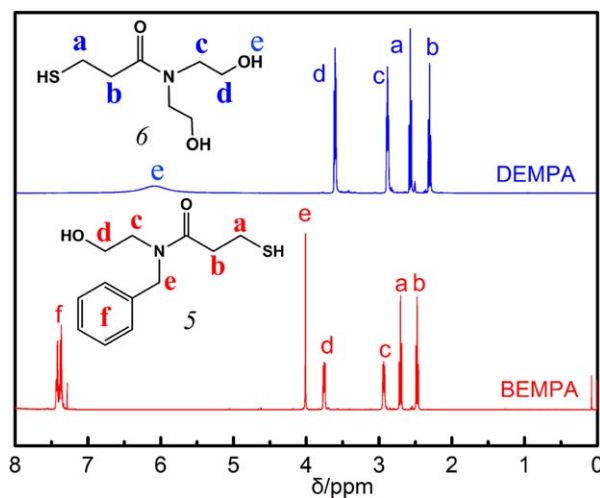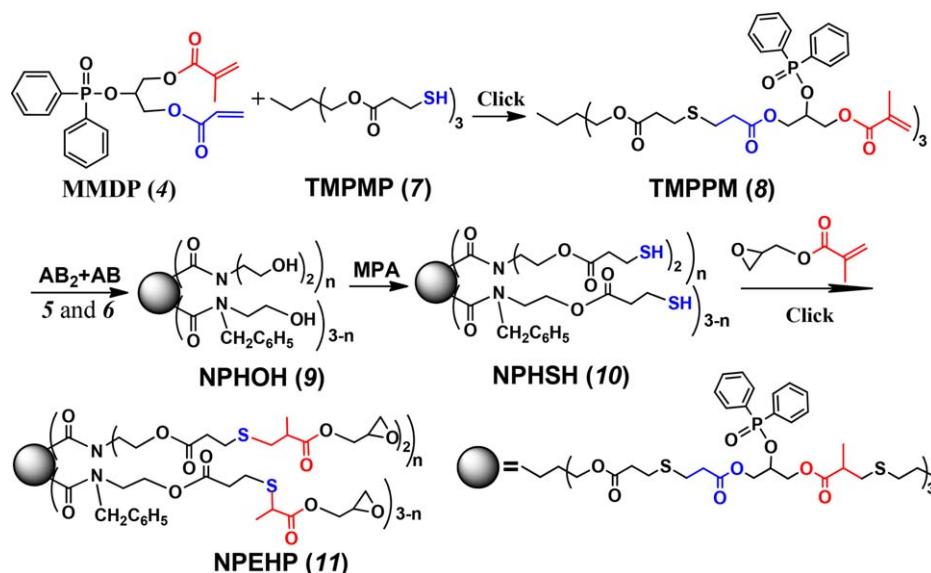

Figure 2. ^{1}H NMR spectra of **5** and **6**. [Color figure can be viewed at wileyonlinelibrary.com.]

Scheme 2. Synthesis scheme of epoxy-ended hyperbranched polymers (NPEHP). [Color figure can be viewed at wileyonlinelibrary.com.]

method of EHPs with controllable DB using a thiol-ene Michael addition reaction. Chemical structure, DB and molecular weight are characterized by FT-IR, ^{1}H NMR, matrix-assisted laser-desorption ionization time-of flight mass spectrometry (MALDI-TOF MS) and sol gel permeation chromatography (GPC) technologies.

RESULTS AND DISCUSSION

Characterization of Monomers

1-(Methyl methacrylate)-1-(methyl acrylate) diphenyl-methyl phosphate (MMDP, **4**) with two different functional double bonds was synthesized by a two-step reaction using the main materials of diphenylphosphinic chloride (DPPC, **1**), glycidyl methacrylate (GMA, **2**), and acrylic acid according to Scheme 1. Both N-benzylethanolamine-3-mercaptopropionamide (BEMPA, **5**) as linear unit (AB) and diethanolamine-3-

Figure 3. ^{1}H NMR spectra of **4**, **7**, and **8**. [Color figure can be viewed at wileyonlinelibrary.com.]

mercaptopropionamide (DEMPA, **6**) as branching unit (AB$_2$) were prepared by an amidations between MPA and BEA and between MPA and DEA according to Scheme 1, respectively. Detailed synthesis processes of all the monomers were supplied in Supporting Information.

Supporting Information Figure S1 compares the FT-IR spectrum of CMDP (**3**) with the FT-IR spectra of compounds **1** and **2**. The peak at 910 cm^{-1} (epoxy group) in the FT-IR spectrum of GMA disappeared and the absorption peaks at 1063 cm^{-1} (P—O—C), 1029 cm^{-1} (P—O), and 754 cm^{-1} (C—Cl) appeared, indicating complete conversion of an epoxy group of GMA. This is further substantiated by the complete disappearance of the chemical shift (δ) peaks of epoxy group at 3.26 ppm and 2.86–2.67 ppm in ^{1}H NMR spectrum of **3** in Supporting Information Figure S2, and the appearance of a new peak at δ 3.83 ppm is attributable to the hydrogen atom of methyl chloride (—CH$_2$Cl).

Compound **4** was then produced by an esterification between the methyl chloride group of **3** and the carboxyl group of acrylic acid (AA) using TBAB as a catalyst. The effects of reaction time and the molar ratio between TBAB and **3** on conversion of methyl chloride group are discussed below with reference to Supporting Information Table S1. Prolonging reaction time from 12 to 24 h resulted in an increase of conversion from 25.9% to 45.5%. Increasing the molar ratio between TBAB and **3** from 0.5:1.0 to 1.0:1.0 led to a significant increase of conversion from 45.5% to 100.0%, as shown in Supporting Information Table S1. This is supported by the fact that the peak area of methyl chloride group at δ 3.83 ppm reduces with the increase of reaction time and molar ratio between TBAB and **3**, as shown in their ^{1}H NMR spectra in Figure 1. The molecular weight of **4** is about 414 g/mol as calculated from its MALDI-TOF mass spectrum data (437 g/mol with Na$^+$) in Supporting Information Figure S3, which is identical with its theoretical value of 414 g/mol. This indicates the complete conversion of **3**
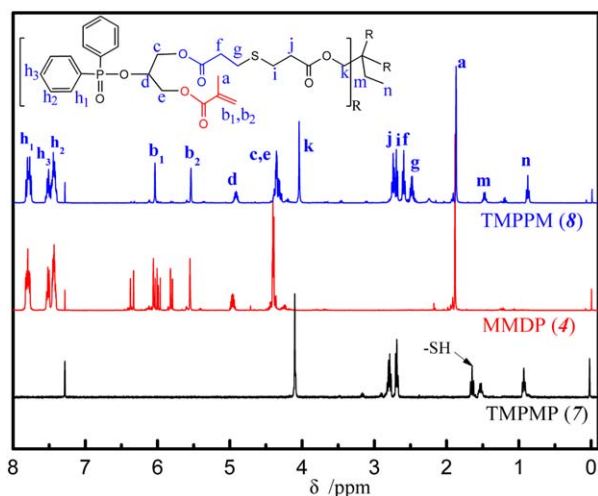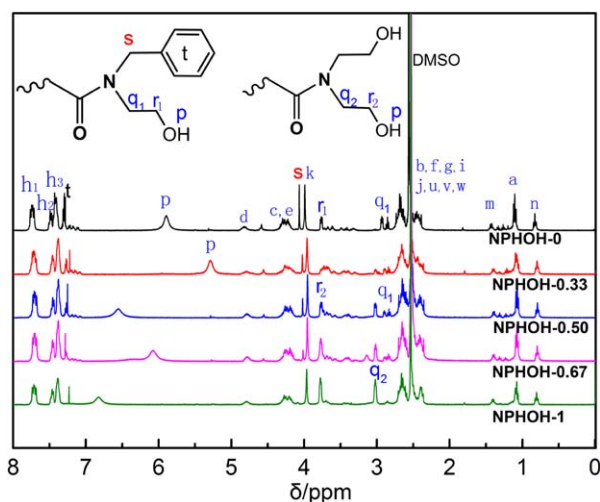
Figure 4. ^{1}H-NMR spectra of NPHOH-n ($n = 0$, 0.33, 0.50, 0.67, and 1). [Color figure can be viewed at wileyonlinelibrary.com.]

into **4** under the reaction time of 24 h and a 1.0:1.0 molar ratio between TBAB and **3**.

Compounds **5** and **6** were synthesized by an amidations between MPA and BEA and between MPA and DEA, respectively. After complete conversion of amino groups in BEA and DEA into amide groups in **5** and **6**, respectively, the thiol group remains unchanged, as demonstrated by the appearance of a new peak at 1563.5 cm^{-1} attributable to stretching vibration of amide group and the disappearance of absorption peak at 1705.1 cm^{-1} attributable to stretching vibration of carboxyl group in Supporting Information Figure S4. The ^{1}H NMR spectra of compounds **5** and **6** are shown in Figure 2. A broad peak at δ 6.0 ppm in the ^{1}H NMR spectrum of **6** is attributed to hydrogen atoms of hydroxy group, and the area ratio among all chemical shift peaks is approximately to its ratio of all hydrogen atoms, suggesting that the products possess the chemical structures of **5** and **6**.

TMPPM (**8**) carrying three methacrylate groups was synthesized by a thoil-ene click reaction between the acrylate group of **4** and the thiol groups of TMPMP (**7**) according to Scheme 2.
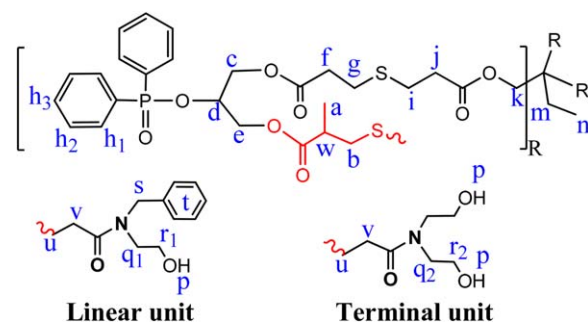
Scheme 3. Chemical structures of NPHOH-n and their main chains. [Color figure can be viewed at wileyonlinelibrary.com.]
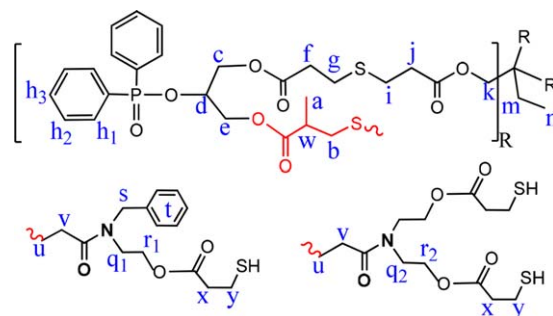
Scheme 4. Chemical structures of NPHSH-n and their main chains. [Color figure can be viewed at wileyonlinelibrary.com.]

Comparing the FT-IR spectrum (Supporting Information Figure S5) of **8** with the FT-IR spectra of **4** and **7**, we find that the peak at 2568.4 cm^{-1} (—SH) disappeared and new peaks appeared at 1636.1, 1408.4, and 810.3 cm^{-1} (methacrylate group). When compared with the ^{1}H NMR spectrum (Figure 1) of **4**, the disappearance of the peaks at δ 6.36 and 5.82 ppm in the ^{1}H NMR spectrum (Figure 3) of **8** can be attributed to hydrogen atoms of acrylate group, and appearance of the peaks at δ 6.06 and 5.58 ppm attributed to hydrogen atoms of methacrylate group. In the system of mercaptopropanoate and **4**, the thiol-ene Michael addition between the thiol group and the methacrylate group and the thiol-ene click reaction between the thiol group and the acrylate group compete with each other because the conditions are quite similar. A thiol-Michael addition that occurs thermally (at room temperature) as a nucleophilic attack to an activated double bond.[28] All the above analyses of FT-IR and ^{1}H NMR spectra of **8** indicate that the acrylate group has been reacted completely and the methacrylate group remains. In other words, the activity of acrylate group is much higher than that of methacrylate group without any catalyst at room temperature although both the methacrylate group and acrylate group of **4** can react with the thiol groups of **7**. The molecular weight of **8** is about 1641 g/mol calculated from its MALDI-TOF mass spectrum data (1664 g/mol with Na$^+$) in Supporting Information Figure S6, which is equal to its theoretical value of 1641 g/mol, confirming the chemical structure of **8**.

Characterization of NPEHP

Synthesis scheme of epoxy-ended hyperbranched polymers with controllable degrees of branching (DBs) is presented as Scheme 2. Firstly, hydroxyl-ended hyperbranched polymers (NPHOH) with controllable degrees of branching were prepared by a thiol-ene Michael addition between the methacrylate group in **8** and the thiol groups in both **5** (AB monomer) and **6** (AB$_2$ monomer), which were used as linear unit and branching unit, respectively. Secondly, the esterification between the hydroxyl groups of NPHOH and the carboxyl group of MPA results in formation of thoil-ended hyperbranched polymers (NPHSH) with controllable degrees of branching. Thirdly, epoxy-ended hyperbranched polymers (NPEHP) with controllable degrees of branching were produced by a thoil-ene Michael addition between the thiol groups of NPHSH and the double bond of GMA. Detailed synthesis processes of NPEHP were supplied in supporting information.

Table I. Calculated and Theoretical DB of NPHOH-n

δ/ppm	3.83 $r_2(N_t)$	3.68 $r_1(N_L)$	3.07 $q_2(N_t)$	2.91 $q_1(N_L)$	BD Calculated value	Theoretical value
NPHOH-0	0	1.97	0	1.97	0	0
NPHOH-0.33	1.36	1.33	1.36	1.31	0.34	0.33
NPHOH-0.50	2.04	0.98	2.03	0.98	0.51	0.50
NPHOH-0.67	2.68	0.67	2.69	0.67	0.67	0.67
NPHOH-1	3.99	0	4.01	0	1.00	1.00

NPHOH-n ($n = 0$, 0.33, 0.50, 0.67, and 1) can be synthesized by a thiol-ene Michael addition between the double bond of **8** and the thiol group of **5** and **6** in their various molar ratios. In the FT-IR spectra (Supporting Information Figure S7) of NPHOH-n (n is between 0 and 1), the absorption peaks at 1722 and 1571 cm^{-1} are attributed to stretching vibration of —C=O and —CON— groups, respectively. The two peaks at 1162 and 1297 cm^{-1} are attributed to stretching vibration of —C—O—C— group. The disappearance of absorption peaks at 1634.06 cm^{-1} attributed to stretching vibration of the double bond and at 810.30 cm^{-1} attributed to bending vibration of the double bond suggest the complete reaction between the thiol and the double bond groups. This is also supported by the disappearance of the absorption peaks of thiol group at 2568.43 cm^{-1}.

The ^{1}H-NMR spectra of NPHOH-n are shown in Figure 4. Chemical shifts of hydrogen atoms are assigned in Figure 4 according to their chemical structures shown in Scheme 3. The disappearance of the peaks at δ 6.06 and δ 5.58 ppm attributed to chemical shift of the methacrylate group suggests its complete conversion. The peak at δ 4.05 ppm is attributable to the chemical shift of hydrogen atom (s, Ph—CH$_2$—) in linear unit (**5**). The chemical shifts of hydrogen atoms (q_1, —N—CH$_2$—) in

linear unit (**5**) and hydrogen atoms (q_2, —N—CH$_2$—) in branched or terminal unit (**6**) appear at δ 2.91 and δ 3.07 ppm, respectively. With an increase in molar ratio (n) between **6** and **5** from 0 to 1, the peak area at δ 4.05 ppm decreases gradually and the peak area at δ 3.07 ppm increases, indicating the decrease of linear unit (**5**) content, which agrees with change of **5** content (Scheme 4).

Degree of branching (DB) is one of the most important parameters of hyperbranched polymers and is usually calculated by NMR spectroscopy[31] according to eq. (1).

$$DB = (N_b + N_t)/(N_b + N_t + N_L) \qquad (1)$$

where N_b is the number of branched units, and N_t is the number of terminal units and N_L is the number of linear units. The chemical chains of NPHOH should be composed of linear units and terminal units (Figure 4). The peaks attributed to the linear unit (N_L) appear at δ 3.68 ppm (r_1, —CH$_2$—OH) and δ 2.91 ppm (q_1, —N—CH$_2$—), and the peaks attributed to the terminal unit (N_t) appear at δ 3.83 ppm (r_2, —CH$_2$—OH) and δ 3.07 ppm (q_2, —N—CH$_2$—). One molar terminal unit contains two molar of —CH$_2$CH$_2$OH groups and one molar linear unit contains one molar of —CH$_2$CH$_2$OH group. Therefore, DB can be calculated using eq. (2):

Table II. GPC data of NPHOH-n, NPHSH, and NPEHP

| Polymers	Theoretical molecular weight/Da	Number-average molecular weight (M_n)	Molecular weight distribution (PDI)
NPHOH-0	2359	1927	1.10
NPHSH-0	2624	2217	1.15
NPEHP-0	3050	2352	1.23
NPHOH-0.33	2313	1875	1.05
NPHSH-0.33	2666	1959	1.09
NPEHP-0.33	3234	2201	1.24
NPHOH-0.5	2290	1840	1.09
NPHSH-0.5	2687	2091	1.11
NPEHP-0.5	3326	2380	1.23
NPHOH-0.67	2267	1786	1.07
NPHSH-0.67	2708	2063	1.09
NPEHP-0.67	3418	2286	1.19
NPHOH-1	2221	1730	1.08
NPHSH-1	2750	1778	1.13
NPEHP-1	3602	1829	1.23
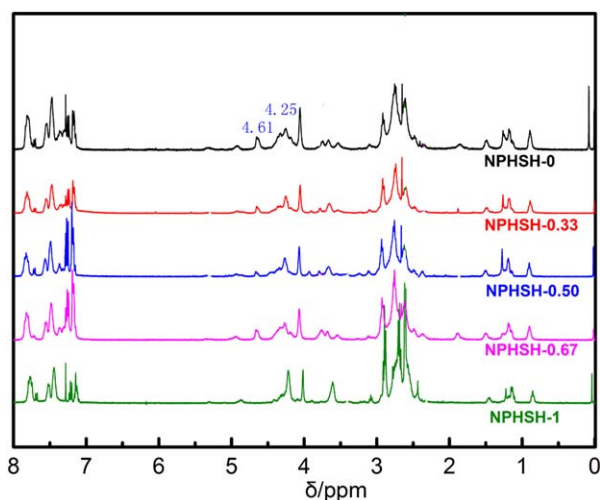
Figure 5. ^{1}H-NMR spectra of NPHSH-n ($n = 0$, 0.33, 0.50, 0.67, and 1). [Color figure can be viewed at wileyonlinelibrary.com.]

$$DB = (N_t)/2/[(N_t/2+N_L)] = N_t/(N_t+2N_L) \qquad (2)$$

As shown in Table I, the calculated DBs of the NPHOH-n ($n = 0$, 0.33, 0.50, 0.67, and 1) from their ^{1}H NMR spectra according to the above equation are very close to their theoretical values, indicating that their DB can be controlled very precisely by tuning the molar ratio between the linear monomer (**5**) and the branched monomer (**6**).

NPHOH-n molecular weights and their distributions from GPC measurement are presented in Table II. The molecular weight of NPHOH-n decreases with the increase of their DBs, which is in good agreement with theoretically derived values. The narrow molecular weight distribution (PDI = 1.05–1.23) also indicates the high efficiency of the Michael addition between the double bond of **8** and the thiol groups of **5** and **6**.

NPHSH-n ($n = 0$, 0.33, 0.50, 0.67, and 1) were synthesized by esterification between MPA and NPHOH-n. In the FT-IR
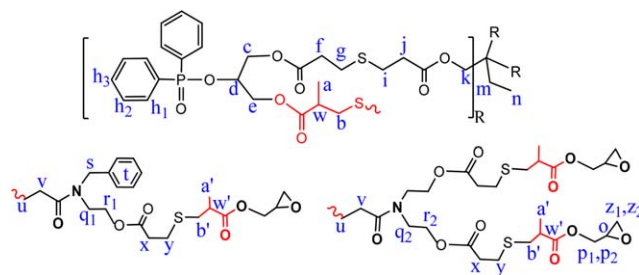
Scheme 5. Chemical structures of NPEHP-n and their main chains. [Color figure can be viewed at wileyonlinelibrary.com.]

spectra (Supporting Information Figure S8) of NPHSH-n, the absorption peaks at 1722 and 1627 cm^{-1} are attributed to stretching vibration of —C=O and —CON— groups, respectively. Both peaks at 1162 and 1297 cm^{-1} are attributed to stretching vibration of —C—O—C— group. In the ^{1}H NMR spectra (Figure 5) of NPHSH-n, the chemical shifts of hydrogen atoms (q_1, q_2, —N—C$\underline{H}_2$—) increased from δ 2.91 ppm and δ 3.07 ppm (refer to Figure 6) to δ 3.51 ppm and δ 3.72 ppm, respectively, and the chemical shifts of hydrogen atoms (r_1, r_2, —C$\underline{H}_2$—OH) increased from δ 3.68 ppm and δ 3.83 ppm (refer to Figure 6) to δ 4.25 ppm and δ 4.61 ppm, suggesting complete esterification of the hydroxyl group of NPHOH-n. NPHSH-n molecular weights (Table II) are more than those of their respective precursors (NPHOH-n), indicating esterification between NPHOH-n and MPA. The narrow molecular weight distribution (PDI = 1.09–1.15) also indicates complete conversion of hydroxyl group of NPHOH-n.

NPEHP-n ($n = 0$, 0.33, 0.50, 0.67, and 1) were synthesized by thiol-ene Michael addition reaction between GMA and NPEHP-n. A thiol-Michael addition occurs thermally (at room temperature) as a nucleophilic attack to an activated double bond.[28] In the system of mercaptopropanoate and glycidyl methacrylate, the thiol-ene Michael addition and thiol-epoxy click reaction
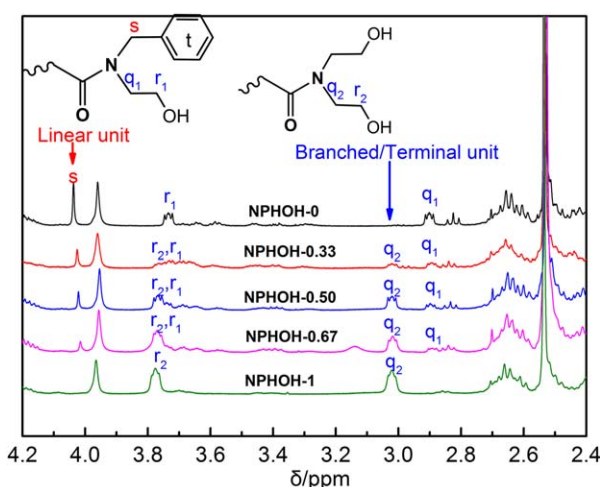

Figure 6. ^{1}H-NMR spectra of linear and terminal units. [Color figure can be viewed at wileyonlinelibrary.com.]
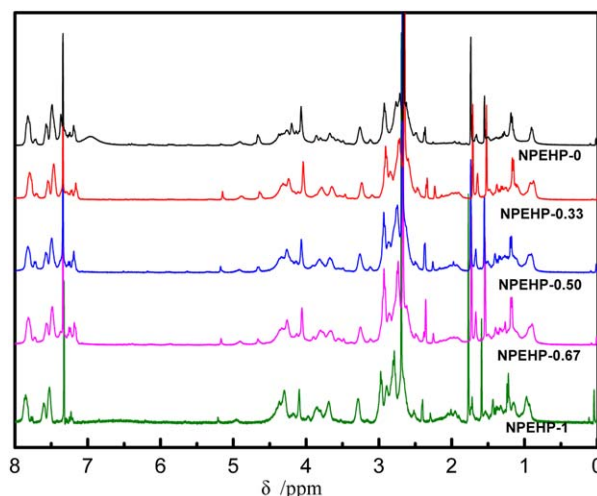

Figure 7. ^{1}H-NMR spectra of NPEHP-n ($n = 0$, 0.33, 0.50, 0.67, and 1). [Color figure can be viewed at wileyonlinelibrary.com.]

compete with each other because the conditions are quite similar.[32] Both thiol-epoxy reaction and homopolymerization of epoxides appear under in the presence of amines.[33] Bowman[34] demonstrated that the thiol-epoxy click reaction took place at a much higher rate than the thiol-ene Michael addition using amine as a catalyst. The partial overlapping of thiol-ene, thiol-epoxy, and epoxy homopolymerization were also observed through radical and anionic initiation.[34] Here, we used azodiisobutyronitrile (AIBN) as catalyst to initiate the thiol-ene Michael addition at reflux temperature and prevent thiol-epoxy reaction. In the FT-IR spectra (Supporting Information Figure S9) of NPEHP-n, the disappearance of the absorption peaks at 1634 and 810 cm^{-1} (double bond of GMA) and the appearance of a new peak at 909 cm^{-1} (epoxy group) suggest grafting of GMA on NPHSH-n, leading to the formation of NPEHP-n. The chemical structure (Scheme 5) of NPEHP-n is verified by the appearance of the chemical shift peaks attributed to double bond of GMA at δ 6.17 ppm and δ 5.61 ppm (Supporting Information Figure S2) and the chemical shift peak of epoxy group at δ 3.20 ppm in ^{1}H NMR spectra (Figure 7). The molecular weights (Table II) of NPEHP-n (n = 0, 0.33, 0.50, 0.67 and 1) are higher than their respective precursors (NPHSH-n), indicating thiol-ene Michael addition between GMA and NPEHP-n. The narrow molecular weight distribution (PDI = 1.19–1.24) also indicates the high efficiency of the Michael addition.

CONCLUSIONS

We proposed and verified a new method for synthesizing nitrogen-phosphor skeleton epoxy-ended hyperbranched polymers (NPEHP) with controllable degree of branching from thiol-ended hyperbranched polymers (NPHSH). NPHSH was obtained by esterification of hydroxyl-ended hyperbranched polymers (NPHOH) and 3-mercaptopropionic acid. NPHOH with controllable DB between 0 and 1 were prepared by a thiol-ene Michael addition between the methacrylate groups of a multifunctional monomer and the thiol groups of linear monomer (AB) and/or branched monomer (AB$_2$ monomer). The degree of branching (DB) of the resultant hyperbranched polymers can be easily controlled by adjusting the molar ratio of AB and AB$_2$ monomers. The experimentally obtained DBs of NPHOH are very close to their theoretical values based on their ^{1}H NMR spectra. FT-IR, ^{1}H NMR, and MALDI-TOF MS spectra have characterized and confirmed the chemical structure and molecular weights of all monomers. The narrow molecular weight distributions of NPHOH, NPHSH, and NPEHP suggest high efficiency of thiol-ene Michael addition. This fast and highly efficient process may open a new avenue for the design and synthesis of hyperbranched polymers.

ACKNOWLEDGMENTS

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