

# Synthesis and properties of novel benzobisthiazole-containing hyperbranched polyamides derived from 2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole

Xiaobing Hu

College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Shaanxi Province Key Laboratory of Phytochemistry, Baoji, Shaanxi, 721013, People's Republic of China

Correspondence to: X. Hu (E-mail: hxb.0917@stu.xjtu.edu.cn)

**ABSTRACT:** In this article, two novel benzobisthiazole-containing hyperbranched polyamides with different end groups were synthesized, by adjusting the feed molar ratio of the reaction monomers, using 1,3,5-benzenetricarboxylic acid and 2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole as monomers, polyphosphoric acid as solvent, and catalyst. The molecular structure of the synthesized hyperbranched polymers were speculated by  $^1\text{H}$ -nuclear magnetic resonance (NMR) analysis,  $^{13}\text{C}$ -NMR analysis, and Fourier transform infrared analysis. The  $M_n$ ,  $M_w$ , and DB of the carboxyl terminated polymer HB-COOH are 3264 g/mol, 3350 g/mol, and 44.1%, respectively, with a polydispersity of 1.03. The  $M_n$ ,  $M_w$ , and DB of amino terminated polymer HB-NH<sub>2</sub> are 3340 g/mol, 3420 g/mol, and 41.7%, respectively, with a polydispersity of 1.02. The thermal stability of HB-NH<sub>2</sub> was higher than HB-COOH in the range of 30 °C–800 °C. These two benzobisthiazole-containing hyperbranched polyamides were completely amorphous and soluble in DMSO. Their DMSO solutions exhibited strong blue fluorescence. The fluorescent intensity of HB-NH<sub>2</sub> was higher than HB-COOH. The prepared polymers were potential useful in the area of blue light emitting and display. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43453.

**KEYWORDS:** hyperbranched polyamide; benzobisthiazole; 2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole; fluorescence spectroscopy; UV-vis spectroscopy

Received 11 November 2015; accepted 18 January 2016

DOI: 10.1002/app.43453

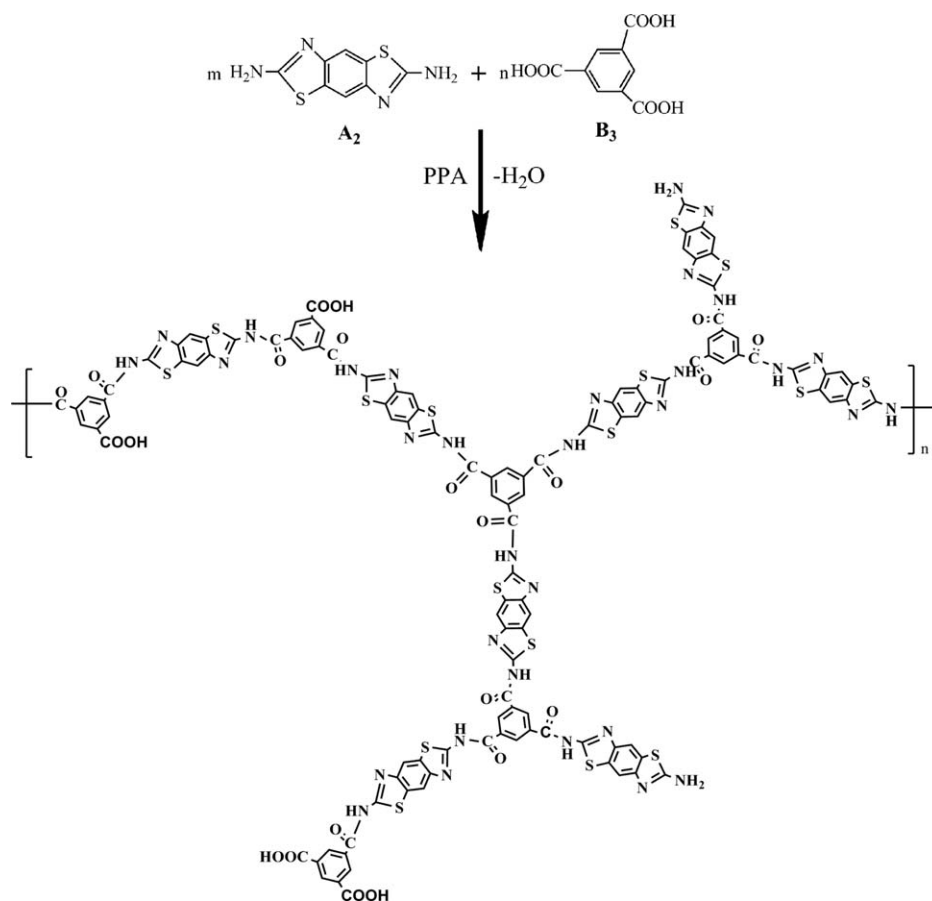
## INTRODUCTION

In the past two decades, hyperbranched polymers have continuously attracted special attention on account of their unique macromolecular structure, meliorative physical and chemical properties, as well as their broad range of applications, such as coatings, surface modification agents, additives, drug delivery vehicles, macromolecular building blocks, nanotechnology, and supramolecular science.<sup>1–8</sup> Hyperbranched polymers are superior to dendritic polymers for that they can be easily synthesized by a “one pot” method. They have highly branched architecture and large numbers of functional end groups and got an advantage over their linear counterpart with their high solubility, low viscosity, good processability, tunable light emission, low crystallinity, and controllable thin film morphology.<sup>9,10</sup> Generally speaking, two kinds of methods are used to synthesize hyperbranched polymers, such as AB<sub>n</sub> (when  $n \geq 2$ ) method and A<sub>2</sub> + B<sub>n</sub> (when  $n \geq 3$ ) method.<sup>11–13</sup> Among these two methods, AB<sub>n</sub> type monomers are usually difficult to synthesize, because there are two different reactive groups in their molecules and they can undergo self-polymerization in some cases. While A<sub>2</sub> + B<sub>n</sub> (when  $n \geq 3$ ) method has the merits of commercially

available monomers and soluble hyperbranched polymer in high yield synthesized by the control of polymerization conditions.<sup>14</sup>

Poly(p-phenylene benzobisthiazole) (PBZT) is a kind of aromatic heterocycle conjugated polymer, which is well known for its excellent mechanical properties (high tensile strength and modulus), high chemical and thermo-oxidative resistance,<sup>15</sup> and large and ultrafast third-order nonlinear optics (NLO) response.<sup>16–20</sup> While the insolubility of PBZT in common organic solvents which deriving from its high degree of molecular rigidity and strong intermolecular interactions makes PBZT difficult to process and impedes more detailed and accurate studies on this type of conjugated polymer. To solve this problem, introducing hyperbranched structure into rigid PBZT backbone by an A<sub>2</sub> + B<sub>3</sub> method was found to be effective in our previous work.<sup>20</sup> The prepared hyperbranched poly(p-phenylene benzobisthiazole)s was soluble in organic solvents and their DMF solutions emit strong blue light under the excitation of ultraviolet (UV) light.<sup>20</sup>

In this work, the author reports the synthesis and characterization of two novel benzobisthiazole-containing hyperbranched



**Scheme 1.** Synthetic approach of benzobisthiazole-containing hyperbranched polyamides.

polyamides by direct polycondensation of 2,6-diaminobenzobisthiazole (DABBT) with 1,3,5-benzenetricarboxylic acid (BTA) via an  $A_2 + B_3$  approach using poly(phosphoric acid) (PPA) as catalyst and solvent under an argon atmosphere. These two benzobisthiazole-containing hyperbranched polyamides are supposed to have special fluorescent properties because of the aromatic heterocyclic benzobisthiazole groups. The synthetic approach is shown in Scheme 1. The condensation polymerization of DABBT and BTA was performed in two manners. In manner 1, DABBT and BTA were added by the molar ratio of 1 : 1 ( $m : n = 1 : 1$ ), in which carboxyl group was excess and carboxyl-terminated hyperbranched polyamide (HB-COOH) was generated. When the molar feed ratio of DABBT and BTA was 9 : 4 (manner 2,  $m : n = 9 : 4$ ), amino-terminated hyperbranched polyamide (HB-NH<sub>2</sub>) was prepared. Photophysical behaviors of the resultant benzobisthiazole-containing hyperbranched polyamides in dimethyl sulfoxide (DMSO) solution were studied spectroscopically.

## EXPERIMENTAL

### Starting Materials

$A_2$  monomer DABBT was synthesized and purified using a slightly modified literature procedure.<sup>21,22</sup>  $B_3$  monomer BTA (>99%) was purchased from Aladdin Industrial Corporation.

PPA and DMSO were purchased from Sinopharm Chemical Reagent Co., Ltd., and were used as received.

### Polymerization

The synthesis procedure of carboxyl terminated benzobisthiazole-containing hyperbranched polyamides (HB-COOH) was as follows. Into a 100 mL dry three-neck flask, 60 mL PPA containing 83.0 wt % P<sub>2</sub>O<sub>5</sub>, 0.445 g (0.002 mol) DABBT and 0.4123 g (0.002 mol) BTA were added with continuous stirring and dry argon gas purging. The reaction mixture was heated to 80 °C with a heating rate of 5 °C/h. And then the heating rate changed to 10 °C/h from 80 °C to 100 °C. After that, the reaction was carried out at 100 °C for 2 h, 110 °C for 1 h, and 120 °C for 0.5 h. After the reaction system was cooled to room temperature, the mixture was poured into a large amount of deionized water. The polymer was collected by suction filtration and washed repeatedly until the pH value of the filtrate become neutral (pH ≈ 7). Then the hyperbranched polymer was collected by suction filtration, and extracted with deionized water in a Soxhlet apparatus for 48 h. Finally, the polymer was dried at 100 °C for 48 h under reduced pressure. The synthesized hyperbranched polymer was named HB-COOH in this manner. The yield of HB-COOH is about 51.3%.

The synthesis procedure of amino terminated benzobisthiazole-containing hyperbranched polyamides (HB-NH<sub>2</sub>) was similar to

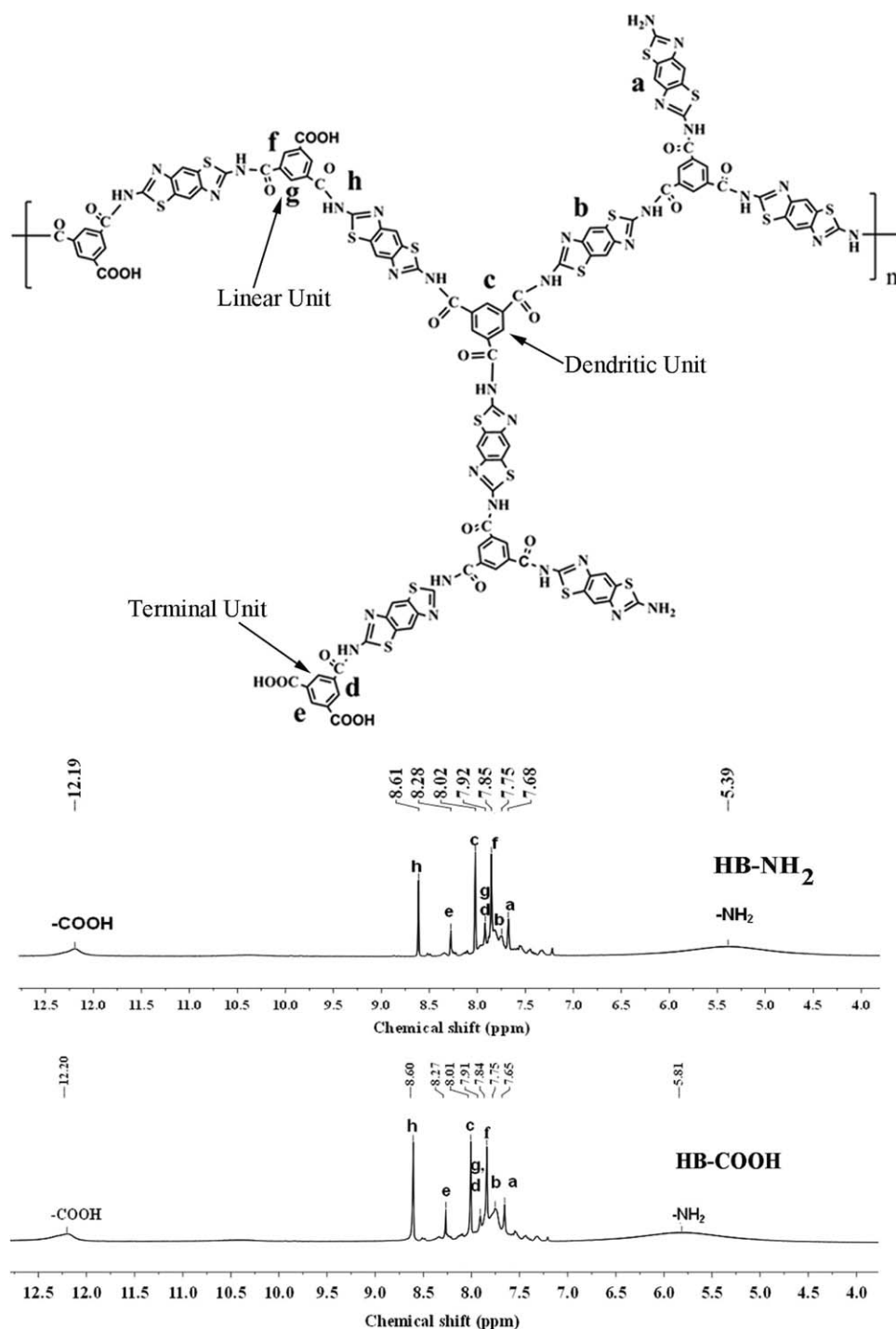
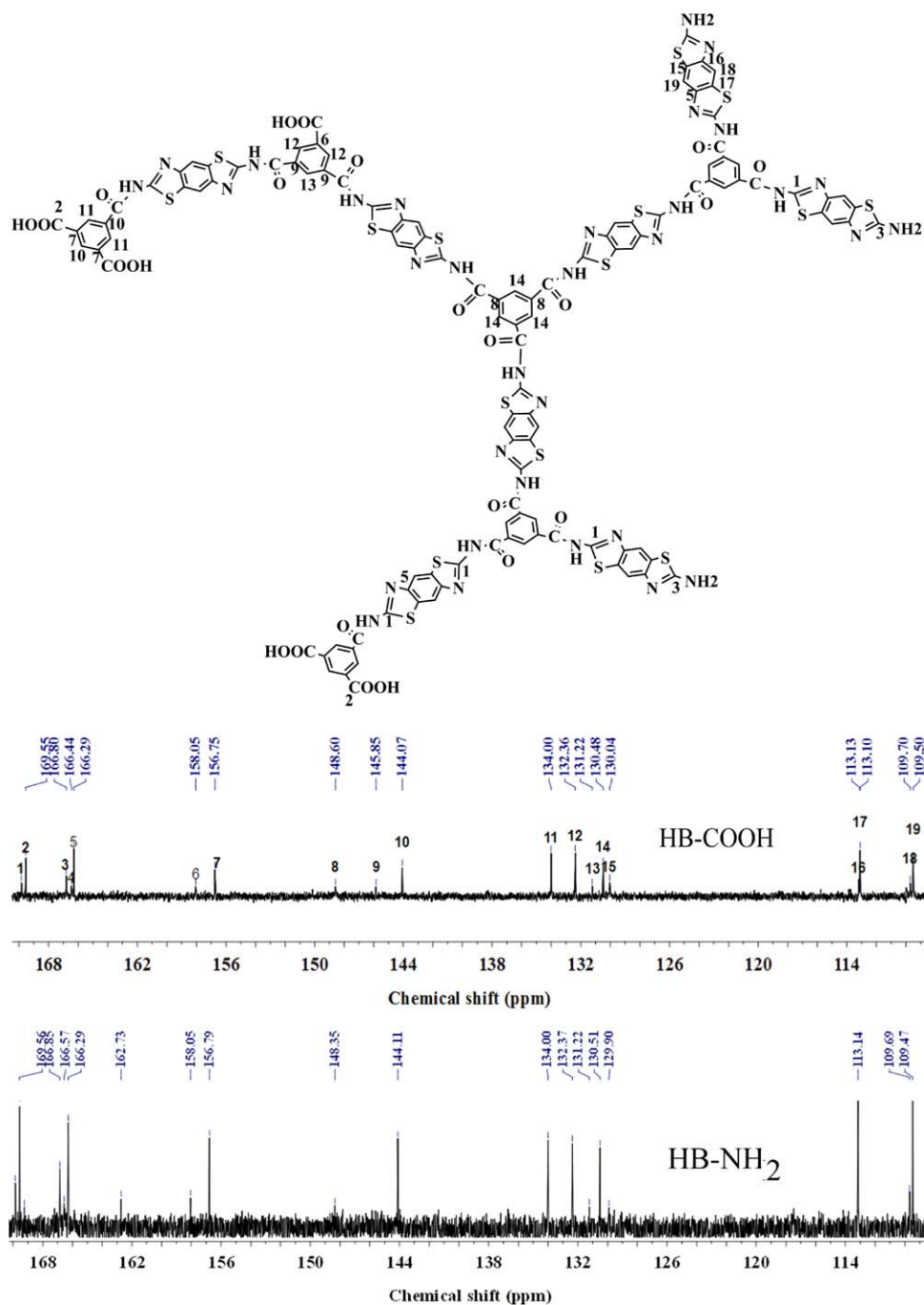


Figure 1.  $^1\text{H-NMR}$  spectra of HB-COOH and HB-NH<sub>2</sub>.

that of HB-COOH with a feeding molar ratio of 9 : 4 (DABBT : BTA). The amino terminated hyperbranched polymer was named HB-NH<sub>2</sub>. The yield of HB-NH<sub>2</sub> is about 69.9%.

Generally speaking, molecular weights normally influence polymer's properties effectively. With the increase of molecular weight, the polymer's aggregation states and mechanical properties should be changed accordingly. While for conjugate polymers, the solubility will be deteriorated when the molecular

weight is higher than a certain level. Especially for hyperbranched conjugated polymers with reactive end groups, when their molecular weights increased to a certain extent, gelation usually happens and insoluble substances are produced. In order to prepare hyperbranched polyamide with high molecular weight, the author has synthesized benzobisthiazole-containing hyperbranched polyamides by a stepwise heating process with an extra heating of 130°C for 1 h. But unfortunately the



**Figure 2.**  $^{13}\text{C}$ -NMR spectra of HB-COOH and HB-NH<sub>2</sub>. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

produced polymers were found to be partial soluble in DMF or DMSO. The appropriate highest reaction temperature is considered as 120 °C and the heating time is 0.5 h.

### Measurements

$^1\text{H}$  nuclear magnetic resonance (NMR) and  $^{13}\text{C}$  NMR spectra were recorded on a Varian 400 MHz NMR spectrometer by using deuterated dimethyl sulfoxide (DMSO- $d_6$ ) as the solvent and tetramethylsilane (TMS) as an internal reference. Fourier transform infrared (FTIR) spectra were recorded on the Perkin-Elmer infrared spectrometer at room temperature. GPC

measurements were performed on a Malvern GPC/SEC-Viscotek 270 max gel permeation chromatography system, using DMF as the eluent at a flow rate of 0.5 mL/min. The temperature is 30 °C. The molecular weights and molecular weight distributions of the polymers were calculated using narrow-molecular-weight polystyrene standards as reference. UV-visible absorption spectra of polymers in DMSO solution were recorded on a METASH UV-8000A spectrometer over the wavelength range of 250–800 nm. Thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements were carried out with a NETZSCH STA 449F3 Jupiter<sup>®</sup> simultaneous TG-DSC under

nitrogen flow with a heating rate of 10 °C/min. The temperature range is from 30 °C to 800 °C. Wide-angle powder X-ray diffraction (XRD) patterns were recorded at room temperature on a Rigaku Ultima IV XRD system using CuK $\alpha$  radiation ( $\lambda = 0.15406$  nm), at a scanning rate of 2°s<sup>-1</sup>. Fluorescence spectra were recorded on a Horiba scientific Fluoromax-4 spectrofluorometer using DMSO as solvent at room temperature. The excitation wavelength was 396 nm.

## RESULTS AND DISCUSSION

### NMR Analysis

The <sup>1</sup>H-NMR spectra of HB-COOH and HB-NH<sub>2</sub> are shown in Figure 1. For both HB-COOH and HB-NH<sub>2</sub>, the 1,3,5-benzenetricarboxylic acid moiety acts as the branching point. The number of remaining carboxylic groups (2, 1, or 0) of 1,3,5-benzenetricarboxylic acid determines the assignment to terminal unit (T), linear unit (L), and dendritic unit (D)<sup>23</sup> as shown in Figure 1.

For HB-COOH, the signals of broad resonance at  $\delta$  5.81 and 12.20 ppm are attributable to the protons of amino group (—NH<sub>2</sub>) and carboxyl group (—COOH) respectively. The signal of resonance at  $\delta$  7.65 ppm is assignable to the protons of terminal benzobisthiazole groups. While the resonance peak at 7.75 ppm attributes to the protons of inner benzobisthiazole groups. The peak at  $\delta$  7.84 ppm is assignable to the protons at the ortho-position of —COOH of the linear units. The resonance peak at  $\delta$  7.91 ppm is attributed to the protons at the para-position of —COOH on the linear units and the protons at the para-position of —COOH on the terminal groups. The resonance peak at  $\delta$  8.01 ppm is attributed to the protons on the dendritic units. The resonance peak at  $\delta$  8.27 ppm is attributed to the protons between two carboxyl groups on the terminal units. The resonance peak at  $\delta$  8.60 ppm is attributed to the protons of amide groups deriving from the condensation reaction of —COOH groups (BTA) and —NH<sub>2</sub> groups (DABBT).

For HB-NH<sub>2</sub>, the signals of broad resonance at  $\delta$  5.39 and 12.19 ppm are attributable to the protons of amino group (—NH<sub>2</sub>) and carboxyl group (—COOH) respectively. The signal of resonance at  $\delta$  7.68 ppm is assignable to the protons of terminal benzobisthiazole groups. While the resonance peak at  $\delta$  7.75 ppm attributes to the protons of inner benzobisthiazole groups. The peak at  $\delta$  7.85 ppm is assignable to the protons at the ortho-position of —COOH of linear units. The resonance peak at  $\delta$  7.92 ppm is attributed to the protons at the para-position of —COOH on the linear units and the protons at the para-position of —COOH on the terminal groups. The resonance peak at  $\delta$  8.02 ppm is attributed to the protons on the dendritic units. The resonance peak at  $\delta$  8.28 ppm is attributed to the protons between two carboxyl groups on the terminal units. The resonance peak at  $\delta$  8.61 ppm is attributed to the protons of amide groups deriving from the condensation reaction of —COOH groups (BTA) and —NH<sub>2</sub> groups (DABBT).

The <sup>13</sup>C NMR data of HB-COOH and HB-NH<sub>2</sub> were listed below and the spectrum was shown in Figure 2. The corresponding relations between the resonance peaks and the molecular structures of HB-COOH and HB-NH<sub>2</sub> were also displayed

**Table I.** Characterization Data for HB-COOH and HB-NH<sub>2</sub>

Sample	DABBT/ BTA <sup>a</sup>	M <sub>n</sub> (g/mol) <sup>b</sup>	M <sub>w</sub> (g/mol) <sup>b</sup>	PDI <sup>b</sup>	DB (%) <sup>c</sup>
HB-COOH	1/1	3264	3350	1.03	44.1%
HB-NH <sub>2</sub>	9/4	3340	3420	1.02	41.7%

<sup>a</sup>Feed molar ratio of monomers.

<sup>b</sup>Number-average molecular weight, weight-average molecular weight and polydispersity (PDI) are determined by GPC.

<sup>c</sup>Degree of branching is estimated by <sup>1</sup>H NMR analysis.

in Figure 2. For HB-COOH, there were nineteen nuclear magnetic resonance peaks in the <sup>13</sup>C-NMR spectrum of HB-COOH, corresponding to nineteen kinds of carbon atoms in HB-COOH molecules, as shown in Figure 2. The <sup>13</sup>C-NMR spectrum of HB-NH<sub>2</sub> was similar to that of HB-COOH beside that the resonance peak at  $\delta$  145.85 ppm was inconspicuous in HB-NH<sub>2</sub> and there was a new resonance peak appeared at  $\delta$  162.73 ppm. The resonance peaks at 113.13 and 113.10 ppm in HB-COOH were merged into one resonance peak at 113.14 ppm in HB-NH<sub>2</sub>.

HB-COOH: <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 169.84, 169.55, 166.80, 166.44, 166.29, 158.05, 156.75, 148.60, 145.85, 144.07, 134.00, 132.36, 131.22, 130.48, 130.04, 113.13, 113.10, 109.70, 109.50.

HB-NH<sub>2</sub>: <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 169.84, 169.56, 169.24, 166.85, 166.57, 166.29, 162.73, 158.05, 156.79, 148.35, 144.11, 134.00, 132.37, 131.22, 130.51, 129.90, 113.14, 109.69, 109.47.

The degree of branching (DB) is one of the most important parameters for the characterization of hyperbranched polymers, which describes the structural perfection of hyperbranched polymers. The DB can be calculated by using Fréchet definition as follows:

$$DB = (D + T) / (D + T + L)^{24-26}$$

In this formula, *D*, *T*, and *L* refer to the number of dendritic, terminal, and linear units in the polymer, respectively. Generally, the values of *D*, *T*, and *L* can be determined by <sup>1</sup>H NMR measurement according to the integrated area of corresponding proton resonance peak. In this research, the DB of HB-NH<sub>2</sub> was determined by the ratio of the integrated area of protons resonance peak at  $\delta$  8.02 ppm (represent the dendritic unit), the protons resonance peak at  $\delta$  7.85 ppm (represent the linear unit) and the protons resonance peak at  $\delta$  8.28 ppm (represent the terminal unit). Similarly, the DB of HB-COOH was estimated by the ratio of the integrated area of the protons resonance peak at  $\delta$  8.01 ppm (represent the dendritic unit), the protons resonance peak at  $\delta$  7.84 ppm (represent the linear unit) and the protons resonance peak at  $\delta$  8.27 ppm (represent the terminal unit). Therefore, the DB of HB-COOH and HB-NH<sub>2</sub> were 44.1% and 41.7%, respectively (see Table I).

### FTIR Analysis

Figure 3 gives the FTIR spectra of HBPA-COOH and HBPA-NH<sub>2</sub>. Sample HBPA-COOH and HBPA-NH<sub>2</sub> have the similar FTIR spectra with a few tiny differences. The absorptions at



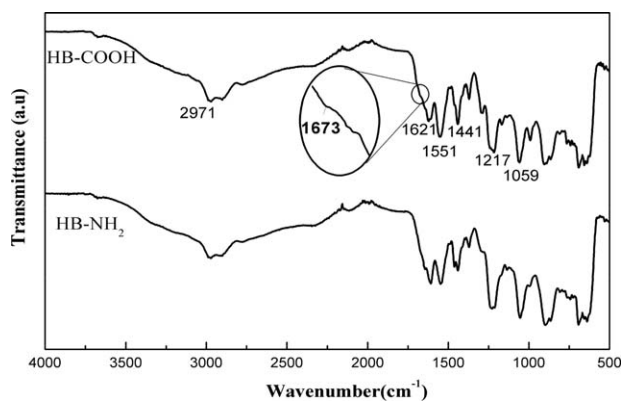


Figure 3. FTIR spectra of HBPA-COOH and HBPA-NH<sub>2</sub>.

about 1621, 1551, and 1441  $\text{cm}^{-1}$  are attributed to the amide groups deriving from the reactions between  $-\text{COOH}$  groups of TBA and  $-\text{NH}_2$  groups of DABBT. Concretely, the signal at about 1621  $\text{cm}^{-1}$  is assigned to the stretching vibration of  $-\text{C}=\text{O}$ , the absorption at around 1551  $\text{cm}^{-1}$  is assigned to the bending vibration of  $-\text{N}-\text{H}$ , and the absorption at about 1441  $\text{cm}^{-1}$  is attributed to the stretching vibration of  $-\text{C}-\text{N}$ . The broad absorption at about 2971  $\text{cm}^{-1}$  is assigned to the stretching vibration of  $-\text{N}-\text{H}$ . The absorption bands around 1217 and 1673  $\text{cm}^{-1}$  can be assigned to the stretching vibration of  $-\text{C}-\text{O}$  and  $-\text{C}=\text{O}$  of  $-\text{COOH}$  groups,<sup>27</sup> indicating the presence of  $-\text{COOH}$  groups remaining in both HB-COOH and HB-NH<sub>2</sub>. The FTIR analysis and NMR analysis indicate that the benzobisthiazole-containing hyperbranched polyamides were successfully synthesized.

#### GPC Analysis

The molecular weights and polydispersity index (PDI) values of HB-COOH and HB-NH<sub>2</sub> are measured by gel permeation chromatography (GPC). The result is shown in Figure 4 and Table I. The number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of HB-COOH are 3264 and 3350 g/mol, respectively. Hence, the PDI value of HBPA-COOH is about 1.03. And for HB-NH<sub>2</sub>, the  $M_n$  and  $M_w$  are 3340 and 3420 g/mol, respectively, with a PDI value of 1.02 (see Table I). Certainly the aforementioned molecular weights of HBPA-COOH and HBPA-NH<sub>2</sub> are slightly inaccurate, because they are esti-

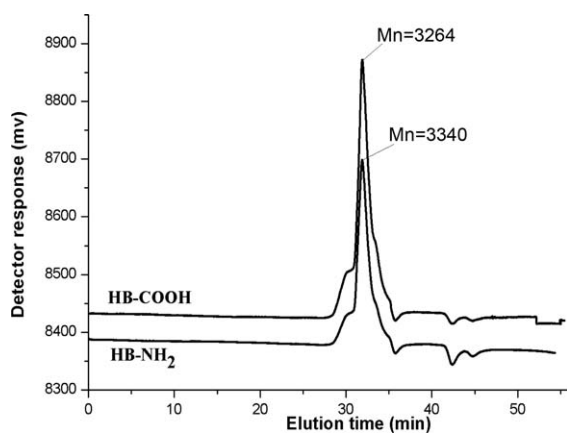


Figure 4. GPC curves of HB-COOH and HB-NH<sub>2</sub>.

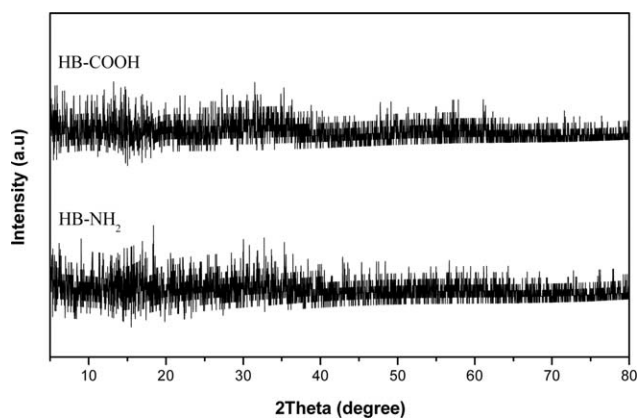


Figure 5. WAXD patterns of HB-COOH and HB-NH<sub>2</sub>.

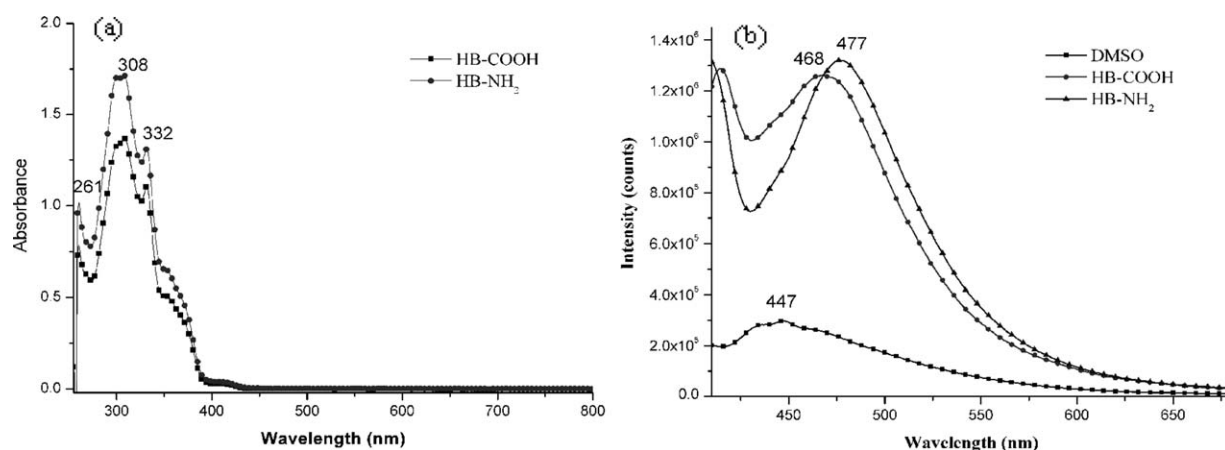
mated by GPC using linear polystyrene as the standard, and the volume of hyperbranched polymers are usually smaller than that of their linear counterparts when their molecular weights are the same.<sup>28,29</sup>

#### XRD Study of Benzobisthiazole-Containing Hyperbranched Polyamides

The wide-angle X-ray diffraction (WAXD) patterns of HB-COOH and HB-NH<sub>2</sub> are presented in Figure 5. There is no obvious sharp diffraction peaks for the two hyperbranched polymers in the 2 theta range of 5°–80°, indicating that the synthesized hyperbranched polymers (HB-COOH and HB-NH<sub>2</sub>) are all amorphous. The results of diffraction studies can be explained by that the introduction of branching in the polymer backbone disrupted the close packing of polymer molecules.<sup>30</sup> In consequence, the crystallinity of hyperbranched polymers is generally greatly decreased compared with their linear counterparts and completely amorphous polymers were obtained. These results are consistent with the DSC analysis (Figure 7), in which no crystalline melting peaks are observed. The amorphous nature of these hyperbranched polymers makes them soluble in DMSO. On this basis, the UV-vis absorption properties and fluorescent properties of HB-COOH and HB-NH<sub>2</sub> were studied for the first time.

#### UV-Vis Spectra and Fluorescence Spectra of HBPA-COOH and HBPA-NH<sub>2</sub>

The UV-Vis spectra and fluorescence emission spectra of HBPA-COOH and HBPA-NH<sub>2</sub> in DMSO solution are shown in Figure 6(a,b), respectively. Figure 6(a) describes the UV-Vis spectra of HBPA-COOH and HBPA-NH<sub>2</sub> in DMSO solution with the concentration of 1.0 mg/mL. Both HBPA-COOH and HBPA-NH<sub>2</sub> show similar absorption in the range of 260–800 nm. Each sample has three absorption bands: the first at  $\lambda_{\text{max}} = 261$  nm, the second at  $\lambda_{\text{max}} = 308$  nm, and the third at  $\lambda_{\text{max}} = 332$  nm. These three absorptions are all within the scope of the ultraviolet region. The absorption intensity of HB-COOH is lower than the absorption intensity of HB-NH<sub>2</sub> in the range of 260–400 nm obviously, which can be attributable to the end-group effect of hyperbranched polymers. Amino group ( $-\text{NH}_2$ ) are electron donating, which will reduce the energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and hence



**Figure 6.** UV-Vis spectra and Fluorescence spectra of HBPA-COOH and HBPA-NH<sub>2</sub> (a) UV-Vis spectra; (b) Fluorescence spectra (excitation wavelength: 396 nm).

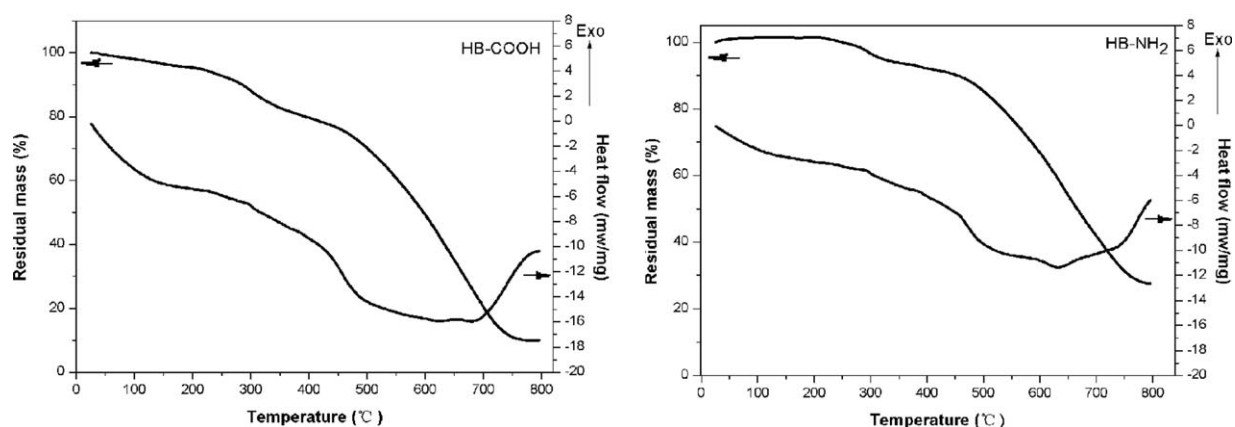
facilitates the corresponding electron transition. While carboxyl group ( $-\text{COOH}$ ) is an electron-withdrawing group which will enhance the energy gap between HOMO and LUMO. Therefore, electron transition between HOMO and LUMO is easier in amino terminated polymer HB-NH<sub>2</sub> than that in carboxyl terminated polymer HB-COOH.

The fluorescence emission spectra of HB-COOH and HB-NH<sub>2</sub> are shown in Figure 6(b), together with the fluorescence spectra of pure DMSO. Both HB-COOH and HB-NH<sub>2</sub> display strong blue light emission when excited at 396 nm in DMSO solution. The concentration of the two samples is 0.033 mg/mL. Sample HB-COOH has a broad emission in the range of 410–680 nm with a maximum emission wavelength of 477 nm. And sample HB-NH<sub>2</sub> shows a broad emission in the range of 410–680 nm with a peak at 468 nm. The solvent DMSO has a weak and broad emission centered at about 447 nm when excited with a light of 396 nm. So the emissions of sample HB-COOH and HB-NH<sub>2</sub> are mainly from the synthesized hyperbranched polymers.

The intense emission of HB-COOH and HB-NH<sub>2</sub> suggests that the hyperbranched structure could maintain the stability of the excited state and help to prevent the aggregation and excimer

formation.<sup>31,32</sup> The fluorescence intensity of HB-NH<sub>2</sub> is higher than that of HB-COOH, which is attributed to the end group effect of hyperbranched polymers. The end group effect on the fluorescent properties of HB-COOH and HB-NH<sub>2</sub> is similar to that of UV-vis absorption properties. HB-COOH is carboxyl terminated polymer with many carboxyl groups in its molecule structure. While HB-NH<sub>2</sub> is amino terminated polymer with large number of amino groups ( $-\text{NH}_2$ ) in its molecular periphery. The  $-\text{NH}_2$  groups are electron-donating, which facilitates the electron transition from HOMO to LUMO. However,  $-\text{COOH}$  is electron-withdrawing, which will weaken fluorescence emission. Therefore, the fluorescence intensity of HB-COOH is lower than that of HB-NH<sub>2</sub>, and the maximum emission wavelength of HB-NH<sub>2</sub> is 9 nm red-shift than that of HB-COOH. This is in accordance with our previous study.<sup>20</sup> These two hyperbranched polymers are potential useful in the area of blue light emitting and display.

In our previous study, three heterocyclic hyperbranched polybenzobisthiazoles (HBPBZTs) were synthesized through an A<sub>2</sub> + B<sub>3</sub> approach by adjusting the mole feed ratios of 2,5-Diamino-1,4-benzenedithiol Dihydrochloride (A<sub>2</sub>) and 1,3,5-benzenetricarboxylate (B<sub>3</sub>). These polymers are conjugated polymers



**Figure 7.** TG and DSC thermograms of HB-COOH (left) and HB-NH<sub>2</sub> (right).

with high rigidity.<sup>20</sup> While in this study, two semi-conjugated benzobisthiazole-containing hyperbranched polyamides with different terminal groups (HP-COOH and HP-NH<sub>2</sub>) were synthesized via an A<sub>2</sub> + B<sub>3</sub> approach by using 2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole (A<sub>2</sub>) and 1,3,5-benzenetricarboxylate (B<sub>3</sub>). Generally speaking, semi-conjugated polymers have higher solubility than conjugated polymers. So the solubilities of HP-COOH and HP-NH<sub>2</sub> are supposed to be higher than HPBPZTs in some polar organic solvents (DMF and DMSO). As a consequence, the processability of these two hyperbranched polyamides is better than HPBPZTs. In addition, the maximum absorption wavelength of HBPBZTs is 336–363 nm. While for HP-COOH and HP-NH<sub>2</sub>, the maximum absorption wavelengths are 332 and 308 nm, respectively. When excited at 370 nm, HBPBZTs emit blue lights in the wavelength range of 439–443 nm. While for HP-COOH and HP-NH<sub>2</sub>, when excited at 396 nm, the maximum emission wavelengths are 468 and 477 nm, respectively. Both HBPBZTs and the benzobisthiazole-containing hyperbranched polyamides (HP-COOH and HP-NH<sub>2</sub>) emit blue lights when excited by ultraviolet. And compare to HBPBZTs, the maximum emission wavelengths of HP-COOH and HP-NH<sub>2</sub> are red-shift.

#### TG and DSC Analysis

The TG and DSC thermograms of HB-COOH and HB-NH<sub>2</sub> are shown in Figure 7. These two polymers show similar thermal degradation behavior in the range of 30 °C–800 °C. There are three stages in the TG curves of HB-COOH and HB-NH<sub>2</sub>. The first stage is from 30 °C to about 300 °C, with weight losses of 11.69% and 3.26% for HB-COOH and HB-NH<sub>2</sub>, respectively. The second stage is from about 300 °C to about 465 °C. The weight losses in this stage are about 13.24% and 7.46% for HB-COOH and HB-NH<sub>2</sub>, respectively. The third stage is from about 465 °C to about 800 °C. The weight loss speed in this stage is much higher than that in the first stage and the second stage. The residual masses at 800 °C are about 9.94% and 27.60% for HB-COOH and HB-NH<sub>2</sub>, respectively. The thermal stability of HB-NH<sub>2</sub> is higher than HB-COOH in whole measurement temperature range. The DSC curves of HB-COOH and HB-NH<sub>2</sub> display wide endothermic peaks in the range of 30 °C to about 150 °C, which is supposed due to the evaporation of absorbed water, owing to the hygroscopic nature of high polar groups on molecular interior and peripheries. While the wide and strong endothermic peaks after 300 °C are ascribed to the thermal decomposition of the hyperbranched polymers, which is in accordance with the TG analysis.

#### CONCLUSIONS

In this research, two different benzobisthiazole-containing hyperbranched polyamides were synthesized via an A<sub>2</sub> + B<sub>3</sub> approach by adjusting the feed mole ratio of the A<sub>2</sub> (DABBT) and B<sub>3</sub> (BTA) monomers using PPA as solvent and catalyst. The molecular structures of the synthesized hyperbranched polyamides were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and FTIR analyses. The M<sub>n</sub>, M<sub>w</sub>, and DB of the carboxyl-terminated polymer HB-COOH were 3264 g/mol, 3350 g/mol, and 44.1%, respectively, with a polydispersity of 1.03. The M<sub>n</sub>, M<sub>w</sub>, and DB of amino-terminated polymer HB-NH<sub>2</sub> were 3340 g/mol, 3420 g/mol, and 41.7%, respectively, with a polydispersity of 1.02. These two polymers were completely amorphous and could be

soluble in DMSO. HB-NH<sub>2</sub> is more stable than HB-COOH in the range of 30 °C–800 °C. Their DMSO solutions exhibit strong blue fluorescence (468–477 nm). The fluorescence intensity of HB-NH<sub>2</sub> is stronger than that of HB-COOH. They are good candidates in the area of blue light emitting and display.

#### ACKNOWLEDGMENTS

The author thanks the Nature science project fund of Shaanxi Educational Committee of China (14JK1041), and the Scientific research project fund of Shaanxi Province Key Laboratory of Photochemistry of China (14JS006) for the support.

#### REFERENCES

1. Gao, C.; Yan, D. Y. *Prog. Polym. Sci.* **2004**, *29*, 183.
2. Androulaki, K.; Chrissopoulou, K.; Prevosto, D.; Labardi, M.; Anastasiadis, S. H. *ACS Appl. Mater. Interfaces* **2015**, *7*, 12387.
3. Tanis, I.; Karatasos, K.; Assimopoulou, A. N.; Papageorgiou, V. P. *Phys. Chem. Chem. Phys.* **2011**, *13*, 11808.
4. Zeng, X.; Zhang, Y.; Wu, Z.; Lundberg, P.; Malkoch, M.; Nystrom, A. M. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 280.
5. Li, J. G.; Xiang, Y. X.; Zheng, S. X. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 368–380.
6. Chen, S.; Zhang, X. Z.; Cheng, S. X.; Zhuo, R. X.; Gu, Z. W. *Biomacromolecules* **2008**, *9*, 2578.
7. Pettersson, B. *Pigm. Resin Technol.* **1996**, *25*, 4.
8. McKee, M. G.; Unal, S.; Wilkes, G. L.; Long, T. E. *Prog. Polym. Sci.* **2005**, *30*, 507.
9. Scott, M. G.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819.
10. Robinson, M. R.; Wang, S.; Bazan, G. C.; Cao, Y. *Adv. Mater.* **2000**, *12*, 1701.
11. Jikei, M.; Chon, S. H.; Kakimoto, M.; Kawauchi, S.; Imase, T.; Watanabe, J. *Macromolecules* **1999**, *32*, 2061.
12. Young, H. K. *J. Polym. Sci. Part a: Polym. Chem.* **1998**, *36*, 1685.
13. Wu, W. B.; Ye, C.; Qin, J. G.; Li, Z. *Macromol. Rapid Commun.* **2013**, *34*, 1072.
14. Kudo, H.; Matsubara, S.; Yamamoto, H.; Kozawa, T. *J. Polym. Sci. Part a: Polym. Chem.* **2015**, *53*, 2343.
15. Herrema, J. K.; Wildeman, J.; Gill, R. E.; van Hutten, P. F.; Wieringa, R. H.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 8102.
16. Lee, J. W.; Wang, C. S. *Polymer* **1994**, *35*, 3673.
17. Roberts, M. F.; Jenekhe, S. A.; Cameron, A.; Mcmillan, M.; Perlstein, J. *Chem. Mater.* **1994**, *6*, 658.
18. Bai, S. J.; Spry, R. J.; Zelmon, D. E.; Ramabadran, U.; Jackson, J. *J. Polym. Sci. Part B: Polym. Phys.* **1992**, *30*, 1507.
19. Vanherzeele, H.; Meth, J. S.; Jenekhe, S. A.; Roberts, M. F. *Appl. Phys. Lett.* **1991**, *58*, 663.
20. Hu, X. B.; Yu, D. M. *Macromol. Chem. Phys.* **2012**, *213*, 738.
21. Wolfe, J. F.; Loo, B. H.; Arnold, F. E. *Macromolecules* **1981**, *14*, 915.



22. Osaheni, J. A.; Jenekhe, S. A. *Chem. Mater.* **1992**, *4*, 1282.
23. Komber, H.; Voit, B.; Monticelli, O.; Russo, S. *Macromolecules* **2001**, *34*, 5487.
24. Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.
25. Liu, N.; Vignolle, J.; Vincent, J.-M.; Robert, F.; Landais, Y.; Cramail, H.; Taton, D. *Macromolecules* **2014**, *47*, 1532.
26. Hazarika, D.; Karak, N. *ACS Sustain. Chem. Eng.* **2015**, *3*, 2458.
27. Xu, H. J.; Chen, K. C.; Guo, X. X.; Fang, J. H.; Yin, J. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1150.
28. Hu, M.; Chen, M. S.; Li, G. L.; Pang, Y.; Wang, D. L.; Wu, J. L.; Qiu, F.; Zhu, X. Y.; Sun, J. *Biomacromolecules* **2012**, *13*, 3552.
29. Hoang, T.; Lee, H.; Park, H.; Cho, J.; Kim, Y.; Kim, I. J. *Polym. Sci., Part A: Polym. Chem.* **2015**, 532557.
30. Unal, S.; Lin, Q.; Mourey, T. H.; Long, T. E. *Macromolecules* **2005**, *38*, 3246.
31. Song, L.; Tu, C. L.; Shi, Y. F.; Qiu, F.; He, L.; Jiang, Y.; Zhu, Q.; Zhu, B. S.; Yan, D. Y.; Zhu, X. Y. *Macromol. Rapid Commun.* **2010**, *31*, 443.
32. Zhu, X. Y.; Zhou, Y. F.; Yan, D. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1277.