

## SYNTHESIS AND CHARACTERIZATION OF HYPERBRANCHED POLYURETHANE-BENZYL TETRAZOLE\*

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**Abstract** A series of hyperbranched polyurethane-benzyltetrazoles (H-PBTZs) with different linkage structures were synthesized *via* the polycondensation of hexamethylenediisocyanate as an  $A_2$  type monomer with (4-(1H-tetrazol-5-yl)benzyl)-diethanolamine (TBDEA) as a  $BB'_2$  type monomer in the absence of catalyst at different temperatures. The FTIR, and  $^{13}C$  and  $^1H$ -NMR spectroscopy were used to characterize the molecular structures of TBDEA and H-PBTZs as well as the counterpart linear polyurethane-benzyltetrazole (L-PBTZ). The molecular composition was determined by the reaction selectivity that the isocyanate group reacted with the hydroxyl group in diethanolamine segment or the active hydrogen atom on tetrazole ring. Raising reaction temperature was propitious to the reaction of isocyanate group with the active hydrogen atom on tetrazole ring. The degrees of branching (DB) for H-PBTZs obtained from the  $^1H$ -NMR spectra increased with raising reaction temperature. The wider molecular weight distribution of 1.7–2.9 for H-PBTZs was obtained *via* GPC analysis. TGA results showed that H-PBTZs had high thermal stability compared with L-PBTZ.

**Keywords:** Synthesis; Hyperbranched polyurethane-benzyltetrazole; Degree of branching; Characterization.

### INTRODUCTION

The hyperbranched polymers with unique tridimensional topological structures have been successfully synthesized in past decades. The conventional approach, that is, polycondensation of  $AB_n$  ( $n \geq 2$ ) type monomers where A and B can react with each other but not with themselves, was extensively applied for preparing different hyperbranched polymers. However, the limitation coming from the monomers which are hardly obtained commercially, and thus have to be synthesized, restricts the developments. In contrast, the  $A_2$  type and  $B_3$  type monomers are easy to be gained and available commercially. Therefore, the “ $A_2 + B_3$ ” type synthesis route is one of the most important approaches to prepare hyperbranched polymers<sup>[1]</sup>. Katimoto and co-workers successfully achieved the hyperbranched aromatic polyamide through the polycondensation of diamide ( $A_2$ ) with trimesic acid ( $B_3$ ) in the presence of pyridine and triphenyl phosphite<sup>[2]</sup>. The major disadvantage of “ $A_2 + B_3$ ” approach is the gelation, which takes place before the completion of polymerization, resulting in the limitation of the method used on large scale. In order to avoid the gelation, stopping the reaction immediately before gelation, polymerization in a dilute solution<sup>[3–5]</sup> and slow addition of monomers<sup>[6, 7]</sup> are adopted. However, such steps directly result in low percent conversion and productivity<sup>[8]</sup>. Yan and coworkers presented a novel approach for synthesizing hyperbranched polymers from  $A_2$  and  $BB'_2$  type monomers based on the different reactivity of B and B' groups, where one B group and two B' groups can react with A group, respectively, in different reaction rates<sup>[9–12]</sup>.

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The tetrazoles without any substituent at the nitrogen atoms show, as a kind of acid<sup>[13]</sup>, significant applications in organic chemistry and coordination chemistry as well as their derivatives<sup>[14, 15]</sup>. A large quantity of research on small molecules and linear polymers containing tetrazole ring has been carried out in past years<sup>[15–17]</sup>. But little was investigated about hyperbranched polytetrazoles not only on the chemical synthesis but also the properties and applications.

In this work, (4-(1H-tetrazol-5-yl) benzyl)-diethanolamine (TBDEA) was synthesized as a BB'<sub>2</sub> type monomer *via* “click chemistry” reaction of nitrile group with sodium azide<sup>[18–22]</sup>. The reactivity of hydroxyl and tetrazole group in TBDEA with isocyanate can be adjusted *via* reaction temperature and catalyst. Hence, the linear/hyperbranched polyurethane-benzyltetrazoles (L-PBTZ/H-PBTZs) were obtained *via* TBDEA reacting with hexamethylenediisocyanate (HDI). The molecular structures were characterized by the FTIR, and <sup>13</sup>C and <sup>1</sup>H-NMR spectroscopy in detail.

## EXPERIMENTAL

### Materials

Diethanolamine (DEA), 4-(chloromethyl)benzonitrile (CBN), benzonitrile (BN), butane-1,4-diol and hexamethylenediisocyanate (HDI) were supplied by Shanghai First Reagent Co., China and used after distillation. Sodium azide (NaN<sub>3</sub>) was supplied by Aldrich and used as received. Zinc chloride (ZnCl<sub>2</sub>), sodium bicarbonate (NaHCO<sub>3</sub>), dibutyltin dilaurate (DBTDL) and all solvents were also purchased from Shanghai First Reagent Co., China. The solvents were dried before use. All chemicals were provided as analytical purity.

### Measurements

The <sup>1</sup>H and <sup>13</sup>C-NMR spectra were conducted on a Bruker 300 MHz NMR spectrometer with CDCl<sub>3</sub> and deuterated water as solvents. The FTIR spectra were recorded with a Nicolet MAGNA-IR 750 spectrometer. The KBr pressed disc method was used to prepare the samples. The element analysis was carried out using an Elementar Vario EL III instrument (950°C in a burning tube, 500°C in a reducing tube). The molecular weight and its distribution were determined with a Waters gel permeation chromatography (GPC) system using a refractive index detector with DMF as an eluent and polystyrene as a standard. The TGA was carried out by using a Shimadzu TG-50 instrument with a heating rate of 10 K min<sup>-1</sup> under nitrogen from room temperature to 700°C.

### Synthesis

#### *N*-4-cyanobenzyl-diethanolamine (CBDM)

DEA (0.1 mol, 10.5 g), CBN (0.11 mol, 16.6 g) and NaHCO<sub>3</sub> (0.11 mol, 9.24 g) were added into ethanol (60 mL) and stirred for 48 h at 80°C under refluxing. The generated salt and residual CBN were removed by filtration. After evaporating ethanol and drying in a vacuum oven, *N*-4-cyanobenzyl-diethanolamine (CBDM) as a white wax was obtained (20.8 g, 93.4%).

#### (4-(1H-tetrazol-5-yl) benzyl)-diethanolamine (TBDEA)

CBDM (0.05 mol, 11.1 g), ZnCl<sub>2</sub> (0.06 mol, 8.12 g) and NaN<sub>3</sub> (0.06 mol, 3.90 g) were added into 100 mL of water, and reacted for 24 h at 100°C under refluxing. Then, the mixture was cooled to room temperature and the pH value was adjusted to 1 by dropping concentrated hydrochloric acid. After the removal of water by distillation the residual solid was dissolved in DMF. The insoluble salt was removed by filtration. The DMF solution was poured into 200 mL of CH<sub>2</sub>Cl<sub>2</sub>, obtaining a white precipitate, which was washed with CH<sub>2</sub>Cl<sub>2</sub> three times. Finally, CH<sub>2</sub>Cl<sub>2</sub> was removed by filtering and drying in a vacuum oven at 40°C for 48 h, obtaining (4-(1H-tetrazol-5-yl) benzyl)-diethanolamine (TBDEA) as a white solid (10.28 g, 78.2%).

#### Linear polyurethane-benzyltetrazole (L-PBTZ)

TBDEA (0.381 g, 14.5 mmol) and DBTDL (0.1 mL) as a catalyst were dissolved in 5 mL of dry DMF. The dissolution of HDI (0.242 g, 14.5 mmol) in DMF (5 mL) was added dropwise into the TBDEA solution, and reacted under nitrogen atmosphere at 30°C until the peak at 2260 cm<sup>-1</sup> for NCO group vibration in the FTIR

spectrum disappeared. Subsequently, the solution was poured into water (50 mL) and precipitated for 12 h. By centrifugation, the linear polyurethane-benzyltetrazole (L-PBTZ) was obtained after drying in a vacuum oven at 60°C for 24 h.

#### *Hyperbranched polyurethane-benzyltetrazoles (H-PBTZs)*

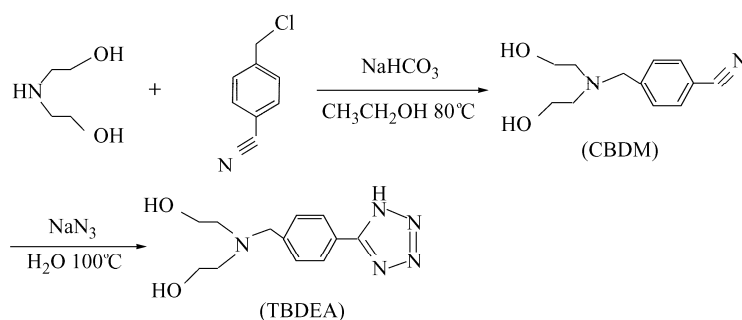
TBDEA (0.381 g, 14.5 mmol) was dissolved in 5 mL of dry DMF. The dissolution of HDI (0.242 g, 14.5 mmol) in DMF (5 mL) was added dropwise into the TBDEA solution, and reacted under nitrogen atmosphere at a given temperature (such as 30°C, 60°C and 80°C) until the peak at 2260  $\text{cm}^{-1}$  for NCO group vibration in the FTIR spectrum disappeared. Subsequently, the solutions were poured into water (50 mL) and precipitated for 12 h. By centrifugation, the hyperbranched polyurethane-benzyltetrazoles, named H-PBTZ-1, H-PBTZ-2 and H-PBTZ-3, prepared at reaction temperatures of 30°C, 60°C and 80°C, respectively, were obtained after drying in a vacuum oven at 60°C for 24 h.

## RESULTS AND DISCUSSION

### *Spectroscopy Characterization*

#### *BB'<sub>2</sub> type monomer TBDEA*

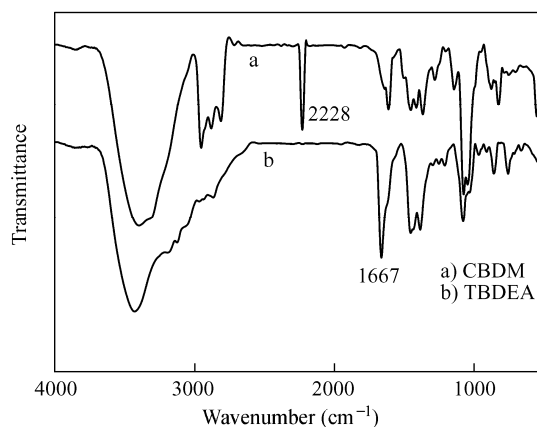
TBDEA was regarded as a BB'<sub>2</sub> type monomer with one active hydrogen atom on the tetrazole ring and two hydroxyl groups in the molecular structure. The synthesis route is shown in Scheme 1. The CBDM was first prepared by the nucleophilic substitution reaction of DEA with CBN. In the presence of Lewis acid or a protonic acid the 5-substituted tetrazoles are usually achieved from organic nitriles *via* cyclic reaction, which is a kind of a “click chemistry” reaction<sup>[18–21]</sup>. The cyclic reaction is carried out at high temperatures (above 100°C) with hydrazoic acid in polar solvents such as DMF, DMAC, DMSO or water. Due to the high toxic of hydrazoic acid, other Lewis acids such as ammonium salts, ammonium, trifluoroacetic acid have been explored. Zinc halides were recommended to be a kind of quite efficient acid. Moreover, zinc chloride and zinc bromide have been investigated extensively in DMF and water. In this study, zinc chloride was used as a Lewis acid for catalyzing the synthesis of substituted tetrazole, TBDEA, showing a high yield with the molar ratio of 1:1.2 for nitrile to  $\text{NaN}_3$  in water.



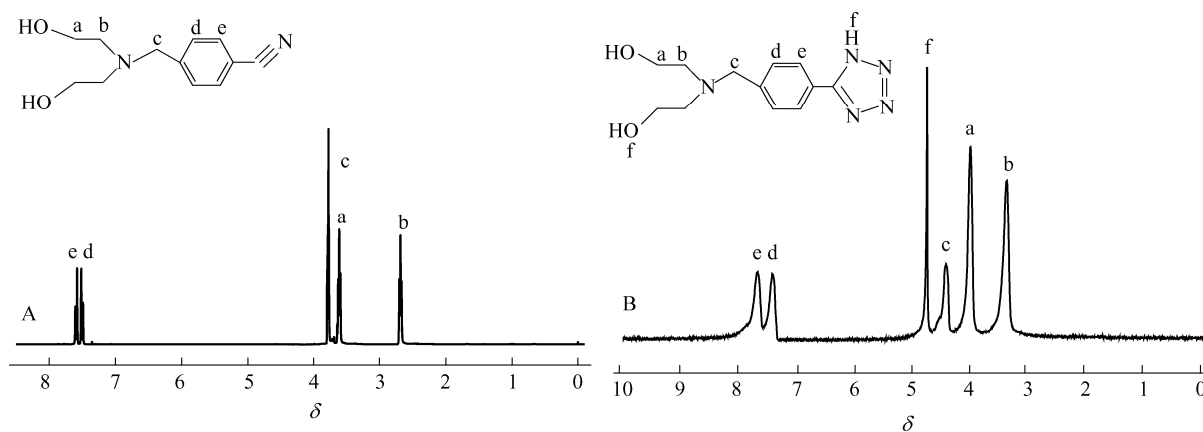
**Scheme 1** Synthesis route of TBDEA

The FTIR spectra of CBDM and TBDEA are shown in Fig. 1. It can be noted that the peak at 2228  $\text{cm}^{-1}$  in the FTIR spectrum of CBDM attributed to the nitrile group completely disappeared in the FTIR spectrum of TBDEA. Moreover, the strong peak at 1667  $\text{cm}^{-1}$  attributed to the N–H flexural vibration of tetrazole ring can be observed from the FTIR spectrum of TBDEA<sup>[16, 17]</sup>.

Figure 2 shows the <sup>1</sup>H-NMR analysis results of CBDM and TBDEA. After the nucleophilic substitution reaction the peaks around  $\delta = 7.51$  attributed to the protons of phenyl group and the peak at  $\delta = 3.78$  attributed to the proton of methylene in benzyl group can be obviously found in the CBDM spectrum (Fig. 2A). However, the peak position in the TBDEA spectrum, as shown in Fig. 2(B), was changed to low chemical shift, and the peak splitting is hardly observed, indicating that the hydrogen bond between hydroxyl group and tetrazole was formed so strongly that the molecular movement was restricted.

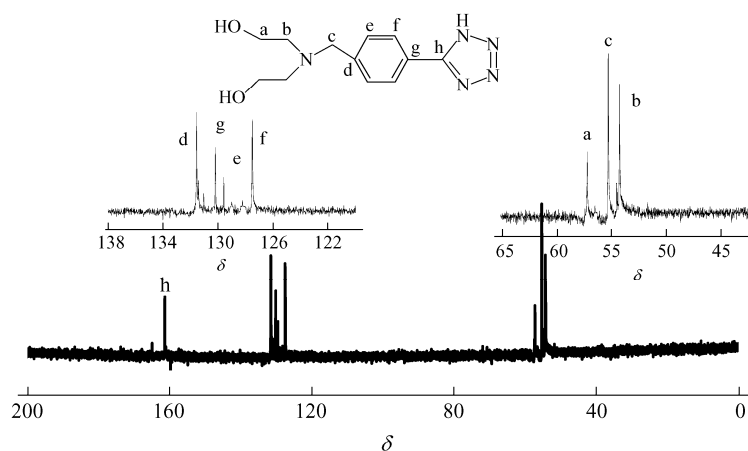


**Fig. 1** FTIR spectra of CBDM (a) and TBDEA (b)



**Fig. 2**  $^1\text{H-NMR}$  spectra of CBDM (A) in  $\text{CDCl}_3$  and TBDEA (B) in deuterated water

In order to confirm the structure of TBDEA further, the  $^{13}\text{C-NMR}$  analysis was carried out, as shown in Fig. 3. The peak observed at  $\delta = 162$  is attributed to the carbon atom in tetrazole group<sup>[11]</sup>, proving that the tetrazole structure has been formed. Other peaks are attributed to the corresponding carbon atoms, as described with the signal assignments in Fig. 3.



**Fig. 3**  $^{13}\text{C-NMR}$  spectrum of TBDEA in deuterated water

Furthermore, the element analysis of TBDEA was investigated to affirm its purity. The calculated result is in accordance with molecular formula  $C_{12}H_{17}N_5O_2$  as follows: C, 54.74; H, 6.51; N, 26.60. And the found result is C, 54.79; H, 6.59; N, 26.49. The element result indicates the higher purity of TBDMA.

#### Linear polyurethane-benzyltetrazole (L-PBTZ)

In consideration of the hydrogen bond density and the similar reactivity of the two end-isocyanate groups (the reactivity ratio is 1:0.5), HDI was selected as a kind of  $A_2$  type monomer to react with TBDEA. Moreover, the reaction temperature directly affects the reactivity of isocyanate with the active hydrogen of tetrazole ring or hydroxyl group of TBDEA. Therefore, it is feasible to control the structure of final product *via* setting the reaction condition.

For the study purpose, the molar ratio of HDI to TBDEA was fixed as 1:1. The  $A_2$  monomer, HDI and  $BB'_2$  monomer, TBDEA react with each other, resulting in two kinds of linkages, amide and imide. For increasing the difference in reactivity of the tetrazole ring and the hydroxyl group with isocyanate, the reaction temperature and catalyst were adjusted.

The FTIR spectra are shown in Fig. 4 for monitoring the polymerization course. The peak at  $1704\text{ cm}^{-1}$  for  $C=O$  in amide<sup>[22]</sup> appears immediately at the early beginning of polymerization, but the peak at  $1620\text{ cm}^{-1}$  for  $C=O$  in imide is absent, indicating that the reactivity of isocyanate with hydroxyl group was improved by the addition of DBTDL, forming the amide structure in priority. However, the reaction of isocyanate with active hydrogen atom in tetrazole ring was restricted, showing no imide structure forming. As a result, a linear polyurethane-benzyltetrazole (L-PBTZ) was prepared at  $30^\circ\text{C}$  in the presence of DBTDL, and the route is shown in Scheme 2.

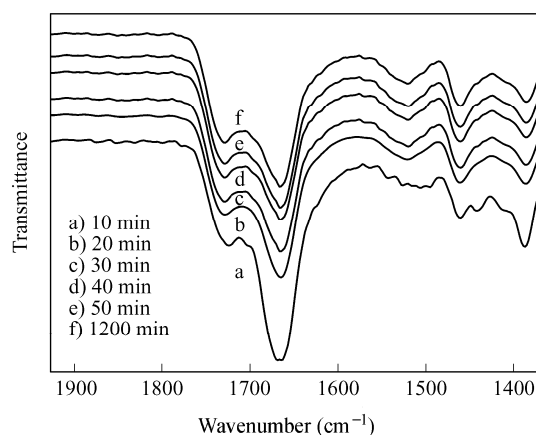
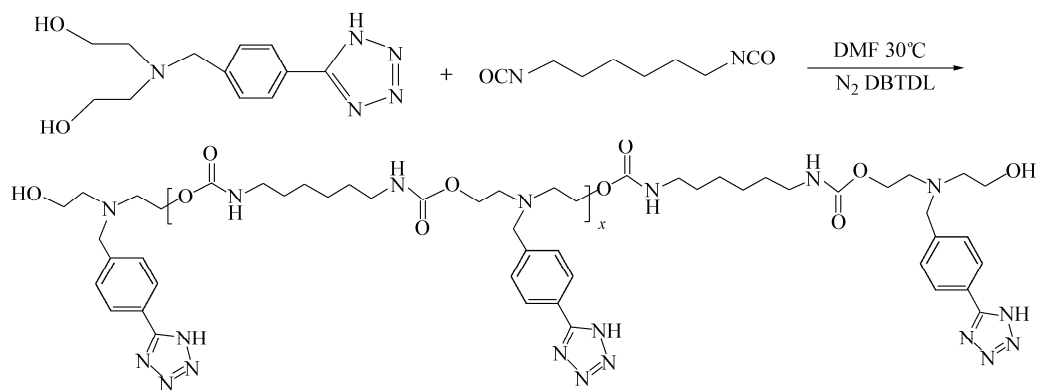


Fig. 4 FTIR spectra of L-PBTZ synthesized at  $30^\circ\text{C}$  with DBTDL



Scheme 2 Synthesis route of L-PBTZ at  $30^\circ\text{C}$  with DBTDL

The  $^1\text{H-NMR}$  spectrum of L-PBTZ obtained at  $30^\circ\text{C}$  with DBTDL addition after reacted for 24 h is shown in Fig. 5 with the signal assignment. The peak at  $\delta = 5.70$  is attributed to the hydrogen in amide structure. The peaks at  $\delta = 4.10$  and  $\delta = 3.75$  are attributed to the hydrogens adjacent to urethane linkage ( $\text{CH}_2\text{-COONH-}$ ) and hydroxyl group ( $\text{-CH}_2\text{-OH}$ ), respectively. Meanwhile, the peaks around  $\delta = 7.50$  and  $\delta = 8.00$  are attributed to the hydrogens in the benzoyl group and the peak at  $\delta = 8.21$  is assigned to the active hydrogen in L-PBTZ.

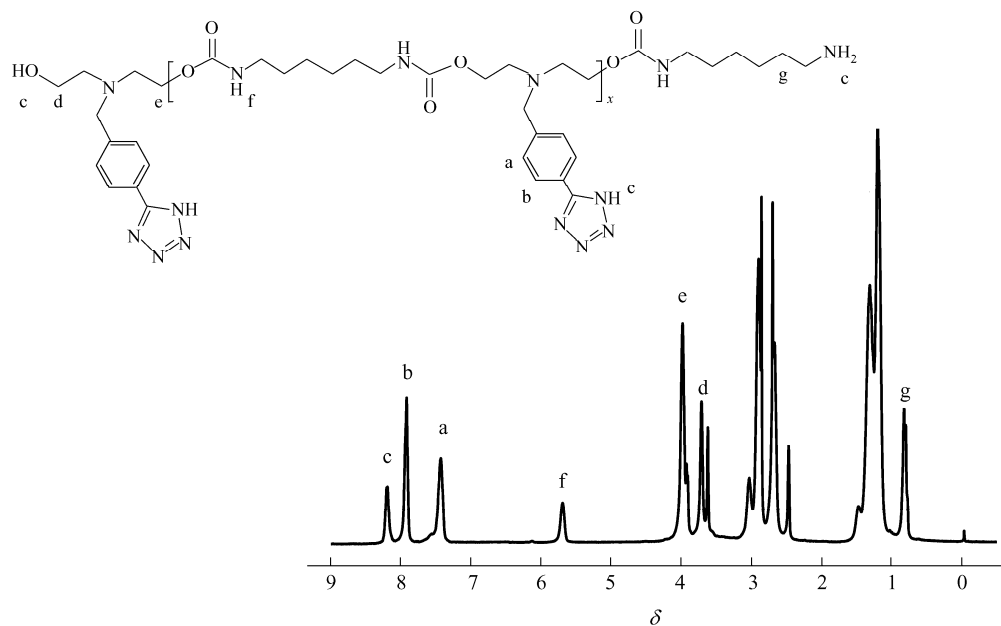


Fig. 5  $^1\text{H-NMR}$  spectrum of L-PBTZ in  $\text{DMSO-d}_6$  synthesized at  $30^\circ\text{C}$  with DBTDL for 24 h

#### Hyperbranched polyurethane-benzyltetrazole (H-PBTZ)

The polymerization was carried out at  $30^\circ\text{C}$  without DBTDL addition. The FTIR spectra measured at different reaction time are shown in Fig. 6. It can be seen that the peak intensity at  $1704\text{ cm}^{-1}$  for  $\text{C=O}$  of amide increases greatly with increasing reaction time. On the other hand, as reacted for 6 h, the peak at  $1620\text{ cm}^{-1}$  for  $\text{C=O}$  of imide can be obviously observed, but increases in a small extent after reacted for 12 h. This indicates that the reactivity of isocyanate with hydroxyl group is much higher than that with the active hydrogen atom on tetrazole ring. Therefore, the amide linkage was formed at the early beginning of reaction. Along with the hydroxyl group

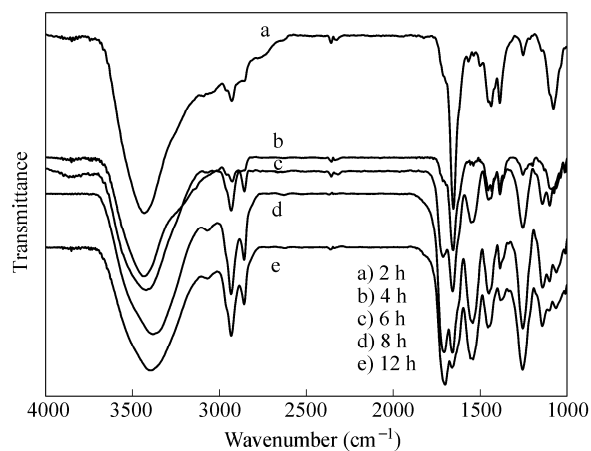
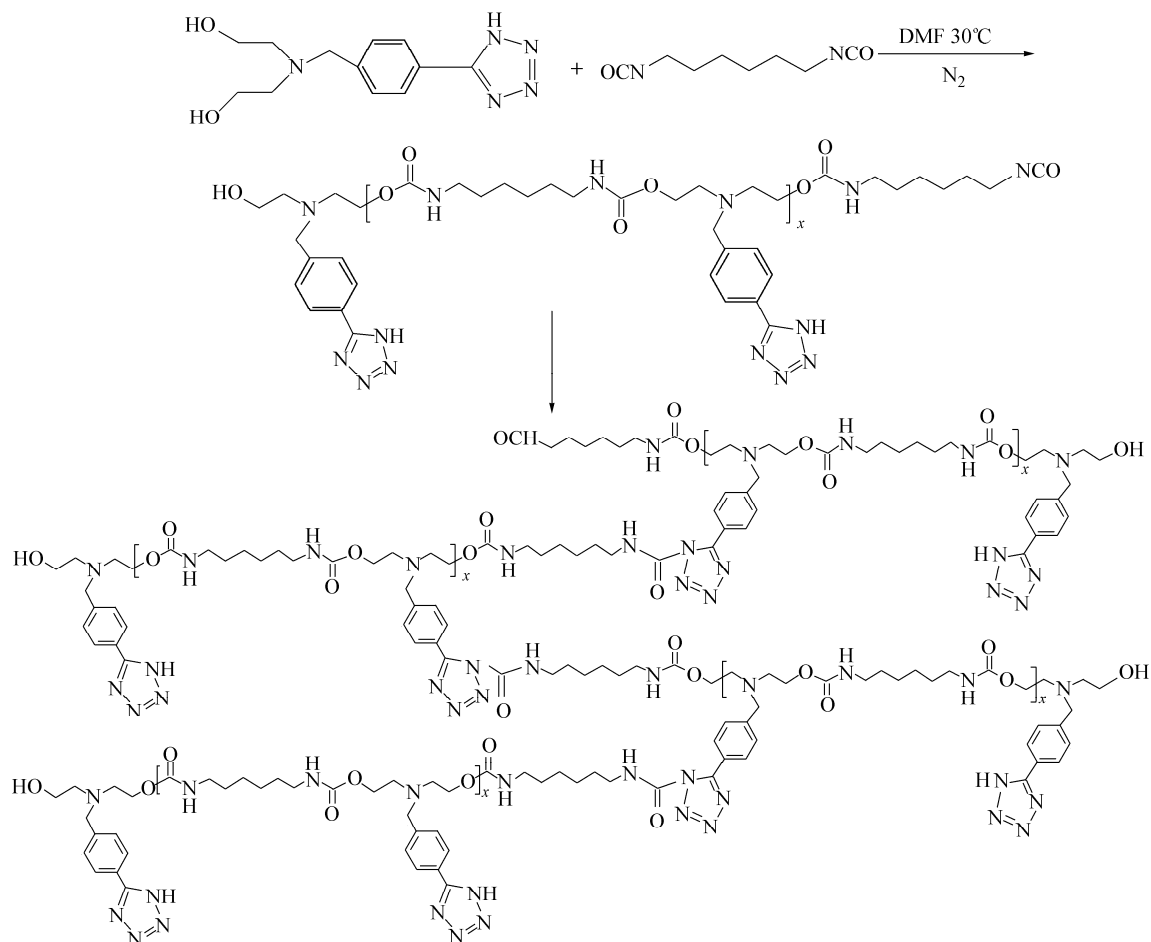


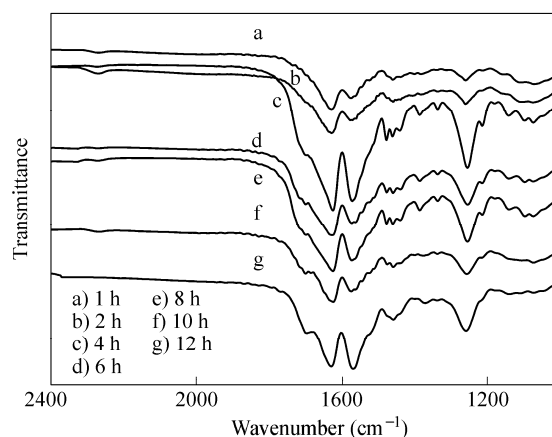
Fig. 6 FTIR spectra of H-PBTZ-1 synthesized at  $30^\circ\text{C}$  without DBTDL

concentration decreasing, the isocyanate group started to react with the active hydrogen atom on tetrazole ring, resulting in the formation of imide linkage. The formed imide groups served as the branched points to generate the hyperbranched structure. The assumable molecular formula of obtained hyperbranched polyurethane-benzyltetrazole, named H-PBTZ-1, at 30°C without DBTDL addition, is shown in Scheme 3.

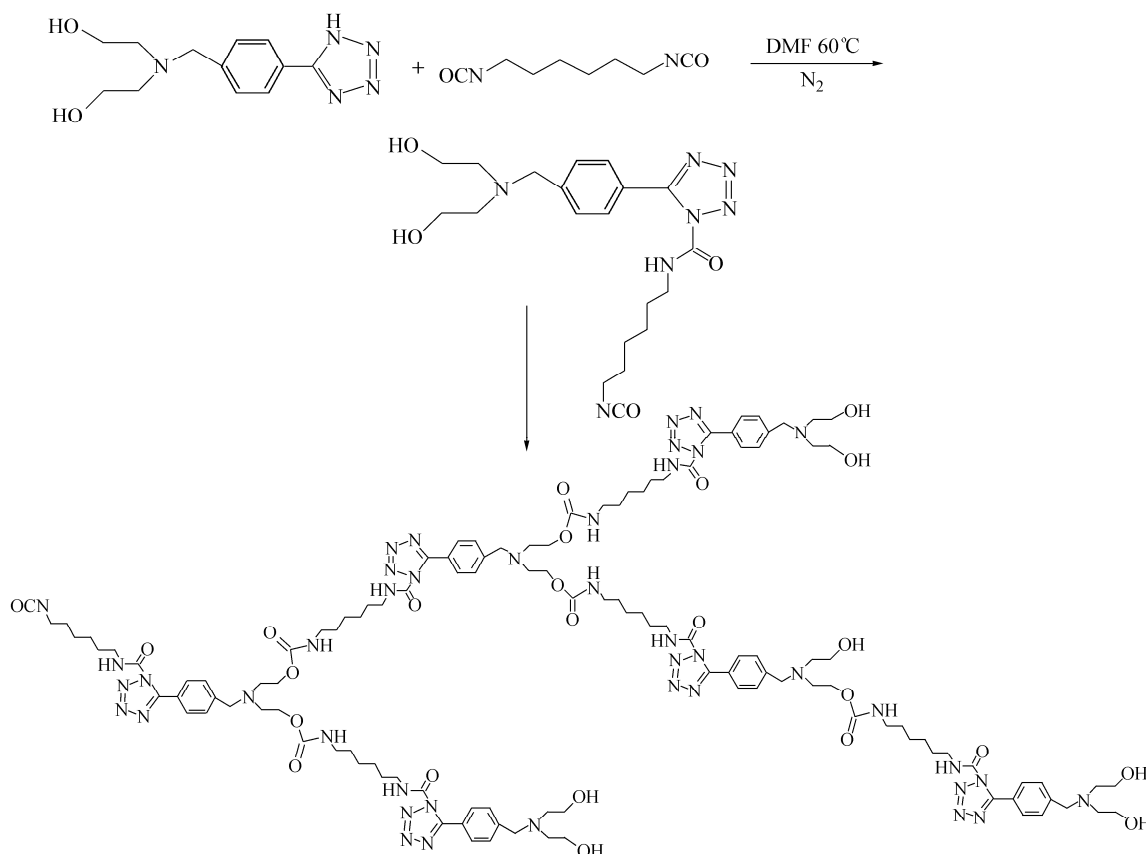


**Scheme 3** Synthesis route of H-PBTZ-1 at 30°C without DBTDL

As the reaction temperature was raised up to 60°C at the absence of DBTDL, the system presented other reaction selectivity. From Fig. 7, it can be seen that the peak at 1664 cm<sup>-1</sup> attributed to the stretching vibration of N—H bond in tetrazole group disappeared, whereas the peak at 1620 cm<sup>-1</sup> attributed to the imide group appeared quickly as the reactant was stirred for 1 h. Moreover, the peak intensity at 1704 cm<sup>-1</sup> for C=O of amide increases gradually with increasing reaction time, indicating the formation of amide linkage during the polymerization. It might be concluded that the isocyanate group had priority to react with the active hydrogen atom on tetrazole ring, and then hydroxyl group at high temperature. Therefore, a kind of new intermediate as a kind of AA-BB'2 type monomer was formed with one isocyanate and two hydroxyl groups, as shown in Scheme 4. Subsequently, the hyperbranched polyurethane-benzyltetrazole with more imide linkage, named H-PBTZ-2, at 60°C without DBTDL addition, was obtained (Scheme 4).



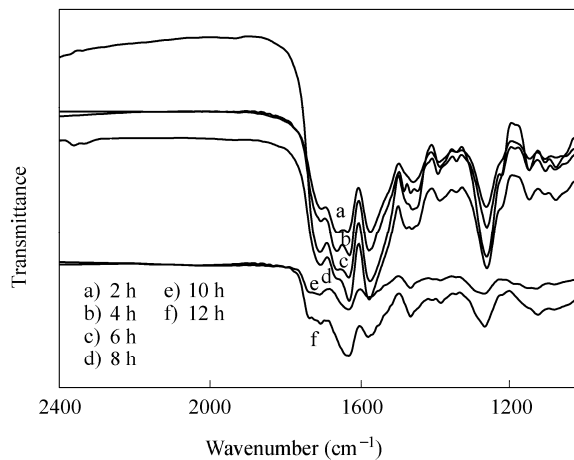
**Fig. 7** FTIR spectra of H-PBTZ-2 synthesized at 60°C without DBTDL



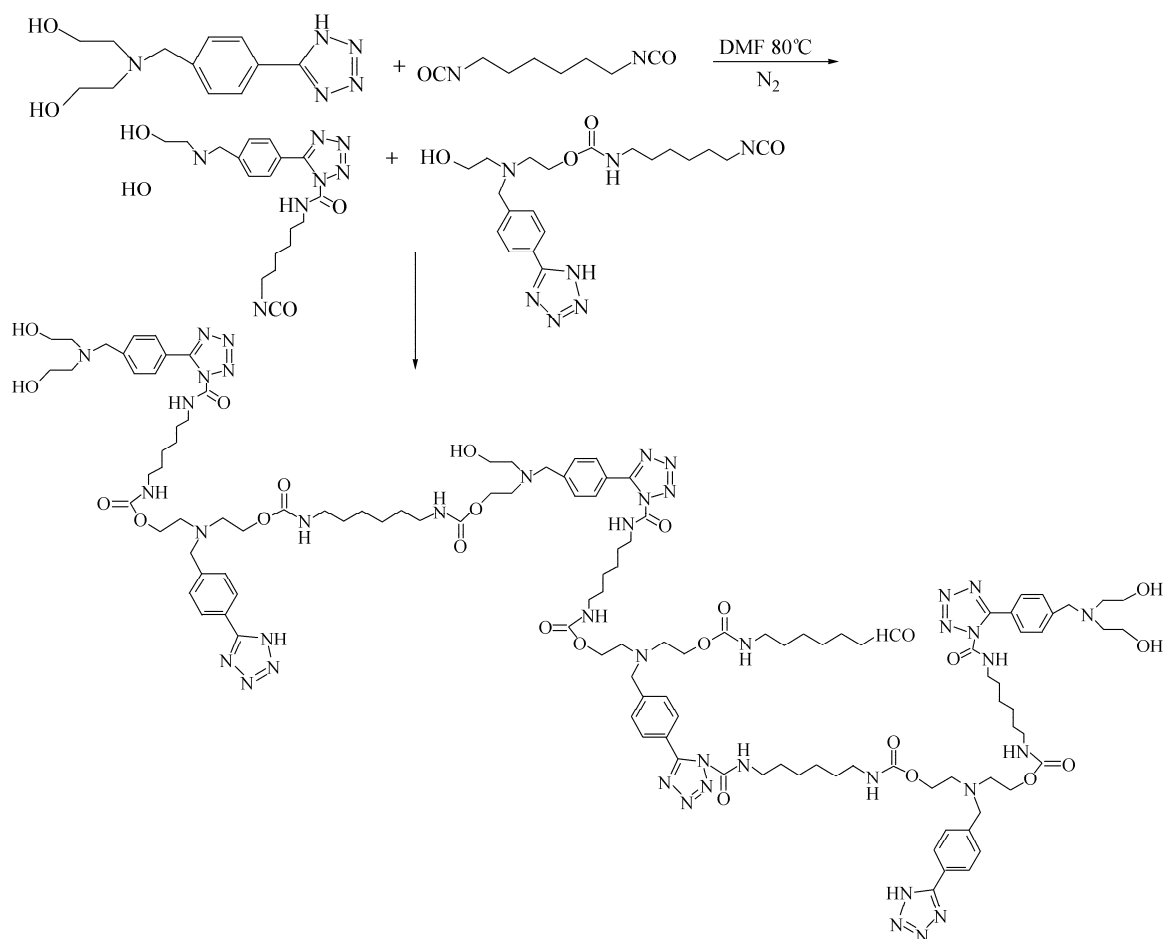
**Scheme 4** Synthesis route of H-PBTZ-2 at 60°C without DBTDL

As the reaction temperature was raised to 80°C, the FTIR spectra results are shown in Fig. 8. All the peaks at 1664, 1704 and 1620  $\text{cm}^{-1}$  can be observed obviously, indicating that three kinds of groups, amide, imide and tetrazole, mentioned above exist in the system. It indicates that the reaction selectivity of isocyanate with the hydroxyl group and the active hydrogen atom on tetrazole ring is not distinct at high temperatures. Hence, the random chain propagation resulted in the formation of a new hyperbranched polyurethane-benzyltetrazole with more complicated structure, named H-PBTZ-3, as shown in Scheme 5.





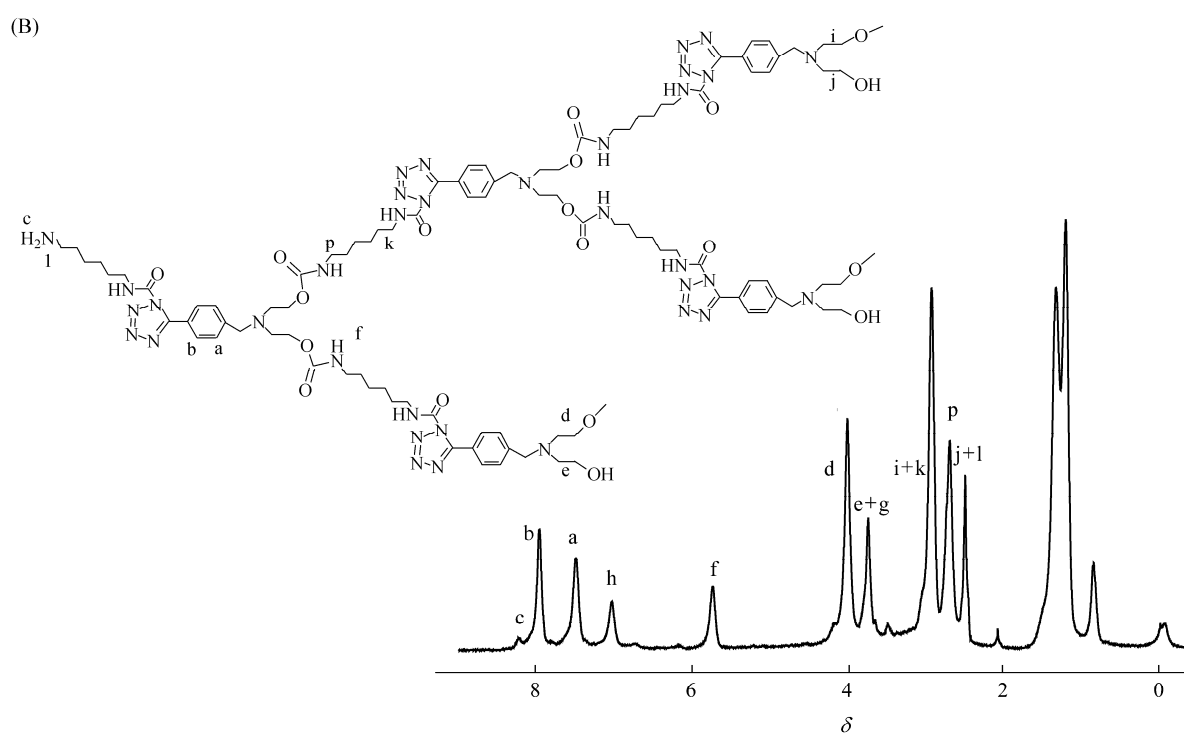
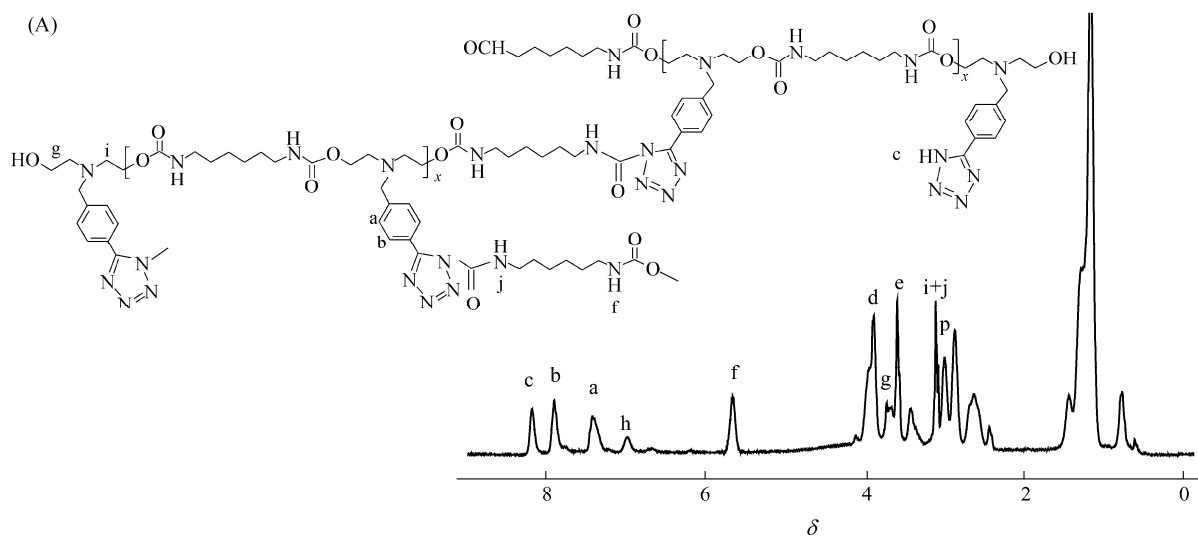
**Fig. 8** FTIR spectra of H-PBTZ-3 synthesized at 80°C without DBTDL



**Scheme 5** Synthesis route of H-PBTZ-3 at 80°C without DBTDL

The  $^1\text{H-NMR}$  analysis results of H-PBTZs with main peak marked after reacted for 24 h are shown in Fig. 9. It can be seen that the new peak at  $\delta = 7.02$  appears in all  $^1\text{H-NMR}$  spectra, which is attributed to the hydrogen in imide structure, indicating the existence of branched structure<sup>[23]</sup>. Meanwhile, the overlap peaks at

$\delta = 3.03$  are assigned to the signals of hydrogen atom near to the imide group ( $-\text{CH}_2-\text{NH}-\text{CO}-\text{N}-$ ) and nitrogen atom in tertiary amine ( $-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}-$ ). It was observed that the peak around  $\delta = 8.23$  with the assignment to hydrogen atom in tetrazole group almost disappeared completely in Fig. 9(B), which can be seen with a strong signal in Fig. 9(A) and 9(C). Hence, the  $^1\text{H-NMR}$  spectrum results are following the reaction course discussed above.



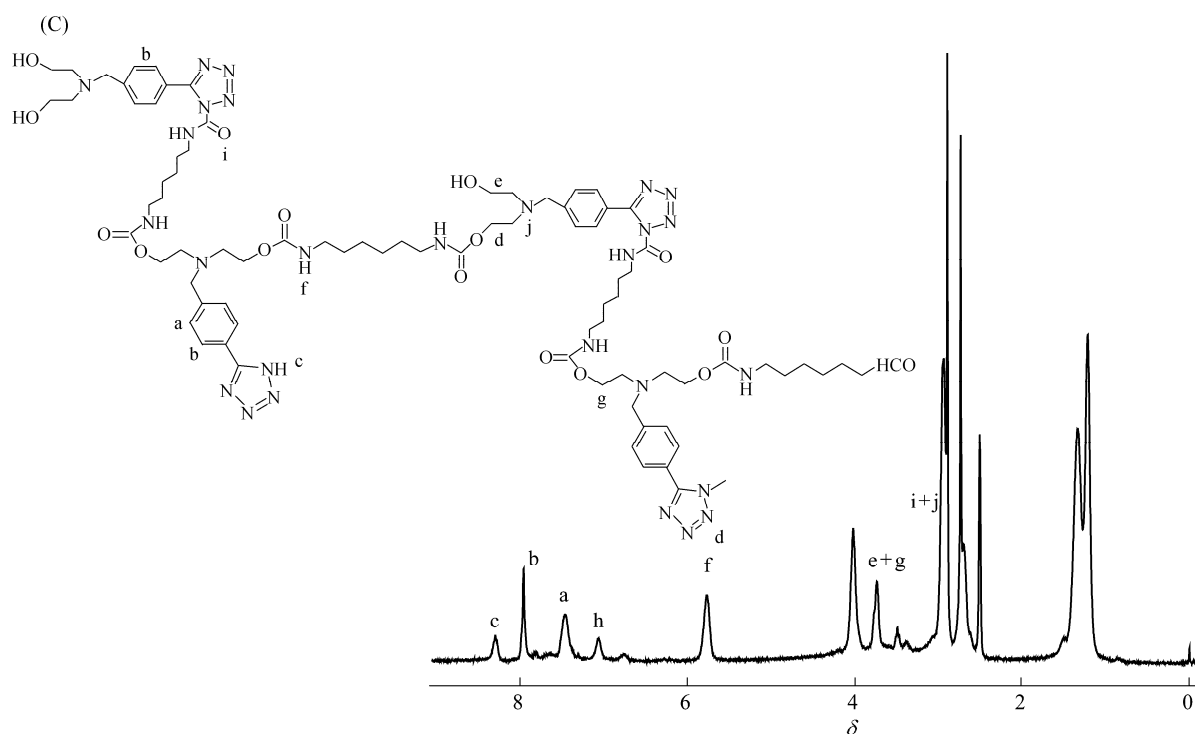


Fig. 9  $^1\text{H-NMR}$  spectra of H-PBTZ-1 (A), H-PBTZ-2 (B) and H-PBTZ-3 (C) in  $\text{DMSO-d}_6$  for 24 h

### Degree of Branching (DB)

According to the assignments of main peaks in the  $^1\text{H-NMR}$  spectra, the degree of branching (DB) was calculated, as listed in Table 2, using the following equation<sup>[24]</sup>:

$$\text{DB} = \frac{D+T}{D+L+T} \quad (1)$$

where  $D$ ,  $T$  and  $L$  are the fractions of dentritic, terminal and linear segments in the hyperbranched polymer, respectively. Table 1 gives the DB values of H-PBTZ-1 obtained at  $30^\circ\text{C}$  without DBTDL addition with different polymerization times. The linear polyurethane-benzyltetrazole with tetrazoles as side groups was first formed (Scheme 3). And then the active hydrogen atom of tetrazole group participated into the polymerization due to the hydroxyl group concentration decreased. The  $D$ ,  $T$  and  $L$  value can be calculated from the peak areas at  $\delta = 7.02$ ,  $3.68$  and  $5.67$  in the  $^1\text{H-NMR}$  spectrum. As a result, the DB values at different stages are rather low, and increase from 0.09 to 0.29 with increasing polymerization time. This can be interpreted by the lower reactivity of isocyanate with the active hydrogen atom on tetrazole ring at low temperature.

Table 1. DB values and GPC results of H-PBTZ-1 synthesized at  $30^\circ\text{C}$

Samples	Time (h)	$D$	$T$	$L$	DB	$M_n$	PDI
H-PBTZ-1a	4	0.11	0.59	7.24	0.09	2397	2.54
H-PBTZ-1b	8	0.25	0.74	7.24	0.12	3219	2.72
H-PBTZ-1c	12	0.40	0.94	7.24	0.19	4328	2.61
H-PBTZ-1d	16	0.64	1.52	7.24	0.23	6982	2.43
H-PBTZ-1e	24	1.19	1.77	7.24	0.29	7484	2.46

The data of  $L$  were set at constant; the data of  $D$  and  $T$  were normalized.

Table 2 lists the DB values of H-PBTZ-2 reacted from 4 h to 24 h at  $60^\circ\text{C}$  without DBTDL addition. The intermediate served as an  $\text{AB}_2$  type monomer was formed at the beginning of reaction due to the fact that the reactivity of isocyanate with the active hydrogen atom of tetrazole ring increased at high temperature. Then the

intermediate generated reacted with each other, resulting in the formation of prepolymers with low molecular weight but high DB value. Therefore, the relatively high DB values by calculating the  $D$ ,  $T$  and  $L$  values from the peak areas at  $\delta = 7.02$ , 5.73, 4.01 and 3.73 in the  $^1\text{H-NMR}$  spectrum were obtained without the obvious correlation with the polymerization time. However, because of the steric effect the obtained H-PBTZs have more defects, leading to the DB values floating.

**Table 2.** DB values and GPC results of H-PBTZ-2 synthesized at 60°C

Samples	Time (h)	$D$	$T$	$L$	DB	$M_n$	PDI
H-PBTZ-2a	4	0.32	0.21	1.25	0.30	2568	1.84
H-PBTZ-2b	8	0.61	0.46	1.25	0.46	4092	1.73
H-PBTZ-2c	12	0.53	0.34	1.25	0.41	6075	1.95
H-PBTZ-2d	16	0.28	0.51	1.25	0.39	8245	1.87
H-PBTZ-2e	24	0.18	0.42	1.25	0.43	10892	1.91

The data of  $L$  were set at constant; the data of  $D$  and  $T$  were normalized.

Likewise, Table 3 lists the DB values of H-PBTZ-3 obtained after reacted from 4 h to 24 h at 80°C. It was found that the reaction selectivity was interfered by raising temperature. The  $D$ ,  $T$  and  $L$  values were calculated from the peak areas at  $\delta = 8.29$ , 7.06, 5.75, 4.02 and 3.73 in the  $^1\text{H-NMR}$  spectrum. The highest DB value of 0.48 was obtained for the sample reacted for 24 h.

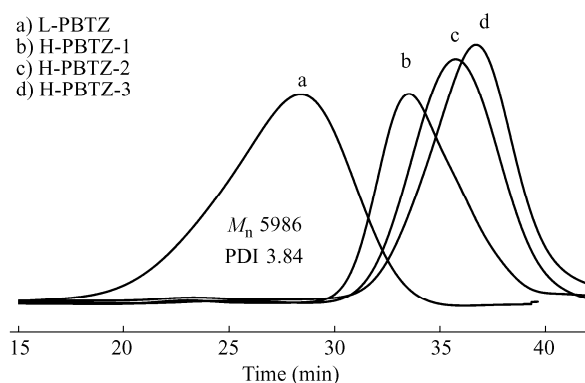
**Table 3.** DB values and GPC results of H-PBTZ-3 synthesized at 80°C

Samples	Time (h)	$D$	$T$	$L$	DB	$M_n$	PDI
H-PBTZ-3a	4	0.86	1.76	8.10	0.24	3158	2.36
H-PBTZ-3b	8	1.45	2.64	8.10	0.34	5987	2.57
H-PBTZ-3c	12	2.34	3.56	8.10	0.42	7432	2.89
H-PBTZ-3d	16	2.87	3.97	8.10	0.46	9709	2.68
H-PBTZ-3e	24	3.12	4.31	8.10	0.48	12820	2.74

The data of  $L$  were set at constant; the data of  $D$  and  $T$  were normalized.

### Number Average Molecular Weights and Their Distribution

In order to determine the number average molecular weights and their distribution (PDI), the H-PBTZs were terminated by acetic anhydride. Therefore, the terminal hydroxyl group was turned into acetic ether, and the tetrazole group was changed into 1,3,4-oxazole group<sup>[25]</sup>. Then the samples were determined by GPC, and the results are shown in Fig. 10. The detail data of  $M_n$  and PDI are listed in Table 1 to Table 3. Among the H-PBTZs, the H-PBTZ-3, which was obtained from the polymerization at 80°C, has the highest molecular weight. Whereas, the H-PBTZ-2 has the smallest PDI value due to the formation of intermediate serving as an AB<sub>2</sub> type monomer, at the beginning of reaction.



**Fig. 10** GPC results of L-PBTZ and H-PBTZs terminated by acetic anhydride

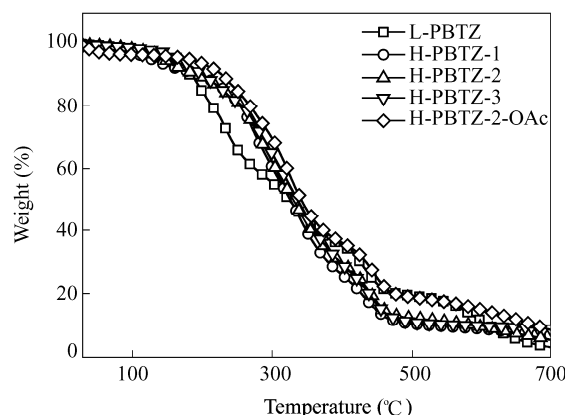


Fig. 11 TGA results of L-PBTZ, H-PBTZs and H-PBTZ-2 terminated by acetic anhydride

### Thermal Property

The thermal decomposition behavior of L-PBTZ and H-PBTZs was investigated using TG analysis, as shown in Fig. 11. It is obvious that H-PBTZs have higher thermal stability compared with L-PBTZ at low temperatures. Moreover, the L-PBTZ experienced three typical thermal degradation stages, as shown in Fig. 11. The degradation at 237°C is considered to be the tetrazole group pyrolysis<sup>[16]</sup> and that at 421°C is assigned to the urethane bond decomposition. The degradation above 550°C indicates that the residual polymers started to break down at high temperatures. Meanwhile, the degradation of H-PBTZs experiences the same trend in two stages due to their similar highly branched structures<sup>[13]</sup>. The H-PBTZ-2-OAc sample terminated by acetic anhydride shows a slow degradation course because of the terminal tetrazole becoming to oxazole group. The decomposition above 500°C may result from the oxazole structure.

### CONCLUSIONS

In this study, the monomer TBDEA possessing the active hydrogen on tetrazole ring and two hydroxyl groups was synthesized successfully *via* the cyclization reaction. The linear polymer L-PBTZ was obtained at 30°C in the presence of DBTDL as a catalyst, with the number average molecular weight of 5986 and wide PDI of 3.84. H-PBTZs were prepared at different temperatures (30°C, 60°C and 80°C) in the absence of DBTDL, and characterized by FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. The DB values were calculated from <sup>1</sup>H-NMR spectra and showed an increasing trends generally along with reaction time. The GPC results showed that the molecular weights increased along with polymerization temperature and time. The H-PBTZ obtained from the polymerization at 80°C has the highest molecular weight. Whereas, the H-PBTZ obtained from the polymerization at 60°C has the smallest PDI value due to the formation of intermediate, which served as an AB<sub>2</sub> type monomer, at the beginning of reaction. From the TGA analysis, H-PBTZs have higher thermal stability than L-PBTZ.

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