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# Synthesis by Different Methods and Characterization of Hyperbranched Polyurethane†

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Hyperbranched polyurethane (HBPU) samples are synthesized by two different methods from isophorone diisocyanate, 1,4-dihydroxybutane and diethanolamine generation by generation. And two series of samples are marked HBPU1s and HBPU2s. FTIR measurement is used to characterize the structure of the samples. DSC and TG measure the thermal properties of the samples. The results indicate that the hyperbranched structure of the polyurethane is consistent with theoretical design through controlling the feed ratio. The intensity of hydrogen-bonded interaction in HBPU1s is stronger than that in HBPU2s. Two series samples have same thermal stability.

**Key Words: Hyperbranched polyurethane, Generation by generation, Hydrogen-bonded interaction, Thermal stability.**

## INTRODUCTION

During the latest decades a new series of the materials-hyperbranched polymers have been created. Hyperbranched polymers are highly branched macromolecules with three-dimensional dentritic architecture. Due to their unique physical and chemical properties and potential applications in various fields such as coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology and supramolecular science, interest in hyperbranched polymers is growing rapidly[1-4]. Generally, the synthetic techniques used to prepare hyperbranched polymers can be divided into two major categories[5]. The one category is the single-monomer methodology, in which hyperbranched macromolecules are polymerized by an $AB_n$ or a latent $AB_n$ monomer. The other category includes methods of the double-monomer methodology, in which direct polymerization of two types of monomers generates hyperbranched polymers. Double-monomer methodology can be divided into two main subclasses based on the selected monomer pairs and different reaction pathways. The one, polymerization of $A_2$ and $B_3$ (or $B_n$, $n \geq 3$) monomers, can be called the '$A_2 + B_3$' methodology and was first adopted intentionally to prepare soluble hyperbranched polymers by Kakimoto and Frechet[6,7]. The other, combination of the basic single-monomer methodology synthetic principle and the multimonomer character of '$A_2 + B_3$' methodology, is called couple-monomer methodology based on *in situ* formation of $AB_n$ intermediates from specific monomer pairs due to the non-equal reactivity of different functional groups[8]. The preparation of hyperbranched polyurethane (HBPU) belongs to couple-monomer methodology.

Because of the high reactivity of isocyanato groups against the nucleophile, it is hard to obtain an $AB_2$ monomer with an isocyanato group. Therefore, hyperbranched polyurethanes cannot be directly synthesized from $AB_2$ monomers. Through the $A_2$+ $BB'_n$ approach, HBPU can be easily prepared by direct polymerization of commercially available diisocyanates and multi-hydroxyl amines[9].

Recently, HBPU has attracted much attention because of its special hyperbranched structure, its large amount of terminal groups and the properties of low viscosity, non-chain entanglement, good solubility *etc.*[10,11]. Hyperbranched polyurethane has good potential prospects in coatings, biological materials, polymer mixture, compound materials and many other fields.

Up to now, the HBPU is synthesized by one-pot method usually[8]. It is very difficult to apply the prepared hyperbranched polyurethanes owing to the complexity of the synthesis and the purification procedures. And the sample purity is too low to study its structure in depth. So in order to research its structure and properties further, it's important to synthesize HBPU with a new method which can obtain high purity samples.

In this work, according to couple-monomer methodology, HBPUs are synthesized from isophorone diisocyanate, 1,4-dihydroxybutane (BDO) and diethanolamine (DEOA) generation by generation. In each generation, the feed ratios are in accordance with the stoichiometric ratio strictly. The structures

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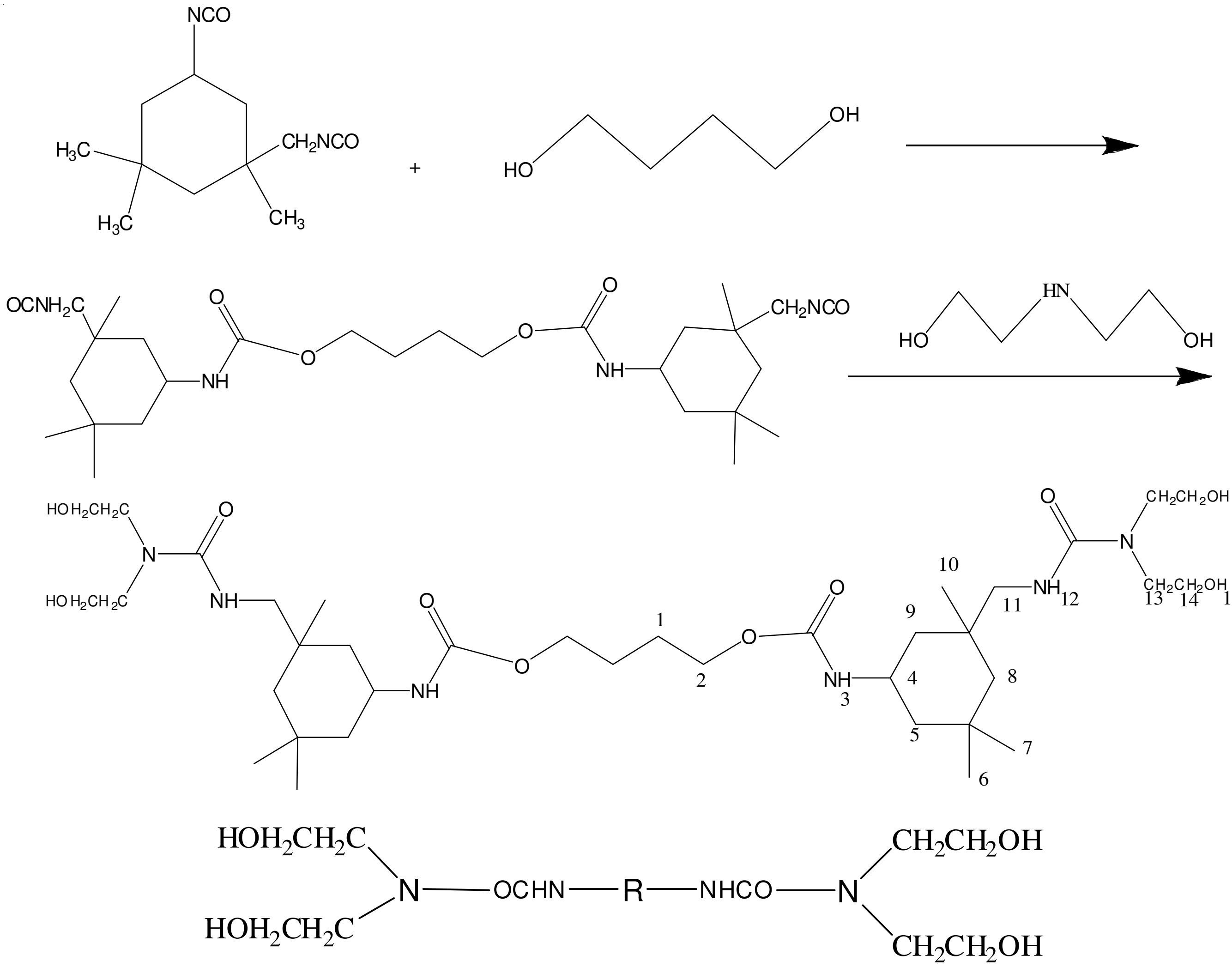


**Scheme-I:** Synthesis routes and structures of the first generation HBPU1-G1

of the HBPU samples are characterized by FTIR. The thermo properties of the HBPUs are analyzed by thermogravimetric analyzer (TG) and differential scanning calorimeter. The results show the hyperbranched structure of the polyurethane is consistent with theoretical design.

## EXPERIMENTAL

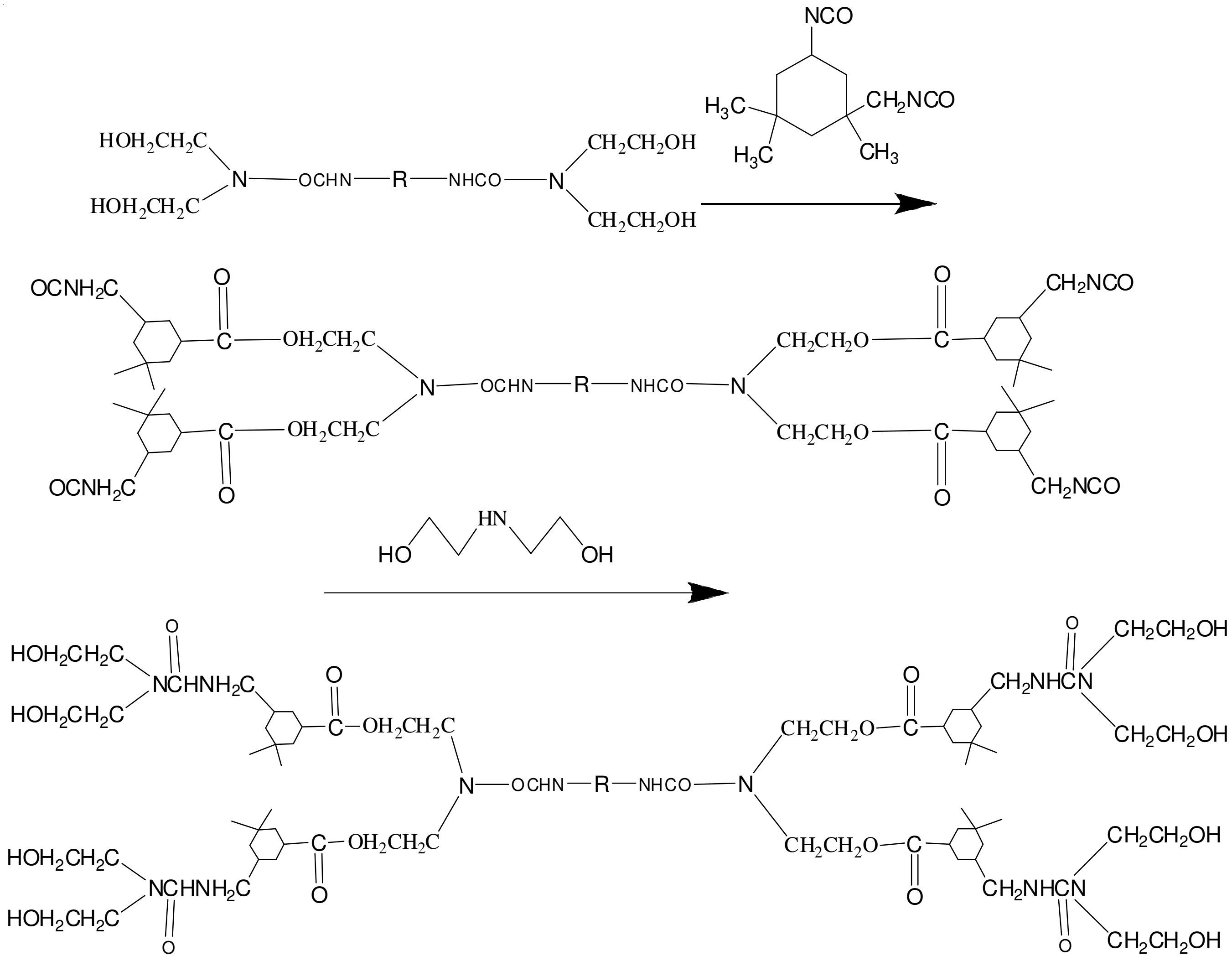
Isophorone diisocyanate was procured from Aldrich, 1,4-dihydroxybutane (BDO), dimethylformamide (DMF) and diethanolamine (DEOA) were obtained from Huipu Chemical Agents Co. Ltd. (Hangzhou China). All the solvents were used as received and freed from moisture by adding 4 Å molecular sieves before use.

Hyperbranched polyurethanes (HBPUs) were synthesized generation by generation. 5.55 g of isophorone diisocyanate was taken in a reaction vessel. 10 mL dimethylformamide contained 1.13 g of BDO were added to the vessel. The reaction time was 6h at 85 ºC. Then the temperature was reduced to 0 ºC. -NCO content was determined by dibutyl amine method which was found to be close to the expected theoretical value[12]. 2.63 g of diethanolamine dissolved in 10 mL dimethylformamide was added in the vessel. The reaction kept 3 h at 0 ºC and the solvent was distilled in vacuum. The first generation sample was obtained which marked HPU1-G1 (**Scheme-I**).

11.1 g of isophorone diisocyanate dissolved in 10 mL dimethyl formamide was taken in a reaction vessel. All of HBPU1-G1 dissolved in 15 mL dimethyl formamide was added in the vessel and kept the temperature at 85 ºC for 6 h. Then the temperature was reduced to 0 ºC. 5.26 g of diethanolamine in 20 mL dimethyl formamide was dropped to the vessel and kept the reaction for 4 h at 0 ºC. The solvent was distilled in vacuum. The second generation was obtained and marked HBPU1-G2 (**Scheme-II**). The rest generations can be done in the same manner.

Another preparation method of HBPU is based on HBPU1-G1. 11.1 g of isophorone diisocyanate dissolved in 10 mL DMF was taken in a reaction vessel. 2.25 g of BDO was added to the vessel and kept the temperature at 85 ºC for 6 h. 4.66 g of HBPU1-G1 dissolved in 15 mL dimethyl formamide was dropped in the vessel and kept the temperature at 85 ºC for 8 h. Then the temperature was reduced to 0 ºC. 2.63 g of diethanolamine in 10 mL dimethyl formamide was dropped to the vessel and kept the reaction for 4 h at 0 ºC. The solvent was distilled in vacuum. The another second generation was obtained and marked HBPU2-G2 (**Scheme-III**).

FTIR spectra (Nicolet Nexus 870, USA) of samples were obtained by the KBr pellet method. Each sample was scanned 32 times with a resolution setting of 2 $cm^{-1}$ and spectra were



**Scheme-II:** Synthesis routes and structure of the second generation HBPU1-G2

determined over the range of 4000-400 cm$^{-1}$. Perkin-Elmer Pyris-1 TGA was used to study the thermal decomposition profile of hyperbranched polyurethane samples at a constant rate of 10 ºC/min in inert nitrogen atmosphere from 20 ºC to 500 ºC. Differential scanning calorimeter was performed on a TA-50 instrument. The samples were heated from 20 ºC to 200 ºC, cooled rapidly to -20 ºC and reheated to 200 ºC under nitrogen atmosphere. The heating rate was 20 ºC /min.

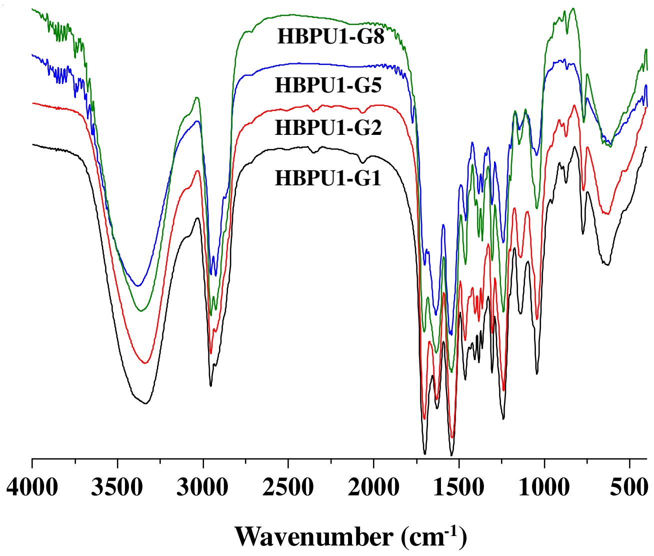
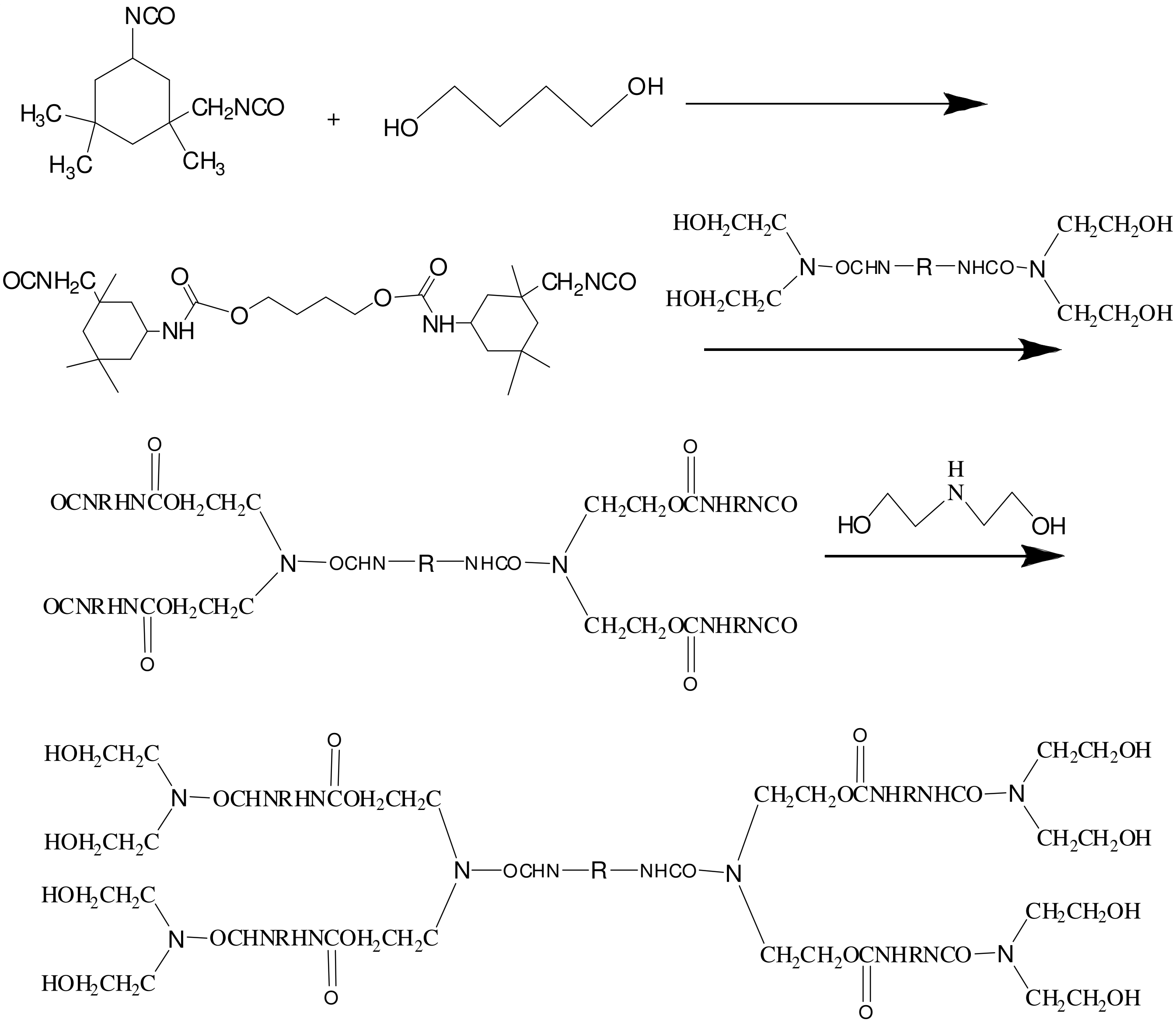


Fig. 1. FTIR spectra for HBPU1s samples

## RESULTS AND DISCUSSION

**FTIR analysis:** Fig. 1 shows the representative FTIR spectra of HBOU1 series in the range 4000-400 cm$^{-1}$. In the spectra, the characteristic absorption band of -NCO groups at 2270 cm$^{-1}$ was not displayed. The results show the all isocyanate groups reacted. From HBPU1-G1 to HBPU1-G8, a strong and broad absorption band exists in the range of 3100-3800 cm$^{-1}$, but the absorption peak shifts to higher wavenumber gradually, from 3336 cm$^{-1}$ to 3382 cm$^{-1}$. Comparing to the absorption band at 1700 cm$^{-1}$, the intensity of the peak at 1635 cm$^{-1}$ enhances gradually. According to the references[13], the peak values at 3600, 3520, 3350 and 3300 cm$^{-1}$ are assigned to free -OH, -NH, bonded -OH and bonded -NH, while the peaks at 1708, 1705, 1648 and 1635 cm$^{-1}$ are due to free urethane, urea, bonded urethane and bonded urea, respectively. Enhancement of the absorption peak at 1635 cm$^{-1}$ indicates the hydrogen bonded between urethane and urea increases. The C=O groups for the urethane and urea can form the hydrogen-bonded



**Scheme-III:** Synthesis routes and structure of the second generation HBPU2-G2

interaction with -NH and -OH. It is obvious that the enhancement of the hydrogen-bonded interaction for C=O groups can not be ascribed to the content -NH groups. The content ratio of -NH/--OH decreases generation by generation in HBPU1 series, as shown in **Scheme-I** and **II**. The content of -OH groups plays the impotant role on the hydrogen-bonded interaction in HBPU1s. Shift to higher wavenumber of the peak in the range 3800-3100 cm$^{-1}$ approves the result.

Interesting result appears in FTIR spectra of HBPU2 series, as shown in Fig. 2. The strong and broad absorption band displays in the range from 3800-3100 cm$^{-1}$. But the peak values hold at 3335 cm$^{-1}$. Meanwhile, compare to the absorption band at 1700 cm$^{-1}$, the intensity of the peak at 1635 cm$^{-1}$ decreased generation by generation in HBPU2 series. According to the synthesis routes as shown in **Scheme-III**, the content ratio of -NH/-OH in HBPU2s is higher than that in HBPU1s. And the arm of each generation in HBPU2s is longer. Free curl of the chain segment for HBPU2s is difficult. So intensity of the hydrogen-bonded interaction for HBPU2s reduces.

**Thermal property study:** Fig. 3 gives the differential scanning calorimeter curves for HBPU1-G5 and HBPU2-G5.

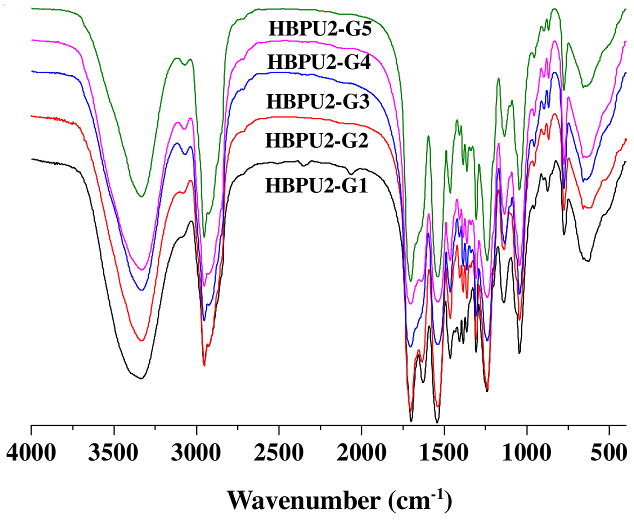


Fig. 2. FTIR spectra for HBPU2s samples

A broad dispersion endothermal peak displays in each curve. For two differential scanning calorimeter curves, endothermal range is from 20 to 120 ºC. The glass transition temperatures for two samples can not be observed distinctly. But it is obvious that the broad endothermal peaks are not attributed to crystalline melt. It can be deduced the broad endothermal peaks are relevant to the disassembly of the hydrogen-bonded interaction. On the other hand, it can be observed that the endothermal enthalpy of HBPU1-G5 is bigger than that of HBPU2-G5 from the curves. Intensity of the hydrogen-bonded interaction for HBPU1-G5 exceeds that for HBPU2-G5. The results are consistent with FTIR.

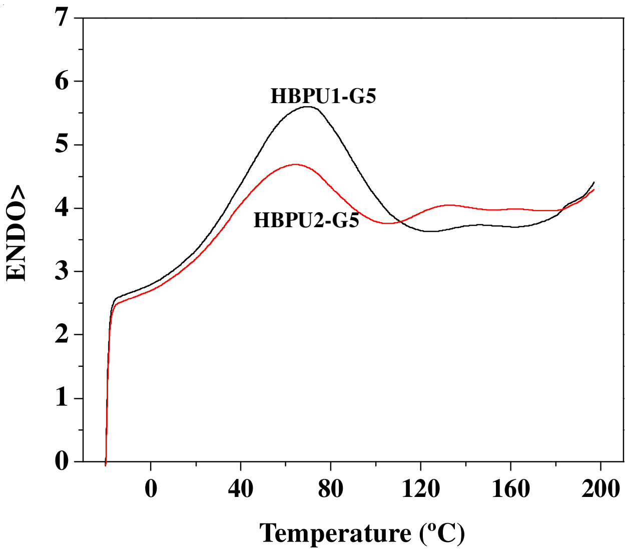


Fig. 3. DSC curves for HBPU1-G5 and HBPU2-G5

The relative thermal stability of HBPU1-G5 and HBPU2-G5 is evaluated from the thermal gravimetric ananlysis in $N_2$ environment (Fig. 4). The decomposition curves for two samples are identical. The characteristic thermal decomposition temperatures such as onset decomposition temperature, temperature corresponding to maximum rate of weight loss and endset decomposition temperature for different samples are equal. HBPU1-G5 and HBPU2-G5 have same thermal stability.

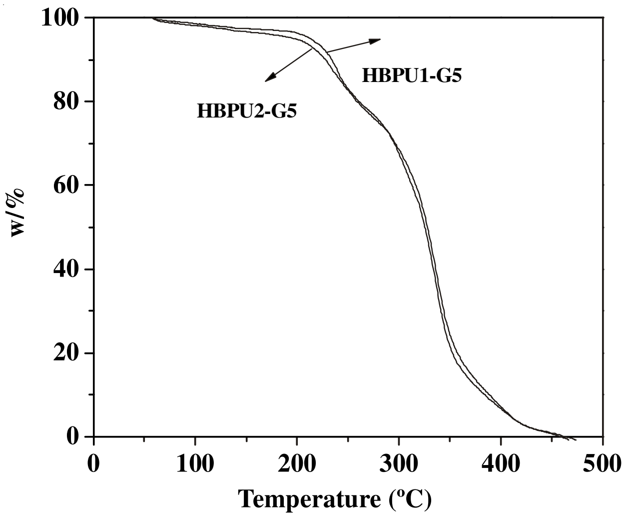


Fig. 4. TG curves for HBPU1-G5 and HBPU2-G5

## Conclusion

Hyperbranched polyurethane samples were synthesized by two different methods and marked HBPU1s and HBPU2s, respectively. FTIR measurement revealed that the hyperbranched structure of the polyurethane is consistent with theoretical design. Thermal properties studied by TG displayed HBPU1s and HBPU2s have same thermal stability. However, only FTIR measurement did not expatiate the structure of the hyperbranched samples well and truly. More characterization methods will be applied in our future work.

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