

Synthesis and Thermal Properties of Carboxyl-Terminated Hyperbranched Polyesters

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A carboxyl-terminated hyperbranched polyester (HBP-COOH) was prepared by hydroxyl-terminated hyperbranched polyester (HBP-OH) and succinic anhydride and the influences of the solvents, catalysts and reaction time on the product's structure and properties were investigated. Hydroxyl-terminated hyperbranched polyester and carboxyl-terminated hyperbranched polyester were characterized by the differential scanning calorimetry (DSC), gel permeation chromatography (GPC), Fourier transform infrared (FTIR), Nuclear magnetic resonance (^1H NMR) and thermogravimetric analysis (TGA). When the molar ratio of succinic anhydride and hydroxyl groups is 3:1 and THF and sodium acetate are used as the solvent and the catalyst respectively and the reaction time is 6 h at 65 °C, the modification degree of the hydroxyl groups is about 99 % and the product yield is about 95 %. The molecular weight of the hyperbranched polyester increases with increasing modification degree. Carboxyl-terminated hyperbranched polyester has much lower glass transition temperature than that of hydroxyl-terminated hyperbranched polyester due to its long and flexible end-groups. The modified hyperbranched polyester is easier to decompose with increasing amount of carboxyl end-groups.

Keywords: Hyperbranched polyester, Hydroxyl, Carboxyl, Succinic anhydride.

INTRODUCTION

As a perfect branched dendrimers, hyperbranched polymers (HBP) exhibit some similar features, such as compact and globular shape, high density of functional end-groups, low viscosity¹⁻³ and so on. By changing the composition and structure of hyperbranched polymers, *e.g.* changing the end-groups, materials with a variety of new special features will be obtained. In many fields, HBP has broad application prospects⁴⁻⁸, such as viscosity modifier, a pharmaceutical carrier, solvent-free coatings, adhesives, thermosetting resins. Carboxyl terminated-hyperbranched polyester (HBP-COOH) is one kind of reactive HBP that may link with other compounds by reactions between the end-groups. Wang *et al.* used the second-generation hydroxyl-terminated hyperbranched polyester (HBP-OH) to react with maleic anhydride and to modify the HBP⁹. Tang *et al.* added maleic anhydride directly to the HBP for modification and the yield of product is 71.3 % and the degree of modification is 88.9 %. The reaction process does not use any solvent so that the post-processing step is easier¹⁰. The glass transition temperature of the modified polymer is significantly reduced. Shi *et al.* modified the HBP-OH with the carboxyl-terminal and then mixed it with metal organic compound to generate a series of organic-inorganic hybrid materials. They used second generation HBP and succinic

anhydride as modified agent in 1,4-dioxane solvent with SnCl_2 as catalyst¹¹. Chen *et al.*¹² dissolved the HBP-OH with succinic anhydride in acetone to prepare HBP-COOH and obtained HBP-COOH with the product yield of 87 % and the caboxylation degree of moderate (60-80 %).

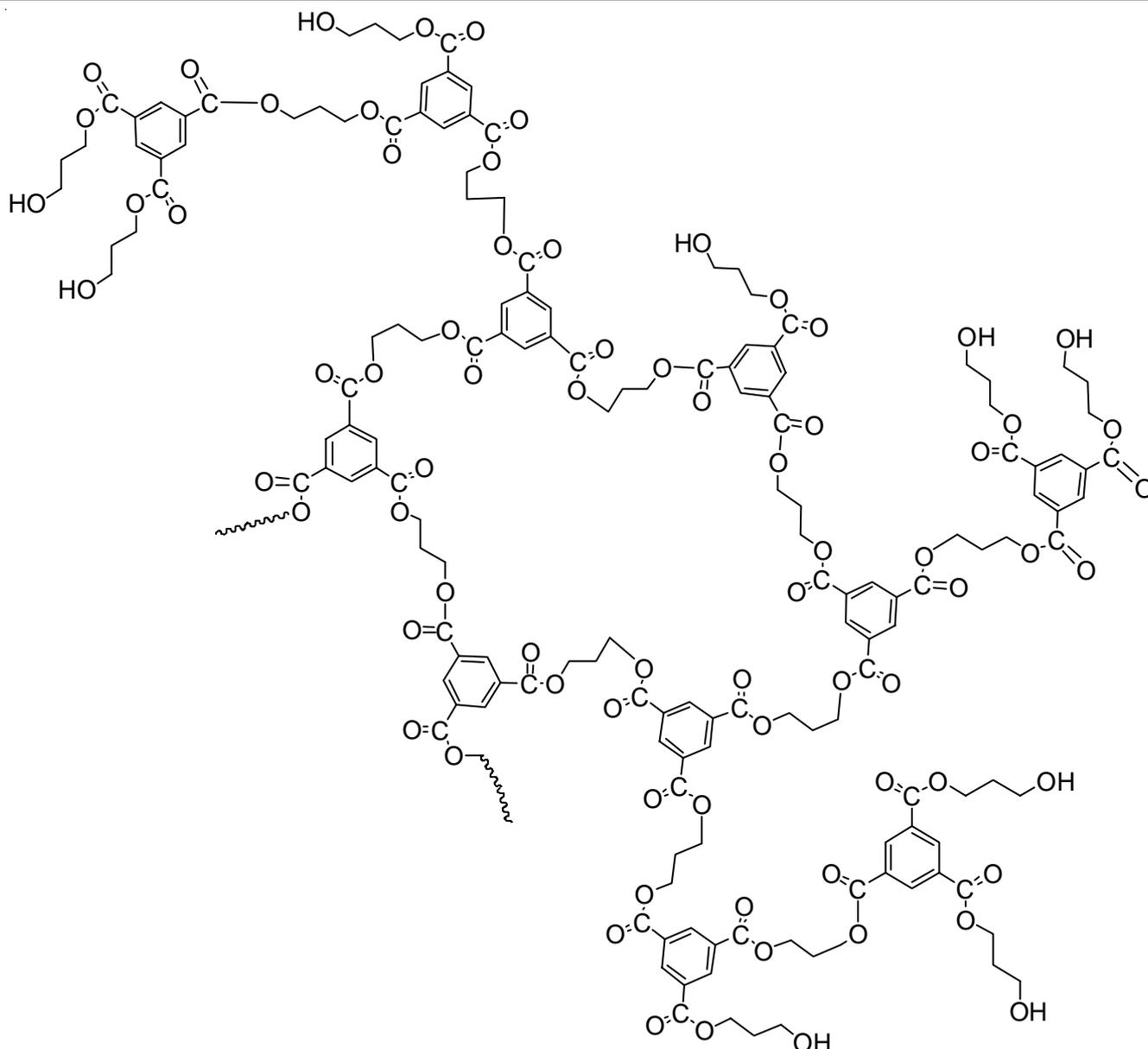
In this work, succinic anhydride was used to modify HBP-OH and the influences of the solvents, catalysts and time on the products were investigated. The modification degree and product yield can reach 99 and 95 % maximum respectively.

EXPERIMENTAL

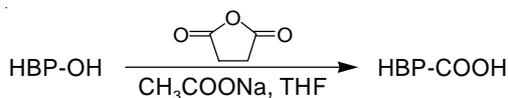
Succinic anhydride (AR), Sinopharm Chemical Reagent Co., Ltd., sodium acetate (AR), Tianjin University Chemical Experiment Plant, zinc chloride (AR); tetrabutyl titanate (AR); DMSO (AR), freshly distilled; DMF (AR), freshly distilled, THF (AR), freshly distilled; anhydrous ether (AR), Tianjin Kermel Chemical reagent Co.

Hydroxyl-terminated hyperbranched polyester was synthesized in our lab with molecular weight (M_n) of 11,000 and the dispersity index of 2.4 measured by GPC; the mass fraction of hydroxyl content is 4.7 %. The molecular formula of HBP-OH is shown in **Scheme-I**.

The preparation of HBP-COOH was shown in **Scheme-II** and the molecular formula of HBP-COOH was shown in



Scheme-I: Molecular formula of HBP-OH



Scheme-II: Reaction formula of modification

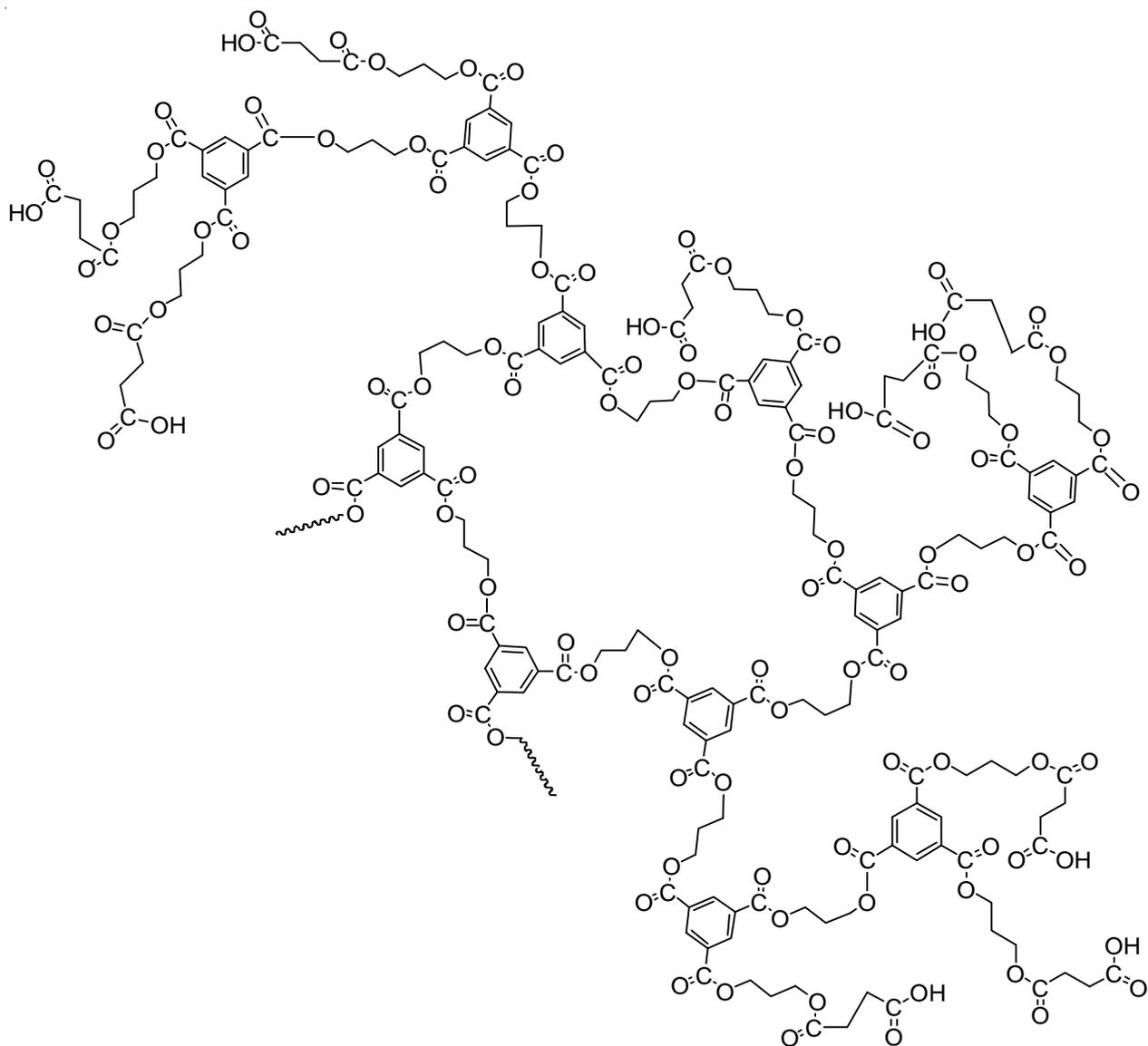
Scheme-III. 0.5 g HBP-OH, 0.2764 g succinic anhydride, 0.01 g (0.005 g) sodium acetate (zinc dichloride, tetrabutyl titanate) and 5 mL THF (DMSO, DMF) were added into a 50 mL single-necked round bottom flask, refluxed, stirred by a magnetic stirrer in an oil bath at 65 °C for 4 h. Post-treatment: the reaction product was precipitated with large amounts of diethylether, then dissolved in THF and then precipitated with ether for three times and finally dried in vacuum oven for 48 h at 35 °C. Experimental phenomena and characterization results were recorded in Table-1.

Fourier transform infrared (FTIR) spectra were recorded with a Varian 640 spectrophotometer (KBr pellet technique) in the wavenumbers from 4000 to 500 cm^{-1} with a resolution

of 1 cm^{-1} and averaged over 32 scans. Nuclear magnetic resonance (^1H NMR) spectra were recorded by an AVIII type NMR spectrometer (600 MHz, Bruker BioSpin Co., Germany) with $\text{DMSO-}d_6$ as solvent, TMS as internal standard. Molecular weight was measured by Waters 200 type gel permeation chromatography (GPC), using THF as solvent and polystyrene as standard.

The thermal stability of different polyesters were studied by the thermogravimetric analyzer (TGA) (Pyris 6, Perkin-Elmer Co., USA) in the following manner: the sample was heated from 30 to 700 °C at a rate of 20 °C/min under a nitrogen atmosphere and the degradation process was recorded. The temperature data at different weight loss were taken from the curves.

DSC heating curves of the samples were performed on a Perkin-Elmer Diamond type DSC instrument (USA), which was calibrated with indium prior to use; the samples weights was approximately 6.0 mg. The dried samples were heated to



Scheme-III: Molecular formula of HBP-COOH

120 °C at a heating rate of 100 °C/min under nitrogen atmosphere, held for 3 min, then cooled to 30 °C at a rate of 100 °C/min, held for 3 min and finally heated again to 120 °C at a rate of 15 °C/min; the second melting processes were recorded.

RESULTS AND DISCUSSION

Table-1 shows the reaction conditions and results. As seen from Table-1, when the catalyst is Lewis acid, such as ZnCl₂

TABLE-1
REACTION CONDITIONS AND THE RESULTS

Sample No.	HBP-OH/SCAE (mol/mol)	Solvent	t (h)	Catalyst	-COOH (mol %)	M _w (10 ⁴)	M _n (10 ⁴)	Colour	Yield (%)
1	1/3	THF	4.0	CH ₃ COONa, 1 wt. %	80	4.8	2.3	White	90
2	1/3	DMF	2.0	CH ₃ COONa, 1 wt. %	100	5.2	2.6	White	70
3	1/3	DMSO	0.5	CH ₃ COONa, 1 wt. %	100	5.3	2.6	Red	80
4	1/3	THF	4.0	ZnCl ₂ , 1 wt. %	–	∞	∞	White	–
5	1/3	DMF	4.0	ZnCl ₂ , 1 wt. %	–	∞	∞	White	–
6	1/3	DMSO	4.0	ZnCl ₂ , 1 wt. %	–	∞	∞	White	–
7	1/3	THF	4.0	Ti(C ₄ H ₉ O) ₄ , 1 wt. %	–	∞	∞	White	–
8	1/3	DMF	4.0	Ti(C ₄ H ₉ O) ₄ , 1 wt. %	–	∞	∞	White	–
9	1/3	DMSO	4.0	Ti(C ₄ H ₉ O) ₄ , 1 wt. %	–	∞	∞	White	–
10	1/3	THF	1.0	Ti(C ₄ H ₉ O) ₄ , 1 wt. %	0	3.7	1.5	White	0
11	1/3	THF	6.0	CH ₃ COONa, 1 wt. %	99	5.2	2.6	White	95
12	1/3	THF	4.0	CH ₃ COONa, 2 wt. %	80	> 100	> 100	White	92

and $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$, the product is cross-linked and not soluble in THF, DMSO, DMF and CF_3COOH and the GPC results of No. 10 is $M_n = 15,000$, which is greater than that of HBP-OH ($M_n = 11,000$). ^1H NMR results show that the product has no carboxyl end-groups, indicating when ZnCl_2 , $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ were used as the catalysts, it mainly leads to cross-linked; when Lewis alkaline like CH_3COONa was used, No. 1, 2, 3 show that the end-groups of the product have $-\text{COOH}$ and GPC displays a increasing molecular weight.

Comparing the experiments of No. 1, No. 2 and No. 3 in Table-1, in the same amount of catalyst CH_3COONa , the reaction in the solvent DMSO reacts fastest, the one in DMF was middle and in THF the slowest. However, the high boiling point of DMSO and DMF made the solvent difficult to remove from the product and it has low solubility in ether in the post-treatment. There were also a lot of side reactions in DMSO, such as the decomposition of DMSO that generates pungent odour and the product was red.

Fig. 1 is ^1H NMR spectra of HBP-OH and different HBP-COOH. For HBP-OH, peak A (δ 1.83) is the methylene hydrogen connected with hydroxyl in the end-groups ($-\text{CH}_2\text{CH}_2\text{CH}_2-\text{OH}$) and peak C (δ 3.53) is the methylene hydrogen on the middle carbon in the end-groups ($-\text{CH}_2\text{CH}_2\text{CH}_2-\text{OH}$). For HBP-COOH with different modification degree, the intensity of peaks A and C decrease with increasing $-\text{COOH}$ modification degree until they disappear in 100 % HBP-COOH. For 80 % HBP-COOH, peak B (δ 2.01) is methylene hydrogen connected with $-\text{OOC}-$ in the end-groups of $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OOCCH}_2\text{CH}_2\text{COOH}$ and its area increases with increasing $-\text{COOH}$ modification degree. For 100 % HBP-COOH, peak D (δ 2.4-2.5) is methylene hydrogen in the end-groups of $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OOCCH}_2\text{CH}_2\text{COOH}$ and the area of which increases with increasing modification degree. These results suggest that HBP-OH can be modified by succinic anhydride in ring opening with CH_3COONa as catalyst and the modification degree can reaches 99 % with proper composition of raw materials.

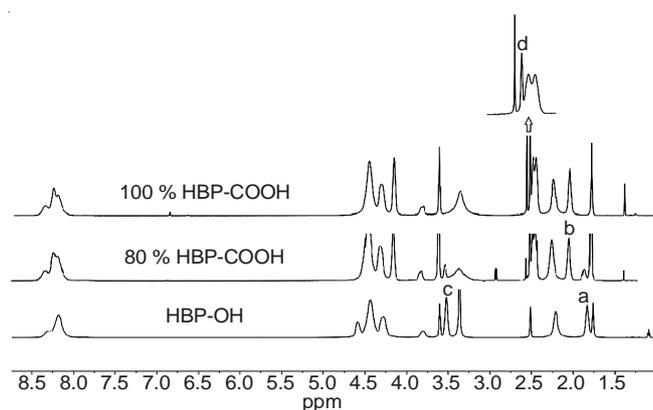


Fig. 1. ^1H NMR spectra of HBP-COOH with different modification degree

The peak at $\delta = 8.2$ ppm is the nuclear magnetic vibration peak of hydrogen on the benzene ring. Compared the hydrogen ratio of carbon backbone chain to the benzene ring in HBP-OH and 80 % HBP-COOH, it does not change with increasing modification degree, suggesting that there is no side reaction occurred in the reaction. However, if DMSO was used as solvent,

the hydrogen ratio of carbon backbone chain of 100 % HBP-COOH sample increases, indicating that side reaction occurred in the reaction process, *i.e.*, the reactions between hydroxyl groups and carbomethoxy groups among macromoleculars.

Fig. 2 shows the FTIR of two products. The stretching vibration of methylene is around 2967 cm^{-1} and its content in HBP-COOH is clearly higher than that in the raw material of HBP-OH. 1784 cm^{-1} is the absorption peak of acid anhydride (SCAE), while it disappeared in HBP-COOH. This shows that the product is pure and does not contain succinic anhydride.

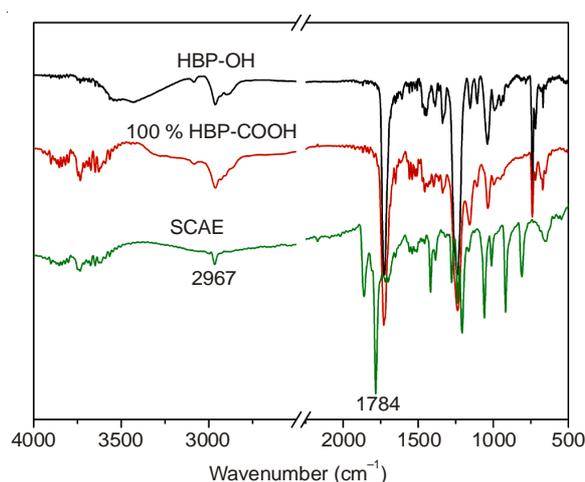


Fig. 2. Infrared spectra comparison of HBP-OH, HBP-COOH and SCAE

Fig. 3 is a comparison GPC chart of HBP-OH and HBP-COOH and the parameters are listed in Table-1. As shown in Fig. 3 and Table-1, the peak of retention time of the HBP-COOH (10.5 min) is significantly shorter than that of HBP-OH (11.2 min), indicating that the molecular weight of HBP-COOH is larger than that of HBP-OH. Moreover, the molecular weight distribution of the HBP-COOH is less than that of HBP-OH (Table-2). The reasons of the occurred phenomena are as follows: (1) the terminal groups of HBP-COOH are longer than that of HBP-OH for the opened anhydride molecule ($-\text{COCH}_2\text{CH}_2\text{COOH}$); (2) the terminal groups of HBP-OH contain a lot of hydroxyl ($-\text{OH}$) and some of methoxy ($-\text{COOCH}_3$), when sodium acetate exists, they can react to each other in the solvent and lead to a larger molecular weight distribution of HBP-COOH; (3) some intermolecular reaction between HBP-COOH and HBP-OH also can result in increasing of the molecular weight of the HBP-COOH.

TABLE-2
MOLECULAR WEIGHT OF DIFFERENT SAMPLES

Sample	M_n	M_w	M_w/M_n
HBP-OH	11000	26400	2.4
80 % HBP-COOH	48300	23100	2.1
100 % HBP-COOH	52400	26300	2.0

Fig. 4 is the TGA curves of HBP-OH, 80 % HBP-COOH and 100 % HBP-COOH. As seen in Fig. 4, when the temperature below $250\text{ }^\circ\text{C}$, the curves of three hyperbranched polyesters almost coincide, suggesting that they are stable below $250\text{ }^\circ\text{C}$. When the temperature rises above $250\text{ }^\circ\text{C}$, their difference of decomposition behaviours occurs. The weight loss increases

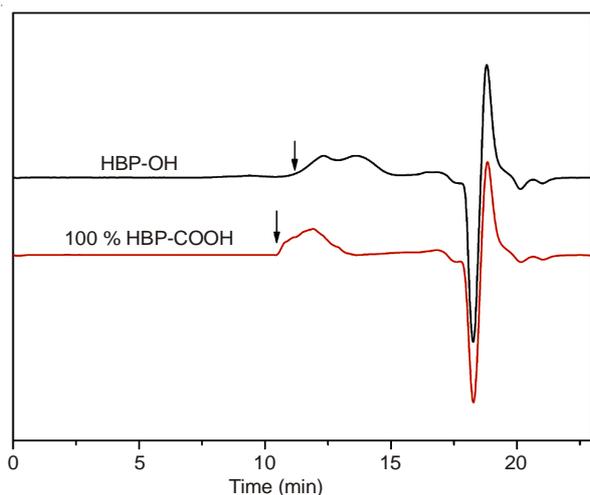


Fig. 3. GPC spectra of HBP-OH and HBP-COOH

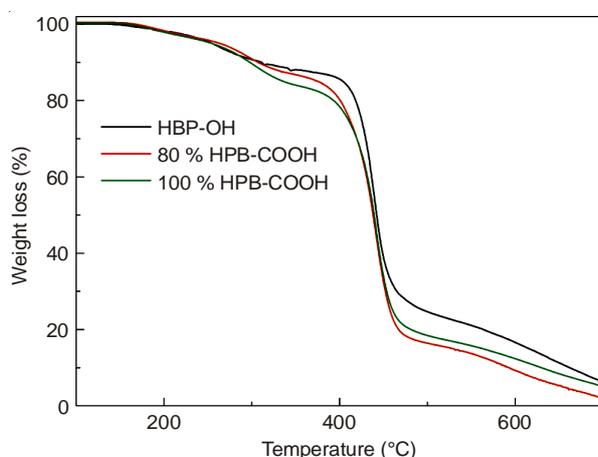


Fig. 4. TGA curves of HBP-OH and HBP-COOH with different modification degree

with increasing modification degree of the hyperbranched polyester and the HB-POH has the least weight loss. In the first decomposition stage, the weight loss of HBP-OH is the loss of hydroxyl end-groups, while the weight loss of HBP-COOH is the loss of the carboxyl end-groups. The modified hyperbranched polyester contains carboxyl end-groups and the decarboxylation reaction producing carbon dioxide gas under heating, which causes the weight loss of the polymer. The decomposition energy of the carboxyl end-groups is lower than that of the hydroxyl end-groups, so the more carboxyl end-groups the polymer have, the larger weight loss occurs in the heating process. On the other hand, three polymers have similar maximum weight loss temperatures (T_{max}) at the second decomposition stage, suggesting that decomposition at this stage is the decomposition of the main backbone of the hyperbranched polymer (Table-3).

TABLE-3
PARAMETERS OF THE TGA CURVES
FOR DIFFERENT SAMPLES

Sample	T_5 (%) (°C)	$W_{350^\circ\text{C}}$ (%)	T_{max} (°C)	$W_{500^\circ\text{C}}$ (%)
HBP-OH	254.3	88.1	440.7	24.6
80 % HBP-COOH	253.5	86.8	442.2	16.4
100 % HBP-COOH	254.3	84.0	440.7	18.4

Fig. 5. is DSC heating curves of HBP-OH and HBP-COOH. It can be seen from the figure that the T_g s of HBP-OH and HBP-COOH are 37 °C and 4 °C respectively and T_g is significantly reduced after modification. This is due to the end-groups of HBP-COOH originated from the SCAE are longer and more flexible than those of HBP-OH, as shown in **Scheme-III**.

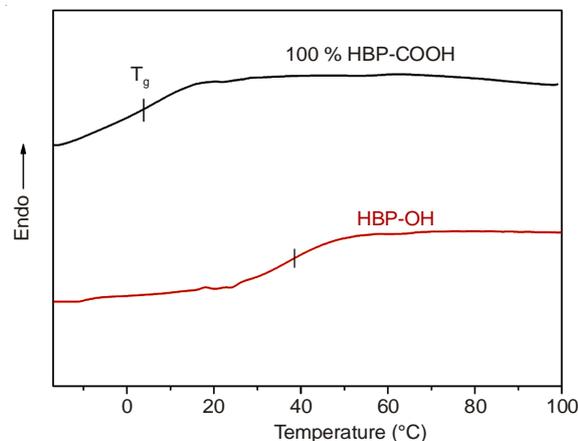


Fig. 5. DSC curves of HBP-COOH and HBP-OH

Conclusion

The terminal function groups in hydroxyl-terminated hyperbranched polyester can be 99 % modified into carboxyl end-groups in tetrahydrofuran at 65 °C for 6 h with sodium acetate as catalyst. The conversion of terminal functional groups can reach 99 % with 95 % yield. The glass transition temperature of HBP-COOH is much lower than that of HBP-OH because of its long and flexible end-group chains. The thermal stability of HBP-COOH is much lower than that of HBP-OH and the decomposition reaction degree of the HBP-COOH increases with increasing amount of -COOH end-groups.

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