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VARIOUS TECHNOLOGIES

Synthesis and Characterization of Aliphatic–Aromatic Hyperbranched Polyesters with High Organosolubility*

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Abstract—Carboxyl-terminated, water soluble, hyperbranched polyesters (HBPET) with aliphatic–aromatic structure were synthesized at three different monomer mole ratios ($A_3/B_3 = 1 : 1, 2 : 1, 1 : 2$, respectively) by melt polycondensation of aconitic acid and phloroglucinol via $A_3 + B_3$ approach. Fourier transform infrared (FTIR) spectroscopy indicated as that was expected HBPET, which showed excellent solubility in a variety of polar solvents such as *N,N*-dimethyl formamide (DMF), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF). The weight-average molecular weight of HBPET ranged from 7792 to 9214 g mol^{-1} and their intrinsic viscosity were varied from 0.17 to 0.34 dL g^{-1}. The degree of branching of the HBPET was estimated to be 0.44–0.49 by ^{1}H and ^{13}C NMR measurement. The thermogravimetric analysis (TGA) measurement revealed that HBPET was of 10% weight-loss at 340°C in N_2.

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INTRODUCTION

In the last two decades, researchers both from academia and industry showed high interest on hyperbranched polymers (HBPs) due to their unique chemical and physical properties such as low viscosity, high solubility and reactivity, and good compatibility with other materials. In addition, terminal groups of hyperbranched polymers can be modified with various functional groups to satisfy numerous possible demands. The easy synthetic accessibility of polymers by one-pot synthesis is a great advantage compared to dendrimers and thus, it allows their large quantity production in industrial scale [1–8].

Among numerous types of HBPs the family of hyperbranched polyesters (HBPET) represents very important polymer. HBPET with the structure ranging from aromatic to aliphatic as well as partial aromatic–aliphatic structures have been investigated in many publications[1, 8–11].

According to the structure and type of monomer, the synthetic methodologies of HBPs can be classified into two categories: single-monomer methodology (SMM) and double-monomer methodology (DMM). SMM refers to the preparation of HBPs based on AB_n monomers or potential AB_n monomers, such as dimethylol propionic acid (DMPA). While DMM refers to the preparation of HBPs through copolymerization reaction of two types of monomers [10].

The synthesis of highly branched aromatic polyester copolymers was first reported by Kricheldorf in 1982 using 3,5-bis(trimethylsiloxy)benzoyl chloride as an AB_2-type monomer[12]. Later, Frechet and coworkers in 1991 successfully developed the thermal self-condensation of the same AB_2-type monomer leading to the synthesis of hydroxyl terminated hyperbranched aromatic polyesters [12].

A large number of HBPs and dendrimers are well described commercialized in the literature, but hyberbranched polyesters with aliphatic–aromatic structure are of special interest, mainly, because of their good processability and the large amount of functional groups distributed in the internal and in the external parts of the molecules. Because of their globular shape, these

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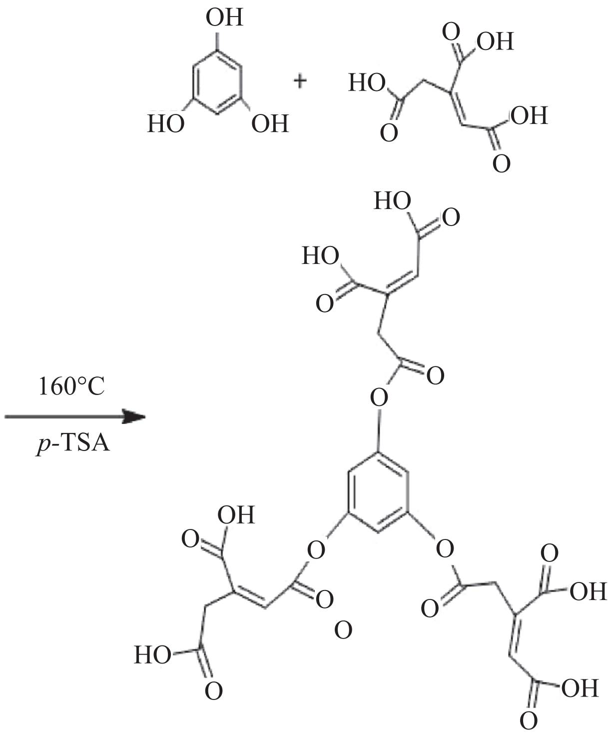
* The text was submitted by the authors in English.

polymers possess low solution and melt viscosities useful, for instance, in applications as rheology modifier in blends [13, 14]. Lusic and Fossum presented the $A_2 + B_3$ HB aliphatic polyesters prepared by reaction of fumaric acid and trimethylolpropane, and the ratio of these two reagents was varied [1, 15]. aliphatic hyperbranched polyester was synthesized by an $A_2 + B_3$ approach using glycerol and adipic acid [9]. Many investigations on the $A_2 + B_3$ route to HB polyesters were also done in the group of Long and several $A_2 + B_3$ HB polyesters were reported by them [16]. Furthermore, the theoretical investigations on the kinetics of HB $A_2 + B_3$ system by polycondensation reactions were carried out by Schmaljohann and Voit [15, 17]. Recently the author synthesised a new type of $A_2 + B_3$ type hyperbranched aromatic–aliphatic polyester with carboxyl end groups [18]. However no work was done on synthesis of carboxyl-terminated aliphatic–aromatic hyperbranched polyester via $A_3 + B_3$ method.

In the work a novel approach for the design of carboxyl-terminated aliphatic–aromatic HBPET was synthesized by melt polymerization of aconitic acid as A3 monomer and phloroglucinol as a B3 monomer at 160°C in the presence of *p*-toluene sulfonic acid (*p*-TSA) as a catalyst. No gelation was observed during the polymerization. The structure of the resulting HBPET and their properties were investigated.

Scheme 1. Synthesis route and possible structure of HBPET.



EXPERIMENTAL

Materials. Aconitic acid, phloroglucinol, and *p*-Toluene sulfonic acid (*p*-TSA) were purchased from Sinopharm Chemical Reagent Co. Ltd (China). THF, DMF, NMP, DMSO, toluene, acetone, and hexane were obtained through Donghua university chemical store. All reagents and solvents were commercial grade and used as received.

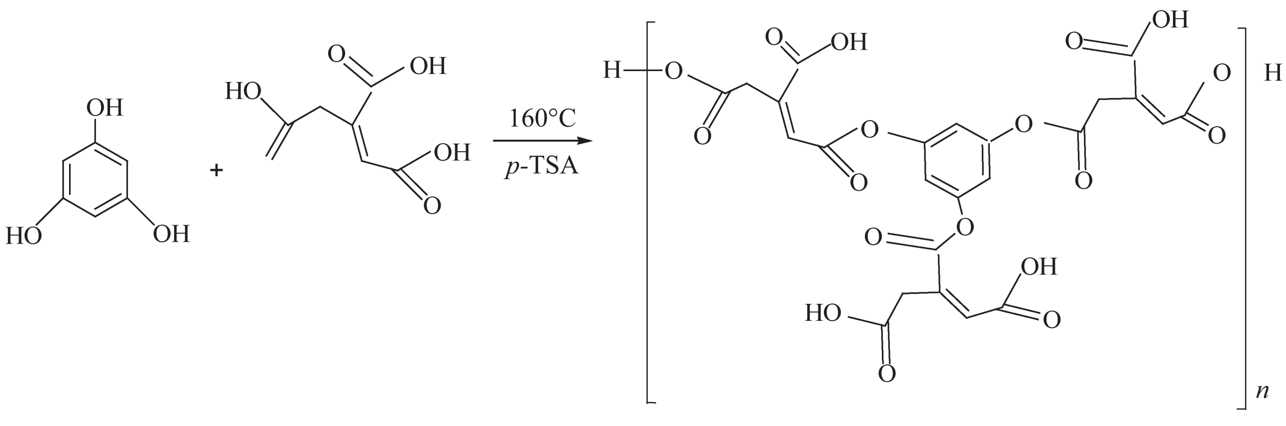
Synthesis of HBPET. The A_3 +B_3 carboxyl-terminated aliphatic–aromatic HBPET was synthesized by melt polymerization of aconitic acid as A3 monomer and phloroglucinol as B3 monomer using different monomer ratios ($A_3 : B_3$). The used monomer amount of aconitic acid were 3.0 g (17 mmol) 6.0 g (34 mmol) and 3.0 g (17 mmol). The monomer amount of phloroglucinol were 3.0 g (23 mmol), 3.0 g (23 mmol), and 6.0 g (46 mmol) corresponding to the A3 : B3 molar ratios of 1 : 1, 2 : 1, and 1 : 2, respectively. In a dry three-necked flask equipped with nitrogen inlet, outlet, condenser and magnetic stirring bar, the phloroglucinol was added into the aconitic acid at 160°C in the presence of *p*-toluene sulfonic acid (*p*-TSA) as a catalyst. The reaction mixture was stirred for 3, 5, and 7 h for HBPE-1, HBPE-2 and HBPE-3, respectively, to ensure high conversion and then the final products were filtrated, purified and precipitated from acetone in hexane to remove the unreacted materials and catalyst then were dried at 70°C under vacuum.

Characterization of polymers. *FTIR spectra analysis.* Fourier transform infrared (FTIR) spectra of the samples were recorded on a Nicolet 5700 FTIR (Thermo Fisher), in which KBr powder were used for the powder samples of the synthesized monomer, the scan of each sample was recorded from 4000 to 800 cm^{-1}.

Thermogravimetric analysis (TGA). Thermal stability of HBPEs was performed using theromgravimetric analysis (TGA) on a simultaneous thermal analyzer (Netzsch TG209F1). The sample weighed between 5–7 mg. The scans were run from room temperature to 600°C at rate of 20°C min^{-1} under nitrogen flow.

Differential scanning calorimetry (DSC). Thermal characterization of the HBPEs was performed with DSC Q20 (TA Instrument-waters LLC). Sealed aluminium pans containing 5–7 mg of the samples were used in all the experiments. To eliminate the thermal history,

Scheme 2. Reaction scheme and chemical structure of HBPET.



all the samples were heated up to 180°C, then rapidly cooled to −50°C. The actual measurements reported were performed during a second heating cycle from 25– 270°C at a heating rate of 20°C/min.

Nuclear magnetic resonance (NMR) Spectroscopy: The ^{13}C and ^{1}H NMR analysis were carried out on a Bruker DRX-400 spectrometer. Chemical shifts were referenced to DMSO-d_6 at 39.43 ppm for the ^{13}C and at 2.5 ppm for the ^{1}H spectra.

Degree of branching: *DB* is the most important parameter of hyperbranched polymers in the description of structural perfection. To calculate *DB*, the assignment of all three possible repeating units [terminal (*T*), linear (*L*) and dendritic (*D*) groups] in hyperbranched polyester are required[19]. Several concepts, such as the definition of repeat units and *DB*, were borrowed from the traditional hyperbranched polymers prepared from AB$_2$-type monomers. Values of *DB* for different pseudo-generations of A HBPE were calculated using the following equation:

$$DB_{\text{fretchet}} = \left(\frac{D+T}{D+T+L}\right), \qquad (1)$$

where *D*, *T,* and *L* refer to the numbers of dendritic, terminal, and linear units in the polymer, respectively.

Gel permeation chromatography (GPC). Gel permeation chromatography (GPC; Shimadzu LC 10ATVP series, Japan) with a refractive index detector. Samples were prepared in THF solvent at a 5 mg mL^{-1} concentration. The flow rate of the mobile phase was kept at 1.0 mL min^{-1}. The instrument was calibrated with polystyrene standards.

Viscometry. The inherent viscosity [η] measurements were performed with an Ubbelohde Viscometer at 25°C in a mixture of phenol and tetrachloroethane (50/50, w/w). The samples were dissolved at room temperature. The solution was filtered through a disposable membrane filter (Teflon).

RESULTS AND DISCUSSION

Synthesis of HBPET. In this work, HBPET were synthesized by single step melt polycondensation of aconitic acid as A$_3$ monomer and phlorogluciol as a B$_3$ monomer via A$_3$ + B$_3$ approach. In contrast to classical hyperbranched polymers synthesized according to the AB$_2$ strategy, the idealized chemical structures of hyperbranched polyesters prepared via the A$_3$ + B$_3$ approach do not display just one focal reactive group but present two different types of functional end groups, as can be seen in Scheme 2. Indeed, OH groups arising from phloroglucinol units, and COOH groups arising from aconitic acid units can coexist within the same macromolecule in different ratios according to the molar ratio of the monomers prior to reaction and, to a certain extent, to the degree of conversion.

Both of the two monomers are commercially available and their properties are very suitable for preparing hyperbranched polyester, which has good solubility, and thermal stability. The reaction was maintained at a relatively low temperature 160°C, to minimize the volatilization of monomers and unwanted side reactions. The reaction was driven toward high conversion as the water formed was removed by using Dean–Stark apparatus. Whereas the composition and structure were analyzed by ^{1}H and ^{13}C NMR spectroscopy. Hydrogen-bonding information was obtained from FTIR spectroscopy. The thermal stability was measured by TGA

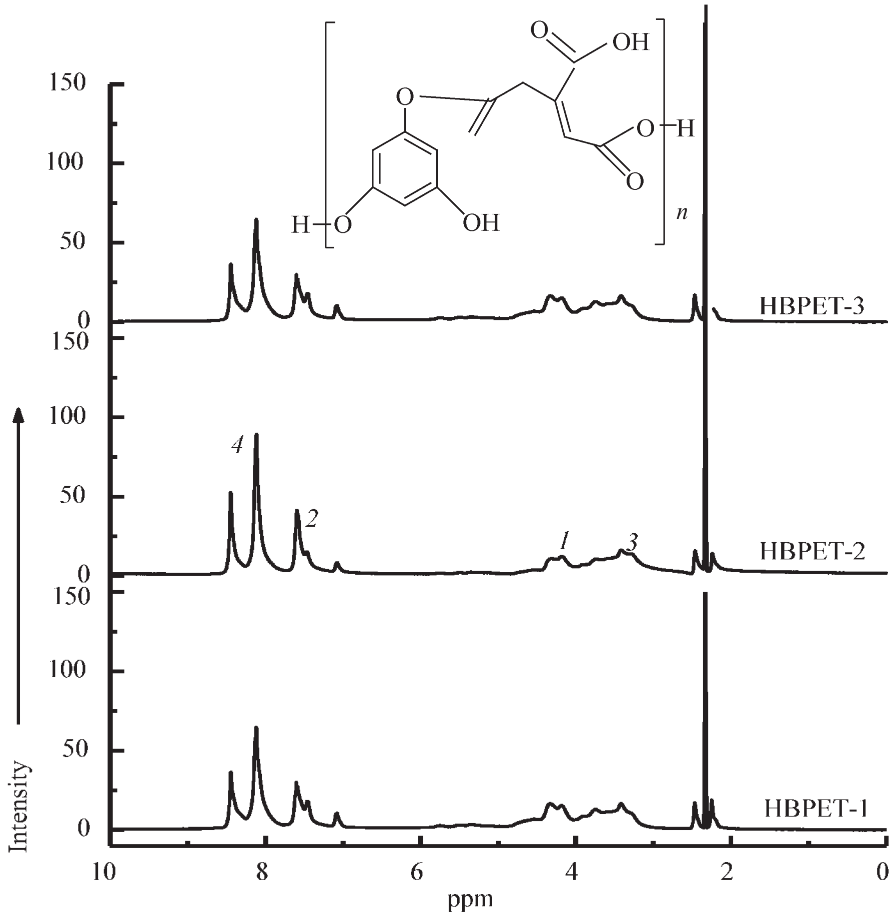


Fig. 1. ^{1}H NMR spectra of the synthesized hyperbranched polyesters.

and DSC. All the synthesized HBPETs exhibited a low intrinsic viscosity as shown in Table 1.

NMR analysis. In order to further confirm the chemical structure and calculate the *DB* values of HBPET, the ^{1}H and ^{13}C NMR measurements were performed. The data of ^{1}H NMR confirmed the structure of the HBPET. In the ^{1}H NMR spectrum of HBPET in Fig. 1, DMSO-d_6 siginal is seen at 2.4 ppm. The signals at 7–7.8 ppm indicated the presence of aromatic rings. Proton signals are for carboxylic protons at 8 ppm. Methylene protons are at 2.4 ppm. Methyl protons are at 2.1 ppm. H protons of aromatic (C–OH) are at 2.3 ppm. And phenolic protons signals are at 8.5 ppm.

Table 1. Feed ratios, reaction time and molecular weight data of HBPET

Polymer	Molar ratio ($A_3 + B_3$)	Reaction time, h	M_w, g mL	M_n, g mL^{-1}	PDI
HBPET-1	1 : 1	3	7792	4926	1.58
HBPET-2	2 : 1	5	8653	5332	1.62
HBPET-3	1 : 2	7	9214	5965	1.54

The ^{13}C NMR spectroscopy is another useful technique to determine the purity and detect structural defects of the hyperbranched polymer fragments. The ^{13}C NMR spectra of HBPET in Fig. 2 showed that the resonances from the carbons in the *T*, *L*, and *D* units had different shifts due to the difference in their chemical environments. In Fig. 2, the peak at 135 ppm could be attributed to the carbonyl carbon of acid or ester (C=O), the peaks at 166–168 ppm are due to the carbons in the benzene ring of phloroglcinol, and the peaks between 125 ppm are due to the methylene of ester units. The peaks between 130–133 ppm arise from quaternary carbons. The percentage of *T*, *L*, and *D* units presented in HBPET, are calculated from the integral area ratios of methylene and the quaternary carbon zone of ^{13}C NMR spectra, as a result, *DB* can be determined by using Eq. (1) and the values of *DB* are shown in Table 1.

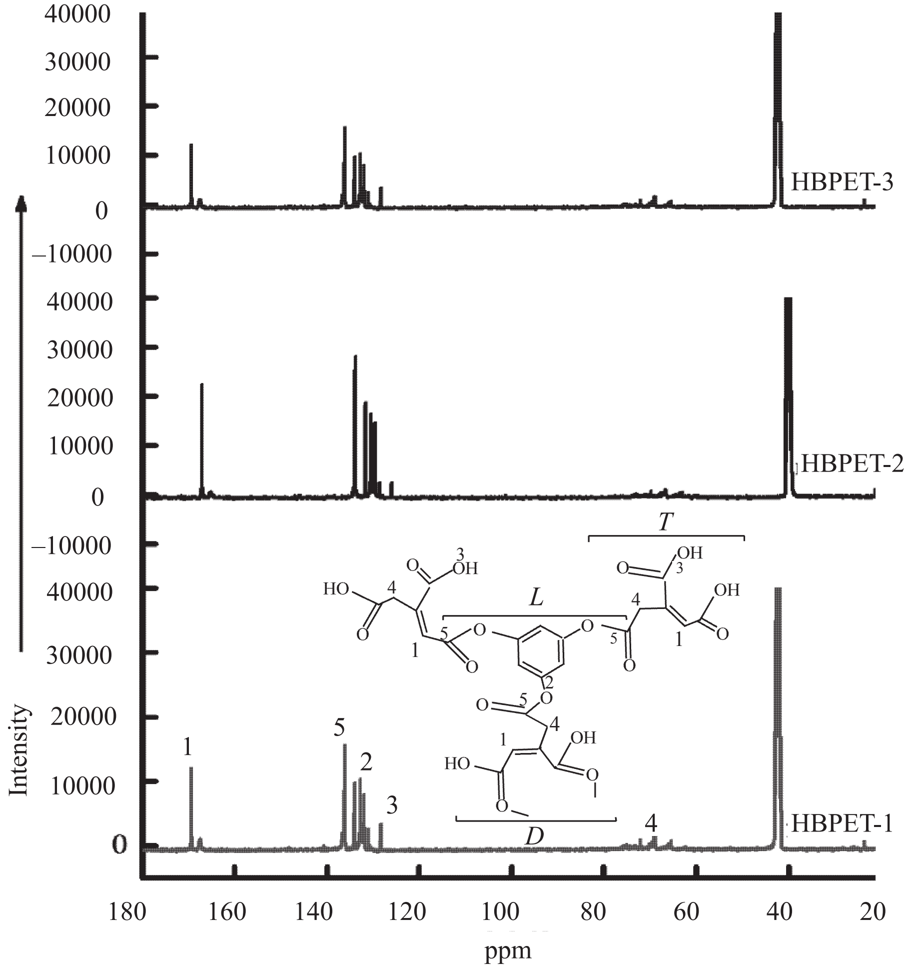


Fig. 2. ^{13}C NMR spectra of the synthesized hyperbranched polyester.

FTIR analysis. The FTIR spectrum of HBPET were shown in Fig. 3. Strong and broad peak around 3495–3350 cm^{-1} confirmed a high concentration of carboxyl groups in HBPET molecules. The peak at 3000 cm^{-1} was the characteristic absorption of methyl, and the peak at 2980 cm^{-1} could be attributed to the absorptions from methylene groups, as well as a peaks at 1263–1324 cm^{-1}, which are due to the presence of the aromatic group originated from phloroglucinol, A strong and broad peak around 1750 cm^{-1} (C=O in ester bond) confirmed a high concentration of carboxyl groups in the HPBET molecule. These data indicated that the polymers contained carboxyl groups, ester bonds, benzene ring, methyl and methylene groups, which were in agreement with our objective polymers.

Molecular weight and polydispersity. The molecular weights of HBPET have been determined by GPC using THF as solvent on the basis of linear polystyrene standards. The weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity index PDI (M_w/M_n) are listed in Table 1. These data show that using the present synthetic strategy can obtain HBPET with moderate molecular weights and narrow molecular weight distributions. It is well known that molecular weight determined by GPC measurements for a hyperbranched polymer is expected to be lower because of the smaller radius of chain gyration in comparison with linear counterparts. As a consequence, in this case, the actual molecular weight may have been higher than the experimental value.

Solubility. HBPET were fairly soluble in common organic solvents. The solubility was evaluated with known concentration of polymers in different solvents at room temperature. In all cases, HBPET were well dissolved in strong polar solvents (Table 2). The introduction of

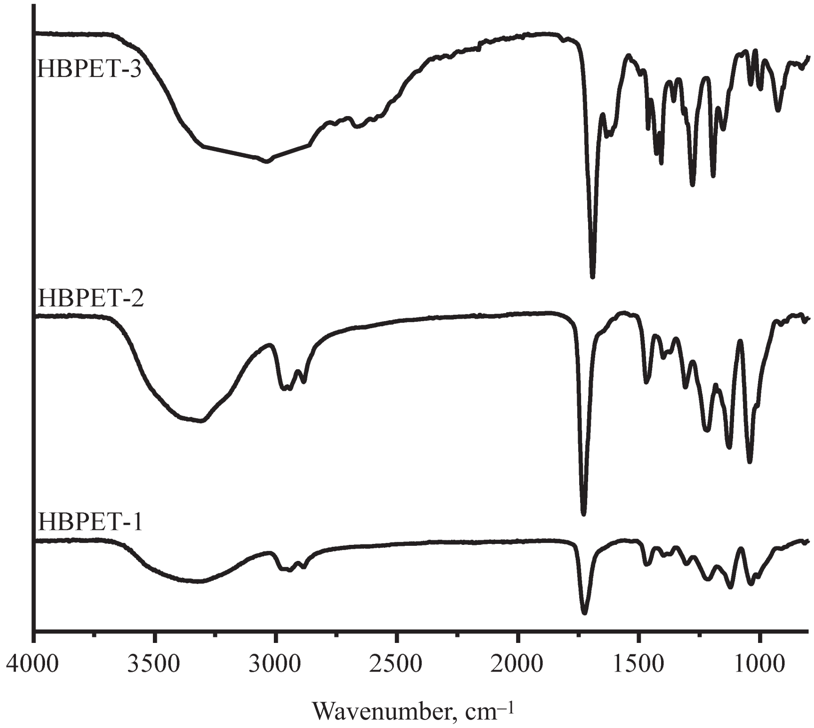


Fig. 3. FTIR spectra of the synthesized HBPET.

Table 2. Solubility behavior of different HBPET samples at room temperature 25°C

Polymer	Solvent[b]					
	H_2O	DMSO	DMF	THF	NMP	$CHCl_3$
HBPET-1	++[a]	++	++	++	+–	–
HBPET-2	++	++	++	++	+–	–
HBPET-3	++	++	++	++	+–	–

[a] Solubility: ++ Soluble; +– partially soluble; – unsoluble.
[b] Scale: 15 mg per 1 mL.

Table 3. Synthesis conditions and characterization data of various HBPET

Polymer	Molar ratio ($A_3 + B_3$)	Reaction time, h	T_m, °C	T_5, °C[a]	T_{10}, °C[a]	Char yield, %[b]	η, dL g[c]	DB_{Fretchet}
HBPET-1	1 : 1	3	154	312	341	9	0.24	0.44
HBPET-2	2 : 1	5	156	300	324	8	0.26	0.46
HBPET-3	1 : 2	7	162	300	317	7	0.27	0.49

[a] At this temperature the weight loss was 5% or 10%.
[b] Residual yield in the TGA at 600°C in N_2.
[c] Intrinsic viscosity.

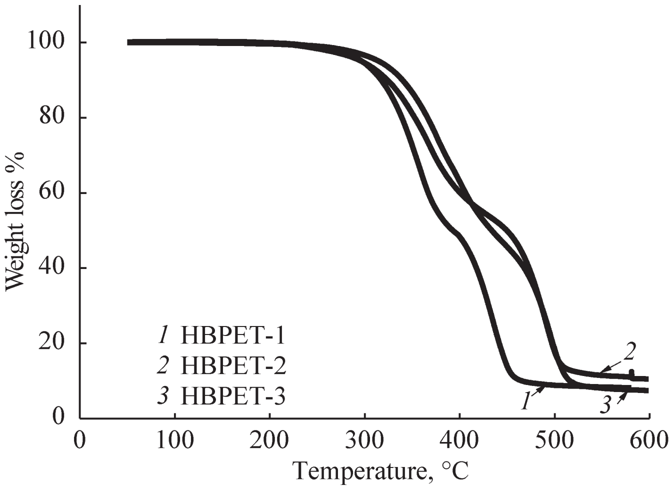


Fig. 4. TGA curves of the synthesized HBPET, the temperature range from 50–600°C.

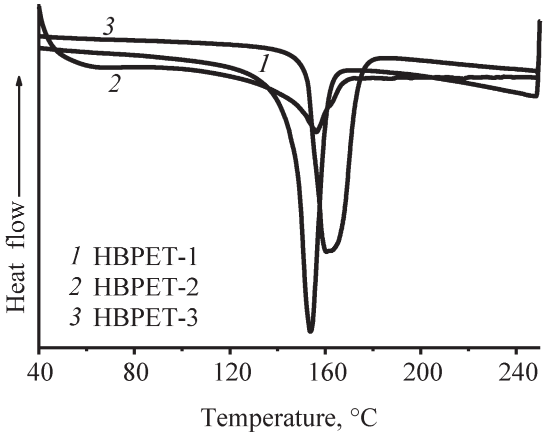


Fig. 5. DSC curves of the synthesized HBPET.

branching units in HBPET had a beneficial effect on solubility in the solvents investigated.

Thermal properties of HBPET. The thermal stability of a polymer can provide an important guidance for its processing and application. The studies of thermal behavior not only can explain the behavior of a polymer at high temperature, but also provide assistance for the establishment of selection criteria for specific applications of polymer materials [20].

The thermal properties of HBPET determined by TGA and DSC are summarized in Table 3. All these HBPET show similar decomposition behavior and good thermal stability in N_2 because they have the same component but different molar ratios. According to the TGA data in Fig. 4, the initial decomposition temperatures (T_5) were about 300–315°C and the temperatures for 10% gravimetric loss (T_{10}), which is an important evidence for thermal stability, were about 317–340°C. The maximum decomposition temperatures ($T_{\max}$) were about 450°C and also char yields of the HBPET at 600°C were 9–7%. DSC studies of the HBPET-1, HBPET-2, and HBPET-3 in Fig. 5 indicate the melting temperatures of the three polymers were 154°C, 156°C, and 162°C, respectively.

Viscometry. In general, factors such as molecular architecture and composition, molecular weight, temperature, and shear rate affect the viscosity of a polymer because the viscosity originates from interactions between the polymer molecules. Moreover, the melt viscosity of a polymer is dependent on the segment density within the volume of a molecule and intermolecular chain entanglement [21]. Because of the sphere like structures of the HBPET, there were few entanglements among molecular chains; this resulted in lower viscosity, which in agreement with properties of hyperbranched polymers (Table 1).

CONCLUSIONS

The first, second and third generations of aromatic–aliphatic hyperbranched polyester (HBPET) were prepared by single step melt polycondension via A_3 + B_3 method, based on aconitic acid (A_3 monomer) and phloroglucinol (B_3 monomer) as a core molecule via melt condensation procedure with *p*-toluene sulfonic acid (*p*-TSA) as a catalyst. HBPET have good solubility in water and some other solvents and good thermal stability. These HBPET had moderate molecular weights and narrow polydispersities from 1.39 to 1.60, and had 10% weight loss at 341°C in nitrogen. The degree of branching (DB) of HBPET-1, HBPET-2, and HBPET-3 were 0.44, 0.47, and 0.49, respectively. The HBPET structure showed the presence of various functional end groups (terminal, dendritic, and linear units) within the same macromolecule, which opens up a high potential for further chemical modifications in order to tune the physical-chemical properties according to the desired applications.

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