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Synthesis and Characterization of Low Viscosity Aromatic Hyperbranched Poly(trimellitic anhydride diethylene glycol) Ester Epoxy Resin

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Low viscosity aromatic hyperbranched poly(trimellitic anhydride diethylene glycol) ester epoxy resin (HTDE) was synthesized from the reaction between epichlorohydrin (ECH) and carboxyl-ended hyperbranched poly(trimellitic anhydride diethylene glycol) ester (HTD). HTD was prepared from inexpensive materials A₂ (diethylene glycol, DEG) and B₃ (trimellitic anhydride, TMA) monomers by a pseudo-one step method. Molecular weight of the HTD was calculated by its acid value with a “Recursive Probability Approach”, and its degree of branching (0.62~0.71) was characterized by model compounds and ¹H-NMR-minus spectrum technology. HTDE has an epoxy equivalent weight of <530 g/mol and its viscosity of <700 cp, respectively. The structure of the AB₂ monomer, HTD and HTDE were also characterized by MS, ¹H-NMR and FT-IR spectra technology. HTDE is an ellipsoid-like molecular with a size of <10.34 nm. This low viscosity novel epoxy resin has important applications in the fields of “no-solvent” coatings.

Keywords: Hyperbranched epoxy resin, low viscosity, NMR, degree of branching, synthesis

1 Introduction

The demand for polymeric materials with novel or improved properties relative to existing materials requires the synthesis and properties evaluation of polymers that possess unique structural features (1,2).

Hyperbranched polymers are of special interest as their easy synthetic accessibility, typically by one pot synthesis, allows for their production in large quantities and their application on an industrial scale. Among the different synthetic approaches, the predominant one is polycondensation, others being (3), e.g., self-condensing vinyl polymerization (SCVP) and ring-opening multi-branching polymerization (4). While the degree of branching and structural precision of HBP is considerably lower than

those of dendrimers, HBP possess a practical competitive advantage for potential commercialization, due to the lower cost that is derived from simpler preparation. Some applications of HBP were used as biodegradable material (5), rheology modifiers (6), additive for cationic photopolymerization of epoxy systems (7), adhesion (8) and macroscopic tubes (9). Some initial studies have been done on toughening of common epoxy resin by HBP (10–12). Several folds increase in GIC toughness value was obtained for a commercial DGEBA epoxy resin using only 5% by weight of a liquid hyperbranched epoxy resin toughener (11), but their strength was found to decrease to some extent for low crosslinking density. Until 2006, we (13–14) reported two kinds of low viscosity aromatic polyester hyperbranched epoxy resins with low epoxy equivalent weight, which not only increased the toughness of diglycidyl ether of bisphenol-A (DGEBA), and but also increased its tensile strength and flexural strength remarkably.

Some preparation technology of hyperbranched epoxy resins was based on expensive raw materials and the synthetic process was also rather complex(3–8). Little literature is available concerning the synthesis of inexpensive low viscosity liquid hyperbranched epoxy resin. The present paper reports the facile synthesis and detailed characterization of a low viscosity hyperbranched polymer from commercially available low cost materials.

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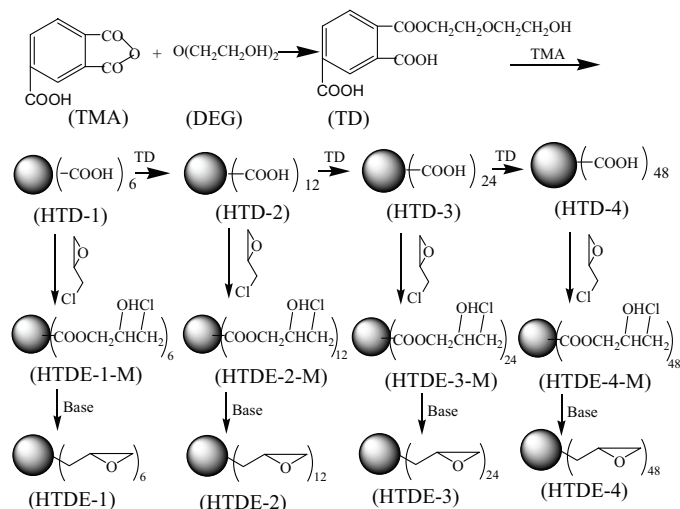


Fig. 1. Synthetic mechanism scheme of hyperbranched epoxy resin HTDE.

2 Experimental

2.1 Materials and Instrumentation

Trimellitic anhydride (TMA), diethylene glycol (DEG), tetrabutyl titanate (TBT), epichlorohydrin (ECH), diglycidyl ether of bisphenol A (DGEBA) containing 5.1 mmol epoxy group per gram of resin and other organic solvents were commercially purchased.

$^1\text{H-NMR}$ measurements were carried out on a 400 MHz Bruker NMR spectrometer with $(\text{CD}_3)_2\text{SO}$ as a solvent. FT-IR measurements were performed on a Bruker Vector 33 spectrometer using a sealed cell (KBr 0.5 mm). A double focusing mass spectrometer (VG ZAB-HS) was used to obtain the fast atom bombardment ion mass spectrum in 3-nitrobenzylalcohol matrix. The viscosity of the HTDE was measured with a Brookfield DV- ϕ + Viscometer with a RV-S06 spindle at 25°C and 20 rpm.

2.2 Synthesis of Low-Viscosity Hyperbranched Epoxy Resin (HTDE)

2.2.1. Synthesis of AB₂ Monomer

0.1 mol TMA, 0.1 mol DEG and 100 ml 1,4-dioxane as a solvent were charged into a four-necked reaction flask equipped with a stirrer, cooler, thermometer and nitro-

gen inlet and were reacted for 3 h at 120°C. White solid AB₂ monomer with an acid value of 380 mg KOH/g was obtained after the solvent was removed under a pressure of 3~5 mmHg at 120°C for 30 min.

2.2.2. Synthesis of Model Compound trimellitic anhydride tri-(diethylene glycol) ester (TTD)

0.1 mol TMA, 0.4 mol DEG, 0.005 mol TBT and 100 ml 1,4-dioxane as a solvent were charged into a four-necked reaction flask equipped with a stirrer, cooler, thermometer and nitrogen inlet and were reacted for 3 h at 150~160°C, and a white solid model compound TTD with the acid value under 3mg KOH/g was obtained after the solvent was removed under a pressure of 3~5 mmHg at 120°C for 40 min.

2.2.3. Synthesis of carboxyl-end Hyperbranched Polymers (HTD)

The HTD was prepared by a pseudo-one step method, as shown in Figure 1, the detailed process was reported in ref. (15).

2.2.4. Synthesis of Low-Viscosity Hyperbranched Epoxy Resin (HTDE)

The HTDE was prepared by the reaction between ECH and HTD shown in Figure 1, the detailed process was reported in ref. (15).

3 Results and Discussion

3.1 Structure and Characterization of the AB₂ Monomer

Theoretically, the reaction of TMA with DEG produces two AB₂ monomer, TD-1 and TD-2, with different structures (Fig. 2); a little TMA-DEG-TMA can also be obtained.

The FT-IR spectra of TMA, DEG and the AB₂ monomer are shown in Figure 3. The appearance of the strong absorption peak at 1711 cm^{-1} and the disappearance of a broad and strong absorption peak at 1720~1863 cm^{-1} from the anhydride group suggest that the anhydride group has reacted completely. From the mass spectrum of the AB₂ monomer in Figure 4, the molecular ion peak of the monomer AB₂ and TMA-DEG-TMA are observed at m/z 297 and 489, respectively, which confirms the structure of the AB₂ monomer and TMA-DEG-TMA compound.

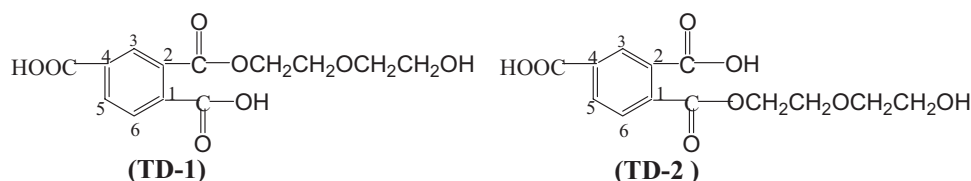


Fig. 2. Structure of TD-1 and TD-2 AB₂ monomers.

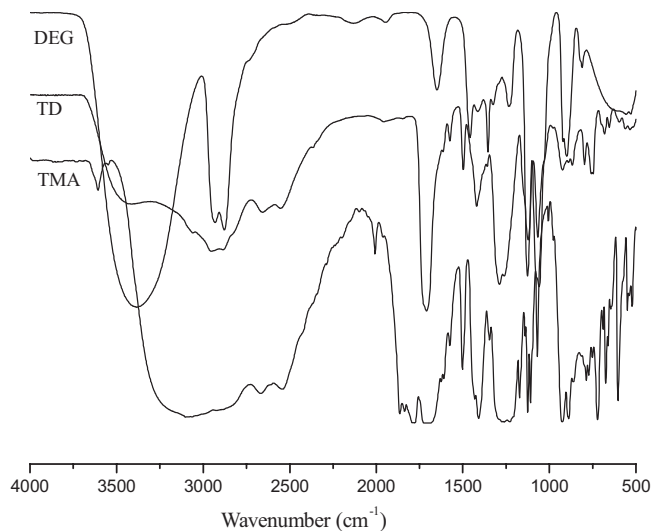


Fig. 3. FT-IR spectra of TMA, DEG and AB₂ monomer.

The ¹H-NMR spectrum of the AB₂ monomer in (CD₃)₂SO (Fig. 5) reflects C₃-H resonance peaks at $\delta = 7.7\sim 7.8$ ppm, C₆-H and C₅-H resonance peaks at $\delta = 8.1\sim 8.3$ ppm of phenyl hydrogen proton, -CH₂- ($\delta = 3.5\sim 4.38$ ppm), -OH ($\delta = 3.4$ ppm) and -COOH ($\delta = 13.52$ ppm) groups (16).

3.2 Characterization of Carboxyl-End Hyperbranched Polymers (HTD)

The ¹H-NMR spectra of the HTD obtained by the pseudo-one step method are shown in Figure 6. Comparing the ¹H-NMR spectrum of the AB₂ monomer with the ¹H-NMR spectra of the HTD, the hydrogen proton of -OH group at 3.4 ppm disappeared and the hydrogen pro-

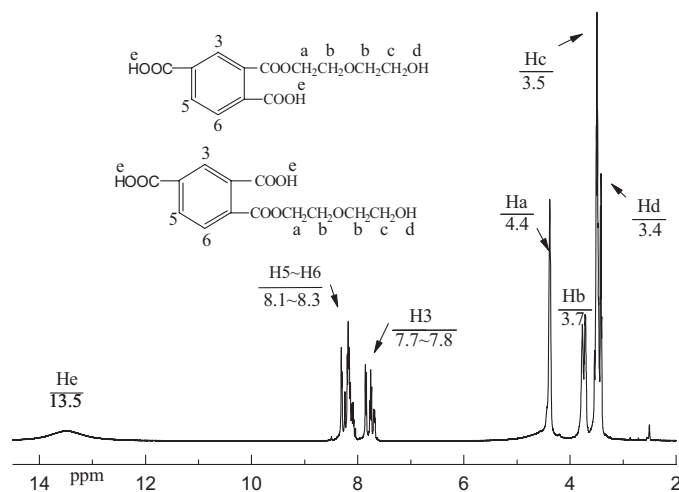


Fig. 5. ¹H-NMR spectra of the HTD and the AB₂ monomer.

ton of -COOCH₂- group at 4.38 ppm become stronger, furthermore, the peak area of 4.38 ppm is almost equal to that of 3.7 ppm. This information confirms that the hydroxy group of the compounds has been reacted completely. The weak peaks at 2.5~3.0 ppm may be attributed to the hydrogen protons of the -OCH₂CH₂CH₂CH₃ group from the TBT catalyst and (CD₃)₂SO. The weak peaks at 3.5 ppm may be attributed to the H* hydrogen proton of -COOCH*₂CH₂CH₂CH₃ which are formed from the reaction between carboxyl-end of HTD and HOCH₂CH₂CH₂CH₃ that resulted from partial hydrolysis of TBT. The existence of the -COOCH*₂CH₂CH₂CH₃ group also results in a decrease of the acid value of HTD, so the experimental acid value is lower than the theoretical acid value of HTD-3 and HTD-4 from Table 1.

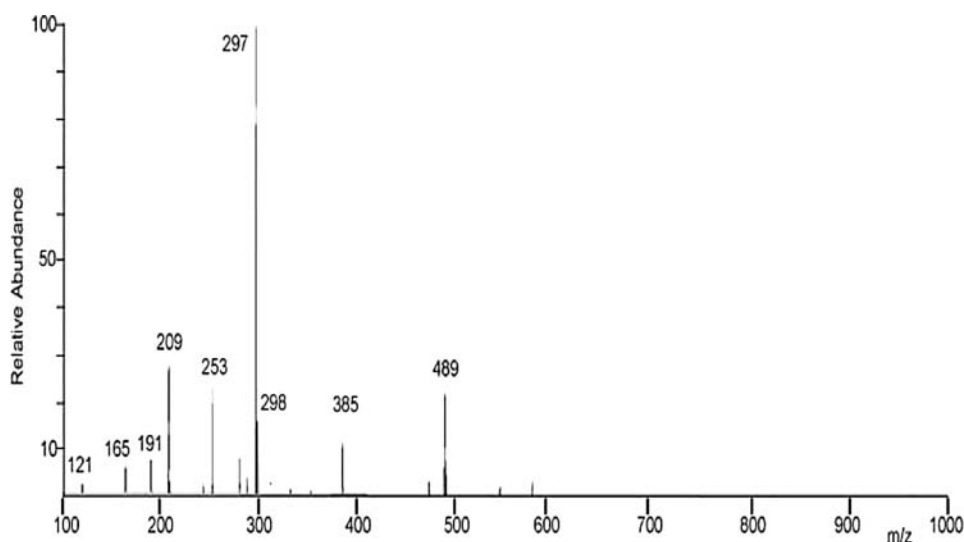


Fig. 4. Fast atom bombardment ion mass spectrum of AB₂ monomer.

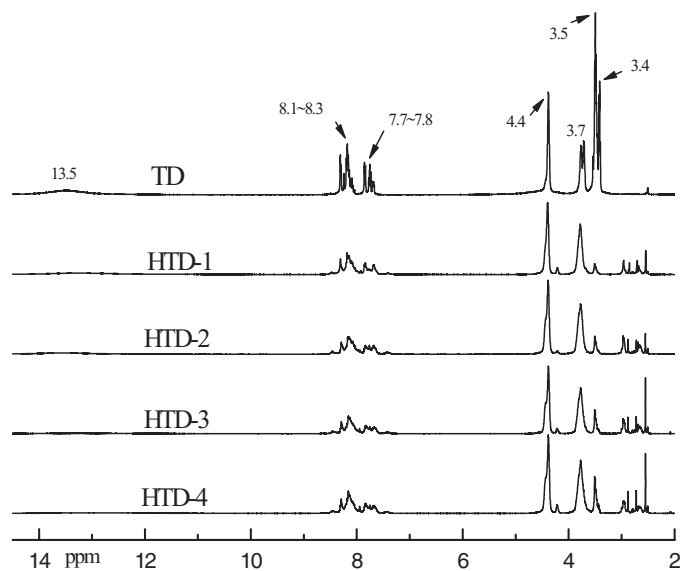


Fig. 6. $^1\text{H-NMR}$ spectra of the HTD and the AB_2 monomer.

According to the polymerization mechanism of the HTD and the definition of the DB (7,17,18), the resulting HTD contains the following units (Fig. 7): (1) branched units (N_b), (2) linear units (N_L) and (3) terminal units (N_t).

The DB is the ratio of branched and terminal units to total units, i.e.,

$$DB = (N_b + N_t) / (N_b + N_t + N_L) \quad (1)$$

NMR spectroscopy represents an important tool for the characterization of hyperbranched polymers since detailed analysis of the spectra permits to extracting of information on both the degree of polymerization and the extent of branching. Therefore, it is appropriate to discuss the results of this method in detail. The hydrogen protons of phenyl demonstrate different chemical shift according to their structure. The proton signals of $\text{C}_3\text{-H}$ appear at 7.7~7.8 ppm, and those of $\text{C}_5\text{-H}$ and $\text{C}_6\text{-H}$ appear between 8.1 and 8.3 ppm (Fig. 6). The chemical shift of $\text{C}_3\text{-H}$ protons depends on the substitution groups of neighboring carbon atom (C_2 and C_4). Therefore, the proton signals of $\text{C}_3\text{-H}$ may be used to characterize the degree of branching of HTD according to the difference of substitution groups

Table 1. Properties of the carboxyl-end hyperbranched polymers (HTD)

Polymer No.	HTD-1	HTD-2	HTD-3	HTD-4
Experimental acid value, mg KOH/g	320.46	247.11	219.72	209.47
p_B	0.333	0.428	0.469	0.485
x	1/3	1/9	1/21	1/45
\bar{X}_n	3.00	8.92	22.69	48.50
\bar{X}_w	3.28	10.00	42.28	154.34
$\text{PDI} = \bar{X}_w / \bar{X}_n$	1.09	1.12	1.86	3.16
Molecular weight from GPC	1228.00	1397.00	1708.00	2875.00
PDI from GPC	1.03	1.06	1.10	1.63
Theoretical molecular weight	1050.84	2732.28	6095.16	12820.92
\bar{M}_n	1050.84	2709.86	6568.77	13801.76

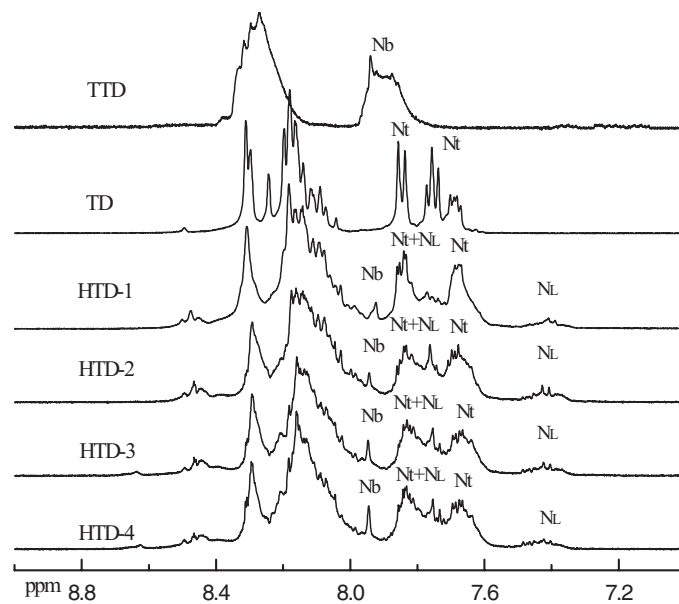


Fig. 8. $^1\text{H-NMR}$ spectra of TTD, TD and HTD- n ($n=1,2,3,4$) between 7.2~8.9 ppm.

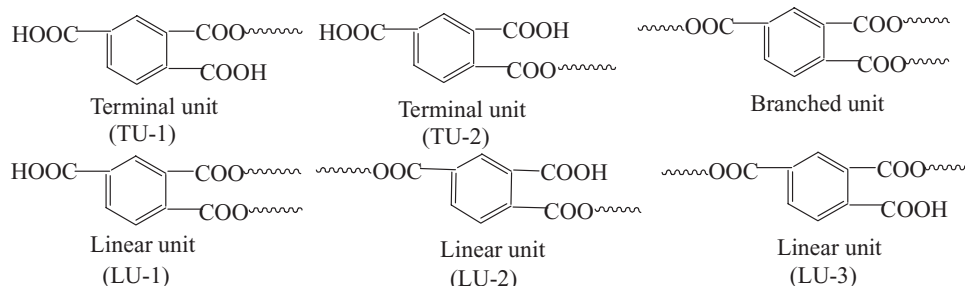


Fig. 7. Structure of terminal, branched and linear units.

from the three structure units at C₂ and C₄ atoms of phenyl resulting. The chemical structure of the model compound TTD is similar to that of the branching unit of HTD (Fig. 8). Moreover, the chemical structure of TD (AB₂ monomer) is similar to that of the terminal unit of HTD, and all the C₃-H proton signals of TD and the terminal unit of HTD

number-average molecular weight. Explicit relationships about theoretical average degrees of polymerization and average molecular weights are established in AB_f+B_g type polymerization by the "Recursive Probability Approach" (20). In such a case, \bar{X}_w , \bar{X}_n , \bar{M}_n and p_A satisfy the following relationships:

$$\bar{X}_w = 1 + \frac{2p_A(f+gx)[f(1-p_A)+gx] + p_A^2[f(f-1)+gx(g-1)]}{(1+x)[f(1-p_A)+gx]^2} \quad (2)$$

$$\bar{M}_n = M_0 + 18 + \bar{X}_n(M_{AB2} - 18) \quad (\bar{X}_n \geq 3) \quad (3)$$

appear between 7.67~7.77 ppm and 7.81~7.85 ppm, with two multiple peaks from two chemical structures (TU-1 and TU-2 in Fig. 7). The peak area ratio of 7.67~7.77 ppm to 7.81~7.85 ppm should remain constant since all B-groups of TD-1 and TD-1 are equally reactive (18,19). While there are three linear units LU-1, LU-2 and LU-3, the chemical structure of LU-1 should be similar to that of LU-2, the C₃-H proton signals of linear units of HTD should have two multiple peaks. The peak area of a linear unit may be obtained by ¹H-NMR-minus spectrum technology (16), i.e., the peak area of a linear unit is equal to the total peak area minus the peak area of branching and terminal units. According to the above analysis, calculation data for the different chemical structure units were obtained and are shown in Table 2.

The molecular weight is very important data for the HBP. The polycondensation between the hydroxy group and carboxy group and the acid value of the HTD can be used to calculate the degree of polymerization and further the

There, \bar{X}_w and \bar{X}_n refer to the mass-average degree and number-average degree of polymerization, respectively. \bar{M}_n refers to the number-average molecular weight. p_A refers to the fraction of A groups that have reacted, and x refers to the ratio of the core B_g to AB₂ monomer. M_0 and M_{AB2} refer to the molecular weight of B_g and AB₂ monomers, respectively.

The acid value (A_v) refers to the milligram number of the KOH needed to neutralize 1 g of resin. In the system, p_B , A_v and \bar{X}_n satisfy the following relationships:

$$A_v = \frac{56100(3 + \bar{X}_n)}{192.12 + 298.24\bar{X}_n - 18(\bar{X}_n - 1)} \quad (4)$$

$$p_B = \frac{\bar{X}_n}{2\bar{X}_n + 3} \quad (5)$$

Therefore, the relationship of A_v and p_B satisfies the following relationship:

$$p_B = \frac{168300 - 210.12A_v}{168300 - 210.12A_v} \quad (6)$$

In the system, since $p_A = fp_B$, $f = 2$, $g = 3$, from Equation 2 to Equation 6, the molecular weight may be calculated and shown in Table 1. Table 1 illustrates that the \bar{M}_n of HTD obtained by "Recursive Probability Approach" are almost equal to their theoretical molecular weight. The relationship also confirms that the hydroxyl group of the compounds were reacted completely, and the results are consistent with the disappearance of the hydroxyl proton signal peak of the HTD at 3.4 ppm in Figure 6.

3.3 Characterization of HTDE

The preparation mechanism of the HTDE comprised of the ring-open reaction between the HTD and ECH and the ring-close reaction of dehydrohalogenation. Therefore, the molecular weight of HTDE is decided by the corresponding molecular weight of the HTD and the number of their epoxy group. The qualitative analysis of the epoxy group is shown in Figure 9. From Figure 9, all absorption peaks of the phenyl at 1634, 1574 and 1450 cm⁻¹, the epoxy group at 1244, 909 and 854 cm⁻¹ and the -COO- group at 1727 cm⁻¹ are observed (16). The quantitative analysis of the epoxy group (Table 3) was measured by a titration method with hydrochloric acid-acetone solution, and other properties also are shown in Table 3.

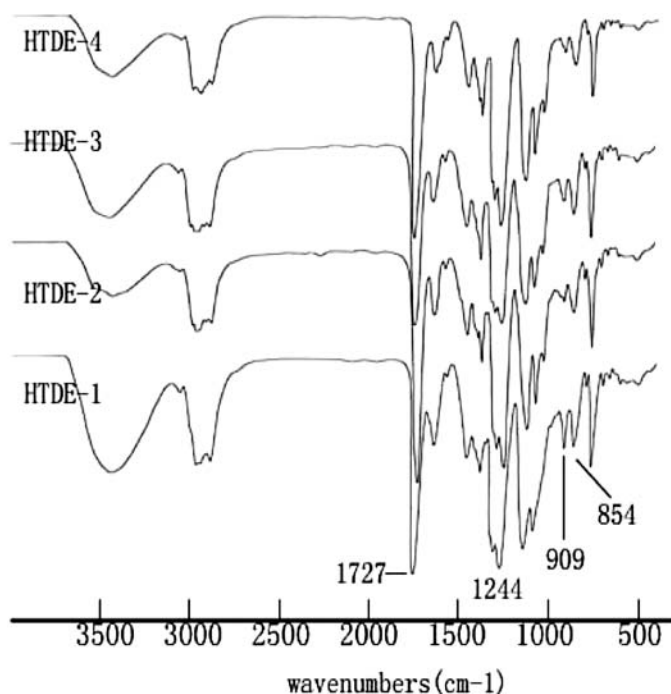


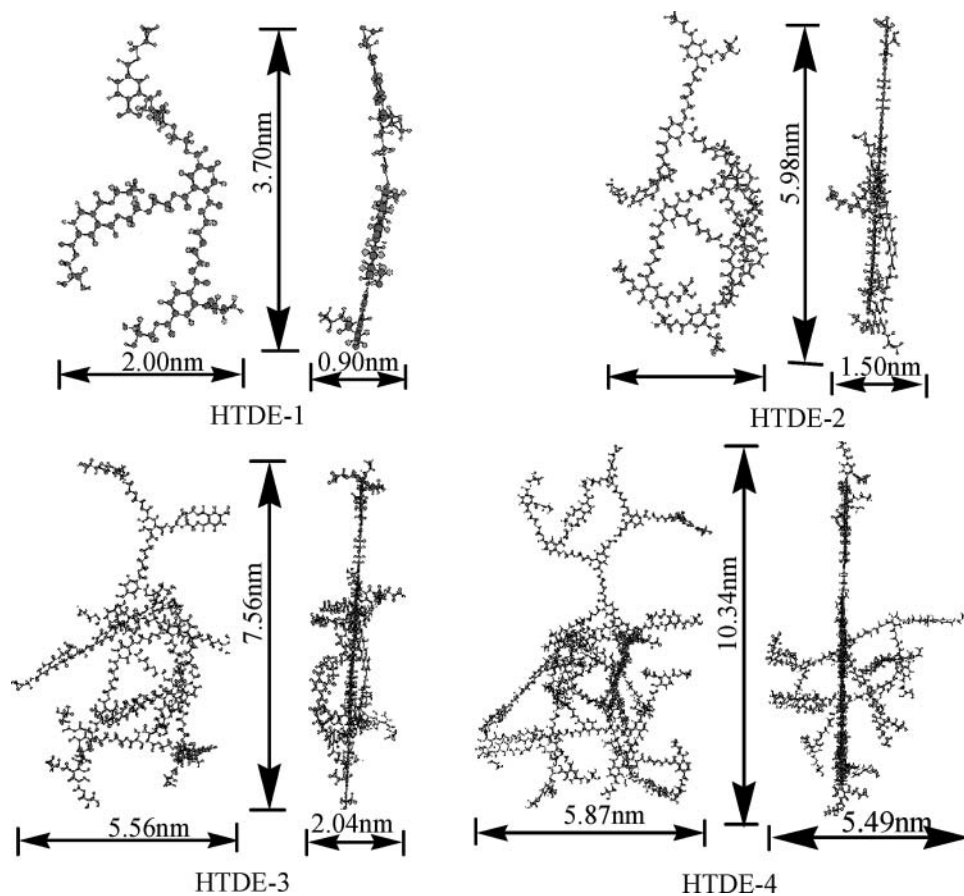
Fig. 9. FT-IR spectra of the HTDE-n (n=1,2,3,4).

Table 2. DB of HTD-1, HTD-2, HTD-3 and HTD-4 and their calculation data

δ (ppm)	7.40~7.43 N_L	7.67~7.77 N_t	7.81~7.85 N_t	7.81~7.85 N_L	7.94 N_b	DB
TTD					1.00	
TD		0.59	0.41			
HTD-1	0.05	0.35	0.24	0.30	0.06	0.65
HTD-2	0.09	0.37	0.26	0.20	0.08	0.71
HTD-3	0.08	0.33	0.23	0.26	0.10	0.66
HTD-4	0.07	0.32	0.22	0.31	0.08	0.62

Table 3. Properties of hyperbranched epoxy resins HTDE

HTDE	Molecular weight from GPC	Theoretical molecular weight	PDI from GPC	Epoxy equivalent weight g/mol	Ring-close degree, %	Viscosity, cp
HTDE-1	1744	1387	1.11	312.5	73.9	550
HTDE-2	2637	3404	2.06	400.0	71.0	700
HTDE-3	3845	7439	1.88	454.5	68.1	500
HTDE-4	3974	15509	1.83	526.3	61.5	350

**Fig. 10.** Simulation structure and shape of HTDE- n ($n = 1,2,3,4$).

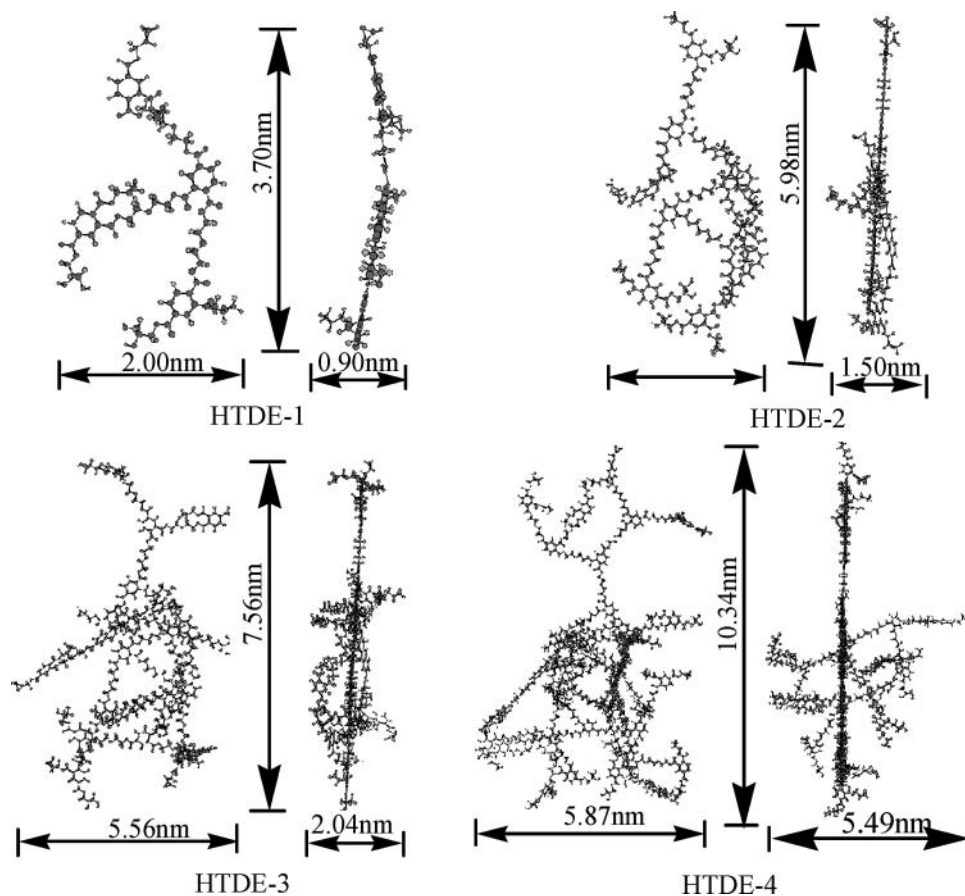


Fig. 11. Effect of the content and molecular weight of HTDE on the viscosity of hybrid resin.

The main characteristics of the HTDE are the low epoxy equivalent weight and low viscosity from Table 3. Low epoxy equivalent weight can increase the curing rate and crosslinking density. Low viscosity property of the HTDE means that it can be used without organic solvent. Moreover, the viscosity of the HTDE has a maximum with increasing the generation or molecular weight, and the minimum viscosity of the HTDE-4 is only 350 cp, which is among the lowest reported value. The relationship between the viscosity and the generation of the HTDE confirms that the structure of the HTDE is hyperbranched and that it has a high DB (21,22). The low viscosity is attributed to the lesser hydromechanical volume and the high DB of the HBP. For the same molecular weight, the viscosity of HBP decreases with decreasing hydromechanical volume and increasing DB (1,22).

Figure 10 shows that molecular simulation sizes of all four kinds of hyperbranched epoxy resins lie in the nanometer range and the thickness of some sections is not more than 1nm (23). Moreover, there are many molecular level cavities in the HTDE structure, and the nanometer size and ellipsoid-like shape of HTDE also would result in lower hydromechanical volume than the stick-like shape of linear polymers. The highly branched structure also results in a

low amount of intra- and intermolecular entanglements and affords a relative low viscosity.

Hyperbranched epoxy resin HTDE were added into bisphenol-A epoxy resin (DGEBA), and the effect of the content and molecular weight of HTDE on the viscosity of HTDE/DGEBA hybrid resin was studied and the results shown in Figure 11.

From Figure 11, the viscosity of HTDE/DGEBA hybrid resins decrease sharply with increase of hyperbranched epoxy resin HTDE. The viscosity of hybrid resins containing 15~20 wt% HTDE is only 3000~4000 cp which is about (1/5~1/6) times of that of DGEBA (≈ 15600 cp).

Therefore, the functional hyperbranched epoxy resin can be used as a reactive thinner in the epoxy resin field, and the characteristics of the HTDE hopefully may be applied widely to thermosetting resin fields, such as environmental resin or no-solvent resin.

4 Conclusions

The TMA and DEG monomers can be successfully used to synthesize carboxyl-end hyperbranched polymers (HTD) by a pseudo-one step method. The low viscosity

and low epoxy equivalent weight hyperbranched epoxy resin (HTDE) also can be successfully prepared by the reaction between carboxyl-end hyperbranched polymers and ECH.

FT-IR, ZAB and $^1\text{H-NMR}$ measurements confirmed that the reaction of TMA and DEG. The DB of HTD was calculated by $^1\text{H NMR}$ -minus spectrum technology. The number-average degree of polymerization and the molecular weight of the HTD were calculated using a "Recursive Probability Approach". Characteristics of HTDE, including molecular size, shape, epoxy equivalent weight and viscosity were obtained by molecular simulation technology and corresponding test methods.

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