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Molecular Simulation of Hyperbranched Polyester

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ABSTRACT

A new types of hyperbranched polyester was synthesized by the 2,2-bis(hydroxymethyl) propionic acid as an AB_2-type monomer and glycerol as the core moiety. Molecular weights were confirmed by Gel Permeation Chromatography. Acid values were titrated by KOH. The hydroxy value was obtained by titration. Furthermore, we calculate logarithmic value of acid value, hydroxy value, and molecular weight, respectively, and the simulation model curves were obtained. Based on the simulation model curves, we establish the empirical equation of the relationship of molecular weight, acid value and hydroxy value.

Indexing terms/Keywords

Hyperbranched; Molecular ; Acid value; Hydroxy value; Equation

Academic Discipline And Sub-Disciplines

Macromolecular Science

SUBJECT CLASSIFICATION

Hyperbranched Polyesters

TYPE (METHOD/APPROACH)

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1. INTRODUCTION

Recently, dendritic polymer including dendrimers and hyperbranched polymer have received increasing attention due to their unique chemical and physical properties. Compared to traditional liner polymer, they have very large numbers of branch points and end groups, low viscosity and excellent solubility[1-6], such as polyesters[7-8], polyamids[9], polysioxysilanes[10] which have been report in past decades.Dendritic polymers mainly include dendrimers and hyperbranched polymers[11]. Dendritic polymer generally synthesized using a multi-step procedure[12-13], however, it is difficult to separate and purity the products. Hyperbranched polymers less regular structure and have more random branches relative to dendrimers, which can be synthesized by simple one-pot polymerization strategies such as polycondensation[14-17], living polymerization (atom transfer radical polymerization[18-19], reversible addition-fragmentation-chain transfer[20]. However, many physical properties of hyperbranched macromolecules have not yet been investigated completely[21].Studies on molecular modeling through atomistic simulations would allow us to know some of their properties before we find their applications.

In this paper, a one-pot synthesis of hyperbranched polyesters by polycondensation using 2,2-bis(hydroxymethyl) propionic acid as an AB_2-type monomerand and glycerol as the core moiety, is presented. Then acid values were titrated by KOH. The hydroxy values were determined by acetylation of hydroxide groups with phthalic anhydride, which was hydroysed. This paper mainly study on the relationship between acid value, hydroxy value and molecular weight.

2. EXPERIMMENTAL

2.1Materials

Dimethylol propionic acid,Glycerol, potassium hydroxide, pyridine(AR), phthalic anhydride, phenolphthalein, and potassium hydrogen phthalate were used as received

2.2 Synthesis of hyperbranched polyester

The reaction was conducted in a 1000mL reaction kettle equipped with a nitrogen inlet tube, a reflux condenser, heating device and a vacuum device. The mixture of glycerol and 2,2-bis(hydroxymethyl) propionic acid (DMPA) was add to the reaction kettle, The reaction mixture was slowly heated to190℃. After the reactants were completely melted, The temperature was maintained between190℃ and 200℃ with the continuous nitrogen flow for about 36h. We monitored the reaction periodically by determining the acid value and stopped reaction until the acid was stabilization. Then keep in vacuum for a certain time.

2.3 Characterization

2.3.1 Acid value

Acid value was determined by titrated by KOH using phenolphthalein as the indicator. In a typical titration procedure, milligrams KOH were required to neutralize free acids in 1g hyperbranched polyester. sample was dissolved in ethanol and ether and neutralized with KOH.The acid value, i.e., the total concentration of the carboxylic groups, was measured by diluting about 1g of the sample to 60 cm^3 neutralized distilled water, then the sample was titrated with 0.8185 mol/L KOH.

2.3.2 Hydroxy value

The hydroxy value is usually determined by titration methods. The hydroxy value was determined by acetylation of the hydroxide groups with phthalic anhydride, which was hydrolysed. The excess acetic acid and the free acid groups in the reaction media were titrated with KOH. The hydroxy value was determined with the acid value according to the ISO standard[23] .

2.3.3 Gel Permeation Chromatography(GPC)

Weight-average molecular weight (Mw), number average molecular weight (Mn) and dispersity (D= Mw/Mn) were obtained using GPC instrument. GPC measurements were carried out using Waters 2414 Series (Japan) with a refractive index detector to determine the molecular weight of the polymer solutions. Samples were prepared in tetrahydrofuran (THF) solvent at a 3 mg/mL concentration. The columns were eluted using THF and calibrated with poly(methyl methacrylate) standards. All calibrations and analysis were performed at 40℃ and the flow rate of the mobile phase was kept at 0.4 mL/min.

2.3.4 NMR

The ^{1}H and^{13}C NMR spectra of the hyperbranched polyesters were recorded on Bruker UXNMR 300 MHz spectrometers in dimethyl sulfoxide d_6 (DMSO-d_6) at ambient temperature.

3 RESULTS AND DISCUSSION

3.1 The acid value, hydroxy value and the number average molecular weight

Different hypherbranched polyesters were synthesis in different conditions, then acid value and hydroxy value was titrated by KOH and number average molecular weight (Mn) was measured by GPC .The dates were shown in the Table 1

Table1 The acid value, hydroxy value and Mn of as-obtained products

experimental	Acid value	Hydroxy value	Mn
1	26.68	120.92	1517
2	38.55	112.72	1376
3	50.54	108.25	1215
4	22.70	153.85	1171
5	20.71	159.03	1460
6	18.58	168.00	1489
7	25.59	173.09	1693
8	33.62	170.64	1691
9	29.92	203.09	1189
10	26.72	254.60	1187

3.1.1 The number average molecular weight (Mn) relationship with acid value

Acid value, Logarithm of acid value, Mn and Logarithm of Mn was listed in the Table 2. According to the data of Table 2 we deduced equations and model curves. Figure 1 showed the model curve of Mn and Logarithm of acid value. The model curve of acid value and Logarithm of Mn was showed on Figure 2. Both the equation of Figure 1 and Figure 2 showed their related coefficient was low, so the two equation are unreasonable.

Table 2 the result of acid value, Logarithm of acid value, Mn and Logarithm of Mn

Acid value	Logarithm of acid value	Mn	Logarithm of Mn
18.58	1.269045710	1489	3.172894698
20.71	1.316180099	1460	3.164352856
22.70	1.356025857	1171	3.068556895
25.59	1.408070286	1693	3.228656958
26.68	1.426185825	1517	3.180985581
26.72	1.426836454	1187	3.074450719
29.92	1.475961589	1189	3.075181855
33.62	1.526597709	1691	3.228143608
38.55	1.586024382	1376	3.138618434
50.54	1.703635238	1215	3.084576278

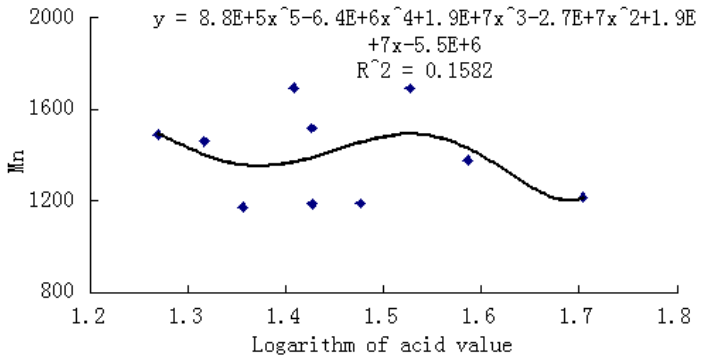

Fig 1: The model curve and equation of logarithm of acid value and M_n

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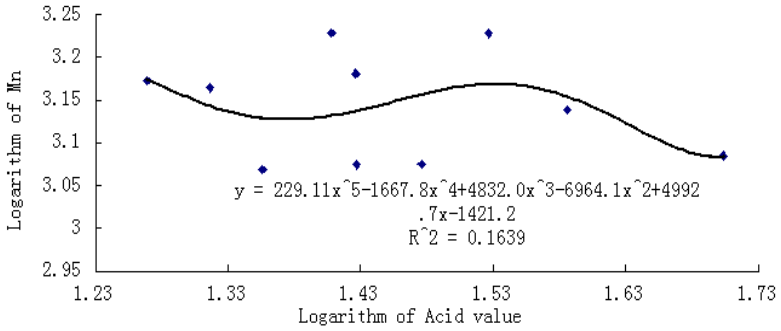

Fig 2: The model curve and equation of Logarithm of acid value and Logarithm of M_n

3.1.2 The number average molecular weight (M_n) relationship with hydroxy value

Hydroxy value, Logarithm of hydroxy value, M_n and logarithm of M_n was listed in Table3.The model curve and calculate equations were on the Fig 3 and Fig 4. Fig 3 showed the model curve and equation of Logarithm of hydroxy value and M_n. Its related coefficient was 0.8754. The model curve and equation of Logarithm of hydroxy value and Logarithm of M_n was shown in Fig 4, its related coefficient was 0.9137 which was higher than Fig 3. Consequently, the model curve and equation of Logarithm of hydroxy value and logarithm of M_n was more reliable than logarithm of hydroxy value and M_n.

Table3: The data of hydroxy value , Logarithm of hydroxy value and M_n

Hydroxy value	Logarithm of hydroxy value	M_n	Logarithm of M_n
120.92	2.034427905	1215	3.180985581
112.72	2.052000980	1376	3.138618434
108.25	2.082498139	1517	3.084576278
153.85	2.187097501	1171	3.068556895
159.03	2.201479059	1460	3.164352856
168.00	2.225309282	1489	3.172894698
173.09	2.232080842	1691	3.228656958
170.64	2.238271978	1693	3.228143608
203.09	2.30768854	1140	3.075181855
254.60	2.405858399	1187	3.074450719

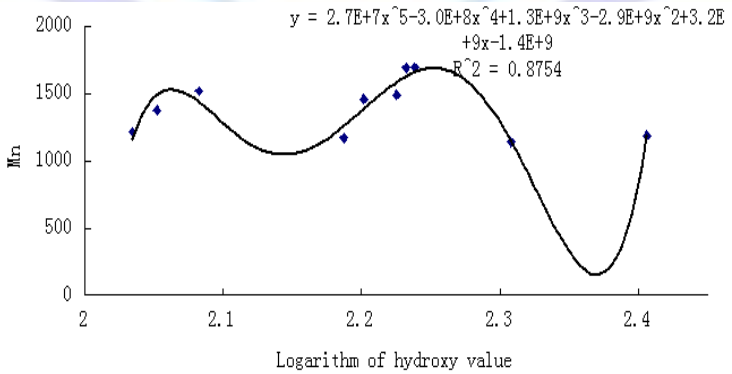

Fig 3: The model curve and equation of logarithm of hydroxy value and M_n

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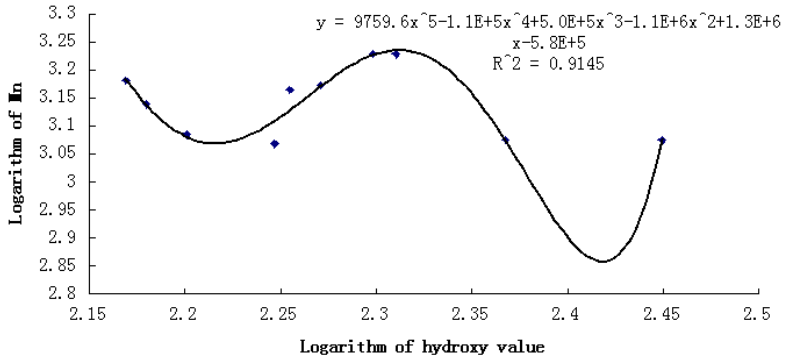

Fig 4: The model curve and equation of logarithm of hydroxy value and logarithm of M_n

3.1.3 The number average molecular weight (M_n) relationship with the correct hydroxy value

The correct hydroxy value and Logarithm of the correct hydroxy value and M_n was listed in table 4.The model curve and equation were shown on the Fig 5 and Fig 6, respectively.

Table 4 The result of the correct hydroxy value, Logarithm of the correct hydroxy value and Mn

The correct hydroxy value	Logarithm of the correct hydroxy value	Mn	Logarithm of the Mn
147.60	2.169086357	1517	3.180985581
151.27	2.179752807	1376	3.138618434
158.79	2.200823149	1215	3.084576278
176.55	2.246867722	1171	3.068556895
179.74	2.254644737	1460	3.164352856
186.58	2.270865089	1489	3.172894698
198.68	2.298154151	1693	3.228656958
204.26	2.310183328	1691	3.228143608
233.01	2.36737456	1189	3.075181855
281.32	2.449200609	1187	3.074450719

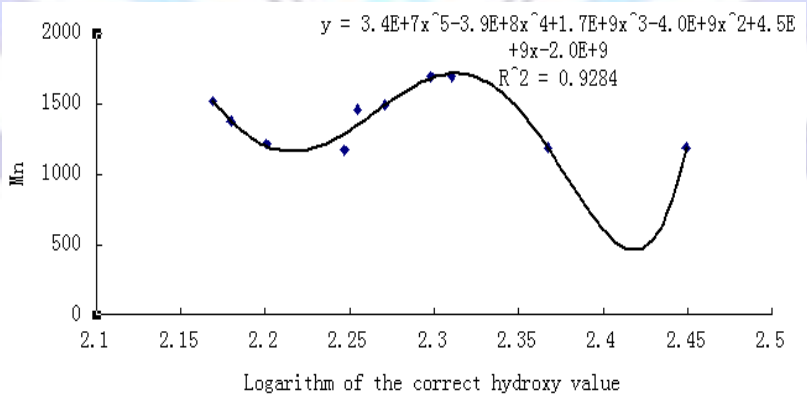

Fig 5: The model curve and equation of logarithm of the correct hydroxy value and M_n

Fig 5 showed the model curve and equation of Logarithm of the correct hydroxy value and Mn, its equation related coefficient R^2 was 0.9284 and the value was higher than the Fig 6 equation related coefficient R^2 i0.9145, the related coefficient of Fig 6 was smaller than Fig 5, but It was higher to Fig 4. Therefore, the model curve and equation of the correct hydroxy value is reasonable. The model curve and equation of Logarithm of the correct hydroxy value and Logarithm of M_n is smallest of all.

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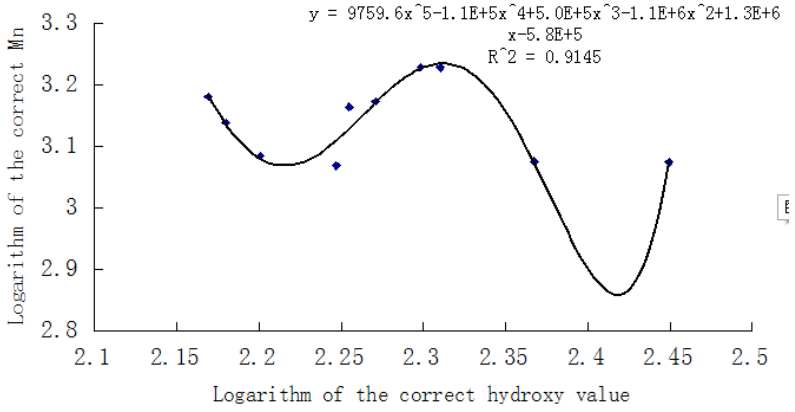

Fig 6: The model curve and equation of logarithm of the correct hydroxy value and logarithm of M_n

3.1.4 NMR

The ^{1}H NMR and^{13}C NMR spectra of the hyperbranched polyester were respectively showed in Fig 7 and Fig 8.

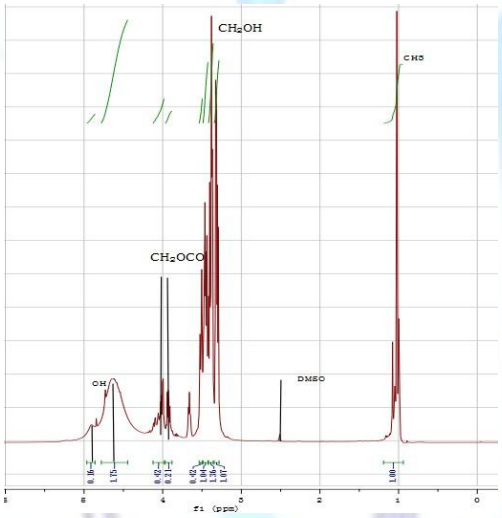

Fig 7: The ^{1}H NMR spectrum of the hyperbranched polyesters

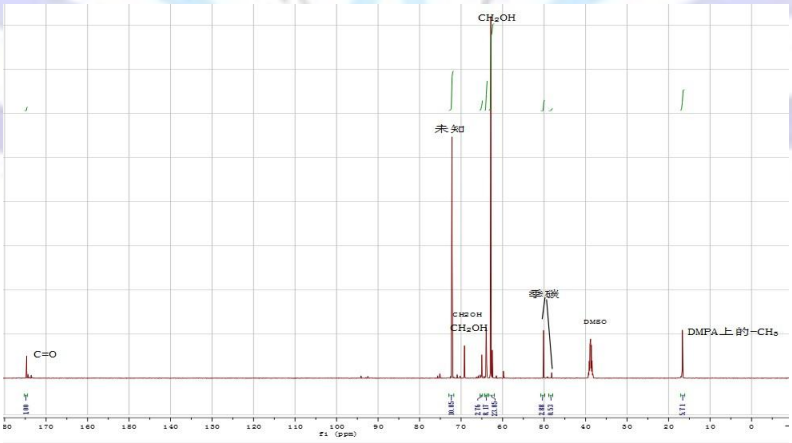

Fig 8 : The ^{13}C NMR spectrum of the hyperbranched polyesters

4 CONCLUSION

Above all, the model curve and equation of Logarithm of the correct hydroxy value and logarithm of Mn is optimum equation to calculate the Mn by acid value and hydroxy value. It's equation is $Mn=9756.6x^5+8x^4+9x^3+9x^2+9x-18$,(x=acid value y=hydroxy value) It's related coefficient R^2 is 0.9284.

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