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\textsubscript{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)

Synthesis, Characterization and Molecular Simulation
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 linear 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], polysioxyasilanes[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 monomer 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 hydrolysed. This paper mainly study on the relationship between acid value, hydroxy value and molecular weight.

2. EXPERIMENTAL

2.1 Materials

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 added to the reaction kettle. The reaction mixture was slowly heated to 190°C. After the reactants were completely melted. The temperature was maintained between 190°C and 200°C 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 of 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 0.0185 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°C and the flow rate of the mobile phase was kept at 0.4 mL/min.

2.3.4 NMR

The 1H and 13C 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 hyperbranched 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.
Table 1: 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   | 3.172894689     |
| 20.71      | 1.316180099            | 1460   | 3.164352856     |
| 22.70      | 1.356025857            | 1171   | 3.068556895     |
| 25.59      | 1.408070286            | 1693   | 3.228659658     |
| 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 Mn.
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 Table 3. 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 $M_n$.

Table 3: 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        | 2.0344427905              | 1215  | 3.180985581        |
| 112.72        | 2.052000980               | 1376  | 3.138618434        |
| 108.25        | 2.082498199               | 1517  | 3.08457278         |
| 153.85        | 2.187097501               | 1171  | 3.068556895        |
| 159.03        | 2.220170598               | 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        | 2.40588399                | 1187  | 3.074450719        |

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

| The correct hydroxy value | Logarithm of the correct hydroxy value | $M_n$ | Logarithm of the $M_n$ |
|---------------------------|----------------------------------------|------|----------------------|
| 147.60                    | 2.169086357                            | 1517 | 3.180985581          |
| 151.27                    | 2.179752807                            | 1376 | 3.138618434          |
| 158.79                    | 2.200823149                            | 1215 | 3.084572678          |
| 176.55                    | 2.246867722                            | 1171 | 3.068556895          |
| 179.74                    | 2.254644737                            | 1460 | 3.164352856          |
| 186.58                    | 2.27065089                             | 1489 | 3.172894698          |
| 198.68                    | 2.298154151                            | 1693 | 3.22656958           |
| 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 $M_n$, 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.
Fig 6: The model curve and equation of logarithm of the correct hydroxy value and logarithm of Mn

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.

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 $\text{Mn}=9756.6x^3+8x^4+9x^5+9x^6+9x^7+1.3E+6$ ($x=\text{acid value}, y=\text{hydroxy value}$) It's related coefficient $R^2$ is 0.9284.
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