Quantitative dependence of crystallinity on degree of branching for hyperbranched poly[3-ethyl-3-(hydroxymethyl)oxetane]

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**Abstract.** A series of hyperbranched poly[3-ethyl-3-(hydroxymethyl)oxetane] samples with various degrees of branching (DB) were adopted to investigate the relationship between crystallinity and DB. The relative degree of crystallization (DC) and DB were determined by x-ray diffraction (XRD) and \(^{13}\)C nuclear magnetic resonance (\(^{13}\)C-NMR) measurements, respectively. The corresponding plot of DC versus DB shows quantitative dependence of the crystallinity on DB for the polyether.

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1. Introduction

The degree of branching (DB) of a polymer is a measurement on the content of branches in the molecular structures [1], which exerts a tremendous influence on the properties of polymers. So far, it has been qualitatively known that the higher the DB, the lower the crystallinity for semi-crystalline polymers. However, the quantitative dependence of the crystallinity on DB of polymers has not yet been systematically studied due to the lack of serial samples with various DBs and a similar molar mass. It is difficult to control DB of polymers in a conventional polymerization. Only few macromolecular isomers with different DBs are available, such as high-density polyethylene (HDPE) made from coordinate polymerization and low-density polyethylene (LDPE) generated from the free radical polymerization, which are insufficient for the systematic investigation of the quantitative relationship between the crystallinity and DB of a polymer. Fortunately, some authors reported that they have prepared poly[3-methyl/ethyl-3-(hydroxyethyl)oxetane] with different DBs and a similar molar mass, and they have preliminarily found that poly[3-methyl/ethyl-3-(hydroxyethyl)oxetane] with a lower DB possess some crystalline properties. For example, Vandenberg and co-workers [2, 3] prepared the completely linear poly[3-ethyl-3-(hydroxyethyl)oxetane] (PEHO), and reported that it was a highly crystalline polymer with a crystalline melting point of 175 or 163 °C. Recently, Hult and co-workers synthesized the hyperbranched PEHOs with various DBs by controlling the conversion of monomers [4], and they found that PEHOs with a lower DB were semi-crystalline polymers with a melting transition between 100 and 130 °C, but PEHOs having a higher DB were amorphous [5]. In a previous work of this laboratory [6], hyperbranched poly[3-methyl-3-(hydroxyethyl)oxetane]s with different DBs were obtained, and the crystalline properties of different samples were measured by differential scanning calorimetry (DSC).

In spite of the progress in the qualitative understanding of the crystalline properties of hyperbranched polymers, no quantitative works have been conducted so far. In the present work, we investigated for the first time the quantitative relationship between the crystallinity and DB of hyperbranched PEHO.

2. Experiment

2.1. Materials

The samples of PEHO, a white powder solid, were obtained according to procedures in the literature [6, 7].

2.2. Characterizations

The hydroxyl value of resulting polymers was measured by titration (acetic anhydride/pyridine method). The PEHO samples were end-capped with benzoyl chloride for determining the molecular weights, and NMR spectra show that few hydroxyl groups exist. Size exclusion chromatography (SEC) in tetrahydrofuran (THF) was performed on a Perkin Elmer Series 200 system at 25 °C (100 µl injection column, PL gel (10 µm) 300 mm × 7.5 mm mixed-B columns, polystyrene calibration), and the flow speed was 1.0 ml min⁻¹. The molecular weights listed in

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Table 1. The characterizations of PEHOs.

| Sample | SEC Mn | PD | Hydroxyl value | DB\(^a\) (%) | D unit content\(^b\) (%) | T unit content\(^c\) (%) | L unit content\(^d\) (%) | Relative DC (%) |
|--------|--------|----|----------------|-------------|-----------------|----------------|----------------|---------------|
| 1      | 5756   | 1.45 | 470           | 5.6         | 2               | 3.6            | 94.4           | 31            |
| 2      | 5538   | 1.53 | 468           | 7.3         | 2.5             | 4.8            | 92.7           | 27            |
| 3      | 5275   | 1.51 | 461           | 13          | 4.5             | 8.5            | 87             | 12            |
| 4      | 4647   | 1.69 | 451           | 25          | 9               | 16             | 75             | 3             |
| 5      | 5536   | 1.57 | 459           | 40          | 15              | 25             | 60             | 0             |
| 6      | 4798   | 1.62 | 442           | 45          | 17              | 28             | 55             | 0             |

\(^a\) DB = (D + T)/(D + L + T) \[1\].
\(^b\) D unit content = D/(D + L + T).
\(^c\) T unit content = T/(D + L + T).
\(^d\) L unit content = 1 − DB.

Table 1 were calculated using the following formula:

\[ M_n(\text{PEHO}) = M_n(\text{end-capped}) \frac{M_n(1)}{[M_n(1) + M_n(2) - M_n(3)]}, \]  

where \(M_n(\text{end-capped})\) represents the molar mass of PEHO end-capped with benzoyl chloride, \(M_n(1)\), \(M_n(2)\) and \(M_n(3)\) stand for the molecular weights of 3-ethyl-3-(hydroxymethyl)oxetane, benzoyl chloride and HCl, respectively. DB values were determined by \(^{13}\)C-NMR and all NMR measurements were performed on a Varian MERCURY plus-400 spectrometer at 20 °C. DMSO-\(d_6\) was used as the solvent. XRD patterns were taken with a Rigaku III Dmax 2500 apparatus using Cu K\(\alpha\) radiation and the voltage and the current were set to 25 KV and 25 mA, respectively. Data were collected at the rate of 4° min\(^{-1}\) with a step size of 0.02° over the range 2\(\theta\) = 3 – 50°. Thermal analyses were carried out on a Perkin Elmer Pyris-1 Series DSC under a constant flow of nitrogen and the heating rate was 10 °C min\(^{-1}\).

3. Results and discussion

The PEHO samples with various DBs were prepared by the cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane (EHO) under different reaction conditions \[6, 7\] (scheme 1).

The samples were characterized by \(^{13}\)C-NMR, SEC, XRD and DSC measurements respectively. A typical \(^{13}\)C-NMR spectrum of PEHO (for sample 6) and the assignments are given in figure 1. In this spectrum, three peaks near 22.50 ppm are attributed to the carbon atoms of the methylene in ethyl groups of the dendritic unit (D), the linear unit (L) and the terminal unit (T), respectively. The peaks near 43.5 ppm from quaternary carbon atoms overlap with one another to form a single peak (b) due to the low resolution. From the integration of signals of the methylene in different ethyl groups, DB value can be calculated in terms of the reported expression, i.e. \(DB = (D + T)/(D + L + T)\) \[1\]. The \(^{13}\)C-NMR spectra near 22.50 ppm measured from various PEHO samples are shown in figure 2 and DB values determined from figure 2 are listed in table 1. The minimum DB value, 5.6%, is the lowest value that can be obtained by our synthesis methods so far. And the maximum DB value, 45%, is close to the theoretical maximum.
value for hyperbranched polymers [8]. In addition, the individual D, T and L unit contents are calculated and listed in table 1 as well.

The molecular weights of the PEHO samples listed in table 1 are around 5000, which are higher than those reported in the previous investigation [5]. It is possible that the observed molecular weights here are much lower than the actual values, because the hydrodynamic volumes of hyperbranched polymers are smaller than the ones of linear polymers used for calibration, and hyperbranched polymers often exhibit aggregation on SEC columns due to their large number of end groups [5], [9]–[11]. The hydroxyl values determined by chemical analysis are close to the theoretical value of 483.7.

To investigate the crystallinity of PEHO, the XRD measurement was performed. Figure 3 exhibits the XRD patterns of various PEHO samples. The crystallization peaks appear near $2\theta = 16^\circ$. Even though sample 1 is the most linear one compared with other hyperbranched PEHO samples, DB of sample 1 is still as high as 5.6%, which is considerably higher than that of a completely linear polymer, so that the crystallization of the PEHO samples is limited and the peak observed is broader. The crystallinity of semi-crystalline polymers is represented by the relative degree of crystallization (DC), which can be estimated from the integration of the crystallization peak area. The relative DC values of the various PEHO samples determined from figure 3 are listed in table 1 as well. Consequently, a plot of DC versus DB is presented in

**Scheme 1.**
Figure 1. $^{13}$C-NMR spectrum of PEHO.

Figure 4(A). The plot shows that the relative DC decreases from 0.31 to 0 with increasing DB from 5.6 to 40%. Obviously, the crystallization becomes more and more difficult with increasing DB of PEHO samples. A gross DC value of the PEHO sample with a certain DB can be evaluated immediately from the plot, which means that the plot shows a quantitative relationship between the crystallinity and DB of PEHO. Furthermore, three curves reflecting the individual influence of D, T and L unit content on the crystallinity of PEHO are presented in figure 4(B). It can be evidently seen that the crystallinity of PEHO decreases with increasing D and T unit content, but goes up with increasing L unit content. It indicates that the more D units, the lower the crystallinity of PEHO. In contrast, the more L units, the higher the crystallinity of PEHO. The variations are in harmony with the relationship between the crystallinity and DB of PEHO.

DSC melting curves of the PEHO samples were measured as well (figure 5), which are similar to those reported for poly[3-methyl-3-(hydroxymethyl)oxetane] [6]. With the enhancement of DB, the melting peak becomes smaller and disappears when DB value goes above 25%. Besides, the melting temperature decreases with increasing DB of PEHO. Hult et al also observed a similar phenomenon in their previous DSC experiments [5]. DSC results offer the conclusion from XRD as a convincing support.

We deduce that the quantitative reduction of crystallinity with the enhancement of DB (or individual D and T unit content) of PEHO may ascribe to the special three-dimensional molecular
structures of hyperbranched polymers [12, 13]. As reported, the three-dimensional architecture of hyperbranched polymers with a higher DB is similar to that of dendrimers which have a spherical shape [14], so most of the hyperbranched polymers with a higher DB cannot crystallize at all. On the other hand, the length of the linear chains is very important for the crystalline properties of polymers. We consider that the longer linear PEHO chains may aggregate in an orderly manner into the crystal domains in the light of the crystallization model proposed by Flory and Yoon [15, 16]. When DB of PEHO is low, the linear segments between two branching points within a species are relatively longer and they can aggregate into the crystal domains. Therefore, PEHO with a lower DB can crystallize partially. When DB increases, the molecular structure of PEHO transforms gradually from a linear shape to a spherical shape (scheme 1), the linear segments between two branching points become shorter and the crystallization gets more difficult, consequently, the crystallinity of PEHO decreases sharply with increasing DB. The reasons are probably why most of the hyperbranched polymers reported in references are weakly crystalline or amorphous although their linear analogues are highly crystalline polymers [14, 17, 18].

Figure 2. Variation of the three peaks near 22.50 ppm in $^{13}$C-NMR spectra of various PEHO samples.
Figure 3. XRD patterns of PEHO samples 1–6.

Figure 4. (A) Plot of relative DC versus DB of PEHO; and (B) curves of DC versus D unit content (■), DC versus T unit content (●) and DC versus L unit content (▲) for PEHO.

It deserves to be mentioned that the casting sheets (about 1 mm thickness) of PEHO with a higher DB were observed to be more brittle than those of PEHO with a lower DB. Further experiments on PEHO are still continued. Hyperbranched PEHO is a flexible hydrophobic polymer with a large population of terminal hydroxyl groups, which shows considerable promise in molecular self-assembly research. Recently, our laboratory prepared a sort of ill-defined amphiphilic hyperbranched macromolecules using hyperbranched PEHO as cores and PEO as...
arms, and discovered that it could self-assemble into macroscopic tubes in acetone solvent [19] and giant polymer vesicles in water [20]. Molecular self-assembly of ill-defined polymers, such as hyperbranched polymers, is a new and promising research topic in the near future.

4. Conclusion

A series of PEHO samples with different DBs were adopted to study the relationship between the crystallinity and DB. The relative DC and DB of PEHO samples were respectively determined by XRD and $^{13}$C-NMR measurements. Consequently, a plot of DC versus DB was obtained, which demonstrates the quantitative dependence of the crystallinity on DB of PEHO. DSC results make a useful compliment to the relationship obtained from XRD and NMR. The quantitative relationship between the crystallinity and DB reflects the effect of the molecular structures on the crystalline properties for hyperbranched PEHO.

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