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A novel biodegradable hyperbranched polyester prepared from cellulose and tyrosine via the synthesis route of glycopeptides

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A novel cellulose-based hyperbranched polyester (CHBP) has been prepared through the polycondensation of the AB_n-type monomer, which was synthesized from the reaction the acetylated oligomeric cellulose bromide with tyrosine via the Koenigs-Knorr reaction, followed by the deacetylation. Its chemical structure, thermal stability as well as biodegradability were preliminarily investigated.

Hyperbranched polymers (HBPs) are one of the major subclasses of dendritic architecture following linear, cross-linked, and chain-branched ones.¹⁻³ Because of unusual structures, unique performance, and a variety of potential applications, such as drug delivery,⁴ coating,⁵ membranes,⁶ biomaterials⁷, and metal ion extractant,⁸ HBPs have attracted increasing attentions in the scientific and industrial community since the first report in the late 1980s, and the field has become a cutting-edge area in current polymer research. Compared to the dendrimers, HBPs have lower branching degree, broader molecular weight distribution, more geometric isomers, and more irregular geometry,⁹⁻¹¹ which impart them some fascinating properties, such as low viscosity, high solubility, and great numbers of functional groups. Once the monomer is obtained, HBPs can be synthesized through the single-step reaction rather than the multi-step ones and no purification procedure is needed.¹²⁻¹⁴ The simplicity and low

synthesis cost make HBPs suitable for scale-up production.^{15,16} Until now, HBPs are mainly synthesized from limited petrochemical reagents (e.g. vinyl alcohol,¹⁷ phenylene vinylene¹⁸ and acrylic ester¹⁹), which limits their practical application. The petroleum-based HBPs have the advantages, such as high chemical stability and specific product structure. However, they tend to suffer from poor biodegradability.

To date, an emerging trend in the synthesis of HBPs is to design and synthesize biodegradable HBPs using a variety of renewable biomass sources as starting materials.²⁰⁻²² As one of the most abundant naturally occurring polymers on earth, cellulose is composed of β -D-glucopyranoside unit linked by 1,4-glycosidic bond, and contains linear long-chain structure. It is renewable, biodegradable, and inexpensive. It is envisioned that the novel biobased HBPs containing cellulose moieties would combine both merits of cellulose and HBPs and have a variety of promising applications. To the best of our knowledge, the synthesis of hyperbranched polyester derived from cellulose, has not been reported yet.

Herein, a novel kind of the cellulose-based derivative was successfully synthesized through the glycopeptide reaction from environmentally friendly oligomeric cellulose and tyrosine as 'green' building blocks and then used as an AB_n-type monomer to prepare a novel biodegradable cellulose-based hyperbranched polyester (CHBP) through

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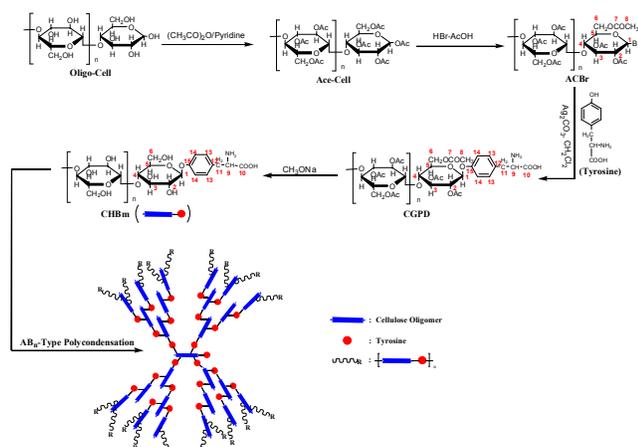
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†Electronic supplementary information (ESI) available: Experimental section and additional solid-state ¹³C-NMR (Fig. S1), FT-IR spectra (Fig. S2) and GPC curve (Fig. S3).

polycondensation reaction. The thermal and biodegradable properties of such prepared polymer were preliminarily studied.



Scheme 1 Synthesis of CHBm and CHBP.

The synthetic route of cellulose-based hyperbranched polyester's monomer (CHBm) as well as the resulting CHBPs is showed in Scheme 1. The acetylated oligomeric cellulose (Ace-Cell) was first synthesized via the acetylation of oligomeric cellulose (Oligo-Cell) using acetic anhydride in the presence of pyridine as catalyst. Due to the strong terminal effect of hemiacetal hydroxyl at the C1 atom of anhydroglucose units of Oligo-Cell,²³⁻³¹ the reaction of hydrogen bromide (HBr) with fully acetylated Oligo-Cell yielded the bromide-substituted derivative of acetylated cellulose (ACBr). Subsequently, the terminal bromide in the ACBr was eliminated by phenolic group of tyrosine to yield the cellulose-based glycopeptide-like derivative (CGPD) through Koenigs-Knorr reaction,³²⁻³⁷ in which silver carbonate (Ag₂CO₃) acted as a neutralizing reagent to absorb the generated HBr. After de-acetylation with sodium methoxide (NaOCH₃), the CHBm monomer containing cellulose and tyrosine moieties was obtained. Finally, the polycondensation of CHBm yielded CHBPs in the presence of dicyclohexyl carbodiimide (DCC) and *p*-toluenesulfonic acid (*p*-TSA).

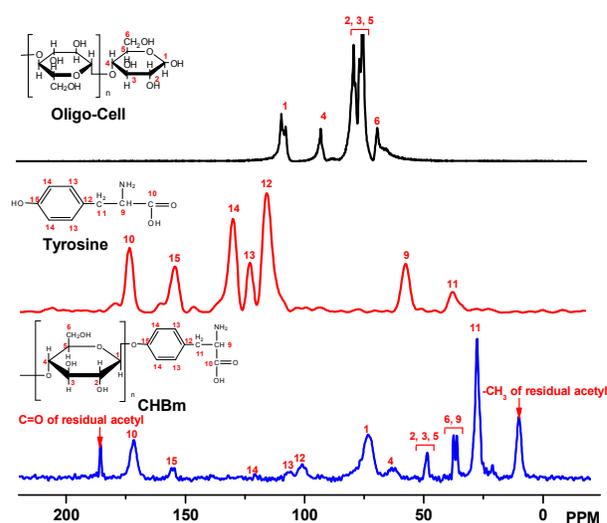


Fig. 1 CP/MAS ¹³C-NMR spectra of Oligo-Cell, tyrosine, and CHBm.

To validate the structure of the CHBm, its solid-state ¹³C-NMR spectrum was recorded together with that of Oligo-Cell and tyrosine as references (Fig. 1). In the case of tyrosine, the peaks at 53.5 and 34.1 ppm are due to the C₉ and C₁₁, respectively, while the one at 172.2 ppm is assigned to the C₁₀. And the C₁₂, C₁₃, C₁₄, and C₁₅ atoms of benzene ring in the tyrosine appear at 114.2, 120.7, 127.7, and 152.6 ppm, respectively. The C₁ atom of oligo-Cell shows a bimodal signal at 106.2 and 104.6 ppm. The signal of 89.5 ppm is attributed to the C₄, while the ones at 65.5 ppm correspond to the C₆. The overlapped signals in the range of 72.0~75.0 ppm originate from the C₅, C₂, and C₃. After the acetylation and subsequent bromination of Oligo-Cell, the new peaks at 10.9 and 175.4 ppm assigned to -CH₃ and -C=O of acetyl group appear for the ACBr (see Fig. S1 in ESI†). The structure CGPD is also verified by the appearance of carbon signals in the range of 114~174 ppm, which are characteristic of tyrosine unit (see Fig. S1 in ESI†). After the deacetylation of CGPD, there are still minor peaks at 30.0 and 190.0 ppm assigned to the -CH₃ and -C=O of acetyl groups, implying the presence of residual acetyl ones. By comparing three ¹³C-NMR spectra in Fig. 1, it can be seen that the signals of carbon skeleton of both Oligo-Cell and tyrosine appear for the CHBm. But the carbon signals assigned to the skeleton of cellulose in the CHBm

consistently shift toward a low frequency with respect to Oligo-Cell. Likewise, the C_{12} , C_{13} , and C_{14} signals associated with carbon atoms of benzene ring in the tyrosine shift toward 103.3, 104.8, 123.1, and 158.7 ppm for CHBm. This change could be attributed to the difference of chemical environment between CHBm and Oligo-Cell.

In order to further determine chemical structure of the above intermediates and products, FT-IR analysis is also given in Fig. 2. A broad and intensive absorption peak in the range of 3200~3500 cm^{-1} attributed to -OH stretching vibration of Oligo-Cell, disappears for the ACBr, indicating the complete acetylation of -OH groups. For the CGPD, both C=O stretching vibration (ca. 1750 cm^{-1}) and C=C stretching vibration (ca. 1600 cm^{-1} , 1510 cm^{-1} , 1450 cm^{-1}) are visible, confirming the indeed attachment of tyrosine unit onto backbone of the ACBr. And much more intensive vibration at 3200~3500 cm^{-1} appears again for the CHBm, confirming the presence of -OH groups. But the existence of weak peak at around 1750 cm^{-1} for the CHBm also evidences the incomplete deacetylation of the CGPD. This result is in accordance with the aforesaid ^{13}C -NMR result. As shown in Fig. S2 (see ESI †), the intensity of -OH stretching vibration of the CHBP-3 is remarkably weakened in comparison to that of the CHBm and meanwhile the C=O absorption of the former becomes much intensive. This is probably indicative of the occurrence of polycondensation between -OH and -COOH groups, resulting in the formation of many ester linkages in the CHBP-3.

Table 1 Number average molecular weight (M_n) and their polydispersity index ($\text{PDI} = M_w/M_n$) of CHBm and different generations of CHBPs

| | Ace-Cell | CHBm | CHBPs | | |
|----------------|----------|------|-------|-----|-----|
| | | | 1st | 2nd | 3rd |
| M_n (kDa) | 11 | 9 | 208 | 210 | 223 |
| PDI | 1.3 | 1.5 | 2.3 | 2.1 | 2.0 |

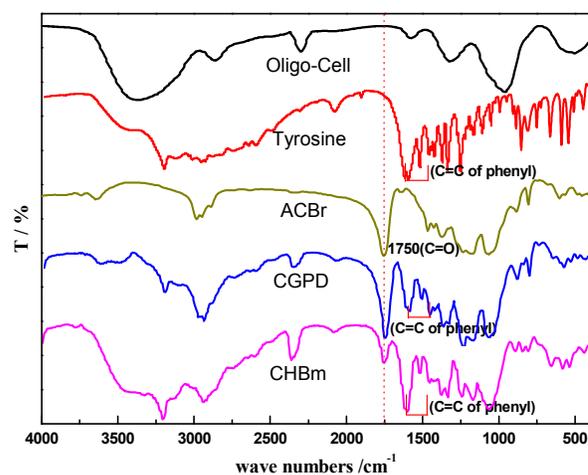


Fig. 2 FT- IR spectra of the raw materials, intermediates and CHBm.

GPC was employed to monitor molecular weight and its distribution of the samples. To overcome poor solubility of cellulose in THF, the acetylated cellulose samples with good solubility in THF were used for GPC measurement. Molecular weight and dates of the samples are listed in Table 1 and their molecular weight distribution curves are showed in Fig. S3 (see ESI †). Note that molecular weight of CHBm is lower than that of Ace-Cell but its polydispersity index (PDI) is somewhat higher than that of the Ace-Cell due to the elimination of acetyl protecting groups from the glycopeptide-like derivative. Unlike the traditional hyperbranched polyester,³⁸⁻⁴³ the PDI values of CHBPs slightly differ from the 1st generation to the 3rd one, presumably due to the inaccessibility of reactive groups (i.e. steric effects) when the polymer becomes more branched. This might suggest that the extent of polymerization of CHBm is almost close to the equilibrium after the 3rd generation CHBP (CHBP-3).

To exclude the possibility of crosslinking structure formed in the CHBP-3, its solubility of in common organic solvents was tested. It was found that the CHBP-3 exhibited a certain degree of solubility in DMSO, THF, and CHCl_3 , among which its solubility degree in DMSO is the highest (0.14g/10mL). Thus, it can be reasonably assumed that the perceptible crosslinking did not occur during

the polycondensation of CHBm.

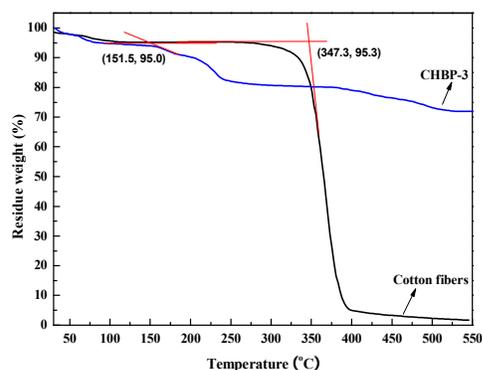


Fig. 3 TGA curves of CHBP-3 and cotton fibers.

Thermal stability is another important concern in the practical applications of biobased materials. Fig. 3 displays TGA curves of cotton fibers and CHBP-3 and their corresponding data are summarized in Table 2. Due to the evaporation of moisture, the weight loss of CHBP-3 up to 110 °C is about 3.1%, which is slightly lower than cotton fibers (4.6%). It can be seen from the Table 2 that the CHBP-3 has lower T_{onset} , T_{d5} , and T_{max} values than cotton fibers, suggesting relatively inferior thermal stability of the CHBP-3. But it is worth noting that char yield of the former exceeds 70 wt%, which is much higher than that of the latter. This may be attributed to the hyperbranched architecture with abundant terminal polar groups which provide strong molecular interaction. And another possibility may lie in the presence of many benzene structural moieties in the CHBP-3. Some investigators have reported that the phenylation of backbone along with the incorporation of ester and amino groups contributed to the improvement in thermal stability of HBPs.⁴⁴ It is expected that such kind of biobased hyperbranched polyesters based on cellulose and tyrosine might have potential applications in high-temp thermal insulation coatings.

Table 2 TGA data of CHBP-3 and cotton fibers

| Samples | Onset weight loss temp, T_{onset} (°C) | Temp of 5% weight loss, T_{d5} (°C) | Maximum weight loss temp, T_{max} (°C) | Char yield (wt%) |
|--------------|--|---------------------------------------|--|------------------|
| Cotton fiber | 347.3 | 335.7 | 368.2 | 1.7 |
| CHPB-3 | 151.5 | 220.7 | 230.7 | 72.1 |

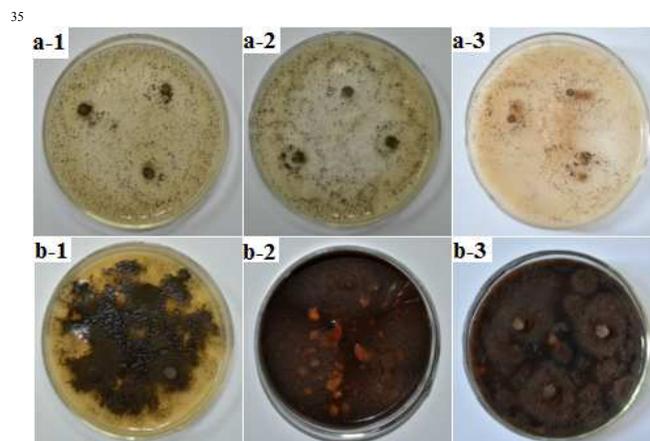


Fig. 4 The *aspergillus niger* colony photos of incubation media with cotton fibers (a) and CHBP-3 (b) after 7 days (a-1 & b-1), 14 days (a-2 & b-2), and 21 days (a-3 & b-3).

The biodegradability of CHBP can be evaluated by observing the colony morphological changes of incubation media. The colony photos of incubation media of the cellulose and hyperbranched polyester are shown in Fig. 4. After one week's microbiological deterioration, the *Aspergillus niger* colony was observed on the incubation media for the cotton fibers and CHBP-3 samples. But the colony size and distribution between them is different. The distribution of *Aspergillus niger* colony on the CHBP-3 is symmetrical, while the distribution range of aspergillus niger colony on cotton fibers is small and focused. This observation indicates that CHBP-3 is more susceptible to the microbial degradation than cotton fibers.

In summary, a novel cellulose-based hyperbranched polyester (CHBP) was successfully designed and synthesized using naturally occurring cotton fibers and tyrosine as the raw materials. The

chemical structure of CHBP and its reaction intermediates were determined in terms of FT-IR and CP/MAS ^{13}C -NMR. TGA results showed that thermal stability of HBP was superior to that of cotton fibers. In addition, the colony degradation experiment confirmed that better biodegradability was achieved for HBP with respect to cotton fibers. The findings of this work demonstrated a novel and feasible route for the design and preparation of hyperbranched polyester using 'green' natural resources.

Acknowledgments

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