Indole as a new sustainable aromatic unit for high quality biopolyesters†

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The aim of this research was to use indole as a new sustainable aromatic unit for polyesters. A series of new polyesters were synthesised by the polycondensation of an indole-based dicarboxylate and five potentially bio-based diols. The new polyesters are amorphous, have superior thermal quality, and can form clear transparent films.

Polymers constitute a major class of plastics (polymers), which are widely used in many applications such as packaging, coating, textile, or components for automobiles and home appliances.1–3 The most widely used polyester is polyethylene terephthalate (PET), which makes up 18% of the total world plastic production.4 An important reason for the wide application of PET is that it contains aromatic units (i.e. terephthalates), which endow PET with excellent thermal and mechanical properties. Without the aromatic units, the physical properties of polyesters are usually inferior (e.g. polyactic acid5,6 and polyhydroxalkanoates).7–10 which limits their application. However, a serious challenge to the use of terephthalate units is that they can only be industrially produced from non-renewable fossil resources, and their production generates considerable amount of CO2.11 Therefore, academia and industry have been actively searching for alternative aromatic units from renewable resources for the production of high quality biopolymers.12,13

Recently, polyesters with furan units (potentially from sustainable resources) have been developed rapidly.14–19 Because of the similar chemical structures of furan and benzene, the thermal and mechanical properties of polyethylene furanoate (PEF) are similar to those of PET.20–24 Furthermore, furan is unsymmetrical along its rotation axis and it has higher polarity; so, its ring-flipping process is restricted (compared with benzene in PET).25 This character makes PEF difficult to be penetrated by gas molecules, which is particularly attractive for food packaging applications.26

Enlightened by the successful development of PEF and other furan-based polyesters, it is of great interest to examine the possibility of using other bio-based aromatic units for polyester production, in order to achieve versatile materials toward various applications. Particularly, larger bio-based aromatic units (than benzene or furan) are attractive, because they have the potential to yield high performance plastics analogous to polyethylene naphthalate (PEN). PEN is a commercial polyester, which has superior thermal (Tg ∼ 120 °C), mechanical, and barrier properties compared with PET.27 These characters make PEN highly durable and amiable for repeated mechanical recycling.28 However, naphthalate is challenging for sustainable production; so, alternative large aromatic units from sustainable resources are of great interest, which can simultaneously address the sustainability and high quality requirements of the society and industry for polyesters.

Indole is a large aromatic unit with two fused cyclic structures (similar to naphthalene).29 Many indole-containing molecules exist in nature, such as mono-substituted (e.g. tryptophan and indole-3-acetic acid), di-substituted (e.g. oxytrofalcatin), or complicated structures (e.g. arnoamine and apparcine). Indole structures can also be conveniently synthetised from bio-sourced chemicals, such as ethylene glycol and aniline derivatives.30 Therefore, indole-derived dicarboxylates can be ideal aromatic units for the production of biopolymers, especially highly durable biopolymers with significant recyclability and added-value (“bioadvantage” materials).31

Surprisingly, such a potentially powerful aromatic unit has been largely ignored in polyester research. Today, indole-based structures are largely limited to the synthesis of conjugated polymers as nonlinear optical materials.32,33 To our knowledge, there was only one indole-containing polyester reported in the 1980s, without the description of its physical properties.34 That polyester contains flexible tetraethylene glycol units, which differs significantly from PET or PEN in physical properties (e.g. Tg and modulus). Therefore, knowledge is still
lacking regarding how the incorporation of indole aromatic units in the polyester backbone will affect its properties. Herein, we present the synthesis of a new indole-based dicarboxylate monomer, which was used to produce a series of bio-polyesters with various aliphatic diols. The molecular structures and thermal properties of the newly synthesized polymers were characterized. The film-forming ability and hydrophilicity of these polyesters were also examined. By this, we demonstrated that indole could be a suitable bio-based aromatic unit for the development of high quality polyesters, which can promote circular economy in the polyester industry.

An indole-based dicarboxylate monomer (3) was synthesised by a facile S$_2$2 reaction of methyl indole-3-carboxylate (1) and methyl 2-bromoacetate (2) (Scheme 1A) under basic conditions. After a convenient purification by recrystallisation, monomer 3 was obtained in 71% yield and high purity (assessed with NMR analyses, Fig. 1A). Afterward, five potentially bio-based aliphatic diols (4a–e, Scheme 1B) were polymerised together with monomer 3 in a two-neck round bottom flask using a modified two-step polycondensation protocol.$^{35,36}$ The first transesterification step was carried out at 180 °C for 3 h, until the methyl ester signals of monomer 3 completely disappeared in the $^1$H NMR spectrum. Afterward, the reaction temperature was raised to 200 °C for the second step (polycondensation). Mesitylene (5 mL) was added for the azeotropic removal of diols (4a–e),$^{37}$ which could effectively increase the molecular weight of the resulting polymer. It was observed that excess mesitylene (>10 mL) could significantly slow down the polymerisation. Therefore, 5 mL of mesitylene was optimal. After the polymerisation, the viscous reaction mixture was dissolved in chloroform and precipitated into methanol to yield a white polymer powder (yields 74%, 71%, 80%, 80% and 69% for 5a–e, respectively). The molecular weights of the obtained polyesters were in a satisfactory range of $M_n \sim 33 \times 10^3$–$44 \times 10^3$ g mol$^{-1}$ (Table 1).

**Table 1** The properties of indole-based polyesters 5a–e. $M_n$, $M_w$, and PDI were determined using GPC. $T_d^{5\%}$ (5% weight loss) and $T_g$ were determined using TGA and DSC, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI</th>
<th>$T_d^{5%}$ (°C)</th>
<th>$T_g$ (°C)</th>
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<tr>
<td>5a</td>
<td>33 400</td>
<td>67 600</td>
<td>2.0</td>
<td>55</td>
<td>354</td>
</tr>
<tr>
<td>5b</td>
<td>35 100</td>
<td>80 900</td>
<td>2.3</td>
<td>63</td>
<td>340</td>
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<tr>
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<td>91 100</td>
<td>2.1</td>
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<tr>
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<td>35 800</td>
<td>71 700</td>
<td>2.0</td>
<td>93</td>
<td>314</td>
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<tr>
<td>5e</td>
<td>41 100</td>
<td>112 300</td>
<td>2.7</td>
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</table>

Polymers 5a–e were characterised using $^1$H NMR analyses. As shown in Fig. 1B–F, all the signals were broad and shifted from the corresponding monomer signals, which indicated the formation of polymers. The monomer methyl signals x and y (Fig. 1A) disappeared after the polymerisation, which showed complete monomer conversion. Furthermore, the CH$_3$ signal at 4.89 ppm (c) and the aromatic signals (d–f) were observed in the spectra of all the polyesters (Fig. 1B–F), which confirmed the incorporation of the indole units in the polyesters. In the meantime, the presence of the aliphatic diol residues was also verified by the corresponding aliphatic signals (a, b, or g). It should be clarified that monomer 3 contains two different ester groups, which can form three different indole residual dyads in the polyesters (h–h, h–t, and t–t, Scheme 1C).

The observation of multiple signals for protons a, b and g was consistent with the presence of different indole-dyads, which further suggested that monomer 3 entered a polymer chain with a random orientation. The random orientation of the indole units in the backbone was expected to diminish the crystallinity of the polymers (compared with the symmetrical polyester PET). Such expected low crystallinity of indole-based polyesters was consistent with the observation in DSC measurements that these polyesters were all amorphous (PET is semi-crystalline). Further investigation of the pattern of signal “a” suggested that higher microstructural regularity (h–t content, see the ESI, Fig. S23†) could be achieved using a sterically hindered diol (4e). Finally, in all the NMR spectra of polyesters 5a–e, no signal corresponding to carboxylic acid or methyl carboxylate end groups was observed, which suggested that the new polyesters contained only OH end groups (ESI, Fig. S24†).

Polymers 5a–e were further studied using $^{13}$C-NMR spectroscopy (Fig. 2). Clearly, signals for the two carbonyl groups...
(m, n), the CH₂ group (d), and the eight indole carbons (e–l) were observed in all the spectra of the monomer and polyesters. Furthermore, the signals corresponding to the methyl groups of 3 (x, y) disappeared after the polymerisation, which confirmed the complete conversion of the monomer.

The signals for the aliphatic carbons (a, b, c and o) were also observed in the spectra of polymers as multiple peaks, which corroborated the formation of different indole-dyads (Scheme 1C). The assignments of the ¹H and ¹³C NMR spectra were all verified by 2D NMR analyses (COSY, HMQC and HMBC, Fig. S2–19, ESI†). In addition, FTIR was used to characterise the polyesters (Fig. S1†), from which the ester C=O stretching (1630–1800 cm⁻¹) and the aliphatic C–H stretching (2790–3180 cm⁻¹) bands were clearly discernible for all the polyesters.

The thermal stability of the new polyesters was assessed using TGA. As shown in Fig. 3A, B and Table 1, all the polyesters were thermally stable with T ᵐ > 300 °C. For the polyesters with linear diol units (5a–d), thermal stability decreased with the decreased length of the diol units (5a > 5b > 5c > 5d).

Furthermore, it was noted that polymer 5e (with two methyl groups in the diol units) exhibited higher thermal stability compared with 5d (polymer with the same length of diol units). This can be explained by the fact that aromatic–aliphatic polyesters primarily degrade through a β-hydrogen transfer via a six-membered cyclic intermediate.38 Therefore, the absence of β-hydrogen atoms in 5e can minimise such a degradation process and thus increase the thermal stability. Finally, isothermal TGA analyses (ESI, Fig. S22 and Tables S1–3†) suggested that the indole-based polyester 5a had lower long-term thermal stability compared with PET.

The thermal behaviour of the polyesters was further studied using DSC. As shown in Fig. 3C and Table 1, all the polyesters were amorphous without a melting endotherm, which was consistent with the random orientation of the indole units in the polymers. The polyesters with linear aliphatic diols (5a–d) had higher Tᵦ as the aliphatic units became shorter, which showed a trend similar to terephthalate- and furan-based polyesters (Fig. 3D).20,39–45 Furthermore, the Tᵦ values of the new polyesters were considerably higher than the values of the corresponding terephthalate- and furan-based polyesters prepared with the same diols, 4a–e (Fig. 3D).39 The highest Tᵦ of the synthesised series of indole-based polyesters was 99 °C (5e), which indicated excellent heat-tolerance of the polyester and thus could enable hot fill processing in food packaging applications.

In addition, the five indole-based polyesters were cast into thin films from their solutions (the casting procedure is described in the ESI†). As shown in Fig. 4, these films were all clear and transparent, which was consistent with the amorphous nature of the polymers according to the DSC results. Qualitatively, the obtained films were soft and non-brittle, and could be easily bent or folded repeatedly without observable cracking. It was noted that some of these films were faint yellow (5b–d), which could be attributed to side reactions during the polymerisation. Although the exact mechanism for such side reactions remained to be unravelled, it was observed that higher polymerisation temperature could lead to deeper colour and lower molecular weight (Mᵣ ~ 12 000) of the polyester 5b (Fig S20, ESI†). Finally, water contact angle (θ) tests (Fig. S21†) revealed that these indole-based polyester films
were generally more hydrophilic ($\theta = 45–62^\circ$) than the films made from PET, PETG, and Akestra ($\theta = 64–75^\circ$) under the same film-casting and measurement conditions. This observation was consistent with the higher polarity of indole (dipole moment 2.13 D), compared with that of benzene rings (dipole moment ~0) contained in PET, PETG and Akestra.

This communication demonstrated the feasibility of using a large bio-based aromatic unit, indole, for the production of high quality polyesters toward various potential applications. A series of indole-based biopolymesters was prepared using a new indole-dicarboxylate monomer and 5 aliphatic diols. Decent series of indole-based biopolyesters was prepared using a new high quality polyesters toward various potential applications. A "project STEPS" (No. 2016/1489). We thank Linda Zellner and Åsa Halldén Björklund from Perstorp AB for providing Akestra.

Conflicts of interest

There are no conflicts to declare.

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