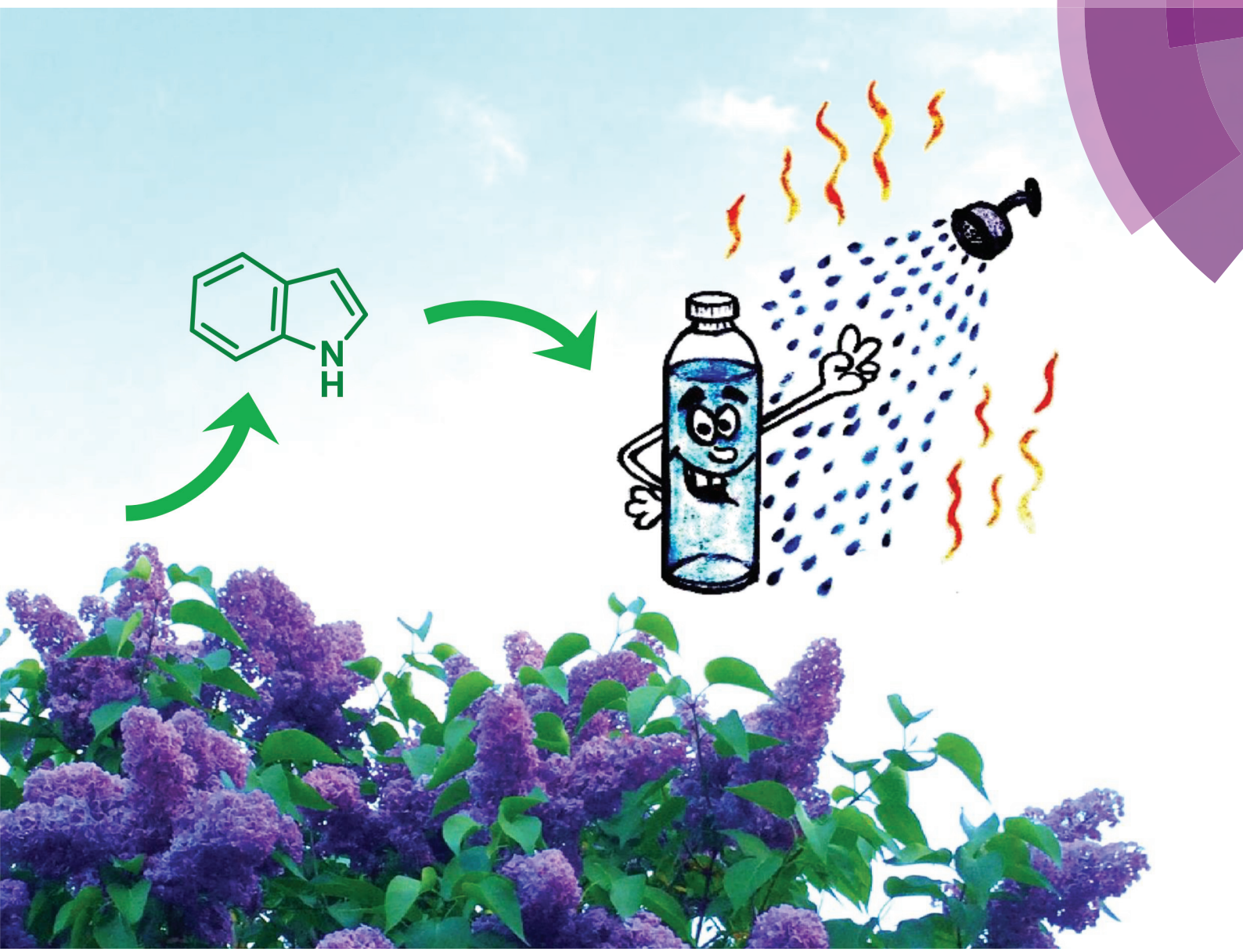
Volume 9 | Number 38 | 14 October 2018 | Pages 4685–4800

Polymer Chemistry

rsc.li/polymers



ISSN 1759-9962

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

Baozhong Zhang *et al.*

Indole as a new sustainable aromatic unit for high quality biopolyesters

Polymer Chemistry

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Polym. Chem.*, 2018, **9**, 4706

Received 27th June 2018,
Accepted 13th August 2018

DOI: 10.1039/c8py00962g

rsc.li/polymers

Open Access Article. Published on 14 August 2018. Downloaded on 3/29/2024 3:11:21 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

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

Ping Wang, Carlos R. Arza and Baozhong Zhang *

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.

Polyesters 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.* polylactic acid[5,6] and polyhydroxyalkanoates),[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 CO_2.[11] Therefore, academia and industry have been actively searching for alternative aromatic units from renewable resources for the production of high quality biopolyesters.[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 (T_g ~ 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 apparicine). Indole structures can also be conveniently synthesised 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 biopolyesters, especially highly durable biopolyesters 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.* T_g and modulus). Therefore, knowledge is still

Lund University, Centre of Analysis and Synthesis, P.O. Box 124, SE-22100 Lund, Sweden. E-mail: baozhong.zhang@chem.lu.se

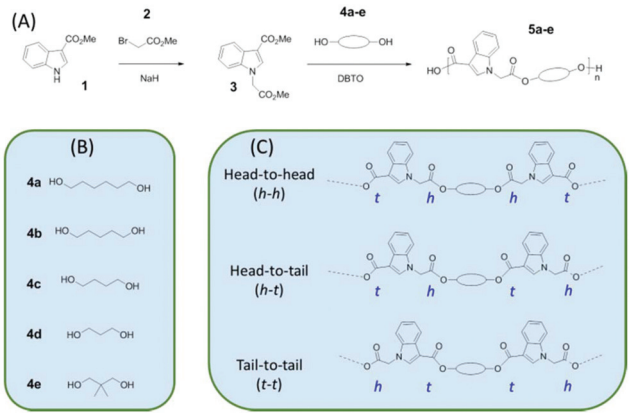
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c8py00962g

This journal is © The Royal Society of Chemistry 2018

Open Access Article. Published on 14 August 2018. Downloaded on 3/29/2024 3:11:21 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

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 new indole-based polyesters 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_N2 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 $M_n \sim 33\,000$–$44\,000$ g mol^{-1} (Table 1).



Scheme 1 (A) Synthesis of indole-based monomer and polyesters. (B) Chemical structures of aliphatic diols **4a–e**. (C) Possible indole dyad structures in the polymers.

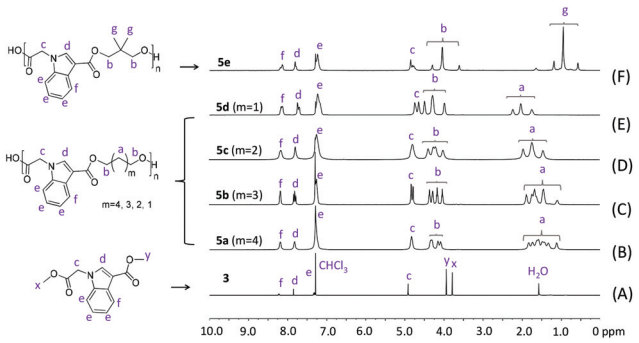


Fig. 1 ^{1}H NMR spectra of monomer **3** and polyesters **5a–e**.

Polyesters **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_2 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 polymers. 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†).

Polyesters **5a–e** were further studied using ^{13}C-NMR spectroscopy (Fig. 2). Clearly, signals for the two carbonyl groups

Table 1 The properties of indole-based polyesters **5a–e**. M_n, M_w, and PDI were determined using GPC. T_d^{95} (5% weight loss) and T_g were determined using TGA and DSC, respectively

	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	T_g (°C)	T_d (°C)
5a	33 400	67 600	2.0	55	354
5b	35 100	80 900	2.3	63	340
5c	43 900	91 100	2.1	75	326
5d	35 800	71 700	2.0	93	314
5e	41 100	112 300	2.7	99	337

Open Access Article. Published on 14 August 2018. Downloaded on 3/29/2024 3:11:21 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

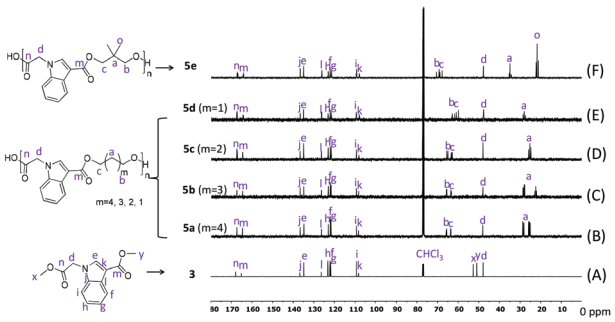


Fig. 2 ^{13}C NMR spectra of monomer **3** and polyesters **5a–e**.

(m, n), the CH_2 group (d), and the eight indole carbons (e-l) were observed in all the spectra of the monomer and polyesters, which proved the incorporation of indole units in the polymers. 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 ^{1}H and ^{13}C 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_d^{95} > 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**).

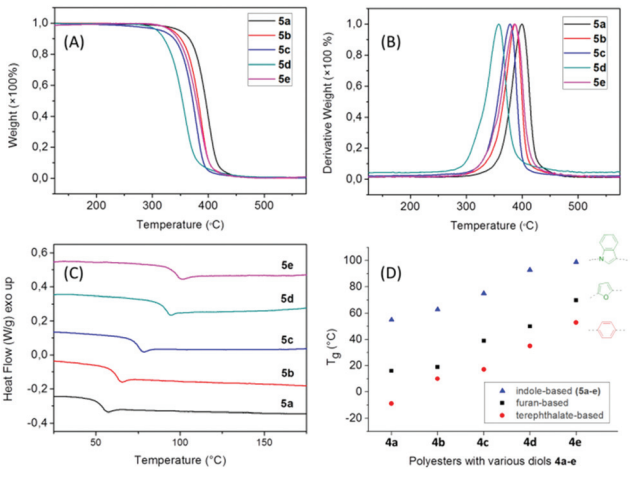


Fig. 3 Thermal behaviour of indole-based polyesters **5a–e**. (A) TGA weight loss and (B) derivative weight loss curves of polyesters **5a–e**. (C) Second heating DSC curves of **5a–e**. (D) T_g of polyesters prepared from diols **4a–e** and different aromatic dicarboxylates.[20,39–45]

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 T_g as the aliphatic units became shorter, which showed a trend similar to terephthalate- and furan-based polyesters (Fig. 3D).[20,39–45] Furthermore, the T_g 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 T_g 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 (M_n ~ 12 000) of the polyester **5b** (Fig S20, ESI†). Finally, water contact angle (θ) tests (Fig. S21†) revealed that these indole-based polyester films

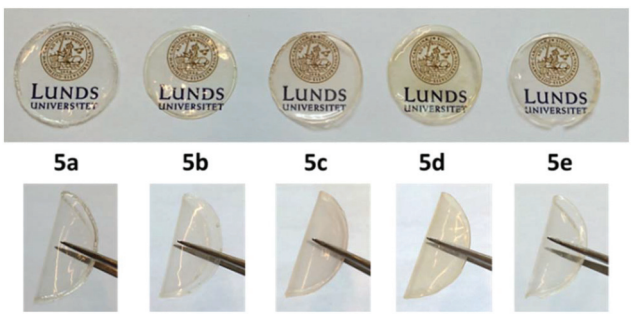


Fig. 4 Thin films of indole-based polyesters (upper row: flat films, lower row: folded films).

This journal is © The Royal Society of Chemistry 2018

Open Access Article. Published on 14 August 2018. Downloaded on 3/29/2024 3:11:21 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

were generally more hydrophilic (θ = 45–62°) than the films made from PET, PETG, and Akestra (θ = 64–75°) under the same film-casting and measurement conditions. This observation was consistent with the higher polarity of indole (dipole moment 2.13 D),[46] 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 biopolyesters was prepared using a new indole-dicarboxylate monomer and 5 aliphatic diols. Decent molecular weights, fair thermal stability and relatively high T_g were obtained. The new polyesters have high T_g values up to 99 °C, which can mimic the thermal quality of commercial heat-tolerant polyesters PETG, Akestra, or Tritan (T_g ~ 90–110 °C). The indole-based polyesters are all amorphous, and can form transparent flexible films, which are slightly more hydrophilic than PET, PETG and Akestra. Further studies on the mechanical and barrier properties of the polyesters are being conducted. Synthesis toward indole-based monomers with different symmetry and substitution patterns is also being explored.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research project was financially supported by the ÅForsk Foundation (No. 16-479), Crafoord Foundation (No. 20160774 and 20180939), and Royal Physiographic Society in Lund. PW thanks the China Scholarship Council for the kind support. BZ thanks the Swedish Foundation for Strategic Environmental Research (Mistra) for the kind financial support through the project "STEPS" (No. 2016/1489). We thank Linda Zellner and Åsa Halldén Björklund from Perstorp AB for providing Akestra.

References

1 A. E. Brown and K. A. Reinhart, *Science*, 1971, **173**, 287–293.
2 C. Vilela, A. F. Sousa, A. C. Fonseca, A. C. Serra, J. F. J. Coelho, C. S. R. Freire and A. J. D. Silvestre, *Polym. Chem.*, 2014, **5**, 3119–3141.
3 S. Vecchiato, J. Ahrens, A. Pellis, D. Scaini, B. Mueller, E. H. Acero and G. M. Guebitz, *ACS Sustainable Chem. Eng.*, 2017, **5**, 6456–6465.
4 S. Yoshida, K. Hiraga, T. Takehana, I. Taniguchi, H. Yamaji, Y. Maeda, K. Toyohara, K. Miyamoto, Y. Kimura and K. Oda, *Science*, 2016, **351**, 1196–1199.
5 K. Madhavan Nampoothiri, N. R. Nair and R. P. John, *Bioresour. Technol.*, 2010, **101**, 8493–8501.
6 S. Farah, D. G. Anderson and R. Langer, *Adv. Drug Delivery Rev.*, 2016, **107**, 367–392.
7 Y. Poirier, D. E. Dennis, K. Klomparens and C. Somerville, *Science*, 1992, **256**, 520–523.
8 B. Hazer and A. Steinbuchel, *Appl. Microbiol. Biotechnol.*, 2007, **74**, 1–12.
9 D. B. Hazer, E. Kilicay and B. Hazer, *Mater. Sci. Eng., C*, 2012, **32**, 637–647.
10 Y. Wang, J. Yin and G. Q. Chen, *Curr. Opin. Biotechnol.*, 2014, **30**, 59–65.
11 S. Spierling, E. Knupffer, H. Behnsen, M. Mudersbach, H. Krieg, S. Springer, S. Albrecht, C. Herrmann and H. J. Endres, *J. Cleaner Prod.*, 2018, **185**, 476–491.
12 A. Rahimi, A. Ulbrich, J. J. Coon and S. S. Stahl, *Nature*, 2014, **515**, 249–252.
13 Y. Q. Zhu, C. Romain and C. K. Williams, *Nature*, 2016, **540**, 354–362.
14 A. S. Amarasekara, L. H. Nguyen, N. C. Okorie and S. M. Jamal, *Green Chem.*, 2017, **19**, 1570–1575.
15 V. Tsanaktsis, Z. Terzopoulou, S. Exarhopoulos, D. N. Bikiaris, D. S. Achilias, D. G. Papageorgiou and G. Z. Papageorgiou, *Polym. Chem.*, 2015, **6**, 8284–8296.
16 Y. Shen, B. B. Yao, G. Yu, Y. Fu, F. S. Liu and Z. B. Li, *Green Chem.*, 2017, **19**, 4930–4938.
17 Z. Terzopoulou, E. Karakatsianopoulou, N. Kasmi, V. Tsanaktsis, N. Nikolaidis, M. Kostoglou, G. Z. Papageorgiou, D. A. Lambropoulou and D. N. Bikiaris, *Polym. Chem.*, 2017, **8**, 6895–6908.
18 T. Kim, J. M. Koo, M. H. Ryu, H. Jeon, S. M. Kim, S. A. Park, D. X. Oh, J. Park and S. Y. Hwang, *Polymer*, 2017, **132**, 122–132.
19 T. P. Kainulainen, J. A. Sirvio, J. Sethi, T. I. Hukka and J. P. Heiskanen, *Macromolecules*, 2018, **51**, 1822–1829.
20 G. Z. Papageorgiou, V. Tsanaktsis, D. G. Papageorgiou, K. Chrissafis, S. Exarhopoulos and D. N. Bikiaris, *Eur. Polym. J.*, 2015, **67**, 383–396.
21 A. Gandini, D. Coelho, M. Gomes, B. Reis and A. Silvestre, *J. Mater. Chem.*, 2009, **19**, 8656–8664.
22 A. F. Sousa, C. Vilela, A. C. Fonseca, M. Matos, C. S. R. Freire, G.-J. M. Gruter, J. F. J. Coelho and A. J. D. Silvestre, *Polym. Chem.*, 2015, **6**, 5961–5983.
23 P. Tao, D. Jin, X. Qing, Z. Yong, G. Qing-Xiang and F. Yao, *ChemSusChem*, 2013, **6**, 47–50.
24 A. F. Sousa, J. F. J. Coelho and A. J. D. Silvestre, *Polymer*, 2016, **98**, 129–135.
25 S. K. Burgess, O. Karvan, J. R. Johnson, R. M. Kriegel and W. J. Koros, *Polymer*, 2014, **55**, 4748–4756.
26 M. Rabnawaz, I. Wyman, R. Auras and S. Cheng, *Green Chem.*, 2017, **19**, 4737–4753.
27 A. Polyakova, R. Y. F. Liu, D. A. Schiraldi, A. Hiltner and E. Baer, *J. Polym. Sci., Part B: Polym. Phys.*, 2001, **39**, 1889–1899.
28 J. K. Money, *J. Coated Fabr.*, 1995, **25**, 24–38.
29 R. B. Van Order and H. G. Lindwall, *Chem. Rev.*, 1942, **30**, 69–96.
30 M. Campanati, S. Franceschini, O. Piccolo and A. Vaccari, *J. Catal.*, 2005, **232**, 1–9.

Open Access Article. Published on 14 August 2018. Downloaded on 3/29/2024 3:11:21 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

31 N. Hernandez, R. C. Williams and E. W. Cochran, *Org. Biomol. Chem.*, 2014, **12**, 2834–2849.
32 B. Dong, B. Li, Y. Cao, X. Meng, H. Yan, S. Ge and Y. Lu, *Tetrahedron Lett.*, 2017, **58**, 35–42.
33 Z. Li, J. Qin, S. Li, C. Ye, J. Luo and Y. Cao, *Macromolecules*, 2002, **35**, 9232–9235.
34 B. Z. Weiner and A. Zilkha, *J. Macromol. Sci., Chem.*, 1980, **A14**, 379–388.
35 C. Japu, A. M. de Ilarduya, A. Alla and S. Munoz-Guerra, *Polymer*, 2013, **54**, 1573–1582.
36 S. Chanda and S. Ramakrishnan, *Polym. Chem.*, 2015, **6**, 2108–2114.
37 K. Komura, A. Ozaki, N. Leda and Y. Sugi, *Synthesis*, 2008, 3407–3410.
38 K. C. Khemani, *Polym. Degrad. Stab.*, 2000, **67**, 91–99.
39 A. Fradet, in *Synthetic Methods in Step-Growth Polymers*, 2003, DOI: 10.1002/0471220523.ch2.
40 P. Malanowski, S. Huijser, F. Scaltro, R. A. T. M. van Benthem, L. G. J. van der Ven, J. Laven and G. de With, *Prog. Org. Coat.*, 2012, **74**, 165–172.
41 J. Zhu, J. Cai, W. Xie, P.-H. Chen, M. Gazzano, M. Scandola and R. A. Gross, *Macromolecules*, 2013, **46**, 796–804.
42 R. J. I. Knoop, W. Vogelzang, J. Haveren and D. S. Es, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 4191–4199.
43 V. Tsanaktsis, Z. Terzopoulou, M. Nerantzaki, G. Z. Papageorgiou and D. N. Bikiaris, *Mater. Lett.*, 2016, **178**, 64–67.
44 L. Genovese, N. Lotti, V. Siracusa and A. Munari, *Materials*, 2017, **10**, 1028.
45 A. Fradet, in *Synthetic Methods in Step-Growth Polymers*, John Wiley & Sons, Inc., 1st edn, 2003, pp. 17–134, DOI: 10.1002/0471220523.ch2.
46 C. Parkanyi, S. R. Oruganti, A. O. Abdelhamid, L. Vonszentpaly, B. Ngom and J. J. Aaron, *J. Mol. Struct.: THEOCHEM*, 1986, **28**, 105–116.

This journal is © The Royal Society of Chemistry 2018