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## Panoramic view of biobased BHMTHF-based polymers

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The biobased platform chemical 5-hydroxymethylfurfural (HMF) is widely recognized as an important precursor for the production of the monomer 2,5-furandicarboxylic acid (FDCA) and, to a lesser extent, 2,5-bishydroxymethylfuran (BHMF), which are used for the production of renewable polymers. Similarly to FDCA and BHMF, 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF) can be synthesized from HMF and can act as a monomer due to its difunctionality. The potential of BHMTHF, also known as 2,5-tetrahydrofurandimethanol (THFDM), for use in the production of innovative biobased polymers is still underexplored. This review summarizes and highlights the different types of polyesters and polyurethanes that are derived from this tetrahydrofuran building block. BHMTHF is predicted to have a bright future as a biobased monomer for the production of sustainable polymers because of its unique heterocyclic rigidity, electronegativity of the ether group and hydrogen bonding ability. This yields various polymers with reduced or absent crystallinity, improved hydrophilicity and pronounced shear thinning behavior.

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### Introduction

Owing to their sustainable characteristics, versatility and comparable or even enhanced performance, biobased polymers have attracted increasing interest in the development of novel polymers.<sup>1,2</sup> An important building block in the transition from fossil-based polymers to biobased polymers is the platform chemical 5-hydroxymethylfurfural (HMF). A major advantage is the great versatility of feedstocks that can be used for the synthesis of HMF: cellulose, starch, inulin, glucose, fructose, sucrose and other carbohydrate sources, such as (non)-edible biomass and food waste.<sup>3–5</sup> Fructose usually results in the highest HMF yield because of its relatively high reactivity.<sup>4</sup>

HMF can be used in numerous different synthesis routes to yield a broad range of various fine chemicals, including 2,5-dimethylfuran (DMF), 2,5-diformylfuran (DFF), 5-methylfurfuryl alcohol (MFA) and 5-methylfurfural (5-MF).<sup>6–10</sup> HMF derivatives can also be used for the production of polymers, especially polyesters; well-known examples are the polyesters produced from 2,5-furandicarboxylic acid (FDCA) and, to a lesser extent, polyesters based on 2,5-bishydroxymethyl furan (BHMF).<sup>11,12</sup> However, in this review, the focus will be on 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF), also known as

2,5-tetrahydrofurandimethanol (THFDM) or 2,5-dihydroxymethyltetrahydrofuran (DHMTHF), which is a relatively underexplored monomer for the synthesis of novel biobased polymers. BHMTHF can be obtained from HMF *via* two different reduction pathways, either *via* hydrogenation of the aldehyde group of 5-hydroxymethyltetrahydrofurfural (HMTHF) or *via* hydrogenation of the furan ring of BHMF, as illustrated in Fig. 1.<sup>13</sup> However, the reduction must be highly selective to ensure that the hydroxyl groups remain unaffected. Currently, much research is being conducted in this field, and very high HMF conversions, BHMTHF selectivities and yields have already been reported and are highlighted in recent literature



Fig. 1 Schematic representation of the reaction pathways for the conversion of HMF to BHMTHF *via* either HMTHF or BHMF. Figure reproduced with permission from ref. 13. Copyright 2024 Chemical Engineering Journal.

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Fig. 2 Structural representations of FDCA, BHMf, BHMTHF (THFDM, DHMTHF) and CHDM.

reviews.<sup>4,14–17</sup> In addition, the Chinese company Sugar Energy started the large-scale production of BHMTHF from HMF.<sup>18</sup>

At first glance, BHMTHF appears structurally similar to BHMf and FDCA, since they all belong to the group of heterocyclic difunctional polyester building blocks derived from HMF (Fig. 2), however there are remarkable differences. FDCA and BHMf are both unsaturated aromatic structures, while BHMTHF is saturated, making it more flexible. This results in different melting points: FDCA (342 °C),<sup>19</sup> BHMf (74–77 °C),<sup>20</sup> BHMTHF (–70 °C),<sup>21</sup> and HMF (30–34 °C).<sup>5</sup> Furthermore, BHMf has relatively limited thermal stability, it is reported to decompose around 120 to 130 °C, while HMF is even more prone to degradation.<sup>22–25</sup> However, both BHMTHF and FDCA, which decomposes around 200 °C, possess high thermal stability, and bulk polymerization synthesis routes are feasible at high temperatures (180 °C).<sup>18,26,27</sup> The high stability of FDCA is attributed to the mesomeric effect of the carbonyl groups on both sides of the furan ring, which are absent for BHMf, HMF and BHMTHF.<sup>28</sup> HMF contains one reactive aldehyde group,<sup>23</sup> and HMF and BHMf contain one and two reactive allylic hydrogens, respectively, which are absent for BHMTHF and might explain its greater stability.

BHMTHF is more structurally similar to 1,4-cyclohexanediol (CHDM) and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO), which are all saturated rigid diols that increase the stiffness of the polymer chain.<sup>29</sup> CHDM-based copolyesters play an important role in the polymer industry by enhancing the thermal, mechanical, chemical and physical properties of polymers.<sup>30</sup> Like CHDM, BHMTHF can be present in the *cis* or *trans* configuration. Stereoregular polymers usually exhibit better properties because of more favorable interactions between the chains.<sup>28</sup> The effect of the *cis*–*trans* configurations of BHMTHF-based polymers will be briefly elaborated in the next paragraphs.

In addition to the fact that BHMTHF can be directly used as a monomer, it can also serve as a biobased intermediate for the synthesis of other well-known monomers. BHMTHF can be converted to 1,2,6-hexanetriol and 1,6-hexanediol, which can subsequently be converted to adipic acid and caprolactone.<sup>4,31–33</sup> In addition, BHMTHF could be used as a biobased (co)solvent or as a precursor for surfactants, lubricants and pharmaceuticals.<sup>18,34,35</sup>

The synthesis of the biobased monomer BHMTHF has currently been studied extensively, but a comprehensive literature review of the current status of the developed polymers is still lacking. Within this review, the potential of BHMTHF as a bio-

based monomer is summarized by discussing and highlighting the interesting features and synthesis of BHMTHF-based polymers.

## BHMTHF-based polyesters

The available literature concerning BHMTHF-based polyesters is limited and mostly very recent. The structures, molecular weights and thermal properties of the BHMTHF-based (co)polyesters are depicted below in Table 1.

To the best of the authors' knowledge, the first attempt to synthesize a BHMTHF-based polyester was performed by Moore and Kelly in 1978.<sup>36</sup> The *cis* and *trans* isomers of BHMTHF were reacted with FDCA, 2,5-furandicarboxylic acid (THFDCA). These polyesters were prepared *via* solution polymerization, demonstrated a low intrinsic viscosity, appeared brown or black, were soluble in chloroform, and had conversions ranging from 70 to 90%. However, qualitative analysis of the polymers was not performed, and it was proposed that 2,5-disubstituted tetrahydrofuran monomers are not suitable for melt-transesterification unless oxygen is excluded and the temperature is below 200 °C.

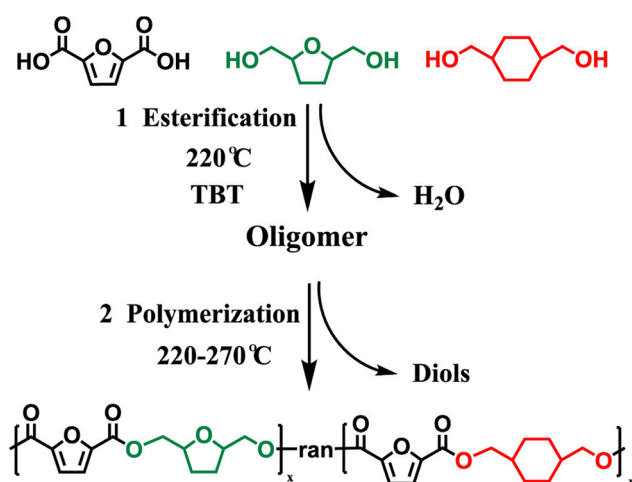


Fig. 3 Schematic representation of the synthesis of poly(1,4-cyclohexyldimethylene-co-hydroxymethyl tetrahydrofuran 2,5-furandicarboxylate) (PCTF) from FDCA, BHMTHF and CHDM. Figure adapted and reproduced with permission from ref. 37. Copyright 2021 ACS Sustainable Chem. Eng.

**Table 1** Polymer names, structural representations, number average molecular weights ( $\bar{M}_n$ ), glass transition temperatures ( $T_g$ ), melting points ( $T_m$ ) and onset thermal decomposition temperatures ( $T_{d5\%}$ ) of BHMTHF-based polyesters reported in the literature

| Name  | Polymer structure | $\bar{M}_n$ (g mol <sup>-1</sup> ) | $T_g$ (°C) | $T_m^a$ (°C) | $T_{d5\%}$ (°C) | Ref.              |
|-------|-------------------|------------------------------------|------------|--------------|-----------------|-------------------|
| PTF   |                   | 10 900–13 200                      | 70–77      |              | 359–381         | 18, 37, 41 and 44 |
| PCTF  |                   |                                    | 78–87      | 230–260      | 366–370         | 37                |
| PTT   |                   | 19 200, 31 700                     | 70         |              | 379–390         | 18 and 38         |
| PETT  |                   | 31 400–48 500                      | 70–80      | 208–239      | 377–396         | 38, 39, 42 and 43 |
| PTS   |                   | 24 700                             | 0          |              | 345             | 18 and 40         |
| PTA   |                   | 20 500                             | –33        |              | 338             | 18                |
| PBTS  |                   |                                    | –32 to –13 | 86–103       |                 | 40                |
| PTPF  |                   |                                    | 56–57      |              | 371–373         | 41                |
| PEIFT |                   |                                    | 81–86      | 217–225      | 392–393         | 43                |
| PBTF  |                   | 18 600–27 400                      | 43–53      | 161          | 367–373         | 44                |

<sup>a</sup> Note that not all copolyesters demonstrate a melting point because high-BHMTHF-content polymers are usually amorphous.

Many years have passed, but the potential of BHMTHF as a monomer was rediscovered by the Wei group in 2021, who produced random copolyesters of poly(1,4-cyclohexyldimethylene-co-hydroxymethyl tetrahydrofuran 2,5-furandicarboxylate) (PCTF) on a kilogram scale *via* melt polycondensations, as illustrated in Fig. 3.<sup>37</sup> A kinetic study revealed that CHDM was more reactive than BHMTHF toward FDCA, which explained the higher CHDM fraction in the copolyester relative to the feed ratio. A detailed crystallization study revealed that the incorporation of BHMTHF units hinders the crystallization ability of this copolyester. The glass transition temperature ( $T_g$ ) increased slightly with increasing CHDM content and ranged from 76 °C for pure poly(hydroxymethyl tetrahydrofuran 2,5-furandicarboxylate) (PTF) to 89 °C for pure poly(1,4-cyclohexanedimethylene furandicarboxylate) (PCF), whereas intermediate values were obtained for the copolyesters. Mechanical analysis *via* tensile tests revealed typical thermo-plastic behavior with high yield stresses ranging from 49–84 MPa.

The same group synthesized the copolyesters poly(ethylene-co-tetrahydrofurandimethanol terephthalate) (PETT), and BHMTHF was proposed as a biobased alternative to CHDM in poly(ethylene terephthalate-co-cyclohexanedimethanol terephthalate) (PETG).<sup>38</sup> In contrast to PET, all the PETT copolyesters were amorphous, except for the one containing only

15 mol% BHMTHF. A higher BHMTHF content resulted in a minor gradual reduction in the  $T_g$ , which ranged from 70 to 75 °C. In addition, the  $T_g$  values of the PETT copolyesters were slightly lower than those of similar PETG polymers, which was attributed to the existence of ether bonds in the BHMTHF units. Oscillatory rheology demonstrated shear thinning behavior, which was more pronounced for higher BHMTHF contents. A higher content of BHMTHF units decreased the water contact angle, which indicates increased hydrophilicity attributed to the abundance of electronegative ether-oxygen atoms. Tensile tests revealed increased elongation at break but a reduced yield strength for a higher BHMTHF content in PETT. These results, and a comparison with those of commercially available polymers, are illustrated in Fig. 4.

In 2022, Chen *et al.* produced PETT copolyesters (named PETF by the authors) containing lower BHMTHF contents to study their spinning performance.<sup>39</sup> PETT containing 5 and 15% BHMTHF units still possesses a melting point ( $T_m$ ), although it is lower than that of pure PET (243 °C). The melting enthalpy ( $\Delta H_m$ ),  $T_m$  and crystallization enthalpy ( $\Delta H_c$ ) decreased with increasing BHMTHF content, which was attributed to a disrupted molecular chain structure. Rheology revealed that a higher BHMTHF content resulted in stronger shear thinning behavior. This was explained by the breaking of the physical entanglements, which originated from the



**Fig. 4** Yield strength and elongation at break of PET, PTT and PTT copolyesters, which are compared with those of commercially available polyesters. Adapted and reproduced with permission from ref. 38. Copyright 2021 European Polymer Journal.

electronegativity of the ether–oxygen bond at higher shear rates.<sup>38,39</sup> Finally, the spinnability of PTT gradually improved with increasing BHMTHF content, which was attributed to the disturbance of the crystallization of PET.

Jin *et al.* expanded the BHMTHF-based polyester library by copolymerization with succinic acid and adipic acid.<sup>18</sup> In addition, they studied the reactivity of BHMTHF toward FDCA and compared it with that of other diols. Generally, cyclic structures, such as BHMTHF and CHDM, have lower reactivities than linear units because of steric hinderance. The *cis-trans* ratio of the BHMTHF monomers in the feed remained rather similar with respect to the ratio in the polymers, although molecular chain energy simulation revealed that the *trans* units were more stable, *i.e.*, lower in energy. DSC analysis demonstrated that all BHMTHF-based polyesters were amorphous. The polyesters derived from BHMTHF and either succinic acid or adipic acid presented relatively low  $T_g$  values of 0 and  $-33$  °C, respectively, and were therefore not subjected to tensile testing.

In a follow-up article by the same authors, biodegradable polybutylene succinate (PBS) was copolymerized with BHMTHF to optimize its performance.<sup>40</sup> Notably, poly(tetrahydrofurandimethylene succinate) (PTS) and the copolyesters poly(butylene-*co*-tetrahydrofurandimethylene succinate) (PBTS), which contain 38 mol% or more BHMTHF, are in a viscous state at room temperature and were considered unsuitable as “plastic” materials, according to the authors. Additionally, although pure PBS was semicrystalline, an increase in BHMTHF content resulted in a decrease in the crystallization ability of the PBTS copolyesters (up to 29% BHMTHF units). Although the rigid ring structure hindered crystallization, the  $T_g$  value increased gradually with increasing BHMTHF content. The semicrystalline PBTS polymers were subjected to tensile testing, which revealed that a higher BHMTHF fraction led to a lower yield stress (16–27 MPa) and greater elongation at break (700–1100%). Finally, the per-

meation coefficients of oxygen and carbon dioxide of the semi-crystalline PBTS polymers were comparable to those of PBS, PLA and PBAT, and the authors predicted that PBTS could be applied in the field of food packaging.

Recently, Hu *et al.* (2023) prepared a series of copolyesters from FDCA, BHMTHF and 1,3-propanediol, which were named poly(2,5-tetrahydrofurandimethanol 2,5-furandicarboxylate)-multi-poly(1,3-propylene 2,5-furandicarboxylate) (PTPF).<sup>41</sup> Partially alternating and partially random copolyesters were prepared by mixing pure PTF and pure PPF at the desired ratios in the molten stage under vacuum. Unsurprisingly, all the copolymers appeared amorphous due to their reduced regularity. The  $T_g$  of PTF (75 °C) was higher than that of PPF (56 °C) and increased slightly for higher tetrahydrofuran units in the copolyesters, which was caused by the higher rigidity of BHMTHF relative to that of 1,3-propanediol.

Liu *et al.* (2024) used low amounts of BHMTHF (2, 4 and 6 mol%) as a comonomer in PET to yield PTT (named PETF by the authors) as an alternative for CHDM and isophthalic acid (IPA) to limit crystallization and allow easier processing.<sup>42</sup> Small fractions of tetrahydrofuran units led to significantly increased hydrophilicity according to water contact angle measurements. The addition of BHMTHF units led to a reduction in the  $T_m$ ,  $\Delta H_m$  and  $T_g$  values. The onset thermal decomposition temperature ( $T_{d5\%}$ ) of PTT (389 °C) was slightly lower than that of PET (399 °C). PTT was shown to be processable for melt spinning, and the obtained fibers had mechanical properties similar to those of PET.

A recent article described the synthesis of poly(ethylene glycol-*co*-2,5-tetrahydrofuran dimethanol-*co*-isosorbide terephthalate) (PEIFT), in which BHMTHF and isosorbide (ISB) were incorporated into PET.<sup>43</sup> An increase in the ISB content improved both the  $T_g$ ,  $T_m$  and thermal decomposition temperature of PEIFT, which was attributed to the rigidity of the ISBs. However, the introduction of ISB and BHMTHF resulted in disrupted crystallinity, slightly lower mechanical strength and lower  $T_m$  than those of PET. The incorporation of the oxygen atoms from ISB and BHMTHF leads to a higher polarity of PEIFT than of PET. This resulted in more entanglements and, consequently, more pronounced shear thinning behavior, as observed with rheology, due to disentanglement at higher shear rates (Fig. 5). This is advantageous during processing and reduces energy consumption. Finally, electrospinning was used to create nanofiber membranes, and an improved spinning performance was observed with increasing BHMTHF content.

In 2025, Cai *et al.* reported the incorporation of BHMTHF in poly(butylene furandicarboxylate) (PBF) to yield the copolyesters poly(butylene furandicarboxylate-*co*-hydroxymethyl tetrahydrofuran furandicarboxylate) (PBTF).<sup>44</sup> DSC analysis revealed that only the PBTF containing 4 mol% BHMTHF units displayed a melting point (161 °C), and the  $T_g$  values increased with increasing tetrahydrofuran content. This is in line with expectations since the  $T_g$  value of PPF (70 °C) is higher than that of pure PBF (40 °C), which was attributed to the high rigidity and steric hinderance of the BHMTHF units.



Fig. 5 Complex viscosity versus angular frequency at 250 °C of PET and BHMTHF- and isosorbide-based polyesters. Figure adapted and reproduced with permission from ref. 43. Copyright 2024 Wiley-VCH GmbH.

Furthermore, the storage modulus, Young's modulus and tensile strength all increased with increasing BHMTHF content. The hydrophilicity, derived from water contact angles, decreased with increasing BHMTHF content in the copolyesters, which was also attributed to the presence of ether linkages.

## BHMTHF-based polyurethanes

In addition to polyesters, BHMTHF can also be used for the synthesis of polyurethanes because of the presence of primary

hydroxyl groups. Only two research groups have so far studied BHMTHF-based polyurethanes, and three related articles are discussed in this paragraph.

The first reported BHMTHF-based polyurethane was developed by Kim *et al.* (2020).<sup>45</sup> They prepared different polyurethanes by reacting a polyol with a trifunctional isocyanate crosslinker and different diols: 1,4-benzenedimethanol, BHMTHF, 1,2-dihydroxyethane or without diol. Compared with aromatic- and aliphatic-based polyurethanes, polyurethanes containing heterocyclic tetrahydrofuran groups presented better mechanical properties and outstanding self-healing behavior after scratching. This was quantified by tensile testing; the material recovered 97, 81 and 87% of the yield stress, elongation at break and Young's modulus, respectively. These enhanced properties were attributed to the unique hydrogen bonding between the urethane group and the ether-oxygen of the BHMTHF unit (Fig. 6), which was illustrated *via* FT-IR analysis of model compounds.

The Han group used BHMTHF as a chain extender for the synthesis of polyurethane, which was blended with nanosheets derived from the natural raw materials hydroxyapatite and polydopamine to yield a nanocomposite.<sup>46</sup> High-strength pure polyurethane (tensile strength of 27 MPa) was obtained, which was attributed to the "optimal hierarchical hydrogen bonding" between the tetrahydrofuran, urea and urethane groups. In addition, the composite demonstrated enhanced mechanical properties, was self-healable and reached good self-repairing efficiencies (55–83%), which were dependent on the nanosheet content, after 24 h at 35 °C. On the basis of the self-healing behavior and corrosion shielding capability of the coatings, these materials are suitable for long-term applications in corrosive environments.

In a follow-up article by the same authors, a similar polyurethane was prepared by using BHMTHF as a chain extender and incorporating aromatic disulfide bonds to improve the self-healing ability (Fig. 7).<sup>47</sup> The polyurethanes were blended



Fig. 6 Schematic representation of the self-healing ability of BHMTHF-based polyurethane. Figure reproduced with permission from ref. 45. Copyright 2020 Polymers.



Fig. 7 Chemical structure of polyurethane containing BHMTHF and aromatic disulfide units. Figure adapted and reproduced with permission from ref. 47. Copyright 2024 Applied Surface Science.

with polydopamine-modified halloysite nanotubes to enhance the mechanical properties. The tensile strength of the pure polyurethane improved to 48 MPa and reached a very high elongation at break (3090%). Additionally, this pure polyurethane and the nanocomposites were shown to be self-healable with similar or even higher self-healing efficiencies, ranging from 70–89%.

In addition, the same authors varied the structure of BHMTHF-based polyurethane by introducing the photothermally responsive monomer 1,4-benzoquinone dioxime.<sup>48</sup> This PU material also demonstrated good mechanical properties and excellent self-healing behavior, which was attributed to the combination of hydrogen bonding and dynamic oxime urethane bonds.

## Biodegradability of BHMTHF-based polymers

The ability and rate of biodegradation of polymers are dependent on both the chemical and physical properties of the polymer, the type and presence of microorganisms and the environmental conditions.<sup>49</sup> For example, amorphous phases degrade faster than crystalline phases of polyesters, and aliphatic polyesters, such as PBS and PCL, are generally more prone to degradation than aromatic-aliphatic polyesters.<sup>49–51</sup> Hence, it would be highly interesting to study the biodegradability of polyesters containing alicyclic tetrahydrofuran units, which are generally poorly crystalline or amorphous, as discussed above.

Currently, only one article has reported the enzymatic degradation of BHMTHF-based polyesters, providing only an indication of their biodegradability. Films of the copolyester poly(butylene-*co*-tetrahydrofuran dimethylene succinate) (PBTS) demonstrated enzymatic degradation over time.<sup>40</sup> Compared with pure PBS, PBTS polymers resulted in greater weight loss, and an increase in BHMTHF content improved degradation (Fig. 8).

PBTF copolyesters were also subjected to hydrolytic degradation experiments under strongly alkaline conditions (pH 12). Both weight loss and <sup>1</sup>H-NMR analysis revealed that the copolyesters containing initially more BHMTHF units were more prone to hydrolysis.<sup>44</sup>

Recently, various furanic-aliphatic BHMTHF-based polyesters were reported to demonstrate biodegradation behavior in activated sludge.<sup>52</sup> In addition, several different copolyesters containing CHDM units have been shown to be enzymatically



Fig. 8 Mass loss versus time of the PBS and PBTS films due to enzymatic degradation. Figure reproduced with permission from ref. 40. Copyright 2022 ACS Sustainable Chem. Eng.

degradable and partially biodegradable in organic compost or simulated municipal solid waste.<sup>53–56</sup> Owing to the structural similarities between BHMTHF, CHDM and BHMTHF, tetrahydrofuran-based polymers could also be biodegradable. Exploring this important polymeric feature of the new class of biobased polyesters is essential for assessing their future role in the circular economy of plastics.

## Future perspective

Although BHMTHF-based polymers are still in their infancy, interesting and promising results have already been reported. First, conventional straightforward high-temperature bulk polymerization is used as the main synthesis route. In addition, relatively large reactors, up to the 5 L scale, are already used for production, which implies easy further upscaling. This finding illustrates once more that BHMTHF, in contrast to BHMTHF and HMF, is stable and easy to handle as a biobased monomer.

Although BHMTHF-based polyesters can be processed into fibers and produce films *via* solvent casting, it is important to

**Table 2** Structure–property relationships in BHMTHF-based polymers

| Property         | Structural effect                                                                                                                                                                                                                                                                         |
|------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Crystallinity    | The incorporation of BHMTHF units typically results in reduced crystallinity or the formation of an amorphous structure, as the rigid tetrahydrofuran ring disrupts the interactions between the chains.                                                                                  |
| Hydrophilicity   | A higher BHMTHF content in the copolyesters results in a lower water contact angle and implies an enhanced hydrophilicity. This is caused by the presence of the electronegative ether-oxygen.                                                                                            |
| Viscosity        | BHMTHF-based polyesters demonstrated a shear thinning behavior with rheology, similar to other polymers. However, the shear thinning effect is more pronounced due to breaking of the physical entanglements, originating from the polar groups of the BHMTHF rings, at higher frequency. |
| Hydrogen bonding | The tetrahydrofuran groups of BHMTHF-based polyurethanes show improved hydrogen bonding with the urethane groups.                                                                                                                                                                         |

study, for example, their detailed behavior during blow molding or extrusion. Furthermore, a deeper understanding of the mechanical behavior is still lacking and could be provided by dynamic mechanical analysis (DMA) or a detailed rheological study.

BHMTHF can be present in the *cis* or *trans* configuration, but is more often a mixture of them. Currently, there is limited information available concerning the importance of the stereochemistry of the polymeric properties. Studying this parameter in more detail is recommended since it is generally known that the monomer configuration can influence the physical properties, such as the thermal transition points, reaction kinetics and crystallization behavior.

A recent study revealed that PBTS could be enzymatically degraded, so it would be valuable to explore the enzymatic polymerization of BHMTHF-based polymers. This technique has already been proven to be highly efficient and selective for FDCA, BHMF and other furan-based polyesters.<sup>52,57–59</sup>

Although enzymatic degradation and polymerization are often related to biodegradability, they are clearly two different processes. Hence, it would be highly interesting to study the biodegradation behavior of various BHMTHF-based polymers in different environments.

Finally, only a limited number of different BHMTHF-based polyesters have been synthesized, as indicated in Table 1. Expanding the library would be worthwhile to explore the versatility of BHMTHF as a biobased monomer. Additionally, other types of polymers derived from BHMTHF, especially polyurethanes, can be explored further because of the unique interactions between the urethane groups and the oxygen of the tetrahydrofuran group (Fig. 6). This would lead to a better understanding of the structure–property relationships in BHMTHF-based polymers in general (Table 2).

## Conclusion

BHMTHF, also known as THFDM and DHMTHF, is similar to FDCA and BHMF, also derived from HMF and can be used for the synthesis of a variety of biobased polymers. Although the synthesis of BHMTHF has shown promising results and is attracting increasing interest, the use of these polymers is currently underemphasized.

The incorporation of BHMTHF units in polyesters generally results in a reduced crystallization ability, usually a slightly reduced thermal stability, relatively high  $T_g$  values, and a reduction or absence in  $T_m$ . In addition, these tetrahydrofuran-based polymers demonstrate enhanced hydrophilicity and shear thinning behavior. All these changes in properties are attributed to the rigidity of the ring structure and the presence of the electronegative ether-oxygen. Furthermore, the copolyesters PETT and PEIFT are proven to be processable *via* melt spinning and electrospinning.

BHMTHF is also used for the synthesis of self-healing polyurethane materials with high mechanical performance. The self-healing ability is attributed to the strong hydrogen bonding between the tetrahydrofuran oxygen and the hydrogen of the urethane group.

Although some BHMTHF-based products have been shown to be enzymatically degradable, proper biodegradation studies are still lacking. However, its amorphous character and similarity to those of CHDM- and BHMF-based polyesters could indicate susceptibility to biodegradation.

Numerous areas remain to be explored to fully understand and assess the future of this monomer in the biobased polymer market. In addition, the synthesis cost, scalability and related availability of BHMTHF in the global market are key parameters for the successful implementation of this monomer in the plastic industry. Nevertheless, BHMTHF has great potential for use in the synthesis of biobased polymers because of its sustainable character, structural rigidity, high thermal stability, good reactivity and hydrophilic character.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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## References

- R. M. Cywar, N. A. Rorrer, C. B. Hoyt, G. T. Beckham and E. Y. X. Chen, Bio-based polymers with performance-advanced properties, *Nat. Rev. Mater.*, 2022, **7**(2), 83–103.
- S. RameshKumar, P. Shaiju, K. E. O'Connor and P. R. Babu, Bio-based and biodegradable polymers - State-of-the-art, challenges and emerging trends, *Curr. Opin. Green Sustainable Chem.*, 2020, **21**, 75–81, DOI: [10.1016/j.cogsc.2019.12.005](https://doi.org/10.1016/j.cogsc.2019.12.005).
- F. Menegazzo, E. Ghedini and M. Signoretto, 5-Hydroxymethylfurfural (HMF) production from real biomasses, *Molecules*, 2018, **23**(9), 1–18.
- A. A. Turkin, E. V. Makshina and B. F. Sels, Catalytic Hydroconversion of 5-HMF to Value-Added Chemicals: Insights into the Role of Catalyst Properties and Feedstock Purity, *ChemSusChem*, 2022, **15**(13), e202200412.
- T. Okano, K. Qiao, Q. Bao, D. Tomida, H. Hagiwara and C. Yokoyama, Dehydration of fructose to 5-hydroxymethylfurfural (HMF) in an aqueous acetonitrile biphasic system in the presence of acidic ionic liquids, *Appl. Catal., A*, 2013, **451**, 1–5, DOI: [10.1016/j.apcata.2012.11.004](https://doi.org/10.1016/j.apcata.2012.11.004).
- W. Fan, C. Verrier, Y. Queneau and F. Popowycz, 5-Hydroxymethylfurfural (HMF) in Organic Synthesis: A Review of its Recent Applications Towards Fine Chemicals, *Curr. Org. Synth.*, 2019, **16**(4), 583–614.
- R. J. Van Putten, J. C. Van Der Waal, E. De Jong, C. B. Rasrendra, H. J. Heeres and J. G. De Vries, Hydroxymethylfurfural, a versatile platform chemical made from renewable resources, *Chem. Rev.*, 2013, **113**(3), 1499–1597.
- C. Chen, M. Lv, H. Hu, L. Huai, B. Zhu, S. Fan, *et al.*, 5-Hydroxymethylfurfural and its Downstream Chemicals: A Review of Catalytic Routes, *Adv. Mater.*, 2024, **2311464**, 1–40.
- W. Zhao, Z. Huang, L. Yang, X. Liu, H. Xie and Z. Liu, Highly efficient syntheses of 2,5-bis(hydroxymethyl)furan and 2,5-dimethylfuran via the hydrogenation of biomass-derived 5-hydroxymethylfurfural over a nickel-cobalt bimetallic catalyst, *Appl. Surf. Sci.*, 2022, **577**, 151869, DOI: [10.1016/j.apsusc.2021.151869](https://doi.org/10.1016/j.apsusc.2021.151869).
- X. Zhu, F. Wang, L. Yang, Z. Chen, K. Zhao, X. Liu, *et al.*, Silica-supported non-precious copper catalyst for catalytic hydrogenation of 5-hydroxymethylfurfural to 2,5-bis(hydroxymethyl)furan, *Mol. Catal.*, 2024, **553**, 113794, DOI: [10.1016/j.mcat.2023.113794](https://doi.org/10.1016/j.mcat.2023.113794).
- X. Fei, J. Wang, X. Zhang, Z. Jia, Y. Jiang and X. Liu, Recent Progress on Bio-Based Polyesters Derived from 2,5-Furandicarboxylic Acid (FDCA), *Polymers*, 2022, **14**(3), 625.
- C. Post, D. Maniar, V. S. D. Voet, R. Folkersma and K. Loos, Biobased 2,5-Bis(hydroxymethyl)furan as a Versatile Building Block for Sustainable Polymeric Materials, *ACS Omega*, 2023, **8**(10), 8991–9003.
- X. Jia, K. Yuan, G. Wang, S. Zhu, M. Dong, J. Wang, *et al.*, Reaction-induced restructuring of partial Pd single atoms to nanoparticles for enhancing HMF selective hydrogenation to BHMTHF, *Chem. Eng. J.*, 2024, **487**, 150482, DOI: [10.1016/j.cej.2024.150482](https://doi.org/10.1016/j.cej.2024.150482).
- A. Prasertsab, W. Nunthakitgason, P. Pornsetmetakul, P. Chaipornchaleram, K. Iamsaard and C. Wattanakit, Selective hydrogenation of 5-hydroxymethylfurfural to 2,5-bis(hydroxymethyl)tetrahydrofuran with NaBH<sub>4</sub> over non-thermal plasma treated Ru supported on hierarchical MFI, *Catal. Today*, 2024, **437**, 114785, DOI: [10.1016/j.cattod.2024.114785](https://doi.org/10.1016/j.cattod.2024.114785).
- J. Tan, J. Cui, Y. Zhu, X. Cui, Y. Shi, W. Yan, *et al.*, Complete Aqueous Hydrogenation of 5-Hydroxymethylfurfural at Room Temperature over Bimetallic RuPd/Graphene Catalyst, *ACS Sustainable Chem. Eng.*, 2019, **7**(12), 10670–10678.
- M. Annatelli, J. E. Sanchez-Velandia, G. Mazzi, S. V. Pandeirada, D. Giannakoudakis, S. Rautiainen, *et al.*, Beyond 2,5-furandicarboxylic acid: status quo, environmental assessment, and blind spots of furanic monomers for bio-based polymers, *Green Chem.*, 2024, **26**(16), 8894–8941.
- C. Chen, M. Lv, H. Hu, L. Huai, B. Zhu, S. Fan, *et al.*, 5-Hydroxymethylfurfural and its Downstream Chemicals: A Review of Catalytic Routes, *Adv. Mater.*, 2024, **36**(37), 1–40.
- C. Jin, L. Liu, Z. Tu, B. Wang, P. Wang and Z. Wei, Melt polycondensation of 2,5-tetrahydrofuran dimethanol with various dicarboxylic acids towards a variety of biobased polyesters, *Polym. Chem.*, 2022, **13**, 5718–5729, DOI: [10.1039/d2py00975g](https://doi.org/10.1039/d2py00975g).
- C. Triebel, V. Nikolakis and M. Ierapetritou, Simulation and economic analysis of 5-hydroxymethylfurfural conversion to 2,5-furandicarboxylic acid, *Comput. Chem. Eng.*, 2013, **52**(2013), 26–34, DOI: [10.1016/j.compchemeng.2012.12.005](https://doi.org/10.1016/j.compchemeng.2012.12.005).
- T. Wang, J. Wei, Y. Feng, H. Liu, X. Tang, X. Zeng, *et al.*, Efficient synthesis of bio-based monomer 2,5-bishydroxymethylfuran by the solvent-free hydrogenation of 5-hydroxymethylfurfural-based deep eutectic mixture, *J. Chem. Technol. Biotechnol.*, 2020, **95**(6), 1748–1755.
- Zhejiang Sugar Energy Technology Co. Ltd, 2, 5-Tetrahydrofuran dimethanol (THFDM), 2024, [cited 2024 Oct 29], Available from: <https://www.sugar-energy.com/product/2-5-tetrahydrofuran-dimethanol.html>.
- F. van der Klis, J. van Haveren, D. S. van Es and J. H. Bitter, Synthesis of Furandicarboxylic Acid Esters From Nonfood Feedstocks Without Concomitant Levulinic Acid Formation, *ChemSusChem*, 2017, **10**(7), 1460–1468.
- F. Aricò, Synthetic approaches to 2,5-bis(hydroxymethyl)furan (BHMF): a stable bio-based diol, *Pure Appl. Chem.*, 2021, **93**(5), 551–560.
- E. H. Choi, J. Lee, S. U. Son and C. Song, Biomass-derived furanic polycarbonates: Mild synthesis and control of the

- glass transition temperature, *J. Polym. Sci., Part A: Polym. Chem.*, 2019, **57**(17), 1796–1800.
- 25 R. J. Kieber, S. A. Silver and J. G. Kennebrew, Stereochemical effects on the mechanical and viscoelastic properties of renewable polyurethanes derived from isohexides and hydroxymethylfurfural, *Polym. Chem.*, 2017, **8**(33), 4822–4829.
  - 26 E. Gubbels, L. Jasinska-Walc and C. E. Koning, Synthesis and characterization of novel renewable polyesters based on 2,5-furandicarboxylic acid and 2,3-butanediol, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**(4), 890–898.
  - 27 C. Liu, K. Su and Z. Li, Studies on FDCA pyrolysis by TG-FTIR-MS characterization and ReaxFF-MD simulation, *J. Anal. Appl. Pyrolysis*, 2024, **183**, 106790.
  - 28 I. Delidovich, P. J. C. Hausoul, L. Deng, R. Pfützner, M. Rose and R. Palkovits, Alternative Monomers Based on Lignocellulose and Their Use for Polymer Production, *Chem. Rev.*, 2016, **116**(3), 1540–1599.
  - 29 K. Walkowiak and S. Paszkiewicz, Modifications of Furan-Based Polyesters with the Use of Rigid Diols, *Polymers*, 2024, **16**(14), 2064.
  - 30 F. Irshad, N. Khan, H. Howari, M. Fatima, A. Farooq, M. Awais, *et al.*, Recent Advances in the Development of 1,4-Cyclohexanedimethanol (CHDM) and Cyclic-Monomer-Based Advanced Amorphous and Semi-Crystalline Polyesters for Smart Film Applications, *Materials*, 2024, **17**(18), 4568.
  - 31 J. He, S. P. Burt, M. Ball, D. Zhao, I. Hermans, J. A. Dumesic, *et al.*, Synthesis of 1,6-Hexanediol from Cellulose Derived Tetrahydrofuran-Dimethanol with Pt-WO<sub>x</sub>/TiO<sub>2</sub> Catalysts, *ACS Catal.*, 2018, **8**(2), 1427–1439.
  - 32 Y. Lee, K.-Y. A. Lin, E. E. Kwon and J. Lee, Renewable routes to monomeric precursors of nylon 66 and nylon 6 from food waste, *J. Cleaner Prod.*, 2019, **227**, 624–633, DOI: [10.1016/j.jclepro.2019.04.194](https://doi.org/10.1016/j.jclepro.2019.04.194).
  - 33 T. Buntara, S. Noel, P. H. Phua, I. Melián-Cabrera, J. G. De Vries and H. J. Heeres, Caprolactam from renewable resources: Catalytic conversion of 5-hydroxymethylfurfural into caprolactone, *Angew. Chem., - Int. Ed.*, 2011, **50**(31), 7083–7087.
  - 34 S. Lima, D. Chadwick and K. Hellgardt, Towards sustainable hydrogenation of 5-(hydroxymethyl)furfural: A two-stage continuous process in aqueous media over RANEY® catalysts, *RSC Adv.*, 2017, **7**(50), 31404–31407.
  - 35 M. H. Tucker, R. Alamillo, A. J. Crisci, G. M. Gonzalez, S. L. Scott and J. A. Dumesic, Sustainable solvent systems for use in tandem carbohydrate dehydration hydrogenation, *ACS Sustainable Chem. Eng.*, 2013, **1**(5), 554–560.
  - 36 J. A. Moore and J. E. Kelly, Polyesters Derived from Furan and Tetrahydrofuran Nuclei, *Macromolecules*, 1978, **11**(3), 568–573.
  - 37 C. Jin, W. Tian, Z. Tu and Z. Wei, Kilogram-Scale Production of Sustainable PCF Copolyesters Based on Novel Cyclic Diol THFDM Derived from 5-Hydroxymethylfurfural: Trade-Off between the THFDM Structure and Various Properties of Copolyesters, *ACS Sustainable Chem. Eng.*, 2021, **9**(39), 13287–13302.
  - 38 C. Jin, F. Ma, C. Li, Z. Tu, H. Wang and Z. Wei, Kilogram-scale preparation of sustainable PETG modified with a bio-based cyclic diol derived from 5-hydroxymethylfurfural: From synthesis to properties, *Eur. Polym. J.*, 2021, **161**(2021), 110832, DOI: [10.1016/j.eurpolymj.2021.110832](https://doi.org/10.1016/j.eurpolymj.2021.110832).
  - 39 Y. L. Chen, Y. S. Mu, Z. J. He, X. M. Pu, D. Q. Wang, M. Zhou, *et al.*, New bio-based polyester with excellent spinning performance: poly(tetrahydrofuran dimethanol-co-ethylene terephthalate), *RSC Adv.*, 2022, **12**(45), 29516–29524, DOI: [10.1039/D2RA04484F](https://doi.org/10.1039/D2RA04484F).
  - 40 C. Jin, B. Wang, L. Liu, Z. Tu and Z. Wei, Biodegradable Poly(butylene succinate) Copolyesters Modified by Bioresourced 2,5-Tetrahydrofuran-dimethanol, *ACS Sustainable Chem. Eng.*, 2022, **10**(34), 11203–11214.
  - 41 Y. Hu, H. Zhang, X. Pu and L. Yang, New Bio-Based Copolyesters Derived from Novel Cyclic Diol 2,5-Tetrahydrofuran-dimethanol, 2,5-Furandicarboxylic acid and 1,3-Propanediol: Synthesis, Thermal Behavior and Rheological Properties, *Polym. Sci., Ser. B*, 2023, **65**(4), 429–437.
  - 42 Y. Liu, B. Zheng, Z. Chen, X. Pu and S. Zhang, 2,5-Tetrahydrofuran-dimethanol as a sustainable comonomer for modification of polyethylene terephthalate: Liter-level pilot test and non-isothermal crystallization kinetics, *J. Thermoplast. Compos. Mater.*, 2024, **37**(4), 1364–1384.
  - 43 D. Wang, X. Pu, Z. He, Y. Mu, Y. Chen, M. Zhou, *et al.*, Bio-Based Copolyester PEIFT: Enhanced Hydrophilicity, Rigidity, and Applications in Nanofibers, *Macromol. Rapid Commun.*, 2024, **45**(12), 1–7.
  - 44 X. Cai, Y. Yang, H. Yu, D. Jiao, L. Xu and D. Zhang, A Sustainable Poly(butylene furandicarboxylate) (PBF)-Based Copolyester Containing a Cyclic Ether Structure: Integrated with High Thermal, Mechanical, and Hydrolytic Degradable Properties, *ACS Sustainable Chem. Eng.*, 2025, **13**(1), 658–668.
  - 45 J. Kim, P. H. Hong, K. Choi, G. Moon, J. Kang, S. Lee, *et al.*, A heterocyclic polyurethane with enhanced self-healing efficiency and outstanding recovery of mechanical properties, *Polymers*, 2020, **12**(4), 968.
  - 46 T. Chen, H. Wu, W. Zhang, J. Li, F. Liu and E. H. Han, A sustainable body-temperature self-healing polyurethane nanocomposite coating with excellent strength and toughness through optimal hydrogen-bonding interactions, *Prog. Org. Coat.*, 2023, **185**, 107876, DOI: [10.1016/j.porgcoat.2023.107876](https://doi.org/10.1016/j.porgcoat.2023.107876).
  - 47 T. Chen, W. Zhang, Y. Li, F. Liu and E. H. Han, A self-healing sustainable halloysite nanocomposite polyurethane coating with ultrastrong mechanical properties based on reversible intermolecular interactions, *Appl. Surf. Sci.*, 2024, **667**, 160399, DOI: [10.1016/j.apsusc.2024.160399](https://doi.org/10.1016/j.apsusc.2024.160399).
  - 48 T. Chen, Y. Li, W. Zhang, F. Liu and E. H. Han, Sustainable photothermal-responsive anti-corrosion nanocomposite coating with distinguished self-healing performance and ultrahigh mechanical properties, *Prog. Org. Coat.*, 2025, **200**, 109070, DOI: [10.1016/j.porgcoat.2025.109070](https://doi.org/10.1016/j.porgcoat.2025.109070).
  - 49 Y. Tokiwa, B. P. Calabia, C. U. Ugwu and S. Aiba, Biodegradability of plastics, *Int. J. Mol. Sci.*, 2009, **10**(9), 3722–3742.

- 50 F. De Falco, R. Avolio, M. E. Errico, E. Di Pace, M. Avella, M. Cocca, *et al.*, Comparison of biodegradable polyesters degradation behavior in sand, *J. Hazard. Mater.*, 2021, **416**, 126231, DOI: [10.1016/j.jhazmat.2021.126231](https://doi.org/10.1016/j.jhazmat.2021.126231).
- 51 J. Huang, C. Cui, G. Yan, J. Huang and M. Zhang, A Study on Degradation of Composite Material PBS/PCL, *Polym. Polym. Compos.*, 2016, **24**(2), 143–148.
- 52 C. Post, D. Maniar, J. A. Jongstra, D. Parisi, V. S. D. Voet, R. Folkersma, *et al.*, Enzymatic bulk synthesis, characterization, rheology, and biodegradability of biobased 2,5-bis(hydroxymethyl)furan polyesters, *Green Chem.*, 2024, **26**(15), 8744–8757.
- 53 Y. Tsai, L. C. Jheng and C. Y. Hung, Synthesis, properties and enzymatic hydrolysis of biodegradable alicyclic/aliphatic copolyesters based on 1,3/1,4-cyclohexanedimethanol, *Polym. Degrad. Stab.*, 2010, **95**(1), 72–78, DOI: [10.1016/j.polymdegradstab.2009.10.006](https://doi.org/10.1016/j.polymdegradstab.2009.10.006).
- 54 X. Cai, X. Yang, H. Zhang and G. Wang, Modification of biodegradable poly(butylene carbonate) with 1,4-cyclohexanedimethylene to enhance the thermal and mechanical properties, *Polym. Degrad. Stab.*, 2017, **143**, 35–41.
- 55 J. S. Ahn, S. M. Kang, M. K. Kim, Y. J. Kim, K. C. Yoon and O. O. Park, Effect of alicyclic monomers on thermal properties of transparent biodegradable polyesters, *Macromol. Res.*, 2016, **24**(7), 609–616.
- 56 H. C. Ki and O. Ok Park, Synthesis, characterization and biodegradability of the biodegradable aliphatic-aromatic random copolyesters, *Polymer*, 2001, **42**(5), 1849–1861.
- 57 D. Maniar, Y. Jiang, A. J. J. Woortman, J. van Dijken and K. Loos, Furan-Based Copolyesters from Renewable Resources: Enzymatic Synthesis and Properties, *ChemSusChem*, 2019, **12**(5), 990–999.
- 58 F. Silvianti, D. Maniar, B. Agostinho, T. C. de Leeuw, A. J. J. Woortman, J. van Dijken, *et al.*, Enzymatic Synthesis of Copolyesters with the Heteroaromatic Diol 3,4-Bis(hydroxymethyl)furan and Isomeric Dimethyl Furandicarboxylate Substitutions, *Biomacromolecules*, 2024, **25**(5), 2792–2802.
- 59 F. Silvianti, D. Maniar, T. C. de Leeuw, J. van Dijken and K. Loos, Enzymatic polymerization of furan-based polymers in biobased solvents, *RSC Sustainability*, 2024, **2**(11), 3436–3450.