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Focus Article, *Mendeleev Commun.*, 2023, **33**, 1–8

Mendeleev
Communications

# Dynamic materials derived from biobased furans: towards the ‘sleeping giant’ awakening

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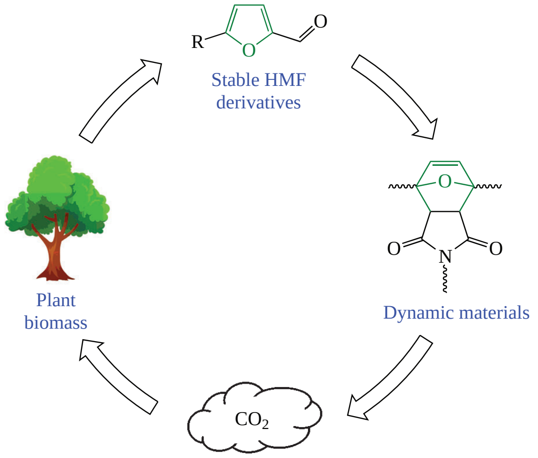
DOI: 10.1016/j.mencom.2023.01.001

**This focus article presents the author’s view on the problems in the development of biorefining strategies based on the use of 5-(hydroxymethyl)furfural (HMF), the key product derived from renewable plant biomass that was recognized as the ‘*sleeping giant*’ of the sustainable chemistry. The several key problems that hinder the large-scale production of HMF and its applicability in the laboratory organic synthesis and industry are discussed. This minireview is also focused on the development of the dynamic cross-linked polymers with controlled three-dimensional structure based on Diels–Alder reaction of biobased HMF-derived furans with maleimides. Realization of scalable technologies for an efficient production of such ‘smart’ analogues of the traditional petrochemical-based materials could be the basis for the realization of the competitive HMF-promoted biorefining.**



*Keywords*: plant biomass, platform chemicals, renewable furans, 5-(hydroxymethyl)furfural, Diels–Alder reaction, dynamers, covalent adaptable networks.

## 1. Introduction

The modern worldwide economy is highly dependent on fossil resources. The world’s oil consumption is around 4 billion tons per year, most of which converts to gasoline and other fuels, and ~10% is used for the needs of the chemical industry to produce high volume chemicals and materials, solvents and various high value-added products.[1] Although the share of the alternative energy (such as hydro-, solar-, nuclear energy and biofuels) is growing but not fast enough: its share grew by only ~4% during the last 5 years, reaching the amount of ~18% of total worldwide generated energy.[1] The dependence of the chemical industry on fossil raw materials is even more evident: only ~10% of chemicals and ~2% of polymeric materials were derived from renewable feedstocks.[2,3] Such a heavy dependence of the global economy on fossil resources resulted in several challenges such as high volatility of fossil resources prices, high carbon dioxide emission and the depletion problems. The only possible approach to solve these limitations is the transition to a circular carbon-neutral economy based on the use of renewable carbon and energy sources.[4,5] The world’s transition to a more sustainable future is currently underway: the reaching of the carbon neutrality for some major developed and developing countries is expected to be around 2030–2050.[6,7]

Biomass that consists mainly of terrestrial plants is one of the largest and virtually inexhaustible sources of renewable carbon. The annual reproduction of biomass is ~150–170 billion metric tons that is more than enough to meet the needs of mankind for energy and materials.[8,9] The main components of plant biomass are cellulose (35–50%), hemicelluloses (20–35%), and lignin (10–25%); the carbohydrate part is more valued than lignin due to its easier processing.[10,11] In 2010, the US department of energy compiled the list of the most valuable carbohydrate-based low-molecular-weight products which can be obtained from lignocellulic biomass by catalytic or biocatalytic conversion that were so-called ‘platform chemicals’.[12] The revised list included twelve compounds involving alcohols, acids, carbohydrates, furans and biohydrocarbons containing from 2 to 6 carbon atoms (Figure 1).[12] It is believed that these renewable building-blocks

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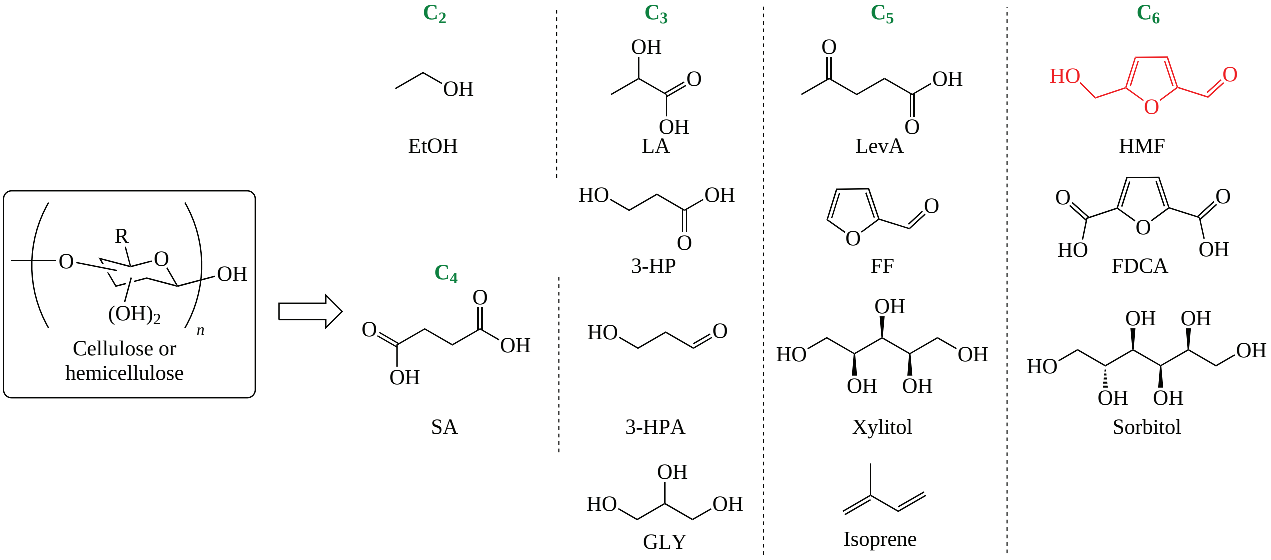


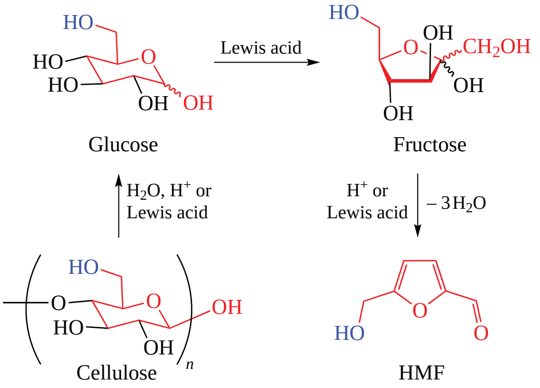
**Figure 1** Top 12 value-added renewable chemicals from plant biomass.

will provide an efficient replacement of exhaustible fossil raw materials for the realization of the carbon-neutral chemical industry to obtain energy, materials, pharmaceuticals and other practically important products.[13–17] Among these products, furanic platform chemicals [furfural, 2,5-furandicarboxylic acid and 5-(hydroxymethyl)furfural (HMF)] have the greatest synthetic and market potential, and HMF was even defined as the 'sleeping giant' of sustainable chemistry.[18–24] It is expected that HMF will be the key element in the transition to a $CO_2$-neutral chemical industry.[23,25]

Currently, the production of new polymer materials from biobased feedstocks is one of the general tasks of the modern chemical science and technology.[26,27] Due to the dienic nature of the furan ring, furanic polymers (that can be obtained employing biobased furfurals) were widely used for the development of the dynamic materials based on the reversible Diels–Alder reaction. This focus article may be viewed as an author's attempt to find the scientific answer to the question of how to awake the 'sleeping giant' HMF. For this, the main problems towards the large-scale industrial synthesis of HMF and its application for the development of dynamic materials based on furan–maleimide Diels–Alder reaction are discussed.

## 2. 5-(Hydroxymethyl)furfural: the 'giant' that is still asleep

Two conceptually different approaches are used for biorefining purposes (Figure 2).[23] The first approach that can be defined as the 'new (or innovative) biorefining' means the use of renewable building blocks as basic raw materials for the production of new practically valuable products, with the aim to substitute the existing products of the petrochemical industry. Usually, these new products have increased oxygen content due to the high oxygenation of the starting plant biomass. The second, 'drop-in', approach means the sustainable production of key products of the petrochemical industry (such as low-oxygenated base and commodity chemicals, materials and high value end-products) starting from renewable biobased feedstocks. From a chemical point of view, the second pathway looks more difficult, since requires the additional stages of the deoxygenation. At the same time, the shifting towards the 'new biorefining' is complicated by the low levels of knowledge about the technological and market potential of the innovative biobased products.



**Scheme 1** General scheme for the conversion of carbohydrates into HMF.

Biobased 5-(hydroxymethyl)furfural is a furanic compound that can be obtained by acid-catalyzed dehydration of different hexose carbohydrates (Scheme 1).[25,28–31] Both ketoses and aldoses can be used for the carbohydrate-to-HMF transformations, but with different efficiency. The highest selectivity in the dehydration of fructose and other ketoses into HMF was achieved using Brønsted acid catalysts.[32,33] The conversion of glucose and other aldoses is less selective since requires a preliminary stage of ketose-to-aldose isomerization. Lewis acids and catalysts with dual functionality have shown highest efficiency in the conversion of aldohexoses into HMF.[25,34,35] The great synthetic potential of HMF is provided by the presence of several reactive functionalities in one molecule: aldehyde and hydroxymethyl groups, and the furan ring. More than 12 thousand articles and patents on the synthesis and chemistry of HMF have been published in the last two decades.[36] Both traditional oil refining products, such as caprolactam, caprolactone, adipic acid and hexanediol, as well as a large number of new furanic and non-furanic derivatives have been obtained *via* the reductive or oxidative upgrading of HMF (Scheme 2) that was highlighted in many recent reviews.[37–44] The development of the HMF-derived biofuels, chemicals and materials for application in different areas, from bioactive compounds and drugs to surfactants and polymers for 3D printing, is being actively studied.[45–51]

Some HMF derivatives are promising substrates in the Diels–Alder (DA) reaction with various dienophiles (alkenes, alkynes, arenes) that was successfully used as a sustainable route to cyclic products with aliphatic or aromatic structure.[50,52–55] The intermolecular furan–alkene DA reaction could be a basis for the HMF-promoted drop-in biorefining by acting as a chemical bridge between carbohydrates and *para*-xylene derivatives which are one of the most important aromatic petrochemicals.[56–59] Regarding 'new' biorefining concept, a furanic monomer 2,5-furandicarboxylic acid (FDCA) and its polymer polyethylene

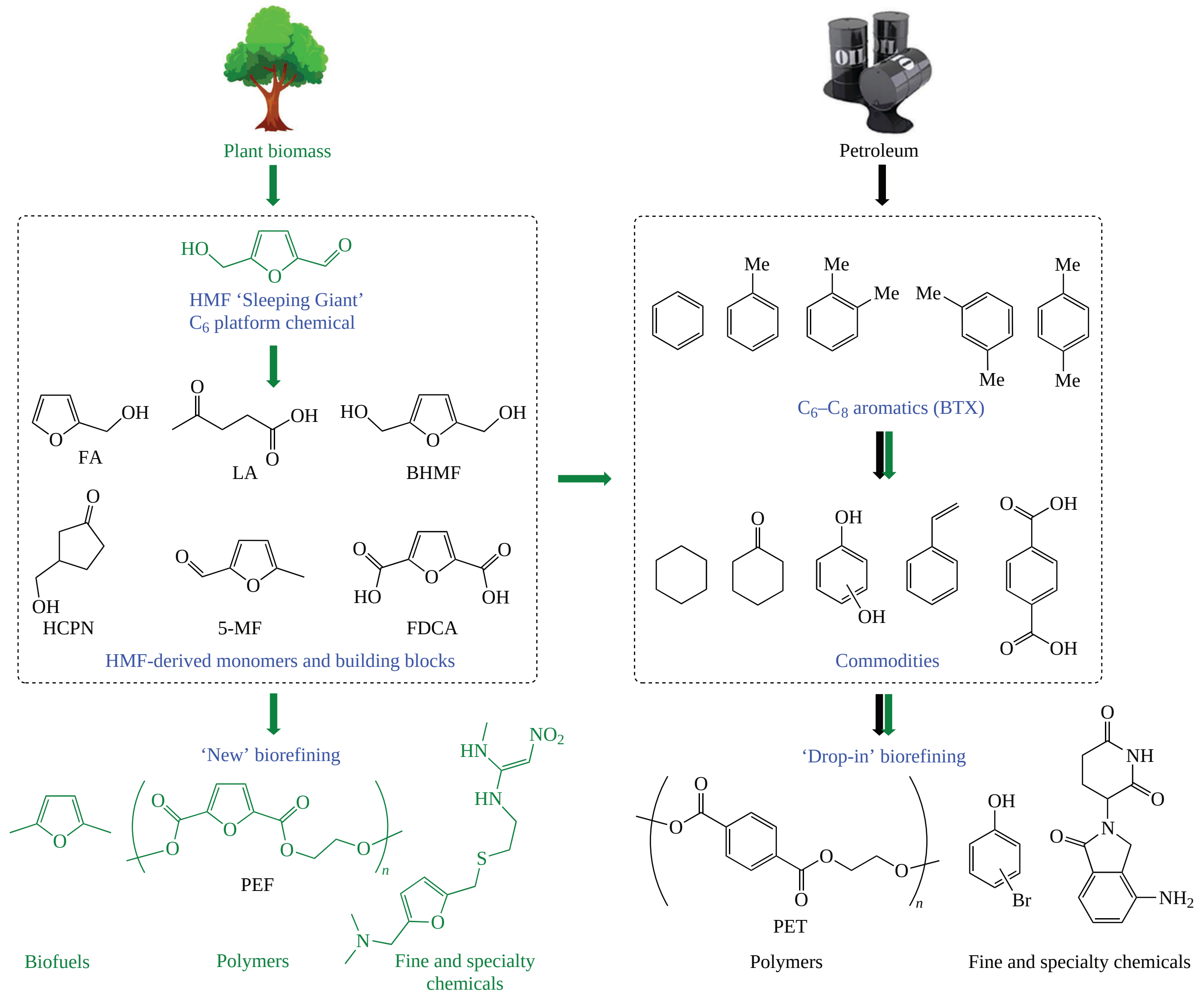
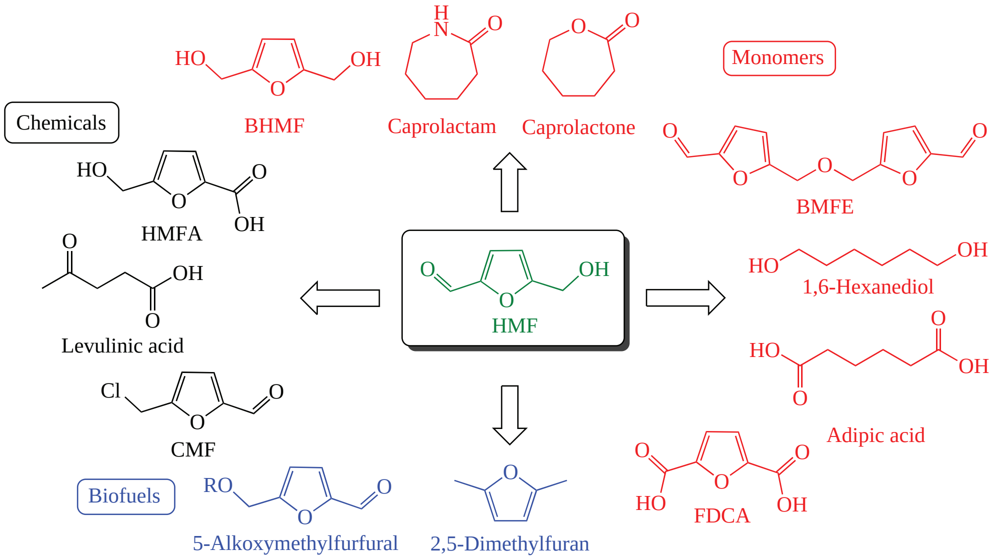


**Figure 2** Two approaches for HMF-based biorefining (indicated by green arrows).

furanoate (PEF), which is a sustainable analogue of the widely used petroleum-based polymer polyethylene terephthalate (PET), become one of the most privileged innovative HMF-based products.[10,60–64] The PEF has better barrier characteristics and low rigid structure than PET and therefore can be considered as more suitable for the use as a packaging material.[65–67] However, despite the apparent benefits of the HMF-derived products and several attempts for its commercialization,[68,69] the large-scale industrial production of HMF is not yet running, the 'giant' HMF is indeed asleep.

Efficient industrialization of HMF is limited by several economical and technical obstacles that results in high price of



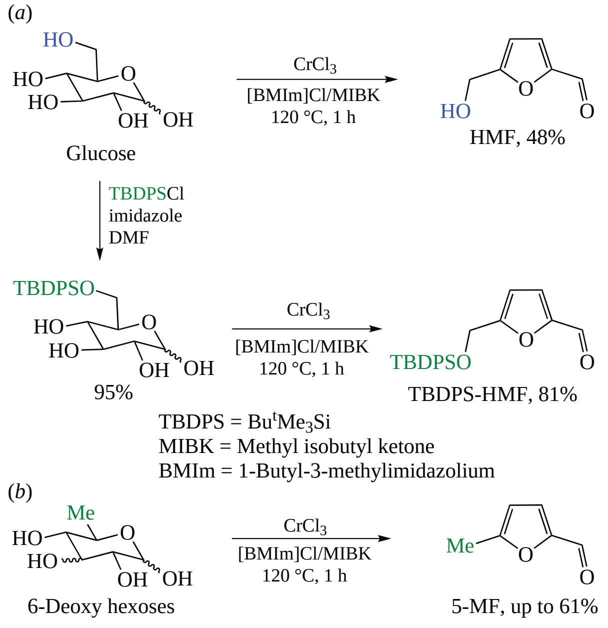
**Scheme 2** Value-added products derived from HMF.

HMF.[68,69] One of the main problems relies on the chemical instability and highly hydrophilic nature of HMF molecule that significantly complicates isolation of HMF and its followed application in organic synthesis.[69–72] It was shown[73] that HMF can undergo a very easy oligo- and polymerization even during storage in an oily state. Highly pure crystalline HMF proved to be more stable and can be stored for a long time without a significant degradation.[73]

The possible solution to the problem of instability of HMF is one-pot conversion of carbohydrates into stable furanic derivatives that may proceeds with or without formation of unstable HMF as an intermediate.[53,74] The Lewis-acid catalyzed dehydration of C6-silylated glucose into *O*-silylated HMF (TBDPS-HMF) in the biphasic [BMim]Cl/MIBK medium showed higher selectivity (~81%) and easier isolation of the resulting product as compared to the conversion of unmodified glucose into HMF under the same reaction conditions [Scheme 3(*a*)].[73] The similar approach was used for the conversion of naturally available L-rhamnose (6-deoxy-L-mannose) or D-quinovose (6-deoxy-D-glucose) into 5-methylfurfural (5-MF) that was considered as a promising renewable platform for biofuels [Scheme 3(*b*)].[75] Recently, high attention was devoted to the synthesis and chemistry of 5-chloromethylfurfural (CMF) which is a highly reactive chlorinated derivative of HMF.[71,76–78] Due to high stability, retained synthetic potential and possibility of high-yielding preparation directly from carbohydrates, this furanic building block was called by Mascal as the ‘new HMF’.[79]

The increasing of the competitiveness of the HMF-based biorefining may also rely on the diversification of HMF into stable multifunctionalized building blocks with high synthetic potential.[53] From this point of view, modification of HMF-derived furans at the α- or β-positions of the furan ring opens access to a variety of polysubstituted furanic monomers and chemicals. In this connection, particular importance has been attributed to the methods for regioselective C−H functionalization of HMF-derivatived furans using transition metal catalysis.[80–85]

The way towards the giant HMF ‘awakening’ may be associated with the application of stable HMF-derived building blocks for the development of end-products with specific practically valuable properties which differ from traditional products derived from petrochemical substrates. In this context, of considerable interest are the dynamic polymers based on the reversible DA reaction of biobased furans with maleimides. These materials have a number of important advantages over the traditional materials, such as the ability to self-healing and shape memory; also, their use provides more opportunities for re-processing and recycling.



**Scheme 3** Conversion of C6-modified carbohydrates (*a*) and naturally available 6-deoxy carbohydrates (*b*) into stable HMF derivatives.

## 3. Dynamic materials based on the furan–maleimide Diels–Alder reaction with HMF-derived furans

The classical DA reaction is the interaction between the electron-rich diene and electron-poor dienophile resulting in the formation of the new six-member ring. The intermolecular furan–maleimide DA (*fm*DA) cycloaddition is characterized by a number of important advantages such as atom economy, high selectivity and efficiency for a wide range of substrates, therefore it may be recognized as a sustainable ‘click’ approach for the development of molecular, macromolecular and organic–inorganic hybrid systems.[86–88] The direct DA reaction of furanic aldehydes with maleimides is thermodynamically unfavorable,[55,89,90] but this type of reactions can be carried out after the modification of the aldehyde into more donor functional group.[55,87,91,92] The nature of the substituent at the C2,5 positions of the biobased furans strongly affects its reactivity in the DA cycloadditions: furans with electron-donating groups are well suited as substrates, while furans containing substituent with electron-accepting properties display low reactivity.[93–95]

The reversibility of the furan–alkene DA reaction may prevent the efficient formation of the corresponding furan–alkene adducts. On the other hand, reverse (retro) Diels–Alder (rDA) reaction of furans with maleimides was efficiently used in the design of ‘smart’ dynamic polymeric systems which exhibit important properties such as self-healing and shape memory (Figure 3). The possibility of creating ‘smart’ dynamic materials employing the biobased furans is provided by the low or moderate thermodynamic barriers of the reverse *fm*DA reaction that is usually performed with after external stimuli such as temperature, light, mechanical or magnetic force. In recent years, the high interest is related to the development of dynamic thermosets, also so-called ‘covalent adaptable networks (CANs)’, based on *fm*DA reaction.[88,96] The presence of dynamic covalent bonds in these three-dimensional materials provides the ability for easy (re)processing and recycling, which is very difficult for the classical covalently crosslinked thermosets.

The numerous recent investigations on the synthesis of linear or three-dimensional dynamic polymers and composites using *fm*DA reaction with biobased furans for application as structural materials, supramolecular systems, hydrogels, and coatings with tunable adhesion which have promising potential for biomedical applications or smart materials development were highlighted in many recent reviews.[86,96,99–104]

Several approaches have been developed for the synthesis of CANs using the *fm*DA reaction (Scheme 4). Two general pathways include: cross-linking of linear furanic pre-polymer by bis-maleimide [Scheme 4(*a*)] and polycondensation of polyfunctional *fm*DA adducts (monomers or polymers) [Scheme 4(*b*)]. Owing to the usually higher reactivity of the C5-unsubstituted furans in the DA reaction, furfural derivatives are usually used for the synthesis of dynamic materials by introduction of the furanic core into the backbone of the linear polymer chain followed by the cross-linking with bis-maleimide.[86,88,96] This type of dynamic polymers can be obtained using HMF, but requires non-atom-economic defunctionalization at the C5 position of the furanic core.

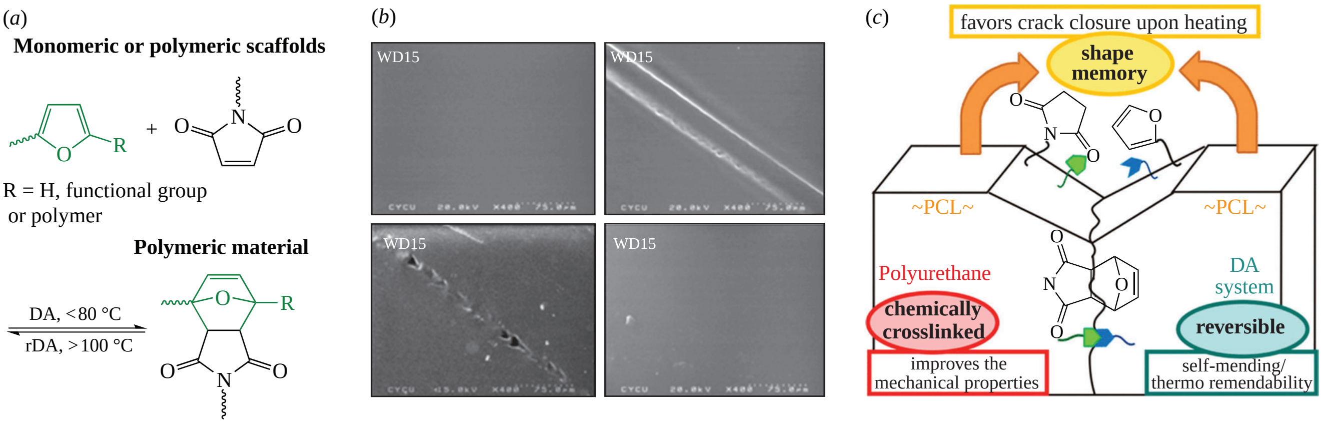
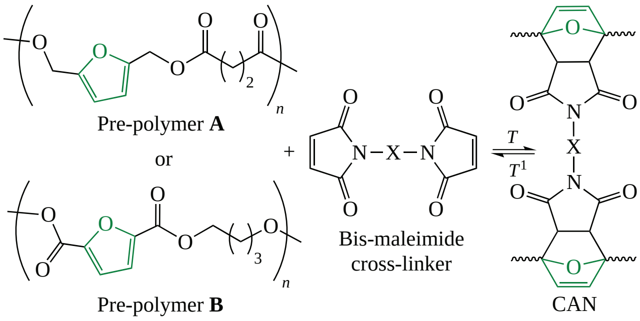
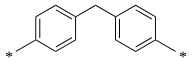


**Figure 3** (*a*) Reversible *fm*DA reaction. (*b*) Scanning electron microscopy visualization of the self-healing process in the thermally remendable epoxy resin. (Reproduced with permission from ref. 97. Copyright 2006, Wiley-VCH). (*c*) Schematic depiction of the shape memory process in the dynamic polyurethane material. (Reproduced with permission from ref. 98. Copyright 2014, American Chemical Society).

Recently, the cross-linking of linear HMF-based polymers with bis-maleimides was used for the preparation of dynamic cross-linked polyesters[105–113] and polyurethanes[114–117] some of which have shown high self-healing ability even without any external stimuli. Bis-maleimides with a long and flexible chain exhibited higher reactivity in a self-healing process than the short and/or rigid linkers (Table 1, entries 1–5). The CANs containing acceptor-type furanic cores displayed self-healing ability only at relatively high temperatures (Table 1, entries 6, 7) due to the higher activation energies of the *fm*DA reaction with acceptor-substituted furans.[101]

**Table 1** Self-healing efficiency for various types of HMF-derived pre-polymers and bis-maleimides.

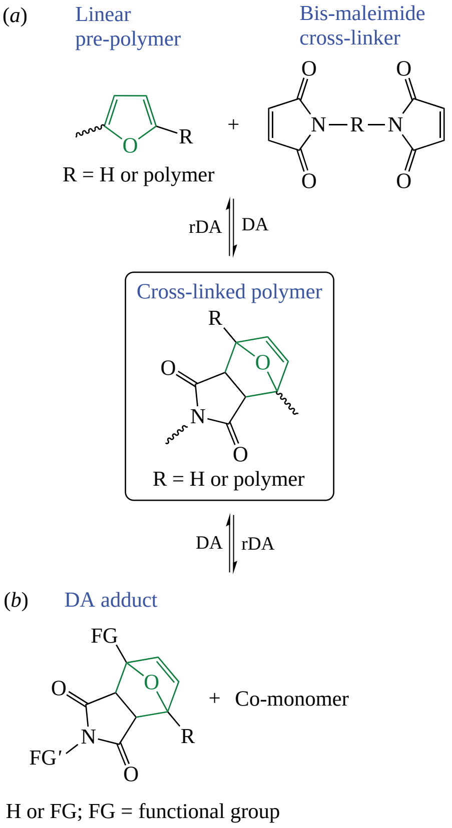


| No. | Pre-polymer | X | F/M$^a$ ratio | $T$/°C | $T^1$/efficiency of self-healing | Ref. |
|---|---|---|---|---|---|---|
| 1 | **A** | $(CH_2)_2$ | 6/1 | 40 | RT$^b$/9 | 105 |
| 2 | **A** | $(CH_2)_6$ | 6/1 | 40 | RT/72 | 105 |
| 3 | **A** | $[(CH_2)_2OCH_2]_2$ | 6/1 | 40 | RT/74 | 105, 106 |
| 4 | **A** | $[(CH_2)_2OCH_2]_2$ | 4/1 | 40 | RT/~22 | 105 |
| 5 | **A** | 1,4-phenylene | 6/1 | 40 | RT/~8 | 105 |
| 6 | **A** |  | 6/1 | 40 | RT/~8 | 105 |
| 7$^c$ | **B** | $(CH_2)_6$ | 6/1 | RT | 30/0 | 107 |
| 8 | **B** | $(CH_2)_6$ | 6/1 | 50 | 50/82 | 107 |

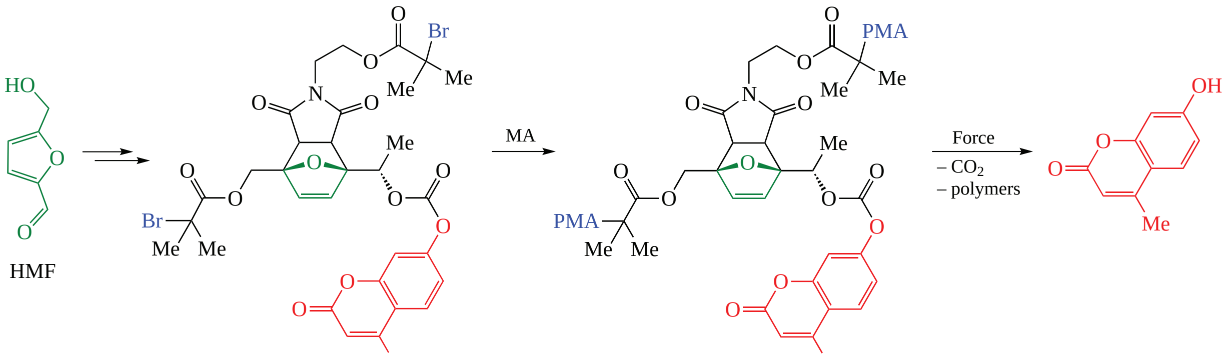
$^a$Furan/maleimide. $^b$RT – room temperature. $^c$The dynamic polymer blended with polyurethane was used.

An alternative strategy for the synthesis of linear or three dimensional dynamic polymers is polycondensation of polyfunctional *fm*DA adducts [Scheme 4(*b*)]. The *fm*DA adducts obtained from furfural-derived building blocks were widely applied for the synthesis of dynamers using this approach,[88] and only limited examples of application of the HMF-derived polyfunctional DA adducts were found in the scientific literature. Robb and co-workers described the preparation of the stimuli-responsive mechanically triggered co-polymer **2** by multistage modification of HMF into DA adduct **1** followed by co-polymerization with methyl acrylate (MA).[118] This mechanophore released a small coumarin-like molecule after the mechanical stress (Scheme 5).[118]

A valuable green approach to the synthesis of recyclable linear and cross-linked sustainable polymers based on HMF-derived acetales was reported by Dumesic and co-workers.[119] Recyclable linear DA polymer obtained by polycondensation of HMF acetale with pentaerythritol and 4,4′-bis(maleimido)-diphenylmethane can undergo acid-catalyzed full depolymerization into monomers. Cross-linking of this polymer with bis-isocyanate afforded polyurethane CAN with self-healing ability (Scheme 6).[119]



**Scheme 4** General approaches for the *fm*DA based dynamic materials employing biobased furans: cross-linking of linear furanic pre-polymer by bis-maleimide (*a*) and polycondensation of polyfunctional *fm*DA adducts (*b*).



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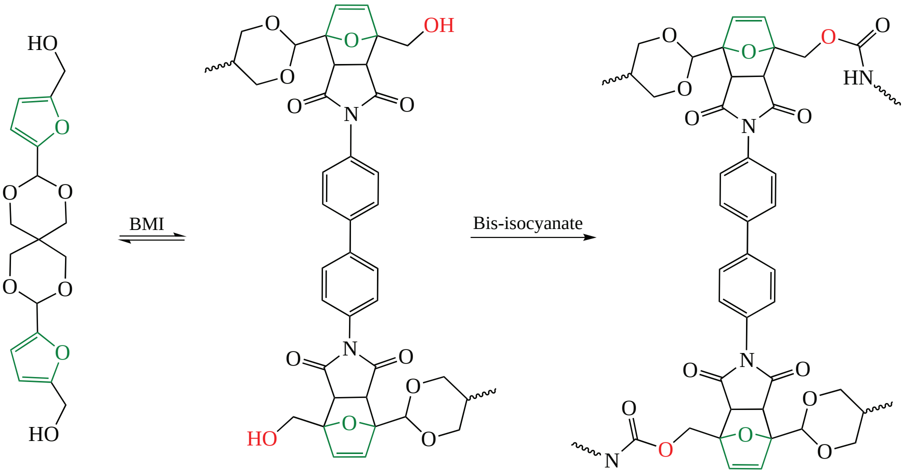
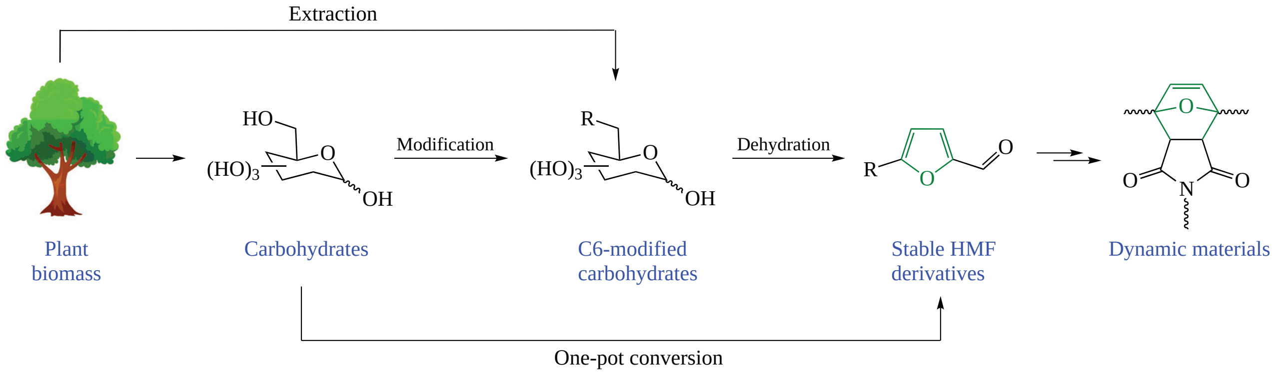
**Scheme 5** Synthesis of stimuli-responsive mechanically triggered polymers from HMF.



**Scheme 6** Synthesis of recyclable linear and cross-linked sustainable polymers based on HMF-derived acetales.



**Scheme 7** The pathways towards ‘sleeping giant’ HMF awakening that have been discussed in this minireview.

## 4. Conclusions

The application of biobased carbohydrates-derived ‘giant’ HMF for the development of practically important products represents an elegant and attractive chemical route towards a sustainable supply of energy, chemicals and materials. The use of HMF and other renewable raw materials as chemical building blocks leads to a reduction in the ‘carbon footprint’ during the industrial production and consumption. Despite the very high synthetic and market potential of HMF and derivatives, their industrial application is only beginning. The key limitations include the chemical instability of HMF and unclear commercial competitiveness of the HMF-based products.

Therefore, one might say that the development of the new approaches to increase the competitiveness of the HMF-based biorefining is required. The possible way to ‘giant’ HMF awakening that was discussed in this minireview may rely on the preparation of stable HMF-derived building blocks and their application for the production of various dynamic polymeric and hybrid systems as ‘smart’ analogues of the traditional petrochemical-based products (Scheme 7). In this context, the central attraction should be attributed to the connection of chemistry of furfural and HMF, and to the development of efficient synthetic methodologies for the use of bioderived furans as diene components in the DA reaction.

This study was supported by the Russian Science Foundation (RSF Grant no. 21-73-20117).

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*Received: 2nd November 2022; Com. 22/7037*