

1

A Brief History

Furfural (F) industrial production, from pentose-rich oat hulls, begun in 1922 at the Quaker Oats cereal mill in Iowa, and soon after its first resins for molding and abrasive tools were on the market in the US. That was followed by furfuryl alcohol (FA) industrial production by the same company in 1934, through an efficient F reduction process, and its resins for the foundry business in 1958 became commercially available. In both instances, these materials were crosslinked polymers with useful thermal and mechanical properties, but little was known about their mechanisms of formation and ultimate structures. It is most likely that the resinification of both these furans was a frequent unwanted event when handling them from their earlier synthetic operations and isolation, given their sensitivity to accidental polymerization, particularly in acidic media. It is moreover particularly relevant to note that since the inception of a series of thermoplastic (cellulose esters) and thermoset (linoleum and vulcanized natural rubber) materials from renewable resources during the second half of the nineteenth century, these furan resins were the first novel materials being produced from renewable resources in the twentieth century. In another vein, F was converted into adiponitrile for the manufacture of Nylon 6,6 and in this du Pont process of 1949, the tetrahydrofuran intermediate was also later utilized to prepare poly(tetramethylene ether)glycol.

A very modest number of other interesting contributions to furan polymers can be found in the period going back to the late 1960s, whereas the following decade saw what should be considered as the beginning of serious research aimed at preparing and characterizing such materials and unravelling the mechanisms of their formation. The first review on furan polymers, published by one of us in 1977 [1], reflects this initial ferment, albeit underlining that much of it was not entirely gratifying in terms of scientific depth or practical success as far the properties of the ensuing materials. It can be argued that this state of affairs stemmed in part from the few and non-communicating groups scattered around the world, with only one laboratory at Havana University doing systematic work on the

polymerization of alkenyl furans and other F-derived monomers. Examples of the paucity of research topics pointed out in that review reflected mostly the rare reports on furan polyesters and polyamides and the absence of studies on polyurethanes, epoxies and other relevant polycondensates. This problem mostly reflected the difficulty in efficiently preparing bifunctional monomers, which were difficult to attain from the monofunctional F and FA.

Some 10 years later, a second review [2] reflected a much-improved situation with a variety of novel investigations covering a wider domain of polymer syntheses and structures, suggesting that the 1980s had brought about a significant awakening concerning the interest of working on furan polymers. But the availability of bifunctional monomers persisted because of the difficulties associated with producing hydroxymethylfurfural (HMF) from hexoses in economically viable quantities.

The overall positive trend was however to continue, as reflected by a third review published a decade later [3], in which the sheer volume of available scientific literature on the subject (reflected by the more than 300 references) was as impressive as much of its scientific and applied quality. This advance was facilitated by the progress in the exploitation of HMF as a source of various bifunctional monomers well suited for the synthesis of polyesters, polyamides and polyurethanes, among other polycondensates.

The research aimed at optimizing the production of HMF became an international effort at the end of the twentieth century, with the primary aim consisting in using it to prepare the corresponding diacid, 2,5-furandicarboxylic acid (FDCA) as the priority monomer, although other difunctional homologues, such as the 2,5-bis(hydroxymethyl)furan (BHMF), were also actively sought, as discussed in a fourth review [4]. The success of this strategy and of other original approaches, notably the application of the Diels–Alder reaction, meant that within another quarter of a century, furan polymers have progressively become a household item to macromolecular scientists, as highlighted by a recent fifth review [5], which represented a skeletal work in progress for the writing of this comprehensive book, which attempts to provide a full picture, going from the pioneering investigations of some 50 years ago to the opening up of brilliant perspectives inspired by the most recent advances.

The numerous breakthroughs that took place in this relatively short saga are documented in detail in each chapter together with a deserved mention to the colleagues who were and are behind these achievements.

References

- 1 Gandini, A. (1977). *Adv. Polym. Sci.* 25: 47–96.
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- 3 Gandini, A. and Belgacem, M.N. (1997). *Progr. Polym. Sci.* 22: 1203–1379.
- 4 Moreau, C., Gandini, A. and Belgacem, M.N. (2004). *Topics Catal.* 27: 11–30.
- 5 Gandini, A. and Lacerda, T.M. (2022). *Macromol. Mater. Eng.* 307: 2100902.