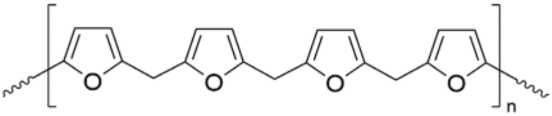
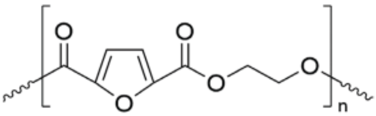
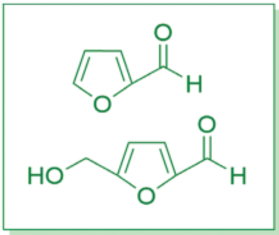
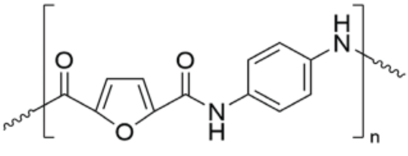
FURAN POLYMERS
AND THEIR REACTIONS

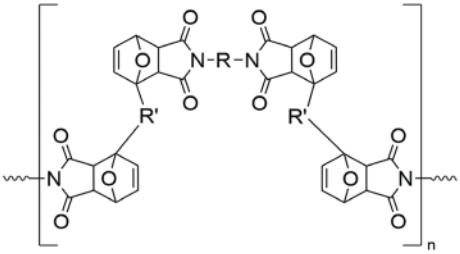
ALESSANDRO GANDINI
TALITA MARTINS LACERDA











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Furan Polymers and their Reactions

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Contents

Foreword

Furan Polymers and their Reactions surveys the chemistry of these crucial renewable heterocyclic compounds and their contributions to polymer synthesis with a large variety of their structures. This book discusses the biorefinery of furans, identifies furfural and 5-hydroxymethyl furfural as the key furan monomer precursors for different polymer synthetic processes, and analyzes all the major reactions the monomers undergo during these processes, as well as the structures, properties, modifications, and applications of the ensuing materials. The results are a vital contribution to the growing field of renewable macromolecular materials.

The book provides an up-to-date and detailed analysis of key polymerization reactions such as chain-growth and step-growth polymerizations and the furan/maleimide Diels–Alder reaction, both as a polycondensation tool and as one of the sources of the chemical modifications of polymers.

Furan Polymers and their Reactions is an essential resource and is highly recommended for researchers and professionals in industrial engineering, polymer science, and biotechnology, as well as for any industry professionals working with platform chemicals or polymer synthesis.

Kris Matyjaszewski
Carnegie Mellon University
Pittsburgh, May 2023

Preface

Eons of evolution have gradually transformed biological structures and functions in all areas of life through increasing molecular complexity and interactions which provided specific adaptations by natural selection. The synthesis of macromolecules in both animal and vegetal species has fulfilled vastly different roles ranging from DNA for genetic information to cellulose and lignin for structural solidity, all being regularly renewed by appropriately adapted pathways in which solar energy is, directly or indirectly, the driving force. In the context of materials science, natural polymers have provided mankind for millennia with valuable sources of living support, including shelter, clothing, tools, and cultural artefacts, aided by technological adaptations, such as natural fiber weaving, papyrus- and then papermaking, leather tanning and construction ingenuities like waterproofing, gluing, as well as hunting and fishing aids. Although some chemistry was unknowingly involved in these activities, the actual suitable chemical modification of natural polymers only begun in the nineteenth century essentially with the preparation of cellulose esters, the vulcanization of rubber, the exploitation of natural resins for making adhesives and sealants, and the controlled drying of plant oils to prepare plastic sheets like linoleum. The major progress, however, occurred throughout the twentieth century because of the chemical revolution associated with the exploitation of fossil resources to prepare monomers and to implement their polymerizations and thus provide an array of synthetic macromolecular materials endowed of different properties and applications. This vigorous development, particularly during the second half of the century, which took the inaccurate name of “plastic revolution”, went for a large part to the detriment of the pursuit of research in the realm of renewable resources as providers of monomers and their polymers, with few novel contributions. This situation started changing toward the end of the century when the paradigm of sustainability begun to make its way within the general conscience in the wake of calls to reduce the dependence on materials and energy providers based on the use of dwindling petroleum and natural gas reserves and to reduce their negative ecological impact to the planet. Research on the alternative exploitation of renewable resources for the same purposes thus resurfaced first timidly, then progressively with more impetus in academy and industry as the century was coming to a close to welcome the new millennium.

This state of affairs is opening a bright scenario in which polymers from renewable resources are witnessing a spectacular growth in the twenty-first century because they represent the response of macromolecular science and technology to the challenges of fighting climate deregulation, together with the equally fundamental search for renewable energy resources, both presently dominated by the exploitation of fossil counterparts. A 2008 monograph provided the first comprehensive state of the art on these materials [1] and numerous reviews followed, with a recent overview of the topic [2] aimed at highlighting the incessant progresses and perspectives in all its domains. The topic is usually subdivided into three major approaches to the elaboration of materials from renewable resources, namely (i) the synthesis of important polymers which are traditionally prepared from fossil resources and can also be prepared now using the same monomers, but derived from renewable counterparts, (ii) the chemical modification of natural polymers to generate novel materials, and (iii) the exploitation of a variety of monomers and macromonomers derived from renewable resources to prepare original macromolecular structures with interesting, or unique, properties and promising applications.

Furans constitute a major class of potential monomers pertaining to the third approach, and this book's title is a minimalist condensation of the important reality of polymers containing furan units derived from natural resources based on polysaccharides and sugars found worldwide as agricultural and forestry side-products, or available in sufficient quantities to justify their exploitation without affecting the food and feed requirements. Two compounds, furfural and hydroxymethylfurfural are readily prepared from these pentoses and hexoses and can be turned into a variety of monomers, thus generating a whole family of sustainable materials covering virtually all structures and properties already found in fossil-based polymers and even previously unattained performances. This situation is unique, since it cannot be achieved with other natural polymer like cellulose, starch, natural rubber and chitosan, or indeed with such natural monomers as terpenes and vegetable oils, because in all these contexts, their inherent chemical structures limits the breadth of polymer properties that can be obtained, notwithstanding the very impressive variety of materials which have and are being successfully prepared and which have so importantly enriched the domain of polymers from renewable resources.

Molecules and macromolecules incorporating the furan heterocycle have been known or synthesized since 1780 when 2-furoic acid was first prepared by Scheele, followed by furfural, furfuryl alcohol and furan itself in the nineteenth century, and by hydroxymethylfurfural and the first industrial furfuryl alcohol resins in the mid-twentieth century. The real event, however, that established furans as a widely recognized branch of chemistry was the publication in 1953 of a seminal book, *The Furans*, by A.P. Dunlop and F.N. Peters (ACS Monograph Series N° 119, Reinhold Publishing Co., New York), two high ranking industrial chemists working at the Quaker Oats Company, the progenitor of furfural and furfuryl alcohol. This monumental monograph of close to 900 pages and covering virtually all furan compounds known then, set the scenario for the development of furans in all major branches of chemistry, including organic synthesis, natural compounds, pharmaceuticals, industrial aspects (particularly for the production of furfural), and the nascent macromolecular field (particularly related to furfuryl alcohol resins). Although numerous book chapters, reviews and patents, based on much published research, have since been covering these topics, no other volume has appeared updating the general field of furans in such a comprehensive treatment. Indeed, the present book is no exception, because its purpose is confined to the area of furan polymers, with the specific message of highlighting the renewable character of these materials and hence providing a contribution to the enhancement of sustainability in the realm of macromolecular science. The field of furan polymers is less than a century old and much younger if one considers materials other than the by-now classic resins based on furfuryl alcohol. It seems fair to point out that serious interest in these materials only begun a few decades ago. Several reviews have covered this area since then but, given the rapid upsurge of important advances in different widening contexts, the need for a more comprehensive and updated monograph prompted us to write this book, which attempts to provide a systematic coverage, while giving more emphasis to recent progress, and to propose ideas about future perspectives and practical developments.

We thought it would be useful to begin with a brief historical sketch and with a chapter devoted to a concise reminder of the chemical peculiarities associated with the furan heterocycle because of their strong implications in determining the behavior and mechanisms of most of the types of polymerizations to be discussed. This introductory chapter is however not intended to cover the organic chemistry of furans, whose synthetic and reactivity aspects fall outside the scope of the book. We also decided to treat the polycondensation of furfuryl alcohol and the ensuing materials in a separate first chapter of the book's main subject because of the unique historical and mechanistic features of what remains today the most important furan industrial material, although this primacy might not last much longer. The rest of the book is organized as in a classical polymer treatise, namely by treating chain- and step-growth systems separately. The properties and potential applications of these materials from renewable resources are outlined when the preparation of each of them is discussed, often comparing their features with those of traditional fossil-based counterparts or emphasizing their unique connotations. We wish to reiterate that the sustainability connotation permeating each section of the book is as essential an ingredient as its actual portrayal of a notable family of macromolecular materials.

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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

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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.

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2

The Peculiar Chemical Features of the Furan Heterocycle and the Synthesis of Furfural and Hydroxymethylfurfural

Following the classic treatise where Dunlop and Peters covered systematically in 1953 the domain of furans in a comprehensive approach [1], several monographs discuss advances in the organic chemistry of furans [2], their naturally occurring compounds [3], and the pharmacological features of some derivatives [4]. This book does not deal with these issues, concentrating instead on furan polymers, but a brief outlook is provided here about the furan-specific chemical properties and reactivity, which are closely related to the polymerization behavior of furan monomers.

The furan heterocycle belongs to the family of five-member ring unsaturated compounds, and its structure can be displayed by the resonant forms shown in Figure 2.1.

Substitution reactions of furans such as alkylation, halogenation, nitration, and sulfonation take place regioselectively at the C2 and/or C5 positions, which indicate that C and D are the dominant structures.

Compared with its sulfur and nitrogen homologues, furan possesses a reduced aromatic character and thus the most dienic, as illustrated in Figure 2.2, where benzene is the reference aromatic compound and cyclopentadiene the reference diene. The Dewar resonance energies decrease from 95 kJ mol^{-1} for benzene to 27 for thiophene, 22 for pyrrole, 18 for furan, and close to zero for cyclopentadiene.

This feature has an important bearing on much of the chemical behavior of furan, as briefly outlined below.

2.1 Free Radical Reactions

The addition of a free radical to a C2-substituted furan heterocycle takes place predominantly at the C2 or C5 position, as shown in Figure 2.3, depending on the chemical nature and steric hindrance of the substituent. The ensuing furyl radical unpaired electron is shared by the remaining three carbon atoms of the ring

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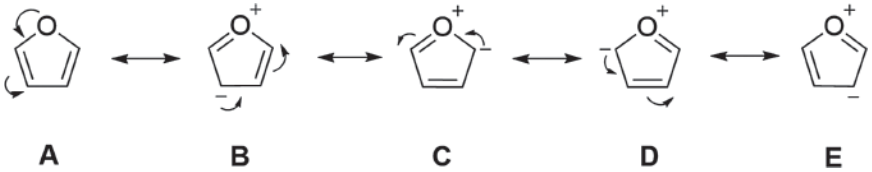

Figure 2.1 The resonance-contributing structures associated with the furan heterocycle.

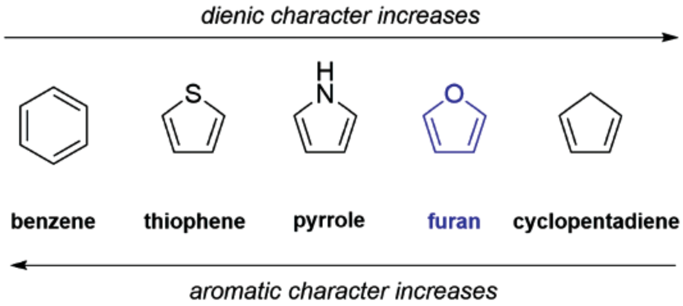

Figure 2.2 The relative dienic and aromatic character of thiophene, pyrrole, and furan in relation to the fully aromatic benzene and the fully dienic cyclopentadiene.

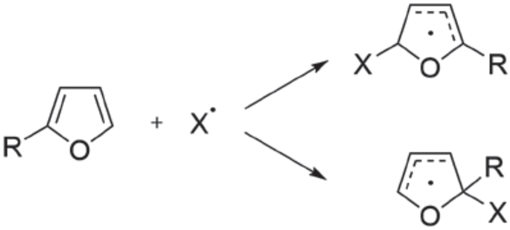

Figure 2.3 The addition modes of a primary radical to furan and 2-monosubstituted furan compounds.

according to its dienic character, which is expected to confer a certain stability to the structure. The reactions of these radicals derived from furan monomers will be discussed in detail when dealing with their behavior in polymerization systems, but their sluggish reactivity must already be mentioned here in the sense that they do not display any tendency to oligomerize with the excess precursor, which emphasize their considerable degree of stabilization. Their termination in a context where the furan derivative is only confronted with primary radicals are illustrated in Figure 2.4, with the formation of a 2,5-dihydrofuran, or the corresponding C5-C5 dimer, depending on the terminating radical. These results were obtained in a systematic study of the bulk reaction of AIBN with furan and a wide selection of furan 2-substituted derivatives [5].

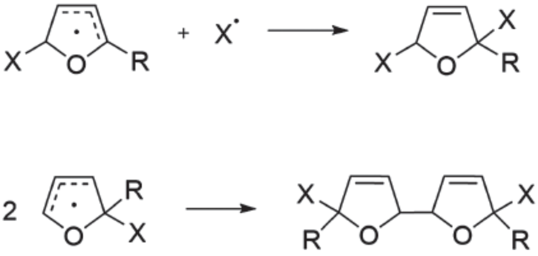

Figure 2.4 Two alternative termination reactions of 2-furyl radicals.

2.2 Electrophilic Reactions

The addition of an electrophile to furan and 2-monosubstituted furans occurs predominantly at the C5 position, as shown in Figure 2.5. This very pronounced regiospecificity, estimated to more than 100:1 with respect to reactions at C3 or C4, is attributed again to the dienic character of the heterocycle, and bears strong consequences to the behavior of the cationic polymerization of furan monomers discussed in the appropriate section. Suffice to note here that the carbocation intermediate in these reactions is stabilized by the dienic property of the furan ring.

2.3 Photochemistry

The electronic spectra of furan and alkyl furans display maxima at 205–215 nm associated with the conjugated diene $\pi \rightarrow \pi^*$ transition. Their mercury-sensitized photolysis produces both molecular fragmentation into CO, cyclopropenes, alkynes and allenes after ring contraction, and isomerization from the excited intermediates, as shown in Figure 2.6 for the case of 2-mehyl furan [6].

When a carbonyl function is attached to the heterocycle, the ring diene is now conjugated to it giving rise, in the case of furfural, to an electronic spectrum with a strong $\pi \rightarrow \pi^*$ transition peak at 260 (gas)-280 (solution) nm and a much weaker $\mathbf{n} \rightarrow \pi^*$ transition at 330 nm in the gas phase, which merges into the red-end of the $\pi \rightarrow \pi^*$ transition in the spectrum of liquid furfural. Furoic acid, HMF and 2-methylfuryl ketone exhibit similar spectral features, which have been exploited for the quantitative analysis of these compounds in processes involving their formation or presence as impurities.

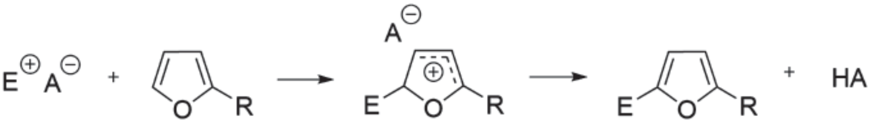

Figure 2.5 Electrophilic substitution reaction to a 2-substituted furan derivative.

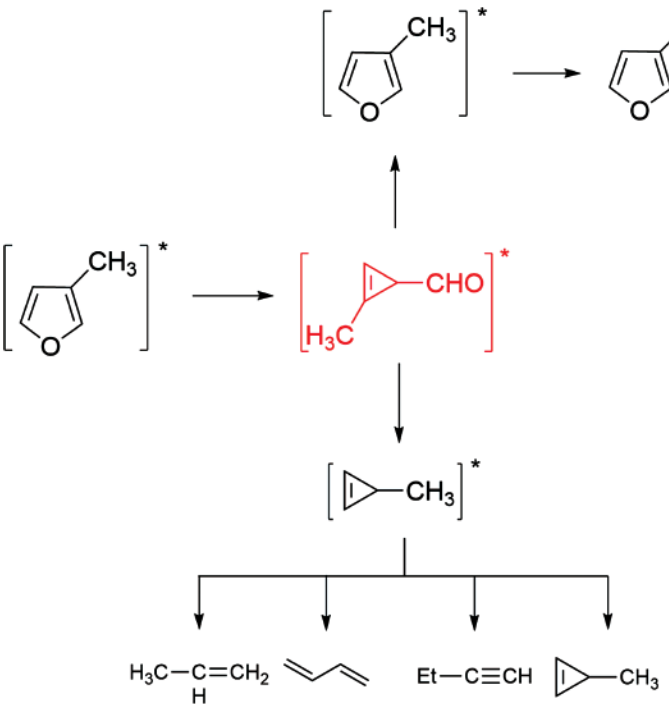

Figure 2.6 The mercury-sensitized photolysis of 2-methyl furan.

The photolysis of furfural in the gas phase has been studied both by direct irradiation of both bands and by mercury sensitization [7]. In all instances, the singlet and triplet excited states rapidly revert to a ground-state vibrationally excited molecule, which either loses a CO molecule to yield furan, or suffers ring contraction, as in the case of furan, to give a cyclopropene dialdehyde intermediate that decomposes into two molecules of CO, propyne, allene, and cyclopropene. At higher pressures, some oligomerization is also observed. On the whole, therefore, this photochemical behavior is similar to that of furan, illustrated in Figure 2.6.

On the other hand, when liquid furfural sealed within a quartz tube is exposed to the full spectrum of a medium-pressure mercury arc for 10–90 h [8], the major product is an oligomeric material generated by two alternative reactions involving furfural excited state and a ground-state molecule, as shown in Figure 2.7. The ensuing vibrationally excited dimer reacts with further furfural molecules to give oligomers with Mn = 500±50, whose structure is close to that shown in Figure 2.8.

Moving to furan molecules with more extended conjugated moieties, 2-furanacrylic acid has been reported to cyclodimerize in the solid state to give cyclobutane

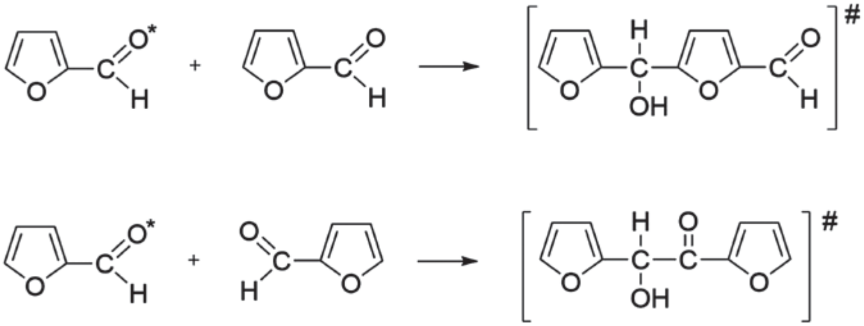

Figure 2.7 The interactions of electronically excited furfural molecules with ground-state counterparts.

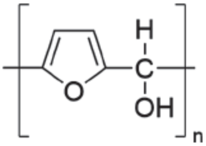

Figure 2.8 The structure of the repeat unit of furfural oligomers produced by liquid-phase photolysis.

isomers [9]. A water slurry of crystals of the corresponding 2,5-diacid (FDA) was irradiated with a 100 W tungsten bulb in a water-cooled reactor giving a near-quantitative conversion into the cyclodimer arising from the [π2+π2] coupling of the excited alkene moiety of a diacid molecule with the ground-state of the second one [10]. The structure of this product, shown in Figure 2.9, was confirmed by a thorough spectroscopic characterization. The use of a simple light bulb (and indeed also sunlight) was sufficient to promote this solid-state reaction stems from the fact that FDA displays a strong peak at 350 nm tailing off towards the visible domain, and photolysis with mercury lamps induced its oligomerization.

It is important to note that the dimer reverted to FDA when heated at 220 °C, a typical behavior related to the breaking down of the strained cyclobutane ring, which will be evoked in other similar systems.

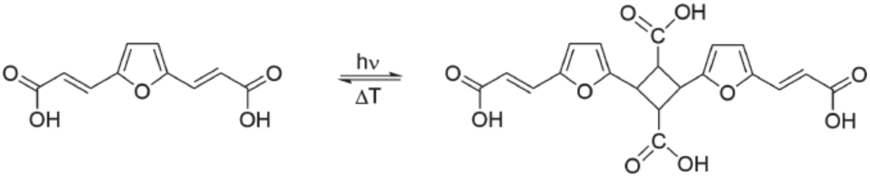

Figure 2.9 The photochemical dimerization of 2,5-furandiacrylic acid.

In the same vein, several furan compounds bearing conjugated *trans* C=C moieties conjugated to carbonyl groups, appended at the C2 position of the heterocycle, were synthesized and submitted to UV irradiation in bulk and solution using a 500W medium-pressure mercury arc provided with a Pyrex filter to limit the excitation to wavelengths higher than 270 nm [11a]. Reactions were followed by FTIR spectroscopy, monitoring the decrease in the C=C band around 1640 cm^{-1}, as well as by UV spectroscopy, monitoring the decrease of the peak around 300 nm. In all instances, cyclodimerization took place via the [π2+π2] coupling of the excited alkene moiety of a molecule with the ground-state of the other, as shown in Figure 2.10, which also illustrates the formation of the two isomeric dimers, identified spectroscopically.

In a systematic study on the photodimerization of furylene-vinylene and thienylene-vinylene compounds, the dimer arising from the self-condensation of 5-methyl furfural (5MF), which gave a UV maximum at 393 nm in methylene chloride, was irradiated in the solid state with both high- and medium-pressure mercury arcs using a filter to cut out any wavelength lower than 300 nm [11b]. The compound readily yielded the symmetrical dimer via the [π2+π2] coupling of the excited alkene moiety of a molecule with the ground-state of the other, as shown in Figure 2.11, which was fully characterized. This reaction was accompanied by

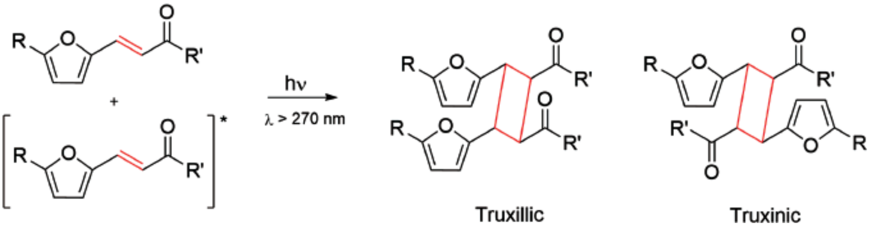

Figure 2.10 Photoinduced cyclodimerization of C2-furan compounds bearing alkene-carbonyl groups.

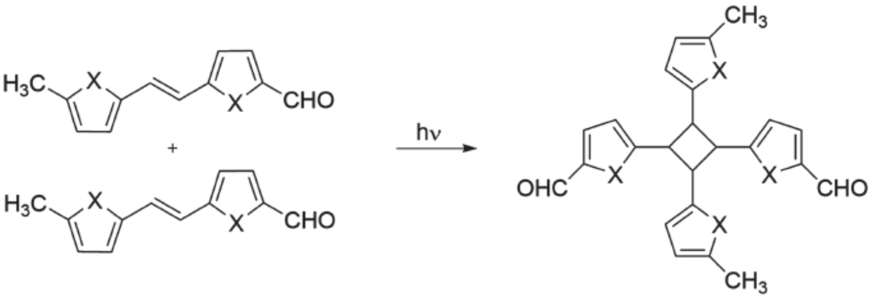

Figure 2.11 The [π2+π2] photochemical dimerization of the 5MF dimer and its thiophene homologue, where X is either oxygen or sulfur.

some trans-cis isomerization of the irradiated molecules. Again, it was observed that heating the crystalline dimer produced a reversion to its precursor starting at about 170 °C. The other furan and thiophene structures bearing ester, and pyridine moieties behaved likewise, but gave rise to a mixture of truxinic and truxillic isomeric dimers.

All these investigations constitute an important basis for their extension to polymerization and polymer cross-linking systems calling upon photochemical activation, as discussed in the specific chapters later in this book.

2.4 Hydrolysis Reactions

The furan heterocycle is susceptible to acid-catalyzed hydrolysis, requiring however fairly aggressive conditions in terms of a large excess of water and a very low pH. The reactions characterizing these processes are illustrated schematically in Figure 2.12. The synthetic relevance of hydrolysis has been exploited with the aim of preparing aliphatic carbonyl compounds. On the whole, however, the vast majority of the polymerization systems discussed in the book do not take place in such environments and are therefore virtually exempt from the interference of ring hydrolysis as an unwanted side reaction. Only when such drastic conditions are involved, the problem will therefore be highlighted, as in the case of polycondensation reactions catalyzed by strong acids that release water molecules at each growth step.

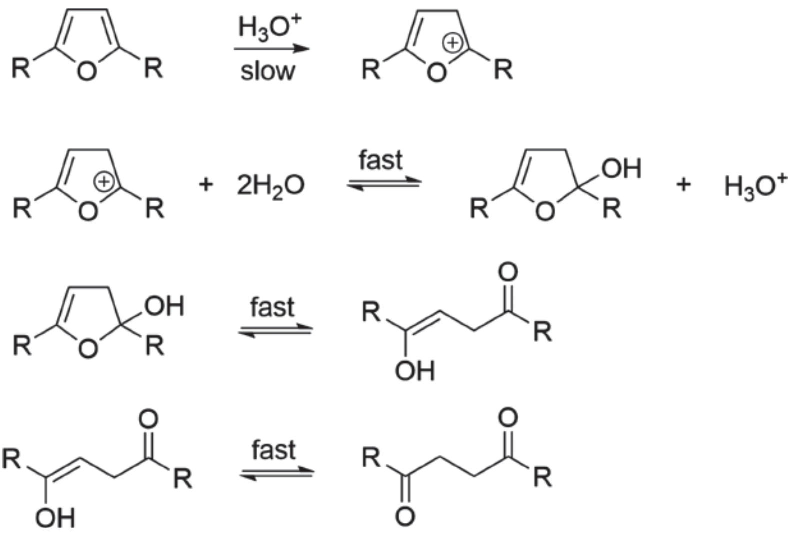

Figure 2.12 The typical reactions associated with the acid-catalyzed hydrolysis of furans.