



The furan/maleimide Diels–Alder reaction: A versatile click–unclick tool in macromolecular synthesis

Alessandro Gandini*

Instituto de Química and Escola de Engenharia de São Carlos, Universidade de São Paulo, 13566-590 São Carlos, Brazil

ARTICLE INFO

Article history:

Received 10 February 2012
Received in revised form 20 April 2012
Accepted 23 April 2012
Available online 28 April 2012

Keywords:

Diels–Alder reaction
Click chemistry
Furans
Maleimides
Thermoreversible polymerizations
Cyclic crosslinking/decrosslinking

ABSTRACT

The purpose of this review is to provide a critical survey covering a few decades of growing interest in the application to polymer chemistry of the Diels–Alder (DA) reaction between furan and maleimide moieties. The major peculiarity of this specific combination of reagents is the fact that their click coupling to generate the DA adduct is thermally reversible, through the retro-DA reaction, at about 100 °C, i.e., a viable and non-degradative temperature in terms of its application to practically all macromolecular structures. The use of furan derivatives constitutes an additional positive feature in this context, because of their renewable character. Attempts were made to insure a comprehensive coverage of the literature, which deals with vastly different approaches and aims concerning the chemistry, the polymer architectures and the possible application of the ensuing materials. The decision to cite all publications available on the subject was deliberate in the sense that in doing so, it was possible to examine them critically and highlight excellence and flaws.

© 2012 Elsevier Ltd. All rights reserved.

Contents

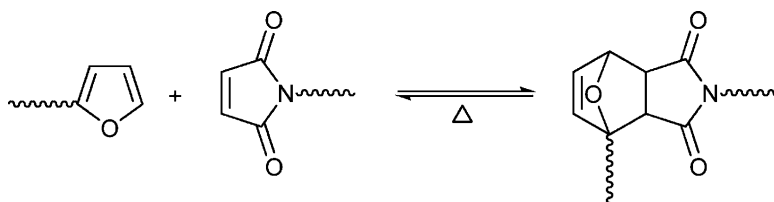
1. Introduction	1
2. Linear polymerizations and thermoreversible or aromatized materials	3
3. Thermoreversible non-linear polymerizations	10
4. Reactions involving polymers	11
5. Stereochemical effects	21
6. Dendrimers and star-like constructs	21
7. Miscellaneous	23
8. Concluding remarks and perspectives	25
References	25

1. Introduction

This review deals specifically with the application of the Diels–Alder (DA) reaction to the thermoreversible polymerization or crosslinking of monomers or polymers incorporating furan (diene) and maleimide (dienophile)

moieties. The choice of these particular systems stems from the fact that the furan/maleimide DA adduct displays a relatively low temperature of decoupling through its retro-DA reaction, which therefore opens the way to interesting applications such as recyclable networks, self-healing materials. The same equilibrium conditions apply to the furan/maleic anhydride combination, but here its extension to macromolecular synthesis is obviously precluded because the unsubstituted maleic anhydride moiety cannot be appended to a polymer or form multifunctional

* Tel.: +55 16 3373 8679; fax: +55 16 3373 9590.
E-mail address: agandini@iqsc.usp.br



Scheme 1. The Diels–Alder equilibrium between furan and maleimide end groups in a stepwise macromolecular synthesis.

molecules. An additional reason for emphasizing the importance of the furan/maleimide couple is the fact that furan derivatives descend from renewable resources and are therefore likely to play a growing role in sustainable approaches to (green) chemistry and materials science.

The Diels–Alder reaction does not require an extensive introduction, given its well-established status in different realms of organic chemistry [1,2]. This [4+2] cycloaddition between a diene and a dienophile typically bearing an alkenyl moiety, occurs through a concerted mechanism and is one of the most attractive members of the click chemistry family [3], particularly because of its thermal reversibility, albeit at different temperature ranges, depending on the actual diene/dienophile combination [4]. Apart from the immense domain of the intervention of the DA reaction in organic synthesis, more specific issues have been tackled concerning its features, such as the role of (i) solvents [5], (ii) Lewis acids or Brønsted acids or bases as catalysts [6,7], (iii) water as a medium [7], including aqueous emulsions [8], and (iv) mechanical energy instead of thermal activation to promote the retro-DA reaction of adducts incorporated into polymer chains [9].

The application of the DA reaction to furan derivatives covers a large field of studies, dominated by synthetic aspects [10], followed in importance by the more recent surge of investigations discussed in this review in which the dienophile counterpart to furans is a maleimide moiety. A remarkably thorough study of the DA reaction between furan and maleimide involving kinetic and stereoselectivity aspects [11] sets an exemplary stage for the extrapolation to macromolecular syntheses based on that reaction, in which of course both heterocycles are now present as *substituted* furans and maleimides. It is unfortunate however that only a small fraction of the investigations discussed here tackle these fundamental kinetic and thermodynamic aspects with sufficient insight, as emphasized in each instance.

It follows that the reversible coupling characterizing all the systems covered here can be simply pictured as in Scheme 1 where the *endo* and *exo* stereoisomers of the adduct are not differentiated, because their role in the formation and thermal reversion of this polymer unit represents a minor issue in most situations. It is important to emphasize that the presence of specific groups in the vicinity of either heterocycle (i.e., on the polymer chain), such as carboxylate, amide and hydroxyl functions, can considerably affect the rates of these DA couplings, as pointed out in the case of reactions involving small molecules [12].

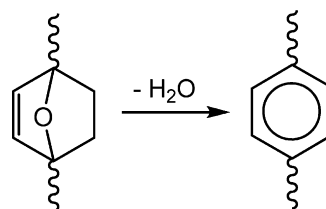
As a rough indication of the role of temperature on the above equilibrium, up to about 60 °C, the left-to-right DA condensation to form the adduct dominates, whereas

above about 110 °C the retro-DA adduct uncoupling becomes preponderant. It is precisely the experimental convenience associated with this range of temperatures, together with the fact that side reactions and possible thermal degradation mechanisms are negligible, that the furan/maleimide couple represents a highly suitable choice for building a large variety of thermoreversible macromolecular architectures. An additional interest in calling upon this combination stems from the possibility of exploiting furan reagents, which are derived from renewable resources [13].

An alternative strategy to exploiting the thermal reversibility of the furan/maleimide adduct in polymeric materials consists in converting them into counterparts that are stable at high temperature, through the chemical modification of the adduct by aromatization, as shown in Scheme 2, and as detailed below. Of course in this case only the initial DA coupling is relevant to the present review, since the adduct is transformed into a thermally stable moiety.

In order to set the stage around this review and underline its peculiar message, it is important to provide a background of recent monographs dealing with cognate topics. Click chemistry has become a standard tool in the hands of polymer scientists, as amply described in recent years [14], but the attention placed in those reviews on the specific issue discussed here was necessarily scant, because of their much wider purpose. The same considerations also apply to essays dealing with healable and mendable polymers, [15], reversible covalent cross-linking [16], and recycling [17], which call upon various strategies, including the thermal reversibility of certain DA reactions. Other reviews have tackled more specifically the DA reaction applied to macromolecular synthesis and to the original properties of the ensuing materials, but again their coverage needs updating [18], or is too broad [19], and hence misses some of the relevant features of the present treatment, or falls outside its area of interest [20].

The specific combination of DA reactants deliberately selected for the present contribution provides therefore a



Scheme 2. Aromatization of a furan DA adduct.

Download English Version:

<https://daneshyari.com/en/article/5208495>

Download Persian Version:

<https://daneshyari.com/article/5208495>

[Daneshyari.com](https://daneshyari.com)