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Where small molecules and polymer materials meet: triazolinedione chemistry at the interface

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Academic Year 2017–2018

Submitted to the Faculty of Sciences of Ghent University, in Fulfilment of the Requirements for the Degree of Doctor of Science: Chemistry

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"Failure is the fog through which we glimpse triumph."

Guy Pearce

Dankwoord

Ik bedank veel personen...

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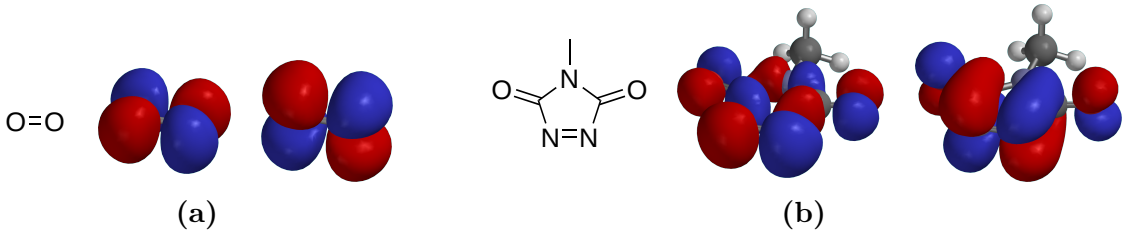
Chapter I

General aim and outline

I.1 Introduction

Dummy reference.[1]

Dit is een test.



(a) **(b)**

Figure I.1: TAD reagents and related reactive compounds: maleimides and singlet oxygen.

Bibliography

1. K. De Bruycker, M. Delahaye, P. Cools, J. Winne, F. E. Du Prez, *Macromol. Rapid Commun.* **2017**, *38*, 1700122.

Triazolinediones (TADs) are very reactive compounds with a long-standing history in various research fields. The very first TAD has been described already in the late 19th century, followed by the first practical applications in organic synthesis and polymer chemistry in the 1970s. Recently, the launch of the concept of 'click chemistry' has renewed the scientific interest in these unique reagents, which has resulted in new applications, such as the bioconjugation to synthetic or natural peptides or proteins and the ultrafast production of various polymeric materials.

The main focus of this research is the application of triazolinedione chemistry in interfacial systems. Both reactions at the solid-liquid interface and in liquid-liquid biphasic systems are investigated. However, in each case, tailored TAD compounds and complementary reaction partners are necessary, of which the synthesis represents the first part of this work. Subsequent parts describe various TAD-based surface modifications. Firstly, fluorinated compounds are applied as reactive additives for polydienes and are shown to greatly influence the surface properties. Secondly, an inorganic yet TAD-reactive substrate is alternatingly submerged in solutions of mutually reactive monomers to afford a coating in a layer-by-layer approach. Finally, similar substrates are used to print a triazolinedione 'ink' via microcontact chemistry, which allows to write, erase and rewrite patterns when reversibility is introduced in the system.

Triazolinedione chemistry proves to be less suitable for reactions in liquid-liquid interfacial systems. Therefore, the next part discusses the limitations of the TAD strategy and introduces the thiolactone-based multi-component reaction as a complementary alternative for the production of polymeric beads. Finally, the latter ligation is demonstrated to be a promising cross-linking method for the synthesis of amphiphilic networks.

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