

# Influence of various catalysts on the 1,3-diacetidine-2,4-dione (uretdione) reaction with hydroxyl groups

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## Abstract

Lowering the curing temperature for powder coatings is desirable with regard to the coating of temperature sensitive substrates. However, commercial available weather-resistant stable powder coatings need curing temperatures  $>180^{\circ}\text{C}$ . The reactivity of various catalysts on the reaction between an uretdione cross-linker and OH groups were carried out on the basis of low molecular model systems. The results were transferred to polymeric systems consisting of the reactive components of a powder coating composition. The investigations were carried out using non-isothermal and isothermal DSC measurements as well as rheological measurements of the complex melt viscosity. However, the curing reaction occurred in a two-step reaction mechanism whereas the first reaction step could be quantitatively separated applying non-isothermal DSC measurements.

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## 1. Introduction

Thermosetting polyurethane powder coatings are widely used in various fields of applications. They are represented in high quality coatings for numerous industrial applications. Isocyanate cross-linkers are highly reactive at low temperatures due to their free isocyanate groups which readily react with the functional groups of the polyester resin. To ensure optimal processing conditions for powder coating extrusion the reactivity of the isocyanate cross-linkers has to be reduced. This premature reaction can be prevented by blocking the free isocyanate groups with a nucleophilic agent (Scheme 1(a)). Most established isocyanate cross-linkers based on IPDI and TDI derivatives are blocked with  $\epsilon$ -caprolactam. The disadvantage of such powder coating systems are the high temperatures of about  $170^{\circ}\text{C}$  required for the deblocking reaction [1]. Furthermore, the blocking agent is set free during the curing process which is on the one hand not desired in view of the VOC guidelines and in addition the blocking agent can cause surface defects during the curing process.

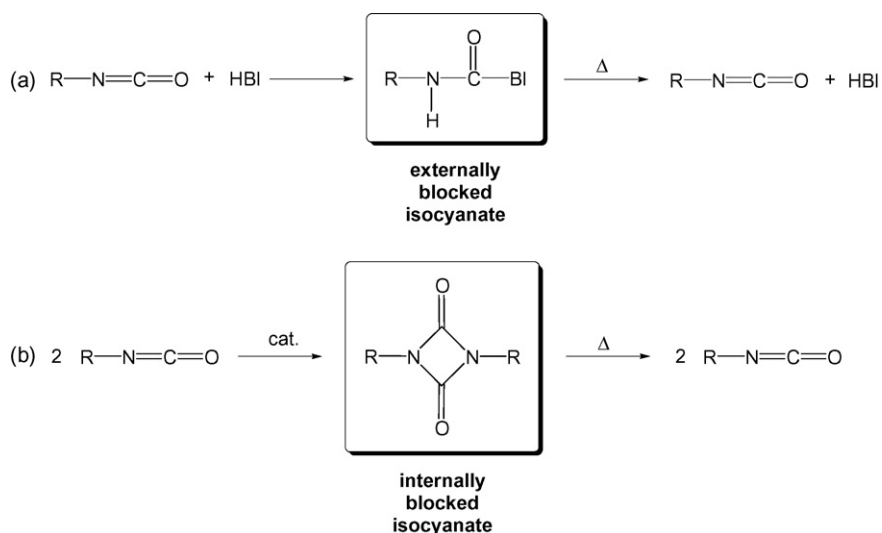
An alternative solution is the use of internally blocked isocyanate cross-linkers which exhibit 1,3-diacetidine-2,4-dione

(uretdione) moieties (Scheme 1 (b)). From the ecological point of view, the uretdione cross-linkers have an increasing interest as no volatile components are emitted. However, in uncatalyzed systems high temperatures ( $190^{\circ}\text{C}$ ) are required for the curing process of such powder coating systems which is the main disadvantage of these systems [2]. The rate-determining step is the high temperature cleavage of the uretdione ring.

In spite of extensive work on the field of catalysis of the uretdione hydroxyl reaction only few catalysts were found to be able to catalyze the deblocking reaction. Until recently, the best results were realized by the use of  $N,N,N'$ -trisubstituted amidines which lower the curing temperatures to  $150^{\circ}\text{C}$  [2]. However, the disadvantage of these catalysts is their tendency to cause yellowing.

The reactivity of a monomeric IPDI based uretdione cross-linker with OH groups was investigated by Degussa. In the presence of dibutyl tin dilaurate and 1,5-diazabicyclo[4.3.0]non-5-en (DBN), the formation of urethanes could be observed at  $150^{\circ}\text{C}$  [3]. Actually new catalysts are published for the uretdione/OH reaction [4]. In the presence of tetraalkyl ammonium carboxylates, the reaction temperature can be lowered to  $120^{\circ}\text{C}$ . However, these model experiments were carried out in solution in the presence of a monoalcohol. In this way, neither curative systems nor diffusion processes were considered.

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Scheme 1. (a) Blocking and deblocking reaction of isocyanate cross-linkers with a nucleophilic blocking agent. (b) Catalytic dimerization of isocyanates to uretdiones and thermal deblocking.

Explorative work on the search of alternative catalysts was done with regard to the yellowing tendency of amidines. During these investigations, a completely new two-stage curing mechanism was found in presence of metal acetylacetonates as catalysts as shown in Scheme 2 [5,6]. In presence of the catalyst, the reaction between OH groups and the uretdione cross-linker gives an allophanate structure at temperatures below 150 °C. The second stage occurs at temperatures higher than 160 °C. The allophanate structure is cleaved to a urethane and free isocyanate groups which react directly with further OH groups to yield another urethane [6–8].

In this paper, comprehensive investigations are described on the reactivity of various catalysts for the reaction between uretdiones and OH groups and the application of these systems in powder coatings.

## 2. Experimental

### 2.1. Materials

All substances were used without further purification. 1,8-Octanediol ( $\geq 98\%$ , Fluka), tetrabutylammonium bromide ( $\geq 98\%$ , Fluka), zirconium acetylacetonate (98%, Aldrich), cal-

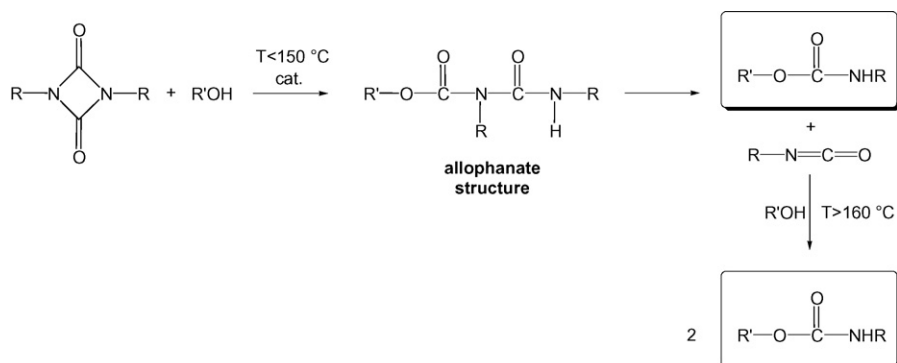
cium acetylacetonate ( $\geq 95\%$ , Fluka). TEGOKAT<sup>®</sup> catalysts, magnesium acetylacetonate and aluminum acetylacetonate were donated by Goldschmidt TIB. Urettdione cross-linker Vestagon<sup>®</sup> BF 1320 ( $T_g$  73 °C; NCO-equivalent 300 g/mol) was donated by Degussa AG. Araldite PT 910<sup>®</sup> (epoxy equivalent 147 g/mol) was donated by Vantico. Hydroxy functionalized polyester DLE 04-210 ( $T_g$  43 °C; acid value 4.5; hydroxyl number 57.0) was donated by Synthopol.

### 2.2. Preparation of low molecular model reaction systems

The substances were weighed in the agate vessel of a laboratory mill Fritsch Pulverisette 23. In order to obtain homogeneous model systems, the samples were mixed for 2 min at a frequency of 50 Hz. Then the pulverized samples were dried at 25 °C in vacuo for 24 h and stored in a desiccator over P<sub>2</sub>O<sub>5</sub>.

### 2.3. Preparation of polymeric reactive model systems

The substances were homogenized in a Haake melt mixer at 90 °C with a rotational frequency of 30 rpm. First the polyester, the uretdione cross-linker and the epoxide were added to the



Scheme 2. Metal acetylacetonate catalyzed reaction between uretdiones and OH groups.

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