



# Kinetic and chemorheological modelling of the polymerization of 2,4-Toluenediisocyanate and ferrocene-functionalized hydroxyl-terminated polybutadiene

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## ABSTRACT

The reaction of 2,4-toluenediisocyanate (2,4-TDI) and a metallocenic-prepolymer derived from hydroxyl-terminated polybutadiene (HTPB) was studied in bulk and under isothermal conditions (50–80 °C) by rheological methods. Two regions distinguished and limited by the gel point, identified as the crossover of loss tangent ( $\tan \delta$ ) at different frequencies, were analysed from different rheological properties during the curing process of this novel metallo-polyurethane (PU). The initial part of this polymerization, dominated by the viscous behaviour (from  $\eta_0 \approx 5$  Pa s to  $\eta = 250$  Pa s), was modelled through the Arrhenius isothermal model, in which the presence of two rheokinetic stages, due to different isocyanate groups in the 2 and 4 positions for this asymmetric monomer, was found until the gelation is reached. The contributions of the main reactions for the region analysed, before the gel point of this polyaddition, are discussed. The gel transition was identified, and the viscoelastic behaviour of the gelation process was studied in depth. In addition, from the evolution of the storage modulus ( $G'$ ) recorded, the overall polymerization reaction was described by a Kamal-Sourour kinetic expression for the reaction rate. The different kinetic parameters obtained for the autocatalytic model used yielded predictions that agree very well with the experimental data, finding a significant autocatalytic effect. An isoconversional method allowed the determination of the dependence of the activation energy on the conversion degree during the network formation of this advanced functional ferrocene-PU, which is of great interest in rocket technology research for the development of the aerospace industry.

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## 1. Introduction

Polyurethanes (PUs) include a practically unlimited number of structures with urethane groups on macromolecular chains. This polymer family thus represents the first example of polymeric material building using a so-called “tailoring” procedure by selecting different isocyanates and polyols and varying the reaction conditions, covering a great number of applications from traditional up to new and expanding areas, such as coatings, biomaterials and high-performance elastomers. The wide variation of PUs presents a difficult challenge because new formulations with completely different kinetic and chemorheological characteristics continue to appear [1–4]. For these reasons, the chemistry of

isocyanates and, more concretely, their reactions with alcohols have been extensively studied from diverse points of view and described in some excellent reviews [5,6].

The mechanistic and kinetic research on numerous substrates, with and without a catalyst, with and without solvents of various polarities, and under equimolar conditions and with an excess of one monomer, has proven that this basic reaction is second-order, with first-order dependences on the concentrations of both the isocyanate and alcohol species [5,7]:

$$-\frac{d[R_1NCO]}{dt} = k \cdot [R_1NCO] \cdot [R_2OH] \quad (1)$$

where  $[R_1NCO]$  is the concentration of the isocyanate compound, and  $[R_2OH]$  is the concentration of the hydroxyl component. However, under certain experimental conditions, deviations from the second-order kinetics may result from the autocatalytic effect

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of the –OH and –NH–COO– groups or from solvent effects. The real dependence should be more complicated and include the reactivities and concentrations of different self or mixed hydrogen bonds and possibly other types of interactions between species present in the reaction medium as well as microgel formation and/or phase separation [8,9]. Unfortunately, such interactions and morphological changes are sometimes difficult to determine directly, and thus the fundamental problem of the urethane reaction still remains open.

Another aspect that is relevant within isocyanate chemistry is the reactivity [5]. A different reactive nature of isocyanates is found, where the aliphatic diisocyanates are fairly less reactive towards alcohols than the aromatic ones. This is a subject that has been extensively studied, but it is necessary to emphasize the fundamental greater degree of complexity associated with asymmetric diisocyanates such as isophorone diisocyanate (IPDI) and 2,4-toluenediisocyanate (2,4-TDI). The latter, which is surely the isocyanate component most extensively used, is an asymmetric aromatic diisocyanate that contains two non-equivalent isocyanate groups, one present in the *ortho* position ( $\text{NCO}_{ortho}$ ) and the other in the *para* position ( $\text{NCO}_{para}$ ), as seen in Scheme 1. The methyl that is adjacent to the  $\text{NCO}_{ortho}$  group causes steric hindrance, making it less reactive than that which is *para*-functionalized [5,6]. When differential reactivities are encountered, a suitable strategy is to consider the entire process as a set of competitive and/or consecutive reactions, and at least two specific rates and stages must be found, one for each isocyanate group [5]. However, to analyse and compare these different reactivities towards alcohols is a difficult task because the lack of similar experimental conditions used for the diisocyanate under study. This is especially relevant when the starting component's nature is changed, such as from simple alcohols to classical macrodiols, and logically with the development of new functional macroglycols by the chemical modification of these latter. A proof of this is found in the great diversity in the values reported in the literature for the reactivity of the –NCO group at the *para* position in comparison with that at the *ortho* position. These differences are also due to the instrumental methods for monitoring the isocyanate-alcohol reaction, ranging from dilatometry and the titration of the free isocyanate groups to chromatographic and spectroscopic techniques to even mass spectrometry, which has been recently used [10]. However, the extremely high viscosity observed when the conversion in urethane reaches a significant level brings analytical problems that have limited the number of systems studied in the bulk polymerization state [11]. This is especially relevant when functional polyols are polymerized. In these cases, the indirect methods cannot be forgotten, as the differential scanning calorimetry (DSC) and the rheology, where a physical property is measured [11–13]. The rate of the conversion depends on the kinetics governed by the chemical reactions, but the physical properties can be functionally related to the extent of the reaction. The rheology will be a particularly major factor of concern, since different rheological parameters, such as the viscosity, during the polymerization may increase by as much as 6–7 orders of

magnitude, and the processability characteristics are of great relevance for the numerous and varied applications of the PU systems [11–13].

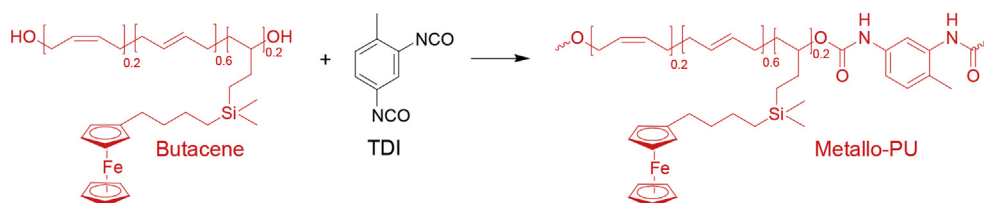
This technique has recently shown great versatility in characterizing the different stages during the formation reaction of PUs and logically the curing of thermosets, which gives rise to dramatic changes in the mechanical properties during the transition from the liquid to the solid state. The evaluation and characterization of the gelation process are crucial to optimize the processing conditions of cross-linked materials. In addition, the universal behaviour of cross-linked polymer systems at the gel point make this phenomenon interesting from a fundamental point of view. Thus, chemorheological analysis is a suitable study to evaluate the curing kinetics of polymers [11,12]. To carry it out, an appropriate empirical model must be selected that describes the behaviour of the reactive system to fit the kinetic data obtained by this indirect methodology [13].

The aim of this work is to study the rheokinetics, the gelation and the kinetics of the reaction formation of a three dimensional network of PU based on a functional metallocenic-prepolymer derived from hydroxyl-terminated polybutadiene (HTPB), called Butacene, and 2,4-TDI in bulk and under isothermal conditions and to obtain a better understanding of the curing behaviour and its mechanism. This metallo-PU belongs to a new class of ferrocene-containing polymers that have attracted much interest in recent years [14]. More concretely, PU based on Butacene can be used as an innovative binder for composite solid propellants in advanced launch vehicles and rockets. Hence, knowing the kinetic and chemorheological models that describe the viscosity and the conversion rate of this system during curing is of great importance and represents a fundamental aspect towards the successful application of this novel reactive system.

## 2. Experimental

### 2.1. Materials

(Ferrocenylbutyl)dimethylsilane grafted to HTPB (Butacene<sup>®</sup>800), was manufactured and provided by the SNPE. According to the supplier, this metallo-prepolymer has an OH value of 0.33 eq/kg and a content of iron of approximately 8% in weight. Butacene synthesis consists of the addition of an organosilicone ferrocene derivative to a low molecular weight HTPB through the pendant vinyl groups. HTPB, synthesized via free radical polymerization route, has a functionality slightly greater than two, with an average value of 2.2–2.4 hydroxyl groups per chain, and a number average molecular weight ( $M_n$ ) of few thousands [15]. The molecular weights of a HTPB and Butacene were evaluated by size exclusion chromatography. The  $M_n$  related to poly(methyl methacrylates) is 4595 and 7555 g/mol and the polydispersity is 2.14 and 2.16 for HTPB and Butacene, respectively [16]. The isocyanate 2,4-TDI was supplied by Aldrich, and it was used as received.



Scheme 1. Reaction of metallo-PU synthesis.

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