

# Cure kinetics of poly (5-ethylidene-2-norbornene) with 2nd generation Hoveyda-Grubbs' catalyst for self-healing applications



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## HIGHLIGHTS

- Polymerization kinetics of 5E2N initiated by Hoveyda-Grubbs' catalyst for low temperatures self-healing applications.
- *In situ* monitoring and analysis of the reaction from room temperature down to  $-30\text{ }^{\circ}\text{C}$  using micro-Raman spectroscopy.
- The reaction at low temperatures follows an Arrhenius behavior showing the temperature dependence of the reaction rates.
- The activation energy of the reaction is measured to be  $64 (\pm 3) \text{ kJ}\cdot\text{mol}^{-1}$  (0.663 eV).

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## ABSTRACT

Self-healing polymer composites based on ring-opening metathesis polymerization (ROMP) incorporating second generation Hoveyda-Grubbs' (HG2) catalyst as polymerization initiator and 5-ethylidene-2-norbornene (5E2N) as healing monomer are promising for self-healing applications. This is particularly true at low temperatures that may persist in the internal environment of an operating space vehicle. By using a systematic micro-Raman spectroscopic analysis and a detailed methodology specifically implemented for the investigation of 5E2N and HG2 reactants, we studied the progression of the ROMP reaction over time from room temperature down to  $-30\text{ }^{\circ}\text{C}$ . The analysis is based on measuring the changes in peak intensity and integrated area of Raman phonons related to the characteristic (C=C) functional groups indicating the progression of the reaction with time. The cure kinetic reaction of the 5E2N/HG2 system at low temperatures is found to follow an Arrhenius behavior showing the temperature dependence of the reaction rates. On this basis, the activation energy of the reaction is measured to be  $64 (\pm 3) \text{ kJ mol}^{-1}$  (0.663 eV), a value that is about 40% higher than the data reported for similar materials.

## 1. Introduction

The self-healing capability of polymer composites used in modern space technologies can mitigate the difficulties, complexities and high costs associated with remote manual repair of damages caused by mechanical loading, space debris and other environmental factors during their operation. Self-healing properties can also ensure the safety and reliability of advanced equipment used in space and extend their useful lifetime, such as epoxy-based materials employed in geostationary satellites, space modules and spacecrafts. However, studies on self-healing polymer composites suitable for extreme temperature applications [1], which is typical of space environments, are limited.

Self-healing of structural polymer composites can be broadly

categorized into two different classes [2–7]: (i) intrinsic self-healing, corresponding to mechanisms where the polymer structure is modified at the molecular level to include new chemical groups that bond reversibly or dynamically [2–5,7], and (ii) extrinsic self-healing, in which external healing agents (e.g. monomer, catalyst, resins, initiators, shape memory alloys, particles etc.) are embedded and dispersed within the polymer matrix, either directly or using breakable storage vessels (e.g. microcapsules, hollow fibers, microvascular networks) [3–7]. The extrinsic approach is generally preferred to the intrinsic one because it is less hampered by light, moisture and other types of degradation, which affect the long-term stability of the healing agents. Many efforts were then made to microencapsulate different healing agent monomers and polymerization initiators to impart self-healing functionality to

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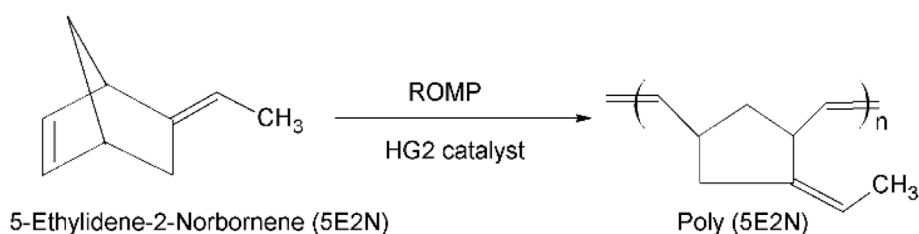


Fig. 1. ROMP of 5E2N.

materials for various applications [8–15]. Among these, Dicyclopentadiene (DCPD) and Grubbs catalyst were widely investigated [16–27], yet DCPD was found to be not suitable for applications at low temperatures as it becomes solid below  $\sim 15^\circ\text{C}$ . Extensive studies have focused on the 5-ethylidene-2-norbornene (5E2N) monomer which remains liquid even at  $-80^\circ\text{C}$  [28] and can also undergo similar ROMP reaction in the presence of Ruthenium catalysts. This ability of 5E2N makes it suitable to be used in spacesuits and space vehicles. However, to better characterize and understand the cure reaction of 5E2N monomer in realistic operating environments, the investigation of its polymerization at low temperatures, and more especially of its kinetics, is essential.

Raimondo and co-workers showed that the self-healing (ROMP) reaction of 5E2N can be triggered at low temperatures (down to  $-50^\circ\text{C}$ ) when initiated by first generation Grubbs (G1) and Hoveyda Grubbs (HG1) catalysts [29]. The reaction was observed to proceed very slowly, taking 1440 min for 52% yields and 450 min for 99% yields, with G1 and HG1 catalysts, respectively [29]. Even if other parameters related to the leakage of the capsules and the diffusion of their core content inside the polymer matrix also contribute to the efficiency of the self-healing process, such a rate is clearly insufficient [30], since a too slow self-healing reaction can cause the diffusion of the healing agent monomer into the matrix material before it polymerizes, resulting in incomplete curing of the material. Hence, measuring and optimizing the cure kinetics of the polymerization reaction is a crucial step towards implementing any self-healing agent [30], especially for those initiated by HG2 catalyst that shows unprecedented chemical stability, recyclability [31–33] and fast rates of initial polymerization [34].

In this work, microcapsules containing 5E2N monomer in poly melamine urea formaldehyde (PMUF) shells are produced following an *in situ* polymerization process [35]. To assess the self-healing ability of the microcapsules, we aim to characterize the polymerization kinetics of the 5E2N core with the 2nd generation Hoveyda-Grubbs (HG2) catalyst. HG2 is particularly known for its chemical stability [34]. This product can also be handled in air and remain stable when coming into contact with a wide variety of functional groups including esters, amides, ketones, aldehydes and even water, alcohols and acids [36].

As such, our work mainly reports on the polymerization kinetics of the ROMP reaction of the 5E2N monomer initiated by HG2 catalyst at low temperatures, as characterized by micro-Raman spectroscopy. This characterization tool was found to be a technique of choice to study the ROMP reaction chemistry of DCPD and Grubbs catalyst [37–40] as well as to determine the kinetics of other polymerization reactions at room temperature and above [8,30,41–44]. However, employing this powerful and non-destructive approach for studying the kinetics of chemical reactions below  $0^\circ\text{C}$  is more challenging due to technical constraints [45]. For example, the formation of ice induces optical scattering effects that deteriorate the signal-to-noise ratio, which complicates both the signal collection and the spectroscopic analysis. Here, an in-depth quantitative analysis of the ROMP reaction kinetics of the 5E2N/HG2 system was systematically conducted from room temperature down to  $-30^\circ\text{C}$ . Our experiments and methodology are designed for enabling an *in situ* monitoring of the ROMP reaction initiated by 5E2N/HG2 self-healing agents. By using a spectral analysis that was specifically developed in this framework, we demonstrate that the polymerization

reaction follows an Arrhenius behavior over the investigated temperature range. On this basis, we can determine the activation energy of the 5E2N/HG2 curing process and compare its value to the data reported for similar materials to show that the reaction kinetics of these micro-encapsulated chemical agents is high enough for application in space environment.

## 2. Background

The ROMP reaction is a type of olefin metathesis chain growth polymerization of a suitable cyclic olefin (e.g. norbornenes, such as 5E2N monomer) and is usually activated by a suitable catalyst (e.g. HG2 catalyst) [46]. During this process, the double bond present in the reactant monomer takes part in the chemical reaction and remains in the produced polymer. This important feature distinguishes ROMP from typical olefin addition polymerization (such as ethylene-polyethylene). The reaction is driven from monomer to polymer by the release of strain associated with the cyclic olefin (ring strain) balanced by entropic penalties [46]. For example, the highly strained norbornene ring of the 5E2N monomer is opened by breaking the carbon-carbon double bond in the presence of suitable catalyst triggering the ROMP reaction to form the polymer (poly 5E2N), preserving the carbon-carbon double bond, as illustrated in Fig. 1.

Fig. 2 shows the conceptual route of the self-healing strategy, originally introduced by White and co-workers [2]. Four basic criteria must be met for the self-healing strategy to be realized, namely: (i) storage, (ii) release, (iii) transport and (iv) re-bonding. In this process, the liquid monomer is initially encapsulated into micro scale polymeric shells (storage). The microcapsules along with the catalyst particles are then dispersed into the host polymer matrix as shown in Fig. 2.

Once a crack is generated in the polymer matrix following a damaging event, its propagation causes the shells of the microcapsules to break, which releases their core content (Fig. 2a). The monomer originating from the core of the broken microcapsules is then transported to the crack plane (Fig. 2b) through capillary action [14] and/or during the crack closure upon unloading. When the monomer meets the dispersed catalyst particles present in the crack plane, it triggers the ROMP reaction. The polymer, thus formed, fills the crack and binds the crack faces together (Fig. 2c), thereby restoring the original functionality and properties of the host material. In addition to these basic criteria, this polymerization reaction must occur quickly, preferably within few minutes depending on the surrounding environment, to prevent further damage or material degradation and to preclude evaporation and diffusion of the monomer from the crack plane [47]. The polymerization kinetics of the healing agents is, thus, one of the most crucial factors for their effectiveness at low temperatures. Its determination is prerequisite for the development of any self-healing system based on ROMP, prior to the optimization of other parameters, such as the concentration, the size and the thickness of the microcapsules, which can also affect the speed and efficiency of the process.

In this work, after microencapsulation of the monomer, the polymerization kinetics of the core 5E2N initiated by HG2 catalysts has been investigated between  $-30^\circ\text{C}$  and  $+21^\circ\text{C}$ , to demonstrate the relevance of using these compounds as self-healing agents at low temperatures.

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