

# Exploring the Scope and Limitations of Pd-catalyzed Carbene Polymerizations

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## Introduction

Rh-catalyzed carbene polymerization (figure 1) was found to be a promising alternative for producing functionalized polymers [1]. Extending this concept to Pd catalysis would make it more cost effective and might affect polymer properties. Using a Pd catalysts might enable carbene-olefin copolymerizations. Copolymerization allows specific tuning of the polar functionalities and the amount in the polymer. This could lead to the synthesis of polymers with a structure that is inaccessible through traditional polymerization routes. Up to now Pd catalysts have produced only low-Mw oligomers [2].

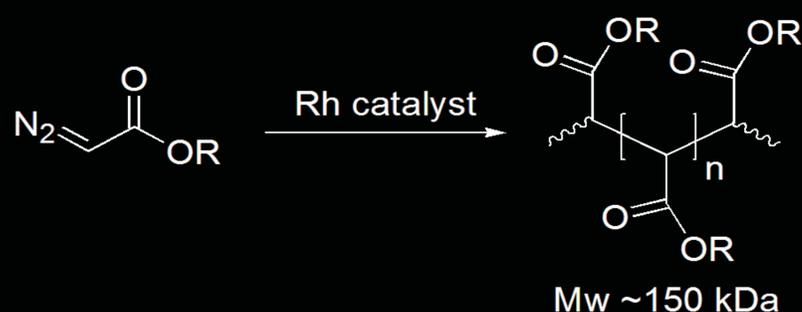


Fig 1. Rh-catalyzed carbene polymerizations.

## Objective

Exploring the behavior of various (defined) Pd catalysts in carbene homopolymerization and carbene-olefin copolymerizations.

## Carbene homopolymerization

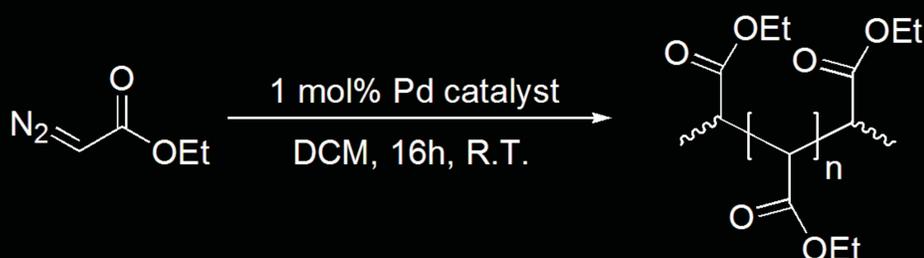
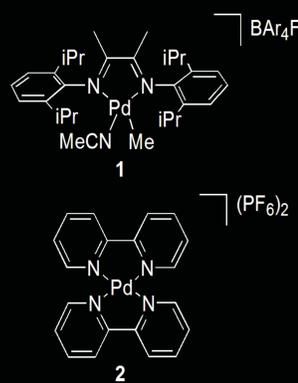


Fig 2. Carbene homopolymerization of EDA with a Pd catalyst.

Table 1. Catalyst screening in polymerization of ethyl diazoacetate (EDA).

| Catalyst   | Mw (Da)  | Mw/Mn | Yield (%) |
|--|----------|-------|-----------|
| <b>1</b>   | 900      | 1.06  | 42        |
| (cod)Pd(Me)Cl  | 2000     | 1.28  | 53        |
| [(cod)Pd(Me)]BAR <sub>4</sub> F                                      | 1500     | 1.32  | 29        |
| [(bipy) <sub>2</sub> Pd](PF <sub>6</sub> ) <sub>2</sub> ( <b>2</b> ) | No olig. | --    | --        |
| Pd(dba) <sub>2</sub>   | 1600     | 1.34  | 72        |
| Pd <sub>2</sub> (dba) <sub>3</sub>                                   | 2000     | 1.20  | 80        |
| (nbd)Pd(ma)  | 1500     | 1.22  | 78        |
| Pd/C   | 1100     | 1.08  | 74        |

Reaction conditions: EDA (0.95 mmol), [Pd] (9 mmol), DCM (5 mL), 16h.



Pd(0) catalysts are more active than Pd(II) species in carbene polymerizations. Due to rapid termination (most likely via  $\beta$ -H elimination) no high-Mw species are observed.

## Scope and Limitations

Pd-catalyzed carbene polymerizations are attractive for selective, high-yielding production of highly functionalized low-Mw oligomers. The active species in these reactions is Pd(0), which hampers carbene-olefin copolymerizations. Higher Mw polymers are available via Pd(0)NHC catalysis, although stereocontrol is not yet achieved.

## Carbene-olefin copolymerizations

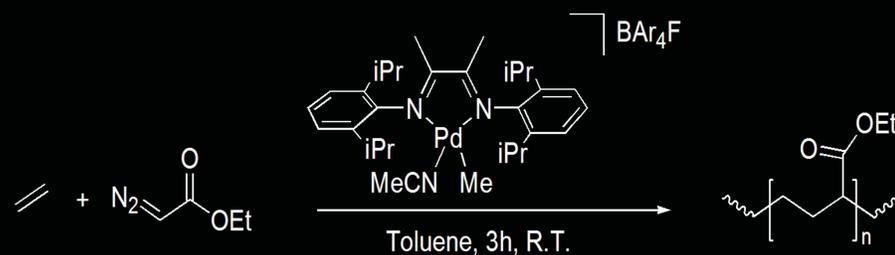


Fig 3. Pd catalyzed copolymerization of EDA and ethylene.

Table 2. Carbene-ethylene copolymerizations.

| Monomer        | P <sub>eth</sub> (Bar) | Product      |
|----------------|------------------------|--------------|
| Ethylene       | 10                     | Polyethylene |
| EDA            | --                     | Oligomers    |
| Ethylene + EDA | 10                     | No reaction  |
| Ethylene + EDA | 1                      | No reaction  |

Reduction of the catalyst to Pd(0) by EDA makes carbene polymerization and olefin polymerization incompatible.

## The curious case of Pd(0)NHC

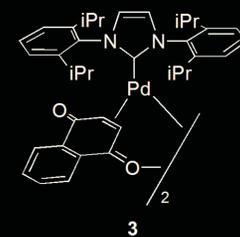
Higher Mw homopolymers of EDA can be obtained with a Pd(0)NHC/BPh<sub>4</sub> catalyst system (table 3). The material is atactic and shows similarities with the product of radical polymerization of diethyl fumarate.



Fig 4. Higher Mw polymer.

Table 3. EDA polymerization catalyzed by **3** under various conditions.

| Additive | [Add]/[Pd] | Mw (Da) | Yield (%) |
|----------|------------|---------|-----------|
| none     | --         | 34000   | 80        |
| TBP      | 0.9        | 44000   | 67        |
| HQ       | 20         | 36000   | 84        |
| MeCN     | 40         | 60000   | 81        |



Reaction conditions: EDA (0.95 mmol), [Pd] (9 mmol), NaBPh<sub>4</sub> (12 mmol), THF (2 mL), 16h.

Radical polymerization is not participating in this reaction, although the exact mechanism is still under investigation.