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Theoretical study on effects of substituent, ligand, and metal on Pd-catalyzed polymerization of norbornene

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ABSTRACT

[(2-R-allyl)Pd(mesitylene)][SbF_6] is a class of highly active catalyst for the polymerization of norbornene (NB). In this work, the detailed mechanism of this polymerization reaction was studied by density functional calculations (B3LYP) augmented with dispersion correction and PCM solvation model. The insertion of the second NB monomer is the initiation step which has the highest activation barrier in the overall cycle. The activation barrier of this step is 11.6 kcal/mol higher than that of polymer chain propagation. The stable intermediate before the second NB insertion is a cationic Pd complex with bidentate coordination of one NB monomer, which is consistent with previously reported crystal structure. However, the resting state of propagation is a cationic Pd complex with two coordinated NB monomers and the growing NB chain. The activation barrier of initiation decreases if electron withdrawing substituents are introduced into the ally moiety. Particularly, the 1,1,2-trichloro-allyl substituent decreases the activation barrier to +10.7 kcal/mol, which is lower than that of propagation. On the other hand, all the examined ligands such as pyridine, NMe_3, PMe_3 and N-heterocyclic carbene increase the activation barrier of initiation. Ni catalyst significantly decreases the activation barriers of both initiation and propagation. However, the barrier of initiation of Ni catalyst is still much higher than that of propagation.

1. Introduction

The polymerization of norbornene (NB) has attracted much research interest because it provides a series of important materials with very useful properties such as high glass transition temperatures, high optical transparency, low dielectric constants, and low birefringence [1]. Catalytic polymerization of NB includes ring-opening metathesis polymerization (ROMP), carbocationic/radical polymerization, and vinyl addition polymerization [2]. ROMP-derived poly(norbornene) has unsaturated vinyl backbone which requires hydrogenation or vulcanization for some applications [1]. Carbocationic and radical polymerizations of NB usually produce low molecular weight polymers with rearranged NB units [3]. On the other hand, transition metal-catalyzed vinyl addition polymerization overcomes the above problems by producing saturated poly(norbornene)s with high molecular weight and no rearrangement of NB units. Generally, Ti [4], Zr [5], and Hf [6,7] catalysts are less active than Ni [8] and Pd [9,10] catalysts for vinyl addition polymerization of NB. Mehler and Risse reported that [$Pd(CH_3CN)_4$][BF_4]$_2$ catalyst produces poly(norbornene) with a number average molecular weight (M_n) up to 60,000 g/mol [9]. Nozaki et al. synthesized ($t$$Bu_3P$)Pd(Me)Cl to accomplish a living polymerization of 5-norbornene carboxylic acid ester (NBE) [10]. Despite these achievements, living polymerization of NB catalyzed by Pd or Ni catalyst has not been reported. The reason is that the initiation step of the polymerization is much slower than propagation. Thus only a small amount of the catalyst is active for polymerization. This makes it difficult to control the molecular weight of poly(norbornene).

Recently, Brookhart et al. developed several highly active cationic (allyl)Pd(II) catalysts for the polymerization of NB (Scheme 1) [11]. A Pd(II) complex in which the NB coordinates to Pd via both the double bond and a γ-agostic interaction of the syn H at C7 was identified. The NB insertion from this complex was supposed to be responsible for the slow initiation of the catalyst. Catalyst precursors with electron withdrawing substituents such as COOMe and Cl on the allyl ligand have a much higher activity. However, living polymerization of NB has not been achieved after these modifications because the rate of initiation is still slower than that of propagation. These observations pose a challenging question: how to make the rate of initiation faster than that of propagation? To answer this question, more mechanistic details of the polymerization are needed, such as the mechanism of catalyst initiation, the structure and activation barrier of the transition state of NB insertion, and factors controlling the relative rate of initiation

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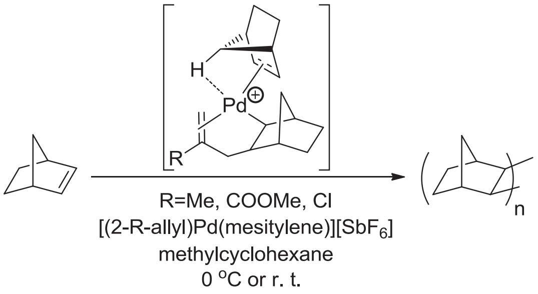

Scheme 1. Pd-catalyzed NB polymerization.

and propagation. Theoretical calculations can provide significant insights into reaction mechanisms [12–16]. Recently, the mechanism of transition metal catalyzed polymerization has been studied extensively [17–20].

As our ongoing research on mechanism of transition metal-catalyzed reactions [21,22], the mechanism of Pd-catalyzed NB polymerization is studied in details by theoretical calculations in this study. Based on the mechanism, possible modifications of the catalyst to increase the rate of initiation relative to propagation are examined and discussed.

2. Results

2.1. Generation of active catalyst

IN1 is the catalyst precursor with $[SbF_6]^-$ as the anionic counterion. The free energy of **IN1** is set to zero. The coordination of NB to **IN1** is exergonic by −3.2 kcal/mol to produce **IN2** (Fig. 1). The activation barrier of NB insertion from **IN2** is +13.3 kcal/mol via **TS2-3**. This low activation barrier is consistent with the experimental observation that NB and **IN1** react to produce **IN3** immediately even at −120 °C [11]. The formation of **IN3** is exergonic by −17.6 kcal/mol. There are two possible ways for the substitution of mesitylene of **IN3** by the second NB to generate **IN6** (Scheme 2). In the first pathway, the dissociation of mesitylene ligand from **IN3** produces **IN4** with a free energy increase of +15.1 kcal/mol. In the second pathway, the free energy increases only slightly by +0.5 kcal/mol when the second NB coordinates to **IN3** to produce **IN5**. The dissociation of mesitylene from **IN5** generates **IN6** with a free energy of −23.9 kcal/mol. The optimized structure of **IN6** shows that NB is a bidentate ligand binding to Pd by both the double bond and a γ-agostic interaction, which is consistent with experimental observation. In addition, the NB ligand is also bidentate in **IN2** or **IN5** but not in **TS2-3**, **IN3** and **IN4**. Thus the γ-agostic interaction between NB and Pd is flexible.

2.2. Insertion of norbornenes

Two pathways are proposed for the second NB insertion from **IN6** (Scheme 3). The activation barrier of NB insertion of **IN6** is +38.9 kcal/mol via **TS6-7**. This activation barrier is too high for a reaction to proceed at room temperature. Thus **IN6** cannot undergo NB insertion directly to form **IN7**. On the other hand, the third NB can coordinate to **IN6** to form **IN8** with a free energy increase of 8.8 kcal/mol. The transition state of NB insertion from **IN8** is located as **TS8-9A** with a free energy barrier of +22.5 kcal/mol relative to **IN6**. Thus **TS8-9A** is more favored than **TS6-7**.

TS8-9A has an isomer, **TS8-9B**, in which the double bond from the allyl moiety coordinates to Pd (Fig. 2). The activation barrier of **TS8-9B** is slightly higher than **TS8-9A** by 0.1 kcal/mol. The product of **TS8-9A** is **IN9** with a free energy of −23.7 kcal/mol whereas the product of **TS8-9B** is **IN10** with a free energy of −31.0 kcal/mol (Fig. 3). Thus **TS8-9B** should compete with **TS8-9A** in the reaction pathway. However, this is not the case when the polymer chain

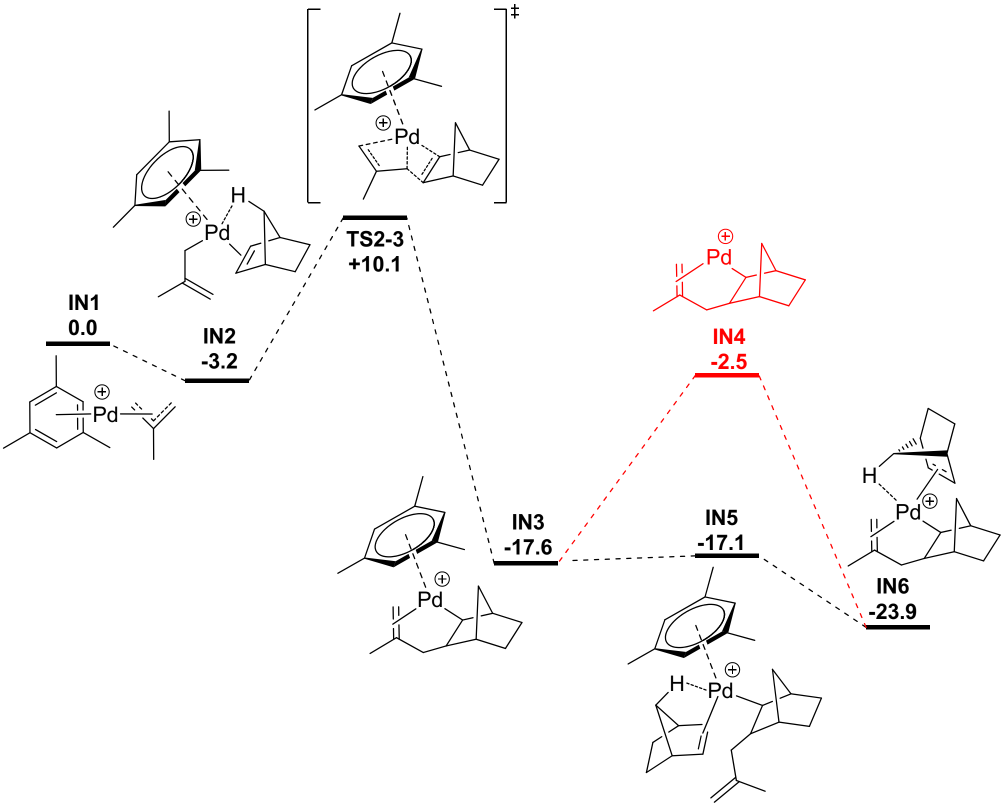

Fig. 1. Free energy profile of catalyst generation (kcal/mol).