Chinese Journal of Polymer Science Vol. 30, No. 5, (2012), 744−758

Chinese Journal of Polymer Science
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Institute of Chemistry, CAS
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A DFT INVESTIGATION OF THE MECHANISM FOR ALTERNATINGCOPOLYMERIZATION OF STYRENE WITH CARBON MONOXIDE CATALYZED BY Pd(II) COMPLEXES*

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Abstract Density functional theory has been employed to study the homogeneous catalytic copolymerization of styrene with carbon monoxide. The copolymerization reaction is catalyzed by Pd(II) coordinated with 2,2′-bipyridine, a conventional nitrogen-containing bidentate ligand with achiral C_{2v} symmetry. The chain propagation mechanism for the alternating copolymerization as well as the side reactions, including multiple insertions of CO and homopolymerization of styrene, has been investigated. This study focused exclusively on regioisomerism and stereoisomerism. We have demonstrated that the strictly alternating copolymerization is kinetically and thermodynamically favored over the side reactions (*i.e.*, multiple insertions of CO and homopolymerization of styrene). The regiochemistry study indicates the 2,1 type. Furthermore, the stereochemistry study shows that the syndiotactic conformation is preferred over the isotactic or atactic conformations.

Keywords: DFT; CO; Styrene; Polyketone; Mechanism.

Electronic Supplementary Material Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s10118-012-1164-9.

INTRODUCTION

Over the past decades, copolymerization of olefins (*e.g.*, ethylene, styrene and *p*-methylstyrene) with carbon monoxide has absorbed many interests of researchers, due to the unusual properties of the products either from an academic point of view or from a industrial point of view[1−5]. This class of copolymerizations catalyzed by cationic Pd(II) complexes with bidentate ligands produces alternating copolymers with regular stereochemistry and regiochemistry. Palladium(II) complex catalysts, modified with carious ligands, including nitrogen-donor chelating ligands[6, 7], phosphino-phosphino derivatives, hybrid phosphino-nitrogen ligands and phosphine-sulfonate ligands, have been successfully employed to prevent catalyst deactivation and to tune the stereoregularity of the copolymerization[8, 9]. The nitrogen-nitrogen ligands are effective in preventing catalyst deactivation, and the copolymerization using these ligands is mild compared to that with phosphine-like ligands[10].

The regioselectivity of α-olefin insertion into a metal-carbon bond (*i.e.*, 1,2-insertion and 2,1-insertion) depends on the nature of the ligands and promoters, acidity, temperature, pressure and some other factors.

* This work was financially supported by the NSFC (Nos. 91127046 and 20974078), KPCME (No. 109043), SRFDP (No. 200800561006), High Performance Computing Center of Tianjin University, China and National Supercomputer Center in Tianjin, China.

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Received December 23, 2011; Revised February 8, 2012; Accepted February 13, 2012
doi: 10.1007/s10118-012-1164-9

Generally speaking, the alternating copolymerization reaction of styrene with carbon monoxide initiated by Pd(II) complexes coordinated to C_{2v} symmetry ligands, (*e.g.*, 1,10-phenanthroline[11], 2,2′-bipyridine[12], a bisoxazoline and other bidentate sp^2 nitrogen compounds[6, 13−16],) resulted in highly syndiotactic polyketones through a chain-end control mechanism, in contrast, Pd(II) complexes coordinated to C_2 symmetric ligands produced highly isotactic polyketones[17]. Recently, it has been reported that the microstructure of CO/styrene or CO/*p*-methylstyrene copolymers can range from atactic to stereoblock isotactic depending on the ligand backbone, which can be visualized either a combination of a fragment having the sp^2 nitrogen atom with a chiral part comprising the sp^3 nitrogen atom[18], or the choice of α-diimine substituents and counterion[19]. The mechanism of copolymerization of the olefin and carbon monoxide is still ambiguous. A deep understanding of the dependence of stereochemistry and regiochemistry on the ligands is valuable for determination of a highly effective catalyst for improved polymerization.

In the present work, a C_{2v} symmetric nitrogen ligand (2,2′-bipyridine) has been used to elucidate the mechanism, the regioisomerism and stereoisomerism of the copolymerization of styrene with carbon monoxide initiated by the methyl carbonyl complex **1** (Fig. 1a)[20]. Although the regioselectivity of the reaction has been demonstrated depending on the nature of the ligands and promoters, acidity, temperature, pressure and some other factors, only the thermodynamic and kinetic properties of all the reaction steps are discussed. The origin of complete 2,1-insertion is shown, and the insertion details are investigated. The alternating copolymerization is also demonstrated by the calculation of multiple CO insertions and homopolymerization of styrene.

COMPUTATIONAL DETAILS

Density functional theory[21, 22] (DFT), B3LYP (Becke's three-parameter hybrid functional[23], the LYP correlation functional[24, 25]) were utilized to fully optimize all the initial geometries on singlet potential energy surfaces without symmetry or geometric constraints, in conjunction with the 6-31g* basis set for main group elements (C,H,O,N) and Lanl2DZ ECP basis sets for palladium element[26−28].

Frequency calculations using the same basis sets have been performed to confirm that the stationary points are minima (zero imaginary frequencies) or transition states (one imaginary frequency) on the potential energy surface. The zero-point energies and the thermal correction data at 101.325 kPa and 298 K are calculated. Intrinsic reaction coordinates (IRC) were employed to verify the connection of the transition states to two relevant minima (*i.e.*, reactants and products). All calculations were performed with the Gaussian 09 suite of programs[29] and the standard "ultrafine" integration grid was used.

RESULTS AND DISCUSSION

The Productive Cycle

As shown in Scheme 1, the productive cycle begins with the methyl carbonyl complex **1** (Fig. 1a) forming the square-planar complex **3** (Fig. 1c) which has a weak β-hydrogen agostic bond through a transition state complex **2** (Fig. 1b). The endothermicity of this reaction step is 32 kJ/mol, and the energy barrier of this step is 59 kJ/mol. The methyl carbonyl complex **1** was selected as starting point because there is a similar complex which has been determined experimentally[20].

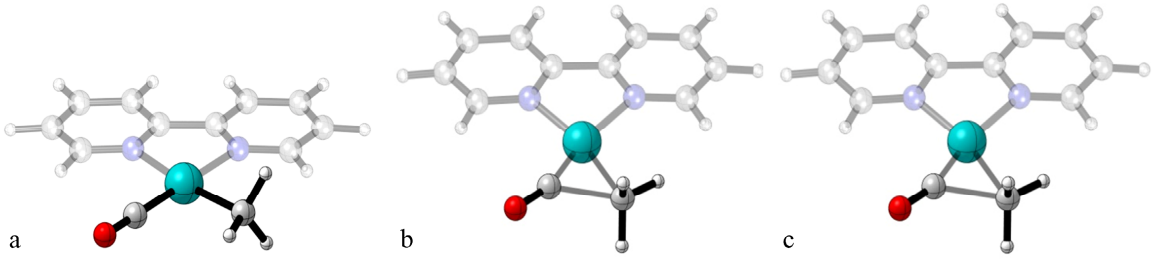
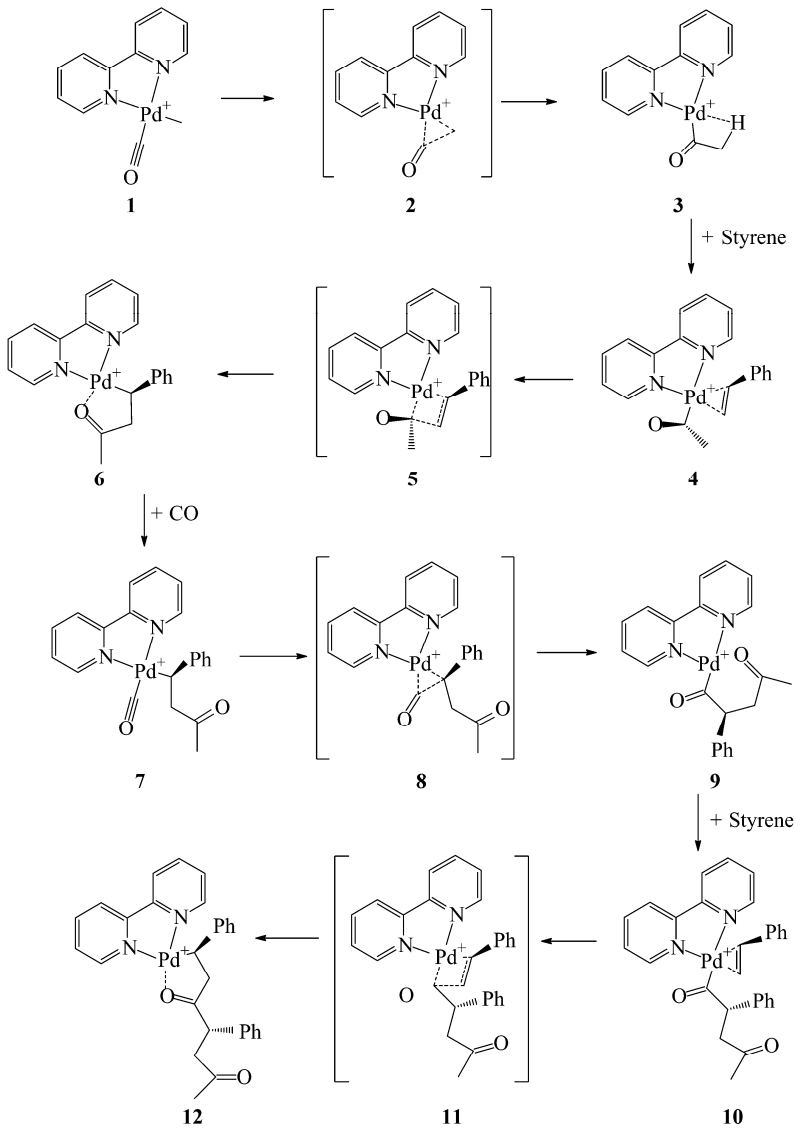


Fig. 1 Molecular structures of methyl carbonyl complex **1** (a), transition state **2** (b) and square-planar complex **3** (c) All structures are drawn by CYLview[30], where the drawing style for bipyridine is set to transparent form.



Scheme 1 Flow chart of the productive section of the catalytic cycle leading to an alternating CO/styrene
The stages of the reaction are identified with numbers; The species in square brackets refer to transition states; All of the species referred to in this work carry a single positive charge.

For the first styrene monomer insertion, the four possible scenarios (**4/I**−**4/IV**, Fig. 2) were considered. The intermediate **4/III** has the highest energy due to the close proximity of the phenyl ring on styrene to the 2,2′-bipyrinyl ring without conjugation (distance between centers of phenyl ring and pyridinyl ring is 0.510 nm). Another reason is that the phenyl ring and the methyl are on the same side of the 2,2′-bipyrinyl plane which makes the energies of intermediates **4/II** and **4/III** higher than the energies of intermediates **4/I** and **4/IV**. Because the Gibbs free energy differences between the four intermediates are small, all of the corresponding transition state structures (Scheme 2) were calculated to determine the most favorable reaction pathway. The corresponding transition states **5/I**–**5/IV** are shown in Fig. 3. Compared with the energy barrier of (77 kJ/mol), the energy barrier from **4/I** to **5/I** is only 70 kJ/mol, which is much less than the energy barrier for conversion of **4/II** to **5/II**. Therefore, the reaction proceeds by following the pathway from **4/I** to **5/I**.

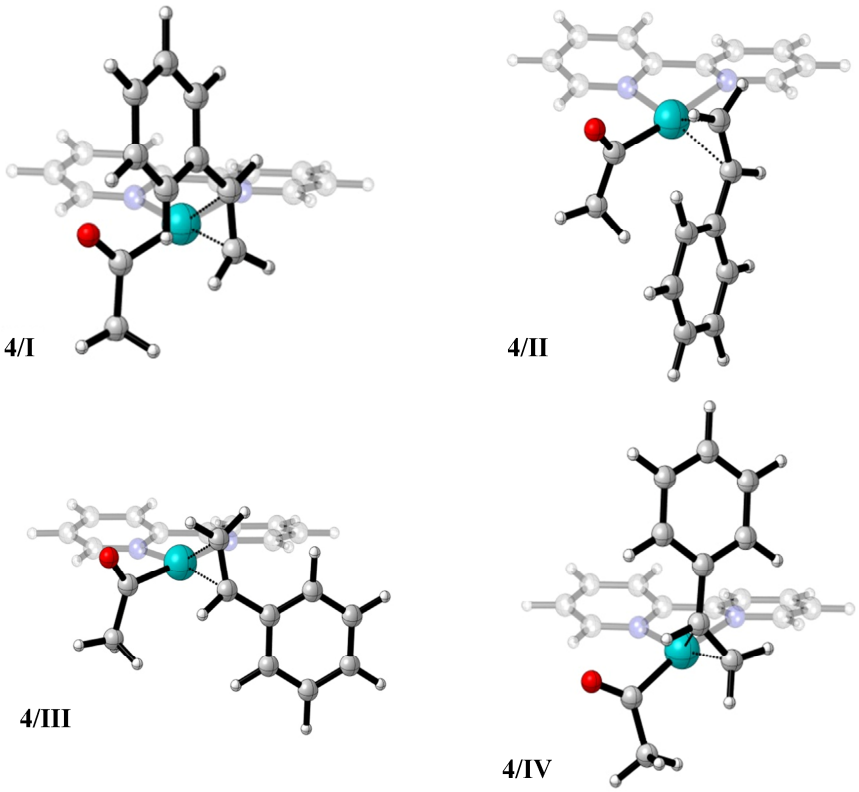
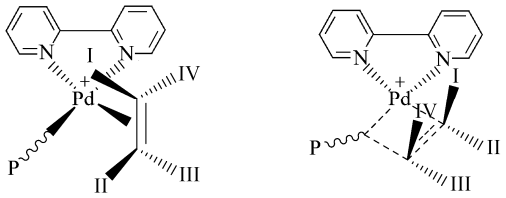


Fig. 2 The structures of intermediates **4/I**−**4/IV** from the coordination of the first styrene unit in the productive cycle



Scheme 2 Sketches of the possible intermediates (left) resulting from the coordination of a styrene unit, and their corresponding transition state isomers (right)
Numbers **I**−**IV** are used to represent styrene units.

A five-membered palladacycle **6/I** (−27 kJ/mol, Fig. 4) with γ-oxygen interaction is generated from 2,1-insertion (*i.e.*, **4/I** to **5/I**), and the energy difference between **6/I** and intermediate **4/I** is 40 kJ/mol. The exothermicity of the reaction is −54 kJ/mol. Two possible β-hydrogen agostic conformations **6/II** and **6/III**, were also investigated. The conformational isomer **6/II** (30 kJ/mol) is optimized from structure **6/I** by moving the γ-oxygen out of the plane through a 49° rotation in the counter-clockwise direction around the C_α-C_β bond. The conformational isomer **6/III** (55 kJ/mol) is obtained by a rotation of 144° in the clockwise direction. These two possible β-hydrogen agostic conformations are not stable, because they are higher in energy than structure **6/I**.

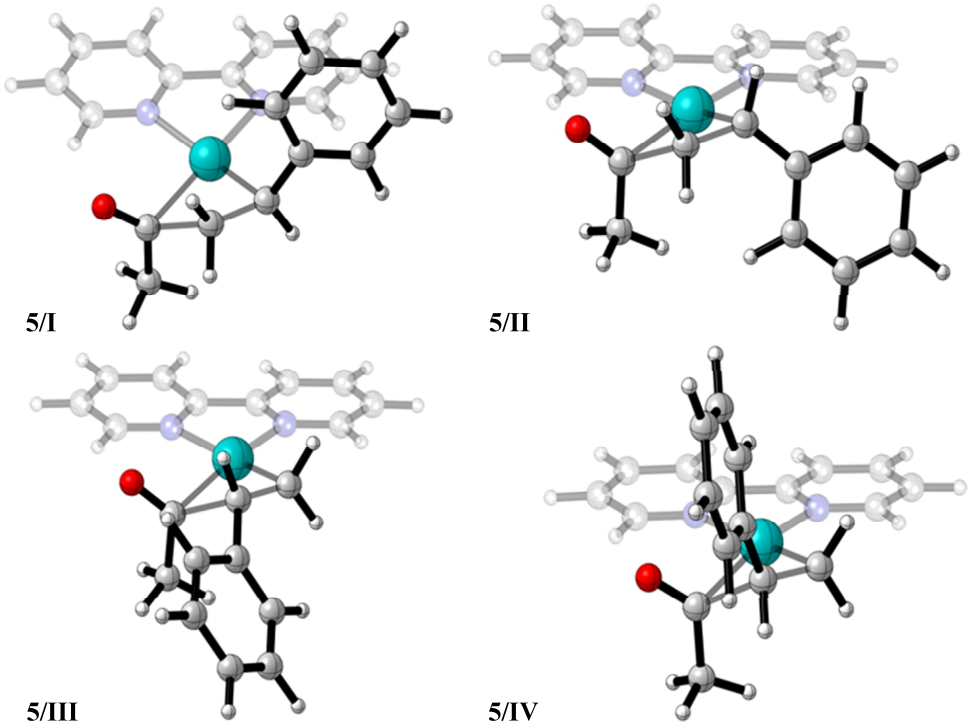


Fig. 3 The structures of transition states **5/I–5/IV** corresponding to the coordination of the first styrene unit in the productive cycle

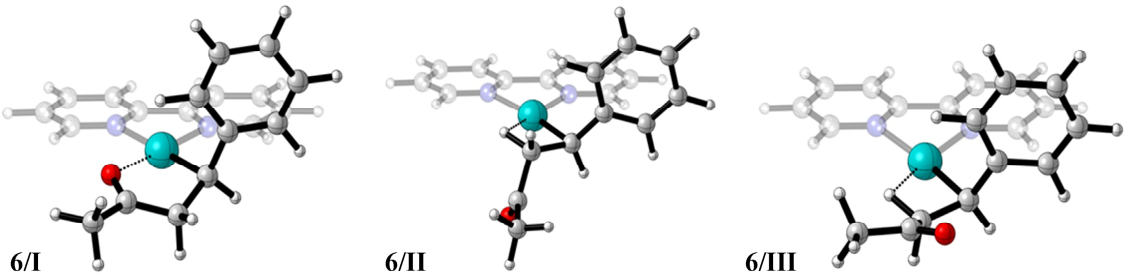


Fig. 4 Molecular structures of the five-membered chelate complex **6/I** and β-hydrogen agnostic complexes **6/II** and **6/III**

The five-membered palladacycle **6/I** formed from the methyl carbonyl complex **1** was experimentally obtained in good yield. The reaction rate constant can be expressed as follows[31]:

$$k(T) = \frac{k_B T}{hc^0} e^{-\Delta G/RT}$$

where k_B is the Boltzmann constant (1.380662×10^{-23} J/K), T is the temperature (K), h is the Planck's constant (6.626176×10^{-34} J s), R is the gas constant (8.31441 J/(mol K)), c^0 is the concentration (taken to be 1) and ΔG is the Gibbs free energy of activation. The Gibbs free energy for the first reaction step to form the square-planar complex **3** with a weak β-hydorgen agostic bond is approximately 58.7 kJ/mol, and the corresponding reaction rate constant is 323.2 s^{-1}. The Gibbs free energy of the second reaction step to form the five-membered palladacycle complex **6/I** is approximately 70 kJ/mol, and the reaction rate constant is 3.4 s^{-1}. This result is consistent with the high yield obtained experimentally[19], which corresponds to high reaction rate constants.

In the chain propagation reaction, a free carbon monoxide attacks complex **6/I** from the same side as the phenyl ring or the opposite side of the phenyl ring. As a result, the γ-oxygen moves out of the coordinating plane to form alkyl carbonyl complexes **7/I** (−11 kJ/mol) and **7/II** (8 kJ/mol), respectively (Fig. 5). Transition state **8** (Fig. 6) for the CO insertion lies 55 kJ/mol above resting state **7/I**. Complex **7/II** can be excluded due to its higher energy. The atoms coordinating with palladium exhibit a small deviation from the square-planar arrangement. The resulting acyl conformation **9/I** (−36 kJ/mol, Fig. 7), which is directly optimized from transition state **8** and forms a six-membered palladacycle by δ-oxygen interaction, lies 25 kJ/mol below alkyl carbonyl conformation **7/I**. The three possible agostic conformations of complex **9/I** are conformational isomer **9/II** (0 kJ/mol), in which the agostic interaction is between the active center and the carbon atom in the phenyl ring, the β-hydrogen agostic conformation **9/III** (26 kJ/mol) and the γ-hydrogen agostic conformation **9/IV** (51 kJ/mol). These conformations exhibit a square-planar geometry (**9/I**, **III**, **IV**) or slightly distorted geometry (**9/II**).

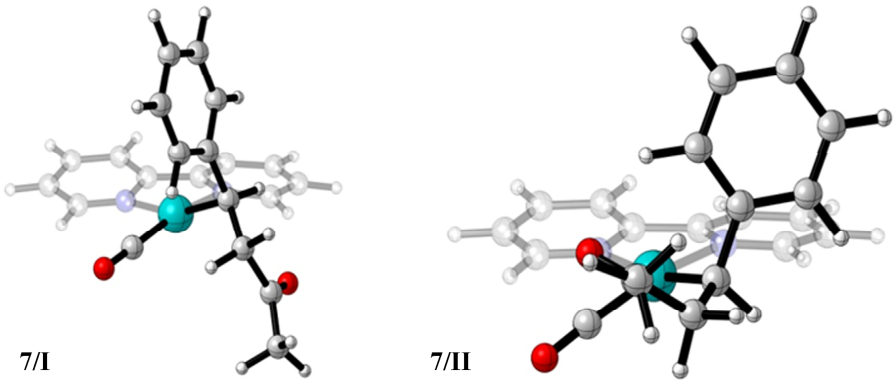


Fig. 5 Molecular structures of complexes **7/I** and **7/II** resulting from the coordinating of the second carbon monoxide

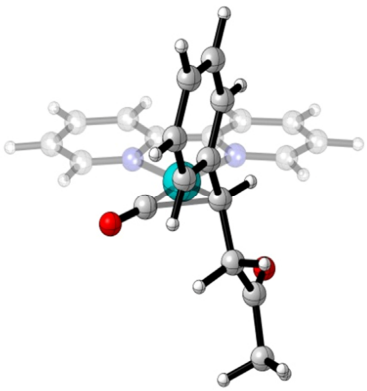


Fig. 6 Molecular structure of transition state **8** corresponding to reactant **7/I**

In the process of adding the second styrene to the growing chain (complex **10**−**12**), the styrene is added to the free apical position of **9/I** leading to the square-planar π-complex **10** (Fig. 8). Intermediate **10** has four possible conformations (Scheme 2) depending on the arrangement of the phenyl ring of the styrene unit with respect to the active center. Their Gibbs free energies are 17, 43, 42 and 13 kJ/mol. These four conformations are all considered because the incorporation of the second styrene determines the regioisomeric and stereoisomeric properties of the alternating polymerization.

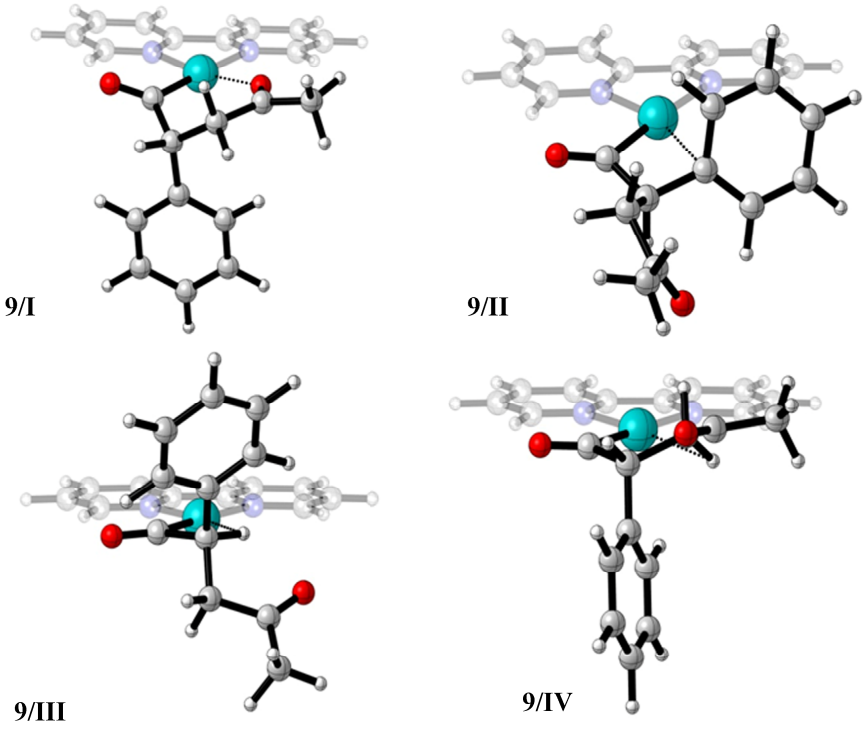


Fig. 7 Molecular structures of the six-membered complex **9/I**, distorted planar complex **9/II**, β-hydrogen agnostic complex **9/III** and γ-hydrogen agostic complex **9/IV**

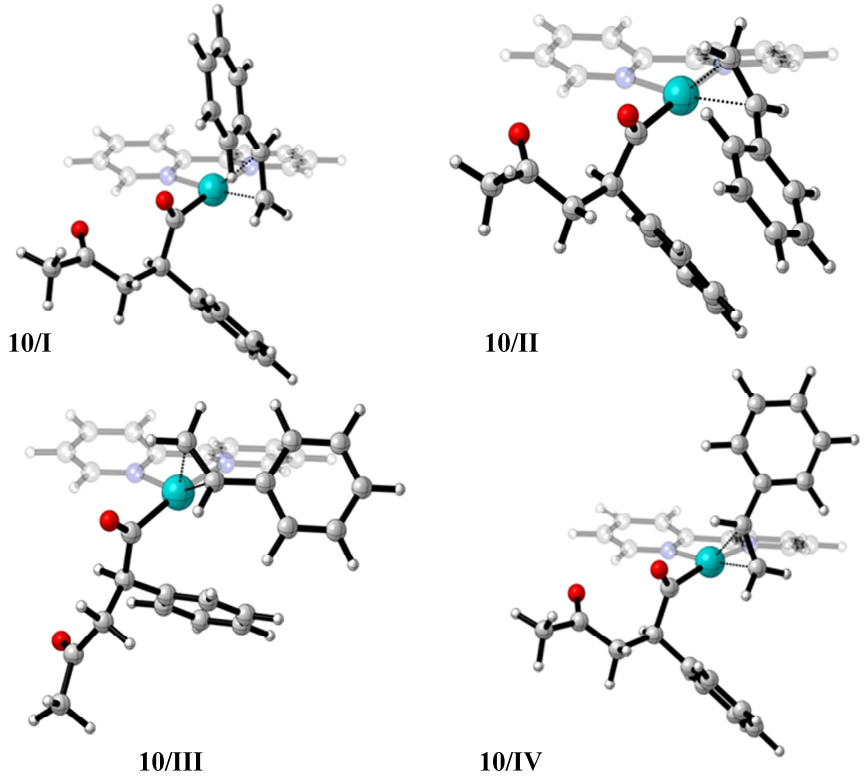


Fig. 8 Molecular structures of the possible intermediates **10** resulting from the coordination of the second styrene unit

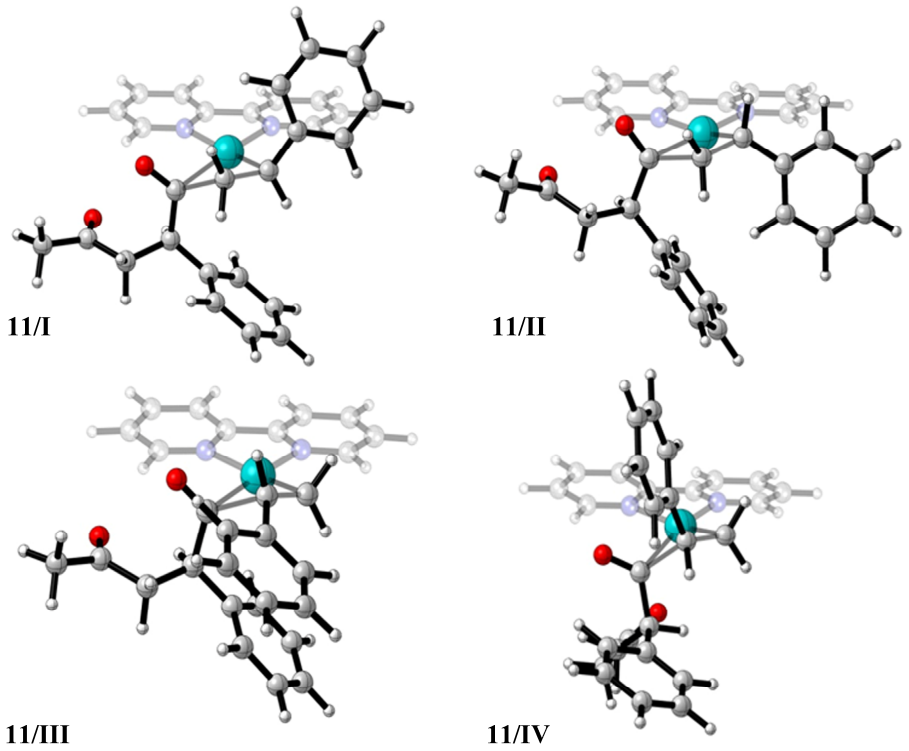


Fig. 9 Molecular structures of the transition states **11** corresponding to the coordination of the second styrene unit

The stereo hindrance of the phenyl ring on the styrene unit plays a critical role in preventing the styrene from turning across the coordinating plane. Intermediate **10** transforms into **12** through the transition state **11** (Fig. 9) by restricting the motion of the phenyl ring. The conformations **10/I** and **10/II** lead to 2,1-insertion, and the conformations **10/III** and **10/IV** lead to 1,2-insertion which is the reverse regiochemistry. Therefore, transition states **11/I**−**11/IV** have the same regiochemistry as complexes **10/I**−**10/IV**. Their activation energies are 81, 72, 116 and 99 kJ/mol, which indicate that the 2,1-insertion is preferred over the 1,2-insertion.

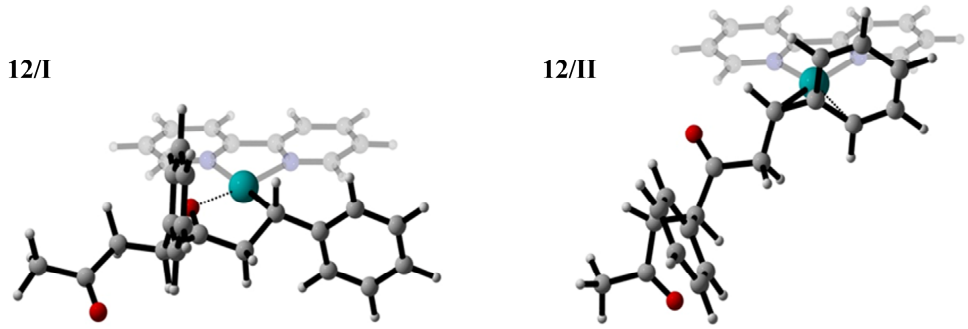


Fig. 10 Molecular structures of the five-membered palladacycle**12/I** and β-hydrogen agostic complex **12/II**

Complex **11/I** generates the isotactic dyad, and complex **11/II** generates the syndiotactic dyad. Furthermore, the energy barrier from **10/I** to **11/I** lies 26 kJ/mol above the energy barrier that from **10/II** to **11/II**, indicating that the syndiotactic conformation is preferred over the isotactic one. Complex **12/I** (−25 kJ/mol, Fig. 10) is a syndiotactic dyad with square-planar geometry and a five-membered palladacycle with a γ-oxygen agnostic interaction. Complex **12/II** (1 kJ/mol, Fig. 10) which has a square-planar geometry with one of the four

coordinating atoms from the phenyl ring, is another possible conformation. Finally, the endothermicity of the reaction from complex **9** to **10** is 7 kJ/mol, and the conversion of **10/II** to **12/I** is exothermic by 44 kJ/mol.

From an energy standpoint, a benchmark for incorporating of a chain segment (the CO/C_8H_8 segment in the productive cycle, the $(CO)_2$ segment in the multiple insertions of CO and the $(C_8H_8)_2$ segment in the homopolymerization of styrene) should be established to demonstrate the predominance of alternating copolymers and to formulate the homopolymerization of styrene and the multiple insertions of CO out of the productive cycle. From the energy profile (Fig. 11), incorporation of a $CO-C_8H_8$ segment recalls −68 kJ/mol.

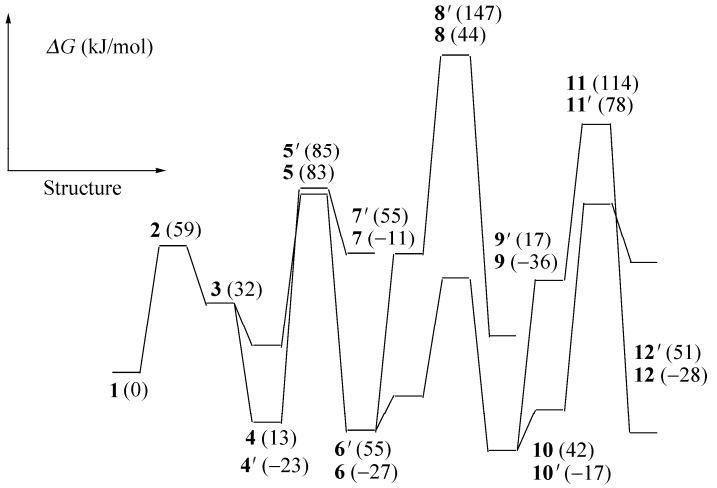
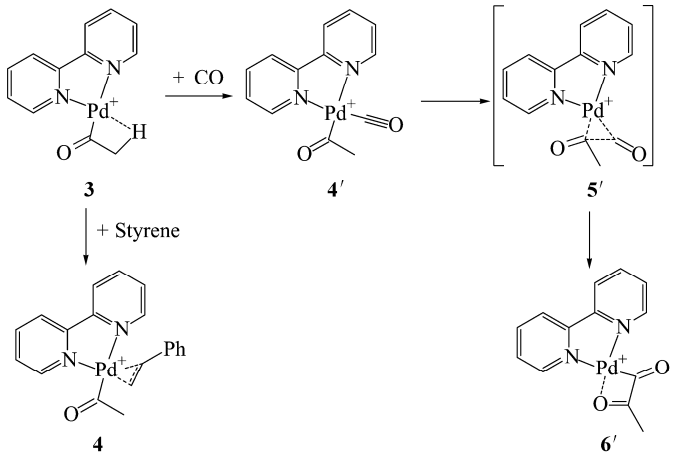


Fig. 11 Energy profile of the alternating copolymerization of styrene with carbon monoxide, as well as the side reactions resulting from multiple insertions of CO and homopolymerization of styrene

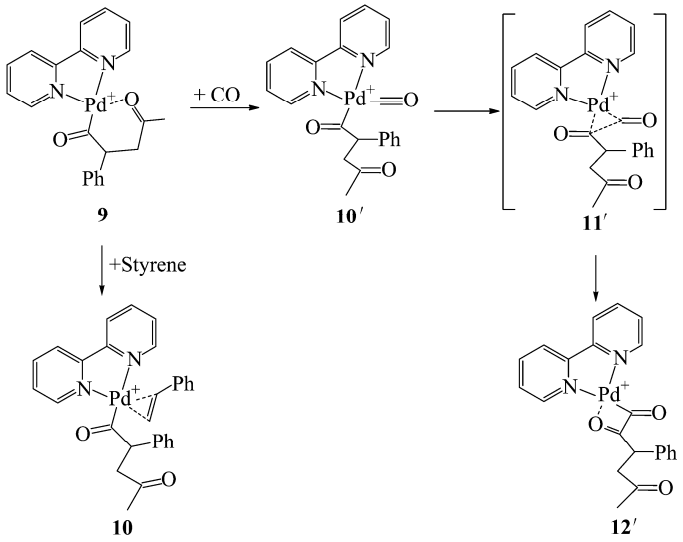


Scheme 3 Flow chart of the CO misinsertion during the catalytic copolymerization of CO and styrene CO misinsertion branches off the productive cycle at stage **3**.

CO Double Insertion

CO misinsertion could occur either before carbonyl complex **3** coordinates to the firstly free styrene in Scheme 3 or after the formation of complex **9/I** in Scheme 4. CO misinsertion can be envisioned as branches in the productive cycle of the reaction. The exothermicities of CO uptake for complexes **3** and **9/I** are −95 and −25 kJ/mol, respectively. The reaction heats of complexes **3** and **9/I** for styrene uptake are −66 and 7 kJ/mol, respectively. The CO uptake process is energetically favorable in the beginning (complex **3**) and in the middle

(complex **9/I**) of the polymerization, which is mainly due to the smaller steric hindrance of the CO molecule compared to the styrene unit.



Scheme 4 Flow chart of the CO misinsertion during the catalytic copolymerization of CO and styrene CO misinsertion branches off the productive cycle at stage 9.

Complex **3** captures a free CO molecule at its fourth ligand position by breaking its β-hydrogen agnostic interaction through a 62° rotation around the Pd-C_α bond. The four ligand atoms of phenyl carbonyl complex **4′** (Fig. 12a) do not maintain a square-planar geometry in contrast to complex **3**. Additional calculations show that transition state **5′** (85 kJ/mol, Fig. 12b) lies 107 kJ/mol above resting state **4′** (−23 kJ/mol), and produces β-oxygen agostic complex **6′** (55 kJ/mol, Fig. 12c) with a square-planar geometry. The endothermicity of this step is 69 kJ/mol.

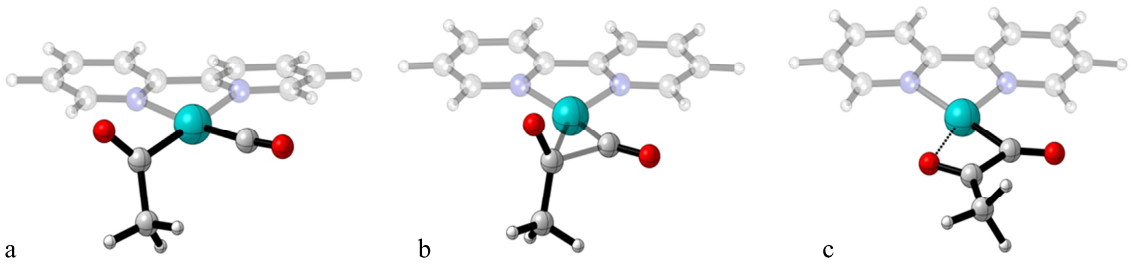


Fig. 12 Molecular structures of the first branch of the carbon monoxide multiple insertions from the productive cycle (a) complex **4′**, (b) complex **5′** and (c) complex **6′**

Complex **9/I** captures a CO molecule from the two sides of the coordinating plane to form complexes **10′/I** (−17 kJ/mol, Fig. 13(a), from the opposite side of the coordinating plane) and **10′/II** (−11 kJ/mol, Fig. 13b, from the same side as the coordinating plane). Complex **9/I** takes up a CO molecule from the opposite side of the coordinating plane to the phenyl ring, which is more stable than CO uptake from the same side of the coordinating plane due to less steric hindrance. The two complexes have distorted planar structures. After taking up a CO molecule, complex **10′/I** transforms into β-oxygen agostic complex **12′** (51 kJ/mol, Fig. 13d with a square-planar geometry) through transition state **11′** (78 kJ/mol, Fig. 13c). The endothermicity of this step is 59 kJ/mol and the energy barrier is 95 kJ/mol.

Comparison with the barriers for alternating insertion (**4/I** to **5/I**: 70 kJ/mol; **10/II** to **11/II**: 72 kJ/mol) shows that the CO double insertion is clearly unfavorable due to high barriers (**4′** to **5′**: 108 kJ/mol; **10′** to **11′**: 95 kJ/mol). Therefore, CO double insertion does not compete with the alternating insertion. The energy profile in Fig. 11 shows that incorporation of a $(CO)_2$ segment equals 78 kJ/mol.

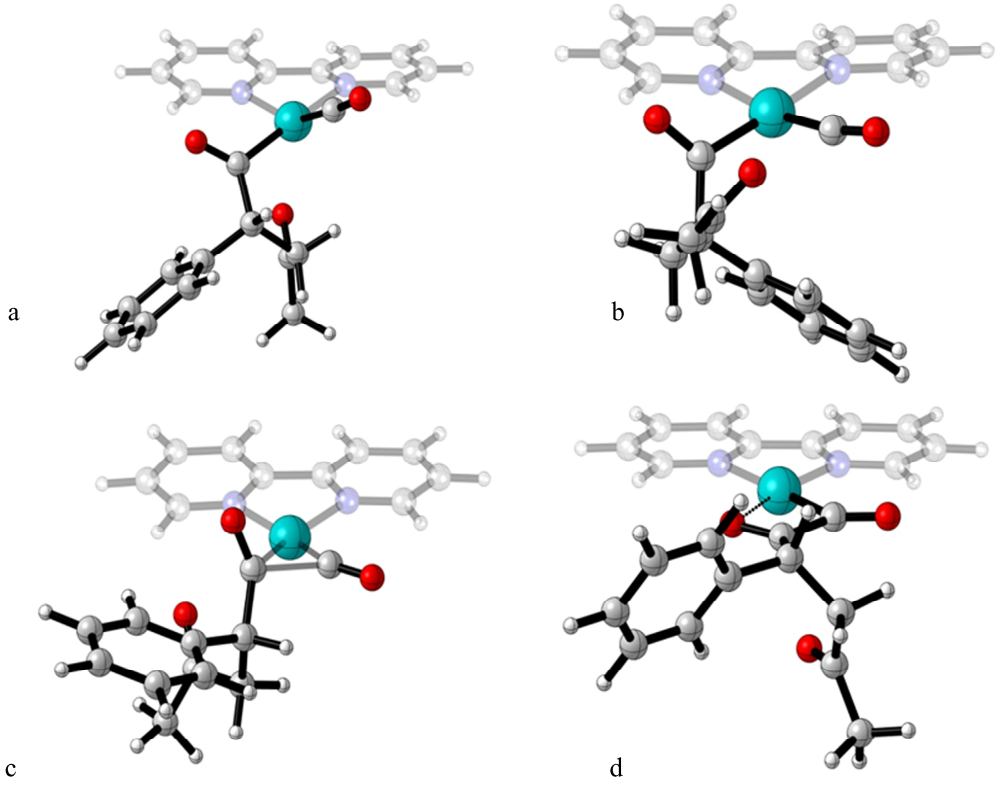
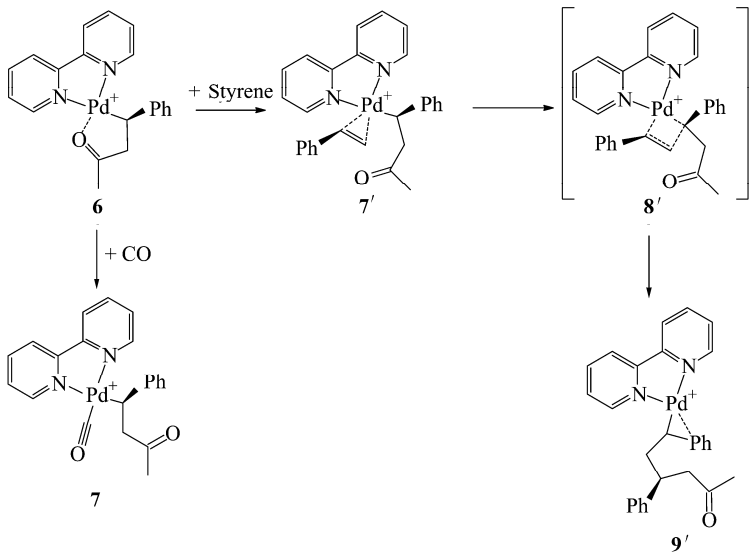


Fig. 13 Molecular structures of the second branch of the carbon monoxide multiple insertions from the productive cycle (a) complex **10′/I**, (b) complex **10′/II**, (c) complex **11′** and (d) complex **12′**

Styrene Double Insertion

The progress of the double insertion of a styrene unit into the polymer chain is shown in Scheme 5. The second insertion can be recognized as branching from the productive cycle originating from complex **6**. When complex **6** takes up styrene, a $(C_8H_8)_2$ segment will be inserted into the growing chain. Styrene uptake by complex **6** occurs at the free apical position by breaking the five-membered palladacycle geometry and converts directly to the distorted planar π-complex **7′** (**I**, **II**, Fig. 14), or 5-coordinate square-pyramid **7′** (**III**, **IV**). Their Gibbs free energies are 52, 55, 49, and 41 kJ/mol, respectively. The energy differences resulted from the arrangement of the styrene unit towards the ligand position. The endothermicity of the styrene uptake step is 55 kJ/mol. Thus, the unproductive styrene uptake by complex 6 is less favorable than the corresponding productive CO addition, which has an exothermicity of −20 kJ/mol. Transition state **8′** (**I**, **II**, **III**, **IV**, Fig. 15) is generated from intermediate **7′** (**I**, **II**, **III**, **IV**) by relaxing the phenyl ring moiety in styrene, and the energy barriers for the four conversions are 98, 92, 116 and 108 kJ/mol, respectively. Therefore, the possible reaction of styrene double insertion would occur from intermediate **7′/II** to transition state **8′/II** because of lowest energy barrier and resulting in an isotactic enchainment of the monomer units. The isotactic product of the styrene double insertion is the 4-coordinate planar-square geometry **9′/I** (17 kJ/mol) in which one of the four coordinate atoms is from the phenyl ring (Fig. 16). Complex **9′/I** lies 34 kJ/mol lower than resting state **7′/II**, and the exothermicity of this styrene double insertion reaction is 30 kJ/mol. Two additional complexes are possible and include: *β*-hydrogen agostic conformation **9′/II** (43 kJ/mol) and *γ*-hydrogen agostic conformation **9′/III** (49 kJ/mol), in which the hydrogen atom occupies one corner of the square-planar configuration.



Scheme 5 Flow chart of the styrene misinsertion during the catalytic copolymerization of CO and styrene Styrene misinsertion branches off the productive cycle at stage **6**.

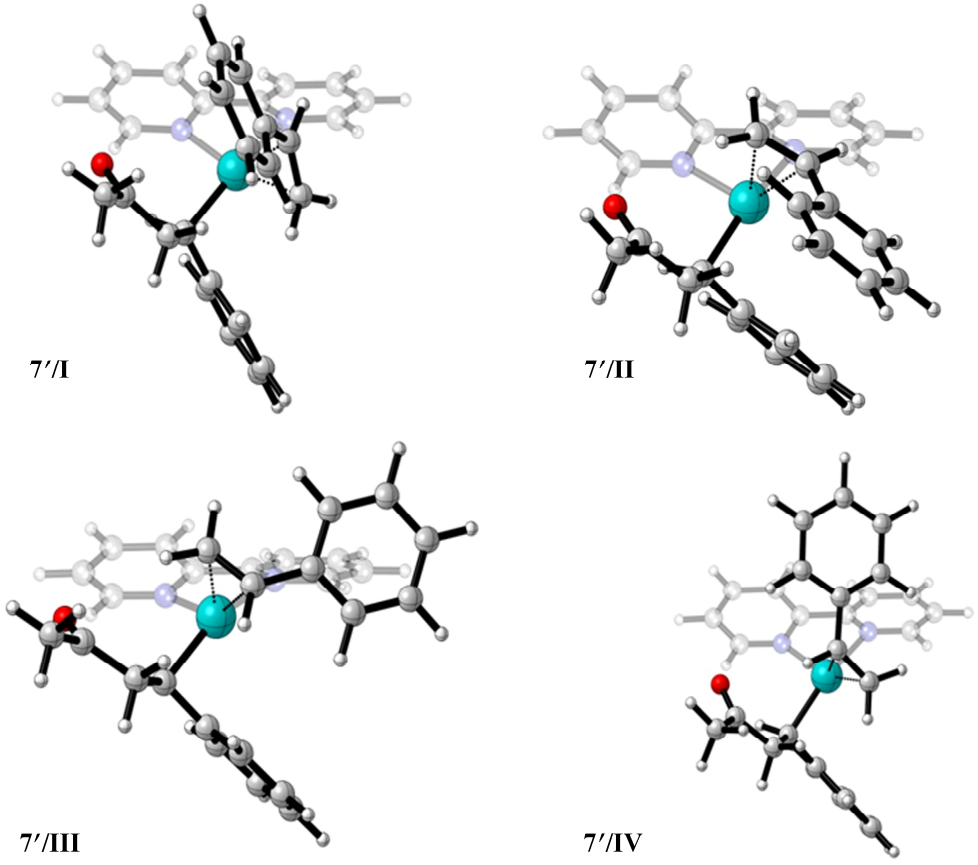


Fig. 14 Molecular structures of the intermediates **7′** resulting from the coordination of the second styrene unit

The Gibbs free energy for the incorporation of a isotactic $(C_8H_8)_2$ segment into the chain is 15 kJ/mol, (−59 and 44 kJ/mol for the first and second styrene insertions, respectively). However, the Gibbs free energy for the

alternating incorporation of a CO/C_8H_8 segment is −68 kJ/mol. Therefore, the strictly alternating insertions are thermodynamically favored because the energy barrier for the alternating reaction is 55 kJ/mol lower than that calculated for the double insertion of styrene (98 kJ/mol).

A good understanding of this branch is important because it controls whether the alternating copolymerization or the styrene double insertion occurs.

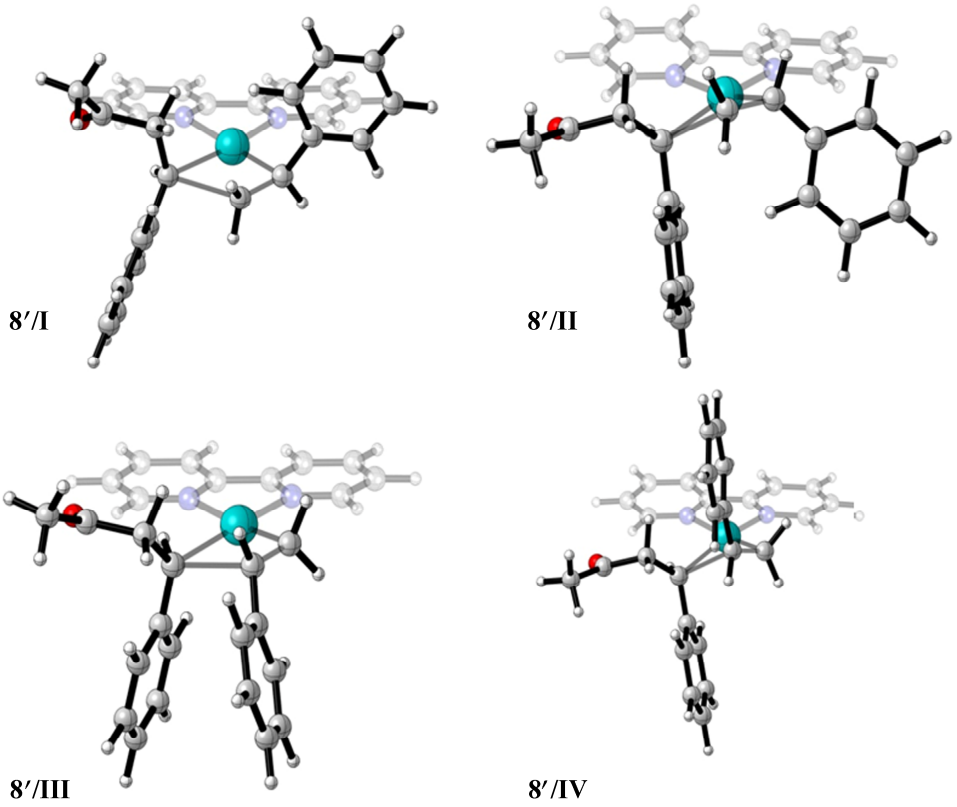


Fig. 15 Molecular structures of transition state **8′** corresponding to the homopolymerization of styrene

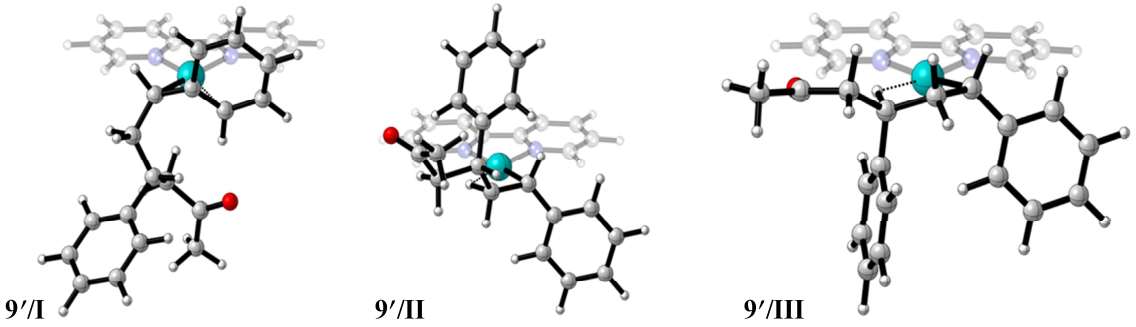


Fig. 16 Molecular structures of complex **9′** resulting from the homopolymerization of styrene

CONCLUSIONS

The chain propagation mechanism for alternating copolymerization of styrene with carbon monoxide catalyzed by an achiral nitrogen Pd(II) complex as well as the misinsertion reactions resulting from multiple insertions of styrene and CO have been investigated, using density functional theory. Strictly alternating copolymerization is thermodynamically favored over both the multiple insertions of CO and homopolymerization of styrene.

Insertion of one CO/C_8H_8 segment into the Pd-methyl bond is exothermic by −170 kJ/mol, whereas insertion of a $(C_8H_8)_2$ segment or a $(CO)_2$ segment is exothermic by −95 and −15 kJ/mol, respectively. Multiple insertions of styrene and CO are kinetically unfavorable compared to the strictly alternating copolymerization. The activation barriers for insertion of a C_8H_8/CO unit into the chain are 70, 55 and 81 kJ/mol, for the multiple insertions of CO are 108 kJ/mol (Scheme 3) and 95 kJ/mol (Scheme 4), and for the homopolymerization of styrene is 98 kJ/mol. From the strictly alternating copolymerization process, a syndiotactic chain is thermodynamically favored over the isotactic chain. The growing polyketone chain is strongly stabilized through the formation of chelate bond between the carbonyl oxygen and the active center. For example, γ-oxygen conformation **12/I** lies 52 kJ/mol below β-hydrogen agostic conformation **12/II**. Finally, although CO incorporation into the growing chain is much easier than styrene incorporation, multiple insertions of CO molecules have the highest activation barriers. Therefore, subsequent multiple insertions of CO are avoided because they are kinetically unfavorable. In addition, the homopolymerization of styrene is kinetically and thermodynamically unfavorable.

AKNOWLEDGEMENT We thank Yakai Feng and Jintang Guo for valuable discussion.

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