

REVIEW

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Light-mediated olefin coordination polymerization and photoswitches

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Polyolefins are important polymeric materials in the plastics industry. While classical Ziegler–Natta catalysts are still superior in global polyolefin production, it is challenging to control their polymerization behavior due to intrinsic heterogeneity. A significant number of molecular olefin polymerization catalysts based on transition metals are capable of harnessing polymerization behavior thanks to their finely-tunable ligand sets, where ligand variation acts as electronic and/or steric factors towards the active metal center. Light has been utilized as a green and specific stimulus in the context of coordination olefin polymerization to mainly alter the electronic state of active catalytic sites, which enables photo-controlled chain propagation. A handful of examples of polymerization catalytic systems that have precise controllability under photoirradiation have been developed to provide a broad range of polyolefins in terms of polymeric (micro)structure. In this Review, we wish to outline photo-responsive, transition metal-based coordination polymerization catalysts ranging from homogeneous to heterogeneous, and monometallic to bimetallic regimes. Specific but varied roles of light depending on the employed catalysts for olefin polymerization are presented with a strong emphasis on the photo-altered properties of the active species.

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1. Introduction

Synthetic polymeric materials are important commodity chemicals in our society, which have been greatly advancing in terms of the polymer's physical and chemical properties to provide people with higher quality and efficiency in life.^{1–3}

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These synthetic polymers are prepared from their monomers largely *via* either step-growth or chain-growth polymerization. A representative example of the former working mode is the condensation reaction of monomers that have reactive multi-functions, which proceeds in a stepwise manner through dimers and oligomers as key intermediates.^{4–6} While this method produces a variety of highly useful thermoplastic polymers such as polyesters and polyamides, the high conversion of monomers is crucial to achieving high molecular weight polymers and the reaction itself is difficult to control due to the nature of the step-growth mechanism.^{7–9} In contrast, chain-growth polymerization requires initiators to generate the active species, which causes polymer chain growth in a controlled manner, being able to give highly modulated polymers. Among them, polyolefins are chain-growth polymers that are widely utilized in modern life. In fact, more than 178 million tons of polyolefins were produced in a single year in 2015, which corresponded to >50% of the global production of synthetic polymers in the same year.^{10,11} Such largescale polyolefin production is likely due to low-cost olefin monomers and them having far less toxicity with broad end-applications of polyolefin products relative to other types of commodity polymers.^{12–14}

Ziegler–Natta catalysts are one of the most practical and powerful catalytic systems for the production of commercialized polyethylene [e.g. high density polyethylene (HDPE), linear low density polyethylene (LLDPE)]. However, these catalytic systems are extremely difficult to study and understand in terms of polymerization mechanism due to their heterogeneous nature.^{15–18} In this regard, a number of well-defined homogeneous catalytic systems based on transition metals have been developed in the last few decades. For example, Kaminsky communicated the first homogeneous catalyst system composed of group 4 metal-based metallocene complexes and methylaluminoxane (MAO) as a cocatalyst for the

coordination polymerization of ethylene and α -olefins leading to HDPE and LLDPE in 1980.^{19–22} In 1995, Brookhart reported Pd and Ni-based complexes with α -diimine ligands as olefin polymerization catalysts to furnish highly branched polyethylene referred to as low density polyethylene (LDPE) under relatively mild conditions, when compared to LDPE production *via* a classical radical process that requires far harsher conditions.^{23–27} Following Brookhart's α -diimine polymerization catalysts, a number of research groups successfully developed well-tailored [N–O] and/or P-based ligand systems of late transition metals (e.g. bis-iminopyridine, salicylaldimine, phosphine sulfonate, *etc.*) for the (co)polymerization of olefins.^{28–30} Molecular olefin polymerization catalysts with electronically and sterically modular ligand systems enable the control of the polymerization profile, including the molecular weight and dispersity, degree of branching, and tacticity of polyolefins.^{31–33} In general, the electrophilic nature of the active metal center stabilized by a non-coordinating counter anion is the key to accomplishing high polymerization catalytic activity, while the electron-donating substituents of the ligands contribute towards suppressed chain transfer to give rise to high molecular weight polymers.^{34–40} The steric bulkiness of ligands is well known to often block an axial coordination site of active metal centers and slow chain-transfer processes, which yields high molecular weight polyolefins with narrow dispersity and enables living polymerization to synthesize various block copolymers.^{41–49} Physical reaction parameters, including temperature and ethylene pressure under certain ligand systems, have also been shown to strongly influence catalyst productivity, polymer molecular weight and microstructure.^{50–53}

Given the well-established relationship between electronic/steric variations in ligand and olefin polymerization behavior, a handful of research groups have been interested in utilizing light as an external stimulus and as a tool for the controlled



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synthesis of polyolefins.^{54–58} There have been remarkable reports on photo-switchable catalysts for non-coordination-insertion polymerization, including ring-opening metathesis polymerization (ROMP),^{59,60} ring-opening polymerization (ROP),^{61–65} and atom-transfer radical polymerization (ATRP),^{66–71} in which photosensitive organo(metallic) catalysts and/or photo-initiators can be reversibly activated to modulate polymerization pathways. The Inagaki and Akita group published a review on visible-light promoted bimetallic catalysis for olefin oligomerization *via* a coordination–insertion mechanism.⁷² Bielawski published a seminal review on switchable polymerization catalysts, including a few examples of photo-responsive polymerization catalytic systems.⁷³ Similarly, Hecht reviewed a series of photoswitchable polymerization catalysts.⁷⁴ Despite the remarkable advances in olefin coordination-insertion polymerization,^{23–33} a review regarding light-mediated olefin coordination polymerization has not been published thus far.

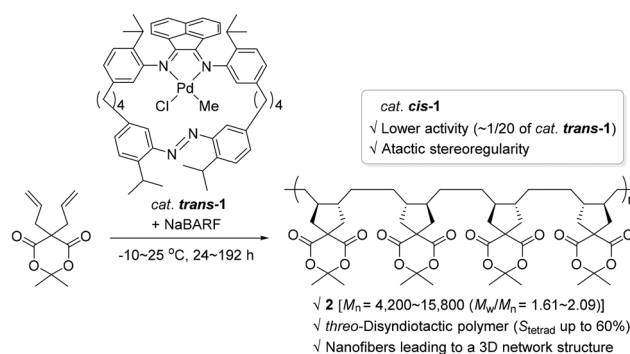
Since light is specific, tunable, and green, light-mediated olefin coordination polymerization (2010–2019) is a promising strategy for the construction of finely-tuned polyolefin architectures. In this regard, we wish to outline in this review the photoresponsive olefin polymerization catalysts ranging from monometallic to bimetallic, and homogeneous to heterogeneous systems. The light-driven electronic and steric alterations in the employed catalytic systems and their effects on polymerization behavior are discussed (Scheme 1).⁷⁵ This review covers the literature up to March of 2020.

2. Monometallic catalytic systems

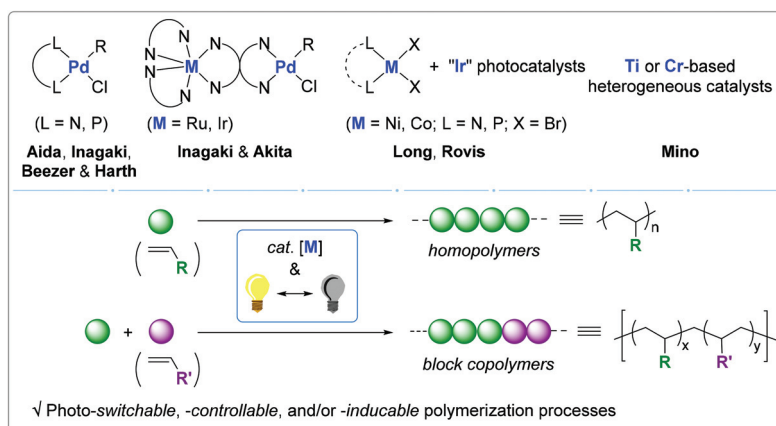
Photochromic moieties on the ligand systems of monometallic olefin polymerization catalysts affect polymerization behavior upon light irradiation generally *via* either of the following modes: (i) a photo-absorbing ligand plays the role of an electronic factor to bring about alteration in the electronic state of the metal center; or (ii) a photo-sensitizing ligand induces reversible changes in the steric environment surrounding an

active metal site. The former working mode involving photo-induced electronic alteration at the active metal center has been well studied, whereas the catalytic system accompanied by significant steric changes in the light has rarely been covered (*vide infra*).

In 2010, Aida and coworkers synthesized a Pd(II) complex **1** with a cyclic α -diimine ligand containing a photo-isomerizable azobenzene moiety, and applied complex **1** [*trans*-**1** or 80% of *cis*-**1** (azobenzene group geometry)] as a catalyst in the known cyclopolymerization^{76–78} of isopropylidene diallylmalonate in an attempt to control its polymerization activity by utilizing light as a switchable external stimulus (Scheme 2).⁷⁹ The cyclopolymerization smoothly proceeded in the presence of catalytic amounts of *trans*-**1** and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF) as a cocatalyst at $-10\sim 25\text{ }^{\circ}\text{C}$ to give the corresponding polymer that has a *trans*-1,2-disubstituted cyclopentane repeating unit (**2**). The molecular weights, M_n , of the obtained cyclic polymer **2** increased up to 15 800 with a molecular dispersity (M_w/M_n) of 1.65 in 192 h. Notably, the nuclear magnetic resonance (NMR) spectroscopic analysis revealed that the tacticity due to relative configurations between the cyclopentane units in **2** prepared *via trans*-**1** catalysis, is rich in *threo*-disyndiotactic tetrad up to 60%.



Scheme 2 Cyclopolymerization of isopropylidene diallylmalonate catalyzed by *trans*-**1** or *cis*-**1**.

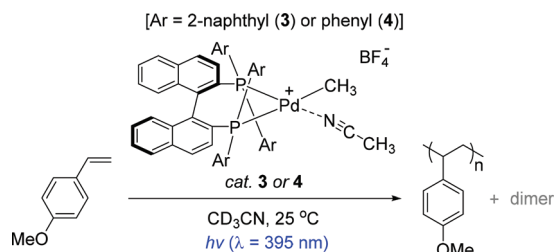


Scheme 1 Catalytic systems for light-mediated olefin coordination polymerization and photoswitches.

This was in stark contrast with the stereooutcome obtained using catalyst **cis-1**, where the syndiotacticity was lower. Another interesting comparison is the highly differing catalytic activities: **trans-1** showed *ca.* 20 times higher diallylmalonate cyclopolymerization activity relative to **cis-1** [k_{obsd} (**trans-1**) = $2.50 \times 10^{-5} \text{ s}^{-1}$ vs. k_{obsd} (**cis-1**) = $0.13 \times 10^{-5} \text{ s}^{-1}$ under the assumption of pseudo-first-order kinetics]. These contrasting stereochemical and kinetic observations indicate that although the azobenzene group with a *trans* or *cis* geometry is embedded far from the Pd center, it counterintuitively and largely influences the catalytic behavior of the Pd species. The obtained polymeric materials rich in syndiotactic sequence formed barb-shaped polymers, which self-assembled into unusual nanofibers to eventually bring about a 3D network structure essential for physical gelation.

The Inagaki and Akita group previously reported a series of bimetallic photocatalysts composed of bipyridyl-ligated Ru-based photosensitizer units and a Pd reactive center linked by a bipyrimidyl ligand, where the naphthyl substituents installed on the ligands played a key role in extending the lifetimes of the metal to ligand charge transfer (MLCT) excited states under light irradiation.^{80,81} Based on the photophysical insights into the Ru-Pd photocatalysts and the known photosensitizing ability of BINAP,^{82–85} the same group developed the naphthyl-substituted BINAP-Pd(II) complex **3** as a catalyst for the preassumed photo-induced styrene polymerization (Scheme 3).⁸⁶

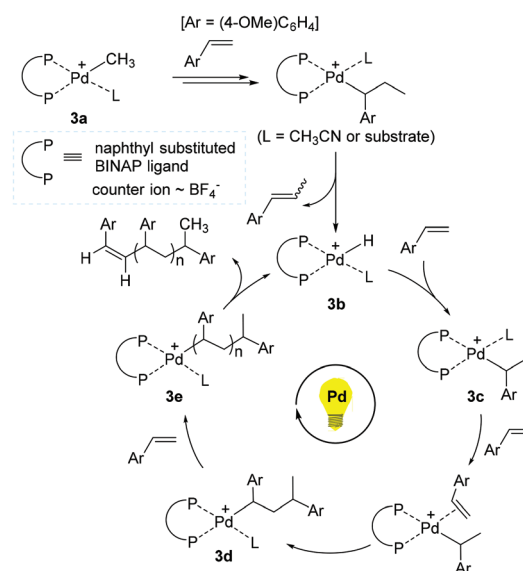
To understand the effects of a naphthyl substituent in terms of photophysical properties and catalytic activity, the Inagaki group prepared a bidentate (*R*)-BINAP Pd complex that has two phenyl groups on each phosphine atom (**4**) for comparison. The polymerization reactions of a handful of styrenes under UV light were examined in the presence of catalyst **3** (1 mol%) to reveal that an electron-rich substrate 4-methoxystyrene underwent chain reaction to give poly(4-methoxystyrene) with a M_n of 14 000 ($M_w/M_n = 1.50$) and small amounts of dimers. This Pd catalysis was perfectly photoswitchable: the reaction stopped under dark conditions, and resumed upon photo-irradiation. It is noteworthy that the overall polymerization outcomes under the light ON-OFF switching sequence were substantially similar to those resulting from continuous light-ON for the same period of time. These results strongly suggest a single site propagating Pd species during polymer



Scheme 3 Polymerization of 4-methoxystyrene catalyzed by a cationic Pd(II)-BINAP complex.

chain growth in the light. In stark contrast, however, catalyst **4** exhibited lower polymerization performance when compared to the catalysis by **3** under identical conditions [polymer yields in 10 h ~60% (**cat. 3**) vs. ~20% (**cat. 4**)]. This result implied that the naphthyl substituent in catalyst **3** serves as a key photochromic moiety to lead to light-mediated styrene polymerization.

On the basis of experimental and theoretical studies, a reaction pathway for the **3**-promoted polymerization of 4-methoxystyrene was proposed (Scheme 4). Initially, the Pd methyl species **3a** is assumed to undergo 2,1-insertion of 4-methoxystyrene, followed by β -hydrogen elimination to generate the Pd hydride **3b** as an active species. **3b** is presumed to consecutively react with 4-methoxystyrene for chain propagation *via* a series of Pd alkyl intermediates such as **3c**, **3d**, and **3e**. Indeed, molecular ions corresponding to intermediates **3c** ($m/z = 1063$) and **3d** ($m/z = 1197$) were detected by electrospray ionization mass spectrometry (ESI-MS), supporting a non-radical, coordination-insertion mechanism. A Pd propagating species with a polymer chain such as **3e** likely liberates the corresponding polymer upon β -H elimination with the regeneration of **3b**. Photoirradiation is proposed to accelerate the insertion of 4-methoxystyrene, and thus to make the overall polymerization reaction facile, while the released polymer bearing alkene chain-ends can be reinserted into the Pd-H bond of **3b** for further chain growth under (repeated) photo-irradiation. Given the fact that styrene and 2-norbornene did not react, while ethyl vinyl ether and methyl acrylate reacted to give the corresponding polymers under the photoirradiation conditions, the polymerization mechanism might vary from coordination to cationic or radical pathways depending on the type of the olefin monomers.



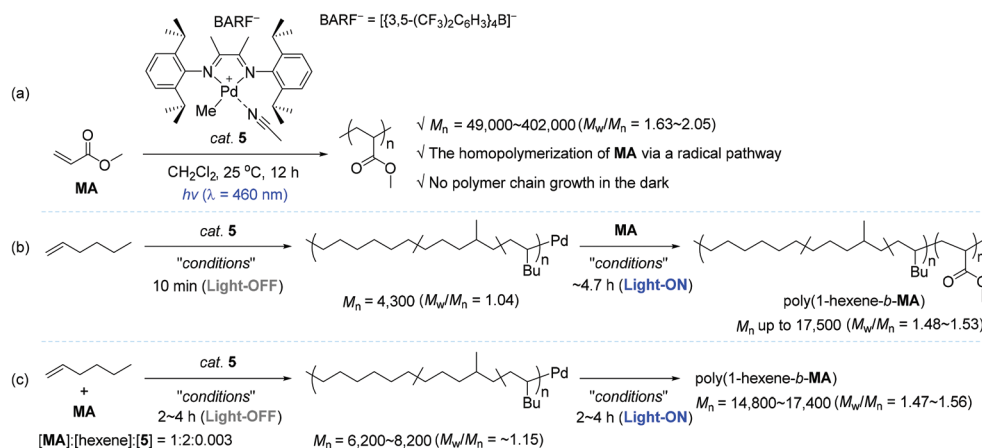
Scheme 4 Proposed pathway for the **3**-catalyzed polymerization of 4-methoxystyrene under UV light.

In the context of coordination–insertion polymerization, despite the significant efforts to increase the incorporation of polar comonomer unit into the polymer backbone under an insertion mechanism, the copolymerization of non-polar olefins with polar olefins generally brings about low comonomer incorporation in the resultant polar functionalized polyolefins. Such low contents of polar comonomer units in the polymer backbone are mainly owing to the stable chelation structure of metallacycles that are *in situ* generated upon the insertion of polar olefin comonomers, followed by isomerization. The chelation structure eventually inhibits the consecutive insertions of the polar comonomers.^{25,28–30,87–91} Being aware of the intrinsic limitation of insertion polymerization in terms of the synthesis of polar polyolefins, a range of research groups applied a radical polymerization strategy for the synthesis of homo- and copolymers of vinyl polar monomers using well-defined organometallic catalysts based on Pd, Ni, and Co.^{92–98} Based on this background, Harth and coworkers conceived the development of a light-sensitive catalyst system for olefin polymerization, in which the catalytic working mode is photoswitchable between coordination–insertion and radical mechanisms. It turned out that an α -diimine Pd complex **5** worked well in such a photoswitchable catalytic mode for the target homo- and copolymerization reactions (Scheme 5).⁹⁹ The **5**-catalyzed homopolymerization reactions of methyl acrylate (**MA**) in various concentrations were conducted under blue light ($\lambda = 460$ nm) to produce poly(methyl acrylate) (poly-**MA**) with a M_n of 49 000–402 000 ($M_w/M_n = 1.63$ –2.05). It should be noted that the linear conversion of **MA** was achieved even through alternating the light irradiation, while no polymerization of **MA** occurred in the dark cycles (Scheme 5a).

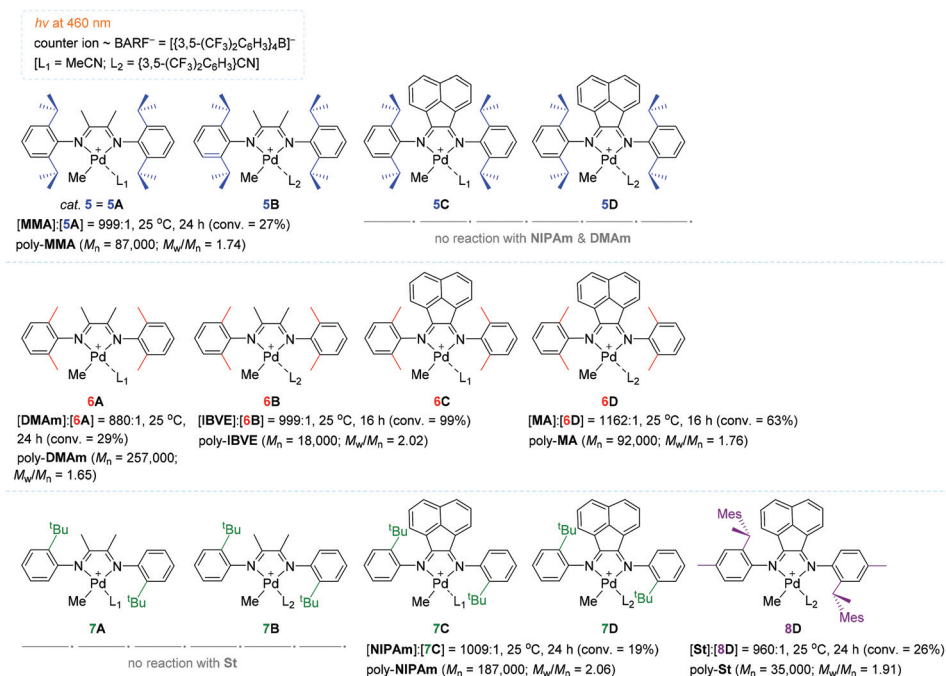
Harth and coworkers were next able to accomplish the synthesis of block copolymers of 1-hexene and **MA** using photo-switchable catalyst **5** under suitable light manipulation (ON/OFF process): the **MA** block was propagated upon photoirradiation *via* a radical process, during which the coordination–insertion mechanism remains non-operative, while the hexene

block was only enchain in the dark *via* a coordination–insertion polymerization. This work represents the first example of diblock polymer synthesis *via* a photoswitchable dual catalytic polymerization pathway. Two polymerization approaches were viable for the block copolymer synthesis. As one approach, the living polymerization of 1-hexene was first conducted in the dark to furnish poly(1-hexene) with a narrow polymer dispersity ($M_n = 4300$, $M_w/M_n = 1.04$), which was subsequently applied as a macroinitiator to create a **MA** block in the light, yielding the desired block copolymer poly(1-hexene-*b*-**MA**) with a M_n of up to 17 500 ($M_w/M_n = 1.48$ –1.53) (Scheme 5b). Notably, hexene polymerization was not substantially observed during the growth of a **MA** block under the UV light conditions. As another strategy leading to poly(1-hexene-*b*-**MA**), the polymerization was performed in the presence of both olefin monomers, and catalyst **5** in a ratio of 1:2:0.003 ([**MA**]:[hexene]:[**5**]) under alternating dark and light conditions. As a result, three different compositions of block copolymers (hexene/**MA** units = 25/75, 50/50, and 75/25) with M_n values of 14 800–17 400 ($M_w/M_n = 1.47$ –1.56) were obtained simply by tuning the period of time of the dark and light cycles (2 h in the dark/4 h in light; 4 h in the dark/4 h in light; 4 h in the dark/2 h in light) (Scheme 5c). The resultant polymeric materials were analyzed by small-angle X-ray scattering (SAXS), which was able to confirm the existence of copolymer blocks.

In a continuous effort to understand in depth of the relationship between the α -diimine ligand structure and polymerization behavior for the light-mediated polymerization of vinyl monomers, Harth and coworkers systematically examined a series of Pd diimine complexes as the polymerization catalyst under both dark and light conditions (Scheme 6).¹⁰⁰ The polymerization of **MA** with catalyst **6D** (~0.1 mol%) proceeded upon blue light irradiation to attain 63% **MA** conversion, providing poly-**MA** with a M_n of 92 000 ($M_w/M_n = 1.76$) in 16 h. However, methyl methacrylate (**MMA**) was less reactive (conversion = 27%) relative to **MA** in the presence of **5** (= **5A**) as the best working catalyst to give poly-**MMA** [M_n 87 000 (M_w/M_n



Scheme 5 Photocontrolled homopolymerization and block copolymerization catalyzed by **5**.



Scheme 6 The α -diimine-Pd catalysts tested for the (photo)-polymerization of vinyl monomers.

= 1.74)]. It is interesting to see that the polymerization reactivity of acrylamides, including *n*-isopropyl acrylamide (NIPAm) and dimethyl acrylamide (DMAm), was highly dependent on the α -diimine ligand structure in the light: catalysts **5C–5D** and **6C–6D** did not react at all with acrylamides, while other ligand variations of the Pd catalysts allowed for the polymerization of acrylamides, albeit in low yields (e.g. 19% conversion of NIPAm in 24 h with catalyst **7C**). The polymerization of styrene (St) proceeded in low conversions irrespective of the presence of light (e.g. 26% conversion of St in 24 h with **8D**). Isobutyl vinyl ether (IBVE) was highly reactive to all Pd catalysts examined in both the light and dark to afford poly-IBVE in high yields (e.g. quantitative conversion of IBVE in 16 h with **6B**). These results indicate that St and IBVE as olefin monomers undergo chain propagation *via* radical and/or cationic mechanisms within the Pd diimine catalyst system.

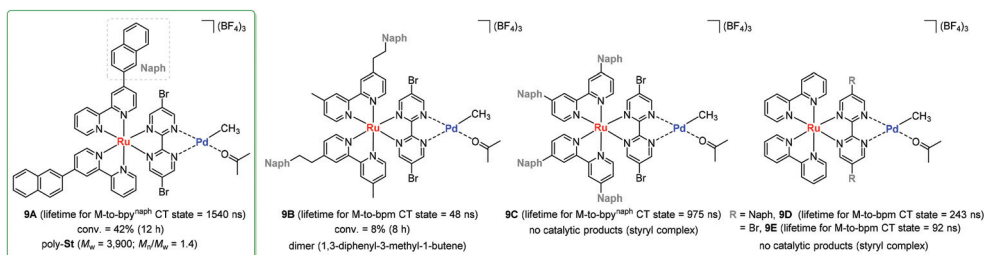
In order to gain insights into the photoexcitation energies of an array of α -diimine Pd complexes, computational studies [density functional theory (DFT) and time-dependent DFT (TD-DFT)] were carried out to show that MLCT transitions from the Pd–Me σ -bonding into the diimine ligand π -bonding orbitals readily occur upon visible light irradiation, causing loss of electron density in the σ -bonding (weakening the Pd–Me bond) and then homolytic cleavage of the Pd–carbon bond to generate a carbon-centered radical capable of initiating radical polymerization.^{101–104} In fact, catalyst **5** was found to decompose upon irradiation with blue light to result in the loss of the methyl group in **5**, while the polymerization of MA did not take place at all in the presence of a radical scavenger (galvinoxyl) under light irradiation. These observations again support the MLCT-led homolysis of a metal–carbon bond

essential for radical polymerization. This result corroborated the radical mechanism as a predominant working mode under visible light conditions. Notably, the simulated HOMO–LUMO gaps were all comparable for the Pd complexes (**5A**, **5C–5D**, **6A–6B**, **7C**) subjected to these calculations, implying that the ligand structure had no significant influence on the photo-initiation process.

3. Bimetallic catalytic system

In a photo-responsible bimetallic polymerization catalyst system, the two metal centers employed play their own catalytic roles: one metal center serves as a photocatalyst to absorb light photons for charge and/or energy transfer, while another metal unit acts as a chain propagating species to bring about polymerization turnovers under the electronic effects derived from an excited state of the photocatalytic species.⁷² Importantly, the light-driven electrochemical alteration at the active metal center by the (catalytic)photoredox species significantly influences the overall catalytic behavior to give rise to unique microstructures of polyolefins that are not achievable *via* conventional coordination polymerization strategies.

Inagaki and coworkers synthesized a new family of bimetallic Ru–Pd complexes supported by a range of bipyridyl (bpy) and bipyrimidinyl (bpm) ligands as photoactive olefin polymerization catalysts [**9A–9D**, and **9E** (control)], where 2-naphthyl groups installed on the ligands were envisioned to lengthen the excited-state lifetimes of the Ru–Pd bimetallic species (Scheme 7).^{80,81} The photophysical properties of these complexes were investigated *via* a series of spectroscopic ana-



Scheme 7 Bimetallic Ru–Pd complexes and their catalytic reactivities towards styrene polymerization under visible light.

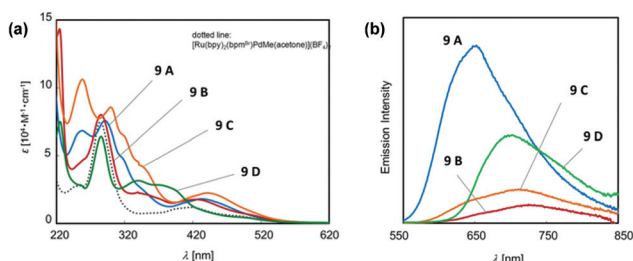


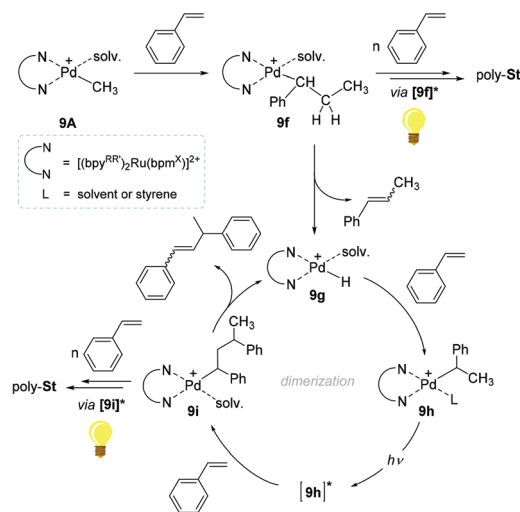
Fig. 1 (a) UV-vis absorption and (b) luminescence spectra of Ru–Pd complexes **9A–9D**.⁸¹

lysis, including UV-vis absorption and luminescence spectroscopies (Fig. 1). Based on the UV-vis spectra of the dinuclear complexes, the naphthyl group as an additional chromophore unit on the bpy or bpm ligands were assumed to enhance light-harvesting capability to cover a wide spectral range (from ultraviolet to visible light) for efficient transfer of the absorbed light energy to the Ru(II) center (Fig. 1a). The luminescence spectra of the complexes **9A–9D** provided key insights into the emission lifetimes of the excited state Ru–Pd species: (i) the metal-to-bpy^{naph} charge transfer (CT) states in **9A** and **9C** have relatively long lifetimes; (ii) the emissions for **9B** and **9D** are dominant in the metal-to-bpm CT states; (iii) the direct connection of a naphthyl group on the bpm ligand in **9D** results in longer lifetimes for the metal-to-bpm CT state relative to that in the parent complex **9E**, which lacks the naphthyl moiety (Fig. 1b).

Based on the photophysical properties of **9A–9D**, Inagaki examined their photocatalytic activities with respect to styrene polymerization under visible light conditions.^{80,81} As a result, **9A** turned out to be active in producing poly-St ($M_w = 3900$, $M_w/M_n = 1.4$), albeit with incomplete conversion (40%), probably due to catalyst decomposition. It is noteworthy that **9B** brought about only styrene dimers under otherwise the same photocatalytic conditions. These contrastive reaction outcomes indicated that the naphthyl unit needs to be directly bonded to the bipyridine ligand *via* a σ bond for effective styrene polymerization. Control experiments involving a set of [**9E** + naphthalene] or {[(bpy^{naph})₂Ru] + [(bpm)PdMe(Me₂CO)]BF₄} again implied that the π -conjugated direct linkage of the naphthyl unit and bridged binding of the Pd-methyl moiety are crucial requirements for intramolecularly photosensitized

polymerization. Unexpectedly, **9C** and **9D** did not display catalytic activities at all, and rather formed stable styryl complexes. In the case of **9C**, the installed two naphthyl substituents on each bpy ligand were presumed to act as an electron-withdrawing factor, which hinders the desired direction of MLCT and thus results in a lack of polymerization activity. **9D** has an excited state lifetime of ~ 200 ns for metal-to-bpm CT as a major contribution, which is much shorter than that of the bpy^{naph}-localized MLCT state in **9A**.

A reaction pathway for **9A**-initiated styrene polymerization was proposed (Scheme 8). The initial step is suggested to involve the 2,1-insertion of styrene into the cationic Pd–Me bond in **9A** to form a Pd-secondary alkyl species (**9f**). The alkyl species **9f** can undergo consecutive insertions of styrene monomers to furnish poly-St *via* a photo-excited species [**9f**]* in light. The existence of the presupposed intermediate **9f**, was in fact corroborated by the observation of β -methylstyrene and the presence of polymer chains with 14 mass difference, ascribed to the two active species bearing Pd–CH₃ and Pd–H moieties. Upon β -hydrogen elimination at **9f**, another active species **9g** is likely formed to undergo a subsequent styrene insertion. The key species leading to chain propagation upon light irradiation/absorption are Pd-alkyl species such as **9f** and **9i**, where the bpy^{naph}-localized MLCT states (*e.g.* [**9f**]*, [**9i**]*)



Scheme 8 Proposed pathway for the polymerization of styrene catalyzed by **9A** under visible light.

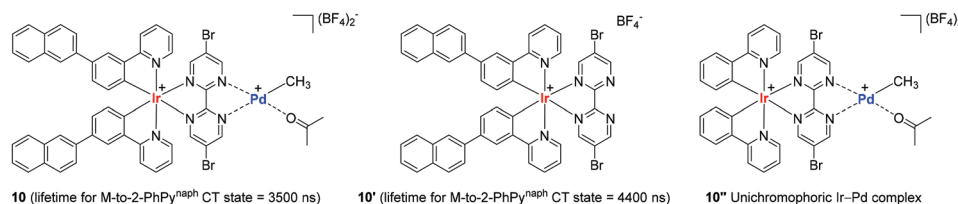
with long lifetimes are supposed to render the Pd center more electrophilic to delay the β -H elimination. From a steric aspect, the excited state's structure in Pd-alkyl species such as $[9i]^*$ can be altered to have the β -H distant from the Pd center, which can be another factor to prevent β -H elimination/chain transfer.^{105,106}

In consideration of the bichromophore-led long MLCT lifetimes (up to 1540 ns) and insufficient polymerization activity observed in the catalytic system of **9A**, Inagaki and coworkers synthesized the naphthyl group-connected bichromophoric Ir-Pd complex **10** as an advanced polymerization catalyst, where the Ir(III) center is supported by both σ -bonds and N-coordination from 2-phenylpyridyl (2-PhPy) and bipyrimidinyl ligands (Scheme 9). Preliminary spectroscopic studies revealed that **10** and its bichromophoric Ir unit **10'** have longer MLCT lifetimes when compared to those of the Ru(-Pd) complexes **9A-9E**.

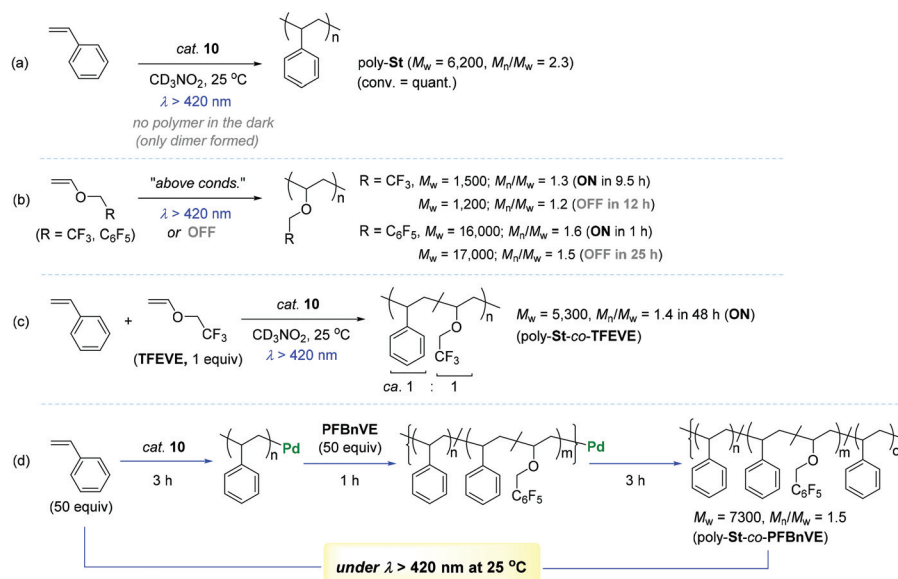
Encouraged by the observed longer MLCT lifetime for **10**, homopolymerization reactions of a range of functional α -olefins, including styrene, and copolymerization of styrene with 2,2,2-trifluoroethyl vinyl ether (TFEVE) or pentafluorophenylbenzyl vinyl ether (PFBnVE) under various photo-irradiation conditions were conducted in the presence of catalytic **10**

(1–2 mol%) at 25 °C (Scheme 10).^{107,108} The homopolymerization of styrene proceeded under light irradiation to attain the quantitative conversion in 8 h with the formation of poly-St ($M_w = 6200$, $M_w/M_n = 2.3$), whereas only dimerization affording *trans*-1,3-diphenyl-1-butene took place in the dark. This indicated that light as an external stimulus is essential for chain propagation (Scheme 10a). Interestingly, the Ir-Pd complex bearing unichromophoric ligand set **10''** catalyzed styrene dimerization under photocatalytic conditions, suggesting the importance of the bichromophore in the Ir(III) cyclometallated ligand system for polymerization. The observed living fashioned photo-polymerization of 4-fluorostyrene (not shown) and constant growth of polymer chains even in the presence of a 2,6-di-*tert*-butyl-*p*-cresol (BHT) radical scavenger strongly supported a non-radical, single site coordination-insertion mechanism.

Unlike the case of styrene, TFEVE and PFBnVE underwent homopolymerization reactions under both light and dark conditions to give poly-TFEVE [$M_w \sim 1500$ ($M_w/M_n \sim 1.3$)] and poly-PFBnVE [$M_w \sim 17\,000$ ($M_w/M_n \sim 1.5$)], respectively (Scheme 10b). To further extend the catalytic utility of **10**, the photocatalytic copolymerization of styrene and TFEVE was examined [**10** (1 mol%), 50 equiv. of St and TFEVE at 25 °C in



Scheme 9 Bi- or unichromophoric Ir(III) cyclometallated complexes and their MLCT lifetimes.



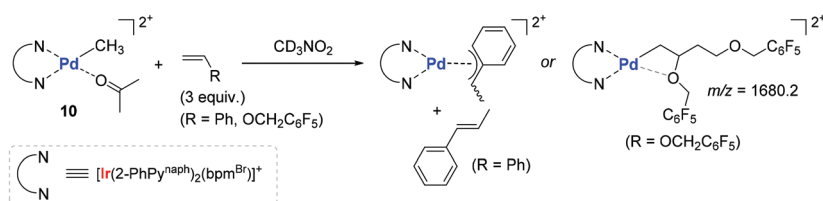
Scheme 10 Catalytic behavior of **10** towards the (co)polymerization of styrenes and vinyl ethers under variable photo-irradiation conditions.

CD_3NO_2 under $h\nu > 420 \text{ nm}$]. As a result, the desired copolymerization proceeded with almost the same consumption rates of the two monomers to yield a random copolymer of styrene and **TFEVE** (poly-**St-co-TFEVE**) with a *ca.* 1 : 1 ratio of comonomer incorporation [$M_w = 5300$ ($M_w/M_n = 1.4$)] (Scheme 10c). In an attempt to synthesize multi-block copolymers consisting of poly-**St** and poly(**St-co-PFBnVE**) blocks, homopolymerization of styrene (50 equiv.) in light was conducted for 3 h at 25 °C to attain ~30% conversion of styrene, into which **PFBnVE** (50 equiv.) was subsequently added to propagate a copolymeric chain as another block on the polystyrene backbone. After 1 h of polymerization, the initially loaded **PFBnVE** was found to be completely consumed, while ~35% of the styrene monomer was still left in the crude polymerization solution. This copolymerization was quenched following another 3 h of polymerization reaction in the light to deliver an unprecedented triblock copolymer [$M_w = 7300$ ($M_w/M_n = 1.5$)] with two distinctive T_g temperatures at 22 and 64 °C (Scheme 10d). Notably, the observed two T_g values were assigned to the polymer blocks poly-**St** and poly(**St-co-PFBnVE**) in a single polymer chain.

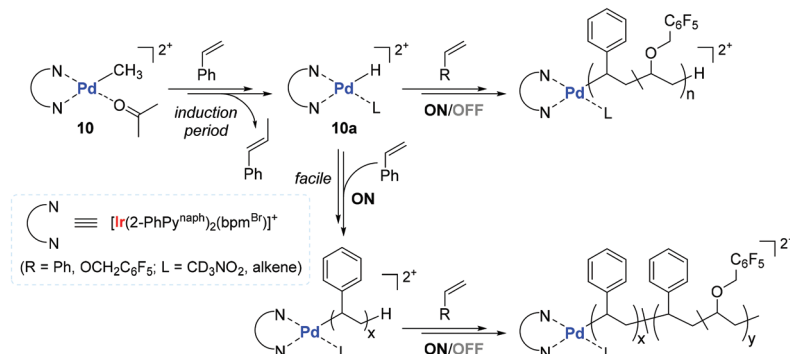
In order to gain more insights into the kinetic behavior of each of the monomers during (co)polymerization, the consumption rates for each monomer in both the homo- and copolymerization reactions were measured to disclose the following insights: (i) the (co)polymerization reactions are generally accelerated upon visible-light irradiation; (ii) the relative reactivity of vinyl monomers under the photocatalytic homopolymerization conditions increases in the order of **PFBnVE** $\gg$ **TFEVE** $\geq$ **St**; and (iii) the consumption rate of styrene upon

irradiation is most dramatically enhanced in the homopolymerization when compared with vinyl ether monomers. Two representative stoichiometric reactions of **10** with **St** or **PFBnVE** were carried out in parallel to show that the reaction with styrene generates *trans*- β -methyl styrene as a β -H elimination product with the formation of a stable π -benzyl complex, while the reaction with **PFBnVE** formed the Pd-alkyl complex through double consecutive insertions of **PFBnVE**, as evidenced by an m/z value of 1680.2 observed in its ESI mass spectrum (Scheme 11). These results again corroborated a coordination-insertion mechanism rather than a radical pathway. Given the fact that vinyl ethers undergo polymerization in the presence of catalyst **10** regardless of photoirradiation, the polymerization reactions of a series of vinyl ethers were examined in order to gain more insights into the catalytic working mode (coordination *vs.* cationic or radical mechanisms). As a result, ethyl vinyl ether and *N*-vinylcarbazole were converted to the corresponding homopolymers, whereas the polymerization of phenyl vinyl ether did not take place under either irradiation or dark conditions. This observed reactivity trend was found to be inconsistent with the vinyl substituent's electronics (*e* or *Q* values), with the conclusion that the polymerization of vinyl ethers by **10** proceeds not *via* a cationic or radical mechanism, but *via* a coordination-insertion mechanism.

Based on stoichiometric observations, a mechanism for the **10**-catalyzed copolymerization of styrene with **PFBnVE** was proposed (Scheme 12). The initial step likely involves the 2,1-insertion of vinyl monomer, followed by rapid β -hydride elimination to form an active species Pd-H (**10a**) with



Scheme 11 Stoichiometric reactions of **10** with styrene or **PFBnVE** in a 1 : 3 ratio.



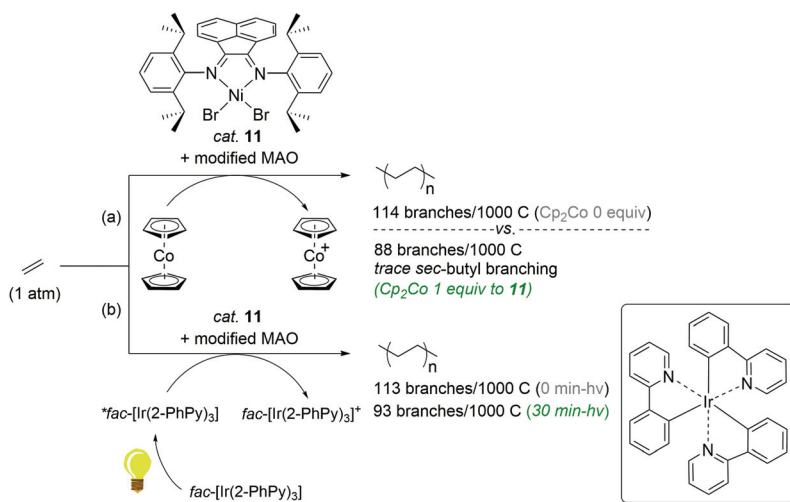
Scheme 12 Proposed mechanism of the **10**-catalyzed copolymerization of styrene with **PFBnVE** under light ON/OFF irradiation conditions.

β -methylstyrene. This initial step has an induction period where styrene is initially inserted into the Pd-methyl bond of **10**. The *in situ* generated **10a** is assumed to undergo consecutive insertions of styrene and/or vinyl ether, during which photo-irradiation greatly accelerates the turnover-limiting monomer insertion step, thus promoting the overall polymerization process.^{107,108} The measured long MLCT lifetimes of the excited-state species¹⁰⁹ and the increased stability from the Ir-C σ -bonded cyclometalate ligand in **10** are considered as the main factors responsible for the observed facile and living polymerization behavior.

The reaction behaviors of well-defined olefin polymerization catalysts based on group 10 transition metals have been known to be influenced by not only reaction parameters (*e.g.* temperature, ethylene feed pressure),^{46,53,110,111} but also ligand-based electronics,⁴⁰ being able to provide polyolefins bearing highly varied microstructures. Inspired by the observed electronic effects of ligands on the polymerization profiles, a handful of research groups recently developed new olefin polymerization catalysts possessing redox-active ligands in an effort to control the branching contents and/or microstructures of the resultant polyolefins *via in situ* alterations of the electronic nature of the catalytically active species.^{112–116} As one example, in 2016, Long and coworkers demonstrated that the microstructure of polyethylene (PE) can be modulated in terms of branching density and branching identity by employing a reductant as an additive in the presence of the Ni-based Brookhart catalyst **11** [$E_{1/2} = -0.80$ V (vs. $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$)] (Scheme 13).^{117,118} For instance, the PE branching density observed *via* the Ni catalysis was decreased in a linear relationship to the equivalents of the cobaltocene additive [$E_{1/2} = -1.33$ V], and *sec*-butyl branching was not substantially observed in the resultant polyethylene. These drastic effects of the cobaltocene reductant indicate that the *in situ* Ni species generated upon reduction by cobaltocene is redox-active and capable of providing a less-branched microstructure of PE (Scheme 13a).¹¹⁷ Based on this precedence, Long next envi-

sioned that the chemical reductant cobaltocene could be replaced with a suitable photoreductant for modulation of the PE microstructure. Considering its similar reduction potential to cobaltocene and its chemical compatibility with **11**, tris(2-phenylpyridinato- C^2,N) iridium(III) [*fac*-Ir(2-PhPy)₃] possessing a photo-excited reduction potential of $E_{1/2}^{\text{IV/III}^*} = -1.73$ V was chosen as a photo-reducing agent for **11**-catalyzed ethylene polymerization under visible light irradiation.¹¹⁸

The Ni-catalyzed polymerization of ethylene was generally performed under 1 atm of ethylene at 20 °C for 30 min in the light (3 W blue LED) with equimolar photoreductant *fac*-Ir(2-PhPy)₃. The catalytic activity of **11** was found to be constant regardless of both light irradiation (<30 min) and the presence of *fac*-Ir(2-PhPy)₃, leading to polyethylene products in similar yields (2.20–2.50 g), whereas the polymer dispersity increased from 1.54 to 1.97 with irradiation time. This trend was also observed when Cp_2Co was used as a reductant,¹¹⁷ suggesting similar roles of *fac*-Ir(2-PhPy)₃ and Cp_2Co in the Ni-catalyzed ethylene polymerization. It is noteworthy that the branching content in the resultant polyethylene remarkably decreased to 93/1000C from 113/1000C upon polymerization under blue LED irradiation (30 min) (Scheme 13b). This outcome showcases the first example of the photo-mediated modulation of the polyethylene microstructure. Similar to the precedence using the reductant Cp_2Co , long exposure times during the Ni catalysis led to a dramatic reduction in *sec*-butyl branching from 6.1 to 1.4%. Such prominent changes in the branching density of PE as a function of light exposure in the presence of *fac*-Ir(2-PhPy)₃ were attributable to the delayed chain-walking process during the polymerization *via* the action of a reduced, more electron-rich propagating Ni species.³² Such a hypothetical relationship between the electron density of the active metal species and the rate of chain-walking was supported by Guan's work, in which catalysts with electron-donating α -diimine ligands exhibited higher rates of ethylene insertion relative to the rates of chain-walking.⁴⁰

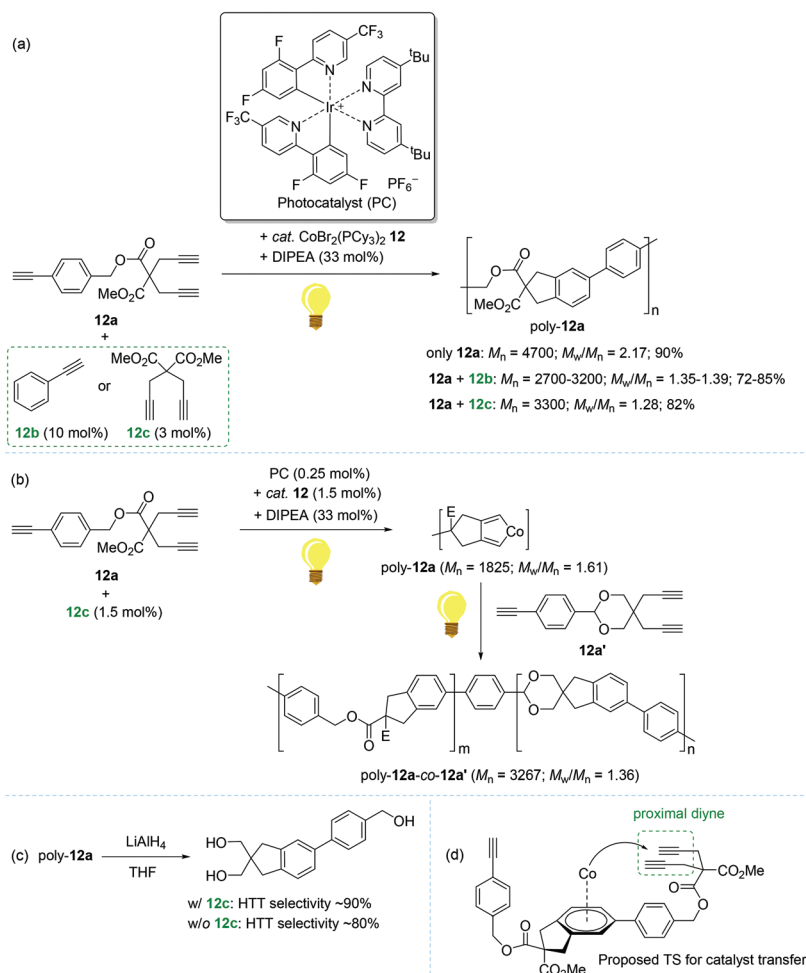


Scheme 13 Polymerization of ethylene catalyzed by **11** in combination with the (photo)chemical reductants [(a) Cp_2Co or (b) *fac*-Ir(2-PhPy)₃].

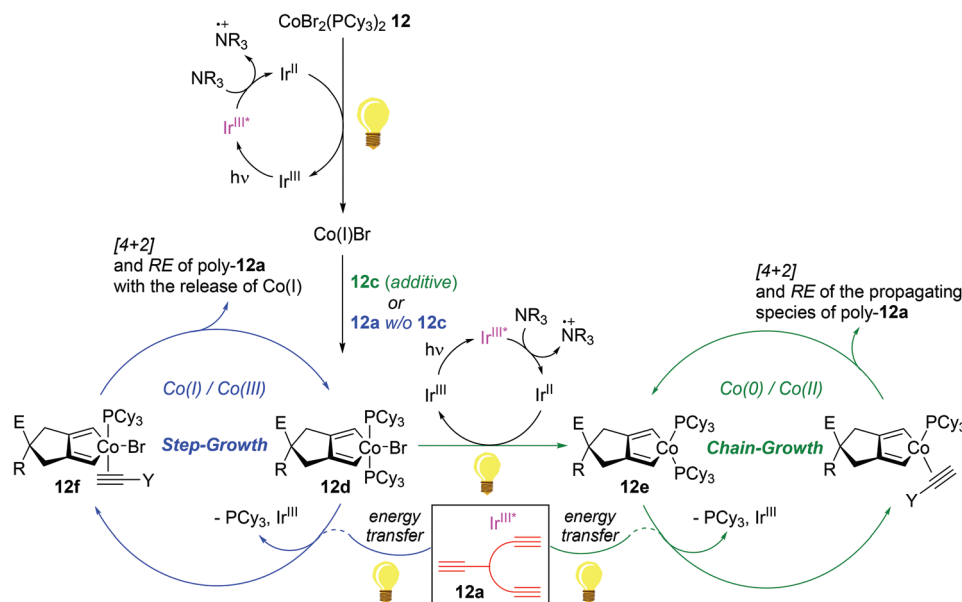
In 2016, Rovis reported the photoswitchable $[2 + 2 + 2]$ cycloaddition of alkynes using a catalyst set of a Co(II) complex and a photoredox catalyst under visible light, in which the reaction clearly responded to the light ON/OFF process during catalytic turnover.¹¹⁹ In 2011, Okamoto succeeded in the Co-catalyzed chain-growth polymerization of triynes based on a conventional $[2 + 2 + 2]$ cyclotrimerization reaction.¹²⁰ Motivated by these findings, Rovis and coworkers recently developed the photocontrolled, Co-catalyzed cycloaddition polymerization of triynes. This work represents the first example of the photocontrolled cycloaddition polymerization of alkynes. The catalytic system was composed of a phosphine-ligated Co(II) complex as a precatalyst $[\text{CoBr}_2(\text{PCy}_3)_2]$, **12**, a fluorinated polypyridyl Ir(III) photocatalyst (PC), and diisopropylethylamine (DIPEA) as a sacrificial reductant (Scheme 14).¹²¹ A standard triyne monomer possessing a malonate moiety (**12a**) was subjected to the preassumed photocontrolled cycloaddition polymerization to find the optimal reaction conditions within a certain catalytic reaction system [**12** (3 mol%), PC (0.5 mol%), DIPEA (33 mol%), MeCN/DCE cosolvent, and additive (3–10 mol%) under visible light at 24 °C].

Without an alkyne additive, the catalytic system afforded a mixture of oligomers and polymers in 90% yield in 16 h ($M_n = 4700$; $M_w/M_n = 2.17$). Interestingly, the introduction of an alkyne additive (**12b** or **12c**) along with minor deviations from the above catalytic reaction system gave rise to the corresponding cycloaddition polymers with relatively reduced M_w/M_n values ranging from 1.28 to 1.39 (poly-**12a**, $M_n = 2700$ –3300) (Scheme 14a). The most efficient polymerization ($M_n = 3300$, $M_w/M_n = 1.28$, and 82% yield in 3 h) was observed, when **12c** (3 mol%) was used as an additive, in particularly with 15 min of preirradiation prior to the addition of the monomer. The light ON–OFF process under the standard polymerization conditions was highly responsible for increasing (ON) and stalling (OFF) monomer conversion and the polymer molecular weight. Such observed precise photo-responsiveness of the present catalytic system implied that the initiation efficiency, involving a Co(I) species *in situ* generated under the light from a combination of **12** and an Ir-based PC, is high.^{122–125}

Being aware of the differing molecular dispersities ($M_w/M_n \sim 2.2$ vs. 1.3) between the polymers obtained with and without an alkyne additive, Rovis assumed that two mechanisms (step-



Scheme 14 Photo-controlled cycloaddition polymerization of triynes catalyzed by **12** in combination with the Ir-based photocatalyst.



Scheme 15 Proposed mechanism of the **12**-catalyzed photo-cycloaddition polymerization of triynes.

growth vs. chain growth) of chain propagation could be operating depending on the addition of an alkyne additive. To gain more insights into the plausible dual polymerization pathways, the light-mediated polymerizations with and without **12c** as an additive were monitored, revealing that the M_n of poly-**12a** increased exponentially as a function of conversion in the absence of **12c**, while a linear relationship was observed between M_n and monomer conversion with the maintaining of narrow molecular dispersities (M_w/M_n) ~ 1.25 in the presence of **12c**. These results strongly indicated that the alkyne additive allows for living chain-growth polymerization.

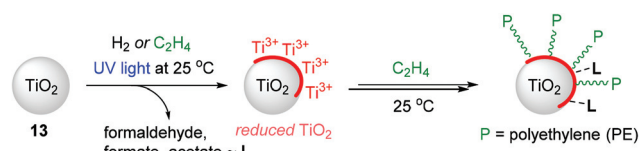
By taking such a living-fashioned polymerization behavior approach, a block copolymer was able to be synthesized through the sequential addition of two monomers **12a** and **12a'**: the $M_n \sim 1800$ of the first homopolymer (poly-**12a**) obviously increased to ~ 3300 as the block copolymer (poly-**12a-co-12a'**) formed after the addition of the second monomer **12a'** (Scheme 14b). This sequential polymer growth supported a chain-growth mechanism, where the monomer is added primarily to the ends of existing chains. It is noteworthy that the LiAlH_4 -reduction of poly-**12a** synthesized with the **12c** additive afforded a slightly larger amount of head-to-tail (HTT) product when compared to the polymer prepared without **12c** (Scheme 14c). The enchainment of the HTT monomer unit was regarded as further evidence of a chain-growth mechanism. Based on the observation of the HTT product, a catalyst transfer transition state during chain propagation was proposed: the Co-benzene η^6 -complex formed upon reductive elimination from the catalytic cycle interacts with a proximal diyne moiety on a HTT polymer chain to cause the transfer of the Co center onto the growing chain end (Scheme 14d).^{126–128}

Experimental observations strongly implied the existence of two distinct redox-active catalytic cycles: (i) a step-growth

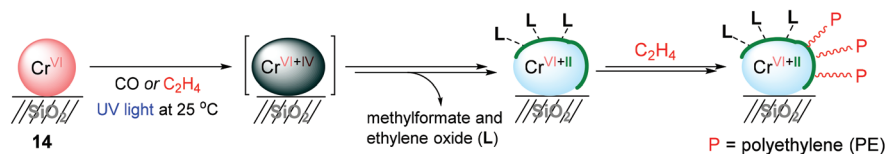
pathway involving Co(I)/Co(III) species and (ii) a chain-growth mechanism involving Co(0)/Co(II) species (Scheme 15). With the pre-reduction process using an alkyne additive such as **12c** in light, precatalyst **12** is assumed to be initially converted to a Co(II) species **12e** via a Co(III) species **12d** to undergo HTT-oriented chain-growth polymerization; meanwhile, **12** is presumed to be initially reduced to Co(I)Br, followed by oxidative addition of a triyne to generate Co(III) **12d**. In the absence of an additive, excess alkyne monomers such as **12a** are suggested to displace a phosphine ligand on **12d** to generate an alkyne adduct **12f** upon energy transfer by the photoexcited Ir species ($\text{Ir}^{\text{III}*}$), which undergoes less HTT-selective, step-growth polymerization accompanied by the release of Co(I) species upon reductive elimination events.

4. Heterogeneous catalytic systems

TiO_2 -based nanostructured materials have application potential in pollution remediation, photovoltaics, and photocatalytic hydrogen generation due to their low toxicity, low cost, and chemical and thermal stability.^{129,130} However, applications utilizing the surface chemical properties of TiO_2 have been limited in the context of olefin polymerization as it is known



Scheme 16 Ethylene polymerization catalyzed by photoreduced **13**.



Scheme 17 Photoreduced ethylene polymerization catalyzed by photoreduced **14**.

that TiO_2 is generally inert toward ethylene polymerization. Groppo and coworkers previously reported the thermal reduction of TiO_2 under H_2 atmosphere as a reducing agent to enable ethylene polymerization without the need of an activator,¹³¹ but this method requires harsh conditions and thus causes undesirable structural modifications.^{132,133} In this regard, Mino developed, for the first time, the light-mediated generation of surface-reduced Ti sites on TiO_2 (**13**) under H_2 or ethylene atmosphere at 25 °C.¹³⁴ The surface-reduced Ti species were found to be capable of polymerizing ethylene at 25 °C without the need for any pre-reduction step (Scheme 16). A range of analytical tools such as electron paramagnetic resonance (EPR), ultraviolet/visible (UV/Vis), near infrared (NIR), and Fourier-transform infrared (FT-IR) spectroscopies were used to observe the effects of UV-light irradiation on TiO_2 in the presence of H_2 or ethylene. In the case of H_2 -photoreduced TiO_2 materials, H_2 splitting and the formation of (sub)surface Ti^{3+} centers were observed on the TiO_2 , and this reduced surface eventually polymerized ethylene upon long contact times to produce high-density polyethylene (HDPE). Interestingly, during ethylene polymerization, ethylene oxidation products such as formaldehyde and formates were detected and suggested to remain absorbed on the surface of TiO_2 .^{135,136}

In the system of ethylene-photoreduced TiO_2 , ethylene was shown to act as a reducing agent to generate Ti^{3+} species in TiO_2 , which simultaneously initiated ethylene polymerization *via* a one-pot process at 25 °C under UV light. Notably, the Ti^{3+} species reduced from TiO_2 by ethylene were mainly generated on the surface rather than the subsurface or bulk lattice Ti^{3+} centers, which were mainly obtained *via* a H_2 -photoreduced process under otherwise identical conditions. The FT-IR analysis showed that the formation of polyethylene at the surface of the TiO_2 sample accompanies the products of ethylene oxidation, as similarly observed in the reaction of ethylene on H_2 -photoreduced TiO_2 .

With a successful example of photoreduced TiO_2 -mediated ethylene polymerization, Mino and coworkers applied a photo-induced polymerization strategy to the Phillips catalyst system, $\text{Cr}^{\text{VI}}/\text{SiO}_2$ (**14**) (Scheme 17),¹³⁷ which is one of the most utilized catalysts in the petrochemical industry.^{138,139} Photoreduction of $\text{Cr}^{\text{VI}}/\text{SiO}_2$ occurred under 0.1 atm of either CO or ethylene at 25 °C. The FT-IR spectra of $\text{Cr}^{\text{VI}}/\text{SiO}_2$ upon UV irradiation under a CO atmosphere showed that a fraction of the Cr^{VI} sites were gradually reduced *via* a Cr^{IV} intermediate to Cr^{II} as an active species for ethylene polymerization. It is noteworthy that the relative amount of highly uncoordinated and thus

accessible Cr^{II} sites formed *via* the photoreduction of Cr^{VI} was much higher when compared with the amount obtained through the thermal reduction in CO at high temperature (350 °C). The UV-vis spectroscopic analysis suggested that the reduction of the Cr^{VI} sites (d^0 species) to low-valent Cr sites (d^n species) was carried out by ethylene upon a short period of UV-vis irradiation (less than 50 s). The ethylene polymerization began to take place after only after 50 s of irradiation, and efficiently progressed with prolonged photo-irradiation time. The FT-IR analysis suggested that surface byproducts containing methylformate and ethylene oxide as a result of ethylene oxidation are formed during the initial steps of photoinduced ethylene polymerization, and remain in the coordination sphere of the reduced Cr^{II} sites, contributing towards defining the ligand sphere around the active Cr sites. The amount of polyethylene produced using this Cr catalysis was too small to conduct a more thorough product characterization.

5. Conclusions

This Review describes the catalytic systems for light-mediated olefin coordination polymerization, enabling photo-controlled and/or -initiated polymer chain propagation. The catalytic reaction systems are all based on transition metals, and encompass monometallic and bimetallic complexes as well as homogeneous and heterogeneous catalytic systems. Most of the catalytic metal species undergo significant alterations in their electronic states *via* charge and/or energy transfer under suitable wavelengths of light irradiation, whereas a single example involves the photoswitchable steric changes of the ligand to influence the coordination sphere of the active metal site for the olefin coordination-insertion process.

In the monometallic catalyst system, Aida disclosed the cyclopolymerization of a diallylmalonate catalyzed by an α -diimine Pd complex possessing a photoisomerizable azobenzene moiety, in which the installed azobenzene group as a photosensitized steric factor was for the first time shown to have an effect on the stereochemistry-determining step of the polymerization under light conditions. On the other hand, Inagaki synthesized a naphthyl-substituted BINAP-Pd complex for photoresponsive styrene polymerization, where the naphthyl moieties were found to improve the excited-state lifetime and stability of the Pd complex. Harth and Beezer showed that photoirradiation as an external stimulus in a series of Pd-based Brookhart catalysts switches the catalytic working mode from a conventional coordination mechanism to a radical

mechanism for olefin polymerization. This photo-responsive-ness allowed the synthesis of not only homopolymers of acrylates, but also block copolymers of α -olefins and acrylates using Brookhart catalysts under photoswitchable conditions.

In terms of bimetallic systems, the Inagaki and Akita group, as major players in this area, contributed towards developing a range of new heterodinuclear organometallic complexes as photosensitizing olefin polymerization catalysts, where one center based on Ru or Ir supported by naphthyl-substituted (2-phenyl)-pyridinyl and bipyrimidinyl ligands works as a photocatalyst in an intramolecular charge transfer process, while another bridged center is a Pd active species for polymer chain propagation. The Long group first revealed that an Ni-based Brookhart catalyst polymerizes ethylene to produce relatively less branched polyethylene, which is attributed to the action of a propagating Ni species photochemically reduced by an Ir-based photosensitizing complex. Rovis and coworkers applied the Co-catalyzed $[2 + 2 + 2]$ photo-cycloaddition reaction of alkynes to the photoswitchable polymerization of triyne monomers. The polymerization proceeds in a living fashion, being able to synthesize cycloaddition block copolymers *via* regulating their M_n values under visible light.

In a heterogeneous catalytic system, Mino and coworkers for the first time showed that the photoreduction of inert TiO_2 under UV light with ethylene as a reducing agent generates Ti^{3+} species on the surface of TiO_2 nanoparticles, which promote ethylene polymerization in a one-pot reaction without the need for alkylating reagents under milder conditions. In a similar manner, the ethylene-photoreduction method was applied to the Phillips catalyst ($\text{Cr}^{\text{VI}}/\text{SiO}_2$) system, in which a fraction of the Cr^{VI} sites are reduced to the active species Cr^{II} by ethylene upon UV-vis irradiation to trigger the polymerization of ethylene.

Overall, the majority of coordination polymerization catalytic systems combined with photosensitizing metal species and/or photochromic moieties are highly responsive to external light irradiation to influence the polymerization activity and/or catalytic working mode as an outcome of electronic alteration on the active propagating metal species. Since the propagating metal center undergoes light-mediated charge and/or energy transfer within a short period of time under mild conditions, good photo-controllability and switchability of the active metal species over the chain growth process are often observed. Despite diverse catalytic systems being known for photocontrolled olefin coordination polymerization, there have been no (systematic) studies on olefin polymerization catalyzed by transition metal complexes with a sterically photoswitchable ligand system. In this regard, developing a new family of olefin polymerization catalysts bearing modular and photoswitchable steric moieties of ligands would be a promising task distinctive from the precedence involving ambiguous photoresponsive electronic effects on the catalytic polymerization behavior. Photoswitchable steric groups installed on the ligand system towards transition metal-catalyzed photocontrolled olefin polymerization will allow the isolation of possible isomeric metal complexes as thermodynamic catalytic

intermediates, and each isomeric metal species will provide straightforward and fundamental insights into the relationship between the ligand's geometric structure (*e.g. cis vs. trans*) and polymerization behavior such as regioselectivity for α -olefin insertion, and chain-walking and chain transfer processes that determine the polymer molecular weight and dispersity. This review will hopefully inspire organometallic chemists to develop new polymerization catalyst systems that enable light-mediated steric and electronic control over the active propagating metal species for olefin coordination polymerization.

Conflicts of interest

The authors declare no competing financial interests.

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