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Visible-light-controlled homo- and copolymerization of styrenes by a bichromophoric Ir–Pd catalyst†

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Visible-light-controlled polymerization was achieved by a bichromophoric organopalladium catalyst which possesses a naphthyl-substituted cyclometallated Ir(III) light-absorbing moiety. The complex was highly active toward styrene polymerization upon visible-light irradiation, and its photoactivity toward polymerization and dimerization was switchable. On the basis of the switching activity, controlled copolymerization of styrene and vinyl ether was achieved upon photo-irradiation to give the corresponding copolymers.

Controlled polymerization by an external stimulus has made a notable impact in materials science for syntheses of well-defined polymers.[1] Since these strategies are potentially useful to create a new class of materials, they have attracted much attention from both scientific and industrial points of view.[2] Especially, external stimuli requiring no additives during a reaction, such as photochemical,[3–8] electrochemical,[9] and mechanochemical[10] controls, are considered to be promising for conducting reactions in a closed system. Among them, light is the most efficient tool to control reactions because it provides a simple, convenient and ecological tactic for achieving a reactivity perturbation. Indeed, a large number of research studies on photopolymerization attempting fine-tuning of polymer properties have been conducted since the pioneering work on the iniferter polymerization controlled by UV-light was demonstrated in the 1960s.[4] Because most of them, however, utilized light for reaction initiation by generating an active species through photodegradation of an initiator, the reaction cannot be controlled once photolyzed. Recently, several strategies for reversible manipulation of photopolymerization have been reported.[6–8] Hawker *et al.* demonstrated the interesting example of the living radical polymerization of methacrylates controlled by visible light using a cyclometallated Ir(III) complex as a photoredox catalyst.[6] Repeated switching of polymerization was achieved by taking advantage of the photoredox catalysis which generates an active species in a reversible manner. External activation of a catalyst by light is expected to open a new way for controlled polymerization.

Meanwhile, catalytic coordination polymerization by late transition metal complexes has also been developed remarkably during the last two decades because of their high functional group tolerance, feasibility to introduce a variety of comonomers, and structural controllability. Specifically, cationic Ni(II) and Pd(II) α-diimine catalysts have been widely used because their activities are tunable to generate polymers with a well-defined structure depending on their molecular designs and reaction conditions.[11] Because the activities are generally fixed by initial conditions, it would be challenging to make the activities controllable during a reaction.

We have been studying photocatalysis by late transition metal complexes with a visible-light absorbing chromophore, and previously reported that the bimetallic Ru–Pd catalyst $[Ru(bpy)_2(bpm^{Br})PdMe(Me_2CO)]^{3+}$ (**2**; bpy = 2,2′-bipyridine, bpm^{Br} = 5,5′-dibromo-2,2′-bipyrimidine) was active for dimerization of terminal olefins upon light irradiation.[12,13] Upon photoexcitation, light energy harvested at the ruthenium polypyridyl chromophore is transferred to the organopalladium catalytic site, which led to activation of the catalyst.[14] Additionally, the bichromophoric Ru–Pd complex containing a 2-naphthyl group on the bipyridyl ligands coordinated to the ruthenium center was found to be active for the photocatalytic polymerization of styrenes.[15] One of the key factors in high polymerization activity is the long excited-state life time compared to the corresponding unichromophoric catalyst. Unfortunately, the activity of bichromophoric Ru–Pd catalyst was not high enough to develop sophisticated control of the reaction. To address this issue, we applied an Ir(III) cyclometallated chromophore expecting improvement of catalyst stability toward photoirradiation, in addition to the above-mentioned bichromophoric effect. From various spectroscopic measurements, it was confirmed that the bichromophoric Ir–Pd complex possesses extraordinary long MLCT lifetimes[16] similar to

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† Electronic supplementary information (ESI) available: NMR data, UV/vis data for **1**, NMR, GPC, DSC, MALDI-MS data for the polymers, and time conversion curves of the reactions. See DOI: 10.1039/c5cc00611b

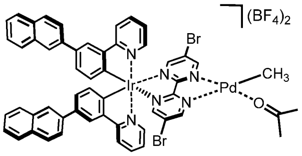

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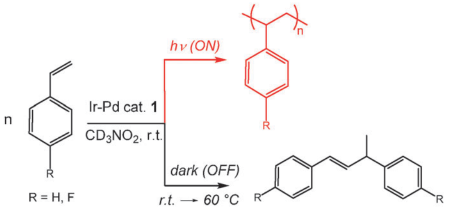
Chart 1 Bichromophoric Ir–Pd complex **1**.

the bichromophoric Ru–Pd analogue.[15,17] We herein demonstrate novel light-controlled photocatalytic polymerization of styrenes by the bichromophoric Ir–Pd complex, which exploits visible-light as an external stimulus and a driving force to accelerate the reaction.

The molecular structure of the bichromophoric Ir–Pd complex, [Ir(ppy^{naph})(bpm^{Br})PdMe(Me$_2$CO)](BF$_4$)$_2$ (**1**) (ppy^{naph} = 2-[3-(2-naphthyl)-phenyl]pyridine) is depicted in Chart 1 and its synthetic procedure is described in the ESI.†[18] In the UV-vis absorption spectrum of **1**, a broad absorption band with shoulders (λ_{max} = 380, 411 nm) was observed in the visible region (~500 nm). This absorption is mainly attributed to the mixed-metal ligand-to-ligand charge-transfer (MMLLCT) bands based on the iridium chromophore (Fig. S1, ESI†).[19]

The photocatalytic activity of the Ir–Pd complex **1** toward styrene was investigated under various irradiation conditions (Scheme 1), and the results are summarized in Table 1. Upon irradiation of 2 mol% CD_3NO_2 solution of **1** ($\lambda_{irr.} > 420$ nm), the styrene polymer precipitated out from the solution with progress of the reaction. The polymer yield reached approximately 96% after irradiation for 12 hours, which was much higher than that obtained using the bichromophoric Ru–Pd catalyst reported previously (entries 1 and 5).[15] In contrast, in the dark, no polymerization took place, but instead, slow dimerization affording *trans*-1,3-diphenyl-1-butene proceeded (entry 2, Fig. 1). Even under the heating conditions (60 °C, dark), a dimer was obtained as the major product (entry 3). These results suggest that light irradiation is essential for the polymerization, and thereby clearly changes the product from that of the thermal reaction. Reversible switching between the polymerization and dimerization was achieved upon ON–OFF intermittent exposure to light (entry 4, Fig. S2, ESI†). The catalyst exhibited rapid-response and high repetitive activity toward the light manipulation. When the reactivity of the corresponding unichromophoric catalyst **2** ([Ir(ppy)(bpm^{Br})PdMe(Me$_2$CO)](BF$_4$)$_2$, ppy = 2-phenylpyridine) was compared, monomer conversion was much lower than that of **1**, and it catalyzed mainly dimerization under the same irradiated conditions (entries 6 and 7). These results clearly show one of the advantages of applying the Ir(III) cyclometallated bichromophore over the photopolymerization.



Scheme 1 Photoreactivity switching of the Ir–Pd catalyst **1** in the catalytic reaction of styrene.

Table 1 Catalytic reaction of styrene by Ir–Pd complex **1** under different irradiation conditions[a]

Entry	Catalyst	Light[b]	*t*/h	Conv./%	Dimer/%	Polymer/%	M_w (M_w/M_n)
1	**1**	ON	8	98	2.0	96	6200 (2.3)
2	**1**	OFF	8	28	28	0	—
3	**1**	OFF (60 °C)	12	64	64[c]	0	—
4	**1**	ON–OFF[d]	12	75	27	48	4500 (1.7)
5[14]	Ru–Pd	ON	12	40	Trace	33[e]	3900 (1.4)
6	**2**	ON	8	26	14	12[f]	—
7	**2**	OFF	8	12	12	0	—

[a] Product distribution in CD_3NO_2 solution at room temperature with 2 mol% catalyst (*ca.* 0.01 M), analyzed by ^1H NMR. [b] $\lambda_{irr.} > 420$ nm (Xe lamp). [c] A mixture of *trans*-1,3-diphenyl-1-butene and the isomerized product, *cis*-1,3-diphenyl-2-butene. [d] ON/OFF switching at 2 h interval. Total of 6 h irradiation. [e] Isolated yield. [f] Trimers.

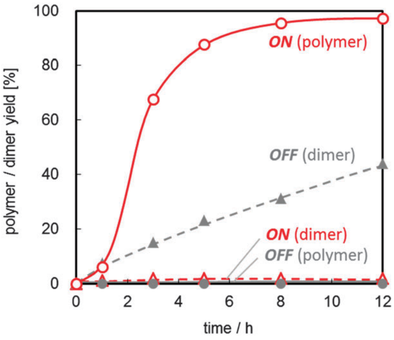
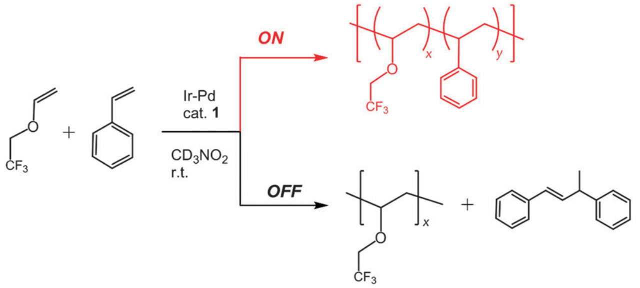


Fig. 1 Polymer yield (solid line) and dimer yield (dashed line) in the catalytic reactions of styrene under light (ON, $\lambda_{irr.} > 420$ nm) or dark (OFF) conditions (cat. 2 mol%, CD_3NO_2, r.t.).

The polymerization was not retarded even in the presence of 4-*tert*-butylcatechol (TBC), a radical scavenger, indicating that the polymerization did not proceed *via* a radical mechanism but *via* a coordination mechanism on the Pd center.[15] Importantly, when 4-fluorostyrene, which produces a polymer soluble in nitromethane, is used, linear dependence of the molecular weight (M_W) of the polymer on the conversion was observed, in the meantime, molecular weight distribution (M_n/M_W) was kept under control (Fig. S3, ESI†). These results suggest that the polymerization proceeds in a living manner.

In order to further develop the photocatalytic performance of **1**, it was subjected to photocatalytic copolymerization of styrene and 2,2,2-trifluoroethyl vinyl ether (TFEVE).[20] When a CD_3NO_2 solution **1** (1 mol%) with styrene (50 eq.) and TFEVE (50 eq.) was irradiated using a Xe lamp ($\lambda > 420$ nm), the irradiation caused consumption of the two monomers at almost the same rates, and yielded a styrene–TFEVE copolymer with a trace amount of styrene dimer (Scheme 2, Fig. S4 and S5, ESI†). In contrast, under the dark conditions (8 h), only polymerization of TFEVE



Scheme 2 Catalytic copolymerization of 2,2,2-trifluoroethyl vinyl ether and styrene by the Ir–Pd cat. **1**.

and dimerization of styrene proceeded to yield the poly(vinyl ether) and the styrene dimer.[21] When the irradiation conditions were changed during the reaction; for example, OFF for 12 h, then ON for 6 h, and the sequence was repeated twice, the corresponding styrene/TFEVE copolymer was also obtained (Table 2, entry 2). A possible structure of the copolymers obtained by intermittent irradiation is the styrene/TFEVE copolymer unit connected to the TFEVE polymer chain (Chart 2).

The resulting copolymer isolated after continuous irradiation was characterized by NMR, and matrix-assisted laser desorption/ionization (MALDI) mass spectroscopy (Fig. S6–S8, ESI†). In the ^{1}H NMR spectrum recorded in tetrachloroethane-d_4 at 100 °C, methylene and methine protons ($-C\mathit{H}PhCH_2-$) in the main chain were observed at around δ 1.2–2.0. On the other hand, the methine ($-C\mathit{H}(OCH_2CF_3)CH_2-$) and methylene ($-OC\mathit{H}_2CF_3$) protons in the vinyl ether unit appeared in the range of δ 3.0–4.0. In the ^{13}C NMR spectrum, broad signals of the main chain were observed at around δ 40 and δ 65 ppm, indicating low stereoregularity of the copolymer. The absence of the peak in the δ 30–35 range suggests that there is no tail-to-tail unit ($-(A)CH_2CH_2(B)-$; A and B are either an aryl or an $-OCH_2CH_3$ group). Thus the obtained copolymer is most probably a random polymer formed by 2,1-insertion of each monomer.[22] MALDI-MS data exhibited a repeated pattern with intervals of the mass numbers corresponding to styrene (m/z = 104) and TFEVE (m/z = 126) (Fig. S8, ESI†).

Table 2 Catalytic polymerization of a mixture of 2,2,2-trifluoro-ethyl-vinylether (V) and styrene (S) under various irradiation conditions[a]

Entry	Initial ratio (V/S)	Irradiation condition[b]	Conv./% V	Conv./% S	Comonomer ratio (V/S)	T_g/°C	M_W (M_W/M_n)
1	1/1	ON (48 h)	97	92	1/1.15	21	5300 (1.4)
2	1/1	(OFF–ON)$_{X2}$[b]	84	79	1/0.88	6.9	4900 (1.4)
3	1/1	(OFF–ON)$_{X2}$[c]	83	82	1/1.07	19	4200 (1.5)
4	0/1[d]	ON (12 h)	0	98	Only S	—[e]	6200 (2.3)
5	1/0	ON (12 h)	97	0	Only V	—[e]	—[e]
6	1/0	OFF (12 h)	94	0	Only V	−21	1200 (1.2)

[a] Product distribution in CD_3NO_2 solution at room temperature with catalyst 1 mol%, analyzed by ^{1}H NMR. [b] ON: *vis*: $\lambda_{irr.}$ > 420 nm (Xe lamp), OFF: dark, (OFF: 12 h, ON: 6 h) × 2 + dark 12 h. [c] (OFF: 12 h, ON: 12 h) × 2. [d] Table 1, entry 1. [e] Not measured.

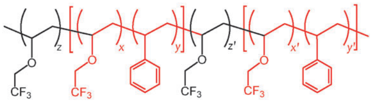
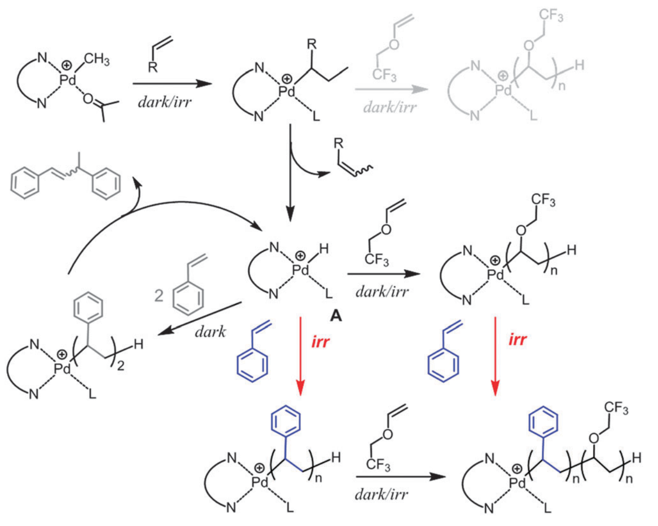


Chart 2 Possible copolymer structure formed under intermittent irradiation conditions.

GPC data of the isolated copolymer showed a single peak (Fig. S9, ESI†). Additionally, differential scanning calorimetry (DSC) data exhibited a corresponding single melting point which are largely different from those of poly TFEVE (−21 °C, Table 2, entry 6) or polystyrene (80–100 °C)[23] (Fig. S10, ESI†). In the DOSY NMR spectrum, aliphatic and aromatic proton signals were observed at a similar diffusion coefficient ($\log D = -9.0$ m^2 s^{-1}, Fig. S11, ESI†). All of the above data clearly exclude the possibility of the obtained polymer being a mixture of the homopolymers.

The copolymers obtained by different switching sequences were analysed by DSC and the data are summarized in Table 2. Although the copolymers possessed similar molecular weight and molecular weight distribution, interestingly, the copolymers obtained under intermittent conditions with two sets of OFF–ON switching sequences showed much lower glass transition temperature (T_g = 6.9 °C) than the one obtained by continuous irradiation (T_g = 21 °C) (Table 2, entry 1). When the reaction mixture was irradiated with a different switching sequence as in entry 3, the copolymer showed much higher T_g (T_g = 19 °C) compared to that of entry 2. The T_g values were similar to that of entry 1 probably because of a similar styrene content. Thus, T_g values of the copolymers were influenced by the comonomer content controlled by light.[24]

The possible copolymerization mechanism is described in Scheme 3. In the case of the dark conditions, a TFEVE monomer replaces an acetone molecule coordinated to the Pd reaction center in **1**, and then inserts into the Pd-alkyl bond successively to form a TFEVE polymer sequence. It is difficult to exclude the possibility of **1** initiating the cationic polymerization of TFEVE, however, observation of intense signals of the Ir–Pd complex with



Scheme 3 Plausible reaction mechanism of homopolymerization and copolymerization of styrene and 2,2,2-trifluoroethyl vinyl ether by the Ir–Pd cat. **1**.

repeating vinyl ether units in the ESI-MS spectrum of the reaction mixture supports this mechanism (Fig. S12, ESI†).[25,26] Under irradiation conditions, styrene insertion is considerably facilitated. Our theoretical study on the Ru–Pd complex indicated that the photoexcitation of the catalyst significantly lowers the activation energy for the insertion of a coordinating substrate on the Pd center,[14] particularly effective for styrene type monomers. In contrast, the consumption rate of TFEVE was not affected by irradiation conditions (Fig. S13, ESI†). According to these results, light exposure dramatically accelerates styrene insertion, and thus, styrene is allowed to be incorporated into a polymer sequence to afford a TFEVE/styrene copolymer. Since the facilitation effect contributes to the reaction only during light irradiation, intermittent irradiation enables the repeated introduction of the styrene/TFEVE unit into a TFEVE polymer sequence.

In conclusion, we have demonstrated the novel light-controlled polymerization of styrene catalyzed by a bichromophoric Ir–Pd complex. To the best of our knowledge, this system is the first example of the light-controlled homo- and copolymerization using the coordination-insertion mechanism by organometallic species. The striking advantage of the reaction system is that a single active site of an organometallic catalyst is reversibly controlled by an external stimulus during a reaction. Since various types of monomers can be employed to fabricate polymer sequences, we believe that this photocatalysis concept has great potential for expanding the versatility of polymer structures and diversity of polymer syntheses. The detailed photophysical properties, and reaction mechanisms are now under investigation.

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