

ENERGY TRANSFER CATALYSIS FOR THE SYNTHESIS OF NOVEL POLYMERS

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Abstract

Catalysis is ubiquitous in the industrial production of commercial products, and understanding the mechanisms behind these catalytic processes gives insight into logical modifications that can be made to increase yields, purity, and efficiency. For the last 20 years, the development of homogeneous transition metal catalysts for use in the polymerization of ethylene has been intensively studied. Traditional early transition metal systems cannot tolerate polar comonomers due to quenching from strong Lewis acid/base interactions, which limits applications of these plastics. The development of late transition metal systems offers improvement but remains limited in its ability to incorporate polar comonomers due to unique interactions in a well-characterized chelate resting state. This project aims to develop a system of chelate opening using a photocatalytic energy transfer to increase the incorporation of polar monomers in copolymerization reactions and perform mechanistic studies. The system developed in this project has synthesized a range of polymers with up to 72 mol% incorporation of polar monomers and 77 branches per 1000 carbons.

Introduction

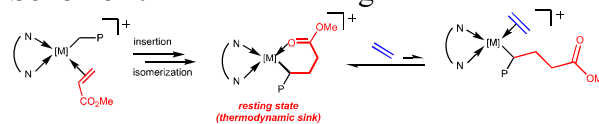
NASA plans to have a manned mission to Mars in the 2030s.¹ This goal requires that materials for space applications be developed to withstand the harsh conditions outside Earth's atmosphere, such as extreme temperatures, vacuum, and radiation.² These materials would also need to be lightweight due to the tremendous cost of transporting material from Earth to space, which can be as high as \$20,000 per pound.²

Polymers are ideal candidates to face these challenges due to their ability to be synthesized to have specific properties.³ They are already utilized by space agencies worldwide as

interior and exterior components of spacefaring vehicles.² This is due to their favorable strength-to-weight ratio and variable thermal, optical, and electrical properties.⁴ Some studies even indicate that polymers could eventually surpass long-established materials due to reduced fuel costs in transportation.²

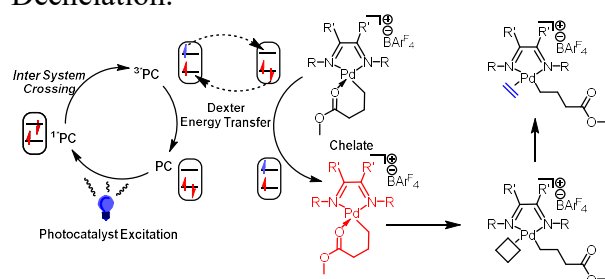
Changing the chemical makeup of a polymer scaffold can greatly change its properties, functions, and architecture.⁵ Functionalization of polymers via polar monomer copolymerization is generally performed using a free radical process, which leads to random incorporation and branching.⁶ Alternate routes of polar functionalization require multiple steps, and the costs associated with synthesizing these polymers are prohibitive enough that free radical reactions are still the most viable option for large-scale production of polar functional group-containing polymers.⁶ When synthesizing branched polyolefins, such as low-density polyethylene (LDPE), early transition metals are used to polymerize ethylene gas with larger comonomers containing α -olefins.⁷ However, Brookhart-type α -diimine nickel and palladium catalysts are capable of synthesizing LDPE using just ethylene gas due to their ability to chain walk.⁸ The diimine ligands and pre-catalyst metal complexes are straightforward to synthesize, and by varying the ligand structure, the microstructures of the polymers can be controlled.⁷ Another advantage of the Brookhart-type catalysts is using unprotected polar monomers in copolymerization with ethylene.⁸ To date, polar comonomer incorporation into polyethylene remains limited due to the strong binding of oxygen to metal centers and a resultant six-membered ring chelate resting state [Scheme 1].⁶

Scheme 1. Chelated Resting State Formation.



Herein we investigate the ability of energy transfer (EnT) catalysis to open these chelated systems [Scheme 2]. EnT catalysis is an emerging field in organometallic chemistry that entails the indirect excitation of molecules and complexes to reactive triplet states, allowing energy barriers to be overcome.⁹ The advantage of EnT is that it allows a reactive triplet state to be accessed under visible wavelengths of light, unlike traditional direct excitation, which requires harsh, short wavelengths.⁹

Scheme 2. Proposed Energy Transfer Induced Dechelation.



Experimental

General Experimental

General Methods: Unless otherwise stated, all reactions were carried out in oven (130°C) dried glassware under an inert atmosphere using standard Schlenk techniques and conducted at ambient temperature (25°C, rt).

Chemicals: All reagents were used as received from commercial sources without further purification. Unless otherwise stated, all solvents were degassed with nitrogen for 30 minutes before use after being passed through activated alumina columns in a solvent purification system.

NMR: All ¹H NMR and ¹³C spectra were acquired on either a 400 or 600 MHz Bruker Avance spectrometer. Deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. Chemical shifts are reported in parts per million (ppm), with the residual

solvent protons used as internal calibration standards.¹⁰

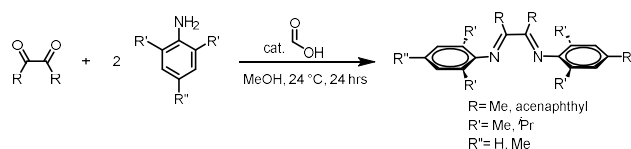
Gel Permeation Chromatography: Gel permeation chromatography data was collected using a Shimadzu refractive index detector, RID-20A, and Wyatt miniDAWN multi-angle light scattering (MALS) detector using Shodex GPC column KF-805L. Polymers were dissolved in 0.5 mL of THF and injected at a 0.7 mL/min flow rate.

Fluorescence: Fluorescence spectra were recorded using an Agilent Cary Eclipse fluorometer. Samples were housed in 1 cm quartz cuvettes with septum-sealed screw caps. Spectra were acquired in DCM.

GC/MS: Gas chromatograph mass chromatograms and spectra were collected on a Shimadzu GCMS-QP2010SE gas chromatograph mass spectrometer. Samples were diluted in 1.5 mL of hexanes and injected via split injection mode. Mass spectrometry data was collected in 0.2-second scans from 35 m/z to 700 m/z.

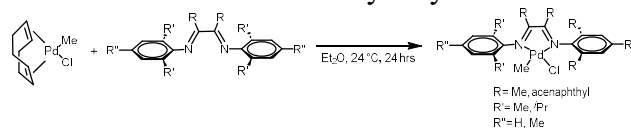
General Synthesis

General Synthesis of α -Diimine Ligands:
Scheme 3. General Ligand Synthesis.



Ligands were prepared according to previously published literature procedures.^{8,11,12}

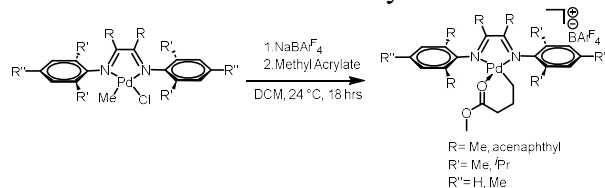
General Synthesis of Precatalysts:
Scheme 4. General Precatalyst Synthesis.



Precatalysts were prepared according to literature.^{8,11,12}

General Synthesis of Chelates:

Scheme 5. General Chelate Synthesis.



Reactions were prepared within an inert atmosphere glovebox in 25 mL Schlenk flasks charged with a stir bar. To those flasks was added 0.28 mmol of the precatalyst, 0.283 mmol of Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, and 25 mL DCM. The flasks were then sealed with a ground glass stopper and connected to a Schlenk line. Under a blanket of nitrogen, an excess of dry and degassed methyl acrylate was added, and the reaction was allowed to run 24 hrs. at room temperature before being concentrated under reduced atmosphere. The precipitate was collected, and the product was used without further purification.

Polymerization Procedure of 1-Hexene:

Reactions were prepared within an inert atmosphere glove box in 1 dram screw capped vials. To those vials, affixed with screw-capped pressure septa, was added 0.005 mmol of the polymerization catalyst, 0.0025-0.005 mmol of the photocatalyst and 750 uL of DCM. Dry and degassed 1-hexene and methyl acrylate were injected via uL syringe in known volumes and allowed to stir at room temperature for 18 hrs. in the presence of blue light (426 nm). Reactions were quenched by exposing them to air and concentrating under reduced atmosphere. The resulting residue was dissolved in hexanes and passed through a pad of silica gel and neutral alumina. The filtrate was concentrated under reduced atmosphere.

Polymerization Procedure of Ethylene:

Reactions were prepared within an inert atmosphere glove box in 75 mL pressure vessels. To those vessels, was added 0.005 mmol of the polymerization catalyst, 0.0025-

0.005 mmol of the photocatalyst, known volumes of dry degassed methyl acrylate, and 3-5 mL of DCM. The vessels were flushed with ethylene gas 3 times before being pressurized to 100 psi and being allowed to stir at room temperature for 18 hrs. in the presence of blue light (426 nm). Reactions were quenched by exposing them to air and concentrating under reduced atmosphere. The resulting residue was dissolved in hexanes and passed through a pad of silica gel and neutral alumina. The filtrate was concentrated under reduced atmosphere.

Equations

Branching per 1000C¹²:

$$(2(\text{CH}_3)/[2(\text{CH}_3)+3(\text{CH}_2+\text{CH})])\times 1000$$
$$\text{CH}_3 = {}^1\text{H Integral } 0.75 \text{ ppm} - 0.95 \text{ ppm} \quad (1)$$
$$\text{CH}_2+\text{CH} = {}^1\text{H Integral } 1.10 \text{ ppm} - 1.50 \text{ ppm}$$

Polar Monomer Incorporation¹²:

$$(4(\text{OMe})/[4(\text{OMe})$$
$$+2(\text{CH}_3)+3(\text{CH}_2+\text{CH})])\times 100$$
$$\text{OMe} = {}^1\text{H Integral } 3.67 - 3.82 \quad (2)$$
$$\text{CH}_3 = {}^1\text{H Integral } 0.75 \text{ ppm} - 0.95 \text{ ppm}$$
$$\text{CH}_2+\text{CH} = {}^1\text{H Integral } 1.10 \text{ ppm} - 1.50 \text{ ppm}$$

Results and Discussion

Fluorescence and Quenching

The chelates and photocatalysts used for the fluorescence and quenching experiments were chosen because they are well studied.^{6-9,12-14} As the concentration of chelate increased the fluorescence intensity of the photocatalysts decreased for both photocatalysts (Figure 1. A, B). When the ratio of intensity of fluorescence with and without quencher is plotted against the concentration of chelate a linear relationship is observed (Figure 1. C, D). These findings implied an intermolecular quenching mechanism and motivated us to investigate the ability of the photocatalysts to open the chelate.

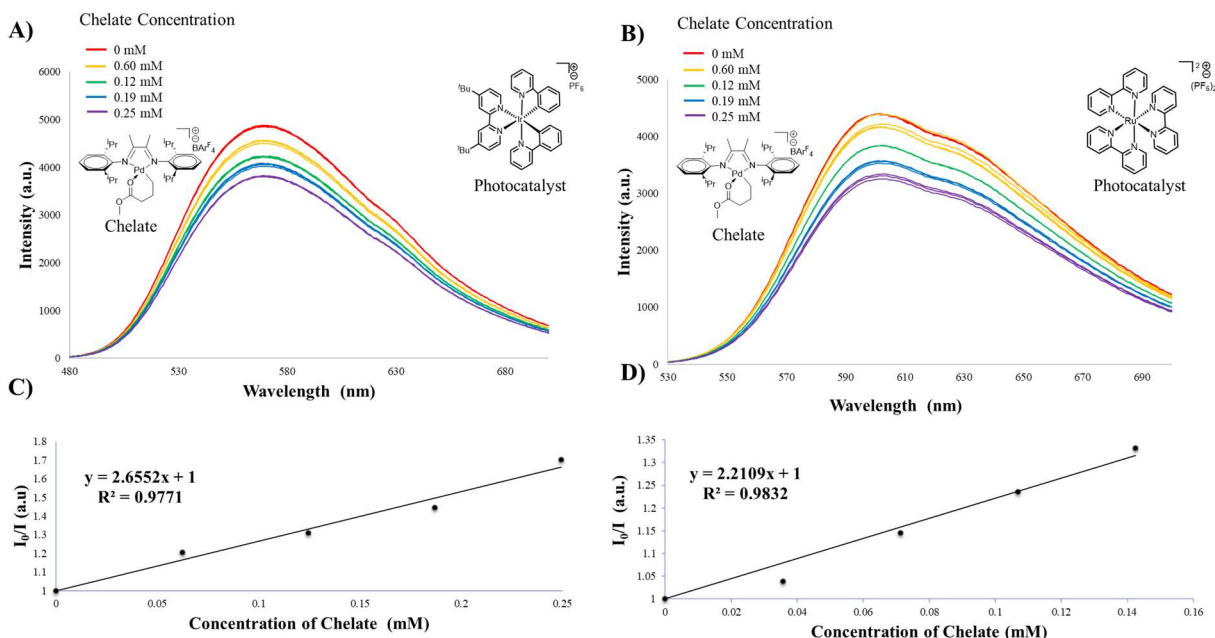


Figure 1. A) Fluorescence spectra of $[\text{Ir}(\text{ppy})_2(\text{dtbpy})]^+$ with different concentrations of chelate, B) Fluorescence spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ with different concentrations of chelate, C/D) Plots of Stern-Volmer relationships from fluorescence spectra.

Photocatalyzed Dechelation

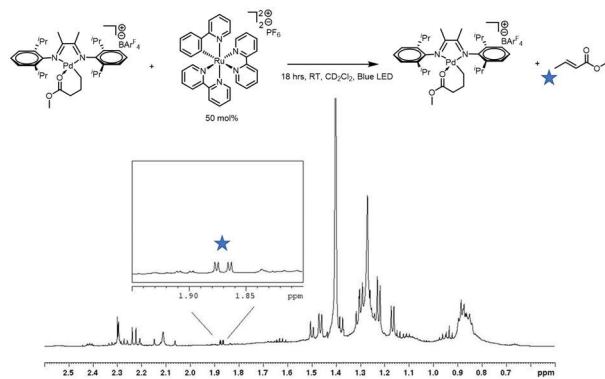


Figure 2. ¹H NMR of chelate-photocatalyst mixture after irradiation with blue light (426 nm).

After irradiating our chelate-photocatalyst mixture for 18 hrs. at room temperature, the sample was analyzed using ¹H NMR and GCMS. This led to the identification of the methyl crotonate CH₃ doublet of doublets at

1.87 ppm, as indicated by the blue star in Figure 2.

Through further experimentation full conversion of the chelate to methyl crotonate was achieved (Figure 3). Photocatalysis was determined to be the primary means of this conversion due to the absence of methyl crotonate when the reaction took place in the

EnT Induced Dechelation



Table 1. Summary of dechelation controls

Entry ^a	Change	Conversion ^b
1	No light	No Conversion
2	No Photocatalyst	Trace
3	Heated at 60°C	No Conversion

dark (Table 1). Full conversion of the chelate **Figure 3.** ^aStandard experimental conditions: solvent CH₂Cl₂; light source CFL; temperature 24 °C; time 18 hrs. ^bConversion determined by ¹H NMR and GCMS. All controls were run for 168 hours.

to methyl crotonate prompted us to investigate the ability of our system to co-polymerize α -olefins with polar monomers.

of 1-hexene to methyl acrylate decreases, branching also decreases and methyl acrylate incorporation increases, up to 72 mol% incorporation with 77 branches per 1000

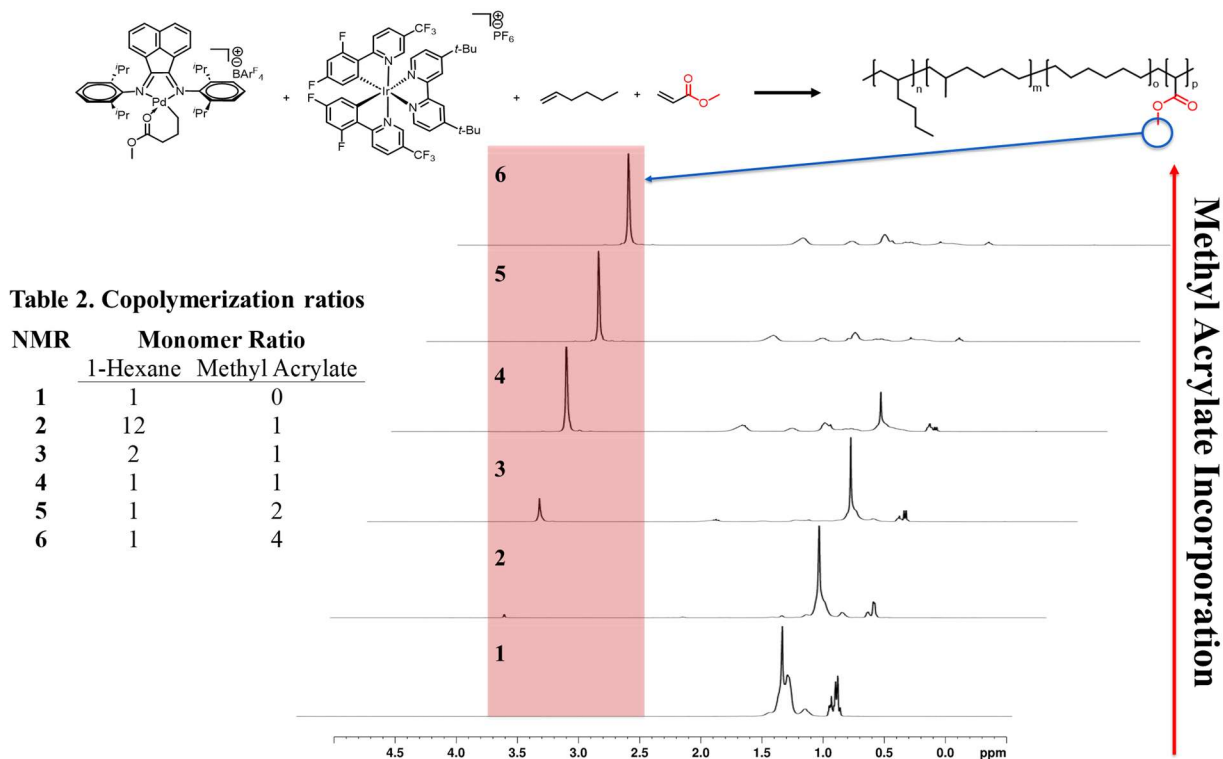


Figure 4. ^1H NMR of hexene copolymers.

Hexene Polymerization

To determine the viability of our system for the co-polymerization of α -olefins with polar monomers 1-hexene was chosen as a model olefin and methyl acrylate as a model polar monomer. During these experiments the optimal chelate ligand-photocatalyst pair was determined to be bis[N-(2,6-diisopropylphenyl)imino]acenaphthene- $(\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy}))^+$ and the optimal light source to be blue LEDs with a wavelength of 426 nm (Figure 4). By varying the mole ratio of 1-hexene and methyl acrylate we observe the resulting polymer backbone changes in branching and polar monomer incorporation (Figure 4). In the absence of methyl acrylate, the resulting polymer is viscous and has 149 branches per 1000 carbons. As the mole ratio

carbons.

Conclusions and Future Work

In summary, a new polymerization technique has been developed for the incorporation of polar monomers in poly α -olefins. Initial investigations show that EnT catalysis using visible light can induce dechelation of Brookhart-type α -diimine polymerization catalysts. ^1H NMR shows synthesized polymers incorporate polar comonomers into their backbones while maintaining some degree of branching. This could allow backbones to be tuned for desired properties based on the branching and polar group incorporation.

Currently the system is being optimized for the polymerization of ethylene gas and polar comonomers. This system could also be

potentially used to synthesize block polymers by quenching a polymerization with a polar monomer, removing unreacted material, adding a new monomer, and dechelating the catalyst using EnT.

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