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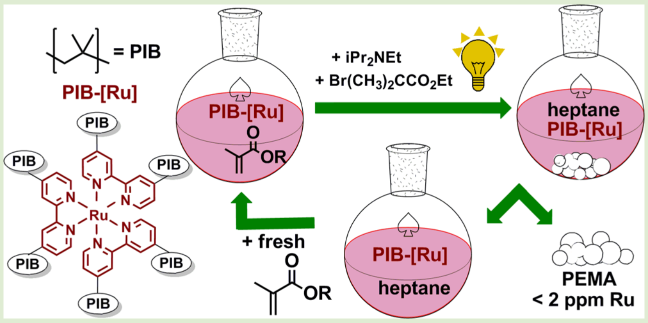
Recoverable Reusable Polyisobutylene (PIB)-Bound Ruthenium Bipyridine ($Ru(PIB\text{-}bpy)_3Cl_2$) Photoredox Polymerization Catalysts

Nilusha Priyadarshani,[†] Yannan Liang,[†] Jakkrit Suriboot,[†] Hassan S. Bazzi,[‡] and David E. Bergbreiter*,[†]

[†]Department of Chemistry, Texas A&M University, College Station, Texas, 77842-3012, United States
[‡]Department of Chemistry, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar

S Supporting Information

ABSTRACT: Polyisobutylene (PIB)-bound ruthenium bipyridine $[Ru(PIB\text{-}bpy)_3]^{2+}$ metal complexes were prepared from PIB ligands formed by alkylation of 4,4′-dimethylbipyridine with polyisobutylene bromide. The product $Ru(PIB\text{-}bpy)_3Cl_2$ complexes with at least one PIB ligand per bipyridine unit function as soluble recyclable photoredox catalysts in free radical polymerization of acrylate monomers under visible light irradiation at 25 °C with ethyl 2-bromoisobutyrate as the initiator in the presence of diisopropylethylamine. The polyacrylate products contained only about 1 ppm Ru contamination. This PIB-bound catalyst was recyclable and showed about 50-fold less Ru leaching as compared to Ru leaching in a polymerization catalyzed by the low molecular weight Ru catalyst, $Ru(bpy)_3(PF_6)_2$.



The development of new strategies for controlled polymerization and controlled radical polymerization, in particular, have had a striking effect on polymer synthesis, providing opportunities for synthesis of new families of materials. These strategies include Ru- or Mo-catalyzed ring-opening metathesis polymerization,[1,2] ADMET polymerization,[3] atom transfer radical polymerization,[4,5] nitroxyl-mediated polymerization,[6] and RAFT.[7,8] The use of transition metal photoredox catalysts for polymerizations by Choi and Hawker has also been described.[9−11]

While each of these polymerization procedures has its advantages, the need to use metals as catalysts in many of these types of polymerizations can lead to issues if the metal has to be separated from the polymer product. While metal removal is inconsequential if the catalyst turnover number is remarkably high,[12] recovering a metal catalyst, its byproducts, or its ligands or separating spent catalyst residues is often necessary because of the toxicity or the undesirable effect of catalyst residues on a product polymer's properties.[12−16] Our prior work has shown that oligomer-bound phase handles can minimize metal contamination in several types of polymerizations.[14−18] Here we show that similar strategies effect the recovery, separation, and reuse of soluble polymer-bound $Ru(bpy)_3Cl_2$ photoredox polymerization catalysts.

Cationic Ru(II)-bipyridine complexes, $[Ru(bpy)_3]^{2+}$, are useful as photocatalysts due to their long excited state lifetime and good chemical stability.[19] The $[Ru(bpy)_3]^{2+}$ complex in its excited state has both reducing and oxidizing properties acting both as an electron donor and as an acceptor with variety of reagents. The use of such catalysts in synthesis began with isolated reports of photo-catalyzed Pschorr reactions[20] and has burgeoned with contributions by many groups.[21−24] Catalytic reactions as diverse as halogenations of alcohols, C−H functionalization, and cycloaddition reactions advantageously use these electron donating and electron accepting properties of excited $[Ru(bpy)_3]^{2+}$ complexes. These same properties have also recently been used in polymerization chemistry.[10,11] In these reports, $[Ru(bpy)_3]^{2+}$ or Ir(tris(2-phenylpyridine)) complexes effect photoredox acrylate polymerizations using α-bromoalkanoate ester initiators. These polymerizations exhibit modest levels of control of polydispersity with polymerization activity that turns on and off in the presence or absence of activating light. However, as in other metal-catalyzed polymerizations, separation of the metal catalyst from the products and its reuse is problematic.[12−16] Bipyridyl metal complexes have previously been immobilized on cross-linked polystyrene or on silica supports for radical or photoredox polymerization or catalysis.[25,26] There are also numerous examples of soluble polymers containing bipyridine-Ru complexes both as pendant and main chain groups. These complexes have generally been used in optio-electronic applications.[27,28] This work shows that $Ru(bpy)^{32+}$ complexes can also be prepared as terminal groups on PIB oligomers and that the resulting complexes are useful as soluble recyclable photoredox catalysts in heptane.

The synthesis of polyisobutylene (PIB) bound bipyridyl ligands began with commercially available alkene terminated PIB (M_n = 2300 Da).[29] Formation of the alcohol **1** led to the primary bromide **3** after an S_N2 reaction of an intermediate

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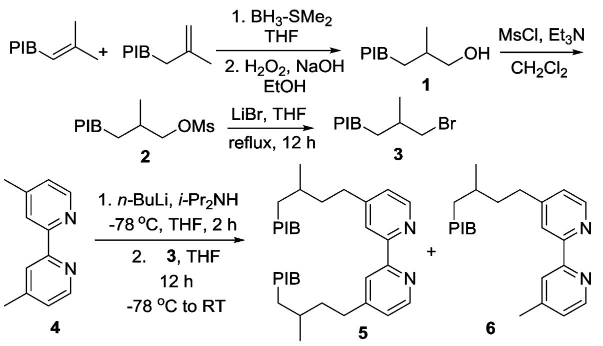
mesylate **2** (Scheme 1). Impurities in **2** due to a small amount (ca. 10%) of unfunctionalized PIB as well as byproducts from some PIB oligomers with an internal carbon−carbon double bond present in **1** were easily separated from the mesylate **2** using column chromatography.

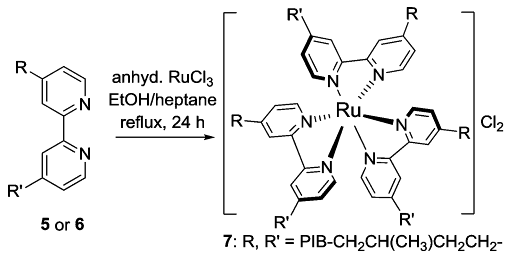
Scheme 1. Synthesis of a Polyisobutylene Bound Alkylating Agent for Synthesis of PIB-Bound Bipyridine Ligands 5 and 6 (PIB = H-$(CH_2C(CH_3)_2)_{39}$)-)



We then used **3** as an alkylating agent for lithiated 4,4′-dimethylbipyridine prepared by deprotonation of **4** at −78 °C (Scheme 1). Addition of **3** consumed all of the starting **4** consistently forming a 1:2 mixture of mono- and dialkylated PIB-bound bipyridine ligands **6** and **5** that contained some PIB-alkene byproduct that presumably forms as a result of an elimination reaction during alkylation of the lithiated 4,4′-dimethylbipyridine by **3**. This alkene was readily separated from the mixture of **5** and **6**. It was also possible to separate **5** from **6** by chromatography, but the mixture of **5** and **6** did not have to be further purified for our purposes (vide infra). The PIB-containing bipyridine ligands were characterized by NMR spectroscopy. While the ^1H NMR spectra of **5** and **6** were similar, ^{13}C NMR spectra showed eight signals from the bipyridine groups in the mixture of **5** and **6**. Purified ligand **5** had only five aromatic peaks at 121.8, 124.3, 149.5, 153.7, and 156.8 δ, resonances that were similar to the chemical shifts for aromatic carbons in **4** (122.0, 125.0, 148.0, 150.0, and 153.1 δ).

We synthesized PIB-bound ruthenium metal complexes from both **5** and the mixture of the PIB-containing bpy ligands **5** and **6**, as in Scheme 2. In this chemistry, pure **5** or the mixture of **5** and **6** were allowed to react with anhydrous $RuCl_3$ in a heptane/ethanol mixture at about 90 °C (Scheme 2). Pure **5** yielded the complex **7**. Using the more readily obtainable mixture that contains a 1:2 mixture of **5**:**6** formed **8**. The complex **7** and the mixture **8** had indistinguishable phase selective solubility and both complexes were soluble in heptane and insoluble in polar solvents (vide infra). Because both were effective polymerization catalysts, the complex **8** was used in the polymerization studies below unless otherwise specified. The formation of the deep red colored Ru(PIB-bpy)$_3Cl_2$ products in these reactions provided a qualitative way to follow the course of the synthesis of the Ru(PIB-bpy)$_3Cl_2$ synthesis. ^1H NMR spectroscopy also was used to follow formation of **7** and **8** from **5** and **6**. In ^1H NMR spectroscopy, the aryl protons of **5** and **6** disappeared and were replaced by a similar pattern of signals for aryl protons at different chemical shift values. Thus, the signals due to the aromatic protons of the free ligands at 8.56, 8.24, and 7.14 δ shifted to 8.47, 7.65, and 7.33 δ in **7** (the aromatic protons in **8** have essentially identical chemical shifts). Similar changes in ^1H NMR chemical shifts were also seen in the formation of a ruthenium complex of 4,4′-dimethylbipyridine. The product Ru complexes **7** and **8** had identical UV−visible spectra (cf., Figure S1 in Supporting Information) with a broad absorbance at a λ_{max} of 463 nm (ε = 15500 M^{-1} cm^{-1}) in hexane that was comparable to the λ_{max} at 452 nm (ε = 14300 M^{-1} cm^{-1}) of $[Ru(bpy)_3]^{2+}$ in acetonitrile.[30]

Scheme 2. Synthesis of Ru(PIB-bpy)$_3Cl_2$ Complexes 7 and 8



7: R, R′ = PIB-$CH_2CH(CH_3)CH_2CH_2$-
8: R = PIB-$CH_2CH(CH_3)CH_2CH_2$- and
R′ = PIB-$CH_2CH(CH_3)CH_2CH_2$- or CH_3-

Complexes $Ru(bpy)_3(PF_6)_2$ (**9**) and $Ru(Mbpy)_3(PF_6)_2$ (**10**) were synthesized using bipyridine (bpy) or 4,4′-dimethylbipyridine (Mbpy) ligands to compare phase selective solubility and catalyst activity with **7** and **8**. PF_6 complexes were prepared instead of chloride complexes because it was easier to isolate the PF_6 salt.

As expected, the Ru complexes Ru(PIB-bpy)$_3Cl_2$ **7** or **8** containing PIB ligands showed thermomorphic phase selective solubility that was different than that of complexes **9** or **10**. As shown in Figure 1, **7** (or the mixture **8**) is phase selectively soluble in a nonpolar solvent like heptane as opposed to the low molecular weight complexes **9** or **10**, which were soluble only in polar solvents such as acetonitrile and *N*,*N*-dimethylformamide and essentially insoluble in heptane (Figure 1).

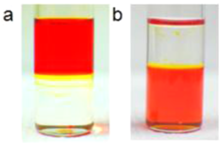


Figure 1. (a) Photograph contrasting the phase selective solubility of **7** in heptane (top) in a thermomorphic heptane/DMF system that is a single red phase hot and biphasic on cooling vs (b) the solubility of the low-molecular weight $Ru(bpy)_3(PF_6)_2$ complex **9** in DMF (lower phase) in the same heptane/DMF thermomorphic solvent mixture.

The heptane soluble PIB-bound ruthenium photocatalyst **7** was first examined in a radical polymerization of ethyl methacrylate (**12**). At a ~0.01 mol % catalyst loading, **7** showed excellent reactivity, forming poly(ethyl methacrylate) at 25 °C. A similar reaction using the more readily available complex **8** containing a mixture of PIB and methyl groups on the bipyridyl groups worked equally well. Using either **7** or **8** as a catalyst formed polymer products in similar isolated yields with similar M_n and PDI values (Table 1). In these experiments, the polymerization of **12** only occurred when the reaction was carried out at ambient temperature under visible light irradiation using a 30 W, household, fluorescent bulb. *N*,*N*-Diisopropylethylamine (*i*Pr_2NEt) and ethyl 2-

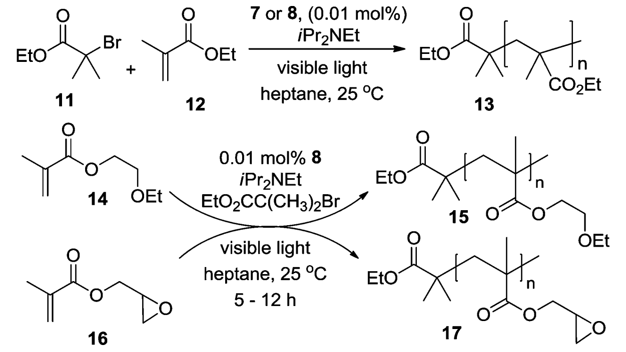
Table 1. PIB-Bound Photoredox Catalyzed Acrylate Polymerization Reactions in Heptane[a]

monomer	cycle	yield[b] (%)	M_n	M_w/M_n
12[c]	1	79	40800	1.2
12	1	82	42800	1.2
12	2	82	40300	1.4
12	3	70	38800	1.4
14	1	75	36600	1.4
14	2	72	45900	1.6
14	3	60	49400	1.4
16	1	70[d]	15600[e]	1.5[e]

[a] Reactions were carried out with 20 mmol of monomer in heptane, monomer/heptane (1:1, vol/vol) using 0.01 mol % of **8**, ethyl 2-bromoisobutyrate, and *N*,*N*-diisopropylethylamine. The reaction was carried out using a 30 W, fluorescent, household bulb irradiation for 24 h. Conversions were ca. 85% for cycle 1 and dropped to 75–80% for cycle 3. [b] Isolated yields of product. [c] This reaction was carried out with catalyst **7**. [d] The yield for cycles 2 and 3 with monomer **16** was 72 and 65%. [e] The PDI was not measured in cycles 2 and 3.

bromoisobutyrate **11** were used as an electron donor and as the initiator, respectively (Scheme 3).

Scheme 3. Free Radical Polymerization of Acrylates Using PIB-Bound Complexes 7 or 8



Given that the Ru catalyst **8** with a PIB ligand is heptane soluble, we developed a catalyst recycling scheme. Because the acrylate monomers are soluble in heptane and the polyacrylate products are insoluble in heptane, we expected that we could carry out a polymerization under homogeneous conditions in heptane and that the product polyacrylate would precipitate and self-separate from **8**. Assuming this occurred, the heptane solution of **8** could be separated from the precipitated polyacrylate product and recycled. This proved to be the case. The results of recycling experiments with **8** are summarized in Table 1. They show that catalyst recycling worked for at least three cycles with a slightly lower yield in cycle 3. This slightly lower yield in cycle 3 could be due either to physical losses in recycling the catalyst or some catalyst decomposition, but is not due to catalyst partitioning into the product polymer phase (vide infra).

To establish the generality of this photoredox catalyst/product separation strategy, two other acrylate monomers were polymerized. Both 2-ethoxyethyl methacrylate (**14**) and glycidyl methacrylate (**16**) were polymerized using light and **8** to form poly(2-ethoxyethyl methacrylate) (**15**) and poly(glycidyl methacrylate) (**17**), respectively (Table 1). In both cases, the products **15** and **17** self-separated from the heptane solution of **8** by precipitation after polymerization, allowing **8** to be recycled.

For comparison purposes, a polymerization reaction of **12** with $Ru(bpy)_3(PF_6)_2$ **9** was also carried out. Due to the insolubility of **9** in heptane, *N*,*N*-dimethylformamide (DMF) had to be used as the solvent. In this experiment, the product **13** is soluble in DMF so it was isolated by precipitation using excess MeOH. The poly(ethyl methacrylate) **13** formed had an M_n of 37200 and a PDI of 1.8, values similar in magnitude to those obtained with either **7** or **8**.

While catalyst recycling was possible with the PIB-bound catalyst **8**, reactivity in a second or third cycle is not in itself a sufficient test of the extent of Ru/product polymer separation. To measure Ru contamination in the product polymer products and to compare the Ru contamination of products with **8** with that for **9**, we analyzed the polymer products for Ru using ICP-MS (Inductively Coupled Plasma Mass Spectroscopy). In these analyses, **13** formed with the low molecular weight catalyst **9** that had been isolated by precipitation into MeOH was analyzed for Ru. For comparison, we analyzed the product **13** from the second cycle of a polymerization using **8** as catalyst also purifying **13** by a MeOH precipitation. ICP-MS analysis of **13** from the second cycle of the polymerization using catalyst **8** showed 1.0 ppm Ru was present. Ru contamination of **13** prepared using the low molecular weight photocatalyst **9** was 48.4 ppm. We also analyzed the polyacrylate **15** formed from **14** using **8** for Ru contamination. In this case, the crude polymer **15** prepared with **8** as catalyst was analyzed directly without purification via solvent precipitation. That analysis showed 1.9 ppm Ru contamination. These results of <1% of Ru leaching into the products with **8** versus ~30% Ru leaching for **9** clearly show that the PIB ligand usefully enhances separation of Ru from the polymer products for these soluble photoredox catalysts.

The precipitation of the products in heptane complicates kinetic studies of the polymerization using **8**, but kinetic studies of the polymerization of **12** using **8** in a 1:1 (vol/vol) solution of **12** and toluene containing 0.01 mol % of **8**, where the product **13** was soluble, were possible. These reactions occur at similar rates to those in Table 1. These studies showed that the polymerization was first order in **12** (Figure S2). The change of PDI with conversion in this system was also followed (Figure 2). The PDI of **13** gradually increased as the polymerization proceeded. This may be because of changes in the rate of reaction between the oligomeric PIB-bound $[Ru(PIB\text{-}bpy)_3]^{2+}$ with the growing macromolecule.

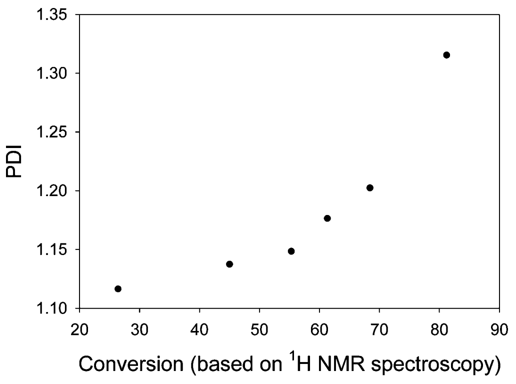


Figure 2. Plot of PDI vs conversion for a polymerization of **12** in toluene (1:1, vol/vol) using **8** as a catalyst.

In summary, the work here shows that a heptane-soluble, PIB-bound $Ru(bpy)_3^{2+}$ complex is an effective recyclable photoredox catalyst. Catalyst/product separation is simple and is effected by precipitation of the polymer products, which self-separates the products from the heptane solution of the reusable catalyst. There is negligible Ru contamination in the recovered polyacrylate. The activity, high separability, and phase selective solubility of these PIB-bound Ru species in polymerizations of acrylates suggests that the use of these heptane-soluble supports should be generally useful for these sorts of catalysts in other photoredox processes.

■ ASSOCIATED CONTENT

Supporting Information

Detailed procedures for ligand and catalyst synthesis, polymerization and recycling experiments, procedure for ICPMS analysis, and spectra data for PIB ligands and PIB−ruthenium complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: bergbreiter@tamu.edu.

Notes

The authors declare no competing financial interest.

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