END FUNCTIONALIZATION OF POLYISOBUTYLENES AND THEIR APPLICATIONS IN DYEING POLYOLEFINS AND IN HOMOGENEOUS CATALYSIS

A Dissertation

by

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ABSTRACT

Non-polar phase selectively soluble polyisobutylene (PIB) is a useful polymer as a polymer support for homogeneous catalysts. Substitution of PIB onto other useful ligands alters the solubility properties of original ligands. However, such chemical modification of PIB polymers is challenging due to its limited synthetic availability. This dissertation describes the end functionalization of this terminal alkene functionalized PIB into variety of other functional groups via variety of chemistries such as electrophilic aromatic substitutions, nucleophilic aromatic substitution reactions and alkylation reactions.

PIB-anilines and PIB-phenols can be prepared *via* electrophilic aromatic substitution reactions of anilines and phenols by PIB-alkene. Excellent oxidative and chemical resistance and nonpolar phase selective solubility of these modified PIB polymers allow these materials to be useful as soluble polymer supports for ligands and transition metal catalysts. This dissertation details immobilization of palladium and ruthenium catalysts on to these modified PIB ligands and their catalytic properties and catalyst recyclability. PIB-bound palladium catalyst was used as a recyclable homogeneous catalyst for cross coupling reactions in a thermomorphic liquid/liquid separation system- biphasic at a lower temperature and monophasic at a higher temperature. Application of a ‘solid solvent’-(Polywax) in place of a organic solvent is also described and improved metal sequestration of this liquid/solid catalyst/product separation compared to the thermomorphic liquid/liquid separation strategy is also investigated. A PIB-bound ruthenium visible light photo-redox catalyst was prepared and its catalytic activity and recyclability in free radical polymerization reactions of acrylates is also reported.

At the end this dissertation details the extension of PIB's utility as a nonpolar phase anchor to functionalize polyolefins with dyes. This is illustrated by preparing PIB-bound metallophthalocyanine dyes in a series of reactions starting with 4-nitro phthalonitrile. The non-polar solvent solubility of these dyes allowed their use in dyeing commercial polyethylene and polypropylene.

DEDICATION

This dissertation is dedicated to my family and my husband, Erosh. A special thank to my parents Peter and Mallika Cancius whose hard work in their lives pushed me for this accomplishment today. My sister Geethani and Brother Nilushan have never left my side are very special. Thank you so much Erosh. I could not have done this without your support.

I dedicate this work to my American host family John and Joyce Schrader for their love and care throughout my academic career. I made it through these seven years with your encouragement. I would not have writing this today without your love and support.

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CHAPTER I

INTRODUCTION

Functional and structural polymeric materials have found many applications in contemporary world in areas, which were unknown or unimagined two decades ago. Some of these areas include plastic electronics, light emitting diodes, drug delivery, consumer goods, pharmaceuticals, automobile industry and so on. In modern industry most of these applications require functional polymers. After the discovery of experimentally practical controlled living radical polymerization (CLRP) techniques expanded upon the prior work on controlled cationic and anionic polymerizations, materials science has revolutionized and has become a truly multidisciplinary research area. In this era, polymer research includes not only synthetic polymers for structural applications (coatings and packaging) but also nanomaterials, opto-electronic devices and biomedical related applications. Controlled polymerization methodologies provide regulated synthesis of materials with defined molecular weights, composition and narrow polydispersities, which allow the design and synthesize complex macromolecular architectures with desired functionalities. While these CLRP methods allow the synthesis of new types of functional polymers, there can still be challenges. For example, while protected functional monomers can be polymerized via controlled polymerization techniques, deprotection of the functionality of the product polymers may not proceed quantitatively. Although, direct polymerization of functional monomers is the ideal strategy for synthesizing functional polymers, conventional radical, anionic or cationic polymerization methods offer very limited possibilities of using directly functional monomers due to their secondary interactions with initiator/catalyst systems which consist of metal salts. Therefore, post polymerization modifications of materials can be an attractive approach and are sometimes the only method for synthesis of functional polymers due to the limited functional group tolerance of polymerization mechanisms.[1]

These post polymerization methods often used to produce end functionalized polymers or telechelic polymers. Such chemistry is of great interest due to its possible applications in synthesis of block copolymers, thermoplastic elastomers, polymer networks, surfactants, macromonomers, macroinitiators and polymeric ligands for catalysts etc..[2-9] The term telechelic refers to a linear polymer chain containing two functional groups at both ends – a type of polymer that is useful either as a cross linker or as a chain extender. While numerous methods have been developed to prepare telechelic, semi-telechelic or multi-telechelic polymers via different CLRP techniques, only the cationic polymerization and related functionalization strategies will be discussed here.

Cationic polymerization is a highly developed industrial practiced methodology especially useful for polymerizations of vinyl monomers that form relatively stable carbocations. Polyisobutylene (PIB) is one of the most commercially produced polymers via a cationic mechanism. This non-polar hydrocarbon polymer of isobutylene (IB) have been explored extensively in recent years due to its many applications in areas such as surface modification, adhesion, as sealants, as lubricants, compatibilization of polymer blends, in the pharmaceutical industry and in the food industry. Polyisobutylene was first developed by the BASF in 1931 and is sold under the trade name “Oppanol B” or “Glissopal” depending on its molecular weight. These commercial materials are produced via cationic polymerization of isobutylene (IB).

The first controlled carbocationic polymerization of IB was reported by Faust and Kennedy in 1980.[10] It has since been a great interest of many material researchers as well as in industrial applications. Polyisobutylene (PIB) is a completely saturated hydrocarbon rubber with interesting chemical and physical properties as extreme chemical inertness, gas impermeable, oxidative resistance, mechanical dampness and excellent biocompatibility.[11-18] These properties are highly desirable in applications such as lubricants, low gas permeable sealants, a soluble support for catalysts and bio medical applications. Therefore production of such a polymer with various functionalities has become an increasing interest among polymer research community. The industrial or conventional production of PIB via cationic polymerization carried out in very low temperatures ca. - 90 ^oC in the presence of a Lewis acid and a proton source as the catalyst system. The head group of the PIB chain is usually hydrogen (from initiation or transfer) and end groups are usually olefins, which are formed as a result of proton transfer and isomerization typical for carbenium ions. Possible unsaturated end groups from such a mechanism are shown in Figure 1. Structures A and B are the most common type of end groups, formed directly from growing chain end. Cations C, D and E are possible from methyl carbanion shift and structure F is obtained after methyl carbanion and hydride shift.[1]

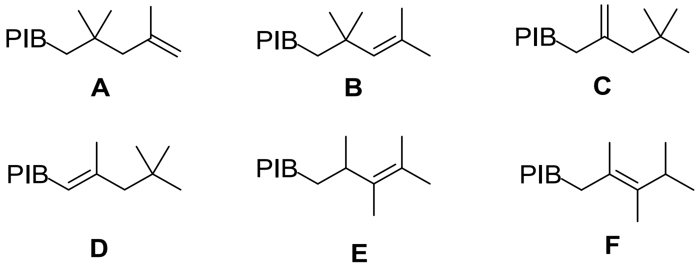
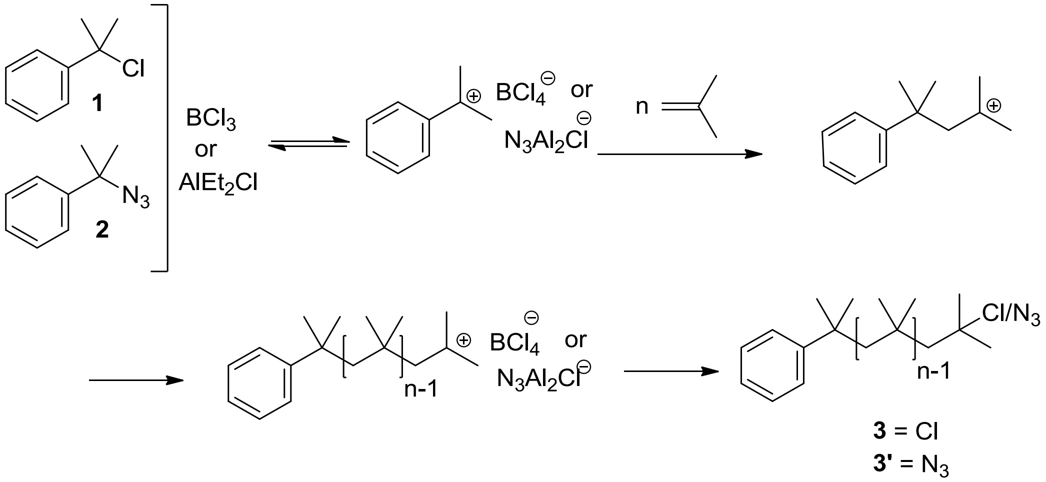


Figure 1. Possible olefinic end groups result in a 'conventional' cationic polymerization.

These di- and tri-substituted alkene terminated PIBs are useful as precursors in synthesis of a variety of other end functionalities via post polymerization modifications. However, elegant chemistries developed with a cationic polymerization process of IB also permit various functionalizations of PIB, either at the initiation step using a functional initiator to form α-end functionalized PIB or at the termination step using a functional terminator or capping agent to form ω-end functionalized PIB. While my work mainly focused on end functionalization of alkene terminated PIB by post polymerization methods, the synthesis of telechelic or semi telechelic PIBs, during a cationic polymerization will be discussed below.

Functionalization using functional initiators

Initiators that induce polymerization are usually consumed during the polymerization and become a part of the polymer chain. The first report of controlled polymerization of IB was described by the Akron polymer group introducing the concept of "inifers".[10,19,20] The term 'inifer' is defined as a compound that acts both as an initiator and as a transfer agent. In a typical IB polymerization cumenyl chloride (CumCl, **1**) acts as the initiator (inifer) and BCl_3 acts as the activator. During the polymerization mechanism chlorine atom is transferred from BCl_4^- counter anion to PIB chain end of the growing polymer to form tertiary chloro ended PIB **3** and reform the Lewis acid BCl_3. With bifunctional initiators (binifers) and trifunctional initiators (trinifers), it was thus possible to prepare macromolecular architectures of PIB such as telechelic or three armed star PIBs (Scheme 1).[21] Another approach to prepare well-defined PIBs was achieved by replacing "catiogenic function" of the halide initiator with the azide initiator **2**. Cheradame et al. showed 1,4-bis(1-azido-methylethyl)benzene **2** as bifunctional initiator in the presence of $AlEt_2Cl$ as the Lewis acid, which initiated IB polymerization following similar chemistry as described above to produce PIB-azide **3'**, which can undergo further functionalizations via 'click' chemistry.[22-25]



Scheme 1. Cationic polymerization of IB with cumenyl chloride and azidocumenyl / Lewis acid as functionalizing initiators.

On the other hand multifunctional initiators are also of great interest, especially in designing ordered PIB-star or branched architectures. Tri and tetra functional initiators can provide a uniform number of arms in a star polymer structure. For example, tetrafuntional initiators 3,3’,5,5’-tetrakis(2-chloro-2-propyl)biphenyl (BPTCC) **4** and a trinifer 1,3,5-tri(2-chloro-2-propyl)benzene (TCC)) **5** have been described as viable initiators for synthesis of four and three arm star telechelic PIBs with tertiary chloride end groups (Figure 2).[2,21]

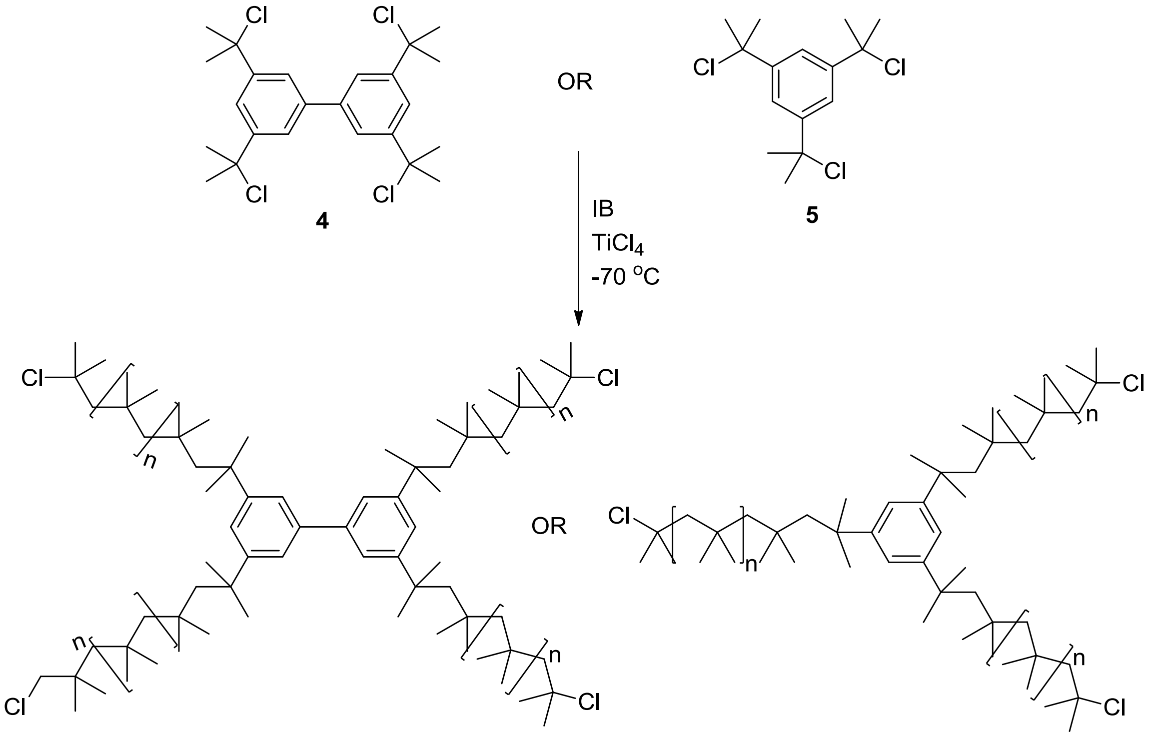
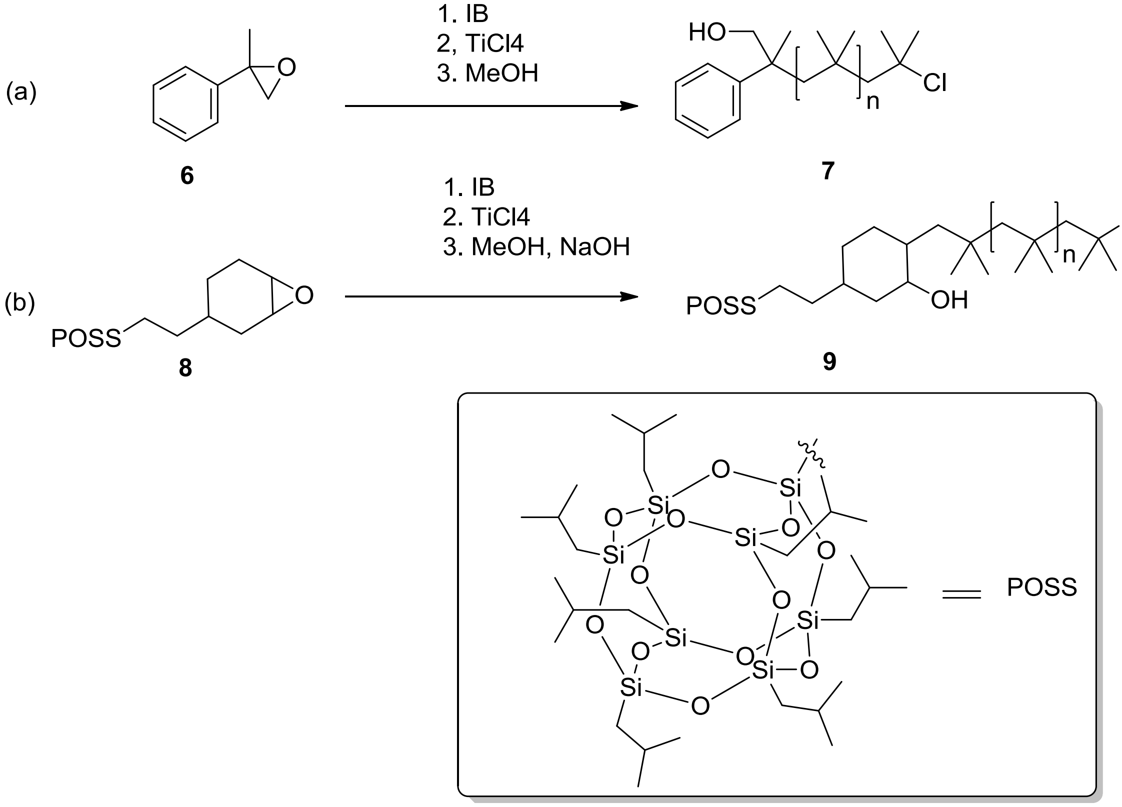


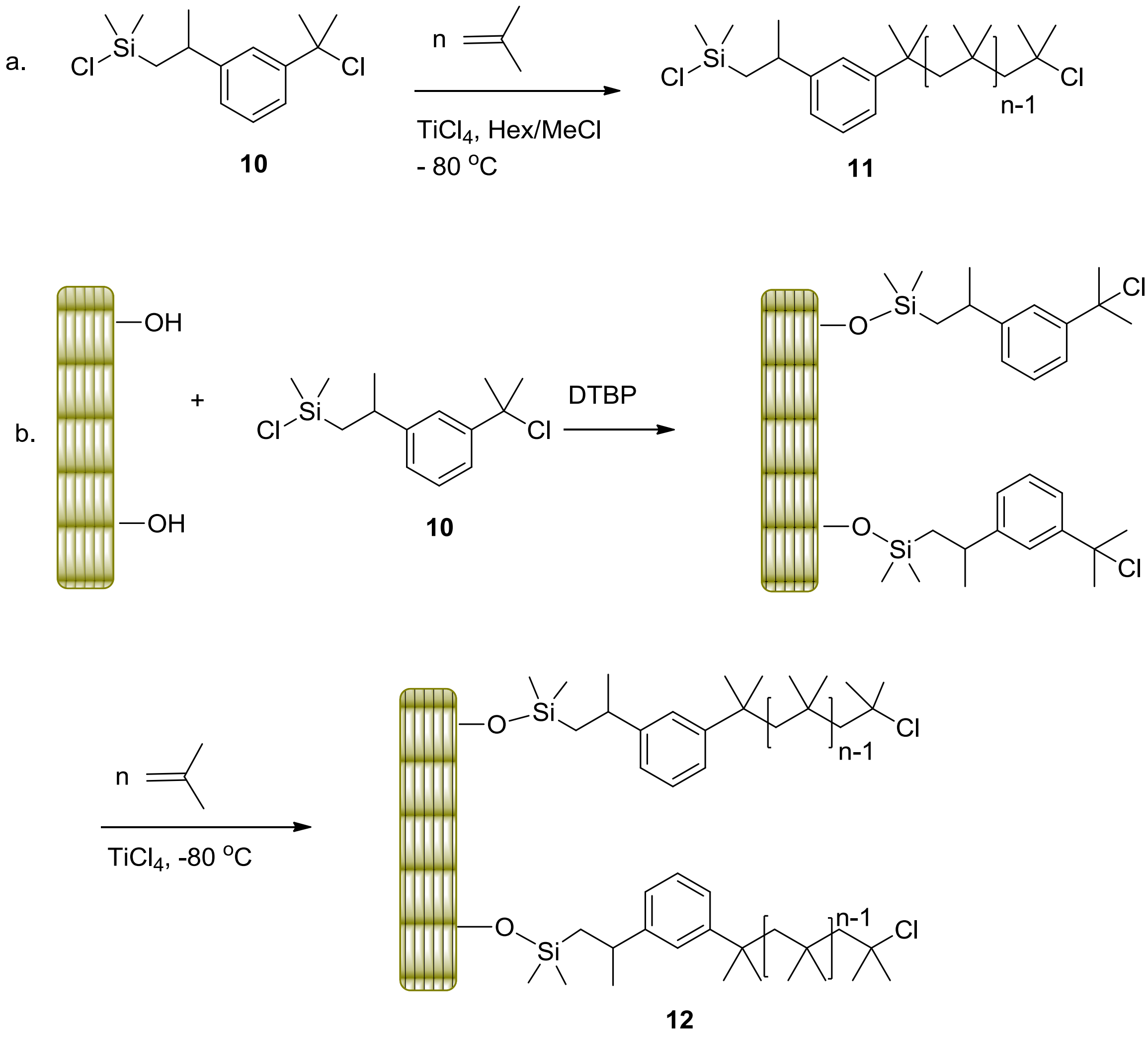
Figure 2. Tri and tetrafunctional initiated multitelechelic three and four arm PIB star structures.

The inifer initiation method generally forms ω-end functionalized PIBs. It is also possible to functionalize a α-end of PIB chain using functional initiators such as substituted epoxides to produce α-hydroxyl and ω-tertiary chloro end functional PIB. Puskas et al. reported that the α-methylstyrene epoxide **6** (MSE)/$TiCl_4$ initiator system efficiently initiated the cationic polymerization of IB to prepare PIB with a primary hydroxyl head group and a tertiary chloride end group functionalized PIB **7** (Scheme 2).[26]



Scheme 2. Initiation of IB polymerization with (a) an MSE/TiCl4 initiator and (b) an epoxycyclohexylisobutyl POSS/$TiCl_4$ initiator.

This epoxide initiator has been improved to synthesize organic-inorganic composite materials, which are of great interest due to enhanced thermal and mechanical properties of the so formed composites. In this case a polyhedral oligomeric silsesquioxanes (POSS) cage is covalently linked to an epoxide initiator for IB polymerization to form α-end POSS and hydroxyl functionalized PIB **9**.[27]

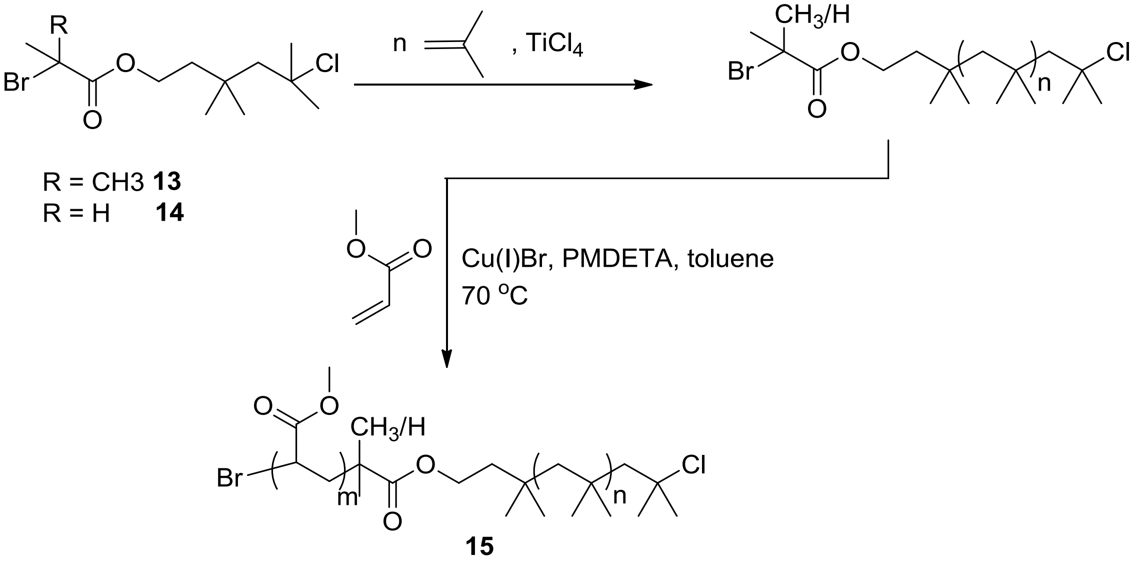


Scheme 3. (a) Synthesis of chlorosilane functionalized PIBs and (b) synthesis of PIB brushes using chlorosilane initiators.

Silicon functional groups are also useful, especially when they are placed in the α-end of the polymer chain. Although these end groups carry Si-Cl reactive bonds they survive the cationic polymerization conditions. Faust at el. reported the use of monochlorosilyl and dichlorosilyl initiators for synthesizing α-chlorosilyl PIBs such as **11** (Scheme 3a). These silicone functional PIBs provide multiple synthetic routes for designing macromolecular architectures. For example, chlorosilyl initiator **10** has been used to fabricate a tethered PIB-brush **12** on a silica surface by grafting from technique where, initiator was immobilized on to the silanol groups of silicon wafers in the presence of di-*tert*-butylpyridine (DTBP). The polymerization of IB was then carried out on the silicon surface to synthesize the PIB-brush (Scheme 3b). [28]

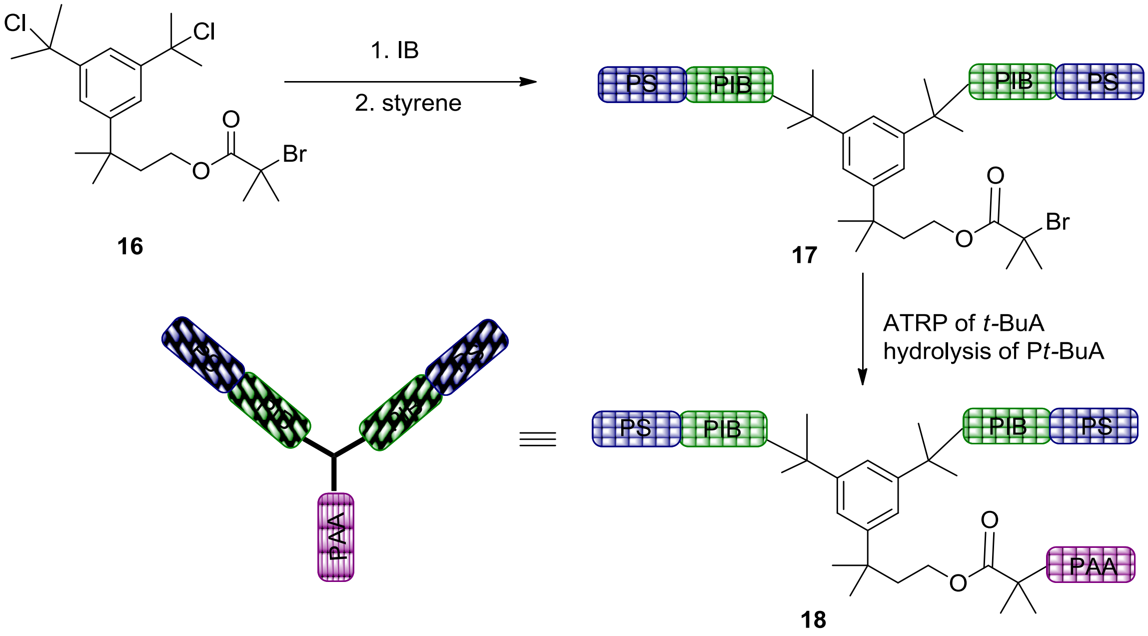
The functional initiator polymerization strategy has also become a great tool for designing block copolymers with different monomers. PIB block copolymer synthesis has attracted much attention due to the flexibility, chemical and oxidative resistance and hydrophobicity that PIB blocks bring to a product copolymer. Incorporating PIB moieties in to a polymer structure not only induces interesting properties into the material, it also endows materials with the ability to self assemble into ordered morphologies. However, isobutylene is one of the rare monomers that undergo cationic polymerization and it is the only method of synthesizing PIB. The sequential monomer addition is the simplest method of copolymerization and it is only limited to those monomers that are polymerizable by the same mechanism.

This issue has been addressed by designing dual initiators, which contain different initiating sites for different polymerization mechanisms.[29,30] For example, developed dual initiators 3,3,5-trimethyl-5-chlorohexyl-2-bromopropionate (IB2BP) **13** and 3,3,5-trimethyl-5-chlrohexyl-2-bromo-2-methylpropionate (IB2BMP) **14** molecules contain a cationic initiating site for IB polymerization and an ATRP initiating ready site. The study demonstrated the utility of these dual initiators to polymerize IB via cationic mechanism while ATRP initiating site remains dormant. At the end of the IB polymerization the ATRP can be performed by addition of acrylate monomers in a sequential manner to form a diblock copolymer **15** (Scheme 4).



Scheme 4. Synthesis of a PIB-*b*-PMA copolymer via dual initiators IB2BP or IB2BMP.

This dual initiator strategy is also useful in synthesizing PIB-based star polymers (Scheme 5). A PIB-based three-arm (miktoarm) star polymer structure has been reported by combining cationic polymerization of IB and styrene and radical polymerization of *tert*-butyl acrylate (*t*-BuA). Therefore, the designed initiator 3-[3,5-bis(1-chloro-1-methylethyl)phenyl]-3-methylbutyl 2-bromo-2-methylpropionate (DCCBMP) **16** contains dicationic initiating sites and a radical initiating site. The polymerization is carried out by first LCP of IB and styrene followed by ATRP of *t*-BuA. Hydrolysis of so formed star polymer can remove *t*-butyl ester from P-*t*BuA block to yield an amphiphilic PIB-star polymer **18** (Scheme 5**)**.[30]

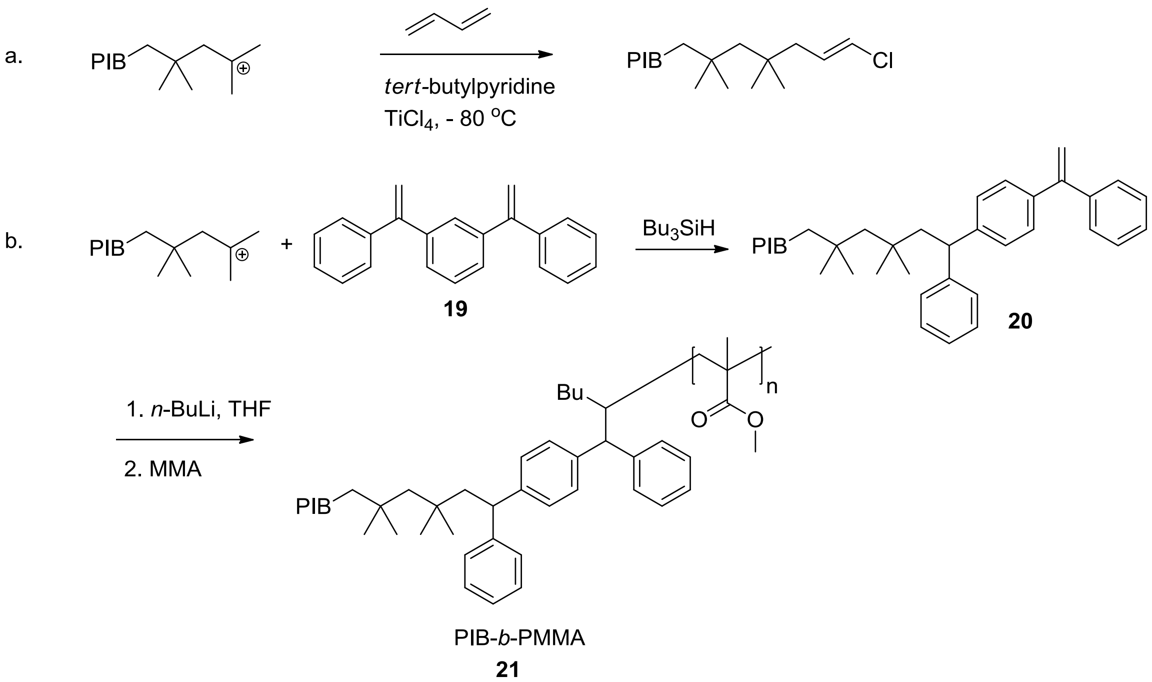


Scheme 5. Schematic diagram of the synthesis of amphiphilic PIB-star polymer, (PS-PIB)$_2$-PAA.

Functionalization using functional terminators

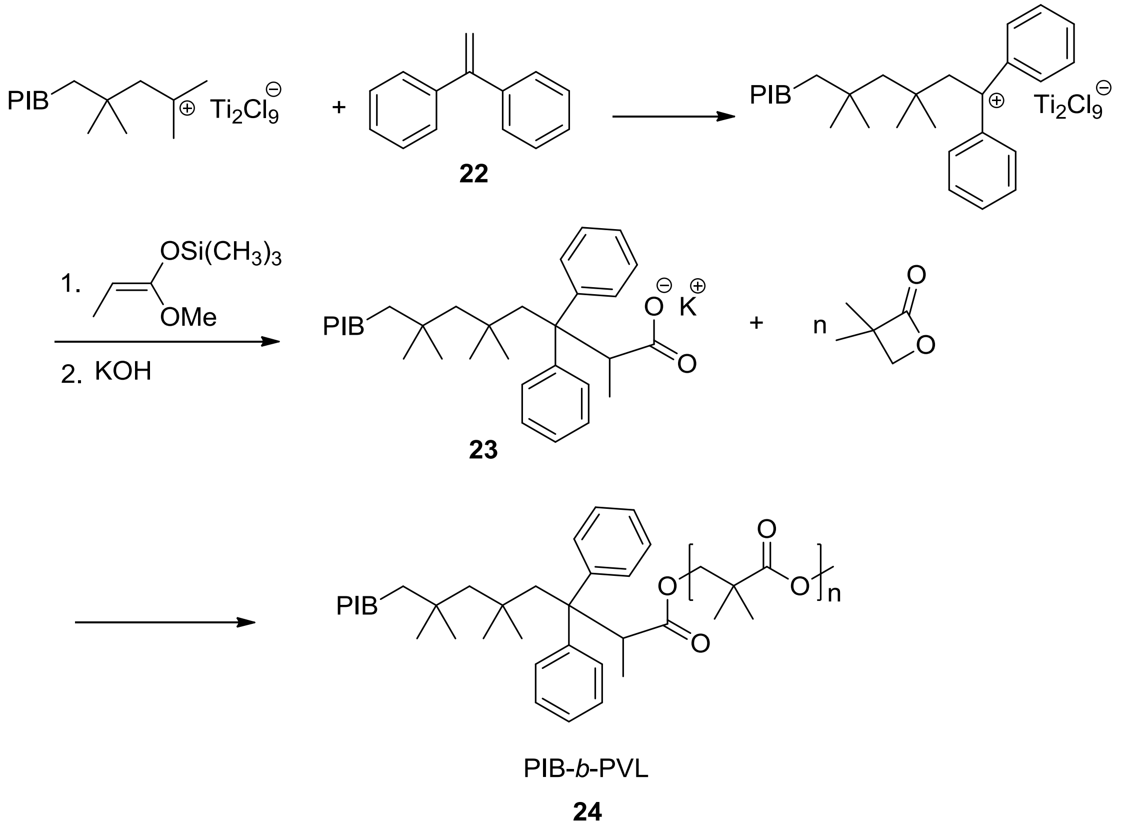
Halide based initiators for cationic polymerization of IB generally yield halide end functionalized PIBs. Nonetheless, termination of living chain end of a polymer with a functional end-capping agent (nucleophile) too is a popular strategy of synthesizing ω-functional PIBs. Olefins, silanes and aromatic compounds have been mostly explored as end-capping reagents in cationic polymerization (LCP) of IB.

End quenching of a growing PIB chain by a C=C bond containing molecules such as butadiene yields C=C end functional PIBs. In a typical example, when 1,3-butadiene (BD) was used as the capping agent, selective 1,4 addition of BD to PIB^+ was observed in the presence of a proton scavenger such as *tert*-butylpyridine (Scheme 6a).[31] These sorts of non-homopolymerizable vinyilidene compounds have been an interest as end-capping reagents and produce relatively stable highly ionized cationic chain ends, which can undergo site transformation chemistry to form living anionic chain ends. This chemistry is an interesting tool for synthesizing block copolymers of PIB.[32-36] Para-double diphenyl ethylene (PDDPE) **19** and diphenyl ethylene (DPE) **22** are widely studied capping reagents that can efficiently quench the living cationic chain end of the PIB^+ and subsequent metallation of formed PIB-end capped derivative with Li, Na/K or Cs yield an anionic chain end which then acts as a macroinitiator for an anionic polymerization (Scheme 6b). In a typical PDDPE **19** end capping process and site transformation, PIB^+ is quenched with excess PDDPE to yield PIB-PDDPE **20**, which can then be lithiated with *n*-BuLi to form anionic PIB chain end and so formed PIB macroinitiator undergoes anionic polymerization with methyl methacrylate (MMA) to form PIB-*b*-PMMA block copolymer **21** in a stepwise one pot reaction (Scheme 6b).



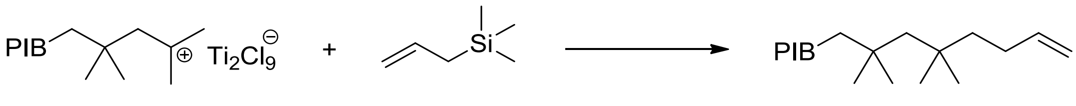
Scheme 6. (a) End capping of PIB$^+$ with BD and (b) end capping of PIB$^+$ with PDDPE and synthesis of PIB-*b*-PMMA.

Faust and coworkers reported another end capping strategy to obtain carboxylate ω-end functionalized PIB by intermediate quenching of PIB$^+$ with DPE **22** and subsequent end- capping of the metallated anionic PIB species with silyl ketene acetals such as 1-methoxy-1-trimethylsiloxypropene (MTSP) to form ω-methoxycarbonyl-PIB (Scheme 7). So formed PIB-methoxycarbonyl undergoes hydrolysis to form a macroinitiator **23** which is a macroinitiator for anionic polymerizations. This PIB ω-carboxylate can initiate anionic ring opening polymerization (AROP) of pivalolactone (PVL) to form PIB-*b*-PVL block copolymer **24** (Scheme 7).[37]



Scheme 7. End capping of PIB$^+$ with DPE and anionic ring opening polymerization of pivalolactone using PIB ω-carboxylate macroinitiator.

In addition to olefins, silanes are also useful capping agents for quenching a carbocationic end of the living polymer chain. The methodology involves using mono or multifunctional initiators to carry out cationic polymerization and subsequent electrophilic derivatization of PIB carbocation with allyltrimethyl silane (ATMS) **25**. Kennedy and coworkers reported the first end capping modification of a living PIB chain end with ATMS to produce allyl telechelic PIB polymers **26** (Scheme 8). Using this chemistry it is also possible to synthesize a variety of telechelic PIBs under different initiator systems containing mono-, di- and trifunctional initiators to form semi-telechelic PIB, telechelic PIB and star PIB structures. [38]



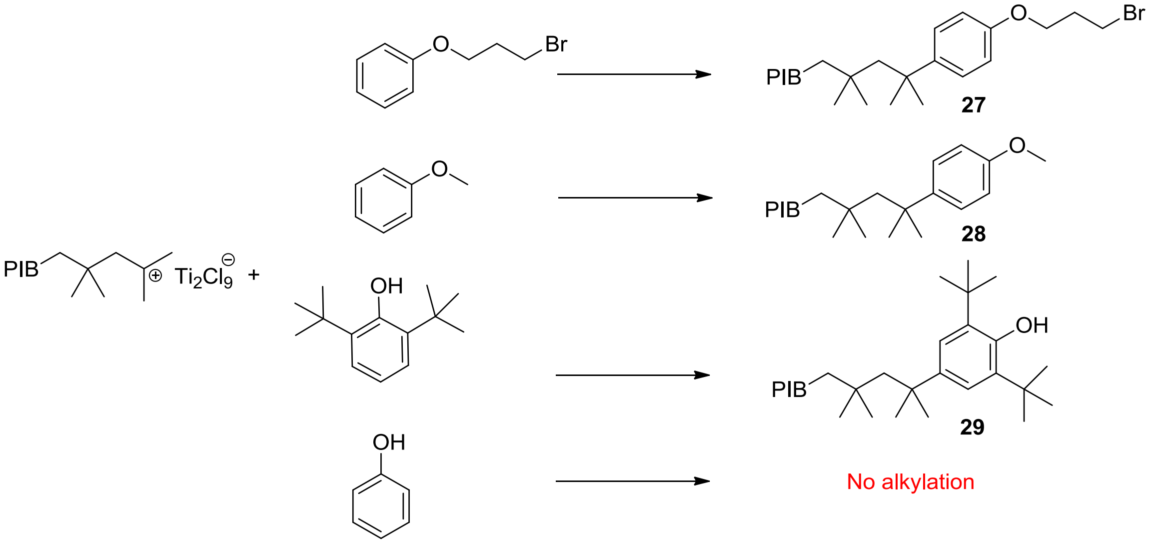
25

26

Scheme 8. End capping of PIB$^+$ with allyltrimethylsilane (ATMS).

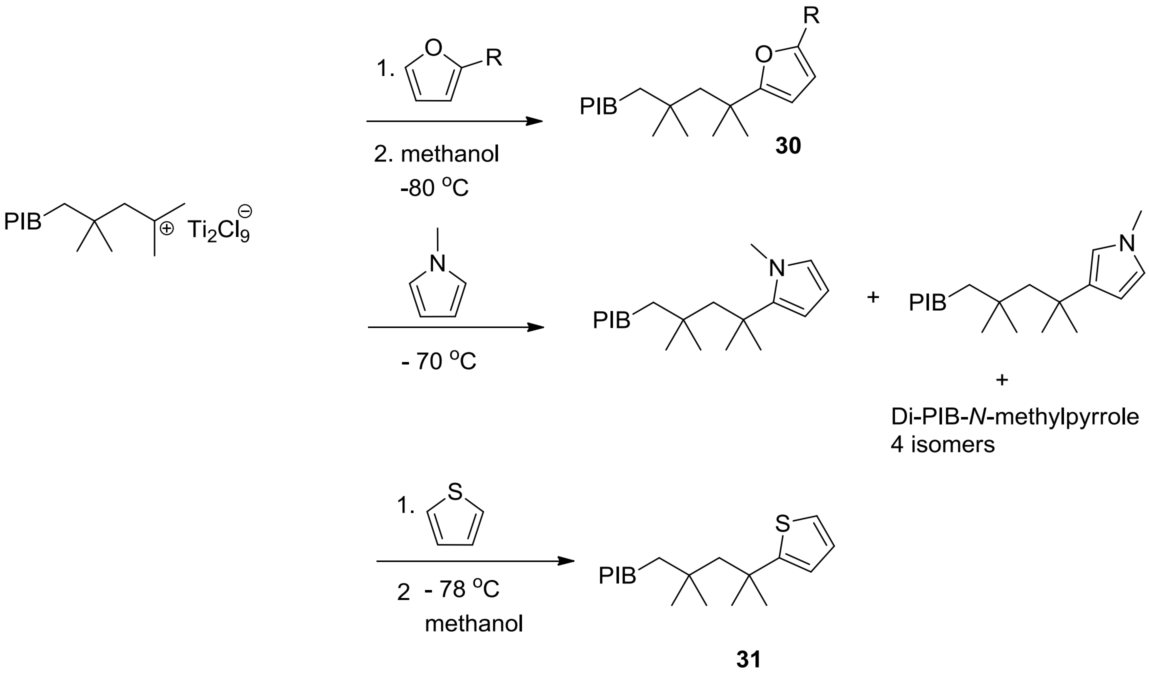
Substituted aromatic compounds are also among widely studied end quenching reagents. Alkoxybenzenes stand out as good candidates for electrophilic end-capping in $TiCl_4$ mediated polymerizations, as they are strongly activated toward electrophilic aromatic substitutions (EAS) and it has no reactivity or secondary interactions with Lewis acids which are catalytic components in the polymerization process. A range of alkoxybenzenes such as anisole, isopropoxybenzene, 2,6-ditert-butylphenol, allyl phenyl ether and 2-bromoethoxybenzene were successfully employed in end capping of PIB$^+$ (Scheme 9).[39] A primary halide, 2-bromoethoxybenzene functionalized PIB **27** is useful due to its versatility as an intermediate for many post chemical transformations, which will be discussed later in this chapter. Although hindered phenols like 2,6-di*tert*-butylphenol underwent facile end capping process to form **29**, unsubstituted phenol did not form PIB-phenol due to complexation with $TiCl_4$ catalyst and became insoluble in the polymerization media.

Heterocyclic aromatic compounds have also been briefly explored as end capping agents. Furan is more reactive than benzene and mainly reactive for electrophilic aromatic substitution at both 2 and 5 equally reactive positions. Therefore, 2-substituted furan has been investigated as end capping reagents. In this study, 2-methylfuran and 2-*tert*-butylfuran were used to cap PIB^+ yielded 2-alkyl-5-PIBfuran **30** quantitatively (Scheme 10).[40]



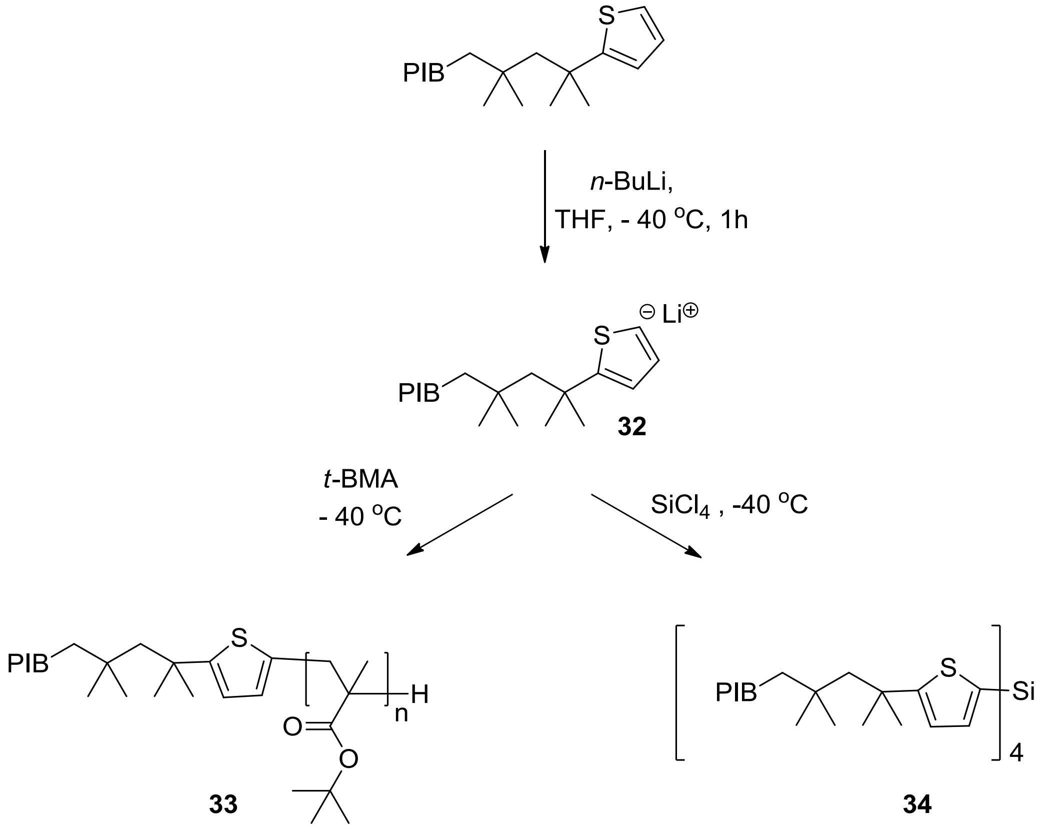
Scheme 9. End quenching of PIB^+ with alkoxybenzenes and phenols.

Among heterocyclic aromatic quenching agents, *N*-methylpyrrole has also been described as a potential quenching agent for living carbocationic polymerizations. In this example, *N*-methylpyrrole can quench living chain end PIB^+ and an equvimolar isomeric mixture of 2- and 3-PIB substituted *N*-methylpyrrole was observed as major products. In addition, an isomeric mixture of PIB-disubstituted *N*-methylpyrrole was also observed as minor products. This diminished selectivity of substitution is justified by both -2 and -3 positions of pyrrole having fairly similar reactivity toward electrophiles.[41] On the other hand, thiophene undergoes regioselective electrophilic substitution of PIB$^+$ to yield only 2-substituted PIB-thiophene **31** (Scheme 10).[42]



Scheme 10. End quenching of PIB$^+$ with heterocyclic aromatic compounds.

While 2-substituted PIB-thiophene is readily available from above end capping reaction, it is also useful in synthesizing block copolymers by site transformation techniques as previously described. The method involves end capping PIB$^+$ living chain end with thiophene and subsequent lithiation with excess *n*-BuLi to produce an anionic PIB macroinitiator **32**. The PIB-thiophene macroinitiator **32** undergoes anionic polymerization with *tert*-butylmethacrylate (*t*-BMA) to form a PIB-*b*-P*t*-BMA block copolymer **33**. This chemistry can also be extended to synthesize four arm star shaped PIB architecture **34** by allowing PIB-thiophene anion **32** reaction with $SiCl_4$, a good coupling agent for anionic chain ends (Scheme 11). [42]

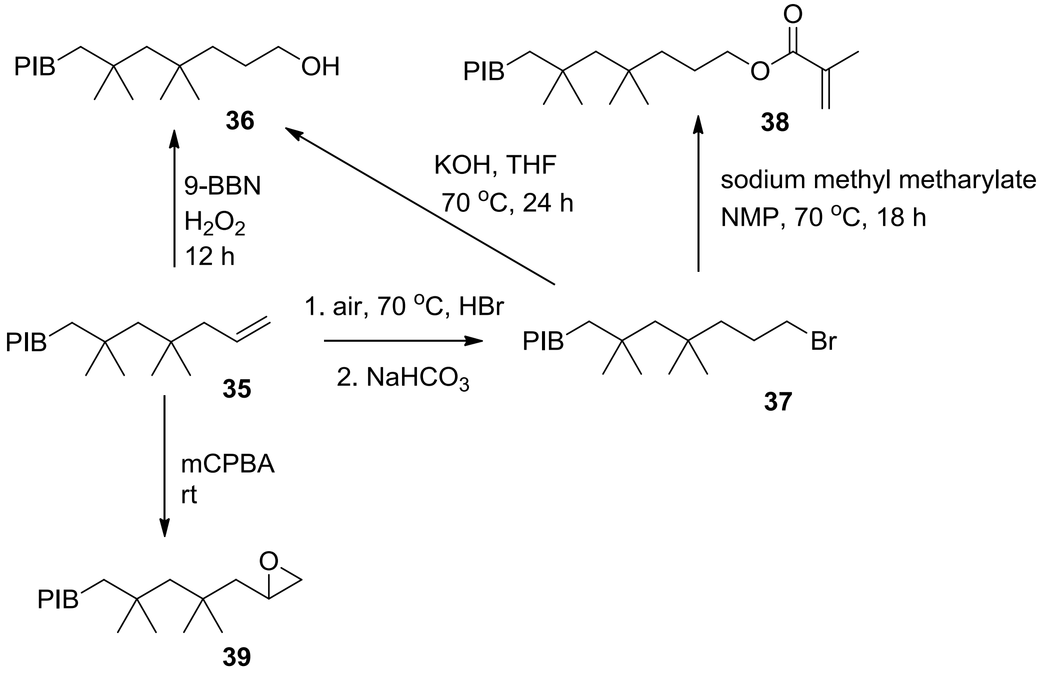


Scheme 11. Synthesis of PIB-*b*-P*t*-BMA and PIB-star polymer using PIB-thiophene.

Post polymerization modifications of PIB

Although, there have been many elegant chemistries developed for end functionalization of PIB in cationic polymerizations, there are still limitations in applying this tool in a broader scope due to functional group tolerance of the cationic polymerization reaction conditions and the fact that cationic polymerizations are not routine reactions in most laboratories. Thus, post polymerization modifications are an attractive tool in this regard. This is illustrated by many reactions where polymers formed in a cationic polymerization are transformed further into other functional groups by classical organic reactions such as addition, nucleophilic aromatic substitution, electrophilic aromatic substitution, eliminations and esterifications.

Allyl terminated PIB **35**, which was reported by Kennedy et al. has been transformed to other functionalities via simple organic reactions. Kennedy also proposed an inexpensive method of converting allyl-PIB to PIB-alcohol **36** using a nucleophilic substitution of a terminal primary bromide **37** by hydroxide in place of hydroboration /oxidation method. In addition, other economical methods for transforming allyl-PIB to -methacrylate **38** and -epoxides **39** have also been discussed (Scheme 12).[43]



Scheme 12. End functionalization of allyl terminated-PIB.

When an allylic halide terminated PIB is available from a cationic polymerization, it can also be further functionalized into variety of other functional groups via typical organic reactions such as nucleophilic substitution, addition elimination and esterifications. Some of these transformations are summarized in Figure 3.[44]

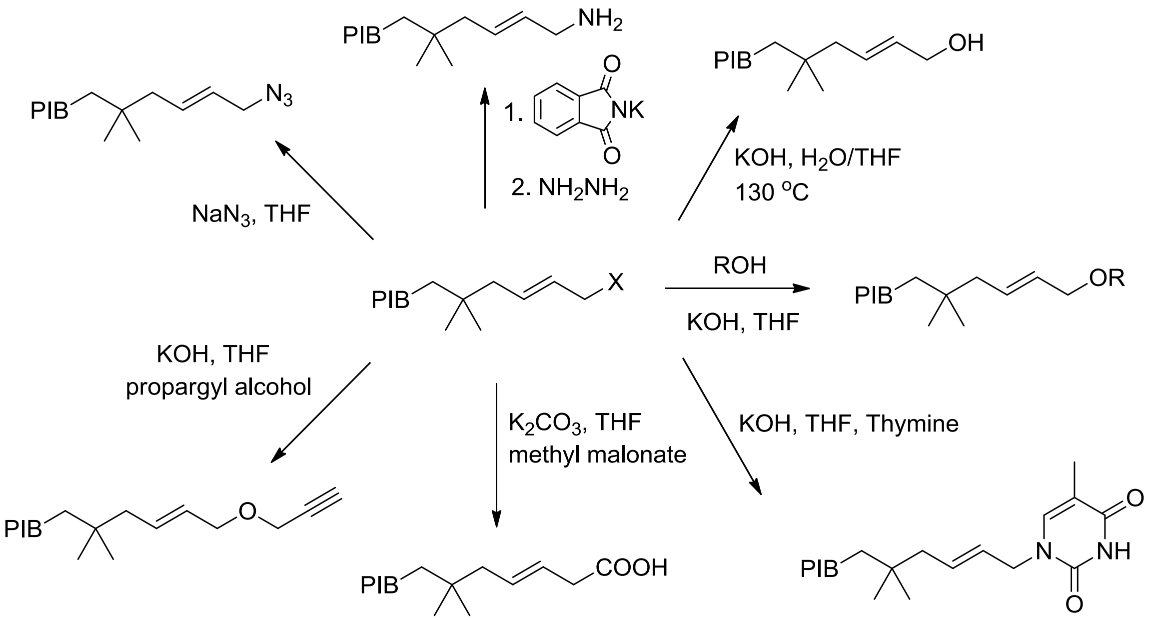
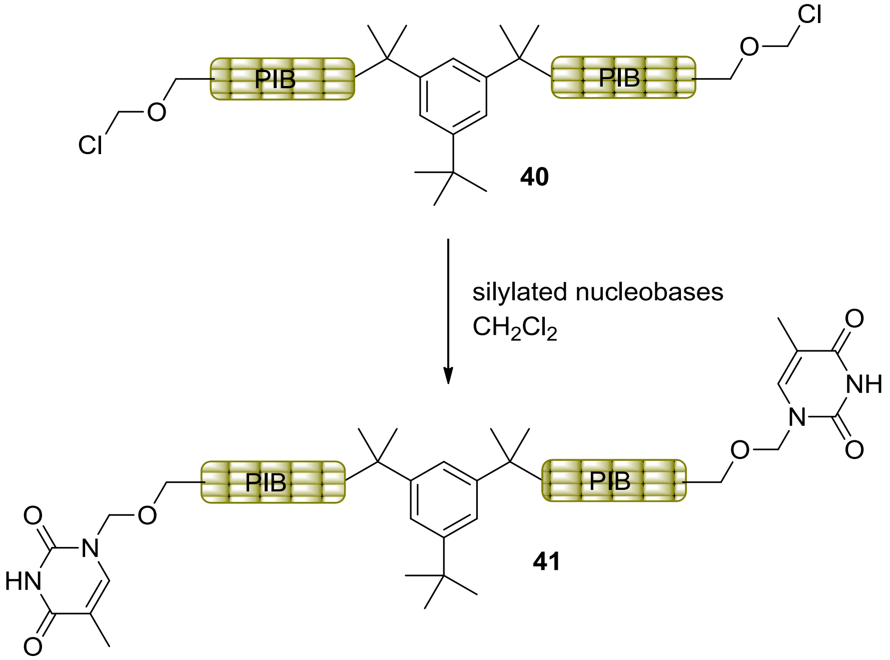


Figure 3. End functionalization of PIB-allyl halide with different nucleophiles.

Controlled synthesis of telechelic polymers with properly oriented hydrogen bonding moieties are of a great research interest for designing macromolecular architectures via non-bonding interactions.[45] Nucleobases are interesting candidates for defined hydrogen bond moieties. Therefore, immobilizing nucleobases on PIB polymer, which is flexible and soluble in many organic solvents, allows the study of the influence in hydrogen bonding on the PIB architecture. In this study, sialylated nucleobases such as thymine, uracil and cytosine were reacted with activated chloromethyl terminated PIB **40** to form nucleobase terminated PIB **41** (Scheme 13).

The Bergbreiter group too has a long-standing interest in developing strategies to use soluble polymer supports for precious ligands and transition metal catalysts. Immobilization of catalysts and reagents onto soluble polymer supports facilitates the green chemical synthesis by providing a strategy for catalyst recyclability that leads to less waste production. In pursuing this goal, polyisobutylene was recognized as a viable candidate as a soluble polymer support given polyisobutylene's properties of high chemical and oxidative inertness, gas impermeability and hydrophobicity. Over the last decade we have explored numerous alkene functionalizing chemistries for modifications of commercial vinyl terminated polyisobutylene and shown that the resulting PIB-end functionalized materials are indeed phase selectively soluble in non-polar solvents such as heptane and toluene.[46]



Scheme 13. Synthesis of thymine end functionalized PIB.

These PIB derivatives are useful as soluble polymer supports for polymeric ligands or for transition metal catalysts providing non-polar phase handles for polymeric ligands otherwise soluble in polar phase.

Unlike other chemistries used in PIB derivatizations that require carbocationic polymerization, PIB oligomers used in this study were commercially available, inexpensive and available under the trade name Glissopal from BASF (MW = 1000, DP = 18 or MW = 2300, DP = 41). The Bergbreiter group is one of a number of other groups that have extensively studied post polymerization modifications of PIB by electrophilic aromatic substitution (EAS) reactions of arene compounds. Although the functionality efficiency of commercially available alkene terminated PIB is as noted in literature not one hundred percent,[43] the presence of unreacted alkane oligomers does not affect the functionalization chemistry. There is also 10-20 % of internal alkene present in these vinyl terminated PIB oligomers. The presence of this isomeric alkene does not affect this EAS chemistry either as the reaction proceeds via the same carbocation regardless of whether the alkene is tri- or disubstituted. I have observed that these substitution reactions on phenol and anisole are highly regioselective and form only para substituted PIB-arene derivatives (Figure 4).[47] However, while phenol and anisole are both good substrates for these EAS reactions, applying similar chemistry for EAS reactions of aniline derivatives to form aniline substituted PIBs were not promising giving no desired product. Fortunately, using a Lewis acid with PIB-aniline derivatives such as 2,6-dimethyl aniline, 2-isobutyl aniline and 2 ethylaniline were successfully alkylated via EAS reactions. However, this chemistry was not successful with unsubstituted aniline because aniline is either immiscible in vinyl terminated PIB at elevated temperature or it forms a complex with $AlCl_3$ Lewis acid and become immiscible in the reaction media.

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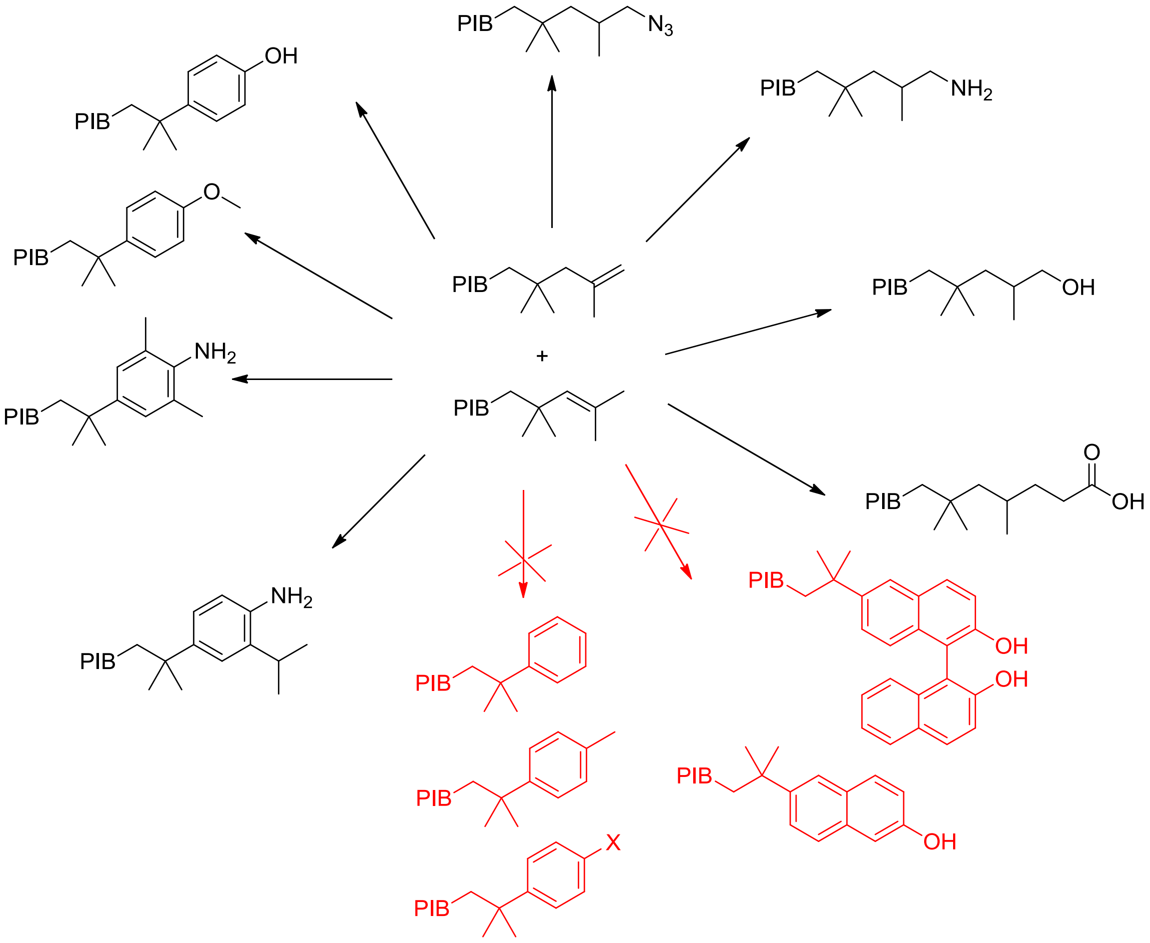

Figure 4. PIB-alkene functionalization *via* post polymerization reactions.

Attempts made towards using EAS reactions on un-activated arene compounds such as toluene and benzene with PIB-alkenes were unsuccessful even with large excess of these arenes as solvents or at elevated temperatures. Instead of substitution, depolymerization of PIB was observed. Given the high success of phenols to EAS reactions with PIB alkenes, we also examined 2-naphthol and BINOL as substrates for Friedel-Crafts arylation of PIB. These substrates too gave unsatisfactory results (Figure 3).

In the subsequent chapters, my work particularly focused on the design and synthesis of end derivatized PIBs via PIB-diazonium salt intermediate, will be discussed first. Some of these synthesized PIB-azo-phenol derivatives can in turn act as ligands for palladium metals and thus form PIB-palladacycles pre-catalysts for Pd-catalyzed cross coupling reactions. The synthesis of a PIB-azophenol palladacycle as a recyclable pre-catalyst and catalyst recovery strategies for such catalysts will also be discussed next. Then I will describe immobilization of another ligand, bipyridine, on PIB support and synthesis of recyclable visible light photo-redox catalyst, PIB-bipyridine ruthenium and its application in free radical polymerization reactions. Finally, I will discuss the use of PIB-derivatives to prepare highly soluble metallophthalocyanines.

CHAPTER II

SYNTHESIS OF TERMINALLY FUNCTIONALIZED POLYISOBUTYLENE DERIVATIVES*

Introduction

Polyisobutylene (PIB) is an important polymer and many procedures can be used to prepare terminally functionalized derivatives of this polyolefin. As mentioned in the Chapter I, a variety of elegant and sophisticated chemistry can be used during a cationic polymerization to introduce terminal groups via functional initiators and during or after a termination step.[10,22,32,33,37,38,40,48-55] However, as PIB polymers with terminal alkene functionality are commercially available, postpolymerization modification reactions are also useful and of interest especially for groups not interested in carrying out living cationic polymerization chemistry. The Bergbreiter group has recently described a number of examples of terminally-functionalized PIB oligomers that are useful in organic synthesis and catalysis.

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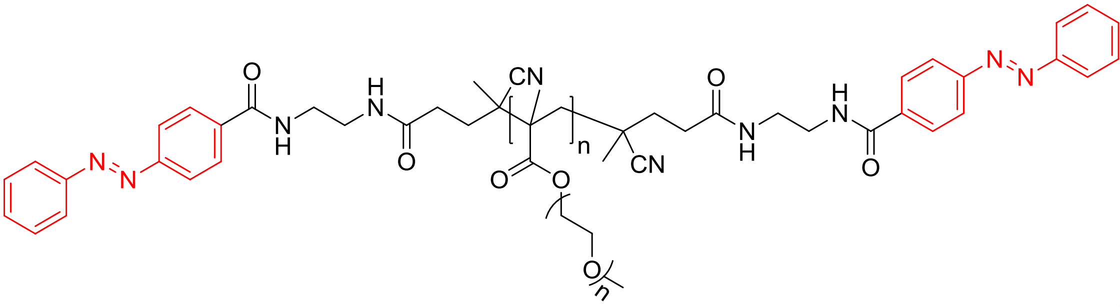
Diazonium salts have been studied as versatile intermediates for many chemical transformations. Synthesis of a PIB-bound diazonium salt too would be a useful route for functionalizing terminal vinyl functionalized PIBs. Diazonium salts can be used to immobilize a variety of activated arenes via electrophilic aromatic substitution reactions; hence PIB chain ends that could be prepared with diazonium groups can be used to incorporate a variety of other arene groups whose direct incorporation would be problematic.

For example, this method provides a synthetic route for synthesis of PIB-bound azo dyes. Azo dyes are the major class of industrially produced dyes that are used to dye textiles and to prepare inks. In addition to highly colored nature of these azodye compounds, the azo moiety also has interesting properties such as photoresponsive behavior as an azo group can isomerizes from the *trans* form to the thermodynamically less stable *cis* form under irradiation by UV light and reverses the isomerization process under visible light irradiation. This light responsive behavior of azobenzene units has been thoroughly investigated in potential applications and has been used to design photo-switchable devices, responsive polymer brushes, optical data storage devices, and to prepare sensors for use in drug delivery systems. If the azobenzene moiety is bound to a polymer into which other responsive properties are engineered, materials can be designed that will be multiresponsive to external stimuli such as light, heat, pH and viscosity.[56-61] Therefore attaching azobenzene groups to other polymers such as poly(ethylene glycol) (PEG) and poly(*N*-isopropylacrylamide) (PNIPAM) or onto macromolecular architectures such as polymer brushes, dendrimers,[62] cyclodextrins

(CDs) and surface functionalized nanoparticles (NPs),[63] extends the various applications of these materials (Figure 5). For example, azobenzene end functionalized poly(oligoethylenemethylether methacrylate) P(OEGMA) **42** showed thermoresponsive solubility of the PEG moiety in aqueous media and light responsive behavior due to *cis*-*trans* isomerization of telechelic azobenzene end groups of the polymer chain. These sorts of PEG derivatized polymers exhibit interesting solubility properties in aqueous media and it shows different lower critical solution temperatures (LCST) - the temperature below which the polymer is soluble in the solvent at all compositions, depending on the length of the PEG side chain. This particular azobenzene end functionalized P(OEGMA) **42** showed LCST values that varied from 43.4 °C - 58.4 °C with the varying molecular weights of 3800 g mol^{-1} – 7900 g mol^{-1} for the PEG moiety.

The LCST of the polymer solution exhibited a strong dependence upon the azobenzene content in the polymer chain too. Polymers with higher hydrophobic azobenzene content showed a decrease in the LCST. The solubility of this polymer **42** was also controlled by light. The isomerization of azo functional group from *cis* to *trans*, is accompanied by a dipole moment change in the polymer structure with the *cis* form being more polar. This increased local polarity increased the LCST ca. ~5 °C.[58]



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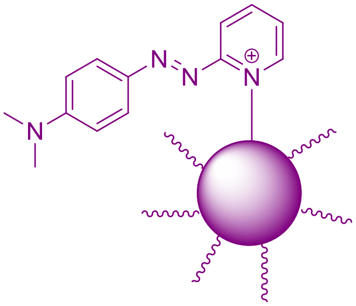

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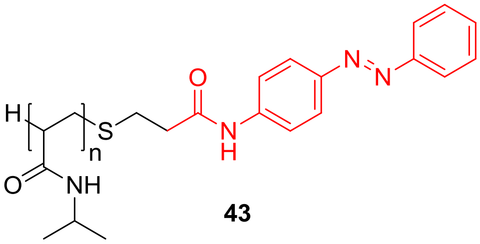

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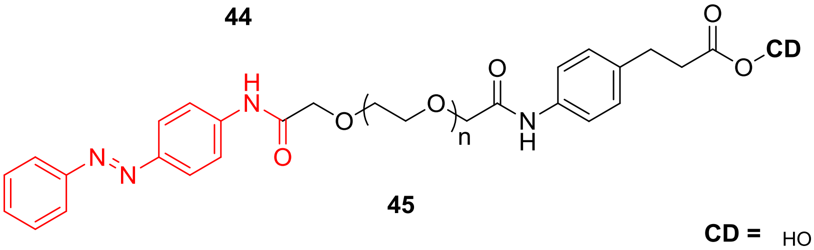

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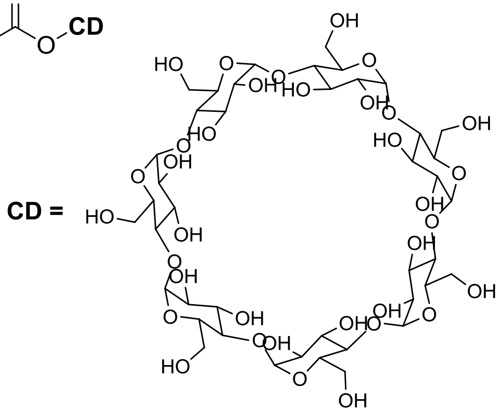

Figure 5. Azobenzene derivatized responsive polymers.

In another study by Ritter et al. synthesized poly(*N*-isopropylacrylamide) polymer **43** which was thermo and pH responsive. This polymer **43** end functionalized with azobenzene moieties with orange color at pH 7 and has a UV_vis absorption at λ_{max} - 460 nm. Upon decreasing the pH from 7 to 2, a large red shift of λ_{max} ca. 550 nm occurred upon protonation of the azodye group.[64]

Dye doped nanoparticles have attracted much attention due to their unique properties and their applications as labeling and sensing tools. Because of their smaller size NPs can be retained in cellular environment with minimal disruption and thus dyed NPs is important in novel sensing devices. Well defined colored NPs have been synthesized with covalently linked azobenzene choromophores. In this study, azobenzene dyes with either electrophilic groups or with nucleophilic groups were first synthesized and were then grafted onto the surface of covalently functionalized NPs. As shown in Figure 5, pyridylazomethylaminobenzene was grafted on to the surface of NPs **44** and the quaternization of the pyridyl moiety occurred with a distinct color change from orange to violet. This color change associated with a change of the azo dye provided an additional advantage as it provided evidence of the extent of success of the reaction where the azodye was grafted to the surface of the NPs.[63]

Stereochemical changers of supramolecular architectures can also be controlled by attaching light responsive azobenzene functional moieties to molecular structure. PEG-substituted β-cyclodextrins (CD) are good candidates for studying stereochemical changers in solution and end functionalization of these sorts of materials with azobenzene moieties can stimulate the photoresponsive conformational changes in the supramolecular architecture. As shown in Figure 5, PEG-CD can be functionalized with an azobenzene end group to form **45.** The conformation of this polymer **45** can be thermally and photochemically controlled. For example, at 1 °C the polymer exists as an elongated chain in the solution while it forms a self-inclusion complex with CD upon heating to 60 °C. Photoresponsive behavior was also seen after irradiating the polymer solution with UV light. In this experiment, the *cis*-azobenzene-PEG-CD polymer formed a self inclusion complex which deforms upon visible light irradiation to form trans-azobenzene-PEG-CD linear polymer.[64,65]

Pioneering work in the Bergbreiter group has also utilized the thermoresponsive behavior of *N*-isopropylacrylamide (PNIPAM) polymer as a phase separable catalyst support. In that work, PNIPAM was labeled with azodyes for spectrometric analysis of the efficiency of the thermoresponsive phase separation of the PNIPAM from the reaction solutions. In this case, a tri block copolymer of PNIPAM, a soluble polymer bound analogue of 4-(dimethylamino)pyridine (DMAP) -4-dialkylaminopyridine (DAAP) and methylred was synthesized. The PNIPAM bound catalyst **46** was soluble in polar solvents such as dimethylformamide or acetonitrile. The catalyst recovery of this sort was accomplished by adding a non-polar solvent (hexane) to the reaction mixture to enhance the polymer precipitation. The efficiency of the precipitation of the catalyst **46** can be visually and spectroscopically observed due to the presence of azodye label (Figure 6).

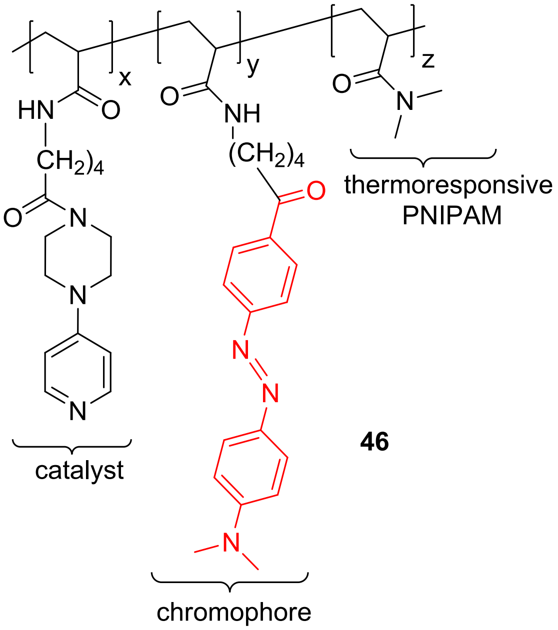

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Figure 6. PNIPAM-DAAP-azodye copolymer.

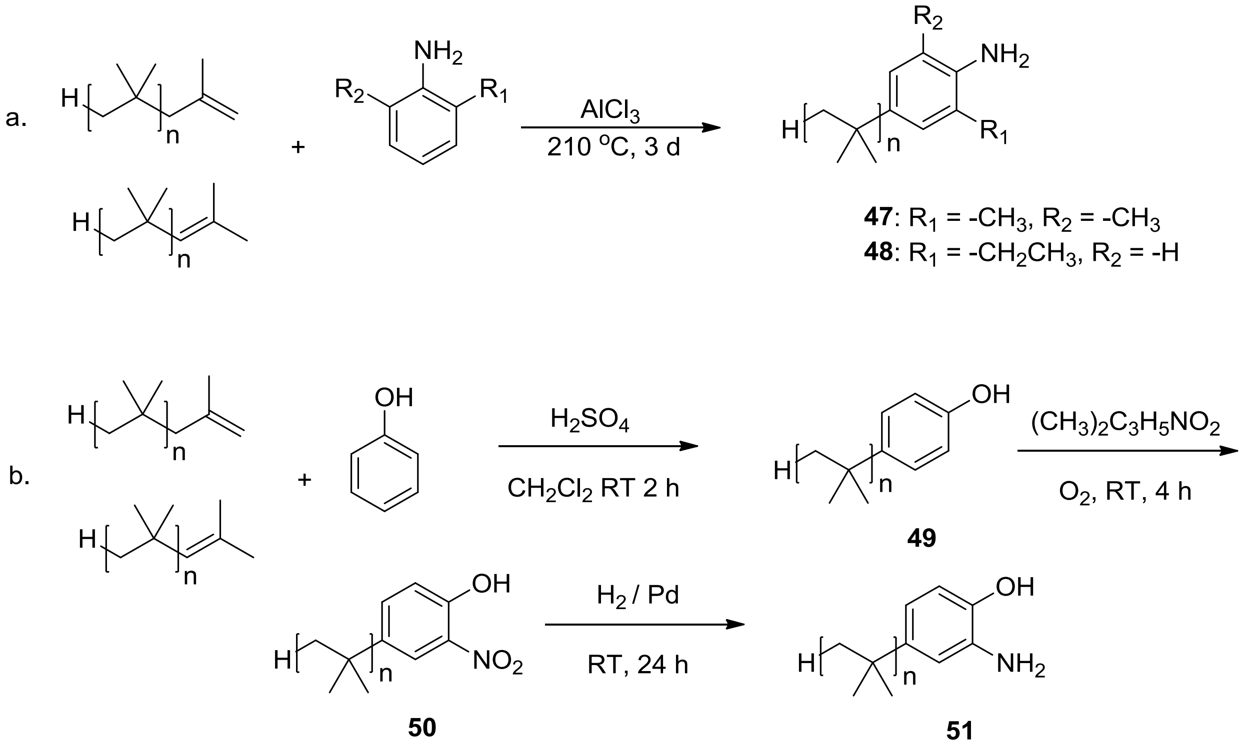
We here describe the advantages and limitations of diazonium salts as intermediates in the end functionalization of PIB. This chemistry uses a versatile reactive intermediate and provides access to a range of terminal functional groups that includes not only PIB -azo dyes but also other useful functional moieties including aryl halides, arenes, and products from Pd catalyzed C-C cross coupling reactions. Such species are potentially useful because they provide functional group handles for attaching ligands or reagents to PIB supports and lead to supported ligands and reagents with spectroscopic diazoarene labels.[60]

The substrates have also allowed us to study the kinetics of an azo substitution reaction of a PIB-bound diazonium salt and to compare this polar substitution reaction at the terminus of PIB in nonpolar solvents with reactions of low molecular weight substrates in polar solvents. The results show that the effects of solvent and substrate in this chemistry are relatively modest.

Results and discussion

Initial objective of this work was to synthesize PIB-bound aniline derivatives as precursors for diazonium salt synthesis. Past work from the the Bergbreiter group has shown that PIB-bound anilines can be synthesized via the electrophilic aromatic substitution (EAS) chemistry shown in Scheme 14a. Commercially available vinyl-terminated PIB precursors can be terminated with either disubstituted or trisubstituted double bonds. Either alkene is equally useful, because each alkene undergoes regioselective protonation under the reaction conditions to form the same electrophilic tertiary carbocation intermediate. The aniline derivatives formed via this chemistry (Scheme 14 a) are chemically analogous to low molecular weight aryl amines that can be used as precursors of aryl diazonium salts.

As mentioned in Chapter I, Friedel Crafts alkylation of phenols of PIB alkene was feasible under much milder conditions compared to the conditions applied with aniline derivatives. Therefore PIB-phenol derivatives were also investigated as potential PIB-aniline precursors. As shown in Scheme 14 b, PIB-phenol can be synthesized under milder reaction conditions- room temperature and shorter reaction times, and so formed PIB-phenol can undergo *ortho*-nitration under aerobic conditions to form PIB-nitrophenol **50**. The catalytic hydrogenation of PIB-nitrophenol readily produced PIB-aminophenol **51**.

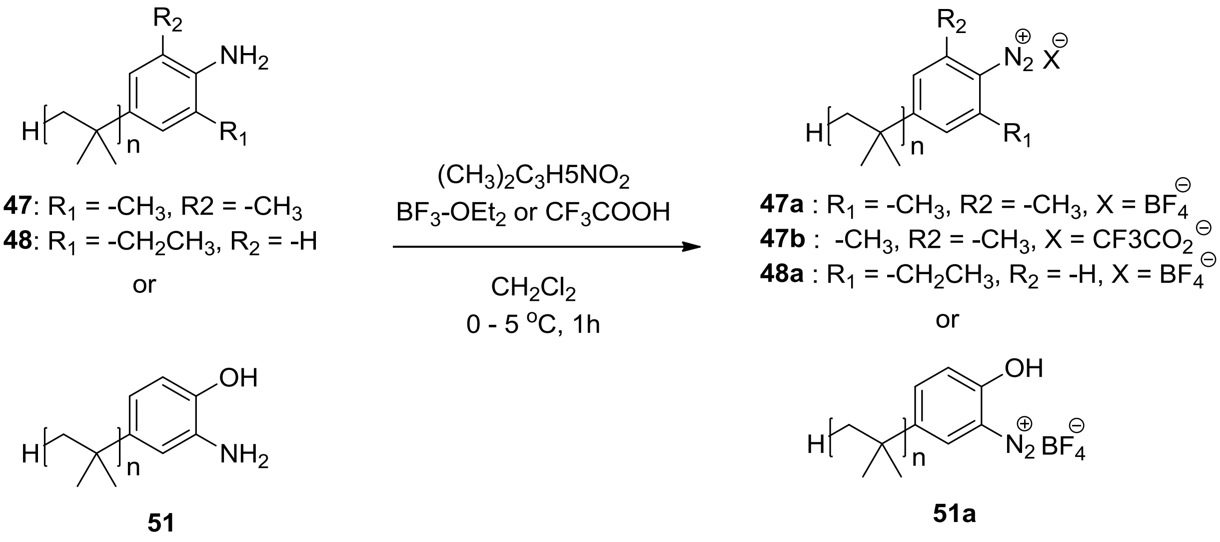


Scheme 14. (a) Synthesis of PIB-substituted anilines 47 and 48 via EAS reaction and (b) Synthesis of PIB-aminophenol 51.

However, the nitrous acid diazotization chemistry most often useful for the conversion of an aryl amine into a diazonium salt is typically carried out in polar solvents, solvents that are incompatible with nonpolar polymers in general and incompatible with nonpolar PIB derivatives like **47**, **48** or **51** in particular. PIB-bound anilines **47**, **48** and **51** are only soluble in nonpolar solvents like heptane, toluene, dichloromethane (CH_2Cl_2) or tetrahydrofuran (THF).

This work describes how we have extended this diazo chemistry to nonpolar polymers that contain anilines using PIB-bound aryl amines as substrates for formation of aryl diazonium salts. These studies then show the scope and limitations of known diazonium chemistry for these polymer-bound diazonium salts. The results of these studies show that these intermediates have broad synthetic use. Kinetic studies also show that substitution reactions that proceeded via polymer-bound diazonium salts in nonpolar solvents proceed without a significant solvent effect and at a rate comparable to that seen for low molecular weight analogs in polar solvents.

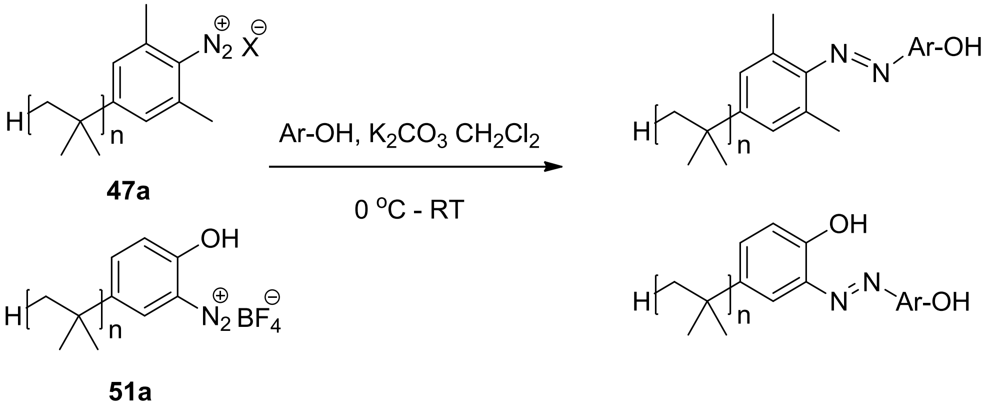
Initial objective of this work was to explore the potential of diazonium salts as intermediates for functionalization of nonpolar polymers by developing diazotization chemistry that could be carried out in relatively nonpolar aprotic solvents - solvents that would be suitable for a nonpolar aryl amine - containing PIB polymers like **47**, **48** or **51.** This was accomplished by using isopentyl nitrite and an acid to effect nitrosation in a nonpolar aprotic solvent. This reagent has been reported previously and was used for the synthesis of 1,3-diaryltriazines of low molecular weight aryl amines in alkanes or mixtures of alkanes and benzene.[66] This reaction is thought to proceed via diazonium salt intermediates. Gratifyingly, we found that the reaction of isopentyl nitrite in CH_2Cl_2 or THF in the presence of boron trifluoride etherate or trifluoroacetic acid with PIB-aniline derivatives -4-polyisobutyl-2,6-dimethylaniline **47**, 4-polyisobutyl-2-ethylaniline **48** or 3-polyisobutyl-6-hydroxyaniline **51** led to complete conversion of these aryl amine-terminated PIB derivatives to form the diazonium salts **47a**, **47b**, **48a** and **51a** (Scheme 15). The conversion of the aryl amine to the diazonium salts in these reactions was monitored by ^1H NMR spectroscopy, where the aryl protons at C3 and C5 of **47** shifted downfield by ca. δ 0.5 ppm and the aryl protons at C3, C5, and C6 of **48** shifted downfield by 0.8, 0.5, and 0.4 ppm on formation of the salts **47** and **48**, respectively.



Scheme 15. Formation of PIB-bound diazonium salts of 47, 48 and 51 in CH_2Cl_2 using isopentyl nitrite and an acid.

The solutions of the diazonium salts **47a**, **47b**, **48a** and **51a** so formed had modest stability. The diazonium salts could be isolated and characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. Either the isolated salts or the solutions of the diazonium salts could be used in further reactions to transform these PIB-bound diazonium salts into other PIB derivatives. In either case, the diazonium salts had to be used promptly, as in solution at 25 °C or on storage as oils over 4 -5 days in a refrigerator some decomposition occurred (cf. the kinetic data for the decomposition of **47a**, vide infra).

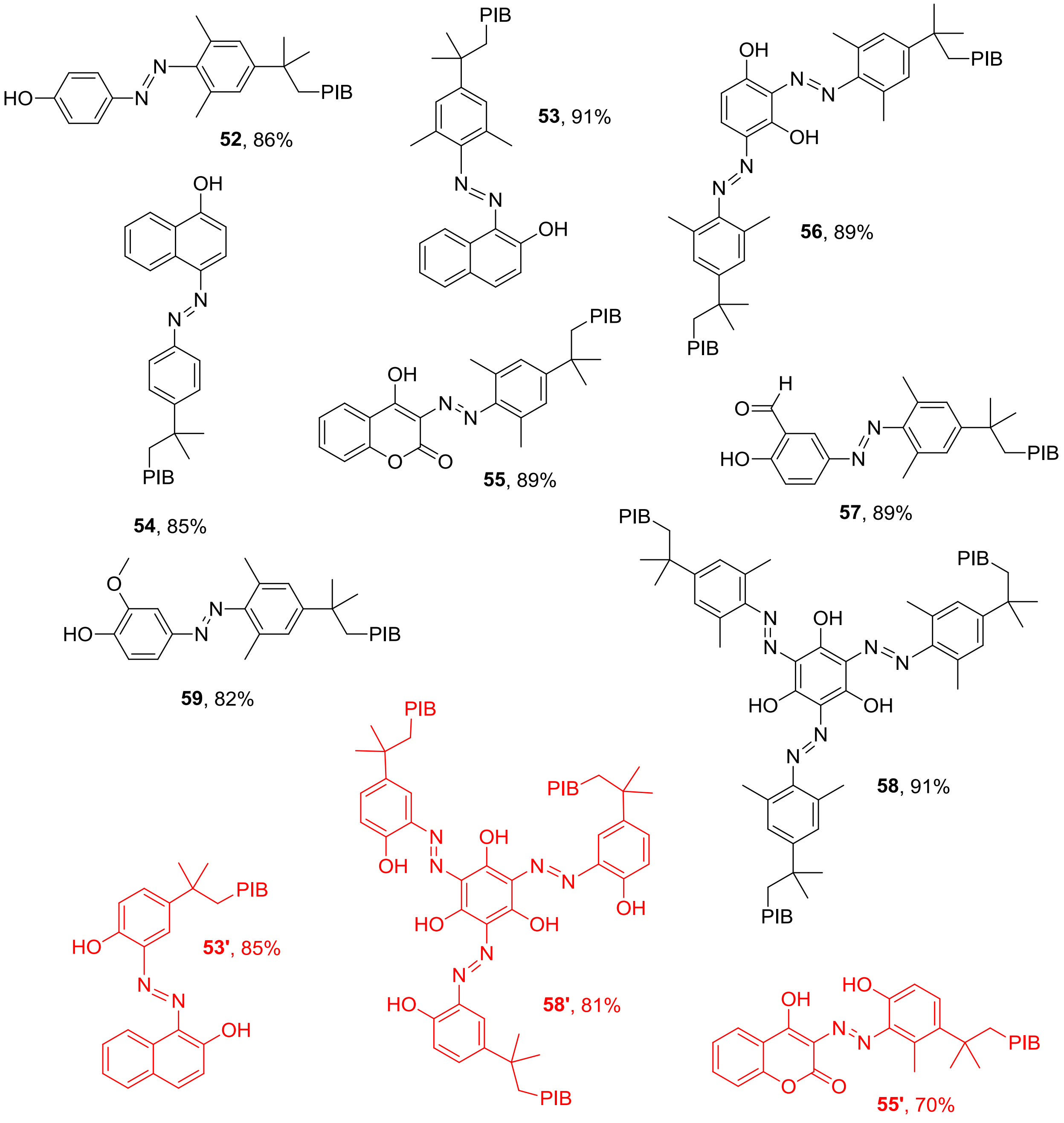
Electrophilic aromatic substitution reactions of PIB-bound diazonium salts and phenols



Scheme 16. Electrophilic aromatic substitution reactions of phenols in CH_2Cl_2 by the diazonium salt 47a and 51a.

We first explored the use of PIB-bound diazonium salts prepared in Scheme 15 as electrophiles in the electrophilic aromatic substitution reactions of phenolic derivatives. This reaction generally worked well in the presence of a base (K_2CO_3 Scheme 16) to form PIB-bound azo dyes useful in our other studies of PIB's phase selective solubility. The yields and scope of these phenolic coupling reactions are summarized in Figure 7.

The principle side reaction observed in the phenolic coupling reactions shown in Scheme 16 was reduction of the aryl diazonium salt to form an arene. This formation of an aryl-terminated PIB product was pronounced when the phenolic coupling partner was a good reducing agent. Indeed, when the dihydroxyarenes hydroquinone or catechol were allowed to react with either **47a** or **47b**, none of the azo dye product was seen. The only product seen was the reduced product. However, while an azo dye was not formed in this chemistry, the reduced PIB product that contains a 3,5-dimethylaryl or 3-ethylaryl substituent that did form is still of interest because weakly or unactivated arene-terminated PIBs are not available directly from the starting vinyl-terminated PIB by electrophilic aromatic substitution. As would be expected, the products of the azo coupling of a polymer-bound diazonium salt and a phenol are highly colored compounds. The λ_{max} for the azo dye-terminated PIB varied depending on the nature of the electron-rich aryl ring in the azo dye as shown in Figure 8. These azo dyes, like their low molecular weight analogs, have colors that vary on protonation with the λ_{max} undergoing a bathochromic shift on formation of the conjugate acid. Typical extinction coefficients for these dyes are in the 10,000–20,000 M^{-1} cm^{-1} range, values that are comparable with those reported for similar low molecular weight dyes.



52, 86%

53, 91%

56, 89%

54, 85%

55, 89%

57, 89%

59, 82%

58, 91%

53', 85%

58', 81%

55', 70%

Figure 7. PIB-bound phenolic azodyes formed by electrophilic aromatic substitution reactions of PIB-diazonium salt 47a and 51a.

Because of the polyisobutyl group, the PIB-bound dyes **52** - **59** shown in Figure 7 are phase selectively soluble in heptane in biphasic mixtures of heptane and a more polar heptane- immiscible solvent. This is illustrated by the photograph in Figure 9, where two examples of these PIB-bound dyes, **52** and **53** are both seen to be selectively soluble in heptane versus acetonitrile.

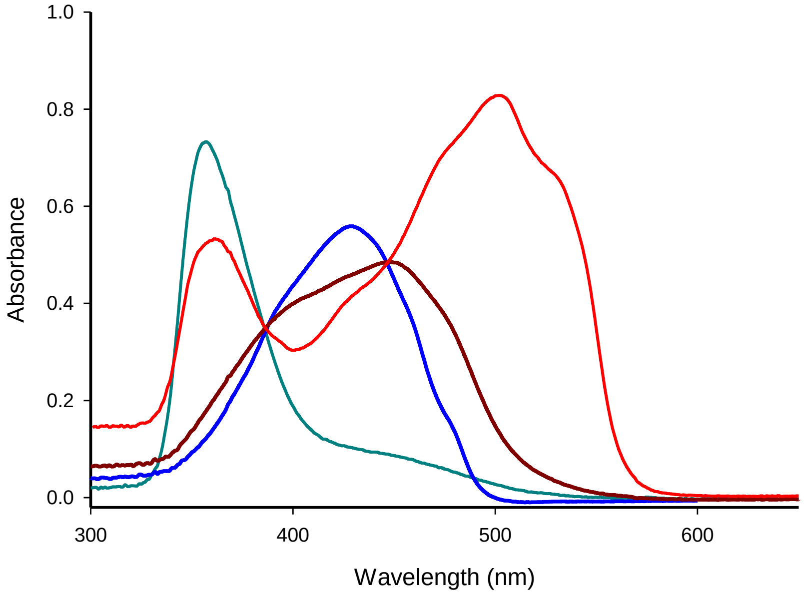


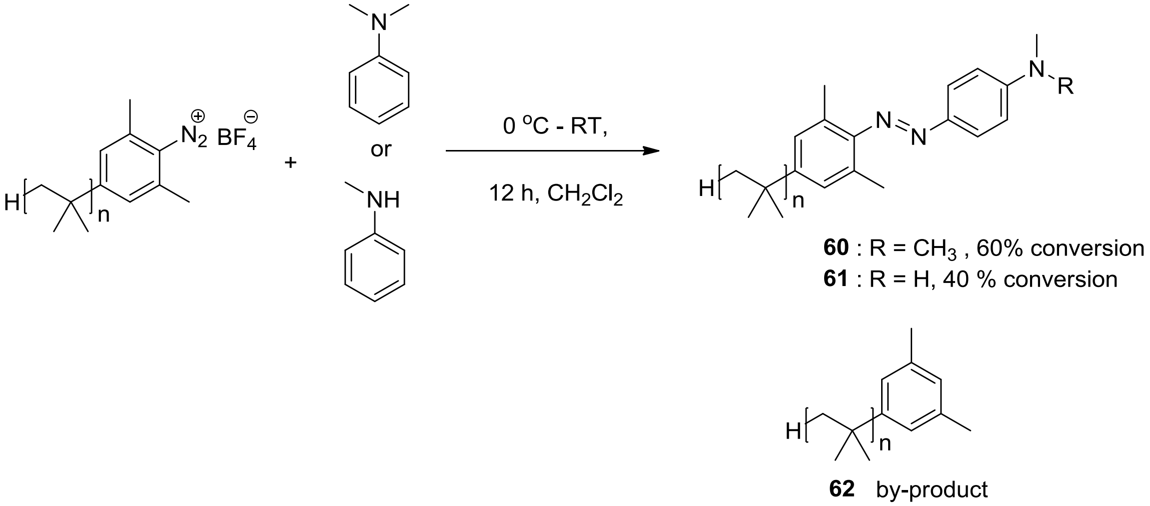
Figure 8. UV–visible spectra of solutions of PIB-bound azodyes, 54 (red, λ_{max} = 503 nm), 55 (maroon, λ_{max} = 470 nm), 56 (blue, λ_{max} = 428 nm) and 52 (green, λ_{max} = 371 nm) in heptane.

Figure 9. Phase selective solubility of the PIB-bound azodyes 52 (yellow) and 53 (red) in heptane (top phase) versus acetonitrile (bottom phase).

Electrophilic substitution reactions of anilines by the PIB-bound diazonium salt 47a

Anilines are another class of electron rich arenes that serve as nucleophiles in electrophilic aromatic substitution reactions of aryl diazonium salts. We briefly examined the reaction of both *N*,*N*-dimethylaniline and *N*-methylaniline with **47a** as an example of this type of chemistry. As shown in Scheme 17, we obtained modest yields of this coupling reaction with both this tertiary- and secondary-amine. In these reactions, **47a** was completely consumed based on ^{1}H NMR spectroscopy.

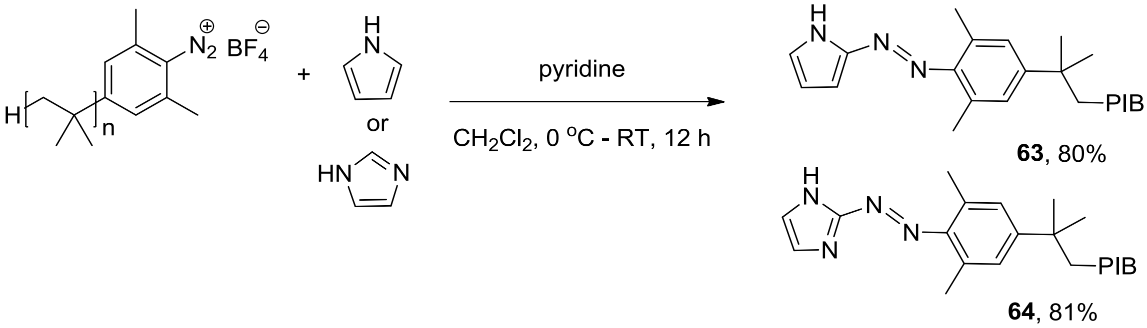
The by-product that formed was the reduced arene. Although we did not attempt to isolate **60** as a pure product, ^{1}H NMR spectroscopy showed it was formed in 60% yield. We were able to show that column chromatography could separate the reduced aryl-terminated PIB derivative from the dye **61** to afford a 54% yield of **61** uncontaminated by the reduced by-product **62**.



Scheme 17. Electrophilic aromatic substitution of *N,N*-dimethylaniline and *N*-methylaniline by the PIB-bound diazonium salt 47a to from azodyes 60 and 61.

Electrophilic substitution reactions of heterocyclic compounds by the PIB-bound diazonium salt 47a

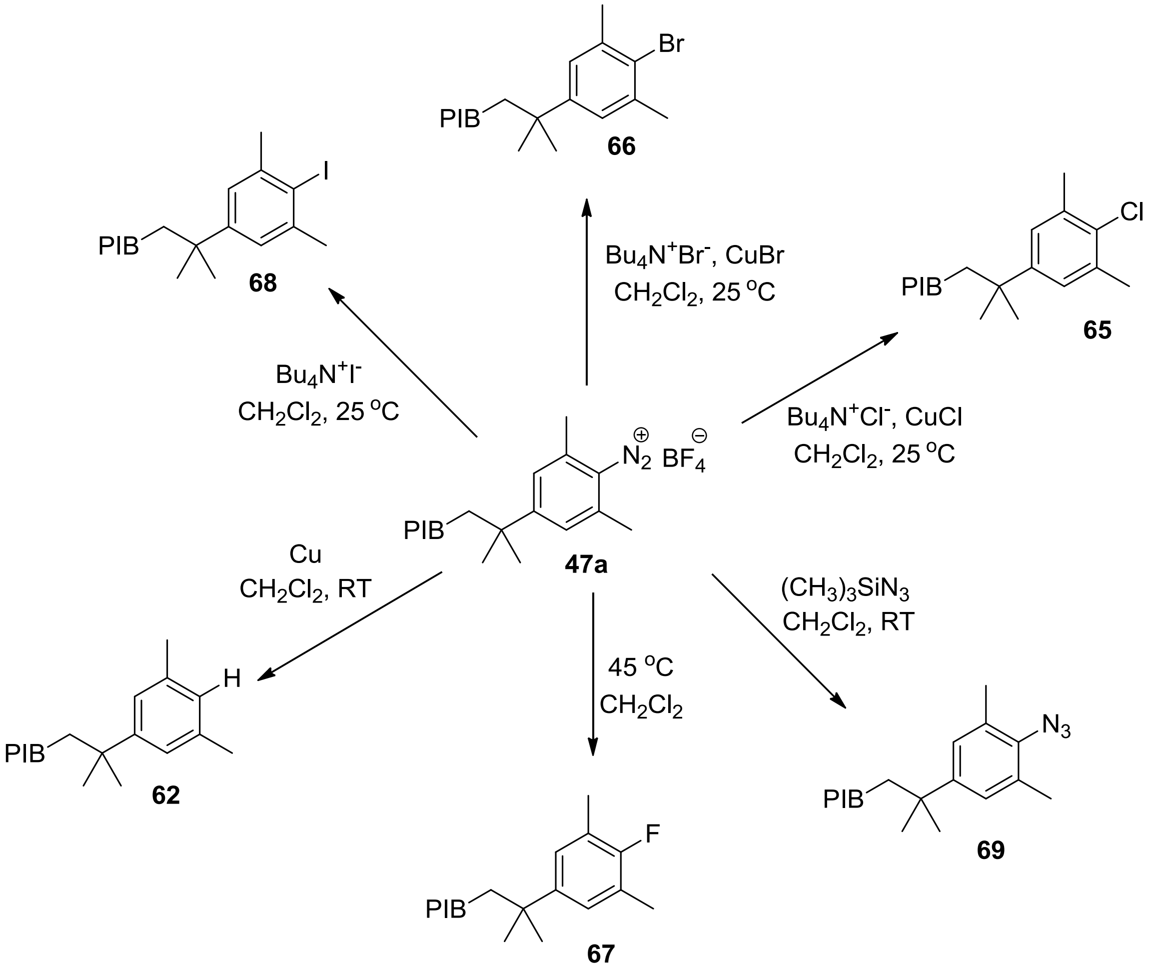
We also examined the use of electron-rich heterocyclic compounds like pyrrole and imidazole as nucleophiles in electrophilic aromatic substitution reactions of low molecular weight diazonium salts. PIB functionalized diazonium salts also react with these heterocycles. For example, as shown in Scheme 18, **47a** and pyrrole undergo an electrophilic aromatic substitution in the presence of pyridine as a base to afford the heterocyclic azo dye **63** in excellent yield. Imidazole as the nucleophile was equally effective in forming **64**. In both reactions, **47a** exhibits high regioselectivity in the substitution reactions as is seen with a low molecular weight diazonium salt.



Scheme 18. Electrophilic aromatic substitution of heterocycles by the PIB-bound diazonium salt 42a to form azodyes 61 and 62.

Substitution reactions of PIB-bound diazonium salts

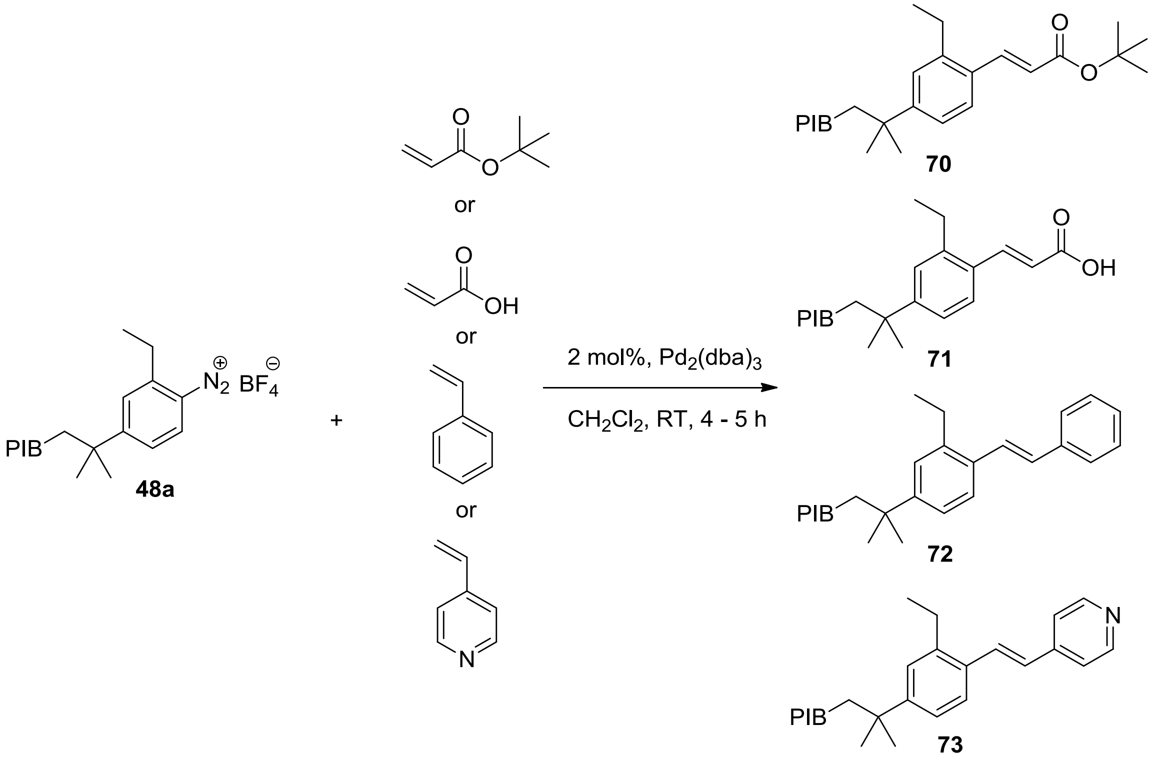
Diazonium salts are widely used as intermediates for the synthesis of substituted arenes. For example, the Sandmeyer reaction is a classical organic reaction that is used to convert aryl amines to aryl halides via aryl diazonium salt intermediates. This chemistry works equally well with PIB oligomers containing terminal diazonium salts as shown in Scheme 19. These substitutions are carried out under a variety of conditions. In the case of both chloro-substitution and bromo-substitution, a Cu(I) catalyst is required for the reaction to proceed. Both reactions worked best with a soluble tetrabutylammonium halide as the source of the chloride or bromide in formation of the chloroaryl- and bromoaryl-terminated PIBs **65** and **66**. A trace amount of the fluoroaryl-terminated polymer **67** (presumably from thermal decomposition of **47a**) was present in the isolated product **65**. Synthesis of the iodoaryl-terminated polymer **68** from **47a** was successful and no Cu(I) catalyst was required. The fluoroaryl-terminated PIB derivative **67** was formed in excellent yield simply by thermal decomposition of **47a**.



Scheme 19. Substitution reactions of PIB-bound diazonium salts to form 62 and 65–69.

Other substitution reactions of PIB-bound diazonium salts were also successful. This included the synthesis of an azide derivative **69** and reduction of the PIB-bound diazonium group by Cu powder to form a 3,5-dimethylaryl substituent (**62**). This latter reaction is noteworthy because it demonstrates that terminally functionalized PIB derivatives can be modified under biphasic conditions.

Palladium catalyzed substitutions of PIB-bound diazonium salts



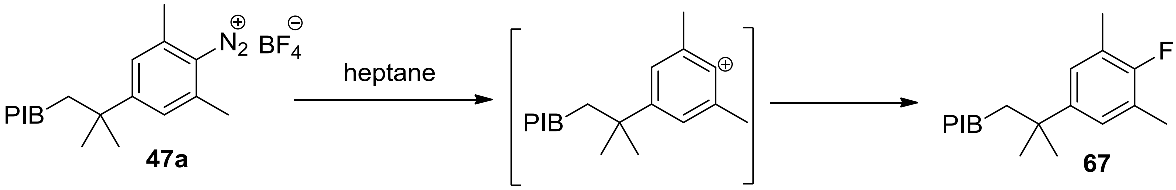
Scheme 20. Mizoroki-Heck cross-coupling reactions using the PIB-bound diazonium salt 48a.

Diazonium salts are also attractive substrates for Pd-catalyzed cross-coupling reactions. Given the broad utility and popularity of Pd-catalyzed cross-coupling reactions in synthesis, we examined the utility of PIB-bound diazonium tetrafluoroborate salts **47a** and **48a** in Pd-catalyzed cross-coupling chemistry. Our initial studies examined **47a** as a substrate in Mizoroki-Heck reaction with *tert*-butylacrylate. The results were disappointing. This reaction produced only 10% of the desired cross coupling product.

The bulk of the product was the reduced arene-terminated PIB derivative **62**. However, reaction of the less crowded diazonium salt **48a** led to a more successful result. Using **48a**, Mizoroki-Heck reactions were successful using olefins as acceptors including *tert*-butylacrylate, acrylic acid, 4-vinyl pyridine, and styrene. These reactions occurred in 4-5 h at room temperature using 2 mol % of the Pd catalyst $Pd_2(dba)_3$ as shown in Scheme 20 above. The lack of success in cross-coupling chemistry seen with **47a** in contrast to the success seen in similar reactions using **48a** is ascribed to the steric hindrance in the substrate **47a** that is absent in **48a**.

Kinetic studies of polar substitution reactions of the PIB-bound diazonium salt 47a

Although our original goal in this work was to develop the synthetic chemistry of PIB-bound diazonium salts as a route to a variety of functional PIB oligomers including dye-labeled materials we could use in other chemistry being explored in our group, the chromogenic properties of these diazonium salts and their convenient decomposition rates in solution allowed us to also examine the kinetics of polar reactions of these nonpolar polymers in nonpolar solvents and to compare these reactions with reactions in more polar solvents or mixed solvents. These studies also have allowed us to compare the kinetic behavior of these polymeric diazonium salts with known chemistry of low molecular weight diazonium salts. These studies followed the thermal decomposition of the tetrafluoroborate salt **47a** (cf. Scheme 21). In the absence of other nucleophiles, a fluoride from the tetra- fluoroborate counterion reacts with the phenyl cation formed after loss of nitrogen to form a fluoroarene-terminated PIB derivative.



47a

67

Scheme 21. Mechanism for the decomposition of the PIB-bound diazonium salt 47a via a phenyl cation to form the fluoroarene-terminated PIB derivative 67.

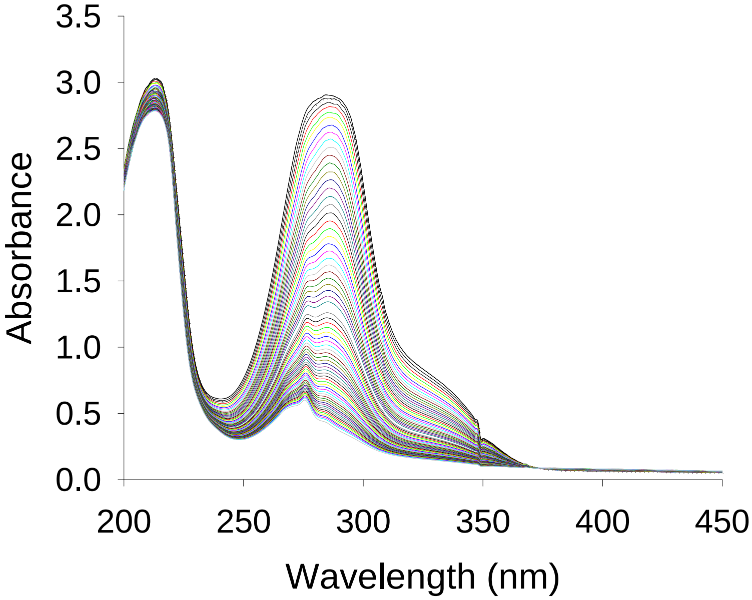


Figure 10. UV_visible spectroscopy studies of the time course for the thermal decomposition of 47a in heptane at 25 ^{o}C. The initial spectrum has a large absorbance at 288 nm that gradually decreases in intensity through the course of the reaction.

Earlier work using low molecular weight diazonium salts is most often discussed in terms of a reactive phenyl carbocation intermediate as shown in Scheme 21. These reactions proceed as first order reactions as if formation of an aryl cation intermediate is the rate-determining step in this reaction.

In the case of **47a**, we followed this decomposition process using UV_visible spectroscopy. A time course for a reaction in heptane at 25 ^{o}C is shown in Figure 10. Similar data were obtained in other solvents at other temperatures. These kinetic data can be analyzed to afford rate constants whose values are listed in Table 1. By examining reactions at various temperatures, we were also able to determine the enthalpy and entropy of activation for these reactions (Table 2).

Table 1. Rate constants for the decomposition of 47a in formation of 67 in various solvents at 25°C.

solvent	***k*** **(10^{-5} sec^{-1})**
heptane	4.3
cyclohexane	4.7
1,2-dimethoxyethane	6.0
methylene chloride	15.7
tetrahydrofuran	6.5
heptane/ 1,2-dimethoxyethane (90/10, v/v)	9.0
heptane/ ethanol (90/10, v/v)	15.3

The results of these studies show that this polar heterolysis reaction on PIB derivatives depends only to a small extent on the solvent, slowest and fastest rate been differed by only a factor of 4 in the various solvents or solvent mixtures. The rate constants we observe are very much comparable with rate constants reported earlier by Swain for dediazoniation of phenyldiazonium tetrafluoroborate. Those rate constants ranged from 1.1 to 4.5 10^{-5} sec^{-1} - values that are very similar to first order rate constants reported in Table 1 for the polyisobutyl-containing 1,4,6-trialkylsubstituted aryldiazonium salts in nonpolar solvents or modestly polar solvent mixtures. Eyring plots for three solvents or solvent mixtures shown in Table 1 had a linear relationship of ln(k/T) versus 1/T and allowed us to calculate the enthalpy and entropy of activation.

Table 2. Activation parameters for the thermal decomposition of 47a to form 67 in various solvents.

solvent	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta S^{\#}$ (cal $mol^{-1}K^{-1}$)
cyclohexane	26.5	9.7
1,2-dimethoxyethane	26.0	10.1
heptane/ ethanol (90/10, v/v)	26.0	10.0

The activation entropy was nearly identical to the favorable $\Delta S^{\#}$ reported earlier by Swain in studies of low molecular weight phenyldiazonium tetrafluoroborate decomposition in a variety of solvents. These results show that this very polar reaction that is thought to proceed via a phenyl cation-like intermediate is unaffected by the presence of a lipophilic nonpolar PIB substituent. These results like our earlier kinetic studies of CO_2/cyclohexane oxide polymerization using a PIB-bound salen catalyst, and our earlier studies of the dynamics of exchange of PIB-bound phosphine ligands on Ag(I) consistently show little or no difference between the kinetic behavior of low molecular weight reagents or catalysts and similar species bound to these PIB oligomers.

Conclusions

In summary, formation of diazonium salts of arylamine-containing nonpolar polymers is feasible using isopentyl nitrite in the presence of boron trifluoride etherate or trifluoroacetic acid. This is illustrated using PIB terminated with arylamines. These studies also show that the resulting PIB-bound diazonium salts undergo chemistry like their low molecular weight diazonium salt counterparts. Thus, these diazonium salts are versatile intermediates for terminal functionalization of PIB oligomers and can afford PIB-bound azo dyes and a variety of other PIB-bound aryl derivatives. Kinetic studies of the thermal decomposition of PIB-bound aryl diazonium tetra- fluoroborate salts were carried out. These studies show that the PIB-bound diazonium salts undergo decomposition presumably via an aryl cation like their low molecular weight counterparts and that these reactions' rates are largely unaffected by either the PIB group or the nature of the solvent.

CHAPTER III

RECYCLING AZOBENZENE PALLADACYCLE PRE-CATALYST USING POLYMERIC PHOSPHINE LIGANDS AND POLYETHYLENE AS A CO-SOLVENT*

Introduction

Carbon-carbon cross coupling reactions are among the most widely studied metal-catalyzed chemical transformations.[67-69] The various cross-coupling processes involving Mizoroki-Heck, Suzuki, Miyaura and Sonogashira reactions are catalyzed both by molecular catalysts that contain phosphine and *N*-heterocyclic carbene ligands and by colloidal palladium catalysts that are formed *in situ*. Regardless of the nature of the catalyst, this chemistry has been widely used in synthesis in academic and industrial laboratories and its importance was recognized by the 2010 Nobel Prize in chemistry to professors Heck, Negishi and Suzuki.

Homogeneous molecular complexes of Pd ligated by phosphine and *N*-heterocyclic (NHC) carbenes are highly active and useful catalysts for Pd-catalyzed cross-coupling chemistry.[70-75]

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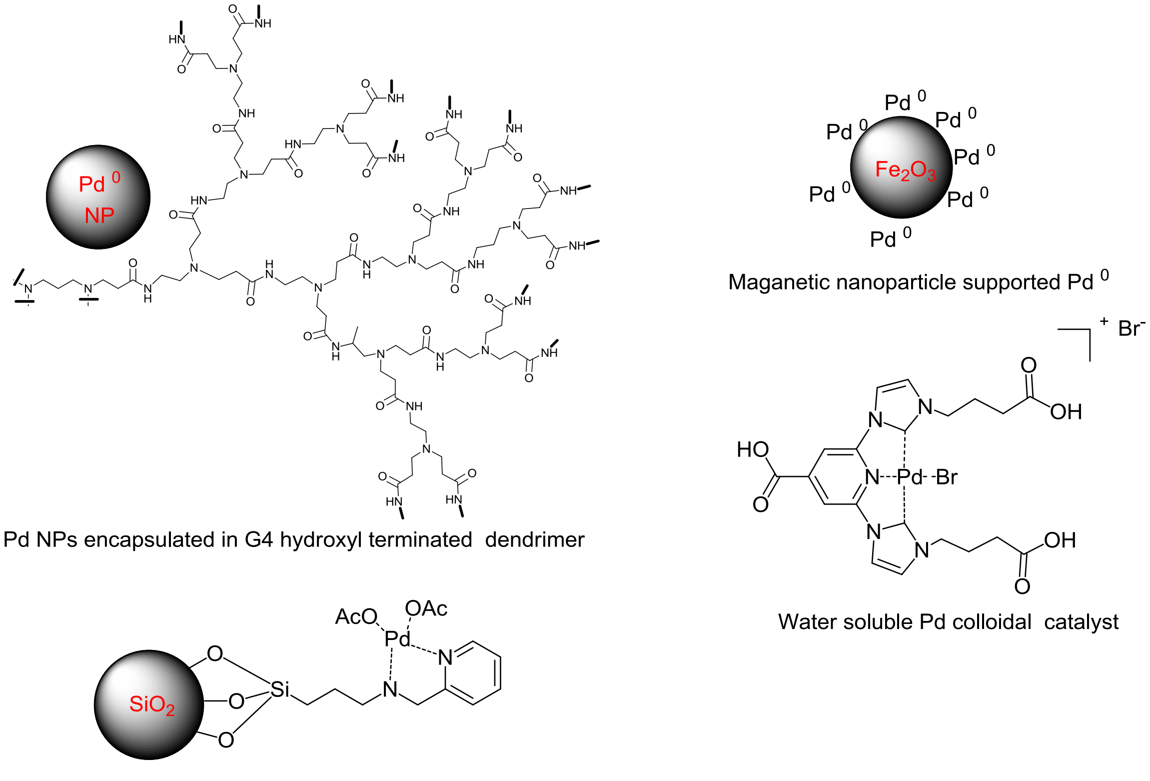
* "Recycling Pd colloidal catalysts using polymeric phosphine ligands and polyethylene as a solvent" Priyadarshani N.; Suriboot, J.; Bergbreiter, D. E. *Green Chem*. **2013**, *15*, 1361, Reproduced by permission of the Royal Society of Chemistry.

However, it has become increasingly apparent that Pd colloids generated in a designed fashion or inadvertently through decomposition or *in situ* reduction of a Pd(II) species are comparably efficient as catalysts for cross coupling chemistry.

The many examples that use what are variously described as colloidal or nanoparticle Pd species show the increasing importance of these sorts of catalysts.[76-81] Thus, some of the attention previously devoted to recycling homogeneous phosphine and NHC-ligated catalysts has now turned to recycling colloidal catalysts.[82-85] Numerous methods of Pd colloidal or nanoparticle (NP) based heterogeneous or homogeneous catalysis have been reported. While heterogeneous catalytic systems are often designed that immobilize NPs on polar supports such as silica or alumina, homogeneous systems that generate NPs *in situ* are also well known and form species that can act similarly to Pd molecular catalysts. In both cases stabilization of the so-formed NPs is essential for maintaining the catalytic activity since agglomeration of the Pd will result Pd black formation and an inactive Pd catalyst. A wide array of Pd NP stabilising strategies have been reported. Physical structures or physical mixtures containing micelles, microemulsions and surfactants for examples reportedly stabilize these NPs. Polymers have also long been used as NP stabilizers. Poly-(*N*-vinyl-2-pyorrolidine) (PVP), polyurea, polyacrylonitrile, polyacrylic acid, polysiloxane, polypyrrole poly(4-vinylpyridine) and dendrimers are among the mostly used polymers for Pd NP stabilization. These strategies are used not only to prevent agglomeration of NPs but also to facilitate green chemical synthesis where catalyst recycling and catalyst product separation is emphasized.[86] For example, dendrimer encapsulated Pd catalysts,[87-89] Pd catalysts on magnetic nanoparticles,[90-93] Pd nanoparticles in the presence of conventional or hyperbranched polymers[94,95] or Pd catalysts localized in a separable solid [86,96] or liquid phase have all been described as effective methods for catalyst and product separation.[96-98] These catalysts are generally designed to achieve several goals – formation of a highly active catalyst, an efficient catalyst/product separation process, and catalyst recyclability with minimal Pd leaching into the product phase (Figure 11).[98,99]



Pd NPs encapsulated in G4 hydroxyl terminated dendrimer

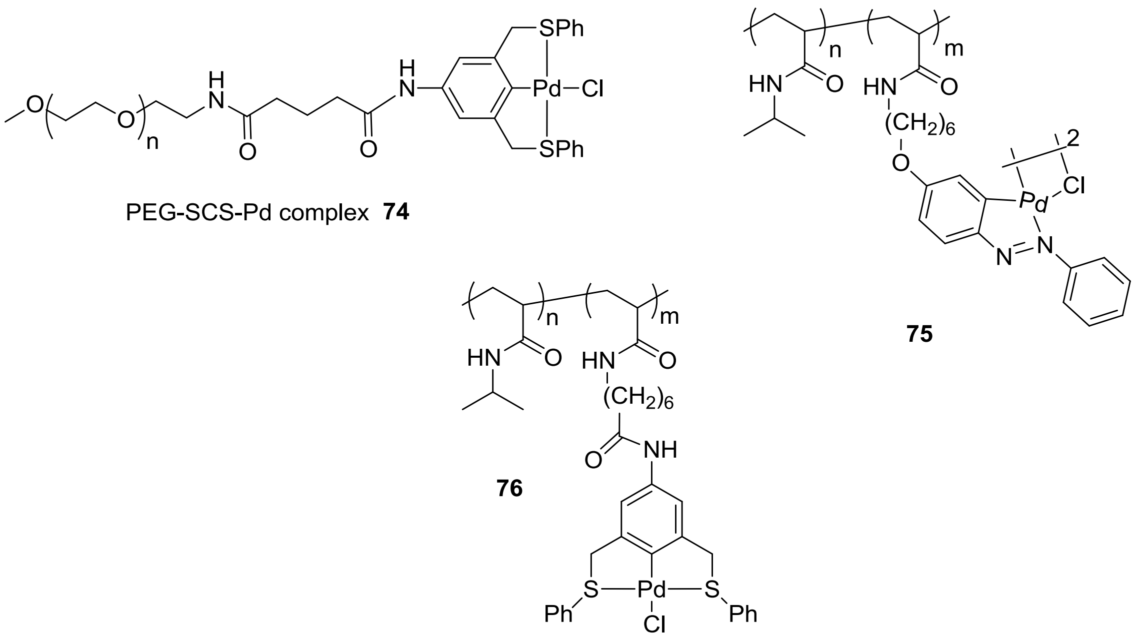
Maganetic nanoparticle supported Pd ^{0}

Water soluble Pd colloidal catalyst

Pd colloidal catalyst immobilized on silica

Figure 11. Recyclable Pd colloidal catalysts.

Past work in the Bergbreiter laboratory has also included such chemistry albeit inadvertently. For example, soluble polymer supported pincer S-C-S Pd complexes were shown to effect catalysis via highly active Pd colloidal catalytic species. In these cases, polymer supported complexes were used for cross coupling chemistry and they are easily recyclable and recovered.[100-102] In this work poly(ethylene glycol) (PEG) bound SCS-Pd catalyst **74** was found to be as efficient in C-C cross coupling reactions as non-supported catalysts (Figure 12). This PEG-SCS-Pd pre-catalyst **74** was active in C-C coupling reactions and the catalyst was reused for 3 cycles by simply precipitating the PEG bound catalyst into diethylether. In a following study, a SCS-Pd pincer complex was also incorporated into a statistical copolymer containing poly(*N*-isopropylacrylamide) (PNIPAM) **76** which has a temperature sensitive phase selective solubility in different solvents. This solubility property was used to separate products from the catalyst. In addition to incorporating a palladium precatalyst onto a polymer that has stimuli responsive solubility behaviour, a poly(N-isopropylacrylamide) polymer containing a dye as a pendent group was also prepared. This azo dye pendent groups in the statistical copolymer which was designed to facilitate the catalyst/product separation was also used as a precursor for preparing Pd(II) complex by *ortho*-metallation. The PNIPAM supported dye labelled Pd(II)complex **75** was then shown to be useful in cross coupling catalysis and had the feature that the pendent azo dye serves as a reporting group to show the location of the catalyst. Since demetallation changed the color of the catalyst, this metallated version of PNIPAM copolymer also provided some information about the Pd(II) complex stability.



PEG-SCS-Pd complex **74**

75

76

Figure 12. Soluble polymer supported Pd pre-catalysts.

The Bergbreiter group has pursued two generic strategies for catalyst/product separation based on the phase selective solubility of these polymer-bound catalysts and products in different solvents: (a) thermomorphic separations and (b) latent biphasic separations systems. Thermomorphic separations include solid/liquid and liquid/liquid separation systems and shown in Figure 13. In a solid liquid thermomorphic system the polymer supported catalyst is insoluble at room temperature and becomes soluble at a higher temperature. This catalyst separation strategy is useful when high temperatures are required for chemical reactions. Then upon cooling the polymer supported catalyst precipitates from the solution while products stay in the solution.

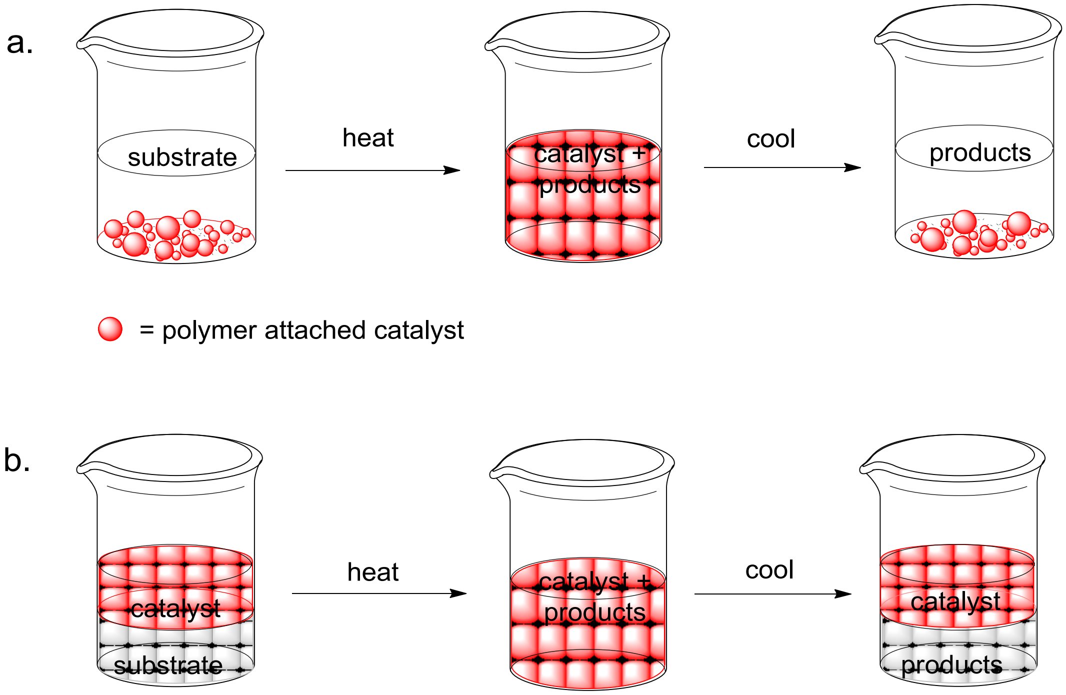


Figure 13 (a) Thermomorphic solid/liquid (b) liquid/liquid separation systems.

Alternatively, thermomorphic liquid/liquid separations can also be useful if the polymer supported catalyst is phase selectively soluble in non-polar solvents at all temperatures and products from the reaction partition into the polar solvent. The requirement for these two solvents to be used in this second sort of thermomorphic system should be miscible at a higher temperature. At this temperature, homogeneous reaction can occur as the catalyst and substrate are in the same phase. If this solvent mixture becomes immiscible at a lower temperature, the phase selectively soluble catalyst would then separate into the non-polar phase which can then be used for catalyst recycling (Figure 13 b).

In Latent biphasic separation system, separation of the polymer attached catalyst from the polar solvent soluble products is shown in Figure 14. This strategy uses two or more solvents that form a single phase solvent mixture that become biphasic upon addition or formation of perturbating agent. In this case it is possible to carry out the catalysis at room temperature and then perturb the system to generate two different phases to recover the catalyst in the nonpolar phase while products stay in the polar phase. For example, heptane and ethanol for a homogeneous solvent mixture at room temperature. However, addition of <5 vol% water produces a biphasic mixture containing heptane rich and an ethanol-rich phases.

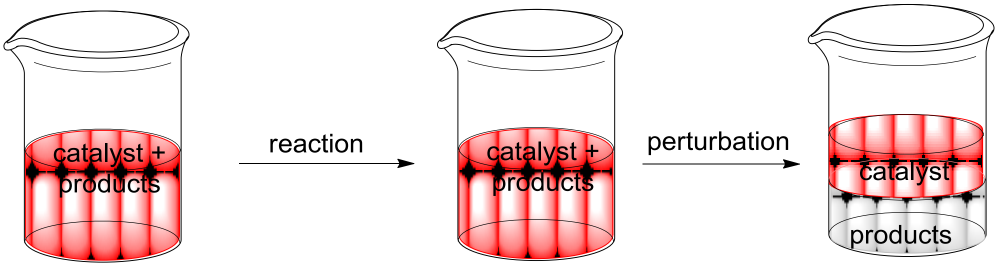


Figure 14. Latent biphasic system.

These latent biphasic and thermomorphic separations are general and are useful ways to separate nonpolar soluble polymer-bound catalysts from polar solutions of products.[15] However, the use of heptane can be eliminated to improve this strategy further if heptane solvent can be replaced with a nonvolatile, nontoxic and fully recyclable solvent. This proved to be the case using Polywax, a commercially available low molecular weight unfunctionalized polyethylene oligomer. In this case a solid polymer is used as a completely recyclable solvent and with the added advantage of entrapping a polymer-bound catalyst to facilitate the catalyst recyclability which provides a well contained reaction scheme Figure 15.

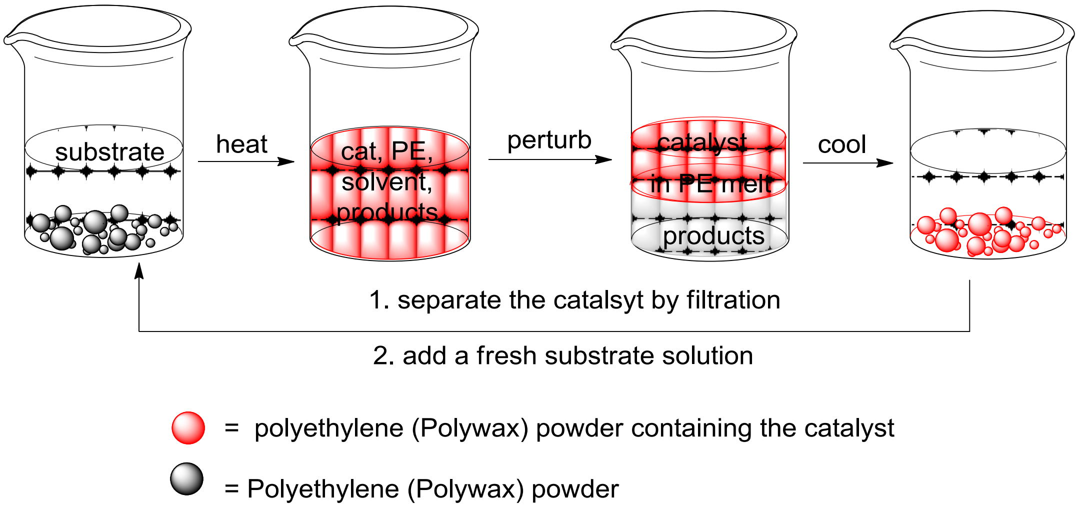
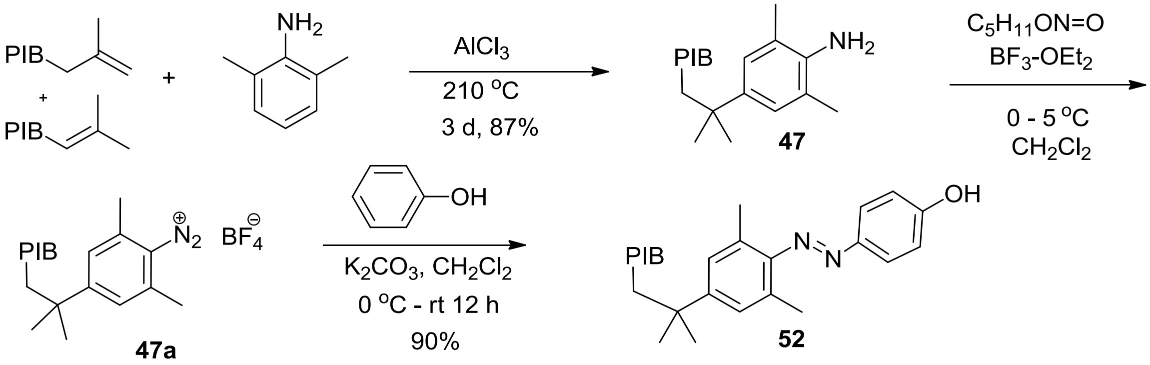


Figure 15. The use of polyethylene as a cosolvent in a thermomophic catalyst separation where the catalyst is isolated as a dispersion in solid polyethylene wax and the products remain in solution after a hot monophasic reaction step is followed by phase perturbation and cooling.

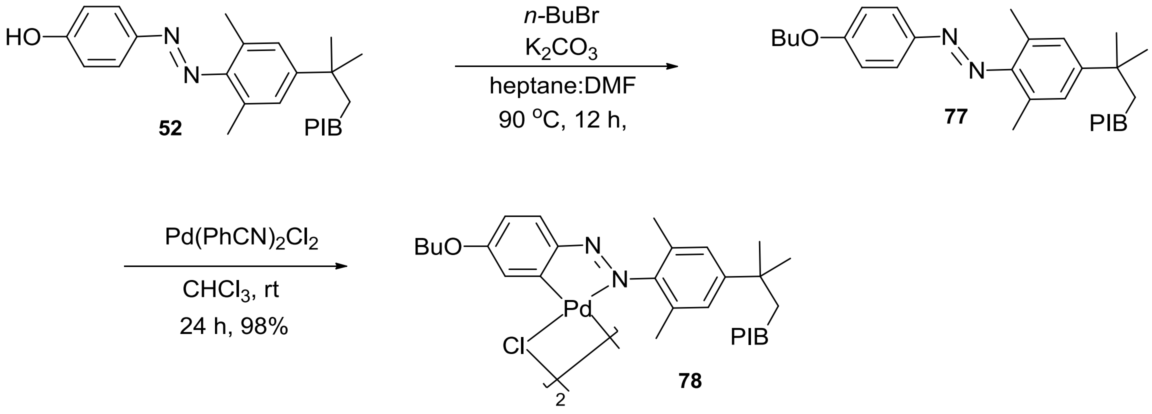
In the studies below, a soluble polymer (PIB) supported palladacycle precatalyst was employed in cross coupling chemistry with the emphasis on improving catalyst recyclability and metal sequestration properties. In this case, thermomorphic liquid/liquid separation system and the use of a more sustainable non-volatile polymer material-Polywax as a solvent for catalytic reactions were studied. A Pd(II) complex of a colorimetric azodyes attached to a soluble polymer-polyisobutylene (PIB) that serves as a pre-catalyst which in turn formed Pd colloids *in situ* was prepared. The activity and recoverability of such Pd-colloidal catalysts can be influenced not just by the presence of a soluble polymer support, but also by the presence of other soluble polymeric ligands such as phosphines that normally are used with molecular Pd complexes. I also coupled this polymer-supported Pd(II) pre-catalyst which forms palladium colloids *in situ* with the novel catalyst product separation strategy to improve the metal sequestration from a catalytic reaction and the reuse of catalyst. My work on this shows that at least part of the solvent that is necessary for separation and recovery (Figure 12) of these colloidal catalysts can be replaced by a low melting Polywax solid. Using Polywax solid solvent and added polymeric ligands together leads to very efficient recovery of the Pd colloidal catalysts in a solid wax phase.

Results and discussion

Initial objective of the work was to synthesize colorimetric polymer-bound palladium (Pd) catalysts that could be used in thermomorphic separations like those in Figure 13. This was accomplished using polyisobutylene (PIB) bound azophenols like **52** (Scheme 22) as the starting material for synthesis of a colored PIB-bound Pd(II) precatalyst. The PIB-bound aniline **47** is easily prepared on a multigram scale as described in the Chapter II. Diazotization of **47** was carried out using isoamyl nitrite in dichloromethane. The product of this reaction was a PIB-bound diazonium salt that was then allowed to react with an electron-rich arene to form a PIB-bound azo dye. For example, a diazonium salt formed from a 2,6-dimethylaniline-terminated polyisobutylene forms an isolable electrophilic diazonium salt **47a** that readily reacts with an excess of phenol to form the azo dye **52**.[46] While this reaction requires excess phenol, the excess phenol is easily separated from the heptane-soluble azo dye by a liquid/liquid biphasic extraction taking advantage of the heptane phase selective solubility of **52**. This reaction can be carried out with PIB oligomers PIB_{1000}, PIB_{1300}, or PIB_{2300} on a multigram scale. It was expected that the electron-rich aryl group of the PIB-bound azo dye **52** would react with Pd(II) to form an *ortho*-palladated intermediate. However, palladation of **52** disappointedly led to a mixture of products based on ^1H NMR spectroscopy. Fortunately, the butyl ether **77** formed from **52** underwent facile metallation with $Pd(PhCN)_2Cl_2$ in chloroform at room temperature to afford the red chloro-bridged PIB-bound palladium (II) complex **78** in quantitative yield (Scheme 23).



Scheme 22. Synthesis of the PIB-bound azophenol dye 3 (PIB = $H\text{-}(CH_2C(CH_3)_2)_{40}\text{-}$)



Scheme 23. Synthesis of the PIB-azobenzene Pd(II) complex 78.

The formation of the PIB-palladacycle was followed by UV_visible and ^{1}H NMR spectroscopy. Ligand **77** has a λ_{max} at ca. 348 nm. On palladation the UV_visible spectrum changes and a new absorbance peak appears at 448 nm (Figure 16b). These spectral changes are comparable to those seen in formation of other similar palladium complexes.[103] ^{1}H and ^{13}C NMR spectra of **78** (Figure 17) were also consistent with metallation in that the aryl protons of the electron rich aryl group in the butoxyarene ring changed from a doublet of doublets to a set of three resonances each integrating to one proton at 7.74, 6.67, and 6.61 δ with an ABX coupling pattern typical for that of a 2,4-disubstituted phenyl ether. ^{13}C NMR spectroscopic analysis confirmed this result. As a result of the palladation, the two aryl C-H signals of the butoxyarene ring were replaced with three new aryl C-H signals and a new peak at 147.2 δ that is consistent with the formation of an aryl-Pd bond.[100,103] A DEPT experiment confirmed that the peak at 147.2 δ was a quaternary carbon and that there were four aryl methine carbons.

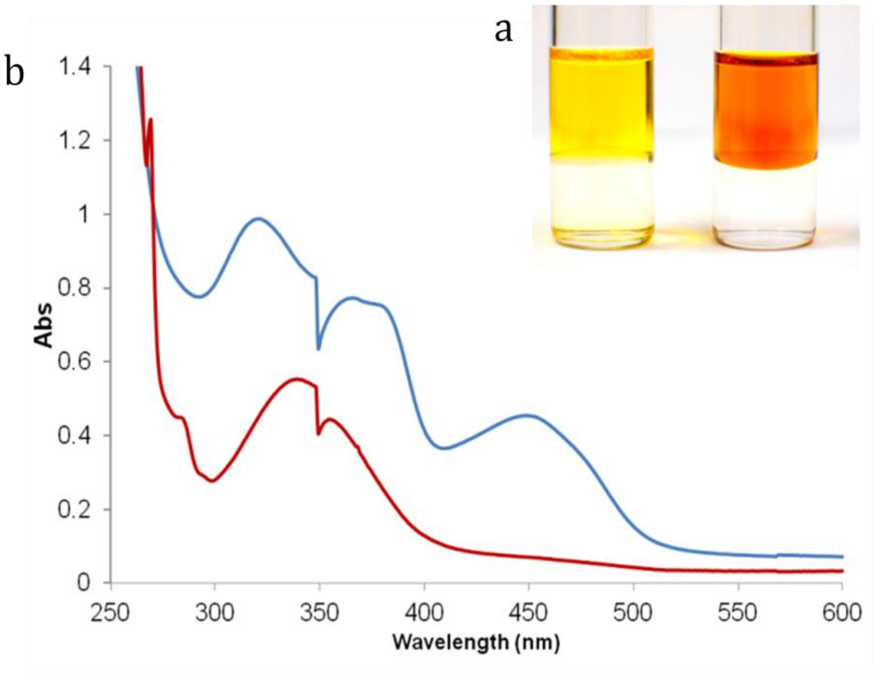


Figure 16. a). Visually evident phase selective solubility of the yellow phenyl butyl ether dye 77 or the red-orange PIB(II) palladacycle 78 in the less dense heptane phase of a biphasic thermomorphic heptane/DMF system; b) UV-Vis spectrum of the azo phenyl butyl ether dye 77 (red) and of the *ortho*-palladated precatalyst 78 (blue) as 2 x 10^{-4} M solutions in hexane.

Initial studies showed that the PIB-bound azo dye **77** and as well as the Pd(II) complex **78** were soluble in a hot equivolume mixture of DMF and heptane but were phase selectively soluble in the heptane phase of the biphasic mixture that formed on cooling based on the absence of color in the polar DMF phase (Figure 16 a). Our expectation was that this PIB-bound Pd(II) complex **78** could be used as a precatalyst for C-C cross coupling reactions where the PIB-bound group would recycle the Pd catalyst in a heptane phase.

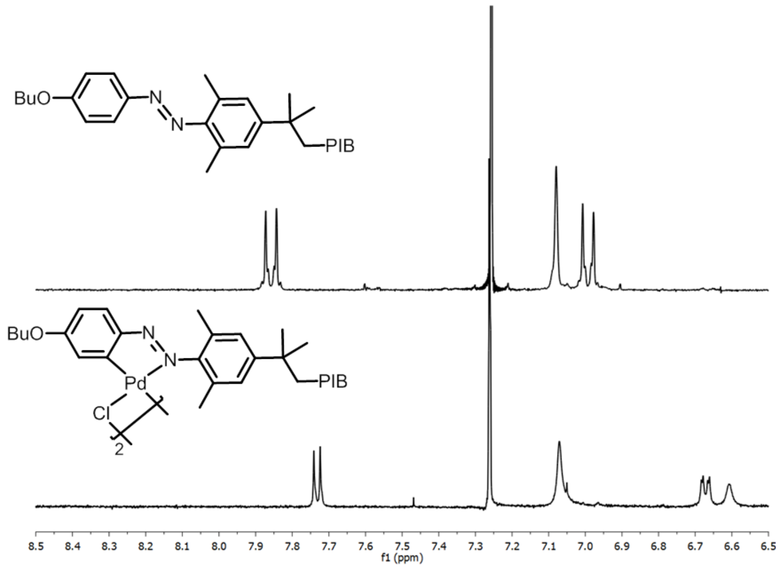
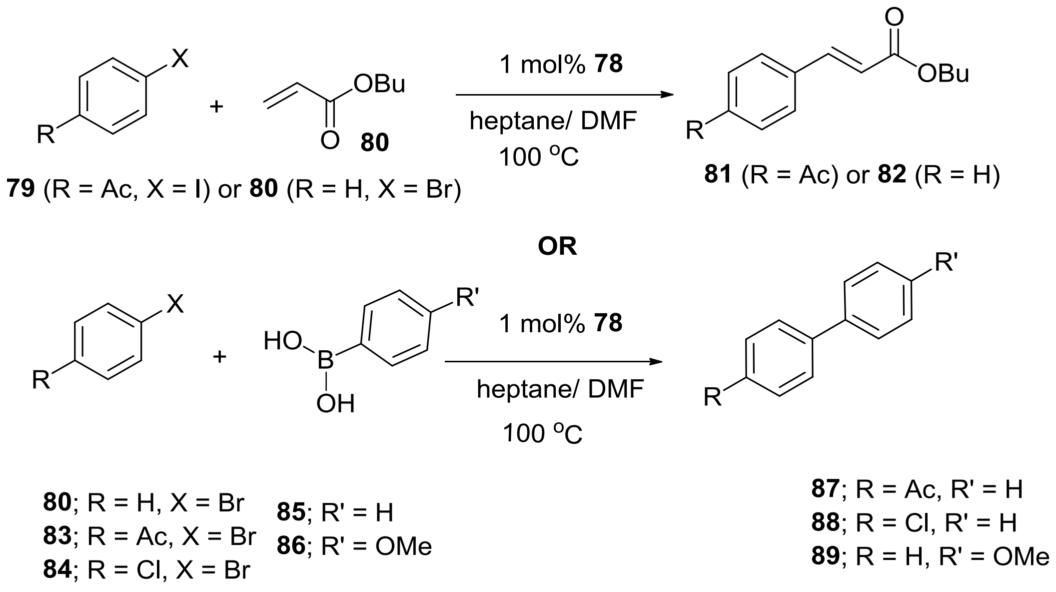


Figure 17. ^{1}H NMR spectrum of the PIB-bound phenyl butyl ether azo dye 77 (above) and the PIB-Pd(II) palladacycle 78.

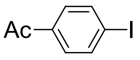
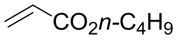
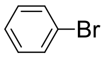
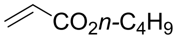
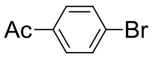
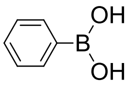
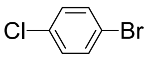
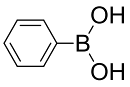
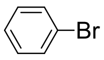
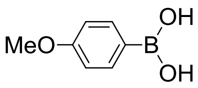
To explore this, a series of C-C coupling reactions were carried out at 100 ºC in a 1:1 (vol : vol) mixture of heptane and DMF using 1 mol% of **78** as shown in Scheme 24. As expected, **78** was competent at Mizoroki-Heck and Suzuki catalysis with a variety of substrates of varying reactivity. In these reactions, the products were isolated from the DMF phase. Catalyst recycling was accomplished by adding a heptane-saturated solution of DMF containing fresh substrate to the recovered heptane catalyst-containing phase.



Scheme 24. Carbon-carbon cross coupling reactions catalyzed by 78 in a thermomorphic heptane/DMF system where catalysts are separated from products and recycled using a liquid/liquid biphasic separation (cf. Figure 13a).

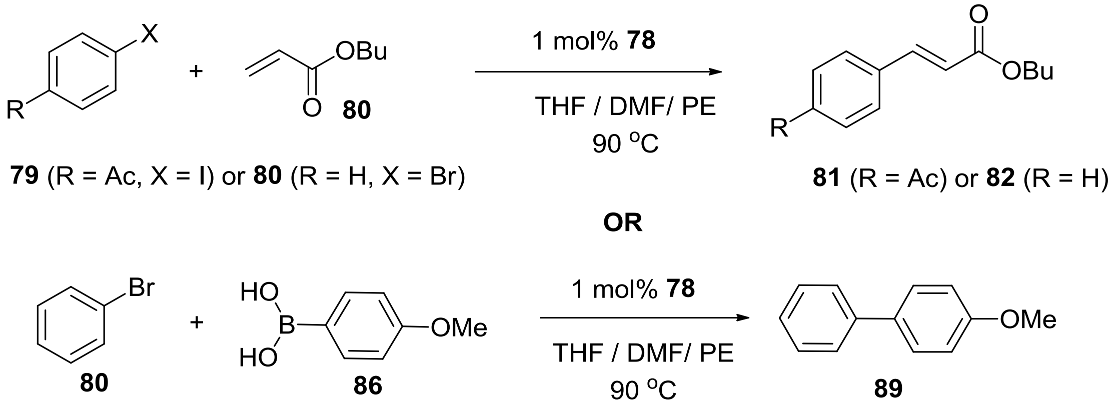
The results of a series of reactions where the catalyst was recycled through 5-6 cycles are summarized in Table 3. The results in this table show that the PIB-azobenzene Pd(II) precatalyst **78** has an activity for cross-coupling chemistry that is similar to that of other low molecular weight Pd precatalysts reported in literature.[104] Visual observation of the colorless DMF phase showed that no significant amount of the complex **78** remained in this phase.

Table 3. Recycling results using precatalyst 78 in a solvent system containing heptane and DMF where the catalyst is separated and recycled by thermomorphic liquid/liquid separation.

aryl halide	acceptor	product	cycles	yield (%)[a]
		**81**	5	92
		**82**	5	90
		**87**	5	96
		**88**	6	94
		**89**	5	89

[a]The reactions were carried out with 1 mmol of the aryl halide and 1.2 mmol of butyl acrylate or 1.4 mmol of phenyl boronic acid using 2 mmol of K_2CO_3 as a base and 0.01 mmol of 78 in a mixture of 2 mL of heptane and 2 mL of DMF. The reaction was stirred under N_2 at 100 °C for 6 - 12 h. [a]The yields are isolated average yields per cycle.

However, ICP-MS analysis showed ca. 7% of the starting Pd leached into the polar product phase after the 4th cycle in a Mizoroki-Heck coupling that formed butyl cinnamate from iodoacetophenone and *n*-butylacrylate (Entry 1, Table 3). Thus, while **78** is an effective precatalyst for cross coupling, the leaching of Pd from solutions of **78** is higher than desired.



Scheme 25. Carbon-carbon cross coupling reactions catalyzed by 78 using a Polywax, THF, and DMF solvent mixture where the catalyst is recycled as a solid dispersion in Polywax (cf. Figure 13b).

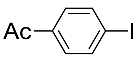
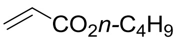
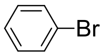
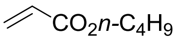
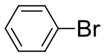
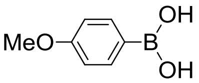
To address this problem of leaching as well to make the overall catalytic reaction more sustainable we examined the use of **78** as a precatalyst in a mixture of THF and DMF replacing the heptane solvent used in Scheme 24 with a commercially available polyethylene oligomer (PE_{Olig}). This Polywax oligomer is a solid at room temperature. This low melting wax can serve as a solvent replacement for alkanes as it dissolves on heating with THF as well as with a 1:1 (vol: vol) mixture of THF and DMF at ca. 80 °C.[105] When these binary or ternary solvent mixtures are perturbed by the addition of water while hot, the Polywax phase separates as a low viscosity hydrocarbon liquid phase that PIB-bound species quantitatively partition into. This solvent system was used here as shown in Scheme 25.

A suspension of polyethylene oligomer ($Polywax_{400}$) in a 1:1 mixture of THF:

DMF containing substrate and **78** was prepared and Polywax was used for this purpose since NMR studies showed Polywax could be separated without contaminating the polar solutions of the product, avoiding the need for chromatography to remove traces of the polymeric solvent. At room temperature, no catalysis occurred and no **78** visually sorbed onto the suspended Polywax powder. However, on heating this mixture to 90 ºC a solution formed and Heck and Suzuki reactions could be effected (Table 4).

After the reaction was complete, the Polywax could be separated by simple cooling. However, while this separation of Polywax from the product solution is quantitative, simply cooling to effect a phase separation leads to precipitation of the Polywax without entrapment of the PIB-bound species. If instead the homogeneous hot solution was perturbed by the addition of hot water, the hot solvent mixture was perturbed and formed a liquid/liquid biphasic mixture with a colored low viscosity Polywax-rich phase and a polar THF-DMF rich phase. Cooling this biphasic mixture led to solidification of the Polywax to form a colored waxy solid that could then be physically separated from the colorless THF-DMF solution that contained the cross coupling product. This waxy catalyst containing Polywax solid was then added to a fresh THF-DMF solution to carry out subsequent reactions cycles. A total of 5 cycles of each Heck and Suzuki reaction were carried out with isolated product yields (Table 4) that were equivalent to those in Table 3.

Table 4. Recycling results using precatalyst 78 in a solvent system consisting of Polywax, THF, and DMF where the catalyst is isolated as a solid Polywax dispersion.

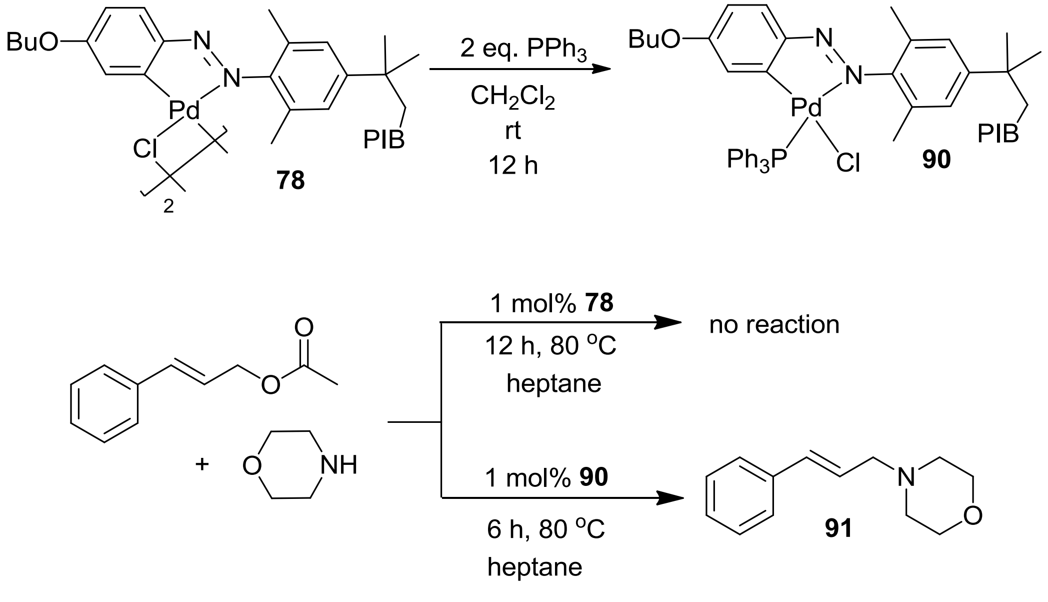
aryl halide	acceptor	product	cycles	yield (%)[a]
		**81**	5	90
		**82**	5	85
		**89**	5	90

[a]The reactions were carried out with 1 mmol of the aryl halide and 1.2 mmol of butyl acrylate or 1.4 mmol of phenyl boronic acid using 2 mmol of K_2CO_3 as a base and 0.01 mmol of 78 in a mixture of 2 mL of THF and 2 mL of DMF and 1.5 g of Polywax (M_n~400). The reactions were stirred under N_2 at 90 °C for 12 h. [a]The yields are isolated average yields per cycle.

While visual observation indicated that there was no red color in the clear polar phase, metal leaching analysis in a Heck reaction showed 1.2 % of the Pd leached into the polar product phase after the 4th cycle. This lower leaching in comparison to Pd leaching seen in the reactions in Scheme 26 suggests that the formation of a solid solvent dispersion of the catalyst helps reduce leaching of the Pd catalyst or precatalyst.

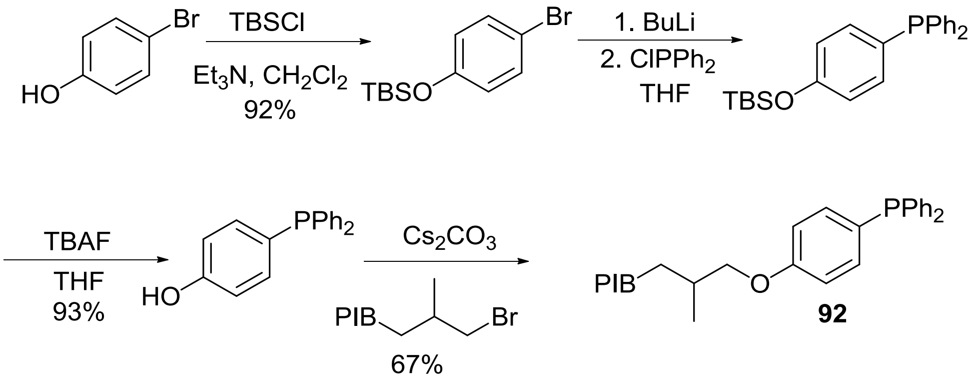
Based on the assumption that **78** is generating a Pd(0) species during these reactions, PIB-palladacycle **78** was examined as a precatalyst for an allylic amination reaction. However, a heptane/DMF solution of **78** did not form any detectable allylic substitution product from cinnamyl acetate and morpholine even after 24 h of stirring at 90 °C. To overcome this unexpected lack of reactivity of **78** in allylic substitution, phosphine ligand was added as an auxiliary ligand since it had been previously reported that phosphines can enhance the reactivity of Pd(0) catalysts in similar chemistry. However, instead of simply adding a phosphine ligand to **78** and heating, we first treated the PIB-bound chloride bridged dinuclear complex **78** with 2 equiv of triphenylphosphine (PPh_3) in dichloromethane at room temperature. Gratifyingly this afforded a PIB-azophenol Pd(II) phosphine complex **90** (Scheme 26) based on ^1H, ^{13}C, and ^{31}P NMR spectroscopic analysis.

Evidence for formation of this complex were the changes in the ^1H NMR spectrum of **90** wherein the resonance for H3 of **90** became a doublet due to ^{31}P-^1H coupling. The chemical shift for this proton also changed from 6.5 to 5.9 consistent with phosphine complex formation.[106] When we examined the use of **90** in an allylic amination reaction using cinnamyl acetate and morpholine in heptane/DMF at 80 °C, complete conversion of the starting cinnamyl acetate to a mixture of structurally isomeric allylic amines occurred (Scheme 26). However, attempted recycling experiments of **90** failed giving no conversion to products in the second cycle.



Scheme 26. Synthesis of PIB-azobenzene Pd(II) phosphine complex 90 and its use in an allylic amination reaction.

Encouraged by the observation that the phosphine complex **90** is active in allylic amination in the presence of added phosphine and by the ability to recycle catalytic species derived from precatalysts like **78**, a more sustainable way was explored to use colloidal Pd catalysts derived from **78** in the presence of phosphines. In this work the use of a PIB-bound phosphine was examined as a ligand to activate **78** for allylic substitutions. This study used a PIB-bound triarylphosphine **92** which had previously been used for organocatalysis. This phosphine was prepared using the chemistry shown in Scheme 27.



Scheme 27. Synthesis of the PIB-bound triarylphosphine 92.

An allylic substitution reaction of cinnamyl acetate by morpholine was carried out using **77** as a precatalyst in the presence of 2 equiv. of PIB-bound aryl phosphine **92** as an additive ligand. This reaction like that seen with the pre-formed phosphine complex **90** was successful. Moreover, in this scheme where the PIB-bound **78** and **92** were used in concert, the catalyst was fully recyclable. In these cases, the catalysis was carried out in heptane at 80 °C. Catalyst recycling was accomplished by cooling to room temperature and extracting the product using acetonitrile. Under these conditions, the catalyst and the PIB-bound phosphine ligand remained in the heptane phase. Additional reaction cycles were then effected by adding fresh substrates to this heptane solution for each subsequent reaction cycle. The catalyst **78** and ligand **92** were successfully recycled for 8 reaction cycles without any decomposition of the phosphine ligand or without any diminution of the product yield. These reactions show that an oligomeric phosphine can be an effective ligand for the presumed Pd colloidal catalyst formed from another oligomer bound species. A further feature of this chemistry is that ICP-MS analysis showed that Pd leaching further diminished when using **78** along with **92**. A metal leaching experiment on the product phase of the 5th cycle using ICP-MS analysis showed only 0.17% of the starting Pd leached into the product phase.

The ability of **92** to lower leaching in the allylic substitution reaction described above suggested that **92** could be similarly useful in cross coupling chemistry. To test this hypothesis, we repeated the Heck coupling reported in Table 3 that involved the reaction of 4-iodoacetophenone and butylacrylate and carried out this reaction using 1 mol% of **78** along with 2 equiv. of **92** using the more sustainable THF/DMF/Polywax solvent system described in Scheme 26 in place of the heptane used in Scheme 25. This cross coupling reaction was carried out through 5 cycles under the conditions used in Table 4. The average yield of product in each cycle in this case was 89%, essentially equivalent to what as seen in Table 4 with the same substrates. Catalyst recycling was accomplished by perturbing the hot THF/DMF/Polywax monophasic mixture with water as described above. Cooling generated a solid Polywax phase that contained a dispersion of the Pd catalyst and **92** that was physically separated from the polar solution of product and then recycled with fresh substrate in a subsequent cycle. ICP-MS analysis for Pd leaching in the 4th cycle showed only 0.12% of the Pd catalyst leached into the product phase. This Pd leaching is almost two orders of magnitude lower than the Pd leaching in a system without Polywax or without a phosphine ligand. This result where one of the volatile solvent has been eliminated and shown the effectiveness of polymeric cofactor ligands suggests the possibility that it should be possible to significantly improve the sustainability of these and other homogeneous catalysts.

While the catalyst recycling experiments and metal leaching data show that Pd catalyst can be recovered in these various reactions and that high levels of Pd separation are possible using added ligands and a Polywax matrix as a cosolvent, the notion that the PIB-bound palladacycle is a precatalyst that forms colloidal palladium during the reaction was conjecture. To confirm that Pd colloidal species formed, we carried out scanning electron microscopy experiments (SEM) on the solid Polywax dispersion of the recycled catalyst isolated from cycle 5 in an experiment using the PIB-bound phosphine **92** as a cofactor and compared it with the recovered Polywax dispersion from an experiment in Table 3 where there was no added **92** present. Both studies examined the recovered Polywax from a Mizoroki-Heck reaction of 4-bromoacetophenone (Figures 18b and 18c, respectively). These SEM images of the Polywax material that was recovered after 5 catalytic cycles showed that Pd colloidal particles with an approximate diameter of 50 nm were dispersed in the solid Polywax matrix in both cases when compared SEM image (Figure 18a) of virgin Polywax material.

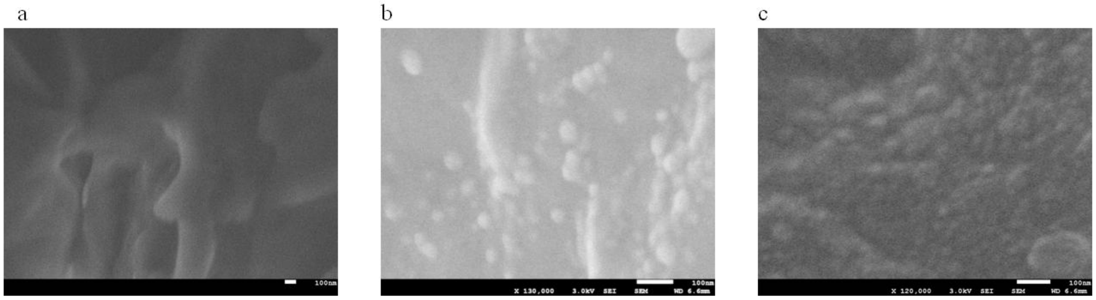


Figure 18: a) SEM image of virgin polywax phase; b) SEM image of Pd colloidal particles entrapped in Polywax, and b) SEM image of Pd colloidal particles entrapped in Polywax solid from a Heck reaction that included added PIB-bound phosphine 92.

Conclusions

In conclusion, the studies in this chapter show that *Ortho*-palladated PIB-bound azo dyes can be used to form Pd(II) complexes that serve as precatalysts useful in catalytic carbon-carbon cross coupling reactions. Good catalyst recyclability was seen. The extent of Pd leaching was reduced significantly when polyethylene oligomers were used as a solvent in place of heptane to separate the catalyst as a solid dispersion of Pd colloidal particles in a solid polyethylene matrix. These Pd colloids were also active in allylic amination reactions when triphenylphosphine was added as an auxiliary ligand. By using a PIB-bound triarylphosphine as an additive in place of triphenylphosphine, the enhanced reactivity resulting from the added triarylphosphine was still observed and the Pd catalyst was recyclable through eight cycles with very low Pd leaching. These latter systems that used an added PIB-bound triarylphosphine and polyethylene oligomers in place of heptane also showed the least Pd leaching both in allylic substitutions and in cross coupling chemistry, suggesting that use of polymeric solvents coupled with multiple polymeric ligands could be a generally useful way to further enhance sustainability of homogeneous catalysts.

CHAPTER IV

GREENER RECOVERABLE POLYISOBUTYLENE-BOUND VISIBLE LIGHT PHOTO-REDOX CATALYST IN FREE RADICAL POLYMERIZATION

Introduction

Sunlight is the most abundant, environmentally benign energy reservoir on earth. Although photochemical synthesis has an enormous impact on industrial scale synthesis as a cost effective and ecology friendly process, the inability of most organic molecules to absorb visible light has limited the broader applicability of photochemical synthesis. This limitation can be overcome by using organic dyes or transition metal complexes, which absorb visible light wavelengths as photosensitizers. Transition metal complexes such as ruthenium(II)-polypyridine $Ru(bpy)_3^{2+}$ and $Ir(ppy)_3$ complexes are well explored as photocatalysts due to their long excited state life time and exceptional chemical and environmental stability of its ground state precursors. [107-109]

The absorption spectrum of $Ru(bpy)_3^{2+}$ exhibits a strong absorption at ~ 452 nm. This absorption corresponds to a metal to ligand charge transfer (MLCT) to produce $Ru^*(bpy)_3^{2+}$ excited state. This $Ru^*(bpy)_3^{2+}$ excited complex has both reducing and oxidizing properties to serve as either an electron donor or as an electron acceptor with variety of quenching reagents (Figure 19). While oxidative quenching of $Ru^*(bpy)_3^{2+}$ forms $Ru(bpy)_3^{3+}$ reductive quenching of the same species provides $Ru(bpy)_3^{+}$. In oxidative quenching, $Ru^*(bpy)_3^{2+}$ reacts with an electron acceptor to form oxidized ground state Ru(III) species (Figure 19, path A). The original Ru(II) complex is then regenerated from Ru(III) complex upon its reaction with a reductant such as triethylamine or triethanolamine. Alternatively, the excited state $Ru^*(bpy)_3^{2+}$ can be reductively quenched with electron rich donors to form $Ru(bpy)_3^+$ (Figure 19, path B). This strongly reducing Ru(I) complex can effectively transfer an electron to other electron acceptors to regenerate the original Ru(II) complex.[107]

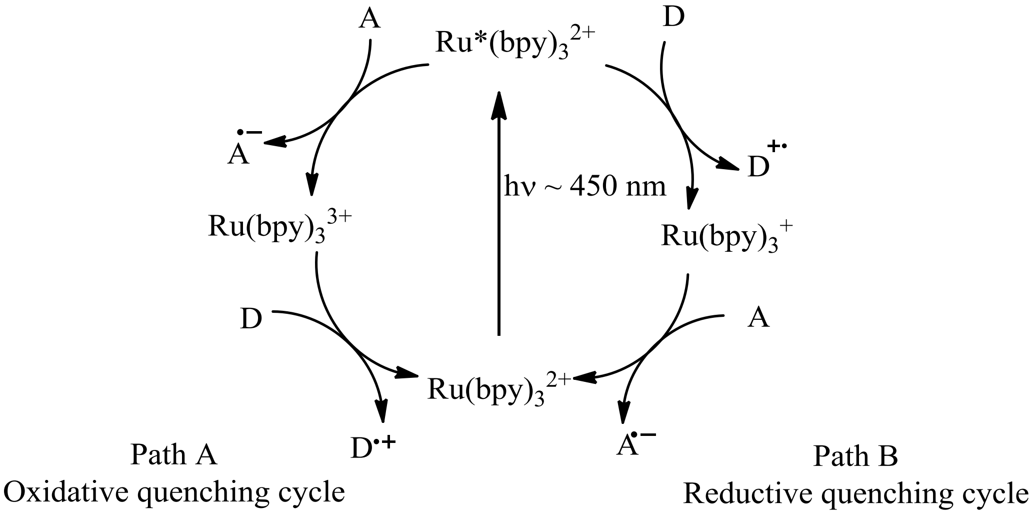
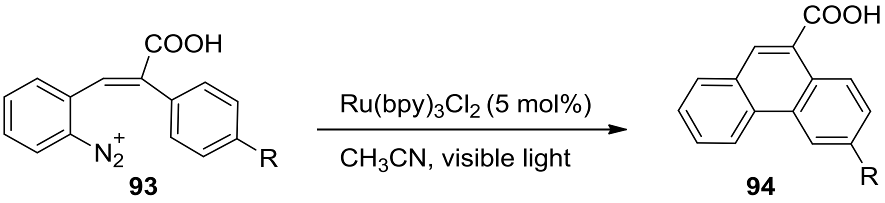


Figure 19. Oxidative and reductive quenching cycles in $Ru(bpy)_3^{2+}$ photochemistry.

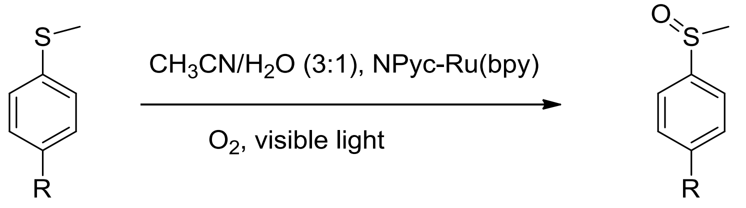
In both these cases excited species $Ru^*(bpy)_3^{2+}$ acts as a single electron donor or acceptor which can be utilized in chemical reactions. Although this excellent photoredox property of ruthenium bipyridine complexes is not new, it has not been explored effectively in organic synthesis until recently. Early reports by Cano-Yelo and Deronzier showed the first examples where $Ru(bpy)_3^{2+}$ catalyst was used in the Pschorr reaction

(Scheme 28). In this case, the diazonium salt **93** is reduced by an electron transfer from the ruthenium bipyridine catalyst and intramolecular radical arylation forms another radical which is oxidized by $Ru(bpy)_3^{3+}$ to produce the product **94**. This photoredox catalytic process mirrored earlier redox chemistry where $Ru(bpy)_3^{2+}$ catalyzed a Pschorr reaction using electrochemical catalysis.[110,111]



Scheme 28. Photocatalytic Pschorr reaction.

Almost 20 years after Deronzier’s reported applications of Ru polypyridine complexes in photochemical reactions, Zen et al. described a method to selectively oxidize sulfides to sulfoxides using a similar Ru photo-redox catalyst (Scheme 29). In these studies a form of heterogeneous $Ru(bpy)_3^{2+}$ catalyst which was incorporated into a Nafion membrane efficiently catalyzed the oxidation of sulfide **95** to yield the desired sulfoxide **96**. This photo oxidation of sulfides to sulfoxides is highlighted by its high selectivity to form only sulfoxides without the over oxidation to form sulfones -a common problem in sulfide oxidation reactions.[112]



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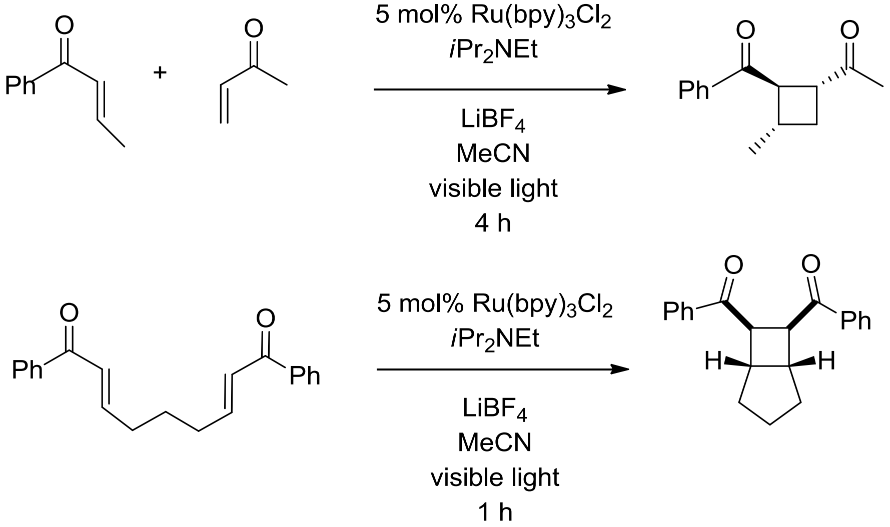
96

Scheme 29. Photocatalytic oxidation of sulfides to sulfoxides.

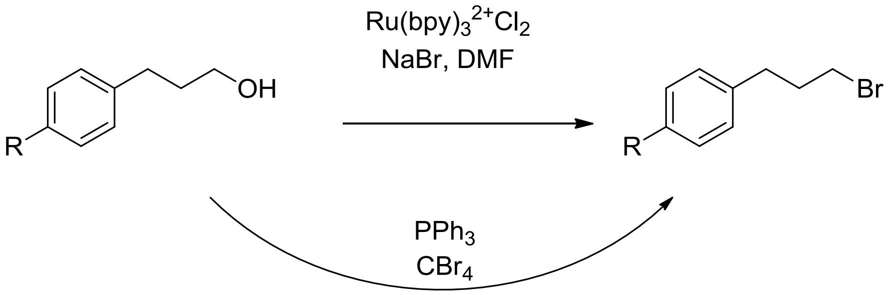
Other than these few examples where visible light photoredox catalysts were used to effect organic transformations, the visible light photochemistry of these sorts of transition metal complexes was underdeveloped in organic synthesis until recent work reported by the Yoon, MacMillan and Stephenson research groups on photocatalysis in radical mediated organic synthesis. These new reactions include halogenations of alcohols, C-H functionalization, cycloaddition reactions and polymerizations and have been efficiently used in the total synthesis of natural products.[107,113-128]

Among these reactions, the 2+2 cycloaddition of bis(enones) has attracted wide attention due to the diastereoselectivity of cyclization of these enones with $Ru(bpy)_3^{2+}$ visible light catalyst compared to that seen in the conventional thermal reaction. Yoon et al. studied these photochemical cycloaddition reactions with intramolecular bisenones and intermolecular enones (Scheme 30). These reactions utilize the reductive quenching pathway of the excited Ru*(II) complex was achieved by *N*,*N*-diisopropylethylamine to form the Ru(I) complex that could do electron transfer to effect the cyclization reaction.[116,129-132]



Scheme 30. Visible light photocatalyzed [2+2] cycloaddition.

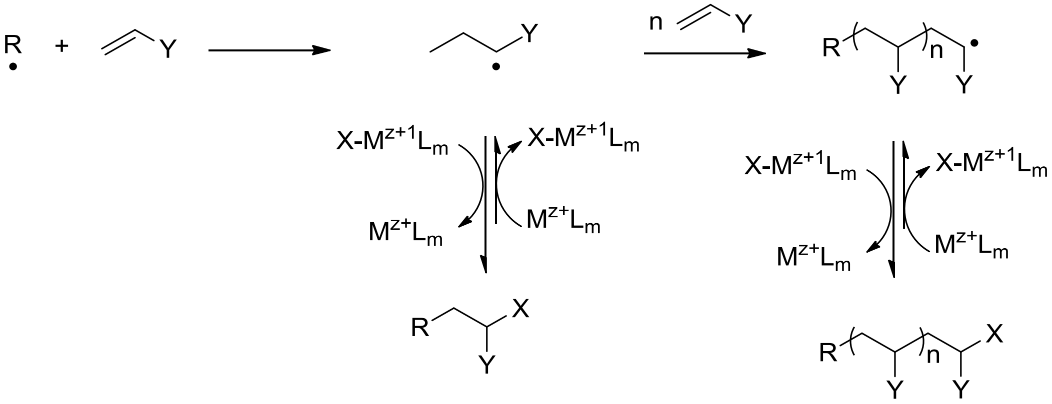
Another recent advancement of this photochemistry was reported by Stephenson and coworkers. The photocatalytic method they described provides a milder and greener method for converting alcohols to halides which is otherwise performed by the Appel reaction which uses triphenylphosphine and a halogen source such as CCl_4 or CBr_4. Triphenylphosphine acts as a two electron reductant in the Appel reaction and it is also one of the least atom economical reactions replacing only a single atom in the starting material. Stephenson et al. reported that a Vilsmeier-Haack type reagent- another reagent that can be used to transform alcohols to alkyl halides, can be generated by oxidative quenching of the $Ru^*(bpy)_3^{2+}$ with halomethane reagents such as CCl_4. The result is that the stoichiometric reagent triphenylphosphine can be replaced by DMF and a Ru photocatalyst to a effect a nucleophilic substitution of an alcohol to form an alkyl halide[133] (Scheme 31).



Scheme 31. $Ru(bpy)_3^{2+}Cl_2$ catalyzed bromination of alcohol.

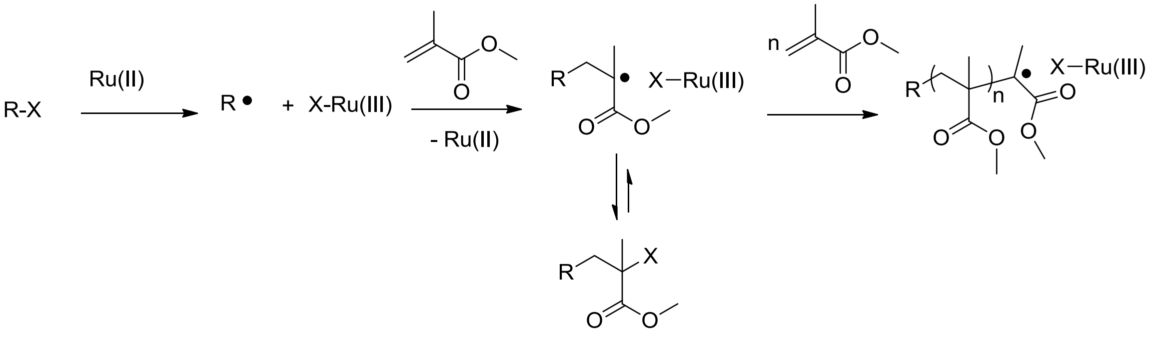
By utilizing the underlying chemistry of the above described photocatalyzed radical reactions, Choi initially and later Hawker have exploited the potential of photoredox catalysts like $Ru(bpy)_3^{2+}$ and $Ir(ppy)_3$ in free radical polymerization (FRP) reactions at ambient temperatures. The $Ru(bpy)_3^{2+}$ based radical initiation method was applied for a variety of polymerization reactions with most work focused on polyacrylates polymerizations.

Haloesters and benzylic halides are common initiators for radical polymerizations such as atom transfer radical polymerizations (ATRP)- a controlled radical polymerization where transition metals are being used as catalysts. This ATRP process is controlled by the reversible reaction of low oxidation state metal complexes with a benzylic halide or a halocarbonyl compound which forms radicals and an oxidized metal complex containing the halide counter anion (Scheme 32). This process is most commonly carried out with Cu catalysts.



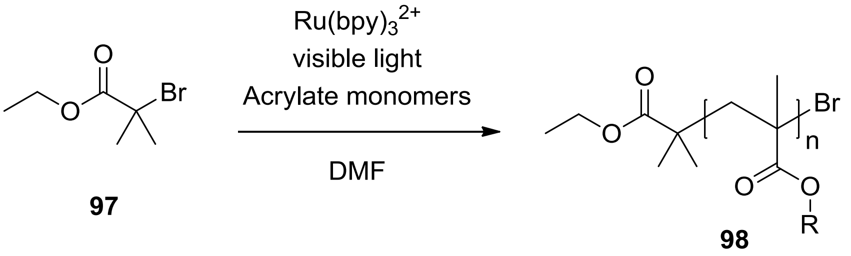
Scheme 32. Metal complex mediated ATRP process.

Other than Cu which is the mostly used transition metal in ATRP as catalysts various other metals have also been applied for mediating the controlled polymerization including Ru, Fe, Rh, Ni, Pd and Co.[134-145] For example, Sawamoto described variety of controlled polymerizations that are initiated and mediated by Ru based metal complexes. In this study dichlorotris-(triphenylphosphine)ruthenium(II) RuCl2(PPh3)3 and methylaluminum bis(2,6-di-tert-butylphenoxide) [MeAl-(ODBP)$_2$] system was applied in the polymerization of methyl methacrylate (MMA). This Ru(II) catalyzed polymerization reaction like the more common Cu catalyzed reaction is based on the reversible homolytic cleavage of a carbon-halogen bond and subsequent addition of the radical with another monomer to form a low concentration of a new larger radical which can then be reversibly quenched by the Ru(III) halide species to reform a dormant species (Scheme 33). The low concentration of radicals makes the overall polymerization process slower but inhibits coupling and other uncontrolled radical reactions that lead to chain termination or polymer polydispersity.



Scheme 33. Ru(II) mediated polymerization.

In the case of these photoredox Ru catalyst both haloesters and benzylic halide initiators can be activated through single electron transfer from Ru(bpy)$_3^+$ complex under visible light irradiation. Choi et al. established that this free radical polymerization method for acrylate monomers is a viable route to various polyacrylates using ethyl 2-bromoisobutyrate (EBiB) 97 as the initiator and *N*,*N*-diisipropylethylamine as a sacrificial electron donor (Scheme 34). This method was versatile and was successfully used with variety of acrylate monomers such as methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA) and benzyl methacrylate (BMA) etc..[146]



Scheme 34. Visible light catalyzed free radical polymerization of acrylate monomers.

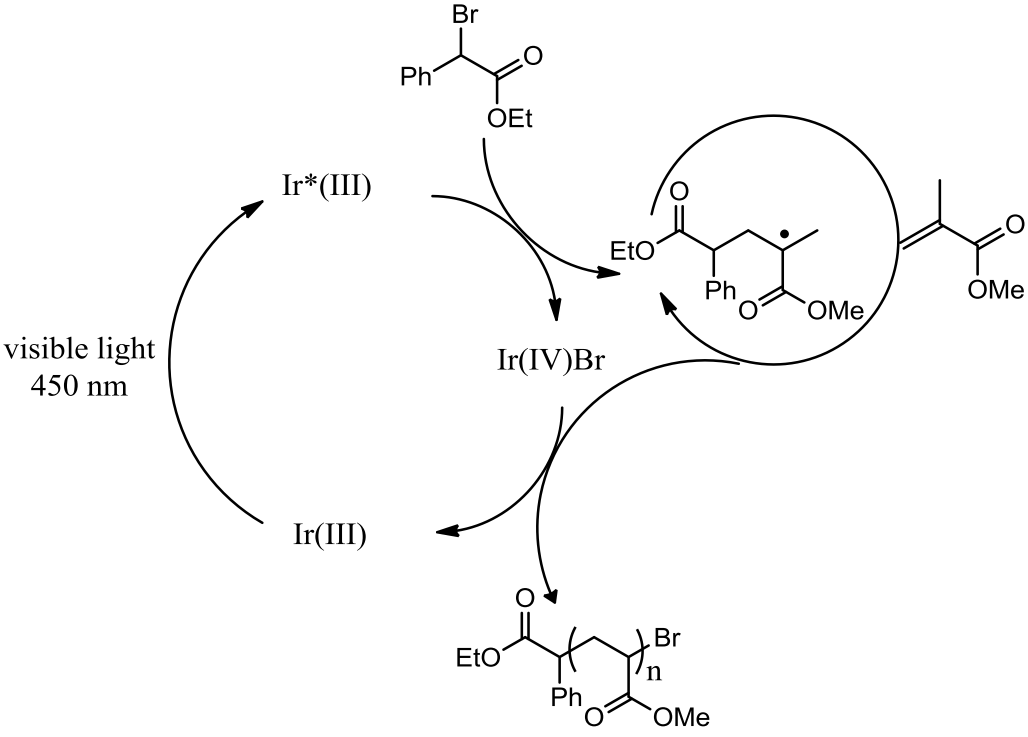


Figure 20. The photoredox catalyst-Ir(ppy)$_3$ (ppy = 2-pyridylphenyl) mediated radical polymerization of MMA.

Hawker et al. also reported a visible light mediated free radical polymerization reaction using Ir(ppy)$_3$ as the photocatalyst. Upon irradiation, the starting Ir(III) complex is excited to form an excited Ir*(III) complex that can reduce the bromophenylacetate initiator to give the initial radical, which starts the polymerization reaction. As shown in the reaction cycle (Figure 20), the Ir(IV) complex that forms is then proposed to react with the radical of the propagating polymer chain to reform the original Ir(III) complex and a dormant chain elongated product. This study also claims that this visible light initiated polymerization is a controlled, living process like atom transfer radical polymerization (ATRP). Interestingly, this visible light mediated polymerization has the advantage of reversibly controlling the polymerization as visible light acts as an external on/off stimulus turning the polymerization 'on' with light and then 'off' in the absence of light (Figure 20).[147]

While all these photocatalytic systems show great promise, they all require the use of expensive and toxic second or third row transition metals. If these metals and their complexes cannot be recovered and reused easily, this could limit the applicability of these complexes in large-scale synthesis. Therefore, as is true for other catalytic reactions, developing strategies for recovering and reusing the catalyst is of interest and will broaden the scope of these transition metal photoredox catalysts.

My work in this Chapter describes a greener approach using a soluble polymer-polyisobutylene (PIB) to immobilize the Ru(bpy)$_3^{2+}$ catalyst which can be recycled and reused as a homogeneous catalyst for FRP reactions. This PIB immobilized ruthenium bipyridine photoredox catalyst is soluble in non-polar solvents such as heptane, toluene, dichloromethane and tetrahydrofuran. However, catalyst/product separation strategies that the Bergbreiter group had developed previously such as thermomorphic liquid/liquid separation systems[148] that were described in the Chapter III will not be applicable in some of these photocatalytic reactions since the ambient temperature and monophasic reaction conditions are employed. However, by carrying out the reaction in a non-polar solvent such as heptane it is possible to separate the polar product. This is illustrated first with a FRP reaction where the product polymer self separates from the solution as a solid. This has added benefit that the catalyst can be recovered by simple filtration of the solid product from solution or decantation of the catalyst solution from the solid.

If the catalyst separation strategy developed for FRP chemistry has the potential to be used to efficiently sequester metal from a variety of reactions like environmentally friendly polymerization processes which include less metal leaching into the polymer material can be beneficial in several ways. For example, metal contamination of products from controlled radical polymerization is a recognized problem if polymers are being prepared for electronic or biomedical applications. The goal of this work is to develop more environmentally benign polymerization process that can employ highly active catalysts which can catalyze the reaction but form products with metal contamination at ppm levels. Ideally, the catalyst/polymer separation strategies will effectively remove the metal catalyst from the polymer product without extensive solvent precipitations.

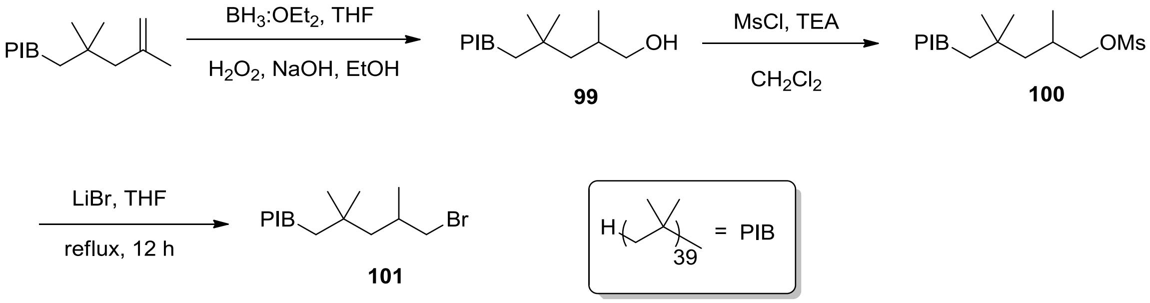
Other approaches to separate catalysts in homogeneous catalysis or in homogeneously catalyzed polymerization reactions include using insoluble polymer supports like polystyrene,[149] soluble polymer supports such as polyethylene glycol[150] and employing green solvents such as Fluorous solvents[151] water, $scCO_2$[152] or ionic liquids. For example, in a recent patent by Du Pont detailed the use of polymer tethered porphyrin and phthalocyanine like metal complexes (Co and Fe) as chain transfer catalysts in the synthesis of polyacrylates. These catalysts are separated from the solution of the polymeric product by a centrifugation or filtration after a homogeneous polymerization reaction.[153]

Previously the Bergbreiter group has reported that immobilization of metal complexes on soluble polymer supports not only serves as a phase anchor to recover the catalyst but also enhances the metal sequestration properties in a variety of polymerization reactions such as PIB-bound Ru catalyzed ring opening metathesis polymerization reactions (ROMP),[154] PIB-bound Cr catalyzed copolymerization of CO_2 and cyclohexene oxides[155] and PIB-bound Cu catalyzed ATRP reactions. [100,105,154,156-159]

My work in this chapter demonstrates that immobilization of the photoredox catalyst ($Ru(bpy)_3^{2+}$) onto a soluble polymer support like polyisobutylene (PIB) allowed the synthesis of a homogeneous catalyst which is recyclable.

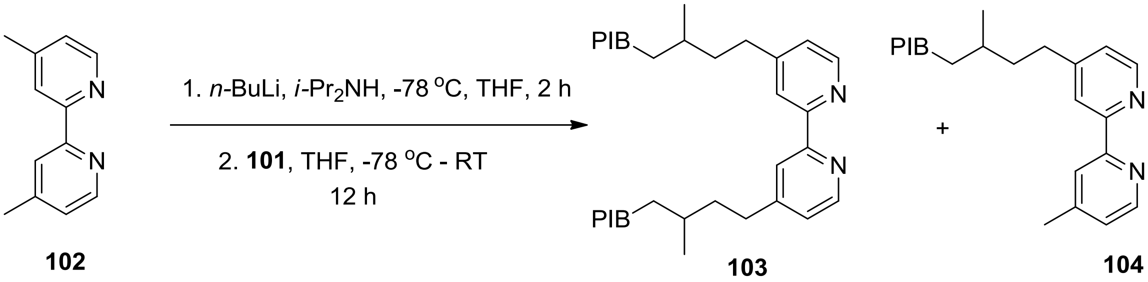
Results and discussion

The synthesis of a polyisobutylene (PIB) bound bipyridyl ligand began using commercially available alkene terminated PIB which is available with M_n values of 1000, 1300 and 2300 Da. However, for this bipyridine ligand synthesis PIB-2300 was used. The terminal alkene functionality of these PIB oligomers was converted to an alcohol **99** via hydroboration which was then be converted to a $-CH_2Br$ group in **101** via an SN2 reaction on an intermediate mesylate ($-PIB-SO_3CH_3$ **100)** (Scheme 35).



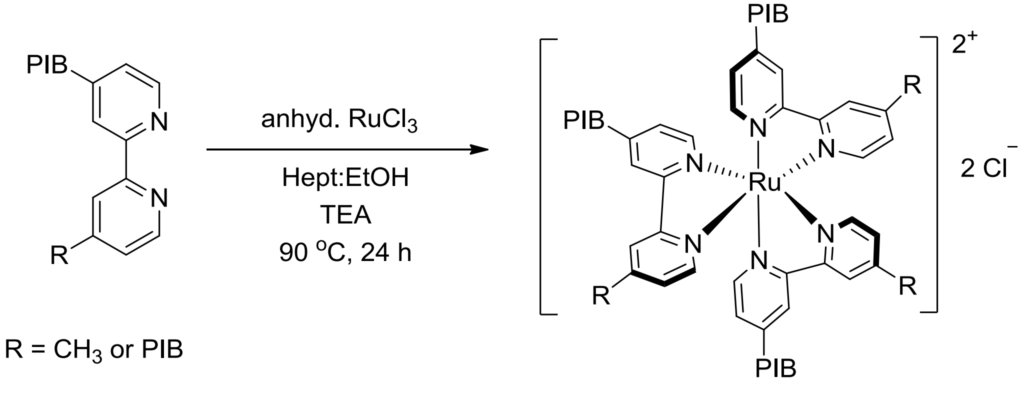
Scheme 35. Synthesis of PIB-Bromide 101.

Deprotonation of 4,4'-dimethylbipyridine (Mbpy) **102** with *in situ* generated lithium diisopropylamine at ca. -78 °C forms a mixture of the mono and di-anion of **102** as a dark brown-black solution. Addition of **101** to this solution yielded a mixture of mono and di-substituted PIB-bipyridine ligands **103 and 104** in good yield (Scheme 36). This mixture did not have to be purified for our purpose. However, it was possible to separate this mixture by silica gel chromatography. These PIB-bipyridine ligands were characterized by ^1H NMR spectroscopy and aromatic signals due to bipyridine portion of the ligands **103** and **104** showed similar chemical shift values.



Scheme 36. Synthesis of Polyisobutylene Bound Bipyridine Ligands (PIB = H-($CH_2C(CH_3)_2)_{40}$)

To synthesize a PIB-bound ruthenium metal complex, the PIB-bpy ligands **103** and **104** were allowed to react with anhydrous $RuCl_3$ in heptane and ethanol (Scheme 37). The use of excess ligands was crucial for avoiding side products with undesired number of ligands substitutions. The formation of the highly red colored Ru(PIB-bpy)$_3{}^{2+}Cl_2$ **105** could be followed both by ^1H NMR and UV_vis spectroscopy. The product complex has a broad absorbance at λ_{max} 463 nm in hexane which is comparable to that of a similar low-molecular weight ruthenium complex in acetonitrile[160] (Figure 21).



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Scheme 37. Synthesis of the Ru(PIB-bpy)$_3^{2+}$Cl$_2$ catalyst 105.

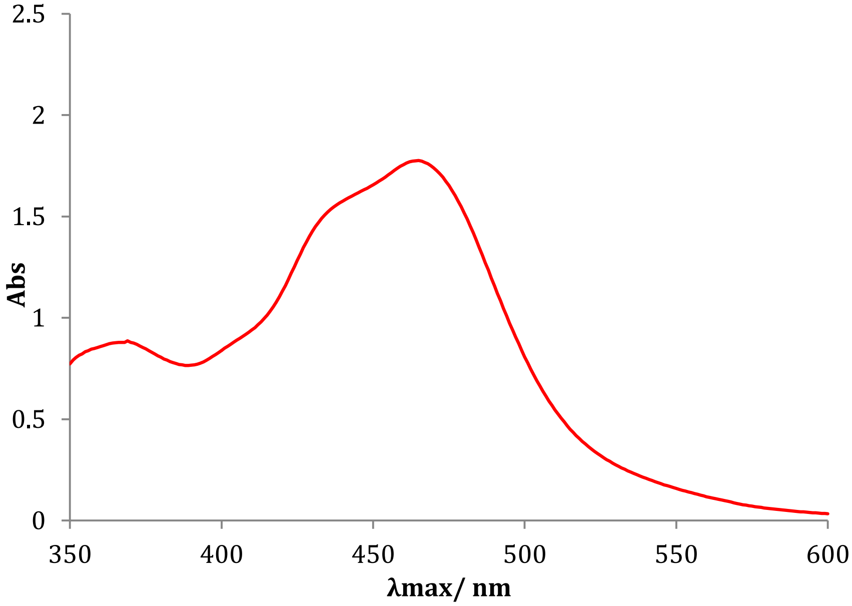
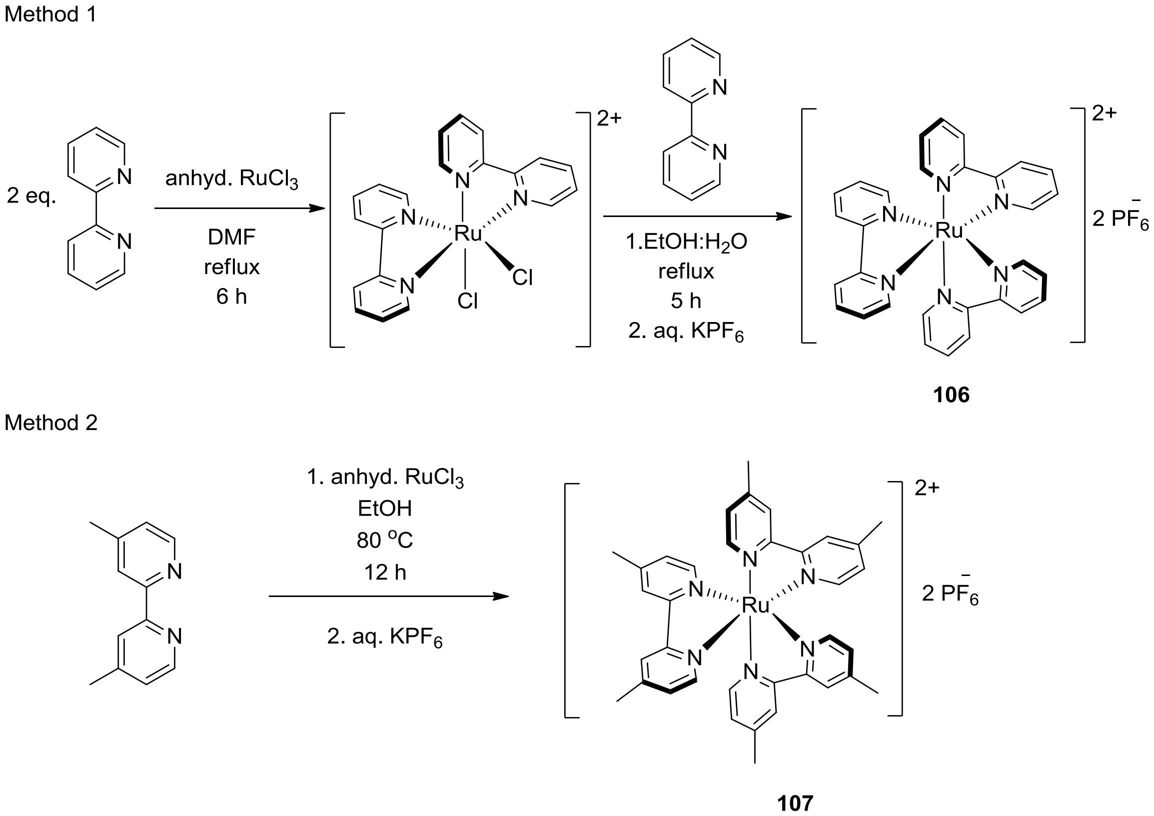


Figure 21. The UV_vis spectrum of the PIB-bound catalyst 105, 2×10^{-4} M solution in hexane.

Another objective of immobilizing the catalyst onto PIB was to examine the extent of Ru metal leaching in FRP reactions catalyzed by **105** compared to leaching of an analogous low molecular weight catalyst in the same polymerization reactions. Therefore, a low-molecular weight analogue of the Ru(PIB-bpy)$_3^{2+}$Cl$_2$ **105** was synthesized by using either 4,4'-dimethyl-2,2'-bipyridine (Mbpy) or 2,2'-bibyridine following either a two step or one step reaction schemes (Scheme 38).



Scheme 38. Synthesis of low molecular weight photoredox catalysts Ru(bpy)$_2$(Mbpy)$^{2+}$Cl$_2$ 106 and Ru(Mbpy)$_3^{2+}$Cl$_2$ 107.

As expected, the PIB-bound Ru catalyst Ru(PIB-bpy)$_3^{2+}$Cl$_2$ **105** complex showed phase selective solubility in a non-polar solvent such as heptane while the low molecular weight complex **107** was exclusively soluble only in polar solvents such as acetonitrile, dimethylsulfoxide and *N*,*N*-dimethylformamide (Figure 22).

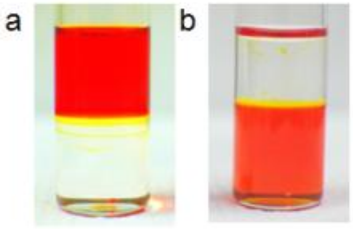
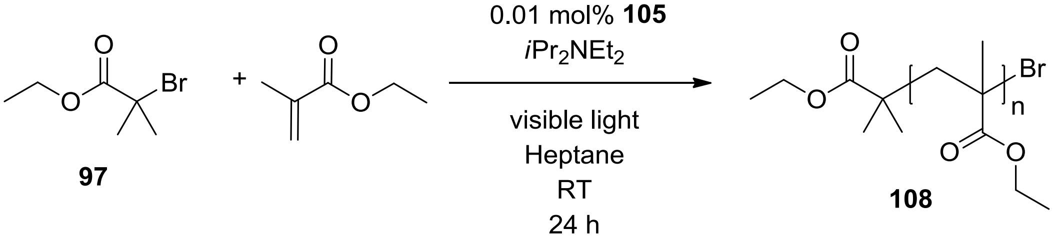


Figure 22. (a) Phase selective solubility of PIB-Ru photocatalyst 105 in heptane (top) in a heptane/DMF thermomorphic system, and (b) of the low-molecular weight Ru(Mbpy)$_3^{2+}$ 107 catalyst dissolved in DMF (lower) in the same heptane/DMF thermomorphic system.

The PIB-bound ruthenium photocatalyst **105** was first examined for its reactivity towards a radical polymerization reaction of a commonly available monomer ethylmethacrylate. The catalyst showed excellent reactivity on this polymerization reaction at a notable low catalyst loading of ca. 0.01 mol%. Encouraged by this initial result a catalyst recovery scheme was developed for the catalyst/polymer separation. As previously mentioned, the catalyst is soluble in heptane whereas the formed polymer was expected to be insoluble and to precipitate as a solid. Fortunately, this was true for the polymer- poly(ethylmethacrylate) (PEMA) and catalyst solution can be force siphoned from the solid polymer after centrifugation. This allowed the catalyst recovery and recyclability by adding new monomer substrates to the recovered catalyst solution for the subsequent reaction cycles. Following above protocol the polymerization of ethyl methacrylate (EMA) was carried out at ambient temperature under visible light irradiation (30W, household fluorescent bulb). In this case, *N*,*N*-diisopropylethylamine (*i*Pr_2NEt) and ethyl 2-bromoisobutyrate (EB*i*B) **97** were used as the electron donor for reductive quenching of the catalyst and as the initiator respectively (Scheme 39).



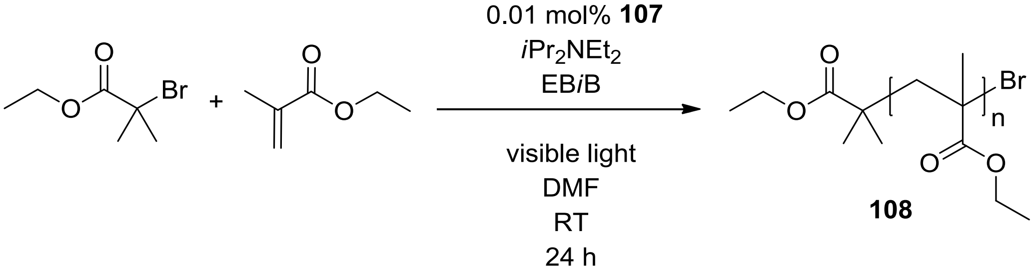
Scheme 39. Free radical polymerization of EMA using PIB-bound catalyst 105.

Above results showed that the catalyst **105** initiated the polymerization efficiently in heptane and polymer was precipitated as expected with reasonably narrow polydispersities (PDI). In this case, second and third polymerization cycles of EMA were also possible with the recovered catalyst in the supernatant from previous reaction solutions. For example, after 24 h of visible light irradiation of each reaction flask the top red colored heptane phase was force siphoned and added to another reaction flask with fresh monomer EMA. However, attempts made for recycling the catalyst for the forth cycle was not ideally successful giving a low yield ca. 40%. These recycling results of Ru(PIB-bpy)$_3^{2+}$Cl$_2$ **105** in polymerization of EMA reactions are summarized in the Table 5.

Table 5. Recycling results for 105 catalyzed polymerization of EMA in heptane.

Cycle	Yield	M_n	M_w/M_n
1	80	42702	1.2
2	72	40303	1.4
3	70	38778	1.4

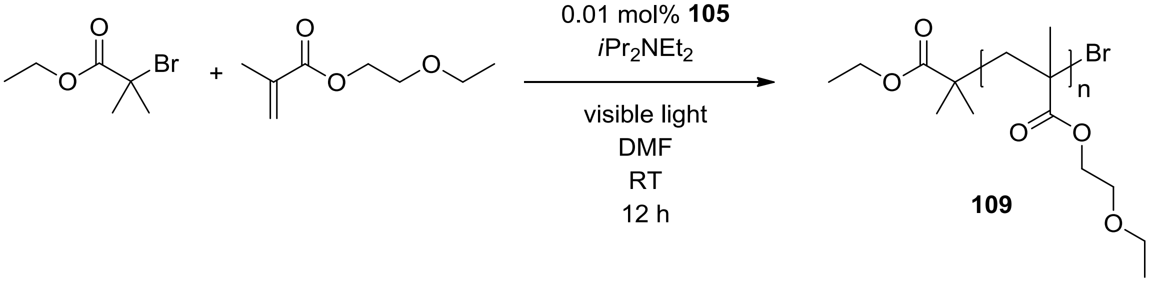
A similar, polymerization reaction of EMA with the low-molecular photocatalyst, Ru(Mbpy)$_3^{2+}$Cl$_2$ **107** was carried out under similar reaction conditions as described in Scheme 40. Due to catalyst **107** insolubility in heptane, *N*,*N*-dimethylformamide (DMF) was used as the solvent. This reaction also provided poly(ethyl methacrylate) (PEMA) with a yield and a molecular weight that was comparable to the PEMA products obtained with the catalyst Ru(PIB- bpy)$_3^{2+}$Cl$_2$ **105**.



Scheme 40. Photocatalyzed radical polymerization of EMA using the catalyst 107.

However, product PEMA formed from the reaction with low molecular weight catalyst **107** was soluble in DMF and the polymer had to be precipitated into methanol to separate it from the Ru catalyst which could not be reused.

To examine Ru leaching, the crude product obtained from the polymerization using the soluble polymer bound catalyst **105** and the initial polymer product obtained using catalyst **107** were both re-precipitated into methanol. The amount of metal leached into the polymer products were then analyzed by ICP-MS (Inductively Coupled Plasma Mass Spectrometer). Interestingly, ICP-MS analysis for ruthenium metal in the polymer **108** obtained from the second cycle of the polymerization reaction which was catalyzed by Ru(PIB-bpy)$_3^{2+}$Cl$_2$ **105** showed that Ru contamination was two orders of magnitudes less (ca. 0.76% (1.04 ppm)) than the metal leached in to polymer product obtained from a reaction which was catalyzed by the low molecular weight photocatalyst Ru(Mbpy)$_3^{2+}$Cl$_2$ (ca. 28.9% (48.38 ppm)).



109

Scheme 41. Photocatalyzed radical polymerization of EEMA using the catalyst 105.

To establish the generality of the developed catalyst/product separation strategy another polymerization of an acrylate monomer was briefly examined. In this case 2-ethoxyethyl methacrylate (EEMA) was polymerized in heptane and as expected poly(2-ethoxyethyl methacrylate) (PEEMA) polymer self separated from the solution of **105** by precipitating in heptane (Scheme 41). The catalyst was reused in two following polymerization cycles. The polymer molecular weights and PDIs were comparable to the results seen with EMA and are summarized in Table 6. It was noted that the polymerization of EEMA was a faster reaction compared to the EMA polymerization and resulted PEEMA polymer also showed higher PDI values compared to PEMA polymers. The faster reactivity may be justified by the more stable tertiary radical formed by EEMA monomer compared to EMA monomer that favors higher radical concentration in the reaction media and faster polymerization with a higher PDI values.

Table 6. Recycling results for 108 catalyzed polymerization of EEMA in heptane.

Cycle	Yield	M_n	M_w/M_n
1	75	35598	1.4
2	72	45961	1.6
3	60	49420	1.4

Conclusions

In summary, the PIB bound ruthenium bipyridine photoredox catalyst **105** effectively catalyzed free radical polymerization reactions of acrylate monomers with excellent catalytic activity. The PIB-bound **105** is soluble in non-polar solvents such as heptane and that solubility property was used in catalyst/product separation and the catalyst recycling. Additional benefits of developed PIB-bound photoredox catalyst lie in its facile reaction setup, ppm level catalyst loading, recycling of the precious metal catalyst and substantial decrease in metal leaching into polymer products. This offers a useful platform for a more sustainable radical polymerization processes especially when the produced polymer materials are applied in electronic materials or in medical devices

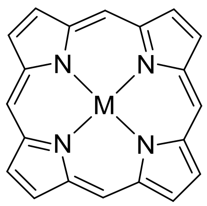
CHAPTER V

POLYISOBUTYLENE-BOUND ORGANO-SOLUBLE METALLOPHTHALOCYANINE

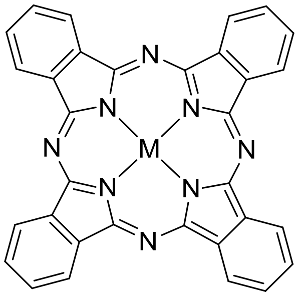
Introduction

Pthalocyanines (Pcs) are an interesting class of macrocyclic 18 π electron aromatic compounds with electronic properties that resemble those of the of more common porphyrin compounds (Figure 23). While a porphyrin like **110** consists of four pyrrole subunits which are linked via four methine carbons, phthalocyanines **111** are comprised of four isoindole units conjugated via four aza nitrogen atoms forming an 18 π electron inner core which is further delocalized into four benzo units. These structural features of phthalocyanines introduce novel chemical and physical characteristics to the structure compared to porphyrins. For example, the extended π conjugation of the macrocycle causes aggregation between phthalocyanine rings making them very insoluble in water and common organic solvents. The four aza nitrogen atoms in phthalocyanine rings in place of the methine carbons in a porphyrin make phthalocyanine molecules more stable compared to porphyrins (Figure 23)[161-163].

The term phthalocyanines (Pc) first used by R.P Linstead et al. at the University of London in 1933 to explain a class of organic dye compounds with blue green colors.[164] The term was originated from Greek terms naphtha for 'rock oil' and cyanine for 'dark blue'. All these metallated or nonmetallated phthalocyanines are highly colored blue or green color materials. Their metalloderivatives has a long history as being used in dyes and pigments industry. [165]



M = metal , H_2 **110**



M = metal , H_2 **111**

Figure 23. General structures of porphyrin 110 and Phthalocyanine 111 molecules.

The UV_vis spectra of metallophthalocyanines provide useful information about their structure and solubility. A typical electronic spectrum of a Pc molecule shows two strong absorption bands named B and Q bands. The strong absorption maxima in the far red end of the visible region (670 nm – 700 nm) (the Q band) is due to π-π* transitions from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbitals (LUMO) in the Pc ring system. The next set of transitions - the B-band lies around 340 nm and this absorption is usually less intense than Q-band. In general, metallophthalocyanines (MPcs) belong to D_{4h} symmetry group and that causes only one absorption peak in the Q band region in the UV_vis spectrum (Figure 24 a). Alternatively, this Q-band appeared as two peaks when the symmetry of the molecule is changed to D_{2h} symmetry as is the case in metal free phthalocyanines (Figure 24 b).

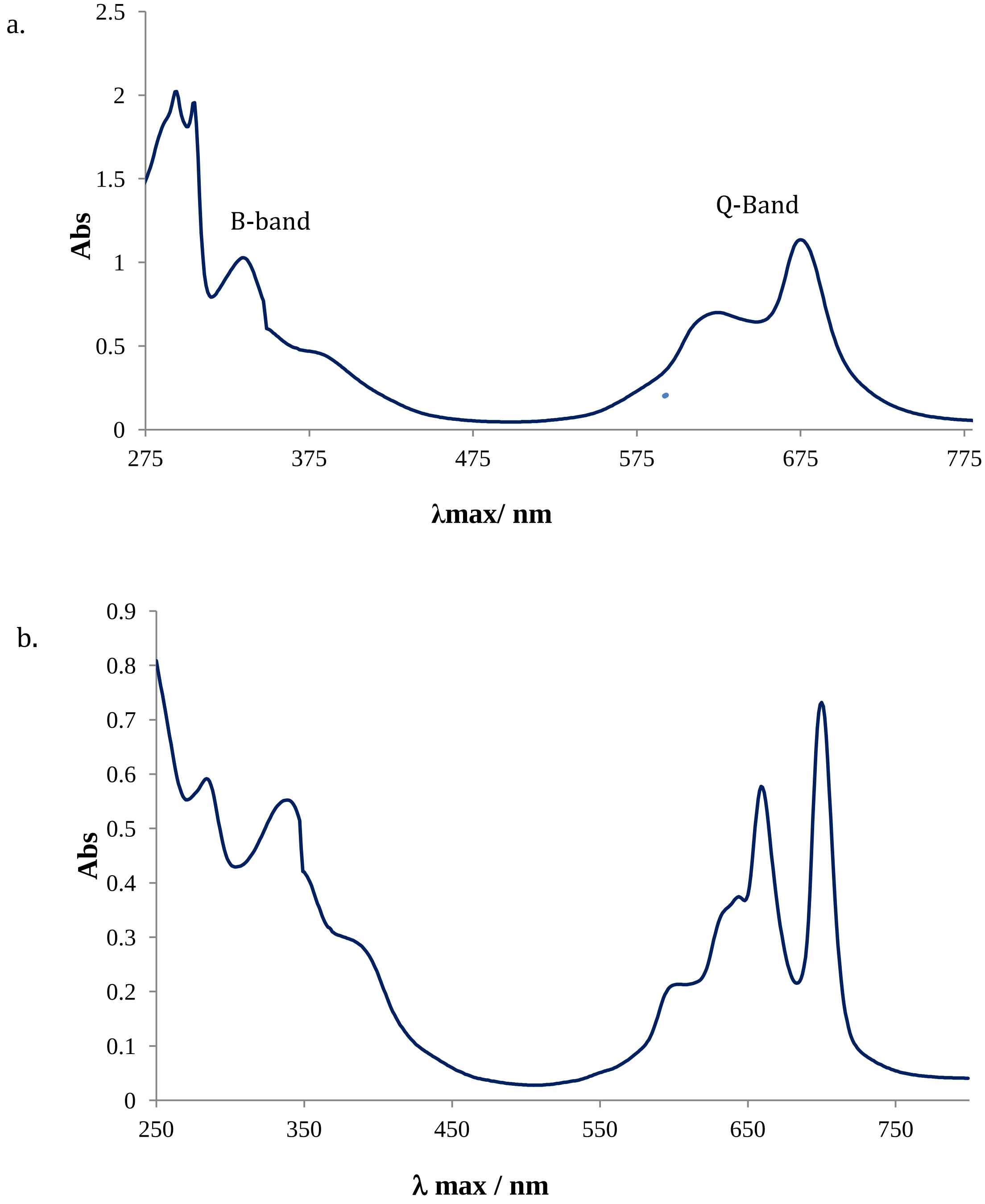
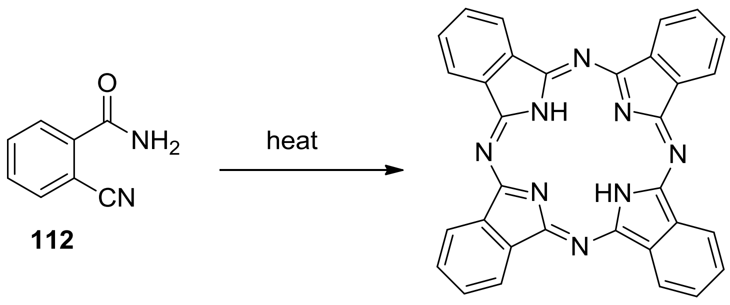


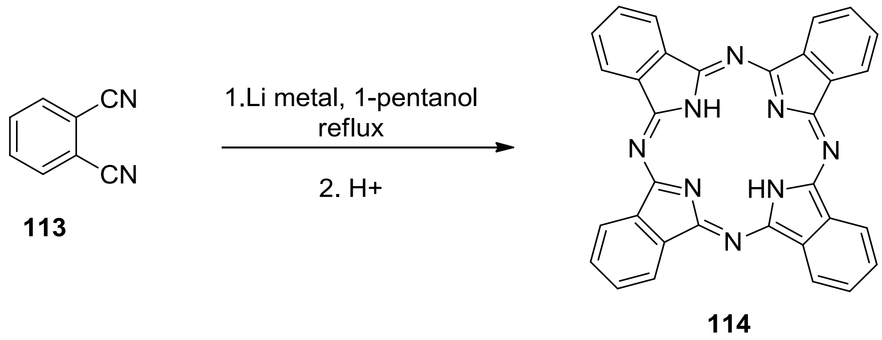
Figure 24 a. Typical UV_vis spectrum of a metallophthalocyanine (MPc): b. UV-vis spectrum of a metal free Pc (PcH_2).

The first synthesis of phthalocyanines was reported in 1907 by Baun and Tcherniac during an experiment to form *ortho*-cyanobenzamide **112** from phthalimide and acetic acid. Instead of the expected product, the high heat led to a formation of a very insoluble dark blue material which was later characterized as a phthalocyanine (Scheme 42).



Scheme 42. The first synthesis of phthalocyanines.

Among the number of different methods for phthalocyanine synthesis the most common and economical method for synthesis of Pcs via the condensation of a phthalonitrile **113** in the presence of lithium metal and a high boiling alcoholic solvent such as pentanol (Scheme 43). The Lithiated phthalocyanine ring can be protonated in an acidic work up yielding the metal free Pc **114**.[166]



Scheme 43. Preparation of phthalocyanines.

The solubility and other chemical properties of Pcs mainly depend on the substituents in the peripheral benzo groups. The most common strategy to introduce functional groups onto the Pc ring is to use a phthalonitrile precursor which has the desired functional groups. However, statistical condensation of this phthalonitrile yields tetrasubstituted phthalocyanines as a mixture of four region-isomers of C_s, C_{2v}, C_{4h} and D_{2h} symmetries in a ratio of 4:2:1:1 (Figure 25).[167]

The characteristic blue green color of these materials makes them excellent as dyes for textiles and as pigment inks. The most common metallophthalocyanine dye is the copper (CuPc) dye which was first manufactured by ICI in 1935. It was synthesized by reaction of phthalic anhydride **115**, urea and copper salts or by condensation of phthalonitrile **116** in the presence of copper salts (Scheme 44). Du Pont followed this work and began manufacturing this CuPc dye in 1937. This CuPc is now produced worldwide. These are interesting compounds as dyes not only because they are highly colored but also due to their high thermal and light stability. Other important properties

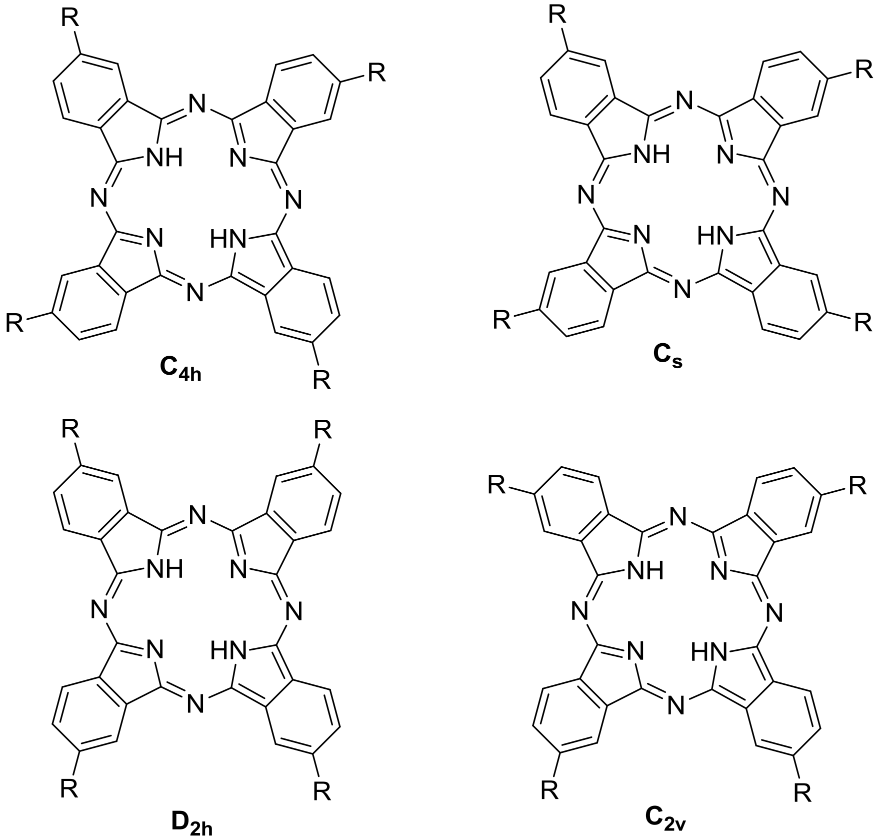
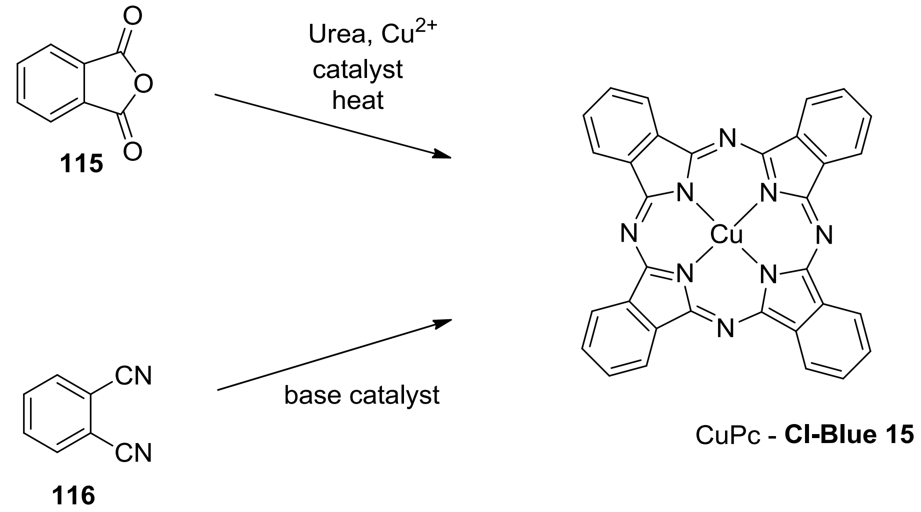


Figure 25. Positional isomers of tetrasubstituted phthalocyanines.

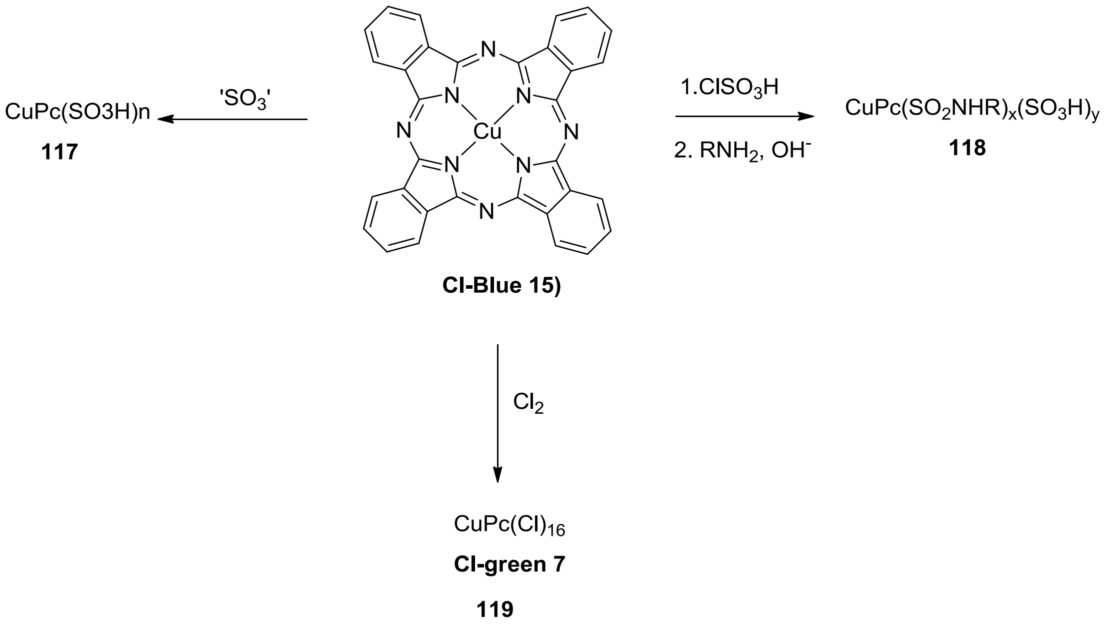
of these dyes such as solvent and oxidative resistance are also useful properties when using these Pcs as pigments for paints and plastics.[165]

While the CuPc dye **CI-Blue 15** has the desired color, it is generally functionalized with other functional groups as shown in Scheme 43 to gain solubility and to improve its. The strategies used generally involve electronic aromatic substitution of the aryl groups in **Blue 15.** For example**,** sulfonation of CuPc to yield sulfonic acid derivatized Pc and di, tri and tetra substituted sulfonic acid derivatives (**117**) that are greatly water soluble affords important and commercially useful dyes. A second route procedure uses chloro-sulfonation of CuPc to form sulfonylchloride derivatives which are then allowed to react with amines to produce cyan dyes **118** that are also used in the textile industry. Finally the copper phthalocyanines **15** can be chlorinated to form more soluble CuPcs **119** (Scheme 45).[165]

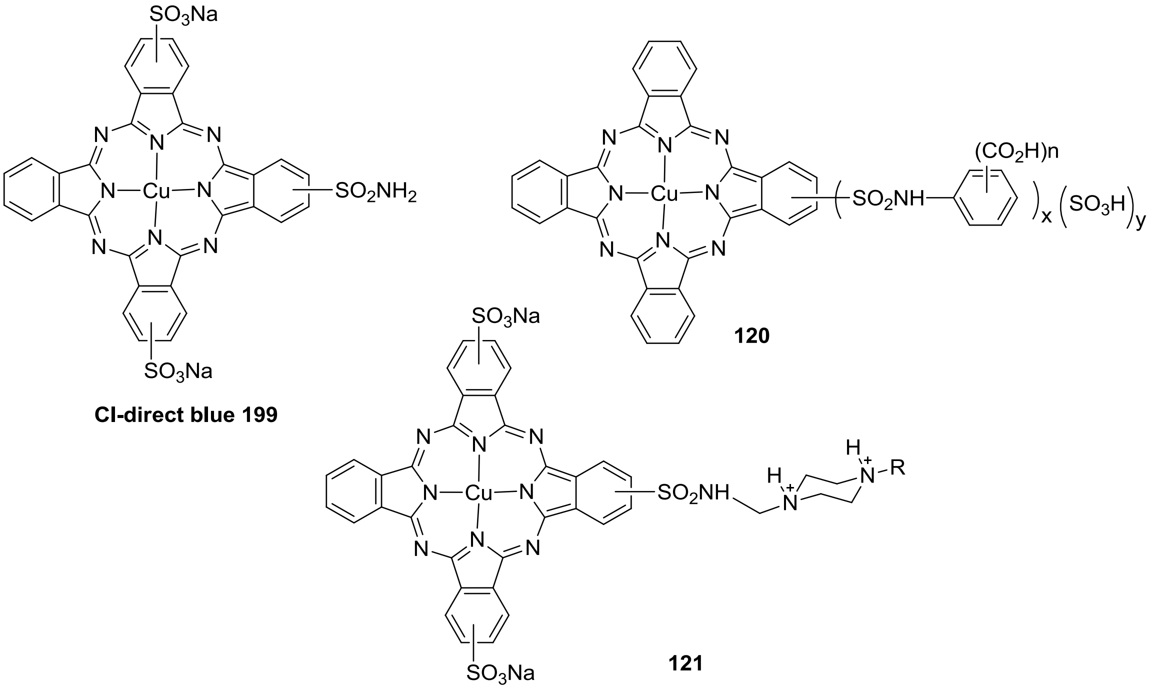


Scheme 44. Synthetic routes for copper phthalocyanine CI-Blue 15.

The commercial impact of these Pcs is principally a result of their beautiful blue-green colors, their excellent chemical stability and the fastness of these dyes to light. For example, first generation of ink jet printers which appeared in the late 1980s used regular Pc dyes like CI-direct Blue **199** (Figure 26). Although dye **Blue 199** was chemically and thermally stable, poor water fastness was a drawback for its use as a pigment in ink jet printing. Improved water and light fastness of this dye was achieved by modifying the peripheral substitution of CuPc as in **120** and in **121**. For example, the dye **120** has the correct pK_a to be soluble in water forming the anion and get protonated on the paper surface to form the free acid which is a water insoluble dye.[165]



Scheme 45. Functionalization of CuPc to form $CuPc(SO_3H)_n$, $CuPc(SO_2NHR)_x(SO_3H)_y$ and $CuPcCl_{16}$.



CI-direct blue 199

120

121

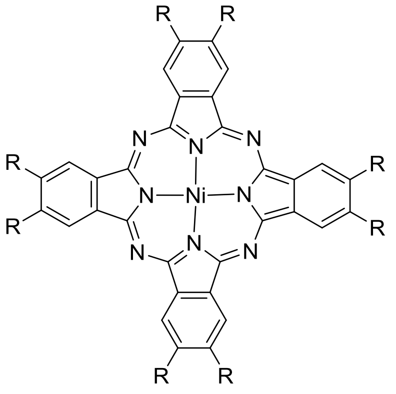
Figure 26. Commercial ink jet inks and their functionalizations.

However, peripherally unsubstituted MPcs and metal free phthalocyanines (H2Pcs) are highly insoluble in most organic solvents. The tendency of these MPcs to self aggregate via π stacking interactions to form dimers or higher order architectures leads to this high insolubility. Introduction of bulky or long chain groups like alkyl or alkyl- thio groups onto periphery of Pcs enhances the solubility of these dyes in organic solvents extending the applications of these materials into many technological fields such as liquid crystals, catalysis, electrochromic and photochromic materials, data storage systems, photodynamic theraphy agents, photoactive units, chemical sensors and nonlinear optical devices.[168-170]

There have been numerous reports in literature describing different substitution chemistries that improve the solubility of MPcs in common organic solvents (Figure 27). In an early report by T. Marks et al. detailed alkyl substituted MPcs showed higher solubility in aromatic solvents compared to unsubstituted MPcs.[171] For example, octabutyl substitution in the phthalocyanine **122** was claimed to increase the solubility of NiPc substantially to ca. 4.2×10^{-5} M in trichlorobenzene where as unsubstituted Pcs were completely insoluble in this solvent. This study also showed that butyl substitution of MPc (**122**) led to a greater solubility compared to methyl substitution MPcs (ca. 1.5×10^{-5} M versus 4.2×10^{-5} M).

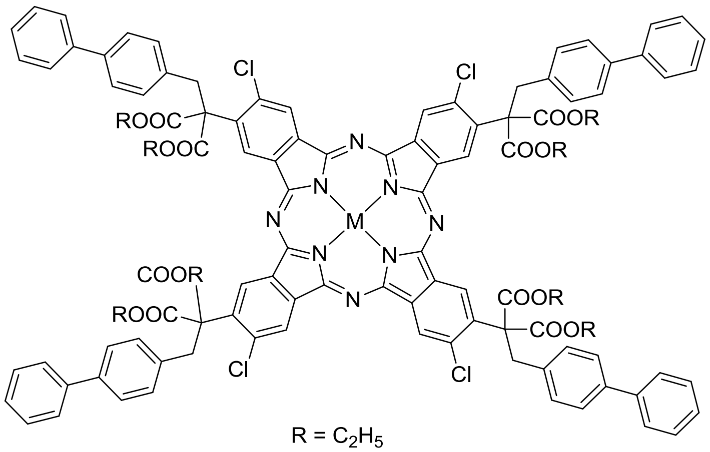
The formation of MPc aggregates in solutions can also be prevented by the introduction of bulky groups in the peripheral positions. In this case stacking interactions by rings in adjacent Pc molecules also become inefficient, facilitating the solubility of MPcs. To accomplish this, MPcs have been functionalized with biphenyl groups as peripheral substituents and with bulky malonic ester pendent groups. For example, **123** shows no aggregation in organic solvents such as DMF, acetonitrile, dimethyl sulfoxide (DMSO) forming solutions that have a concentration of 10^{-6} M .[172]

Phthalocyanine's ability to form aggregates was also used as a useful tool in the synthesis of MPcs which were substituted by crown ethers **124.** These molecules showed higher aggregation tendency by solvents and by cations. Hence they are useful compounds in colorimetric determination of cations and served as ion channels for transporting ions due to the stacking of the crown ether rings.[166]



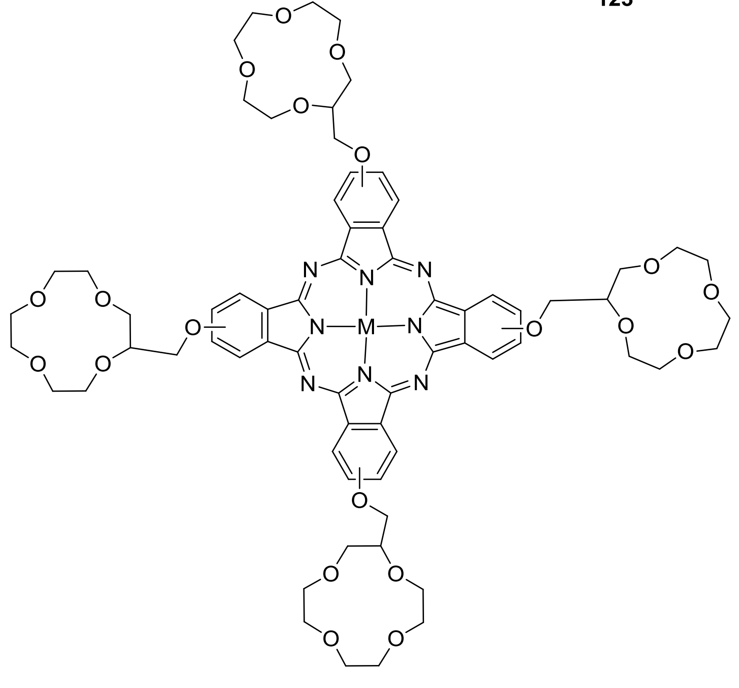
R = n-C_4H_9

122



R = C_2H_5

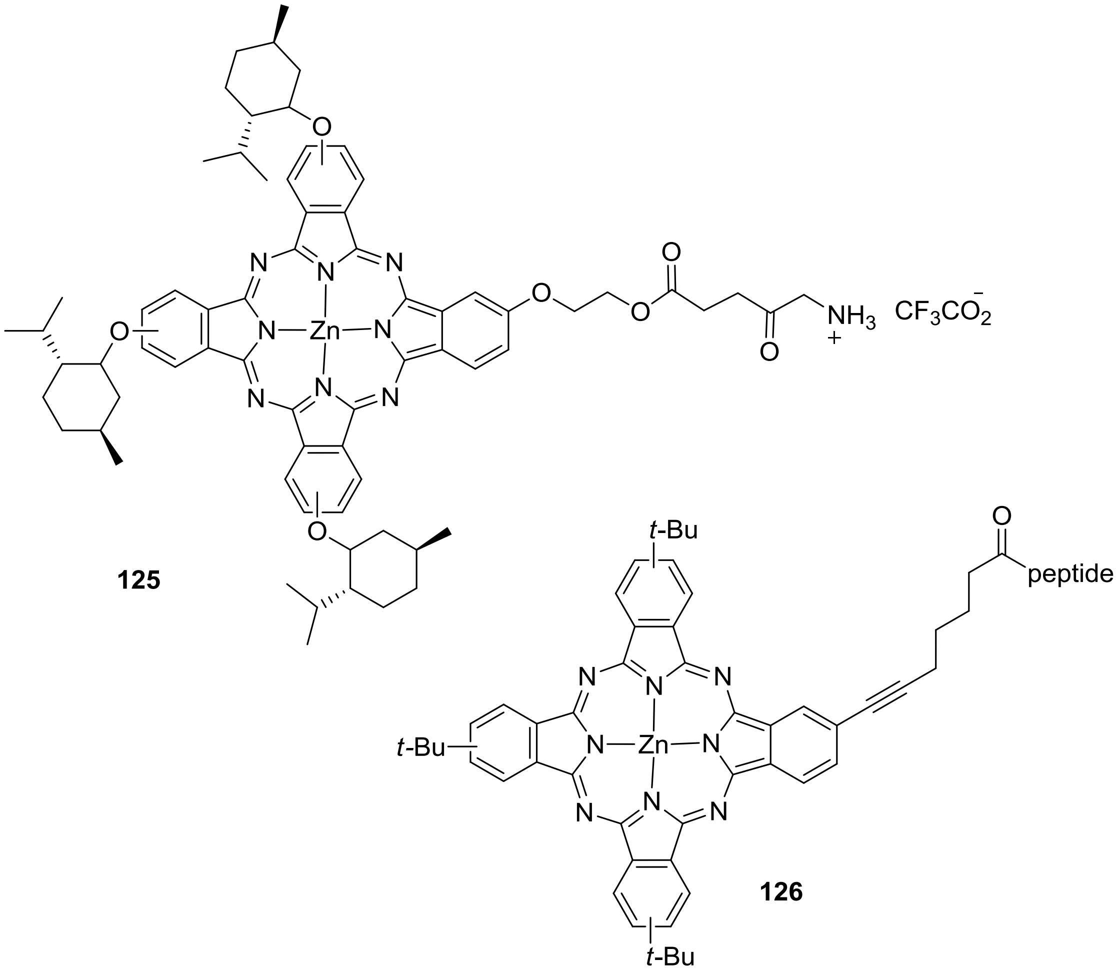
123



124

Figure 27. Peripherally modified phthalocyanines.

As previously described, organic solvent soluble phthalocyanines broaden the scope of the applications of MPcs. Likewise; water soluble phthalocyanines are also of interest as they can serve as photosensitizers in photodynamic therapy (PDT). PDT is a noninvasive treatment for many diseases including cancer which involves light, a



125

126

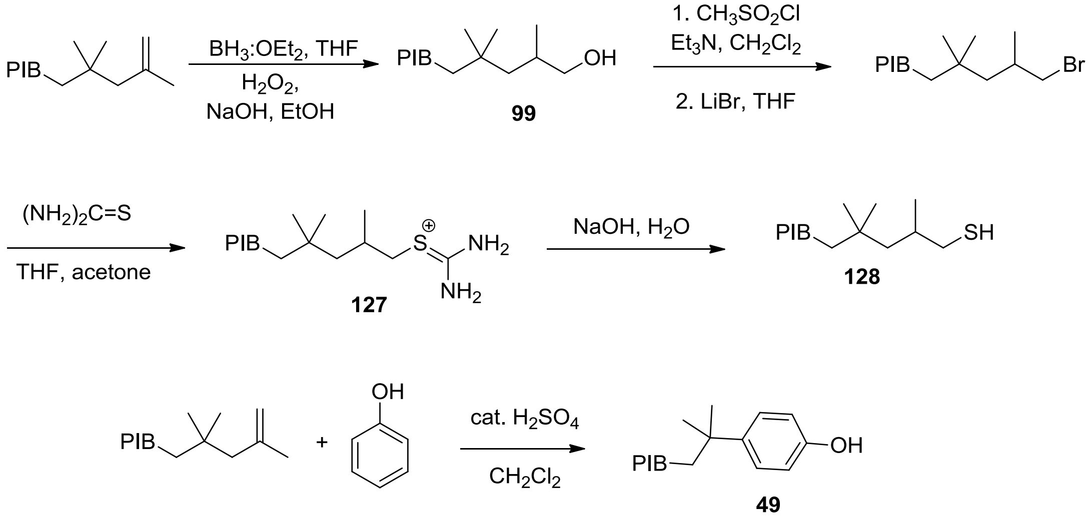
Figure 28. Water soluble Zn-Pcs for PDT applications.

photosensitizer (PS) and oxygen. Most of the photosensitizers are hydrophobic molecules and tend to accumulate in hydrophobic sites within the cell. Functionalization of phthalocyanines which are active photosensitizers (PS) can alter the hydrophilicity of an MPc and provides a useful method of increasing the utility of MPcs as photosensitizers in PDT. For example, 5-aminolevunic acid (ALA) substituted phthalocyanine **125** acts as PSs to kill tumor cells in vitro. These peripherally mono-5-aminolevulnic acid (ALA) substituted ZnPc **125** was reported to be highly soluble in polar organic solvents such as dimethylsulfoxide (DMSO) and water without any aggregation mainly due to the presence of the bulky menthyl group (Figure 28). Peptide bound Pcs like **126** are also popular substituents in PDT applications. These peptide moieties can improve cell targeting and the water solubility of the Pc by reducing aggregation.[168,169,173-176]

The work described in this Chapter is focused on the synthesis of a variety of peripherally substituted MPcs with polyisobutylene groups. The idea was that PIB groups would enhance the solubility of these MPcs in hydrocarbon solvents such as heptane and hexane and in other weekly polar solvents just as PIB groups are used in other work described in this dissertation to form phase selectively soluble azo dyes. These studies thus parallel to other work done by the Bergbreiter group directed toward the development of soluble polymer-bound catalysts and ligands where, polyisobutylene oligomers have been used as a non-polar phase handle to prepare these phase selectively soluble catalysts.[177]

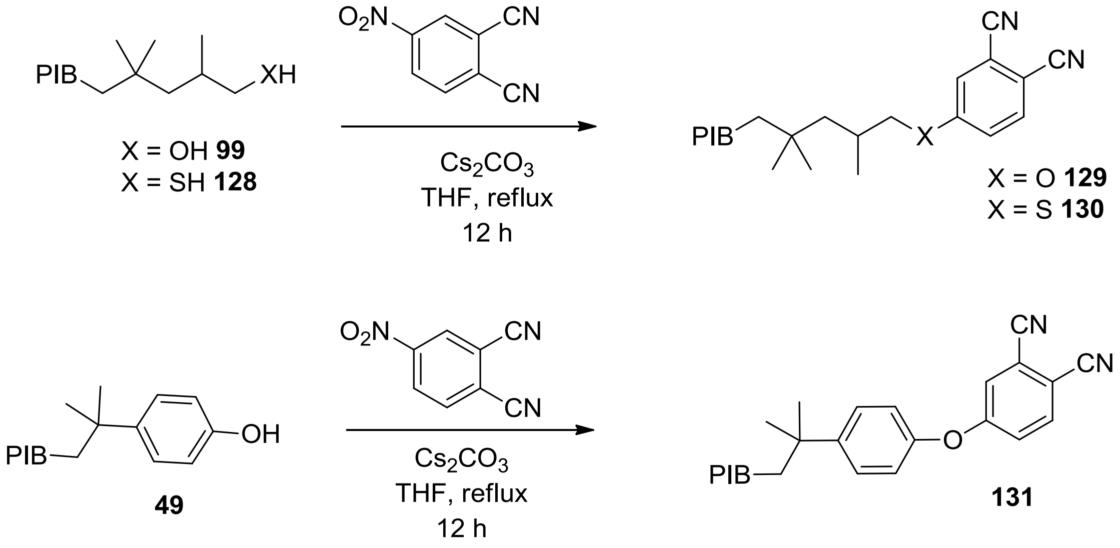
Results and discussion

To prepare PIB-substituted MPcs, PIB oligomers terminated with hydroxyl **99**, thiol **128**, and phenol **49** groups were prepared from commercially available vinyl terminated PIB-oligomers using the chemistry shown in Scheme 46. Working with a summer REU student (Mr. Chase Benzine), the PIB-attached alcohol **99** was synthesized using the hydroboration/oxidation procedure as described in Chapters II and III.



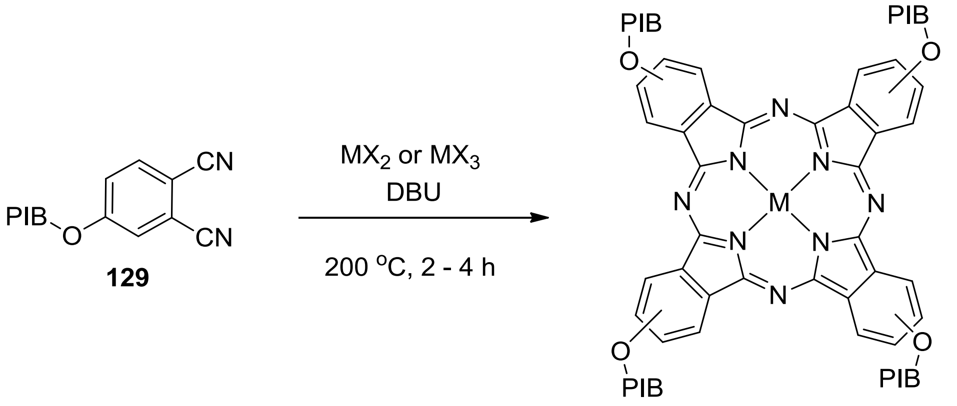
Scheme 46. Synthesis of PIB-bound nucleophiles with hydroxyl, thiol or phenol groups.

Activation of this PIB alcohol as a mesylate followed by nucleophilic substitution of this mesylate first by bromide and then by thiourea formed a thiouronium salt **127** that on hydrolysis formed a thiol **128** (This work was carried out by a coworker – Dr. Dongmai Zhang). Electrophilic aromatic substitution of the commercially available alkene-terminated polyisobutylene oligomers with phenol provides a simple route to the PIB-terminated phenol **49**. All the functionalized PIB-oligomers and intermediates were characterized by ^{1}H and ^{13}C NMR spectroscopy. There was some unfunctionalized PIB-oligomer also present in the starting alkene terminated PIB. That was removed by a column chromatography from the polar products **99**, **128** and **49**. All of these polyisobutylene oligomers proved to be suitable nucleophiles for a nucleophilic aromatic substitution of the nitro group of 4-nitrophthalonitrile (Scheme 47). This well known chemistry has been previously used to introduce a variety of groups onto a phthalonitrile precursor for a metallophthalocyanine.[172] Most relevant to this work, it has been previously used by a DuPont group to prepare a 4-polyethylated-4-hydroxyphthalonitrile.[178]

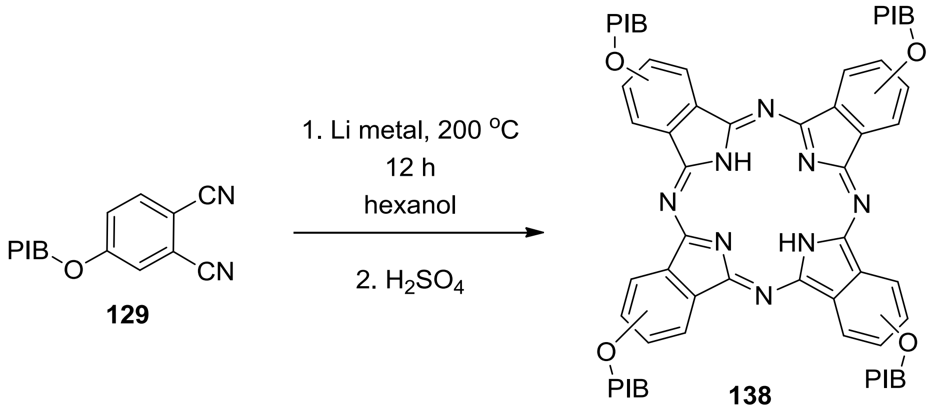


Scheme 47. Synthesis of PIB-bound phthalonitriles 129 – 131 by nucleophilic substitution of 4-nitrophthalonitrile.

Following the approach reported by the DuPont that used hydroxyl-terminated polyethylene oligomers to prepare a thermomorphically soluble polyethylene derivatives of a cobalt metallophthalocyanine, phthalonitriles containing polyisobutyl derivatives were also cyclicized in the presence of metal salts to form metallophthalocyanines (Scheme 48). The products prepared from this statistical condensation method are a mixture of four different metallophthalocyanines. Since the orientation of the PIB groups in the phthalonitrile residues in positions of the metallophthalocyanines is not controlled, a 4:2:1:1 mixture of isomers with different symmetries presumably formed.[167] This cyclization reaction worked equally well with a variety of metals like Cu, Co, Pd, Ni, Zn, and Cr. PIB-bound metallophthalocyanines **132** – **137** were prepared using the 4-polybutylenoxy-substituted phthalocyanide **129**. The metal free analogue of these metallophthalocyanines was also synthesized via Li metal catalyzed macro-cyclization of **138** in a high boiling alcohol as a solvent followed by an acidic work up (Scheme 48).



MX_2 or MX_3; **132**; $CuCl_2$, **133**; $Co(OAc)_2$, **134**; PdC_{l2}, **135**; $NiCl_2$, **136**; $ZnCl_2$, **137**; $CrCl_3$



Scheme 48. Synthesis of PIB-bound metallophthalocyanines 132 – 137 and PIB-bound metal free phthalocyanine 138.

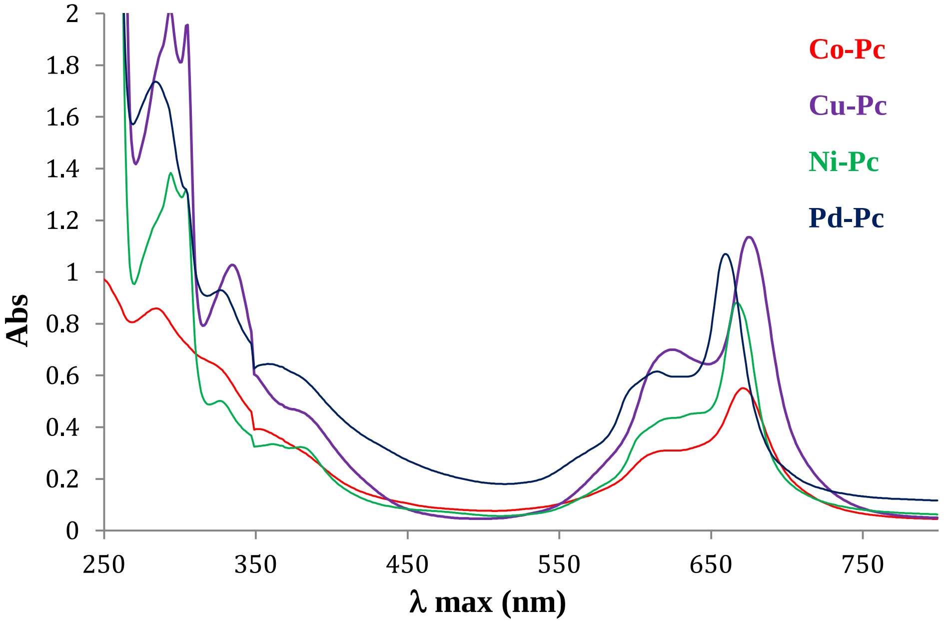


Figure 29. UV_vis spectra of PIB-bound metallophthalocyanines 133-138 in hexane.

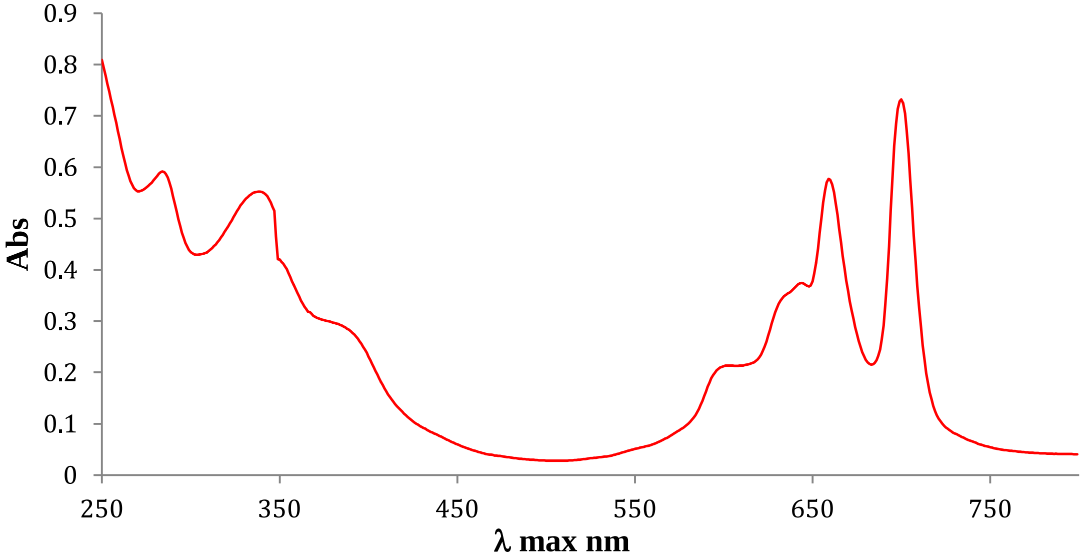
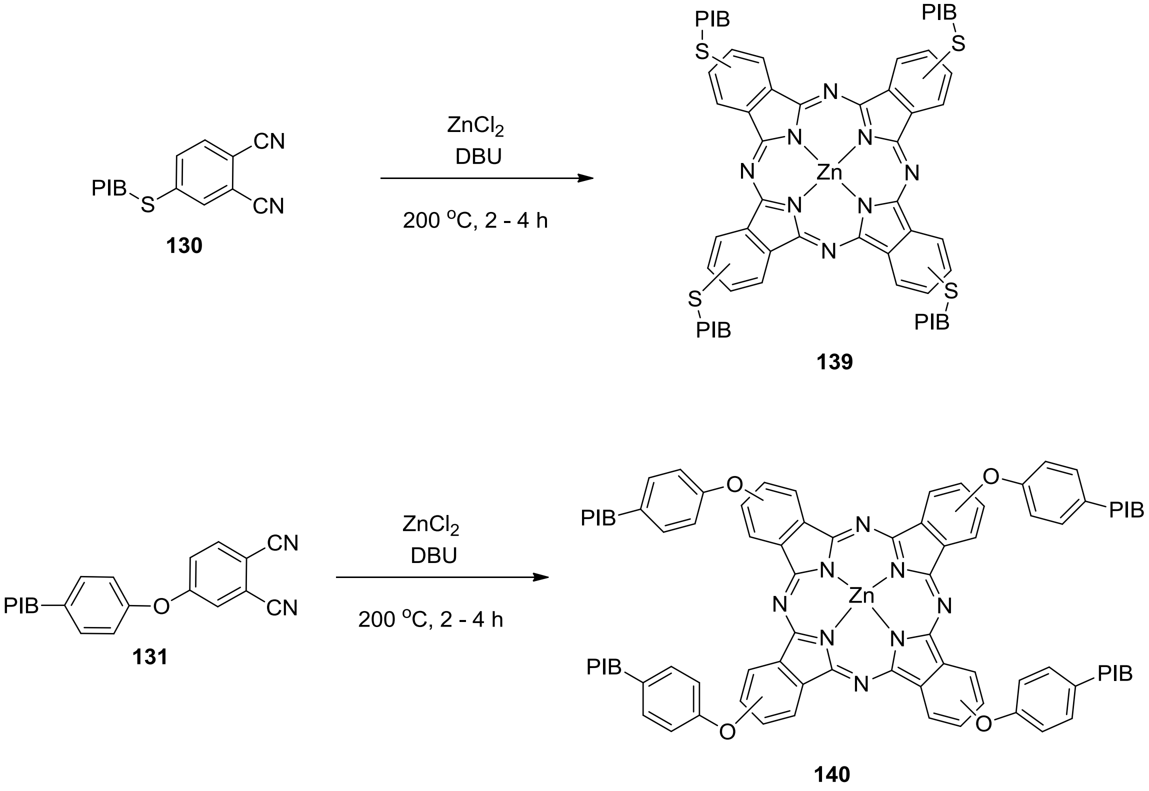


Figure 30. UV_vis spectrum of PIB-bound metal free phthalocyanine 139.

UV_visible spectroscopy was a general tool for characterizing these metallophthalocyanines. The spectra showed that the MPcs differed modestly from one another and Figure 29 illustrates UV_visible spectra for the PIB-bound **132**, **133**, **134** and **135** metallophthalocyanines. While most of the metals do not distort the symmetry of the macro cycle, certain larger metal ions cause some distortion to the phthalocyanine and that can effect deviations in the UV_vis spectroscopy. PIB-bound metal free phthalocyanine **138** is less symmetric than metallophthalocyanines and was evident from its UV_vis spectrum that has two distinct sharp Q bands in the far red end of the visible spectrum (Figure 30).

The thiol and phenol functionalized phthalonitriles **130** and **131** was also cyclicized successfully in work done in collaboration with an undergraduate – Mr. Ben Cassidy. In this case PIB-thiol-phthalocyanide **130** was used to prepare zinc metallated MPc **139** and 4-polyisobutylphenoxy-substituted phthalocyanide **131** to form metallophthalocyanine **140** (Scheme 49).



Scheme 49. Synthesis of PIB-bound ZnPc 139 and 140.

a.

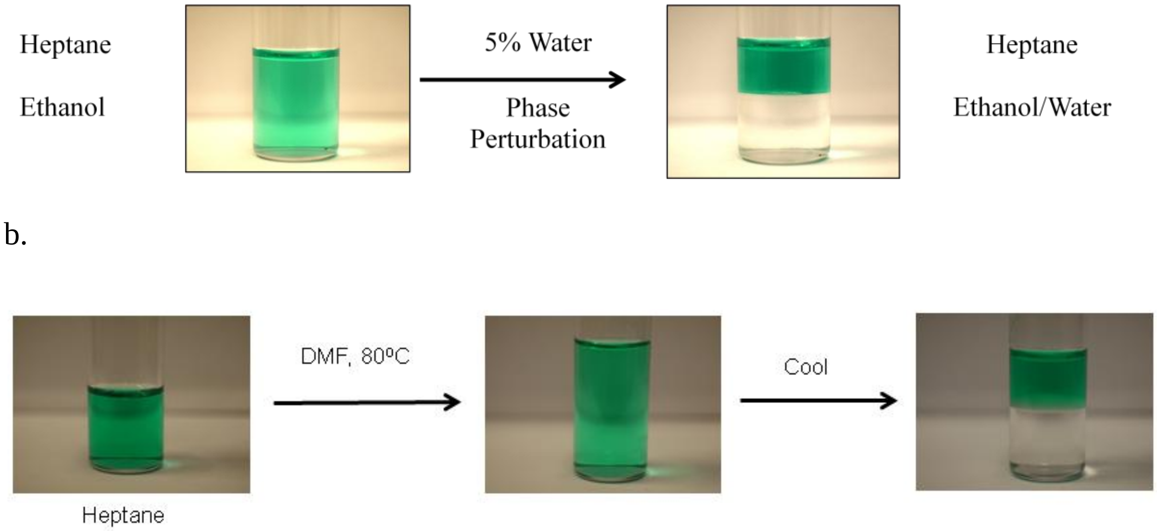


Figure 31a. Phase selective solubility of PIB-bound metallophthalocyanine 133 in a heptane/ethanol latent biphasic solvent mixture; 31b. Phase selective solubility of PIB-bound metallophthalocyanine 135 in a heptane/DMF thermomorphic solvent system.

All these PIB modified metallophthalocyanines have excellent solubility in non-polar solvents such as heptane and in moderately polar solvents such as tetrahydrofuran and dichloromethane. These phthalocyanines were also heptane phase selectively soluble in thermomorphic mixtures of heptane and a polar organic solvent such as dimethyl formamide (DMF). They are heptane soluble in biphasic mixtures of heptane and acetonitrile. This is illustrated by the photographs in Figure 31a where the PIB-bound Co^{2+} metallophthalocyanine **133** is initially soluble in a miscible monophasic heptane-ethanol solution but phase selectively soluble in the heptane phase of the biphasic mixture that forms when this system is perturbed by the addition of 5 vol% water (Figure

31a). Similar solubility is seen in a thermomorphic heptane/DMF solvent mixture where the PIB-bound Zn^{2+} metallophthalocyanine **135** is exclusively soluble in the heptane phase in a heptane/DMF mixture, soluble in the hot miscible equivolume mixture of heptane and DMF, and heptane phase selectively soluble in the heptane rich portion of the biphasic mixture which forms on cooling this thermomorphic solvent mixture (Figure 31b).

Since these PIB-metallophthalocyanines are highly soluble in hydrocarbon solvents, the miscibility of these materials in commercially available low molecular weight (M_n values of 400 and 700) polyethylene waxes was also examined. Interestingly, these PIB-phthalocyanine dyes were observed to be readily dispersed in hot wax phase forming a blue-green solid product. Finally, the solubility of the PIB-metallophthalocyanines in a commercially available high density polyethylene (HDPE) and High Density Polypropylene (HDPP) melt was briefly examined by dissolving these blue green PIB-metallophthalocyanines in molten HDPE and HDPP using a Haake-Rheocordmixer (Figure 32). The solid dyed HDPE produced in this process was highly colored with a 5 wt% loading of **133** as a dye. Diluting this dye to form a 1 wt% mixture in HDPE produced light blue-green solid (Figure 32c).

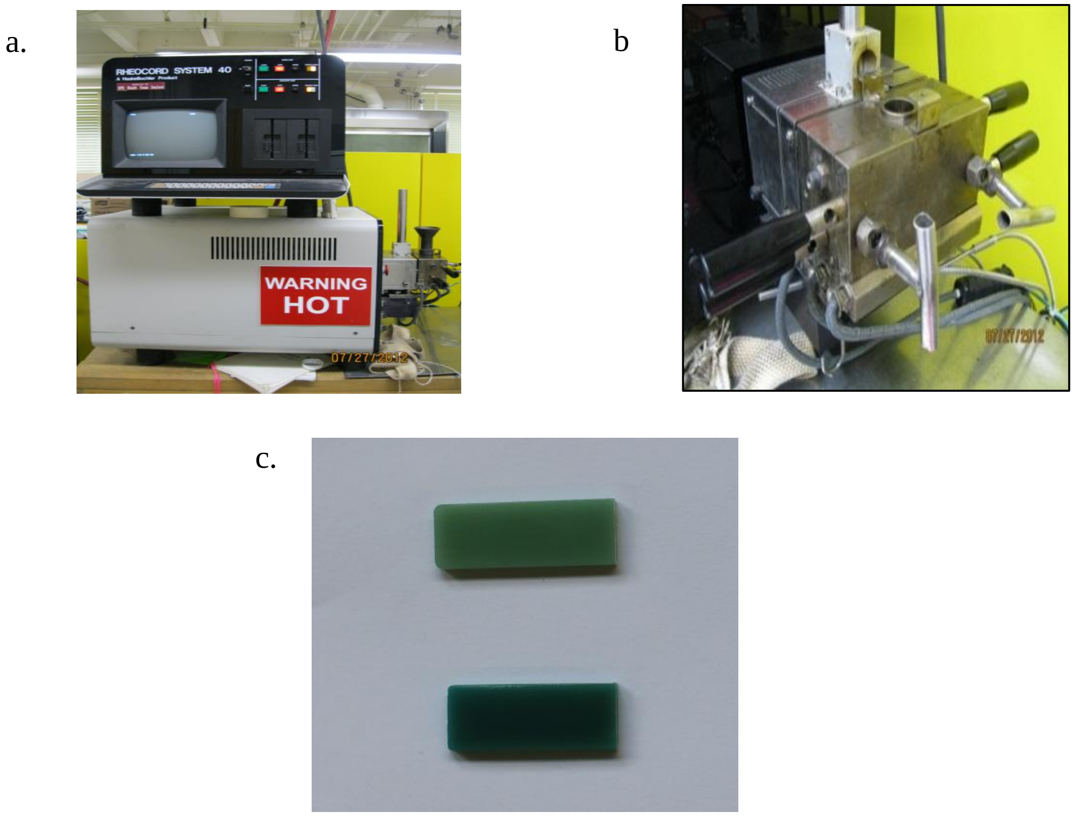


Figure 32. a. Haake-Rheocordmixer for melting HDPE; b. HDPE melting chamber of the mixer; PIB-MPc 133 dyed HDPE.

Conclusions

In conclusion, PIB-substituted metallophthalocyanines were succesfully prepared via a cyclization reaction of differently functionlized PIB-phthalonitrile derivatives **129** - **131**. These prepared PIB-MPcs are higly colored viscous materials which showed excellent heptane phase selective solubility compared to other polar organic solvents such as DMF and acetonitrile. The utility of these PIB-phthalocyanine dyes in dyeing commericial High Density Polyethylene (HDPE) and High Density Polypropylene (HDPP) was also examined by melt mixing of the PIB-MPc materials into the HDPE and HDPP. The visual uniformity of the dyed HDPE and HDPP materials showed the PIB-MPc dyes can disperse homogeneously into these polyolefins.

CHAPTER VI

EXPERIMENTAL SECTION

General methods

Vinyl-terminated PIB oligomers (Glissopal 1000, 1300 and 2300, M_n of 1000, 1300 and 2300 were obtained from BASF. The unfunctionalized polyethylene oligomer (POLYWAX 400, M_n of 400) was supplied as a gift from Baker-Hughes. Commercial high density polyethylene (HDPE) and high density polypropylene (HDPP) materials were supplied from INEOS-olefins-USA. All other reagents and solvents were purchased from commercial sources and used without further purification unless otherwise specified. ^{1}H NMR spectra were obtained on Varian Inova 300 or 500 spectrometers operating at 299.96 and 499.71 MHz, respectively.^{13}C NMR spectra were measured on these spectrometers operating at 75.433 and 125.66 MHz. Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) (δ) relative to residual proton resonances in the deuterated solvent (CDCl3). ^{31}P NMR spectra were recorded on spectrometers operating at Varian Inova 300 MHz spectrometers operating at 121.43 MHz. Chemical shifts of ^{31}P NMR spectra were reported in ppm and were referenced to external 85% H_3PO_4 aqueous solution at room temperature. ^{11}B NMR spectra were recorded using an Inova 400 broadband spectrometer using $BF_3{:}OEt_2$ as an external standard. Coupling constants (*J* values) were reported as Hertz (Hz) and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), b (broad), and m (multiplet). UV-vis spectra were recorded on a Cary 100 UV_vis spectrometer and scanning electron microscopic imagers (SEM) were obtained on a JEOL-JSM-7500F microscope. All reactions were carried out under nitrogen atmosphere unless otherwise noted.

Melting points were measured by Stanford Research Systems OptiMelt apparatus and uncorrected. Gel permeation chromatrography (GPC) data were collected using a Viscotek I-MBMMW- 3078 mixed bed column (30 °C) in DMF and THF solvents. The Viscotek instrument was equipped with a VE 3210 UV-Vis detector, a 270 Viscometer and Light Scattering Dual Detector, and a VE 3580 RI detector. The molecular weights and polydispersity index (PDI) of polymers were calculated using the OmniSEC software (v. 4.6.1) based on polystyrene standards.

2,6-Dimethyl-4-(polyisobutyl)aniline (47). A mixture of 9.32 g (76.9 mmol) of 2,6-dimethylaniline, 10.10 g (7.77 mmol) of PIB-1300 alkene and 1.52 g (10.2 mmol) of anhydrous aluminum chloride were stirred for 3 days at 200 °C in a pressure vessel. Then the reaction mixture was cooled and added to 100 mL of water. After extraction with 200 mL of hexane, the organic layer was washed with three 100 mL portions of 90% ethanol/ water. The hexane phase was dried with Na_2SO_4 and the solvent was removed under reduced pressure to afford a brown-colored viscous oil. Column chromatography using hexane and CH_2Cl_2 was used to purify the product leading to **47** as a viscous oil (8.80 g, 60%). ^1H NMR (300 MHz, $CDCl_3$) δ: 0.8-2.0 (m), 2.19 (s, 6 H), 3.50 (broad, 1H), 6.95 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 18.26, multiple poorly resolved peaks between 30–40 and 55–60, 121.28, 126.30, 140.06, 140.27.

2-Ethyl-4-(polyisobutyl)aniline (48). A mixture of 2.94 g (24.3 mmol) of 2-ethylaniline, 3.17 g (2.4 mmol) of PIB-1300 alkene and 0.48 g (3.64 mmol) of anhydrous aluminum chloride were allowed to react using the procedure used for **47**. After column chromatography, **48** was obtained as a viscous oil (2.2g, 65%). ^{1}HNMR (300MHz, $CDCl_3$) δ: 0.82 (m), 2.53 (q, 2H), 6.61 (d, 1H, *J* = 7.4 Hz), 7.00 (d, 1H, *J* = 7.4 Hz), 7.05 (s, 1H), 3.50 (bs, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: multiple poorly resolved peaks between 11–40 and 57–60, 115.21, 124.56, 126.85, 127.61, 140.77.

General procedures for diazotization of 47 and 48. Two general approaches were used using either trifluoroacetic acid or BF_3-Et_2O as the acid. Representative examples of these procedures are described for the synthesis of **47a, 47b** and **48a** below.

(2,6-Dimethyl-4-polyisobutyl)benzenediazonium tetrafluoroborate (47a). A solution of **47** (0.99 g, 0.83 mmol) in 3.5 mL of CH_2Cl_2 was cooled to 0 °C and mixed with cold $BF_3.Et_2O$ (0.15 mL, 0.83 mL). After stirring for few minutes, isopentyl nitrite (0.14 mL, 0.98 mmol) was added and the reaction mixture was stirred for 2 h at 0 °C. The solvent was removed at reduced pressure to afford the product as a viscous oil in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.8-2.0 (m), 2.80 (s, 6 H), 7.45 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: multiple poorly resolved peaks between 10-42 and 54-63, 127.37, 129.28, 144.94, 168.23. ^{19}F NMR (300 MHz, $CDCl_3$, BF_3:OEt_2 external standard) δ: 1.66; ^{11}B NMR (100 MHz, $CDCl_3$, BF_3:OEt_2. external standard) δ: 1.50.

(2,6-Dimethyl-4-polyisobutyl)benzenediazonium trifluoroacetate (47b). A solution of **47** (0.36 g, 0.30 mmol) in 3 mL of CH_2Cl_2 was cooled to 0 °C using an ice bath. Then trifluoroacetic acid (0.04 mL, 0.527 mmol) was added by a syringe and the reaction mixture was stirred for few minutes. Then isopentyl nitrite (0.04 mL, 0.301 mmol) was added and the reaction mixture was stirred at 5 °C to 0 °C for an additional 2 h. At this point, the reaction was complete and the product was isolated in 80% yield. FT-IR: 2533 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.8–2.0 (m), 2.80 (s, 6 H), 7.45 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: multiple poorly resolved peaks between 11-41 and 57–61, 110.90, 117.06 (q, *J* = 273.2 Hz), 128.22, 144.40, 161.20 (q, *J* = 33.8 Hz).

(2-Ethyl-4-polyisobutyl)benzenediazonium tetrafluoroborate (48a). A solution of **48** (0.83 g, 0.70 mmol) in 3.5 mL of CH_2Cl_2 was allowed to react with $BF_3.Et_2O$ (0.13 mL, 0.70 mL) and isopentyl nitrite (0.12 mL, 0.836 mmol) to form **48a**, which was isolated as a viscous oil in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.8-2.0 (m), 3.12 (q, 2 H), 7.63 (s, 1 H), 7.71 (d, 1 H), 8.79 (d, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: multiple poorly resolved peaks between 14-27 and 31-69, 129.09, 129.70, 134.50, 149.95, 150.05, 152.52, 167.82; ^{11}B NMR (128.19 MHz, $CDCl_3$, BF_3:OEt_2 external standard) δ: 1.50.

General procedure for electrophilic substitutions of phenolic compounds. A solution of a diazonium salt (e.g. **47a**) prepared as described above dissolved in CH_2Cl_2 was added drop wise to 2 eq. of a solution of phenol and K_2CO_3 in CH_2Cl_2 at 0 °C. After 12 h stirring at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in hexane and washed with 90% ethanol solution, aqueous $NaHCO_3$, and water. The hexane phase was dried with Na_2SO_4 and the solvent was removed under reduced pressure at 0 - 5 °C to afford the product azo dye as a highly colored viscous material. Yields and spectral data for the various products formed in this reaction are provided below.

1-[(2,6-Dimethyl-4-polyisobutyl)phenyl]azo-4-phenol (52). The reaction was carried out on a 100-mg scale and the product was isolated as an orange viscous oil in 86% yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.8–2.0 (m), 2.40 (s, 6 H), 6.95 (d, 2H), 7.09 (s, 2 H) 7.84 (d, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ: 19.45, multiple poorly resolved peaks between 31-60, 115.68, 124.44, 127.04, 130.34, 147.60, 148.61, 150.46, 158.01.

1-[(2,6-Dimethyl-4-polyisobutylphenyl)azo]-2-naphthol (53). The reaction was carried out on a 100-mg scale and the product was isolated as a red viscous oil in 91% yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.8–2.0 (m), 2.60 (s, 6 H), 6.94 (d, 1 H), 7.17(s, 2 H), 7.39(t, 1 H), 7.55(t, 1 H), 7.65(d, 1 H, *J* = 10.5 Hz), 7.73 (d, 1H, *J* = 9.3 Hz), 8.45 (d, 1H, *J* = 9.3 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ: 20.99, multiple poorly resolved peaks between 31-38 and 58-60, 126.13, 127.64, 127.95, 128.65, 129.79, 133.75, 138.65, 138.90, 164.99, 171.30.

4-[(2,6-Dimethyl-4-polyisobutylphenyl)azo]-1-naphthol (54). A reaction carried out on a 100-mg scale led to the product that was isolated in 85% yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.8–2.0 (m), 2.55 (s, 6H), 6.99 (d, 1H, *J* =9.2Hz), 7.16 (s, 2H), 7.23 (d, 1H, *J* = 2.5Hz), 7.44 (m, 1H), 7.58 (m, 2H), 8.46 (d, 1H, *J* = 7.6Hz). ^{13}CNMR (75 MHz, CDCl$_3$) δ: multiple poorly resolved peaks 30-39 and 58-61, 120.39, 126.56, 127.21, 128.20, 128.52, 129.13, 130.30, 131.00, 132.36, 133.42, 137.77, 138.22, 150.24, 172.69.

4-Hydroxy-3-[(2,6-dimethyl-4-polyisobutylphenyl)azo]-2-benzopyranone coumarin (55). A reaction carried out on an 80-mg scale led to the product that was isolated as a colored viscous oil in 94% yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.8–2.0 (m), 2.60 (s, 6 H), 7.19 (s, 2 H), 7.29 (m, 2 H), 7.62 (t, 1 H), 8.19 (d, 1 H, *J* = 8.4 Hz); ^{13}C NMR (75

MHz, $CDCl_3$) δ: 20.13, multiple poorly resolved peaks between 29-39 and 58-60, 120.46, 122.26, 124.49, 126.68, 128.47, 130.09, 134.80, 135.95, 151.38, 154.47, 159.71, 177.87.

2,4-Bis[(2,6-dimethyl-4-polyisobutylphenyl)azo]-1,3-benzenediol (56). A reaction carried out on a 100-mg scale led to the product that was isolated in 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.8–2.0 00 (m), 2.50 (s, 6 H), 2.60 (s, 12 H), 6.25 (d, 1 H), 7.05 (s, 2H), 7.10 (s, 2 H), 7.30 (d, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.91, 19.86, multiple poorly resolved peaks 30-39 and 58-60, 120.63, 127.62, 129.09, 130.20, 130.88, 131.66, 135.69, 142.66, 148.80, 150.42, 177.39, 182.45.

2-Hydroxy-5-[(2-ethyl-4-polyisobutylphenyl)azo] benzaldehyde (57). A reaction carried out on a 200-mg scale using triethylamine as the base led to the product that was isolated as an orange colored viscous oil in 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.8–2.0 (m), 3.20 (q, 2 H), 7.15 (d, 2 H, J = 7 Hz), 7.32 (dd, 1H, J = 8.4 and 10 Hz), 7.37 (s, 1 H), 7.62 (d, 1 H, J = 7 Hz), 8.17 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.01, 38.27, 59.27, 114.65, 118.85, 120.57, 124.58, 127.82, 129.54, 130.49, 143.86, 146.53,147.68, 154.36, 163.53, 165.25, 196.94.

2,4,6-Tris[(2,6-dimethyl-4-polyisobutylphenyl)azo]-1,3,5-benzenetriol (58). A reaction carried out on a 100-mg scale led to the product that was isolated as a viscous maroon-colored oil in 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.8-2.0 80 (m), 2.60 (s, 18 H); ^{13}C NMR (75 MHz, CDCl3) δ: 11.46, 14.14, 19.83, 20.72, 22.67, multiple poorly resolved peaks between 30–339 and 58–60, 124.34, 127.53, 128.91, 130.05, 135.79, 149.98, 178.51.

2-Methoxy-4-[(2,6-dimethyl-4-polyisobutylphenyl)azo] phenol (59). A reaction carried out on a 100-mg scale led to the product that was isolated in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.8-2.0 (m), 2.60 (s, 18 H), 2.40 (s, 6 H), 3.99 (s, 3 H), 7.07 (d, 1 H, *J* = 8.3 Hz), 7.12 (s, 2 H), 7.48 (d, 1 H, *J* = 2.1 Hz), 7.58 (dd, 1 H, J = 2.1 and 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: multiple poorly resolved peaks between 12 and 34, 102.31, 114.85, 121.10, 124.90, 127.98, 130.88, 147.73, 147.78, 149.37, 151.07, 182.29.

Synthesis of N-methyl-4-[2-(2,6-dimethyl-4-polyisobutylphenyl) diazenyl] benzenamine (61). A solution of N-methylaniline (50 mg, 0.47 mmol) in 4 mL of CH_2Cl_2 was allowed to react with a CH_2Cl_2 solution of **47a** first at 0 °C and then at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was dissolved in hexane and washed with 90% ethanol solution, saturated $NaHCO_3$ solution, and water. After drying with anhydrous Na_2SO_4, the hexane was removed under reduced pressure and the crude product was purified by chromatography to afford **61** in 54% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.8–2.0 (m), 2.38 (s, 6 H), 2.97 (s, 3 H), 6.67 (d, 2 H, *J* = 8Hz), 7.01 (s, 2 H), 7.82 (d, 2 H, *J* = 8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 19.93, 23.32, 25.93, multiple poorly resolved peaks between 31-39 and 58-61, 112.39, 125.20, 127.51, 129.48, 130.37, 131.57, 145.66, 149.81, 150.14, 152.22.

Procedure for reduction of 47a with copper metal to form alkyl-substituted arene-terminated PIB derivative (62). The diazonium salt **47a** was added at room temperature to a suspension of Cu metal powder (1.2 mg-atom) in CH_2Cl_2 and vigorously stirred under N_2 for 4 h. After that time, the reaction mixture was poured into brine (10 mL) and organic layer was separated. The CH_2Cl_2 was removed under reduced pressure and the residue was dissolved in 10 mL of hexane. This hexane was washed with two 5 mL portions of CH_3OH and two 5 mL portions of brine and dried with anhydrous Na_2SO_4. The arene-terminated PIB was then isolated by removal of solvent at reduced pressure and the product was isolated as colorless viscous material in 92%. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.8 - 2.0 (m), 2.31 (s, 6 H), 6.80 (s, 1 H), 6.90 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.31, multiple poorly resolved peaks between 31 - 39 and 58 - 61, 124.73, 127.36, 137.49, 151.00.

Synthesis of 2[(2,6-Dimethyl-4-polyisobutylphenyl)]azo pyrrole (63). Reaction of 2 mL of a CH_2Cl_2 solution of pyrrole (0.008 g, 0.132 mmol) and pyridine (0.12 mL, 1.610 mmol) with 1 mL of a CH_2Cl_2 solution of **47a** (0.066 mmol) for 12 h produced a 80% yield of a green-colored viscous oil after solvent removal. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.80–1.80 (m), 2.38 (s, 6 H), 6.37 (dd, 1 H, *J* = 7 and 3.8 Hz), 6.85 (dd, 1 H, *J* = 1.5 and 2.8 Hz) 6.95 (dd, 1 H, *J* =1.5 and 3.8 Hz), 7.05 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: multiple poorly resolved peaks between 12 and 60, 111.84, 114.70, 121.36, 127.76, 131.08, 146.72, 148.84, 150.55.

Synthesis of 2-[(2,6-Dimethyl-4-polyisobutylphenyl)] azoimidazole (64). The procedure used to prepare 16 was used with imidazole on a 100 mg scale to afford a 81% yield of **63** as a red-colored viscous oil was washed with two 5 mL portions of methanol (5 mL 2), two 5 mL portions of $NaHCO_3$ and finally with two 5 mL portions of brine. Then the organic layer was dried with an- hydrous Na_2SO_4 and solvent was removed under reduced pressure to yield the product as a light yellow viscous material in 77% yield. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.8–2.0 (m), 2.51 (s, 6 H), 7.12 (s, 1H) 7.14 (s, 2H), 7.40 (s, 1H), 9.75 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: multiple poorly resolved peaks between 12 and 60, 114.71, 119.01, 120.75, 127.35, 133.55, 143.77, 153.75.

Synthesis of 2,6-Dimethyl-4-polyisobutylchlorobenzene (65). A solution of tetrabutylammonium chloride (0.6 M, 1.53 mL) in CH_2Cl_2 was prepared and CuCl (0.26 g, 0.002 mmol) was added to this solution. After stirring for 2 min under N_2, the diazonium salt **47a** (0.009 mmol) dissolved in 3 mL of CH_2Cl_2 was added all at once. The resulting reaction mixture was heated for a further 3 h under N_2. Then the reaction mixture was poured into 25 mL of water. The organic layer was separated and the solvent was removed under reduced pressure. The residue was dissolved in hexane, and the organic layer was dried with anhydrous Na_2SO_4 and solvent was removed under reduced pressure to yield the product as a light yellow viscous material in 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.8–2.0 (m), 2.45 (s, 6 H), 7.06 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: multiple poorly resolved peaks between 12 and 60, 127.29, 132.18, 135.97, 149.09. This sample contained ~20 mol % of the reduced product, 3,5-dimethylpolyisobutylbenzene.

Synthesis of 2,6-Dimethyl-4-polyisobutylbromobenzene (66). To a solution of tetrabutylammonium bromide (0.6 M, 1.53 mL) in CH_2Cl_2 was added CuBr (0.26 g, 0.002 mmol). Then the diazonium salt **47a** (0.01 mmol) in 3 mL of CH_2Cl_2 was added all at once and the reaction mixture was heated for 3 h under N_2. After stirring, the reaction mixture was poured into a separatory funnel that contained 25 mL of water. The organic layer was separated and the solvent was removed under reduced pressure. The residue was dissolved in hexane, and the hexane was washed with two 5 mL portions of

CH_3OH, two 5 mL portions of $NaHCO_3$, and with two 5 mL portions of brine. The hexane was dried with anhydrous Na_2SO_4 and removed under reduced pressure to afford **65** as a light yellow viscous oil in 87% yield. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.8–2.0 (m), 2.48 (s, 6 H), 7.06 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.00, 26.10, multiple poorly resolved peaks between 31-39 and 48-61, 127.02, 135.43, 137.58, 165.65. This sample contained ~ 10% of the fluoroarene as a contaminant.

Synthesis of 2,6-Dimethyl-4-polyisobutylfluorobenzene (67). A solution of **47a** in heptane was heated to 50 °C for 2 h. Then the solvent was removed under reduced pressure and the product fluoroarene product was isolated in 98% yield. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.80-1.80 (m), 2.26 (s, 6 H), 6.97 (d, 2 H, J = 6.91 Hz); ^{13}CNMR (75MHz, $CDCl_3$) δ: multiple peaks between 12 - 39 and 58-60, 123.60 (d, J = 17.63), 127.10 (d, J = 4.47 Hz), 145.71, 158.49 (d, J = 250.51 Hz).

Synthesis of 2,6-Dimethyl-4-polyisobutyliodobenzene (68). A solution of tetrabutylammonium iodide (0.03 g, 0.18 mmol) in 1 ml of CH_2Cl_2 was stirred at room temperature for 2 min. Then the diazonium salt **47a** (0.09 mmol) dissolved in 1 mL of CH_2Cl_2 was added all at once, and the reaction mixture was stirred for 3 h under N_2. The solvent was removed under reduced pressure and the residue was dissolved in hexane. This hexane solution was washed with two 5 mL portions of CH_3OH (5 mL 2) and with two 5 mL portions of brine. After drying with anhydrous Na_2SO_4, the solvent was removed under reduced pressure to yield **67** as a viscous oil in 75% yield. ^1H NMR (300 MHz, $CDCl_3$) d: 0.8-2.0 (m), 2.45 (s, 6 H), 7.06 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: multiple poorly resolved peaks between 12-40 and 58-61, 104.74, 124.63, 125.75, 127.28, 137.36, 141.55, 150.54, 150.86.

Synthesis of 2,6-Dimethyl-4-polyisobutylazidobenzene (69). A solution of diazonium salt **47a** (0.007 mmol) in 0.5 mL of CH_2Cl_2 (0.5 mL) was added to a solution of trimethylsilylazide ($TMSN_3$; 0.015 g, 0.013 mmol) in 0.6 mL of CH_2Cl_2 and the resulting mixture was stirred at room temperature for 6 h under N_2. The solvents were removed under reduced pressure and the residue was dissolved in 5 mL of hexane. This hexane solution was washed with two 5 mL portions of 90% ethanol/water and with two 5 mL portions of brine. After drying with anhydrous Na_2SO_4, the hexane was removed under reduced pressure to yield **69** as a viscous oil in 96% yield. FTIR, 2087 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.80-1.80 (m), 2.45 (s, 6 H), 2.58 (s, 6 H), 6.90 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: multiple poorly resolved peaks between 14-39 and 58-60, 126.74, 131.04, 133.96, 148.01.

General procedure for Pd-catalyzed coupling reactions of 48a. The diazonium salt **48a** in 2 mL of CH_2Cl_2 was added to a solution of *tert*-butyl acrylate (0.139 g, 1.045 mmol) and triethylamine (0.105 g, 1.04 mmol) in 1 mL of CH_2Cl_2 containing $Pd_2(dba)_3$ (0.012 g, 0.013 mmol) as catalyst. After stirring at room temperature under N_2 for 5 h, the reaction mixture was poured into water. The organic layer was separated and concentrated under reduced pressure evaporation. Then the residue was dissolved in 10 mL of hexane and washed twice with 5 mL of methanol, twice with 5 mL of 90% ethanol/ water, and finally with two 5 mL portions of brine. The hexane layer was dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to obtain the product which was purified by a column chromatography (hexane: CH_2Cl_2, 1:1).

This afforded a 87% yield of *tert*-butyl 3-(2-ethyl-4-polyisobutylphenyl)propionate (**70**) on a100-mg scale. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.8 - 2.0 (m), 2.80 (q, 2 H, *J* = 7 Hz), 6.30 (d, 1 H, *J* = 16 Hz) , 7.20 (m, 2 H), 7.50 (d, 1 H, *J* = 9 Hz), 7.95 (d, 1 H, *J* = 16 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 16.61, 26.63, 28.21, multiple poorly resolved peaks between 30–39 and 58 - 60, 120.03, 124.26, 125.94, 127.33, 129.65, 141.12, 143.30, 152.76, 166.78.

4-(Polyisobutyl)phenol (49). To a 500-mL round bottomed flask equipped with a stir bar and rubber septum were added PIB-1000 alkene (15 g, 100 mmol), phenol (8.9 g, 8.9 mmol) in CH_2Cl_2 (200 mL), and conc. H_2SO_4 (1.05 g). The mixture was then stirred under N_2 for 12 h at room temperature. At this point, the solvent was removed under reduced pressure and 250 mL of hexane was added to the viscous oil. The hexane solution was washed with 3 150-mL portions of N,N-dimethylformamide and 3 150-mL portions of 90% ethanol/water. The organic phase was dried over Na_2SO_4 and filtered and solvent was removed under reduced pressure to give 8.27 g of **49** as a viscous, light yellow oil, in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23 (d, *J* = 8.79 Hz, 2 H), 6.75 (d, *J* = 8.79 Hz, 2 H), 1.8 (s, 2 H), and 0.8 - 1.6 (m, 140 H). ^{13}C NMR(125 MHz, $CDCl_3$) δ: 153.1, 142.9, 127.5, 114.7, multiple poorly resolved peaks between 58 and 60, 38-39, and 30-33.

PIB(1000)-nitrophenol (50). To a solution of 2.00g (1.83 mmol) of PIB-phenol **49** in 18 mL of THF was added 0.73 mL (5.49 mmol) isoamyl nitrite. The reaction mixture was stirred for 4 hours under oxygen at room temperature. The THF was then rotovaped and the product dissolved in hexane. The organic layer was then washed with three 50 mL portions of acetonitrile and the hexane was removed under reduced pressure to obtain **50** as yellowish oil in 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.52 (s, 1 H), 8.05 (d, *J* = 2.51, 1 H), 7.63 (dd, *J* = 8.71, *J* = 2.32, 1 H), 7.10 (d, *J* = 8.77, 1 H) 1.92 - 0.83 multiple peaks poorly resolved. ^{13}C NMR (300 MHz, $CDCl_3$) δ: 153.0, 142.9, 135.6, 133.1, 121.5, 119.1, 59.2, 38.10, 34.98-14.3 multiple peaks.

PIB(1000)-aminophenol (51). To a solution of 2.00g (1.75 mmol) of PIB-nitrophenol **51** in 18 mL of THF was added 186 mg (0.18 mmol) of 10% Pd/C. This reaction mixture was then stirred under H_2 at 20 bar for 24 h. After this time, the Pd/C was filtered and THF was removed under reduced pressure. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.77 (d, *J* = 1.79, 1 H), 6.67 (m, 2 H), 1.44-0.8 (m); ^{13}C NMR (300 MHz, $CDCl_3$) 165.4, 153.3, 143.1 136.4, 133.0, 122.0, 119.1, 105.0, 59.9, 59.2-12.3 multiple peaks.

PIB-2-naphthol azo-dye (53'). A solution of 0.02g (0.16 mmol) of 2-napthol in 2 mL of CH_2Cl_2 was added 0.05 mL (0.20 mmol) of triethylamine and cooled to 0 °C. To this solution was then added 0.20g (0.08 mmol) of PIB-diazonium salt drop wise. The reaction mixture turned red and was allowed to stir for 5 hours at room temperature. The CH_2Cl_2 was then removed under pressure and the product was extracted with hexane. The organic layer was then washed with three 50 mL portions of 90% ethanol/water and one 50 mL portion of acetonitrile before drying with $MgSO_4$ and hexane was removed under reduced pressure to yield **53'** in 57.3% yield. UV-Vis (hexane) λ_{max} 471 nm, 2.92×10^{-6}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.26 (d, *J* = 8.34, 1 H), 7.85 (d, *J* = 9.19, 1 H), 7.81 (d, *J* = 7.93, 1 H), 7.64 (m, 2 H), 7.48 (d, *J* = 7.60, 1 H), 7.40 (dd, *J* = 8.55, *J* = 2.24, 1 H), 7.21 (d, *J* = 9.19, 1 H), 7.05 (d, *J* = 8.87, 1 H), 2.0-0.80 (m).

PIB(2300)-4-hydroxy coumarine-dye (55'). Following the above procedure which was used to prepare 53', the PIB-bound coumarin dye **53'** was synthesized in 56% yield. UV-Vis (hexane) λ_{max} 467 nm, 3.85×10^{-6}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.11 (d, *J* = 6.52, 1 H), 7.69 (t, *J* = 8.36, 1 H), 7.36 (m, 3 H), 7.24 (m, 2 H).

PIB(2300)-phloroglucinol-dye (58'). Following a similar procedure as in 55', the PIB-bound phloroglucinol dye **58'** was prepared in 68% yield. UV-Vis (hexane) λ_{max} 479 nm, $8.41\times10^{-}6$; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.42 (dd, *J* = 9.84, *J* = 2.43, 3 H), 6.90 (d, *J* = 2.60, 3 H), 6.66 (d, *J* = 9.89, 3 H), 1.99-0.81 (m).

4-Butoxyphenyl-4-(2,6-dimethyl-4-polyisobutylphenyl)diazene (77). To a 25-mL round-bottomed flask was added **52** (1.96 g, 0.78 mmol) in 5 mL of heptane, *n*-butyl bromide (0.13 mL, 1.17 mmol), K_2CO_3 (1.57 mmol, 0.21 g) in 5 mL of dimethyl formamamide. The reaction mixture was heated at reflux overnight. The reaction solution was cooled to room temperature and added to a separatory funnel. The bottom DMF phase was removed and 100 mL of hexane was added to the funnel. The hexane phase was washed with 3 10-mL portions of 10% aq. Ethanol, with 3 10-mL portions of brine, dried over anhydrous Na_2SO_4, and filtered. Then the filtrate was concentrated under reduced pressure to obtain bright orange color viscous oil as a pure product in quantitative yield (1.5 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 8.8, 2 H,), 7.10 (s, 2 H), 6.95 (d, *J* = 8.8, 2 H), 2.39 (s, 6 H), 0.76 – 1.82 (m); ^{13}C NMR (125 MHz, CDCl3) δ: 162.0, 150.7, 149.1, 147.6, 130.6, 127.6, 124.5, 115.1, 60.6–14.4 multiple peaks.

Palladation of 4-butoxyphenyl-4-(2, 6-dimethyl-4-polyisobutylphenyl)diazene (78). To a 50-mL round-bottomed flask equipped with a magnetic stir bar was added **76** (0.72

g, 0.30 mmol), $Pd(PhCN)_2Cl_2$ (0.132 g, 0.344 mmol) in 30 mL of chloroform. The resulting homogeneous solution was stirred for 24 h at room temperature. Then the solvent was evaporated under reduced pressure and 100 mL of hexane was added to the oily residue. The solution was transferred to a separatory funnel and the hexane solution was washed with first with 3 50-mL portions of acetonitrile and finally with 50 ml of brine. The organic phase was dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuum to obtain red viscous oil in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.74 (d, J = 8.5, 1 H), 7.08 (s, 2 H), 6.68 (d, J = 8.5, 1 H), 6.61 (s, 1 H), 3.98 (t, 2 H), 2.33 (s, 6 H), 1.75 – 0.89 (m); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.7, 160.0, 157.7, 150.5, 147.2, 130.8, 130.0, 125.9, 118.9, 111.6, 59.3 – 13.9 multiple peaks.

General procedure for the Mizoroki-Heck and Suzuki reactions in heptane/DMF under thermomorphic conditions. A 10-mL Schlenk tube equipped with a stir bar was charged with catalyst **77** (0.01 mmol) dissolved in 2 mL of heptane and 2 mL of DMF containing 1 mmol of aryl halide, 1.2 mmol of *n*-butyl acrylate or 1.4 mmol of phenyl boronic acid and 2 mmol of K_2CO_3. The mixture was stirred at 100 °C for 6 - 12 h. After the reaction was complete, the solution was led to cool to room temperature at which point the heptane and DMF separated into two phases. Then the bottom DMF phase was isolated by a gravity separation and the solvent was removed under reduced pressure to obtain a crude product which was purified by silica gel column chromatography (hexane/ethyl acetate: 4:1) to afford the pure product. Recycling the catalyst was achieved by adding 2 mL of heptane saturated DMF containing fresh substrates in the appropriate amounts followed by heating as described above.

General procedure for the Mizoroki-Heck and Suzuki reactions in THF/DMF/Polyethylene system. A 10-mL screw-capped vial equipped with a stir bar was charged with catalyst **77** (0.01 mmol) dissolved in 2 mL of THF, aryl halide (1 mmol), *n*-butyl acrylate (1.2 mmol) or phenyl boronic acid (1.4 mmol) and K_2CO_3 (2 mmol) in 2 mL of DMF. Polyethylene (Polywax 400) (1.5 g) was also added to this reaction mixture. The mixture was stirred with heating at 90 ºC for 12 h. At this point, the solution was perturbed to form two phases by adding a small amount of hot water (~ 2 mL). The upper liquid Polywax phase solidified on cooling. That solid wax was separated from the solution by vacuum filtration and the waxy phase was rinsed with methanol (5 mL). Then the filtrate was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1) to afford pure coupling product. The catalyst was recycled by adding fresh THF/DMF containing substrates in appropriate amounts to the waxy solid followed by heating as described above. Reactions carried out in the presence of **92** using Polywax were carried out in a similar manner.

Butyl (*E*)-3-(4-acetylphenyl)-2-propenoate (81). The reaction was carried out on a 1 mmol scale and the product was isolated as colorless oil in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 7.5, 2 H), 7.69 (d, *J* = 16.7, 1 H), 7.61 (d, *J* = 7.5, 2 H), 6.53 (d, *J* = 16.7, 1 H), 4.22 (t, *J* = 7.4, 2 H), 2.62 (s, 3H), 1.67 (m, 2H), 1.43 (m, 2H), 0.94 (t, *J* = 7.3, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:197.9, 167.2, 143.6, 139.4, 138.6, 129.5, 128.8, 121.5, 65.3, 31.4, 27.3, 19.83, 14.39.

Butyl (*E*)-3-phenyl-2-propenoate (82). The reaction was carried out on a 1 mmol scale and the product was isolated as colorless oil in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 16.7, 1 H), 7.54 (m, 4 H), 7.40 (m, 2 H), 6.45 (d, *J* = 16.6, 1 H), 4.22 (t, *J* = 6.9, 2 H), 1.70 (m, 2 H), 1.45 (m, 2 H), 0.97 (t, *J* = 8.2, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.9, 144.3, 134.2, 130.0, 127.9, 118.5, 64.3, 31.0, 19.2, 13.9.

Phenylacetophenone (87). The reaction was carried out on a 1 mmol scale and the product was isolated in 94% yield as a white solid; **mp =** 122 - 124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 6.4, 2 H), 7.67 (m, 4 H), 7.48 (m, 3 H), 2.60 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.6, 146.1, 139.1, 135.6, 129.0, 127.4 (m), 27.0.

1-Chloro-4-phenylbenzene (88). The reaction was carried out on a 1 mmol scale and the product was isolated in 90% yield as a white solid; **mp** = 75 - 78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.54 (m, 4 H), 7.43 (m, 4 H), 7.37 (t, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 140.5, 140.3, 134.1, 129.6, 129.5,128.9, 128.1, 127.4.

4-(4-Methoxyphenyl)benzene (89). The reaction was carried out on a 1 mmol scale and the pure product was isolated in 89% yield as a white solid; **mp** = 86 - 89 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.56 (m, 4H), 7.43 (t, 2H), 7.33 (t, 1H), 7.00 (d, 2H, *J* = 8.39), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 156.6, 138.1, 130.9, 126.0, 125.6, 124.4, 124.1, 112.0, 53.0.

PIB-bound azo-Pd(II) complex with triphenylphosphine (90). To a Schlenk tube equipped with a stir bar was added PIB-azo-Pd complex (**77**) (0.015 mmol), triphenylphosphine (0.029 mmol) in 2 mL of dichloromethane. Then the tube was sealed with a rubber septum and degassed the reaction solution using three freeze thaw pump cycles. Then the reaction solution was stirred 12 h at room temperature. After 12 h time period the solvent was evaporated under reduced pressure and the residue was purified by a flash column with hexane:ethyl acetate (vol:vol, 4:1) to obtain **90** as a bright yellow color oil in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.9, 1 H), 7.70 (m, 5 H), 7.39 (m, 10 H), 7.03 (s, 2 H), 6.60 (dd, *J* = 8.65, *J* = 2.59, 1 H), 5.95 (m, 1 H), 3.14 (t, 2 H), 2.36 (s, 6 H), 1.80-0.8 (m); ^{31}P NMR (122 MHz, ^{1}H-decoupled, H_3PO_4 as an external standard, $CDCl_3$) δ: 28.9.

4-(3-Phenyl-2-propenyl) morpholine (91). To a Schlenk tube equipped with a magnetic stir bar was added cinnamylacetate (1 mmol), morpholine (4 mmol), catalyst **77** (0.01 mmol) and polyisobutylene-bound phosphine (**92**) (0.02 mmol) in 5 mL of heptane. The tube was sealed with a rubber septum and the reaction solution was degassed using three freeze thaw pump cycles. Then the reaction mixture was heated with an oil bath regulated at 80 ºC for 12 h. After the reaction was complete the reaction mixture was cooled to room temperature and the products were extracted with 2 5-mL portions of acetonitrile. The acetonitrile phases were combined and evaporated under vacuum to obtain the crude product which was purified by silica gel column chromatography to afford the pure product in 86% yield as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 8.62, 2 H), 7.30 (t, 2 H), 7.22 (t, 1 H), 6.53 (d, *J* = 15.4, 1 H), 6.25 (m, 1 H), 3.73 (m, 4 H), 3.15 (m, 2 H), 2.49 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.2, 134.2, 129.0, 128.2, 127.0, 126.9, 126.5, 67.6, 62.1, 54.2.

PIB–CH_2OH (99). The starting vinyl-terminated PIB (50 g, 50 mmol) was dissolved in 100 mL of hexane and then was allowed to react with neat BH_3.SMe_2 (8.5 mL, 17 mmol). After 24 h, the reaction mixture was cooled to 0 °C and 40 mL of ethanol and 12 mL of 4 N NaOH were added, oxidation to form the alcohol was accomplished by drop wise addition of 8 mL of 30% H_2O_2. The oxidation was allowed to proceed for 2 h at which point 300 mL of H_2O was added. The solution was extracted with hexane (100 mL), and then washed with H_2O (3 50 mL), brine (1 50 mL). The organic phase was dried over $MgSO_4$, filtered and hexane was removed under reduced pressure. After drying under vacuum for 24 h, a total yield of 52 g (102% yield possibly containing trace hexanes) of product (PIB–CH_2OH) was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.75–1.46 (m, 180 H), 3.31 (dd, *J* = 7.5, 10.2 Hz, 1 H), 3.48 (dd, *J* = 5.4, 10.2 Hz, 1 H).

PIB–$CH_2OSO_2CH_3$ (100). PIB–CH_2OH **99** (10 g, 9.8 mmol) was dissolved in 100 mL of CH_2Cl_2 and cooled to 0 °C. Then methanesulfonyl chloride (2.3 mL, 29 mmol) and triethylamine (4.3 mL, 31 mmol) were added drop wise. The reaction mixture was allowed to stir for 2 h after warming to room temperature. The solvent was removed under reduced pressure and the resulting mixture was taken up with 300 mL of hexane, washed with H_2O (3 30 mL) and 90% EtOH (4 50 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. A total yield of 10.5 g (97.8%) of product was obtained after drying under vacuum for 24 h. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.88–1.39 (m, 180 H), 1.95 (m, 2 H), 2.96 (s, 3 H), 3.88 (dd, *J* = 7.5, 9.3 Hz, 1 H), 4.06 (dd, *J* = 5.4, 9.3 Hz, 1 H).

PIB–CH_2Br (101). A mixture of **100** (10 g) was dissolved in THF (100 mL) and LiBr (9 g, 103 mmol) was heated to 65 °C for 12 h. After cooling to room temperature, THF was removed under reduced pressure and 200 mL of hexane was added to the reaction flask.

The resulting alkane phase was washed with 90% EtOH (2 10 mL), H_2O (2 20 mL), and dried over Na_2SO_4. The solvent was removed and residue was dried under vacuum to give 9.4 g (88.6%) of product **101**. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.76 - 1.49 (m, 180 H), 3.27 (dd, J = 6.9, 9.6 Hz, 1 H), 3.41 (dd, J = 4.8, 9.6 Hz, 1 H).

Synthesis of polyisobutylene (PIB)-bipyridine ligands (103 and 104). To a 100 mL round bottom flask was added freshly distilled anhydrous tetrahydrofuran (THF) 10 mL and closed with a rubber septum. This solution was cooled to -78 °C in a dry ice/acetone bath for few minutes. *n*-butyl lithium (3.4 mL, 5.43 mmol) in hexane and diisopropylamine (0.77 mL, 5.43 mmol) were added to the above reaction flask and stirred for 40 minutes. At this point a solution of 4,4'dimethyl-2,2'-bipyridine (0.40 g, 2.17 mmol) in 10 mL THF was added to the reaction flask and the temperature was maintained at -78 °C for another 2 h. Formation of bipyridine anions were observed by sudden change of color from light yellow to dark brown-black solution. After 2 h string, the flask was charged with polyisobutylene bromide **102** (10.57 g, 4.34 mmol) in 20 mL of THF. This solution was allowed to stir over night at room temperature. At this point 5 mL of water was added to reaction mixture and THF was evaporated under reduced pressure. The resulting viscous oil like material was dissolved in 100 mL of hexane. The organic phase was washed with 3 50-mL portions of 10% aq. ethanol and 1 50-mL portion of brine. Then the organic layer was dried with anhydrous sodium sulfate and hexane was evaporated under reduced pressure to obtain PIB-bipyridine ligand as a mixture of mono and di substituted products in 85% yield with respect to the starting PIB-Br_2.

Polyisobutylene (PIB)-bipyridine ligand (103). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.56 (d, 2 H), 8.24 (s, 2 H), 7.14 (d, 2 H), 2.69 (m, 2 H), 2.45 (s, 3 H), 1.71 – 0.68 (m); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 165.5, 156.8, 153.7, 149.5, 124.3, 121.8, 60.40, 41.3-15.0 (multiple peaks).

Polyisobutylene (PIB)-bipyridine ligand (104). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.56 (d, 2 H), 8.22 (s, 2 H), 7.13 (d, 2 H), 2.67 (m, 4 H), 1.71 – 0.68 (m); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 165.5, 156.8, 153.7, 149.5, 124.3, 121.8, 60.40, 41.3-15.0 (multiple peaks).

Synthesis of Ru(PIB-bpy)$_3^{2+}$Cl$_2$ catalyst (105). A solution of PIB-bipyridine ligand **103** and **104** (0g, 0 mmol) in 2 mL of heptane and a solution of anhydrous RuCl$_3$ (2 mg, 2 mmol) in ethanol were mixed in a pressure vessel and closed with a rubber septum. This solution was bubbled with N$_2$ stream for 15 minutes. Then the rubber septum was quickly replaced with the pressure vessel lid and closed tightly. This reaction vessel was heated to 90 °C for 12 h at which point the reaction mixture turned to a dark orange red color. Then the reaction solution was cooled to room temperature and poured in to 250 mL separatory funnel to which 5 mL of water was added. The solution was separated into two phases, upper heptane layer and lower aq. layer. Another 100 mL of hexane was added to the funnel and organic phase was washed with 10% aq. Ethanol 3 50-mL portions. Then the organic layer was dried with anhydrous sodium sulfate and evaporated under reduced pressure. This bright red color crude product was purified by a neutral alumina column and dichloromethane: methanol (10:1, v/v) as the eluent to obtain the catalyst in 61 % yield. UV-Vis (hexane) λ_{max} 463 nm; ^{1}H NMR (300 MHz,

$CDCl_3$) δ: 8.47 (m, 2 H), 7.65 (m, 2 H), 7.37 (m, 2 H), 2.85 (bs), 2.64 (bs); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 1546.4, 156.2, 154.7, 150.8, 150.6, 150.6, 129.1, 127.9, 125.1,124.1, 59.0-57.0 (multiple peaks), 38.0 – 21.5 (multiple peaks).

Synthesis of $[Ru(bpy)_3{}^{2+}2PF_6$ catalyst (106). A 25 mL RB flask equipped with a stir bar was charged with 2,2'-bipyridine (0.5 g, 3.2 mmol) dissolved in DMF (10 mL), LiCl (16 mmol, 1.0 g) and $RuCl_3$ (0.32 g, 1.6 mmol). This solution was purged with N_2 for 10 minutes and then refluxed 6 h upon which a dark purple solution was obtained. This purple solution was cooled to room temperature and 10 mL of acetone was added to the reaction flask. This solution was stored in the refrigerator for 12 h and the resulting shiny purple crystals were filtered under suction. These crystals were washed ether and the solid was collected and dried in the vacuum to obtain the product. Then the purple solid was transferred to another 25 mL RB flask and a mixture of ethanol : water (1:1) 10 mL was added. To this flask was added 2,2'-bipyridine (0.4 g, 2.6 mmol) and the solution was refluxed another 6 h to obtain dark orange red solution. To this solution was added a saturated aq. solution of KPF_6 (8 mL). at this point dark orange red solid precipitated in aq. solution and the solid was filtered under suction filtration. The solid was washed with diethylether (2 3 mL portions) and dried in the vacuum to obtain the product 106 in 69% yield. UV_vis (CH_3CN) λ_{max} : 469 nm, 287 nm; ^1H NMR (300 MHz, DMSO) δ: 8..81 (d, J = 11 Hz , 2 H), 8.15 (t, J = 8.1 , 2 H), 7.72 (d, J = 5.7, 2 H), 7.52 (t, J = 7.3 , 2 H).

Synthesis of $Ru(Mbpy)_3{}^{2+}2PF_6$ catalyst (107). A 25 mL RB flask equipped with a stir bar was charged with 4,4'dimethyl-2,2'-bipyridine (1 g, 4.3 mmol) dissolved in ethanol

(15 mL) and $RuCl_3$ (0.18 g, 0.86 mmol). This solution was purged with N_2 for 10 minutes and then refluxed 24 h upon which a dark reddish orange solution was obtained. This solution was cooled to room temperature and added a saturated aq. solution of KPF_6 (10 mL). At this point dark orange red solid precipitated in aq. solution and the solid was filtered under suction filtration. The solid was washed with diethylether (2 3 mL portions) and dried in the vacuum to obtain the product 106 in 80% yield. UV_vis (CH_3CN) λ_{max}: 453 nm, 280 nm; ^{1}H NMR (300 MHz, CD_3OD) δ: 8.51 (m, 6 H), 8.11 (m, 6 H), 7.30 (m, 6 H), 2.49 (bs, 18 H).

General procedure for Photocatalyzed polymerization and recycling of the catalyst 105. A 10 mL Schlenk tube equipped with a stir bar was charged with Ru(PIB-bpy)$_3^{2+}$Cl$_2$ **105** (10 mg, 1.33 μmol) dissolved in 2.5 mL of heptane and ethyl methacrylate (2.5 mL, 20 mmol). This solution was purged with N_2 for 15 minutes and then degassed three times using freeze pump thaw method. At this point *N*,*N*-diisopropylethylamine (170 μL, 1 mmol) and ethyl 2-bromoisobutyrate, EB*i*B (75 μL, 0.5 mmol) were added. Then the reaction tube was irradiated with 30 W household fluorescent bulb for 24 h at which point the solid polymer was precipitated in the reaction tube. Then the supernatant liquid was force siphoned and transferd to another Schlenk tube with fresh monomer substrates. The volume was adjusted to 5 mL by adding heptane and this second solution was degassed three times using freeze pump thaw method. By adding fresh initiator (EBiB) and iPr2NEt continued to the second cycle of the polymerization. The precipitated solid polymer was dissolved in 5 mL of *N*,*N*-dimethylformamamide (DMF) and precipitated into 70 mL of methanol. This precipitate was filtered under vacuum. The solid was dried in vacuum over night to obtain the polymer in 70 – 80 % yield.

Poly(ethylmethacrylate) PEMA (108). The reaction was carried out in a 20 mmol scale and polymer was isolated as 73% yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 4.03 (q, 2 H), 1.96-1.70 (m, 2 H), 1.60 (m, 0.3 H), 1.45 (m, 0.22 H), 1.03 (s, 1 H), 0.88 (bs, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 177.8, 177.5, 176.8, 60.8, 54.1, 44.7, 31.4, 18.5, 16.6, 13.8.

Poly(ethoxyethylmethacrylate) PEEMA (109). The reaction was carried out in a 20 mmol scale and polymer was isolated as 77% yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 4.09 (t, 2 H), 3.53 (t, 2 H), 3.50 (t, 2 H), 1.84-2.02 (m, 2 H), 1.22 (t, 3 H), 0.92 (t, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 177.6, 67.7, 66.5, 63.9, 54.1, 17.3, 13.4.

PIB-bound phthalonitrile (129). To a solution of 3.0g (2.95 mmol) of PIB-CH$_2$OH **102** in 30 mL of THF was added 4-nitrophthalonitrile (1.53g, 8.85 mmol) and 1 eq. of cesium carbonate (2.87g, 8.85 mmol). This reaction mixture was refluxed under nitrogen for 3 hours at which time a second portion (8.85 mmol) of cesium carbonate was added. A third and final portion was added 3 hours after each previous addition. Three hours later, the reaction mixture was cooled to room temperature and the THF was removed. Then the product was dissolved in hexane and washed three 50 mL portions of 90% ethanol/water. The organic layer was then dried with MgSO$_4$ and evaporated under reduced pressure. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 7.73 (d, *J* = 8.89, 1 H), 7.28 (d, *J* = 2.54, 1 H), 7.20 (dd, *J* = 8.76, *J* = 2.46, 1 H), 3.88 (dd, *J* = 8.78, *J* = 5.85, 1 H), 3.76 (dd, *J* = 8.78, *J* = 7.28, 1H), 2.08 (m, 1 H), 1.61-0.93(m); ^{13}C NMR (300 MHz, CDCl$_3$) δ: 162.3, 135.3, 119.5, 119.4, 117.5, 115.8, 115.3, 107.1, 59.54, 59.19-13.98 (m).

PIB-bound-thiol phthalonitrile (130). Following a similar procedure as in **128**, **129** was prepared in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.54, 1 H), 7.56 (d, *J* = 1.99, 1 H), 7.49 (dd, *J* = 8.34, *J* = 2.06, 1 H), 2.97 (dd, *J* = 11.66, *J* = 6.09, 1 H), 2.87 (dd, *J* = 11.79, *J* = 7.25, 1 H), 1.97-0.85 (m); ^{13}C NMR (300 MHz, CDCl3) δ: 165.0, 133.1, 130.1, 129.9, 77.51, 77.08, 76.65, 60.85-14.18 multiple peaks.

PIB(2300)-phenol-phthalonitrile (131). Following a similar procedure as in **128**, **130** was prepared in 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) 7.71 (d, *J* = 8.49,1 H), 7.46 (d, J= 8.48, 2 H), 7.26 (d, *J* = 2.00 1 H), 7.22, (dd, *J* = 8.48, *J* = 2.51, 1 H), 6.98 (d, *J* = 8.48, 2 H), 1.92-0.84 (m); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 162.8, 151.5, 149.6, 135.9, 129.3, 128.7, 122.0, 121.7, 120.7, 120.3, 118.4, 116.1, 115.7, 109.2, 60.1, 38.8-12.1 multiple peaks.

General procedure for the synthesis of PIB-metallophthalocyanines. A mixture of 0.50g (0.309 mmol) of PIB-phthalonitrile (1**28**), 0.019g (0.077 mmol) metal salt and 0.024g (0.155 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were stirred for 2 hours at 200 °C in a pressure vessel. The reaction mixture was cooled and the product was extracted with hexane. The organic layer was then washed with two 50 mL portions of 90% ethanol and two 50 mL portions of acetonitrile. The hexane phase was dried with $MgSO_4$ and the solvent was removed under reduced pressure to afford a blue-colored dye.

PIB-CuPc (132). The reaction was carried out in a 1 mmol scale and PIB-MPc was isolated as 62 % yield. UV-Vis (hexane) λ_{max} 676 nm ($\varepsilon = 1.06\times 10^{4}$ $M^{-1}cm^{-1}$).

PIB-CoPc (133). The reaction was carried out in a 1 mmol scale and PIB-MPc was isolated as 88 % yield. UV-Vis (hexane) λ_{max} 670 nm ($\varepsilon = 1.50\times 10^4$ $M^{-1}cm^{-1}$).

PIB-PdPc (134). The reaction was carried out in a 1 mmol scale and PIB-MPc was isolated as 54 % yield. UV-Vis (hexane) λ_{max} 660 nm ($\varepsilon = 1.38\times 10^4$ $M^{-1}cm^{-1}$).

PIB-NiPc (135). The reaction was carried out in a 1 mmol scale and PIB-MPc was isolated as 52 % yield. UV-Vis (hexane) λ_{max} 667 nm ($\varepsilon = 1.80\times 10^4$ $M^{-1}cm^{-1}$).

PIB-ZnPc (136). The reaction was carried out in a 1 mmol scale and PIB-MPc was isolated as 47 % yield. UV-Vis (hexane) λ_{max} 663 nm ($\varepsilon = 1.0\times 10^4$ $M^{-1}cm^{-1}$); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.73 (m, 4 H), 8.28 (m, 4 H), 7.44 (m, 4 H), 4.14 (m, 8 H), 2.2 - 0.8 (m).

PIB-CrPc (137). The reaction was carried out in a 2 mmol scale and PIB-MPc was isolated as 52 % yield. UV-Vis (hexane) λ_{max} 693 nm ($\varepsilon = 1.49\times 10^4$ $M^{-1}cm^{-1}$).

PIB-phenol-ZnPc (140). The reaction was carried out in a 2 mmol scale and PIB-MPc was isolated as 52 % yield. UV-Vis (hexane) λ_{max} 677 nm ($\varepsilon = 1.99\times 10^4$ $M^{-1}cm^{-1}$); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46-7.04 (Ar-H), 2.25-0.80 (m).

PIB-metal-Free Pc (138). To a high pressure reaction vessel was added 0.50g (0.437 mmol) of PIB-phthalonitrile, 1.31 mL hexanol, and roughly 6mg of lithium metal. This reaction mixture was heated to 160 °C for 12 hours in a sand bath and then cooled to room temperature before the product was extracted with hexane and poured into 3.5 mL of conc. H_2SO_4. The reaction mixture was then stirred for 15 min before being washed with acetonitrile, dried with $MgSO_4$, filtered, and the solvent removed under pressure.

UV-Vis (hexane) λ_{max} 660 nm, 1.92×10-^{6}, λ_{max} 701nm, 2.51×10-^{6} ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.01(d, *J* = 8.26, 4 H) 7.31 (d, *J* = 2.03 4 H) 7.06 (dd, *J* = 8.63, *J* = 2.42, 4 H), 3.88 (dd, *J* = 9.12, *J* = 5.34, 4 H), 3.75 (dd, *J* = 9.12, *J* = 7.55, 4 H), 2.2 - 0.8 (m).

CHAPTER VII

CONCLUSIONS

This dissertation describes end functionalization of alkene terminated polyisobutylene (PIB) into variety of functionalities to immobilize phase selectively soluble behavior of PIB onto useful ligands. Bergbreiter lab has intensively studied non-polar phase soluble PIB as s soluble support for ligands in homogeneous catalysis. This work is a continuation of using PIB as a highly soluble non-polar phase tag for different applications. Commercially available olefin terminated PIB can be functionalized via Friedel –Crafts arylation reactions under Lewis/mineral acidic conditions. Following this electrophilic aromatic substitution reactions of aniline derivatives such as 2,6-dimethyl aniline and 2-ethylaniline can be immobilized onto the PIB chain end to form **47** and **48.** Synthesis of a versatile intermediate such as diazonium salt was accomplished by using these PIB bound anilines **47** and **48.** This PIB-oligomer bound diazonium salt was utilized in azo-coupling reactions to form polymer bound azodye compounds which were highly colored viscous oil materials. These PIB-materials showed non-polar phase selective solubility compared to analogue low molecular weight azodye compounds which are normally soluble in polar organic solvents such as acetonitrile, methanol or *N*,*N*-dimethylformammide (DMF). This non-polar solvent solubility property of PIB-azodye compounds was later used in dyeing highly unfunctionalized non-polar commercial polymer materials such as high density polyethylene (HDPE) and high density polypropylene (HDPP).

PIB bound diazonium salt was also used in diazonium displacement reactions to form substituted arene compounds. In this case it was thus possible to expand the synthesis of halides (F,Cl, Br, I) terminated PIB aryl compounds which were difficult to synthesize *via* aromatic substitution reactions. The diazonium salt functionality can also be displaced by an azide group to synthesize PIB-azides **69** which can be further functionalized by click type chemistry. This PIB-diazonium salt **48a** was successfully used as a substrate for Heck-Mizoroki reaction and a variety of olefinic compounds were coupled to PIB-diazonium salt under Pd catalyzed conditions.

Continuation of the PIB-bound azodye synthesis and their utility as soluble ligands for palladium metal was also studied and PIB-azophenol dye **52** was orthopalladated to obtain PIB-supported palladium pre-catalyst **78** which can catalyze cross-coupling reactions. This PIB-immobilized azopalladacycle **78** was heptane phase selectively soluble compared to polar solvents such as acetonitrile and DMF. The catalyst recovery and reuse was accomplished by performing these catalytic reactions in liquid/liquid thermomorphic separation system. A new catalyst separation strategy where polyethylene was used as a solid solvent in entrapping and separating the catalyst from the product solution was also established. The developed polyethylene as solid-solvent method was considered to be greener compared to conventional solvents due to its non-toxicity, non-volatility and reusability. This more sustainable catalyst/product separation strategy improved metal sequestration from the product phase substantially.

Combining the concepts of using PIB as a support for recyclable catalysts and using a green energy source for catalytic reactions also led us to explore the immobilization of an interesting visible light photo-redox catalyst- Ru(bpy)$_3$Cl$_2$ onto PIB. PIB bound photoredox catalyst was synthesized by reacting 4,4-dimethylpyridine with PIB-Br in an alkylation reaction. The synthesized polymer attached Ru(PIB-bpy)$_3$Cl$_2$ photoredox catalyst was successfully used as a single electron transfer radical initiator for free radical polymerization reactions of methacrylate monomers. This novel polymer attached visible light photo catalyst showed excellent reactivity in initiation of the radical polymerizations. More importantly, the catalyst **105** was soluble in non-polar hydrocarbon solvents such as heptane and hexane. This non-polar phase selective solubility of the catalyst **105** provided the advantage of performing the reaction in homogeneous conditions in a hydrocarbon solvent such as heptane and the catalysts's solubility in heptane also was useful as the formed polar polymer product was directly precipitated as it was formed. This autonomous catalyst/polymer separation strategy was advantages since it eliminates the need of extra solvent precipitation steps for the polymer separation.

Phthalocyanine (Pc) an important ligand for almost 70 metals in the periodic table has been a wide interest in electronic applications, photodynamic therapy and in catalysis. However this material has been widely used as a dye material in textile and ink industry. However, the limited solubility of these materials in any of the organic media precluded its wide applications in these fields. Therefore, immobilization of metallophthalocyanines (MPcs) onto PIB was successful in increasing the solubility of these highly insoluble low molecular MPc materials.

In all, this dissertation described the solubility switch of useful materials from polar solvents to non-polar hydrocarbon solvents upon their immobilization onto soluble polymer materials such as PIB. The recoverability and reusability properties which were introduced by this soluble PIB-immobilization facilitated green chemical synthesis.

REFERENCES

(1) Goethals, E. J.; Du, P. F. *Prog. Polym. Sci.* **2007**, *32*, 220.

(2) Shim, J. S.; Asthana, S.; Omura, N.; Kennedy, J. P. *J. Poly. Sci. Part A: Poly. Chem.* **1998**, *36*, 2997.

(3) Kwon, Y.; Faust, R.; Chen, C. X.; Thomas, E. L. *Macromolecules* **2002**, *35*, 3348.

(4) Binder, W. H.; Kunz, M. J.; Kluger, C.; Hayn, G.; Saf, R. *Macromolecules* **2004**, *37*, 1749.

(5) Higashihara, T.; Faust, R. *React. Funct. Polym.* **2009**, *69*, 429.

(6) Nagy, M.; Szollosi, L.; Keki, S.; Faust, R.; Zsuga, M. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2009**, *46*, 331.

(7) Ojha, U.; Kulkarni, P.; Singh, J.; Faust, R. *J. Poly. Sci. Part A: Poly. Chem.* **2009**, *47*, 3490.

(8) Wu, Y. B.; Guo, W. L.; Li, S. X.; Gong, H. Q. *J. Appl. Polym. Sci.* **2009**, *112*, 3294.

(9) Wu, Y. B.; Ren, P.; Guo, W. L.; Li, S. X.; Yang, X. P.; Shang, Y. W. *Polym. J.* **2010**, *42*, 268.

(10) Ivan, B.; Kennedy, J. P.; Chang, V. S. C. *J. Poly. Sci. Part A: Poly. Chem.* **1980**, *18*, 3177.

(11) Kang, J.; Erdodi, G.; Kennedy, J. P. *J. Poly. Sci. Part A: Poly. Chem.* **2011**, *49*, 3891.

(12) Tuncaboylu, D. C.; Okay, O. *Langmuir* **2010**, *26*, 7574.

(13) Ojha, U.; Kulkarni, P.; Cozzens, D.; Faust, R. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 3767.

(14) Nagy, M.; Zsuga, M.; Racz, D.; Keki, S. *J. Poly. Sci. Part A: Poly. Chem.* **2010**, *48*, 2709.

(15) Kali, G.; Georgiou, T. K.; Ivan, B.; Patrickios, C. S. *J. Poly. Sci. Part A: Poly. Chem.* **2009**, *47*, 4289.

(16) Erdodi, G.; Kang, J. M.; Kennedy, J. P.; Yilgor, E.; Yilgor, I. *J. Poly. Sci. Part A: Poly. Chem.* **2009**, *47*, 5278.

(17) Sen, M. Y.; Puskas, J. E.; Ummadisetty, S.; Kennedy, J. P. *Macromol. Rapid Commun.* **2008**, *29*, 1598.

(18) Sipos, L.; Som, A.; Faust, R. *Biomacromolecules* **2005**, *6*, 2570.

(19) Kennedy, J. P.; Carlson, G. M. *J. Poly. Sci. Part A: Poly. Chem.* **1983**, *21*, 3551.

(20) Kennedy, J. P.; Hongu, Y. *Polym. Bull.* **1985**, *13*, 115.

(21) Taylor, S. J.; Storey, R. F. *J. Poly. Sci. Part A: Poly. Chem.***2004**, *42*, 5942.

(22) Cheradame, H.; Andreolety, J. P.; Rousset, E. *Makromol. Chem.* **1991**, *192*, 901.

(23) Cheradame, H.; De, l. C. H. J.; Rousset, E.; Chen, F. *Makromol. Chem.* **1991**, *192*, 2777.

(24) Cheradame, H.; Gojon, E. *Makromol. Chem.* **1991**, *192*, 919.

(25) Buchmann, W.; Desmazieres, B.; Morizur, J.-P.; Nguyen, H. A.; Cheradame, H. *Macromolecules* **2001**, *34*, 2783.

(26) Song, J.; Bodis, J.; Puskas, J. E. *J. Poly. Sci. Part A: Poly. Chem.* **2002**, *40*, 1005.

(27) Soytas, S. H.; Lim, G. T.; Puskas, J. E. *Macromol. Rapid Commun.* **2009**, *30*, 2112.

(28) Kim, I. J.; Faust, R. *J. Macromol. Sci. Pure App. Chem.* **2003**, *A40*, 991.

(29) Mei, L.; Zhu, X.-Q.; Cheng, J.-P. *Chin. Sci. Bull.* **2010**, *55*, 2824.

(30) Zhu, Y.; Storey, R. F. *Macromolecules* **2012**, *45*, 5347.

(31) De, P.; Faust, R. *Macromolecules* **2006**, *39*, 6861.

(32) Bae, Y. C.; Faust, R. *Macromolecules* **1998**, *31*, 9379.

(33) Feldthusen, J.; Iván, B.; Müller, A. H. E. *Macromolecules* **1998**, *31*, 578.

(34) Ivan, B.; Chen, X. Y.; Kops, J.; Batsberg, W. *Macromol. Rapid Commun.* **1998**, *19*, 15.

(35) Schlaad, H.; Erentova, K.; Faust, R.; Charleux, B.; Moreau, M.; Vairon, J.-P.; Mayr, H. *Macromolecules* **1998**, *31*, 8058.

(36) Schafer, M.; Wieland, P. C.; Nuyken, O. *J. Poly. Sci. Part A: Poly. Chem.* **2002**, *40*, 3725.

(37) Kwon, Y.; Faust, R.; Chen, C. X.; Thomas, E. L. *Macromolecules* **2002**, *35*, 3348.

(38) Ivan, B.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 89.

(39) Morgan, D. L.; Storey, R. F. *Macromolecules* **2009**, *42*, 6844.

(40) Hadjikyriacou, S.; Faust, R. *Macromolecules* **1999**, *32*, 6393.

(41) Storey, R. F.; Stokes, C. D.; Harrison, J. J. *Macromolecules* **2005**, *38*, 4618.

(42) Martinez-Castro, N.; Lanzendorfer, M. G.; Muller, A. H. E.; Cho, J. C.; Acar, M. H.; Faust, R. *Macromolecules* **2003**, *36*, 6985.

(43) Peetz, R. M.; Kennedy, J. P. *Macromol. Symp.* **2004**, *215*, 191.

(44) Ojha, U.; Rajkhowa, R.; Agnihotra, S. R.; Faust, R. *Macromolecules* **2008**, *41*, 3832.

(45) Sen, M. Y.; Puskas, J. E.; Dabney, D. E.; Wesdemiotis, C.; Absalon, C. *J. Poly. Sci. Part A: Poly. Chem.* **2010**, *48*, 3501.

(46) Bergbreiter, D. E.; Tian, J.; Hongfa, C. *Chem. Rev.* **2009**, *109*, 530.

(47) Bergbreiter, D. E.; Hobbs, C.; Tian, J.; Koizumi, H.; Su, H.-L.; Hongfa, C. *Pure Appl. Chem.* **2009**, *81*, 1981.

(48) Rooney, J. M. *J. Appl. Polym. Sci.* **1980**, *25*, 1365.

(49) Wu, G. Y.; Cheng, B.; Zhao, Y. X. *Polym. Bull.* **1988**, *20*, 229.

(50) Wu, G. Y.; Cheng, B.; Zhao, Y. X. *Polym. Bull.* **1988**, *20*, 221.

(51) Jerome, R.; Henrioulle-Granville, M.; Boutevin, B.; Robin, J. J. *Prog. Polym. Sci.* **1991**, *16*, 837.

(52) Nemes, S.; Kennedy, J. P. *J. Macromol. Sci. Chem.* **1991**, *A28*, 311.

(53) Everland, H.; Kops, J.; Nielsen, A.; Ivan, B. *Polym. Bull.* **1993**, *31*, 159.

(54) Nielsen, L. V.; Nielsen, R. R.; Gao, B.; Kops, J.; Ivan, B. *Polymer* **1997**, *38*, 2529.

(55) Allen, A. J.; Kennedy, J. P. *Des Monomers Polym* **1999**, *2*, 29.

(56) Hua, Y.; Flood, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 12838.

(57) Inoue, Y.; Kuad, P.; Okumura, Y.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2007**, *129*, 6396.

(58) Jochum, F. D.; zur Borg, L.; Roth, P. J.; Theato, P. *Macromolecules* **2009**, *42*, 7854.

(59) Lenahan, K. M.; Wang, Y.-X.; Liu, Y. J.; Claus, R. O.; Heflin, J. R.; Marciu, D.; Figura, C. *Adv. Mater.* **1998**, *10*, 853.

(60) Li, C.; Bergbreiter, D. E. *Chem. Ind.* **2003**, *89*, 545.

(61) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139.

(62) Tsuda, K.; Dol; Gensch, T.; Hofkens, J.; Latterini, L.; Weener; Meijer; De, S. *J. Am. Chem. Soc.* **2000**, *122*, 3445.

(63) Cannizzo, C.; Amigoni-Gerbier, S.; Frigoli, M.; Larpent, C. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3375.

(64) Kemnitz, M.; Ritter, H. *Beilstein J. Org. Chem.* **2012**, *8*, 2176.

(65) Tomatsu, I.; Hashidzume, A.; Harada, A. *J. Am. Chem. Soc.* **2006**, *128*, 2226.

(66) Vernin, G.; Siv, C.; Metzger, J.; Parkanyi, C. *Synthesis* **1977**, 691.

(67) Molnár, A. *Chem. Rev.* **2011**, *111*, 2251.

(68) Suzuki, A. *Angew. Chem.,. Int. Ed.* **2011**, *50*, 6722.

(69) Yamamoto, Y.; Takizawa, M.; Yu, X.-Q.; Miyaura, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 928.

(70) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195.

(71) Billingsley, K.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358.

(72) Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046.

(73) Lee, D.-H.; Kim, J.-H.; Jun, B.-H.; Kang, H.; Park, J.; Lee, Y.-S. *Org. Lett.* **2008**, *10*, 1609.

(74) Prasad, B. A. B.; Buechele, A. E.; Gilbertson, S. R. *Org. Lett.* **2010**, *12*, 5422.

(75) Salvi, L.; Davis, N. R.; Ali, S. Z.; Buchwald, S. L. *Org. Lett.* **2011**, *14*, 170.

(76) Astruc, D. *Inorg. Chem.* **2007**, *46*, 1884.

(77) Cirtiu, C. M.; Dunlop-Briere, A. F.; Moores, A. *Green Chem.* **2011**, *13*, 288.

(78) Costa, N. J. S.; Kiyohara, P. K.; Monteiro, A. L.; Coppel, Y.; Philippot, K.; Rossi, L. M. *J. Catal.* **2010**, *276*, 382.

(79) Harraz, F. A.; El-Hout, S. E.; Killa, H. M.; Ibrahim, I. A. *J. Catal.* **2012**, *286*, 184.

(80) Karimi, B.; Fadavi, A. P. *Chem. Commun.* **2011**, *47*, 7686.

(81) Laska, U.; Frost, C. G.; Price, G. J.; Plucinski, P. K. *J. Catal.* **2009**, *268*, 318.

(82) Cassol, C. C.; Umpierre, A. P.; Machado, G.; Wolke, S. I.; Dupont, J. *J. Am. Chem. Soc.* **2005**, *127*, 3298.

(83) Chauhan, B. P. S.; Rathore, J. S.; Chauhan, M.; Krawicz, A. *J. Am. Chem. Soc.* **2003**, *125*, 2876.

(84) Li, J.; Shi, X.-Y.; Bi, Y.-Y.; Wei, J.-F.; Chen, Z.-G. *ACS Catal.* **2011**, *1*, 657.

(85) Moreno-Mañas, M.; Pleixats, R.; Villarroya, S. *Organometallics* **2001**, *20*, 4524

(86) Polshettiwar, V.; Len, C.; Fihri, A. *Coord. Chem. Rev.* **2009**, *253*, 2599.

(87) Bernechea, M. a.; de Jesús, E.; López-Mardomingo, C.; Terreros, P. *Inorg. Chem.* **2009**, *48*, 4491.

(88) Garcia-Martinez, J. C.; Lezutekong, R.; Crooks, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 5097.

(89) Yeung, L. K.; Lee Jr, C. T.; Johnston, K. P.; Crooks, R. M. *Chem. Commun.* **2001**, 2290.

(90) Baruwati, B.; Guin, D.; Manorama, S. V. *Org. Lett.* **2007**, *9*, 5377.

(91) Liu, J.; Peng, X.; Sun, W.; Zhao, Y.; Xia, C. *Org. Lett.* **2008**, *10*, 3933.

(92) Ranganath, K. V. S.; Kloesges, J.; Schafer, A. H.; Glorius, F. *Angew. Chem., Int. Ed. Engl.* **2010**, *49*, 7786.

(93) Stevens, P. D.; Li, G.; Fan, J.; Yen, M.; Gao, Y. *Chem. Commun.* **2005**, 4435.

(94) Sreedhar, B.; Reddy, P. S.; Devi, D. K. *J. Org. Chem.* **2009**, *74*, 8806.

(95) Tabuani, D.; Monticelli, O.; Chincarini, A.; Bianchini, C.; Vizza, F.; Moneti, S.; Russo, S. *Macromolecules* **2003**, *36*, 4294.

(96) Churruca, F.; SanMartin, R.; Inés, B.; Tellitu, I.; Domínguez, E. *Adv. Synth. Catal.* **2006**, *348*, 1836.

(97) Bergbreiter, D. E.; Liu, Y.-S.; Osburn, P. L. *J. Am. Chem. Soc.* **1998**, *120*, 4250.

(98) Bergbreiter, D. E.; Su, H.-L.; Koizumi, H.; Tian, J. *J. Organomet. Chem.* **2011**, *696*, 1272.

(99) Bergbreiter, D. E.; Osburn, P. L.; Frels, J. D. *J. Am. Chem. Soc.* **2001**, *123*, 11105.

(100) Bergbreiter, D. E.; Osburn, P. L.; Liu, Y.-S. *J. Am. Chem. Soc.* **1999**, *121*, 9531.

(101) Sommer, W. J.; Yu, K.; Sears, J. S.; Ji, Y.; Zheng, X.; Davis, R. J.; Sherrill, C. D.; Jones, C. W.; Weck, M. *Organometallics* **2005**, *24*, 4351.

(102) Yu, K.; Sommer, W.; Richardson, J. M.; Weck, M.; Jones, C. W. *Adv. Synth. Catal.* **2005**, *347*, 161.

(103) Shin, R. Y. C.; Goh, C. L.; Goh, L. Y.; Webster, R. D.; Li, Y. *Eur. J. Inorg. Chem.* **2009**, 2282.

(104) Beletskaya, I. P.; Cheprakov, A. V. *J. Organomet. Chem.* **2004**, *689*, 4055.

(105) Yang, Y.; Priyadarshani, N.; Khamatnurova, T.; Suriboot, J.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **2012**, *134*, 14714.

(106) Naya, L.; Vázquez-García, D.; López-Torres, M.; Fernández, A.; Vila, J. M.; Gómez-Blanco, N.; Fernández, J. J. *J. Organomet. Chem.* **2008**, *693*, 685.

(107) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102.

(108) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem.* **2010**, *2*, 527.

(109) Zeitler, K. *Angew. Chem,. Int. Ed.* **2009**, *48*, 9785.

(110) Cano-Yelo, H.; Deronzier, A. *J. Chem. Soc., Per. Trans. 2* **1984**, *0*, 1093.

(111) Elofson, R. M.; Gadallah, F. F. *J. Org. Chem.* **1971**, *36*, 1769.

(112) Zen, J.-M.; Liou, S.-L.; Kumar, A. S.; Hsia, M.-S. *Angew. Chem. Int. Ed.* **2003**, *42*, 577.

(113) Narayanam, J. M. R.; Tucker, J. W.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2009**, *131*, 8756.

(114) Nguyen, J. D.; D'Amato, E. M.; Narayanam, J. M. R.; Stephenson, C. R. J. *Nat. Chem.* **2012**, *4*, 854.

(115) Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2011**, *133*, 4160.

(116) Parrish, J. D.; Ischay, M. A.; Lu, Z.; Guo, S.; Peters, N. R.; Yoon, T. P. *Org. Lett.* **2012**, *14*, 1640.

(117) Pham, P. V.; Nagib, D. A.; MacMillan, D. W. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 9232.

(118) Pham, P. V.; Nagib, D. A.; MacMillan, D. W. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 6119.

(119) Shih, H.-W.; Vander, W. M. N.; Grange, R. L.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2010**, *132*, 13600.

(120) Tucker, J. W.; Narayanam, J. M. R.; Krabbe, S. W.; Stephenson, C. R. J. *Org. Lett.* **2010**, *12*, 368.

(121) Tucker, J. W.; Narayanam, J. M. R.; Shah, P. S.; Stephenson, C. R. J. *Chem. Commun.* **2011**, *47*, 5040.

(122) Tucker, J. W.; Nguyen, J. D.; Narayanam, J. M. R.; Krabbe, S. W.; Stephenson, C. R. J. *Chem. Commun.* **2010**, *46*, 4985.

(123) Tucker, J. W.; Stephenson, C. R. J. *Org. Lett.* **2011**, *13*, 5468.

(124) Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617.

(125) Tucker, J. W.; Zhang, Y.; Jamison, T. F.; Stephenson, C. R. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 4144.

(126) Tyson, E. L.; Farney, E. P.; Yoon, T. P. *Org. Lett.* **2012**, *14*, 1110.

(127) Wallentin, C.-J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 8875.

(128) Wallentin, C.-J.; Nguyen, J. D.; Stephenson, C. R. J. *Chimia* **2012**, *66*, 394.

(129) Ischay, M. A.; Ament, M. S.; Yoon, T. P. *Chem. Sci.* **2012**, *3*, 2807.

(130) Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. *J. Am. Chem. Soc.* **2008**, *130*, 12886.

(131) Ischay, M. A.; Lu, Z.; Yoon, T. P. *J. Am. Chem. Soc.* **2010**, *132*, 8572.

(132) Lu, Z.; Yoon, T. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 10329.

(133) Dai, C.; Narayanam, J. M. R.; Stephenson, C. R. J. *Nat. Chem.* **2011**, *3*, 140.

(134) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.

(135) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 2819.

(136) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070.

(137) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 6746.

(138) Kotani, Y.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 6979.

(139) Nishikawa, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2244.

(140) Nishikawa, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 2204.

(141) Senoo, M.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 8005.

(142) Takahashi, H.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3820.

(143) Ueda, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6762.

(144) Ueda, J.; Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 557.

(145) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2249.

(146) Zhang, G.; Song, I. Y.; Ahn, K. H.; Park, T.; Choi, W. *Macromolecules* **2011**, *44*, 7594.

(147) Fors, B. P.; Hawker, C. J. *Angew. Chem., Int. Ed.* **2012**, *51,* 8850.

(148) Bergbreiter, D. E.; Tian, J.; Hongfa, C. *Chem. Rev*. **2009**, *109*, 530.

(149) Toy, P. H.; Janda, K. D. *Tetrahedron Lett.* **1999**, *40*, 6329.

(150) Bergbreiter, D. E.; Hamilton, P. N.; Koshti, N. M. *J. Am. Chem. Soc.* **2007**, *129*, 10666.

(151) De Campo, F.; Lastécouères, D.; Vincent, J.-M.; Verlhac, J.-B. *The J. Org. Chem.* **1999**, *64*, 4969.

(152) Wells, S. L.; DeSimone, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 518.

(153) Bryndza, H. E.; Grady, M. C.; Kristjansdottir, S. S.; Older, C. M.; Page, M. A.; Ritter, J. C.; Tam, W.; Recoverable polymer-bound homogeneous catalysts for catalytic chain transfer processes, US Patent 2007024634, 2007.

(154) Hongfa, C.; Tian, J.; Bazzi, H. S.; Bergbreiter, D. E. *Org. Lett.* **2007**, *9*, 3259.

(155) Hongfa, C.; Tian, J.; Andreatta, J.; Darensbourg, D. J.; Bergbreiter, D. E. *Chem. Commun.* **2008**, 975.

(156) Bergbreiter, D. E.; Liu, Y.-S.; Osburn, P. L. *J. Am. Chem. Soc.* **1998**, *120*, 4250.

(157) Bergbreiter, D. E.; Osburn, P. L.; Frels, J. D. *J. Am. Chem. Soc.* **2001**, *123*, 11105.

(158) Bergbreiter, D. E.; Su, H.-L.; Koizumi, H.; Tian, J. *J. Organomet. Chem.* **2011**, *696*, 1272.

(159) Bergbreiter, D. E.; Yang, Y.-C.; Hobbs, C. E. *J. Org.Chem.* **2011**, *76*, 6912.

(160) Hage, R.; Dijkhuis, A. H. J.; Haasnoot, J. G.; Prins, R.; Reedijk, J.; Buchanan, B. E.; Vos, J. G. *Inorg. Chem.* **1988**, *27*, 2185.

(161) Claessens, C. G.; Hahn, U.; Torres, T. *Chem. Rec.* **2008**, *8*, 75.

(162) de la Torre, G.; Vázquez, P.; Agulló-López, F.; Torres, T. *Chem. Rev.* **2004**, *104*, 3723.

(163) Mack, J.; Kobayashi, N. *Chem. Rev.* **2010**, *111*, 281.

(164) Linstead, R. P. *J. Chem. Soc.* **1934**, *0*, 1016.

(165) Gregory, P. *J. Porphyrins Phthalocyanines* **2000**, *4*, 432.

(166) Biyiklioğlu, Z.; Kantekin, H. *Dyes and Pigments* **2009**, *80*, 17.

(167) Wang, A.; Long, L.; Zhang, C. *Tetrahedron* **2012**, *68*, 2433.

(168) Akkurt, B.; Hamuryudan, E. *Dyes and Pigments* **2008**, *79*, 153.

(169) Ribeiro, A. O.; Tomé, J. P. C.; Neves, M. G. P. M. S.; Tomé, A. C.; Cavaleiro, J. A. S.; Iamamoto, Y.; Torres, T. *Tetrahedron Lett.* **2006**, *47*, 9177.

(170) Salih Ağırtaş, M. *Dyes and Pigments* **2007**, *74*, 490.

(171) Cuellar, E. A.; Marks, T. J. *Inorg. Chem.* **1981**, *20*, 3766.

(172) Dinçer, H. A.; Gonca, E.; Gül, A. *Dyes and Pigments* **2008**, *79*, 166.

(173) de Oliveira, K. T.; de Assis, F. F.; Ribeiro, A. O.; Neri, C. R.; Fernandes, A. U.; Baptista, M. S.; Lopes, N. P.; Serra, O. A.; Iamamoto, Y. *J. Org. Chem.* **2009**, *74*, 7962.

(174) Ranyuk, E.; Cauchon, N.; Klarskov, K.; Guérin, B.; van Lier, J. E. *J. Med. Chem.* **2013**, *56*, 1520.

(175) Kudrevich, S.; Brasseur, N.; La Madeleine, C.; Gilbert, S.; van Lier, J. E. *J. Med. Chem.* **1997**, *40*, 3897.

(176) van Lier, J. E.; Tian, H.; Ali, H.; Cauchon, N.; Hasséssian, H. M. *J. Med. Chem.* **2009**, *52*, 4107.

(177) Li, J.; Sung, S.; Tian, J.; Bergbreiter, D. E. *Tetrahedron* **2005**, *61*, 12081.

(178) Michael, G.; Soley, K.; Wilson, T.; Christina, O.; Joachim, R. In *Catalysis of Organic Reactions*; CRC Press: 2008; pp 319.