HYDROCARBON SOLUBLE POLYMER SOLVENTS AND CATALYSTS

A Dissertation

by

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ABSTRACT

Solvents are most often the major component of chemical reactions. Indeed, global solvent demand and cost are growing exponentially every year. Thus, solvent waste and efficient solvent recycling are big environmental issues.

This work discusses solvent systems based on oligomeric hydrocarbons, poly(α-olefin)s (PAOs), whose low toxicity, low vapor pressure, low flammability, and simple gravity-based separations and recyclability make them promising as green alternative solvent systems. However, while PAOs can serve useful as solvents in stoichiometric and catalytic reaction, they are still alkanes with low polarity that sometimes are poor solvents for polar substrates. Here two strategies for introducing polar moieties into nonpolar media like PAOs will be discussed: hydrogen bond assisted solubilization of poly(*N*-isopropylacrylamide) (PNIPAM) and end-group modification of polyisobutylene (PIB) with hexamethylphosphoramide (HMPA).

The first case will illustrate how a polar polymer can be dissolved in heptane using H-bonding cosolvents. This study further shows that this chemistry can be sued with polymeric Rh(I) hydrogenation catalysts and that it is a feasible way to recycle catalysts using a gravity-based liquid/solid separation. Second, an organocatalyst, a PIB-bound HMPA was used to catalyze allylation of different aromatic aldehydes and reduction of α, β-unsaturated carbonyl compounds in PAOs. In this case, the catalyst and solvent are easily isolated from the organic products by liquid/liquid separation.

In addition, we also examined several polymerizations to form polar block onto PIB to form hydrocarbon soluble polar polymers. With several failed radical and controlled radical polymerization, we enabled to optimize the RAFT chemistry to build up a hydrocarbon soluble PMMA, PEMA, PNIPAM and PDMAA. Finally, we have shown that the polarity of PAO and a substrate can be markedly affected by even small amounts of cosolvent. Studies using solvatochromatic dyes show that 0.2- 2.0 M cosolvent creates microheterogeneity in otherwise miscible solvent mixtures. A polymer ester compound was synthesized and applied in the solvatchromic dyes' polarity studies. The fluorescence behavior affected by the polymer ester compound is similar to the one with a low molecular weight polar cosolvent. The kinetic studies further show that this microheterogeneity translates into large rate changes in reactions.

DEDICATION

This dissertation is dedicated to my beloved family, especially my mother, my father, my sister and my best partner, Chin-An, who always support me, love me and believe me unconditionally.

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Contributors

This work was supervised by a dissertation committee consisting of Professor David Bergbreiter and Professors Daniel A. Singleton and Lei Fang of the Department of Chemistry, and Professor Jamie Grunlan of the Department of Materials Science and Engineering.

In chapter 3, the preliminary solubilizations of PNIPAM were conducted by Camila Perales and Todd Eliason. In chapter 4, solvatochromic Nile Red studies were conducted by Yunuen Avila Martinez.

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NOMENCLATURE

CED Cumulative energy demand

DCM Dichloromethane

THF Tetrahydrofuran

DMF Dimethylformamide

EtOAc Ethyl Acetate

MeCN Acetonitrile

HMPA Hexamethylphosphoramide

LCA Life cycle assessment

VOC Volatile Organic Compound

EHS environmental, health and safety

GHG greenhouse gas

sCO_2 supercritical carbon dioxide

MeTHF 2-methyltetrahydrofuran

ILs ionic liquids

DES deep eutectic solvents

DBSA dodecylbenzenesulfonic acid

SDS sodium dodecyl sulfate

HBD hydrogen bonding donors

PAGs Poly(alkylene glycol)s

PAO Poly(α-olefin)

PE Polyethylene

PIB Polyisobutylene

PEG Poly(ethylene glycol)

PNIPAM Poly(*N*-isopropyl acrylamide)

PPG Poly(propylene glycol)

PDMS polydimethylsiloxane

PTHF poly(tetrahydrofuran)

PNODAM poly(*N*-octadecylacrylamide)

PMMA poly(methyl methacrylate)

LCST lower critical solution temperature

ATRP atom transfer radical polymerization

RAFT reversible addition/fragmentation chain transfer polymerization

QLCP quasiliving carbocationic polymerization

MMA methyl methacrylate

EMA ethyl methacrylate

BMA benzyl methacrylate

NIPAM *N*-isopropyl acrylamide

DMAA *N*,*N*-dimethylacrylamide

tert-BA *tert*-butyl acrylate

CAT catalyst

SUB substrate

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

CHAPTER I

INTRODUCTION

1.1 Green solvents

Most chemical productions are carried out in solvents as they provide suitable milieu for reaction, alleviate heat generation and way to control concentrations of reaction substrates. In particular, large amounts of solvents are used in industrial process, which cause a significant environmental impact if used solvents are not recycled. In the past decades, developing sustainable solvents has become a topic of growing interest in both academic and industrial chemist as way to minimize pollution, energy usage and other related impacts of solvent on climate change. Indeed, the idea of "green" solvent has become a popular theme both for chemical suppliers and chemical users.[1]

In 1998, Anastas and Werner provided a framework of green chemistry as a guideline for chemists to carry out chemistry with smaller impacts to our environment.[2] The 12 principles they proposed outlined how to invent new products, new synthetic routes and new processes in a sustainable way. These principles focus on issues that include 1) prevent waste, 2) atom economy, 3) less hazardous synthesis, 4) design benign chemicals, 5) benign solvents & auxiliaries, 6) design for energy efficiency, 7) use of renewable feedstocks, 8) reduce derivatives, 9) catalysis, 10) design for degradation, 11) real-time analysis for pollution prevention and 12) inherently benign chemistry for accident prevention. In the ensuing decades, 1000s of articles have been published that claim that their research fulfills one or more green tenets. Since solvents take major part of most of

reactions, development of sustainable solvent systems has been a significantly important theme in this large collection of work. This work with solvents has typically focused on the broad issues shown in Figure 1.1 below.

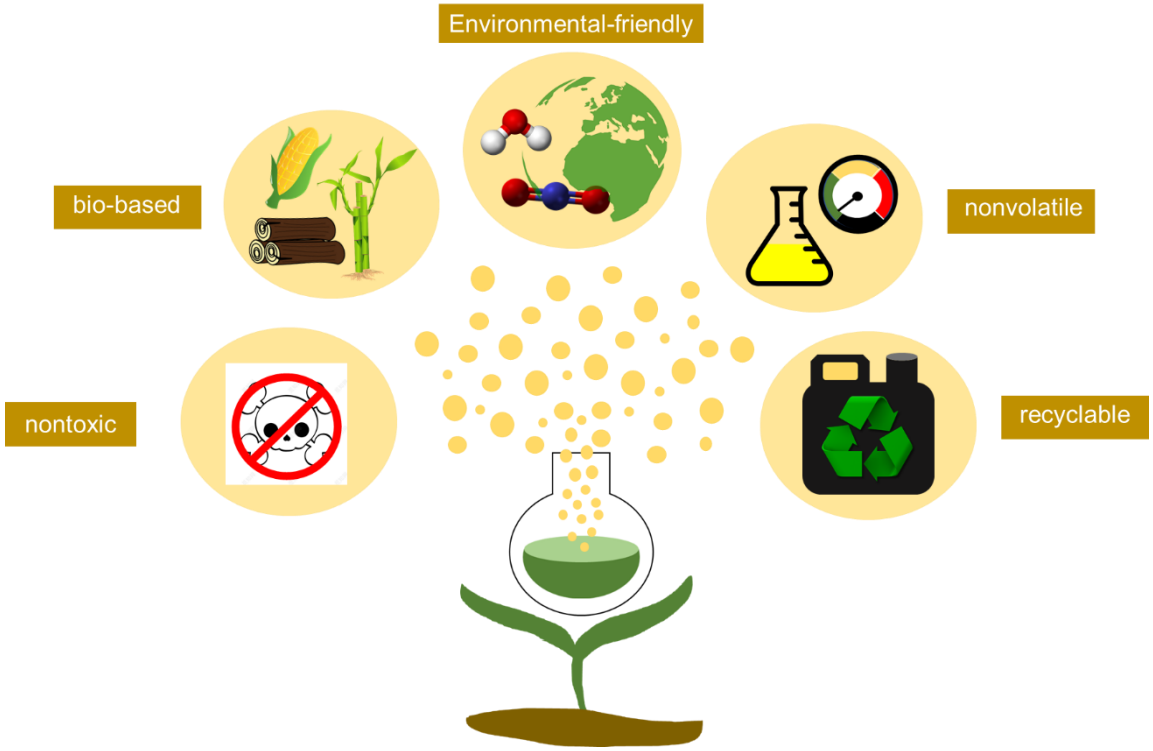


Figure 1.1. Five directions to develop sustainable solvent systems.

When choosing green solvents for reactions, there are five issues (see Figure 1.1) that could be taken into consideration: 1) choose the substitute solvents such that they have better EHS (environmental, health and safety) properties, 2) use "bio-solvents" generated from renewable resources, 3) select environmental harmless alternative solvents, 4) sue solvents with low vapor pressure and 5) search for solvents that can be recycled in a feasible and energy-economic way.[3] There are many examples using these strategies, a few of which are illustrated and discussed in the following paragraphs.

Hoogenboom et al. reported a green process in production of poly(2-ethyl-2-oxazoline) (PEtOx) in which the polymerization occurred in ethyl acetate instead of the commonly used acetonitrile and chlorobenzene.[4] According to table that assess solvent,[5] ethyl acetate is a better solvent than the other two because of its lower toxicity and renewability of its precursors – ethanol and acetic acid. In contrast, acetonitrile and chlorobenzene are derived from petrochemical sources. The difference between ethyl acetate and acetonitrile and chlorobenzene can be assessed in terms of the greenhouse gas (GHG) generation associated with these solvents use. This reflects the fact that a cradle to grave analysis of a petrochemically derived solvent that is not recycled inexorably leads to a net increase in GHGs. In contrast a bio-derived solvent would not lead to a net increase in GHGs.

There are many bio-based alternatives that have been discussed as replacements for conventional ones that were petrochemically derived. By the definition of bio-based solvents, they are produced with plant feedstock.[6] For example, d-limonene can be obtained from citrus wastes, γ-valerolactone can be derived from corn starch, and cyrene and 2-MeTHF can be derived from lignocellulosic biomass. In addition to renewable feedstocks, bio-derived solvents generated much interest in chemical production because it could encourage cultivation of crops and trees and therefore bring positive impact on climate changes. Despite the benefits using bio-derived solvents, there are still several concerns that limit their use as green solvents. First, their production involves GHG generation as discussed below. In addition, these solvents can have other undesirable properties: d-limonene and other terpene solvents have been found recently to have moderate inhalation toxicities and high photochemical ozone creation potentials

(POCPs).[7] Cyrene has a stability issue due to its sensitivity toward acidic/basic conditions as well as strong oxidizing/reducing agents. On the other hand, γ-valerolactone is a robust solvent but the high production cost (ca. $3/kg) may hinder its large-scale industrial application.

In general, two environmental assessment of solvents are often used to evaluate the environmental impact of solvents. The first method is EHS (environmental, health and safety) assessment. The EHS method screens potential hazards of chemical substances based on their physical and chemical properties, toxicity, environmental and safety aspects. Capello et al. reported an EHS assessment of 26 pure solvents as shown in Figure 1.2.[3] Overall solvents with high EHS scores include acetic acid, acetonitrile, dioxane, formaldehyde and formic acid. While acetonitrile shows a relatively low score of air hazards, it has high scores in fire /explosion hazards. Formic acid has high scores on air hazard, chronic toxicity, irritation and acute toxicity. On the other hand, methyl acetate, ethanol and methanol are found to be solvents with low overall scores due to their inherently low environmental hazards and relatively low health hazards. The numbers from EHS assessments provides an overview of potential hazards of each compound in a variety of aspects that need to be considered when using a certain solvent in a chemical process.

Life Cycle Assessment (LCA) is another method to measure "green-ness" of solvents. LCA analysis studies emissions to the environment generated from petrochemical solvent production and the following waste-solvent treatment, such as distillation or incineration.[3] The cumulative energy demand (CED) is used as a screening indicator for the assessment

of solvent manufacturing as well as the following recycling process. Ecosolvent software tool was employed to analyze those environmental factors.[8] In general, solvents which require little energy to be synthesized or even further recycled are considered an environmental friendly solvent, one of the green properties in Figure 1.1. As shown in Figure 1.3, the solvent production energies (MJ/kg) reflects the fact that the closer the solvent (e.g. heptane) to the petrochemical solvent production (e.g. natural gas, naphtha) the lower environmental impact it would generate. On the other hand, highly elaborated solvents (e.g. EtOAc, acetonitrile and THF) has a higher CED as they need more than five steps starting from petrochemicals to be manufactured.[9] The bagasse-based solvent, 2-MeTHF, has a lower CED than the other organic solvents. The production energy varies if a different lignocellulosic feedstock is used. The low CED of 2-MeTHF attributes to the short synthetic route (< 5 steps).[10] It has been calculated that the renewable 2-MeTHF synthesis significantly reduces solvent emissions by 97% relative to the THF production.[11] However, there are some studies showed that biomass cultivation could generate more greenhouse gases than the chemical process of 2-MeTHF.[12] There are additional greenhouse gas (GHG) emissions associated with the solvent's synthesis and there are also GHG costs associated with solvent recycling. To effectively mitigate the rapid climate changes, reductions in greenhouse gases (CO_2, CH_4, N_2O and etc.) emissions are required. The calculation of GHG generation in solvent manufacturing is particularly complicated as many processes including petrochemicals recovery, transport, processing, chemical production and purification are all taken into accounts when estimating the GHG

emissions. The amount of CO_2 generated from solvent combustion is another critical factor in evaluating LCA.

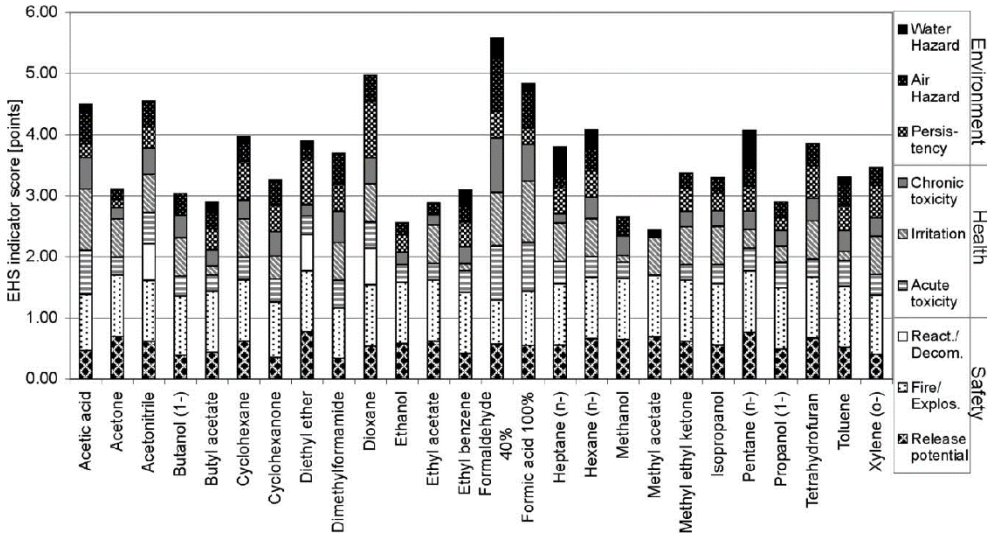


Figure 1.2. Results of the EHS method for the 26 pure organic solvents.[3]

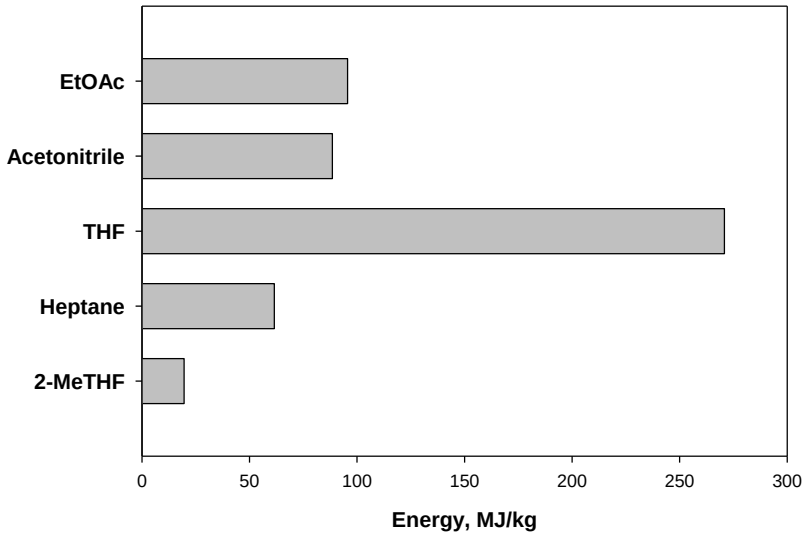


Figure 1.3. The energy required to manufacture 1kg of EtOAc,[3] acetonitrile,[3] THF,[3] heptane[3] and 2-MeTHF.[10]

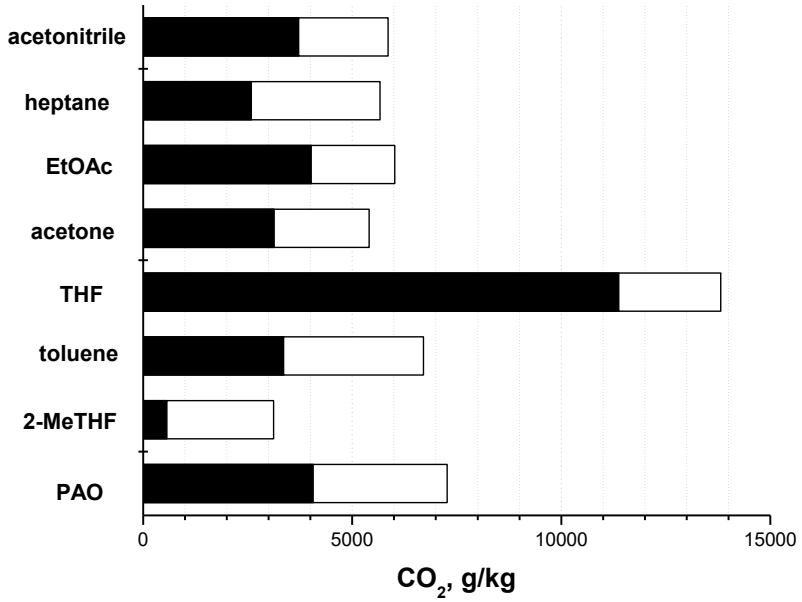


Figure 1.4. Greenhouse gas emissions resulting from the energy consumed during manufacture[3,10,13] (solid bars, assuming 0.042 g CO_2 emissions per kJ) and from the eventual oxidation or combustion (hollow bars) of 1 kg of solvent.

As shown in Figure 1.4, greenhouse gas emissions from solvent manufacture and solvent incineration can also be compared. There are two issues. First, the more steps there are in solvent production, the more GHG emissions there are. The best solvents would be those with the least GHG emissions if this were the only criterion. However, the eventual fate of the solvent has to be considered. Any volatile solvent (2-MeTHF, heptane, EtOAc) can in principle be recycled by distillation. However, recycling is most often not done and would in any case have a cost in terms of GHG emission due to the energy costs associated with distillation. Moreover, in many cases, solvents are contaminated with other species and the products of distillation or the process itself may not be desirable or safe. For

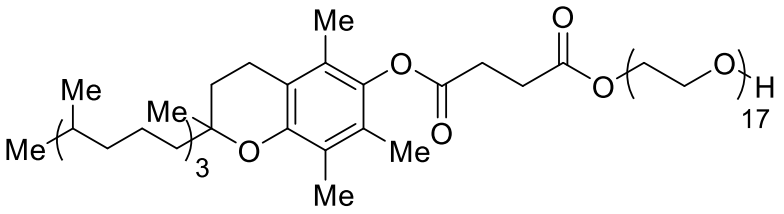
example, MeTHF, like THF, forms peroxides and distillation residues for this solvent could be a significant hazard. If one simply considers the most common fate of these solvents, it would be biodegradation to form CO_2 or combustion to form CO_2. As shown in the bar graph above, all the solvents are roughly similar in that regard.

In most analyses, the LCA of 2-MeTHF has the lowest life cycle footprint relative to other solvents. Some LCA studies on the production on 2-MeTHF disregard the environmental impact like GHG emission during the production of the feedstock like empty fruit bunches or rice straw. The environmental impact from the biomass cultivation is needed to be taken into account when evaluating the greenness of solvents. However, while 2-MeTHF is bioderived and while there may not be a 'net' production of CO_2 on solvent disposal via combustion for this or other bio-derived solvents, combustion of this solvent or of any solvent does produce GHG emissions. Recycling, while it is impractical for this solvent, would not produce GHG emissions. Indeed, infinite recycling of this or any solvent would completely avoid the combustion related emission of GHGs and contribute to the desired outcome of reducing the amount of chemicals produced (i.e. the so-called Moore's Law for Green Chemistry).[14] Recycling would also effectively attenuate the GHGs associated with any solvent's production assuming the recycling process itself was not a significant source of GHGs. Another consideration in using acetonitrile, chlorobenzene, or their greener substitute ethyl acetate is that these are all volatile organic solvents (VOCs). As such, they may cause health, safety and environmental risks and they themselves can be GHGs. Solvent volatility also affects the efficiency of solvent recycling.

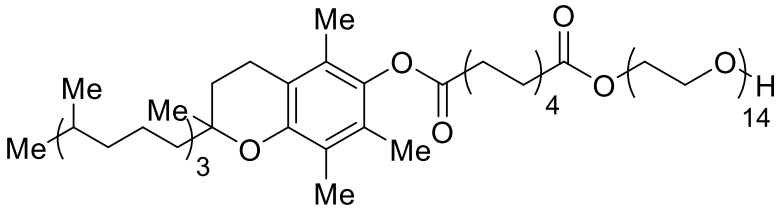
Bio-sourcing isn't the only factor needed that has been considered in developing sustainable solvents. Supercritical carbon dioxide ($scCO_2$) has been recognized as a green alternative in replace of traditional organic solvents because of its natural abundance, nontoxicity, facile removal, recyclability and sustainability. Additionally, exploitation of greenhouse gas like CO_2 normally generated as a by-product in various industrial processing is a great step toward a circular economy. Supercritical CO_2 has been extensively used in both industry and academia in a wide range of applications including drying, extraction, separation, impregnation of porous material, chemical synthesis and other solvent intensive processes. In 1994, Jessop et al. described a hydrogenation by using $scCO_2$ as a solvent and also a substrate to afford formic acid.[15] In this process, hydrogen is highly miscible in this supercritical phase and the initial reaction rate in $scCO_2$ is faster than the one in tetrahydrofuran under the same conditions. Along with its great gas miscibility, $scCO_2$ possess low viscosity. The result is high diffusivity of substrates that can lead to significant rate increases in some gas-involved reaction such as hydrogenation, hydroformylation and oxidation.

However, despite its merit as a promising alternative to replace conventional solvents, $scCO_2$ has some issues. First, it has limited solvation power toward solid reagents and products because pure $scCO_2$ has a low polarity. As a consequence, cosolvent or additives are often introduced to increase the solubility of insoluble material in $scCO_2$.[16–18] Second, to achieve a supercritical state requires pressurized apparatus (T_c = 31 °C, p_c = 72.8 atm). CO_2 recovery and reuse thus requires expensive equipment intensive depressurization/pressurization cycles, which may raise potential operation safety risk.

Another alternative solvent is water. Recycling water is a solved problem and water is an abundant material. Water has also been suggested to have some advantages. For example, several pericyclic reactions found to be accelerated in aqueous solution due to an "on water" effect.[19] It is believed that the hydrogen bonding between two hydrophobic molecules are stronger in water that in less polar solvent medium. However, these reactions were mostly carried out either in dilute aqueous condition (0.4-10 mM)[20] or with cosolvents to enhance the solubility of substrates.[21] Because water is incompatible and immiscible with polar organic substrates, surfactants like dodecylbenzenesulfonic acid (DBSA) or sodium dodecyl sulfate (SDS) are often added to create emulsion droplet in water and further solubilize substrates.[22,23] For the metal-catalyzed cross-couplings, the amphiphiles that are predominantly used are shown in Figure 1.5.[24] PTS was utilized as a surfactant in Heck, Suzuki−Miyaura, Sonogashira, olefin cross-metathesis and other Pd-catalyze processes by Lipshutz group.[25–28] Later, TPGS-750-M was synthesized and described as a better version of PTS as TPGS-750-M provides an economically practical feature and more attractive outcome in many cross-couplings, such as Heck, Suzuki−Miyaura, Sonogashira, and Negishi-like couplings.[29] Based on the observations by dynamic light scattering (DLS), TPGS-750-M formed a larger micelle averaging 50-60 nm in water than the micelle PTS assembled (average size 23 nm). It's believed that the nanoreactor on the order of 50+ nm best accommodates reactants in Pd-catalyzed cross-couplings. This illustrates a possible disadvantage of this approach. Because a surfactant is crucial in reactions in water, different reactions may have to introduce different amphiphilic additives in reaction mixtures, which may narrow to the generality of this approach in chemical production.



TPGS-750-M



PTS

Figure 1.5. Structure of PTS, and the more recently engineered surfactant TPGS-750-M.

As discussed so far, better EHS properties, renewability and environmental harmlessness are important elements to be considered when identifying a green solvent. Solvents with low vapor pressure too can be important as that could minimize emission to air. Neoteric solvents like ionic liquid (ILs) and deep eutectic solvents (DES) are examples of greener media that have a great advantage over other conventional solvents because of their nonvolatile features.[30] Ionic liquids are molten salts at room temperature. These are ionic compounds which are liquid below 100 °C with physiochemical properties modified by tuning the combination of cations and anions. Their high enthalpy of evaporation (ΔH_{vap}) significantly reduces solvent loss during reactions and separation processes.[31,32] Their ionic nature can also be tuned with alkyl groups. Thus, ILs have good solubilizing capacity for a broad class of organic compounds. Accordingly, ionic liquids can be used in organic

reactions,[33–35] catalysis,[36,37] nanoparticle syntheses[38,39] and polymerizations.[40] As mentioned earlier, ILs can be tuned by changing the composition of their anionic and cationic components. However, while over 10^{18} various ILs can be synthesized, they are costly solvents. The inherent moisture sensitivity of ILs can be a hindrance to their use as a solvent in water sensitive reactions. In other cases, the corrosiveness and cytotoxicity of ILs could negate their economic and environmental benefits.[41,42] They are not considered bio-sourced. Thus, while ILs are useful solvents, they are not necessarily regarded as green solvents.

Another neoteric solvent system with low vapor pressure would be deep eutectic solvents (DES). These solvents have attracted rapidly growing interest. Formed by non-covalent interaction like ILs, DES are derived from mixtures of Brønsted or Lewis acids and bases where the liquid mixture has a lower melting point than the two individual components. Like ILs, DES possess low vapor pressures and are non-flammable. An example of a DES is a solvent formed from the quaternary ammonium cation choline [also known as the cholinium cation, (2-hydroxyethyl)-trimethylammonium cation or $HOCH_2CH_2N^+(CH_3)_3$] and a hydrogen bonding donor (HBD) like urea, a carboxylic acid or a glycol.[43] This type of DES has been widely studied and has received significant commercial attention. Many organic syntheses, redox reactions, organometallic reactions, and bio-catalyzed processes have been successfully carried out in DES solvents that contain choline chloride and these hydrogen bond donors.[44] In contrast to ILs, DES is a more interesting alternative to traditional solvents due to their simple synthesis and their inexpensive and environmentally benign components such as glycerol, sugar, urea and natural acids.[45]

Although DES possess many "green" requirements, DES like ILs are often highly viscous fluids. Also, while DES can made from bio-derived molecules, the property of the formed complex can be quite different from its ingredients. Hayyan et al. have studied the toxicity and cytotoxicity of four choline-based DES (with glycerine, ethylene glycol, triethylene glycol and urea as HBDs).[46] Their results suggested these DES have higher cytotoxicity than its individual components.

Still other green alternatives exist. Switchable solvents, i.e. smart solvents, are a unique class of sustainable solvents. Switchable solvents can reversely change their physiochemical properties upon stimulus such as light, chemical and heat.[47–50] CO_2 is a common chemical trigger to perform reversible nonpolar-to-polar solvent system. Jessop et al. has shown that introducing CO_2 into a non-ionic liquid (hexanol and DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene)) formed a new solvent mixture as polar as dimethylformamide.[51] The CO_2-responsive polarity change also could be a feasible and inexpensive work-up procedure to separate products and catalysts when reactions are over. In the past few decades, many CO_2-triggered switchable solvents like switchable polarity solvents (SPSs), switchable hydrophobicity solvents (SHSs), and switchable water (SW) has been discovered and applied in extractions and organic synthesis.[48,52–58] Although the polarity changes don't require a high pressure of CO_2 like using $scCO_2$ (72.8 atm), CO_2 solubility in non-ionic mixture is critical and parameters like gas flow rates and temperature have to well-controlled. In addition, switchable functional groups, such as alcohols and amines, are potentially reactive to reaction substrates. Thus, a careful consideration of choosing reactants and substrate is needed. Hence, in order to achieve a

significant property changes after a stimulus, switchable solvents usually require sophisticated design and cosolvents or additives. Consequently, the advantages of using switchable solvent may be balanced out against the cost and work to remove those cosolvents and additives.

Since switchable solvents are relatively new, the thorough assessments about the toxicity and environmental impact are still inadequate. Therefore, more LCA data will be needed when evaluating the potential of switchable solvents as a new sustainable choice in chemical process.

Other less polar alternative solvents have recently gained some attention. Fluorous solvents like perfluoroalkane, perfluoroethers and other perfluorinated compounds (fluorine-rich) have a number of features that make them advantageous as alternative solvents: low vapor pressure, low flammability, low toxicity and low partition coefficients to general organic compounds.[59,60] Two major advantages of fluorous solvents are their separability and recyclability. In terms of separation, mixtures of fluorous solvents and traditional organic solvents can be used in thermomorphic separations which allows a feasible way to separate products and catalysts via liquid/liquid separation.[61–68] However, the key factor that holds flurorous solvents back from being widely used is their high costs and issues associated with their lack of biodegradability, a problem highlighted recently by issues associated with the environmental persistence of perfluorinated surfactants.[69]

In Table 1.1, some advantages and disadvantages of common green solvents ($scCO_2$, water, ionic liquid, deep eutectic solvents, and switchable solvents) are compiled.

Table 1.1 Comparison between common green solvents

Common solvents	**Advantages**	**Limitations**
$scCO_2$	- natural and abundant - nontoxicity - great recyclability - exploitation of greenhouse gas - low viscosity	- low polarity (cosolvent needed) - pressurized apparatus - operational safety risk
Water	- natural and abundant - nontoxicity - nonflammability	- immiscible with organic compounds due to high polarity - use of surfactants required
Ionic liquid (ILs)	- excellent solubility for organic compounds - tunable property - great recyclability - nonflammability - low vapor pressure	- often toxic - multi-step synthesis - expensive production - limits in H_2O-sensitive reactions - high viscosity - corrosiveness
Deep eutectic solvent (DES)	- nonflammability - low vapor pressure - cheaper production than ILs - bioderived source	- potential cytotoxicity - electrochemical instability
Switchable solvents	- bioderived source - reversible polar-nonpolar polarity upon a stimulus - feasible and cheap work-up procedure	- refined design to different reaction - cosolvents or additives are sometimes needed - undiscovered the toxicity and environmental impact
Fluorous solvents	- low partition coefficients to organic compounds - low vapor pressure - low toxicity - low flammability	- expensive production - poor biodegradability

1.2 Liquid polymers as green solvents

Liquid polymers (LPs) have also gained some attention as alternative green solvents. Polymers are ubiquitous in our daily life and they are often sourced from petroleum chemicals. The synthesis of polymers is relatively inexpensive and they are available on industrial scales often at low cost. Due to their macromolecular nature, liquid polymers are usually considered to have a low volatility. As shown in Figure 1.6, poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), polydimethylsiloxane (PDMS), poly(tetrahydrofuran) (PTHF) and polyolefins have been utilized as solvents. In the following paragraphs, some reported examples of using LPs in organic synthesis will be discussed.

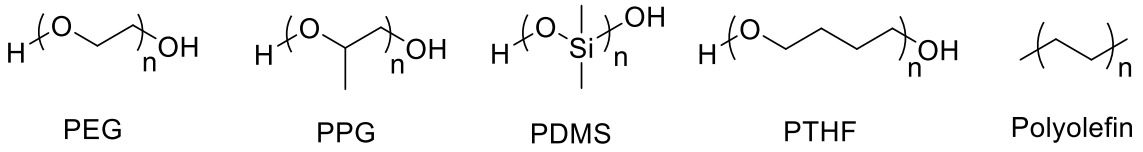


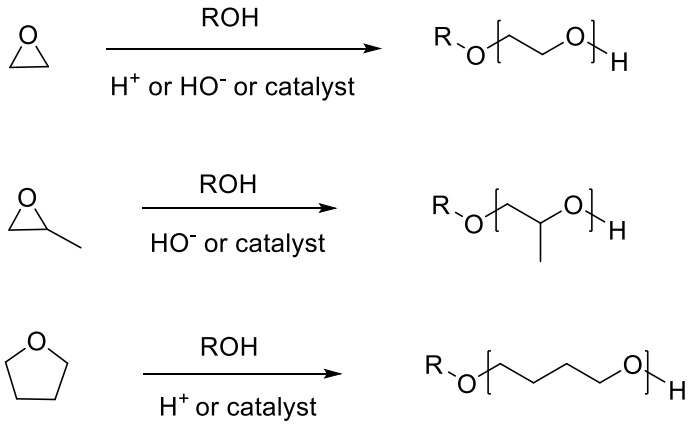
Figure 1.6. Chemical structures of liquid polymers used as solvents: (left to right) poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), polydimethylsiloxane (PDMS), poly(tetrahydrofuran) (PTHF) and a polyolefin.

1.2.1 Polyether (PEG, PPG and PTHF)

Polyethers like polyethylene glycol and low molecular weight of polypropylene glycol (M_w <500 Da) are water-soluble or wax-like solid widely used in cosmetics, lubricant, as wetting agents in biomedical applications.[70] Poly(alkylene glycol)s (PAGs) like PEG and PPG are often synthesized through a cationic or anionic ring opening polymerization of epoxides as shown in Scheme 1.1.[71] The polymerization can be initiated by acid, base or by using a metal catalyst. Ethylene oxide and propylene oxide are typically made in

industry from ethylene and propylene respectively via either direct oxidation with oxygen.[72] Since the monomer source of PEG and PPG can be formed in industrial scale in two-step of oxidation from crude oil, producing PEG and PPG are relatively inexpensive compared with ionic liquids. The polymerization of ethylene oxide can be well controlled and different molecular weights of PEG can be prepared by changing the ratio of ethylene oxide to initiators. Low molecular weight (M_w <600 Da) poly(ethylene glycol)s are colorless fluids at room temperature and are a common polymer used as a solvent. PEGs with molecular weight above 800 Da are white waxy solids and can also be a solvent but at an elevated temperature. Another polyether shown here, poly(tetrahydrofuran) or poly(tetramethylene oxide), is also synthesized via ring open polymerization of tetrahydrofuran. Tetrahydrofuran is not considered to be a green solvent as its complicated multi-step synthetic process is energy-consuming.[9] It is derived from petroleum and its peroxide-forming property increases its potential hazard over time. Thus, PEG and PPG are more desirable sustainable solvent choices than PTHF in terms of economic production and safety concerns. PEG, in particular, is also known for its low toxicity and biodegradability. The negligible toxicity of PEG (LD_{50} 17 to 76 g kg^{-1}, orally, rat/rabbit/guinea pig)[73] allows PEG to be commonly applied as drug carriers for biomedical uses and additives in cosmetic applications. PPG presents a slightly higher toxicity (LD_{50} 2 g kg^{-1}, orally, rat)[74] than that of PEG but significantly lower than that of ionic liquids. For example, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) (LD_{50} 300 to 500 mg kg^{-1}, orally, rat)[75] is much more toxic than PPG. Additionally, biodegradability is also an important criterion of a green solvent. As shown

in Table 1.2, Kawai compared the biodegradation of various polyethers including PEG, PPG and PTHF by activated municipal sewage sludge.[76] PEG and PTHF showed a great biodegradable property, whereas PPG only had a moderate extent of degradation.



Scheme 1.1. Synthesis of poly(ethylene glycol), poly(propylene glycol) and poly(tetrahydrofuran)

Table 1.2. Extent of biodegradation of polyethers by activated municipal sewage sludge after 14 days exposure[76]

Polymer	M_n	Biodegradation (%)
PEG	390	99.7
PEG	1500	95.9
PEG-DME[a]	1500	9.4
PPG	410	69.7
PTHF	660	99.8

[a] PEG-dimethylether, $MeO(CH_2CH_2O)_nMe$

Additionally, PEG is water soluble due to the hydration of the ether group and terminal group. Using the UV absorbance of the solvatochromic dye, Nile Red, the polarity of PEG can be estimated to be like dichloromethane but lower than ionic liquids.[77] As a reaction medium, PEG has extensively studied in organic and organometallic synthesis (Table 1.2).

Several carbon-carbon bond formation reactions (Suzuki coupling, Heck reaction, Stille coupling and Sonogashira coupling) are reported to have a comparative or a higher reaction rate in comparison with conventional solvents. Furthermore, common organic reactions like Knoevenagel condensations, Ru-catalyzed hydrogenations, Michael additions and 1,3-dipolar cycloadditions can also be conducted successfully in PEG. Because the great solubility of PEG toward polar organic substrate, additives or cosolvents usually aren't needed to make reaction mixtures homogeneous. On the flip side, separation of polar product from such polyether solvent isn't always easy as it may require another solvent such as diethyl ether or ethyl acetate to extract product out. Furthermore, many reactions in PEG are conducted in high temperature (>100 ^{o}C) because of the high viscosity of PEG (92 cSt) at room temperature. The issue is also found in ionic liquids as the highly viscous fluid may limit its ability to carry solutes. As for other polyethers, PPG is less polar than PEG. PPG also has an unusual inverse temperature-solubility relationship in water, along with a rapid decrease in water solubility as the molecular weight increase.[78] Therefore, PPG could possibly provide a way to effect a biphasic separation to partition product out upon heating. However, the poor solubility in water may also impede its applicability in aqueous systems. Several reactions listed in Table 1.3, are shown to be catalyzed in PPG. The reaction performance of CO_2 hydrogenation in PPG is superior to the ones in PEG and PTHF. PTHF is also used in running reductions but its applications as solvents are less common.

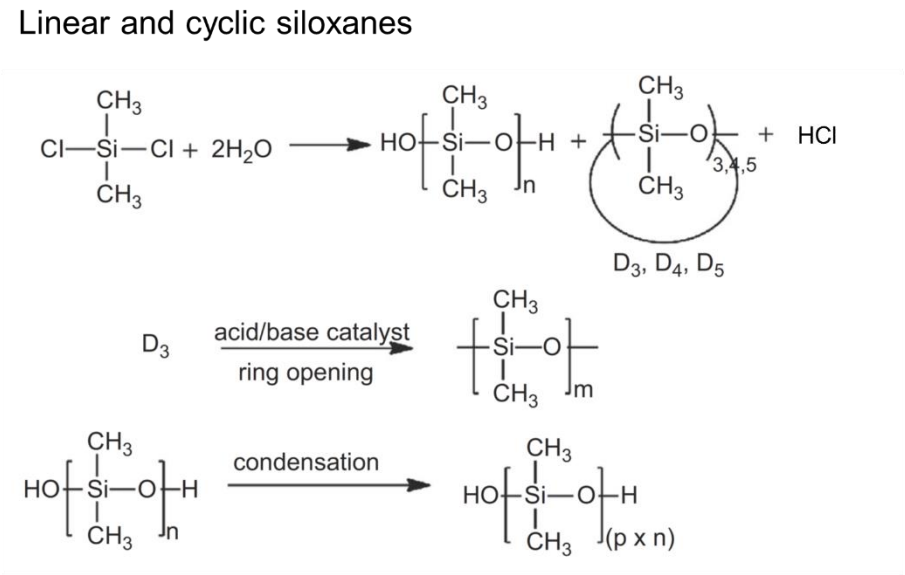
Table 1.3. organic reactions used liquid polyethers as solvents

Polyether solvents	Reactions	Yields
Poly(ethylene glycol) (PEG)	Suzuki coupling	74-90%[79]
	Heck reaction	87-95%[80]
	Stille coupling	75-95%[81]
	Sonogashira coupling	>99%[82]
	Knoevenagel condensation	92-96%[83]
	Ru-catalyzed hydrogenation	91-97%[77]
	Michael addition reaction	98-99%[84]
	CuAAC reaction	90-98%[85]
Poly(propylene glycol) (PPG)	Indium mediated allylation reactions	34-96%[86]
	Ru-catalyzed hydrogenation of alkene	>99%[77]
	Ru-catalyzed CO_2 hydrogenation	52%[77]
	Yeast-catalyzed reductions	100%[77]
Poly(tetrahydrofuran) (PTHF)	Ru-catalyzed hydrogenation of alkene	>99%[77]
	Ru-catalyzed CO_2 hydrogenation	30%[77]

1.2.2 Polysiloxane

Polysiloxane is another example of a liquid polymer used as a solvent in organic reactions. It also exhibits low vapor pressure that would minimize solvent loss and environmental damage from solvent evaporation. Poly(dimethylsiloxanes) (PDMS) is a widely used silicone-based organic polymer with applications as antifoams, lubricants, adhesives, hydraulic fluids, and for degreasing clothes and circuit boards. PDMS is an inert, optical, colorless, nonvolatile, nontoxic and biocompatible liquid polymers, which make PDMS an attractive solvent choice in synthetic chemistry. High gas permeability of PDMS allows the diffusion of gases like oxygen and carbon dioxide and makes it more appropriate in medical applications like wound dressing and contact lenses Additionally, low molecular weight of PDMS (2000 Da) has a low viscosity (20 cSt) that would be superior to other polyether solvents (e.g. PEG, 46-55 cSt).[87] To date, there are few reactions reported using

PDMS as solvents, for instance, Diels-Alder cycloaddition between cyclopentadiene and either methyl acrylate or acrolein,[88] biphasic sodium borohydride reduction of aliphatic aldehydes,[88] and Ru-catalyzed hydrogenation of unsaturated organic acids.[89] PDMS a provide nearly non-polar solvent medium and thus cosolvent may need in the solvent system in order to expand its use in organic synthesis. PDMS can be formed through three different routes: from hydrolyzing dimethyldichlorosilane (Me_2SiCl_2), from ring-opening polymerization of cyclosiloxane, or from polycondensation of diol-functionalized oligo(dimethylsiloxane) resulting from hydrolysis of Me_2SiCl_2 (Scheme 1.2).[90] However, while PDMS synthesis is straightforward, the monomer Me_2SiCl_2 and oligomers are not really green precrusors. They are synthesized from exhaustive industrial processing from copper-catalyzed reactions of alkyl halides (chloromethane and dichloromethane) and ground silicon. Additionally, the cycloalkylsiloxanes (trimers or tetramers) will require energy-extensive fractional distillation to isolate out. Overall, the non-environmentally friendly sources (e.g. dichloromethane) of PDMS and its expensive production of monomers may disqualify its candidacy of sustainable alternative to conventional volatile organic solvents.



Scheme 1.2. Synthesis of linear poly(dimethylsiloxanes) (PDMS)[90]

1.2.3 Polyethylene (PE)

Back in 2010, DuPont released a patent of a recoverable PE-bound cobalt porphyrins for catalyzing polymerizations of olefinic monomers.[91] The low molecular weight PE-bound metal complex are designed to be soluble at elevated temperature, where the polymerization would occur. Upon cooling, the polymer-bound catalysts would precipitate out and be recovered. Furthermore, some thermomorphic separations of PE-bound catalysts and product by using PE oligomer as a cosolvent were developed by Bergbreiter group.[92–95] For example, PE oligomers are used as a polymer support and a cosolvent to facilitate the catalyst separation.[94] From the results, the PE-bound Grubbs catalyst enabled to carry out ring opening metathesis polymerization (ROMP) reactions at 80 ^{o}C in THF with 1 mol% of unfunctionalized PE as a cosolvent. When the polymerization was done and the reaction mixture was cooling back to room temperature,

the unfunctionalized PE entrapped the PE-bound catalysts and precipitated out. Therefore, the PE cosolvent and PE-bound catalyst can be easily separated from the products by a simple filtration. In addition to effect the separation, a nonvolatile and nontoxic PE solid can also protect a catalyst from adventitious decomposition by polar reagents. One issue of using PE as a solvent is the high melting temperature (80-110 ^{o}C). In order to have PE as a liquid form to solubilize reagents, reactions are often needed to be proceed at a high temperature. For some catalysts that undergo thermal decomposition, the PE solvent system may not be seen that useful.

1.2.4 Poly(α-olefin)s (PAOs)

This section discusses the final example of a polymeric solvent, polymers that are alkane like. An example of these solvents relevant to my work is a synthetic base fluid, called a poly(α-olefin) (PAO). Since 1990s, PAOs has been extensively used in applications as diverse as automotive, crankcase oil, gear oils and cosmetics, in refrigeration, in textile synthesis, as dielectric fluids, as brake fluids, as shock absorption fluids and other ways. PAOs are produced from linear alpha olefins usually including 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene. As shown in Scheme 1.3, there are two steps synthesizing poly(α-olefin)s starting from linear alpha olefins: oligomerization of long alkenes and hydrogenation of unsaturated residues of the oligomers. To control the degree of polymerization to obtain low molecular weight PAOs, boron trifluoride (BF_3) coupled with a protic co-catalyst (e.g. water, alcohol or weak carboxylic acid) is used.[96] With a careful control of ratio between BF_3 and alcohol, trimer of 1-decence is the predominant oligomer found in the product mixture. Other than boron

trifluoride, aluminium chloride ($AlCl_3$) is another Lewis acid catalyst that is commonly seen to produce higher molecular weight of PAOs.[97] Metallocene and heterogeneous chromium (II) catalysts are also reported to yield high molecular weight of PAOs.[97,98] The important point in PAO synthesis is that a careful choosing the catalyst and tuning the reaction condition allows industry to control the properties of PAOs like degree of polymerization, the degree of branching and the polymer distribution can be properly controlled. The second step of PAO synthesis, hydrogenation of unsaturated oligomers, typically uses nickel or palladium catalysts. The hydrogenation is quite vital because it could enhance the chemical inertness and oxidative stability. Therefore, the maturity of PAO synthesis allows producers to manufacture different PAOs that satisfy customer end-use requirements. As listed in Table 1.4, the common liquid PAOs derived from 1-decene are PAO2 (dimer), PAO4 (trimer), PAO6 (tetramer), PAO10 (pentamer), PAO40 (13mer) and PAO65 (18mer), which are usually named after their corresponding viscosity (cSt) at 100 ^{o}C. In the following discussion, this nomenclature of PAO will be continued used for convenience.

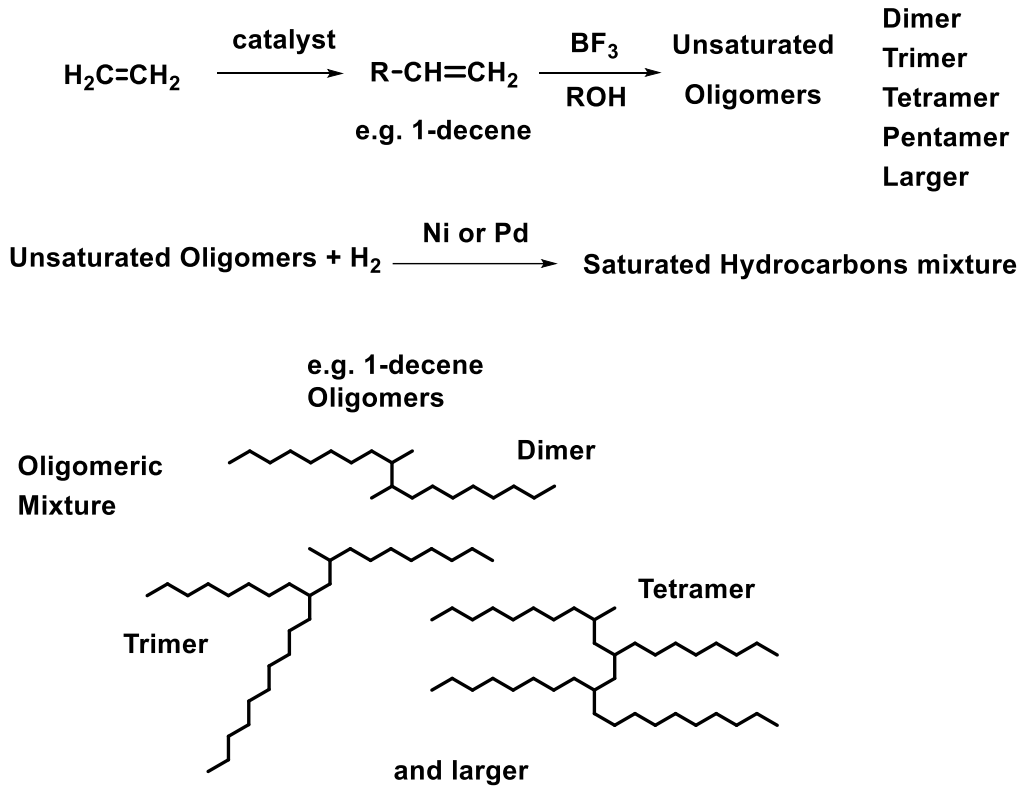
Compared to another hydrocarbon oligomer derived from distillation of petroleum, mineral oil, synthetic based stocks PAOs have several advantages. PAOs have a wider operational temperature range, oxidative stability, hydrolytic stability, biodegradability (for low molecular weight of PAOs), low toxicity and high purify as a linear alkane (with no cyclic alkanes and no unsaturation).[96] More importantly, PAOs have relatively homogeneous molecular weights due to their applications as lubricants that requires defined viscosity.

While biodegradability of PAOs is not their feature, it is noteworthy that PAO2 and PAO4 demonstrate a superior biodegradability to some equi-viscous commercial paraffinic and naphthenic base stock in the biodegradability test (CEC L-33-T-82), which is a standard industry method for assessing the biodegradability of oil products (Figure 1.7).[99] While there is a widespread misperception that PAOs are not generally biodegradable, low M_w of PAOs do degrade to some extent (>70 %) over time. PAO fluids are also reportedly not skin irritants to mammals.[99]

As noted above, PAOs possess more uniform molecular distribution than mineral oils (Figure 1.8) because PAOs are synthesized in a controlled polymerization whereas mineral oil are straightly distillated from crude oil. This feature is attractive because solvent recyclability is a critical for e a green solvent. The narrow distribution of nonpolar PAOs offers a great phase selectivity when other polar solvent is added. In other words, while a less nonpolar solvent would partition to an extent to a polar phase, mineral oil could have a small portion of short hydrocarbons leaching to a polar phase in a biphasic separation. PAOs similarly exhibit less leaching (<0.01%) to polar phases than conventional nonpolar solvents like hexanes do (4 %). PAOs also have an "antileaching" effect, which they are better than heptane at recycling hydrocarbon-bound catalysts.[100]

Finally, PAOs have a high flash point (e.g. 200 ^{o}C for PAO4) which is distinctly different than hexanes that has its flash point at -26 ^{o}C. Thus, PAOs are barely flammable under normal range of reactions temperatures. Previous work has shown that pyrophoric compounds like *tert*-butyllithium could stay stable in PAOs upon exposure to air.[101] Moreover, alkyllithium reagents are as reactive in PAOs as they are in low molecular

weight alkanes. Several reactions including anionic polymerization, metalation, and nucleophilic addition were all successfully carried out in PAO4 with yields of products that were unchanged from those in hexanes and heptane.



Scheme 1.3. Synthetic flow of poly(α-olefin)s (PAO)s.

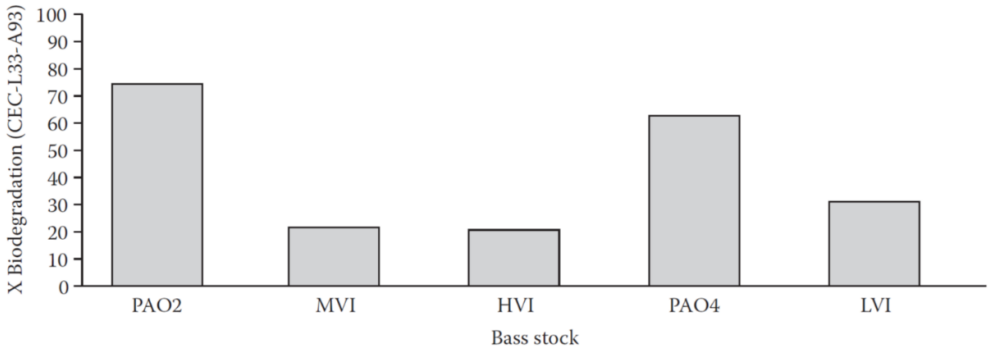


Figure 1.7. Biodegradability of base stocks poly(α-olefins) versus equi-viscous mineral oils: MVI, medium viscosity index (naphthenic base stock, aromatic content 1.9%); HVI, high viscosity index (paraffinic base stock, aromatic content 2.6%); LVI, low viscosity index (naphthenic base stock, aromatic content 12.3%).[96]

Table 1.4. Poly(α-olefin) (PAO) Alternative Solvents.

PAOs	Molecular Weight (M_n)	Number of Carbons	Viscosity at 100 ^oC (cSt)
PAO2	283	20	2
PAO4	432	30	4
PAO6	570	40	6
PAO10	687	50	10
PAO40	1785	130	40
PAO65	2505	180	65

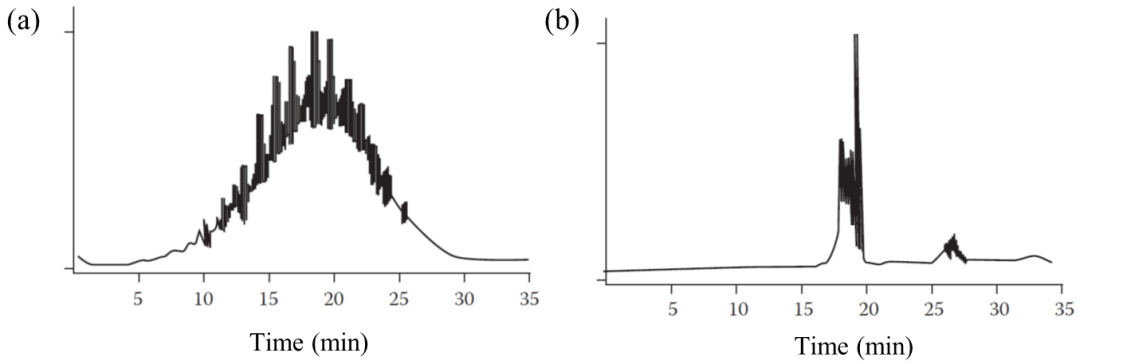


Figure 1.8. Gas chromatography traces of (a) mineral oil and (b) PAO4.[96]

Given the fact that PAOs are nonvolatile, nontoxic, non-flammable, potentially biodegradable, PAOs are believed to be a sustainable choice to replace small alkane solvents like hexanes and heptane. To date, some organic reactions have been studied by our group. In general, these experiments show comparative or better reaction performance in PAOs when comparing with the ones in hexanes or heptane. Malinski studied the thermal isomerization of a hydrocarbon soluble azo dye in PAO4 and heptane (Figure 1.5), monitoring its UV-visible absorbance at 430 nm (λ_{max} of trans azo dye) to study the rate of isomerization of the Z to E form of they dye.[95] The rate constant in PAO4 (2.6×10^{-4} s^{-1}) was similar to the rate constant in heptane (2.2×10^{-4} s^{-1}). Another example of using PAOs a solvent is a nucleophilic substitution reaction. In that case, Samusual and Bergbreiter studied the S_N2 reaction of butyl bromide by potassium acetate in PAO4 (Figure 1.6), using solid potassium acetate as a nucleophile and a polyisobutylene (PIB)-tethered phase transfer agent as a catalyst (PIB-PTC).[102] While she did not study the kinetics in PAO, she was able to show that the yields of butyl acetate in PAO4 or heptane were almost identical in the same time frame. Moreover, using PAO4 and the PIB-PTC

could be recycled and reused over multiple cycles without changes in yield while a similar recycling in heptane was less successful. The higher recyclability of the catalyst was rationalized by the fact that small alkane solvents are prone to leach into the polar phase (MeCN in this case) more than PAOs are. In addition, a portion of PIB-PTC catalyst may be lost in each extraction step using heptane, a supposition that has support in prior work by Harrell and Liang showed that PAOs were better than heptane at preventing leaching of PIB-bound catalysts.[100] Ongoing work by others in the Bergbreiter group showed that PAOs are also useful in Bronsted acid-catalyzed processes and in nucleophilic catalysis.

While PAOs have advantages, they are still alkanes. As nonpolar solvents, PAOs has an intrinsic drawback that they are poor solvents for many organic substrates. PAOs are also immiscible with many polar protic solvents (methanol, ethanol and isopropanol). While some of these solvents and some polar aprotic solvents (e.g. dimethylforamide) will form a homogeneous solution with PAOs at an elevated temperature, the solubility of many of these cosolvents in PAOs at ambient temperature is low. The thermomorphic behavior of PAOs with some of these solvents does though have a potential in that it could be a way to carry out a reaction in a polar mixture and then to separate a polar solvent solution of polar products upon cooling. Still other polar solvents like acetonitrile (MeCN), dimethylsulfoxide and water are not miscible with PAOs even on heating. They could in principle be used to extract products from PAO after a reaction without contaminating the PAO phase.

The low polarity of PAOs means that like $scCO_2$ and PDMS, PAOs would need cosolvents to enhance their polarity in order to expand the scope of their use. PAOs are

miscible with solvents with an intermediate polarity (dichloromethane, ethyl acetate and tetrahydrofuran). Thus, there is a possibility for PAO modification through polarization with an added cosolvent. This possibility has been explored already in collaborations with a prior student, Thomas Malinski. However, that work used volatile organic solvents that are not recyclable. In the work I've discussed below, I have explored ways to address this issue by designing scheme that retain polar additives including catalysts in PAOs during separation methods that either separate additives after a reaction or reuse them along with the PAO.

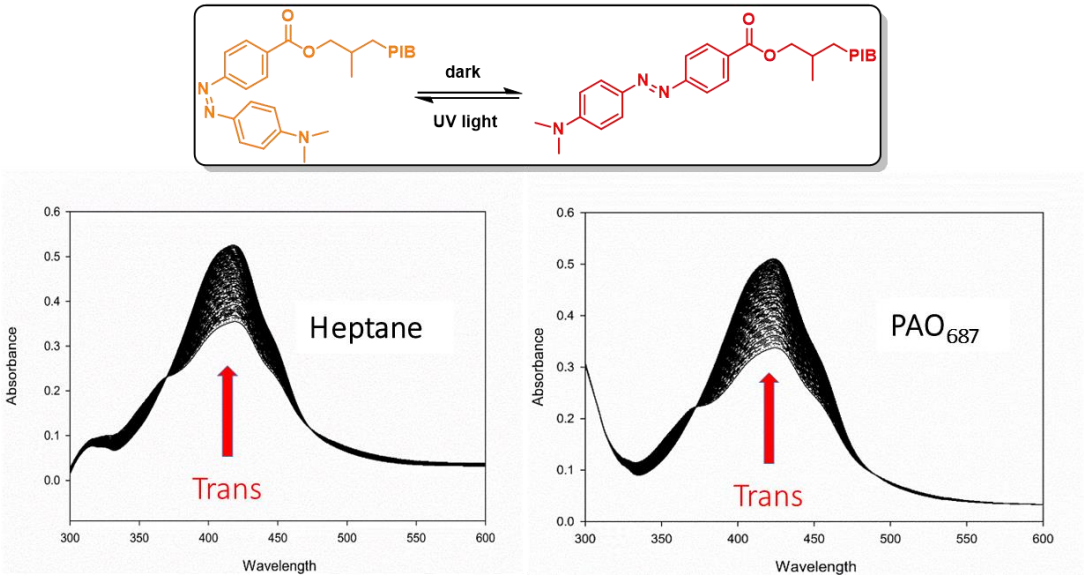


Figure 1.9. UV-visible spectra of the thermal isomerization of PIB-bound para-methyl red in heptane (left) and PAO_{687} (right).[95]

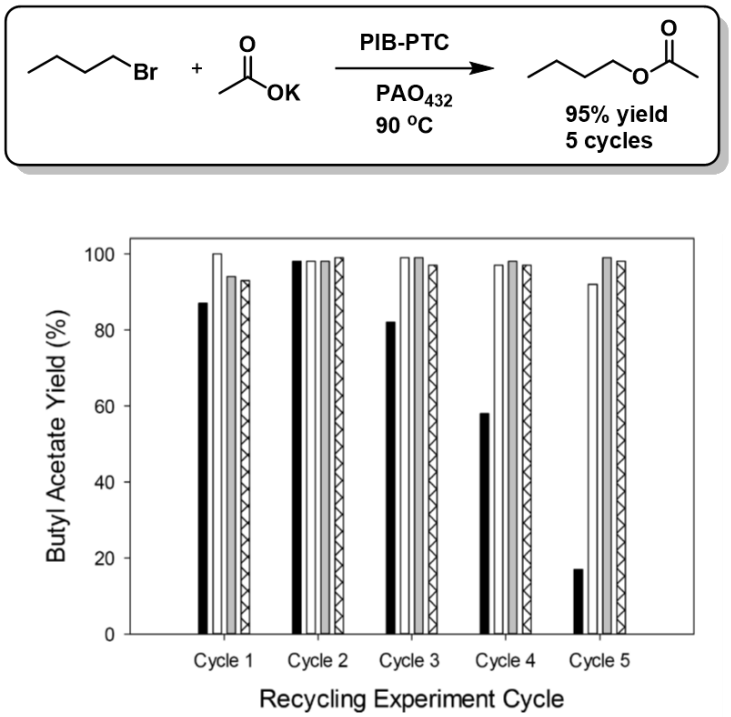


Figure 1.10. Recycling of PIB-PTC catalyst in phase-transfer-catalyzed esterification of butyl bromide by potassium acetate in heptane (black bar), PAO2 (white bar), PAO4 (grey bar) and PAO6 (cross-hatched bar).[102]

1.3 Recyclable polymer-supported catalysis

Catalysis is ubiquitously used in modern chemical industry. Over 90 % of all chemical products has at least one catalytic step in their manufacturing.[103] Homogeneous catalysts especially offers several advantages over heterogeneous catalysts in terms of better accessibilities of substrates to active sites and tunability of catalyst selectivity with ligand modification.[104] However, homogeneous catalysts are often difficult to separate from a reaction mixture. Such separability many not matter in a 1-mmol scale academic reaction but can become an issue in an industrial scale process. Exacerbating this problem is the modest stability of many homogeneous catalysts and their ligands. Thus, these leads to problems when it comes to conventional separation method like product distillation or even a filtration where air exposure occurs. Generally, there are two types of strategies to address the difficulties in homogeneous catalyst separation and reuse: the use of a biphasic solvent system or the use of a polymer-supported catalyst.[105] Ionic liquids and water are commonly utilized in biphasic catalysis where the polar solvents dissolve catalysts, substrates and product but where another phase can be used to extract or separate the product.[35,106] Polymer-supported catalysts can be soluble or insoluble. In soluble polymer supported catalysts initially received the most attention for homogeneous catalyst separation. However, while some examples like polystyrene sulfonic acids are now used commercially, most studies that focused on homogeneous organo or transition metal catalysts found the immobilization of a catalyst on an insoluble polymer altered the catalyst's activity.[107] The alternative was soluble polymer supported catalysts that could be obtained through a synthetic modification binding a catalyst moiety onto polymer chain

ends or side chains. The Bergbreiter group has been a pioneer in this latter approach and has shown that suitably designed polymer-bound catalysts could possess phase-selective solubility and readily recovered by either a biphasic workup or by a solid/liquid separation (Figure 1.11).[108] By using polymers with the appropriate physical property, catalysts can be selectively soluble in a polar or nonpolar phase or quantitatively precipitate from all solvents after a reaction. In some cases, catalysts can be separated under biphasic condition after a monophasic reaction by perturbing the reaction mixture with small amounts solvents or other perturbing agents. Another strategy is to alter the reaction conditions such that a soluble polymer becomes insoluble. This can involve a temperature change or solvent addition. Stimuli-responsive polymer-supported catalyst, in particular, have been received some attentions because the polymers could precipitate out upon external stimuli (heat, pH or etc.). An example of my work that addressed this problem of solid/liquid separation and some related chemistry will be further discussed in chapter 3. These general strategies of polymer bound catalyst/product separation will be briefly described below.

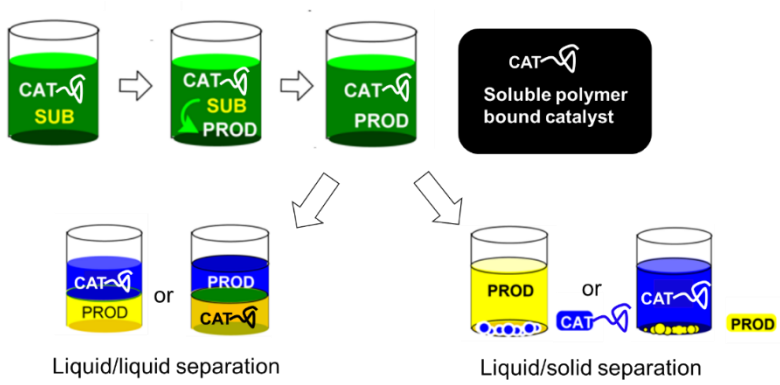


Figure 1.11. Strategies for separation of soluble polymer bound catalyst (CAT) from products (PROD) after homogeneous reaction with a substrate (SUB).

Common polar polymer supports include polyacrylamides and poly(ethylene oxide). Either polymer can be used to support catalysts in water or polar organic solvents. Poly(*N*-isopropylacrylamide) (PNIPAM) is a thermoresponsive polymers. Its inverse solubility (insoluble at high temperature) in water makes it possible to separate PNIPAM from water by simple heating above PNIPAM's LCST (low critical solution temperature). This property of PNIPAM enabled our group to design smart catalysts with on/off reactivity as the temperature went below/above its LCST.[109] Our group also used PNIPAM in mixed thermomorphic solvent systems containing an equivolume mixture of heptane and 90% EtOH that was a single phase on heating (>70 ^{o}C) but biphasic at ambient temperature (Figure 1.12). Since PNIPAM was insoluble in heptane, a heptane soluble product could be separated from a PNIPAM bound catalysts themormorphically. While this chemistry worked, it only worked for alkane soluble substrates. Therefore, the phase preference of PNIPAM was altered by making the acrylamide's *N*-alkyl group into a more lipophilic octadecyl group. This new polymer, poly(*N*-octadecylacrylamide) (PNODAM), was preferentially soluble in heptane versus aq. EtOH and could be used to prepare more polar products in cross coupling chemistry.[110] PNODAM was also soluble in an equivolume heptane/*N*,*N*-dimethylacetamide mixture. After few drops of water was added, two phases mixture generated with PNODAM exclusively in the nonpolar phase.

Polyethylene (PE) and polyisobutylene (PIB) oligomers, have been widely used by our group as phase anchors for separating and recycling catalysts. PE oligomers have only been used in reactions where they are soluble hot and insoluble cold.[93] PIB on the other hand is always a viscous oil. PE oligomers are generally insoluble in any solvent at

ambient temperature. However, while PE oligomers insolubility can be an issue, functional PE oligomers are commercially available and have been used to make commercially viable thermomorphic catalysts for acrylate polymerization.[111] PIB is generally soluble in any solvent heptane or hexane dissolved in.

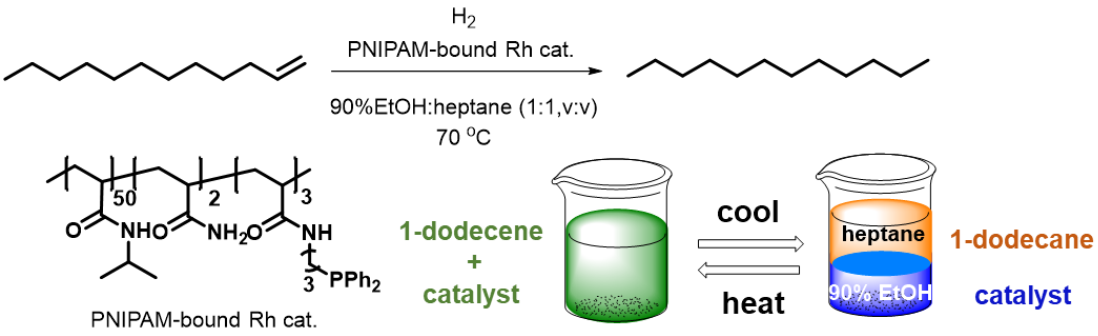


Figure 1.12. Thermomorphic PNIPAM-bound rhodium(I) catalyzed hydrogenation.[110]

Most recent work by the Bergbreiter group has focused on using PIB oligomer supports because their solubility facilitates catalyst synthesis, analysis and use. Vinyl-terminated PIB oligomer (450,1000 and 2300 Da) is commercially available.[112] The terminal alkene of PIB is easily modified by conventional chemistry and PIB oligomers can be converted to form many soluble polymeric reagents and catalysts. The potential of PIB as a hydrocarbon soluble support ligand has been extensively explored by our group. Catalysts including a Grubbs−Hoveyda catalyst,[92,113] a Cr(III)-salen catalyst,[114] a Pd(0) cross-coupling catalyst,[93] a Ru(II) bipyridine dichloride complex,[115,116] Rh(II) catalyst,[100] a Co(II) phthalocyanines catalyst,[117] a polyoxometalates catalyst,[118] a phase transfer catalyst[102] and photoredox organocatalysts[119] have all been reported. Due to the

preferential solubility of PIB bound ligands and reagents in heptane, both thermomorphic and latent biphasic separation (heptane/MeCN or heptane/DMF) can be used to separate catalysts and products after reactions.

Some elected examples of PE oligomer and PIB oligomer supported catalysts include the following. In 2011, Bergbreiter group showed a thermomorphic ring-closing metathesis (RCM) reaction could be catalyzed by a PE-supported olefin metathesis catalyst (Figure 1.13).[120] This PE catalyst is insoluble in toluene at 25 °C but can catalyze RCM reactions at 65 °C as a homogeneous catalyst. These PE-supported catalysts could be recycled upon cooling and reused by adding fresh diene substrate up to 10 times with a consistent high yield. The separation was so efficient that different reactions with different dienes could be affected in series simply by washing the recovered solid catalyst with toluene.

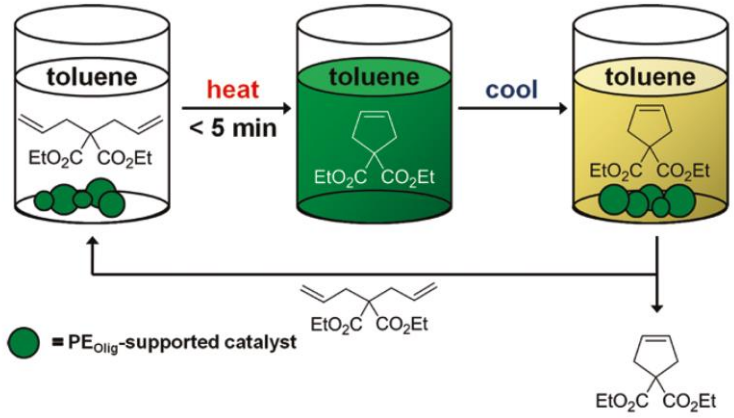


Figure 1.13. Thermomorphic polyethylene-supported olefin metathesis catalysts.[120]

PIB bound catalysts are soluble in hydrocarbons like heptane or PAO. Thus, they are most commonly separated from products using a thermomorphic process or by extraction with a solvent like acetonitrile. However, it is sometimes possible to use PIB-bound catalysts in heptane without a liquid/liquid separation. For example, Priyadarshani used a PIB bound Ru (II) photoredox catalyst in a radical polymerization of acrylate monomers under visible light irradiation at 25 °C with ethyl 2-bromoisobutyrate as the initiator in the presence of diisopropylethylamine (Figure 1.14).[115] In this case, the polymer precipitated as it formed. From their results, the polymerization from each cycle formed polymer products in similar isolated yields with similar M_n and PDI values. Furthermore, the polyacrylate products had minimal (e.g. 1ppm) Ru contamination that was 50-fold less than products from a similar polymerization catalyzed by a low molecular weight Ru catalyst.

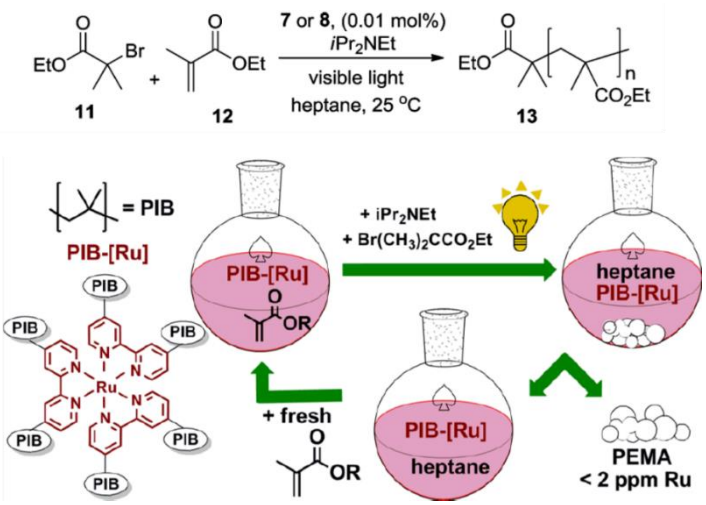


Figure 1.14. Recoverable reusable polyisobutylene (PIB)-Bound Ru (II) photoredox polymerization catalysts.[115]

In summary, catalysis is a key component in green chemistry. Soluble polymers have an established role in catalyst/product separation. Unlike small organic molecule, polymers usually have phase preferential solubility. The phase selectivity allows a polymer bound catalyst to be separable from product of reaction if the product is soluble in different liquid phase.

CHAPTER II

RECYCLABLE POLYISOBUTYLENE-BOUND HMPA AS AN ORGANOCATALYTST IN RECYCLABLE POLY(ALPHA-OLEFIN) SOLVENTS*

2.1 Introduction

As mentioned in chapter I, over 90 % of all chemical products have at least one catalytic step in their manufacturing processes. However, while catalysts by definition are not consumed in reactions,[103] the sustainability and recyclability of organocatalysts continue to be problematic. That in part reflects the fact that organocatalysts often have higher mol% loading than transition metal catalysts.[107,121] These issues also are important because more efficient catalyst recycling strategies are needed to reduce waste production and because catalyst separation can minimize hazards if a catalyst has inherent toxicity or contaminates products.

An additional issue in homogeneous catalysis is the solvent used. Solvents are the major component of most chemical processes and are required in homogeneous catalysis. While most reported organocatalytic reactions historically used conventional solvents like tetrahydrofuran (THF) and dichloromethane (DCM), green solvents are now available as substitutes. Such green solvents are commonly derived from renewable resources.[6,122] An advantage of these green solvents is that they do not have any net greenhouse gas (GHG) impact because as bio-derived solvents they are derived from CO_2 in contrast to solvents derived from a non-renewable petrochemical source However, greenhouse gas

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generation (GHG) inexorably occurs if these greener solvents are not recycled. Most organic solvents including these green solvents are also volatile. Volatile organic solvents (VOCs) often have health, safety and environmental risks. Accordingly, a recent thrust of our research has been exploring the use of highly recyclable nonvolatile poly(α-olefin)s (PAOs). While such solvents are not at present bioderived, they are highly recyclable and are safer than conventional more volatile solvents.[95,101,122] However, they are simply large alkanes and as alkanes, their applicability in synthesis and more specifically to organocatalytic processes involving polar catalysts has to be experimentally established.

Our prior work has shown that vinyl-terminated PIB is broadly useful as a precursor for formation of recyclable ligands, catalysts, and reagents that can be easily separated from products.[100,116,117,119,123–125] Such separations are effective because terminally functionalized PIB oligomers have excellent phase selective solubility in nonpolar alkanes versus polar solvents like acetonitrile (MeCN), MeOH and water. They are also highly soluble in poly(α-olefin)s (PAOs) like PAO_{432}, the fully saturated trimer formed from trimerization of 1-decene.[96] Our prior work has also shown that PIB-bound species are even more phase selectively soluble in PAOs than heptane in liquid/liquid separations involving polar organic phases.[95,122] This prior work has also shown that terminally functionalized PIB-bound catalysts or reagents in the same solvents as their low molecular weight analogs have equivalent reactivity.[92,93,100,114–117,119,122,123,125,126] However, when PIB is used in an alkane, reactivities are less predictable because alkanes have not historically been studied as solvents for reactions of polar catalysts. Indeed, prior studies have shown that switching from a solvent like THF or CH_2Cl_2 to an alkane like

heptane or its recyclable analog PAO can lead to higher, different, equivalent or no reactivity for a recyclable PIB-bound catalyst in a pure alkane because of the minimal ability of alkanes to solvate reactants, transition states, or products.[100,115,122,123]

Hexamethylphosphoramide (HMPA) is both an organocatalyst and a useful polar aprotic solvent. Its applications as a catalyst and solvent have been described in reactions like allylations,[127–131] aldol additions,[130,132] reductions,[133–138] reductive aldol reactions,[135,136] reductive alkylations,[139] alkyne additions,[140] ring opening reactions[141] and radical polymerizations.[142] However, whether HMPA is used as a catalyst or as a solvent, its use like that of other dipolar aprotic solvents has been limited because of its toxicity and the difficulty of separating it from products. The carcinogenic and mutagenic toxicity of HMPA is of special concern since separating HMPA either from an organic phase, from a product, or from an aqueous waste phase after a reaction is problematic.[143–145] Specifically, HMPA has a high boiling point and is miscible both with many organic solvents and with water, making it difficult to separate after a reaction.

There is a long history wherein polymer supports have been used to design safer versions of dipolar aprotic solvents including HMPA.[146,147] The earliest reports of a polymer-bound phosphoramide described synthesis of a DVB-crosslinked polystyrene (PS) supported phosphoric triamide as an organocatalyst for biphasic reactions like S_N2 reactions and reductions.[148] Similar PS-supported HMPA analogs were also shown to be useful organocatalysts in catalytic aldol reactions.[149–151] However, while these polystyrene supported HMPA resins could be recycled by a simple filtration, polystyrene supported

HMPA resins' activity sometimes decreased on recycling.[149] These PS-bound HMPA analogs also required a conventional volatile organic solvent. Other examples of polymers containing HMPA analogs included a polymeric phosphoramide (poly(HMPA)) that was formed by post-modification of linear poly(ethylenimine)[152] or by a ring opening polymerization of *N*-bis(dimethylamino)phosphorylpropylenimine.[153] While this polymer analog of HMPA reportedly had good solubility in water, methanol, acetonitrile, *N*,*N*-dimethylformamide, chloroform and dichloromethane, its applicability as a cosolvent or catalyst in synthesis was not described. Later work by the Haag group showed that a dendritic HMPA analog that had a phosphoramide covalently attached onto a hyperbranched polyglycerol (hPG) as a support was useful as a soluble polymeric catalyst for allylation and Mukaiyama aldol reactions.[131] This polymer-bound HMPA analog could be separated by membrane filtration. However, those reactions and the membrane filtration required relatively large amounts of conventional volatile organic solvents.

HMPA-catalyzed reactions whether with HMPA itself or with polymer-bound analogs all use conventional solvents like toluene, tetrahydrofuran (THF) and dichloromethane (DCM). Moreover, the recyclability of HMPA as an organocatalyst has not always been well described or is not simple and efficient. In this chapter, I describe a portion of my work wherein I developed a more sustainable way to use the equivalent of HMPA as an organocatalyst. In this chemistry, I also further explored the potential of alternative nonvolatile PAOs as fully recyclable solvents showing that this sort of highly polar organocatalyst was as or even slightly more competent. This involved synthesizing a PAO-anchored polyisobutylene (PIB)-bound HMPA analog as an organocatalyst and

exploring its reactivity and use for aldehyde allylation and enone reduction in PAO_{432}. The results below show that this PIB-bound HMPA analog has comparable reactivity to HMPA in both a conventional solvent and in this recyclable PAO_{432} solvent. We show that both this PIB-bound HMPA-like organocatalyst and the PAO solvent phase can be readily separated and recycled through at least five cycles separating products and the PAO phase containing the PIB-bound catalyst by simple gravity separations (Figure 2.1).

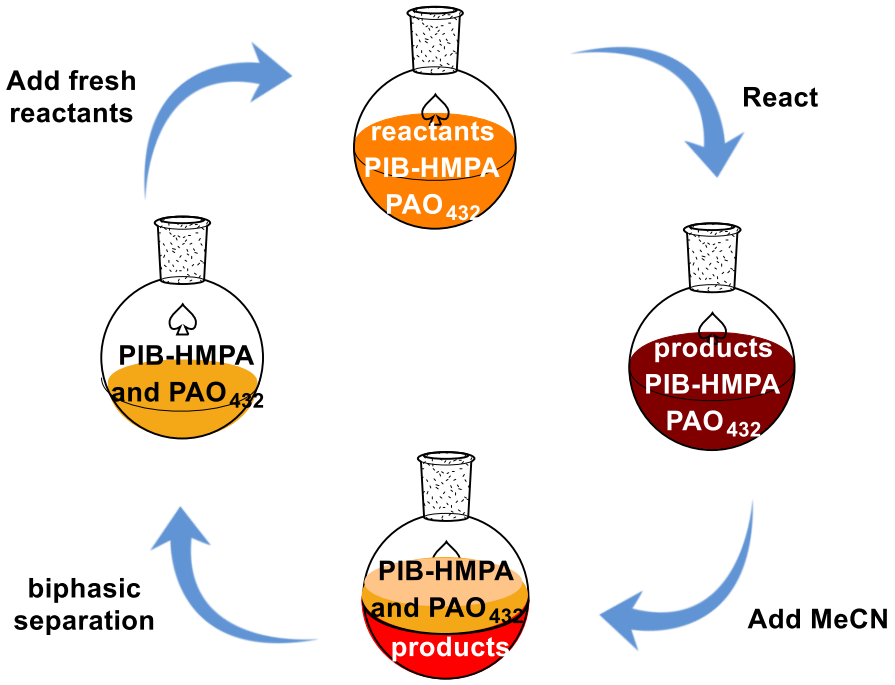
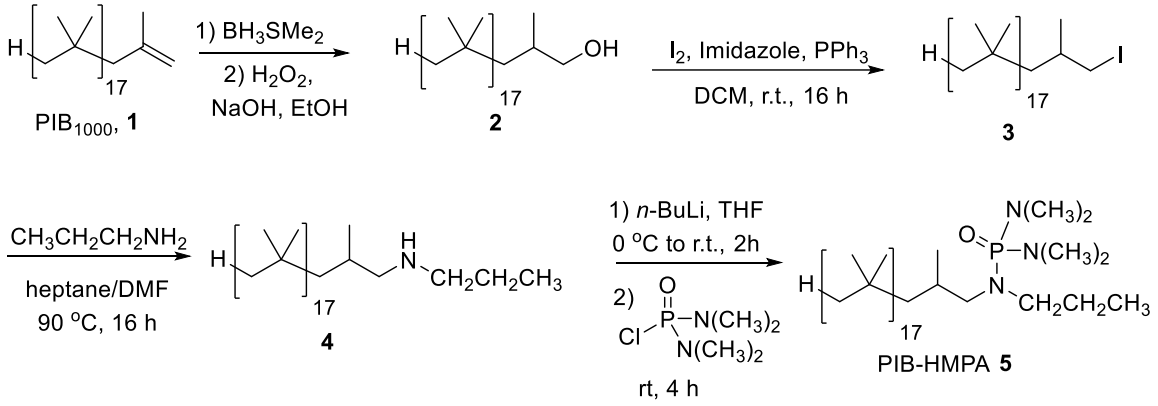


Figure 2.1. Scheme for use of a recyclable alkane soluble PIB-bound hexaalkylphosphoramide analog of HMPA (PIB-HMPA) in catalysis using PAO_{432} as a recyclable alkane solvent. Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

2.2 Results and discussion

The synthesis of a PIB-bound hexaalkylphosphoramide (PIB-HMPA, **5**) is shown in Scheme 2.1. In this synthesis, a commercially available alkene terminated PIB oligomer **1** (M_n = 1000 Da) was first converted to a PIB-bound alcohol **2** which was then allowed to react with iodine in presence of triphenylphosphine and imidazole to generate the PIB-bound iodide **3**. The iodide **3** was used to form a secondary amine **4** by allowing it to react with excess propylamine in a thermomorphic solvent mixture (heptane/DMF). A liquid/liquid separation isolated the PIB-bound secondary amine **4** as a heptane solution with any excess amine and any polar byproducts phase separating into the DMF-rich phase. Lithiation of a THF solution of the amine **4** with *n*-butyllithium formed a lithium amide *in situ* that was allowed to react with excess *N*,*N*,*N*',*N*'-tetramethyl-phosphorodiamidic chloride to form **5**. After solvent removal, the crude product **5** was isolated as a viscous oil that was further purified by trituration with MeOH to remove any non-PIB bound phosphoramide species. The product was characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. ^{31}P NMR spectroscopy in particular was important as it allowed us to compare the ^{31}P NMR spectra of HMPA with that of **5** (See Figure 2.2). In this ^{31}P spectrum, **5** had essentially the same ^{31}P NMR chemical shift as HMPA consistent with formation of a hexaalkylphosphoramide.



Scheme 2.1. Synthesis of hexaalkylphosphoramide-terminated PIB oligomer **5** (PIB-HMPA). Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

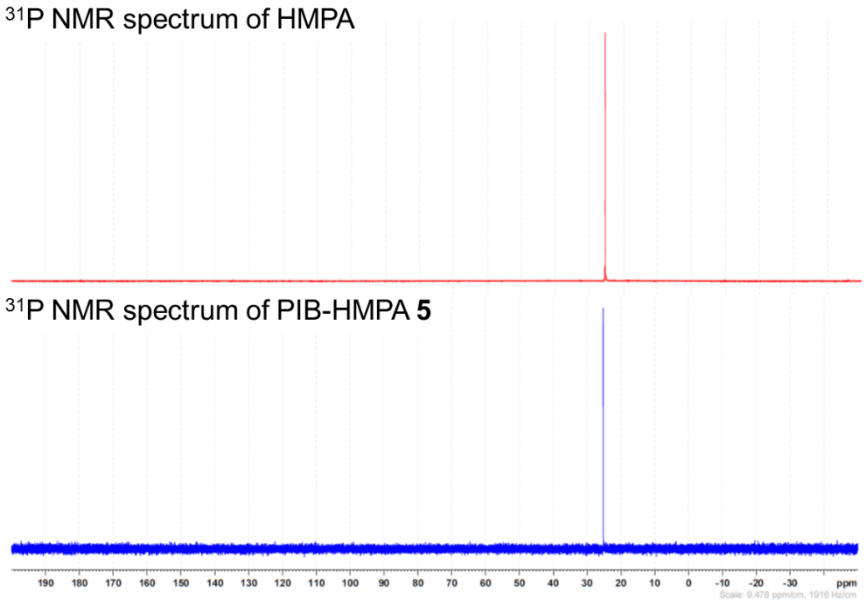


Figure 2.2. Overlay of ^{31}P NMR spectrum of HMPA (top) and PIB-HMPA **5** (bottom). Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

We next explored the phase separability of **5**. Our prior work has shown that PIB-bound dyes can be separated in a gravity-based liquid/liquid separation using heptane and a polar solvent like methanol with >99.9% of the PIB-bound species partitioning into the alkane phase.[95] We anticipated similar phase selective solubility would accrue to **5.** That proved to be the case. In the experiment that probed the phase separability of **5**, we vigorously mixed a 0.05 M solution of **5** with a methanol solution that contained 0.03 M phosphoric acid. ^{31}P NMR spectroscopy analysis of the methanol phase after 48 h showed that there was no detectable **5** presented indicating that the concentration of **5** in MeOH was <0.001 M (Figure 2.3, >99.8% phase selective solubility for **5** in PAO_{432} vs. MeOH). A similar experiment was also carried out with heptane as the alkane phase. In this case, we did detect a small concentration of **5** in the MeOH phase (>95% phase selective solubility for **5** in heptane vs. MeOH, see Figure 2.4).

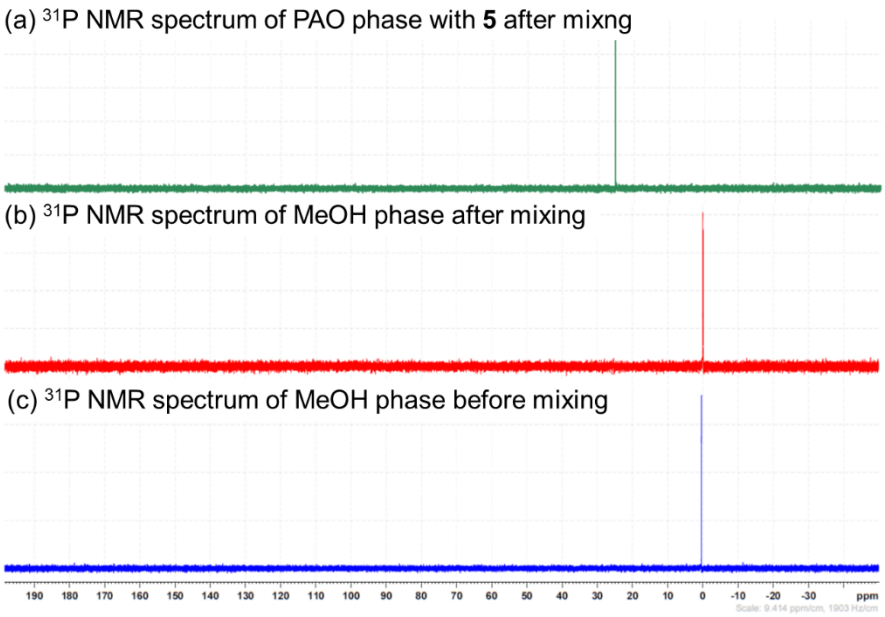


Figure 2.3. Overlay of ^{31}P NMR spectra showing the phase selective solubility of **5** in PAO_{432}: (a) the only phosphorus signal in the PAO_{432} phase after mixing is the PIB-HMPA **5**; (b) the absence of a signal for **5** in the MeOH with the only phosphorus signal being that of the 0.03 M phosphoric acid that was used as an internal standard) and (c) the MeOH phase with 0.03 M of phosphoric acid before mixing showing a single signal due to the phosphoric acid. As expected, the phosphoric acid is insoluble in the PAO_{432} but phase selectively soluble in MeOH. Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

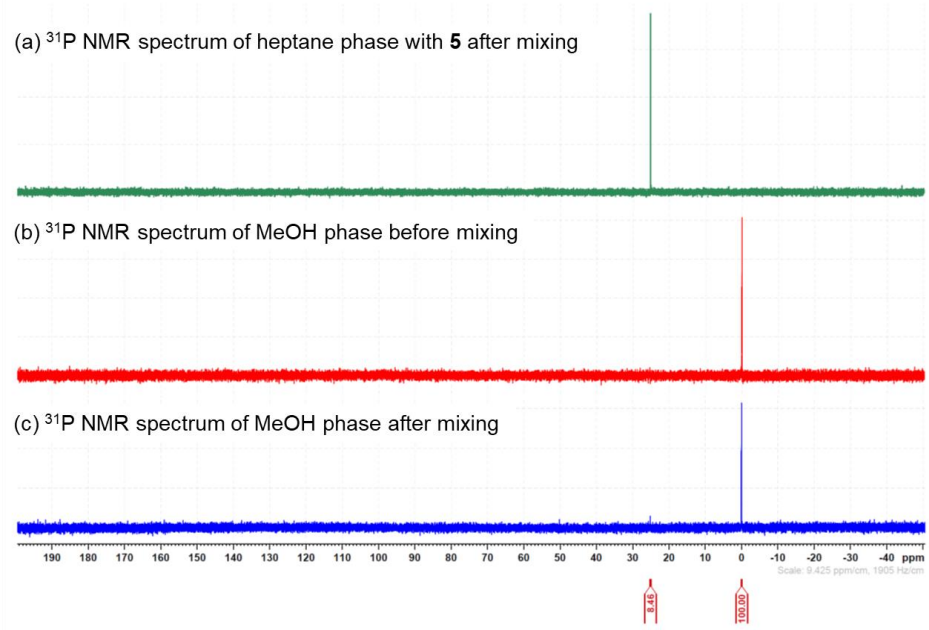
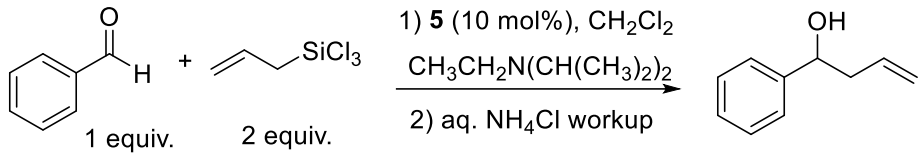


Figure 2.4. Overlay of ^{31}P NMR spectra showing the slightly less phase selective solubility of 5 in the heptane phase of a heptane/MeOH mixture: (a) the only phosphorus signal in the heptane phase after mixing is the PIB-HMPA **5**; (b) the presence of a small amount of **5** in the MeOH phase with the predominant signal being that of the 0.03 M phosphoric acid that was used as an internal standard) and (c) the MeOH phase with 0.03 M of phosphoric acid before mixing showing a single signal due to the phosphoric acid. As expected, the phosphoric acid is insoluble in heptane but phase selectively soluble in MeOH. Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

Next, we examined the use of **5** as a catalyst. The initial reaction we studied was the allylation of benzaldehyde in CH_2Cl_2 using allyltrichlorosilane. This reaction has been reported using HMPA as a catalyst and has been studied by others using polymer-supported formamides as catalysts so it provides a good way to evaluate the utility of this PIB-bound HMPA analog as an organocatalyst.[150,154–156] We first compared the reactivity of **5** with HMPA in CH_2Cl_2 in order to confirm that **5** acts like HMPA in this allylation chemistry (Scheme 2.2). We then examined the reactivity of **5** as an allylation catalyst in

heptane and PAO_{432}. Overall, we examined five systems; no catalyst in CH_2Cl_2, HMPA in CH_2Cl_2, **5** in CH_2Cl_2, **5** in heptane, and **5** in PAO_{432}.



Scheme 2.2. Allylation of benzaldehyde catalyzed by the PIB-bound organocatalyst **5**. Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

This work like the prior work with HMPA as a catalyst included an equivalent of *N*,*N*-diisopropylethylamine (DIPEA).[157] These studies of the conversion versus reaction time profile for the allylation of benzaldehyde are shown in Figure 2.5. As expected, no reaction occurred without catalyst. Allylations with **5** in CH_2Cl_2 were comparable but marginally faster than with HMPA in CH_2Cl_2. While **5** appeared to be slightly more active than HMPA in this solvent, the difference was modest to explore in more detail. More importantly, allylations with **5** in PAO_{432} converted benzaldehyde into 1-phenylbut-3-en-1-ol quantitatively essentially as fast as was the case for HMPA in CH_2Cl_2. An experiment using **5** in heptane showed that allylation occurred at a rate that was indistinguishable from that for **5** in PAO_{432}. The overall conclusion is that **5** as a catalyst for this allylation chemistry is equivalent to HMPA in CH_2Cl_2, in heptane or PAO_{432}.

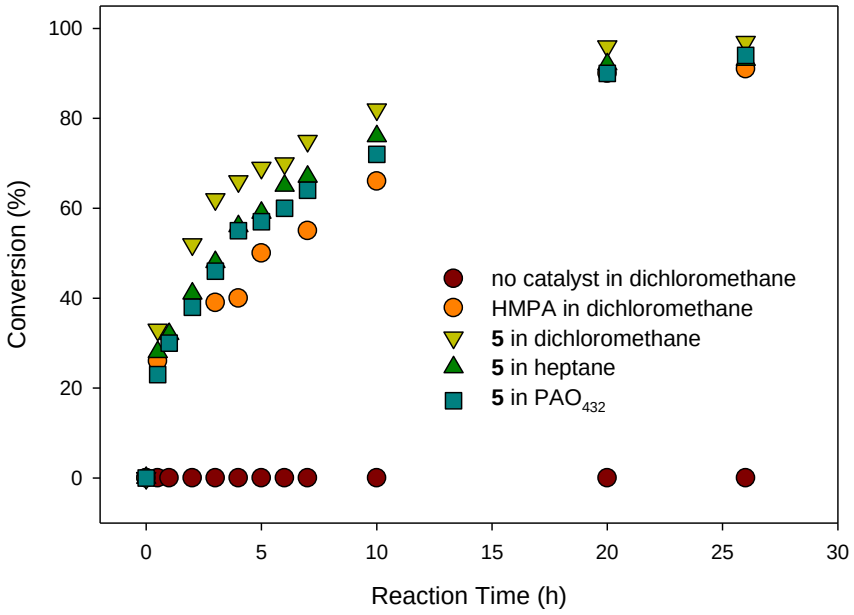


Figure 2.5. Kinetic studies of allylation of benzaldehyde with 10 mol% of HMPA or **5** in various solvents at 25 °C: no catalyst in dichloromethane (red circle), HMPA in dichloromethane (orange circle); **5** in dichloromethane (light green triangle), **5** in heptane (green triangle); **5** in PAO_{432} (malachite green square). Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

After confirming the comparative reactivity of **5** versus HMPA and showing that **5** is reactive in PAO_{432}, we explored the recyclability of **5** in benzaldehyde allylation in PAO_{432}. This included developing procedures for separation of **5** in PAO_{432} from the products using MeCN as an extraction solvent. To this end, we examined the phase selective solubility of **5** and the product (1-phenylbut-3-en-1-ol) in a biphasic PAO_{432}/MeCN mixture. In this experiment, 0.25 g of **5** and 0.1 mL of 1-phenylbut-3-en-1-ol were dissolved in 2 mL of PAO_{432} and then mixed vigorously with 2 mL of MeCN. After a gravity separation, an aliquot (100 μL) from each phase was dissolved in $CDCl_3$

with 0.2 M of dichloroethane as an internal standard and further analyzed by ^{1}H NMR spectroscopy. Based on these ^{1}H NMR spectra (see Figure 2.6), > 99% of **5** stayed the in PAO_{432} phase while more than 98% of 1-phenylbut-3-en-1-ol was present in the MeCN phase. This result is in accord with our prior observations that PIB derivatives have little or no solubility in acetonitrile phases.[95,100]This phase selective solubility wherein **5** is in the PAO_{432} phase and the small organic compound is in the MeCN phase assured an excellent separation of catalyst from product via a liquid/liquid (PAO_{432}/MeCN) separation in recycling studies in the following reactions. However, a complication was observed in an examination of the PAO_{432} phase in a similar separation by ^{31}P NMR spectroscopy of an experiment where allyl trichlorosilane was present. Under those conditions, we observed that the original signal for **5** at 25.3 ppm in PAO_{432} disappeared and that a new signal at 32.3 ppm appeared (see Figure 2.7). Since allyl trichlorosilane can readily hydrolyze to form HCl with adventitious water, we considered that this downfield shift might be the result of protonation of the phosphoramide catalyst by adventitious HCl formed from the chlorosilane. Since a protonated catalyst **5** is incapable of activating allyltrichlrosilane to form six-member ring transition state,[157] we added an additional step and treated the recovered PAO phase with 4 N NaOH. After this base treatment, the ^{31}P NMR signal in the PAO phase changed back to 25.3 ppm suggesting that experiments to recycle catalyst **5** should include a second NaOH treatment to insure that the PAO phase is recycling the active catalyst **5**. Notice that ca. 3 equivalent of DIPEA was added as an additive to accelerate the reaction. However, DIPEA was not

observed as a base to neutralize the protonated 5 from the early trials. We speculated that this may reflect the fact that acidities in this PAO medium differ from water.

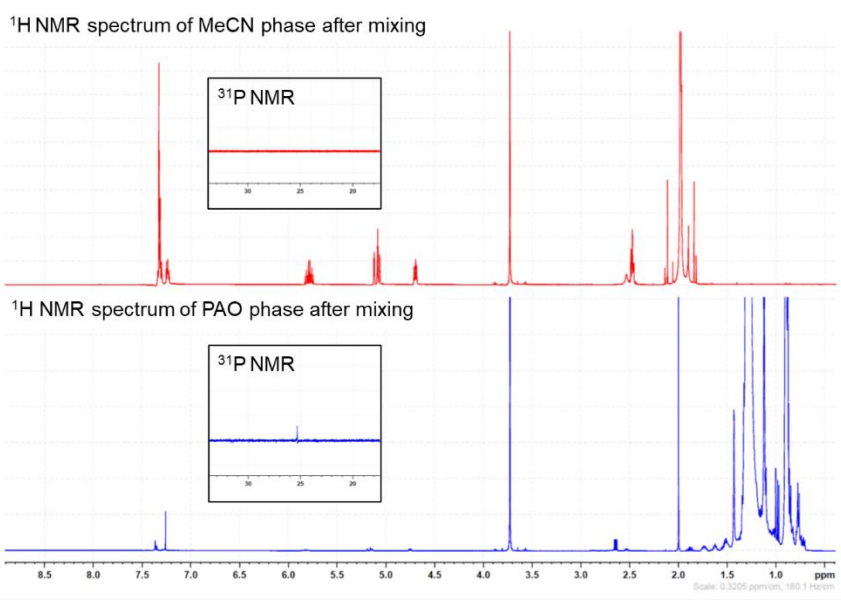


Figure 2.6. ^{1}H and ^{31}P (inset plot) NMR spectra of the MeCN (top) and PAO_{432} (bottom) phases in a phase selective solubility test of 1-phenylbut-3-en-1-ol and 5 in MeCN/PAO_{432} mixture after a vigorous mixing (0.2 M dichloroethane was used as an internal standard). Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

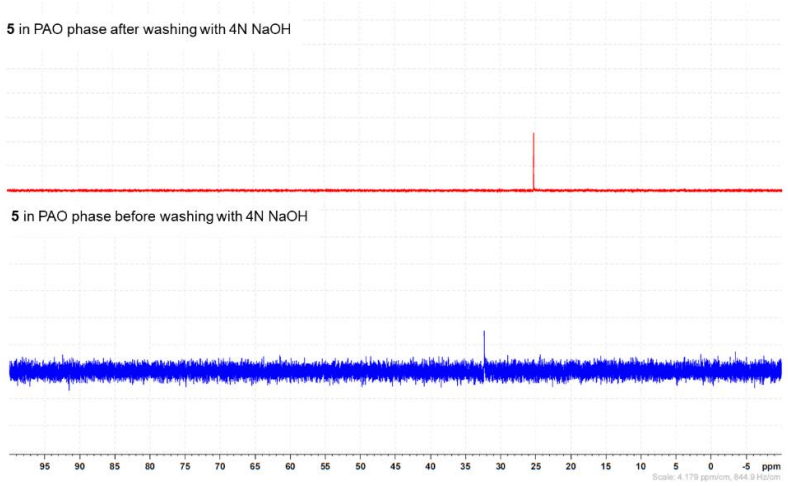


Figure 2.7. ^{31}P NMR spectrum of the PAO_{432} phase in presence of allyl trichlorosilane (bottom) and a ^{31}P NMR spectrum showing regeneration of **5** after washing the PAO_{432} phase with 4 N NaOH (top). Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

The performance and recyclability of the allylation of benzaldehyde catalyzed by HMPA or **5** in alkane solvents (heptane or PAO_{432}) is shown in Table 2.1. In an initial experiment, we first examined HMPA-saturated PAO_{432} as a reaction medium. Separate experiments showed that PAO_{432} saturated with HMPA had ca. 0.02 M HMPA. Thus, HMPA could in principle itself function as a catalyst in PAO_{432}. In the event, allylation of benzaldehyde by allyl trichlorosilane did occur with a 51% conversion of benzaldehyde over 24 h at room temperature. However, on recycling, the conversion dropped to <0.1%. In contrast, **5** either in heptane or PAO_{432} was a recyclable catalyst for the allylation chemistry. The difference between using **5** in heptane versus in PAO_{432} was that recycling in heptane was simply less successful. While **5** in heptane afforded a higher conversion (96%) of benzaldehyde in heptane in the first cycle, the conversion decreased in cycles 2-5. This presumably reflects the ca. 5% catalyst loss of **5** due to leaching of **5** into the

heptane-saturated acetonitrile phase. In contrast, using **5** in PAO_{432} led to a consistently high conversion for five cycles. These synthetic studies used a 6.5 mol% loading of **5** versus the 10 mol% loading of **5** which was used in the kinetic study (Figure 2). This lower catalyst loading leads to only ca. 80% conversion with **5** in PAO_{432} over 24 h. However, this level of conversion was constant through 5 cycles, showing the recyclability of **5** is very high and that the activity of **5** in cycles one and five. If a significant amount of **5** had leached from PAO into the acetonitrile phase or if **5** were not recyclable, this conversion would have dropped. We also noted that there was no visible change in volume of the PAO_{432} phase suggesting complete recycling of the solvent, something we noted in other work.[122]

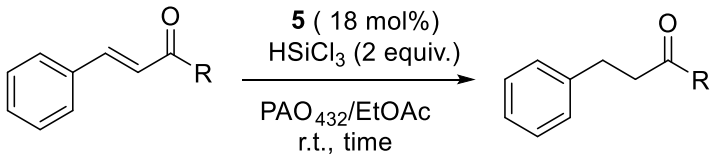
Table 2.1. Recyclability of **5** in the allylation of benzaldehyde by allyl trichlorosilane in heptane or PAO_{432}. The conversions were calculated by taking and analyzing the MeCN layer from a biphasic separation (MeCN/PAO_{432} or MeCN/heptane). Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

Entry	Catalysts	Cycle	Solvent	Catalyst Loading (mol%)	Conversion (%)
1	HMPA	1	PAO_{432}	4	51
2	HMPA	2	PAO_{432}	-	<0.1
3	PIB-HMPA **5**	1	heptane	6.5	96
4	PIB-HMPA **5**	2	heptane	-	95
5	PIB-HMPA **5**	3	heptane	-	87
6	PIB-HMPA **5**	4	heptane	-	81
7	PIB-HMPA **5**	5	heptane	-	74
8	PIB-HMPA **5**	1	PAO_{432}	6.5	83
9	PIB-HMPA **5**	2	PAO_{432}	-	77
10	PIB-HMPA **5**	3	PAO_{432}	-	74
11	PIB-HMPA **5**	4	PAO_{432}	-	80
12	PIB-HMPA **5**	5	PAO_{432}	-	84

To verify the synthetic utility of this chemistry, we carried out allylations of several other aromatic aldehydes in addition to benzaldehyde. Since Figure 2 had shown that 10 mol% catalyst afforded higher conversions, all of these synthetic reactions were carried out with this catalyst loading. In each case, the acetonitrile phases from five reaction cycles using **5** in PAO_{432} cycles was isolated and combined and the allylation products were isolated and characterized by IR, ^{1}H and ^{13}C NMR spectroscopy. As shown in Table

2.2, PIB-HMPA **5** is an efficient catalyst for the allylation of all of these aromatic aldehydes. The allylic alcohol products were obtained in a steady and moderately high conversion. In the product layers from each cycle, there is no observable signal for **5** in a ^{31}P NMR spectrum, suggesting no catalyst leaching to the product layer occurred with these different aromatic aldehydes. Additionally, ^{1}H NMR spectroscopy showed negligible PAO_{432} was present in the product layer (MeCN phase) in agreement with our prior work.[95] Average isolated yields of products for each of these reactions were consistent with the observed conversions measured by ^{1}H NMR spectroscopy.

As noted in the introduction, HMPA and its polymer bound analogs catalyze a variety of reactions. To confirm that the catalyst **5** has similar versatility, we also studied using **5** as a recyclable catalyst in a conjugate reduction in PAO_{432} (Scheme 2.3) since a similar reduction catalyzed by HMPA in CH_2Cl_2 has been reported.[135]



Scheme 2.3. Reduction of an α,β-unsaturated carbonyl compound (1 equiv.) with trichlorosilane (2 equiv.) in PAO_{432}/EtOAc using 18 mol% **5** as a catalyst. Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

α,β-Unsaturated carbonyl compounds including benzylideneacetone, (*E*)-1,3-diphenyl-2-propen-1-one (chalcone), dibenzylideneacetone, β-ionone, (*E*)-2-benzylidenecyclopentan-1-one and methyl cinnamate where examined as substrates.

Amongst these substrates, β-ionone and methyl cinnamate were soluble in PAO_{432}. The other substrates had poor solubility in PAO_{432}. We addressed this by adding 1.8-3.4 M ethyl acetate (EtOAc) as a cosolvent. EtOAc was chosen for three reasons. First, EtOAc has good miscibility with PAO_{432}, it is considered a green solvent, and its volatility means it can be removed from the product solution and potentially recycled.[4] In the presence of catalyst **5** and trichlorosilane as a reducing agent, benzylideneacetone, chalcone, dibenzylideneacetone and β-ionone all underwent 1,4-reduction to form a saturated ketone in high conversion (Table 2.3). In each case, the polar MeCN product-containing phase was analyzed by ^{1}H and ^{31}P NMR spectroscopy. Similar to the results of the allylation, there was no significant leaching of catalyst or the PAO solvent leaching to the polar product phase. However, in the cases using (*E*)-2-benzylidenecyclopentan-1-one and methyl cinnamate as substrates, the reduction reactions proceed in low conversion. The poor conversion of (*E*)-2-benzylidenecyclopentan-1-one could be attributed to the unfavored six-membered cyclic transition state between trichlorosilane and the *s-cis* conformation of (*E*)-2-benzylidenecyclopentan-1-one.[135] In any case, a similar low conversion (<1%) of (*E*)-2-benzylidenecyclopentan-1-one in an HMPA-catalyzed reduction in CH_2Cl_2 was also seen. As for the reduction of methyl cinnamate, the reduction using HMPA as the catalyst to reduce the unsaturated ester in CH_2Cl_2 in presence of $HSiCl_3$ also showed a negligible conversion (<1%) to the desired reduced product. These failures suggested that both failures were due to the inapplicability of these α,β-unsaturated carbonyl compounds in this type of reduction rather than a limitation of **5** or a nonpolar milieu like PAO_{432}.

Table 2.2. Scope of allylation reactions of aromatic aldehydes with different substituents catalyzed by PIB-supported catalyst **5** (10 mol%) in PAO_{432}. The conversions were calculated by taking and analyzing the MeCN layer from a biphasic separation (MeCN/PAO_{432}). The average product yields were calculated after combining the MeCN layers from cycle 1 to 5 and purifying via a column chromatography. Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

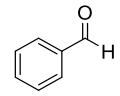
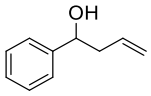
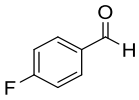
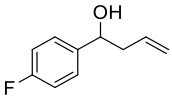
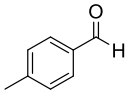
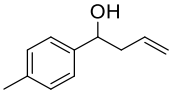
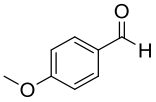
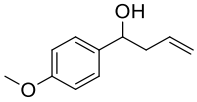
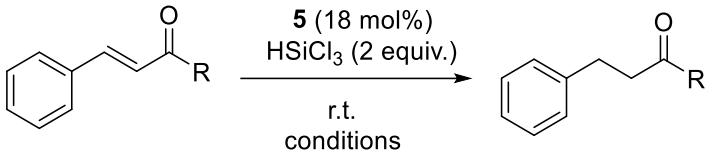
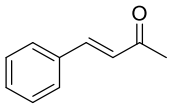
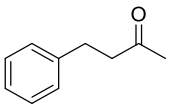
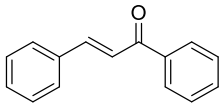
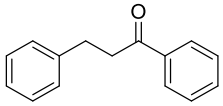
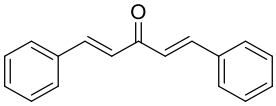
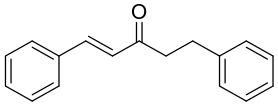
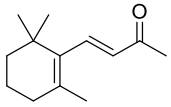
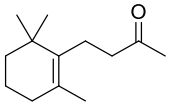
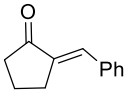
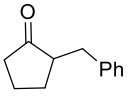
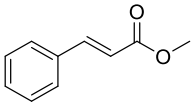
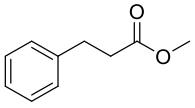
Substrate	Product	Conversion (%)					Avg. yield %
		Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	
		92	87	84	93	89	83
		81	78	74	90	85	75
		82	73	73	86	78	70
		74	72	87	71	78	67

Table 2.3. Scope of Lewis base-catalyzed conjugate reduction of various α,β-unsaturated carbonyl compounds. Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.



Substrate	Condition	Product	Conversion (%)	Yield (%)[a]
	PAO_{432}, EtOAc (1.8 M), 2 h		94	83[b]
	PAO_{432}, EtOAc (1.8 M), 2 h		>99	>99
	PAO_{432}, EtOAc (3.4 M), 4 h		84	80
	PAO_{432}, 4 h		>99	98
	PAO_{432}, EtOAc (1.8 M), 12 h		16	-
	PAO_{432}, 12 h		<0.1	-

To further establish the synthetic utility of these transformations and to examine recyclability of **5** and the PAO solvent in these reductions, we examined reduction of benzylideneacetone in more detail. In these reactions we first removed the EtOAc at reduced pressure using a rotary evaporator. The product was then separated from the PAO_{432} phase by adding MeCN using the same work-up procedure used above in the allylation chemistry. Then fresh substrates and EtOAc were added to the PAO_{432} phase with **5** that was separated from the acetonitrile product phase. As shown in Figure 2.8, **5** could be recycled with consistently high conversions for 6 cycles. As was true for the allylation chemistry, the recyclability of catalyst **5** and the solvent system makes this a greener process than the prior work that used HMPA and dichloromethane. We also showed that this product afforded good isolated yields by combining the product phases from all six cycles and isolating the product. The isolated yield was averaged 83%/cycle.

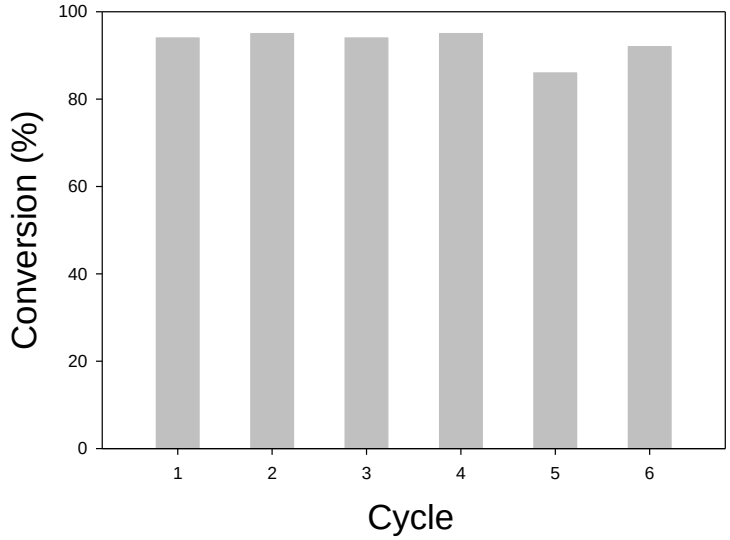


Figure 2.8. Recyclability data of **5** in catalytic reduction of benzylideneacetone with $HSiCl_3$ in PAO_{432} containing 1.8M of EtOAc as a cosolvent. Reprinted with permission from *ChemCatChem* **2020**, just accepted. Copyright 2020 by John Wiley & Sons, Inc.

2.3 Conclusion

This work describes a PIB supported HMPA analog as a safer and recoverable version of a highly toxic HMPA low molecular weight catalyst. The phosphoramide terminated PIB oligomer **5** served as a catalyst in allylation reactions using a variety of aromatic aldehyde substrates. Kinetic studies showed that catalyst **5** was at least as reactive if not more reactive as HMPA in CH_2Cl_2 in benzaldehyde allylation and that the reactive of 5 in heptane or a recyclable PAO solvent was comparable to the reactivity of HMPA in CH_2Cl_2. Catalyst **5** was also a competent alternative to HMPA as a recyclable catalyst for the conjugate reduction of various enones by $HSiCl_3$. In all of these reactions, catalyst **5** along with the PAO reaction solvent was successfully recovered by a simple liquid/liquid (PAO_{432}/MeCN) extraction for at least 5 cycles with no significant loss in activity.

CHAPTER III

REVERSIBLE SOLUBILIZATION OF POLAR POLYMERS AND POLYMERIC-CATALYSTS IN NONPOLAR SOLVENTS*

3.1 Introduction

Polymer solubility is an important property of polymers. Solubility can be important in processing or characterizing a polymer. It can also be important in a polymers' eventual applications. To dissolve a polymer, it is necessary to pair a solvent with a polymer and to find conditions that effect and/or affect polymer solubility. In many cases, solvents that dissolve a particular polymer can be chosen from handbooks and or by using solubility parameters.[158] Such data enable pairing the nature of a polymer's repeating units and their relative hydrophobicity or hydrophilicity with the properties of a given solvent. In these cases, a mixture of enthalpically favorable strong and weak interactions of solvents with a polymer's repeating units leads to solubility. Miscibility in solvent mixtures is also important and also relies on intermolecular interactions. Deep eutectic solvents would be an example where H-bonding stabilizes the solvent mixture.[159]

Polymer stimuli-responsive and phase-selective solubility are also of interest. Indeed, stimuli responsive changes in polymers' solubility properties has become an increasingly important area of study in polymer chemistry. Studies of this type of solubility behavior have shown that polymers can exhibit stimuli responsive properties

*Reprinted with permission from "110th Anniversary: Reversible Solubilization of Polar Polymers and Polymeric Catalysts in Nonpolar Solvents" by Fu, Y.-H.; Perales, C.; Eliason, T.; Bergbreiter, D. E. *Ind. Eng. Chem. Res.* **2019**, *58*, 14579. Copyright 2019 by ACS.

that vary depending on the polymer microstructure, the solvent, solutes, and a chemical or physical stimulus.

A common example of a polymer with stimuli responsive solubility is poly(*N*-isopropylacrylamide) (PNIPAM). PNIPAM is a thermoresponsive polymer whose water solubility and a modest lower critical solution temperature (LCST) derives from a favorable ΔH due to hydrogen bonding with water and an unfavorable ΔS due to the organization of these water solvent molecules with the many repeating units of the PNIPAM polymer.[160] Water soluble polymers with LCSTs like PNIPAM, poly(2-oxazoline)s, proteins, and polypeptoids have LCSTs that depend not only on temperature but also on the nature of cosolute anions and cations.[161–164] That type of responsive behavior has led to applications of these and other polymeric materials in drug delivery,[165] in separations,[166] in catalysis and synthesis,[167] in the design of responsive surfaces,[168] and in the synthesis of stimuli responsive membranes.[169]

Light or chemical stimuli that change the character of the repeating units in a polymer are other examples of stimuli that can reversibly change a polymer's solubility. For example, photoactivated ring closure reactions that can be reversible can be used to make polymers dissolve or precipitate.[170] Similar chemistry has been reported for polymers that contain azo groups that isomerize from trans to more polar cis forms with light and then reversibly convert back to the less polar and differentially soluble trans azo groups.[171] Acid/base chemistry is an example of another covalent modification that changes solubility. In this case, addition of an acid or base can reversibly convert a polymer's basic or acidic repeating units into conjugate acid or base salts – chemistry that

can be used to alter the solubility of poly(acrylic acid)s or polymeric bases. This sort of chemistry has many applications – for example, it is the basis for many photoresists.[172]

While there are many applications of stimuli responsive polymers that use a polymer's solubility to advantage, the focus of much of our prior work and of others' work on responsively-soluble and phase-selectively polymers has been on the applications of such systems in homogeneous catalysis. We were among the early groups to show that polymers with LCSTs coupled to homogeneous catalysts could turn these catalysts' activity off in response to an exotherm and then turn these catalysts' activity back on since after the reaction stopped the reaction mixture cooled.[173,174] We and others have also coupled the stimuli-responsive solubility of polymers and the temperature dependent miscibility of solvent mixtures to develop so-called thermoregulated catalysts or thermomorphic catalysts.[110,175–177]

Polymer phase-selective solubility is useful too as a way to control catalyst separation after a homogeneous reaction. This has involved using hydrophilic polymers like poly(ethylene glycol) with a terminally bound catalyst or a hydrophilic polymer like poly(acrylic acid) with pendant functionality to separate catalysts in a polar organic or aqueous phase from a nonpolar or less polar organic product-containing phase.[178,179] More often, we have used hydrophobic polymers like terminally modified polyisobutylene or poly(4-alkylstyrene)s with pendant catalyst groups to separate catalysts in an alkane or poly(α-olefin) (PAO phase from a polar organic phase after a monophasic reaction. In all of these cases we designed the polymer to be phase selectively soluble in one phase of a biphasic mixture.[124,180] For example, using poly(*N*-alkyl acrylamide)s as catalysts

supports, we used these polar polymers and thermomorphic solvent mixtures to effect homogeneous catalysis in a heated miscible solvent mixture and to then separate alkane-soluble products from DMF or aqueous ethanol solutions of a PNIPAM bound catalysts on cooling after the reaction was over.[110] We subsequently showed that poly(*N*-alkyl acrylamide)s with octadecyl groups could separate catalysts as heptane solutions from polar organic phases.[181] Similar chemistry used fluorous acrylates, recovering catalysts or metals in fluorous phases.[182] We also explored the effect of alkyl chain length on the phase selective solubility of poly(*N*-alkylacrylamide)s using a combinatorial synthesis of various poly(*N*-alkylacrylamide)s from polyacrylates that containing an *N*-hydrosuccinimide active ester.[183] All these approaches used covalent modification of a polymer to change the character of the repeating unit to control solubility and all involved a liquid/liquid separation.

Separations that employ a biphasic liquid/liquid separation of a soluble polymer-bound catalyst phase and a product phase require two solvents. Often, these are volatile organic solvents–solvents that have issues of flammability and recyclability. Even when the solvents are chosen to be "sustainable", they are typically not recycled but are discarded as waste since they either contaminate water waste streams or are not economically recyclable by distillation.

The alternative to a biphasic liquid/liquid separation is to use a catalyst that separates as a solid. In that case, a physical separation via a filtration or centrifugation is a practical method for catalyst product separation. We used that approach with polyethylene oligomer bound catalysts—chemistry that others have described as

commercially viable technology.[92,120,184] In the case of polyethylene, heat and a suitable solvent like xylene served to dissolve polyethylene-bond catalysts to generate a homogeneous solution of catalyst and substrate. After formation of products, cooling quantitatively precipitated the polyethylene oligomers and catalyst.

In the work described below, we show how simple hydrogen bonding using the pendant amide groups of PNIPAM and readily available carboxylic acids can be used to make polar polymers reversibly soluble in nonpolar solvents including alkanes, PAO, and toluene. In this chemistry, insoluble PNIPAM in hydrocarbon solvents form H-bond adducts when treated with carboxylic acids that dissolve in these nonpolar solvents. This solubilized polymer can then be precipitated on treatment with a base or on exposure to other H-bonding solvents. This solubilization/precipitation can be repeated through multiple cycles. This same process can also be used to make a PNIPAM-bound analogue of Wilkinson's catalyst that is unreactive as a suspension dissolve to form an active hydrogenation catalyst that can solubilized in toluene. By addition of a base or another H-bond acceptor, this PNIPAM-bound catalyst can be quantitatively precipitated, recovered as a solid from a solution of the product, and recycled through four reaction cycles. These results suggest a new approach to stimuli-responsive soluble polymers and related catalytic systems that could be expanded to include other molecular recognition chemistry and used to prepare other sorts of recyclable catalysts.

3.2 Results and discussion

As noted in the introduction, it is not necessary to covalently modify a polymer to control polymer solubility. In the case of polymers with LCSTs like PNIPAM,[160] poly(2-oxazoline)s,[162] peptides like elastin,[164] PEG derivatives,[185] and cellulose derivatives,[165] the enthalpically favorable hydrogen-bonding (H-bonding) of water makes polymers soluble at low temperature. However, this weak H-bonding is entropically unfavorable so at higher temperatures these polymers phase separate. Like a protonation or deprotonation reaction, these solubility changes are reversible though in this case the stimulus for reversible solubility is temperature. When this solubility behavior is coupled with support of a catalyst on these polymers, this sort of thermal stimulus has been used to design smart or recyclable catalysts.

Our prior interest in poly(*N*-alkylacrylamide) polymers, their LCST behavior, and their response to cosolutes and our success in solubilizing salts in hydrocarbons like heptane or poly(α-olefin)s using reversible ion exchange reactions[102] with lipophilic catalysts suggested to us that lipophilic H-bonding agents might have potential to solubilize polymers with H-bond acceptor groups. Our hypothesis was that just as H-bonding with water solubilizes the otherwise insoluble PNIPAM in water an alkane soluble H-bond donor like a carboxylic acid would be capable of H-bonding to PNIPAM's amide groups to make it soluble in nonpolar solvents like alkanes. Moreover, we thought that such solubilization could be reversible either thermally or chemically.

The scheme we proposed to make PNIPAM soluble in nonpolar solvents like alkanes and toluene is shown in Figure 3.1. In this scheme, PNIPAM in the absence of any cosolute is an insoluble solid because the hydrocarbon solvent cannot solvate the polar amide backbone of the polymer. However, as we know from prior work, if these amide repeating units were modified to contain a sufficiently lipophilic group, the modified polyamide would dissolve. That work showed that an azo dye labeled poly(*N*-alkylacrylamide) containing an *n*-octyl group was phase selectively soluble in the heptane phase of an equivolume mixture of heptane and 90% aqueous EtOH.[183]

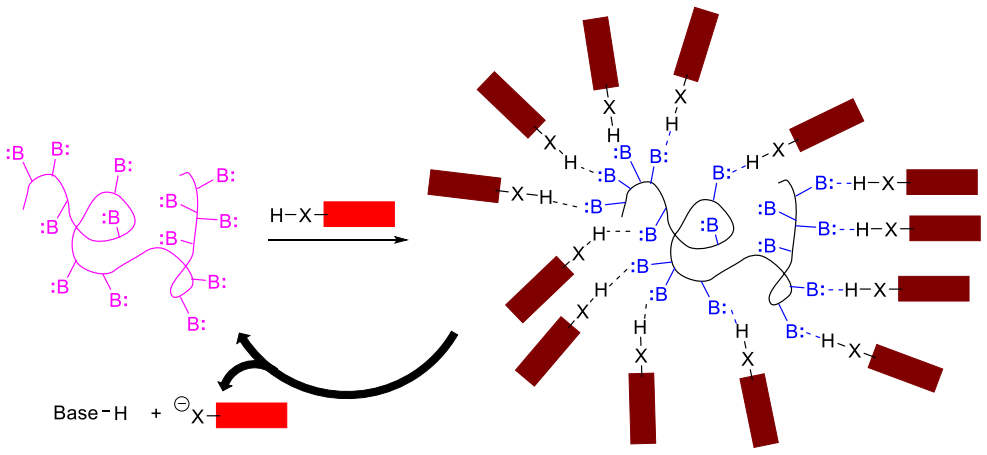
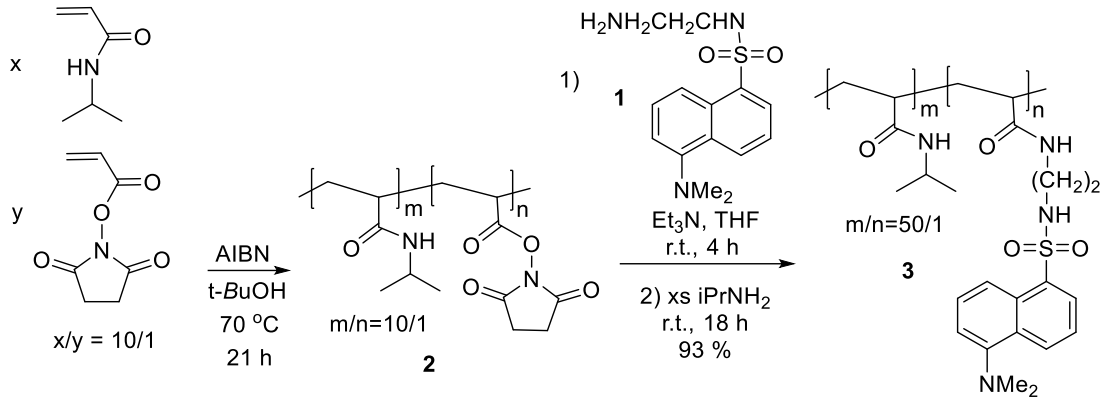


Figure 3.1. Schematic representation of a H-bonding approach to make PNIPAM reversibly soluble in hydrocarbon solvents. Reprinted with permission from *Ind. Eng. Chem. Res.* **2019**, *58*, 14579. Copyright 2019 by ACS.

In the chemistry described, we envisioned solubilizing PNIPAM using H-bonding carboxylic acid groups. Prior studies of carboxylic acids in heptane or PAO showed carboxylic acids exist as H-bonded dimers even at 0.01 M and that H-bonding agents like a polyisobutylene-bound catechol are strong H-bonding agents in these hydrocarbon solvents.[95,186] Thus, we thought that introducing aliphatic acids to a nonpolar solvent

could enable PNIPAM solubilization by coupling the aliphatic acid to PNIPAM's pendant groups. If a sufficient number of the carboxylic acids were to couple to the PNIPAM, we would *in situ* form a brush-like derivative of PNIPAM containing a hydrocarbon shell.

To test this hypothesis, we prepared a dye-labeled PNIPAM using an amine derivative of a dansyl fluorophore. In this chemistry, we first prepared a copolymer of PNIPAM and poly(*N*-acryloxysuccinimide) by conventional radical polymerization. A ten-fold excess of the *N*-isopropylacrylamide relative to the *N*-acryloxysuccinimide monomer was used to ensure that the product polymer contained a random mixture of active ester and *N*-isopropylamide pendent groups. Then 0.2 equivalents of the 2-dansylaminoethylamine **1** relative to the active ester groups was added to form a dansyl-labeled polymer. Any unreacted active ester groups were then converted into *N*-isopropylamide groups using excess isopropyl amide (Scheme 3.1). ^{1}H NMR spectroscopic analysis showed the resulting polymer had a 50/1 ratio of *N*-isopropy/*N*-2-dansylaminoethyl groups. The product polymer was as expected soluble in polar solvents and had a λ_{EX} of 498 nm in dichloromethane.



Scheme 3.1. Synthesis of PNIPAM-co-PNASI **2** and a dansyl-labeled PNIPAM 3 from the ethylene diamine derivative of dansyl (**1**). Reprinted with permission from *Ind. Eng. Chem. Res.* **2019**, *58,* 14579. Copyright 2019 by ACS.

To explore the potential for hydrocarbon solutions of carboxylic acids to solubilize PNIPAM in solvents it would otherwise be insoluble in, we examined the alkyl length of carboxylic acids and the nature of the host solvent polarity of poor solvents to PNIPAM. These studies involved shaking a suspension of PNIPAM in a solvent with a carboxylic acid. The amount of the solubilization cosolute was measured at the point where the solid PNIPAM visually dissolved.

First, we examined acetic acid and octanoic acid as cosolutes that could change the character of PNIPAM to make it soluble in solvents in which it is otherwise insoluble (Figure 3.2). Octanoic acid was chosen because poly(*N*-octylacrylamide) is phase selectively soluble in a heptane phase of an equivolume heptane/90% aqueous ethanol mixture that is miscible hot and biphasic at room temperature. The solvents chosen were hexane, toluene, benzene, diethyl ether, methyl *tert*-butyl ether and dibutyl ether. As shown below, either acetic acid and octanoic acid as cosolutes can make PNIPAM soluble

in any of these solvents. For most solvents other than hexane, acetic acid and octanoic acid were roughly comparable solubilizing agents though octanoic acid was typically more effective. Benzene and toluene required the least cosolute. More cosolute was required for diethyl ether or tert-butyl methyl ether, possible because these solvents compete as H-bond donors. Hexane and dibutyl ether required the most additional solubilizing cosolute. Separate experiments with a C_{30} PAO showed it behaved like hexane though using PNIPAM with it required five equivalents of octanoic acid per equivalent of the acrylamide repeating unit of PNIPAM.

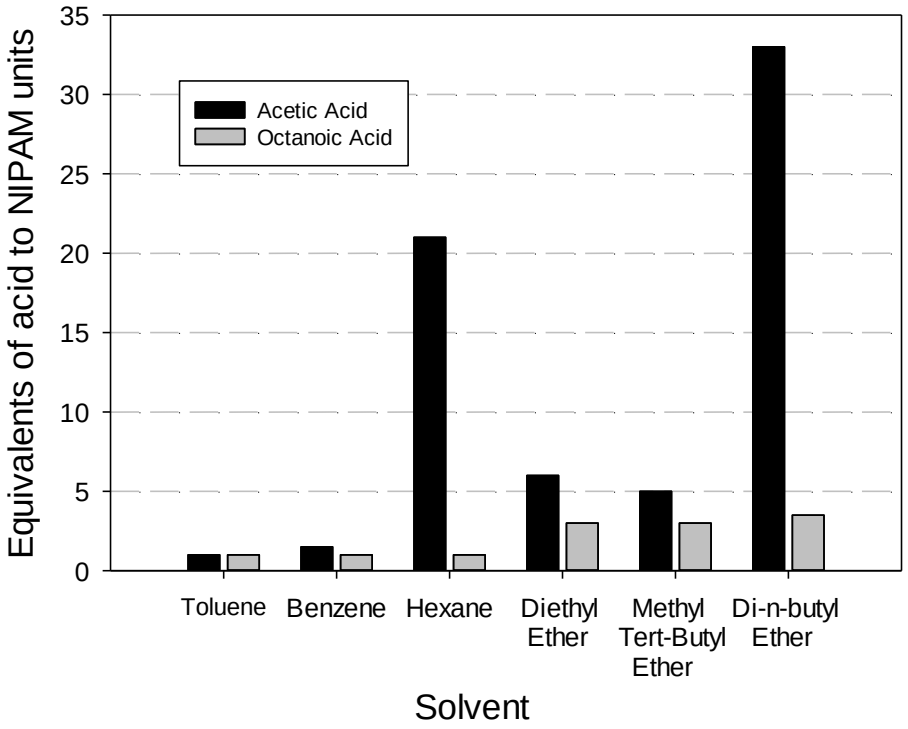


Figure 3.2. Visual solubilization of PNIPAM with varying ratios of acetic or octanoic acid relative to the repeating NIPAM monomer units of PNIPAM. Reprinted with permission from *Ind. Eng. Chem. Res.* **2019**, *58*, 14579. Copyright 2019 by ACS.

In a second set of experiments, we carried out a similar solubilization test in hexane varying the nature of the carboxylic acid groups. Carboxylic acids with different alkyl chain lengths (acetic, pentanoic, octanoic and oleic acids) that dissolve in hexane were used. The results show that pentanoic, octanoic, and oleic acid all were roughly similar as solubilizing cosolutes though octanoic acid was slightly more effective requiring less equivalents of acid on a mole: mole basis (Figure 3.3).

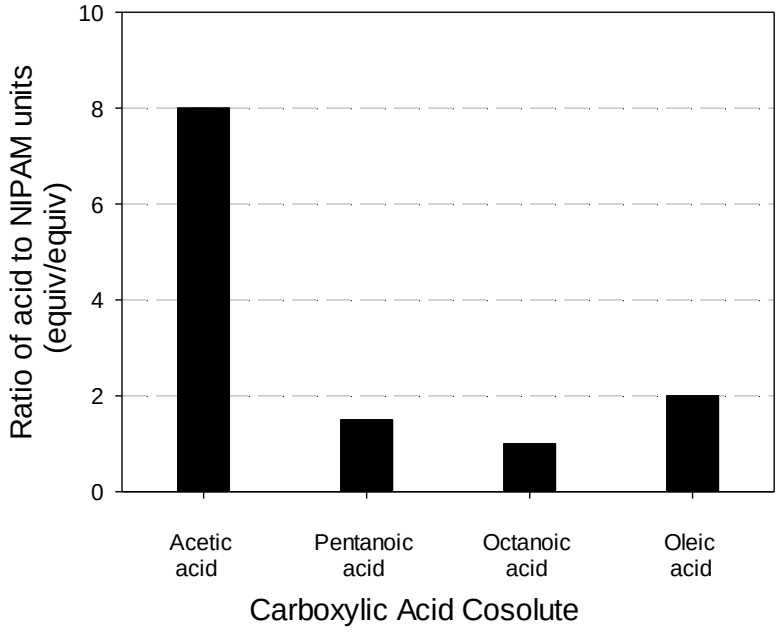


Figure 3.3. The effect of varying the size of the aliphatic chains of carboxylic acids on solubilization of PNIPAM in hexane based on a visual examination of solubility of PNIPAM as the ratio of the equivalents of the carboxylic acid/NIPAM monomer units was varied. Reprinted with permission from *Ind. Eng. Chem. Res.* **2019**, *58*, 14579. Copyright 2019 by ACS.

We next studied the reversibility of the solubilization process in Figure 3.1. We had made an analogy between water molecules having a favorable enthalpically solubilizing effect for PNIPAM in water and octanoic acids making PNIPAM soluble in hexane. However, while heating and the unfavorable entropy in the PNIPAM/water leads

to PNIPAM precipitation on mild heating, PNIPAM solutions in hexane solubilized by octanoic acid did not precipitate on heating. Presumably this is because the entropy term in the octanoic acid case is not as unfavorable as it is for PNIPAM in water.

However, since carboxylic acid were being used as the H-bond donors in solubilizing PNIPAM in hexane and since these H-bond donors are acidic, we reasoned that adding a base would break the hydrogen bonds between the PNIPAM and the solubilizing agent. Two solvents were examined – hexane and toluene. Triethylamine (Et_3N), was chosen here because it's soluble in both of these solvents. While triethylammonium octanoate, the conjugate acid formed, is also soluble in hexane and toluene and while it too could be an H-bonding solubilization cosolute, we reasoned that it would be a poorer solubilization cosolute because it is much less acidic that octanoic acid. Moreover, if the PNIPAM precipitated as expected, its solubility would allow us to study recycling experiments.

These studies of the repeated solubilization precipitation used the fluorescently labeled PNIPAM **3** prepared in Scheme 3.1. In these experiments, a suspension of **3** in hexane or toluene was prepared. This suspension was stirred for 30 min and any solids were allowed to settle. The supernatant was then examined by fluorescence spectroscopy. Control experiments in both hexane and toluene showed that the solubility of **3** in hexane or toluene (Figure 3.4a and 3.4b) was negligible. Then these suspensions of **3** in hexane or toluene were allowed to react with 1.5 equivalents of octanoic acid relative to the repeating unit of **3**. After 30 min stirring, the apparent solution was again assayed by

fluorescence spectroscopy. We observed an intense fluorescence with a λ_{EM} at 498 nm that is consistent with the dansyl group of **3** being in solution. These fluorescent results were consistent with the visual observation that no significant amount of solid polymer remained after the solubilization process.[a)] Then these solutions were treated with 1 equivalent of Et_3N relative to the octanoic acid.[b)] Again, the reaction mixtures were stirred for 30 min. We visually observed an almost immediate formation of solids. After allowing these suspensions to settle, we analyzed the supernatant hexane or toluene (Figures 4a and 4b). In most cases, >98% of the fluorescence disappeared. As shown in Figure 4, this cycle of dissolution/precipitation was repeated five times.

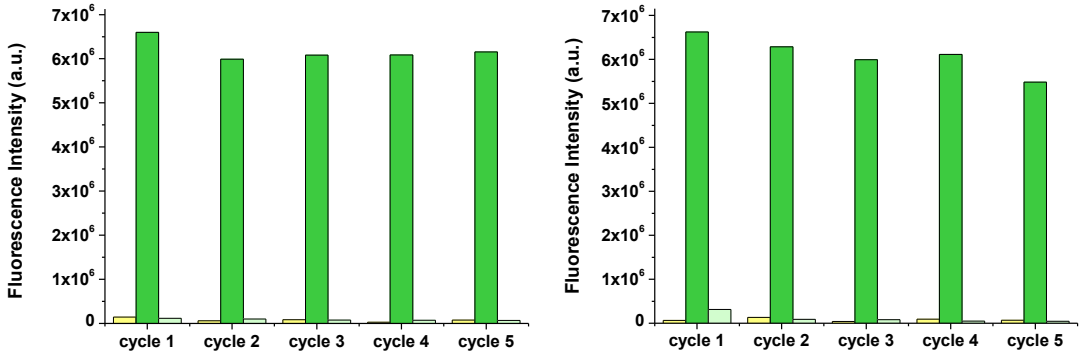
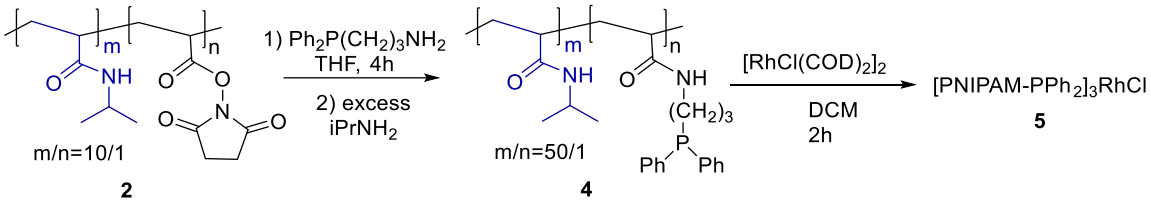


Figure 3.4. a) Fluorescence data for PNIPAM **3** in hexane before addition of octanoic acid (yellow bar), after addition of octanoic acid (green bar), and after precipitation of PNIPAM **3** with Et_3N (light green bar) through five cycles. b) Fluorescence data for a similar experiment in toluene for five cycles. Reprinted with permission from *Ind. Eng. Chem. Res.* **2019**, *58*, 14579. Copyright 2019 by ACS.

Gravimetric measurements were also carried out. Analysis of the combined supernatant from five cycles of solubilization/precipitation in toluene showed that only 2% polymer **3** was not recovered after the Et_3N treatment.

We also briefly examined an alternative method of precipitating **3** using DMF as an additive in toluene. The idea in this case was that DMF would compete with the amide groups of PNIPAM for the octanoic acid. These experiments paralleled the experiments shown in Figure 4b and used 5.8 equivalents of DMF relative to the equivalent acrylamide units of PNIPAM **3**. As was the case in Figure 4b, these experiments that used DMF as a precipitation agent were repeated for three cycles in toluene and are graphically shown in the supporting information (Figure S2).



Scheme 3.2. Synthesis of a PNIPAM-bound phosphine ligand (**4**) and an analog of Wilkinson's catalyst (**5**). Reprinted with permission from *Ind. Eng. Chem. Res.* **2019**, *58*, 14579. Copyright 2019 by ACS.

Finally, since we were able to dissolve, quantitatively precipitate, and redissolve PNIPAM **3** in hexane and toluene, we examined the potential of this solubilization/precipitation process for recycling a homogeneous catalyst. Rh(I)-catalyzed hydrogenation was chosen as a proof-of-concept for this chemical-responsive catalytic system. Using the chemistry in Scheme 3.2, we prepared the PNIPAM-bound rhodium catalyst **5**. We then examined this catalyst for hydrogenation of 1-decene. The polymer-bound catalyst **5** is insoluble and relatively inactive in the absence of octanoic acid. While we did see ca. 29% conversion of 1-decene to decane, we believe this was due to unreacted [RhCl(cod)$_2$] used in the synthesis of **5**. In any case, **5** could be solubilized by addition of

1 equivalent of octanoic acid relative to the repeating acrylamide units of **5**. As a soluble catalyst, it hydrogenated observed to dissolve on addition of octanoic acid and the resulting solutions were active catalysts for decene hydrogenation. In a comparison to Wilkinson's catalyst, **5** had roughly equivalent reactivity (Figure 3.5). In previous work, we had prepared other soluble polymer-bound analogues of Wilkinson's catalysts. Those studies too showed that soluble polymer-bound Rh(I) catalysts were kinetically comparable to a conventional Wilkinson's catalyst.[68,187] Moreover, the catalyst 5 like the fluorescently labelled PNIPAM **3** could be precipitated by addition of Et_3N, separated as a solid, redissolved with octanoic acid and recycled. To evaluate this catalyst recycling, we carried out kinetic studies whose results are shown in Table 3.1. These studies showed that decene hydrogenation using catalyst **5** solubilized in toluene with octanoic acid occurred with high yields over 6 h and that the initial rates of hydrogenation were largely invariant over 4 reaction cycles. We did note that the yield of the hydrogenation did drop in later cycles. In some preliminary experiments we noted that the catalyst **5** was susceptible to decomposition to phosphine oxidation and we speculate that the drop in yield in the last two cycles may reflect that inadvertent oxidation. We also measured the Rh content in the supernatant after precipitation of catalyst 5 in cycle 3. That Rh content was 14 ppm (2% of the measured 668 ppm Rh content in the first cycle).

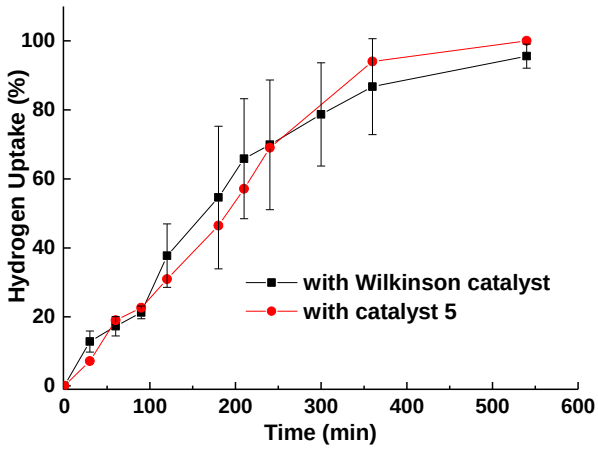


Figure 3.5. A comparative plot for a Rh(I)-catalyzed hydrogenation of 1-decene in toluene for Wilkinson's catalyst (black dots) and the octanoic acid solubilized catalyst 5 (red dots) at 25 °C. Reprinted with permission from *Ind. Eng. Chem. Res.* **2019**, *58*, 14579. Copyright 2019 by ACS.

Table 3.1. Reaction rates and product yields of hydrogenation of 1-decene using Wilkinson catalyst or catalyst **5** that was solubilized in octanoic acid in toluene at 25 °C. Reprinted with permission from *Ind. Eng. Chem. Res.* **2019**, *58*, 14579. Copyright 2019 by ACS.

Entry	Catalyst	Octanoic acid added	Reaction rate[a] (mL of H_2/min)	Yield[b] (%)
1	$RhCl(PPh_3)_3$	no	2.3×10^{-2}	100
2 (1^{st}cycle)	catalyst **5**	yes	2.2×10^{-2}	100
3 (2^{nd}cycle)	catalyst **5**	yes	4.6×10^{-2}	100
4 (3^{rd}cycle)	catalyst **5**	yes	3.5×10^{-2}	87
5 (4^{th}cycle)	catalyst **5**	yes	3.2×10^{-2}	82

[a]The reaction rate was measured in the first 180 min with a H_2-filled gas buret using a 0.002 M solution of the Rh catalyst in toluene at 25 °C. [b] Yields were determined by gas chromatography using cyclooctane as an internal standard.

3.3 Conclusion

This work shows that carboxylic acids as hydrogen bonding agents can facilitate solubilization of PNIPAM in solvents in which this polar polymer is otherwise insoluble. This includes nonpolar solvents like hexane, a C_{30} poly(α-olefin), toluene and benzene. In hexane, the more lipophilic octanoic acid was a much more effective solubilizing agent. Using a fluorescently labeled PNIPAM polymer, we also showed that this H-bonding solubilization was reversible. Five cycles of solubilization/precipitation were carried out in both hexane and toluene. Finally, we have shown that this reversible solubilization of a polar polymer can be used in catalysis. Using a PNIPAM-bound Rh(I) analog of Wilkinson's catalyst, we showed that we could affect hydrogenations in toluene homogeneously and then recover and reuse the catalyst through four cycles with little or no loss in catalyst activity. These results suggest a new approach stimuli-responsive soluble polymers and related catalytic systems that could be expanded to include other molecular recognition chemistry and used to prepare other sorts of recyclable catalysts.

CHAPTER IV

BLOCK COPOLYMERS DERIVED FROM POLYISOBUTYLENE OLIGOMERS*

4.1 Introduction

Polyisobutylene (PIB) and polypropylene alkene-terminated polyolefin oligomers are commercially available, nontoxic and inexpensive polymers that are highly soluble in alkanes and moderately polar solvents like dichloromethane and tetrahydrofuran. These materials are avail-able with terminal alkene groups that are easily converted into functional groups such as hydroxyl, thiol, azide, ester, amide and aryl groups – chemistry we and others have used in a variety of applications in catalysis and green chemistry.[124] These materials' phase selective solubility in alkane solvents like heptane and poly(α-olefin)s (PAOs) makes these oligomer hydrocarbon derivatives excellent phase anchors for immobilization of ligands and catalysts.[100,188–191] Such functional polyisobutylene derivatives also are useful in that they make otherwise insoluble materials like phthallocyanines,[117] inorganic clusters,[118] and nanoparticles soluble in hydrocarbon solvents and in polyolefins.[95,192] Here we explore chemistry to modify the properties of PIB exploring possible routes to block copolymers using the terminal alkene groups of the commercially available PIB oligomers as handles to couple polar monomers to these preexisting PIB oligomers. Our goal was to introduce polyvalent functionality onto these PIB oligomers while maintaining the alkane phase selective solubility of the PIB group by

* Reprinted with permission from "Block copolymers derived from polyisobutylene oligomers" by Fu, Y.-H.; Bergreiter, D.E. *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

controlling the degree of polymerization of the polar block such that it was less than that of the polyisobutylene block.

A variety of prior studies have examined radical grafting onto polyisobutylene or other polyolefins.[193–199] These studies have shown that click chemistry followed by other reactions is one route to diblock PIB derivatives. Other chemistry including quasiliving radical polymerization to prepare polyolefin block copolymers are also known. However, the synthesis of PIB block copolymers whose polar block has a degree of polymerization that is less than that of the polyisobutylene block that are alkane soluble has not been described. Based on other work, we believe such materials could be used as cosolvents with alkane oligomers,[95] as fully miscible polyolefin additives,[200] or as polyvalent ligands to solubilize nanoparticles.[118]

In this work, we examined three different synthetic routes to block copolymers from PIB oligomers with terminal alkene groups (Scheme 1): hydroboration/oxygen initiation; atom transfer radical polymerization (ATRP); and reversible addition/fragmentation chain transfer polymerization (RAFT). These studies examined block copolymers using the same precursor PIB, PIB_{1000}, an alkene-terminated PIB with a molecular weight of 1000 Da.[112] This PIB derivative is commercially available but contains a mixture of di- and trisubstituted alkenes as a terminal functional group. PIB oligomers with better defined end group chemistry can be prepared.[193] However, the alkene functionality on commercially available PIB oligomers has been adequate in our past work[100,188–191] in designing alkane phase anchored species and the use of

commercially available PIB facilitates use of this chemistry by others without expertise in cationic polymerization.

The first procedure (Scheme 4.1) we studied was based on earlier studies by our group that had used the residual unsaturation in polyethylene (PE) films as a grafting site to graft poly(methyl methacrylate) (PMMA) onto polyethylene films through hydroboration and O_2-induced radical polymerization.[201] We had hoped that this chemistry that uses an experimentally simple hydroboration and an inexpensive commercially available alkene-terminated PIB followed by oxygen-induced radical formation could be a simple route to PIB block copolymers. This route relies on chemistry wherein alkylboranes and oxygen serve as a precursor for radicals, chemistry that was used for polymerizations in the 1950s and later used later by many groups in organic synthesis.[202–204] Hydroboration followed by radical generation has also been extensively investigated by Chung's group who have shown that this chemistry is broadly applicable in polyolefin modification. Chung's group has shown that this chemistry generates alkyl or alkoxyl radical species that readily polymerize vinyl monomers.[205–208] In the work described here, we hoped to similarly use alkylborane groups produced from the terminal alkene group of PIB by hydroboration with BH_3-SMe_2 to form tris(polyisobutyl)borane. This tris(polyisobutyl)borane was then expected to react with oxygen to generate polyisobutyl radicals which could in turn initiate radical chain reactions in presence of vinyl monomers (e.g., acrylates, methacrylates, and acrylamides).

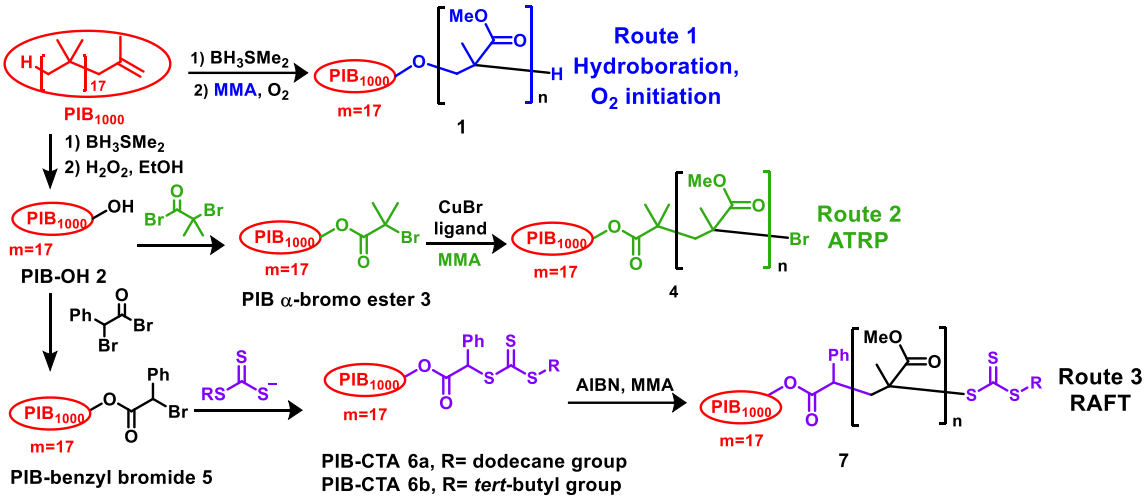
A second route shown in Scheme 4.1 that uses a PIB-bound 2-bromoisobutyrate ester **3** as an ATRP initiator was also explored. Low molecular weight initiators in the

form of bromides activated by an ester,[209] phenyl,[210] amide,[211] or cyano groups,[212,213] are known in ATRP chemistry. PIB-bound macroinitiators derived from quasiliving carbocationic polymerization (QLCP) of isobutylene that afforded benzyl halide or α-bromoester end groups had previously been used in ATRP chemistry with both styrene and acrylate esters.[214,215] We prepared similar PIB macroinitiators by esterification of hydroxyl groups derived from hydroboration of commercially available alkene terminated PIB (Scheme 4.1).

The third route to PIB copolymers we investigated used RAFT polymerization. Prior work has also shown that RAFT initiators bound to the terminus of PIB can effect RAFT polymerization.[199] Our work used a similar RAFT agent that contained a thiocarbonate group on the polyisobutylene chain end that served as a chain transfer agent to prepare PIB block polymers. The necessary PIB-bound RAFT agent PIB-CTA **6a** or **6b** could be prepared from PIB_{1000} by the multistep synthesis shown in Scheme 4.1.

The results of our studies show that each of these three routes can be used to effect block copolymerization using PIB macroinitiators with polar monomers. The first route was synthetically very inefficient. However, while the ATRP and RAFT chemistry was more efficient at formation of a PIB block copolymer, unless a relatively hydrophobic monomer were used, the chemistry in routes 1, 2, and 3 generally formed alkane insoluble block copolymers instead of the desired alkane soluble block copolymers. Only RAFT chemistry was used successfully with a variety of polar monomers to prepare alkane soluble block copolymers. In these cases, PIB macroinitiators coupled with a relatively

high amount of 2,2′-azobis(2-methylpropionitrile) allowed us to control the size of the block such that polar polymer blocks whose degree of polymerization is less than that of the PIB are formed even with relatively small PIB oligomers.



Scheme 4.1. Preparation of PIB-*b*-PMMA via hydroboration/O_2 initiation, ATRP and RAFT polymerization reactions. Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

4.2 Results and discussion

Hydroboration/O_2 Initiation of Radical Polymerization with PIB Macroinitiators

As mentioned before, the alkyl or alkoxyl radicals generated from bond cleavage of a alkylperoxyboron compound intermediate are known to be able to initiate radical polymerization reactions.[204,207,208] In our studies of synthesis of PIB-block copolymers from alkene-terminated PIB macromonomers, we initially explored a grafting-from radical polymerization of MMA using borane intermediates following the procedures described by Chung.[205] As expected, graft polymerization was successful using tri(polyisobutyl)borane and oxygen. However, from the GPC trace of the crude reaction product, the bulk of the graft polymer products formed had a much higher molecular weight fraction of the graft polymer than we desired (Figure 4.1, black curve). This graft copolymer could be isolated by precipitation in cold hexane (Figure 4.1, red and blue curve). Any hexane soluble product could be isolated by removal of the hexane under reduced pressure. The precipitated solid and the hexane soluble material were then further analyzed by ^{1}H NMR spectroscopy (see Figure 4.2). ^{1}H NMR spectroscopic analysis of the residue after evaporation of hexane from the filtrate contained an insignificant amount of signals characteristic of the methoxy peaks from PMMA. As shown in entry 1 of Table 4.1, the solid hexane-insoluble polymer product isolated by hexane precipitation did contain acrylate and PIB. The copolymer ratio of these polymers was analyzed by ^{1}H NMR spectroscopy. The result showed that the PIB_{1000} which had an average degree of polymerization of 18 contained a polyacrylate block with an average degree of polymerization of 65. This reaction used a 1/5 mole/mole ratio of PIB_{1000}/methyl

methacrylate. To increase the number of initiating groups from the intermediate tris(polyisobutyl)borane we tried adding excess oxygen. However, when we altered this chemistry introducing excess oxygen to the solutions of tris(polyisobutyl)borane, the major PIB graft product was still hexane insoluble (Table 4.2 and Figure 4.3-4). Under these conditions, the copolymers were also formed in lower yields (5 %). This suggests that the introduction of excess oxygen did not effectively generate more initiating groups or control the size of the polymers. While a PIB-*b*-Poly*(tert*-BA) block copolymer was prepared in this way was hexane soluble and while it could be separated from the PIB-OH by chromatography, the *tert*-BA block still had a higher degree of polymerization than the PIB block (see Figure 4.5). Thus, while we were able to use hydroboration and oxidation to form PIB block copolymers, we were unable to use this chemistry to control the size of the polar blocks. In these studies, the molecular weight distributions observed (Đ = ca. 2.0) were similar to the Đ seen in Chung's work using alkyl-9-BBN and oxygen to polymerize EMA.[205]

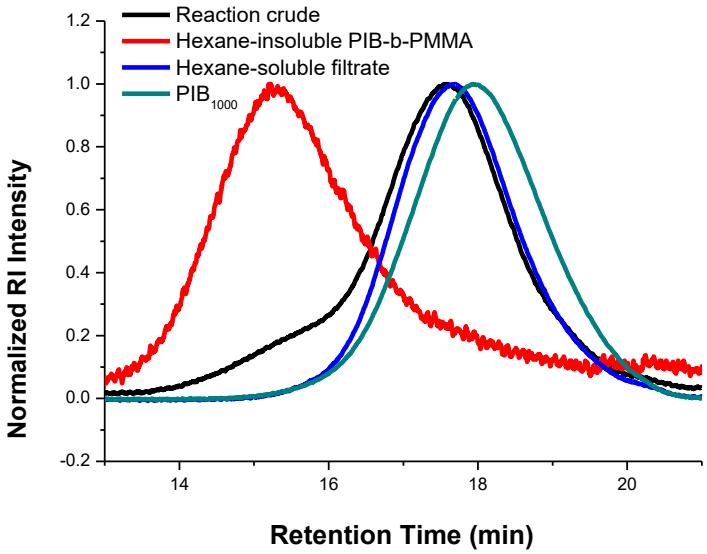


Figure 4.1. GPC traces of the crude reaction mixture (black curve) of PIB-*b*-PMMA, hexane-soluble PIB-*b*-PMMA (red curve), hexane-soluble filtrate (blue curve) from route 1 and PIB_{1000} (green curve). Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

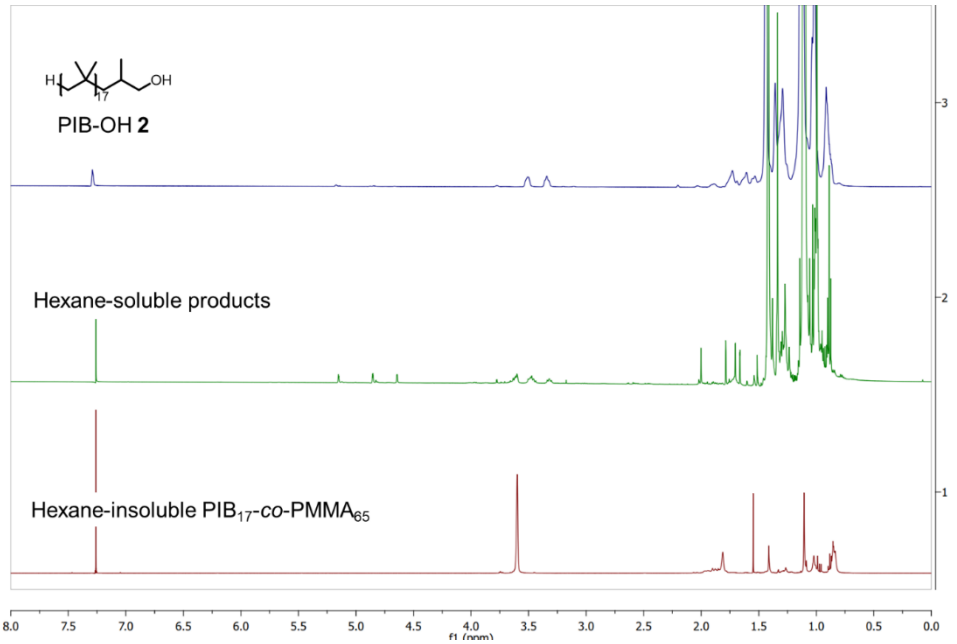


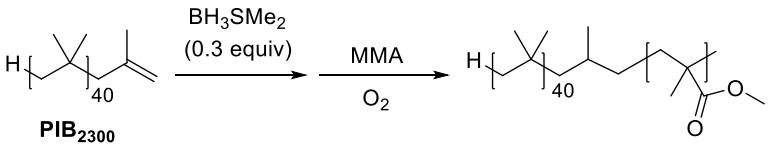
Figure 4.2. ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of PIB-OH **2**, the hexane-soluble products, and the hexane-insoluble PIB_{17}-*b*-$PMMA_{65}$ from route 1 from a hydroboration/O_2 initiated polymerization. Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

Table 4.1. Characterization data for PIB-bound oligoacrylates and oligomethacrylates formed via a hydroboration/O_2 initiation grafting-from radical polymerization using 6.5 mol% of oxygen relative to the moles of the PIB_{1000} used to prepare the tris(polyisobutyl)borane. Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

Entry	Monomer	Monomer to PIB_{1000}	M_n[a]	m/n[a]	M_n[b]	M_w[b]	Đ[b]	Yield %[c]
1	MMA	5/1	9,900	17/65	8,700	20,400	2.3	34
2	EMA	5/1	17,100	17/141	32,800	55,600	1.7	15
3	*tert*-BA	5/1	10,000	17/70	6,100	10,800	1.7	40

[a] Determined by ^{1}H NMR spectroscopy.
[b] Measured by size exclusion chromatography; d*n*/d*c* = 0.093 was used to calculated the polymer molecular weight and molecular weight distribution.
[c]The isolated yield of block copolymer is based on starting weight of PIB_{1000} and monomer.

Table 4.2. Effect of the amount of oxygen in hydroboration/O_2 initiated graft polymerization of MMA onto polyisobutylene. Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.



entry	Mon.	O_2 mmol %	Mon. /[MI]	Part	M_n (NMR)	M_n (GPC)	M_w (GPC)	Đ	Yield[b] (g)
1	MMA	xs[a]	10/1	Crude	-	3,000	7,300	2.4	-
				Supern-atant	-	2,600	6,200	2.4	
				Solid	20,400	18,200	38,200	2.1	0.5 g
2	MMA	6.5	10/1	Crude	-	2,400	6,400	2.7	-
				Supern-atant	-	2,400	6,400	2.7	
				Solid	42,300	32,800	123,800	3.7	1.5 g

[a] To a flask containing vinyl-terminated PIB_{2300} (4.34 mmol, 10 g) in THF (20 mL) was added BH_3-SMe_2 (1.32 mmol, 0.12 mL). The resulting reaction mixture was allowed to stir at room temperature for 2 h. Then methyl methacrylate (43.4 mmol, 4.6 mL) was added into the reaction mixture. Air was added to the solution by purging underneath the solution surface for 16 h. After 16 h, any unreacted acrylate monomer was removed under reduced pressure to yield the crude reaction product. The crude product was further purified by hexane precipitation. In that process, the crude product was dissolved in a minimal amount of a good solvent like THF and then added to a ca. 40-fold excess of cold hexane. Centrifugation separated the hexane-soluble products from the insoluble products. The hexane was removed under reduced pressure to isolate the hexane-soluble reaction product(s). The crude reaction mixture, hexane-soluble and -insoluble products were analyzed via GPC and ^{1}H NMR spectroscopy. [b]Yield of PIB-bound copolymers from 10 g of PIB_{2300}.

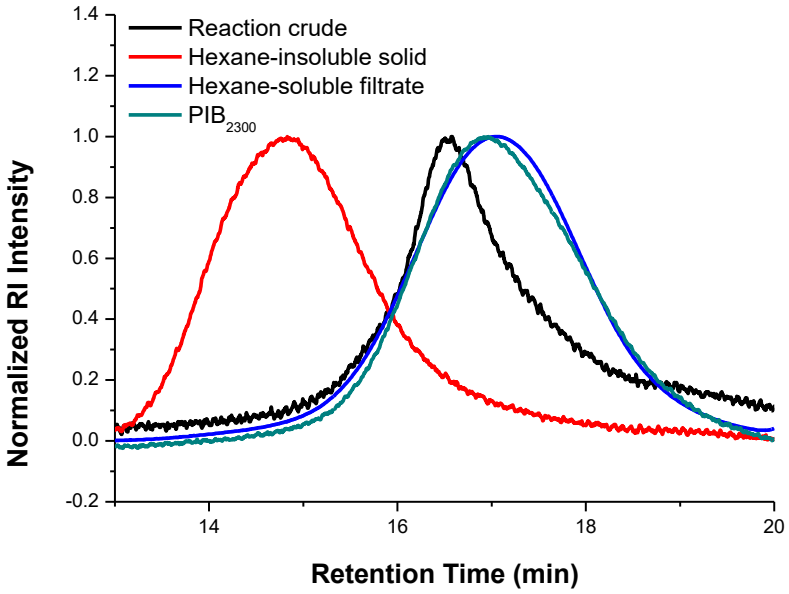


Figure 4.3. GPC traces of the crude reaction product, the hexane-soluble products, and the hexane-insoluble products from hydroboration/O_2 initiated polymerizations using excess oxygen. A GPC trace of the starting PIB_{2300} is also included in the Figure 4.3. Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

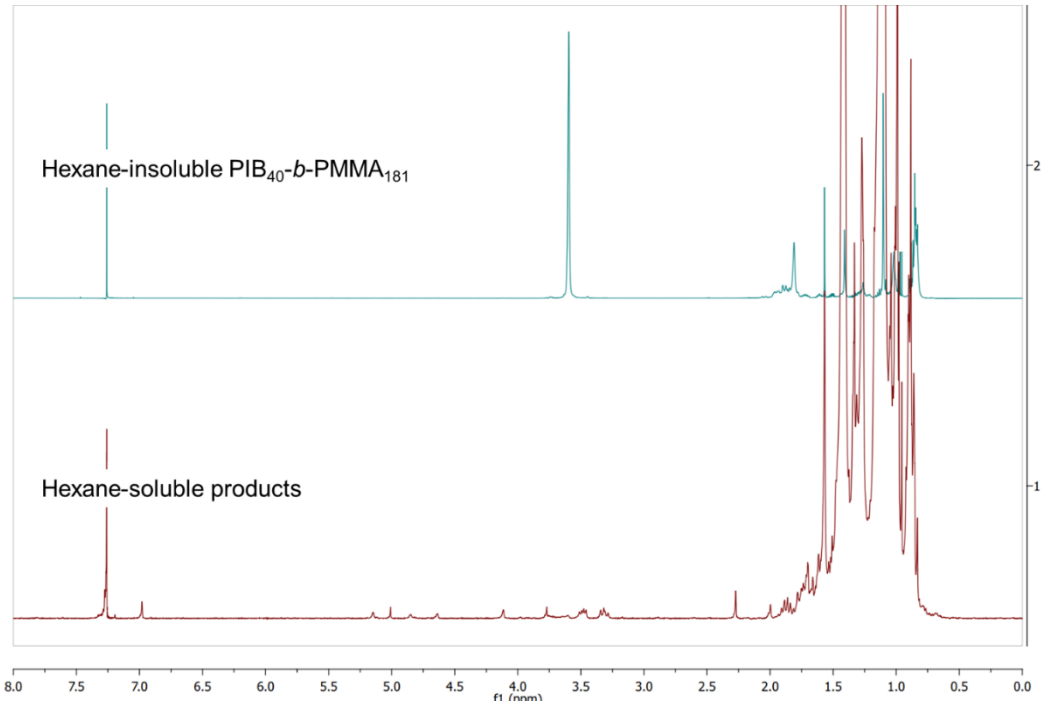


Figure 4.4. ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of hexane-insoluble PIB-*b*-PMMA and the hexane-soluble products from a hydroboration/O_2 initiated polymerization that used excess oxygen. 2,6-Dimethyl-4-tert-butylphenol (BHT) was found (6.98, 5.01 and 2.27 ppm) in hexane-soluble products due to the inhibitor in THF. Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

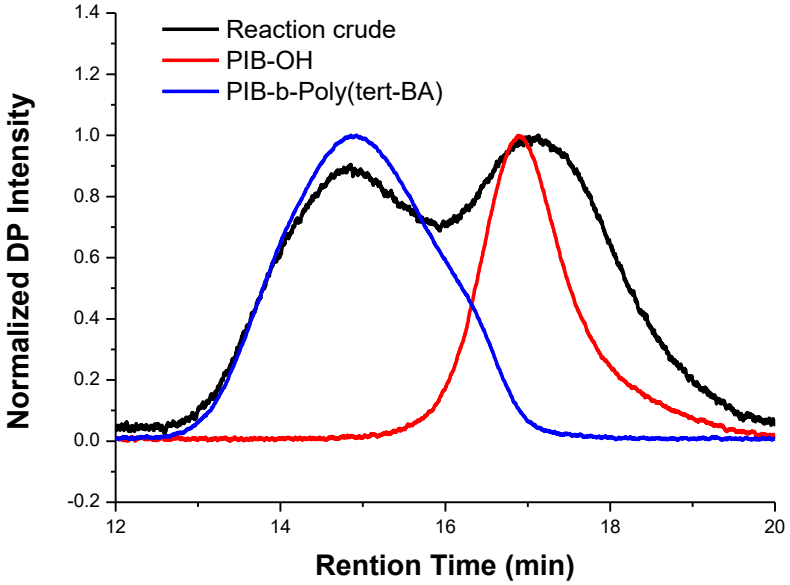


Figure 4.5. GPC traces of reaction crude, PIB-*b*-Poly(*tert*-BA) and PIB-OH from hydroboration/O_2 initiated polymerizations separated via column chromatography (Hexane/Acetone=4/1, followed by Hexane/Acetone= 1/1). Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

ATRP Copolymerization Using PIB Macroinitiators

The second route we explored for synthesis of an alkane soluble PIB-graft copolymer used the PIB-bound 2-bromoisobutyrate ester **3** as an ATRP initiator (Scheme 4.1, route 2). The necessary macroinitiator **3** was synthesized through in an esterification reaction using a hydroxyl-terminated PIB **2** and α-bromoisobutyryl bromide. PIB-bound copolymers were successfully synthesized with various kinds of vinyl monomers including MMA, benzyl methacrylates (BMA), *tert*-BA, and *N*,*N*-dimethylacrylamide (DMAA). However, the products in each of these cases were not alkane soluble because the degree of polymerization of the polar block of these diblock copolymers was higher than desired (Table 4.3, entry 1-3). The synthesis of PIB-derived block copolymers via ATRP did however provide better yields of product and better control over the size of the copolymers than was achieved using tris(polyisobutyl)-borane initiators in route 1. The copolymerization of MMA is an illustrative example (Table 4.3, entry 1). In this case, the 18-mer PIB_{1000} starting material produced a block copolymer with a MMA block with an average degree of polymerization that was also 34. However, while this copolymer contained a 1:2 ratio of the repeating units in the polar block relative to the PIB repeating units, it too was insoluble in hexane as evidenced by the fact that this block copolymer was isolated by precipitation from cold hexane. An examination of the hexane filtrate showed it only contained a small amount of the unreacted macroinitiator **3** and no PIB block copolymer. As was the case with *tert*-BA as a comonomer in first route, the PIB-bound oligo(*tert*-BA) was hexane-soluble. We have not fully studied the reasons why we could not get more control for the size of the polar grafts in these cases but speculate that

the PIB-α-bromo ester **3** is less reactive than the bromo-terminated PIB-bound acrylate or acrylamide intermediates. In any case, while ATRP reactions do lead to block copolymers that effectively change the properties of PIB, this chemistry did not in our hands serve as a general way to synthesize the alkane soluble block copolymers we desired.

Table 4.3. Characterizations of PIB-bound oligoacrylates and oligomethacrylates via ATRP. Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

Entry	Monomer	Monomer to Initiator **3**	M_n[a]	m/n[a]	M_n[b]	M_w[b]	Đ[b]	Yield %[d]
1	MMA	10/1	4,600	17/34	5,600	7,300	1.3	43
2	BMA	10/1	6,300	17/29	11,800	16,200	1.4	57
3	DMAA[c]	10/1	6,500	17/54	19,000	21,500	1.1	24
4	*tert*-BA	10/1	2,500	17/10	2,500	3,300	1.3	88

[a] Determined by ^{1}H NMR spectroscopy.
[b] Measured by size exclusion chromatography; d*n*/d*c* = 0.093 was used to calculate the polymer molecular weight and molecular weight distribution.
[c] The polymerization was proceeded under reflux in toluene. [d]The isolated yield of block copolymer is based on starting weight of PIB_{1000} and monomer.

RAFT Copolymerization Using PIB Macroinitiators

The third approach for synthesis of alkane-soluble PIB block copolymers used RAFT chemistry. In this case a RAFT agent on the PIB terminus was used as a chain transfer agent to form block copolymers from PIB macroinitiators using MMA, EMA, DMAA and *N*-isopropylacrylamide (NIPAM) as monomers. The RAFT initiator, PIB-CTA **6a** ,

was prepared from PIB by a multistep synthesis (route 3 in Scheme 4.1). We initially explored a RAFT polymerization using 1 mol % AIBN relative to the MMA monomer. As was true in ATRP polymerizations, the degree of polymerization of the polar polymer block in this case was typically larger than what was predicted based on the PIB-CTA/monomer ratio and we did not isolate alkane soluble block copolymer. This suggests that the initiator **6a** does not efficiently initiate the polymerization. The higher than expected dispersities of the product are consistent with this notion. However, by using 5 mol % of AIBN (relative to monomer) versus 1 mol % of AIBN, we were successful in activating all the macroinitiators **6a**. In this case, we did successfully obtain block copolymers with acrylate monomers and acrylamides. In these cases, the degrees of polymerization of the polar blocks were noticeably lower than that of PIB (Table 4.4, entries 1–4). In these polymerizations, the PIB-dominated block copolymers were separated from the non-hydrocarbon soluble portions by precipitation in cold hexane. These hexane soluble block copolymers made from RAFT polymerization still had higher dispersities than typical in RAFT chemistry ($Đ$ = 1.3-2.1). The GPC traces of RAFT polymerizations (see Figure 4.6) showed that the products and the PIB macroinitiator **6a** largely overlap. This is consistent with the ^{1}H NMR spectroscopy analysis that showed the degree of polymerization of the polar block was relatively low (3–8 repeating units). Notably, while the GPC analysis could not distinguish between unreacted **6a** and the hexane soluble block copolymers, ^{1}H NMR spectroscopy did show that there was no detectable **6a** in the copolymer products. This suggests that the product copolymers are not an admixture of the starting material and block copolymer. As

expected, these hexane soluble block copolymers were also soluble in higher molecular weight hydrocarbons like poly(α-olefin)s. As such, they are candidates for use in other ongoing work both as recyclable cosolvents and for use in nanoparticle solubilization studies.

Table 4.4. Characterization of hexane soluble PIB-bound oligoacrylates, oligomethacrylates, and oligoacrylamides via RAFT. Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

entry	Monomer	Monomer to CTA **6a**	AIBN mol%	M_n[a]	m/n[a]	M_n[b]	M_w[b]	Đ[b]	Yield %[c]
1	MMA	10/1	5	1,700	17/3	1,800	2,900	1.6	40
2	EMA	10/1	5	2,300	17/8	1,300	2,700	2.1	80
3	NIPAM	10/1	5	1,800	17/3	1,800	2,900	1.6	50
4	DMAA	10/1	5	2,200	17/8	2,400	3,100	1.3	84

[a] Determined by ^{1}H NMR spectroscopy.
[b] Measured by size exclusion chromatography; d*n*/d*c* = 0.093 was used to calculate the polymer molecular weight and molecular weight distribution.
[c] The isolated yield of block copolymer is based on starting weight of PIB_{1000} and monomer.
[d] The PIB-bound CTA with *tert*-butyl group as a Z group (PIB-CTA **6b**) was used and its synthesis is the same as PIB-CTA **6a** using *tert*-butyl thiol instead of dodecanethiol. Synthesis of **6a** was preferred because dodecanethiol is less malodorous.

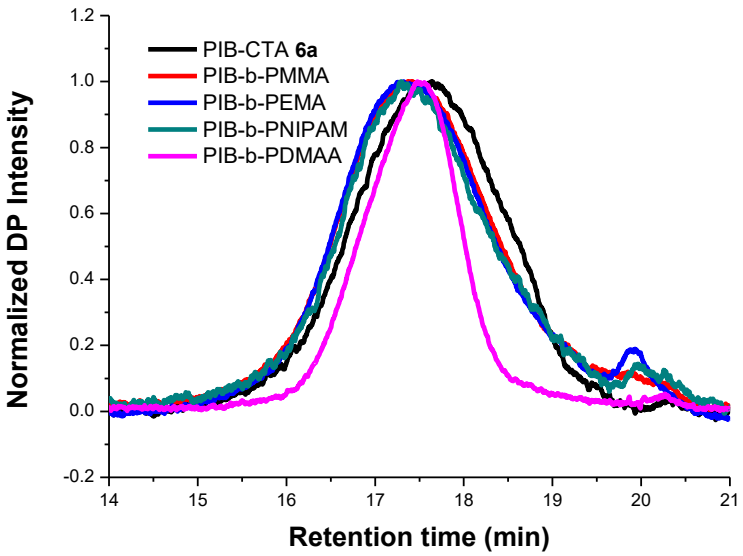


Figure 4.6. GPC traces of PIB-*b*-PMMA, PIB-*b*-PEMA, PIB-*b*-PNIPAM, PIB-*b*-PDMAA from RAFT polymerization and PIB-CTA **6a**. The molecular weight and its polydispersity (*Đ*) of PIB-CTA **6a** measured by GPC are listed as follows: M_n 1,600 g mol^{-1}, M_w 2,700 g mol^{-1}, *Đ* 1.69. Reprinted with permission from *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1860, Copyright 2018 by John Wiley & Sons, Inc.

4.3 Conclusion

Three copolymerization processes were explored as routes to make hexane soluble PIB-based block copolymers from vinyl-terminated PIB_{1000} where the degree of polymerization of the polar block was controlled so as to be less than that of the PIB block. Hydroboration/O_2 initiated polymerizations proceed under mild conditions. However, the yields of the block copolymers in this chemistry were modest and the degree of polymerization of the polar poly(methyl methacrylate), poly(ethyl methacrylate) and poly(*tert* -butyl acrylate) block was larger than that of the PIB block. With the exception of the poly(*tert* -butyl acrylate) case, the product block copolymers were all alkane insoluble. Using hydroxyl-terminated PIB **2,** an ATRP macroinitiator **3** was also synthesized. This macroinitiatior was successful in ATRP polymerizations using a variety of vinyl monomers (MMA, EMA, BMA, *tert* -BA, and DMAA). However, while these polymerizations were more controllable that polymerizations using a tris(polyisobutyl)borane initiator based on ^{1}H NMR spectroscopic and GPC analyses, the block copolymers were still not alkane soluble. However, when the hydroxyl-terminated PIB **2** was used to prepare the RAFT agent **6a,** RAFT polymerizations could be carried out with vinyl monomers like MMA, EMA, DMAA and NIPAM. In these RAFT polymerizations, using a higher amount of AIBN successfully formed short polar blocks on PIB_{1000} where the degree of polymerization could be controlled producing block copolymers of PIB and polar monomers that were soluble in hexane and poly(α-olefin) hydrocarbon solvents.

CHAPTER V

KINETIC STUDY OF ORGANIC REACTIONS IN PAO AND POLAR MIXTURES

5.1 Introduction

Solvents are a necessary component of nearly all chemical processes. Solvents serve useful roles in mitigating exotherms, in providing a suitable milieu for reactions, in controlling relative concentrations of reacting species and in purifying chemical and polymers. They are essentially required in homogeneous catalysis. However, solvents pose environmental issues and introduce additional costs in any system. Most often solvents are incinerated after being used for reactions causing tremendous amount of greenhouse emissions (GHGs) and requiring the production of more solvents. To recycle solvents, they often have to be recovered by energy intensive processes like distillation. Ideally, solvents should be easily recyclable by a simple physical process which requires far less energy.

My first chapter discusses the pros and cons of current greener and more environmentally benign solvents that include new types of solvents as well as more benign and more sustainable organic solvents. However, it is difficult if not impossible to design solvents that meet all the desired criteria for a green solvent. For example, sustainable bioderived organic solvents are often still volatile and as such can introduce unwanted pollutants into the environment. Furthermore, while the environmental of a new solvent compared to the solvents they replace is important, reactions in alternative solvents ideally should proceed equally well in both solvents if not better in the greener more sustainable solvent system. A green solvent which has poor performance compared to the traditional

solvent is not likely to be widely adopted. Solubility of substrates, reagents, and catalysts is another critical factor in choosing an alternative greener or more sustainable solvent alternative. For example, when $scCO_2$ is used as a reaction medium, it has advantages of renewability, environmental-friendly properties and high diffusivity for reaction substrates. However, cosolvents are often needed to enhance the solubility of reactants and reagents because of its low polarity.[16–18] This second issue wherein a single solvent is used with another solvent is common practice in organic chemistry. Indeed, this has been a theme both in my research with PAOs as alternative solvents and in prior work by the Bergbreiter group. In my work and in prior work by others in the Bergbreiter group, this has typically involved adding conventional or 'greener' solvents to heptane or PAOs to make the solvent mixture more polar. That prior work typically used heptane or PAO to recycle catalysts and most often required cosolvents to either enhance the reactivity of a catalyst or to insure solubility of reactants and reagents. In that work, our group developed thermomorphic and latent biphasic separation schemes to effect liquid/liquid separations in these solvent mixtures after a reaction.

An example where a second solvent is required because of solubility issues is the Lewis base-catalyzed reduction of enones discussed in chapter 2. In that work, I added ethyl acetate (1.7-3.4 M) to a PAO solvent to form a reaction mixture that made it possible to dissolve the α,β-unsaturated reactants. Others in our group too have recently described this approach in studies of nucleophilic catalysis.[122]

A general thesis of the work in earlier chapters and by others in the Bergbreiter group is that PAOs are good alternatives to heptane. PAOs behave much like heptane in reactions but are greener solvents and more sustainable solvents due to their lower volatility, low flammability, low toxicity akin to mineral oil, and easy biphasic separability. They are also commercially available from many sources at relatively low cost. Although their low volatility means they cannot be separated from products via distillation, they can be separated from their products via liquid-liquid extractions. Recent studies demonstrated that PAO as solvents are just as functional as heptane and barely leach into polar phases. Thus, they are easily recycled and do not significantly contaminate products.[95] However, just as heptane is a poor solvent from many polar species, the nonpolar nature PAOs makes them poor solvents, narrowing the breadth of their potential utility in reactions. The obvious solution mentioned above is to add a cosolvent like toluene or ethyl acetate to enhance the solubility of substrates and reagents.[122, chapter 2] However, while much of the emphasis on cosolvents has focused on addressing solubility issues, introducing cosolvents to form cosolvent/PAOs systems also affects reaction mixture polarity which is a second issue that directly affects reaction performance.

The effects of changing from heptane to PAO and from one PAO to another have been studied previously. For example, Malinski had studied the thermal isomerization *Z* to *E* PIB-bound *para*-methyl red in nonpolar solvents (heptane versus PAOs).[95] His kinetic studies showed the rate constant of the thermal isomerization of the PIB-bound *para*-methyl red in all of the PAOs (PAO_{283}, PAO_{432}, PAO_{687}, PAO_{1785} and PAO_{2505}) regardless of their viscosity were essentially identical to the rate constant of the isomerization in

heptane. Studies of reaction rates in PAO versus heptane or PAO/cosolvent mixtures have been studied too but only to a limited extent. For example, recently Thavornpradit studied the rate of the Boc-protection reaction of 2,6-dimethylphenol in PAO, heptane, toluene, THF, PAO/toluene, and PAO/THF using a PIB-bound nucleophilic catalysts. While the difference seen were <10-fold, there reactions were slightly faster in nonpolar media (Table 5.1). These rates were also shown to be comparable to rates measured previously for similar chemistry carried out with a low molecular weight catalyst. I also made similar observations in Chapter 3. In general, our group has observed that reactions as diverse as Boc-protection, esterfications, addition of trimethylsilyl cyanide to aldehydes, Knoevenagel, allylation of benzaldehydes, and reduction of α,β-unsaturated compounds, can be successfully carried out in PAOs or PAOs/cosolvent mixtures.

Table 5.1. Effects of solvent on the rate of Boc-protection of 2,6-dimethylphenol.[122]

Solvent	Rate constant (min^{-1})
Heptane	6.0×10^{-3}
PAO_{506}	5.4×10^{-3}
5 M toluene/PAO_{506}	2.9×10^{-3}
5 M THF/PAO_{506}	2.4×10^{-3}
Toluene	2.5×10^{-3}
THF	1.9×10^{-3}

Reactions were carried out at 0 °C using 0.2 M 2,6-dimethylphenol, 0.24 M $(Boc)_2O$, 0.5 mol% of PIB-bound DMAP catalyst and were monitored using ^1H NMR spectroscopy.

Since PAOs or PAOs/cosolvent mixtures have broad applicability as a sustainable and recyclable reaction medium our group has further explored these solvent mixtures. For example, in unpublished work, Malinski carried out a series of polarity studies of PAOs and PAOs/cosolvent systems using solvatochromic fluorophores (a PIB-bound dansyl dye and Nile Red). These dyes have different emission wavelength (λ_{EM}) based on the polarity of the solvent that the dye encounters. In that work, Malinski hypothesized that by adding a small amount of polar cosolvent to PAO might lead to a local environment in the solvent system that might resemble the bulk polar cosolvent even with very modest amounts of the added cosolvent. This concept that a low concentration of a cosolvent can affect a solute is known as microheterogeneity and has been discussed by others.[216,217]

In Malinski's fluorescence experiments, the λ_{EM} of a dye in PAO and a polar solvent was measured. Then the $\Delta\lambda_{EM}$ for the dye in PAO containing varying amounts of polar solvents was measured. The solvatochromic study of PIB-bound dansyl dyes and Nile Red in varying amount of polar solvent (THF and DCM) showed two distinctive features. First, both solvatochromic fluorophores had virtually identical responses to cosolvent addition in heptane or any of the low viscosity PAOs. Second, a nonlinear shift in the plot of % shift (the $\Delta\lambda_{EM}$) from the nonpolar solvent to the pure polar cosolvent vs the molarity of the cosolvent was measured. In the low concentration ranging from 0 to 15% THF or DCM, the significant increase (40-60%) in $\Delta\lambda_{EM}$ occurred with the λ_{EM} changing rapidly to resemble the dye's λ_{EM} in the more polar solvent. This is shown in Figure 5.2 where ca. 1-4 M of THF lead to a 60-70% λ_{EM} change. Similar phenomena were also seen in the solvatochromic studies ethyl acetate/heptane, hexanoic acid/PAO_{432},

and alcohol mixtures with heptane or PAO_{432}. Other polymeric polar additives in PAO_{432} behaved similarly.[218] This presumably reflects the fact that the fluorophore is being solvated by the polar cosolvent. Polar solvent acts as a stabilizer for dyes' excited states whereas the heptane or PAO alkane solvents only provide a nonpolar dispersive medium for polar solvents and dyes. This is an exciting finding because it could reduce the need of polar solvents when using PAOs as the bulk of the mixed solvent system, which significantly minimize the solvent wastes. Furthermore, if the polar molecules could be modified and anchored in PAO phase, the whole solvent system could be recycled. If polar moieties can serve not only as a cosolvent but also a catalyst for a reaction, a clean, catalytic and recyclable solvent system can potentially be developed that would be more sustainable than conventional solvents. Indeed, it would allow chemists to use the power of synthesis to tune solvent properties in chemical manufacturing. In this chapter, I further examine these microheterogeneity effects by studying the kinetics of some common organic reactions.

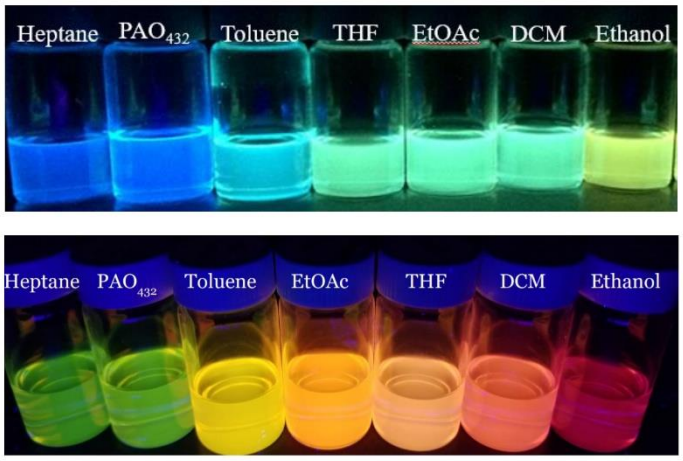


Figure 5.1. Solvatochromic fluorescence of dansyl sulfonamide (top) and Nile Red (bottom).[218]

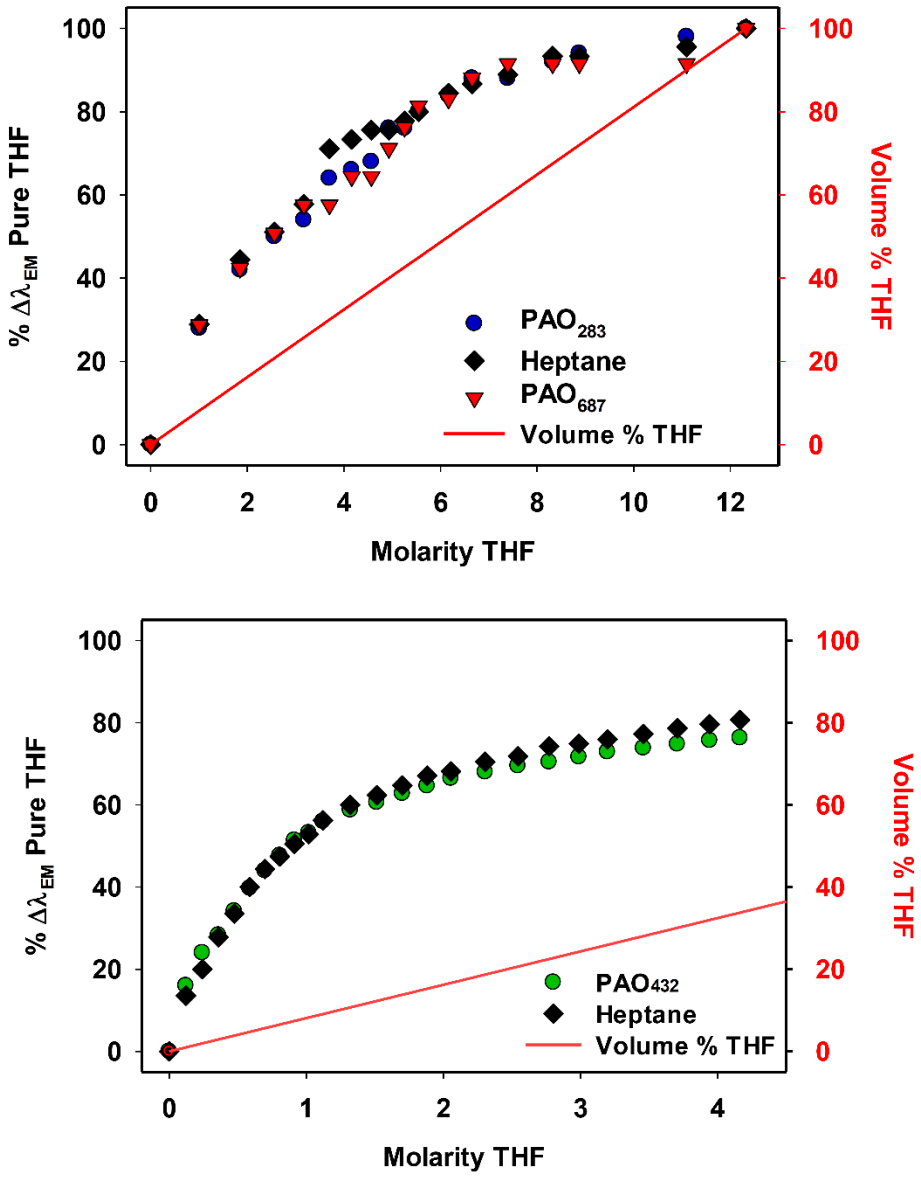


Figure 5.2. Solvatochromic shift of PIB-bound dansyl sulfonamide adding THF as a cosolvent in heptane, PAO_{283}, and PAO_{687} (top) and Nile Red in heptane and PAO_{432} (bottom). The red line is the volume % THF added.[218]

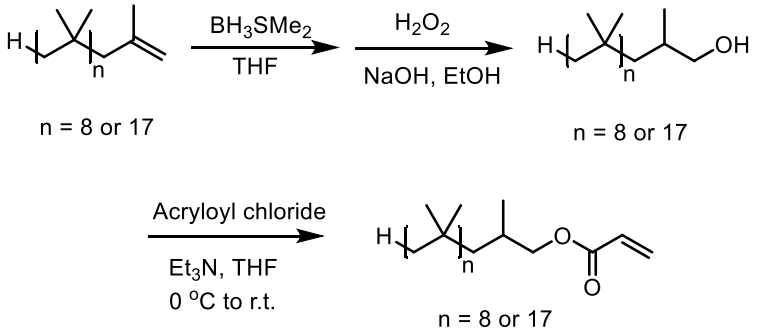
5.2 Results and discussion

As mentioned earlier, microheterogeneity in hydrocarbon/polar solvents is common with conventional polar solvents. However, we were interested in exploring the similar fluorescent behavior when using PAO-anchored polar molecules as a cosolvent. Polymer supports have been widely used in prior work in Bergbreiter's group to generate phase anchored, phase selectively soluble species. Whether the polymer is polyethylene, poly(ethylene glycol) and polyisobutylene, this work has established that a polymer support is generally useful for synthesizing organic ligands or catalysts.[93,100,113–119,125,126,219]

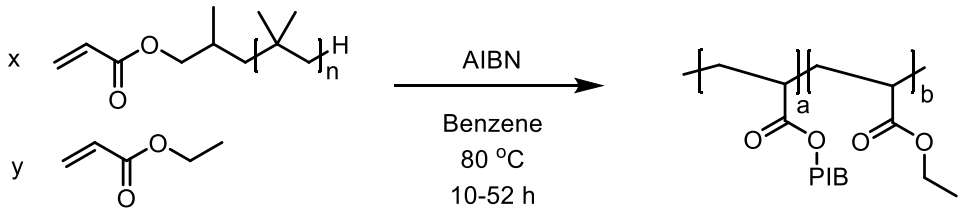
In the syntheses I developed, I examined copolymerization of monomers with a polymer (phase anchor) and a functional group and direct end-group modification onto a polymer as two common ways to make polymer supported oligomeric cosolvents. In this particular case, I opted to introduce more polar groups into PAO phase using a copolymerization of PIB-bound monomers and polar monomers to form a polyvalent hydrocarbon-soluble macromolecule that possess a higher equivalent of polar groups in a single polymer chain than the one from an end-group modification. To accomplish this, I prepared a vinyl-terminated PIB oligomer (n = 8 or 17) from hydroxyl-terminated PIB oligomers. This was accomplished by reaction of acryloyl chloride with a hydroxyl-terminated PIB oligomer (see scheme 5.1). The PIB supported acrylate was then copolymerized with a commercially available ethyl acrylate via a random radical polymerization to form a polymer version of ethyl acetate (see scheme 5.2). Both

monomers had the same polymerizable group (i.e. an acrylate) as way to minimize block copolymer formation. For example, if a different polymerizable group with a different reactivity ratio such as methacrylate was chosen, we anticipated more problems.[220] However, even with our precautions, we cannot exclude that a block copolymer formed. The PIB group may have formed micelle-like microstructures in a nonpolar medium. However, our goal was to prepare a PAO-soluble copolymer that contained PAO-anchorable functionality so the actually polymer microstructure is not as important as the polymer's solubility. In the initial radical polymerizations of a PIB-bound acrylate and ethyl acrylate (see Table 5.2), 0.5 mol% of AIBN and 0.5 M of PIB-bound acrylate (n =17) were used to copolymerize with different equivalent of ethyl acrylates (1, 2, or 3 equivalents) under 80 ^{o}C for 10 h. However, the conversions of PIB-bound acrylate (n =17) were relatively lower than an ethyl acrylate. The unreacted PIB-bound acrylate cannot be isolated from the copolymers via an extraction or a precipitation. Additionally, from the TLC plates, the PIB acrylate and copolymers both located at the same spot; therefore, it's also not possible to purify the copolymer via a column chromatography. To make an easier purification process, several reaction parameters are changed: the loading of AIBN was increased (0.5% to 2%), the concentration of the monomers was increased (0.5 M to 1M) and the reaction times were extended (10h to 48h). Under those, the conversion of a PIB-bound acrylate (n = 17) was nearly completed (>99 %). After a solvent removal under a reduced pressure, the copolymer (a/b = 2/1) was directly used for the following fluorescence studies. Applied with the same condition, PIB-bound acrylate

(n = 8) were able to copolymerize with an ethyl acrylate to form a copolymer (a/b = 2/1) and PIB-bound acrylate (n = 8) showed almost 100 % conversions.



Scheme 5.1. Synthesis of PIB-bound acrylate (n = 8 or 17, PIB_{450} or PIB_{1000} respectively).



Scheme 5.2. Synthesis of polymer bound ester cosolvents by copolymerization of a PIB-bound acrylate (n = 8 or 17, PIB_{450} or PIB_{1000} respectively) and an ethyl acrylate.

Table 5.2. Radical polymerization condition of PIB-bound acrylates (n = 8,17) and ethyl acrylates.

n	x/y	[PIB-bound acrylate]	AIBN mol%	Reaction time	Conversion (%) of PIB-bound acrylate	a/b
17	1/1	0.5	0.5	10 h	50	-
17	1/2	0.5	0.5	10 h	75	-
17	1/3	0.5	0.5	10 h	61	-
17	1/1	1	2	48 h	>99	2/1
8	1/1	1	2	52 h	>99	2/1

As shown in Figure 5.3, the λ_{EM} shift of both the Nile Red and PIB-bound dansyl sulfonamide solvatochromic fluorophores are affected by these PAO soluble polymer bound ester cosolvents. These studies also compared the results for microheterogeneity introduced by a polymer-bound cosolvent to the changes seen for addition of low molecular weight cosolvents. For example, an ethyl ester-terminated PIB bound oligomer (n =17) was also synthesized and used as a polymer bound cosolvent. In the event, the polymer bound cosolvent affected the dye solute in the same way as the low molecular weight analogs at the same concentration regardless of the length of alkane solvent anchoring polymer chain. Introducing the polymer supported ethyl ester or the PIB-bound ethyl ester into alkane solvents (heptane and PAO_{432}) provided a more polar environment for the fluorophore, thus influenced the λ_{EM} shift. In addition to polymer supported ethyl esters, other polymer version polar additives (e.g. polymer supported alcohols and carboxylic acids) were also tested in the solvatochromic fluorescence experiments.[218]

Given that solvatochromic shifts suggest that we can significantly affect polarity at low concentrations of a conventional or polymeric cosolvent, we hypothesized that the same microheterogeneity phenomena could affect kinetics of reactions. In these prior fluorescence studies, a small amount (1-4 M) of THF was shown to lead to a 60-70 % increase in $\Delta\ \lambda_{EM}$. Thus, we elected to study a simple transesterification reaction (Scheme 5.3) studying its rates in PAOs with varying amounts (0, 1.2, 2.4, 6 and 12M) of THF as a polar cosolvent. To ensure the miscibility of the aromatic substrates with PAO, a PIB support (M_w 450 Da) is incorporated onto a 2-nitrophenyl acetate. The basic nucleophile used was lithium octoxide which was prepared *in situ*. This alkoxide was chosen because

its eight-carbon aliphatic chain insured this reagents solubility in PAO. The transformation from nitrophenyl acetate to nitrophenolate was chosen as a model reaction because the formation of the nitrophenolate anion lead to a significant change in the wavelength of maximum absorption (λ_{max}, 268 to 450 nm).[221–223] The distinctive λ_{max} shift after the reaction allowed us to follow the reaction kinetic via UV-visible spectroscopy.

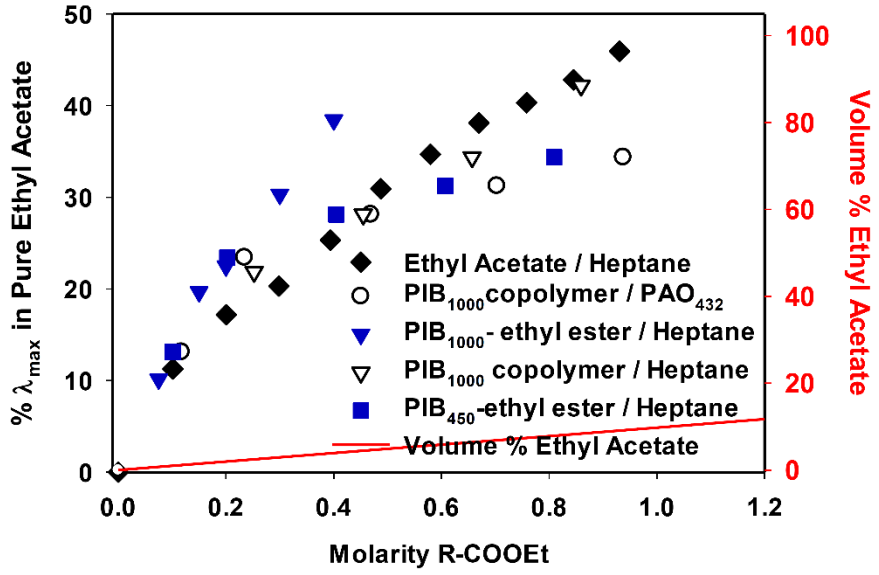
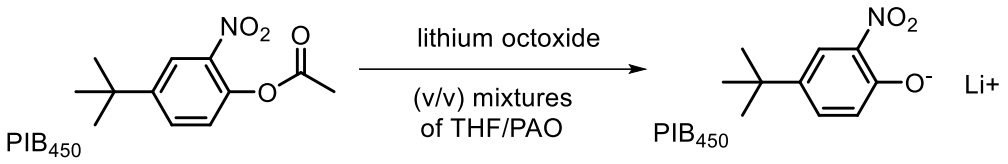


Figure 5.3. Solvatochromic shift of fluorophores adding polymer bound cosolvents. Solvatochromic shift of Nile Red with polymer bound carboxylic acids as cosolvents into heptane and PAO_{432} (top), solvatochromic shift of Nile Red with polymer bound ester as cosolvents into heptane and PAO_{432} (middle), and solvatochromic shift of PIB-bound dansyl sulfonamide (n = 17, PIB_{1000}) with a polymer bound alcohol as a cosolvent into heptane (bottom).[218]



Scheme 5.3. The transesterification between a PIB-bound nitrophenyl acetate (n = 8, PIB_{450}) and lithium octoxide.

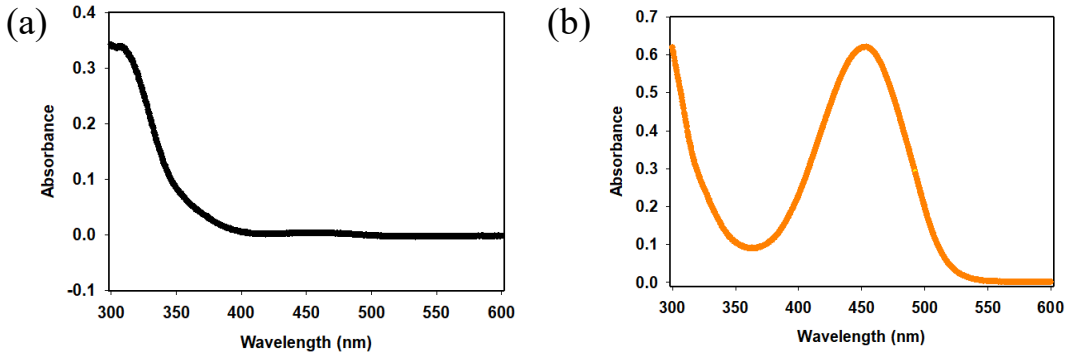
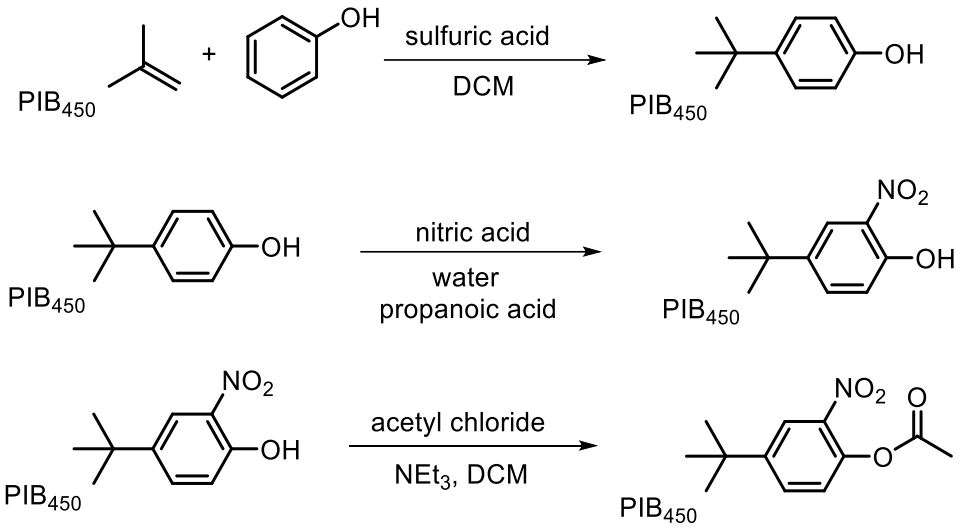


Figure 5.4. The UV-visible spectrum of (a) PIB-bound nitrophenyl acetate (n = 8, PIB_{450}) and (b) lithium PIB-bound nitrophenolate (n = 8, PIB_{450}).



Scheme 5.4. The synthesis of PIB-bound nitrophenyl acetate acetate (n = 8, PIB_{450}).

The synthesis of the PIB-bound nitrophenyl acetate is shown in see Scheme 5.4. In this synthesis, vinyl-terminated PIB (M_w 450 Da) was allowed to react with phenol under acidic conditions to yield a PIB-bound phenol via an electrophilic aromatic substitution reaction.[124] Then a nitro group was introduced by nitration with nitric acid. As expected, the nitro group was successfully introduced at the ortho position to afford a PIB-bound nitrophenol. Then, the nitrophenol was further functionalized with acetyl group via a nucleophilic acyl substitution to yield a PAO soluble PIB-bound nitrophenyl acetate. The exact amount of the nitrophenyl acetate per gram was determined by ^{1}H NMR spectroscopy using dichloroethane as an internal standard.

Due to the large extinction coefficient of the nitrophenyl group, modest concentrations (3×10^{-4} M) of the ester was used in these UV-visible analyses of the transesterification. THF used in the kinetic studies was distilled to remove an inhibitor (BHT) that is used to prevent THF from forming peroxides. In initial studies, BHT in THF (250 ppm, ca. 1.3×10^{-3} M) reacted with lithium octoxide (3×10^{-4} M) converting the anionic alkoxide into a relatively unreactive alcohol. The use of distilled THF my also be important in avoiding the potential complication of adventitious water presented in THF. In the event, lithium octoxide, was freshly prepared by treating octanol with *n*-butyl lithium and the exact concentration of lithium octoxide was calibrated by a titration with 0.01M HCl.

A final issue that complicated these experiments was the present of some absorbance peaks in the UV-visible spectra of PAO432 from ExxonMobil. These peaks complicated studies of the changes in absorption of PIB-bound nitrophenyl acetate.

Fortunately, the 200-300 nm range was much cleaner using an alternative PAO solvent. Thus, PAO_{506} from Chevron Phillips was used to carry out these kinetic studies.

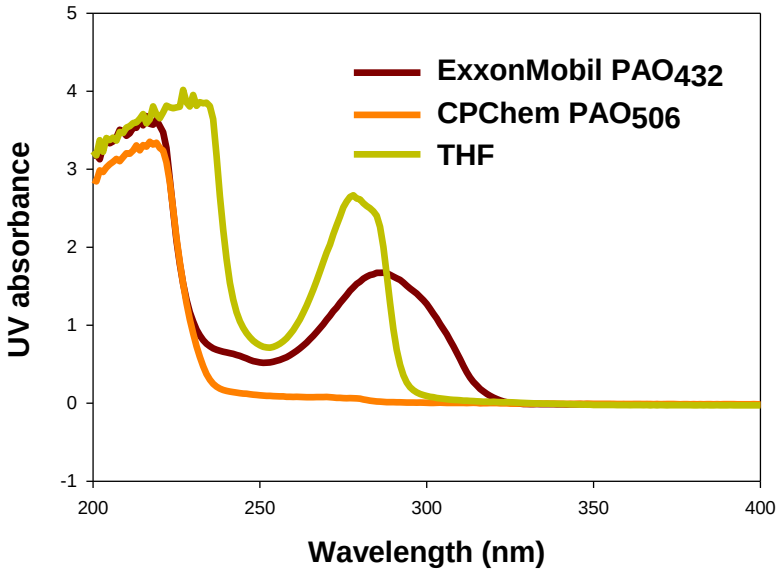


Figure 5.5. The UV-visible spectra of PAO_{432} from ExxonMobil (red curve), PAO_{506} from Chevron Phillips (orange curve) and THF (green curve).

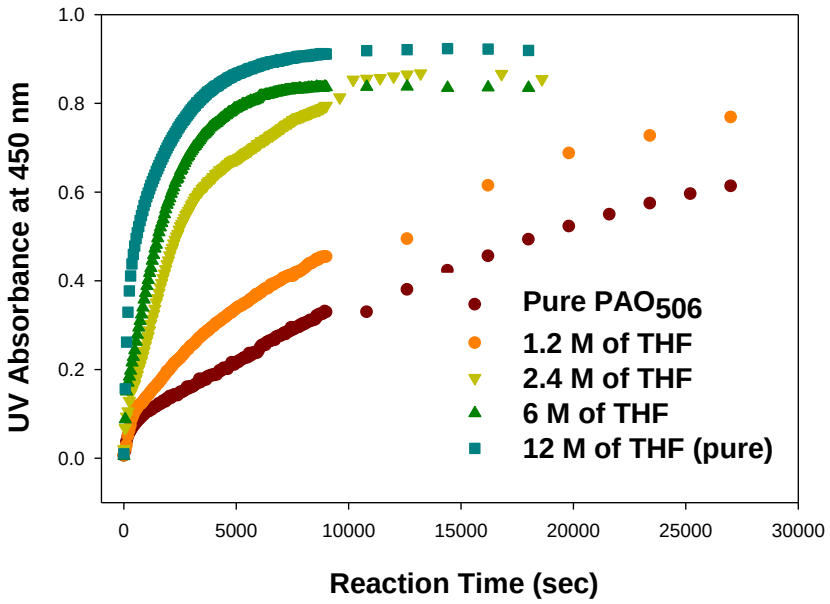


Figure 5.6. UV-visible spectra of the transesterification of PIB-bound nitrophenyl acetate with lithium octoxide in 12 M THF (pure), 6 M THF in PAO_{506}, 2.4 M THF in PAO_{506}, 1.2 M THF in PAO_{506} and pure PAO_{506}.

After optimizing the transesterification condition, the conversions of PIB-bound nitrophenolate anion at different times in different molarities of THF in PAO_{506} were recorded by UV-visible spectroscopy. As expected, the reaction rate in pure PAO_{506} gave the slowest reaction curve, whereas the reaction in pure THF presented the fastest transesterification rate (see Figure 5.5). While the two substrates in this reaction were used in a 1 to 1 ratio, a second order kinetic plot for the for the disappearance of the starting material for the first 15-20 % of the reaction was linear (Figure 5.6-10) and allowed us to calculate rate constants (Table 5.3).

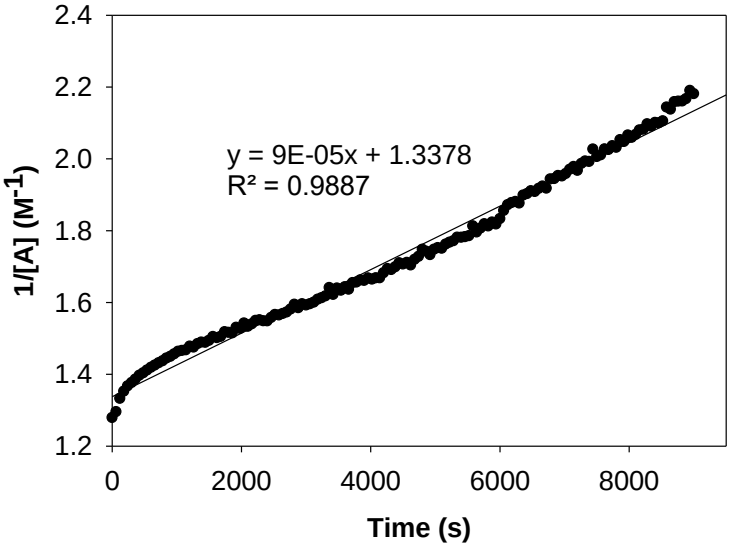


Figure 5.7. 2nd order of kinetic plot of PIB-bound nitrophenyl acetate to PIB-bound nitrophenolate anion in PAO_{506}.

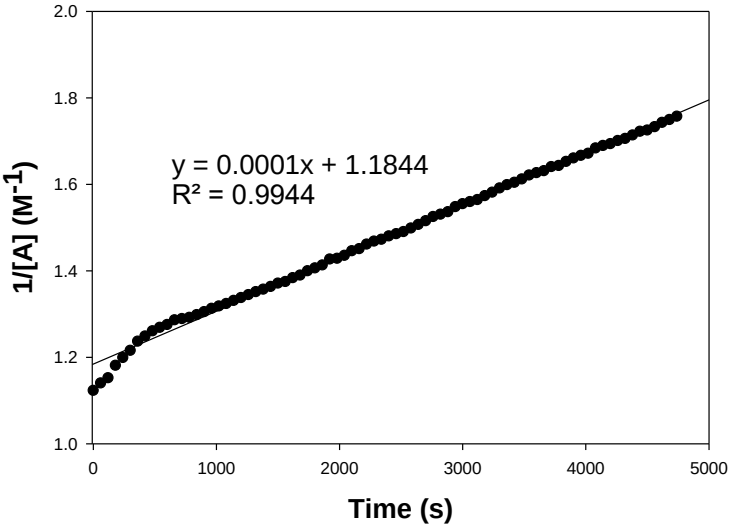


Figure 5.8. 2nd order of kinetic plot of PIB-bound nitrophenyl acetate to PIB-bound nitrophenolate anion in 1.2 M THF in PAO_{506}.

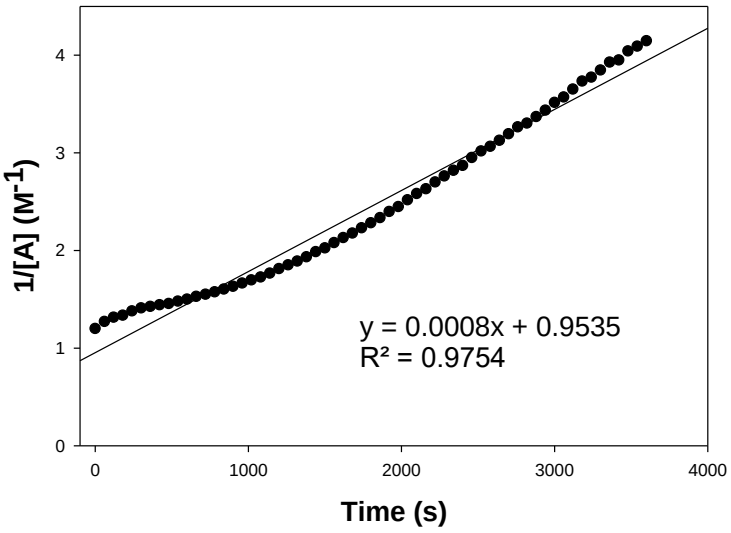


Figure 5.9. 2nd order of kinetic plot of PIB-bound nitrophenyl acetate to PIB-bound nitrophenolate anion in 2.4 M THF in PAO_{506}.

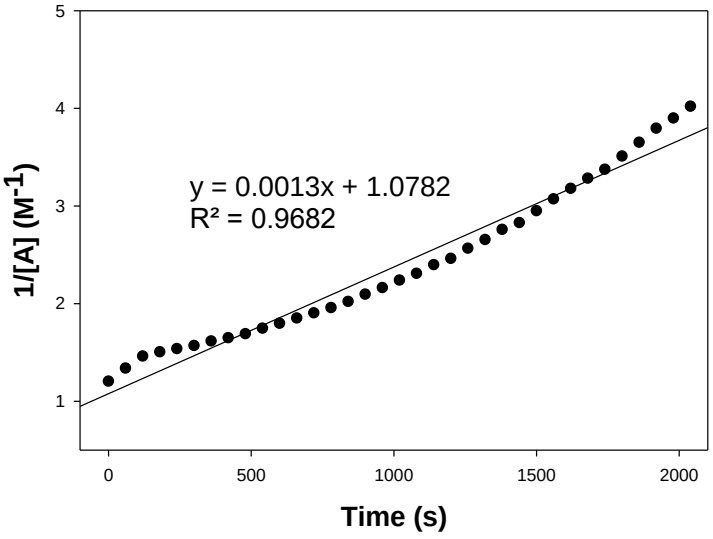


Figure 5.10. 2nd order of kinetic plot of PIB-bound nitrophenyl acetate to PIB-bound nitrophenolate anion in 6 M THF in PAO_{506}.

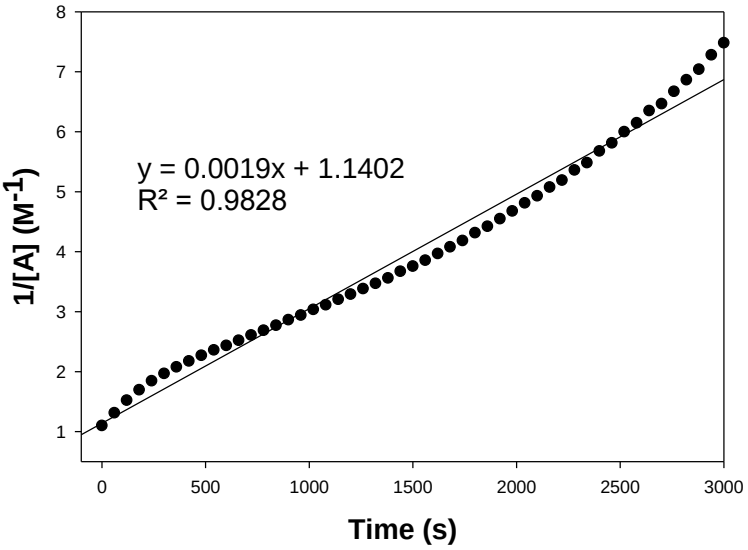


Figure 5.11. 2nd order of kinetic plot of PIB-bound nitrophenyl acetate to PIB-bound nitrophenolate anion in pure THF.

Table 5.3. Effects of solvent on the rate of transesterification of PIB-bound nitrophenyl acetate.

Solvent	Rate constant (1/M·s)
Pure PAO	9×10^{-5}
1.2 M of THF	1×10^{-4}
2.4 M of THF	0.8×10^{-3}
6 M of THF	1.3×10^{-3}
12 M THF (pure)	1.9×10^{-3}

The kinetic comparison is shown in Table 5.3, the reaction with a higher THF molarity give a faster rate in PAO_{506}. The trend is expected because the polar environment can stabilize the tetrahedral intermediate. The reaction constant in THF (1.9×10^{-3} $M^{-1}s^{-1}$) is higher than the one in PAO_{506} (9×10^{-5} $M^{-1}s^{-1}$) by 22 times. With 1.2 M of THF was added into PAO506, the reaction constant (1×10^{-4} $M^{-1}s^{-1}$) didn't have a significant enhancement. Notably, the rate was increased by approximately 10 factors (0.8×10^{-3} $M^{-1}s^{-1}$) when 2.4 M of THF was introduced. Based on the prior solvatochromic study (Figure 5.2) that 2 M of THF can bring about 40% polarity to PAO_{432}. The reaction rate in 2.4 M of THF in PAO_{506} is 42% to the rate in pure THF (1.9×10^{-3} $M^{-1}s^{-1}$), which agreed with the previous polarity study.

In the following kinetic study, we are interested in using 1-octyl-2-pyrrolidone as a cosolvent in a S_N2 reaction. A 1-alkyl-2-pryrrolidone structurally resembles the common polar aprotic solvent, *N*,*N*-dimethylformamide. The compound with an octyl group is miscible with PAO. Moreover, in a preliminary polarity study (Figure 5.11), the polarity in PAOs can be increased to 70 % to the polarity of pure 1-octyl-2-pyrrolidone with only 0.45 M of 1-octyl-2-pyrrolidone was added. The model reaction we proposed to examine the microheterogeneity in reactions is a simple S_N2 reaction of a bromobutane reacting with a PAO soluble benzoate ion. as shown in Table 5.4. A *N*,*N*-diethyl-*N*-methylammonium terminated PIB oligomers with benzoate anion was prepared to insure the solubility of nucleophile in PAO. Similar solvent effects on S_N2 kinetics has been demonstrated in prior work in Bergbreiter group.[102] We anticipated the microheterogeneity phenomena could be observed in this S_N2 reaction.

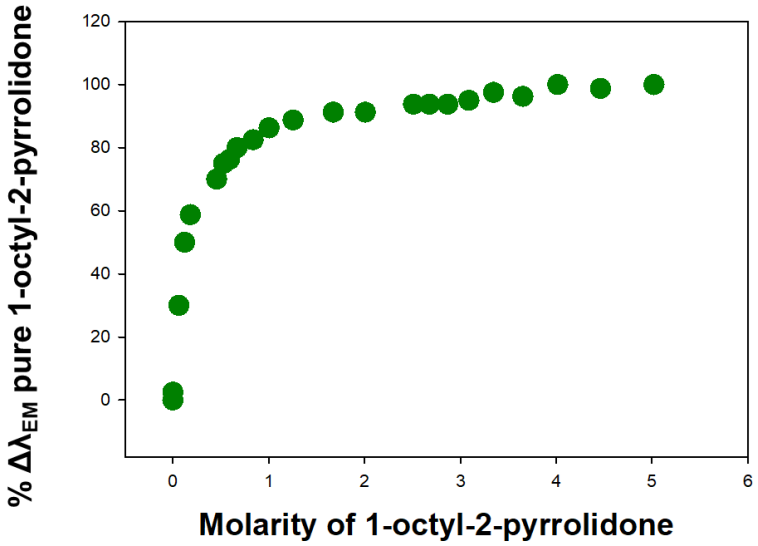
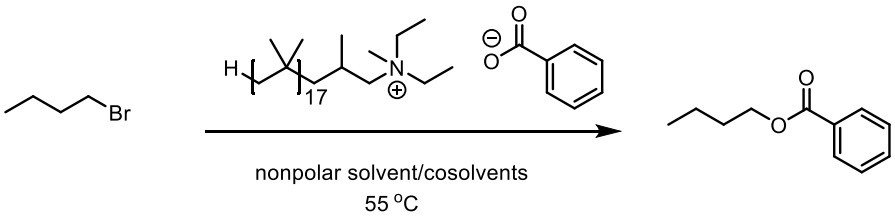


Figure 5.12. Solvatochromic shift of Nile Red with 1-octyl-2-pyrrolidone as cosolvents into PAO_{432}.

Table 5.4. Effects of solvent on the S_N2 reaction of 1-bromobutane with *N*,*N*-diethyl-*N*-methylammonium terminated PIB oligomers with benzoate anion.



Solvent	Rate constant (1/ M·s)
Heptane[102]	0.0023
Heptane (this work)	0.0018
PAO_{506}	TBD
PAO_{506}/1-octyl-2-pyrrolidone (0.5 M)	TBD
PAO_{506}/1-octyl-2-pyrrolidone (0.25 M)	TBD
PAO_{506}/1-octyl-2-pyrrolidone (0.12 M)	TBD
PAO_{506}/1-octyl-2-pyrrolidone (1 M)	0.0061
1-octyl-2-pyrrolidone (4.6 M, neat)	TBD

CHAPTER VI

EXPERIMENTAL SECTION

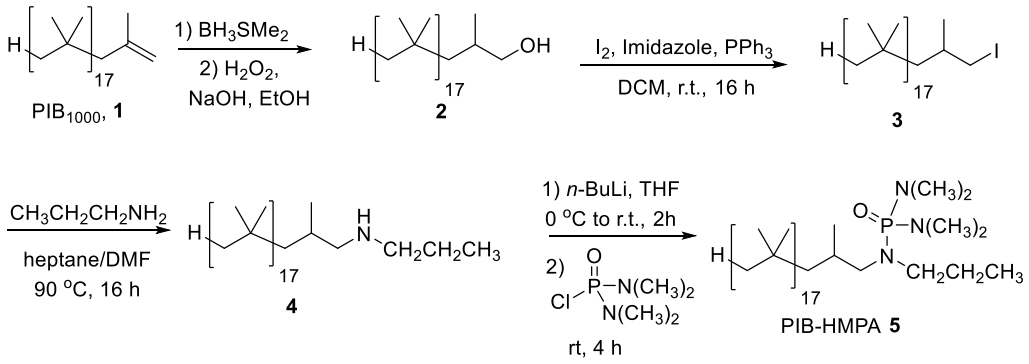
General Experimental

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Dichloromethane (DCM) was purified using a SPBT-1 Bench Top Solvent Purification System before use. Alkene-terminated PIB with a molecular weight (M_n) of 1000 Da is commercially available and was obtained from Texas Polymer Corp.[112] The poly(α-olefin) (PAO) solvent used had a reported molecular weight (M_n) of 432 Da and was obtained from Exxon Mobil.[224] ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian 500 MHz spectrometer interfaced to a Linux computer and were worked up using VNMR-J software and on Bruker Avance Neo 400 instruments. Chemical shifts are reported in ppm and referenced to the residual proton in $CDCl_3$, and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), and m (multiplet). For ^{31}P NMR spectroscopy, phosphoric acid (85 wt% in H_2O) at 0 ppm was used as an external standard. Infrared spectra (IR) were recorded on a Shimadzu IRAffinity-1S IR spectrophotometer. UV-visible spectra were recorded using a Shimadzu UV-2600 UV-visible spectrophotometer. A multi-detector Viscotek gel permeation chromatograph (GPC) and a Viscotek LT400L column was used to analyze the molecular weight of the polymer products at a flow rate of 1 mL/m using THF as the eluent. A value for dn/dc = 0.093 was utilized to calculate the PIB molecular weight and molecular weight distribution.[225] A value for dn/dc of 0.107 was used to calculate the PNIPAM molecular weight and molecular weight distributions.[226] The GPC data analysis was carried out

using Omnisec software version 4.7. Gas chromatography analyses were performed on a Shimadzu instrument equipped with a 15-m SPB-5 fused-silica capillary column. Fluorescence spectra were measured on Horiba FluorEssenceTM fluorescence spectrometer. ICP-MS analyses were performed using a PerkinElmer NexION 350 ICP-MS spectrometer.

Synthesis and Experimental Procedures

Synthetic scheme of PIB-bound HMPA:



Hydroxy-Terminated PIB Oligomer 2. Compound **2** was prepared using a reported procedure[124] which yielded 9.98 g of 2 (98% yield). ^{1}H NMR ($CDCl_3$) δ: 0.75−1.46 (m, 208H), 3.33 (dd, 1H), 3.50 (dd, 1H). ^{13}C NMR ($CDCl_3$) δ: 19.7, multiple peaks between 29.1 and 38.3, 49.5, multiple peaks between 56.8 and 59.6, 69.7.

Iodide-Terminated PIB Oligomer 3. Compound **3** was prepared using a reported procedure[124] on a 26 g scale to afford 3 as a viscous oil (89% yield). ^{1}H NMR ($CDCl_3$) δ: 1.00−1.43 (m, 220H), 3.13 (dd, 1H), 3.27 (dd, 1H). ^{13}C NMR ($CDCl_3$) δ: 20.8, 23.9, multiple peaks between 29.1 and 38.3, 52.7, multiple peaks between 56.9 and 59.4.

Propylamine-Terminated PIB Oligomer 4. To a 50 mL heptane solution of iodide-terminated PIB oligomer (**3**) (20 g, 20 mmol) was added a 50 mL DMF solution of propylamine (18 mL, 200 mmol) to form a biphasic reaction mixture. Upon heating to 90 °C, the biphasic mixture became single phase. After 24 h, the reaction mixture was cooled to room temperature to reform a biphasic mixture. The two layers were separated, and the heptane phase was washed with DMF (2 × 25 mL), water (2 × 25 mL), and brine (1× 25 mL). The heptane layer was then dried with $MgSO_4$, and the solvent was removed under reduced pressure using a rotary evaporator. The product viscous oil was purified by column chromatography (Brockmann aluminum oxide) to afford 19.2 g of 4 (96% yield). ^{1}H NMR ($CDCl_3$) δ: 1.00−1.41 (m, 308 H), 2.18 (1H), 2.31 (dd, 1 H), 2.48 (dd, 1 H), 2.53 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ: 11.8, 14.0, 21.3, 22.7, 23.2, multiple peaks between 29.0 and 38.1, 47.3, 51.7, 51.9, multiple peaks between 58.4 and 59.5.

PIB-HMPA 5. Propylamine-terminated PIB oligomer **4** (9.93 g, 9.9 mmol) was dissolved in 50 mL of anhydrous THF and allowed to react with. 5 mL of ^{n}BuLi (2.5 M) which was added dropwise. The reaction solution was allowed to stir for 2 h at room temperature. Then *N*,*N*,*N'*,*N'*-tetramethylphosphorodiamidic chloride (2 mL, 14 mmol) was added and the reaction mixture was stirred for 6 h at room temperature. The solvent was then removed under reduced pressure using a rotatory evaporator until ca. 10 mL of reaction residue remained. This viscous residue was then added to a 40-fold excess volume of cold methanol. The supernatant MeOH was removed by decantation. The insoluble oil that remained was re-dissolved in 10 mL of THF. A second solvent trituration using a 40-fold excess volume of cold methanol to afford the desired product. The MeOH was again

removed and the viscous residue was collected and dried under vacuum overnight to afford 7.89 g of 5 as a dark orange oil. ^{1}H NMR ($CDCl_3$, δ): 2.62-2.87 (m, 16H), 1.0-1.41 (m, 272H). ^{13}C NMR ($CDCl_3$, δ): 11.6, 14.1, multiple peaks between 20.6 and 32.5, 34.6, 35.9, multiple peaks between 36.0 and 38.2, 45.8, multiple peaks between 51.1 and 59.5. ^{31}P NMR ($CDCl_3$, δ): 25.3 ppm. GPC data: M_n = 1,700 g·mol^{-1}, M_w = 2,800 g·mol^{-1}, Đ = 1.65. The exact amount of the phosphoramide per gram was determined by ^{1}H NMR spectroscopy using dichloroethane as an internal standard and varied from 0.4 to 0.25 mmol/g.

Phase Selectivity Solubility of Catalyst 5 in PAO_{432} or heptane versus MeOH. 0.25 g of **5** was dissolved in 2 mL of PAO_{432}. Then the PAO_{432} phase was vigorously mixed with 2 mL of 0.03 M of H_3PO_4 in MeOH for 48 h. The biphasic mixture was transferred into a centrifuge tube and underwent a 15-min centrifugation. 0.4 mL of the MeOH and PAO_{432} phase was taken individually and directly analyzed by ^{31}P NMR spectroscopy. The phase selectivity of **5** in heptane with MeOH was also studied and analyzed via the same procedure. The catalyst **5** showed high phase selectivity solubility in PAO_{432} (>99.9 %) and the MeOH phase showed no detectable signal from **5**. The internal standard H_3PO_4 also had no leaching to the PAO_{432}. However, a phase selectivity solubility of **5** in heptane versus MeOH showed ca. 4.8% 5 leached from heptane to the MeOH phase.

Phase Selectivity Solubility of Catalyst 5 and 1-phenylbut-3-en-1-ol in PAO_{432} versus MeCN. 0.25 g of **5** was dissolved in in 2 mL of PAO_{432} and vigorously mixed with 2 mL of 0.5 M of 1-phenylbut-3-en-1-ol in MeCN for 1 min. The biphasic mixture was transferred into a centrifuge tube and underwent a 15-min centrifugation. An aliquot (100

μL) was taken from both the MeCN and PAO_{432} phase and analyzed by ^1H NMR spectroscopy in $CDCl_3$ using 0.2 M of dichloroethane as an internal standard. The amount of **5** that leached into the MeCN phase was calculated to be <0.1 % and the amount of leaching of 1-phenylbut-3-en-1-ol into the PAO_{432} phase was calculated to be 1.6 % based on ^1H NMR spectroscopy.

Typical Procedure for Kinetic Studies of Allylation of Benzaldehyde. For the kinetic studies, benzaldehyde (0.1 mL, 1 mmol), DIPEA (0.5 mL), and catalyst **5** (0.25 g, 0.1 mmol) were dissolved in 2 mL of CH_2Cl_2. HMPA or **5** was then added at a concentration of 10 mol% (0.1 mmol of an HMPA equivalent). Allyltrichlorosilane (0.29 mL, 2 mmol) was then added into the reaction mixture. The reaction was stirred at room temperature and aliquots (50 μL) of the reaction mixture were removed at different time intervals. Each aliquot was diluted with 1 mL of CH_2Cl_2 and washed with 1 mL of aqueous ammonium chloride (NH_4Cl). The mixture was separated by centrifugation, the two phases were separated, and the CH_2Cl_2 phase was concentrated at reduced pressure using a rotary evaporator. The residue dissolved in $CDCl_3$ and analyzed by ^1H NMR spectroscopy.

Benzaldehyde Allylation and Recycling of Catalyst 5. A scintillation vial containing a solution of benzaldehyde (0.1 mL, 1 mmol), DIPEA (0.5 mL), catalyst **5** (0.25 g, 0.0625 mmol) and PAO_{432} (2 mL) was prepared. Allyltrichlorosilane (0.29 mL, 2 mmol) was added into the reaction mixture via a syringe. After 24 h stirring, the reaction was quenched by adding 5 mL of MeCN. The reaction mixture was then transferred into a centrifuge tube the phases separated with a 15 min centrifugation. The bottom layer (MeCN phase) separated and the conversion was analyzed as described above. The PAO

phase was washed with 5 mL of NaOH (4 N) and returned to a scintillation vial for the next cycle. To isolate the product, the MeCN phase from the five cycles was combined, the solvent was removed at reduced pressure and the crude 1-phenylbut-3-en-1-ol was purified by a column chromatography. The product was all characterized by ^{1}H, ^{13}C NMR and IR spectroscopy.

1-Phenylbut-3-en-1-ol: The product was isolated by flash chromatography (CH_2Cl_2/hexanes = 8/1, v/v) as colorless liquid (0.6 g, 0.12 g of product/cycle (81%)). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.19 (1H), 2.53 (m, 2H), 4.74 (m, 1H), 5.17 (m, 2H), 5.82 (m, 1H), 7.27-7.37 (m 5H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 43.7, 73.3, 118.3, 125.7, 127.5, 128.3, 134.4, 143.8. IR (neat) data: 3386, 3066, 3031, 2909, 1641 cm^{-1}.

Lewis Base-Catalyzed Allylation of Other Aromatic aldehydes. These reactions were all carried out on a 0.1 mmol scale following the procedure used for benzaldehyde. **5** used here was the other batch from the experiment of benzaldehyde allylation and recycling of catalyst **5**. The HMPA amount was calculated accordingly (0.25 g, 1mmol). Products from the combined MeCN phases from 5 cycles were further purified by a column chromatography and characterized by ^{1}H, ^{13}C NMR and IR spectroscopy.

1-(*p*-Tolyl)but-3-en-1-ol: ^{1}H NMR (500 MHz, $CDCl_3$, δ): The product was isolated by a flash chromatography (EA/hexanes = 1/4, v/v) as colorless liquid (0.57 g, 0.11 g of product/cycle (70 %)). 1.97 (d, J = 3Hz, 1H), 2.35, (br, s, 3H), 2.51 (m, 2H), 4.71 (m, 1H), 5.14 (m, 2H), 5.81 (m, 1H), 7.16 (d, J = 8 Hz, 2H), 7.25 (d, J = 8 Hz, 2H). ^{13}C NMR (125

MHz, $CDCl_3$, δ): 21.1, 43.7, 73.2, 118.2, 125.7, 129.1, 134.6, 137.2, 140.9. IR (neat) data: 3391, 3076, 2935, 2929, 2924, 1640, 1514 cm^{-1}.

1-(4-Methoxyphenyl)but-3-en-1-ol: The product was isolated by a flash chromatography (EA/hexanes = 1/4, v/v) as yellow liquid (0.6 g, 0.12 g of product/cycle (67 %)). ^1H NMR (500 MHz, $CDCl_3$, δ): 1.96 (s, 1H), 2.51 (m, 2H), 3.81 (s, 3H), 4.69 (m, 1H), 5.14 (m, 2H), 5.79 (m, 1H), 6.88 (d, J = 8.5 Hz), 7.28 (d, J = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 43.7, 55.2, 72.9, 113.7, 118.1, 127.0, 134.6, 136.0, 158.9.IR (neat) data: 3428, 3076, 2972, 2932, 1611, 1512 cm^{-1}.

1-(4-fluorophenyl)but-3-en-1-ol: The product was isolated by a flash chromatography (EA/hexanes = 1/5, v/v) as yellow liquid (0.63 g, 0.13 g of product/cycle (75 %)). ^1H NMR (500 MHz, $CDCl_3$, δ): 2.04 (s, 1H), 2.48 (m, 2H), 4.72 (m, 1H), 5.16 (m, 1H), 5.79 (m, 1H), 7.03 (m, 2H), 7.32 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 43.9, 72.6, 115.1, 115.2, 118.6, 127.4, 127.5, 134.1, 139.5, 161.1, 163.1. IR (neat) data: 3393, 3077, 2976, 2934, 1641, 1603, 1509 cm^{-1}.

Reduction of Various α,β-Unsaturated Carbonyl Compounds by 5 in PAO_{432} and Catalyst Recycling. A 10-mL round-bottomed flask containing α,β-unsaturated carbonyl compounds (0.5 mmol), ethyl acetate (0-3.4 M), **5** (0.25 g, 0.1 mmol) and PAO_{432} (2 mL) was prepared. Trichlorosilane (0.1 mL, 1 mmol) was then added into the reaction mixture via a syringe under N_2. The reaction was monitored by TLC. After the starting material was consumed or no significant change was observed, the cosolvent EtOAc was removed at reduced pressure using a rotary evaporator. Then 5 mL of MeCN was introduced to

form a biphasic mixture of **5** in PAO_{432} and the product in MeCN. A 15-min centrifugation separated the phases. The PAO phase was washed with 5 mL of NaOH and reused as described above. The bottom MeCN phase was analyzed as described above to determine conversions and the products were either directly analyzed or purified by a silica gel column chromatography. In the reduction of benzylideneacetone, the reduced product from the combined MeCN phases from 6 cycles was obtained after solvent removal and purified by a column chromatography and analyzed by ^{1}H, ^{13}C NMR and IR spectroscopy.

4-Phenyl-2-butanone: The product was isolated by a flash chromatography (EA/hexanes = 1/4, v/v) as colorless liquid (0.37 g, 0.061 g of product/cycle (83 %)). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.12 (s, 3H), 2.74 (t, J = 7.5 Hz, 2H), 2.88 (t, J = 7.5 Hz, 2H), 7.16 (m, 3H), 7.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 29.7, 30.0, 45.1, 126.1, 128.2, 128.4, 140.9, 207.8. IR (neat) data: 3027, 2959, 1714, 1602 cm^{-1}.

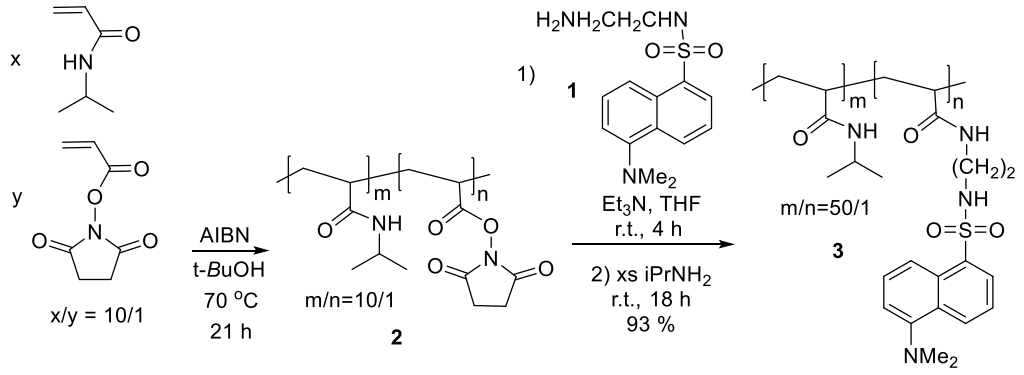
1,3-Diphenylpropan-1-one: The product was directly characterized as a white solid (105 mg, >99%) without a further purification removal of MeCN. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.07 (t, J = 7.5 Hz, 2H), 3.31 (t, J = 7.5 Hz, 2H), 7.19-7.31 (m, 5H), 7.45 (t, J = 10 Hz, 2H), 7.56 (t, J = 10 Hz, 1.25 Hz, 1H), 7.96 (d, J = 10 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 30.1, 40.4, 126.1, 128.0, 128.4, 128.5, 128.6, 133.0, 136.8, 141.3, 199.2. IR (neat) data: 3074, 3024, 2951, 2922, 1680, 1595 cm^{-1}.

(E)-1,5-Diphenylpent-1-en-3-one: The product was isolated by a flash chromatography (EA/hexanes = 1/15, v/v) as a colorless liquid (95 mg, 80 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.01 (s, 4H), 6.74 (d, J = 16 Hz, 1H), 7.19-7.25 (m, 3H), 7.28-7.32 (m, 2H), 7.38-7.41

(m, 3H), 7.52-7.56 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 30.1, 42.4, 126.0, 126.1, 128.2, 128.3, 128.5, 128.9, 130.4, 134.4, 141.2, 142.6, 199.2. IR (neat) data: 3057, 3028, 2918, 1681, 1608, 1573, 1558 cm^{-1}.

4-(2,6,6-Trimethylcyclohex-1-en-1-yl)butan-2-one: The product was directly characterized as a yellow oil (95 mg, 98%) without a further purification after removal of MeCN. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 0.96 (s, 6H), 1.39 (m, 2H), 1.55 (m, 5H), 1.89 (m, 2H), 2.12 (s, 3H), 2.h24 (t, J = 7.5 Hz, 2H), 2.48 (t, J=7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 19.3, 19.6, 22.1, 28.3, 29.7, 32.6, 34.9, 39.6, 44.4, 127.7, 135.8, 208.9. IR (neat) data: 2954, 2927, 2866, 1716 cm^{-1}.

Synthetic scheme of Synthesis of PNIPAM-co-PNASI 2 and a dansyl-labeled PNIPAM 3 from the ethylene diamine derivative of dansyl (1).:



Synthesis of Dansyl-Labeled Amine 1. Ethylene diamine (3.2 mL, 55.2 mmol) was dissolved in DCM (15 mL) in a round-bottomed flask and cooled to 0 °C using an ice bath. Dansyl chloride (0.504 g, 1.9 mmol) was dissolved in DCM (8 mL) and added dropwise into the ethylene diamine solution. This reaction mixture was allowed to stir overnight at

room temperature. Then aqueous hydrochloric acid (1M) was the added. The organic phase was separated and the aqueous phase was washed with 3 20-mL portions of DCM. The combined organic phases were then dried with $MgSO_4$. The DCM was then removed at reduced pressure using a rotary evaporator to afford a greenish solid polymer product. Yield: 0.4 g (72 %) mp: 144.6-147.9 ^oC. ^1H NMR (500 MHz, $CDCl_3$, δ): 8.52 (d, J= 9 Hz, 1H), 8.31 (d, J= 9Hz, 1H), 8.23 (d, J= 7.5, 1H), 7.52 (m, 2H), 7.16 (d, J= 7.5 Hz, 1H), 2.916 (m, 2H), 2.87 (s, 6H), 2.72 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 151.96, 134.63, 130.38, 129.87, 129.58, 128.38, 123.16, 118.73, 115.19, 45.39, 45.12, 40.73.

Synthesis of PNIPAM$_m$-*co*-PNASI$_n$ 2, m/n=10/1. *N*-Acryloxysuccinimide (NAS) (0.9 g, 5.3 mmol) was prepared using a literature procedure[30] and was added to a two-necked round-bottomed flask along with *N*-isopropylacrylamide (NIPAM) (6 g, 53 mmol) and azoisobutyronitrile (AIBN) (46.4 mg, 0.28 mmol). The flask was sealed with a rubber septum and was then flushed with N_2 for 1 h. Then *tert*-butyl alcohol (50 mL) was transferred into the flask and the solution was degassed by nitrogen exchange for 30 min. The reaction mixture was then heated up to 70 ^oC and stirred for 16 h under a nitrogen flow. The polymerization was cooled to room temperature and the *tert*-butyl alcohol was removed at reduced pressure using a rotatory evaporator. The crude copolymer product solid was then redissolved in 20 mL of DCM and precipitated by addition to 400 mL of cold hexane. The product copolymer (5.99 g) was collected by a vacuum filtration and dried under vacuum overnight. ^1H NMR (500 MHz, $CDCl_3$, δ): 4.00 (br s, 2.5H), 2.87 (br s, 1H), 1.54-5.17 (m, 7.5H), 1.13-1.27 (br s, 15H). This polymer was not analyzed by GPC

because of it contained reactive NASI residues. GPC and molecular weight data for its derivatives though are reported below.

Synthesis of Dansyl-Labeled PNIPAM 3. A solution of 3.2 g of copolymer **2** in 30 mL of anhydrous THF was prepared in a 100 mL round-bottomed flask. Then 144 mg (0.49 mmol) of amine **1** and triethylamine (0.51 mL, 3.66 mmol) in 30 mL of THF were added. After stirring for 4 h, isopropylamine (0.4 mL) was added to consume any unreacted NAS groups. After 18 h, the resulting suspension was filtered and the THF was removed at reduced pressure using a rotatory evaporator. The resulting crude product was dissolved in ca. 10 mL of THF and precipitated in 400 mL of cold diethyl ether. The product pale-yellow polymer product (2.81 g) was collected by a vacuum filtration and dried under vacuum overnight. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.00 (br s, 33H), 2.88 (br s, 4H), 2.75 (br s, 1H), 1.36-2.12 (m, 100H), 1.13 (br s, 200H). GPC data: M_n = 11,900 g·mol^{-1}, M_w = 12,000 g·mol^{-1}, Đ = 1.01.

Synthesis of PNIPAM-Bound Diphenylphosphine 4. Copolymer **2** (1.73 g) was added to a 100-mL round-bottomed flask and the flask was flushed with N_2 for 30 min. Then 50 mL of degassed THF was transferred via syringe into the flask. After the polymer dissolved, DPPA (73.4 mg, 0.3 mmol) in 10 mL of THF was added. The reaction mixture was allowed to stir for 5 h at which point 0.25 mL of isopropylamine (0.25 mL, 3 mmol) was added. The reaction mixture was stirred for an additional 12 h at which point any precipitates were separated by centrifugation. The filtrate solution containing the polymer product was then concentrated at reduced pressure using a rotary evaporation. The crude copolymer **4** was further purified by precipitation using 400 mL of degassed hexanes that

was cooled to 0 ℃ using an ice bath. The precipitated copolymer **4** was isolated by filtration and dried under vacuum overnight to give 1.42 g of a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.38 (br s, 3H), 7.30 (br s, 4H), 3.98 (br s, 33H), 3.12 (14H), 2.72 (1H), 1.32-2.09 (m, 100H), 1.12 (br s, 200H). ^{31}P NMR (200 MHz, $CDCl_3$, δ): −16.68 ppm. GPC data: M_n = 9,990 g·mol^{-1}, M_w = 10,400 g·mol^{-1}, Đ = 1.04.

Synthesis of PNIPAM-bound Rh(I) catalyst 5. A solution of copolymer **4** (400 mg) in 30 mL of degassed DCM was prepared. To this was added a solution of $[RhCl(COD)_2]_2$ (11.6 mg, 0.024 mmol) in 8 mL of degassed dichloromethane. The resulting yellow solution was stirred for 4 h and the solvent was removed at reduced pressure using a rotatory evaporator. The crude product was dissolved in ca. 2 mL of degassed DCM and added to 100 mL of cold degassed diethyl ether. The product PNIPAM-bound Rh(I) catalyst **5** was collected by a vacuum filtration as a yellow solid and dried under vacuum overnight before use to obtain 400 mg of polymer **5**.

Representative Procedure for Solubilization of PNIPAM in Different Solvents. To evaluate the amount of carboxylic acid cosolute required to dissolve PNIPAM in a given solvent, 250 mg of PNIPAM that would have 2.2 equivalent acrylamide units was placed in two vials separately with 10 mL of toluene. Acetic acid (0.13 mL, 2.2 mmol), octanoic acid (0.35 mL, 2.2 mmol) were added such that there would be one equivalent of the acid/acrylamide repeating unit. Each PNIPAM solution was stirred at room temperature for 30 min in the given solvent. If the PNIPAM solid was still present a vial, an additional equivalent of acid was added. This process was repeated until there visually was no solid left. We also carried out quantitative fluorescence experiments with octanoic acid where

1 equivalent of octanoic acid per acrylamide repeating unit was used for solubilization of the dansyl-labeled polymer **3** and showed that extended sonication times did not change the extent of solubilized polymer **3**.

Repeated Dissolution/Precipitation of Dansyl-Labeled PNIPAM 3 in Heptane. Polymer **3** (333 mg, 2.9 equivalents of the acrylamide repeating units) was added to a 50-mL centrifuge tube along with 10 mL of heptane. The centrifuge tube was placed in sonication bath for 10 m. The sample was then centrifuged for 15 min (3000 rpm). An aliquot (2 μL) of the supernatant was removed and diluted with 12 mL of DCM to analyze the solution for any fluorophore that dissolved before octanoic acid was added. This same centrifuge tube was then treated with 0.9 mL (5.66 mmol) of octanoic acid. The solution was sonicated for 30 min at which point all solids had visibly dissolved. Then 2 μL of the solution was removed and diluted in 12 mL of dichloromethane to measure the fluorescence intensity of the solubilized dansyl-labelled PNIPAM **3**. Then triethylamine (0.85 mL, 6.09 mmol) was added to the solution. Solids began to form immediately. This reaction was then mixed using a Vortex mixer for ca. 30 s. At that point the suspension was centrifuged and 2 μL of the supernatant removed and added to 12 mL of dichloromethane to determine how much of the fluorescent polymer **3** remained in solution. The rest of the supernatant was decanted from the precipitate and the precipitate was washed with 10 mL of fresh heptane. The resulting solid was then used in a subsequent cycle of solubilization and precipitation. The fluorescence analyses for each step in each cycle used an excitation wavelength of 354 nm. The emission in the 375-600 nm was analyzed with the λ_{EM} maximum typically occurring at 498 nm.

Repeated Dissolution/Precipitation of Dansyl-Labeled PNIPAM 3 in Toluene. These experiments used the same procedure used with heptane with the exception that 0.57 mL of octanoic acid and 0.5 mL of trimethylamine were used to solubilize or precipitate polymer **3**. This experiment also included a gravimetric analysis of the polymer **3** that did not precipitate with the Et_3N treatment. That experiment combined the supernatant after reprecipitation of polymer 3 for each of the five dissolution/precipitation cycles. The result show that a total of 0.032 g of polymer 3 was lost over five cycles, a loss per cycle of 0.006 g (ca. 2% per cycle) cycle.

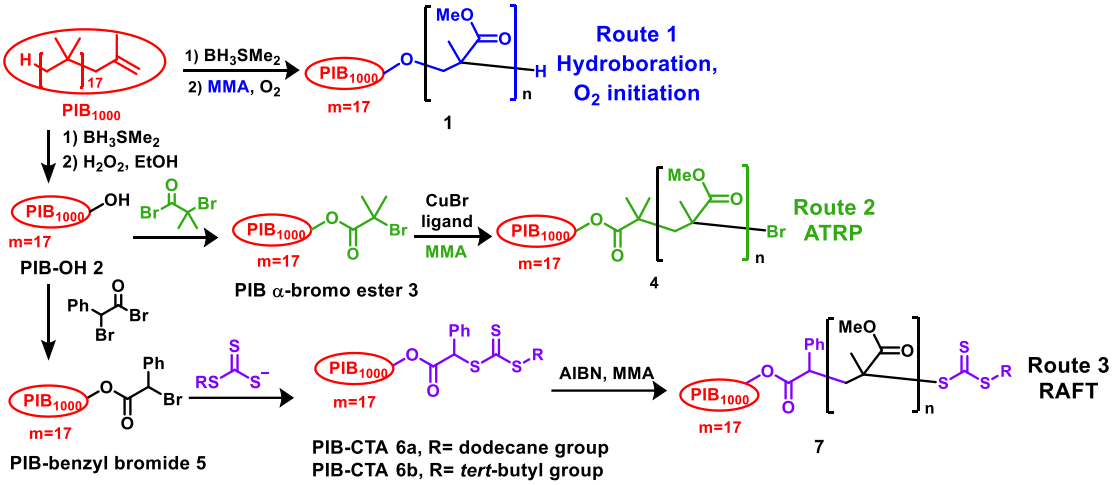
General Procedure for Hydrogenation using PNIPAM-bound Rh(I) Catalyst 5 in Toluene. A septa-sealed scintillation vial containing catalyst **5** (333 mg) was prepared an flushed with N_2. Then 8 mL of a solution of 0.45 mL of octanoic acid in degassed toluene was introduced via a syringe. The scintillation vial was then placed in a sonication bath under a N_2-filled balloon for approximately 1-h sonication until polymer **5** was fully dissolved. The resulting yellow solution was then transferred into a Schlenk reaction flask with an adapter leading to a H_2 gas buret. The reaction flask was flushed with hydrogen 4 times. Then 2 mL of toluene containing 1-decene (0.37 mmol) and cyclooctane (0.37 mmol) was added to this flask. The final reaction volume was 10 mL. The temperature of the reaction was controlled through a water bath and kept between 23 and 25 ^oC. The H_2 uptake volume over the first 3 h of the reaction was measured using a constant stirring rate for the reaction mixture to monitor the rate of the hydrogenation. To confirm that hydrogenation proceeded, an aliquot of the reaction mixture was taken and analyzed by GC. After the reaction was done, the reaction solution was transferred to a centrifuge tube

using a syringe. The catalyst **5** was then precipitated out by treating the reaction mixture with triethylamine (0.3 mL, 2.15 mmol) and DMF (0.19 mL, 2.52 mmol). The precipitate that formed was separated from the solution with 15 min of centrifugation (3000 rpm). The supernatant was decanted and the recovered catalyst was washed with 10 mL of fresh degassed toluene. After drying the recovered polymer under vacuum overnight, a second hydrogenation cycle was carried out in the same fashion.

Digestion Procedure for ICP-MS Analyses. The sample to be analyzed was added to a glass vial along with 2 g of concentrated nitric acid. The mixture was heated to 120 °C for 24 h. At this point, 2 g of concentrated sulfuric acid was added, and the system was heated again to 120 °C for 24 h. The clear solution that formed was then allowed to cool to room temperature and was diluted with 1% nitric acid aqueous solution as necessary to produce an ICP-MS analysis sample. The diluted sample solution was then analyzed using ICP-MS, which allowed us to determine the ppm of the metal in the diluted ICP-MS sample, which could be converted by simple math into micrograms of metal/grams of the analysis sample (ppm).

(continued)

Synthesis of block copolymers derived from polyisobutylene oligomers



Synthesis of PIB-bound oligoacrylates via hydroboration/O_2 initiation

Grafting from radical polymerizations that used borane/O_2 initiation starting from vinyl-terminated PIB included two steps: hydroboration and oxygen-induced radical polymerization. Two approaches were tried. The first used excess oxygen relative to the tris(polyisobutylborane) intermediate (See Table 4.2). The second used a deficiency of oxygen in order to diminish overoxidation of boranes to boronates and borates which are poor initiators for polymerizations.[203] The following procedure using the synthesis of PIB-*b*-PMMA is an illustrative example of the second procedure. To a flask containing a solution of vinyl-terminated PIB_{1000} (5 mmol, 5 g) in THF (15 mL) was added BH_3-SMe_2 (1.66 mmol, 0.16 mL). The resulting reaction mixture was allowed to stir at room temperature for 2 h. Then methyl methacrylate (50 mmol, 5.3 mL) was added into the reaction mixture. Oxygen (0.325 mmol, 7.8 mL) was introduced by injecting oxygen gas by syringe underneath the solution surface. After 16 h, any unreacted acrylate monomer

and solvents were removed under reduced pressure. The residue was then dissolved in a minimal amount of THF and the resulting solution was added to excess cold hexane. The hexane phase was separated from the solid precipitate that formed and the hexane was removed. ^{1}H NMR spectroscopy was used to determine if there were hexane any soluble block copolymer present. In the event, the only block copolymer product formed was hexane insoluble unless *tert*-butyl acrylate was used as the graft monomer. The yields of the block copolymer in these reactions varied from 15-40%. Other experiments compared the effect of using a deficiency (6.5 mol% oxygen) versus using excess oxygen using a different PIB monomer – PIB_{2300} (M_n = 2300 Da). In that case, the yield of block copolymer product using MMA was more modest with most of the starting polyisobutylene being isolated as a hydroxyl terminated PIB oligomer after workup in air. When excess oxygen was used with this same monomer, most of the tris(polyisobutyl)-borane was oxidized to form a PIB containing an alcohol terminal group. The yield of block copolymers was even less than when a deficiency of oxygen was used (See Table 4.2). Regardless of whether PIB_{1000} or PIB_{2300} were used and regardless of whether a deficiency of oxygen or an excess of oxygen was used, the ratio of the MMA repeating units in block polymers relative to the PIB repeating units was large as determined by ^{1}H NMR spectroscopy. That analysis used the normalized ratio of the integrals for signals in the 1.08-1.14 δ region (two methyl groups on PIB backbone, 6H) and the 3.55-3.63 δ region (methoxy groups on PMMA, 3H) in the ^{1}H NMR spectrum of the product.

Synthesis of PIB-α-bromo ester 3

PIB–OH **2** was made from vinyl-terminated PIB_{1000} based on a reported procedure.[124] To a solution of PIB–OH **2** (10 mmol, 10 g), triethylamine (12 mmol, 1.7 mL) in anhydrous THF (40 mL), α-bromoisobutyryl bromide (12 mmol, 1.5 mL) was added dropwise at 0 °C. The reaction mixture was then stirred for 16 h at room temperature. The triethylammonium bromide precipitate was removed by filtration. Then ethyl acetate was added to the filtrate. The combined organic phase was washed with deionized water three times and then with brine. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure using a rotary evaporator. The crude product was further purified by flash column chromatography on silica gel with hexane-acetate (40:1) as an eluent to provide 9.3 g of the desired product. ^{1}H NMR ($CDCl_3$) 1.08-1.14 (m, 112H), 1.26-1.40 (m, 49 H), 1.94 (s, 6H), 3.89 (dd, J = 7 Hz, J = 10.5 Hz, 1H) 4.04 (dd, J = 7 Hz, J = 10.5 Hz, 1H). The ^{1}H NMR spectrum also contained a trace of hexanes based on the presence of signals in the 0.8-1.0 δ range.

General synthesis of PIB-bound oligoacrylates via ATRP

The following procedure using the synthesis of PIB-*b*-PMMA is an illustrative example of this approach to ATRP grafting from a terminally functionalized PIB oligomer. A solution of PIB-α-bromo ester **3** (1.2 mmol, 1.2 g), MMA (12 mmol, 1.3 mL), *N,N,N',N'*-tetraethyldiethylenetriamine (0.12 mmol, 31 μL), and THF (5 mL) were degassed by three freeze–pump-thaw cycles. Then CuBr(I) (0.12 mmol, 19 mg) was added to a three-necked

round-bottomed flask sealed with rubber septa and that flask was then flushed with N_2 for 30 min. The degassed solution of the monomer, the PIB-bound initiator and the ligand in THF was then injected into this three-necked round-bottomed flask and the reaction mixture was heated to 70 $^{\circ}$C. The reaction was stirred for 16 h, then cooled to room temperature and exposed to air to quench the reaction. THF was then added to the reaction mixture and the reaction mixture was passed through a basic aluminum oxide column in order to remove all copper and ligand complexes. The solvent was removed at reduced pressure and the crude product was dissolved in a minimal amount of THF and added to a 40-fold excess volume of cold hexane. A precipitate that formed was collected by a vacuum filtration. If the hexane phase were cloudy due to incomplete filtration, centrifugation was used to separate any solids. The hexane was then removed from the clear filtrate or supernatant at reduced pressure to isolate any hexane soluble products. Results for these reactions are listed in Table 4.3.

Synthesis of PIB-benzyl bromide 5

To a solution of α-bromophenylacetic acid (9.2 mmol, 2 g), DMF (cat. amount, few drops), and THF (10 mL), oxalyl chloride (10.2 mmol, 0.86 mL) was added in an ice bath. The resulting reaction mixture was allowed to stir for 1 h. The solvent and excess oxalyl chloride were removed at reduced pressure to afford α-bromophenylacyl chloride. The crude product was then dissolved in THF (5 mL) and allowed to react with PIB-OH (11 mmol, 11 g) in THF (10 mL) and triethylamine (11 mmol, 1.54 mL) at room temperature

for 16 h. The ammonium salts that formed were removed by filtration and ethyl acetate (15 mL) was added into the filtrate. The resulting solution was washed with deionized water three times and brine. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under a reduced pressure to yield 11 g of a light-yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.08-1.14 (m, 149H), 1.26-1.40 (m, 58 H), 1.91 (bs, 1H), 3.90 (m, 1H) 4.03 (m, 1H), 5.37 (s, 1H), 7.39 (t, J = 8 Hz, 3H), 7.52 (dd, J = 1.5 Hz, J = 8 Hz, 1H), 7.57 (dd, J = 1.5 Hz, J = 8 Hz, 1H). The ^{1}H NMR spectrum also contained a trace of hexanes based on the presence of signals in the 0.8-1.0 δ range.

Synthesis of PIB-CTA 6a

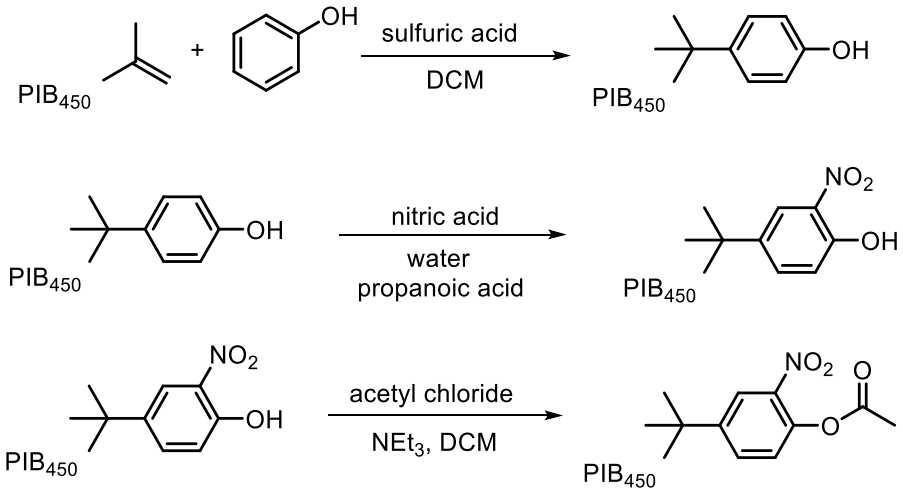
A solution of 1-dodecanethiol (4.9 mmol, 1.17 mL) in THF (15 mL) containing NaOH (6 mmol, 0.24 g) in water (1 mL) was prepared. After 1 h, the solution was cooled to 0 $^\circ$C using an ice bath and carbon disulfide (6 mmol, 0.36 mL) was slowly added. The mixture was stirred for 1 h at which point the resulting orange solution was treated with polyisobutyl 2-bromophenylacetate (**5**) (6 mmol, 6 g). The resulting mixture was allowed to warm to ambient temperature. After stirring for 16 h, the suspension was filtered to remove sodium bromide. The dark orange filtrate was washed with deionized water three times and washed with 10 mL of brine. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed at reduced pressure using a rotary evaporator to afford a dark orange crude product. This crude product was further purified by flash column chromatography on silica gel using hexane as an eluent to afford a dark orange oil (4.77

g). ^{1}H NMR spectrum ($CDCl_3$) 0.99-1.12 (m, 121H), 1.26-1.41 (m, 64 H), 1.64-1,72 (m, 2H), 1.86 (m, 1H), 3.31-3.36 (t, 2H), 3.38-3.86 (dd, J = 7 Hz, J = 10.5 Hz, 1H), 3.95-3.99 (dd, J = 7 Hz, J = 10.5 Hz, 1H), a pair of roughly equally intense singlets at 5.81 and 5.82 (due to the diastereotopic benzylic proton attached to the thioester), 7.34-7.41 (m, 3H), and 7.42-7.44 (m, 2H). The ^{1}H NMR spectrum also contained a trace of hexanes based on the presence of signals in the in the 0.8-1.0 δ range.

General synthesis of PIB-bound oligoacrylates via RAFT

The following procedure describing the synthesis of PIB-*b*-PMMA is an illustrative example. PIB-chain transfer agent **6a** (PIB-CTA **6a**) (0.35 mmol, 0.5 g), MMA (3.5 mmol, 0.37 mL), and AIBN (0.2 mmol, 30 mg) were dissolved in THF (10 mL). This solution was then subjected to three freeze-pump-thaw cycles and the degassed solution was transferred by forced siphon into a three-necked round-bottomed flask which was pre-heated to 68-70 °C. The reaction was terminated after 16 h by cooling the reaction flask to ambient temperature followed by exposure to air. The product was then dissolved in a minimal amount of THF and added to excess cold hexane to remove any insoluble PIB-*b*-PMMA. The hexane filtrate was concentrated at reduced pressure and the residue was analyzed by ^{1}H NMR spectroscopy and GPC. In one experiment 1 mol% of AIBN was used instead of 5 mol% of AIBN. In that case, no hydrocarbon-soluble product block copolymer was formed (the block copolymer that was formed had had a 17/81 ratio of PIB/MMA repeating units and was isolated by hexane precipitation in 50% yield. Thus, other block copolymers were all prepared using 5 mol% of AIBN. Results for these reactions are listed in Table 4.4.

Synthetic scheme of PIB-bound nitrophenyl acetate:



Synthesis of PIB-bound phenol

Alkene terminated polyisobutylene or 20 g (44.4 mmol) was dissolved in 200 mL of DCM in a round bottom flask with a stir bar. Then 18.8 g (200 mmol) of phenol was added and cooled to 0 ^{o}C, followed by 6 mL of concentrated sulfuric acid. The reaction was allowed to stir overnight, and then the DCM was removed via reduced pressure, and the crude residue was taken up in 200 mL hexane. The product was washed with 70% EtOH 30% water 3 times and washed with brine twice. Afterwards the compound was dried with sodium sulfate, filtered, and solvent was removed via reduced pressure.16.8 g (84%) yield of a viscous pale, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J= 8.0 Hz, 2 H), 6.77 (d, J=8.0 Hz, 2 H), 1.83 (s, 2 H), 1.4-0.8 (m, 80 H)

Synthesis of PIB-bound nitrophenol

PIB-phenol (4.5 g or 10 mmol) was dissolved in 20 mL of propionic acid in a round bottom flask with a stir bar. Then, 2.5 ml of water and 2.5 ml of HNO_3 were added at 0 ^oC and allowed to react for 1 h to yield nitrophenol. The product was obtained by washing with 30 ml of water and 20 ml of hexane. The hexane layer was dried with Na_2SO_4, filtered, and the solvent was removed via reduced pressure. 4.2 g (93%) yield of a viscous pale orange oil (d, J=8.5 Hz, 1 H), 7.08 (d, J=8.5 Hz, 1 H), 1.81 (s, 2 H), 1.4-0.8 (m, 80 H).

Synthesis of PIB-bound nitrophenyl acetate

PIB-nitrophenol (4.5 g, 10 mmol) was dissolved in 50 mL of DCM in a round bottom flask with a stir bar. Then, 3 g or 30 mmol of triethylamine was added to the solution which turned a dark orange color. The solution was cooled to 0 ^oC and 2 g or 25 mmol of acetyl chloride was added dropwise, and allowed to stir overnight. The reaction was then refluxed for 2 h, cooled to room temperature, and the solvent was removed via reduced pressure. The residue was taken up in 10 mL hexane, filtered, and then washed with acetonitrile (3x 10 mL), 90% ethanol/water (3x 10 mL), and brine (1x 10 mL). The organic phase was dried with Na_2SO_4, filtered, and the solvent was removed via reduced pressure to yield 3.1 g (69%) yield of a viscous pale ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1 H), 7.65 (d, J=9 Hz, 1 H), 7.14 (d, J=9 Hz, 1 H), 2.37 (s, 3 H), 1.87 (s, 2 H), 1.4-0.8 (m, 80 H). The exact amount of nitrophenyl acetate was calculated by ^1H NMR spectroscopy by using dichloroethane as an internal standard: 1.2 mmol/g.

Synthesis of PIB-bound acrylate

To a flame dried 100 mL round bottom flask equipped with 50 mL of anhydrous THF and a magnetic stir bar, 5 g (ca. 5 mmol) of hydroxyl-terminated PIB oligomers (M_w 1000 Da) was added. After fully the substrate is dissolved in THF, triethylamine (6.5 mmol, 0.66 g) was subsequently introduced into the flask. Followed by an addition of acryloyl chloride (6 mmol, 0.54 g) dropwise under an ice bath, the reaction mixture was allowed to stir for 16 h under room temperature. Then THF was removed by a rotatory evaporator. The reaction mixture was re-dissolved in heptane (30 mL) and extracted with aqueous solution (10 mL x 3) and brine (10 mL). The organic layer was dried over $MgSO_4$. Then heptane was removed by a rotatory evaporator to yield an orange crude product (4.9 g, 98%). The PIB-bound acrylate (M_w 450 Da) was prepared in the same procedure.

Copolymerization of PIB-bound acylate and ethyl acrylate

A PIB-bound acrylate (M_w 1000 Da, 3 mmol, 3g), an ethyl acrylate (3 mmol, 0.3 g) and benzene (6 mL) were added into a flame dried 10 mL round bottle flask and degassed by three freeze–pump-thaw cycles. Then AIBN (0.03 mmol, 5 mg) was added to a three-necked round-bottomed flask sealed with rubber septa and that flask was then flushed with N_2 for 30 min. The degassed solution of the monomers in benzene was then injected into this three-necked round-bottomed flask and the reaction mixture was heated to 80 $^{\circ}$C. An aliquot (0.1 mL) was taken after 16 h through a canula and dissolved in 0.4 mL of $CDCl_3$. The reaction conversion was analyzed by ^{1}H NMR spectroscopy. The reaction was stirred

for 48 h until all the PIB-bound acrylate was consumed, then cooled to room temperature and exposed to air to quench the reaction. Benzene and the unreacted ethyl acrylate were removed by a rotatory evaporator. The ratio of PIB and ethyl acetate was determined by ^{1}H NMR spectrum by comparing the integral of the -CH_2- group next to the chiral carbon of the PIB (3.6 and 3.9 ppm) with the integral of the -CH_2- group next to the oxygen of the ester (4.1 ppm). Additionally, no unreacted monomer and benzene were observed in the ^{1}H NMR spectrum. The polymer bound esters were used directly in the following solvatochromic study.

Procedure for studies of transesterification rates of PIB-bound nitrophenyl acetate with lithium octoxide using UV-Visible Spectroscopy

The PIB-bound nitrophenyl acetate was dissolved in PAO_{506} to form a 3 x 10^{-3} M solution of PIB-bound nitrophenyl acetate. 0.5 mL of the PIB-bound nitrophenyl acetate solution was diluted with different ratios of THF/PAO_{506} solution to afford a 3 x 10^{-4} M of PIB-bound nitrophenyl acetate. For example, 0.5 mL of PIB-bound nitrophenyl acetate solution (3 x 10^{-3} M) was diluted with 4 mL of PAO_{506} and 0.5 mL of THF in making 10 v/v% (1.2 M of THF) of THF/PAO_{506} solution. After the dilution, the prepared PIB-bound nitrophenyl acetate solution (4 mL) was transferred into an UV-Visible cuvette and ready to react upon the nucleophile addition. To prepare lithium octoxide solution, 0.13 g (1 mmol) of octanol was dissolved in 9.6 mL of THF. Then 0.4 mL of ^{n}butyl lithium (2.5 M in hexanes) was added into the octanol solution and allowed the solution to stir for extra 5 minutes. The lithium octoxide solution was directly titrated with 0.1 M of HCl aqueous solution to determine the actual concentration of the lithium octoxide (0.07 M). The

lithium octoxide solution (ca. 17 μL) was added into the UV-Visible cuvette with PIB-bound nitrophenyl acetate solution (3×10^{-4} M). This solution was then used to follow the rate of transesterification of the nitrophenyl acetate to the nitrophenolate ion in a spectrometer. This transesterification was monitored using UV-visible spectroscopy with 150-160 scans, 60 seconds between scans in the first 150 scans, and a fast sampling speed (7 nm/s). The rate constant of this isomerization was calculated from the slope of the second order plot obtained by plotting 1/(Aeq-At) versus time using the λmax of 450 nm where Aeq is the absorbance at equilibrium, At is the absorbance at time t.

Procedure for solvatochromic shift studies

Solutions of Nile Red (1×10^{-8} M) were prepared in both 1-octyl-2-pyrrolidone and PAO_{432} to be tested. The fluorescence experiments were performed by taking 2 mL of the Nile Red PAO solution in a fluorescence quartz cell, and then adding small volumes of 1-octyl-2-pyrrolidone and measuring the emission spectra. The solutions of Nile Red were excited at 420 nm. Spectra of the fluorophores in pure alkane solvent or polar cosolvent were used to determine the $\Delta\lambda_{EM}$ of the fluorophore in a solvent mixture.

CHAPTER VII

CONCLUSIONS

In summary, the projects described in this dissertation have explored greener chemical processes that minimize solvent or chemical wastes. The two main approaches in my work are 1) developing new recyclable catalysts for organic reactions, and 2) exploring how poly(α-olefin)s (PAOs) can be used as a green solvent alternative for organic reactions since PAOs possess several green properties superior to conventional alkane solvents - low toxicity, low vapor pressure, feasible recyclability and negligible contamination to products.

The first two chapters focused on one major issue facing chemists who want to use PAOs or hydrocarbons as a green solvent: the poor solubility of polar organic substrates or catalysts in PAOs and hydrocarbons. The use of end-group modification of PIB was then applied in making a PAO soluble organocatalyst in Chapter 2. This work involved the synthesis of a PIB-bound hexamethylphosphoramide (HMPA) analog and its applications as a recyclable catalyst in allylation of aldehydes and reduction of enones in a recyclable poly(α-olefin) (PAO) polymeric solvent. Kinetic studies of the allylation reaction show that this PIB-bound HMPA analog is slightly more active than HMPA in dichloromethane in allylation of benzaldehyde by 1.3 times. The catalyst was as active in PAO as HMPA in dichloromethane and the activity in PAO was indistinguishable from this PIB-bound catalyst's reactivity in heptane and in a PAO solvent. Separate studies showed that this PIB-bound HMPA catalyst has high phase selective solubility in PAO versus a polar solvent so it could easily be separated from the polar products whose

solubility in PAO was minimal. While this catalyst was also phase selectively soluble in heptane, a small amount of catalyst leaching and a measurable amount of heptane leaching occurred using a conventional hydrocarbon solvent. By using this catalyst in a nonvolatile separable PAO solvent, this catalyst recyclability was successfully coupled to solvent recyclability, something that is less feasible in a conventional heptane solvent. The result was recycling of catalyst and solvent through at least 5 cycles using simple gravity-based liquid/liquid extractions. This is in contrast to HMPA in conventional solvents which is not easily separable form products or recyclable.

In chapter 3, I took a different approach to making polar polymers soluble in alkanes. Taking the advantage of the polyvalency of polymers, I developed a procedure to alter the solubility of polar polymers and polar polymer-bound catalysts in hydrocarbons. This was accomplished by using a poly(*N*-isopropylacrylamide) (PNIPAM) that was initially phase selectively soluble in a polar organic phase in DMF. While this polymer has no solubility in the hydrocarbon phase, the addition of octanoic acid formed hydrogen bonds to the amide pendant groups of the polymer, *in situ* forming a brush-like polymer that was now hydrocarbon soluble. This solubility was completely reversible. By adding a base to the polar solvent, I showed that a fluorescent labeled PNIPAM partitioned into the hydrocarbon phase on addition of carboxylic acids like octanoic acid. This fluorescence analysis of a dansyl-labeled polymer showed that adding base reversed this solubilization behavior and that this solubilization in hydrocarbons and separation from hydrocarbons could be repeated through five cycles. This same hydrogen bonding network scheme was then used to make a responsively soluble PNIPAM

supported Rh(I) hydrogenation catalyst that was active in alkanes when modified by a carboxylic acid but separable and recyclable after the carboxylic acid was converted to a non-hydrogen bonding sodium salt. This catalyst's activity was comparable to that of a low molecular weight catalyst, but the polymeric catalyst was successfully recoverable and recyclable through four cycles of dissolution/precipitation in toluene. While I did not further explore this idea, I believe this chemistry could be expanded to include other molecular recognition chemistry and used to prepare other sorts of recyclable catalysts.

In chapter 4, I explored the solubility of block copolymers in hydrocarbon solvents. I examined a variety of polymerization chemistries to add a polar polymer to a terminally functionalized polyisobutylene to make block copolymers that were phase selectively soluble in hydrocarbons versus polar solvents. Most of these efforts including some controlled radical polymerization chemistry failed – while the products sometimes dissolved in an alkane solvent, they were more soluble in a separate polar phase. I was finally able to prepare a phase selectively soluble diblock polymer containing polyisobutylene as the phase anchor with PMMA, PEMA, PNIPAM and PDMAA as the polar block using RAFT chemistry. For example, that chemistry allowed me to form PEMA with an average degree of polymerization of 8 and I was able to show that a PIB with an Mn of 1000 Da with this size polar block was selectively soluble in hexanes.

Finally, in Chapter 5, a polymer version ethyl acetate was synthesized through a radical polymerization of PIB-bound acrylate and ethyl acrylate. The PIB-bound ester was then investigated as a polar additive to PAOs solution. Based on prior work in our group, it was known that small amounts of polar cosolvents added to heptane or PAO have a

nonlinear effect on the local environment of solvatochromic dyes. Based on these fluorescence studies, small amounts of polar solvent produce most of the solvatochromatic effect as a pure polar solvent and small amounts of alkanes hardly affect the dye's the λ_{EM}. In my work, I showed that the $\Delta\lambda_{EM}$ (the percentage of the change of the λ_{EM} (in PAO or heptane) versus the λ_{EM} (in a polar solvent) was similar for a polymeric analog of ethyl acetate and for these polymers bound ester copolymers. Similar studies showed that a polar DMF like end group on PIB exhibited similar microhetereogeneity effects on Nile Red's λ_{EM}. In a final set of experiments, I probed the he polar effects of microheterogeneity on actual organic reaction rates. The first of these studies used a mixture of THF and PAO and showed that ca. 15% THF added to PAO produced rates that were comparable to those in pure THF and significantly different than rates in PAO. Specifically, a transesterification reaction of a PAO-bound nitrophenol ester was examined kinetically by studying its reaction with the lithium salt of octanol in solvents containing just PAO, just THF, or different ratios of THF to PAO. This kinetic study suggested that the transesterification proceeded faster as the cosolvent system became more polar. Interestingly, the nonlinear polarity increases previously seen for a dye was also observed in this transesterification rates since 2.4 M of THF in PAO_{506} (ca. 20% of THF) led to a reaction rate that was much faster than in PAO alone and almost 50% of the rate in pure THF.

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