

NOVEL APPLICATIONS OF
POLY(ALPHA-OLEFIN)S AS SOLVENTS AND SUPPORTS

A Dissertation

by

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ABSTRACT

Solvents are needed to perform nearly every reaction in chemistry. They are needed not only to provide the medium in which the reaction occurs, but also have important roles controlling the temperature and concentrations of reactants throughout the reaction. However, many common solvents have drawbacks that include safety, health, and environmental hazards which can be further compounded by the cost and energy intensive nature of recycling. To circumvent these issues, attention has been turned to alternative green solvents. In this dissertation, I will discuss alternative uses of poly(α -olefin) (PAO) oligomers as safer, recyclable solvents, and their use in water purification applications. PAOs can be used as safer, recyclable alternative solvents to hexane and heptane for reactions. These PAOs have very low vapor pressure, and do not contaminate water or polar organic solvents like acetonitrile or DMF when used in biphasic reactions or in extractions. Furthermore, addition of polar cosolvents to PAOs can broaden the usability of these solvent systems. Cosolvents preferentially solvate fluorophores to create microheterogeneity in PAOs the same way as in heptane. Additionally, polymer bound cosolvents affect the fluorophores in the same way as their low molecular weight counterparts and can lead to fully recyclable tunable solvent systems. PAOs, due to their high flash points, are also safer solvents than traditional alkane solvents for pyrophoric reagents like alkyllithiums, trialkylaluminums, and alkyl zinc reagents. Finally, PAOs alone or coupled with phase anchored additive can be used as recyclable alternatives to activated carbon for removing organic impurities from

water. The oligomers which make up the extracting phase have virtually no solubility in water, so they do not contaminate the water which is being purified. These systems are easily recyclable by simply purging the oligomers with an inert gas.

DEDICATION

This dissertation is dedicated to my family, especially my mother Rita and my stepfather Larrie, without whom this would never have been possible.

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NOMENCLATURE

CED	Cumulative energy demand
CMC	Critical micelle concentration
DCM	Dichloromethane
DMF	Dimethylformamide
HMF	5-hydroxymethylfurfural
LCA	Life cycle assessment
LDA	Lithium diisopropylamide
M	Molarity
MeCN	Acetonitrile
MeTHF	2-methyltetrahydrofuran
PAO	Poly(α -olefin)
PCBs	polychlorinated biphenyls
PIB	Polyisobutylene
PEG	Poly(ethylene glycol)
PNIPAM	Poly(<i>N</i> -isopropyl acrylamide)
PPG	Poly(propylene glycol)
Ppm	Part per million
SCW	Supercritical water
SCWO	Supercritical water oxidation
t	Time

T	Temperature
TEA	Triethylamine
THF	Tetrahydrofuran
VOC	Volatile Organic Compound

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CHAPTER I

INTRODUCTION

The need for new and sustainable solvents for chemical transformations is a significant area of research in green chemistry. Solvents are ubiquitous in nearly every reaction performed in chemistry. Solvents serve not only as the media in which reactions occur, but also serve to control the concentration of reactants as well as to control the thermal environment. They are required in homogeneous catalysis. Current solvents are often volatile organic solvents (VOCs) which pose health, safety, and environmental risks. These solvents often make up 80-90% of the mass of a batch chemical reaction, and produce the vast majority of the waste generated from chemical reactions. The solvent used is often not recycled. If the solvent is separated, it is often only incinerated, not recycled.

Paul Anastas and John Warner proposed 12 principles of green chemistry in 1998.¹ These principles outlined the ways in which chemists could perform chemistry which had less of an impact on the environment. Anastas and Warner suggested green chemistry should 1) prevent waste 2) have high atom economy 3) strive for less hazardous synthesis 4) design more benign chemicals 5) design more benign solvents and auxiliaries 6) have high energy efficiency 7) use renewable feedstocks 8) reduce derivatives 9) use catalysts to replace stoichiometric reagents 10) design for degradation 11) analyze for pollution prevention and 12) strive for accident prevention. The search for new sustainable solvents can easily fulfill many of the tenants of green chemistry,

including waste prevention, solvent design can lead to safer solvents and new solvents can be based on renewable feedstocks or be designed to facilitate recycling.

Chemists have developed some helpful tools to determine whether a solvent can be considered a green alternative. Life cycle assessment (LCA) analyzes the impact a given solvent has across the entire lifespan of a solvent, from generation to use and eventual disposal. Additionally, a number of different companies and groups including Sanofi, GlaxoSmithKline, and the ACS Green Chemistry Institute Pharmaceutical Roundtable have developed solvent selection guides which help chemists weigh the health and environmental impact a given solvent may have.²⁻⁴ These guides compile factors like environmental, health, and safety to grade the usability of a given solvent. While there is no perfect solvent for all reactions, these guides can help chemists determine the best overall solvents and offer greener alternatives to conventional solvents.

Biological Sources for Greener Solvents

While most solvents have historically been derived from non-renewable resources, renewable biological sources are of considerable current interest for the replacement of solvents. This interest was reflected in a recent report by Gu and Jérôme who expanded on the 12 principles of green chemistry and posed their own principles 12 principles of green solvents.⁵ They proposed that in order to be a green solvent, a solvent must have 1) availability 2) competitive price 3) recyclability 4) high purity 5) low energy production 6) low toxicity 7) biodegradability 8) a competitive performance

9) chemical stability 10) low flammability 11) be safely storable and 12) be renewably sourced. Solvents from biological sources have advantages over solvents derived from petroleum sources. This fits criterion 12 and also has the advantage that such solvents availability and price is not tied strongly to petroleum prices. Several biologically sourced solvents which have generated interest as green solvents including glycerol and glycerol derivatives, 2-methyltetrahydrofuran (MeTHF), and terpene derivatives shown in Figure 1.1. Glycerol and MeTHF are produced primarily as a by-product of carbohydrate production, and terpene derivatives are derived from natural plant-based sources such as orange peels or conifer trees.

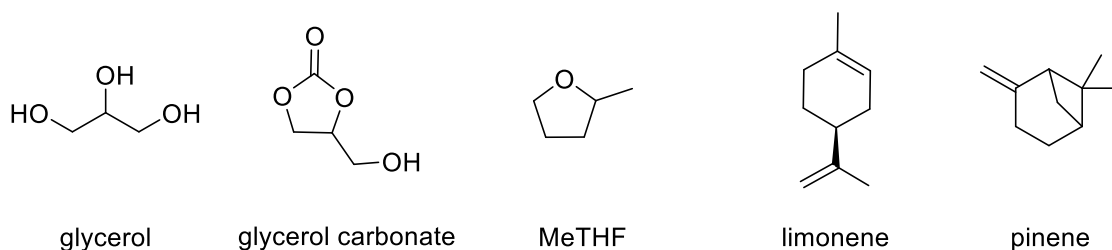


Figure 1.1. Common bioderived solvents

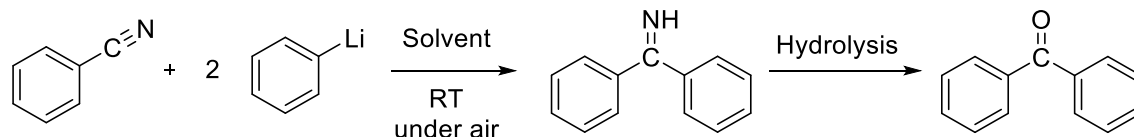
Glycerol is an attractive green replacement for a host of different solvents. Glycerol is derived from renewable sources, and it is relatively non-flammable. The alcohol functional groups in the molecule make it a promising alternative to other alcohol solvents (i.e. methanol or ethanol). The alcohol functional groups can also be easily modified into other functional groups, which further increases the usability of glycerol as a green solvent. Glycerol however does have a higher boiling point (290 °C) compared to many common solvents which makes purification of the solvent by

distillation much more energy intensive. The relatively high melting point of glycerol (17.8 °C) also limits its use as a solvent for low temperature reactions.

The use of glycerol as a green solvent was first realized by Wolfson where glycerol was used as the solvent for the catalytic hydrogenation of prochiral β -keto esters and ketones.⁶ In this work, it was shown that as a solvent, glycerol was comparable to water and superior to hydrocarbon solvents in conversion, enantioselectivity, and yield in the reduction of ethyl acetoacetate by immobilized baker's yeast. The authors noted that organic substrates often had much greater solubility in glycerol vs. water. They also noted that glycerol had much lower vapor pressure and toxicity than traditional hydrocarbon solvents, making it a much safer solvent to use.

Another fascinating use of glycerol as a solvent was shown in the 2018 work by Hevia and coworkers where glycerol was used as the solvent for reactions using aryllithium reagents.⁷ In this work, glycerol was used as the solvent for phenyllithium addition to benzonitrile or to aryl ketones. Reactions using organolithium reagents generally require low temperatures and oxygen free conditions. Very interestingly, the reactions using glycerol were both air and temperature stable. Table 1.1 shows the conditions and yields of the reaction and subsequent hydrolysis of phenyllithium with benzonitrile. The authors proposed that the reaction did not occur in glycerol, but instead "on glycerol". The reactants used were not soluble in the glycerol solvent, so the reaction happened heterogeneously. This hypothesis was probed by testing how the use of stirring affected the yield of the reaction. Stirring the reaction increased the yields

from 51% to 83%, which the authors attributed to increasing the surface area for the reaction to occur.



Solvent	Glycerol	Ethylene Glycol	MeOH	Glycerol (no stirring)	MeTHF
% Yield of Ketone	83	53	8	51	47

Table 1.1. Yields of benzophenone via nucleophilic addition of phenyllithium to benzonitrile and subsequent hydrolysis in different solvents by Hevia and coworkers

Glycerol derivatives can be used as greener alternatives to a wide variety of solvents. Glycerol can easily be functionalized with a wide variety of ether or carbonate functionalities, which allow for fine tuning of the solvent properties.⁸ Such glycerol derivatives are non-volatile, and their toxicities are often low. Glycerol carbonate, for example, is often used as an additive in the cosmetic industry as a preservative.⁹ Glycerol derivatives have been used in a wide variety of other applications. For example, glycerol or glycerol derivatives have been used for membrane preparation, as nonaqueous solvents for enzyme catalyzed reactions, and in the production of chemical feedstocks like 5-hydroxymethylfurfural (HMF) from fructose.⁹⁻¹¹ However, the chemical processes used for derivatization of glycerol often requires the use of non-green solvents and conditions, a sometimes hidden disadvantage which could impact the

use of such derivatives as sustainable greener replacements for conventional solvents. Furthermore, glycerol is most often not reused after a reaction.

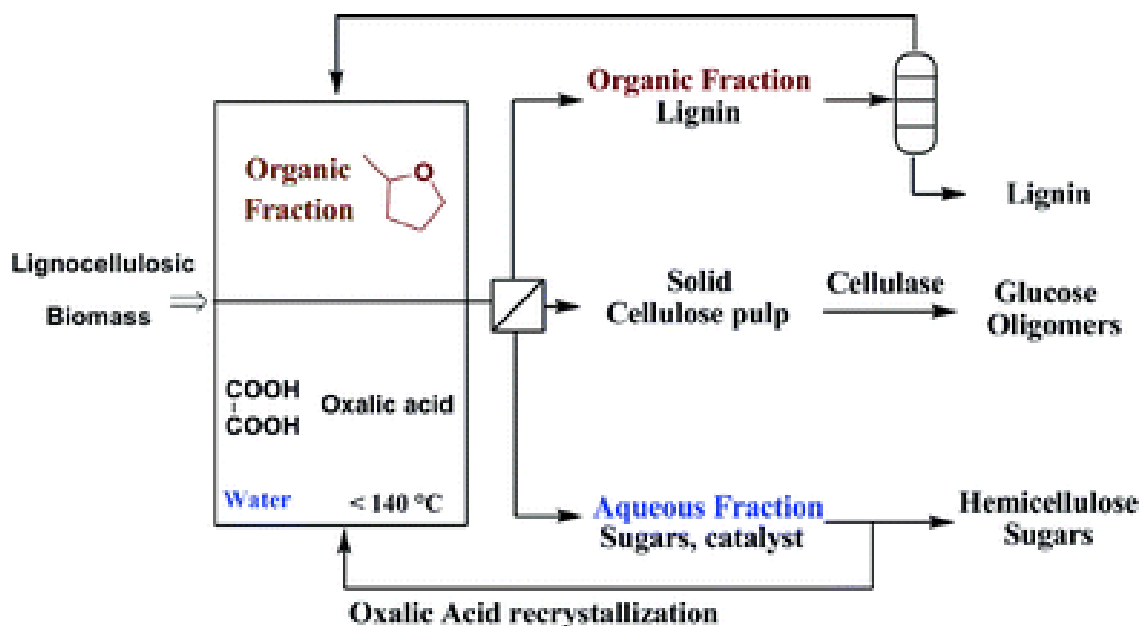
MeTHF has generated interest as a greener solvent particularly as a replacement for tetrahydrofuran (THF). MeTHF is produced via the hydrogenation of furfural, which is sourced from C₅ sugars that in turn are sourced from renewable resources, such as cellulose, hemicellulose, and lignin. MeTHF acts similarly to THF in that it is Lewis-basic and will readily coordinate with organometallic reagents. MeTHF has advantages as a solvent for organometallic reagents over THF in that it has lower rates of reactivity with organometallic reagents such as *n*-butyllithium, making it a better solvent choice for these solvents. MeTHF has less solubility in water than THF, which makes it a candidate for extracting polar organic species from water.¹² The higher boiling point of MeTHF vs. THF (80 °C and 66 °C, respectively) and lower melting point of MeTHF vs. THF (-136 °C and -108 °C, respectively) expands the temperature range available for reactions. It has also been reported that MeTHF has lower mutagenic risks compared to THF.¹³ These factors, along with the higher stability and lower vapor pressure of MeTHF vs THF led GlaxoSmithKline to classify MeTHF as a solvent with some issues vs THF as a solvent with major issues. However, MeTHF, like THF is not normally recycled. Further, MeTHF, like THF is expected to form peroxides by autooxidation with air and the peroxides formed by MeTHF like peroxides formed from THF are likely to be potentially explosive.

MeTHF and THF comparisons can illustrate how the life cycle of solvents is used in order to determine if a new solvent is actually a green replacement for a

conventional solvent. MeTHF is produced from 2-furfuraldehyde, which can be derived from carbohydrates or from the byproducts of carbohydrate production like corn cob waste.¹⁴ Some studies on the production on MeTHF disregard the environmental impact like greenhouse gas generation during the production of the starting materials for MeTHF, because those environmental factors are present during the production of the agriculture. It has been reported that the agricultural process of growing the biomass produces more greenhouse gasses than the chemical transformations needed to convert the biomass byproducts to MeTHF.¹⁵ However, if biomass is cultivated for the sole purpose of generating solvents, a hidden drawback becomes the greenhouse gases generated from cultivation of the biomass. It has been reported that greenhouse gas emissions could be as much as 1600 times higher if deforestation is used to acquire land for biomass vs. using waste from carbohydrates for the conversation to solvents.¹⁶ Furthermore, the greenhouse gas production can vary by wide margins depending on the carbohydrate source used to make MeTHF.¹⁷ Unlike MeTHF, THF is produced from 1,4-butanediol which is produced from petroleum sources which increases the CED (cumulative energy demand) of the THF.¹⁵ The CED of THF is among the highest of many commonly used solvents.¹⁸ The end fate of the solvent must also be considered when assessing the environmental impact and ultimately the “greenness” of a solvent. It is suggested that the environmental impact from the burning of CO₂ is mitigated due to the fact that the CO₂ produced from the incineration of the MeTHF originally came from the atmosphere. This means that any greenhouse gasses produced are from the chemical transformations in producing the chemical.¹⁵ Any CO₂ produced from the incineration

of THF introduces new CO₂ into the atmosphere. While there are certainly advantages for alternative solvents to be derived from biomass sources, using renewable resources does not automatically make a solvent green, and the drawbacks from cultivating the biomass must be considered.

One example of the use of MeTHF as a green solvent was work by Domínguez de María and coworkers where a biphasic system of MeTHF and water was used to separate biomass into lignin, soluble oligomers, and cellulosic pulp in a one pot procedure.¹⁹ Scheme 1.1 shows the system which was used to separate the biomass. In this study, oxalic acid in water was used to depolymerize hemicellulose found in biomass into water soluble sugars. Once liberated from the biomass, the lignin from the biomass was extracted *in situ* into the organic MeTHF phase, leaving only solid cellulose. The use of MeTHF to extract the lignin is important when refining biomass because lignin can be used for in a wide range of applications including as a precursor to activated carbon, as a bioderived platform for pharmaceutical applications, and as a chemical platform for the production of monomers for bioderived polymers and fine chemicals.²⁰⁻²³ This system for the production of lignin was superior to current methods such as the organosolv process or kraft or sulfite pulping. The biphasic system used modest temperatures (>140 °C) by pressurizing the reaction with CO₂ and avoided the use of harsh mineral acids which are commonly used in the current methods.



Scheme 1.1. Separation scheme of lignin, cellulose, and hemicellulose sugars using MeTHF/H₂O biphasic system used by Domínguez de María and coworkers. Reprinted with permission from (19)

While there are a number of examples of green solvents for the replacement of polar solvents, there are far fewer examples of replacements for non-polar solvents, such as *n*-hexane. *n*-Hexane is a very useful solvent for extraction of relatively nonpolar substrates from water, and because it only has unreactive C-C and C-H bonds, it is a solvent for very reactive reagents like *tert*-butyllithium. While it is a useful solvent, *n*-hexane has drawbacks that it is very flammable which makes it dangerous to use as the solvent for pyrophoric reagents. Additionally, *n*-hexane has neurotoxicity issues due to its conversion in the body to hexane-2,5-dione.²⁴ While replacements such as heptane or pentane limits its use. Heptane is considered an ‘acceptable’ solvent in many solvent tables though it still has significant volatility, flammability, and is also generally not recycled.⁴

Some of the more appealing bioderived green replacements for *n*-hexane are terpenes. Pinene, for example, is derived from pine resin, and (*R*)-(+)-limonene which is sourced from citrus peels is recognized as the U.S. Food and drug administration as a safe chemical. Unlike hexane, which is sourced from petroleum sources, terpenes are readily derived from renewable resources and thus have received interest as alternative solvents.

Chemat and coworkers have shown that pinene could be used as a solvent for the extraction of bioactive compounds from biological feed-sources. For example, Pinene was used by to extracted carotenoids, the chemicals which give root vegetables their characteristic yellow color, from carrots.²⁵ Pinene extracted the carotenoids at a higher efficiency when compared to *n*-hexane (95% to 78%, respectively). Furthermore, Sherwood and coworkers have shown that (*R*)-(+)-limonene can be used as an alternative solvent to replace common solvents for esterification and amidation reactions.²⁶ In this study, it was shown that both the synthesis of butyl butanoate from butanoic anhydride and 1-butanol and the synthesis of *N*-benzyl-4-phenylbutanamide from 4-phenylbutanoic acid and benzylamine proceeded at faster rates in (*R*)-(+)-limonene compared to many different organic solvents including chloroform, acetonitrile, and toluene.

While terpenes have generated interest as green alternatives to alkane solvents, they do have drawbacks. Terpenes have a much higher boiling point (155 °C for pinene, 176 °C for (*R*)-(+)-limonene) compared to traditional alkane solvents (<100 °C). The higher boiling point of terpenes requires more energy for distilling and recovering the solvent. The unsaturation of (*R*)-(+)-limonene also may pose problems. Liu and

Mamidipally noted that while using (*R*)-(+)-limonene to extract rice bran oil from rice bran that some of the (*R*)-(+)-limonene was oxidized.²⁷ In order to circumvent this problem, (*R*)-(+)-limonene may readily be hydrogenated to *p*-cymene which cannot be oxidized like (*R*)-(+)-limonene. Terpenes are also more expensive than alkane solvents which can hinder their widespread acceptance as alternative solvents.

Sourcing conventional solvents and chemicals from renewable sources is also a route to greener solvents. The vast majority of solvents and chemicals produced today come from nonrenewable petroleum sources. Bioethanol for example, has wide ranges of uses as solvent or as a chemical feedstock. Ethanol is one of the most common solvents used in chemistry. Ethanol currently is often made via the hydration of ethylene, which is sourced from the cracking of naphtha. Renewable sources can be used for the production of ethanol via the fermentation of sugars. Bioethanol is chemically identical to ethanol produced from petroleum sources, and thus bioethanol can be directly used as a solvent in place of ethanol produced from ethylene. Furthermore, bioethanol can be further transformed into a vast array of chemicals or solvents. For example, bioethanol is a precursor of ethylene and has been used to make ethylene commercially by Braskem.²⁸ Adding renewable sources to solvents and chemicals which generally come from non-renewable sources can help stabilize the cost of these commodities which could fluctuate based on the price of oil.

Water as a Green Solvent

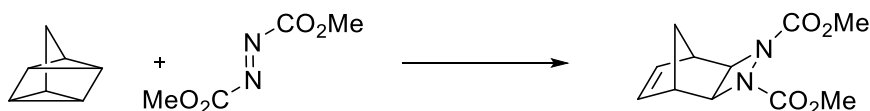
Finding green alternatives for existing solvents is important for chemists. However, many organic solvents have drawbacks that they are toxic. Most organic solvents are also volatile and the volatility of the solvent can make them dangerous to work with. The most common solvent used in nature is water, and thus should be considered by chemists. Water is integral to life on earth, and non-toxic. It is readily available, and is inexpensive. Ideally, chemists can use water alone as a solvent for chemical reactions. Unfortunately, many organic substrates have low solubility in water. In order to circumvent the solubility issues, chemists have turned to techniques such as micellar chemistry or using supercritical conditions to utilize water as a solvent.

The simplest use of water as a solvent avoids the use of cosolvents or harsh conditions. One of the most common uses of water as a solvent is in Diels-Alder reactions. It has been noted that the solvent has a significant role in the rate of Diels-Alder reactions.²⁹ Breslow noted the Diels-Alder reactions of cyclopentadiene with butanone or acrylonitrile and anthracene-9-carbinol and *N*-ethylmaleimide are significantly accelerated in water compared to when isooctane, acetonitrile, or methanol were used as the solvent.³⁰ The increase in this rate was attributed to hydrophobic effects. Adding lithium chloride to the reaction increased the polarity of the water and increased the hydrophobic effect which increased the rate of reactions.

Chemists can use the low solubility of organic substrates in water to their advantage to facilitate reactions. In 2005, Sharpless reported reactions performed “on water”.³¹ Reactions performed “on water” take advantage of the insolubility of the

organic reagents and use water as only a supporting medium. Very interestingly, this phenomenon is not due to the reagents effective concentration being increased.

Sharpless showed that the reaction of quadricyclane with dimethyl azodicarboxylate was faster “on water” than neat, and required less time and lower temperatures compared to when the reaction was run in the conventional solvent, toluene, as shown in Table 1.2. It was further shown that reactions like Claisen rearrangements and nucleophilic epoxide openings were accelerated “on water” compared to conventional solvents.



Solvent	Concentration (M)	T (°C)	t	Yield (%)
neat	4.53	0	2 h	0
neat	4.53	23	48 h	85
toluene	1	80	24 h	74
on water	4.53	0	1.5 h	93
on water	4.53	23	10 min	82

Table 1.2. Reaction of quadricyclane with dimethyl azodicarboxylate by Sharpless and coworkers

Using micelles to do chemistry in water is an interesting way to reduce organic waste. In this process, chemists use molecules that are amphiphilic. Figure 1.2 shows some typical micelle forming surfactant molecules, along with the minimum

concentration of the molecules to form micelles, the critical micelle concentration (CMC).³² One end of the molecule has a hydrophilic end which dissolves the molecule in water while the other hydrophobic end functions as the organic solvent where the reaction can occur. Generally, the amount of these molecules needed in order to form micelles is 10^{-3} to 10^{-4} M.³³ Lipshutz has discussed five considerations which chemists need to be aware of when performing micellar chemistry in water rather than in traditional organic solvents.³⁴ Chemists need to be aware of the size and the shape of the micelles, how all the species in water are transitioning between micelles and the water, the competition between different species in terms of access into the micelle core, the concentration of reactants within the micelle, and how well the micelle binds to other organic species and to itself.

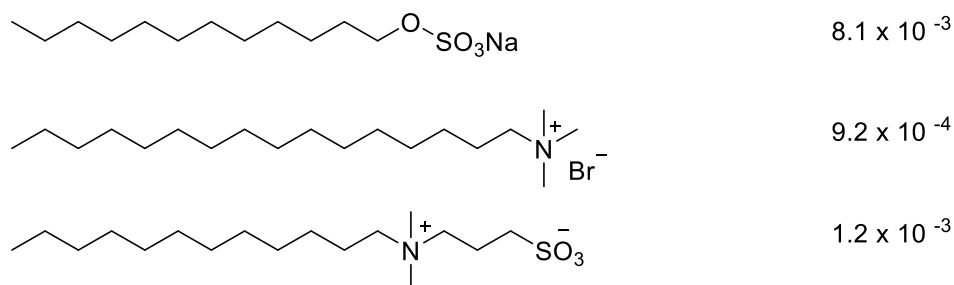


Figure 1.2. Commonly used surfactants for micellular chemistry

Chemists have used micelles to perform a wide array of reactions in water. An interesting use of this system uses ppm levels of metal catalyst to perform reactions. Richard Heck, Ei-ichi Negishi, and Akira Suzuki received the Nobel Prize in 2010 for their work focusing on cross coupling reactions. Cross coupling reactions often rely on

expensive precious metal catalysts like Pd. In 2015, Lipshutz reported using the natural ppm abundance of Pd in Fe to produce nanoparticles which could be to facilitate Suzuki-Miyaura reactions using micelle chemistry in water.³⁵ In this work, iron nanoparticles with 300-350 ppm Pd were ligated with SPhos and added to water with the surfactant TPGS-750-M (2 wt% in water) to cross couple a large substrate scope with high (generally > 80%) yield. This system could be recycled as many as 5 times by extracting the product from the micelle/water phase using an organic solvent and then reusing the micelle/water phase, although recycling the system did require some Pd to be doped back into the system.

Supercritical water (SCW) has also generated substantial interest as an alternative solvent. Supercritical fluids are gasses which are heated and pressurized to above their critical point. Above a material's critical point, a substance acts as a gas and can move through solids and fill the container it is in, but also acts as a liquid, and can dissolve materials. Supercritical fluids are very tunable – slight changes in pressure or temperature can drastically change the density and polarity of the solvent.³⁶ Supercritical fluids are easily separated from reactions by simply depressurizing the reaction system. This allows the supercritical fluid to vent off in the gas form.

One of the most promising uses for supercritical water is for water purification. Supercritical water oxidation (SCWO) is useful for purifying water because when water becomes a supercritical fluid, the polarity of the water switches such that organic impurities become soluble while salts precipitate.³⁷ SCWO can be used to destroy a wide range of contaminants, including chlorinated species. Saito and coworkers used

SCWO to remove polychlorinated biphenyls (PCBs) from water.³⁸ PCBs are compounds which have high toxicity. In this work, PCBs were oxidized in SCW with hydrogen peroxide in both flow and batch reactions to form CO₂, H₂O, and HCl. The authors reported >99.9% conversion of the PCBs using hydrogen peroxide which was much higher than 14.3% conversion when only oxygen was used. While the PCBs did quantitatively degrade, the authors reported no further purification of byproducts of the SCWO and the water product contained species such as 3-chlorophenol, 2-monochlorodibenzofuran, and biphenyl among others. Further work examined SCWO for municipal excess sludge and alcohol distillery waste water.³⁹ While SCWO was efficient at breaking down the water contaminants, the major products from this SCWO were corrosive compounds like acetic acid and ammonia. No further purification of the water was done to remove these impurities

While supercritical water can be very useful for water purification, it does suffer from drawbacks which have hindered its adoption. Reactions and extractions using supercritical water rely on potentially prohibitively expensive high pressure and high temperature equipment. The specialized equipment needed for supercritical water can make scaling reactions difficult. Reactor corrosion from halogenated organics reduces the feasibility of supercritical water oxidation for water purification.³⁶ Furthermore, precipitated salts can plug reactors.⁴⁰ High energy input in order to form supercritical water is required to reach temperatures over 373 °C and pressures over 221 bar also has hindered the adaption of SWO for water purification.

Ionic Liquids as Greener Solvents

Ionic liquids are a recently developed alternative to conventional solvents. Ionic liquids are salts that have a low melting point (below 100 °C). The low melting point of ionic liquids make them suitable for a wide range of applications, including use in water purification, as fuel additives, MALDI-TOF matrices, solvents, among many others.⁴¹⁻⁴⁴ The history of ionic liquids can be traced back to the early 1900s. Walen is credited with synthesizing the first room temperature ionic liquid in 1914 when he reported the synthesis of ethylammonium nitrate with a melting point of 12 °C.⁴⁵ Figure 1.3 shows several of the most common ionic liquids used today. The low melting point of these compounds compared to many other ionic compounds is due to the lower symmetry of the ionic liquid, and the charge on the organic component is often delocalized. The asymmetry of the ionic liquid and the delocalization of charge reduce the ability of the molecule to pack to form crystalline solids, leading to the characteristic low melting point. Beyond the low melting point of these compounds, ionic liquids have many other interesting attributes which make them attractive as solvents. Due to the fact that these materials are salts, ionic liquids have very low volatility. They are thus relatively non-flammable, and do not have the same inhalation hazards and volatility that plague most conventional solvents.

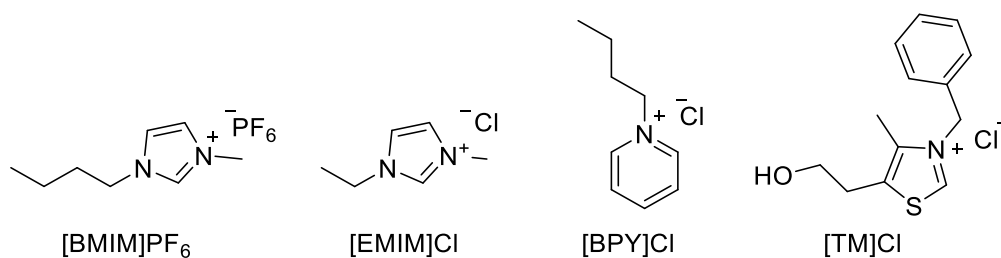


Figure 1.3. Common ionic liquids

Ionic liquids are often referred to as designer solvents due to the ease at which they may be modified. Holbrey and Seddon showed that changing the alkyl substituent on 1-(C_nH_{2n+1})-3-methylimidazolium tetrafluoroborate salts decreased the glass transition temperature of the salt from over 0 °C when n=2 to -80 °C when n=5.⁴⁶ The glass transition temperature rose by increasing the chain length from n=5 to n=9 from -80 °C to -70 °C. When the chain was further lengthened to n=9, the glass transition became a melting point and rose to nearly 0 °C. Further studies by Carmichael and Seddon used the solvatochromic dye Nile Red to probe how changing the identity of the anion affected solvent polarity. The researchers showed that the anion determined the polarity of 1-alkyl-3-methylimidazolium ionic liquids for short alkyl chains, and that the length of the alkyl chain determined the polarity of 1-alkyl-3-methylimidazolium ionic liquids when the alkyl chains were long.⁴⁷ This facile tunability of ionic liquids makes them very attractive for a wide variety of applications.

An interesting application of ionic liquids is the conversion of sugars to 5-hydroxymethylfurfural (HMF). HMF is a versatile building block which can be used to produce fine chemicals normally sourced from petroleum sources. Zhang and coworkers showed that using catalytic amounts of CrCl₂ in the ionic liquid [EMIM]Cl converted

glucose to HMF in 70% yield.⁴⁴ The authors also noted that catalytic amounts of the CrCl_2 catalyst in the ionic liquid solvent stabilized HMF. Further study by Raines and coworkers expanded the use of ionic liquids for HMF production when they used phenylboronic acids in conjunction with magnesium chloride and mineral acids in $[\text{EMIM}]\text{Cl}$ to directly convert cellulose to HMF.⁴⁸ The ionic liquid was critical for this application, as the ionic liquid was able to dissolve the cellulose, enabling a homogeneous reaction of the cellulose with the acids.

While ionic liquids are interesting alternatives to conventional solvents, there are drawbacks associated with their use. Many ionic liquids have melting points at or just above room temperature, which can limit their use as low temperature solvents. While there are examples of ionic liquids with melting points as low as $-150\text{ }^\circ\text{C}$, these materials are very sensitive to impurities, and thus have to be very carefully synthesized and used. Ionic liquids also have very high boiling points which precludes the use of distillation as a tool for purifying the solvent. This can be a problem as byproducts that are soluble in the ionic liquid form and accumulate. Finally, while ionic liquids can be separated from products in many cases and reused, ionic liquids are relatively expensive.

Oligomeric and Polymeric Solvent Systems

The use of oligomers or polymers as solvents is yet another approach to greener solvents. Generally, the molecules used as solvents have few repeat units, and thus are classified as oligomers opposed to polymers. Higher weight polymers generally are not used as solvents. Due to the higher molecular weight of the oligomers compared to

traditional solvents, oligomers are much less volatile. The non-volatility of the oligomers decreases the flammability and some of the health risks associated with conventional VOCs. Common oligomers that are used as solvents have low toxicity. Poly(ethylene glycol) (PEG) with a molecular weight of 400 has an LD₅₀ of 12.9 g/kg in mice, and poly(α -olefin) (PAO) with a molecular weight of 432 has an LD₅₀ of >5 g/kg in rats.^{49, 50} Many polymers are also biodegradable.⁵¹ The low toxicity and biodegradability of these polymers make them excellent safe candidates as alternative solvents. Examples of polar polymers used as solvents include polyethers like PEG and poly(propylene glycol) (PPG). Examples of non-polar polymers used as solvents include polyethylene (PE), polyisobutylene (PIB), and PAO. Examples of both polar and nonpolar polymers used as solvents are shown in Figure 1.4.

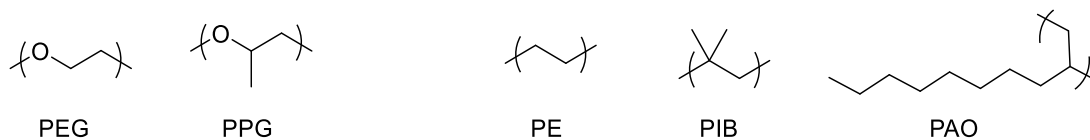


Figure 1.4. Common polymers used as solvents

Polyethers are some of the most studied polymeric solvents. In 1995, Drago and Naughton reported one of the first uses of polyether solvents when they used PEG as a non-volatile hydrophilic solvent for the hydroformylation of 1-hexene using a rhodium catalyst.⁵² Since then, polyethers like PEG and PPG have been extensively studied as polymer solvents. Low molecular weight polyethers are liquids at room temperature. After reactions are complete, products can be removed from the polymer solvent via

distillation or extraction with an immiscible solvent.⁵³ The monomers for PEG and PPG (ethylene oxide and propylene oxide, respectively) are normally derived from petroleum sources, although it may be economically feasible to derive them from biological sources.^{54, 55}

Early work by Wang and coworkers used solid PEG₄₀₀₀ as the solvent for cross coupling reactions.⁵⁶ In this study, aryl halides were added to PEG and Pd(OAc)₂ as a catalyst and heated to 120 °C for 4 hours to form biaryl compounds. Once the reaction was complete, the solution was cooled to room temperature and the product was extracted from the PEG solvent with diethyl ether. The PEG solvent and Pd(OAc)₂ catalyst could be recycled up to 6 times without decrease in yield. However, while PEG is an alternative solvent, it is worth noting that the workup required using a conventional solvent. Indeed, in this case the amount of ether solvent (60 mL each cycle) used to extract the product far exceeded the amount of PEG which was used (3.5 mL).

PEG is also an excellent solvent for use in biological systems. PEG₄₀₀ has been shown to be an excellent solvent for the solubilization of popular nonsteroidal anti-inflammatory drugs (NSAID) like Celecoxib, Rofecoxib, Leoxicam, and Nimesulide.⁵⁷ NSAID drugs are the most widely prescribed drugs, but have low water solubility which hinders oral bioavailability, so biologically safe solvents are of great interest. The high solubility of the NSAIDs in PEG is most likely due to the mixture of polar alcohol end groups and nonpolar ether repeat units.

An interesting application of PEG is its use in formation of aqueous two-phase systems (ATPS). ATPS are solvent systems using two incompatible polymers or salts

which are water soluble to form two aqueous phases, essentially separating water from water.⁵⁸ Using these aqueous solvent systems for the extraction of biomolecules are of interest because they are much greener than other methods like precipitation and chromatography which rely on excess solvents. PEG as a cosolvent has been shown to make inexpensive ATPS with a variety of salts such as PEG/phosphate, PEG/citrate, and PEG/dextran.⁵⁹⁻⁶¹ ATPS are especially useful for extracting a wide range of biomolecules including proteins, enzymes, and nucleic acids without harming the bioactivity of the molecule.⁶² Recently, it was shown that a PEG/phosphate ATPS system could be used in a continuous flow extraction to extract C-phycoyanin, a protein with a wide range of pharmaceutical applications, from algae.⁶³ The use of flow extraction for biomolecules further reduces the amount of solvent needed vs batch extraction which further increases the green nature of ATPS.

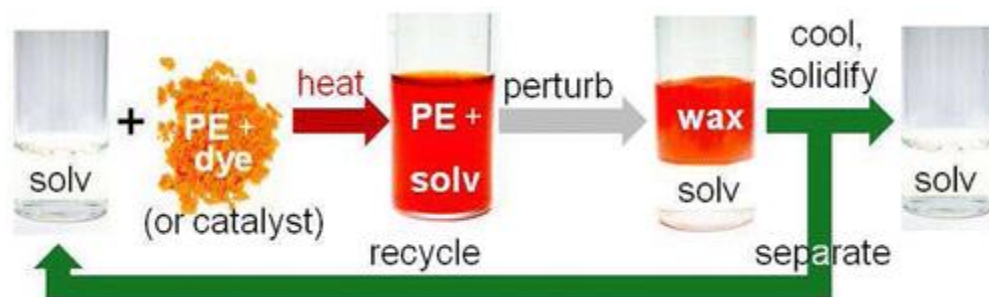
PPG is another polyether which can be used as a solvent. Though it has not received as much study as PEG, PPG is an interesting solvent because it is much more hydrophobic than PEG. It can be considered a green solvent because it can be sourced from renewable sources.⁶⁴ Raston and coworkers used PPG as a solvent for Barbier reactions to form homoallylic amines.⁶⁵ In this work, various aldimines were sonicated with allyl bromide and indium powder in PPG, and the resulting homoallylic amine could either be extracted with a small amount of ether or by vacuum distillation. The PPG solvent could be recycled at least 3 times in the reaction of benzylidene aniline with allyl bromide and indium powder. The authors did note a slight loss in yield which they

attributed to the incomplete removal of water which was used to remove inorganic salts after the reaction.

While the most commonly used polymer solvents are polyethers, there has been research focusing on using non-polar polymers as solvents. Research into alternative non-polar solvents is of interest due to the relative lack of replacements compared to more polar solvents. The Bergbreiter group has a history of using non-polar polymers as supports for recyclable homogeneous catalysts and using non-polar oligomers such as low melting (PE), (PIB), and PAOs as recyclable nonpolar solvents or cosolvents. PE is a waxy solid at room temperature, PIB is a viscous oil, and low weight PAOs have viscosity akin to vegetable oil. Similar to polyethers, products from reactions run in nonpolar polymers can be removed via distillation or by extraction with an immiscible solvent.

The Bergbreiter group reported some of the first examples of using PE as a solvent in 2012 when they used low melting Polywax with a molecular weight of 400 Da as a replacement for heptane.⁶⁶ In this work, the phase selectivity of a PIB-bound azo dye was first tested. The dye was added to a solvent system containing a 1.5:2:2 by volume mixture of Polywax, THF, and DMF. The solution had to be heated to 80 °C in order for the solution to become homogeneous. This latent biphasic system was then perturbed via addition of 10-20 vol% of water. This produced a biphasic mixture where the Polywax phase was separated from the denser water-THF-DMF phase. UV/Visible spectroscopy analysis showed that the dye was over 99.9% phase selective in the Polywax over the water-THF-DMF solution. Experiments using Polywax as a

recyclable solvent in homogeneous catalysis was then tested. Scheme 1.2 shows typical reaction and recycling conditions used. In these experiments, the reactions were carried out at 80 °C or higher to ensure that the Polywax was a liquid and to ensure that monophasic reaction mixtures were formed with polar cosolvents. In these experiments, Polywax was shown to be a recyclable solvent in an allylic substitution reaction using a PIB-bound Pd(0) catalyst in a Polywax/THF solvent system and in PIB-bound SCS-Pd catalyzed Heck reactions in a Polywax/THF/DMF solvent systems. In these reactions, water was added to perturb these latent biphasic solvent mixtures. The non-polar phase separated as a liquid at 80 °C from the product containing polar phase. The Polywax phase was however not separated under these conditions but was isolated as a solid at room temperature. It was also shown that Polywax/toluene could be used with a PIB-bound Grubbs catalyst for RCM reactions without the need of water to perturb the two phases. While these studies showed that Polywax could be used as a recyclable solvent, these reactions used a large ratio of non-recycled polar solvent to Polywax (as high as 3:1 by weight).



Scheme 1.2. Reaction and recycling conditions used for reactions using Polywax solvents. Reprinted with permission from (66)

Another study by the Bergbreiter group utilized PIB as a non-polar cosolvent to create an anti-leaching effect.⁶⁷ In this study, a biphasic system of acetonitrile and heptane was used in cyclopropanation reactions to segregate a nonpolar phase anchored PIB-bound Rh catalyst from ethyl diazoacetate to slow the rate of dimer formation – a reaction which usually utilizes a syringe pump to limit dimer formation due to reaction of the Rh catalyst with the polar ethyl diazoacetate reactant. Typically a syringe pump would be used to slowly add the ethyl diazoacetate to a dichloromethane solution of the alkene substrate and catalyst. Such a process normally requires long reactions time but would lead to cyclopropanated product in a 71% yield with a minimal (2-3 %) dimer formation. By using a biphasic mixture of heptane and acetonitrile without a syringe pump, a similar 69% average yield of cyclopropanated product could be obtained over three cycles. In this case, the phase isolation of the polar ethyl diazoacetate and the PIB-bound Rh catalyst limited average dimer formation to ca. 7%. Gratifyingly, when PIB with a molecular weight of 2300 was added to the nonpolar phase, the average yield of the cyclopropanation reaction was still a respectable 61% over 3 cycles. However, the PIB cosolvent further reduced the average dimer formation to ca. 4.5%. The reduction in yield and dimer formation was attributed to the reduction of PIB-bound Rh catalyst leaching into the polar acetonitrile. Other studies of this effect using a PIB-bound azo dye showed that adding a nonpolar polymer cosolvent in a heptane/methanol solvent system reduced the leaching of the azo dye by roughly 30% in a heptane/methanol. However, these studies were limited to using PIB as a cosolvent with heptane because the high viscosity of PIB disfavored its use as a pure solvent.

While PIB was usable as a cosolvent and had excellent anti-leaching properties as a cosolvent, interest turned to nonpolar polymers which could be used as solvents alone. Thus, attention was turned to low viscosity PAOs as green alternatives to alkane solvents. PAOs are commercially available from many sources in a variety of viscosities as they are commonly used as lubricants, as heat transfer fluids, and in hydraulic systems. The viscosity of the PAO increases as a function of the molecular weight. PAOs are produced from the oligomerization of α -olefins like decene or dodecane to form dimers, trimers, tetramers, and higher oligomers. Subsequent hydrogenation forms alkane oligomers which are fully saturated. While PAOs are more expensive than traditional alkane solvents like hexane (ca. \$4.5/kg and \$3/kg for PAOs and hexane, respectively), much of their cost can be mitigated by the fact that PAOs are inherently more recyclable than their lower weight analogs.

In order to assess the usability of PAOs as solvents, an LCA of the solvent and of a conventional solvent like heptane is needed. Unlike THF, the CED and the overall environmental impact of heptane is relatively low.¹⁸ This is due to the fact that heptane comes directly from petroleum refining. The synthesis of PAOs begins with ethylene which is normally produced via the cracking of naphtha, but a growing portion of ethylene comes from ethylene rich shale.⁶⁸ The fracking of ethylene rich shale has driven the price of ethylene down, making it more cost effective to generate ethylene products.⁶⁹ The vast majority of α -olefins used for oligomerization to PAOs are produced via the Shell Higher Olefin Process (SHOP). Developed by the Shell Development Company, SHOP employs a catalyst which generates α -olefins from

ethylene for the synthesis of detergents.⁷⁰ Figure 1.5 shows the process which is used to generate an α -olefin like decene. Once the α -olefins have been made, it can be undergo a cationic polymerization using an initiator like boron trifluoride or metallocene catalyst to generate the unsaturated oligomer.⁷¹ A final hydrogenation step is performed to generate the saturated PAO. The extra steps needed to produce PAOs vs hexane hurt the LCA of the PAOs. These extra steps, however, are mitigated by the fact that the ethylene used as a monomer for PAO production is already a direct product of oil refining.⁷² PAOs can also be derived from biological sources. Bioethanol can be dehydrated to bioethylene using supported phosphoric acid or activated alumina.²⁸ Cross-metathesis chemistry of unsaturated fatty acids and fatty acid esters with ethylene using Grubbs-type ruthenium catalysts is currently used by Elevance Renewable Sciences to form a variety of chemicals, including α -olefins.⁷³ However, PAOs derived from renewable biological sources would suffer from the same land-use drawbacks as listed previously for MeTHF.

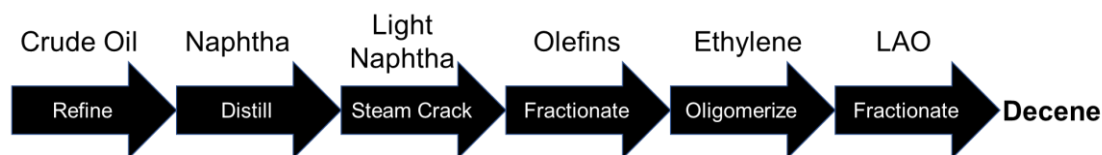
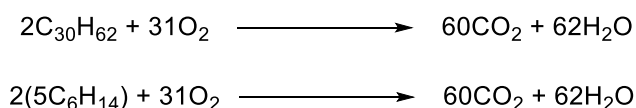


Figure 1.5. Generation of decene from petroleum sources

The end fate of the solvent must be considered in a LCA. Due to the low environmental impact of producing heptane, recycling of heptane is not energy efficient, and it heptane often incinerated to generate energy.¹⁸ When burned for energy, PAOs will produce the same amount of green-house gasses as the same mass of conventional

alkane solvents (Equation 1.1). In 1 kg of the decene trimer PAO, there are 2.3 moles of PAO. In 1 kg of hexane, there are 11.3 moles of hexane, corresponding to 5 times as many moles of hexane compared to decene trimer PAO. Burning 1 kg of either PAO or hexane produces roughly 3.2 kg of CO₂. It has been calculated that 4 kg of CO₂ are produced in the process of making 1 kg of PAO.⁷⁴ This means that simply burning the PAO produces nearly as much CO₂ as is produced in making the PAO.



Equation 1.1. Balanced equation of the products formed from burning equal masses of PAO (top) and hexane (bottom)

While PAOs can be incinerated for energy, they are also more recyclable than heptane when used as solvents.⁷⁵ As noted above, 3.2 kg of CO₂ are produced by burning 1 kg of PAO, on top of 4 kg of CO₂ generated in the production of the PAO. If the PAO solvent is recycled more than 2 times, the greenhouse gas emitted drops below what is generated when using hexane as a solvent.

When used as a solvent, products can be extracted from PAOs via distillation or with a minimal amount of PAO immiscible solvent. In one experiment, it was shown that PAO with a molecular weight of 432 Da did not contaminate polar organic solvents. It was shown that in a thermomorphic system of DMF and PAO₄₃₂ that only 0.02% of the PAO leached into the DMF phase. This leaching was further reduced to 0.002% with the addition of 10% water to the polar organic phase. Another study showed that

using PAO with a molecular weight of 432 could act as a recyclable nonpolar solvent for a phase transfer catalyzed esterification of butyl bromide with potassium carbonate. Conversely, the reaction was not recyclable when heptane was used as a solvent. Furthermore, impurities in the PAO can be easily removed to recycle the solvent. Impurities can be removed from the PAO via extraction with a small amount of PAO immiscible solvent like water or acetonitrile, by sparging with an inert gas, or via vacuum distillation. Even at high temperatures, PAOs, unlike hexane, do not evaporate.⁷⁶ The low vapor pressure reduces the loss of solvent due to evaporation while also reducing inhalation hazards normally associated with traditional solvents. While the production of PAOs requires more steps than heptane, the inherent recyclability of PAOs make them attractive green alternatives to traditional alkane solvents.

CHAPTER II

PAO AND PAO SOLVENT MIXTURES AS RECYCLABLE SOLVENT SYSTEMS*

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, and in controlling relative concentrations of reacting species. 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 releasing greenhouse gasses 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.

Lists of greener and more environmentally benign solvents that include new types of solvents as well as more benign and more sustainable organic solvents exist.^{2, 4,}
⁵ However, it is difficult if not impossible to design solvents that have 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, in addition to having less of an impact on the environment compared to the solvents they replace, reactions in alternative solvents ideally should proceed

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identically in both solvents. A green solvent which has poor performance compared to the traditional solvent is not likely to be widely adopted.

One approach to replacing solvents with greener alternatives is using polymers or oligomers as solvents. Polymers have advantages over traditional solvents that they have lower vapor pressure, thus reducing inhalation hazards associated with traditional solvents. Furthermore, schemes have been developed for recycling the oligomeric solvent like precipitation of the solvent or liquid-liquid extractions to remove products from the solvent.^{56, 75} The most commonly utilized oligomeric solvent is poly(ethylene glycol) (PEG). PEG has been used as a recyclable solvent for many applications including hydroformylation and cross coupling reactions.^{52, 56} While PEG is an interesting alternative solvent, the polar nature of the PEG oligomers can make it difficult to separate from products. In the most common examples, product/PEG separation requires solvent precipitation – a process that requires a large excess of solvent to separate products from the solvent.

Previously, the Bergbreiter group utilized PIB as a non-polar cosolvent to create an anti-leaching effect.⁶⁷ In this study, a biphasic system of acetonitrile and heptane was used in cyclopropanation reactions to segregate a nonpolar phase anchored PIB-bound Rh catalyst from ethyl diazoacetate to slow the rate of dimer formation – a reaction which usually utilizes a syringe pump to limit dimer formation due to reaction of the Rh catalyst with the polar ethyl diazoacetate reactant. Typically, a syringe pump would be used to slowly add the ethyl diazoacetate to a dichloromethane solution of the alkene substrate and catalyst. Such a process normally requires long reactions time but would

lead to cyclopropanated product in a 71% yield with a minimal (2-3 %) dimer formation. By using a biphasic mixture of heptane and acetonitrile without a syringe pump, a similar 69% average yield of cyclopropanated product could be obtained over three cycles. In this case, the phase isolation of the polar ethyl diazoacetate and the PIB-bound Rh catalyst average dimer formation to ca. 7%. Gratifyingly, when PIB with a molecular weight of 2300 was added to the nonpolar phase, the average yield of the cyclopropanation reaction was still a respectable 61% over 3 cycles. However, the PIB cosolvent further reduced the average dimer formation to ca. 4.5%. The reduction in yield and dimer formation was attributed to the reduction of PIB-bound Rh catalyst leaching into the polar acetonitrile. This antileaching effect is shown in Figure 2.1, where a PIB-bound Ru bipyridine complex visually leaches less from a nonpolar alkane phase into a polar phase consisting of ethanol and DMF when PIB₂₃₀₀ is added to the nonpolar phase. However, these studies were limited to using PIB as a cosolvent with heptane because the high viscosity of PIB disfavored its use as a pure solvent.

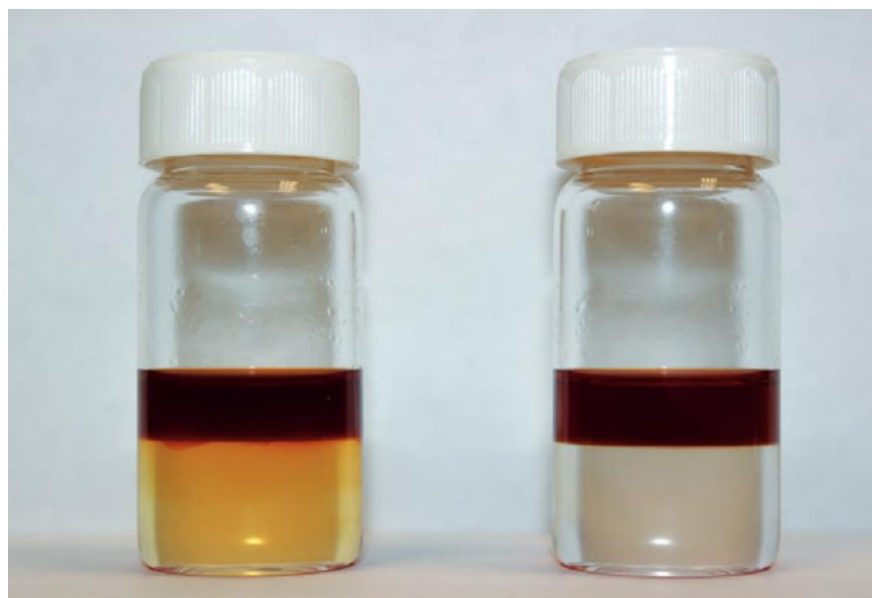


Figure 2.1. Leaching of a PIB-bound Ru bipyridine complex into a DMF/ethanol polar phase from heptane (left) and in a solvent system consisting of ca. 10% PIB₂₃₀₀ in heptane. Reprinted with permission from (67)

While PIB was usable as a cosolvent and had excellent anti-leaching properties as a cosolvent, it could not be used as a solvent itself because of its viscosity. It would also have to be hydrogenated to make a non-reactive alkane-like solvent. Thus, our interest turned to nonpolar hydrocarbon polymers which could be used as solvents alone. Originally, this effort focused on polyethylene oligomers that were modestly viscous liquids above their melting point and solids at room temperature.⁶⁶ We showed that these solvents could sequester and protect catalysts and that they could also be used with other conventional solvents to recover and reuse catalysts in a variety of transition-metal catalyzed reactions where the catalyst ligands were phase selectively soluble in the

molten polyethylene phase of a hot biphasic mixture of molten polyethylene and a more polar organic solvent.

An alternative was to use low viscosity PAOs as green alternatives to alkane solvents. PAOs are commercially available from many sources in a variety of viscosities as they are commonly used as lubricants, as heat transfer fluids, and in hydraulic systems.⁷⁷ The viscosity of PAOs increases as a function of the molecular weight. PAOs are produced from the oligomerization of α -olefins like decene or dodecene to form dimers, trimers, tetramers, and higher oligomers which have a wide range of structural connectivities.^{78, 79} Subsequent hydrogenation yields the commercial PAO alkane oligomers which are fully saturated.

PAOs have properties which make them good candidates as replacements for traditional alkane solvents. PAOs have only C-C and C-H bonds, making them functionally equivalent to traditional alkane solvents like pentane, hexane, or heptane. Unlike traditional alkane solvents, PAOs have very low volatility which eliminates hazards associated with inhalation. PAOs also have flash points which generally exceed 220 °C making them much less flammable than traditional alkane solvents and thus safer to work with.⁷⁶ Furthermore, PAOs are not toxic, and have been approved for uses with incidental food contact and are kosher certified.⁸⁰ PAOs as have similar solvating properties to traditional alkane solvents in that they will dissolve non-polar and moderately polar substrates or cosolvents and exclude polar substrates or cosolvents.⁸¹ Finally, unlike polyethylene oligomers, they can be separated from polar organic phases at ambient temperature.

Results and Discussion

In order to test how reactions proceeded in the PAO solvents vs a traditional alkane solvent like heptane, we chose to study the thermal isomerization of the PIB-bound azo dye *para*-methyl red. The azo dye was PIB-bound to increase the solubility of the polar dye in the nonpolar alkane solvents. In visible light, the azo dye is in the higher energy *cis* conformation, and in the dark undergoes a thermal isomerization to the lower energy *trans* conformation. The synthesis of the PIB-bound *para*-methyl red is shown in Figure 2.2, and the spectra of the isomerization of the dye in heptane and PAO₆₈₇ are shown in Figure 2.3. This isomerization can easily be tracked via UV-visible spectroscopy by tracking the absorbance at 420 nm which corresponds to the *trans* isomer of the PIB-bound *para*-methyl red. This isomerization was studied kinetically and the kinetics of this reaction were successfully modeled using first order kinetics.⁸²

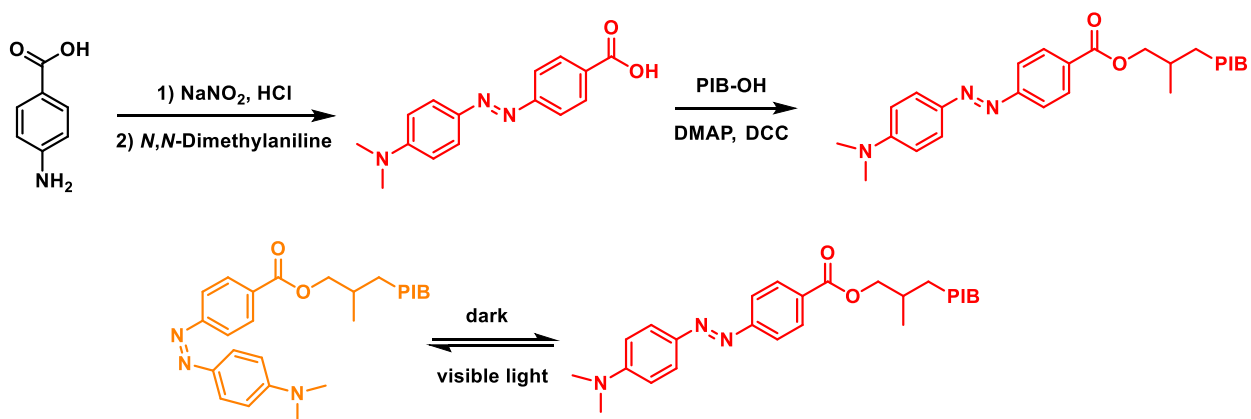


Figure 2.2. Synthesis and isomerization of PIB-bound *para*-methyl red

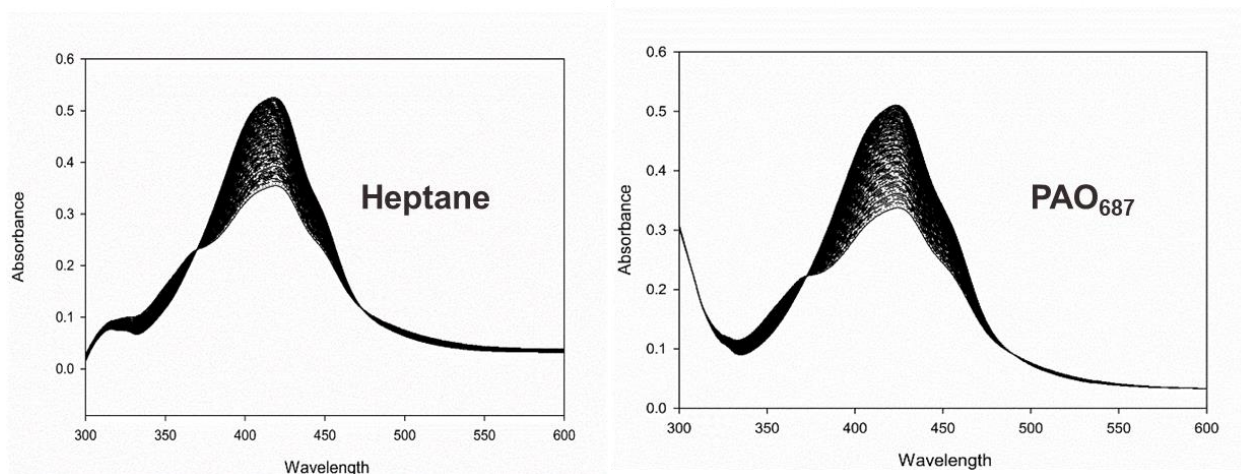


Figure 2.3. UV-visible spectra of the thermal isomerization of PIB-bound *para*-methyl red in heptane (left) and PAO₆₈₇ (right).

We determined the rate constant of the isomerization of the PIB-bound *para*-methyl red in PAOs with viscosities ranging from 2 cSt at 100 °C to 65 cSt at 100 °C and compared these rate constants to the rate constant of the dye in heptane which are listed in Table 2.1. An unknown trace acid impurity catalyzed the isomerization of the azo dye in the PAO₁₇₈₅ and PAO₂₅₀₅ solvents, resulting in rate constants of 4.2×10^{-4} and 1.2×10^{-3} for PAO₁₇₈₅ and PAO₂₅₀₅ respectively. It is known that acids can catalyze the isomerization of azo dyes.⁸³ This acid impurity was quenched by adding an excess of triethylamine, resulting in rate constants of 2.2×10^{-4} and 2.4×10^{-4} for PAO₁₇₈₅ and PAO₂₅₀₅ respectively. The rate constant of the thermal isomerization of the PIB-bound *para*-methyl red in all of the PAOs regardless of their viscosity was virtually identical to the rate constant of the isomerization in the traditional alkane solvent heptane.

Conversely, the isomerization of the PIB-bound azo dye in DCM was too fast to be observed, indicating that the isomerization rate constant is solvent dependent.

Solvent	Rate Constant (s ⁻¹)
Heptane	2.2 x 10 ⁻⁴
PAO ₂₈₃	2.5 x 10 ⁻⁴
PAO ₄₃₂	2.6 x 10 ⁻⁴
PAO ₆₈₇	2.3 x 10 ⁻⁴
PAO ₁₇₈₅	2.2 x 10 ⁻⁴
PAO ₂₅₀₅	2.4 x 10 ⁻⁴
Dichloromethane	Too fast to observe

Table 2.1. Observed rate constant of the thermal isomerization of PIB-bound *para*-methyl red.

To determine how using PAOs as solvents affect catalytic reactions, we studied the acid catalyzed isomerization of the PIB-bound *para*-methyl red azo dye. As noted above, acids can act as catalysts for the isomerization. Acids catalyze this reaction by protonating or associating with the basic azo nitrogen ultimately reducing the bond order between the azo nitrogens allowing for free rotation around the sigma bond. To test how the acids affected the rate of isomerization in a PAO vs the traditional solvent heptane, we chose three carboxylic acids with different chain lengths, including a PIB-bound carboxylic acid. We observed that regardless of the carboxylic acid chain length and alkane solvent that the rate constant for the isomerization increased linearly with the

molarity of the carboxylic acid squared as shown in Figure 2.4. The rate constant for the PIB-bound carboxylic acid mirroring the low molecular weight carboxylic acids at the same concentration supports our previous findings that polymer supports with adequate spacing from the main polymer chain like the terminally functionalized polyisobutylene chain does not affect the reactivity of terminal groups.⁸⁴⁻⁸⁶ Furthermore, the linear increase in rate constant when plotted against the molarity of the carboxylic acid squared indicates that the carboxylic acid catalyzing the isomerization is in the dimer form in these hydrocarbon solvents at all concentrations studied. This result mirrors the findings of DeTar and Silverstein who reported that acetic acid is primarily the dimer in carbon tetrachloride whereas in acetonitrile which is more polar, acetic acid is primarily monomeric at similar concentrations.⁸⁷ These results suggest that polar species in alkane solvents have a high affinity for aggregation and association. This appears to be especially true for H-bonding species like carboxylic acids that form H-bonded dimers. In this instance, the carboxylic acid cannot H-bond to the alkane solvent because the alkane does not contain any atoms that can be H-bond acceptors. Thus, enthalpy favors dimer formation in spite of the unfavorable entropy of dimer formation at low concentrations.

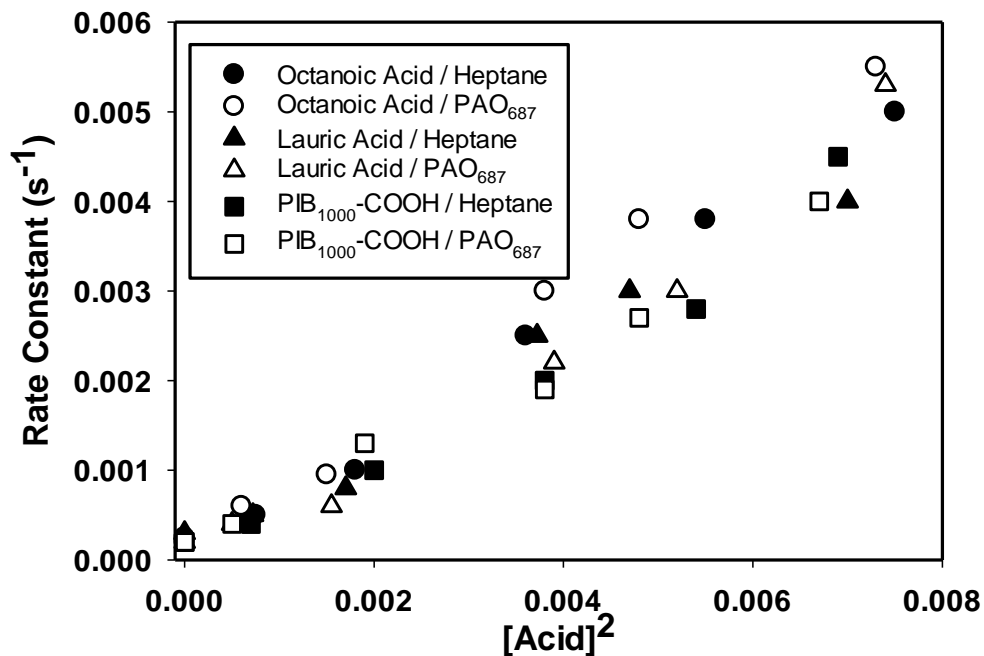
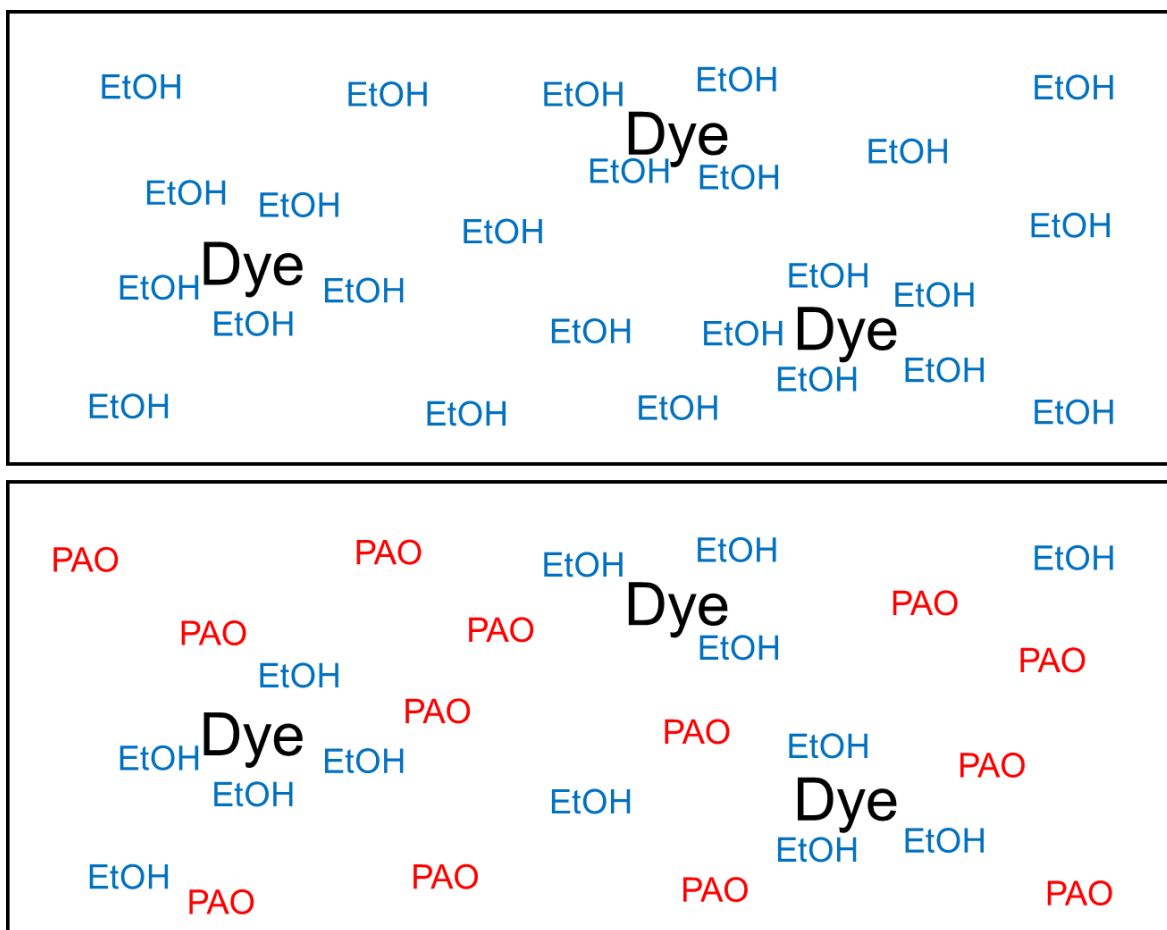


Figure 2.4. Carboxylic acid catalyzed isomerization of PIB-bound *para*-methyl red in PAO₆₈₇ and in heptane

The experiments above showed that PAO behaves like heptane in these azo dye isomerization reactions. They showed that acid catalysis of these azo dye isomerization reactions is similar in heptane and PAOs. Other data suggests that PAOs are a better solvent at separating a PIB-bound azo dye from a polar solvent than heptane. In addition, studies of the separation chemistry showed that PAO₆₈₇, PAO₁₇₈₅, or PAO₂₅₀₅ did not significantly contaminate polar solvents unlike heptane.⁸¹ However, the PAOs PAO₆₈₇, PAO₁₇₈₅, or PAO₂₅₀₅ studied initially are relatively viscous. They thus would only be useful as solvents with the addition a low viscosity cosolvent. PAO₂₈₃ or PAO₄₃₂ or similar dimers and trimers derived from dodecene could be potential lower viscosity substitutes for PAO₆₈₇, PAO₁₇₈₅, or PAO₂₅₀₅. These PAOs with lower

molecular weights should not be any different than heptane in their ability to function as solvents. However, while these lower molecular weight PAOs would be like heptane and while in the event we showed that they were as separable as their higher molecular weight analogs, they still are just alkanes. This is a significant limitation on the use of PAOs since alkanes are among the least useful solvents in organic chemistry because most organic chemistry involves species with little or limited solubility in pure alkanes. The observations above and particularly the observation that even modest concentrations of a carboxylic acid exist as dimers that can interact with a polar dye suggested that even low concentrations of a cosolvent can affect a solute. This concept has been described in the literature as microheterogeneity.^{88,89} This suggests that even small amounts of added cosolvents could affect the local environment experienced by a solute in a mixed solvent system. In the case of this azo dye, the polar carboxylic acids act as catalysts but could also be considered to be cosolvents preferentially solvating the azo dye solute. Presumably the acids associate with the basic H-bond acceptor sites on the azo dye while nonpolar solvents or cosolvents do not. This phenomenon is highlighted in Scheme 2.1. We hypothesized that by adding a small amount of polar cosolvent to a PAO might have the same effect and that the low amounts of a cosolvent would lead to a local environment in the solvent system that might resemble the bulk polar cosolvent. If the local environment in these solvent systems resembled the polar solvent, it would expand the potential of PAO solvents for catalysis and synthesis. First it would allow one to use these recyclable solvents more broadly. Second, it would be possible to reduce the amount of polar solvent needed for reactions by using the PAO as the bulk of the mixed

solvent system, ultimately reducing solvent waste. Third, if the cosolvents could be designed so that they were anchored in the PAO, the entire solvent system could be recycled. This last possibility is the most speculative but is intriguing in that it suggests that schemes might be developed where solvents could be designed and synthesized in a tailored way to affect chemical reactions. Currently, this is not an option because solvents are typically not recycled easily or quantitatively with the only real exception being ionic liquids that are sometimes tailor for specific applications.



Scheme 2.1. Example of microheterogeneity in a polar solvent (top) and a mixed solvent system consisting of polar and nonpolar solvents (bottom)

The use of solvatochromic fluorophores to determine the polarity of solvents has a well-documented history.⁹⁰ Solvatochromic fluorophores change emission wavelengths based on the polarity of the solvent in which they are dissolved. Most solvatochromic dyes experience a bathochromic or red shift in increasingly polar solvents. Bathochromic shifts occur due to the polar solvent stabilizing the polar excited state of the fluorophore, which results in the fluorophore emission occurring at a lower energy. The most common solvatochromic dye used for determining the polarity of solvents is Reichart's dye (Figure 2.5). This dye has, for example, been used to probe polarity in room temperature ionic liquids, another potentially environmentally benign alternative solvent.⁹¹ However, this dye was judged to not be a good choice for our purposes as it is unlikely to have much if any solubility in alkane rich media. Fortunately, others have used other dyes that do have reasonable alkane solubility for similar studies. For example, the solvatochromic fluorophore Nile red has been used by Rimmer and coworkers to investigate the effect of branching on the local environment of poly(*N*-isopropyl acrylamide) (PNIPAM) polymers in polar solvent systems.⁹² It is also a dye that has solubility in alkanes.

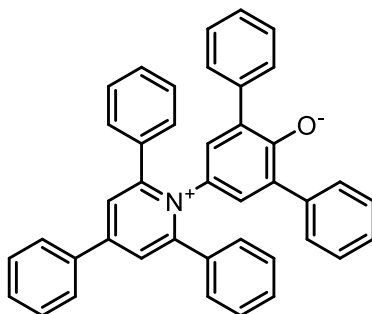
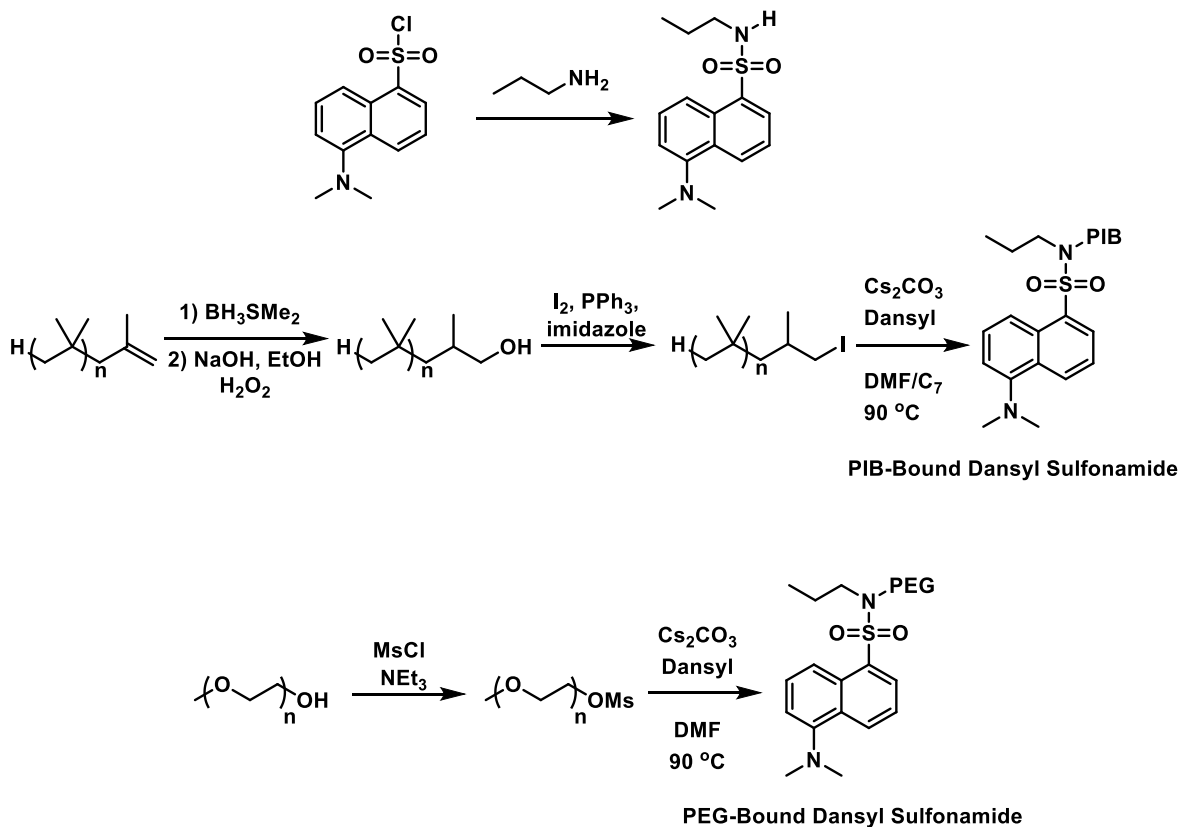


Figure 2.5. Structure of Reichart's Dye – a commonly used solvatochromic dye

In order to test effect of cosolvents on the local environment of a solute in the solvent systems of interest to us, we used two solvatochromic fluorophores – Nile red and dansyl dyes (Figure 2.6). These dyes were chosen because they could be used as is or as a modified material in a range of solvents and in alkane/polar solvent mixtures. Nile red is soluble in nonpolar solvents like heptane or PAO and in polar solvents like ethanol. While low molecular weight dansyl dyes are not soluble in nonpolar solvents, we have previously used dansyl sulfonamides which were bound to polymers as phase tags to quantify the leaching of the nonpolar anchored polymer bound catalysts into polar solvents. These latter dansyl dye derivatives were prepared as a PIB-bound dansyl sulfonamides or PEG-bound dansyl sulfonamides (Scheme 2.2). As noted above, the solubility of these dyes or readily prepared derivatives in nonpolar solvents make them more attractive than other common solvatochromic dyes like Reichert's dye which itself is not soluble in nonpolar solvents and is not easily modified.



Scheme 2.2. Synthesis of polymer bound dansyl sulfonamides

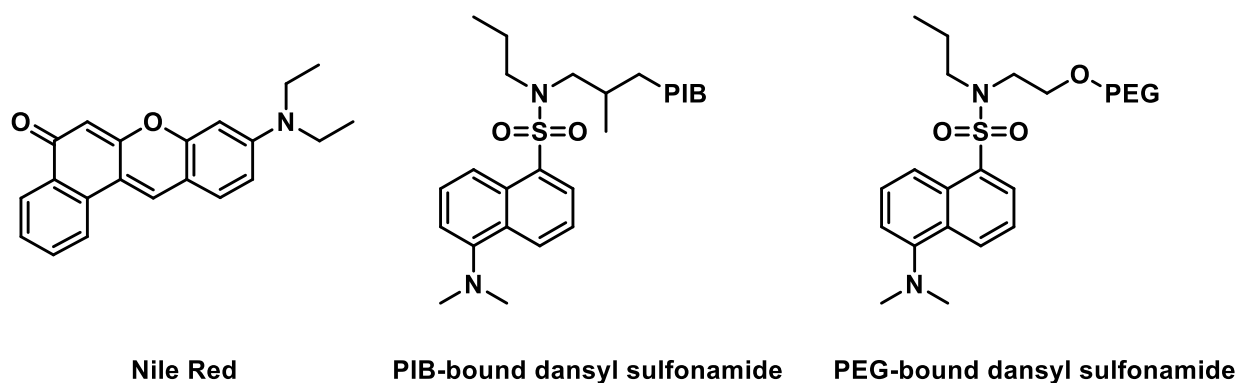


Figure 2.6. Solvatochromic dyes used to study the polarity experienced by solutes in mixed solvent systems

Fluorescent dyes like Nile red and dansyl sulfonamide derivatives are advantageously used to test the local environment in cosolvent systems for two reasons. First, a fluorescent dye can be studied at relatively low concentration and thus requires only modest solubility of the dye in any given solvent or solvent mixture. Second, dyes are an inexpensive surrogate for solutes or catalysts in actual reactions. Both Nile red and dansyl sulfonamides exhibit large bathochromic shifts for the λ_{EM} of their fluorescence as the solvent polarity increases as is evident in Figure 2.7. Finally, the dansyl sulfonamides could be modified to make it soluble in various solvents. For example, it could be modified to be either PIB-bound or PEG-bound species. This allowed us to solubilize this dye in a range of solvents with different polarities. The PIB-bound dansyl dye was used to test the local environment of a solute in nonpolar and moderately polar solvents. The PEG-bound dansyl sulfonamide was used to test the local environment of a solute in polar solvents. We later explored the second fluorescent dye - Nile red. Nile red did not need to be polymer functionalized as it had acceptable solubility in most of the solvents studied.

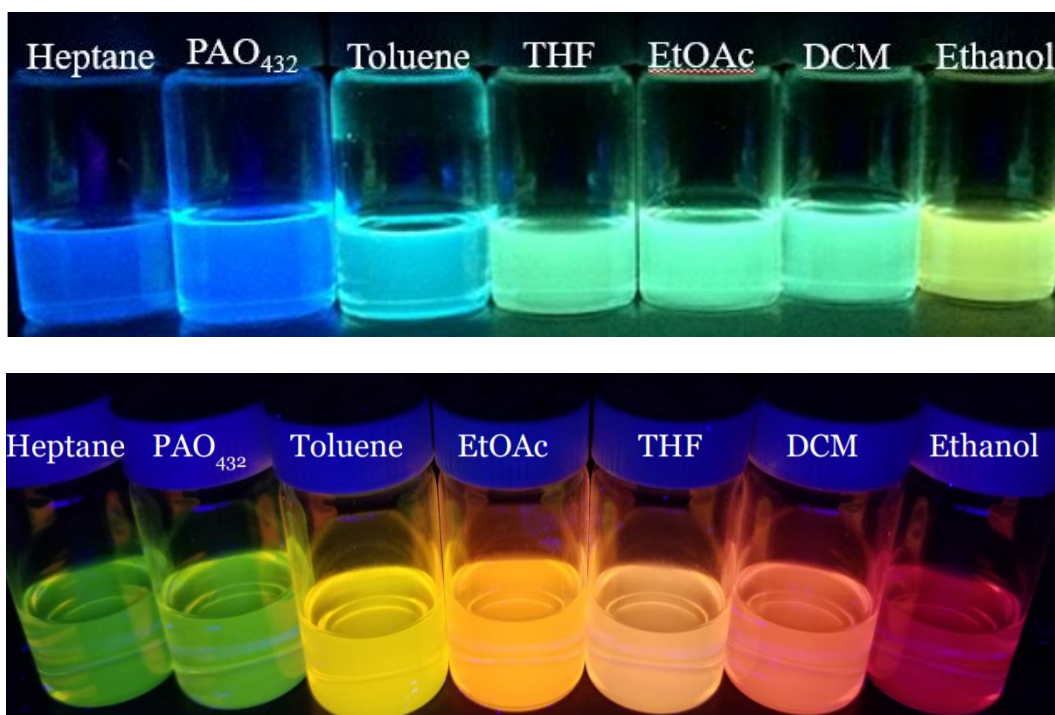


Figure 2.7. Solvatochromic fluorescence of dansyl sulfonamide (top) and Nile red (bottom)

We first tested the emission of the fluorophores in the bulk solvents. Table 2.2 lists the λ_{EM} of the dyes in different solvents. As was the case with the dye isomerization, the dye response in heptane vs. in any of the PAOs was virtually identical. The λ_{EM} of the PIB-bound dansyl sulfonamide was 447 nm in heptane and 448 to 449 nm in the PAOs. The λ_{EM} of Nile red was 525 nm in heptane and 529 to 531 nm in the PAOs. As the polarity of the solvent increased, so did the λ_{EM} of each of the dyes. The PIB-bound dansyl sulfonamide has a working range of 65 nm which corresponds to the difference between the λ_{EM} of the fluorophore in heptane and ethanol (447 nm and 510 nm, respectively). Nile red has a working range of 98 nm corresponding to the difference between the λ_{EM} of the fluorophore in heptane and ethanol (525 nm and 623

nm, respectively).

Solvent	Polymer-bound Dansyl Emission (nm)	Nile Red Emission (nm)
Heptane	447	525
PAO ₂₈₃	448	529
PAO ₄₃₂	448	530
PAO ₆₈₇	449	531
Toluene	471	565
THF	493	589
EtOAC	494	587
DCM	494	597
EtOH	512 (90 % in heptane)	620
1-butanol	510 (90% in heptane)	623
Hexanoic acid	N/A	609

Table 2.2. λ_{EM} of PIB-bound dansyl and Nile red in different solvents

To examine microheterogeneity in alkane/polar solvent mixtures we looked at the fluorescence of Nile red and/or polymer bound dansyl sulfonamide in heptane or PAO and studied how adding varying amounts of polar solvents affected the λ_{EM} of the dye. To begin, we studied the microheterogeneity of two common moderately polar solvents, THF and DCM using heptane, PAO₂₈₃ PAO₄₃₂ or PAO₆₈₇ as the nonpolar phase. To compare the effect of how cosolvents affected the local environment of the

dye, known small volumes of cosolvent was added to the nonpolar solvent and the λ_{EM} of the fluorophore was recorded. The emission was then plotted as a % shift from the nonpolar solvent to the pure polar cosolvent vs the molarity of the cosolvent. For example, the λ_{EM} of Nile red is 525 nm in heptane and 597 in DCM. The $\Delta \lambda_{EM}$ is 72nm. When 1 M DCM is present as a cosolvent, the λ_{EM} is ca 555 nm, or 40% of the $\Delta \lambda_{EM}$ of the λ_{EM} of heptane vs THF. Figures 2.8 and 2.9 show the $\% \Delta \lambda_{EM}$ of the dye vs the molarity of the polar cosolvent in THF and DCM, respectively.

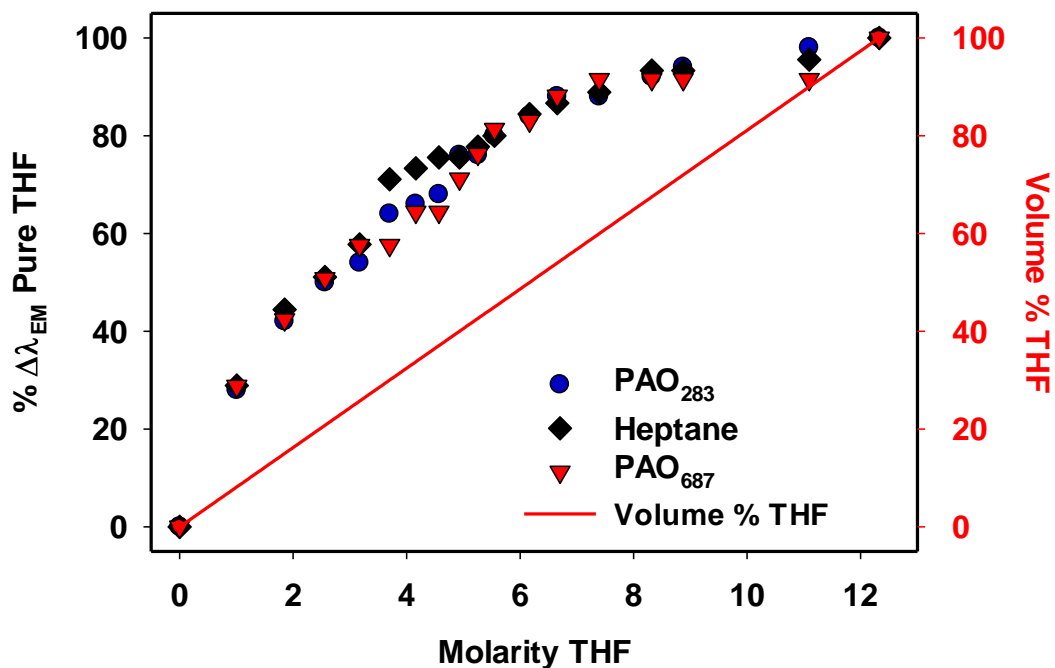


Figure 2.8. Solvatochromic shift of PIB-bound dansyl sulfonamide adding THF as a cosolvent in heptane, PAO₂₈₃, and PAO₆₈₇ (top) and Nile red in heptane and PAO₄₃₂ (bottom). The red line is the volume % THF added.

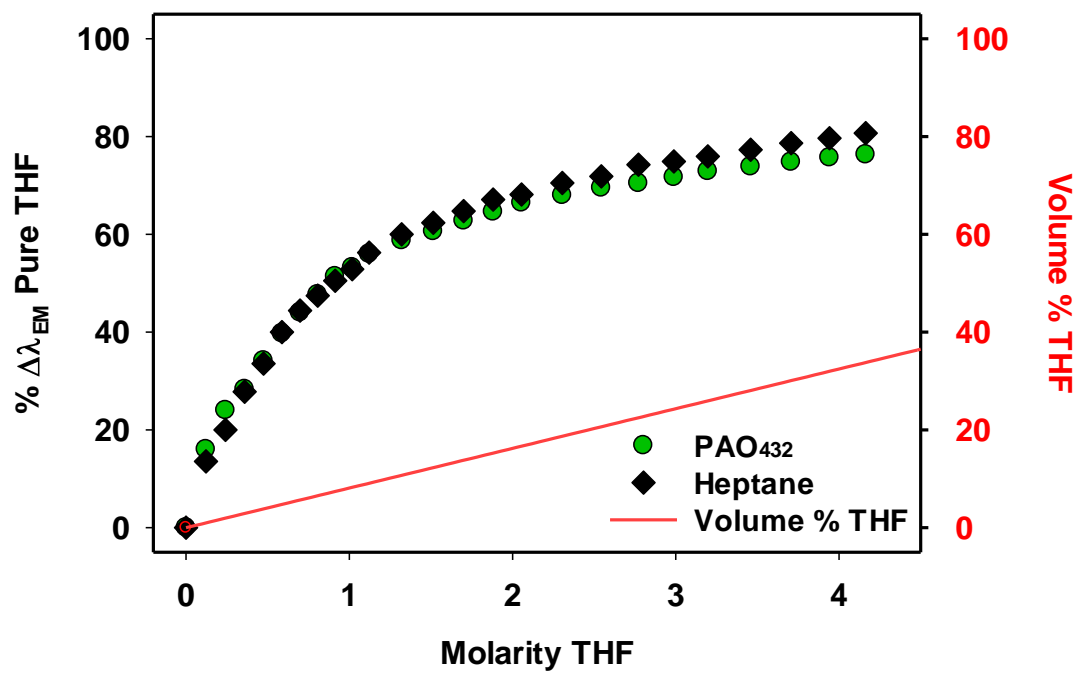


Figure 2.8 Continued

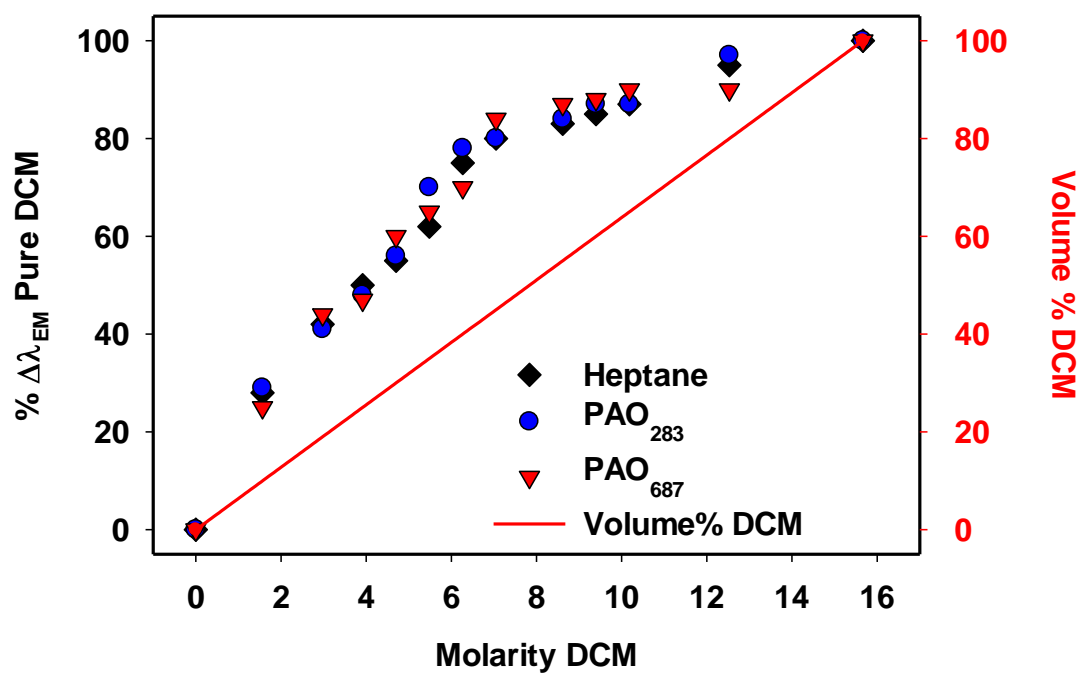


Figure 2.9. Solvatochromic shift of PIB-bound dansyl sulfonamide adding DCM as a cosolvent in heptane, PAO₂₈₃, and PAO₆₈₇(top) and Nile red in heptane and PAO₄₃₂ (bottom). The red line is the volume % DCM added.

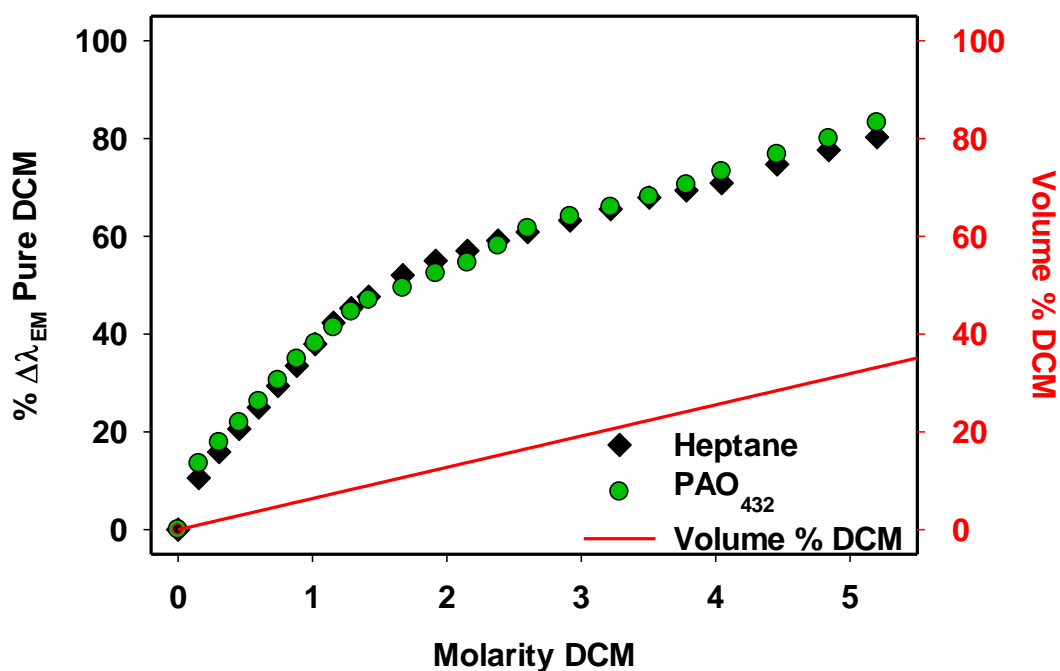


Figure 2.9 Continued

As shown in Figures 2.8 and 2.9, both solvatochromic fluorophores had virtually identical responses to cosolvent addition in heptane or any of the low viscosity PAOs. Furthermore, both fluorophores exhibited a nonlinear shift in emission compared to the molarity of the polar cosolvent added. This is best exhibited by comparing the shift in emission to the volume % of polar cosolvent added. Figures 2.8 and 2.9 both show that both PIB-bound dansyl sulfonamide and the Nile red fluorophores have fluorescence that is largely unchanged when the cosolvent mixture is >40% THF or DCM. However, going from 0% THF or DCM to 15% THF or DCM leads to a 40-60% $\Delta\lambda_{EM}$ in these dyes' fluorescence. We suggest that this is due to the fact that the fluorophore is being solvated by the polar cosolvent selectively. The heptane or PAO alkane solvents only

have dispersive interactions with a solute dye while the polar solvent can stabilize the dyes' excited states by polar interactions. Thus, adding alkane or PAO to a pure polar solvent leads to only a modest $\% \Delta \lambda_{EM}$ change because there is a high concentration of polar solvent molecules that maintain a local environment for the dye that resembles that in pure polar solvent. However, the situation is different in solutions where the molarity of the alkane solvent is high. In those cases, even a small amount of polar cosolvent can lead to a significant solvation of the dye because the dyes' excited state is not solvated to any significant extent by the alkanes.

Our hypothesis is that the polarity difference between alkanes like heptane or PAO lead to microheterogeneity effects on the λ_{EM} of different fluorophores and that the microenvironment, the solvent polarity experienced by the fluorescent dye, is thus nonlinear. This effect is presumably magnified by the use of two solvents with disparate polarity. However, if two similar solvents both of which can solvate a dye were used, these microheterogeneity effects should be absent or much diminished. To explore this, we examined the fluorescence of the PEG-bound dansyl sulfonamide dye in mixtures of ethanol and water (Figure 2.10). When compared to solvents more disparate in polarity like heptane and ethyl acetate (Figure 2.11), adding water into ethanol resulted in a roughly linear shift in the $\% \Delta \lambda_{EM}$ of the dansyl sulfonamide fluorophore.

These experiments show that in media which have wide ranges in polarity that solvation of polar substrates is preferential, where in solvents with similar polarity, there is little to no preferential solvation. This observation suggests that small amounts of polar solvents

can usefully polarize PAOs, making them at least somewhat similar to conventional polar solvents for catalytic and synthetic reactions.

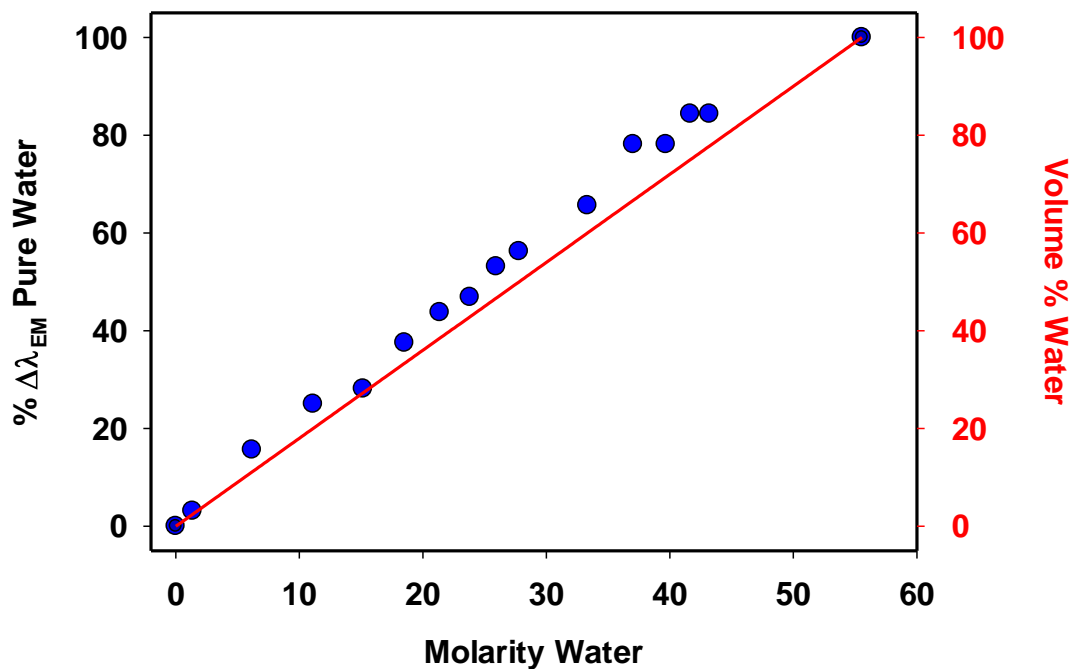


Figure 2.10. Solvatochromic shift of PEG-bound sulfonamide. In this case, there is little deviation of the $\% \Delta\lambda_{EM}$ linearity suggesting that there is nearly no difference in how these solvents solvate the fluorophore resulting in nearly no microheterogeneity in this solvent system.

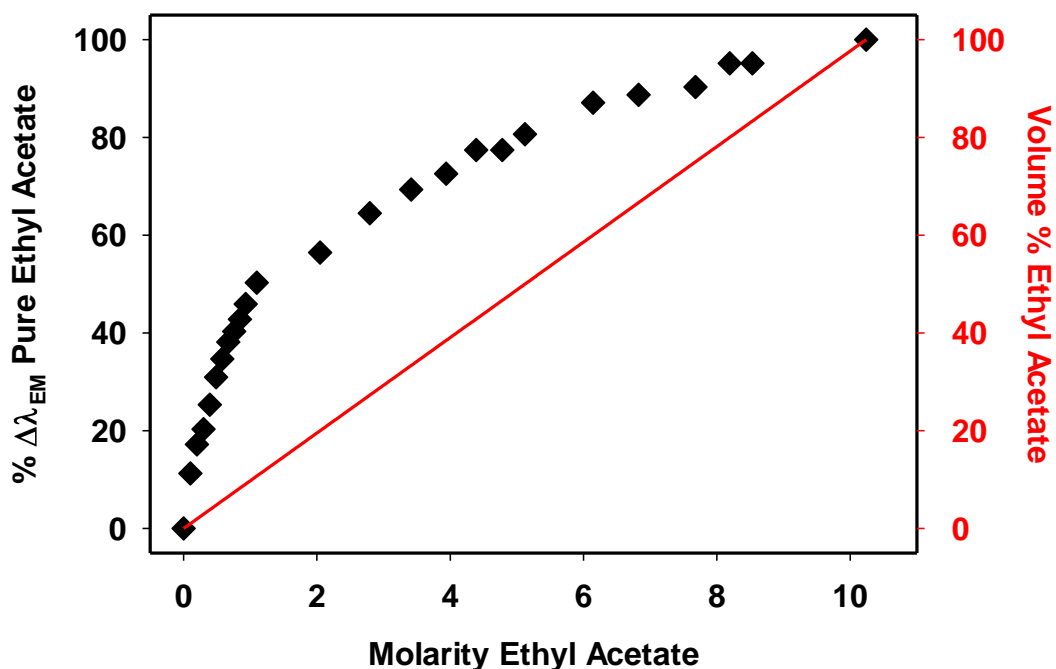


Figure 2.11. Solvatochromic shift of Nile red adding ethyl acetate into heptane. The red line is the volume % of ethyl acetate as a function of ethyl acetate molarity. The deviation of the $\% \Delta\lambda_{EM}$ (■ experimental data) from the red line indicating volume % ethyl acetate shows the microheterogeneity of this cosolvent system and how dye solvation differs from simple additive effect of the two solvents on the dye fluorescence

Solvents like THF, DCM, and ethyl acetate presumably stabilize the excited state of Nile red and the polymer bound dansyl sulfonamide leading to bathochromic shifts in dye fluorescence. They presumably interact with the fluorophores through dipole-dipole interactions. We believed that solvents which have a more specific interaction with a fluorophore would have a much more profound effect on the λ_{EM} shifts we observed. Thus, we turned our attention to hydrogen bonding cosolvents like acids and alcohols. Based on our previous results studying the acid catalyzed isomerization of the PIB-bound *para*-methyl red, we knew that H-bonding cosolvents interact with polar solutes

preferentially in alkane solvent systems. In order to further probe how H-bonding cosolvents interacted with solutes, we first tested how carboxylic acids as cosolvents affected the λ_{EM} of Nile red. Figure 2.12 shows the $\% \Delta \lambda_{EM}$ change when hexanoic acid was used as a cosolvent. The effect of the hexanoic acid on the λ_{EM} of the Nile red fluorophore is much more pronounced at low concentrations compared to solvents like THF or DCM which cannot hydrogen bond with the fluorophore. For example, 1M THF in an alkane solvent produces a ca. 40 $\% \Delta \lambda_{EM}$ of the Nile red fluorophore, where 1M hexanoic acid produces a ca. 60% $\Delta \lambda_{EM}$. This large difference is attributed to the fact that unlike THF or DCM, hexanoic acid can have a direct H-bond interactions with the Nile red fluorophore which stabilizes the excited state of the fluorophore.

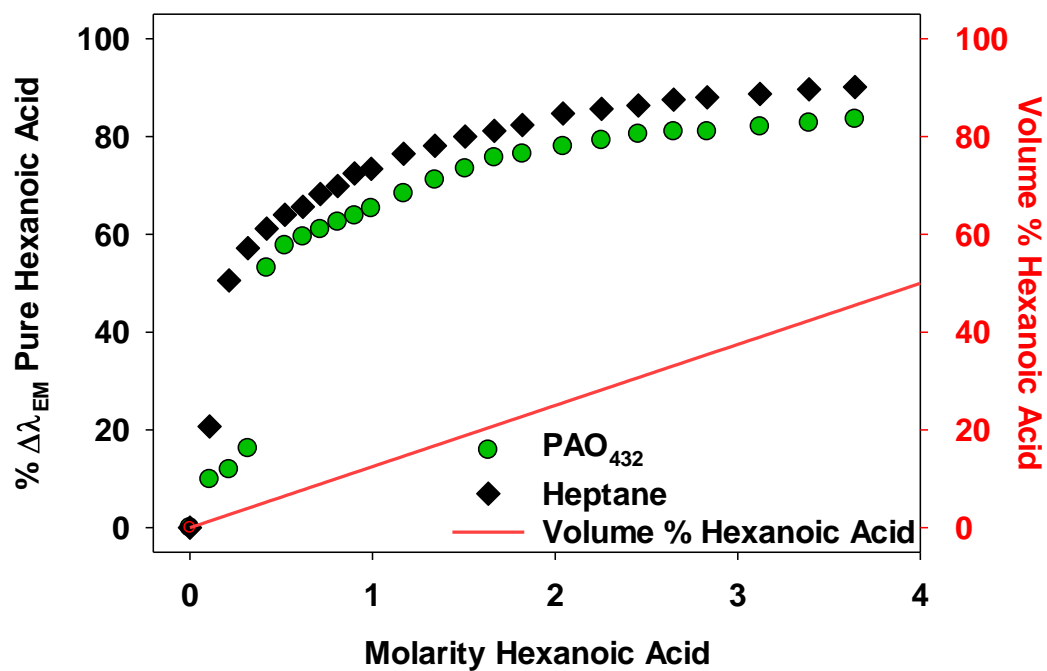


Figure 2.12. Solvatochromic shift of Nile red adding hexanoic acid in heptane or PAO₄₃₂. The deviation from volume % shows the microheterogeneity of this cosolvent system and how dye solvation differs from simple additive effect of the two solvents on the dye fluorescence.

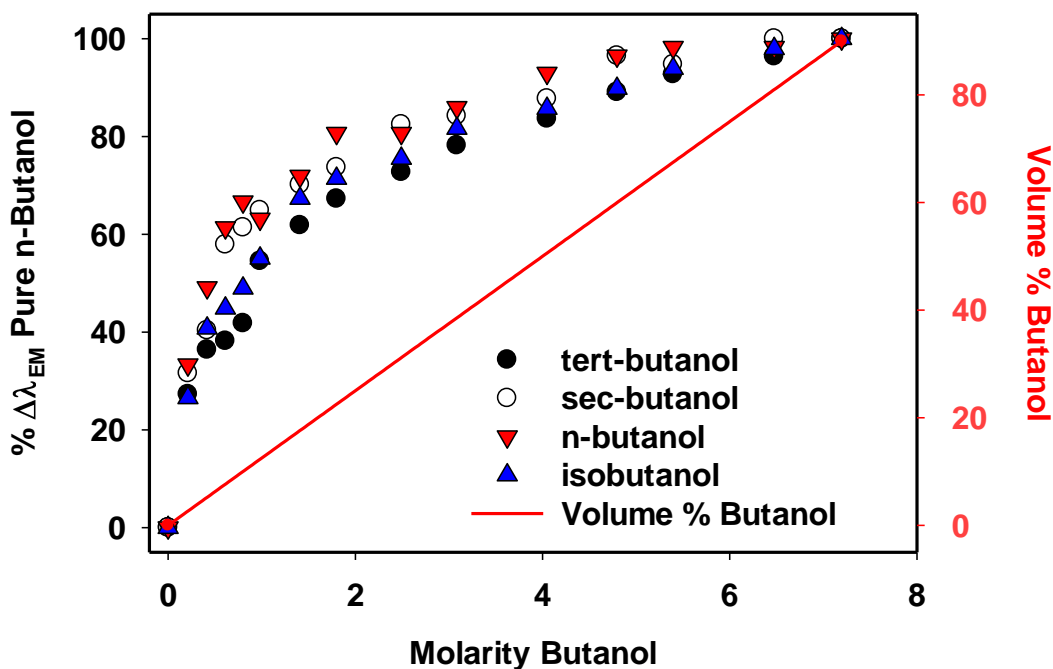


Figure 2.13. Solvatochromic shift of PIB-bound dansyl sulfonamide adding butanol in heptane. The deviation of the $\% \Delta\lambda_{EM}$ (■ experimental data) from volume % shows the microheterogeneity of this cosolvent system and how dye solvation differs from simple additive effect of the two solvents on the dye fluorescence.

We further tested this hypothesis by examining the effect of alcohols as cosolvents in heptane had on the λ_{EM} of PIB-bound dansyl sulfonamide (Figure 2.13). As was the case with hexanoic acid, the presence of even relatively small amounts of hydrogen bonding n-butanol has a large effect on the λ_{EM} of the fluorophore at low concentrations. At 2M n-butanol, the PIB-bound dansyl sulfonamide has a ca. 80 $\% \Delta\lambda_{EM}$ compared to 30 $\% \Delta\lambda_{EM}$ for either THF or DCM. Even at 0.2 M n-butanol, the fluorophore shift is ca. 30 $\% \Delta\lambda_{EM}$ for the PIB-bound dansyl sulfonamide. This further supported our hypothesis that H-bonding donors that can directly interact with solutes in alkane solvent systems have more of an effect on the solutes than polar solvents which

cannot directly interact with the solute. We further investigated how incorporating steric hindrance into the cosolvent affected the ability of the H-bonding solvent to affect solutes. Sec-butanol, isobutanol, and tert-butanol were all compared to n-butanol to determine how steric hindrance affected the ability of the alcohol to solvate the PIB-bound dansyl sulfonamide fluorophore. As the steric hindrance around the alcohol increased, the effect the cosolvent has on the solvatochromic dye decreases. For example, 2M n-butanol results in a ca. 80 % $\Delta\lambda_{EM}$ of the PIB-bound dansyl sulfonamide, where 2M tert-butanol results in a ca. 60 % $\Delta\lambda_{EM}$ of the same fluorophore. This is presumably because as steric hindrance increases around the alcohol, the ability of the alcohol to pack around the fluorophore to solvate it decreases, and thus not having as drastic effect on the local environment around the fluorophore. This effect is well known in classical organic chemistry and in inorganic chemistry and illustrated by the Tolman cone angle.⁹³

These results indicate that it would be possible to use PAO as an alternative recyclable bulk solvent and fine-tune the polarity experienced by polar solute molecules by adding a small volumes of polar cosolvents to approximate many of the effects of a pure polar solvent. Using conventional solvents this could significantly reduce the amount of solvent needed for a reaction. For example, 2 M DCM instead of pure DCM in a reaction with a recyclable PAO would require only 13% of the non-recyclable solvent. Likewise, using 2 M THF in a reaction with a recyclable PAO would require only 16% of the non-recyclable solvent. This idea should be general and could also be extended to more sustainable low molecular weight cosolvents like EtOAc. However,

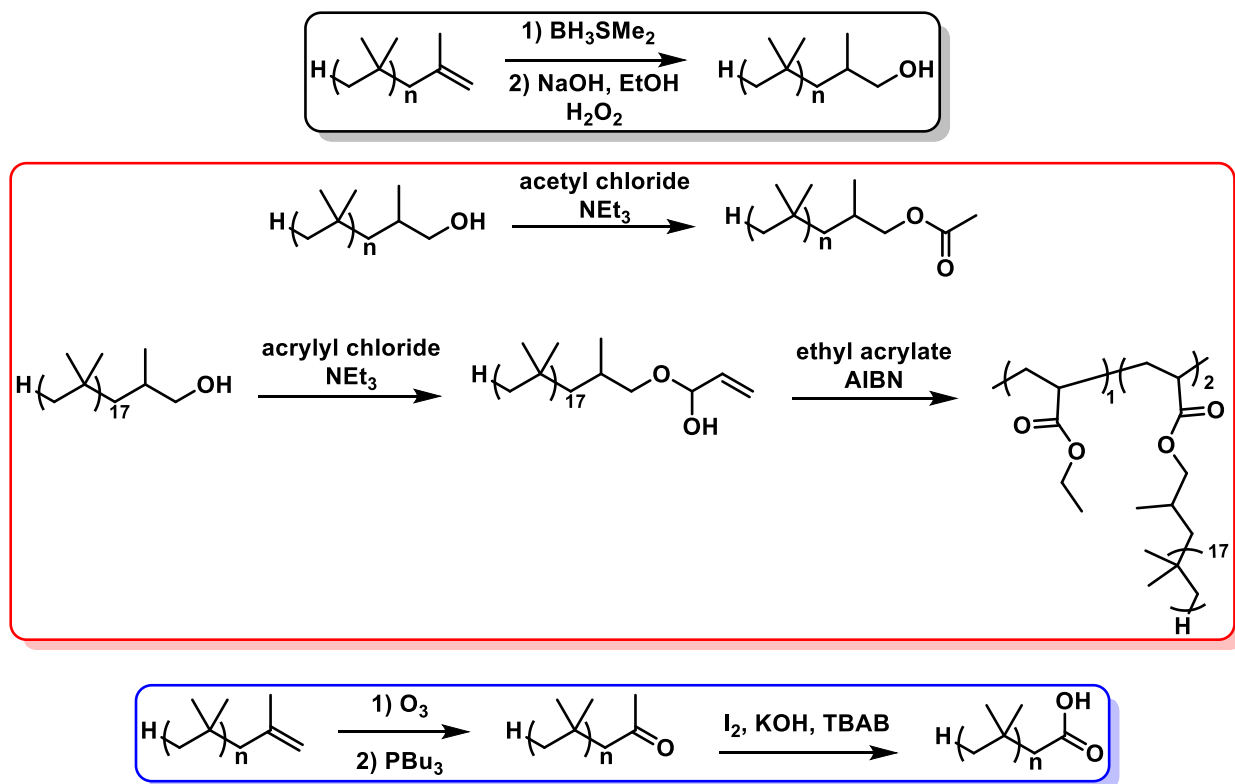
these schemes still require some low molecular weight solvent. In other work where we used PAO as a recyclable solvent, we separate it from products by a liquid/liquid biphasic separation. In these separations, a low molecular weight solvent like DCM or THF would substantially partition to the polar phase. Thus, while we could lower the amount of the polar solvent we would use, we would not eliminate it. That would mean that these schemes will not completely eliminate the toxicity associated with DCM or the hazards of peroxide formation associated with THF.

Previous work in the Bergbreiter lab has shown that soluble homogenous polymer bound catalysts perform identically to low molecular weight catalysts when activity is compared under similar conditions.^{84-86, 94, 95} We envisioned that this general observation could be extended to include a polymer bound moiety that functioned as a cosolvent. In this concept, we would imagine preparing a PAO anchored polymer bound DCM, EtOAc, butanol, or hexanoic acid. Such species have already been prepared as part of ligand syntheses. If such a polymeric solvent could tune the polarity of the PAO phase like its low molecular weight analog, we could develop fully recyclable polarized PAO solvent systems.

Our initial experiments to determine if polymer bound solvents affected solutes in the same way as low molecular weight analogs have used the same solvatochromic fluorophores Nile red and the PIB-bound dansyl sulfonamide we used in the studies above of the effects of low molecular weight cosolvents on solute solvation. These initial studies used PIB-bound esters, PIB-bound alcohol, and PIB-bound carboxylic acids as analogs of ethyl acetate, butanol, and hexanoic acid. The synthesis of these

polymer bound cosolvents is shown in Scheme 4.1. These syntheses for the most part parallel the chemistry we developed earlier for ligand syntheses of terminally functioned polyisobutylenes.⁹⁶ The exception was the synthesis of PIB copolymers of acrylates. This work was carried out in collaboration with Ying-Hua Fu and involved the free radical polymerization of ethyl acrylate and a PIB-bound acrylate.

We chose to test these cosolvents because the low molecular weight analogs of these polymer bound cosolvents had significant effects on the environment experienced by the fluorophores. H-bonding agents like butanol and hexanoic acid had significant effects even at 0.2 M. An ester like ethyl acetate had more modest effect but still had 50% of the $\% \Delta \lambda_{EM}$ of the Nile Red at ca. 1 M. This is important because the polymer chains needed to anchor the cosolvent in the PAO phase also decrease the loading of the cosolvent. For example, pure PIB-bound alcohol is roughly 2M, where pure butanol is ca. 12M. Furthermore, the viscosity of PIB requires that these polymer-bound cosolvents need to be modulated by diluting with PAO or heptane. This means that the maximum usable molarity of the PIB-bound alcohol is roughly 1M.



Scheme 4.1. Synthesis of polymer bound alcohol cosolvent (top, black), polymer bound ester cosolvents (middle, red), and polymer bound carboxylic acid cosolvent (bottom, blue)

Once the polymer bound cosolvents were synthesized, we tested how they affected the λ_{EM} shift of both the Nile red and PIB-bound dansyl sulfonamide solvatochromic fluorophores and compared the results to the low molecular weight solvents (Figure 2.14). As was the case we had previously seen using polymer bound catalysts compared to low molecular weight catalysts, the polymer bound cosolvents affected the 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. Adding the polymer chain to the cosolvent not only does not affect how the polymer bound solvent interacts with the fluorophore, but it also allows for solvents which are not

generally miscible with the nonpolar solvents like heptane or PAO to become miscible. For example, ethyl acetate does not have any appreciable solubility in PAO₄₃₂, but the PIB phase anchoring tails makes the polymer bound solvent infinitely miscible in alkane solvents like heptane or PAO.

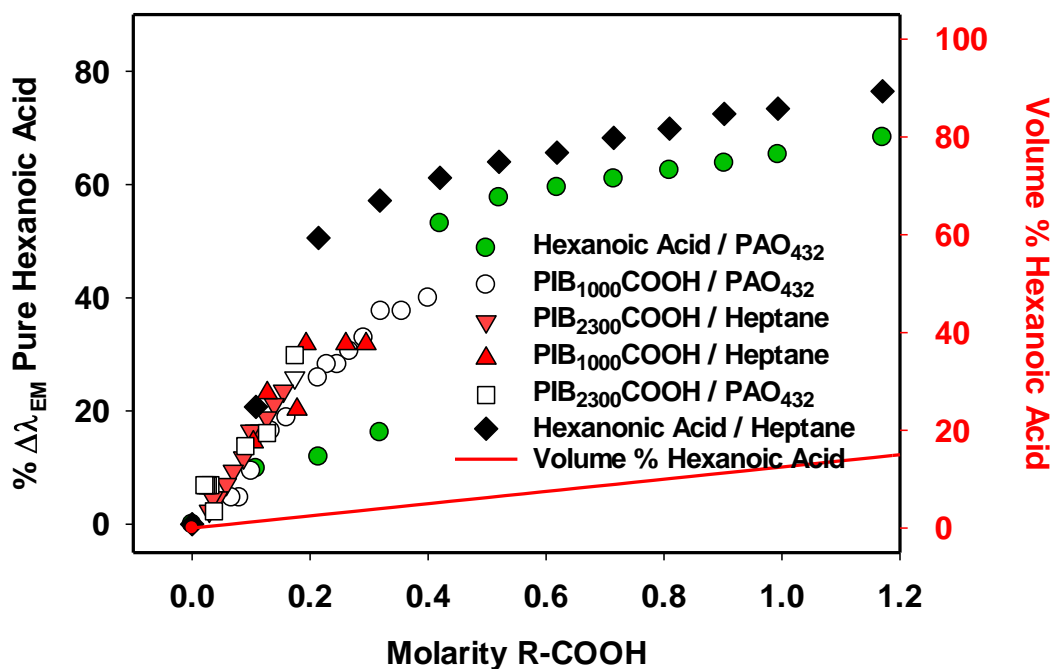


Figure 2.14. Solvatochromic shift of fluorophores adding polymer bound cosolvents. Solvatochromic shift of Nile red with polymer bound carboxylic acids as cosolvents into heptane and PAO₄₃₂ (top), solvatochromic shift of Nile red with polymer bound ester as cosolvents into heptane and PAO₄₃₂ (middle), and solvatochromic shift of PIB-bound dansyl sulfonamide with a polymer bound alcohol as a cosolvent into heptane (bottom)

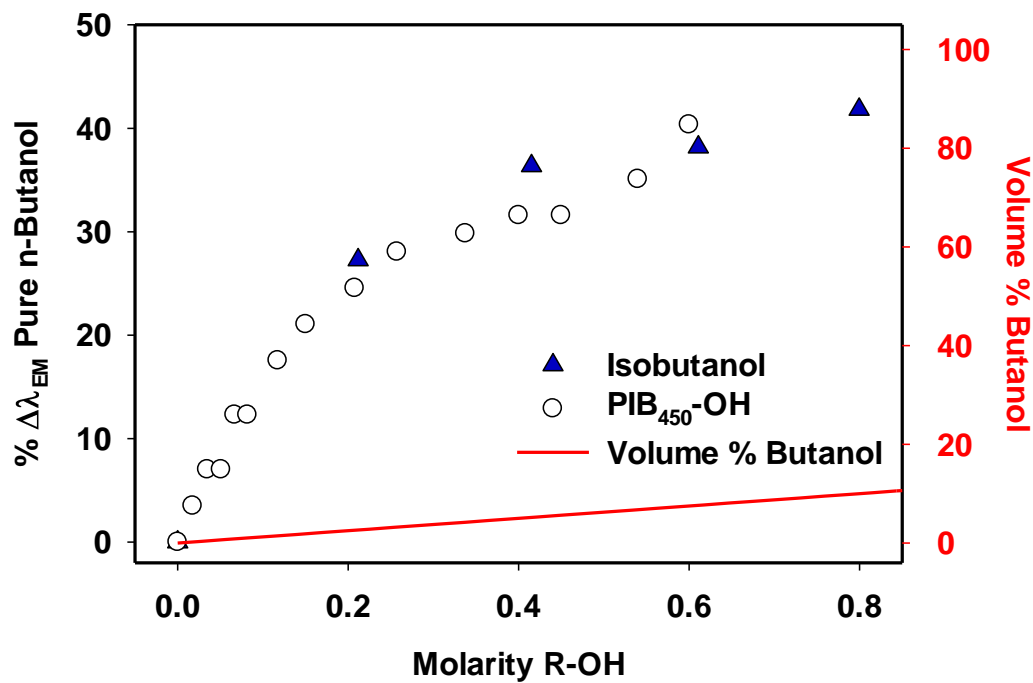
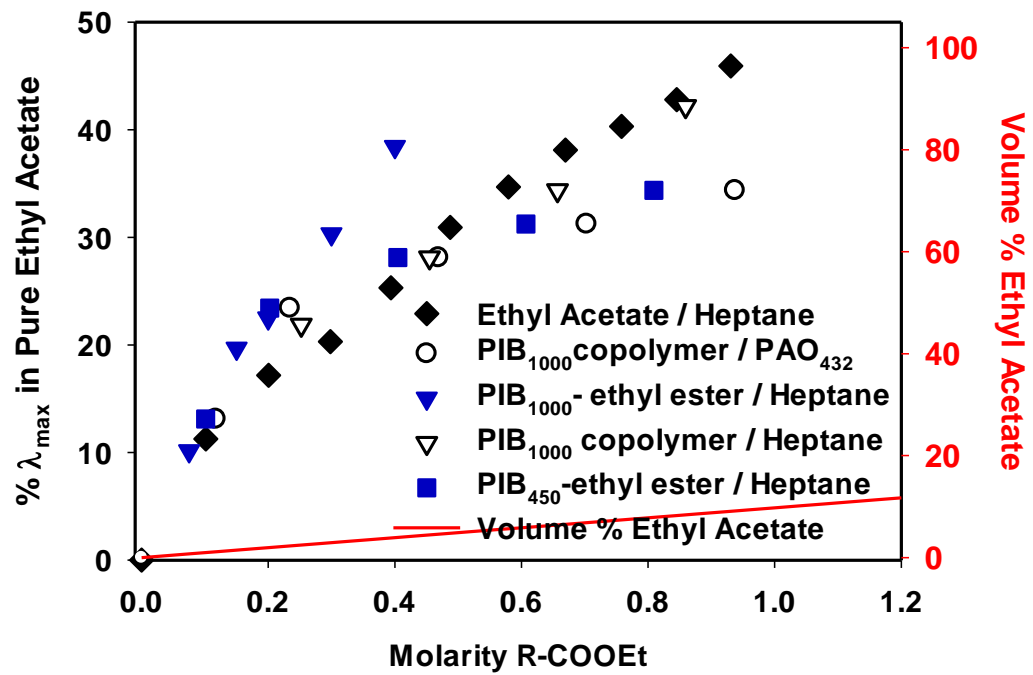


Figure 2.14 Continued

If these solvent systems were to be used for solvents for synthetic reactions, one concern would be how products could be separated from PAO. Unlike many common solvents, the boiling point of PAO is very high. For example, a TGA experiment indicated that when heated to 150 °C, there was only ca. 1% solvent loss of PAO₄₃₂ over 2 hours.⁷⁶ The high boiling point of the PAOs makes it nearly impossible to remove the PAO from the products of synthetic reactions via distilling off the PAO. We have devised several different ways to recycle these solvent systems. The simplest way to separate products from PAO solvent systems is if the product of a reaction auto-separates from the reaction solution. For example, current work in our lab shows that using a PIB-bound nucleophilic catalyst in a PAO/toluene solvent system catalyzes condensation reactions where the product precipitates and can be easily separated via centrifugation and decanting the PAO solvent which can be subsequently reused. A second way to separate products from PAOs is to take advantage of the high boiling point of the PAOs and distill the product off. This method is also being investigated in the Bergbreiter group to remove ester products from PAO solvent systems which use PIB-bound sulfonic acids PAOs to catalyze transesterification reactions. A final solution to separate products from PAOs is to extract the product in a liquid-liquid extraction using a small amount of polar solvent.⁷⁵ This method takes advantage of the low miscibility of the PAOs and PIB with polar organic solvents like acetonitrile.⁷⁶ While this method works, it does require the use of a small amount of a less recyclable polar solvent.

Conclusion

In summary, the work presented in this chapter shows that hydrocarbon oligomers can be used as alternatives for heptane for reactions. Reactions like the thermal isomerization or carboxylic acid promoted isomerization of an azo dye occurs at the same rate in heptane and in PAOs. Experiments to polarize the PAOs to expand their usability as a bulk recyclable solvent were conducted. Small amounts of polar cosolvent affect solvatochromatic fluorophores nonlinearly identically in both PAOs and in heptane. Cosolvents which can directly interact with the fluorophores like hydrogen bond donating cosolvents have a much more pronounced effect on the local environment of the fluorophores compared to solvents which can only interact through dipole-dipole interactions. Furthermore, polymer bound cosolvents affect the local environment of the fluorophore solutes in the same way as the low molecular weight cosolvents, indicating that they could be used to form a fully recyclable solvent system. Further experiments testing reactions in PAO mixed solvent systems are underway.

CHAPTER III

PAOS AS SAFER SOLVENTS FOR REACTIVE PYROPHORIC REAGENTS*

Introduction

Reactive organometallic reagents have important uses in organic chemistry. Alkylolithium reagents for example were the initial examples of imitators for living polymerizations and are still used in that application.⁹⁷ Alkylolithium reagents are also used to metalate of aryl halides, as nucleophiles for 1,2-addition to electrophilic functional groups like aldehydes, ketones and esters, as strong bases for generation of regioselective hindered bases like lithium diisopropylamide (LDA), or as reagents for C-H activation in arenes with that form stabilized anions from arenes that have suitable directing groups.⁹⁸⁻¹⁰¹ However, while alkylolithium reagents like *n*-butyl-, *sec*-butyl-, or *tert*-butyllithium that serve in these roles are commercially available and sold in bulk, these reagents are extremely hazardous. At high concentration, the commercially available products that are sold in solutions in alkanes like pentane or hexane can ignite on contact with air. Even in more modest concentrations, their exothermic reaction with water generates sufficient heat to ignite the volatile alkane solvents used to in these commercial reagents, making their use a serious laboratory hazard.^{102, 103} While these issues have been known for decades, their importance was highlighted in a recent tragic

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incident at UCLA where a reaction using *tert*-butyllithium led to a fire that resulted in the death of a young researcher.

Similar issues exist for other reactive organometallics like KH, alkali metal dispersions, dialkylzinc reagents, alkylmagnesium bromides and dialkylmagnesium reagents, trialkylboron reagents, and alkylaluminum reagents. While there are safe ways to handle these reagents, none of these reagents can ever be considered nonhazardous. Indeed, fires due to the use of these reagents are unfortunately not uncommon in industry. These reagents' hazards can be mitigated (but not eliminated) in several ways. First, substitution of the pyrophoric reagent can be considered. For example, *n*-hexyllithium can be used as a substitute for *n*-butyllithium. The reactivity of *n*-hexyllithium is the same as *n*-butyllithium in many applications, and has several advantages. Solutions of *n*-hexyllithium are not pyrophoric, even at 85 wt% *n*-hexyllithium in hexane.¹⁰⁴ Furthermore, *n*-hexyllithium is safer than *n*-butyllithium because it produces hexane in deprotonation reactions which is a liquid and less flammable than the gaseous butane produced from *n*-butyllithium. If substitution of the pyrophoric reagent is not feasible, they can be handled safely by using inert atmosphere techniques. Their hazards can also be lessened by dispersing these reactive metal dispersions as suspensions in inert solvents or by dilution of these reagents in an inert solvent.¹⁰³ While the latter strategy introduces a solvent that itself is highly flammable, this strategy is commonly used to mitigate the hazards of highly pyrophoric reagents like alkylaluminum reagents and they are often sold as solutions in an inert alkane solvent.¹⁰⁵
¹⁰⁶ While the hazards associated with pyrophoric compounds can be mitigated by

diluting the compound in an inert solvent, these solvents are themselves flammable, adding fuel to the fire if the pyrophoric reagent catches fire. The hazard of reagents like *tert*-butyllithium can be reduced by using solvents with higher flash points.¹⁰⁷ Solutions of *tert*-butyllithium in heptane are commercially available. While these solutions are still pyrophoric, the higher flash point of heptane reduces the pyrophoric hazard compared to solutions of *tert*-butyllithium in pentane.¹⁰⁴

Alkane flash points vary with the alkane molecular weight because alkane volatility is a function of molecular weight. Table 3.1 shows the flash points of alkane solvents that are used for alkyllithium reagents. As noted in the table, even a low molecular weight PAO has a flash point that is over 200 degrees higher than heptane. As would be expected from the data in this table, we have observed that poly(α -olefins) (PAOs)' flammability is demonstrably different than conventional alkanes.⁷⁶ However, while PAO and conventional alkane alkyllithium solvents vary widely in flash point and volatility, we have observed that the reactions occur virtually identically in PAOs and traditional alkane solvents.^{75, 81} Here we describe studies that show that PAOs can serve as inert solvents for alkylaluminum reagents, diethylzinc, alkylborane reagents, and alkyllithium reagents like *n*-butyl-, *sec*-butyl-, and *tert*-butyllithium. In that role, they behave like conventional alkane solvents.

A second consideration is separation of the solvent from products. While a conventional low molecular weight solvent can be removed from products by distillation at reduced pressure, that is not an option for PAOs. One way to separate PAOs from polar organic products is to use chromatography. While that option works, it is

undesirable in terms of green chemistry as it produces significant waste. Fortunately, the simpler process of using a physical gravity-based separation works well. A significant factor in this separation is that PAOs are refined such that the lower molecular weight versions we use as solvents have a narrow molecular weight range. In that sense they differ from similar materials like mineral oil. Since alkanes with 20, 24, 30, or 36 carbons have solubility in polar solvents that is often at levels of 100 ppm or less and since this solubility can be lowered further with modest amounts of water, gravity separations effectively lead to products with minimal PAO contamination.

Solvent	Flash Point
Pentane	-49 °C
Hexane	-26 °C
Cyclohexane	-20 °C
Heptane	-4 °C
PAO ₄₃₂	220 °C

Table 3.1. Flash point of alkane solvents commonly used for alkyllithium reagents

While the use of PAOs as solvents for reactions like those discussed below had not been known prior to our work, the general idea that a higher molecular weight alkane medium can serve as a safer and more convenient vehicle for a reactive organometallic species has precedent. For example, Taber described using solid paraffin to prepare dispersions of potassium hydride or Grubbs' catalyst.^{108, 109} Our group earlier noted that

as waxy solids, they protected transition metal catalysts from reaction with polar reagents and later described using polyethylene oligomers as sometimes solid solvents.⁶⁶ ¹¹⁰ Subsequently, the Buchwald group noted that solid paraffin can be used as a protective vehicle for many other catalysts.¹¹¹⁻¹¹³ Mineral oil is commonly used for sodium dispersions. Finally, alternative solvents for the reactions involving alkyllithium reagents have been explored.¹¹⁴ However, while work like that of the Hevia group that used deep eutectic solvents as a reaction media is interesting, that work only addresses the medium used for a reaction. There is no suggestion that those solvents could be used as solvents for the alkyllithium reagents themselves.

While solid paraffins can be used as vehicles for catalysts and as a way to stabilize reactive metals like sodium, they are unlikely to be useful for alkyllithium reagents. While it is possible to disperse reactive organometallics and related reagents like Na or KH in paraffin, paraffin has to be melted to deliver the reagent in the eventual reaction. This precludes their use for preparation of an alkyllithium dispersion. That is because paraffins or polyethylene oligomers would require heating to > 70 °C to melt the hydrocarbon solid, a problem for thermally unstable organometallics like alkyllithium reagents that undergo decomposition by lithium hydride formation at these temperatures.¹¹⁵

An alternative liquid hydrocarbon medium that has seen use for dispersions of reactive metals and related species is mineral oil. Mineral oil is generally considered a relatively safe material with a history of use as an over-the-counter laxative, as a skin moisturizer, and as cleaning product. It has a low flash point and is non-volatile.

However, mineral oil contains a mixture of hydrocarbons ranging from with 12-50 carbons and can also include some aromatic species.¹¹⁶ The later species could react with some alkyllithium reagents once a dispersion was formed.¹¹⁷ Furthermore, the high viscosity of mineral oil could be a drawback when handling dissolved pyrophoric reagents. Finally, the use of mineral oil poses problems in separation because of the dispersity of mineral oil. Specifically, the smaller molecular weight hydrocarbons contaminate an organic product separated in a liquid-liquid separation necessitating a column chromatography purification. Mineral oil contamination can be easily removed before or after a reaction by an extraction with hexanes or by column chromatography after a reaction. However, either scheme generates extra solvent and/or solid waste. The PAOs described below are fully hydrogenated oligomers derived from alkenes like decene (or dodecene) that are fractionated into fractions containing ca. 20 (24), 30 (36), or more carbons. The work here uses dimers and trimers of decene containing ca. 20 or 30 carbons that have M_n values of ca. 283 and 432 Da and modest viscosities. This avoids the problems of mineral oil. While higher molecular weight PAOs could be used too and would have separability like that of a C20 or C30 PAO, higher molecular weight PAOs have increased viscosity and are likely less useful as solvents because of these viscosity issues. The other important difference between PAOs and mineral oil is their separability. All PAOs and especially those with 30 or more carbons have the property that they minimally contaminate polar organic phases in a biphasic liquid/liquid separation. Such gravity separations require little or no energy and with PAOs as solvents avoid the need for an extra purification step. As noted above and as shown in

our results below, PAO₄₃₂ contamination of a polar organic solvent is most often in the 10-100 ppm range, a level of contamination that as the discussion below shows can be further minimized by adding small amounts of water to the polar phase.

Results and Discussion

While we have initially described using PAOs with M_n values ranging from 687 Da to 2505 Da as solvents, these PAOs have 50 to 180 carbons and a higher than desired velocity.⁸¹ Thus, this work used PAOs that were decene dimers or trimers that have viscosities of 2 and 4 cSt and reported M_n values of 283 and 432 Da, respectively. We first examined these lower molecular weight materials' separability. We previously described how higher molecular weight and higher viscosity PAOs are separable from solvents like DMF, MeOH, aqueous EtOH and CH₃CN.⁸¹ Similar behavior is seen for PAO₂₈₃ and PAO₄₃₂. In experiments that resemble the batch type liquid/liquid extractions typically used to work-up a reaction, contamination of PAO₂₈₃ and PAO₄₃₂ was consistently small (Table 3.2). Moreover, even what contamination of the polar phase that was seen could be reduced ca. 10-fold by adding 10 vol% water to the polar organic phase.

We further examined PAO₄₃₂ leaching in an experiment where PAO₄₃₂ was continuously extracted by CH₃CN for an extended period. After 1 day the as received PAO₄₃₂ contaminated the CH₃CN phase to the extent of 700 ppm. A second 4 day of continuous extraction of this 'extracted' PAO₄₃₂ led to only 200 ppm contamination of

the PAO₄₃₂ in CH₃CN. A further 10 day of continuous extraction led to essentially no further extraction of the PAO₄₃₂ into the CH₃CN (i.e. <50 ppm).

	DMF	DMF _{aq}	MeOH	MeOH _{aq}	CH ₃ CN
PAO ₂₈₃	0.10	0.01	0.21	0.007	0.04
PAO ₄₃₂	0.02	0.002	0.015	0.005	0.001

Table 3.2. Percent Leaching of PAO into Polar Solvents^a.

^aLeaching was measured by heating an equivolume mixture of the PAO with MeOH and DMF until the solvent mixture was miscible and then cooling this thermomorphic mixture to room temperature with or without addition of 10 vol% water. The experiments with CH₃CN involved 24 h stirring of a biphasic mixture of PAO and CH₃CN

We next studied these materials' volatility. In this study, thermogravimetric analysis (TGA) of the PAO samples was conducted. Both PAO₄₃₂ and the previously studied PAO₆₈₇ had minimal mass loss on heating from room temperature to 150 °C (Figure 3.1). PAO₂₈₃ (not shown) did gradually lose significant mass at 150 °C, had a ca. 3% mass loss over 2 h at 100 °C. PAO₄₃₂ and PAO₆₈₇ showed no mass loss even at 150 °C in this same timeframe. While the volatility of PAO₂₈₃ at higher temperatures may prohibit its use as a solvent for some applications, it should not affect the use of PAO₂₈₃ for ambient or sub-ambient applications.

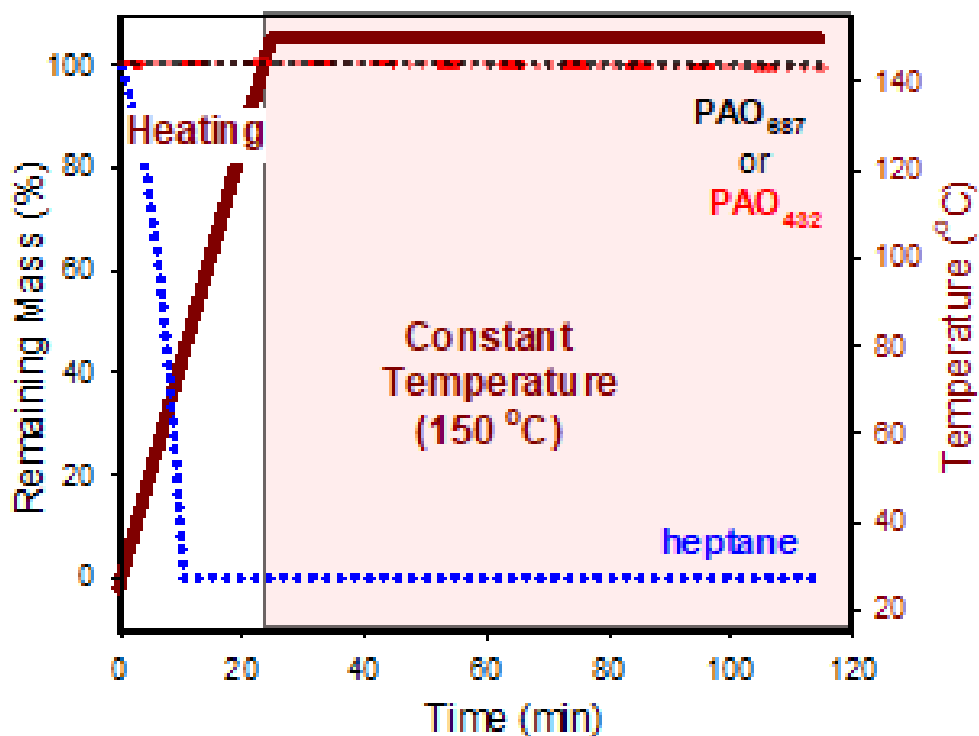


Figure 3.1. TGA analysis of heptane (blue curve), PAO₄₃₂ (red curve), and PAO₆₈₇ (black curve).

We next tested how PAOs could be used as solvents for pyrophoric reagents. These initial studies focused on using PAO₂₈₃ and PAO₄₃₂ as solvents because these solvents had lower viscosities more amenable for synthetic chemistry. To test the applicability of PAOs as safer solvents for pyrophoric reagents, we prepared PAO solutions of alkyllithium reagents starting with commercial samples of these reagents in lower molecular weight volatile alkane solvents. The PAO solutions of *n*-butyl-, *sec*-butyl-, and *tert*-butyl-lithium were prepared by transferring commercial hexane or cyclohexane solutions of these alkyllithium reagents by forced syphon to a round-bottomed flask containing a known volume of PAO₂₈₃ or PAO₄₃₂. The hexane or

cyclohexane was then removed from these solutions at reduced pressure until the solution volume approximated that of the PAO₂₈₃ or PAO₄₃₂ solvent. This generally led to a clear solution of the alkyllithium reagent whose titer was measured by a standard titration for alkyllithium and total base.¹¹⁸ These titrations involved first adding the alkyllithium solutions to water, and titrating with standardized acid to determine the total amount of base in the solution. A separate aliquot of butyllithium solution was then added to an excess of 1,2-dibromoethane which consumed all of the alkyllithium reagent by reaction of the alkyllithium reagents with the dibromide. This solution was then added to water and titrated with standardized acid to determine the amount of residual base. The difference of these two titrations is the concentration of the alkyllithium reagent in solution. Titrations of alkyllithium reagents are necessary because contact of the alkyllithium reagent with water leads to the formation of lithium hydroxide, or with air leads to the formation of the butyl peroxide which can react with excess alkyllithium to form lithium butanoates.¹⁰⁷ The solutions of *n*-butyllithium in PAO were typically ca. 2.7 M. The solutions of *sec*-butyllithium in PAO were typically ca. 1.5 M. The solutions of *tert*-butyllithium in PAO were typically ca. 1.0 M. While this work still used commercially alkyllithium reagents in low molecular weight alkane solvents, commercially available alkyllithium reagents could be directly sold in a PAO solvent, circumventing the need for any low molecular weight alkane solvent.

To demonstrate the lower flammability of the PAO solvents compared to hexane, ca. 20 mL of hexane, 20 mL of PAO₄₃₂ or 20 mL of 1.60 M *tert*-butyllithium in PAO₄₃₂ was transferred to a petri dish in open air. Notably, the *tert*-butyllithium solution in

PAO₄₃₂ did not ignite, behavior that was also seen when a similar experiment with 1.21 M *n*-butyllithium in hexanes was similarly transferred by forced siphon to a petri dish in open air.

To further examine flammability, we exposed these solutions to an open flame in the form of a gas torch. These videos are available in a supplementary file with this dissertation. As expected, the hexane immediately ignited on exposure to a gas torch. The PAO solutions of the alkyllithium reagents also ignited immediately on exposure to a gas torch and in all of these experiments, the solutions burned until the solution was completely consumed. However, PAO₄₃₂ that did not contain an alkyllithium reagent was much less flammable. It could be heated with a gas torch for 30 seconds without igniting. Further heating did cause the PAO₄₃₂ to smoke (Figure 3.2) and to eventually ignite though without continued heating by the gas torch, the flame self-extinguished within a few seconds. This behavior was seen in repeated versions of the same experiment as well as with any of the higher molecular weight PAO variants. Finally, we also added several 2-mL samples of *n*-butyl- and *tert*-butyllithium in PAO₄₃₂ to water. None of these experiments led to an ignition event though a similar experiment with *tert*-butyllithium in pentane did lead to ignition.

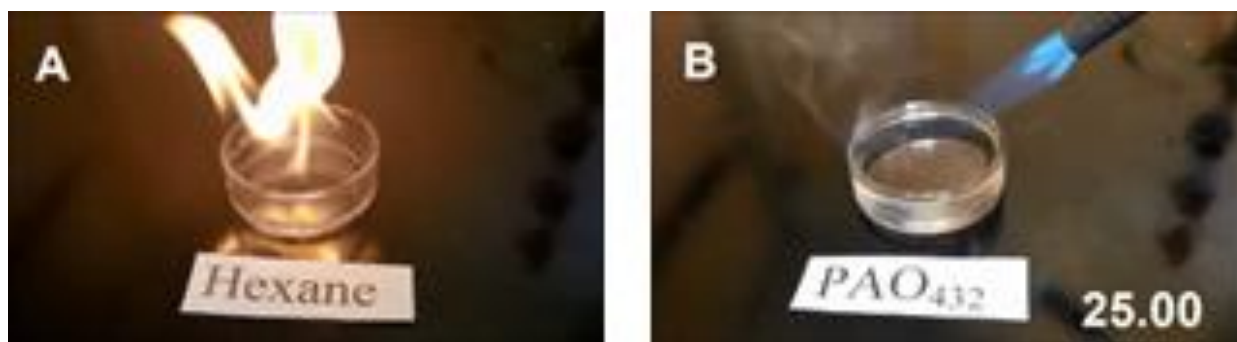


Figure 3.2. A still picture of (A) hexane immediately and (B) PAO₄₃₂ after 25 s of contact with a gas torch.

We were also able to show that PAO solutions of alkyllithium reagents had modest stability even standing in air. In experiments that tested the flammability of alkyllithium reagents in PAO solvents, the PAO solutions of *n*-butyllithium, *sec*-butyllithium, and *tert*-butyllithium were sampled after they were transferred to the petri dish and analyzed for active alkyllithium reagent. Those titrations showed that >80% of the alkyllithium reagent was present even after 30 min. Surprisingly, up to 50% of the active *n*-butyllithium remained after standing in open air overnight.

To establish the equivalence of alkyllithium reagents in PAO solvents relative to their commercial analogs in low molecular weight alkanes in synthesis, we examined reactions typical for these reagents. This included polymerization reactions, metalation chemistry where the alkyllithium is allowed to react with an aryl bromide to generate an aryllithium reagent, 1,2-additions to aldehydes where the alkyllithium reagent serves as a nucleophile, LDA chemistry where the alkyllithium reagent serves as a base for formation of LDA that is in turn used to form lithium enolates, and C-H activation

chemistry where the alkyllithium acts as a strong base to abstract an aryl C-H from a relatively acidic hydrocarbon or from an aryllithium stabilized by a ligating group. The first reaction we examined in hexanes versus PAO₄₃₂ was the polymerization of styrene (Figure 3.3). In an example of this reaction, we added a solution of *n*-butyllithium to a toluene solution of styrene at 25 °C produced a red solution. A MeOH quench led to a clear solution. Solvent removal at reduced pressure afforded white solid that was purified by precipitation in hexane to afford polystyrene in 97% yield (M_n 4100 Da, $\bar{D} = 2.5$). A reaction with slightly more styrene that used *n*-butyllithium in PAO₄₃₂ at 25 °C afforded a similar product (M_n 8300, $\bar{D} = 1.8$) in 98% isolated yield. Similar experiments were carried out by adding *tert*-butyllithium in pentane and PAO₄₃₂ to a toluene solution of styrene. In those cases, polystyrene was isolated in a similar manner with 94 and 96% yield (M_n 3920 Da, $\bar{D} = 2.0$ and M_n 5160, $\bar{D} = 1.6$, respectively).

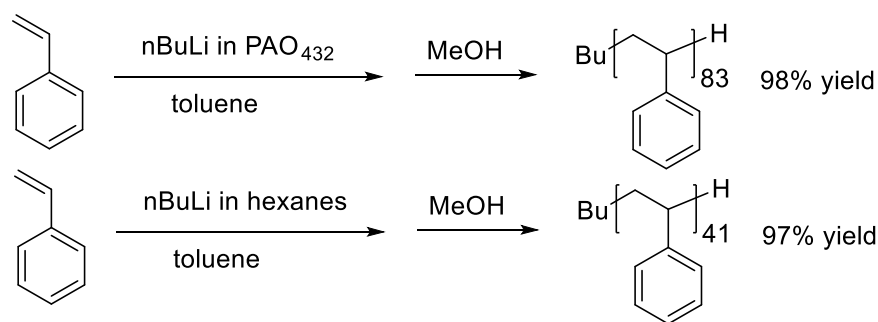


Figure 3.3. Styrene polymerizations using either *n*-butyllithium in hexanes or PAO₄₃₂ as an initiator.

The second reaction we examined in hexanes versus PAO₄₃₂ was a transmetallation (Figure 3.4). In this case, *n*-butyllithium in hexanes was allowed to

react with bromobenzene in THF at $-78\text{ }^{\circ}\text{C}$ for 30 min. Propanal was then added as an electrophile, and the reaction was allowed to warm to room temperature. After a dilute aqueous acid quench, the product alcohol was isolated in 89% yield. The same procedure starting with *n*-butyllithium in PAO₄₃₂ afforded the 1-phenylpropanol product in 85% yield.

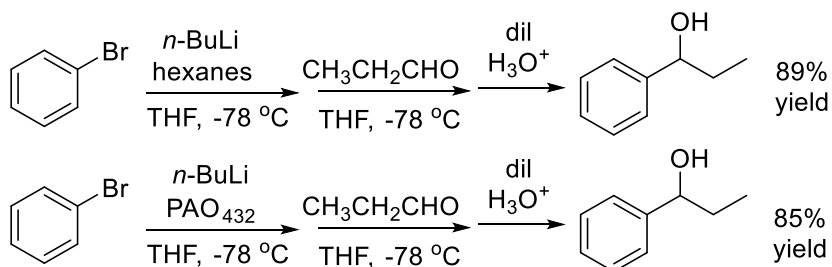


Figure 3.4. Transmetalation of bromobenzene to form phenyllithium using either *n*-butyllithium in hexanes/THF or *n*-butyllithium in PAO₄₃₂/THF followed by reaction of the aryllithium reagent with propanal.

A third example of the comparability of alkyllithiums in hexanes and PAOs is the 1,2 addition of *n*-butyllithium to benzaldehyde (Figure 3.5). The conventional addition of *n*-butyllithium in hexanes to a THF solution of benzaldehyde at $-78\text{ }^{\circ}\text{C}$ followed by warming to room temperature and a dilute aqueous acid quench afforded the expected secondary alcohol product in 82% yield. The same procedure starting with *n*-butyllithium in PAO₄₃₂ afforded the same product in 84% yield.

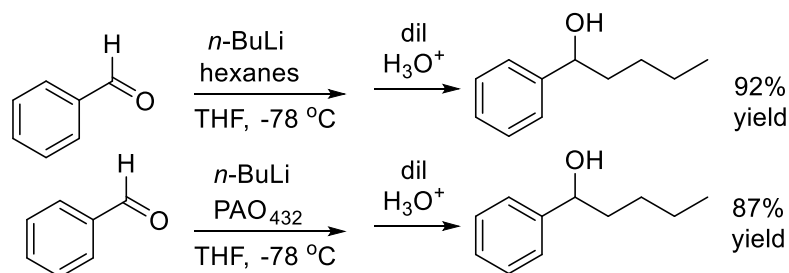


Figure 3.5. 1,2-Addition of *n*-butyllithium in either hexanes/THF or PAO₄₃₂/THF to benzaldehyde.

Using either *n*-butyllithium in hexanes or *n*-butyllithium in PAO₄₃₂ to form LDA to effect an aldol reaction was also equally effective (Figure 3.6). In this case, the LDA was prepared at -78 °C from a THF solution of diisopropylamine by addition of the alkyl lithium reagent. This LDA solution that contained a modest amount of hexane or PAO₄₃₂ was then allowed to react with acetophenone to form a THF solution of the lithium enolate that was in turn allowed to react with methyl iodide. After warming to room temperature and acidification with dilute acid, the expected aldol product was isolated in 92% and 87% yields, respectively.

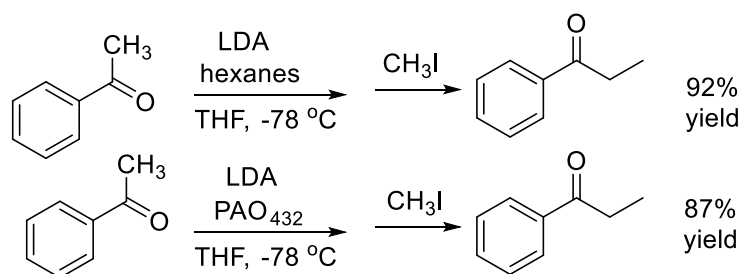


Figure 3.6. Methylation of the enolate of acetophenone with methyl iodide using LDA prepared from *n*-butyllithium in either hexanes/THF or PAO₄₃₂/THF.

A final example of the equivalence of volatile alkane solutions of alkyllithium reagents with PAO solutions of alkyllithium reagents is their use in metalation of C-H bonds. There are many examples of this chemistry used both in academic and industrial settings. Figure 3.7 shows that *n*- and *tert*-butyllithium either in hexanes or in PAO₂₈₃ readily deprotonates fluorene. Other metalation chemistry including formation of an aryllithium reagent by a TMEDA facilitated ortho-lithiation of *N,N*-diethylbenzamide using *sec*-butyllithium in cyclohexane or PAO₄₃₂ as a solvent was equally effective.

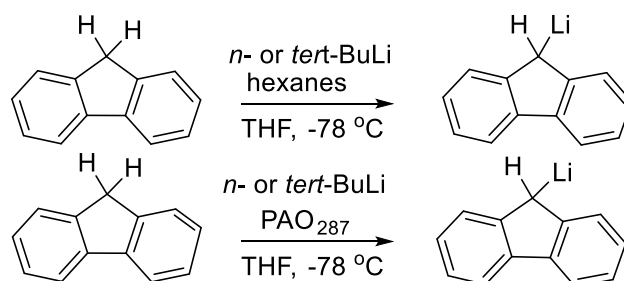


Figure 3.7. Lithiation of fluorene by either *n*- or *tert*-butyllithium in either hexanes/THF or PAO₂₈₃/THF.

To further expand on the use of PAOs as safer solvents for pyrophoric reagents, we examined the use of PAOs as solvents for trialkylboranes. Trialkylboranes like triethylborane are commonly used reagents in radical reactions where their reaction with in situ oxygen generates ethyl radicals that serve as radical initiators.¹¹⁹⁻¹²¹ Similar to diethylzinc and the alkyllithium reagents, we first attempted to transfer commercially available triethylborane in hexane into the same volume of PAO₄₃₂ and then remove the hexane via reduced pressure. In this case however, the low boiling point (95 °C) of triethylborane resulted in its removal from the PAO solution along with the hexane.

This PAO did not catalyze the reaction of styrene, where the original triethylborane solution in hexane readily polymerized styrene.

To avoid the issues encountered with triethylborane's volatility, we turned to an alkylborane with a higher boiling point. Trihexylborane was prepared by reacting 1-hexene with borane dimethyl sulfide in THF, removing the solvent, and then adding heptane or PAO₄₃₂ so that the concentration of the reagent was 1.0 M. Unlike triethylborane, trihexylborane did not readily ignite in air. A similar flame test to the alkyllithium reagents was performed with the PAO₄₃₂ or heptane solutions of trihexylborane (Figure 3.8). When exposed to the propane torch flame, the solution of trihexylborane in heptane immediately ignited and burned with a bright yellow flame. Only after all of the heptane had burned did the flame turn green, characteristic of burning boron containing compounds. The solution of trihexylborane in PAO₄₃₂ conversely burned bright green when exposed to the propane torch, but would self-extinguish after a few seconds when the torch was removed. This experiment suggests that PAO solvents could be safer solvents for trialkylborane reagents.

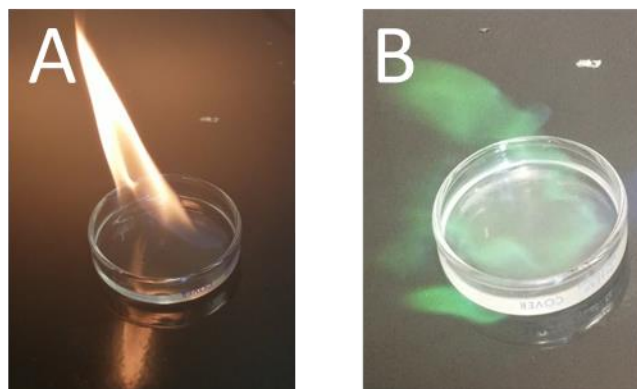


Figure 3.8. A still picture of (A) trihexylborane in hexane immediately and (B) trihexylborane in PAO₄₃₂ after 5s of contact with a gas torch.

We then tested the reactivity of the trihexylborane in PAO₄₃₂ and in heptane. Acrylonitrile was polymerized in hexane using a trihexylborane solution in either heptane or in PAO₄₃₂ as an initiator. Using trihexylborane in hexane and PAO both produced an insoluble white polymer in 93% and 88% yield for the trihexylborane in hexane and PAO respectively. The polymers were characterized by SEC and polymer from the trihexylborane in hexane had an M_n of 21000 and \bar{D} of 2.1 and the polymer from the trihexylborane in PAO had an M_n of 23000 and \bar{D} of 1.85.

We investigated the use of PAOs as solvents for other pyrophoric reagents as well. Experiments using diethylzinc and triethyl aluminum were conducted. Exposure of the commercially available diethylzinc in hexane (1.0 M) or triethylaluminum in toluene (2.5 M) to air resulted in an immediate ignition. A known volume of diethylzinc in hexane or triethylaluminum in toluene was then added to the same volume of PAO₄₃₂ and the low molecular weight solvent was removed via reduced pressure. Exposure of

these solutions of diethylzinc or triethylaluminum in PAO₄₃₂ to air did not lead to an ignition.

Conclusions

The results above show that PAO solvents are safer solvents than alkanes like pentane, hexane, and heptane for reactive organometallic solvents. While PAOs have reactivity comparable to conventional alkanes like pentane, cyclohexane or hexanes higher flash point makes solutions of these reagents less hazardous. In contrast to conventional alkanes like hexanes or cyclohexane, PAO solvents do not catch on fire even when exposed to flame. Thus solutions of pyrophoric reagents like alkyllithiums, trialkylboranes, triethylaluminum, or diethylzinc in PAO do not readily inflame. While replacing a low molecular weight alkane with PAO does not make these highly reactive pyrophoric reagents completely safe, it does mitigate their hazard. We also showed that substitution of PAO for a low molecular weight alkane did not affect the reactivity of organometallic reagents. We first showed this for reactions of alkyllithium in reactions like polymerizations, metallations, 1,2 additions, and formation of hindered bases. Direct comparisons of commercial reagents in low molecular weight alkane solvents with reagents in PAO₄₃₂ showed these reactions proceeded in comparable yields. The products in these reactions could also be separated from PAO by a simple gravity biphasic extraction. Contamination of the polar phase and products was minimal. We further showed that alkylboron reagents in PAOs can be used in polymerizations. Such polymerizations proceed like their analogous reactions in heptane. These results suggest

that these PAO solvents merit consideration as a vehicle for use with these and other reactive organometallic reagents.

CHAPTER IV

PAOS AS RECYCLABLE ALTERNATIVES TO ACTIVATED CARBON FOR WATER PURIFICATION APPLICATIONS*

Introduction

Trace organic contaminants in water that arise from natural and unnatural sources are an increasingly important issue that impacts the availability of clean water for human consumption, agriculture, and industry. The desire for greener and low energy methods for water purification have led to increasing interest in new ways to remove trace organics from water. Activated carbon is commonly used for water purification applications, but there is extensive research into alternative methods. For example, recent work has described using MOFs, modified porous polymers, functionalized membranes, and various other heterogeneous porous sorbents that use molecular recognition and novel materials to remove trace organics from water.¹²²⁻¹²⁸

Activated carbon is readily available for water purification applications. Activated carbon is generally produced from the forestry industry, although there is widespread research examining alternative sources like agriculture waste products.^{129, 130} Activated carbon purifies water of trace organic impurities via adsorption as it can be produced to have high surface area and porosity.¹³¹ While activated carbon can

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effectively remove trace impurities from water, recycling of the activated carbon requires heating the spent sequestrant to temperatures between 700 and 1100 °C. Thus, the energy cost of recycling activated carbon often makes disposal more attractive than recycling.

Due to the high costs associated with recycling activated carbon, focus has turned to alternative methods of purifying water of trace organic impurities. Current alternative approaches for water purification such as using MOFs, porous polymers, or fluorinated polymers can be engineered such that they have advantages over activated carbon in terms of recyclability, selectivity, and activity. However, these methods have drawbacks due to the cost of the starting materials and sometimes complicated synthesis. For example, Dichtel and coworkers have shown that a porous β -cyclodextrin polymer could efficiently remove contaminants like bisphenol A (BPA) more rapidly than activated carbon.¹²² While the porous β -cyclodextrin worked very well and could be recycled via simply washing the impurity away with methanol, the relatively high cost of the porous β -cyclodextrin monomer and the need to synthesize the specialty polymers reduce the usability of the sequestrant (Figure 4.1).

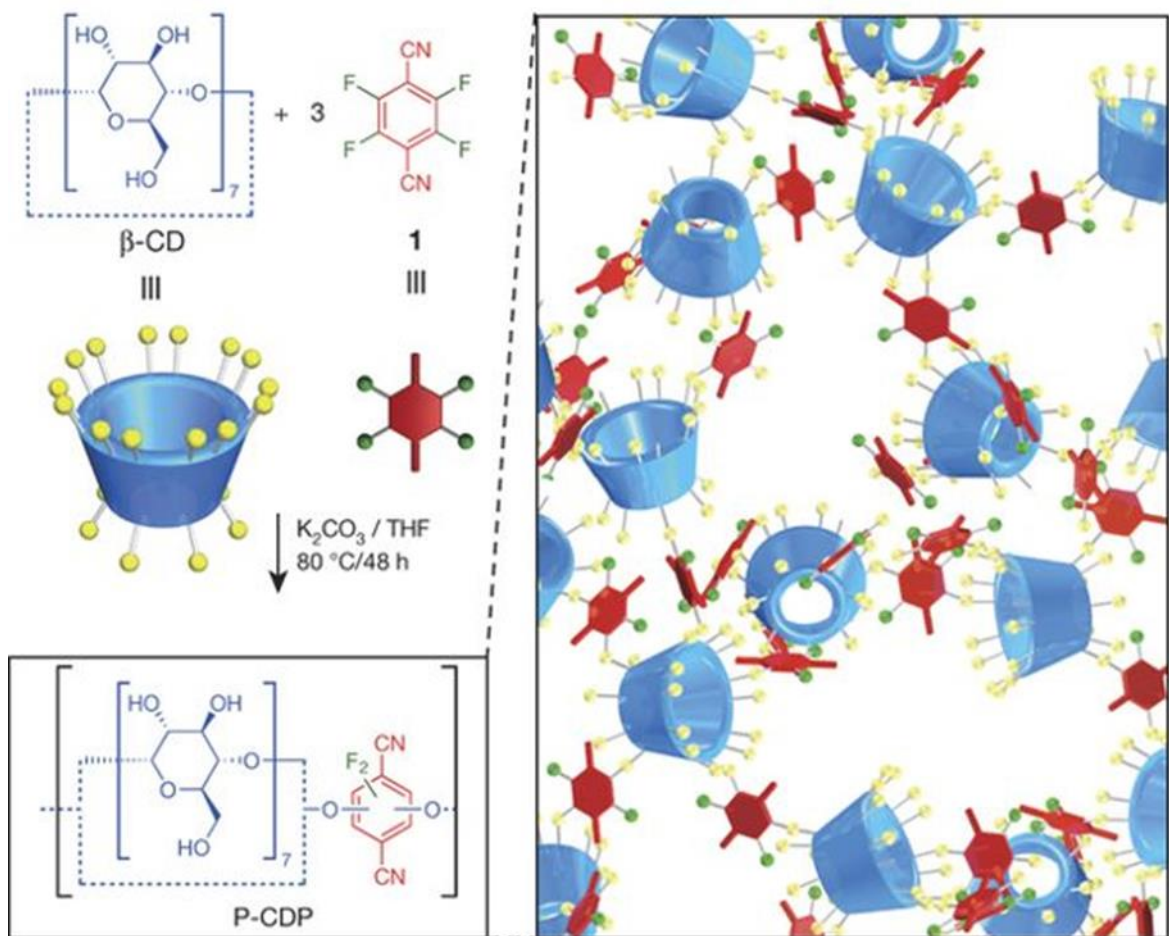


Figure 4.1. Synthesis of a porous β -cyclodextrin polymer for water purification applications. Reprinted with permission from (122)

Here we describe an alternative approach wherein liquid hydrocarbon polymers alone or with phase anchored cosolvents act as sustainable solvent systems to achieve similar goals. In this approach, liquid nontoxic hydrocarbon oligomers alone remove >99% of trace nonpolar organic compounds like hexane or benzene after a few minutes of mixing by an extraction process. If a functional oligomer which is anchored in the hydrocarbon phase is added as a cosolvent, even water miscible materials like tetrahydrofuran (THF), triethylamine (TEA), or phenols can be sequestered in the

hydrocarbon phase in this biphasic separation. In effect, this process is like an extractive workup that is commonly used in organic synthesis. However, solvents used to extract a compound in an organic synthetic process are typically chosen such that they can be easily removed from the extracted species. Most often this is accomplished using volatile organic solvents that are not recycled. The work below describes a process that uses nonvolatile recyclable solvents instead, which can be easily recycled.

Using low molecular weight compounds including lower molecular weight hydrocarbons like pentane, hexane, or heptane introduce further problems because they can contaminate the water that is being purified. These compounds also have issues in terms of cost, low recyclability, and safety. While heptane is generally regarded as an acceptable solvent, pentane has too low a flash point and hexane can metabolize to form neurotoxic intermediates. Thus, while heptane could extract benzene from water, the heptane would itself contaminate the water. This would replace one pollutant for another. An example of this would be a patent that describes the use of diesel fuel to remove trace nonpolar organics from water.¹³² This patent uses diesel fuel #2 to remove trace organic impurities from water. While the separation chemistry described in the patent works, the reality is that the diesel fuel used contains 8-10 weight % aromatic compounds which subsequently contaminate the water. Given that diesel fuel #2 is itself toxic, this is a solution to separating some trace organics from water that itself requires a solution to purify the 'purified' water. Furthermore, the patent recommends that the diesel fuel is incinerated for energy after it is used. This generates greenhouse gasses and necessitates using more of the diesel fuel for further extractions.

Our past work used hydrocarbon soluble phase anchors that separate catalysts from polar organic solvents and organic products.¹³³ Those separations were designed to be quantitative and when successful resulted in separation of 99.9 wt% of the phase anchored catalyst. As part of that work, we recently described low viscosity poly(α -olefin) oligomers (PAOs) that are green alternatives to typical alkane solvents in catalysis and synthesis.^{75, 76, 81} These PAOs are commercially available and are commonly used lubricants. We have shown that these PAO solvents enhance separations of hydrocarbon-anchored soluble catalysts and dyes and serve as safer solvents for reactive organometallics. As part of ongoing work, we noted that adding water to a polar organic phase during a biphasic liquid/liquid separation enhances the ability of these same hydrocarbon oligomer solvents to extract a nonpolar catalyst, ligand, or catalyst surrogate and that contamination of water or polar organic solvents by PAOs is negligible. This suggested to us that these same hydrocarbon oligomers could be used either alone or in concert with PAO-anchored cosolvents as media to remove trace organics from water solutions. We have noted that PAOs have virtually no solubility in water, meaning that they would not contaminate the water phase if used in water purification applications.⁷⁶ Even if the water was contaminated with trace amounts of PAO, PAOs are non-toxic and can even be kosher certified. The results described below confirm this hypothesis. PAOs alone are efficient at rapid (<5 min) separations of alkanes, arenes, and halogenated alkanes from water.

While PAOs alone are effective for removing nonpolar contaminants from water, they were expected to be less effective for substrates that have high water solubility.

Our previous work has shown that polyisobutylene (PIB) bound catalysts and dyes had high selectivity for nonpolar solvents over polar organics or water. While functionalized PIB itself is too viscous to be easily used for water purification applications, a modest amount of the functionalized PIB could be used as a cosolvent in PAO to increase the extraction efficiency of the PAO.

For example, using PAO-anchored PIB-bound hydrogen bond donating cosolvents as part of a hydrocarbon oligomer solvent system can facilitate sequestration of water-soluble hydrogen bond accepting trace organics like tetrahydrofuran (THF) in a liquid/liquid separation. To extract hydrogen bond donating trace organics like BPA, PAO-anchored PIB-bound hydrogen bond accepting cosolvents be used as part of a hydrocarbon oligomer solvent system to facilitate the sequestration in a liquid/liquid separation.

The conventional approach to removing trace organic materials from water uses granular activated carbon (GAC) as a solid sorbent.^{134, 135} While this solid sorbent is widely used, recent studies have emphasized the potential of designed solid sorbents and modified membranes in place of this generic solid sorbent. Such designed materials act faster than GAC, have chemical specificity, and can be regenerated without using as much energy. However, while these new sorbents have advantages of chemical elegance in terms of form and function, liquid/liquid separations with a soluble sorbent could be another alternative to GAC, if an economical, nontoxic, non-volatile, and regenerable phase could be used to trace organic contaminants from water using a gravity separation. We reasoned that this could be accomplished by mixing a contaminated water solution

with a commercially available PAO solvent. As is true for polar organic solvents and PAO, the immiscibility of water and PAO or PAO with PAO anchored cosolvents and their density difference ensures that a biphasic mixture of water and PAO can be separated by gravity. In this case, the PAO phase simply extracts the organic contaminant from water as shown in Figure 4.2. Such a process requires minimal amounts of energy input.

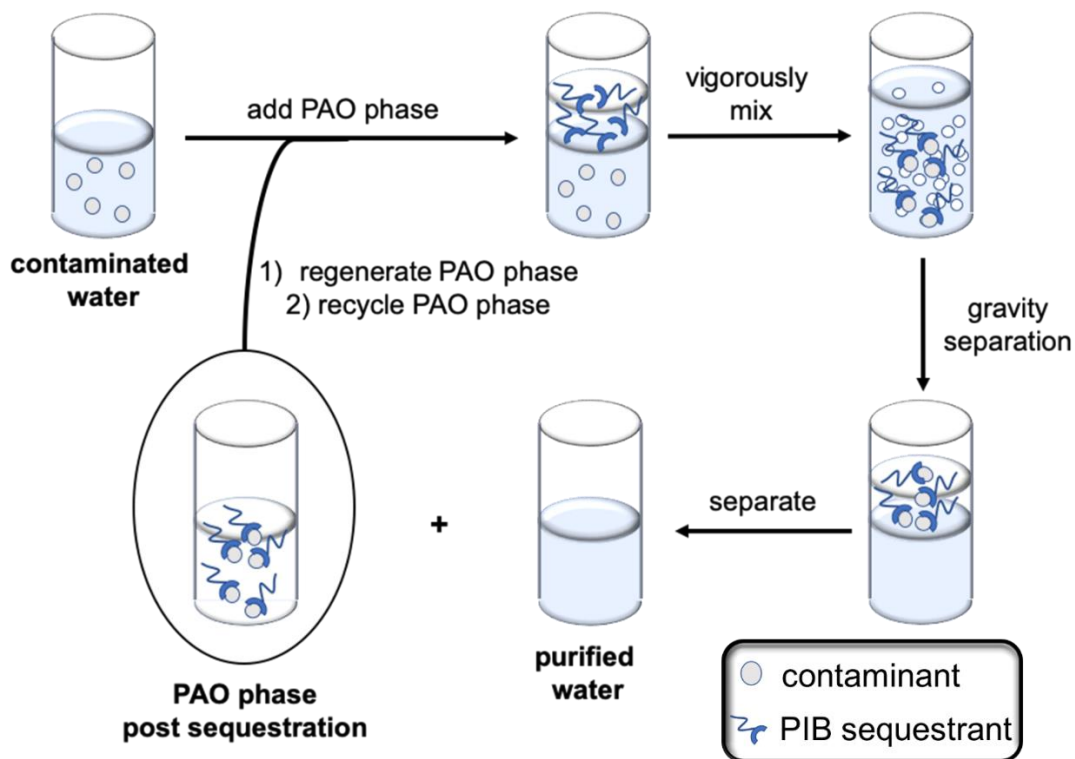


Figure 4.2. Mixing and recycling of a PAO / PAO anchored cosolvent sequestering phase purifying water contaminated by a water-soluble contaminant

Results and Discussion

Our first experiments explored two types of hydrocarbon-contaminated water samples - ca 900 ppm solutions of benzene in D₂O and a ca. 800 ppm hexane/water mixture. The benzene was present as a solution in the D₂O. The hexane was a physical dispersion. In the event, 3.5 g of these contaminated water phases were physically mixed with 1.5 g of a 432 Da PAO₄₃₂ phase for 1 min using a vortex mixer. A ¹H NMR spectroscopic analysis compared the amount of benzene or hexane in the D₂O phase before PAO treatment with the amount of benzene or hexane remaining in the PAO-extracted D₂O phase after mixing using the ratio of the signals for benzene or hexane vs. the HOD peak. Using this analysis procedure, this simple extraction removed >99% of the benzene or hexane contaminant (Table 4.1).

Trace Organic Impurity (ppm)	Residue in H ₂ O After Sequestration (ppm)	Percent Sequestered
Benzene (900) ^a	7.0	99 %
Benzene (24) ^b	< 0.1	> 99 %
Hexane (800) ^{a, d}	< 0.1	> 99 %
Dichloromethane (1450) ^b	72	95 %
Benzene (550) ^c	3.4	99%
Benzene (450) ^d	8.1	98%
1,2-Dichloroethane (650) ^c	40	94%
1,4-Dichlorobenzene (17) ^c	<0.1	>99%
Dichloromethane (7000) ^c	350	>99%
Tetrahydrofuran (11,100) ^c	7,700 (2820) ^e	30% (76%) ^e
Tetrahydrofuran (2820) ^c	330 ^e	88% ^e
Triethylamine (15,000) ^c	4,500 (600) ^e	70% (96%) ^e
Nitrobenzene (1560) ^c	142 (<0.2) ^e	90% (>99%) ^e
Perfluorooctanoic acid (1300) ^c	1130 (190) ^e	17% (83%) ^e

Table 4.1. Sequestration of Trace Amounts of Organic Contaminants from Water by PAO₄₃₂. ^[a]Sequestration was carried out by mixing 3.5 g of the D₂O solution containing the organic impurity with a vortex mixer with 1.5 g of the PAO₄₃₂ for 1 min. The D₂O phase was then analyzed by ¹H NMR spectroscopy by comparing the ratio of the signals for the trace organic component to the HOD peak of the D₂O before and after sequestration. ^[b]Sequestration was carried out by mixing 3.5 g of an aqueous solution containing the organic impurity with a vortex mixer with 0.15 g of the PAO₄₃₂ for 1 min. The D₂O phase was then analyzed by ¹H NMR spectroscopy using an MPEG₂₀₀₀ internal standard. ^[c]Sequestration was carried out by mixing 3.5 g of a D₂O solution containing the organic impurity with a vortex mixer with 1.5 g of the PAO₄₃₂ for 1 min. The D₂O phase was then analyzed by ¹H NMR spectroscopy using an MPEG₂₀₀₀ internal standard. ^[d]The concentration of benzene was measured by UV-visible spectroscopy. ^[e]The PAO phase contained 0.9 M PIB₄₅₀-catechol.

While these initial experiments were promising, using the residual HOD as a standard is problematic because the HOD peak is broad vis-à-vis the peaks for the organic contaminants and because D₂O can sorb H₂O from air. For more quantitative analyses and as a comparison to GAC we carried out two other experiments using 3.5 g of an aqueous solution containing either 24 ppm benzene or 1450 ppm of dichloromethane (DCM), extracting these solutions with 0.15 g of GAC or PAO₄₃₂. In this case, we used a quantitative ¹H NMR spectroscopic analysis with a methoxy-terminated poly(ethylene glycol) (MPEG₂₀₀₀, 2000 Da) as an internal standard.^{136, 137} Using this internal standard, we could use the signals of the repeating unit of PEG (the –CH₂CH₂O–), the CH₃O– end group, or the ¹³C satellite peaks of the MPEG₂₀₀₀, and compare them to peaks for benzene and DCM before extraction and after extraction by PAO or GAC to carry out an analysis. The equation used to determine the extraction efficiency of the system is shown in Equation 4.1. The results of these experiments showed that PAO sequestered >99% of the benzene and 95% of the DCM. GAC under the same conditions sequestered 91% of the benzene and 86% of the DCM suggesting that PAO and GAC were comparable in their efficiency.

$$\frac{1000 \text{ mg PEG}}{1 \text{ kg D}_2\text{O}} \times \frac{1 \text{ mmol PEG}}{2000 \text{ mg PEG}} \times \frac{3 \text{ H PEG}}{1 \text{ mmol PEG}} \times \frac{\text{integral of impurity}}{100 \text{ H PEG integral}} \times$$

$$\frac{1 \text{ mmol Benzene}}{6 \text{ H Benzene}} \times \frac{78.11 \text{ mg Benzene}}{1 \text{ mmol Benzene}}$$

Equation 4.1. Equation for determining the extraction efficiency of PAO for extracting benzene from water

To further explore the scope of PAO as a sequestrant, we carried out a broader set of experiments using H₂O and or D₂O solutions a variety of trace organics. These experiments variously used the ¹H NMR analysis with MPEG₂₀₀₀, described above or a UV-visible spectroscopy assay analyzing the absorbance of benzene at 253.5 nm. These analyses all used a 3.5/1.5 g/g ratio of the contaminated aqueous solution/PAO₄₃₂ sequestering phase. The results of these experiments are shown in Table 4.1. They show that benzene at various concentrations, chlorinated hydrocarbons, and chlorinated arenes can all be sequestered by PAO with sequestration efficiency typically being >98% after 1 minute of agitation to perform the extraction. However, while PAO was efficient at sequestering nonpolar contaminants, sequestrations of more polar water contaminants were less successful. Extraction of an aqueous THF or TEA contaminated solution with just PAO₄₃₂ showed that only 30% of the THF in a 11,000 ppm aqueous solution or 70% of the TEA in a 15,000 ppm aqueous TEA solution was sequestered under conditions where >98% of less polar chloroalkanes, chloroarenes, benzene, and

hexane were sequestered. Water immiscible polar substrates like nitrobenzene and perfluorooctanoic acid were sequestered too with good and low efficiency, respectively.

To explore the capacity of PAO₄₃₂ for benzene sequestration, we separately prepared solutions of PAO₄₃₂ containing 2000, 5000, or 10,000 ppm benzene and mixed them with D₂O. Analysis of the D₂O phase after 1 min of mixing the benzene/PAO₄₃₂ mixtures with benzene-free D₂O showed 1.9, 4.4, and 11.1 ppm of benzene in a D₂O phase (0.22, 0.20 and 0.25%, respectively) based on a ¹H NMR spectroscopic analysis. This showed that leaching of benzene from a highly contaminated PAO phase is minimal. We also used the same PAO₄₃₂ sample to extract a series of 900 ppm benzene/H₂O solutions using UV-visible spectroscopy to assay the PAO's effectiveness through multiple cycles of extraction with a relatively high level of benzene in water. The recycled PAO phase was effective through 5 cycles in significantly reducing the amount of benzene in these 900 ppm solutions but the amount of residual benzene in the aqueous phase gradually increased from 7 to 31 ppm first through fifth cycles when the same 1.5 g sample of PAO was used to treat 5 3.5 g samples of a 900 ppm benzene solution as shown in Figure 4.3. This PAO phase was recycled by sparging N₂ gas following the procedure described below to regenerate the PAO phase. This recycled PAO₄₃₂ was then used to extract another 5 cycles of 900 ppm benzene. Sparging the PAO phase increased the extraction efficiency of the hydrocarbon phase so that the recycled PAO performed similarly to the original PAO. A similar experiment that started with a lower 7 ppm benzene solution showed no detectable benzene after 5 serial

extractions using the same 1.5 g of PAO to extract 5 3.5 g samples of benzene contaminated water.

We verified that the extraction efficiencies seen in these small-scale experiments were scalable by extracting 500 g of H₂O containing 250 ppm benzene or 16 ppm 1,4-dichlorobenzene with 22 g of PAO₄₃₂. In the benzene case, we removed 98.1, 98.3 and 97.8% of the benzene in three successive extractions using the same PAO₄₃₂ sequestration phase. In these experiments, the PAO₄₃₂ was quantitatively recovered based on volume and was reused after bubbling air through it to remove the sequestered benzene. In a separate experiment, the same PAO₄₃₂ phase sequestered >99% of a 1,4-dichlorobenzene contaminant without any purification through three cycles.

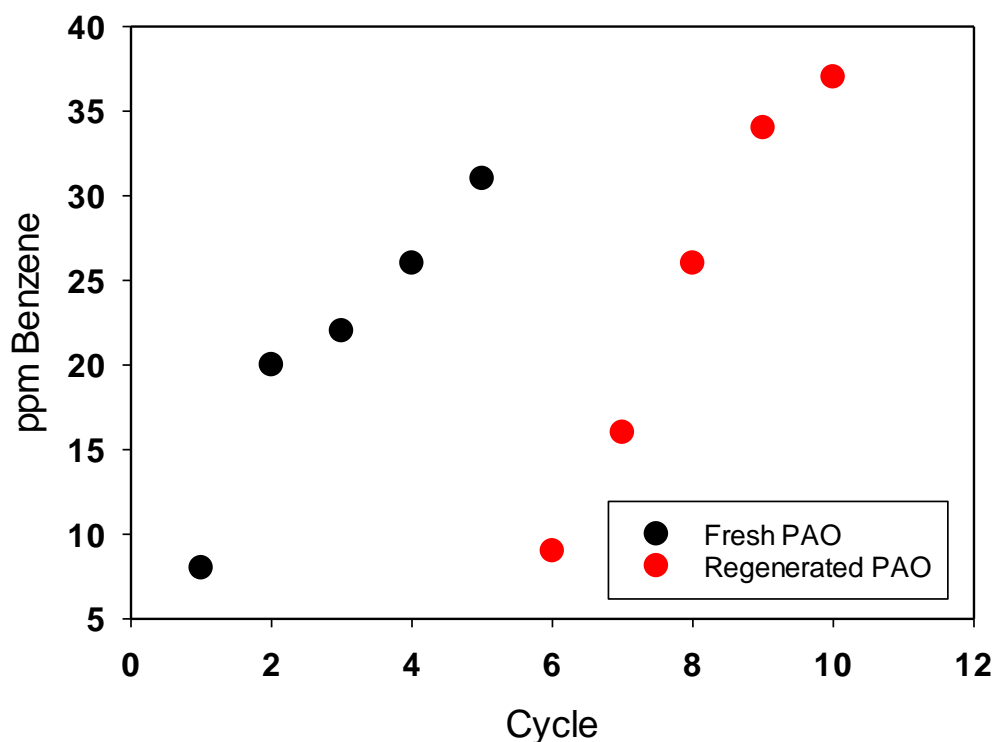


Figure 4.3. Benzene sequestration efficiency of 1.5 g of fresh and recycled PAO₄₃₂ extracting 3.5 g of D₂O containing 900 ppm benzene

To address the issue of more pedestrian sequestration levels for polar organics, we explored modifying PAO with a PAO-phase anchored cosolvent to generate a sequestering phase that contained molecular recognition elements. Our experience with polyisobutylene (PIB)-bound dyes, ligands, catalysts, and polar nanoparticles is that hydrocarbon oligomeric solvents are very effective at phase anchoring PIB-bound polar species.^{67, 81, 138, 139} Thus, we reasoned that a PIB with a hydrogen-bonding terminal catechol group could be phase anchored in PAO. The synthesis of this PIB-bound catechol is shown in Figure 4.4. We hypothesized that this PIB-bound catechol could be used to facilitate sequestration of polar groups in PAO because the ability of catechol to

form hydrogen bonds, a property that would be enhanced in a hydrocarbon like PAO where there are no competing hydrogen bond acceptors. This premise has precedent in water separation with membranes.¹²⁸ Thus, we prepared a catechol derivative from alkene terminated PIB₄₅₀ (450 Da M_n) using the chemistry below and used this PIB derivative as a PAO phase anchorable hydrogen bonding agent.

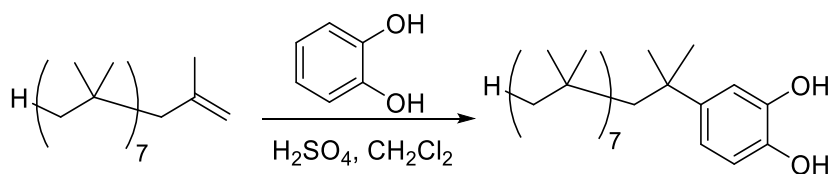


Figure 4.4. Synthesis of hydrogen bonding catechol-functionalized polyisobutylene cosolvent

A preliminary experiment using PAO, 1 M PIB₄₅₀-catechol, and an aqueous solution of *p*-methyl red suggested this strategy would be effective since the methyl red visually transferred from water to the PAO phase, forming a red PAO solution consistent with strong hydrogen bonding of the PIB₄₅₀-catechol to the methyl red dye. This PIB-bound catechol also significantly increased the effectiveness of PAO for THF and TEA sequestration. In the event, >70% of the THF in a 11,000 ppm solution of THF in D₂O could be sequestered and >90% of the TEA in a 15,000 ppm TEA solution in D₂O could be sequestered in a PAO₄₃₂/0.6 N PIB₄₅₀-catechol mixture. After a 11000 ppm THF/D₂O solution was extracted using PAO₄₃₂/0.6 N PIB₄₅₀-catechol mixture, the D₂O layer contained 2860 ppm THF resulting in an extraction efficiency of 76%. A second extraction with fresh PAO₄₃₂/0.6 N PIB₄₅₀-catechol lowered the concentration of THF to

351 ppm THF. This second extraction had an extraction efficiency of 88%, and left 3% of the original THF concentration. These results and results using other concentrations of PIB₄₅₀-catechol are shown in Figure 4.5 and in Table 4.1.

Nitrobenzene and PFOA and nitrobenzene are two other examples of polar organics that are problematic trace contaminants in water. While PAO₄₃₂ alone as sequestrant did a good job of sequestering 90% of the nitrobenzene in a 2000 ppm solution of nitrobenzene in water, the extent of nitrobenzene sequestration could be raised to 99% using 0.6 M PIB₄₅₀-catechol as a cosolvent with PAO₄₃₂. As shown in Figure 4.5 and Table 4.1, PAO₄₃₂ alone was less successful at sequestering PFOA from a 3000 ppm solution of PFOA in water too became a more viable sequestration medium. Adding up to 1.0 M PIB₄₅₀-catechol as a phase-anchored co-solvent to the PAO led to 89% sequestration of PFOA. Analysis of the PFOA in water was determined using ¹⁹F NMR spectroscopic analysis using D₂O containing 700 ppm of trifluoromethanesulfonic acid as an internal standard.

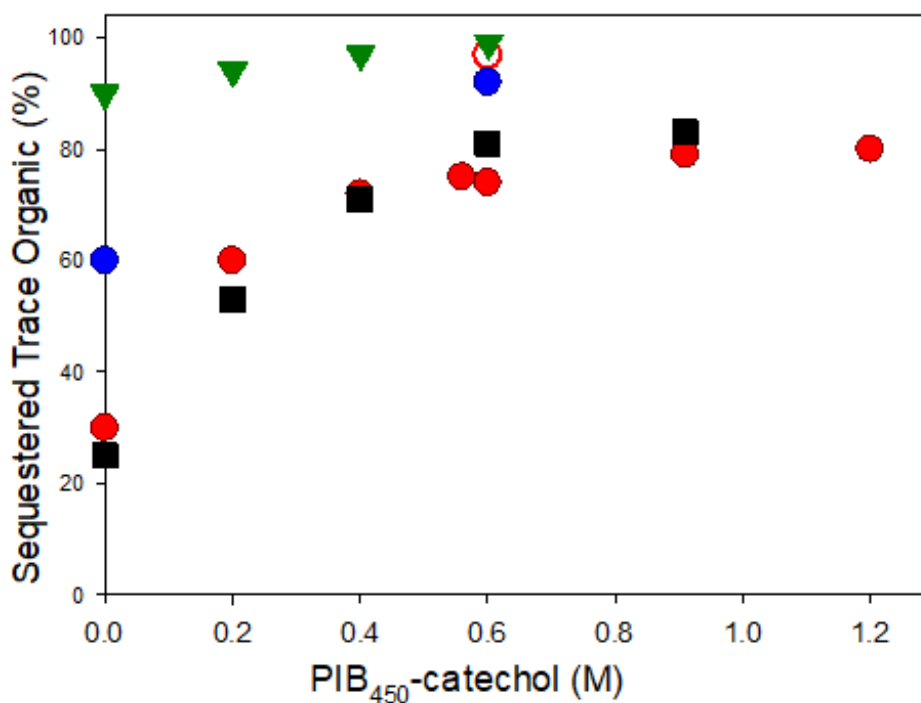


Figure 4.5. Enhanced sequestration of water miscible and water immiscible polar trace organics using catechol-functionalized PIB₄₅₀-catechol as a PAO phase-anchored cosolvent: THF in D₂O [THF]_o = 11,100 ppm ●; THF in D₂O [THF]_o = 2,820 ppm (a second sequestration of using 0.6 M PIB₄₅₀-catechol ○); Et₃N in D₂O [Et₃N]_o = 20,200 ppm ●; PFOA in D₂O [PFOA]_o = 1130 ppm ■; C₆H₅NO₂ in D₂O [C₆H₅NO₂]_o = 1560 ppm ▼

Based on the encouraging results obtained using PIB-bound catechol as a hydrogen bond donating cosolvent, Mr. Neil Rosenfeld and Mr. Ethan Quinn investigated the use of PIB-bound hydrogen bond accepting cosolvents to extract hydrogen bond donating impurities. PIB-bound amines were chosen as hydrogen-bond accepting cosolvents, and their synthesis is shown in Figure 4.6.

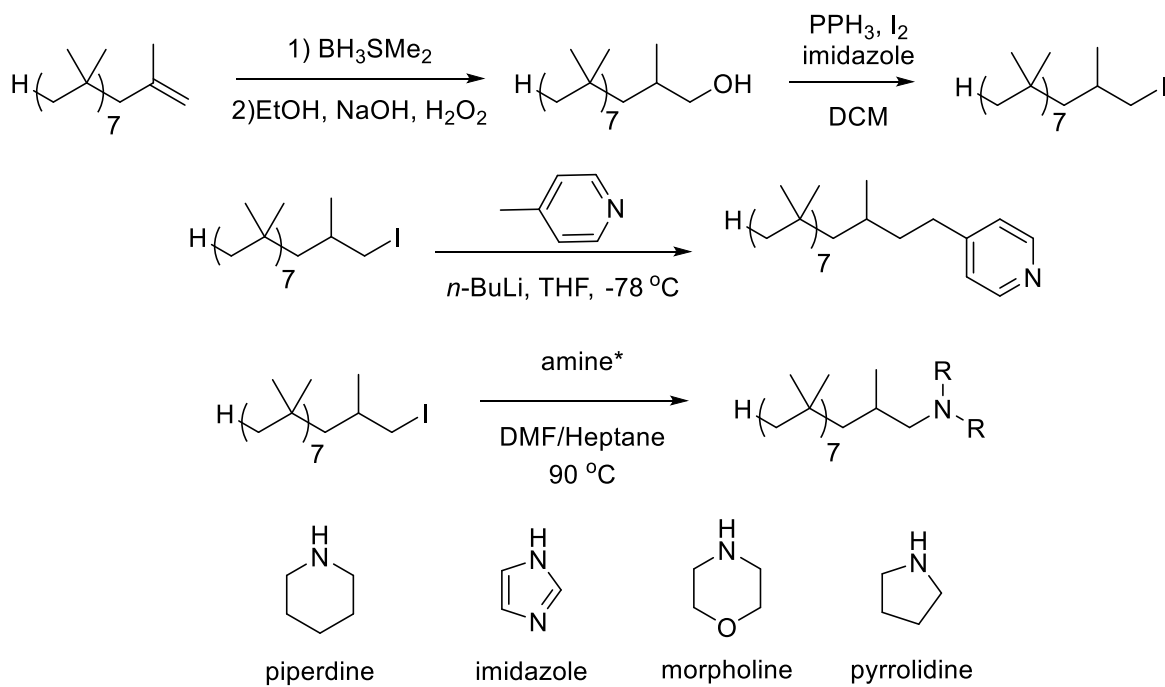


Figure 4.6. Synthesis of hydrogen bond accepting polyisobutylene cosolvents

Mr. Neil Rosenfeld and Mr. Ethan Quinn then used these hydrogen bond accepting cosolvents to extract phenols from water. In these experiments, 1.5 g of PAO/hydrogen bond accepting cosolvent was added to 3.5 g of H₂O contaminated with 300 ppm BPA. As was the same for previous experiments, this biphasic mixture was vigorously vortexed for 1 minute, allowed to stand for 10 minutes, and then centrifuged. A 0.5 g aliquot of the H₂O phase was then added to 0.5 g of D₂O containing 1000 ppm mPEG internal standard, and analyzed via ¹H NMR spectroscopy utilizing solvent suppression software to suppress the H₂O peak. While all of the PIB-bound hydrogen bond accepting cosolvents increased the extraction efficiency of the BPA, PIB-bound imidazole was the champion cosolvent, removing >99% of BPA using only 0.2 M

cosolvent. Mr. Rosenfeld expanded the use of PIB-bound imidazole to extract other phenols, and the results of some of these extractions are shown in Figure 4.7.

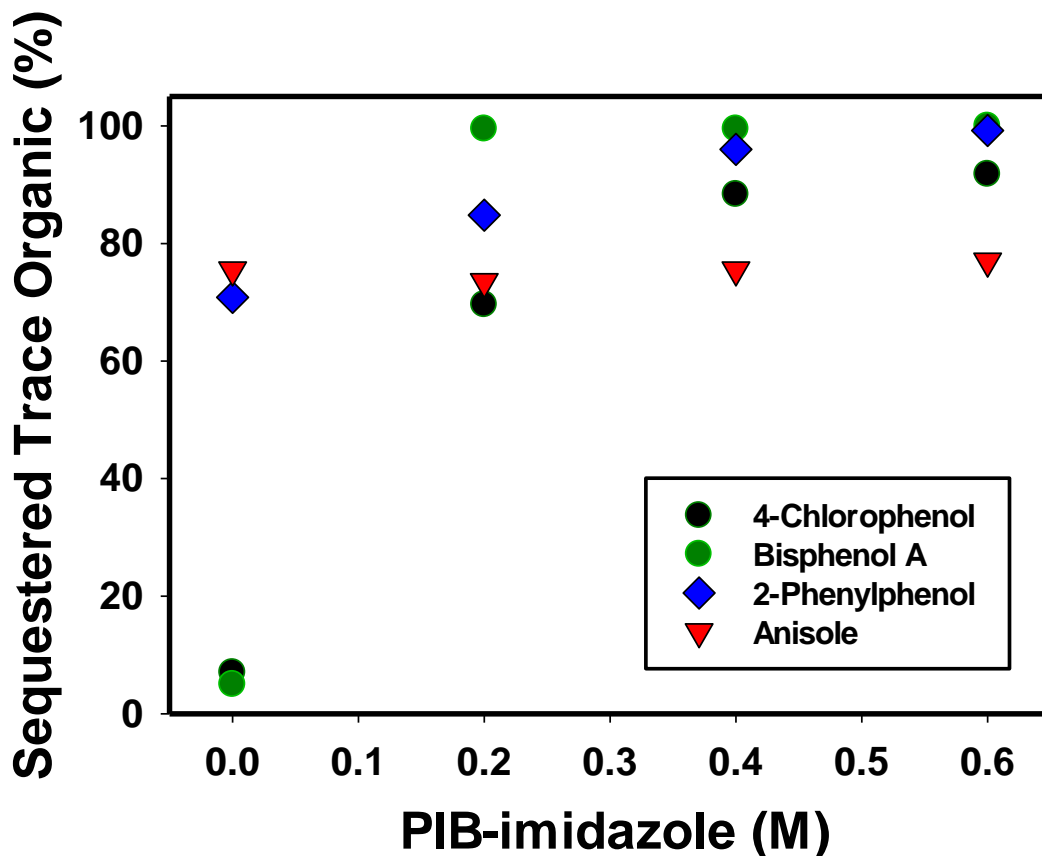


Figure 4.7. Extraction of various impurities using PAO with PIB-bound imidazole as a cosolvent

Another interesting experiment conducted by Mr. Rosenfeld involved using the PIB-bound imidazole cosolvent to extract anisole. The purpose of this experiment was to show that the cosolvent was removing the impurities via accepting of hydrogen bonds, not via polarization of the extracting phase. These experiments used a system of 0.5g of PAO/PIB-imidazole cosolvent and 20 g of H₂O contaminated with 57 ppm anisole. When no PIB-bound imidazole cosolvent was added to the PAO, the hydrocarbon phase

sequestered 75.5% of the anisole. When PIB-bound imidazole was added as a hydrogen bond accepting cosolvent at 0.2, 0.6, and 0.9M, the extraction efficiency of the anisole was 73.5%, 75.5%, and 77% respectively. These experiments show that as the concentration of the hydrogen bond accepting PIB-bound imidazole increases, the extraction efficiency of the anisole remained constant. This result indicates that the PIB-bound imidazole was extracting the phenolic impurities by accepting hydrogen bonds, and not by simply polarizing the hydrocarbon sequestering phase.

An important consideration in the development of alternative materials for trace organic sequestration is the eventual fate of the sequestration phase. Existing materials like GAC are often disposed of after use, but can be regenerated. This process requires shipping the spent sequestrant to a facility that regenerates the activated carbon by heating to temperatures in excess of 800 °C, procedures that add cost and that are energy intensive.¹⁴⁰ In the case of PAO₄₃₂, there are several alternatives to this process.

The first scheme simply involves bubbling N₂ or other inert gas through a PAO phase. This process was tested by bubbling N₂ through PAO₄₃₂ containing 7,900 ppm benzene at ambient temperature. After 1 h, 88% of the benzene was removed and more than 99% of the benzene was removed after 4 h (Figure 4.8). The amount of benzene removed from the PAO was determined by ¹H NMR spectroscopic analysis by adding a known amount of the benzene contaminated PAO to a known amount of CDCl₃ and comparing the benzene peak to the ¹³C satellite peaks of the CDCl₃. We did not recover the benzene in this experiment but commercially available cryogenic methods used for

separation of volatile siloxanes from landfill gas could be used for this purpose to avoid environmental contamination by benzene.¹⁴¹

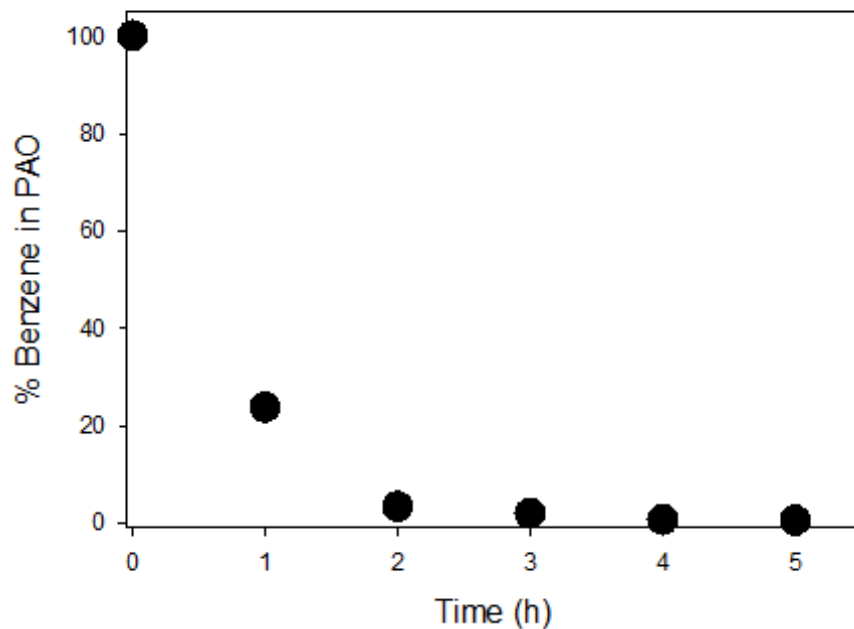


Figure 4.8. Aeration of a benzene contaminated PAO₄₃₂ phase containing 100 ppm of benzene using air removes >99% of the benzene contamination after 4 h based on a ¹H NMR spectroscopic analysis of the PAO₄₃₂ phase.

A second approach to remove less volatile impurities would involve extracting the impurities from the PAO using a polar organic solvent or water. This method would involve extracting the PAO with a small volume of sacrificial polar solvent and could be used for impurities with a low vapor pressure which would not be easily removed from the PAO phase via purging with an inert gas. We have previously reported that PAO has solubility in the 10-100 ppm range in acetonitrile, and virtually no solubility in water.⁷⁶ The low solubility of the PAO in acetonitrile or water ensures that no PAO will be lost to the sacrificial polar solvent during the regeneration process. We have previously shown

that removing ester products from PAO can be accomplished by extracting the PAO with a small amount of acetonitrile.⁷⁵ Furthermore, acid/base chemistry can be utilized to extract suitable compounds. For example, a PAO/PIB-bound imidazole sequestering phase that was used to sequester phenolic compounds would not likely be purified by sparging with an inert gas. If the solution was extracted with a 4 N aqueous sodium hydroxide solution, the phenolic compounds would be deprotonated and have far greater solubility in the water phase.

Conclusion

These initial studies suggest that the use of PAO as a liquid version of activated carbon could be broadly useful as a strategy to sequester nonpolar trace organics from water. The ability to further modify such a PAO sequestering phase with a phase-anchored cosolvent or a PIB-bound molecular recognition group can expand the scope of this liquid/liquid biphasic strategy, enabling sequestration of a variety of polar organic trace contaminants including polar organic species like PFOA or nitrobenzene which have limited water solubility as well as organic compounds like THF or NEt_3 that are fully miscible with water. Since these experiments use hydrocarbon oligomers with ca. 30 carbons, the extracting solvent or cosolvent has no detectable solubility in the aqueous phase. Indeed, solvents like PAOs have only ppm solubility even in polar organic phases.¹¹ The PAO sequestering phase can be easily recycled by simply sparging with an inert gas, and alternative recycling methods are currently being explored. In continuing work we are exploring the potential of other types of cosolvents

and recognition groups and exploring the potential of these systems for sequestration of other classes of trace organic and inorganic contaminants from dilute aqueous solutions.

CHAPTER V
EXPERIMENTAL SECTION

General Experimental

PAOs were obtained from Exxon Mobil, Chevron Phillips Chemical, or Ineos and extracted with acetonitrile to remove any impurities before use. Polyisobutylene (PIB) was obtained either from BASF or Texas Polymer Corporation. Granular activated carbon (GAC) was obtained from Cabot Norit Americas Inc. Other reagents were purchased from commercial sources and used without further purification unless otherwise stated. ^1H NMR spectra were recorded on Inova NMR spectrometers operating at 300 MHz and 500 MHz or Bruker NMR spectrometers operating at 400 MHz. Chemical shifts were reported in ppm with reference to CHCl_3 at 7.26 ppm or DMSO at 2.50 ppm. ^{13}C NMR spectra were recorded on Inova NMR spectrometers operating at 75 MHz and 125 MHz or Bruker NMR spectrometers operating at 100 MHz. Chemical shifts are reported in ppm with reference to CHCl_3 at 77.00 ppm or DMSO at 39.5 ppm. Coupling constants are given in Hz and the spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), br (broad peak) and m (multiplet). Infrared spectra were recorded on a Shimadzu IRAffinity-1S FT-IR spectrophotometer, UV-visible spectra were recorded using a Shimadzu UV-2600 UV-visible spectrophotometer, and fluorescent measurements were recorded on a Horiba Scientific Fluoromax-4 spectrofluorometer. Size exclusion chromatography was performed using two Viscotek LT4000L columns in

series and THF as the eluent. Polymer molecular weights were determined using triple detectors (refractive index, right angle light scattering, and viscometry) and polystyrene as a standard. Thermogravimetric analysis was performed using about 40 mg of the sample heated on a TGA Q500 thermogravimetric analyzer from room temperature to either 100 or 150 °C at a rate of 5 °C·min⁻¹ under argon flow of 20 mL / min⁻¹. Videos of the flame tests of the PAOs are included as a supplementary file with this dissertation.

Synthesis and Experimental Procedures

Synthesis of *para*-Methyl Red

To a 500-mL Erlenmeyer flask, 3.2 g (30.2 mmol) of sodium carbonate and 8.0 g (58.3 mmol) of 4-aminobenzoic acid were added to 100 mL of water and heated until dissolution to form a yellowish brown solution. After cooling to room temperature, 4.20 g (60.9 mmol) of sodium nitrite was added. This solution was then added to 50 mL of 2 M HCl at 0 °C, at which time the solution became thick and turned a dark rust orange color. After stirring for 30 min, 6 mL (47.3 mmol) of *N,N*-dimethylaniline and 4 mL (70 mmol) of glacial acetic acid were added dropwise, and the solution warmed to room temperature over 1 h. The crude solution was filtered and recrystallized from hot DMF/water to give 8.5 g (67%) of dark red crystals. mp 240-242 °C (decomposition) (lit. 263 °C) ¹H NMR (500 MHz, DMSO-d₆) δ 8.07 (d, J = 8.6 Hz, 2H), 7.83 (broad doublet with J_{avg} = 8.9 Hz, 4 H), 6.86 (d, J = 9.2 Hz, 2H), 3.09 (s, 6H). ¹³C NMR (125 MHz, DMSO-d₆) δ 167.5, 153.6, 143.2, 131.0, 125.8, 122.2, 112.1.

Synthesis of PIB-bound Alcohol

PIB₁₀₀₀ terminated alkene (20 g, 20 mmol) was dissolved in 100 mL of hexanes in a 250 mL round bottomed flask charged with a stir bar. To this solution, 2 mL Boron dimethylsulfide was then added dropwise and the reaction was stirred for 24 h at room temperature. After 24 h, the reaction solution was cooled to 0 °C and 20 mL of ethanol, 6 mL of 4M NaOH were slowly added, and then 4 mL of 35% hydrogen peroxide was added dropwise and the resulting reaction mixture was allowed to stir for 2 h after which 150 mL of water was added. The hexanes phase was separated and the aqueous phase was washed with hexanes (1 x 50 mL). The combined hexanes phase was then washed with water (3 x 100 mL), brine (1 x 150 mL), dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure to yield 18.2 g of product. ¹H NMR (300 MHz, CDCl₃): δ 3.48 (dd, J = 5.5 Hz, 10.2 Hz, 1H), 3.32 (dd, J = 7.5 Hz, 10.2 Hz, 1H), 0.8-1.6 (m, 180 H)

Synthesis of PIB-bound *para*-Methyl red

This dye had previously been coupled to a terminal hydroxyl group on a polyolefin oligomer using the acid chloride derivative of *para*-methyl red. In our hands, a Mitsunobu reaction proved more convenient. In this Mitsunobu reaction, a 100-mL round-bottomed flask was charged with a stir bar, 2.0 g (2 mmol) of PIB₁₀₀₀-bound alcohol, 0.91 g (4 mmol) of *para*-methyl red, and 0.02 g (0.2 mmol) of DMAP which were dissolved in 50 mL of DCM and cooled to 0 °C. To this solution, 0.82 g (4 mmol) of DCC was added and the resulting solution was stirred overnight. The suspension that

formed was filtered, and solvent was removed from the filtrate under reduced pressure. The crude product was purified via silica column chromatography (95% hexanes / ethyl acetate) to give 1.41 g (71%) of a viscous red oil. ^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 8.5$ Hz, 2H), 7.91 (d, $J = 9.1$ Hz, 2H), 7.87 (d, $J = 8.5$ Hz, 2H), 6.77 (d, $J = 9.1$ Hz, 2H), 4.19 (dd, $J = 6.0$ Hz, 10.5 Hz, 1H), 4.04 (dd, $J = 7.6$ Hz, 10.5 Hz, 1H), 3.12 (s, 6H), 0.97-1.65 (m). ^{13}C NMR (125 MHz, CDCl_3) δ 166.4, 155.8, 152.9, 143.7, 125.7, 125.6, 125.6, 121.9, 111.6, multiple poorly resolved peaks between 30-39 and 58-60.

Synthesis of tert-Butyl Isobutyrate

To a 250-mL round-bottomed flask charged with a stir bar, 15.7 g (212 mmol) of tert-butanol and 18.3 g (150 mmol) of DMAP were added to 100 mL of DCM at 0 °C. Then, 15.0 g (142 mmol) of isobutyryl chloride was added dropwise over 5 minutes, during which time a white precipitate formed. The resulting suspension was left to stir overnight. The solution was filtered, and the solvent was removed under reduced pressure. The crude product was dissolved in hexanes (50 mL), and extracted with saturated sodium bicarbonate (3 x 50 mL) and brine (1 x 50 mL) and dried over sodium sulfate. Solvent was removed via reduced pressure, and the product was passed through a short alumina pipette column to yield 15.6 g of a clear colorless liquid. ^1H NMR (500 MHz, CDCl_3) δ 2.35 (m, $J = 7.0$ Hz, 1H), 1.36 (s, 9H), 1.05 (d, $J = 7.0$ Hz, 6H). FT-IR (neat) 1730 (C=O). ^{13}C NMR (100 MHz, CDCl_3) δ 176.7, 79.6, 34.8, 28.0, 18.6

Synthesis of PIB-bound Iodide

To a 250-mL round-bottomed flask charged with a stir bar, 25.0 g (25 mmol) of PIB₁₀₀₀-bound alcohol was dissolved in 100 mL of DCM. To this solution, 8.1 g (32.5 mmol) of iodine, 8.5 g of (32.5 mmol) triphenylphosphine, and 2.2 g of (32.5 mmol) imidazole were added and the solution was stirred overnight. The orange solution was filtered, and solvent was removed under reduced pressure. The product was purified via silica column chromatography (hexane) to give 22.1 (88%) of a clear viscous oil. ¹H NMR (500 MHz, CDCl₃) δ 3.19 (dd, J = 4.2, 9.3 Hz, 1H), 3.05 (dd, J = 6.8, 9.3 Hz, 1H), 0.87-1.47 (m). ¹³C NMR (125 MHz, CDCl₃): δ multiple poorly resolved peaks between 30-39 and 58-60, 20.9.

Synthesis of PIB-bound *tert*-Butyl Isobutyrate

To a 250-mL flame-dried round-bottomed flask equipped with a flame dried dropping funnel charged with a stir bar, 5.76 g (40 mmol) of *tert*-butyl isobutyrate dissolved in 50 mL of dry THF was added dropwise over 30 minutes into 20 mL (40 mmol) of lithium diisopropylamide (nominally 2M in THF) in 50 mL of dry THF at -78 °C. The solution was allowed to react for 2 h. PIB₁₀₀₀-bound iodide (20.0 g, 20.0 mmol) dissolved in 100 mL of dry THF was then added dropwise over 10 min at -78 °C, and the solution was allowed to warm to room temperature overnight. The reaction was quenched with saturated ammonium chloride, and solvent was removed under reduced pressure. The crude product was dissolved in 100 mL of hexanes and extracted with saturated sodium bicarbonate (3 x 100 mL), 1 M HCl (3 x 100 mL), DMF (3 x 50 mL), 95% ethanol (3 x

50 mL), and brine (1 x 50 mL). After drying with sodium sulfate, hexane was removed under reduced pressure to yield 16.3 g (82%) of a yellow orange oil. ^1H NMR (500 MHz, CDCl_3) δ 0.84-1.46 (m). ^{13}C NMR (125 MHz, CDCl_3) δ 177.9, 79.6, multiple poorly resolved peaks between 30-39 and 58-60. FT-IR (neat) 1730 (C=O).

Synthesis of PIB-bound Isobutyric Acid

To a 250-mL round-bottomed flask charged with a stir bar, 16.3 g (16.3 mmol) of PIB-bound tert-butyl isobutyrate was dissolved in 200 mL of DCM. To this solution, 4.0 g of sulfuric acid was added and allowed to react overnight at which point the solution turned a reddish color. The solvent was removed under reduced pressure, and the crude product was dissolved in 100 mL of hexanes and washed with saturated sodium bicarbonate (3 x 100 mL), 1 M HCl (3 x 100 mL), DMF (3 x 50 mL), and 95% ethanol (3 x 50 mL), and dried over sodium sulfate. The solvent was removed under reduced pressure, and the product was passed through a short silica column (100% hexanes, then 90% hexanes /ethyl acetate) giving 6.1 g (37%) of product. Since we had noted that the purifications in multistep synthetic processes can lead to fractionation of PIB derivatives and since we wanted to compare PIB-COOH solutions with a known concentration of the -COOH group, we did an end group analysis of this final product rather than assume it was the same as the 1000 Da starting material. This analysis showed that the M_n of the PIB-COOH was 1616 Da based on titration in THF/water to a phenolphthalein endpoint. ^1H NMR (500 MHz, CDCl_3) δ 0.86-1.47 (m). ^{13}C NMR (125 MHz, CDCl_3) δ 185.4, multiple poorly resolved peaks between 30-39 and 58-60. FT-IR (neat) 1699 (C=O)

Synthesis of PIB-bound Dansyl Sulfonamide

To a round bottomed flask equipped with a magnetic stir bar, 2.63 g (44.5 mmol) of *n*-propylamine was dissolved in 50 mL of MeCN, dansyl chloride (1.00 g, 0.370 mmol) was added at 0 °C. The solution was allowed to stir at room temperature for 3 h and then the solvent was removed under reduced pressure. The residue was then dissolved in 100 mL of DCM and washed with water (3 x 30 mL). The organic phase was then filtered through silica and the solvent was removed under reduced pressure. The residue was taken up in a 1:1 mixture of 95% aqueous ethanol and water was then added and the crude product was placed in an ice bath. The crystals obtained were then isolated by suction filtration to give the product in 60% yield. ¹H NMR (300 MHz, CDCl₃): δ ¹H (300 MHz, CDCl₃) δ: 8.53 (d, J = 9.0 Hz, 1H), 8.26 (t, J = 8.0 Hz, 2H), 7.54 (m, 2H), 7.19 (d, J = 6.0 Hz, 1H), 3.30 (m, 2H), 3.06 (m, 2H), 2.90 (s, 6H), 1.6-0.8(m, 180H).

Synthesis of PEG-OMs

To a round bottomed flask equipped with a magnetic stir bar, methoxy terminated PEG2000 (MPEG₂₀₀₀) (10 g, 5 mmol) and triethylamine (1.5 g, 15 mmol) were dissolved in 100 mL DCM and cooled to 0 °C. Then, tosyl chloride (1.75 g, 15 mmol) was added and the reaction was allowed to stir overnight. The reaction was then washed with 2 N NaOH_(aq) (5 x 50 mL) and brine (1 x 50 mL) and dried over sodium sulfate. Solvent was removed via reduced pressure and the product was purified via precipitation in cold diethyl ether to yield 7.5 g (75%) of a white powder. ¹H NMR (300 MHz, CDCl₃): δ 4.40 (m, 2 H), 3.45-3.70 (m, 180 H), 3.38 (s, 3 H), 3.08 (s, 3 H)

Synthesis of Dansyl-Terminated PEG Monomethyl Ether

To a round bottomed flask equipped with a magnetic stir bar, dansyl-n-propyl sulfonamide (1.10 g, 3.76 mmol) was dissolved in 100 mL of DMF and 0.72 g (3.8 mmol) of cesium carbonate was added. After the solution was allowed to stir for 1 h, 2 g (1 mmol) of PEG-OTs was added and the solution was stirred at 90 °C for 96 h. The solvent was then removed via reduced pressure, and the residue was taken up in 50 mL DCM and washed with water (3 x 100 mL). The crude product was purified by precipitation in diethyl ether (300 MHz, CDCl₃): δ 8.51 (d, 1 H, $J = 8.5$ Hz), 8.29 (d, 1 H, $J = 8.5$ Hz), 8.15 (d, 1 H, $J = 7.5$ Hz), 7.51 (m, 2 H), 7.18 (d, 1H, $J = 7.5$ Hz), 3.5-3.7 (m), 3.37 (s, 3 H), 3.30 (m, 2 H), 2.89 (s, 6 H), 1.55 (m, 2 H), 0.76 (t, 3 H, $J = 7.5$ Hz). ¹³C NMR (125 MHz, CDCl₃) δ 151.6, 135.6, 130.1, 130.0, 130.0, 128.9, 127.9, 123.1, 119.7, 115.1, multiple poorly resolved peaks between 70-73, 61.7, 59.0, 50.4, 46.5, 45.4, 21.6, 11.0.

Procedure for Studies of Isomerization Rates of PIB-bound *para*-Methyl Red using UV-Visible Spectroscopy

The PIB-bound *para*-methyl red dye was dissolved in heptane or PAO to form a 1.5 x 10⁻⁵ M solution of the dye in heptane or PAO. This solution was then used to follow the rate of thermal isomerization of the dye to an equilibrium mixture of E and Z isomers in a spectrometer. This thermal isomerization was monitored using UV-visible spectroscopy with 100 scans, 100 seconds between scans, and a fast sampling speed (7 nm/s). Once the solution had reached equilibrium, the cuvette was removed from the

UV-Vis spectrometer and allowed to isomerize in room light for 12 h to a different Z-enriched E/Z mixture of 9. This solution was then placed in the spectrometer and the isomerization was again followed by UV-visible spectroscopy. A similar procedure was followed when studying the rate of carboxylic acid promoted thermal isomerization of the dye to an equilibrium mixture of E and Z isomers using various concentrations of both low and high molecular weight carboxylic acids. The rate constant of this isomerization was calculated from the slope of the first order plot obtained by plotting $\ln[(A_{\text{eq}}-A_t)/(A_{\text{eq}}-A_o)]$ versus time using the λ_{max} of 420 nm where A_{eq} is the absorbance at equilibrium, A_t is the absorbance at time t, and A_o is the absorbance at time 0.

Procedure for Solvatochromic Shift Studies

Solutions of dansyl sulfonamide (1×10^{-6}) or Nile red (1×10^{-8} M) were prepared in both solvents to be tested. The fluorescence experiments were performed by taking 2 mL of a solvent in a vial, and then adding small volumes of cosolvent and measuring the emission spectra. The solutions of dansyl sulfonamide were excited at 354 nm, and 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 $\Delta\lambda_{\text{EM}}$ of the fluorophore in a solvent mixture.

Preparing Organolithium Reagents in PAOs

To an oven dried 50 mL glass centrifuge tube equipped with a stir bar, 15 mL of dried, degassed PAO was added under a nitrogen atmosphere. Then, 15 mL of the butyllithium

reagent in low molecular weight solvent was added via forced syphon, and the low molecular weight solvent was removed via reduced pressure overnight.

Determining Concentration of Active Organolithium Reagent

A solution of NaOH (0.1024M) was prepared and standardized via titration with KHP and used to determine the concentration of a standard HCl solution (0.1425). To determine the total base concentration of the organolithium reagents, 0.5 mL of the organolithium solutions were added to 20 mL of water, then titrated with the standard HCl solution to a phenolphthalein endpoint. To determine the residual base concentration of the organolithium reagents, 0.5 mL of the organolithium solutions were added to 2 mL 1,2-dibromoethane, added to 20 mL of water, and then titrated to a phenolphthalein endpoint. The active butyllithium concentration was the difference of these two values.

Determining Leaching of PAOs into Polar Solvents

In a vial equipped with a magnetic stir bar, 3 mL of purified PAO₄₃₂ or PAO₂₈₃ were added to 3 mL of the polar solvent and stirred at 90 °C for 10 min for MeOH and DMF, and for 24 h for MeCN. The solution was then cooled to room temperature, and water was added to the aqueous samples. The contents of the vials were then transferred to separatory funnels and allowed to stand for 1 h. The phases were separated, and the polar phase was centrifuged for 15 min at 1500 RPM. A small sample of the polar phase was then collected and analyzed via ¹H NMR spectroscopy to determine the amount of

PAO contamination. A sample equation showing the contamination of methanol with PAO₄₃₂ is shown as follows

$$\frac{\text{X Integral of PAO peaks } (\delta \text{ 0.8} - \text{1.4})}{\text{Integral of MeOH satellite peaks}} \times \frac{3 \text{ H in } ^{13}\text{CH}_3\text{OH}}{1 \text{ mmol } ^{13}\text{CH}_3\text{OH}} \times \frac{1 \text{ mol } ^{13}\text{CH}_3\text{OH}}{132.04 \text{ g } ^{13}\text{CH}_3\text{OH}}$$

$$\times \frac{0.0103 \text{ g } ^{13}\text{CH}_3\text{OH}}{1 \text{ g } ^{12}\text{CH}_3\text{OH}} \times \frac{1 \text{ mol PAO}}{64 \text{ H in PAO}} \times \frac{432 \text{ g PAO}}{1 \text{ mole PAO}} = \frac{\text{g PAO}}{3 \text{ mL MeOH}}$$

Equation 5.1. Equation used to determine the amount of PAO contaminating methanol

Synthesis of 1-Phenyl-1-Propanol

To a flame dried 50 mL round bottomed flask equipped with a magnetic stir bar, 0.32 mL (3 mmol) of bromobenzene in 15 mL dry THF was added at -78 °C. Then, *n*-butyllithium (1.32 mL, 3.3 mmol, 2.5 M in hexane or PAO₄₃₂) was added dropwise and allowed to react for 30 minutes, at which time propionaldehyde (0.26 mL, 3.6 mmol) in 15 mL dry THF was added dropwise. After 1 h, the reaction was quenched with 20 mL saturated ammonium chloride. The phases were separated, and the aqueous phase was washed once with 15 mL hexane. The combined organic phases were washed once with 15 mL 2 M HCl. The organic phase was then dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was then taken up in 10 mL hexane and extracted once with 10 mL MeCN. Solvent from the MeCN phase was then removed via reduced pressure to give the product. (89% yield hexanes, 85% yield PAO) ¹H NMR (500 MHz, CDCl₃) δ=7.25-7.38 (m, 5H), 4.60 (t, J= 6.5 Hz, 1H), 1.90 (bs, 1H),

1.79 (m, 2H), 0.92 (t, J=7.5 Hz, 3H) ^{13}C NMR (125 MHz, CDCl_3) δ =144.6, 128.4, 127.5, 125.97, 76.0, 31.9, 10.1

Synthesis of 1-Phenyl-1-Pentanol

To a flame dried 25 mL round bottomed flask equipped with a magnetic stir bar, (0.30 mL, 3 mmol) of benzaldehyde in 3 mL dry THF was added at $-78\text{ }^\circ\text{C}$. Then, *n*-butyllithium (1.32 mL, 3.3 mmol, 2.5 M in hexane or PAO₄₃₂) was added dropwise and allowed to react for 2 hours, at which time the reaction was quenched with 10 mL saturated ammonium chloride. The phases were separated, and the aqueous phase was washed once with 10 mL hexane. The combined organic phases were washed once with 10 mL 2 M HCl. The organic phase was then dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was then taken up in 10 mL hexane and extracted once with 10 mL MeCN. Solvent from the MeCN phase was then removed via reduced pressure to give the product. (92% yield hexanes, 87% yield PAO) ^1H NMR (500 MHz, CDCl_3) δ =7.25-7.38 (m, 5H), 4.60 (t, J= 5 Hz, 1H), 2.02 (bs, 1H), 1.80 (m, 1H), 1.72 (m, 1H), 1.35 (m, 4H), 0.90 (t, J=7 Hz, 3H) ^{13}C NMR (125 MHz, CDCl_3) δ =144.9, 128.4, 127.5, 125.97, 74.7, 38.8, 28.0, 22.6, 14.0

Synthesis of Propiophenone

To a flame dried 50 mL round bottomed flask equipped with a magnetic stir bar, (0.35 mL, 3.3 mmol) of diisopropylamine in 10 mL dry THF was added at $-78\text{ }^\circ\text{C}$. Then, *n*-butyllithium (1.32 mL, 3.3 mmol, 2.5 M in hexane or PAO₄₃₂) was added dropwise and

allowed to deprotonate for 30 minutes, at which time acetophenone (0.35 mL, 3 mmol) was added and allowed to react for 30 minutes. Then, methyl iodide (0.22 mL, 3.6 mmol) was added in 10 mL dry THF. After 4 h, the reaction was quenched with saturated ammonium chloride. The phases were separated, and the aqueous phase was washed once with 5 mL hexane. The combined organic phases were washed once with 10 mL 2 M HCl. The organic phase was then dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was then taken up in 10 mL hexane and extracted once with 10 mL MeCN. Solvent from the MeCN phase was then removed via reduced pressure to give the product. (86% yield hexanes, 89% yield PAO) ^1H NMR (500 MHz, CDCl_3) δ =7.95-7.98 (m, 2H), 7.54-7.58 (m, 1H), 7.44-7.49 (m, 2H), 3.02 (t, J = 7.2 Hz, 2H), 1.24 (t, J =7.2 Hz, 3H) ^{13}C NMR (125 MHz, CDCl_3) δ =200.8, 136.9, 132.9, 128.5, 127.9, 31.8, 8.2

Synthesis of *N,N*-Diethylbenzamide

To a 250 mL round bottomed flask equipped with a magnetic stir bar, 6.1 g (50 mmol) benzoic acid and 5.48 g (75 mmol) DMF were dissolved in 100 mL DCM and cooled to 0 °C. Then, oxalyl chloride (6.35 g, 50 mmol) was added dropwise, and allowed to react for 2 h, at which time a mixture of diethylamine (5.49 g, 75 mmol) and triethylamine (10.12 g, 100 mmol) was added dropwise, and allowed to react overnight. The resulting suspension was filtered, and the solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (DCM) to yield the product as a yellow oil (6.1 g, 69% yield). ^1H NMR (500 MHz, CDCl_3) δ =7.35-7.41 (m, 5H),

3.56 (bs, 2H), 3.27 (bs, 2H), 1.26 (bs, 3H), 1.12 (bs, 3H) ^{13}C NMR (125 MHz, CDCl_3) δ =171.3, 137.3, 129.1, 128.4, 126.3, 43.3, 39.2, 14.2, 12.9

Synthesis of *N,N*-Diethyl-2-Methylbenzamide

To a flame dried 50 mL round bottomed flask equipped with a magnetic stir bar, *sec*-butyllithium (3.3 mmol, 1.4 M in cyclohexane or PAO₄₃₂) and TMEDA (3.3 mmol) were added to 5 mL dry THF at -78 °C. Then, diethylbenzamide (3 mmol) in 10 mL dry THF was added dropwise and allowed to react for 40 minutes, at which time methyl iodide (7.5 mmol) in 5 mL dry THF was added dropwise. After 4 h, the reaction was quenched with 10 mL saturated ammonium chloride. The phases were separated, and the aqueous phase was washed once with 5 mL hexane. The combined organic phases were washed once with 10 mL 2 M HCl. The organic phase was then dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was then taken up in 10 mL hexane and extracted once with 10 mL MeCN. Solvent from the MeCN phase was then removed via reduced pressure to give the product as a yellow liquid. The product was further purified by column chromatography (DCM) (62% yield cyclohexane, 66% yield PAO) ^1H NMR (500 MHz, CDCl_3) δ =7.14-7.28 (m, 3H), 3.74 (bs, 1H), 3.40 (bs, 1H), 3.11 (q, J=7 Hz, 2 H), 2.28 (s, 3H) 1.25 (t, J=7 Hz 3H), 1.02 (t, J=7 Hz, 3H) ^{13}C NMR (125 MHz, CDCl_3) δ =170.8, 137.1, 133.8, 130.3, 128.5, 125.7, 125.4, 42.6, 38.6, 18.8, 14.0, 12.9

Synthesis of Polystyrene

To a flame dried 100 mL round bottomed flask equipped with a magnetic stir bar, 4.0 mL (34.5 mmol) of styrene was added to dried, degassed toluene at room temperature. Then, 0.63 mmol of organolithium reagent in low molecular weight solvent (*n*-butyllithium in hexane, *sec*-butyllithium in cyclohexane, *tert*-butyllithium in pentane) or in PAO₄₃₂ were added in one quick addition. After 1 h, the reaction was quenched with 10 mL methanol, and the solvent was removed via reduced pressure. The crude product was then dissolved in 10 mL DCM and precipitated into 400 mL methanol at 0 °C. The product was filtered and dried under vacuum to give the product as a white powder. (*n*-butyllithium in hexane – 97% yield, M_n 4100 Da, $\mathcal{D} = 2.5$, *n*-butyllithium in PAO₄₃₂ – 98% yield, M_n 8300, $\mathcal{D} = 2.5$, *tert*-butyllithium in pentane – 94% yield, M_n 3920 Da, $\mathcal{D} = 2.0$, *tert*-butyllithium in PAO₄₃₂ – 96% yield, M_n 5160, $\mathcal{D} = 1.6$)

General Procedures for Adding Impurities to Water

Small scale stock solutions of impurities in D₂O or H₂O were made via two methods. For impurities which were not miscible with water, approximately 4 mL of the impurity was sonicated with 20 mL of D₂O or H₂O for 2 h. The mixture was allowed to stand for 1 h. The aqueous phase was then separated by pipette and diluted with D₂O or H₂O as necessary to a desired concentration before use. D₂O miscible impurities were added gravimetrically. Large scale stock solutions were made by sonicating 2 L of water with 20 mL of benzene or 1,4-dichlorobenzene for 2 h. The mixture was allowed to stand for

1 h, and the aqueous phase was separated from any undissolved benzene or 1,4-dichlorobenzene via gravity separation or filtration.

Small Scale Procedure for Extracting Impurities from D₂O using PAO or PAO / PIB₄₅₀-Catechol or PIB₄₅₀-Imidazole

1.5 or 0.15 g of PAO₄₃₂ or PAO₄₃₂ containing PIB₄₅₀-catechol was added to 3.5 g of D₂O containing various organic trace contaminants. This biphasic mixture was vortexed for 1 min and then transferred to a separatory funnel and allowed to stand. Then the bottom aqueous phase was removed and centrifuged for 15 min at 1500 RPM. The aqueous phase was then analyzed via UV-Vis or ¹H NMR spectroscopy to determine the amount of impurity which was extracted as detailed below. Comparison of the extraction efficiency in 10 separate experiments showed that the average extraction efficiency for benzene was 98.9% ± 0.5%.

Large Scale Procedure for Extraction of Impurities from H₂O using PAO₄₃₂

500 g of H₂O containing impurities was added to 22 g of PAO₄₃₂ and was mixed in a blender for 10 min, transferred to a separatory funnel and allowed to stand for 1 h. The aqueous phase was removed and centrifuged for 15 min at 15000 RPM. The aqueous phase was then analyzed to determine the amount of impurity which was extracted as detailed below. In the case of benzene, the PAO₄₃₂ phase was regenerated between each cycle via bubbling with N₂ gas for 2 h. The same PAO₄₃₂ phase was used for 3 cycles.

General Procedure for Extracting Impurities from Water using Granular Activated Carbon

0.15 g of Norit[®] GAC 1240 was added to 3.5 g of D₂O containing impurities. This biphasic mixture was vortexed for 1 min and allowed to stand for 1 h. Then, the mixture was centrifuged for 15 min at 1500 RPM. The aqueous phase was then analyzed to determine the amount of impurity which was extracted as detailed below.

Procedure for ¹H NMR Analysis of Water Samples

0.50 g of the stock D₂O solution containing various impurities before extraction was added to 0.50 g of D₂O containing either 2600 ppm methoxy terminated PEG₂₀₀₀ for samples with high concentrations of impurities or 260 ppm methoxy terminated PEG₂₀₀₀ for samples with low concentrations of impurities in order to determine the starting concentration of impurity. Then, 0.50 g of extracted D₂O was added to 0.50 g of D₂O containing the same concentration of methoxy terminated PEG₂₀₀₀ to compare with the starting solution to determine the extraction efficiency of the PAO₄₃₂ or PAO₄₃₂/PIB₄₅₀-catechol solvent system. The ¹H NMR spectra shown below both illustrate the efficiency of extraction and the absence of PAO₄₃₂ or PIB₄₅₀-catechol contamination.

Procedure for ¹⁹F NMR Analysis of Water Samples

0.50 g of D₂O contaminated with perfluorooctanoic acid before extraction was added to 0.50 g of D₂O containing 700 ppm of trifluoromethanesulfonic acid in order to determine the starting concentration of impurity. Then, 0.50 g of extracted D₂O was

added to 0.50 g of D₂O containing the 700 ppm trifluoromethanesulfonic acid standard to compare with the starting concentration of impurity to determine the extraction efficiency of the PAO₄₃₂ or PAO₄₃₂/PIB₄₅₀-catechol.

Equations for Determining Concentration of Impurity by NMR Spectroscopy

$$\frac{mg \text{ mPEG}}{kg \text{ D}_2\text{O}} \times \frac{1 \text{ mmol mPEG}}{2000 \text{ mg mPEG}} \times \frac{3 \text{ H methoxy}}{1 \text{ mmol PEG}} \times \frac{\text{integral of impurity}}{100 \text{ integral methoxy}} \\ \times \frac{1 \text{ mmol impurity}}{\# \text{ of H in impurity signal}} \times \frac{mg \text{ impurity}}{1 \text{ mmol impurity}} = \frac{mg \text{ impurity}}{kg \text{ D}_2\text{O}}$$

Equation 5.2. Equation for Determining Concentration of Impurity by ¹H NMR Spectroscopy

$$\frac{mg \text{ CF}_3\text{SO}_3\text{H}}{kg \text{ D}_2\text{O}} \times \frac{1 \text{ mmol CF}_3\text{SO}_3\text{H}}{150.08 \text{ mg mPEG}} \times \frac{3 \text{ F CF}_3\text{SO}_3\text{H}}{1 \text{ mmol CF}_3\text{SO}_3\text{H}} \times \frac{\text{integral of impurity}}{100 \text{ integral CF}_3\text{SO}_3\text{H}} \\ \times \frac{1 \text{ mmol impurity}}{\# \text{ of F in impurity signal}} \times \frac{mg \text{ impurity}}{1 \text{ mmol impurity}} = \frac{mg \text{ impurity}}{kg \text{ D}_2\text{O}}$$

Equation 5.3. Equation for Determining Concentration of Impurity by ¹⁹F NMR Spectroscopy

Procedure for Recycling PAO₄₃₂ Phase for Benzene Extraction

1.5 g of PAO₄₃₂ was added to 3.5 g of benzene contaminated H₂O, vortexed for 1 min, and then added to a separatory funnel and allowed to stand for 1 h. The aqueous phase was then separated from the PAO₄₃₂ phase. The aqueous phase was analyzed via UV-Vis spectrometry measuring the absorbance at 253.5 nm, using the molar extinction coefficient of 210 cm⁻¹/M reported by Berlman.¹ The PAO₄₃₂ phase was recycled 4 times extracting a fresh 3.5 g aliquot of the benzene contaminated water each time. After 5

cycles, nitrogen was bubbled through the PAO₄₃₂ phase to remove residual benzene to regenerate the PAO, which was subsequently used for another five cycles.

Procedure for Tracking Benzene Removal from PAO₄₃₂ via Nitrogen Purge

40 g of a 10,000 ppm benzene solution in PAO was prepared. At time 0, a 0.050 g aliquot was removed and added to 5.00 g of CDCl₃. Then, nitrogen was bubbled through the sample using a gas dispersion rod. 0.050 g aliquots were removed every hour and added to 5.00 g of CDCl₃. The amount of benzene in each sample was determined by comparing the integral of the benzene peak at 7.36 to the ¹³C satellite peaks of the CDCl₃ at δ 7.48 or 7.06

Synthesis of PIB₄₅₀-Catechol

In a 250-mL round-bottomed flask equipped with a magnetic stir bar, PIB₄₅₀-alkene (10 g, 22 mmol) and catechol (11 g, 100 mmol) were added to 150 mL of DCM and cooled to 0 °C using an ice-water bath. Then, 6 mL of concentrated sulfuric acid was added at which time the clear solution turned dark brown. The reaction was allowed to warm to room temperature overnight, filtered, and the solvent removed via reduced pressure. The residue was taken up in 150 mL of hexane and filtered a second time. The hexane phase was washed 5 times with 150 mL of 75% aqueous ethanol, 3 times with 150 mL of brine, dried over sodium sulfate, filtered, and the solvent was removed via reduced pressure. The product was purified via silica column chromatography (95:5

hexane:ethyl acetate) to yield the product as a brown viscous oil. (7.8 g, 78% yield). ^1H NMR (500 MHz, CDCl_3) δ = 6.75-6.95 (m, 3H), 5.26 (bs, 1H), 5.19 (bs, 1H), 1.77 (s, 2 H), 2.28 (s, 3H) 0.8-1.45 (m, 80 H). ^{13}C NMR (125 MHz, CDCl_3) δ = 144.1, 142.9, 140.7, 118.7, 114.7, 113.8, multiple poorly defined peaks between 0-60 ppm

Synthesis of PIB₄₅₀-Imidazole

In a 100-mL round bottomed flask equipped with a magnetic stir bar, PIB₄₅₀-I (10 g, 22 mmol) and imidazole (6.4 g, 100 mmol) were dissolved in 20 mL heptane and 20 mL DMF. The reaction solution was heated to 90 °C for 96 hours, and then cooled to room temperature. The heptane phase was removed and washed with MeCN (3 x 20 mL), 80% aqueous ethanol (3 x 20 mL), and brine (1 x 20 mL) and dried over Na_2SO_4 . The solvent was removed via reduced pressure to yield a pale yellow viscous oil (8.7 g, 87% yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.45 (s, 1H), 7.06 (s, 1H), 6.89 (s, 1H), δ 3.81 (dd, J = 6.4, 13.8 Hz, 1H), 3.61 (dd, J = 8.2, 13.8 Hz, 1H) (s, 3H) 1.6-0.8 (m, 80 H). ^{13}C NMR (100 MHz, CDCl_3) δ = 137.5, 129.4, 119.1, multiple poorly defined peaks between 0-60 ppm

CHAPTER VI

CONCLUSIONS

In summary, the work presented in this dissertation focuses on the uses of poly(α -olefins) (PAOs) as oligomeric alternatives to traditional alkane solvents. These PAOs are inexpensive as they are commercially available in a wide range of viscosities as lubricants. They are the fully hydrogenated oligomers of α -olefins like decene or dodecane and are and are recyclable, non-toxic, and non-volatile. PAOs do not leach in any appreciable amount into polar organic solvents or water, and their low vapor pressure leads to flash points which are much higher than traditional alkane solvents. PAOs have been shown to be replacements for traditional alkane solvents. PAOs exhibit antileaching properties similar to other nonpolar polymeric cosolvents like polyisobutylene, but can be used as solvents or cosolvents due to their low viscosity. Reactions in PAOs are identical to reactions in traditional alkane solvents, as was demonstrated by both the thermal and acid-catalyzed isomerization of PIB-bound *para*-methyl red. The use cosolvents to polarize the PAOs to expand the usability of PAOs as alternative solvents was investigated. It was shown that whether in PAOs or heptane that small amounts of polar cosolvents have the same nonlinear effect on the local environment of solvatochromic dyes. Furthermore, it was shown that nonpolar phase anchored polymer bound cosolvents like a PIB-bound alcohol, a PIB-bound carboxylic acid, or PIB-bound esters affect the local environment of these dyes in the same way as butanol, hexanoic acid, or ethyl acetate, respectively. These results suggest that PAOs

can be used as a bulk solvent and the polarity of the solvent can be fine-tuned by adding small amounts of polar cosolvent.

The use of PAOs as solvents for pyrophoric reagents was also explored. Many pyrophoric reagents are sold in alkane solvents like hexane due to the high reactivity of reagents. However, the solvent that the reagents are sold in are very flammable with low flash points, which increases the dangers associated with using them. We have shown that pyrophoric reagents like *n*-butyllithium, *sec*-butyllithium, *tert*-butyllithium, diethylzinc, and triethylaluminum dissolved in PAOs do not readily ignite in air. Furthermore, as much as 80% of *n*-butyllithium or *tert*-butyllithium was still active butyllithium reagent after being exposed to air for 1 hour. Finally, the reactivity of the pyrophoric reagents dissolved in PAO is identical to the reactivity of the reagents dissolved in low molecular weight alkane solvent. This was demonstrated with the use of butyllithium reagents in reactions like polymerizations, transmetallations, 1,2-additions, and in formation of hindered bases.

Finally, PAOs were used as recyclable replacements for activated carbon for purifying water of trace organic impurities. Activated carbon is often used for purifying water of trace organic impurities, but recycling the spent activated carbon is very energy intensive. PAOs can be used to purify water by vigorously mixing the PAO and water phase, and then separating the two phases in a simple liquid-liquid separation. The PAOs do not contaminate the purified water because PAOs have virtually no solubility in water. PAOs alone are capable of rapid (less than 5 minute) removal of nonpolar contaminants like hexane or benzene from water. More polar contaminants like

tetrahydrofuran or bisphenol A can be removed from the water phase via the addition of a nonpolar phase anchored polymer bound sequestering agent. PAO anchored H-bond donating sequestering agents can be used to remove H-bond accepting impurities and PAO anchored H-bond accepting sequestering agents can be used to remove H-bond donating impurities. Furthermore, the PAO phase can be easily regenerated by simply removing volatile impurities via sparging the PAO with an inert gas like N₂.

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