USING POLYISOBUTYLENE AS NONPOLAR PHASE SOLUBILIZING AGENTS

AND POLYMER SUPPORTS FOR CATALYSTS AND REAGENTS

A Dissertation

by

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ABSTRACT

Diethylamine terminated PIB and *N,N*-diethyl-*N*-methylammonium terminated PIB oligomers are used to help solubilize different types of anions in nonpolar solvents. Metal salts are important in many organic transformations, yet their uses in organic solvents and more particularly in hydrocarbon solvents have not been fully explored due to their insolubility in these media. Although much work has been done to solve this problem by using phase transfer catalysts, such as tetrabutylammonium salts, the solubility of these salts is still limited in very nonpolar solvents. Moreover, these salts are often hard to isolate from the product and are not recyclable. This work describes the synthesis of diethylamine terminated PIB and *N,N*-diethyl-*N*-methylammonium terminated PIB oligomers and their use to help solubilize oxidative catalysts, such as polyoxometalate clusters and perruthenate anions, in heptane. The oxidation reactions were found to be efficient, and the PIB-supported catalysts can be easily recovered by biphasic separation and recycled multiple times.

We have also explored using a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer to do simple reactions, exploring both their competence and how the hydrocarbon solvent affects a conventional reaction's kinetics. This was accomplished using studies of the rates of S_N2 reactions with various kinds of anions in conventional solvents like DMF, MeCN, MeOH, and in heptane using a *N,N*-diethylamine-*N*-methylammonium terminated PIB oligomer. The reaction in heptane is assumed to have minimal solvent effects because it is nonpolar and has no hydrogen bonding. Moreover,

the catalytic activity of the *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer was also investigated in a solid/liquid phase catalysis. *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer was used as a phase solubilizing catalyst to solubilize anions from solid metal salts in heptane. We also expanded our work to use poly(α-olefins) (PAOs) as alternatives for low molecular weight conventional alkane solvents. Not only are poly(α-olefins) nontoxic and nonvolatile, the leaching of PAOs into the polar phase was less than the leaching of heptane into a polar phase. This feature is important for catalyst recycling.

In addition to the oxidation reactions using POM cluster and perruthenate anion, we also investigated another class of oxidizing agents, hypervalent iodine compound. 2-Iodoxybenzoic acid (IBX) was immobilized on to PIB oligomer by a covalent ester linkage. The PIB-supported IBX was efficient in oxidizing various types of alcohols. It can also be easily recovered by simple biphasic separation and can be recycled multiple times.

DEDICATION

This dissertation is dedicated to the loving memory of my father, Kasem Samunual, whom I still miss every single day. I also dedicate this dissertation to both my mother, Busara Samunual, and grandmother, Anong Lamsam, for their love, patience, and support.

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CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supervised by a thesis committee consisting of Professor David E. Bergbreiter, Professor Daniel Romo, and Professor Daniel A. Singleton of the Department of Chemistry and Professor Melissa A. Grunlan of the Department of Biomedical Engineering.

The applications of diethylamine terminated and *N,N*-diethyl-*N*-methylammonium terminated PIB oligomers with polyoxometalates (POMs) in the oxidation reactions in chapter 2 were conducted by Rana Yahya, Michael Craven, Elena F. Kozhevnikova, Alexander Steiner, and Professor Ivan V. Kozhevnikov of the Department of Chemistry at the University of Liverpool.

All other work conducted for the dissertation was completed by the student independently.

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CHAPTER I

INTRODUCTION

Many researchers have become increasingly aware of and concern with the negative impacts of chemical processes on the environment. In 1998, Paul Anastas and John Warner introduced the twelve principles of green chemistry as a guideline for scientists to consider when designing or developing chemical processes as shown in Figure 1. The primary goal of these principles is to reduce or eliminate the generation and use of hazardous substances in chemical products or processes.[1] The practice of green chemistry
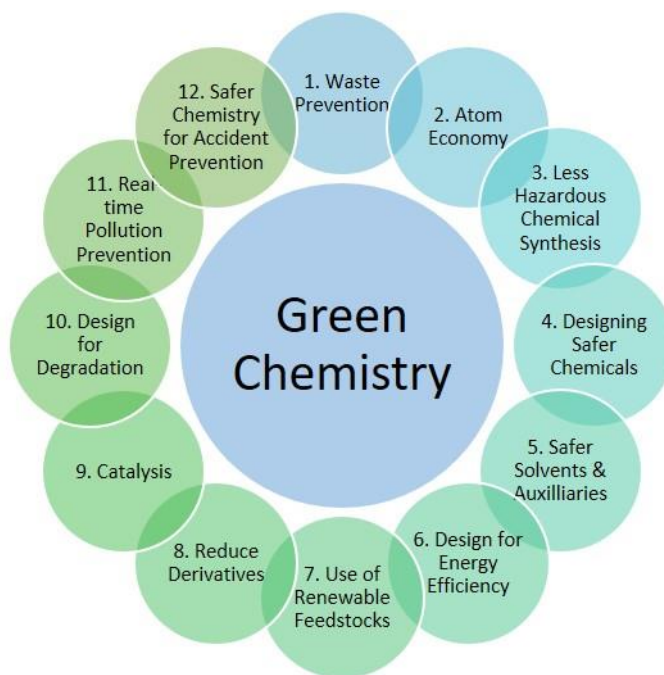
Figure 1. The twelve principles of green chemistry

has become more prevalent in both the academic and industrial sector and some distinguished accomplishments include the discovery of metathesis and the development of fully biodegradable plastic bags. The Nobel Prize in Chemistry in 2005 was awarded to work done on metathesis, which was shared between Robert H. Grubbs, Yves Chauvin, and Richard R. Schrock. Metathesis in organic synthesis is extremely useful, especially in the pharmaceutical industry, and the process has low environmental factor. The chemical process uses less energy, is stable to air, produces less waste, has fewer steps, and can be used with green solvents.[1] The industrial sector also produces more sustainable products such as the fully biodegradable bag, Ecovio®, that was developed by BASF. Ecovio® is made from compostable polyester film, cassava starch, and calcium carbonate and decompose into water, carbon dioxide, and biomass. To further advance and contribute to the field of green chemistry, my research projects aim to integrate the concept of green chemistry and tackle ongoing problems specifically on waste reduction, renewable feedstocks, and reduced toxicity in organic transformation by using polymer as the key component.

Previous studies have been done to investigate the uses of polymer supports on catalysts or reagents to facilitate product isolation and catalyst/reagent recovery and recyclability in chemical transformations. Various kinds of polymer supports, both heterogeneous and homogeneous, have been used. Merrifield introduced the use of insoluble polymer supports, such as divinylbenzene (DVB) cross-linked polystyrene resins, for the synthesis of peptides. He received the Noble prize for this invention now known as the solid-phase synthesis technique.[2] With this technique, the C-terminus of the

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peptide chain was attached to the insoluble DVB cross-linked polystyrene resins. The reagents required for the next peptide bond were then added to the resins. Because the peptide was attached to insoluble polymers, the resins were simply filtered and washed after the reaction. This simple washing isolated the resin-bound product, avoiding a much more complicated purification process that generates considerable waste and requires considerable time to isolate the peptide chain. This process can be continued until the desired peptide is synthesized, then the completed peptide can be released from the insoluble DVB cross-linked polystyrene resins by cleaving the benzyl ester. This technique simplifies the purification process of peptide synthesis, and since then, many work have been built upon the idea. More recently, Imada et al. synthesized polystyrene-supported flavins that were used in aerobic reduction of olefins. These insoluble polymers can be used to prepare separable polymer-supported catalysts that can be recovered and recycled.[3] While conceptually as simple as solid phase peptide synthesis, the use of these supports for practical catalysis has been less successful. Although heterogeneous polymer supports, such as insoluble DVB cross-linked polystyrene, allow homogeneous catalysts to be separated easily by filtration, the actual catalysts often have different activity than their homogeneous counterparts. The catalysts themselves are also more difficult to characterize. Moreover, in cases where catalysts are immobilized by dative ligands (e.g. phosphines), leaching often occurs.

As an alternative to insoluble polymer supports, soluble polymer supports also have received attention for organic synthesis and catalysis. Using soluble polymer supports, such as those shown in Figure 2, may be advantageous, because the homogeneity
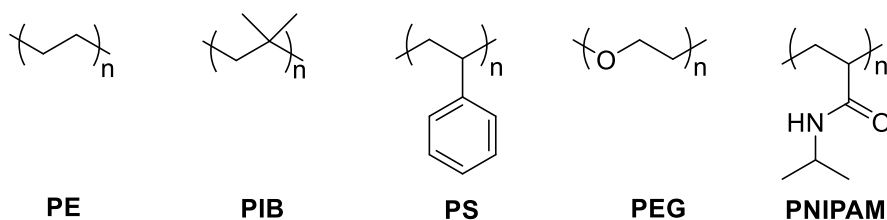
Figure 2. Common soluble polymers
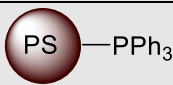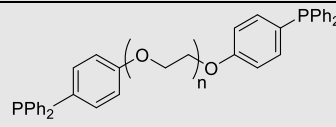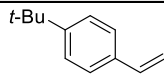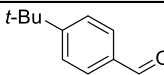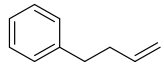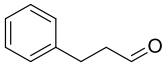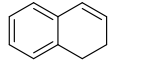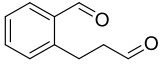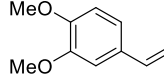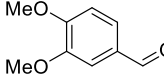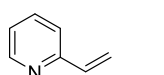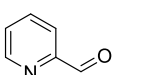
of the polymer-bound species during a reaction allows a supported catalyst or reagent to work more efficiently in solution. These soluble polymer-bound supports include both polar and nonpolar supports. Poly(ethylene glycol) (PEG) and linear polystyrene (PS) were among the earliest examples of soluble polymer supports. PEG and linear PS were initially proposed as an alternative to Merrifield resin for liquid-phase polymer-supported peptide synthesis.[4] Such supports had the advantages that the peptide products can be easily characterized by UV-Vis, IR, and NMR spectroscopies. However, the products had to be isolated by solvent precipitation. In this process, the polymer-bound species were diluted with a solvent that induced the precipitation of the polymer-bound product. Similar to the solid-phase peptide synthesis, the polymer-bound species were filtered from the solution that contained excess reagents and other contaminants. In peptide synthesis, this isolation procedure has a major flaw. Specifically, in a peptide synthesis, the peptide eventually begins to alter the solubility of the polymer since in essence a diblock copolymer is being formed. Thus, isolation becomes increasingly problematic as the peptide becomes larger.

The change in solubility of the polymer-supported species due to modification is less of a problem in catalysis, because the polymer can be designed so as to insure that the polymer is large enough to be a phase selective solubility handle for a specific catalyst. This was noted early on Bayer's group who used both polyethylene glycol and polystyrene supports in catalysis.[5] However, after Bayer's initial work, the use of soluble polymers instead of insoluble polymers in catalysis was less common. In other work, soluble polymers were mostly used if they had a specific advantage. For example, work by Whitesides showed that MeO-PEG-supported bis(phosphine)-ligated catalysts were easily prepared and useful for rhodium-catalyzed hydrogenation of different types of olefins in water.[6] By attaching MeO-PEG, the phosphine ligands became more soluble in water, where the reaction occurred. Janda also reported immobilizing cinchona alkaloid ligands on PEG to recover and reuse these expensive chiral ligands. These PEG-supported cinchona ligands were used in the Sharpless asymmetric dihydroxylation reaction and afforded enantioselectivities and yields similar to the original Sharpless ligands.[7] The PEG-supported chiral ligands can be recovered and reused five times without any loss of reactivity for the dihydroxylation reaction of *trans*-stilbene. Unlike polystyrene-supported chiral ligands, the soluble polymer-supported species tended to have reactivity more like their low molecular weight counterparts. However, using solvent precipitation to recover the PEG-bound species still generates significant waste, making it inherently not a green process.

While soluble supported catalysts or reagents that are isolated by solvent precipitation are not especially green, they still have some advantages over insoluble

supported analogs. For example, Janda also demonstrated the superiority of soluble

polymer supports against insoluble supports through his work on poly(ethylene glycol)-

supported triarylphosphine reagent.[7-8] The PEG-supported reagent were found to be more

reactive than the insoluble polystyrene-supported phosphine as shown in Table 1. For

Table 1. Comparison of Ozonide Reduction between Solution-Phase, Solid-Phase, and Liquid-Phase Triphenylphosphine

No.	Alkene	Product	Yield, %[a]		
			PPh_3	PS—PPh_3	
1			94	58	98
2			80	73	92
3			84[b]	60[b]	97[b]
4			51	56	77
5			72	62	63

[a] Reaction conditions: the respective triphenylphosphine (2 equiv) was added to the ozonide (1 equiv) of the alkene in DCM and left to stir for 2 h. Yields are based on HPLC comparison to the authentic product standards. [b] Isolated yield

example, a reductive workup of the ozonolysis reaction of *tert*-butyl styrene with the

insoluble polystyrene-supported triphenylphosphine only resulted in 58% yield while the

yields of the reactions with the low molecular weight triphenylphosphine and the soluble

PEG-supported triphenylphosphine were 94% and 98% yield respectively.

The need for solvent precipitation of a soluble PEG-supported catalyst can be addressed if a biphasic separation is used. The Bergbreiter group demonstrated the use of PEG and PNIPAM as polymer supports for tridentate sulfur-carbon-sulfur (SCS) Pd(II) catalysts.[9] The PEG-bound and PNIPAM-bound SCS-Pd(II) catalysts were air stable and competent for the Heck and Suzuki cross-coupling reactions, and the catalysts can be easily isolated from the product and recyclable by undergoing the liquid/liquid biphasic separation – a system that was subsequently described as a thermomorphic separation since temperature was used to induce a phase change. In these cases, a 90% aqueous DMA/heptane system was employed, and the reaction started out being biphasic at room temperature. Although the reaction did not become completely miscible, there was a significant change in the volume of each phase at 95 °C, allowing the reaction to take place. After the reaction, the mixture become biphasic with the products being in the heptane phase and the PEG-supported or PNIPAM-supported catalysts being in the aqueous DMA phase. This work inspired the Bergbreiter group to explore the use of biphasic separation with other types of polymer supports, specifically nonpolar polymer supports, where other types of biphasic separation systems will be described later in this chapter.

Our group has also extensively studied soluble nonpolar supports as alternatives to polar supports. The rational was that suitably chosen nonpolar polymer supports, such as polyethylene (PE) and polyisobutylene (PIB) could be as efficient in synthesis and

catalysis as polar supports but be separable by either liquid/solid or liquid/liquid separation without the need for excess solvent.[10–12] The initial work using nonpolar polymer supports used polyethylene oligomers as polymer supports that were prepared from ethylene by anionic polymerization.[13,14] Such oligomers had the property that they are completely insoluble at room temperature in all solvents but soluble at 70-105 °C in suitable nonpolar or weakly polar solvents. Thus, catalysts on such supports could be used homogeneously but separated by solid/liquid separation. Subsequently, DuPont used similar polyethylene oligomers that were commercially available from Baker Hughes in acrylate polymerization, describing these supports as commercially viable.[15] The commercial availability of these polyethylene oligomers has led our group to further studies these supports in catalysis. For example, polyethylene oligomers were used as soluble polymer supports for ring-opening metathesis polymerization (ROMP) catalysts and unfunctionalized polyethylene oligomers were used as a cosolvent to reduce ruthenium contamination in the polymer products as shown in Figure 3.[16] The PE oligomers allowed the polymerization reaction to be conducted under homogeneous conditions at 80 °C. However, since polyethylene oligomers are insoluble at room temperature, the PE_{Olig}-bound Ru-catalyst residues can be removed by filtration. The leaching of ruthenium into the products was less than 0.5%. This work followed the same general concepts used in the first example of PE_{Olig}-bound catalysis where phosphite-functionalized PE oligomers were also used as ligands for Ni(0)-catalyzed cyclooligomerization of butadiene.[17] The

catalysts were entrapped along with the precipitates of PE oligomers at room temperature, which allow the catalysts to be separated, recovered, and recycled. Most importantly, the ability for the catalytic reaction to be run under homogeneous reaction with the PE-bound Ni(0) catalysts at elevated temperature results in the same product selectivity and catalytic reactivity seen with their homogeneous analogs.
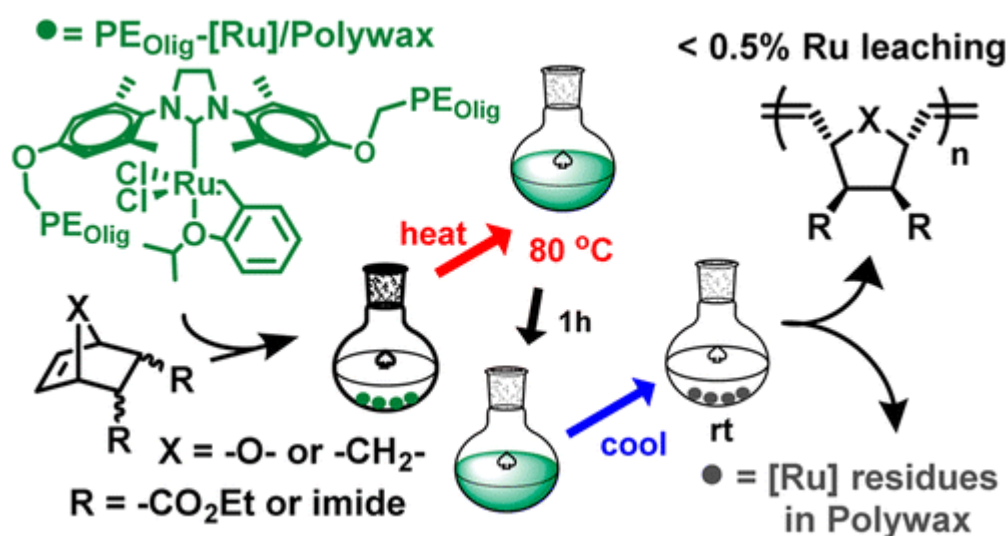
Figure 3. PE-bound Ru-Catalyst for ROMP[*]

Another soluble nonpolar polymer supports of greater recent interest is polyisobutylene (PIB). Vinyl-terminated PIB is a commercially available, nontoxic, and

inexpensive polymer that is often used as oil and fuel additive. Studies done by the Bergbreiter and other research groups have shown that vinyl-terminated PIB can be modified into useful ligands and supports for catalysts and reagents by simple conventional chemistry.[18–21] These PIB supports are soluble in nonpolar solvents such as heptane or hexanes, and some polar solvents such as DCM and THF. However, they are not soluble in polar solvents such as acetonitrile, methanol, and DMF. Because of this unique property of the PIB polymer supports, the Bergbreiter research group was able to develop strategies, as mentioned earlier, in which the reaction can be conducted homogeneously in a mixed solvent system during the reaction. Perturbation of this mixed solvent system can make it biphasic after the reaction to facilitate separation and recovery of the catalysts or reagents from the products. The two strategies used in this process are known as the thermomorphic liquid/liquid system and the latent biphasic system and are described schematically in Figure 4. The thermomorphic liquid/liquid system can be illustrated using heptane and DMF as the solvents. In this case, the reaction starts out being biphasic at room temperature. When employing nonpolar polymer supports, the PIB-supported catalysts or reagents are soluble in heptane and the substrates are most likely soluble in DMF. The reaction mixture is then heated to form a completely miscible monophasic reaction mixture, allowing the reaction to take place. The reaction mixture is then cooled down to room temperature upon completion and becomes biphasic, where the PIB-supported catalysts/reagents can be physically separated and isolated from the product. The heptane phase along with the PIB-supported catalysts and reagents can then be reused and recycled. The latent biphasic system also uses a solvent mixture, for

example heptane and ethanol. However, in this case, the reaction mixture starts out being monophasic. Upon completion, the reaction mixture is perturbed with water to become biphasic. The PIB-supported catalysts can then be recycled in similar fashion as mentioned
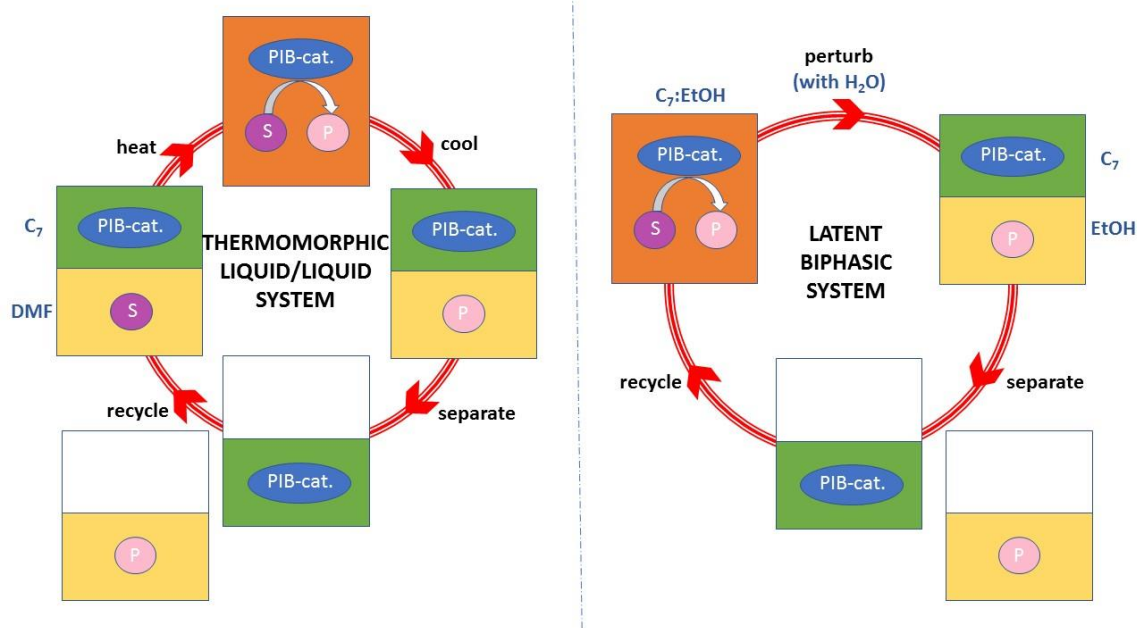
Figure 4. Recycling strategies developed by the Bergbreiter group

above. Because the PIB-supported catalysts/reagents are selectively soluble in nonpolar solvents, the PIB-support catalysts/reagents can also be isolated by a simple gravitational separation. The solubility of PIB-supported catalysts/reagents along with the development of these recycling strategies make the separation and recycling of many precious catalysts less tedious. These strategies were found to be successful with many catalysts. For example, a PIB-supported Cr(III)-Salen catalyst that was used for ring-opening of

epoxides with various nucleophiles was shown to be practically recyclable using these schemes. Generally, the PIB-supported Cr(III)-Salen catalysts were recovered and recycled without any loss of reactivity after six cycles. For example, the yields of the ring-opening of cyclohexene oxide by 4-methoxythiophenol with the PIB-supported catalysts were greater than 90% for four cycles as shown in Figure 5. Moreover, the leaching of
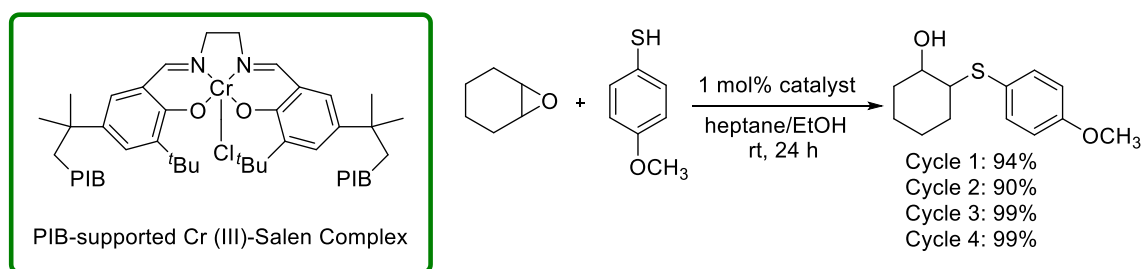
Figure 5. Ring-opening of epoxides with thiol catalyzed by PIB-supported Cr (III)-Salen Complex

the metal was found to be less than 0.3%.[22] These catalysts can also be used in flow chemistry. This was seen in work by both the Bergbreiter research group using PIB-bound Rh(II) carboxylate cyclopropanation catalysts and by earlier work by the Reiser group.[20] Reiser's group was the first to demonstrate the use of these PIB-bound catalysts in flow chemistry. In their work, they showed that a PIB-tagged *fac*-Ir(ppy)₃ complex could be used and recycled as a photocatalyst in the isomerization of cinnamyl acetate as shown in Figure 6. The *Z/E* ratio was observed to be 82:18, which was the same as the ratio of the reaction with the analogous low molecular weight *fac*-Ir(ppy)₃ catalyst. This work and the
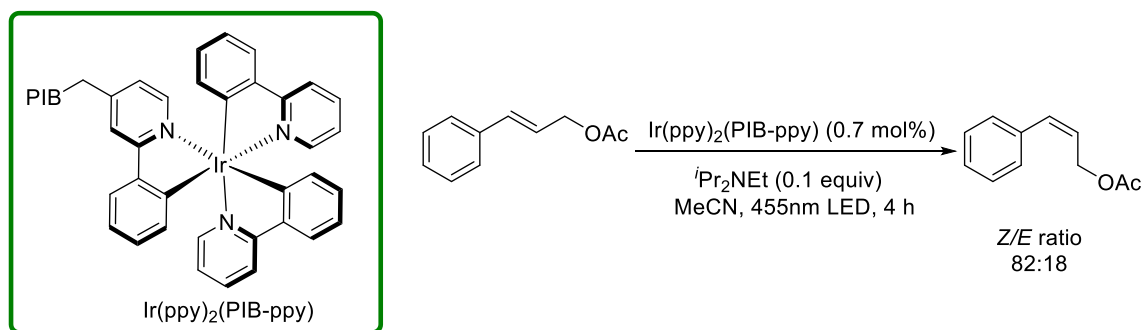
Figure 6. Isomerization of cinnamyl acetate with PIB-tagged *fac*-Ir(ppy)₃ complex

later work by the Bergbreiter group showed how the phase selectivity of these PIB-supported photocatalysts in nonpolar solvents make them suitable in continuous flow chemistry, where they can constantly be recycled in this process as described in Figure 7. This set-up could be important as a strategy in a larger-scale production process.[19,20]
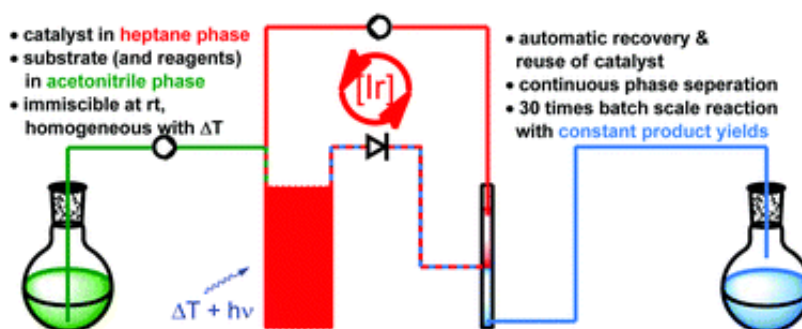
Figure 7. PIB-bound catalysts in continuous flow chemistry[*]

While the use of PIB polymer supports to help recover and recycle precious metal catalysts/reagents has been the most common use of PIB in our group, PIB polymer supports can also play a large role in making compounds that are normally insoluble in organic solvents soluble. This is illustrated by recent work where terminally functionalized PIB, specifically PIB-bound catechol was used to modify the solubility of magnetic nanoparticles to form stable suspensions of these polymers even in nonpolar solvents like heptane. In this work, the magnetic oils contained up to 32 wt% magnetic nanoparticles and were found to be stable to centrifugation, magnetic separation, and external reagents.[21] Most interestingly, PIB-modified nanoparticles can be used in hydrocarbon sequestration. It was observed a heptane solution that contained a sufficient amount of the magnetic oil (i.e. the PIB modified magnetic nanoparticles), can be attracted to an external magnet as shown in Figure 8. The role of PIB supports to facilitate solubilization was also illustrated in chemistry with metallophthlocyanines (MPcs). MPcs are not commonly used in homogeneous catalysis due to their low solubility in organic solvents. In 2016, PIB-bound cobalt phthalocyanines were synthesized and used in nitroarene reduction.[23] Not only does the PIB support helped solubilize the MPcs, they also allowed the catalysts to be recycled up to 10 times with little leaching and no detectable loss of reactivity. With PIB having such unique properties, my studies are largely on immobilizing quaternary ammonium salts, a very useful functional group, on PIB.

Quaternary ammonium salts have been shown to be useful in a wide variety of applications. For example, they can be used as surfactants, phase-transfer catalysts, and

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solvent replacements. Some examples of surfactants are shown in Figure 9. Bales and

Zana illustrated the formation of micelles by using of quaternary ammonium surfactants,
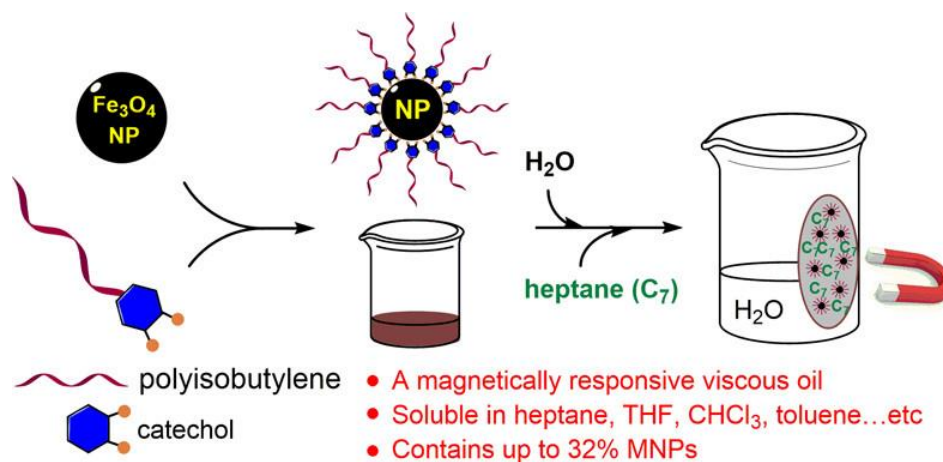
Figure 8. PIB-modified magnetic nanoparticles[*]

dodecyltrimethylammonium bromide (DTAB) and dodecyltrimethylammonium chloride

(DTAC), where different physical properties of these micelles were studied.[24] Above the

critical micelle concentration, these surfactants form micelles that can serve as reaction

sites, where the reagents are brought together in close proximity. Typically, the

hydrophobic tails of surfactants form the interior of the micelles, while the polar heads are

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Figure 9. Some examples of surfactants

exposed to the water-micelle interface. Cationic micellar media was observed by Bhat to

enhance the reaction rates and yields of the Morita-Baylis-Hillman (MBH) reaction.[25] In

this work, many types of surfactants, both cationic and anionic, were screened. It was

found that the reaction proceeded better with cationic surfactants such as
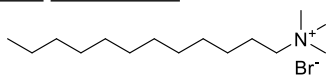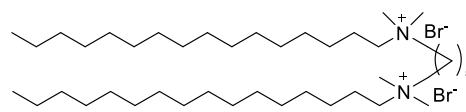
cetyltrimethylammonium   bromide   (CTAB)   and   penanediyl-1,5-
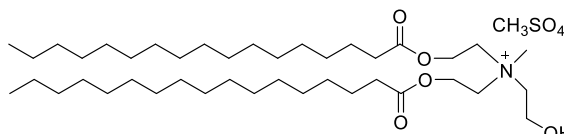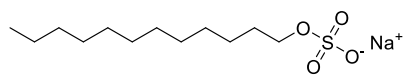
bis(dimethylethylammoniumbromide) than with anionic surfactants such as sodium

dodecylsulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS). It was believed that
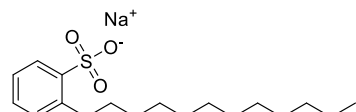
cationic head of the surfactants help stabilized the enolate intermediate in the conjugate

addition step of the reaction illustrated in Figure 10. Surfactants are also often used in

many household and personal care items. Esterquat, for example, are often used in fabric

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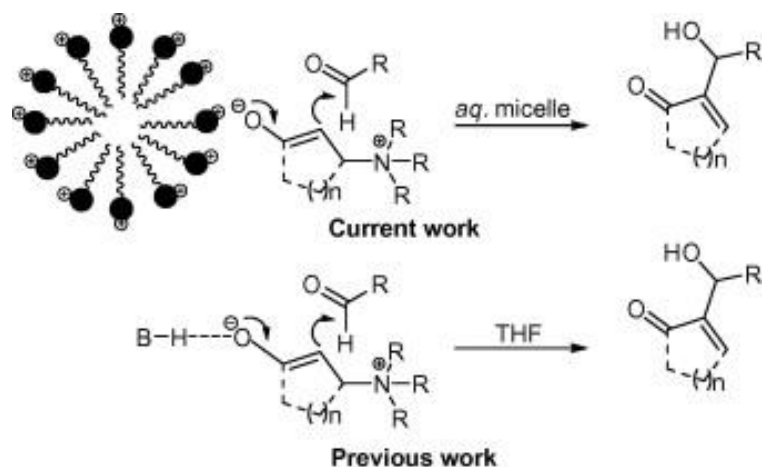
Figure 10. Mechanism of MBH reaction with micelles[*]

softener and haircare due to their antistatic property.[26] The positive charges of the cations

were believed to help neutralize the negative charges on the surfaces of fabric. For this

reason, the quaternary ammonium salts have to be highly dispersed in water so that they

can be absorbed on fabric, making them soft. The benefit of using Esterquat, rather than

the older generation surfactants, is because of their biodegradability, which results in

lower environmental impact.

Another important application for quaternary ammonium salts is their use as

phase-transfer catalysts. Phase-transfer catalysts play a large role in synthetic organic

chemistry, promoting reactions between reagents with different solubility. Phase-transfer

catalysts function by transporting a reagent from one phase to another phase, bringing the

reagents together and allowing the reaction to take place. The mechanism of the phase-

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transfer catalyst reaction was proposed by Stark as is described in Figure 11.[27] The

quaternary ammonium salts that serve as phase-transfer catalysts are soluble in the

aqueous phase that contains the metal salts. The quaternary ammonium salts undergo an

ion-exchange reaction with the anions of the metal salts. The new ion pair, then, can

diffuse to the organic phase due to their lipophilic nature. Depending on the types of
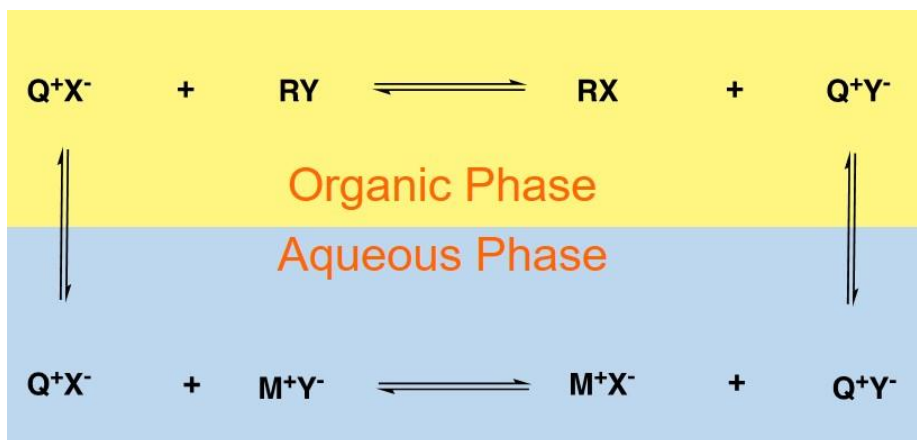
Figure 11. Mechanism of typical phase-transfer catalysts

organic reaction, the anions can react with the substrates that are in the organic phase. This

cycle is repeated until the reaction is completed. Stark also demonstrated that phase-

transfer catalysts can help facilitate and enhance displacement reactions, ester hydrolyses,

oxidations of olefins with potassium permanganate, and borohydride reductions. For

example, an oxidation reaction of 1-octene and aqueous potassium permanganate led to

no reaction at all, because the 1-octene and permanganate reagents are phase isolated from

one another. However, when a small amount of quaternary ammonium catalysts was added to this biphasic reaction mixture, the reaction proceeded immediately. Similarly, borohydride reduction of 2-octanone with quaternary ammonium catalysts in benzene and solution of $NaBH_4$ in 2 N NaOH was shown to be 20-30 times faster than the reaction without the phase-transfer catalysts.

Chiral phase-transfer catalysts also play a large role in a wide range of organic transformations. Some examples of chiral phase-transfer catalysts are shown in Figure 12. Dolling, O'Donnell, and Corey reported the uses of chiral phase-transfer catalysts that
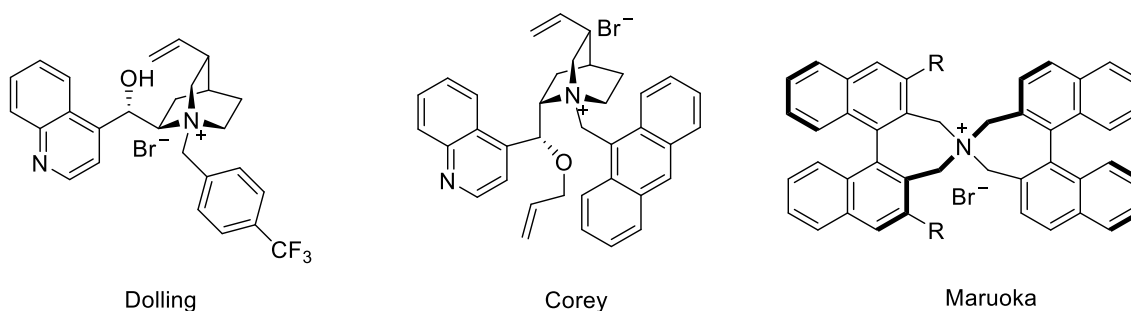
Figure 12. Examples of chiral phase-transfer catalysts

were derived from cinchona alkaloids. Dolling reported the use of *N-(p-*(trifluoromethyl)benzyl)cinchoninium bromide as a catalyst in the methylation of 6,7-dichloro-5-methoxy-2-phenyl-1-indanone with chloromethane in aqueous NaOH and toluene to obtained (S)-(+)-6,7-dichloro-5-methoxy-2-methyl-2-phenyl-1-indanone in up to 92% *ee* and 95% yield. This seminal work stimulated many more studies on using chiral

quaternary ammonium salts in organic transformations, especially in the alkylation of glycine Schiff base esters as shown in Figure 13. O'Donnell demonstrated that catalytic quantities of the enantio-control element can be utilized in asymmetric synthesis of α-amino acids.[28] In this work, 10 mol% of *N*-benzylcinchoninium ions, catalysts similar to those used in Dolling's work, were used as catalysts in the alkylation of *tert*-butyl glycinate-benzophenone Schiff base with various alkyl bromide substrates in 17%
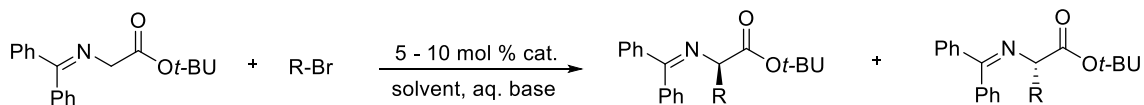
Figure 13. Alkylation of glycine Schiff base ester

aqueous NaOH and toluene. However, the reaction did not achieve high enantioselectivities, with only 66% *ee* and 75% yield when using allyl bromide as the substrate. To improve the efficiency of the asymmetric reaction, Corey modified the chiral catalyst by attaching a 9-anthracenylmethyl group to the bridgehead nitrogen to make *O*(9)-allyl-*N*-(9-anthracenylmethyl)cinchonidinium bromide. The new catalysts prepared in this way were shown to be efficient, affording products with very high enantioselectivity. The alkylation of glycine ester Schiff base with allyl bromide achieved 97% *ee* and 89% yield. The success of the modified catalysts was attributed to the rigidity and well-defined geometry of the quaternary ammonium salt.[29] Other than the cinchona

derived phase-transfer catalysts, other types of asymmetric phase-transfer catalysts were also investigated. The Maruoka catalyst, for example, is a commercially available C_2-symmetric chiral phase-transfer catalyst. The Maruoka catalyst was used to catalyze the enantioselective alkylation of glycine ester as well. With this catalyst, only 1 mol% loading of the catalyst was required to achieve the desired product in excellent yields and high enantioselectivity in only 1 h. The reaction with allyl bromide and the glycine ester resulted in 94% *ee* and 84% yield. With this usefulness, the Maruoka catalyst was proven to be successful in synthesizing biologically active molecules.[30] In addition, an improved version of Maruoka catalysts were also synthesized and investigated in recent years.[31]

Quaternary ammonium salts can also be used as alternatives for volatile organic solvents. In the past decades, many efforts have been made to replace volatile solvents, such as dichloromethane, to reduce toxicity and environmental harms in chemical processes. Ionic liquids, known as "designer solvents", are salts that are liquid at temperature less than 100 °C as shown in Figure 14. The physical properties of these ionic liquids, such as their melting point, viscosity, density, solubility, and hydrophobicity, can be tailored for a chemical process by modifying the cationic and anionic components. For ionic liquids to be liquid at room temperature, the cation should be unsymmetrical. This can be accomplished by having different alkyl groups in the dialkylimidazolium cation. In addition, the length of the alkyl chain groups and the identity of the anions can also influence the hydrophobicity and hydrophilicity of the ionic liquid components. For example, butylmethylimidazolium tetrafluoroborate (emimBF$_4$) is soluble in water,

whereas butylmethylimidazolium hexafluorophosphate (emimPF$_6$) is insoluble in water.

There are three generations of ionic liquids as shown in Figure 15.[32] The first generation

Common Cations

R^4-N$^\pm$-R^2 with R^1 and R^3

Tetraalkylammonium

Di, Tri, and Tetraalkylammonium

Alkylpyridinium

Dialkylpyrrolidinium
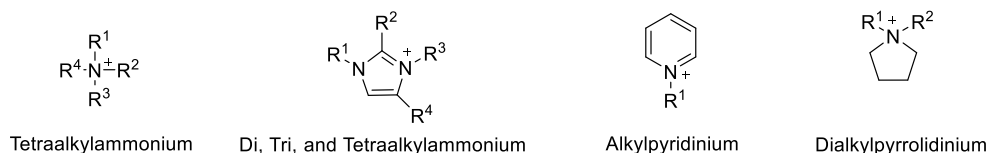
Common Anions

BF$_4^-$, PF$_6^-$, AlCl$_4^-$, CF$_3$CO$_2^-$, SCN$^-$, etc.

Examples

BF$_4^-$

vs.

PF$_6^-$

bmimBF$_4$
soluble in water

bmimPF$_6$
insoluble in water
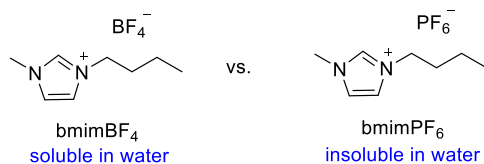
Figure 14. Common ionic liquids

of ionic liquids used dialkylimidazolium cations and chloroaluminate anions. These first

generation ionic liquids were found to be useful for Friedel-Crafts chemistry. Typically,

Friedel-Crafts alkylation and acylation reactions are conducted in an inert solvent with

suspended or dissolved aluminium (III) chloride as the catalyst. These reactions produce

a mixture of isomeric products.[33] However, with the use of ionic liquids as both the

solvent and catalyst for the reaction, it was observed that the reaction proceeded faster
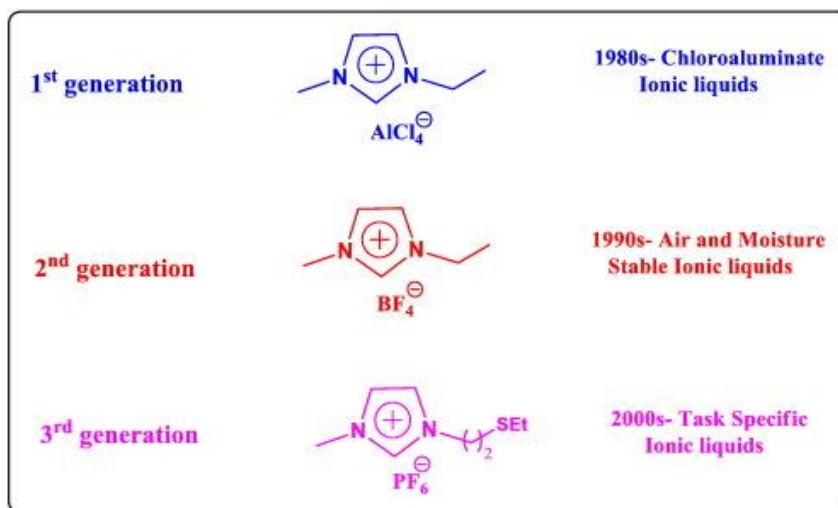
Figure 15. Generation of ionic liquids[*]

with 100% conversion and most often forming a single product. The main drawback of the first generation of ionic liquids is that the anions are highly reactive with water. To solve this problem, the second generation of ionic liquids were developed that replaced chloroaluminate anions with other kinds of anions to make these ionic liquids more stable to water and air and useful in other reactions in organic chemistry.[34] Recently, researchers have become interested in the third generation of ionic liquids called task-specific ionic liquids. Task-specific ionic liquids are ionic liquids that have a functional group covalently tethered to the cation, anion, or both the cation and anion. For example, the normal Brönsted acidic ionic liquids were found to be useful in esterification reactions

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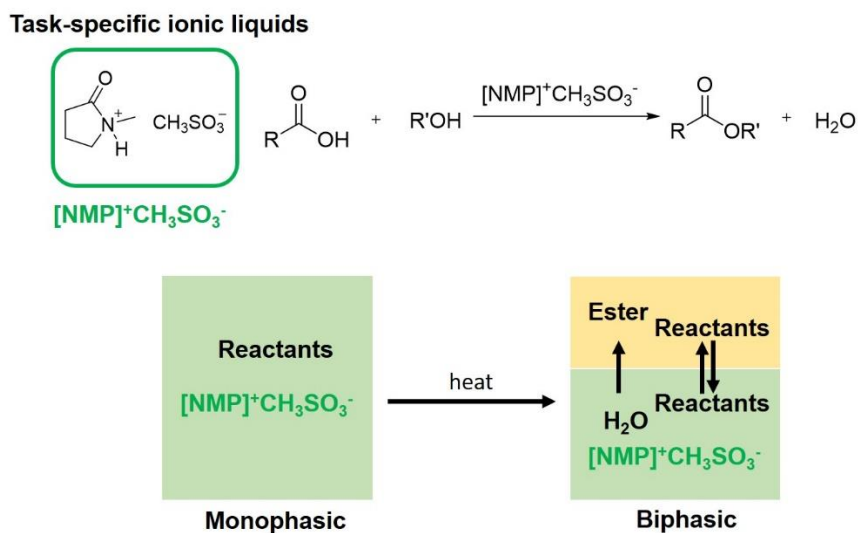
Figure 16. Esterification by using task-specific ionic liquids

between alcohols and carboxylic acids as shown in Figure 16. Zhou illustrated that *N*-methyl-2-pyrrolidonium methyl sulfonate can be used as solvents and catalysts for this reaction, which resulted in good conversion rates and high selectivity. The reason is because the ester products formed a separate phase. Because esterification is a reversible reaction, the ability for the ester products to self-separate can improved the yield of the reaction. Moreover, the task-specific ionic liquids can be recycled after removal of water under reduced pressure.[35]

Given the many ways ammonium salts have been used in organic chemistry, it could be expected that others would have examined their use on using polymer supports. Most of this work on immobilizing tetraalkylammonium used either DVB cross-linked polystyrene or polyethylene glycol as shown in Figure 17. An example of this would be Montnari's work using 2% cross-linked polystyrene as polymer supports for quaternary
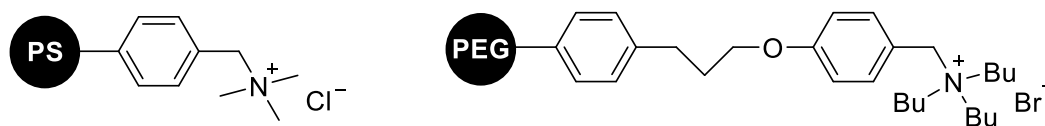
Figure 17. Polymer-supported quaternary ammonium salts

ammonium salts.[36] Although under optimized condition, the catalytic activity of these salts was comparable with that of soluble phase-transfer catalysts, the reaction rates were dependent on the stirring speed of the reaction and often required higher temperatures and longer reaction times. Soluble polar polymer, such as polyethylene glycol, was also used as supports for quaternary ammonium salts. The poly(ethylene glycol) supported quaternary ammonium salt was used under phase-transfer catalysis conditions and were found to be efficient in many organic transformations. One example would be the benzylation of phenol and pyrrole which only required 1 mol % of the catalyst and resulted in yields of ≥95%. The poly(ethylene glycol) supported quaternary ammonium salts were recovered and recycled by precipitation and filtration.[37] Itsuno also immobilized chiral quaternary ammonium salts onto polymer supports. In this case, benzylcinchonidinium chloride was allowed to react with sodium *p*-styrene sulfonate in water to make a monomer containing the chiral ammonium salt. This chiral monomer was then co-polymerized with styrene and divinylbenzene under a radical condition to generate the polymer supported chiral quaternary ammonium salts as shown in Figure 18. The polymer supported chiral
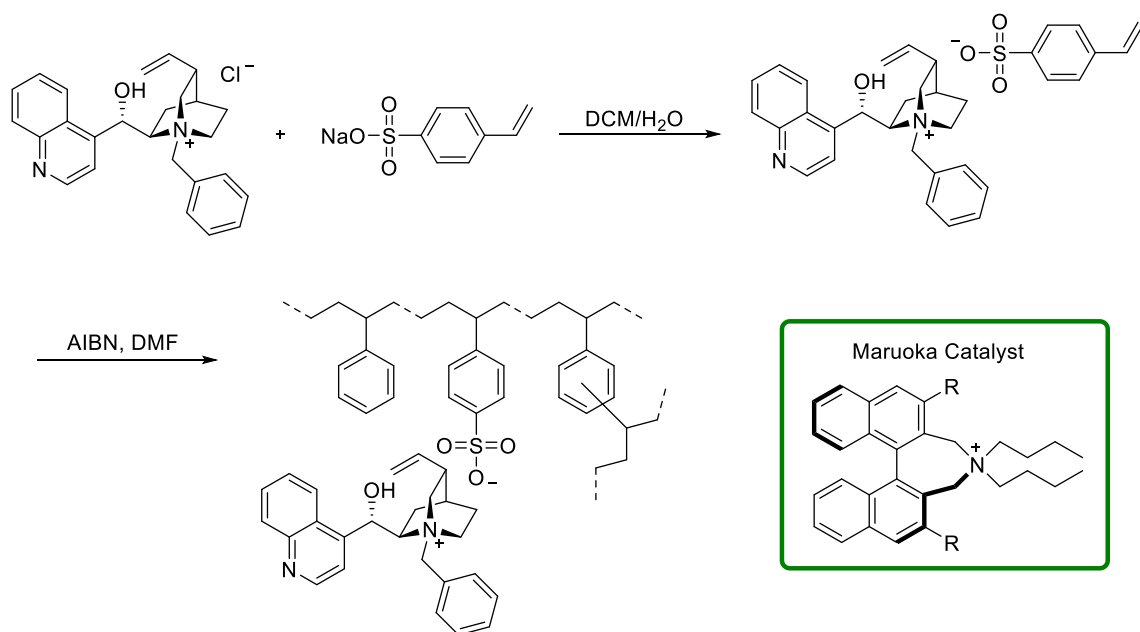
Figure 18. Polymer-supporter chiral phase-transfer catalyst

quaternary ammonium salts were found to be effective and recyclable. In comparison to the low molecular weight catalysts, the alkylation of glycine ester with benzyl bromide had a yield of 78% and 69 % *ee* while the polymer-supported catalysts afforded a yield of 66% and 78% *ee*. Other quaternary ammonium salts were also investigated. A polymer-supported Maruoka catalyst was also prepared in similar fashion and was also found to be even more successful in asymmetric alkylation with 84% yield and 98 % *ee* in less than 0.5 h. Although the mechanism of the reaction was not clear, it was proposed as shown in Figure 19 that polymeric sulfonate must be closely involved in the transition state.[38] In addition, Ding just recently demonstrated that polymer-supported ionic liquids were highly efficient catalysts for conversion of carbon dioxide to cyclic carbonates in a batch

and continuous flow fixed-bed reactor. The polymer-supported ionic liquids also have high stability after being investigated in the flow reactor for 130 hours.[39]
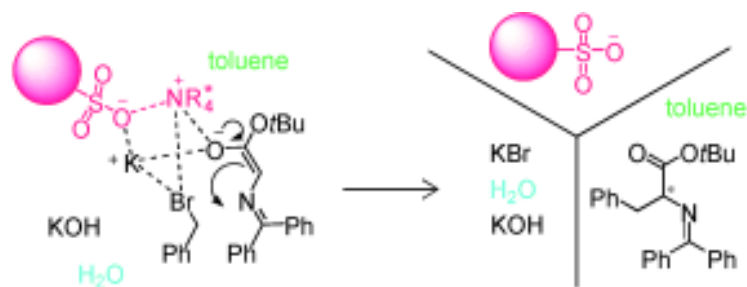
Figure 19. Proposed mechanism of polymer-supported chiral quaternary ammonium salts[*]

Because PIB oligomers and quaternary ammonium salts were found to be advantageous for a wide variety of applications, my research integrated these two components together by using PIB as polymer supports for quaternary ammonium salts. The idea was that we could use PIB with a molecular weight of 1000 Da to recover, recycle, and solubilize catalysts and reagents. Based on our prior studies, it was through that PIB solubility would render ammonium salts soluble in heptane and allow for reactions that involved a wide variety of anionic species in hydrocarbons. In the following

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[*] Reprinted with permission from "An Immobilization Method of Chiral Quaternary Ammonium Salts onto Polymer Supports" by Arakawa, Y.; Haraguchi, N.; Itsuno, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 8232, Copyright 2008 by John Wiley & Sons

chapters, I discuss conducting reactions solely in a nonpolar solvent, such as heptane, and under a biphasic catalysis system, such as in a heptane:water mixture. The recycling strategy for when the reaction is run solely in nonpolar solvent is shown in Figure 20. Similar recycling and separation strategies can also be applied to the biphasic catalysis system. In the biphasic catalysis system, the two solvents are immiscible. The quaternary
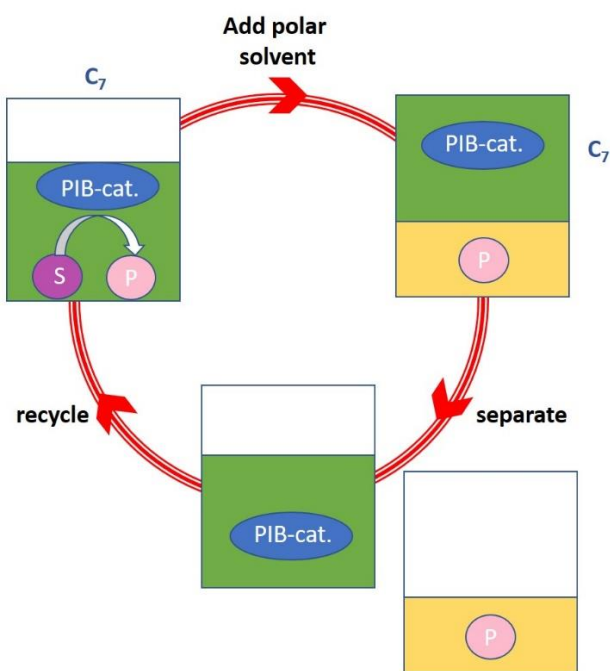
Figure 20 Recycling strategy for reaction done solely in heptane

ammonium terminated PIB oligomer that serves as a catalyst or a reagent will be soluble in the nonpolar phase and the substrates can either be in the polar phase or in both phases. During the reaction, the mixture is vigorously stirred to allow mixing of the catalyst and the substrate. Upon completion, the catalyst will still remain in the nonpolar phase. The

objectives of using quaternary ammonium terminated PIB oligomer are 1) to dissolve reagents that are not normally soluble in organic solvent or reagents that are not soluble in nonpolar solvent 2) to explore the recyclability of the quaternary ammonium terminated PIB-supported catalysts or reagents, and 3) to investigate the rate of organic transformations that are not normally done in nonpolar solvents due to the insolubility of reagents in these solvents. In chapter two, I described my success using a diethylamine terminated PIB oligomer and a quaternary ammonium terminated PIB oligomer to help solubilize oxidative catalysts, such as polyoxometalate clusters and perruthenate anions, in heptane. The oxidation reactions were found to be efficient, and the PIB-supported catalysts were easily recovered by biphasic separation and recycled multiple times. Chapter three focuses on investigating simple reactions with quaternary ammonium terminated PIB-supported reagents, exploring both their competence and how the hydrocarbon solvent affects a conventional reaction's kinetics. This was accomplished using studies of the rates of S_N2 reactions with various kinds of anions in conventional solvents like DMF, MeCN, MeOH, and in heptane using a quaternary ammonium terminated PIB oligomer. The reaction in heptane is assumed to have minimal solvent effects because it is nonpolar and has no hydrogen bonding. The results show that the rates of S_N2 reactions in heptane and MeCN are comparable. While my work largely focused ionic immobilization of catalysts and reagents on PIB oligomers, my last chapter describes the use of PIB supports on the ester of 2-iodoxybenzoic acid (IBX). This work, which was an extension of my studies on oxidation chemistry, attached PIB to IBX, which is typically only soluble in DMSO. Instead of an ionic bond, the IBX was attached to the PIB support

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by a covalent ester bond. The PIB-supported IBX were found to efficient in oxidation of alcohols to their corresponding ketones or aldehydes and could be recycled multiples. The ultimate goal of these studies is to contribute to the field of green chemistry by making chemical process more environmentally-friendly by minimizing the amounts of reagents and solvents used and wastes generated through the recycling strategies and using less toxic solvent such as heptane in organic transformations.

CHAPTER II

AMINE AND AMMONIUM TERMINATED POLYISOBUTYLENE OLIGOMERS

AS POLYMER SUPPORTS FOR CATALYSTS

Introduction

Alkene-terminated polyisobutylene (PIB) is a commercially available, nontoxic, and inexpensive nonpolar polymer that can be modified and used as polymer supports for many precious catalysts. Several groups have successfully demonstrated the use of PIB supports with Hoveyda-Grubbs catalysts,[16] photoredox catalysts,[19,20] and cross-coupling catalysts.[40] The PIB supports allow the catalyst to be conducted under homogeneous conditions and facilitate the isolation and recovery of the catalysts by simple phase separation in liquid/liquid separation. Most importantly, the use of PIB supports make chemical transformations more environmentally-friendly by reducing the amount of catalysts used by recycling, minimizing the amounts of solvents required in the process, and also using heptane as a solvent that is known to be greener than halogenated solvents and even some hydrocarbon solvents such as hexanes and benzene.[41] Not only that, PIB supports also help make insoluble catalysts soluble in organic solvents, making these insoluble catalysts more useful in a wide variety of applications.[23] In this work, we discuss the synthesis of a diethylamine terminated PIB oligomer and a quaternary ammonium terminated PIB oligomer and described the advantages and limitation of the use of these functionalized polyisobutylene oligomers as polymer supports for oxidation catalysts using as examples polyoxometalates (POMs) and perruthenate anions.

Polyoxometalates (POMs) are valuable in many disciplines, including their uses as corrosion resistant coatings, dyes and pigments, and precursors for oxide films.[42] Their applications in catalysis were, however, of most interest to me. In catalysis, they are used in large-scale industrial processes, such as in the oxidation of methacrolein to methacrylic acid, the hydration of alkenes to alcohols, and the synthesis of ethyl acetate by direct addition of acetic acid to ethylene.[43] POMs are comprised of O-sharing MO_x polyhedra, with $M = Mo^{VI}$ and W^{VI}. POMs with Keggin type polyanions, $[XM_{12}O_{40}]m^-$ {$X = P^V$ (m = 3) and Si^{IV} (m = 4)}, are known to be useful in environmentally benign biphasic oxidations with hydrogen peroxide. Such Keggin type polyanions are of specific interest in oxidative desulfurization and olefin epoxidation reactions. In these reactions, they have been used both as homogeneous catalysts in benzene and in two-phase systems containing toluene or 1,2-dichloroethane and aqueous H_2O_2.[44–48] With excess hydrogen peroxide in solution, Keggin type polyanions are transformed to peroxo polyoxometalates species {$PO_4[WO(O_2)_2]_4$}$^{3-}$, the active intermediates for oxidation. Biphasic oxidations in organic solvent-water system, for example in a toluene and aqueous H_2O_2 system, are also particularly attractive because in these systems the product and catalyst are easily separated after a reaction. In these two-phase systems, the oxidation reactions typically require some sort of phase-transfer catalysis, where the peroxo polyanions are transported through the organic-water interface by using phase-transfer agents such as quaternary ammonium cations with C_8-C_{18} alkyl groups. Recently, the Kozhevnikov group demonstrated that cyclophosphazenes can also be used as effective phase transfer agents too.[49] However, while this issue has been explored, there is still a need for more efficient

biphasic oxidation processes using POM/H_2O_2 systems, especially for alkane-water two-phase systems. Systems that afforded catalysts with high stability and recyclability would be particularly important for reactions such as the POM-catalyzed oxidative desulfurization with aqueous hydrogen peroxide as the "green" oxidant as a method for deep desulfurization of transportation fuel.[46]

Perruthenate anions are also another important oxidation catalyst used in organic transformations. However, a potential oxidation catalyst like potassium perruthenate is only soluble in water. It is insoluble in organic solvents. For this reason, tetra-*n*-propylammonium perruthenate (TPAP) was developed by the Ley group as a catalyst using *N*-methylmorpholine-*N*-oxide as the penultimate oxidant to oxidize alcohols to the corresponding aldehydes and ketones. However, while TPAP can be used catalytically as a mild oxidizing agent, Ru is an expensive metal. Therefore, there is value in attempting to recycle this transition metal oxidant. Prior reports have described using both crosslinked polystyrene resins as polymer supports and inorganic or inorganic-hybrid supports to recover and recycle this Ru oxidant using either NMO or oxygen as the penultimate oxidant. However, these reactions were done under heterogeneous conditions, conditions that limit reactivity of some substrates. The catalyst recyclability was also modest and leaching was not well described. This led us to consider the use of PIB oligomer as a potential polymer support for perruthenate anions because PIB supports will solubilize an anion like perruthenate in nonpolar and modestly polar solvents, allowing an oxidation reaction with a perruthenate anion to be carried out under homogeneous conditions. Also, the PIB supports would be expected to make perruthenate anions phase-selectively soluble

in nonpolar solvents such as heptane, which could make it possible to recycle these catalysts if they were stable under the reaction conditions.

The results below show that diethylamine terminated and quaternary ammonium terminated PIB oligomers are indeed efficient hydrocarbon solubilizing agents for POM clusters and perruthenate anions. Both diethylamine terminated PIB and *N,N*-diethyl-*N*-methylammonium terminated PIB oligomers were explored as supports for Keggin type POM catalysts in oxidative desulfurization and alkene epoxidation with hydrogen peroxide in a heptane-water two-phase system. *N,N*-diethyl-*N*-methylammonium terminated PIB and *N*-methylimidazolium terminated PIB oligomers were used as polymer supports for perruthenate anions. In the case of the perruthenate oxidations, the reactions were conducted in heptane. Then a subsequent extraction with heptane immiscible solvent and a liquid/liquid separation was used to isolate the product from the catalyst to explore catalyst recycling.

Results and Discussion

As discussed in chapter 1, past work by the Bergbreiter group has shown that alkene-terminated polyisobutylene (PIB) oligomers can be converted into a variety of ligands and catalysts that facilitate the recovery and recycling of homogeneous catalysts. My work extended these studies specifically exploring the synthesis and use of a diethylamine terminated PIB oligomer, a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer, and a *N*-methylimidazolium PIB oligomer as polymer supports for catalysts. The resulting PIB-modified oligomers contained were used to ionically support

polyoxometalate clusters and perruthenate anions. The resulting species were all found to be highly soluble in heptane. While a biphasic system of heptane-water is used with the PIB-supported polyoxometalates, a monophasic system of heptane is utilized with the PIB-supported peruthenate. In both cases, however, PIB supports played significant roles as both nonpolar phase-anchored species in separation after reactions and also highly soluble catalysts for reactions with substrates that can be readily conducted under homogeneous conditions.

PIB oligomers as supports for polyoxometalate clusters (POM)

This research using PIB as polymer supports for POM catalysts was done in collaboration with the Kozhevnikov group at the University of Liverpool. Commercially available vinyl-terminated PIB with a molecular weight, M_n, of 1000 Da was chemically modified so that the terminal vinyl group was transformed into a diethylamino or an ammonium salt. These nitrogen functional groups on PIB oligomers were then used to bind to POM clusters. A PIB-oligomer with a terminal diethylamino group (**6**) was synthesized as shown in Figure 21. The starting alkene-terminated PIB underwent an ozonolysis, a haloform reaction, activation of the carboxyl group, amidation, and finally reduction to form **1**. The diethylamine terminated PIB oligomer was dissolved in heptane to form a 0.5 M heptane solution. To solubilize a POM cluster, the 0.5 M heptane solution of the diethylamine terminated PIB oligomer was used to form the PIB-supported precatalyst as described in Figure 22. This solution was then added to the reaction mixture containing heptane, dodecane (GC internal standard), aqueous H_2O_2, and heteropoly acid
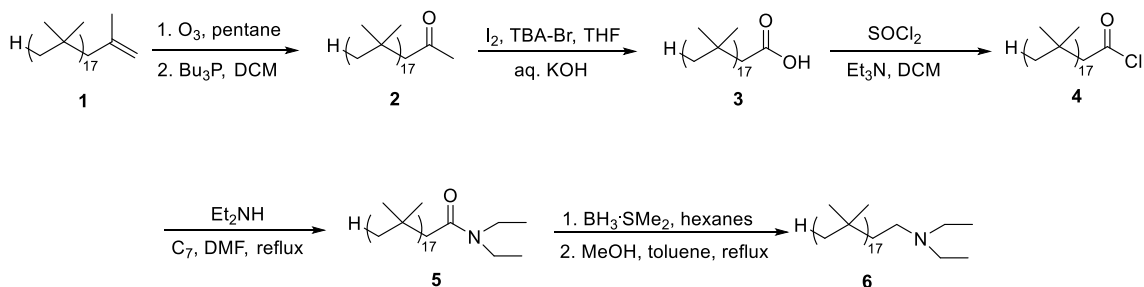
Figure 21. Synthesis of a diethylamine terminated PIB oligomer
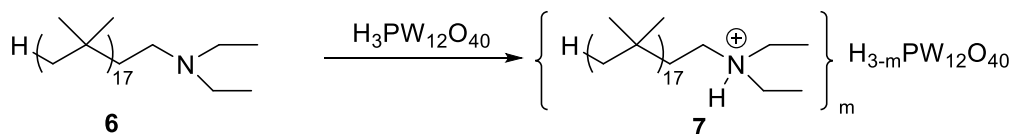
Figure 22. Synthesis of PIB-supported POM catalyst

in specified quantities. The active catalyst was generated *in situ*. The POM can either be the heteropoly acid hydrate $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, or $H_4SiW_{12}O_{40}$, all of which contain roughly 20 H_2O molecules per Keggin Unit. The POMs were abbreviated as PW, PMo, and SiW respectively. The oxidations of dibenzothiophene (DBT) were carried out in a two-phase system with heptane as an organic solvent and aqueous H_2O_2 at 25-60 °C. The DBT oxidation reactions, as described in Figure 23, were monitored by taking aliquots from the organic phase and submitting them to GC analysis to determine substrate conversion and product yield. The results for DBT oxidations are shown in Table 2. As expected, the catalyst activity increased with the PIB/POM molar ratio, levelling off at a ratio of 4:1-6:1 (Entries 1-4). More remarkably was that the catalyst was more reactive
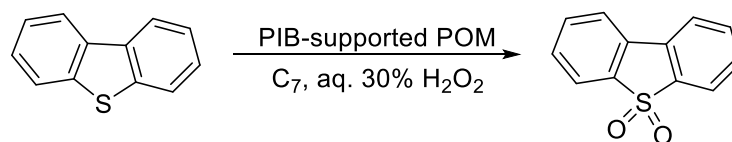
Figure 23. Oxidation of dibenzothiophene (DBT)

than a catalyst formed with similar POMs using conventional C_8-C_{18} quaternary ammonium surfactants. At a 1:1 PIB/POM molar ratio, the reaction had a 70% DBT conversion in 0.5 h (Entry 1) and 100% in 1 h. This can be explained by the higher phase-transfer efficiency of the PIB surfactant due to its much longer hydrocarbon chain.

Table 2. Oxidation of DBT in heptane-water biphasic system in the presence of PIB-bound POM catalysts

Entry	POM	PIB/POM (mol mol^{-1})	Temp. (°C)	Conv. (%)	H_2O_2 (%)
1	PW	1:1	60	70	>99
2	PW	2:1	60	96	>99
3	PW	4:1	60	97	>99
4	PW	6:1	60	100	>99
5	PW	4:1	40	49	>99
6	PW	4:1	25	30	>99
7	PMo	4:1	60	73	>99
8	SiW	4:1	60	0	>99

^{a} Heptane (10 mL), DBT (0.5 mmol, 1 wt%), aqueous 30% H_2O_2 (0.15 mL); molar ratios: DBT/POM = 90:1, DBT/H_2O_2 = 1:3; 0.5 h reaction time. DBT sulfone was the only product observed

In addition, the reactivity of different POMs were compared as illustrated in Figure 24. PW was found to exhibit the highest activity followed by PMo (Entries 3, 7). The reaction with PW at 60 °C and a PIB/PW molar ratio of 4:1 had a conversion of 97% in 0.5 h. On the other hand, SiW showed no reactivity at all within the 0.5 h reaction time, with a slow conversion rate after 1 h induction period. This is in agreement with the well-known stability of SiW to degrade in solution and its resistance to form peroxo species. It is important to note that practically no decomposition of H_2O_2 to molecular oxygen
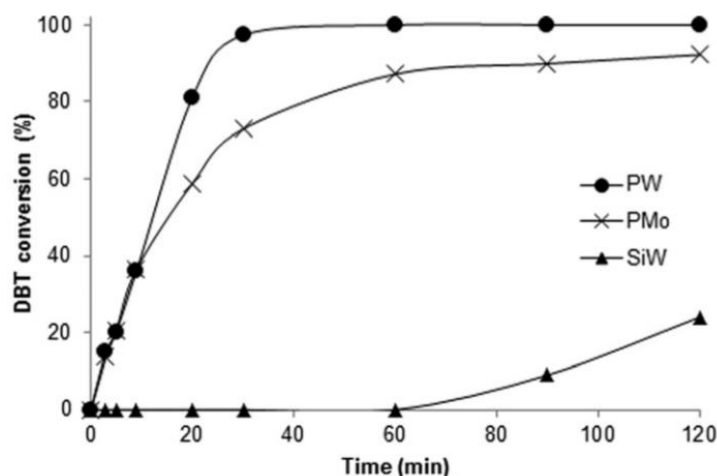
Figure 24. Effect of POM on DBT conversion (60 °C, heptane (10 mL), DBT (0.5mmol), aqueous 30 % H_2O_2; molar ratios: PIB/POM = 4:1, DBT/POM = 90:1, DBT/ H_2O_2 = 1:3).[*]

took place in the PIB-POM reaction system, giving >99% efficiency of H_2O_2. The catalytic performance of PIB-supported POM catalyst was comparable or better than the best results obtained previously. Jiang demonstrated the use of amphiphilic decatungstate $[(CH_3)_3NC_{16}H_{33}]_4W_{10}O_{32}$ as catalyst under similar conditions and observed similar DBT conversion (99.6%). However, the H_2O_2 efficiency was not reported.[45] Another catalyst, $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$, was also studied. However, this catalyst had to be pre-synthesized by a laborious procedure that is not required for the PIB-POM systems.[46]

In addition to the use of a diethylamine terminated PIB oligomer as a hydrocarbon solubilizing agent, a quaternary ammonium terminated PIB oligomer was also tested as solubilizing agents for a POM catalyst used in the oxidation of DBT. PIB oligomer with an *N,N*-diethyl-*N*-methylammonium salt was synthesized by the alkylation of **6** with iodomethane. The *N,N*-diethyl-*N*-methylammonium terminated PIB-supported precatalyst (**9**) was formed as described in Figure 25. The active catalyst was again generated *in situ*. However, in this case, the catalytic activity of a reaction using **9** as a precatalyst was found to be slower than **7**, producing only 30% conversion of DBT to DBT sulfone at 60 °C with a PIB/PW molar ratio of 4:1 in 0.5 h. We hypothesized that this was because the ion-exchange reaction of the POM with the quaternary ammonium terminated PIB oligomer was less successful than the acid-base reaction of the basic diethylamine terminated PIB oligomer with acidic sites on the POM clusters.

As expected, the PIB-supported POM oxidants were easily separated from the products and were recycled multiple times. In this particular case, the DBT sulfone product self separated in that it precipitated as white powder. However, while the product

formed as a precipitate, the workup actually involved a biphasic liquid/liquid separation.

The heptane phase was further extracted with water, acetonitrile, or dimethylformamide
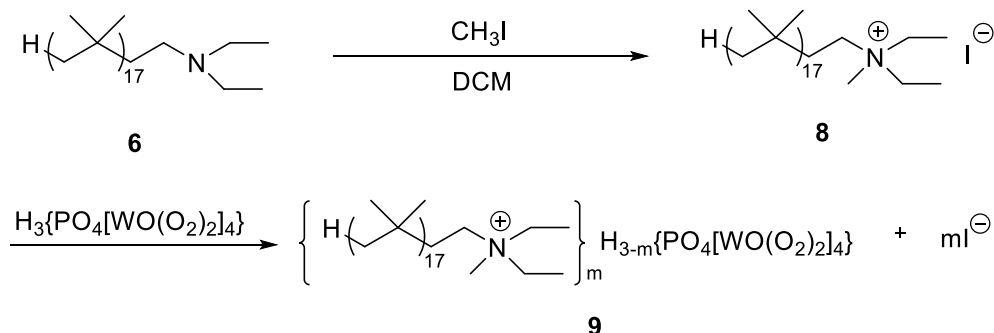
Figure 25. Synthesis of quaternary ammonium salt terminated PIB-supported POM catalyst

to ensure that DBT sulfone was completely removed. Since the PIB-supported POM

catalysts were phase-selectively soluble in heptane, recycling simply involved reusing the

heptane phase. The phase behavior and catalyst recycling using extraction with acetonitrile

is demonstrated in Figure 26. Test tube 1 demonstrated the initial reaction system with the

heptane phase (top) and aqueous H_2O_2 phase (bottom). Then, test tube 2 showed the

system after the first run was completed, where the DBT sulfone precipitated out of the

reaction mixture. In test tube 3, the heptane phase was extracted with acetonitrile, and

finally in test tube 4, fresh amounts of DBT and hydrogen peroxide were added for the

next cycle. The PIB-supported PW catalyst was shown to have excellent recyclability

illustrated in Figure 27, where the catalyst can be recovered and reused five times without any loss of activity.
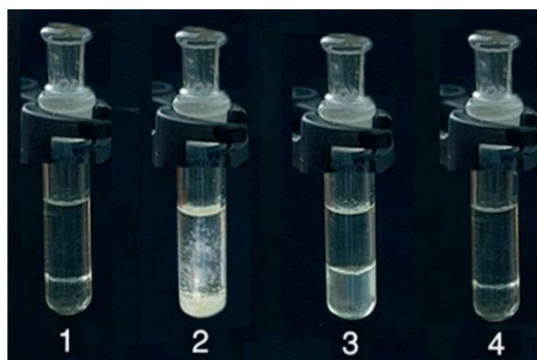
Figure 26. Catalyst recycling and phase behavior in DBT oxidation in heptane-water biphasic system catalyzed by PIB-PW[*]
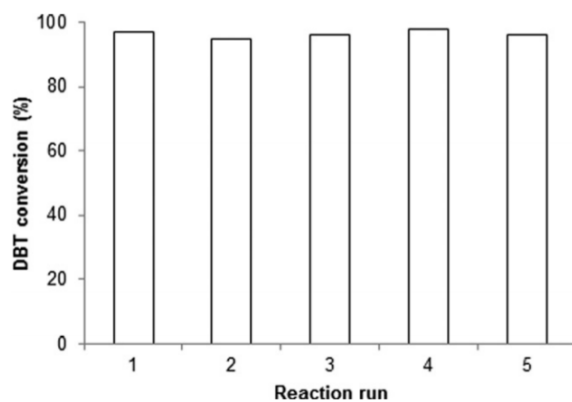
Figure 27. Catalyst reuse in DBT oxidation*

The PIB-supported POM catalysts were also found to be efficient for the epoxidation of cyclooctene in a heptane-water biphasic system. This oxidation reaction, as shown in Figure 28, has been used by others as a standard test for epoxidation catalysts and was used here as a proof of concept.[50] Typically, the reaction of POM and cyclooctene
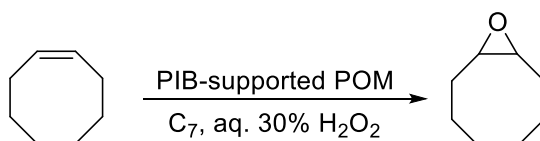
Figure 28. Epoxidation of cyclooctene

to form epoxycyclooctane with H_2O_2 is conducted under both homogeneous and biphasic conditions using more toxic organic solvents such as aromatics and chlorinated hydrocarbons. Therefore, using PIB-supported POM catalyst in a heptane-water biphasic system for olefin epoxidation has an important advantage in process safety due to the use of a greener solvent. The reaction was carried out at 30-60 °C using 10% H_2O_2 as the oxidant and PIB-bound PW or PMo as the catalyst at a PIB/POM molar ratio of 1:1 to 6:1. The results were demonstrated in Table 3. Similar to the results obtained for the oxidative desulfurization of DBT, the PW catalyst was found to be the most reactive. The reaction was already efficient at 30 °C, yielding 94% epoxycyclooctane in 2.5 h (Entry 6) and 100% at 60 °C in 0.5 h. The decomposition of H_2O_2 was negligible, and the catalyst could be recycled. The *N,N*-diethyl-*N*-methylammonium terminated PIB-supported POM, **9**, was found to be less efficient than the diethylamine terminated PIB-support POM, **7**, giving only 18% yield of epoxycyclooctane when the reaction was conducted at 60 °C

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Table 3. Epoxidation of cyclooctene by 10% H_2O_2 catalyzed by PIB-POM in heptane-water biphasic system[a]

Entry	POM	PIB/POM (mol mol^{-1})	Temp. (°C)	Time (h)	Yield (%)	Initial rate[c] (mmol min^{-1})
1	PMo	6:1	60	0.5	99	0.059
2	PW	6:1	60	0.5	100	0.083
3	PW	5:1	60	0.5	97	0.085
4	PW	4:1	60	0.5	92	0.075
5	PW	3:1	60	0.5	96	0.080
6	PW	3:1	30	2.5	94	0.031
7	PW	2:1	60	0.5	92	0.065
8	PW	1:1	60	0.5	88	0.056

[a] Heptane (10 mL), cyclooctene (9.71 mmol, 1 mL), aqueous 10% H_2O_2 (1 mmol, 0.3 mL), $H_3PW_{12}O_{40}.20H_2O$ or $H_3PMo_{12}O_{40}.28H_2O$ (6.48 µmol). [b] Yield based on the initial amount of H_2O_2. [c] Initial rate calculated over the first 10 min of the reaction.

with a PIB/PW molar ratio of 6:1 in 1.5 h. The PIB-supported PW catalyst was compared to the lacunary silicotungstate, $(nBu_4N)_4[SiW_{10}O_{34}(H_2O)_2]$, that was reported by Kamata.[50] The lacunary silicotungstate, $(nBu_4N)_4[SiW_{10}O_{34}(H_2O)_2]$, epoxidized cyclooctene with 30% H_2O_2 in homogeneous MeCN solution at 32 °C, giving 99% yield and >99% H_2O_2 efficiency. However, the synthesis of PIB-supported POM catalyst is more straightforward than the synthesis of lacunary silicotungstate.

The ability of the PIB supports to transport a POM catalyst from the aqueous phase to the organic phase was also investigated. It was observed that the catalytic activity

decreased with decreases in the PIB/PW molar ratio. The extent of PW phase transfer was estimated separately in the PW-PIB-heptane-water system using UV-Vis spectroscopy by monitoring the PW charge transfer band at 275 nm at different PIB/PW molar ratios. The amount of PW transferred into the heptane phase and the initial rate of cyclooctene epoxidation as a function of the PIB/PW ratio was shown in Figure 29. It can be seen clearly that both the concentration of the PW in the heptane phase as measured by absorbance and the initial rate change in parallel with the PIB/PW ratio.

PIB supports with perruthenate anions

Perruthenate anions are oxidizing agents that are typically used as metal salts or tetraalkylammonium salts. Potassium perruthenate, for example, is a useful oxidant that is highly soluble in water. However, it is not soluble in organic solvents. To make perruthenate more useful in organic chemistry, the Ley group replaced the potassium cation in these perruthenate salts with tetra-*n*-propylammonium to form tetra-*n*-propylammonium perruthenate (TPAP). In my work, I explored the potential for *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer and *N*-methylimidazolium terminated PIB oligomer as polymer supports for perruthenate anions to facilitate solubilization and recycling of the catalyst. The necessary PIB-oligomer terminally functionalized with *N,N*-diethyl-*N*-methylammonium iodide (**8**) was synthesized as described above in Figure 25. It was then dissolved in DCM along with TPAP. An ion-exchange reaction with tetra-*n*-propylammonium perruthenate (TPAP) was presumed to occur to generate the PIB-supported perruthenate (**10**) as shown in Figure 30. We assumed
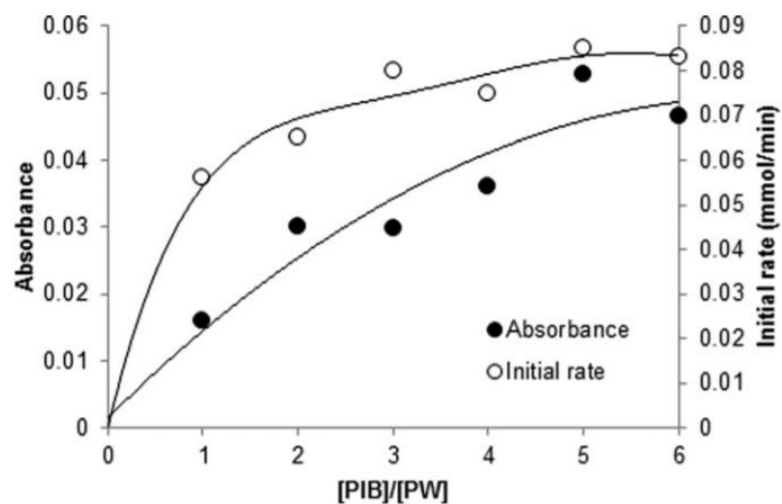
Figure 29. Absorbance of PIB-bound PW in heptane phase at 275 nm and initial rate of cyclooctene epoxidation catalysed by PIB-PW in heptane-water system as a function of PIB/PW molar ratio[*]

Figure 30. Synthesis of a PIB-bound tetraalkylammonium perruthenate oxidation catalyst

a 1:1 equilibrium mixture of **8** and **10** formed when the reaction was carried out with equal amounts of TPAP and **8**. DCM was removed from the reaction mixture under reduced

pressure and hexanes was added to the crude product. To remove the low molecular weight tetra-*n*-propylammonium perruthenate and iodide, which are insoluble in hexanes, from the hexanes soluble PIB species, **8** and **10,** the hexane solution was either passed through Celite in a pipette to separate the solids or washed with acetonitrile. The solubility of the low molecular weight perruthenate and the PIB-supported perruthenate (**10**) was easily tested visually because the perruthenate anion was highly colored. As shown in Figure 31, the heptane phase was highly colored when the perruthenate anions were immobilized on PIB supports. This solubility contrasted with that of TPAP which was phase-selectively soluble in acetonitrile under the same conditions.

To probe the utility of this heptane soluble PIB-supported perruthenate as an oxidizing catalyst, the catalyst was used along with *N*-methylmorpholine-*N*-oxide (NMO) to oxidize alcohols to their corresponding aldehydes and ketones. The reaction of 1-phenylethanol to form acetophenone was tested. The results of these studies are shown in Table 4. At room temperature in DCM in the presence of molecular sieves, the reaction

Figure 31. Phase solubility of TPAP and PIB-bound perruthenate[*]

Table 4. Catalytic activity of *N*,*N*-diethyl-*N*-methylammonium terminated PIB-bound perruthenate (10) in the oxidation of 1-phenylethanol to form acetophenone

Solvent	Time (h)	Temp. (°C)	Conversion (%)
DCM	12	25	Cycle 1: 91
			Cycle 2: 69
Heptane	12	80	Cycle 1: 93
			Cycle 2: 73

[a] The conversion of substrate to product was measured using ^{1}H NMR spectroscopy

proceeded in 91% conversion based on ^{1}H NMR spectroscopy in 12 h. Oxidation of 1-phenylethanol was also successful in heptane though it required elevated temperature (80 °C) to effect a similar 93% conversion of alcohol to ketone. In the first case, the DCM solvent was removed under reduced pressure. The residue from that reaction was then dissolved in heptane and that solution was extracted with acetonitrile from a heptane solution of **10**. Recycling was then explored. However, attempts to recycle the recovered heptane solution of **10** were only modestly successful. A second cycle using the recovered **10** led to only 70% conversion. Similar problems of diminished yields in recycling of polystyrene supported TPAP had been noted previously.[51,52] In our experiments, we also noted formation of traces of an insoluble material at the interface of the heptane/acetonitrile phases in the biphasic product separation after an oxidation leading us to believe that some decomposition of **10** occurred.

A possible reason of decomposition of the *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer is the base-induced elimination reaction. Thus, we briefly explored an alternate quaternary ammonium terminated PIB oligomer, *N*-methylimidazolium terminated PIB oligomer **13**. This cationic nitrogen salt cannot undergo such an elimination reaction. The synthesis of **13** is shown in Figure 32. In this
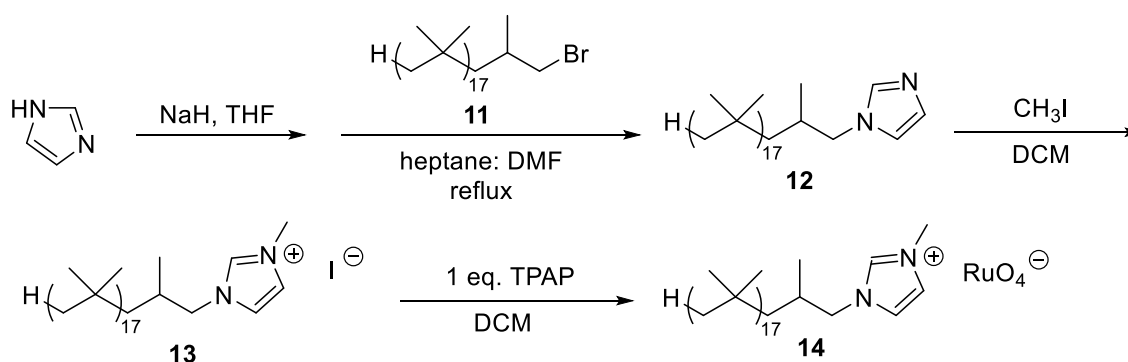
Figure 32. Synthesis of *N*-methylimidazolium terminated PIB-bound perruthenate

synthesis, NaH was used to promote the reaction of the imidazole with the bromide terminated PIB oligomer **11** to form the imidazole terminated PIB oligomer **12**. Imidazole terminated PIB oligomer **12** was then allow to react with iodomethane to make *N*-methylimidazolium iodide terminated PIB oligomer **13**. Finally, **13** underwent an ion-exchange reaction with TPAP to generate *N*-methylimidazolium terminated PIB-bound perruthenate **14**. Similar to *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer (**10**), **14** was phase-selectively soluble in heptane, allowing the PIB oligomer to be isolated from the product by a liquid/liquid separation with MeCN. To explore the utility and

recyclability of **14** as a catalytic oxidant, 10 mol % of **14** was used to oxidize benzyl alcohol to benzaldehyde using NMO as the penultimate oxidant. The results shown in Table 4 demonstrated that the *N*-methylimidazolium terminated PIB-bound perruthenate catalyst worked well in cycle 1. However, like **7**, the activity decreased in cycle 2 to 65% and 61% conversion in DCM and heptane respectively.

Table 5. Catalytic activity of *N*-methylimidazolium terminated PIB-bound perruthenate (14) in oxidation of benzyl alcohol to form benzaldehyde

Solvent	Time (h)	Temp. (°C)	Conversion (%)
DCM	3	25	Cycle 1: 98
			Cycle 2: 65
Heptane	12	80	Cycle 1: 86
			Cycle 2: 61

[a] The conversion of substrate to product was measured using ^{1}H NMR spectroscopy

Conclusion

This chapter describes the synthesis and use of a diethylamine terminated PIB oligomer, a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer, and a *N*-methylimidazolium terminated PIB oligomer as polymer supports for oxidation catalysts such as polyoxometalate clusters and perruthenate anions. Initially, this work demonstrated the use of a diethylamine terminated PIB oligomer and a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer to ionically support Keggin type POMs. The

PIB-supported POM catalysts were highly efficient for environmentally benign biphasic oxidations with hydrogen peroxide, especially in the oxidation of DBT to DBT sulfone and in cyclooctene epoxidation, in a heptane-water biphasic system. The precatalysts were formed by simply mixing commercial Keggin type POMs and PIB supports. The PIB supports also allow the POMs catalysts to be easily recovered and reused. I also examined the use of a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer and a *N*-methylimidazolium terminated PIB oligomer as polymer supports for a perruthenate anion In this case, the goal was to the explore potential of these same supports to recycle a commonly used Ru complex that is known to oxidize alcohols to aldehydes or ketones. The PIB-bound perruthenate catalyst formed was found to be a competent oxidant. However, recycling of the perruthenate catalyst immobilized on PIB was only modestly successful. In addition, the reaction was also slower in heptane than in the commonly used solvent, DCM.

CHAPTER III

EXPLORING THE SCOPE OF AMMONIUM TERMINATED PIB OLIGOMERS AS

HYDROCARBON SOLUBILIZING AGENTS AND CATALYSTS IN HEPTANE

AND HYDROCARBON OLIGOMERIC SOLVENT ALTERNATIVES FOR S_N2

REACTIONS

Introduction

Bimolecular nucleophilic substitution reaction also known as an S_N2 reaction, is one of the most common reactions in organic chemistry. The discovery of bimolecular nucleophilic substitution reactions has involved many giants in chemistry. For example, Walden first observed an inversion of pure enantiomeric (+)-malic acid to (-)-chlorosuccinic acid in the presence of PCl_5. (-)-Chlorosuccinic acid was then treated with Ag_2O to form (-)-malic acid. When (-)-malic acid was used as a substrate, the reaction proceeded in similar fashion, obtaining (+)-malic acid as the final product.[53] The rates of bimolecular nucleophilic substitution reactions were also found to be dependent on the concentrations of the substrates and the nucleophiles, making them a second-order reaction. The mechanism of the bimolecular nucleophilic substitution reaction, as shown in Figure 33, was proposed by E. D. Hughes and Christopher Ingold in 1935.[54] The transition state involves the incoming nucleophile attacking the alkyl halide carbon at 180° from the leaving group, inverting the stereochemistry of the carbon. In their work, they studied both the stereochemistry and kinetics of S_N2 reactions.
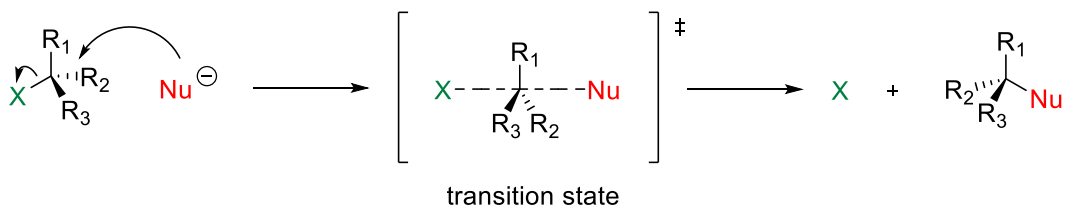
Figure 33. Mechanism of S$_N$2 reaction

Some factors that influenced the rates of S$_N$2 reactions are the characteristics of the substrate, the nucleophile, the leaving group, and the solvent. The work in this chapter is focused on the solvent effects on S$_N$2 reactions. Prior studies have demonstrated that S$_N$2 reactions proceeded faster in polar aprotic solvents, such as in MeCN and in DMF, than in polar protic solvents, such as water and MeOH.[55] This is because polar protic solvents can hydrogen bond to the nucleophiles, lowering their reactivity and energy as shown in Figure 34. On the other hand, polar aprotic solvents cannot form these hydrogen
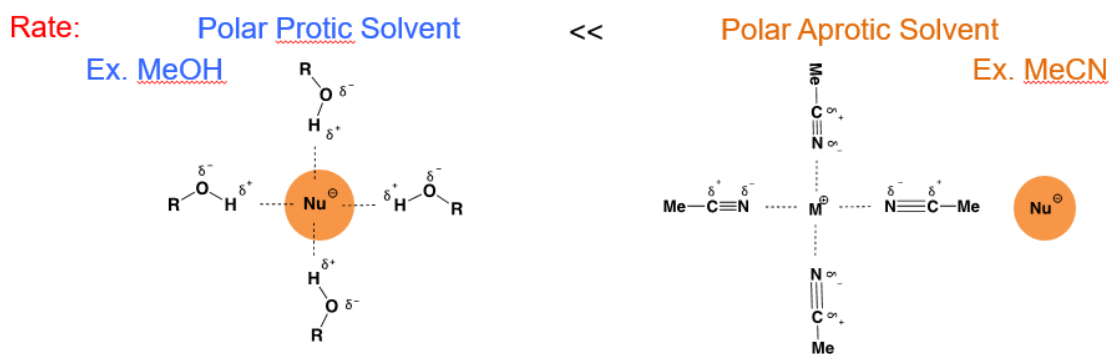
Figure 34. Effects of polar solvents on S$_N$2 reactions

bonds. Instead of solvating the nucleophiles, these polar aprotic solvents solvate the cations. This enhance the rates of S_N2 reactions by increasing the nucleophilicity of the bare unsolvated nucleophiles and by providing a polar milieu for these polar reactions.

An issue with some S_N2 reactions that involve metal salts of anionic nucleophiles is that the metal salts and the organic substrates often have different solubility. Therefore, the substrates and the nucleophilic anions are often in two different phases. This can slow the reaction as the reagents cannot readily come in to contact with each other. To solve this heterogeneity problem, strategies that make these anions soluble in organic solvents by using tetrabutylammonium cations have been developed. Suitable ammonium ions like tetrabutylammonium cations are generally soluble in polar solvents. In some cases, cationic tetrabutylammonium ions can be used catalytically as phase-transfer catalysts. In these cases, the reactions are conducted under biphasic conditions. The phase-transfer catalysts help transfer the anions from the aqueous phase to the organic phase where the reaction occurs as illustrated in Figure 35. Kinetic studies of the S_N2 reactions in aqueous organic two-phase reactions and homogeneous conditions were done by Landini, Maia, and Montanari.[56] Those studies showed that while phase-transfer catalysts solve the problem of heterogeneity, the reactions proceeded slower under phase-transfer conditions than in homogeneous conditions. Phase-transfer catalysts that are recoverable and recyclable have also been immobilized on insoluble cross-linked polystyrene resins and used in S_N2 reactions.[36] The reactivity of this cross-linked polystyrene supported phase-transfer catalysts were found to be similar to catalysts used under conventional
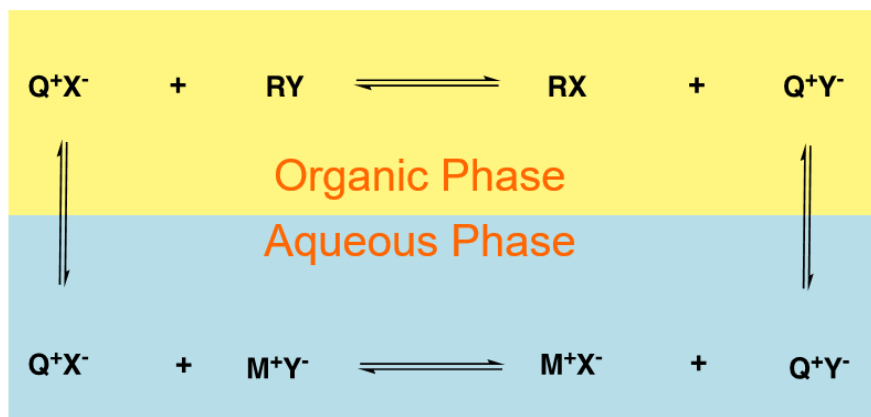
Figure 35. S$_N$2 reactions with a phase-transfer catalyst

phase-transfer conditions. More recently, studies have been done to explore the rate of S$_N$2 reactions in nanoreactor consisting of ionic liquids entrapped in reverse micelles. In these work, benzyl-*n*-hexadecyldimethylammonium chloride (BHDC) was used as the cationic surfactant in toluene/ionic liquid systems.[57,58] In these studies, they explored the nucleophilicity of chloride anion in an S$_N$2 reaction with dimethyl-4-nitro-phenylsulfonium trifluoromethanesulfonate. It was demonstrated that the protic ionic liquid (IL), ethylammonium nitrate, that was confined inside toluene/BHDC reverse micelles was suitable for S$_N$2 reactions. This result was in contrast to when the protic IL was used as a homogeneous media. It was believed that when the ionic liquid was entrapped in the reverse micelles, due to the strong interactions of the hydrogen bonds, the protic IL behaved like an aprotic-like IL. Therefore, the protic IL did not decrease the nucleophilicity of the chloride in the S$_N$2 reaction and allowed the S$_N$2 reaction to proceed.

In my work, I explored using *N,N*-diethyl-*N*-methylammonium terminated PIB oligomers as hydrocarbon phase-solubilizing agents for nucleophilic anions to study the rates of S$_N$2 reactions in heptane, a nonpolar solvent that cannot significantly stabilize anions or cations. Although the rates of S$_N$2 reactions in polar aprotic and polar protic solvents in homogeneous conditions have been investigated previously, the rates of S$_N$2 in nonpolar solvents have not been fully studied due to the insolubility of either the metal salts or tetrabutylammonium salts in these solvents. Exactly how heptane will effect such a reaction is also unclear. Unlike polar solvents, these solvents have no hydrogen bonding and polarity.

To explore the S$_N$2 reactions in heptane, *N,N*-diethyl-*N*-methylammonium terminated PIB oligomers were used as hydrocarbon phase-solubilizing agents to help solubilize nucleophilic anions, allowing the S$_N$2 reactions to take place homogeneously in heptane. As part of this study, S$_N$2 reactions in conventional solvents such as in MeOH, MeCN, and DMF were studied as comparisons for the reactions in heptane. We then further extend our work to investigate the use of *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer as a catalyst to transfer insoluble anions from the solid metal salts to the heptane phase. Finally, we explored the use of poly(α-olefins) (PAOs) as alternatives for conventional alkane solvents in S$_N$2 reactions in a model study. The advantages in using these PAO solvents are that they are nonvolatile and relatively nontoxic. In addition, the leaching of the PAOs and the PIB oligomers into the polar phase is lesser than the leaching of a low molecular weight conventional alkane solvent, a result noted previously in earlier work from the Bergbreiter group.[59]

Results and Discussion

Chapter 2 describes how a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer was synthesized via an ozonolysis, a haloform reaction, activation of the carboxyl group, amidation, amide reduction, and methylation. To improve the synthesis route to a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer, a new method was introduced to reduce the numbers of steps, time, and amount of reagents to make this PIB oligomer. The improved method is described in Figure 36. Alkene-terminated PIB
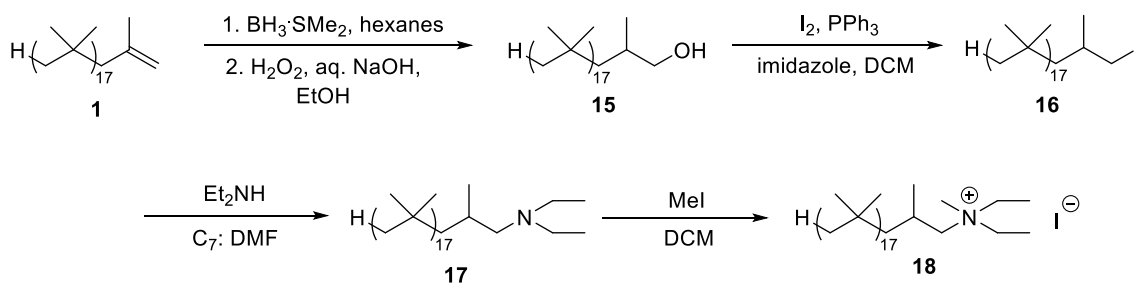
Figure 36. Improved synthesis route for *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer

oligomer underwent a hydroboration-oxidation reaction to generate an hydroxy-terminated PIB oligomer **15**. Then, the Appel reaction was conducted to transform **15** into an iodide terminated PIB oligomer **16**. To make the diethylamine terminated PIB oligomer **17**, an excess amount of diethylamine in DMF was added to a solution of **16** in heptane. Upon heating at 90 °C, the two phases become miscible and the substitution reaction took place. The diethylamine terminated PIB oligomer **17** was then methylated by using

iodomethane to generate a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with an iodide anion **18**. Other anions like benzoate and phenolate were immobilized on to a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer **18** by an ion-exchange reaction using an ion-exchange column. Amberlite® IRA400 (hydroxide form) resins were first treated with a solution of sodium hydroxide until the eluent was basic. The basicity and the acidity of the eluents in this process were tested with pH papers. This ensured that the ammonium functional groups on the resins were present as ammonium hydroxide salts. The resins were then rinsed with water until the eluent has a pH of 7 to remove any excess aqueous NaOH. A solution of benzoic acid or phenol in methanol was then added into the ion-exchange column until the eluent has the same pH as the starting solution. Again, the resins were rinsed with either methanol, acetonitrile, or heptane until the eluent has a neutral pH. Lastly, a solution of **18** in heptane was passed through the column to generate either *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with benzoate anion **19** or *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with phenoxide anion **20** illustrated in Figure 37. The solution of **18** in heptane can be passed
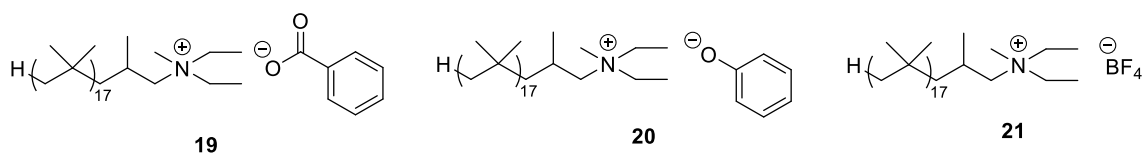
Figure 37. *N,N*-**diethyl-***N*-**methylammonium terminated PIB oligomers with benzoate anion and phenolate anion**

through the ion-exchange column until all the iodide anions were exchanged into the desired anions. The formation of **19** and **20** was confirmed by ^{1}H NMR spectroscopy. The resins were also reusable by retreatment with solutions of aqueous NaOH and benzoic acid or phenol to recycle the resins used in the ion-exchange reaction. Low molecular weight tetra-*n*-butylammonium bromide can also be used to generate tetra-*n*-butylammonium benzoate (TBA-benzoate) and tetra-*n*-butylammonium phenol-phenolate (TBA-phenol-phenolate) in similar fashion. TBA-benzoate can also be synthesized by using a solution of tetra-*n*-butylammonium hydroxide in methanol and benzoic acid, using magnesium sulfate to remove water that was generated in the reaction.

S$_N$2 reactions were first investigated using commercially available tetra-*n*-butylammonium iodide (TBA-iodide). The kinetics of S$_N$2 reactions were studied first in methanol and acetonitrile. Subsequently, the same substrates were studied in heptane using a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with an iodide anion **18**. In these studies, 1-bromooctane was used as the substrate, and the reactions were conducted at 35 °C in different solvents and the approach to equilibrium was studied using GC analysis. Cyclooctane was used as an internal standard for gas chromatography (GC) analysis. When the reactions were conducted in MeCN and in MeOH, an aliquot of the reaction mixture was removed at various time intervals, diluted with diethyl ether, and extracted with water. The two layers were then separated, and the diethyl ether phase was dried with anhydrous sodium sulfate. The diethyl ether phase was analyzed by gas chromatography (GC). When the reaction was done in heptane, an aliquot of the reaction mixture was passed through a silica gel pipette column to remove the PIB species, and the

pipette column was washed with hexanes. The eluent was then analyzed by GC. The S_N2

reactions in these cases were second-order opposing reactions, which mean that the

reactions were reversible. For this reason, using the classical method, the k constant was

calculated by plotting $\frac{x_e}{2a_0(a_0-x_e)}\ln\left[\frac{x(a_0-2x_e)+a_0x_e}{a_0(x_e-x)}\right]$ $vs.$ time (s), where a_0 is the starting

concentration of the substrate, x is the concentration of the product at time t, and x_e is the

amount of product present at equilibrium.[60] The rate constant, k, can be determined from

the slope of the line. Graphs showing this plot for heptane, MeCN, and MeOH are shown

in Figure 38. The R^2 values for the linear plots are 0.9981, 0.9897, and 0.9982 respectively.

Because the calculations through this method is complicated and not straightforward, we

used a modern method to calculate the rate constant by using the Solver add-in in excel to

fit nonlinear curve. With this modern method, the concentrations of the substrate and

product (M) were plotted versus time (s). Solver, then, minimized the chi-squared error to

fit the experimental data to the theoretical data by changing a variable or variables. In this

case, the variables are k and k_{-1}. The results of these studies are summarized in Table 1.

The results from both methods were similar, but with the modern method, we can calculate

the rate constants for both the forward and reverse reactions. The reactions in MeCN was

comparable to heptane. The rate constants in heptane and MeOH were 0.0014 and 0.0003

respectively using the classical method and 0.0013 and 0.0003 respectively using the

modern method, which means the S_N2 reaction in heptane is faster than a polar protic

solvent, MeOH.

The reaction of 1-bromooctane with 1-iodooctane is, as noted, complicated

because it is an equilibrium process. Iodide can replace bromide and bromide can replace

iodide. Thus, simpler non-opposing reactions were also investigated by using a different substrate, 1-octylmesylate. In these reactions, using the classical method, $1/[A]$ (M^{-1}) was plotted against time (s) to obtain the rate constant from the slope of the line, where [A] is the concentration of the substrate at time t. The S_N2 reactions with 1-octyl mesylate were

a)

$$\frac{x_e}{2a_0(a_0 - x_e)} \ln\left[\frac{x(a_0 - 2x_e) + a_0 x_e}{a_0(x_e - x)}\right] (M^{-1})$$

y=0.0014x-0.6313
R^2=0.9981

b)

$$\frac{x_e}{2a_0(a_0 - x_e)} \ln\left[\frac{x(a_0 - 2x_e) + a_0 x_e}{a_0(x_e - x)}\right] (M^{-1})$$

y=0.0036+1.9238
R^2=0.9897
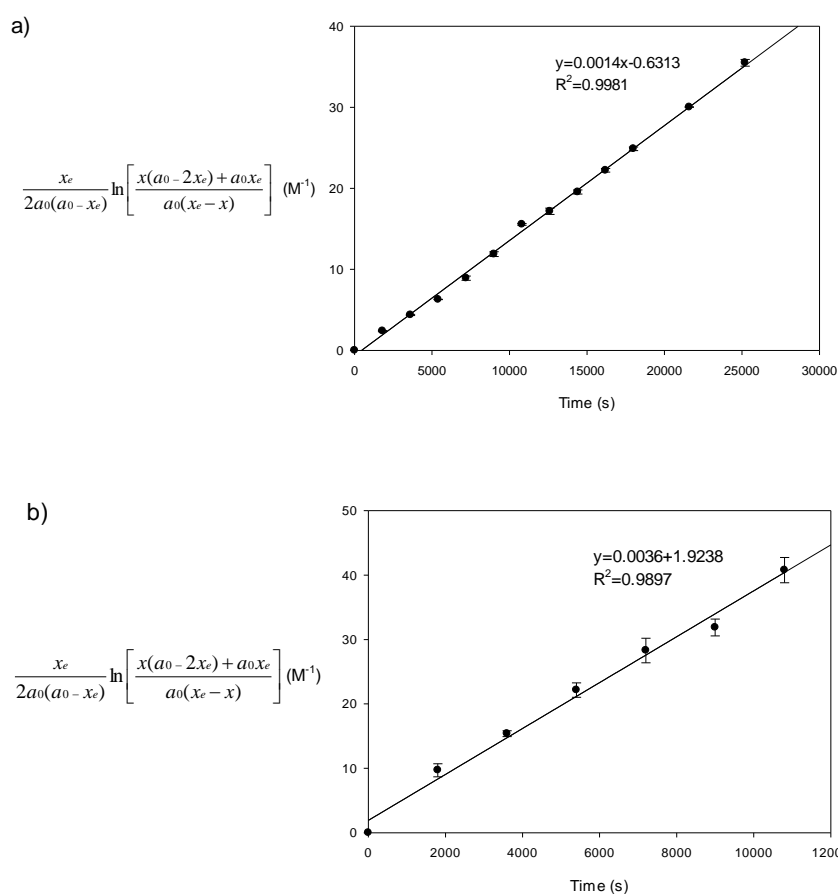
Figure 38. Kinetics of 1-bromooctane to 1-iodooctane a) in heptane, b) in MeCN, and c) in MeOH

c)

$$\frac{x_e}{2a_0(a_0 - x_e)} \ln\left[\frac{x(a_0 - 2x_e) + a_0 x_e}{a_0(x_e - x)}\right] (M^{-1})$$
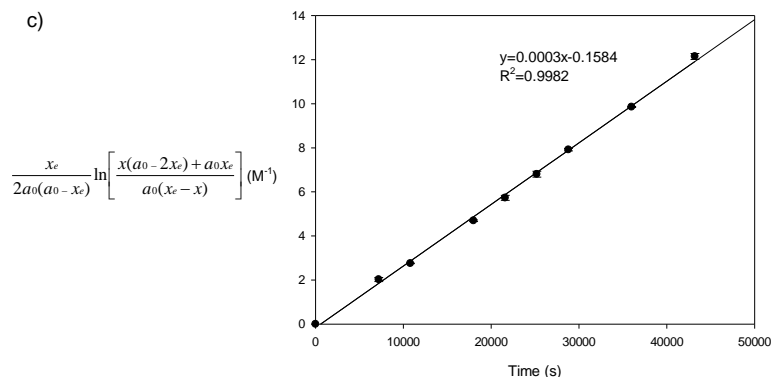
Figure 38. Continued

Table 6. Rates of S_N2 opposing reactions 1-octylbromide and iodide anions
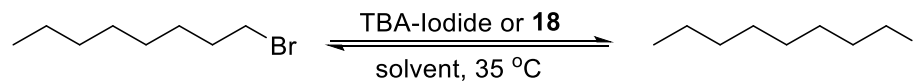
Solvent	Nucleophile	Classical k (1/M·s)	Modern k_1, k_{-1} (1/M·s)
Heptane	PIB-ammonium iodide	0.0014	0.0013, 0.0016
MeCN	TBA-iodide	0.0036	0.0047, 0.090
MeOH	TBA-iodide	0.0003	0.0003, 0.0022

conducted at 55 °C with TBA-iodide in DMF, in MeCN, and in MeOH and **18** in heptane.

The graphs of these reactions are shown in Figure 39. In these cases, the rate of the

reaction in heptane and in MeCN have rate constants of 0.0211 and 0.0018 respectively

using the classical method and 0.0184 and 0.0022 respectively using the modern method.

With these cases, the variable is the rate constant for the forward reaction. Results for these reactions are shown in Table 2. Again, the reaction in MeOH was the slowest.

Other nucleophiles, such as benzoate and phenolate, were also investigated for the rates of S_N2 reactions. Tetra-*n*-butylammonium benzoate (TBA-benzoate) or tetra-*n*-butylammonium phenol-phenolate (TBA-phenol-phenolate) was used for the kinetic studies of S_N2 reactions with 1-bromobutane or 1-butylmesylate in both polar protic and polar aprotic solvents. In the reactions where heptane was used as the solvent, either *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with benzoate anion **19** or *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with phenolate anion **20** was used
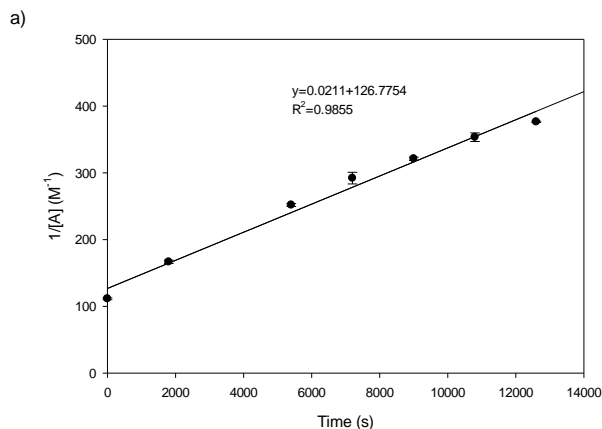
Figure 39. Kinetics for 1-octylmesylate to 1-iodooctane a) in heptane b) in DMF c) in MeCN, and d) in MeOH

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b)

y=0.0076+118.8492
R^2=0.9941

1/[A] (M^{-1})

Time (s)

c)

y=0.0018x+98.0962
R=0.9825

1/[A] (M^{-1})

Time (s)

d)

y=0.0016x+118.9005
R^2=0.9849

1/[A] (M^{-1})

Time (s)
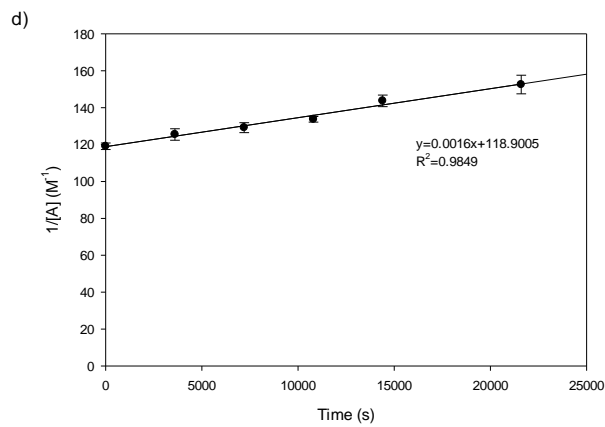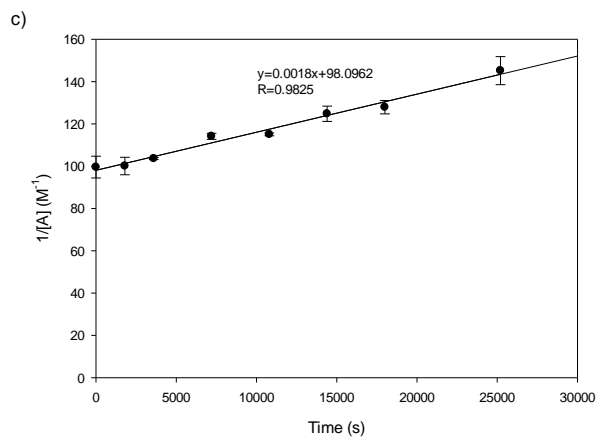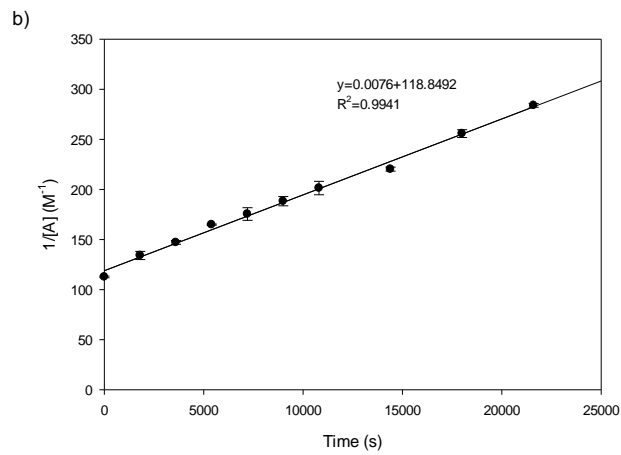
Figure 39. Continued

Table 7. Rates of S$_N$2 reactions with 1-octylmesylate and iodide anions

$$\text{(structure) OMs} \xrightarrow[\text{solvent, 55 °C}]{\text{TBA-Iodide or } \mathbf{18}} \text{(structure) I}$$
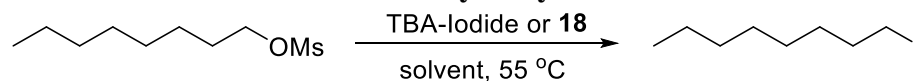
Solvent	Nucleophile	Classical k (1/M·s)	Modern k$_1$ (1/M·s)
Heptane	**18**	0.0211	0.0184
DMF	TBA-iodide	0.0076	0.0079
MeCN	TBA-iodide	0.0018	0.0022
MeOH	TBA-iodide	0.0016	0.0017

as a nucleophile source. The graphs of these reactions are shown in Figure 40, 41, and 42.

The results of these reactions are summarized in Table 3, 4 and 5. In general, the rates of

reactions proceeded fastest in DMF, followed by the reactions in MeCN and heptane. The

reactions in methanol tended to be the slowest as expected due to the hydrogen bonding

of in methanol to the nucleophile.

a)

y=0.0255x+107.8829
R^2=0.9793

1/[A] (M^{-1})

Time (s)
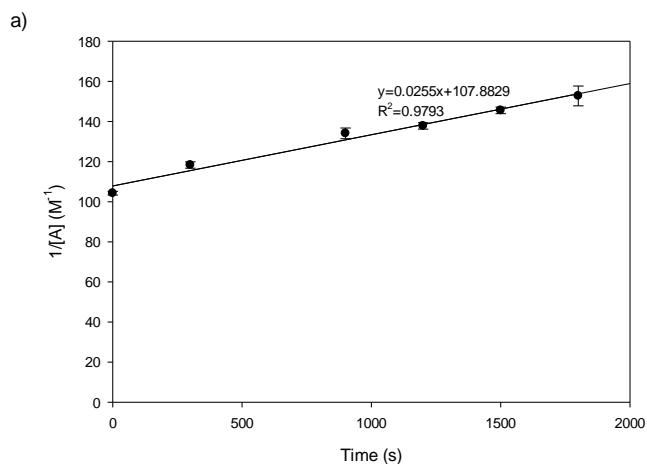
Figure 40. Kinetics of 1-butylmesylate to 1-iodobutane a) in heptane, b) in DMF, and c) in MeCN. There was barely any reaction in MeOH.

b)

y=0.1108x+115.35
R^2=0.9886

c)

y=0.0230x+106.9260
R^2=0.9905
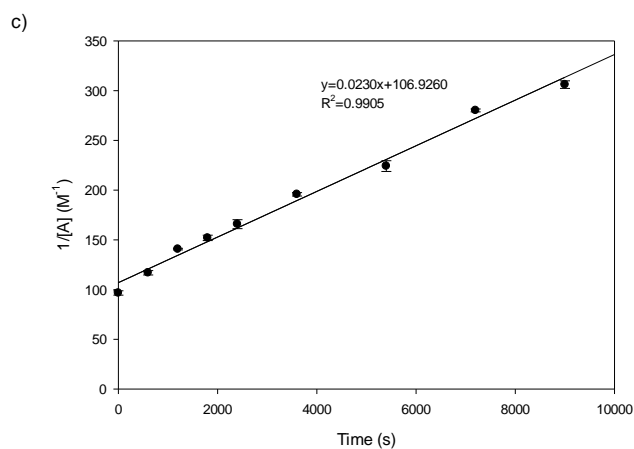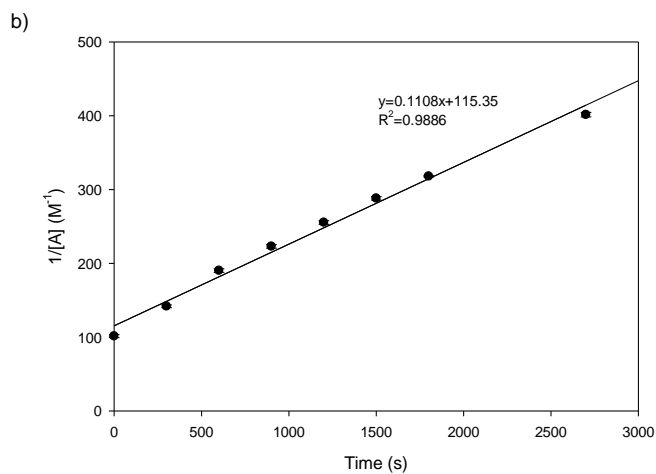
Figure 40. Continued

Table 8. Rates of S$_N$2 reactions with 1-butylmesylate and iodide anions
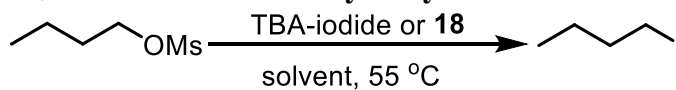
Solvent	Nucleophile	Classical k (1/M·s)	Modern k_1 (1/M·s)
Heptane	**18**	0.0255	0.0264
DMF	TBA-iodide	0.1108	0.1316
MeCN	TBA-iodide	0.0230	0.0279
MeOH	TBA-iodide	very slow	very slow

a)

b)
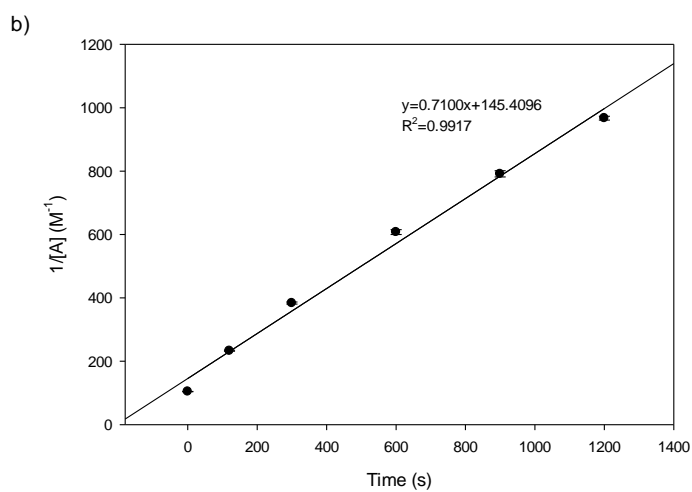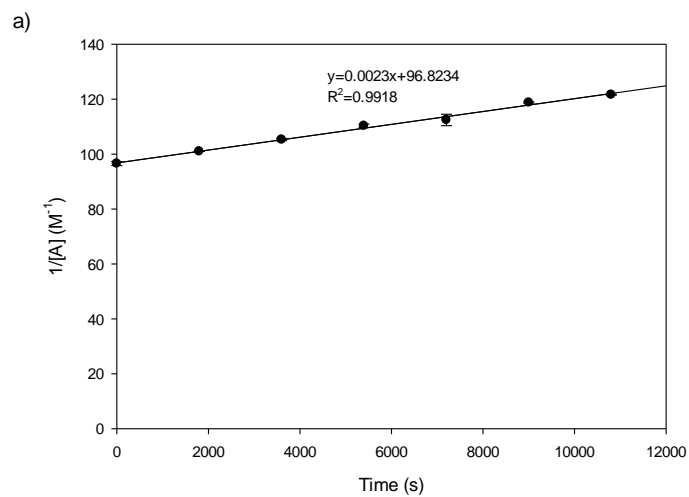
Figure 41. Kinetics of 1-bromobutane to 1-butylbenzoate a) in heptane, b) in DMF, c) in MeCN, and d) in MeOH

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c)

y=0.0616x+135.0354
R²=0.9875

d)

y=2.9737E-0006x+1.1908
R²=0.9889
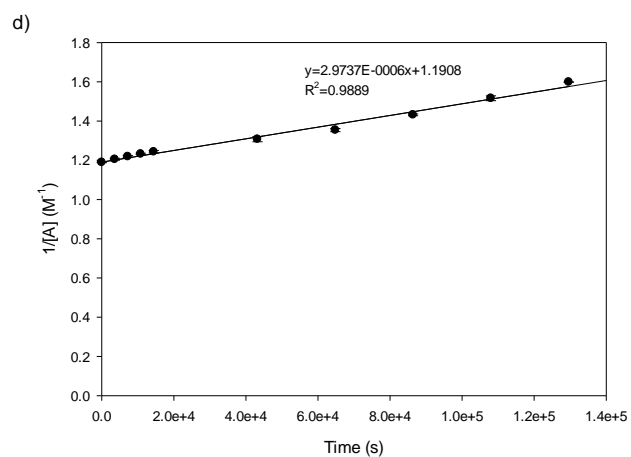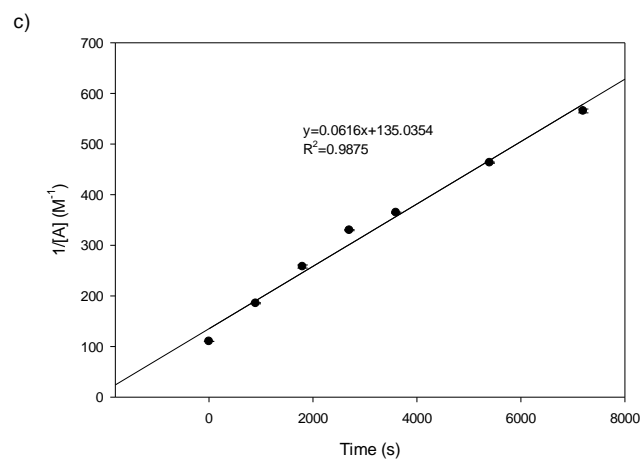
Figure 41. Continued

Table 9. Rates of S$_N$2 reactions with 1-bromobutane and benzoate anions
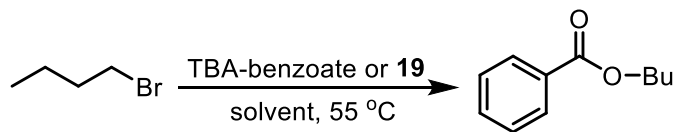
Solvent	Nucleophile	Classical k (1/M·s)	Modern k_1 (1/M·s)
Heptane	**19**	0.0023	0.0020
DMF	TBA-benzoate	0.7100	0.9025
MeCN	TBA-benzoate	0.0616	0.0651
MeOH	TBA-benzoate	2.97×10^{-6}	1.63×10^{-6}

a)

b)
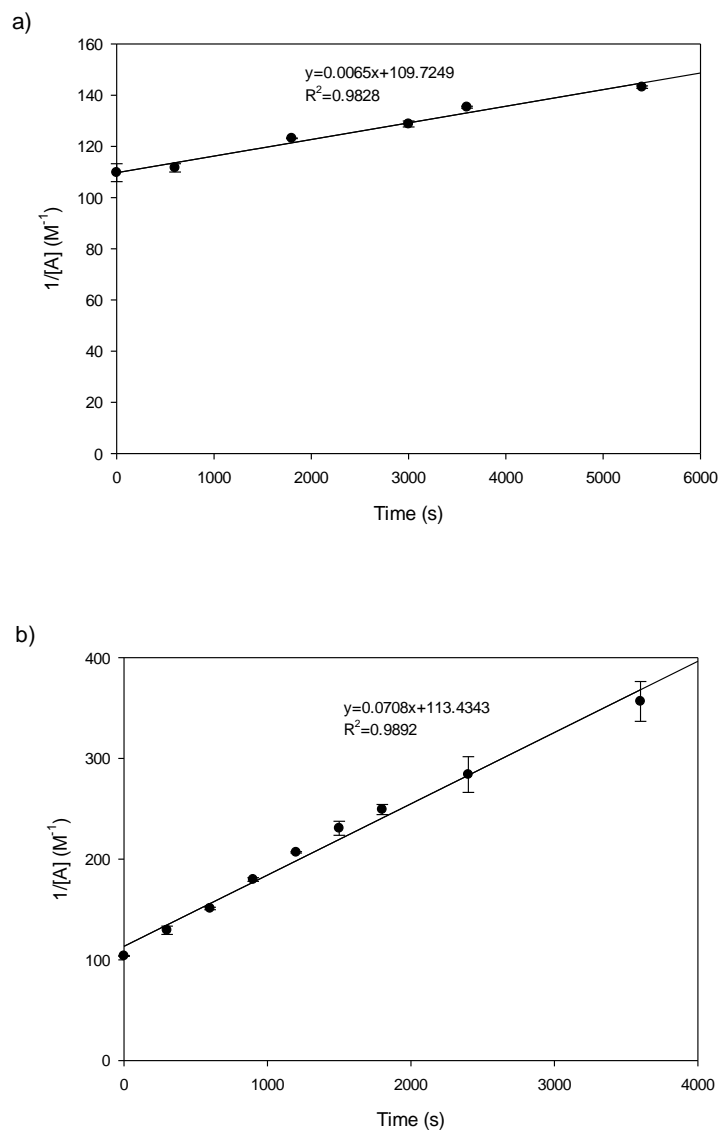
Figure 42. Kinetics of 1-bromobutane to 1-butylphenylether 1) in heptane, 2) in DMF, 3) in MeCN, and 4) in MeOH

c)

d)
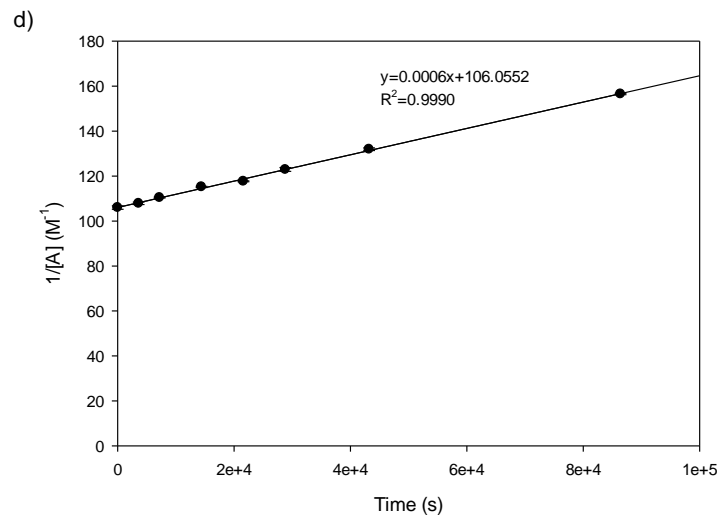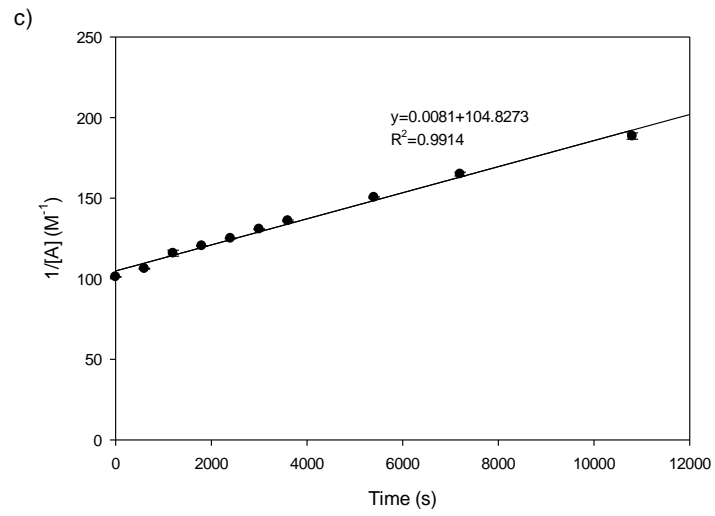
Figure 42. Continued

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Table 10. Rates of S$_N$2 reactions with benzoate and phenolate anions
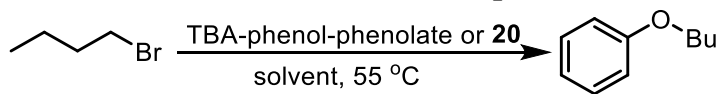
Solvent	Nucleophile	Classical k (1/M·s)	Modern k_1 (1/M·s)
Heptane	**20**	0.0065	0.0059
DMF	TBA-phenol-phenolate	0.0708	0.0771
MeCN	TBA-phenol-phenolate	0.0081	0.0092
MeOH	TBA-phenol-phenolate	0.0006	0.0004

Since the rates of reactions in heptane were comparable to rates of reactions in acetonitrile, we further investigated the use of the *N,N*-diethyl-*N*-methylammonium
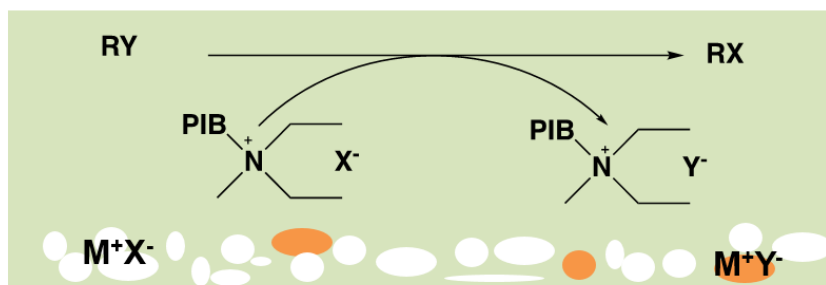
Figure 43. The mechanism of solid/liquid catalysis

terminated PIB oligomer as a hydrocarbon phase-solubilizing catalyst. The catalytic activity of the *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer was investigated in a solid/liquid phase catalysis as shown in Figure 43. In these reactions, the insoluble solid metal salts were used directly in the reaction, where the *N,N*-diethyl-*N*-

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methylammonium terminated PIB catalyst can solubilized the nucleophilic anions in the heptane phase. **18** underwent an ion-exchange reaction with sodium tetraborohydrate to form *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with tetraborohydrate anion **21** before being used as a catalyst. This was to minimize the possible side reaction that can occurred from the nucleophilic iodide anion in an S_N2 reaction. 1-Bromobutane was used as the substrate with 3 eq. of KOAc in heptane at 90 °C. Without the presence of **21**, no reaction occurred. With the presence of **21** in the reaction mixture, the reaction obtained a 100% conversion in 24 h as demonstrated in Figure 44. The conversion was determined by GC analysis using cyclooctane as the internal standard. The reaction also worked well with (3-bromopropyl)benzene as shown in Figure 45. The reaction had a conversion of 97% in 5 h.
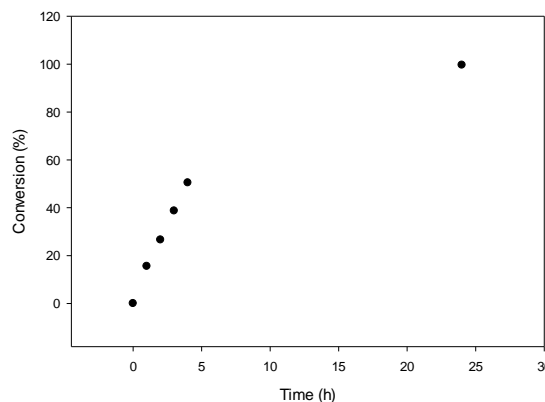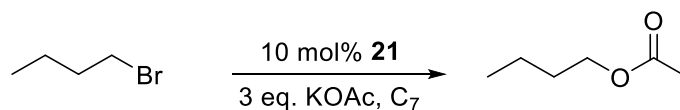
Figure 44. Solid/liquid catalysis with 21 and 1-bromobutane

71
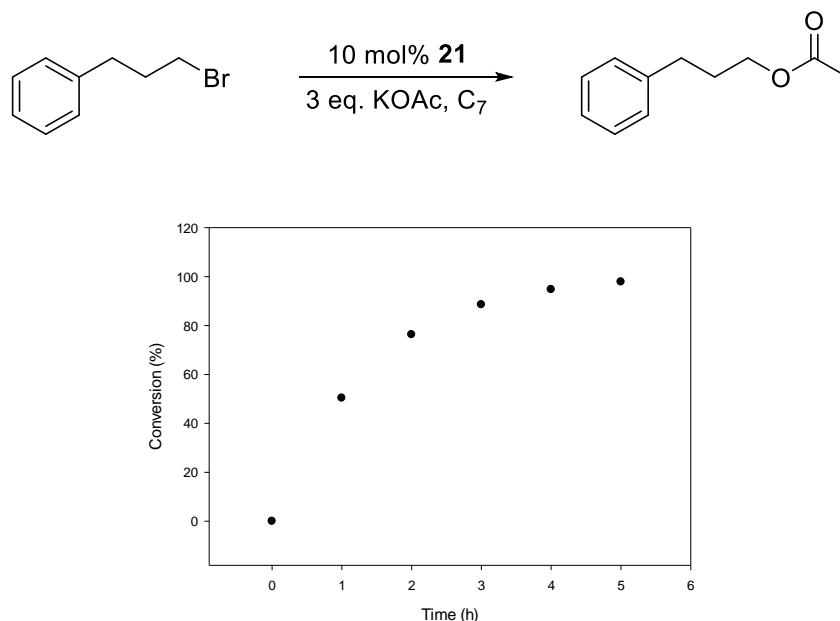
Figure 45. Solid/liquid catalysis with 21 and (3-bromopropyl)benzene

Since the reaction work efficiently in heptane, we assumed that the reaction would also proceed well in the greener hydrocarbon oligomeric PAO solvents our group recently described. That recent work described alternatives for low molecular weight conventional alkane solvents. Solvents such as hexanes and heptane have inhalation toxicity due to their volatility. Therefore, we turned our attention to poly(α-olefin)s (PAOs), which are inexpensive and commercially available. In addition to being nontoxic and nonvolatile, the recent work by the Bergbreiter group has also shown that the leaching of PAOs into the polar phase was less than leaching of heptane into a polar phase.[59] This feature can be beneficial for catalyst recycling because the concentration of the PIB-supported catalyst in these hydrocarbon solvents will be constant and because alkane solvent will not be lost in each recycling step. In the event, S_N2 reactions using 1-bromobutane, 3 eq. KOAc, and 10 mol% **22** were tested with 2 cST PAO, 4 cST PAO, and 10 cST PAO and the

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solid/liquid catalysis was found to be successful. The recycling of the catalysts in these S_N2 reactions in heptane, 2 cST PAO, 4 cST PAO, and 10 cST PAO was also investigated. PAOs can be recycled in the same fashion as the heptane:acetonitrile biphasic system. In the recycling processes, after 24 h, the reactions were extracted and centrifuged with acetonitrile. The two phases were separated and equivalent amount of cyclooctane (internal standard) was added into the acetonitrile phase before submitting the solution for GC analysis. The heptane phase was then recycled by adding fresh amount of substrate and KOAc. The results are demonstrated in Figure 46. The reactivity of the S_N2 reaction in heptane started to diminish in cycle 4. The reason for the decreased reactivity may result from the leaching of the heptane phase containing the *N,N*-diethyl-*N*-methylammonium terminated PIB catalyst into acetonitrile during extraction. The amount of heptane phase was visually observed to lessen in further recycling cycles. The reactivity of the S_N2 reaction in 2 cST PAO started to decrease in cycle 5 as well. Less leaching was observed in 4 cST PAO and 10 cST PAO. Therefore, there was no loss of reactivity in these S_N2 reactions.

Conclusion

In this study, comparative kinetic studies of S_N2 reactions in polar aprotic, polar protic, and nonpolar solvents were investigated. The reactions in heptane were conducted by using *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer as hydrocarbon phase-solubilizing agents. These *N,N*-diethyl-*N*-methylammonium terminated PIB

oligomers help solubilized the nucleophilic anions in heptane. In general, the rates of the S_N2 reactions was fastest in DMF, followed by MeCN and heptane. The reaction in MeOH
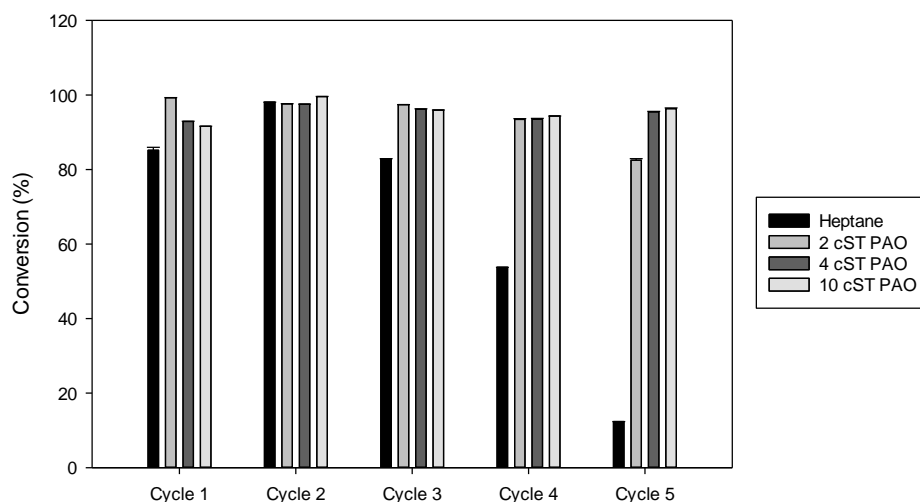
Figure 46. Recycling of the hydrocarbon phase in heptane, 2 cST PAO, 4 cST PAO, and 10 cST PAO

was slowest due to the hydrogen bonds that decrease the nucleophilicity of anions. We

further examined the use of *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer as

a phase-solubilizing catalyst in a solid/liquid phase catalysis. The S_N2 reaction with the

N,N-diethyl-*N*-methylammonium terminated PIB catalyst worked efficiently in heptane,

but a loss of reactivity was observed when the catalyst was recycled due to the leaching

of the heptane phase into acetonitrile phase. For this reason, we explored alternatives for

conventional alkane solvents by investigating PAOs, which can be used as hydrocarbon

oligomeric solvents. PAOs were found to leach lesser than conventional alkane solvents

in to the polar phase. Not only that, these hydrocarbon oligomeric solvents are relatively

nontoxic and nonvolatile, making them a much more greener solvent replacement. The

S$_N$2 reactions worked well in these hydrocarbon oligomer solvents, especially in 4 cST

PAO and 10 cST PAO, where no loss of catalytic reactivity was observed in recycling.

CHAPTER IV

POLYISOBUTYLENE OLIGOMERS AS POLYMER SUPPORTS FOR

HYPERVALENT IODINE REAGENT

Introduction

Oxidation is one of the most important transformations in organic chemistry. While chapter 2 describes the use of polyoxometalate clusters and perruthenate anion as catalysts for oxidation reactions, this chapter focuses on another class of oxidizing agents, hypervalent iodine compounds. Hypervalent iodine reagents are used as mild, safe, and economical alternatives to heavy metal reagents, such as mercury (II), thallium (III), lead (IV), osmium (VIII) and chromium (VI). Some examples of organohypervalent iodine compounds are shown in Figure 47. These compounds can be categorized into two main classes, trivalent iodine derivatives known as λ^3-iodanes and pentavalent iodine derivatives known as λ^5-iodanes. The mechanism of these hypervalent iodine reagents as oxidants and electrophilic reagents typically involve ligand exchange, reductive elimination, and ligand coupling reactions.[61]

The most common version of hypervalent iodine compounds is 2-iodoxybenzoic acid (IBX) or derivatives like the ester shown in Figure 48. IBX is known to be an efficient and mild oxidant used for the oxidation of primary and secondary alcohols. Although IBX has valuable properties, its application in organic synthesis can be limited. While IBX is soluble in DMSO, it is relatively insoluble in many common organic solvents. To address this issue, structural modifications of IBX have been investigated. For example, Zhdankin
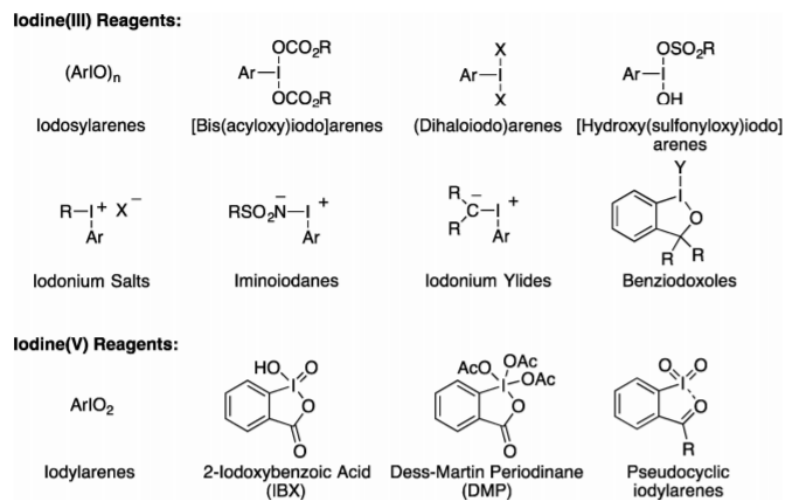
Figure 47. Main classes of organohypervalent iodine reagents[*]
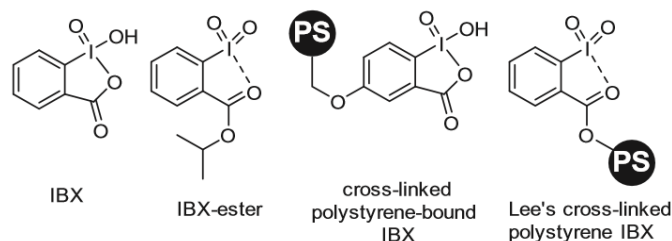
Figure 48. Analogs of IBX[†]

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[*] Reprinted with permission from "Advances in Synthetic Applications of Hypervalent Iodine Compounds" by Yoshimura, A.; Zhdankin V.V. *Chem. Rev.* **2016**, *116*, 3328, Copyright 2016 by American Chemical Society

[†] Reprinted with permission from "Recyclable soluble polyisobutylene-bound oxidizing agents" by Samunual P.; Bergbreiter, D. E. *Tetrahedron Lett.*, **2016**, *57*, 3272, Copyright 2016 by Elsevier

et al. described IBX esters and IBX amides that were both stable and soluble in polar organic solvents.[62] Unlike the common hypervalent iodine reagents, these compounds have an additional intramolecular non-covalent coordination at the iodine center. This feature gives rise to a new class of hypervalent iodine reagents known as the pseudocyclic hypervalent iodine compounds. The pseudocyclic hypervalent iodine compounds have higher thermal stability, better solubility, and improved reactivity compared to the common hypervalent iodine reagents.[63]

Another issue with IBX is that this reagent is often used stoichiometrically. This opposes the basic concept of green chemistry that emphasizes on the superiority of catalytic and recyclable reagents over stoichiometric reagents. Thus, recycling of this reagent in an efficient and simple manner would be desirable. Prior studies have focused on using a variety of insoluble supports for this purpose.[56] These previous studies have reported the use of both inorganic supports like silica gel and organic polymer supports like cross-linked polystyrene, which were precedented by earlier work by the Moss group that immobilized iodobenzoate reagents on insoluble cross-linked polystyrene. [64–67] These reagents were catalysts for phosphate ester hydrolyses, where the insoluble cross-linked polystyrene facilitated workup and separation of spent oxidant and product.[67] Soluble polymer-supported IBX oxidants too have been investigated. The Janda group reported the synthesis of soluble polystyrene-supported IBX.[68] While these soluble oxidants had some advantages and while they too could be separated from products, the separation process involved solvent precipitation and required excess solvent.

This work here explores a different approach to immobilize and recycle an IBX oxidizing agent that uses the soluble PIB oligomer. It relies on the phase-selective solubility of PIB phase anchor after an oxidation process to separate the oxidant from the product using a liquid/liquid biphasic separation. The synthesis of the PIB-supported IBX ester oxidant was straightforward, and the oxidant was shown to be competent for alcohol oxidations. We were able to separate spent PIB-bound IBX ester from the product efficiently and were also able to show that it was possible to both readily regenerate and reuse this spent oxidant.

Results and Discussion

Previous chapters described how a diethylamine terminated PIB oligomer and a quaternary ammonium terminated PIB oligomer were used as solubilizing and recycling handles for catalysts and reagents. While the catalysts and reagents discussed earlier were bound ionically to the PIB supports, here we describe a different approach to immobilize catalysts or reagents to PIB oligomers by a covalent ester linkage. This chapter explored the potential for these same soluble hydrocarbon oligomer supports for a stoichiometric hypervalent iodine oxidant, 2-iodoxybenzoic acid, showing how the support facilitates its recyclability and solubility in organic solvents.

The synthesis of the PIB-supported IBX ester analog was accomplished as shown in Figure 49. Alkene-terminated PIB oligomer (**1**) with M_n values of 1000 Da was subjected to a hydroboration-oxidation reaction to generate the hydroxy terminated PIB oligomer (**15**). The hydroxy terminated PIB oligomer was esterified using 2-iodobenzoic

acid with DCC and DMAP to form the PIB-supported 2-iodobenzoic acid (**22**). After

purification by column chromatography, the PIB-supported 2-iodobenzoic acid (**22**) was
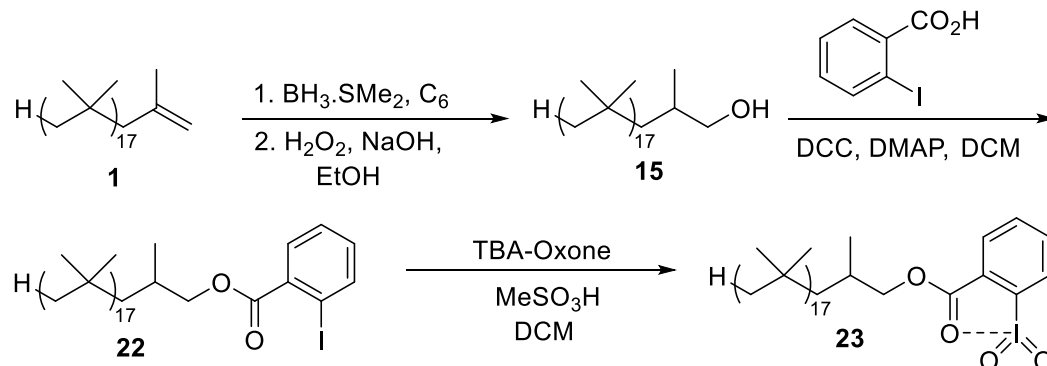
Figure 49. Synthesis of PIB-supported IBX analog

oxidized to make the desired PIB-supported IBX ester (**23**) using tetrabutylammonium

oxone (TBA-Ox) and MeSO$_3$H in DCM. In this chemistry, the oxidant, TBA-Ox, was

prepared by a procedure described by Borhan and co-workers and its oxidative activity

(82%) was measured by iodometric titration before its use in the formation of **23**. The

conversion of PIB-supported 2-iodobenzoic acid to PIB-supported IBX ester was

determined by using ^{1}H NMR spectroscopy, looking at the ratio of the diastereotopic -

CH$_2$O- signal of **22** at 4.33 ppm and the signal of the same group in **23** at 4.03 ppm. The

average conversion of **22** to **23** in six different reactions was 87% and ranged from 81%

to 94%. The solution of the PIB-supported IBX ester so formed was then directly used in

oxidations without isolation of **23**.

The oxidation reaction of benzyl alcohol to benzaldehyde was initially investigated

to determine the best reaction conditions with **23** as an oxidizing agent. The extent of the

oxidation reaction was measured by ^{1}H NMR spectroscopy. These studies are shown in Table 9 and demonstrated that the reaction did not progress well unless an acid promoter, such as trifluoroacetic acid (TFA) or boron trifluoride etherate, was utilized. The use of these acid promoters is known to also increase the reactivity in the oxidations with the low molecular weight IBX.[62] Interestingly, we observed an unexpected solvent effect, where the oxidation reaction in heptane was found to be more efficient than the reaction in

Table 11. Conversions of oxidation of benzyl alcohol with PIB-supported IBX ester (23) at 25 ° C

23 (equiv)	Solvent	Promoter	Time (h)	Conversion[a] (%)
2.38	DCM	None	24	4
2.26	Heptane	None	24	33
1.76	DCM	1 equiv TFA	24	30
2.42	Heptane	1 equiv TFA	24	94
1.67	Heptane	None	1	100[b]
1	Heptane	1 equiv $BF_3 \cdot OEt_2$	<0.5	97
1.64	$CDCl_3$	1 equiv $BF_3 \cdot OEt_2$	0.2	91

[a] The conversion of substrate to product was measured using ^{1}H NMR spectroscopy
[b] The reaction was carried out at 80 °C
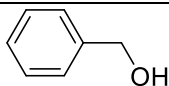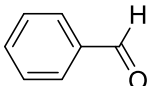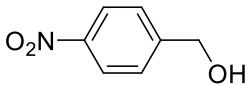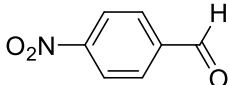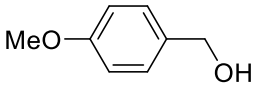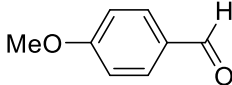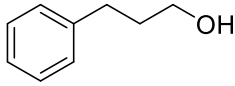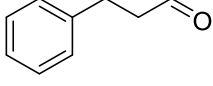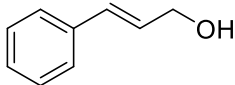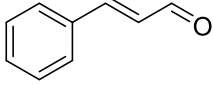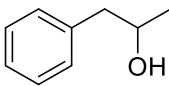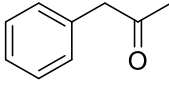
dichloromethane, which is the typical solvent used for IBX oxidant. TFA and boron trifluoride etherate were found to be both efficient in the conversion of benzyl alcohol to

benzaldehyde, but boron trifluoride etherate was preferred over TFA for two main reasons. First, the reaction time using **23** as the oxidizing agent and TFA as the promoter was significantly longer than the same reaction with a crosslinked polystyrene-supported IBX ester. Second, there was a formation of white precipitate during the reaction. This precipitate was insoluble in d_6-DMSO, CDCl$_3$, and d-benzene. Therefore, we could not identify these white solids. Since these problems were not observed in the oxidation reaction with **23** using boron trifluoride etherate as the promoter, we focused on using boron trifluoride etherate as the acid promoter in this study. The oxidation reaction of benzyl alcohol to benzaldehyde with **23** and boron trifluoride etherate in heptane resulted in quantitative conversions, 97%, in less than 0.5 h.

Given that the oxidation of benzyl alcohol was found to be successful, other types of alcohols were tested using the PIB-supported IBX ester **23** as the oxidants, boron trifluoride etherate as the acid promoter, and heptane as the solvent. As shown in Table 10, the oxidation reactions with the described reaction condition were highly successful, with conversions ranging from 95-100%. The reactions with **23** were highly efficient in oxidizing benzyl alcohols with an electron-withdrawing group and an electron-donating group with conversions of 100% and >94% respectively. Reactions with non-benzylic alcohols were also examined, where the oxidation reactions with cinnamyl alcohol and 3-phenyl-1-propanol had conversions of >96% and 100% respectively. Lastly, the oxidation of secondary alcohol, 1-phenyl-2-propanol, with **23** and boron trifluoride etherate was also found to be effective, having a conversion of 100%.

Because both the low molecular weight IBX and the PIB-supported IBX ester are stoichiometric reagents, the original goal of this work was to recycle the oxidant to minimize the amount of reagent utilized. A key advantage was that unreacted or spent **23**,

Table 12. Survey of substrate scope of oxidation reactions using PIB-supported IBX ester (23)

Substrates	Products	Conversion[a] (%)
		100
		100
		>94
		>96
		100
		100
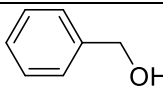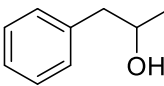
[a] The conversion of substrate to product was measured using ^{1}H NMR spectroscopy

having PIB as a phase selectively heptane soluble anchor, can be easily isolated from the product. In addition, the ketone or aldehyde product from the oxidation reaction were more likely soluble in acetonitrile than heptane, which meant that the heptane phase along with

the PIB-supported IBX ester can be recycled after undergoing extractions with acetonitrile. Recycling of the PIB-supported IBX ester **23** was conducted with both benzyl alcohol and 1-phenyl-2-propanol and were found to be successful up to 5 times as shown in Table 11. After the biphasic separation, the heptane solution of the spent PIB oxidant was not generally isolated but was simply re-oxidized using TBA-Ox as described in Figure 49. However, if desired, the spent oxidant could be isolated and analyzed by ^{1}H NMR spectroscopy.

Table 13. Conversions for alcohol oxidations in five cycles of the PIB-supported IBX ester 10[a]

Substrates	Cycle 1 (%)	Cycle 2 (%)	Cycle 3 (%)	Cycle 4 (%)	Cycle 5 (%)
	>94	>99	>99	>99	80
	>99	>98	100	>92	100

[a] The conversion of substrate to product was measured using ^{1}H NMR spectroscopy

Conclusion

The results above show that IBX can be immobilized on a PIB oligomer by an ester linkage to form a polymer-supported pseudocyclic hypervalent compound, PIB-supported IBX ester. The PIB-supported IBX ester was found to be a competent oxidant for the oxidations of different types of alcohols in the presence of BF_3-etherate as a Lewis acid promoter. Unexpectedly, the oxidation reaction of benzyl alcohol to benzaldehyde was faster in heptane than in DCM. This is beneficial in that heptane is known to be a greener solvent than a chlorinated solvent like DCM. Moreover, the PIB-bound hypervalent iodine oxidant was highly soluble in a solvent like heptane and was readily separated from the product by a liquid/liquid separation with MeCN. This property allowed the spent PIB-supported IBX ester to be reoxidized and reused multiple times without any loss of reactivity. Recycling of the spent PIB-bound IBX ester was successful with both a primary alcohol and a secondary alcohol.

Instrumentation

^{1}H NMR spectra were obtained using Varian Inova 300, Mercury 300, AvanceIII 400, or Varian Inova 500 spectrometers at 300 MHz, 400 MHz, or 500 MHz. ^{13}C NMR spectra were obtained using Varian Inova 300, Mercury 300, AvanceIII 400, or Varian Inova 500 spectrometers at 75 MHz, 100 MHz, or 125 MHz. The spectra were calibrated using residual non-deuterated solvent as an internal reference (e.g. CDCl3: 1H NMR = δ 7.27 ppm; 13 C NMR = δ 77.2 ppm). Analysis by gas chromatography (GC) was done using Shimadzu GC-2010 equipped with FID and a 30 m × 0.32 mm × 0.5 μm HT5 capillary column.

Syntheses of PIB Oligomers with Different Functionalities
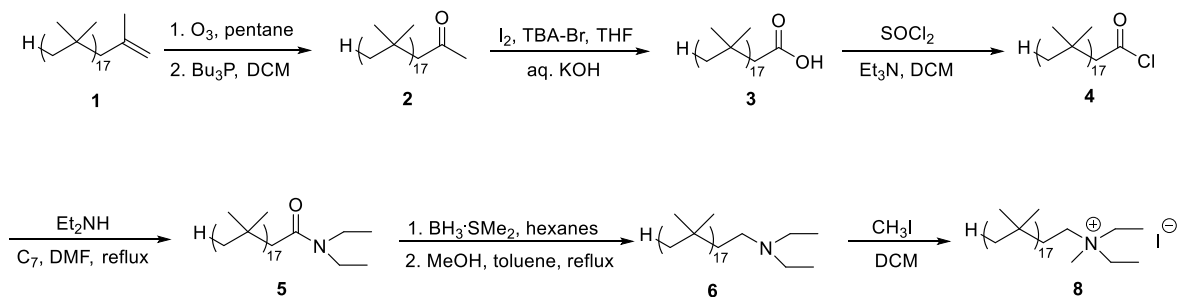
Alkene-terminated PIB (1). Alkene-terminated PIB with a molecular weight, M$_n$, of 1000 Da is commercially available and was obtained from BASF and Texas Polymer

Corporation. The starting material has some saturated PIB and a small amount of alkene isomer. It was used without further purification.

Ketone terminated PIB oligomer (2). The starting alkene-terminated PIB (**1**) (40.29 g, 40.29 mmol) was dissolved in 200 mL of pentane. The resulting solution was cooled in an acetone-dry ice bath and was purged with oxygen for 10 min. Ozone was bubbled into the reaction mixture until the solution turned blue. Then the reaction mixture was purged with oxygen again to remove excess ozone from the solution until the solution became colorless. To reduce the ozonide, tributylphosphine (20 mL, 80 mmol) was added to the reaction mixture. The reaction mixture was stirred at room temperature under nitrogen for 24 h to complete this reaction. At this point, the reaction mixture was tested for peroxides with Baker Testrips. The solution was concentrated by removing pentane under reduced pressure only after the test was negative. The resulting mixture was dissolved in 200 mL of hexanes, which was washed with 90% EtOH (4 x 50 mL) and brine (1 x 50mL). The organic phase was dried over anhydrous sodium sulfate and filtered. Hexane was removed under reduced pressure using a rotary evaporator, and the crude product was purified with silica gel column chromatography to obtain an isolated yield of 90% (36.40 g, 36 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.00-1.49 (m, 220 H), 2.12 (s, 3 H), 2.44 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: multiple peaks between 30.0 and 38.4, multiple peaks between 56.1-59.8, 209.0.

Carboxylic acid terminated PIB oligomer (3). Ketone terminated PIB oligomer (**2**) (19.91 g, 19.91 mmol) was dissolved in 600 mL of THF. Iodine (19.20 g, 75.65 mmol)

was added into the reaction mixture, followed by a solution of KOH (70.53 g, 1.07 mol) in 600 mL of deionized water. Tetrabutylammonium bromide (TBAB) (4.56 g, 14.15 mmol) was added into the reaction mixture and the resulting biphasic mixture was stirred for 48 h under nitrogen. After the iodoform reaction was complete, the aqueous layer was removed by extraction and THF was removed under reduced pressure using a rotary evaporator. The crude product was dissolved in 150 mL of hexanes and this hexane solution was washed with 6 M HCl (2 x 40 mL), 90% EtOH (4 x 40 mL), and brine (1 x 40 mL). The organic phase was dried over anhydrous sodium sulfate and filtered and the solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by silica gel chromatography to afford an isolated yield of 79% (15.66 g, 15.59 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.01-1.52 (m, 211 H), 2.35 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: multiple peaks between 28.2 and 60.0, 178.8.

Acid chloride terminated PIB oligomer (4). Carboxylic acid terminated PIB oligomer (**3**) (4.25 g, 4.23 mmol) was dissolved in 40 mL of dichloromethane. Thionyl chloride (1 mL, 13.77 mmol) and a catalytic amount of DMF (8 drops) were added and the reaction was stirred at room temperature under nitrogen for 24 h. The solvent was then removed under reduced pressure using a rotary evaporator. The crude acid chloride terminated PIB oligomer (**4**) was used without further purification.

Amide terminated PIB oligomer (5). Acid chloride terminated PIB oligomer (**4**) (4.25 g, 4.16 mmol) was dissolved in 40 mL of dichloromethane. Diethylamine (2.50 mL, 21.28

mmol) was added into the solution, which was stirred at room temperature for 24 h. After the reaction was complete, the solvent was removed under reduced pressure using a rotary evaporator. The viscous oil residue was dissolved in 80 mL of hexanes and this hexane solution was washed first with 90% EtOH (4 x 40 mL) and then brine (1 x 40 mL). The organic phase was dried with anhydrous sodium sulfate, filtered, and the solvent was removed by reduced pressure using a rotary evaporator. The isolated yield of the amide product was 91%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.00-1.53 (m, 200 H), 2.28 (s, 2 H), 3.33-3.38 (m, 4 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.4, 14.6, multiple peaks between 30.1 and 45.7, multiple peaks between 57.0-59.8, 171.3.

Diethylamine terminated PIB oligomer (6). Amide terminated PIB oligomer (**5**) (21.46 g, 20.26 mmol) was dissolved in 200 mL of dichloromethane. The solution was placed under nitrogen for 15 min at which point 10 M BH$_3$·SMe$_2$ (10.73 mL, 107.3 mmol) was added. The reaction was stirred at room temperature for 24 h. After the reaction was complete, solvent was removed under reduced pressure using a rotary evaporator. The viscous residue was dissolved in 200 mL of toluene. Then 20 mL of methanol was added and the solution was stirred under reflux for 24 h to form trimethylborane. At this point, toluene was removed under reduced pressure using a rotary evaporator and 150 mL of hexanes was used to dissolve the crude **6**. The hexane solution was washed with 90% EtOH (4 x 50 mL) and brine (1 x 50 mL), dried with anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure using a rotary evaporator. Two methods were used to purify diethylamine terminated PIB oligomer. First, the amine could

be purified using column chromatography (Brockmann aluminum oxide). Alternatively, a sequestration/release method we developed earlier using Amberlyst 15 could be used.[69] In this latter method, the crude amine (17.19 g, 16.45 mmol) was dissolved in 160 mL of dichloromethane. The Amberlyst 15 (22.3 g, 0.104 mol eq.) was added. This suspension was then shaken for 24 h. At this point, the Amberlyst-bound ammonium salt formed by an acid-base reaction was isolated by filtration and washed successfully with hexane, acetonitrile, and dichloromethane. The Amberlyst species was then placed in a flask with 160 mL of dichloromethane and treated with triethylamine (40 mL, 0.28 mol). The mixture was again shaken for 24 h. The triethylammonium salt on Amberlyst 15 was then removed from the solution of **6** by filtration. Dichloromethane was removed under reduced pressure using a rotary evaporator. To insure that all the triethylamine was removed, the viscous oil product was dissolved with 150 mL of hexane and washed with 90% EtOH (4 x 50 mL) and brine (1 x 50 mL). The hexane solution was then dried with anhydrous sodium sulfate, filtered, and the solvent was removed by reduced pressure using a rotary evaporator to afford the amine **6**. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.00-1.50 (m, 190 H), 2.52 (m, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ: 11.8, multiple peaks between 30.0 and 38.2, 46.9, 48.17, multiple peaks between 56.0-59.5.

***N,N*-Diethyl-*N*-methylammonium iodide terminated PIB oligomer (8)**. Diethylamine terminated PIB oligomer (**6**) (3.6 g, 3.44 mmol) was dissolved in 30 mL of dichloromethane. Iodomethane (0.325 mL, 5.27 mmol) was added and the reaction solution was stirred at room temperature overnight. Dichloromethane was removed from

the product ammonium salt by reduced pressure using a rotary evaporator and the crude product was purified by aluminum oxide column chromatography to afford the ammonium salt **7**. ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.00-1.56 (m, 221 H), 3.30 (s, 3 H), 3.35 (m, 2 H), 3.60 (m, 2 H), 3.73 (m, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 8.4, multiple peaks between 28.9 and 38.1, 48.3, multiple peaks between 56.6 and 59.5.

PIB-supported POM (7) and (9). 0.5 M solutions of diethylamine terminated PIB oligomer (**6**) and 0.5 M solutions of *N,N*-diethyl-*N*-methylammonium iodide terminated PIB oligomer (**7**) in heptane were initially prepared. The PIB-supported POMs were generated *in situ* with the presence of heteropoly acid hydrates H$_3$PW$_{12}$O$_{40}$ (99%), H$_3$PMo$_{12}$O$_{40}$ (99.9%) or H$_4$SiW$_{12}$O$_{40}$ (99.9%) containing approximately 20 H$_2$O molecules per Keggin unit and an aqueous solution of H$_2$O$_2$.

***N,N*-diethyl-*N*-methylammonium terminated PIB-supported perruthenate (10).** *N,N*-diethyl-*N*-methylammonium iodide terminated PIB oligomer (**7**) (2.0 g, 1.91 mmol) was dissolved in 20 mL of dichloromethane. Tetra-*n*-propylammonium perruthenate (TPAP) (0.33 g, 0.94 mmol) was added and stirred 6 h. After the reaction was completed, dichloromethane was removed under reduced pressure using a rotary evaporator. Hexane was added to the crude product and the hexane solution was either passed through celite in a pipette to isolate the low molecular weight tetra-*n*-propylammonium perruthenate and iodide. The hexane solution can also be washed with acetonitrile to remove these low molecular weight compounds.
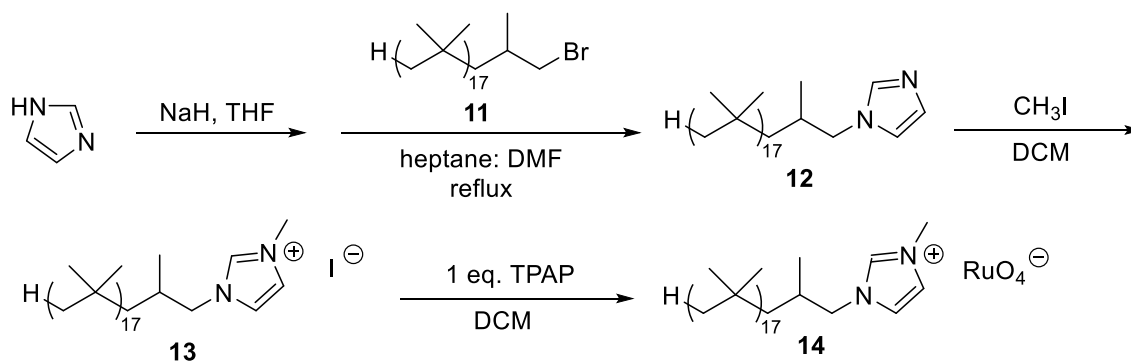
Bromide terminated PIB oligomer (11). Hydroxy terminated PIB oligomer (**16**) (5 g, 4.91 mmol) was dissolved in 50 mL of dichloromethane. The reaction solution was cooled to 0 °C and methane sulfonyl chloride (1.15 mL) and triethylamine (2.15 mL) were added dropwise. The reaction was stirred for 2 h and the solvent was removed under reduced pressure using a rotary evaporator. The viscous oil was then dissolved with 100 mL of THF, followed by the addition of LiBr (4.5 g). The reaction was stirred under reflux at 80 °C for 24 h. At that point, the THF solvent was removed under reduced pressure using a rotary evaporator and the residue was dissolved in hexane (20 mL). This hexane solution was washed with 90% EtOH (2 x 15 mL) and brine (2 x 15mL). The hexane layer was dried with Na_2SO_4 and filtered, and the solvent was removed under reduced pressure using a rotary evaporator to afford **3**. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.76-1.49 (m, 180H), 3.27 (dd, 1H), 3.41 (dd, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 22.0, 29.0, 29.2, multiple peaks between 30.8 and 31.6, 32.4, 32.6, 35.8, multiple peaks between 37.8 and 38.1, 43.7, 51.1, 56.8, 58.2, 58.8, multiple peaks between 59.3 and 59.5.

Imidazole terminated PIB oligomer (12). Imidazole (0.94 g, 13.80 mmol) was dissolved in 20 mL of THF. Sodium hydride (0.56 g, 14 mmol) was added into the reaction mixture

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and the reaction mixture was stirred at room temperature for 2 h. THF was removed by reduced pressure and 30 mL of DMF was then added into the flask followed by 20 mL of a solution of bromide terminated PIB oligomer (**11**) (1 g, 0.93 mmol) in heptane. The reaction was refluxed at 90 °C overnight. The reaction was cooled to room temperature where upon two layers formed. The two layers were separated and the heptane layer was extracted with DMF (2 x 15 mL), water (3 x 15 mL), and brine (1 x 15mL). The heptane layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure using a rotary evaporator to afford **12**. ^1H NMR (300 MHz, CDCl$_3$) δ: 0.80-1.80 (m, 239H), 3.61 (dd, 1H), 3.82 (dd, 1H), 6.90 (s, 1H), 7.07 (s, 1H), 7.47 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 14.1, 20.1, 22.7, multiple peaks between 28.8 and 38.1, 49.7, multiple peaks between 57.1 and 59.5, 121.7, 122.6, 138.3

Imidazolium iodide terminated PIB oligomer (13). Imidazole terminated PIB oligomer (**12**) (1 g, 0.94 mmol) and iodomethane (0.71 g, 5.0 mmol) were dissolved in 10 mL of DCM. The reaction mixture was then allowed to stir at room temperature for 24 h. The DCM was removed at reduced pressure using a rotary evaporator and the residue was dissolved in hexanes. This hexane solution was washed with water (3 x 15 mL) and brine (1 x 15 mL). The hexane layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure using a rotary evaporator to afford the product **13**. ^1H NMR (300 MHz, CDCl$_3$) δ: 1.00-1.80 (m, 169H), 4.13-4.18 (m, 5H), 7.17 (s, 1H), 7.27 (s, 1H), 10.94 (s, 1H)

Imidazolium terminated PIB-supported perruthenate (14). Imidazolium iodide terminated PIB oligomer (**13**) (1 g, 0.94 mmol) was dissolved in 10 mL of dichloromethane. Tetra-*n*-propylammonium perruthenate (TPAP) (0.33 g, 0.94 mmol) was added and stirred 6 h. Hexanes was added to the crude product and the hexane solution was either passed through celite in a pipette to isolate the low molecular weight tetra-*n*-propylammonium perruthenate and iodide. The hexane layer can also be washed with acetonitrile to isolate these low molecular weight compound.
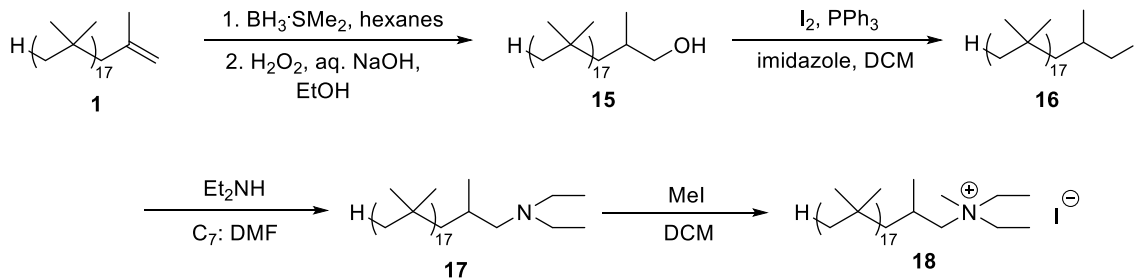

Hydroxy terminated PIB oligomer (**15**). The starting alkene-terminated PIB (**1**) (10 g, 10 mmol) was dissolved in 20 mL hexanes. The reaction mixture was stirred under N_2 and 0.34 mL of $BH_3 \cdot SMe_2$ (10M) was added into the reaction mixture. After stirring at room temperature for 24 h, the reaction mixture was cool to 0 °C. Then, 8 mL of EtOH and 2.4 mL of 4N NaOH were added into the reaction mixture and followed by dropwise addition of 1.6 mL of 30% H_2O_2. The reaction mixture was stirred for 2 h at room temperature and 60 mL of water was added to form a biphasic mixture. The hexane layer was washed with water (3x15 mL) and brine (1x15 mL). The hexane layer was then dried with Na_2SO_4 and the solvent was removed under reduced pressure using a rotary evaporator. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.75-1.46 (m, 208H), 3.33 (dd, 1H), 3.49 (dd, 1H). ^{13}C NMR (75 MHz,

CDCl$_3$) δ: 19.9, multiple peaks between 29.1 and 38.3, 49.5, multiple peaks between 56.8-59.6, 69.7.

Iodide terminated PIB oligomer (16). Hydroxy terminated PIB oligomer (**15**) (25.56 g, 25.1 mmol) was dissolved in 250 mL of DCM. The reaction mixture was charged with iodine (8.23 g, 32.6 mmol), triphenylphosphine (8.55 g, 32.6 mmol), and imidazole (2.22 g, 32.6 mmol) and stirred for 24 h. DCM was then removed under reduced pressure using a rotary evaporator and hexanes was added to dissolve the crude product. The hexane layer was extracted with DMF (3x75mL), (2x75 mL), and brine (1x75 mL). The hexane layer was dried with Na$_2$SO$_4$ and the solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by column chromatography and afforded an isolated yield of 89%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.00-1.43 (m, 220H), 3.13 (dd, 1H), 3.27 (dd, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ: 20.8, 23.9, multiple peaks between 29.1 and 38.3, 52.7, multiple peaks between 56.9-59.4.

Diethylamine terminated PIB oligomer (17). To a 50 mL heptane solution of iodide terminated PIB oligomer (**16**) (5.27 g, 4.7 mmol), a 50 mL of DMF solution of diethylamine (3.42 g, 46.7 mmol) was added to form a biphasic reaction mixture. Upon heating to 90 °C, the biphasic mixture became miscible. After 24 h, the reaction mixture was cooled to room temperature where the reaction became biphasic again. The two layers were separated and the heptane phase was washed with DMF (2x25 mL), water (2x25 mL), and brine (1x25 mL). The heptane layer was dried with Na$_2$SO$_4$ and the solvent was removed under reduced pressure using a rotary evaporator. **17** was purified by column

chromatography (Brockmann aluminum oxide) and afforded an isolated yield of 82%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.00-1.50 (m, 308 H), 2.02 (dd, 1 H), 2.16 (dd, 1 H), 2.49 (m, 4 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ: 11.8, 14.0, 21.6, 22.6 multiple peaks between 30.7 and 38.0, 47.3, 51.5, multiple peaks between 57.1-62.4.

***N,N*-Diethyl-*N*-methylammonium terminated PIB oligomer with iodide anion (18)**.
Diethylamine terminated PIB oligomer (**17**) (4.71 g, 4.2 mmol) was dissolved in 50 mL of dichloromethane. Next, iodomethane (2.96 g, 20.8 mmol) was added into the reaction solution and was stirred for 24 h. Dichloromethane was removed by reduced pressure using a rotary evaporator. *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer was purified by aluminum oxide column chromatography and afforded an isolated yield of 83%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.00-1.56 (m, 221 H), 3.20 (dd, 1 H), 3.32 (s, 3 H), 3.40 (dd, 1 H), 3.70 (m, 4 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 8.6, 14.0, multiple peaks between 20.7 and 38.1, 48.8, 53.2, multiple peaks between 57.1 and 59.6, 69.5.

19   **20**   **21**
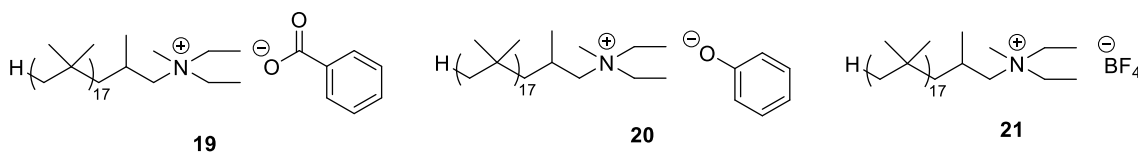
***N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with benzoate anion (19) and phenolate anion (20)**. In general, the ion-exchange reaction was done by using an ion-exchange column made up of Amberlite® IRA400 (hydroxide form) resins. The resins were first treated with a solution of sodium hydroxide to ensure that the ammonium functional groups on the resins were present as ammonium hydroxide salts. After the

eluent was tested to be basic by using a pH paper, the resins were then rinsed with water until the eluent has a pH of 7 to remove any excess aqueous NaOH. A solution of benzoic acid or phenol in methanol was then added into the ion-exchange column until the eluent has the same pH as the starting solution. Again, the resins were rinsed with either methanol, acetonitrile, or heptane until the eluent has a neutral pH. Lastly, a solution of **18** in heptane was passed through the column to generate either *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with benzoate anion **19** or *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with phenoxide anion **20.** The solution of **18** in heptane can be passed through the ion-exchange column until all the iodide anions were exchanged into the desired anions. The heptane solvent was removed under reduced pressure using a rotary evaporator. The formation of **19** and **20** was confirmed by ^{1}H NMR spectroscopy. The resins were also reusable by retreatment with solutions of aqueous NaOH and benzoic acid or phenol to recycle the resins used in the ion-exchange reaction. *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer with benzoate anion **19**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.86-1.92 (m, 420 H), 3.15 (dd, 1 H), 3.30 (dd, 1 H), 3.32 (s, 3 H) 3.73 (m, 4 H), 7.33 (m, 3 H), 8.08 (m, 2 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 8.1, 14.0, multiple peaks between 23.3 and 38.1, 48.4, 53.0, multiple peaks between 57.4 and 59.5, 68.8, 127.7, 129.6, 130.5, 135.6, 171.4. *N,N*-Diethyl-*N*-methylammonium terminated PIB oligomer with phenolate anion **20**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.93-1.45 (m, 364 H), 3.12-3.28 (m, 5 H), 3.67 (m, 4 H), 6.73 (m, 1 H), 6.85 (m, 2 H), 7.16 (m, 2 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 8.0, 23.2, 24.7, multiple peaks between 29.0 and 38.1, 48.2, 53.0, 56.6, multiple peaks between 57.6 and 59.5, 68.5, 115.8, 117.4, 129.3, 135.6, 162.7.

N,N-diethyl-N-methylammonium terminated PIB oligomer with boron tetrafluoride anion (21). Diethylamine terminated PIB oligomer (**17**) (10 g, 8.2 mmol) was dissolved in 100 mL of heptane. Then, acetone (100 mL) and potassium acetate (4.91 g, 50 mmol) were added into the reaction mixture. The reaction was stirred for 24 h. The solvents were removed under removed pressure using a rotary evaporator. Then, hexane was added into the crude product, where the hexane solution was extracted with water (3x50 mL). The hexane layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure using a rotary evaporator. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.68-1.82 (m, 276 H), 2.92-3.29 (m, 5 H), 3.29-3.60 (m, 4 H).
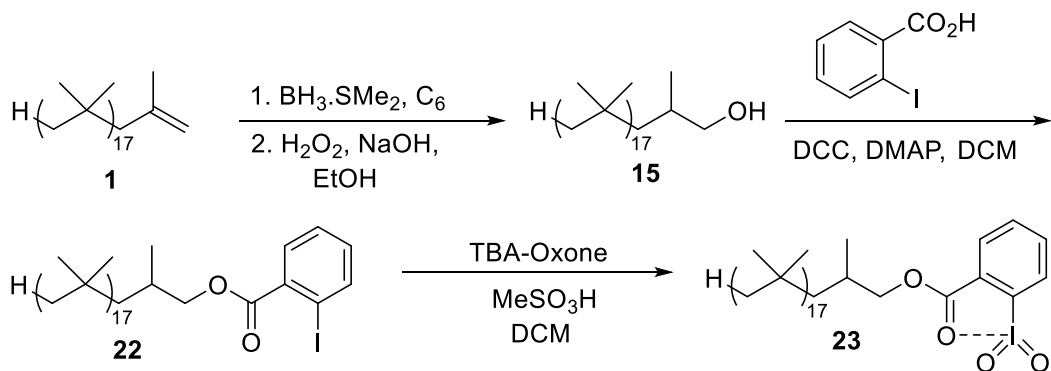
PIB-bound 2-iodobenzoic acid ester (22). PIB-bound alcohol (29.64 g, 29.12 mmol) was dissolved in 300 mL of dichloromethane. 2-Iodobenzoic acid (9.67 g, 38.99 mmol), *N,N'*-dicyclohexylcarbodiimide (8.04 g, 38.96 mmol), and 4-dimethylaminopyridine (0.48 g, 3.90 mmol) were then added to the solution of the PIB alcohol. The reaction mixture was stirred for 24 h at room temperature. Dichloromethane was removed under reduced pressure and the PIB product was dissolved in 200 mL of hexanes. Extraction with DMF (3 x 150 mL) and then water (3 x 150 mL) afforded a hexanes solution that was then dried

with Na_2SO_4 and finally concentrated under reduced pressure to yield a crude PIB product. This crude product was purified by silica gel column chromatography affording a final product ester. ^{1}H NMR (300 MHz, CDCl_3) δ: 0.80-2.00 (m, 190H), 4.03 (dd, 1H), 4.20 (dd, 1H), 7.16 (td, 1H), 7.41 (td, 1H) 7.82 (dd, 1H), 8.01 (dd, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ: 20.4, 28.7, 29.1, multiple peaks between 30.8 and 32.4, 35.9, multiple peaks between 37.8 and 38.1, 49.4, multiple peaks between 56.8 and 59.5, 94.3, 128.0, 131.0, 132.7, 135.8, 141.6, 166.8.

PIB-bound IBX (23). PIB-bound 2-iodobenzoic acid (2.20 g, 1.74 mmol) was dissolved in 20 mL of DCM. Then TBA-Ox (5.59 g, 11.0 mmol) and $MeSO_3H$ (1.06 g, 11 mmol) was added into the reaction mixture and the reaction mixture was stirred overnight. DCM was removed under removed pressure and the crude underwent an extraction with hexanes (30 mL), DMF (3 x 20 mL) and water (3 x 20 mL). The hexane layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude product which contained some unreacted PIB-bound 2-iodobenzoic acid was dried under reduced pressure overnight and was used without further purification. The amount of the PIB-bound IBX relative to the unreacted PIB-bound 2-iodobenzoic acid ester was readily measured by ^{1}H NMR spectroscopy as the PIB bound IBX shows some distinguishable integrable peaks at 4.37 δ. ^{1}H NMR (300 MHz, CDCl_3) δ: 0.80-2.00, 4.37 (dd, 1H), 8.19 (dd, 1H), 8.56 (dd, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ: 20.2, multiple peaks between 28.6 and 32.6, 35.9, multiple peaks between 37.8 and 38.1, 49.3, multiple peaks between 56.9 and 59.5, 94.3, 125.2, 126.9, 130.7, 133.0, 135.5, 168.5.

Syntheses of Low Molecular Weight Compounds

Tetrabutylammonium Oxone (TBA-Ox). TBA-Ox was prepared by a procedure described by Borhan.[4] Oxone monopersulfate granular with the formula $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (10 g, 16.25 mmol) and tetrabutylammonium hydrogen sulfate (11 g, 32.40 mmol) were dissolved in 100 mL of water. The aqueous solution was extracted with DCM (4 x 150 mL). The DCM layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure. The oxidative activity of the product was determined by iodometric titration.

Tetrabutylammonium benzoate (TBA-benzoate). The same procedure as mentioned in the synthesis of **19** and **20** can we used. In this case, heptane was not used as a solvent. This compound can also be made by using 1 M solution of tetra-*n*-butylammonium hydroxide in MeOH and equivalent amount of benzoic acid. The reaction was stirred for 24 h in the presence of magnesium sulfate. The reaction mixture was filtered and the solvent of removed under reduced pressure using a rotary evaporator. Then the white solids were dried under vacuum for another 24 h. ^1H NMR (400 MHz, CDCl$_3$) δ: 0.91 (m, 12 H), 1.37 (m, 8 H), 1.47 (m, 8 H), 3.40 (dd, 1 H), 3.2 (m, 8 H), 7.21 (m, 3 H) 8.00 (m, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 13.4, 19.4, 23.7, 58.32, 127.1, 128.7, 129.3.

Tetrabutylammonium phenol-phenolate (TBA-phenol-phenolate). The same procedure as mentioned in the synthesis of **19** and **20** can we used. In this case, heptane was not used as a solvent. ^1H NMR (400 MHz, CDCl$_3$) δ: 0.92 (m, 12 H), 1.29 (m, 8 H),

1.36 (m, 8 H), 2.97 (dd, 1 H), 3.2 (m, 8 H), 6.58 (m, 2 H), 6.86 (m, 4 H), 7.06 (m, 4 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 13.6, 19.5, 23.8, 58.3, 115.8, 117.1, 129.2, 162.1

General Procedures

Typical procedure for oxidation of dibenzothiophene (DBT) and epoxidation of cyclooctene by PIB-bound POMs. This part was done by the Kozhevnikov group at the University of Liverpool. Oxidation of DBT and epoxidation of cyclooctene were carried out in a two-phase system containing heptane as an organic solvent and aqueous H$_2$O$_2$ at 25-60 °C In a typical run, heptane (10 mL), dodecane (GC internal standard), diethylamine terminated PIB, aqueous H$_2$O$_2$ and heteropoly acid in specified quantities were added into the reactor. Once the reactor was heated to the required temperature, the substrate (DBT or cyclooctene), was added to start the reaction. DBT oxidation was carried out at a DBT/ H$_2$O$_2$ molar ratio of 1:3, which is typical of this reaction. A ten-fold excess of cyclooctene over H$_2$O$_2$ was applied in the epoxidation reaction. Both reactions were carried out at a stirring speed of 1000 rpm; at stirring speeds above 500 rpm, the reaction rate did not depend on the stirring speed. The reactions were monitored by taking aliquots from the organic phase and submitting them to GC analysis (Varian CP-3380 gas chromatograph equipped with FID and a 25 m × 0.32 mm × 0.5 μm BP1 capillary column) to determine substrate conversion and product yield. After reaction, the amount of remaining H$_2$O$_2$ was determined by titration with KMnO4 for the efficiency of hydrogen peroxide.

Recycling of PIB-supported POMs. This part was done by the Kozhevnikov group at the University of Liverpool. In the oxidation of DBT, after each run, DBT sulfone was extracted by MeCN and fresh DBT and 30% H_2O_2 were added. Then, the reaction was run as described above. In cyclooctene epoxidation, the catalyst was separated by complete evaporation of the reaction mixture, washed with methanol and reused by adding fresh cyclooctene and 10% H_2O_2. The reaction was continued as the method mentioned above.

UV-Vis study of POM phase transfer. This part was done by the Kozhevnikov group at the University of Liverpool. For UV-Vis study of PW phase transfer facilitated by PIB, PW (0.648 µmol, 2 mg), water (3 mL) and diethylamine terminated PIB oligomer **6** in heptane (10 mL) were added to a stoppered test tube and shaken vigorously at room temperature (~20 °C). The mixture was then left to settle for 2 h at room temperature. An aliquot of the organic phase was taken, spun in a centrifuge and analyzed via UV-Vis spectrophotometry (CARY 50 Probe UV-Vis spectrometer) at 275 nm.

Typical procedure for oxidation of alcohols by PIB-bound perruthenate. The alcohol substrate (0.5 mmol) and 1.5 equiv. NMO were added to a solution of PIB-bound ammonium perruthenate (at least 5 mol%) in 5 mL of dichloromethane along with 0.20 g of 4Å molecular sieves. The resulting reaction mixture was stirred overnight (typically 12 h) at room temperature. At that point ^{1}H NMR analysis showed that the reaction was essentially complete. Then the molecular sieves were removed by filtration and the solvent DCM removed under reduced pressure. Heptane and acetonitrile were added. The product partitioned to the acetonitrile phase and PIB-bound ammonium perruthenate

partitioned into the heptane phase. Visually, no PIB-bound ammonium perruthenate was present in the acetonitrile phase. Then, the two layers were separated. The solvent was removed from the heptane phase and the residue was dried overnight at reduced pressure for use for the next cycle. The conversion of the substrate to product was determined by ^{1}H NMR spectroscopy after removed of acetonitrile from the product phase under reduced pressure. When reactions were carried out in heptane, the reaction was carried out at 80 °C and the workup simply involved extracting the product from the heptane phase using acetonitrile.

Typical procedure for kinetic studies of S$_N$2 reactions. For the kinetic studies, 0.1 M solution of equivalent amounts of the substrates, the nucleophile source, and cyclooctane was prepared in MeOH, MeCN, DMF, and heptane. The reaction was either stirred at 35 °C or 55 °C. An aliquot (100 µL) of the reaction mixture was taken at different time intervals. In cases where polar solvents were used, the aliquot was diluted with 1 mL of diethyl ether and washed with 1 mL of water. The two phases with separated and the organic layer was dried with anhydrous sodium sulfate. The solution was then submitted for GC analysis. In the case of heptane, an aliquot (100 µL) of the reaction mixture was passed through a pipette silica gel column using 1 mL of hexanes. The eluent was submitted in the GC for analysis. The rate constant, k, was calculated by plotting a second-order (1/[A] *vs.* time) to find the slope of the line.

Typical procedure for solid/liquid phase catalysis and their recycling process. The reaction was done by making a 0.1 M solution of 1-bromobutane and 10 mol% of **21** in

heptane (10 mL). Potassium acetate (3 eq) was added into the reaction mixture and the reaction was stirred for 24 h at 90°C. After the reaction, MeCN (2x10 mL) was added to separate the low molecular weight species. For better separation, the biphasic mixture was centrifuged for 15 min at 25 °C with a spinning speed of 3000 rpm. The two layers were separated as well as the solids from the metal salts. The MeCN layers were from two extractions were combined and equivalent amount of cyclooctane was added as an internal standard before submitting the solution into the GC for analysis. For recycling, fresh 1-bromobutane and potassium acetate were added and the reaction mixture was performed under the same procedure as described above. The same process was also tested with 2 cST PAO, 4 cST PAO, or 10 cST PAO as the solvent.

Typical procedure for oxidation of alcohols using PIB-bound IBX. The desired alcohol (0.5 mmol) and 2 equivalents of PIB-bound IBX were dissolved in heptane. Then 2 equivalents of boron trifluoride diethyl etherate was then added into the reaction mixture and the reaction mixture was stirred at room temperature for 30 min. An aliquot of the heptane reaction mixture was taken and diluted with $CDCl_3$ to determine the conversion of the substrate to product by ^{1}H NMR spectroscopy. Kinetic studies where a reaction mixture in $CDCl_3$ was directly analyzed by ^{1}H NMR spectroscopy had previously been used to show that this was a sufficient time for complete conversion of alcohols to their product aldehyde or ketone. As described above, the products were separated from the heptane solution of any unreacted or spent oxidant by an extraction with acetonitrile. The heptane from the solution of polyisobutylene-bound substrates was then removed at reduced pressure and the PIB species isolated were reoxidized as described above. The

reoxidized PIB-bound IBX was always characterized by ^{1}H NMR and the ratio of PIB-bound IBX to the ester of PIB-bound 2-iodobenzoic acid was always calculated before a subsequent cycle.

CHAPTER VI

CONCLUSIONS

The major goal of my research projects is to make organic transformations greener by using polymer as a key component to help tackle ongoing problems specifically on waste reduction, renewable feedstocks, and reduced toxicity. We explored the uses of PIB oligomers as polymer supports for catalysts and hydrocarbon phase-solubilizing reagents/catalysts. We also explored using poly(α-olefins) (PAOs) as solvent alternatives for conventional alkane solvents. PAOs are relatively nontoxic and nonvolatile. They were also found to have lesser leaching into the polar phase than the low molecular weight alkane solvents, which is an important feature in the recycling of catalysts.

This work initially describes the synthesis of a diethylamine terminated PIB oligomer, a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer, and a *N*-methylimidazolium terminated PIB oligomer and their use as polymer supports for oxidation catalysts such as polyoxometalate clusters and perruthenate anion. The PIB-supported POM catalysts were highly efficient in the oxidation of DBT to DBT sulfone and in cyclooctene epoxidation, using an environmentally benign heptane-water biphasic system in the presence of hydrogen peroxide. The PIB supports also allow the POMs catalysts to be easily recovered and reused. I also examined the use of a *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer and a *N*-methylimidazolium terminated PIB oligomer as polymer supports for a perruthenate anion. The PIB-bound perruthenate catalyst formed was found to be a competent oxidant, oxidizing alcohols to aldehydes or

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ketones. However, recycling of the perruthenate catalyst that was immobilized on PIB oligomer was only modestly successful.

We then explored the use of *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer as a hydrocarbon phase-solubilizing agent. In this study, the rates of S_N2 reactions in polar aprotic, polar protic, and nonpolar solvents were investigated. Here, the reactions in heptane were conducted by using *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer to help solubilized the nucleophilic anions. In general, the rates of the S_N2 reactions was fastest in DMF, followed by MeCN and heptane. The reaction in MeOH was slowest due to the hydrogen bonds that decrease the nucleophilicity of anions. We further examined the use of *N,N*-diethyl-*N*-methylammonium terminated PIB oligomer as a phase-solubilizing catalyst in a solid/liquid phase catalysis. The S_N2 reaction with the *N,N*-diethyl-*N*-methylammonium terminated PIB catalyst worked efficiently in heptane, but a loss of reactivity was observed when the catalyst was recycled due to the leaching of the heptane phase into the acetonitrile phase. We solved this problem by using PAOs as the hydrocarbon oligomeric solvents. PAOs were found to leach lesser than conventional alkane solvents into the polar phase. Not only that, these hydrocarbon oligomeric solvents are relatively nontoxic and nonvolatile, making them a much more greener solvent replacements. The S_N2 reactions worked well in these hydrocarbon oligomer solvents, especially in 4 cST PAO and 10 cST PAO, where no loss of catalytic reactivity was observed when recycled up to five cycles.

Lastly, we explored another class of oxidizing agent, hypervalent iodine compounds. 2-Iodoxybenzoic acid can be immobilized on a PIB oligomer by an ester

linkage to form a polymer-supported pseudocyclic hypervalent compound, PIB-supported IBX ester. The PIB-supported IBX ester was found to be a competent oxidant for the oxidations of different types of alcohols in the presence of BF_3-etherate as a Lewis acid promoter. Moreover, the PIB-bound hypervalent iodine oxidant was highly soluble in a solvent like heptane and was readily separated from the product by a liquid/liquid separation with MeCN. This property allowed the spent PIB-supported IBX ester to be reoxidized and reused multiple times without any loss of reactivity. Recycling of the spent PIB-bound IBX ester was successful with both a primary alcohol and a secondary alcohol.

REFERENCES

(1) ACS Green Chemistry Institute® - American Chemical Society

https://www.acs.org/content/acs/en/greenchemistry.html (accessed May 23, 2017).

(2) Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149.

(3) Arakawa, Y.; Kawachi, R.; Tezuka, Y.; Minagawa, K.; Imada, Y. *J. Polym. Sci.*
Part Polym. Chem. **2017**, *55*, 1706.

(4) Gravert, D. J.; Janda, K. D. *Chem. Rev.* **1997**, *97*, 489.

(5) Bayer E.; Schurig, V. *Angew Chem Int Ed Engl* **1975**, *14*.

(6) Nuzzo, R. G.; Feitler, D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 3681.

(7) Toy, P. H.; Janda, K. D. *Acc. Chem. Res.* **2000**, *33*, 546.

(8) Dickerson, T. J.; Reed, N. N.; Janda, K. D. *Chem. Rev.* **2002**, *102*, 3325.

(9) Bergbreiter, D. E.; Hughes, R.; Besinaiz, J.; Li, C.; Osburn, P. L. *J. Am. Chem. Soc.*
2003, *125*, 8244.

(10) Bergbreiter, D. E. *ACS Macro Lett.* **2014**, *3*, 260.

(11) Bergbreiter, D. E.; Tian, J. *Tetrahedron Lett.* **2007**, *48*, 4499.

(12) Tao, G.; Gong, A.; Lu, J.; Sue, H.-J.; Bergbreiter, D. E. *Macromolecules* **2001**, *34*,
7672.

(13) Bergbreiter, D. E.; Blanton, J. R.; Chandran, R.; Hein, M. D.; Huang, K.-J.;
Treadwell, D. R.; Walker, S. A. *J. Polym. Sci. Part Polym. Chem.* **1989**, *27*, 4205.

(14) Bergbreiter, D. E.; Chandran, R. *J. Am. Chem. Soc.* **1987**, *109*, 174.

(15) Grady, M.; Kristjansdottir, S.; Tam, W.; Older, C.; Ritter, J. In *Catalysis of*
Organic Reactions; Chemical Industries; CRC Press, 2008; pp 319–328.

(16) Suriboot, J.; Hobbs, C. E.; Guzman, W.; Bazzi, H. S.; Bergbreiter, D. E. *Macromolecules* **2015**, *48*, 5511.

(17) Bergbreiter, D. E.; Chandran, R. *J. Org. Chem.* **1986**, *51*, 4754.

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

(19) Liang, Y.; Watson, C.; Malinski, T.; Tepera, J.; Bergbreiter, D. E. *Pure Appl. Chem.* **2016**, *88*.

(20) Rackl, D.; Kreitmeier, P.; Reiser, O. *Green Chem* **2016**, *18*, 214.

(21) Chao, C.-G.; Kumar, M. P.; Riaz, N.; Khanoyan, R. T.; Madrahimov, S. T.; Bergbreiter, D. E. *Macromolecules* **2017**, *50*, 1494.

(22) Bergbreiter, D. E.; Hobbs, C.; Hongfa, C. *J. Org. Chem.* **2011**, *76*, 523.

(23) Chao, C.-G.; Bergbreiter, D. E. *Catal. Commun.* **2016**, *77*, 89.

(24) Bales, B. L.; Zana, R. *J. Phys. Chem. B* **2002**, *106*, 1926.

(25) Shairgojray, B. A.; Dar, A. A.; Bhat, B. A. *Tetrahedron Lett.* **2013**, *54*, 2391.

(26) Friedli, F. E.; Koehle, H. J.; Fender, M.; Watts, M.; Keys, R.; Frank, P.; Toney, C. J.; Doerr, M. *J. Surfactants Deterg.* **2002**, *5*, 211.

(27) Starks, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 195.

(28) O'Donnell, M. J.; Bennett, W. D.; Wu, S. *J. Am. Chem. Soc.* **1989**, *111*, 2353.

(29) Corey, E. J.; Xu, F.; Noe, M. C. *J. Am. Chem. Soc.* **1997**, *119*, 12414.

(30) Tan, J.; Yasuda, N. *Org. Process Res. Dev.* **2015**, *19*, 1731.

(31) Shirakawa, S.; Maruoka, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 4312.

(32) Vekariya, R. L. *J. Mol. Liq.* **2017**, *227*, 44.

(33) Holbrey, J. D.; Seddon, K. R. *Clean Technol. Environ. Policy* **1999**, *1*, 223.

(34) Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc. Chem. Commun.* **1992**, No. 13, 965.

(35) Zhang, H.; Xu, F.; Zhou, X.; Zhang, G.; Wang, C. *Green Chem.* **2007**, *9*, 1208.

(36) Molinari, H.; Montanari, F.; Quici, S.; Tundo, P. *J. Am. Chem. Soc.* **1979**, *101*, 3920.

(37) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F.; Tocco, G. *Org. Lett.* **2000**, *2*, 1737.

(38) Arakawa, Y.; Haraguchi, N.; Itsuno, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 8232.

(39) Wang, T.; Wang, W.; Lyu, Y.; Chen, X.; Li, C.; Zhang, Y.; Song, X.; Ding, Y. *RSC Adv* **2017**, *7*, 2836.

(40) Khamatnurova, T. V.; Zhang, D.; Suriboot, J.; Bazzi, H. S.; Bergbreiter, D. E. *Catal Sci Technol* **2015**, *5*, 2378.

(41) Byrne, F. P.; Jin, S.; Paggiola, G.; Petchey, T. H. M.; Clark, J. H.; Farmer, T. J.; Hunt, A. J.; Robert McElroy, C.; Sherwood, J. *Sustain. Chem. Process.* **2016**, *4*.

(42) Katsoulis, D. E. *Chem. Rev.* **1998**, *98*, 359.

(43) Kozhevnikov, I. *Catalysis by Polyoxometalates*; Wiley, Chichester, 2002.

(44) Collins, F. M.; Lucy, A. R.; Sharp, C. *J. Mol. Catal. Chem.* **1997**, *117*, 397.

(45) Jiang, X.; Li, H.; Zhu, W.; He, L.; Shu, H.; Lu, J. *Fuel* **2009**, *88*, 431.

(46) Jiang, Z.; L?, H.; Zhang, Y.; Li, C. *Chin. J. Catal.* **2011**, *32*, 707.

(47) Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587.

(48) Venturello, C.; Alneri, E.; Ricci, M. *J. Org. Chem.* **1983**, *48*, 3831.

(49) Craven, M.; Yahya, R.; Kozhevnikova, E.; Boomishankar, R.; Robertson, C. M.; Steiner, A.; Kozhevnikov, I. *Chem Commun* **2013**, *49*, 349.

(50) Kamata, K.; Yonehara, K.; Sumida, Y.; Yamaguchi, K.; Hikichi, S.; Mizuno, N. *Science* **2003**, *300*, 964.

(51) Hinzen, B.; V. Ley, S. *J. Chem. Soc. [Perkin 1]* **1997**, No. 13, 1907.

(52) Ley, S. V.; Ramarao, C.; Smith, M. D. *Chem. Commun.* **2001**, No. 21, 2278.

(53) Walden, P. *Eur. J. Inorg. Chem.* **1896**, *29*, 133.

(54) Hughes, E. D.; Ingold, C. K. *J. Chem. Soc. Resumed* **1935**, 244.

(55) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1.

(56) Landini, D.; Maia, A.; Montanari, F. *J. Am. Chem. Soc.* **1978**, *100*, 2796.

(57) Blach, D.; Pessêgo, M.; Silber, J. J.; Correa, N. M.; García-Río, L.; Falcone, R. D. *Langmuir* **2014**, *30*, 12130.

(58) Crosio, M. A.; Correa, N. M.; Silber, J. J.; Falcone, R. D. *Org Biomol Chem* **2016**, *14*, 3170.

(59) Harrell, M. L.; Malinski, T.; Torres-López, C.; Gonzalez, K.; Suriboot, J.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **2016**, *138*, 14650.

(60) Keith J. Laidler. *Chemical Kinetics*, 3rd ed.; HarperCollinsPublishers.

(61) Yoshimura, A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328.

(62) Zhdankin, V. V.; Koposov, A. Y.; Litvinov, D. N.; Ferguson, M. J.; McDonald, R.; Luu, T.; Tykwinski, R. R. *J. Org. Chem.* **2005**, *70*, 6484.

(63) Yoshimura, A.; Yusubov, M. S.; Zhdankin, V. V. *Org Biomol Chem* **2016**, *14*, 4771.

(64) Muelbaier, M.; Giannis, A. *Angew. Chem. Int. Ed.* **2001**, *40*, 4393.

(65) Sorg, G.; Mengel, A.; Jung, G.; Rademann, J. *Angew. Chem. Int. Ed.* **2001**, *40*, 4395.

(66) Chung, W.-J.; Kim, D.-K.; Lee, Y.-S. *Tetrahedron Lett.* **2003**, *44*, 9251.

(67) Moss, R. A.; Bolikal, D.; Durst, H. D.; Hovanec, J. W. *Tetrahedron Lett.* **1988**, *29*, 2433.

(68) Reed, N. N.; Delgado, M.; Hereford, K.; Clapham, B.; Janda, K. D. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2047.

(69) Liu, Y.-S.; Zhao, C.; Bergbreiter, D. E.; Romo, D. *J. Org. Chem.* **1998**, *63*, 3471.