

Liquid/Liquid Biphasic Recovery/Reuse of Soluble Polymer-Supported Catalysts

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Abstract: Liquid/liquid separations using gravity and two phases of different density are a practical and viable way to recover, separate and reuse soluble polymer-supported catalysts. Such separations are facilitated by using polymers that have phase-selective solubility under biphasic conditions. Such polymers can be designed to be soluble either in a non-polar or a polar phase. Since catalyst and ligand loading can be at a low mole percent level on the polymer, the polymer's intrinsic solubility can be maintained with a variety of ligands and catalysts making such separation strategies general. Catalysis with such soluble polymer-supported species can either be carried out under biphasic or monophasic conditions. In the former case, aqueous/organic, fluorous/organic or other biphasic regimes can be used. In the later case, thermomorphic or latent biphasic conditions can be employed. In either case, catalyst separation and re-

covery can be accomplished simply without using significant quantities of additional solvent.

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1 Introduction

Polymer supports have been utilized for facilitating catalyst and reagent recovery since the 1960s. Most of this work involved insoluble polymers as would be expected based on the extensive literature from that era describing insoluble polymeric ion exchange resins and because of Merrifield's pioneering work in solid-phase synthesis.^[1,2] However, early on, Bayer and others showed that a soluble polymer could be equally efficient in enabling the recovery of a supported substrate or catalyst. As was true for insoluble polymers, this recovery of a supported molecule or catalyst was possible because of the macromolecular properties of the polymeric support.^[3–5] These initial descriptions of the recovery of these polymers emphasized solid-liquid separations after solvent precipitation of the polymer-bound catalyst. In some cases, the size differences between soluble polymers and products were also exploited using membrane filtration to effect a separation. These separation methods can serve as adequate methods for the separation of a po-

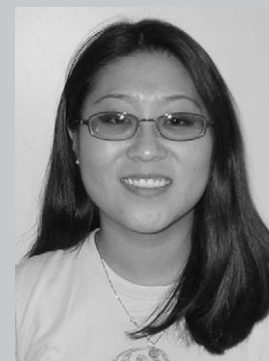
lymer-supported catalyst from a product, but these separation methods have a number of problems that make them difficult to use in large-scale syntheses. For example, such separation strategies often generate significant volumes of solvent waste or are not as efficient as desired. Subsequent and future advances in membrane technology may eventually mitigate or eliminate some of these problems.^[6] However, alternative separation strategies that employ biphasic liquid/liquid separations provide yet another attractive separation strategy. Such biphasic liquid/liquid separations employing phase-selectively soluble polymers have proven to be simple alternatives to these earlier strategies. The review below discusses both the historical context for and some recent examples where such liquid/liquid separation schemes are used for separation of a homogeneous catalyst from products and to facilitate catalyst reuse.

The idea of using a biphasic liquid/liquid mixture for catalyst separation from products and for catalyst reuse and recovery has a variety of precedents that do not necessarily even involve polymers. The essence

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Shayna Sung began her Ph.D. work in 2001 working in Dr. D. E. Bergbreiter's group at Texas A&M University. Her thesis work focused on the attachment of catalysts, ligands, or reagents to non-polar polymer supports for use in thermomorphic, latent biphasic, or biphasic systems. She received her Ph.D. in 2006 and she is presently working with Exxon-Mobil Corporation in Paulsboro, New Jersey.



of this simple idea is that one can achieve a practical separation using gravity and a pair of immiscible liquid phases of different density when schemes can be devised that ensure a catalyst is in a different liquid phase than the product after a reaction. The practicality of this approach is evidenced by its application in several industrial processes. Two classic examples include the Shell higher olefins process (SHOP) for the preparation of long-chain α -alcohols and the Ruhrchemie/Rhône-Poulenc (RCH/RP) oxo process for the production of butyraldehyde from propene. The SHOP utilizes a soluble nickel hydride catalyst that is anchored in a solvent such as 1,4-butanediol by virtue of its polarity. This catalyst effects the oligomerization of ethylene and comprises the first of four synthetic steps that end in the production of the long-chain primary alcohols. As the oligomerization occurs in SHOP, the non-polar, linear α -olefin products phase separate from the polar phase containing the catalyst. The catalyst phase of this immiscible biphasic system can then be recycled and the product phase can be used in the next step.^[7–9]

The RCH/RP oxo process is a second but conceptually different example of practical liquid/liquid separation in an industrial setting. This RCH/RP oxo process differs from the SHOP process in that the system is a two-phase liquid-liquid biphasic system throughout the entire course of the reaction. In this example, an aqueous/organic biphasic system converts propene and synthesis gas (CO and H₂) to butyraldehyde on an annual scale of 9.2 million tons.^[10] Immobilization of the rhodium catalyst in the aqueous phase is achieved by phase tagging the catalysts' triphenylphos-

phine ligands with sodium sulfonate residues. This water-soluble ligand makes the catalyst complex water soluble. Throughout the reaction there is a liquid-liquid biphasic system consisting of a water phase containing the immobilized catalyst and an organic substrate phase comprised of propene and product. Efficient mixing is required for this biphasic system. After completion of the reaction, the butyraldehyde product phase separates from the aqueous phase, allowing separate isolation of both a catalyst and a product phase and recycling of the catalyst.

The success of the liquid-liquid biphasic systems for the simplification of product and catalyst recovery in both the SHOP and the RCH/RP process is attested to by the prolonged and successful use of these strategies in industry. However, both systems suffer from limitations. In both cases, the systems have been optimized to ensure the solubility of the catalyst in a particular single solvent phase and to achieve useful rates and separations with a single substrate or product. Attempts to adapt the RCH/RP process for the production of higher aldehydes demonstrate the significance of this last criterion. While the conversion of propene to butyraldehyde works phenomenally well, increasing the hydrophobicity of the substrate is severely detrimental to the rate of the reaction. Attempts to perform the hydroformylation of 1-hexene and other higher α -olefins with the RCH/RP process are hindered by the insolubility of the higher alkenes in the aqueous catalyst phase.^[11,12] For this reason, the RCH/RP process is effectively restricted to the production of butyraldehyde.

Methodology to circumvent the problems experienced with these biphasic systems has received more attention as the catalysis and synthesis community has begun to appreciate the significance of separation as a strategic issue.^[13] This has led to the development of new solvent systems that rely upon novel solvents such as fluorous solvents, scCO_2 , and ionic liquids.^[14] The resulting body of work has shown that facilitating a separation step can lead to new chemistry or simplify existing chemistry. Other schemes that use solvent systems that allow homogeneous reaction conditions during a reaction with a later biphasic separation protocol have also received increasing attention. Examples of such schemes include the thermomorphic^[15–23] and latent biphasic^[24,25] solvent systems.

Processes carried out with fluorous solvents, scCO_2 , or ionic liquids often but not always resemble the Scheme used in the aqueous/organic biphasic RCH/RP process described above. Most commonly in these systems two phases are present during the reaction and also during the separation phase of the synthetic or catalytic process. Such systems typically employ low molecular weight phase tags on ligands of an ionic catalyst to ensure that the catalyst is phase separated from the products at the end of a reaction. In most cases, separations in fluorous, scCO_2 , or ionic liquids involve a biphasic liquid/liquid separation, although alternatives to liquid/liquid separations are also being studied.

Thermomorphic behavior is demonstrated by a number of different solvent mixtures. Thermomorphic solvent mixtures are solvent mixtures that miscibilize with the application of heat or immiscibilize on cooling. Equivolume mixtures of heptane with either *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), or 90% aqueous ethanol all miscibilize on heating. Such mixtures of heptane with these polar solvents are biphasic at 25°C but are a single phase at 70°C. Other examples of thermomorphic systems include Horvath's initial fluorous/organic biphasic system. This system consists of perfluoromethylcyclohexane, toluene, and hexanes and is biphasic at room temperature and a single phase at 36.5°C.^[26] While the only examples of thermomorphic systems employed in catalysis use heating to achieve miscibilization and cooling to induce formation of a biphasic mixture, it is worth noting that inverse behavior is known. Triethylamine and water, for example, are a single phase at 0°C but are biphasic at room temperature.

Latent biphasic solvent systems are solvent mixtures that are a homogeneous, single phase at ambient or even subambient temperatures. These systems typically consist of two or more solvents that are miscible but that are at the cusp of immiscibility. In such solvent mixtures, the addition of solute, the formation of a different product, the consumption of starting mate-

rial, or the addition of a small volume percent of another solvent, salt, or water is sufficient to slightly perturb the original miscible mixture to induce a separation to form a biphasic system. Mixtures of (1:1, v/v) heptane and ethanol or heptane and DMA are examples of such systems where phase separation occurs upon addition of less than 10 vol% water or formation of an ammonium salt as a product of a Heck reaction.

Using thermomorphic or latent biphasic systems in catalysis allows reactions to be run completely homogeneously, avoiding the problems caused by mass transfer limitations, while the separation post reaction is performed under biphasic conditions (Figure 1). In

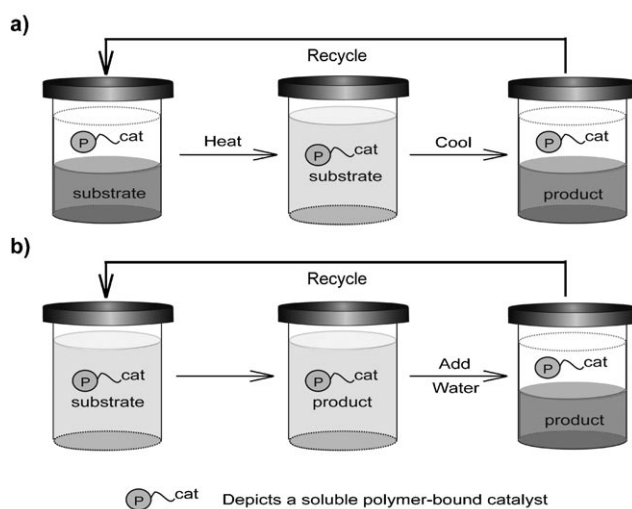


Figure 1. A depiction of **a)** thermomorphic and **b)** latent biphasic systems used in catalysis with a soluble, non-polar polymer-supported catalyst.

these systems, soluble polymer-supported catalysts have the advantage of being completely soluble in the binary or ternary mixture of solvents during the homogeneous stage of catalysis. After perturbation or cooling of the system, the polymer is designed to be phase-selectively soluble in one of the two phases of the biphasic system present at work-up. Thus, liquid-liquid separation after perturbation or cooling separates the product and catalyst phases. The phase containing the catalyst can then be mixed with a fresh substrate solution in the appropriate solvent and the reaction can be repeated. Such thermomorphic or latent biphasic systems require either a small amount of perturbant or sometimes no additional solvent at all.^[15,16,24,25,27–29] This minimizes volume and concentration changes and avoids the production of excess waste streams common to previously mentioned solvent precipitation and membrane filtration strategies.

A final example where a biphasic system can be used to separate catalysts and products would be a

case where a simple extraction post-reaction is used with a highly phase-selectively soluble polymer-bound catalyst to recover products in a process that could be described as “selective product extraction.” This technique provides another method that uses monophasic reaction conditions with biphasic conditions only at the separation stage. This last method is really little more than a batchwise catalyst separation using an ordinary extraction like that used at the end of many synthetic operations, the soluble polymer support's phase-selective solubility ensures complete catalyst recovery after the washing step that removes the product.

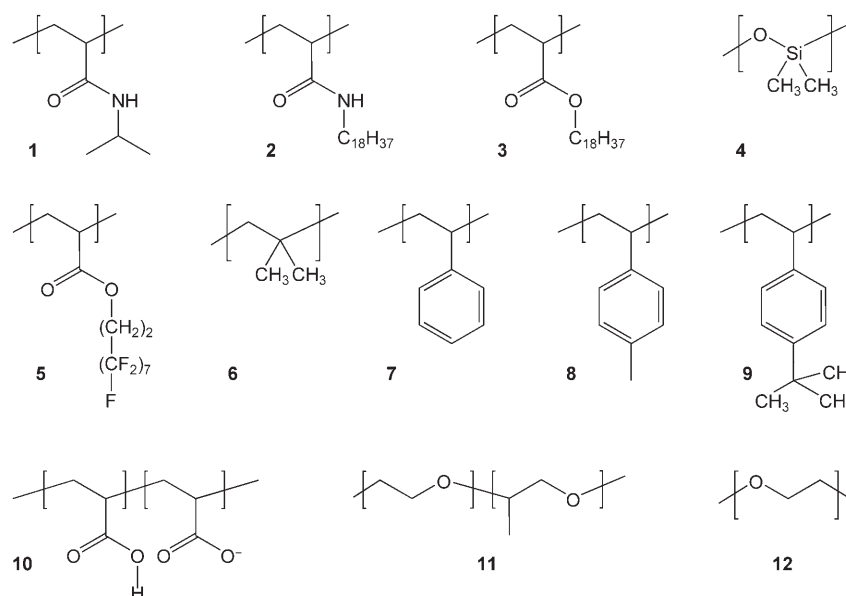
Any of the aforementioned biphasic-type systems can be used to facilitate the recovery and reuse of a catalyst. However, as is true in the case of “selective product extraction,” each of these procedures requires that the catalyst first be phase labeled to provide it with phase-selective solubility in either a polar or non-polar phase of the a biphasic mixture at the separation step. This phase labeling allows for quantitative recovery and recycling of the catalytic material. While low molecular weight materials may suffice in some cases, soluble polymer supports afford a general way to obtain highly phase-selective behavior for a catalyst or ligand. Furthermore, catalysts or ligands that are covalently supported by soluble polymers only have to be present at a low mole percent loading on the polymer. Thus, a polymer's inherent solubility is little modified by the ligand and catalyst and the catalyst can then be prepared with predictable phase-selective solubility.

The fact that polymers can have highly phase-selective solubility is well known. Our group and others

have extended this chemistry, exploring a variety of ways to design or test the feasibility of phase-selective, soluble polymers for use as supports for catalysts, reagents, or substrates. A diverse selection of both polar and non-polar polymers has been synthesized and shown to exhibit good to excellent phase-selective solubility in a variety of solvent systems. Examples of these polymers are shown in Scheme 1 below. Variation of the polymer's main chain or pendant groups affords a wide variety of materials with excellent ($>100,000:1$) to good ($500:1$) phase-selective solubility in various solvent mixtures based on dye labeling. These polymers include fluoropolymers, alkylated polystyrene derivatives, polyacrylamides, polyacrylates, poly(ethylene glycols), polydimethylsiloxanes, poly(ethylene imine), poly(acrylic acid) salts, and polyisobutylenes. Applications of these phase-selectively soluble polymer supports for catalyst immobilization, separation, recovery, and reuse in the context of the previously mentioned liquid/liquid separation strategies are discussed below.

2 Aqueous/Organic Biphasic Catalysis

Water is readily abundant, inexpensive, non-flammable and perhaps the most environmentally benign solvent. For these reasons, water has been considered to be an ideal reaction media. Furthermore, the use of water as a solvent can serve to greatly enhance reaction rates and selectivities as well as providing access to previously inaccessible reactions.^[8,30–34] Biphasic reactions utilizing water often allow for near ideal separation conditions due to the high partition coeffi-



Scheme 1. A dozen examples of representative sorts of phase-selectively soluble polymers that can serve as supports for recoverable catalysts.^[30–32]

cient between water and most other organic solvents. Given the success of aqueous/organic biphasic catalysis in hydroformylation, it is not surprising that separations utilizing homogeneous polymer-supported catalysts, reagents, or substrates have been reported by a number of groups over the years.^[27,35,36] In many cases, ionic groups on a ligand or catalyst serve as phase labels. However soluble polymers can be designed to serve this purpose as well.

Recent work by Jin's group has presented a novel strategy for the production of higher aldehydes in an aqueous/organic biphasic system. As mentioned previously, the hydroformylation of 1-hexene and other higher alkenes is typically unsuccessful in aqueous/organic biphasic systems due to mass transfer limitations between the catalyst and substrate phases. However, application of thermoregulated phase transfer ligands and catalysts allows production of these higher aldehydes.^[37–39] This is a result of using polymer-supported ligands like **13–15** that have lower critical solution temperature (LCST) behavior (Figure 2) because

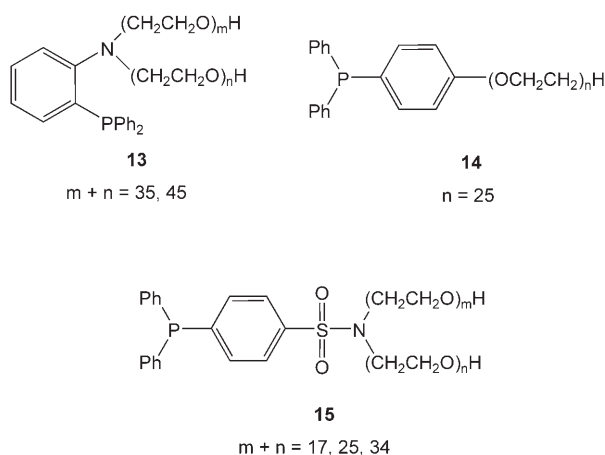


Figure 2. Thermoregulated phase transfer ligands.

of the poly(alkene oxide) polymer support. Such polymers have so-called thermoregulated solubility – their solubility in water decreases as temperature increases. In pure aqueous solutions, such polymers' LCST behavior leads to precipitation or formation of a separate oil-in-water polymer phase.^[40,41] Such behavior has been used to design smart catalysts.^[42] In the presence of a second organic phase, the LCST property of the soluble polymer support can lead to the soluble polymer ligated catalyst moving from the aqueous phase to the organic phase as a function of temperature (Figure 3). The resulting preferential solubility in either the organic or aqueous phase means that the catalyst can be phase cycled from one phase to another for reaction with the organic soluble substrate and for separation after a reaction. This phase switchable property is potentially very attractive in catalysis as it

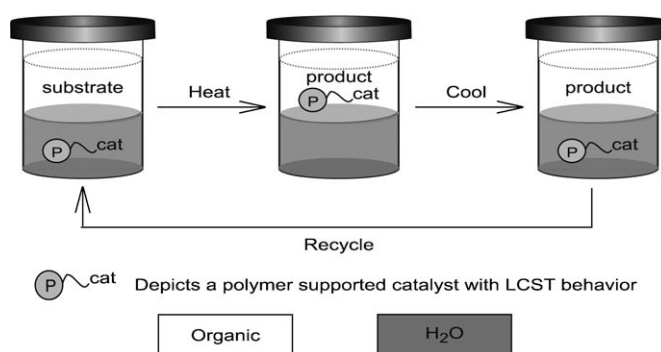
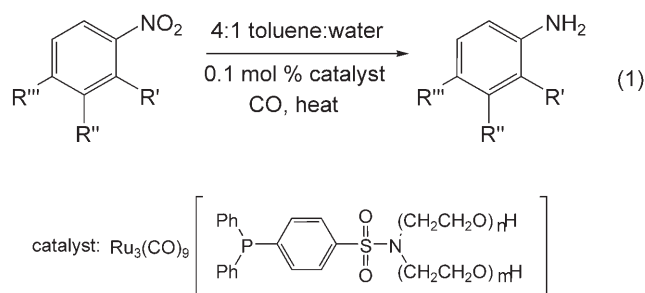


Figure 3. Recycling of a thermoregulated phase-transfer catalyst by manipulation of the system's temperature.

provides a system with two favorable features. Specifically, mass transfer problems are eliminated since the catalyst or ligand is soluble in the same phase as the substrate at reaction temperatures and simple cooling of the system allows recovery of the catalyst from the aqueous phase post reaction.

The application of such behavior has been demonstrated by the hydroformylation of higher alkenes in aqueous/organic biphasic solvent systems. In all cases, a dramatic increase in product yield is observed at temperatures above the LCST of the polymer-supported catalysts. This increase in product yield corresponds to the temperature at which the solubility of the polymer changes so as to phase switch the supported catalyst from the aqueous to the organic phase, thereby eliminating the mass transfer problem. However, the high temperature needed to reach the LCST of the material leads to an *n:iso* selectivity decrease as temperature is increased due to increased rate of isomerization at elevated temperatures. A non-polar organic phase is used to ensure that the supported catalyst can be completely recovered in the aqueous phase of the system post reaction. Metal leaching analyses indicated that the metal loss in such systems was in the order of 1.5 to 2.5% by ICP-AES.^[37] Later work by the same group has also recognized that metal colloids produced by catalyst decomposition during the reaction may also be contributing to the catalytic activity seen in these systems.^[43] To further demonstrate the applicability of these thermoregulated phase-transfer ligands and catalysis, Jin's group has also examined these materials in other biphasic catalysis reactions.^[44] The selective reduction of aromatic nitro compounds to the respective aniline derivatives provides access to a variety of compounds that are valued for their application in dyes, pigments, pharmaceuticals, and pesticides. Jin's procedure for the reduction of these nitroarene compounds utilizes a ruthenium cluster catalyst and CO as the reductant to chemoselectively reduce the aromatic nitro functionality to the corresponding amine [Eq. (1)]. As was seen in the hydroformylation reactions, dramatic



increases in reactivity were observed at temperatures above the supported catalyst's LCST. Additional evidence regarding the efficacy of this catalyst in these biphasic systems was provided by the results obtained for a variety of other ligands with varying solubilities in water. Use of a ruthenium catalyst complexed by the organic soluble triphenylphosphine ligand gave product conversions comparable to the thermoregulated, PEG-supported catalyst (>99%). However, changing the polarity of the low molecular weight ligand to a water-soluble TPPTS ligand resulted in a significant decrease in conversions to 38%. This was attributed to poor accessibility of the water-soluble TPPTS ligated catalyst to the substrate. The polymer-supported thermoregulated catalyst was also successfully recycled over seven cycles with minimal losses in catalytic activity.

Other water-soluble polymeric materials include the salts of poly(acrylic acid). These polymers exhibit good solubility in water and have been utilized as supports for enantioselective hydrogenation reactions in always biphasic aqueous/organic systems (Figure 4).^[45]

Attachment of a chiral phosphine moiety to the polymer *via* an amide linkage produces a ligand (**16**) that can be utilized to complex rhodium by addition of $[\text{Rh}(\text{NBD})_2]\text{OTf}$ to a water solution of the polymer (Figure 5). Application of the resulting catalyst in a biphasic system composed of ethyl acetate and water allows recycling of the catalyst by recovery and reuse of the water phase by liquid-liquid separation. This

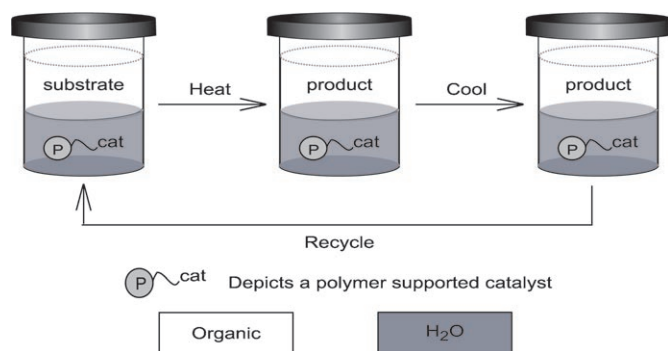


Figure 4. Recycling of a polar-soluble polymeric catalyst in an always biphasic aqueous/organic system.

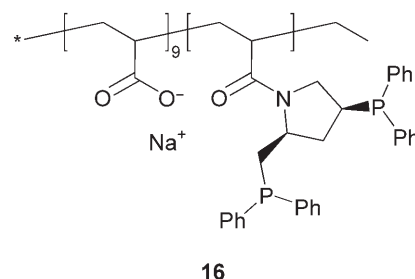


Figure 5. A water soluble, poly(sodium acrylate)-supported ligand for application in aqueous/organic biphasic catalysis.

water-soluble polymer-supported catalyst was active in the reduction of α -acetamidocinnamic acid to produce *N*-acetyl-(*R*)-phenylalanine in 100% yields and 58 to 89% *ees*. Recycling experiments showed that the aqueous catalyst phase could be reused without a detectable decrease in the enantioselectivity. While ICP analysis was not reported, the lack of discoloration of the organic phase was suggested to be indicative of low rhodium loss.

Another recent contribution describing a water-soluble polymer-supported catalyst is from Weberskirch's group who have prepared polymer-supported catalysts for the aqueous Heck reaction and the hydroformylation of 1-octene. In their work, they prepared amphiphilic block copolymers containing *N*-heterocyclic carbenes that could be used to complex palladium or rhodium (Figure 6).^[46,47] The resulting polymers **17a** through **17c** form micellar aggregates in solutions of water that can in turn be used in catalysis. The palladium catalysts, for example, are active in the Heck coupling of iodobenzene and styrene. Improved reactivities were seen in catalysts whose polymer supports had a minimum spacer length of six methylene groups or more (**17b** and **17c**). Recycling of **17c** was achieved by selective product extraction with ether. While no assays for metal leaching were reported and while the identity of the actual palladium catalyst in reactions of this sort is not always clear, the aqueous catalyst phase was reused over five cycles, giving conversions of 76–89% in each cycle.^[46]

Weberskirch also used catalyst **18** in an aqueous biphasic hydroformylation of 1-octene. In this case, the turnover frequency of 1100 h^{-1} increased to 2360 h^{-1} in the fourth cycle. The authors have suggested that this increase in activity is the result of exchange of a bromide for a carbonyl in the active catalytic species. Similar to the previously discussed RCH/RP process, the product nona-aldehydes separate from the water-containing catalyst phase and can be removed by decantation. The *n:iso* selectivity of the catalysts decreases from 2.6 in the first cycle to 1.22 in subsequent cycles. The activity of this catalyst is comparable to the activity of a similar low molecular weight catalyst in benzene solvent where the TOF was

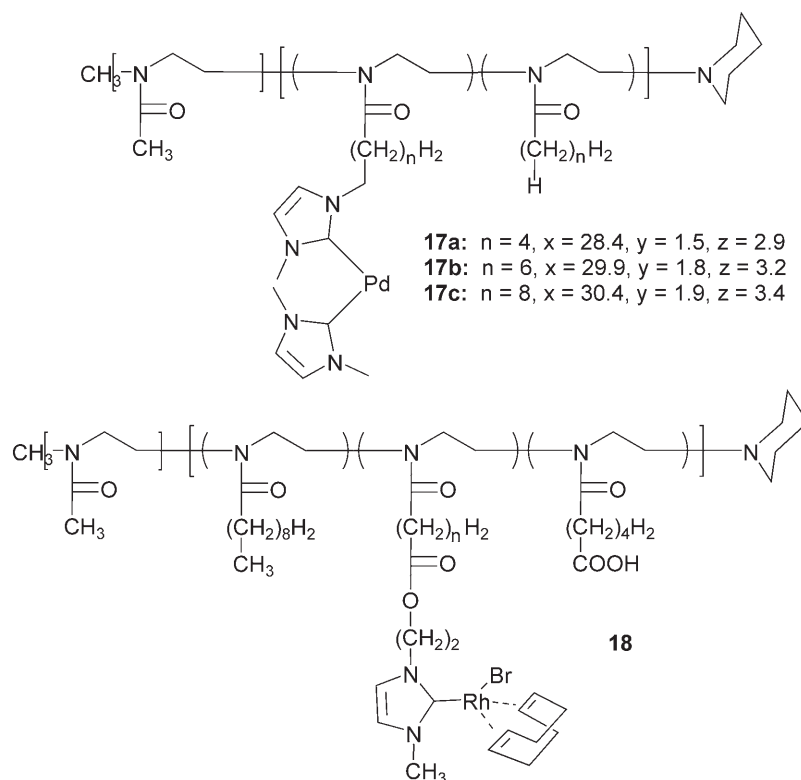


Figure 6. Amiphilic polymer-supported catalysts for Heck and hydroformylation reactions.

2400 h⁻¹. In benzene, the *n:iso* selectivity was also modest (0.66). Metal leaching experiments using ICP-OES testing on the aldehyde phase after cycle 1 showed the presence of 0.4 ppm rhodium in the product phase. Rhodium leaching is common in hydroformylations, and in this case may also be a result of the catalyst's covalent attachment to the polymer support *via* an ester linkage. Experimental examination of the catalyst's stability indicated that as much as 2.7% of the NHC ligand could be hydrolytically cleaved from the polymer in each cycle. While this could account for the rhodium in the product phase, it also brings into question whether the active catalytic species is in fact polymer-supported or if the catalytic activity can be accredited to a low molecular weight analogue that is slowly being released into the reaction medium from the polymer by hydrolysis.^[47]

PEG supports have been used to prepare water-soluble catalysts for many years.^[48] A recent application of a PEG support to induce water solubility of a catalyst has been reported by Grubbs' group. Previous efforts to prepare a metathesis catalyst for application in aqueous systems had until now experienced limited success.^[49–52] However, this recent report shows that it is feasible to prepare PEG-supported ruthenium metathesis catalysts that show excellent activity and stability in aqueous media (Figure 7).^[53] This example, like the examples from Kobayashi's^[54] and Weberskirch's work, may be classified as biphasic as this

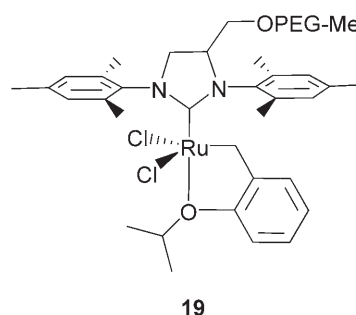


Figure 7. A highly active water-soluble olefin metathesis catalyst.

metathesis catalyst is thought to form micelle-like structures in water due to the hydrophobicity of the catalytic ruthenium center. This initial report did not discuss recyclability of the catalyst.

3 Fluorous/Organic Biphasic Catalysis

Perfluoroalkanes, perfluorodialkyl ethers, and perfluorotrialkylamines exhibit poor miscibility with many common organic solvents such as toluene, THF, and acetone. The similarity of these materials' and water's immiscibility with organic solvents led Horvath to coin the term "fluorous" to parallel the term "aqueous."^[55,56] While fluorous/organic systems can

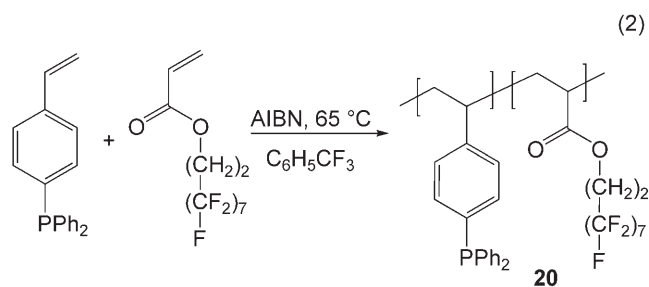
be used under biphasic conditions, a number of fluororous and organic solvent pairs exhibit thermomorphic behavior.^[26] This thermomorphic property presents a situation for an ideal biphasic system, where a reaction can be conducted under homogeneous conditions and separated under heterogeneous conditions through cooling of the system. The variation available regarding solvent pairs as well as the reversible heterogeneity of the system serves to expand the scope of accessible reactions that can be performed under liquid-liquid biphasic conditions. In a manner similar to the aqueous/organic liquid-liquid biphasic systems, a catalyst could be anchored in the fluororous phase by modification with fluororous moieties or “ponytails” while the product preferentially partitions either to its own phase or into a separate organic solvent phase.

Fluororous polymers containing pendant groups with Teflon “ponytails” have been shown to have high partition coefficients favoring their solubility in the fluororous phase of a biphasic fluororous/organic solvent mixture. The high phase selectivity that a fluorinated polymer exhibits towards the fluororous phase of such a system and the ready availability of fluorinated acrylate monomers makes these polymers excellent candidates as soluble polymeric phase tags.^[57–59] In addition, fluorinated polymers also exhibit excellent solubility in scCO_2 , making them useful as polymer supports in reactions carried out in scCO_2 systems.^[60–64]

Yao's group has recently reported application of a fluororous acrylate in the recovery and recycling of a ruthenium metathesis catalyst (Figure 8). The catalyst exhibits excellent solubility in fluororous solvents such as PhCF_3 and FC-72 but is completely insoluble in organic solvents like dichloromethane and ethyl acetate. This allows olefin metathesis reactions to be performed in biphasic solvent systems such as PhCF_3 /dichloromethane. The catalyst can be recovered and reused by simple extraction with FC-72. The catalyst was examined for activity and recyclability in the ring closing metathesis of an extensive variety of di-, tri-, and tetrasubstituted diene and enyne substrates. This fluororous labeled Hoveyda-type catalyst gave excellent conversions (94 to 98%) over 20 cycles for the RCM

of *N*-tosyldiallylamine. The success of RCM with other substrates served to further demonstrate the efficacy of this catalyst, often giving conversions in excess of 90% over 5 cycles.^[22]

A second example of a fluorinated polymer being used in a biphasic liquid/liquid separation after a monophasic reaction is seen in work by Xiao's group.^[59] In this case, a phosphine-containing styrene monomer was copolymerized with a fluorinated acrylate to form a fluorocopolymer-supported ligand [Eq. (2)] that was soluble in benzotrifluoride or perfluoro-



methylcyclohexane. On formation of a Rh complex using $[\text{Rh}(\text{CO})_2(\text{acac})]$, the Xiao group was able to carry out a successful hydroformylation. Unlike the Yao's Hoveyda-type metathesis catalyst, the *in situ* Rh complex solution prepared using the soluble fluororous polymer **20** in a mixture of hexane, toluene, and perfluoromethylcyclohexane was a single phase at the reaction temperature of 50 °C. This thermomorphic solvent mixture phase separated on cooling. The hydroformylation catalyst prepared in this manner had a 100:1 *n*:*iso* selectivity in the hydroformylation of 1-decene and a turnover frequency (TOF) of 136 mol of aldehyde per hour per mole of rhodium catalyst. Both the selectivity and TOF were superior to those of a similar water-soluble polymer-bound catalyst. Rhodium leaching was measured and was 1 ppm.

4 Organic-Organic Biphasic Catalysis

In addition to the well known aqueous/organic biphasic systems, many organic solvent mixtures can be immiscible pairs. These biphasic systems can also be utilized to facilitate the recovery and recycling of a soluble polymer-supported catalyst. Plenio's group has prepared both polar and non-polar phase-selective polymeric phosphines for application in such systems (Figure 9). PEG labeled phosphines **21–25** were, for example, examined as ligands for palladium catalysts in the palladium-catalyzed Suzuki–Miyaura, and Sonagashira reactions.^[65,66] Ligands **21**, **22**, and **25**, were utilized in a biphasic Sonagashira reaction employing the immiscible mixture, heptane-DMSO. Palladium ligated by **22** and **25** was capable of coupling aryl bro-

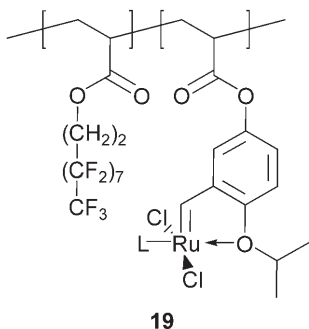


Figure 8. A fluororous olefin metathesis catalyst.

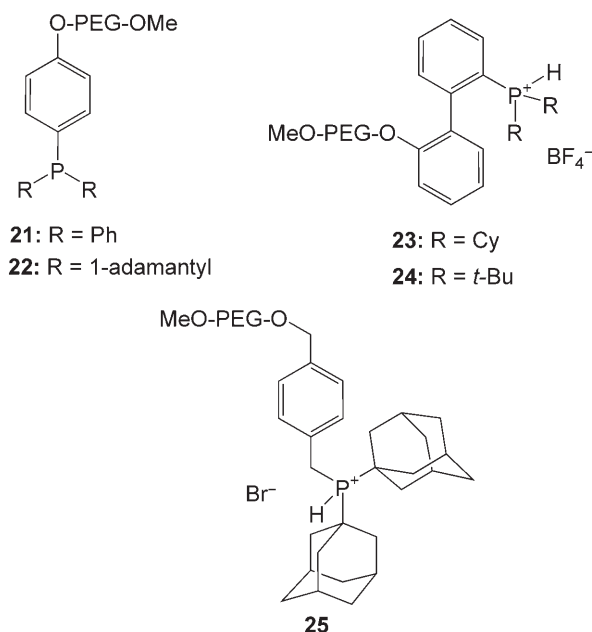


Figure 9. PEG-containing polymeric phosphines useful for reactions in organic-organic biphasic systems.

mides and alkynes in high yield over five cycles when the catalyst-containing polar DMSO phase was separated and reused. Small but significant decreases in the TOF over the reuse cycles were noted but were ascribed to deactivation of the catalyst rather than leaching. Reactivation of the catalyst by addition of CuI was observed and the catalyst deactivation was presumed to result from the adventitious oxidation of the Cu^I to Cu^{II}. Catalyst leaching studies used total reflection X-ray fluorescence (TXRF) and showed that retention of both the palladium and copper species in the DMSO phase was > 99.995 %.^[66]

Ligands **23**, **24**, and **25** also were useful in forming palladium catalysts for the Suzuki–Miyaura coupling of aryl chlorides and phenyl boronic acid in DMSO. These materials were recycled through three to five cycles by selective extraction of the products with heptane. High yields and a minimal decrease in TOFs were seen. Metal analysis of the recovered crude product layer indicated catalyst retention in the polar phase of > 99.95 %.^[65]

A non-polar analogue of ligand **25** was also prepared, and palladium complexes of this ligand were used in both the Sonagashira and Suzuki couplings (Figure 10).^[28] The polymeric phosphine **26** was used to form *in situ* a Pd(0) complex. The resulting polymer-supported catalyst was then used in a biphasic system composed of cyclohexene and DMSO or nitromethane, producing high yields and good recyclability over five cycles for both the Sonagashira and Suzuki couplings. Catalyst leaching studies demonstrated > 99.8 % catalyst retention in the non-polar phase of

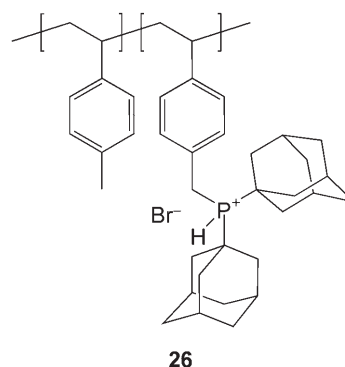


Figure 10. A non-polar polymer-supported phosphine ligand for application organic-organic biphasic systems.

the biphasic systems.^[28] While these results are promising, adventitious oxidation of these phosphine-palladium complexes remains a problem in batch-type reactions.

5 Biphasic Catalysis in Ionic Liquids

Another alternative solvent for the recovery and recycling of catalysts are the ionic liquids (ILs). The ILs are a unique set of solvents that are composed entirely of ions. However, unlike molten salts such as liquid NaCl (which is molten at 803 °C), ILs in this context are liquids at ambient temperature (often below 100 °C).^[67] The cations utilized in ILs are often tetraalkylammonium, tetraalkylphosphonium, *N*-alkylpyridinium, or asymmetric *N,N*-alkylated imidazolium, or *N,N*-alkylated pyrrolidinium cations. The anions can be varied extensively, although commonly used anions include [PF₆]⁻, [BF₄]⁻, [NO₃]⁻, [CF₃SO₃]⁻ and [N(CF₃SO₂)₂]⁻.^[68,69]

These ILs have been recognized for their excellent solvation power, especially for many catalytically active transition metal species that have previously shown poor solubility in non-polar organic solvents. The solubility of such materials in ILs has lead to the examination of anchoring such species in an IL phase by virtue of this solubility preference.

However, the unique characteristics of ILs also impose limitations on the standard chemical techniques and procedures that can be applied to recovering and recycling catalysts dissolved in ILs. Due to the ionic character of ILs, these liquids have no appreciable vapor pressure. For this reason, product isolation techniques are restricted to distillation, sublimation or precipitation of the product from the IL or extraction of the product into another solvent. These methods become compromised if the product is high boiling, thermally unstable, or sufficiently polar to exhibit phase preference in the IL. Hence, the application of phase-selectively soluble polymers in IL biphasic sys-

tems converts the limitations of IL systems into methods for recovery and reuse of a catalytic material.^[69]

Several recent reports have discussed ways to use ionic liquids and polymers or polymer supports. Several examples have described how ionic liquid immobilized catalysts can be used to prepare soluble polymers.^[70–72] In such cases, the insolubility of the polymer and the ionic liquid facilitate a separation (although the catalyst is not attached to a soluble polymer at the separation stage). This suggests that a soluble polymer-bound catalyst could be used in a multistep reaction with an ionic liquid.^[73] Other reports have described ionic liquids immobilized on a solid support^[74] or have discussed cross-linked organic polymer-bound ionic liquid catalysts.^[75,76]

One recent report has described a linear polymeric ionic liquid support using poly(diallyldimethylammonium chloride) as a mixture with a 1-butyl-3-methylimidazolium hexafluorophosphate with cationic transition metal catalysts like **27** and **28** for hydrogenations (Figure 11).^[77] In this case, rhodium and ruthenium

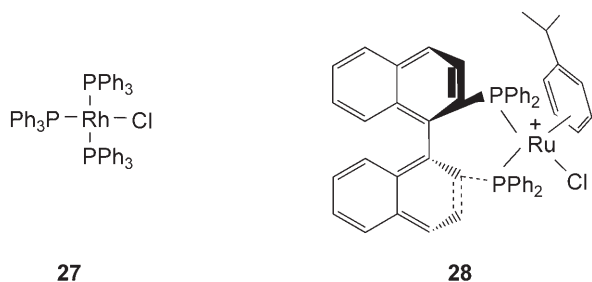


Figure 11. Transition metal catalysts utilized in an ionic liquid biphasic system.

catalsys **27** and **28** were immobilized in the ionic liquid-ionic polymer phase. Hydrogenations studied included hydrogenation of cyclohexenone and selective monohydrogenation of 1,3-cyclooctadiene. An asymmetric hydrogenation of methyl acetoacetate using the Ru catalyst **28** was also studied. Hydrogenations generally proceeded better than similar hydrogenations using the ionic liquid alone without polymer. Atomic absorption analyses did not detect any leached rhodium or ruthenium and the catalysts were recycled with little change in activity (TOF) or enantioselectivity (using a chiral catalyst like **28**).

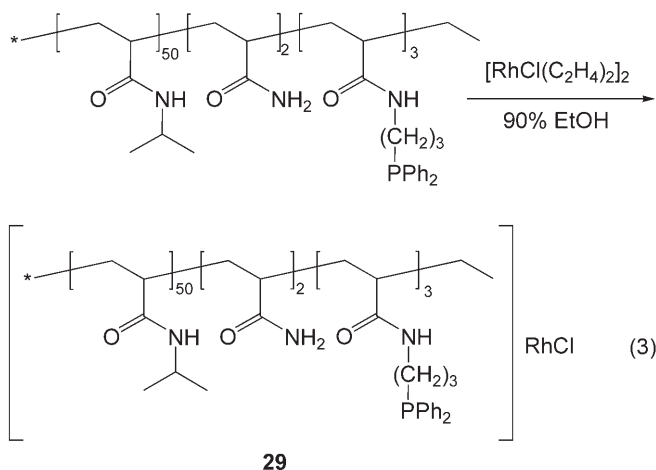
6 Thermomorphic and Latent Biphasic Catalysis

Our group was the first to coin the term thermomorphic to describe the behavior of many solvent pairs whose miscibility changes with temperatures. We have

worked extensively to develop both the temperature-induced phase changes in such thermomorphic biphasic systems and to also use latent biphasic systems for application in catalysis. Such systems have the potential to combine the advantages of homogeneous and biphasic catalysis while minimizing the disadvantages of each system.^[18,24,25,29,78–85]

6.1 Application of Polar Phase-Selectively Soluble Polymers

The first work illustrating the idea of using a soluble polymer and a thermomorphic system in catalysis was our work that used a polymeric phosphine for the complexation of a Rh(I) species to produce a poly(*N*-isopropylacrylamide) (PNIPAM)-supported version of Wilkinson's catalyst [Eq. (3)]. The catalyst **29** was



studied in the hydrogenation of 1-octadecene or 1-dodecene in a heptane-90% aqueous ethanol thermomorphic system. Comparison of **29**'s activity in this chemistry to that of a low molecular weight analogue showed that the soluble polymer-bound catalyst had comparable activity and that the polymeric catalyst could be recycled four times with no loss in catalytic activity.^[17]

Palladium precatalysts containing pincer-type Pd(II) complexes have been used by our group and others for cross-coupling reactions under thermomorphic conditions.^[16,18] More recently, end-functionalized PEGs containing sulfur-carbon-sulfur (SCS) ligated Pd complexes have been shown to be effective in cross-coupling chemistry in a 10% aqueous DMA-heptane thermomorphic system with microwave activation.^[86] However, while complexes on PEG-modified ligands and while other pincer complexes on soluble supports are catalytically active over reuse cycles, the identity of the catalytically active species has since come into question. Studies by us and

others have since identified the active catalytic species in these reactions to be Pd colloids.^[87–89]

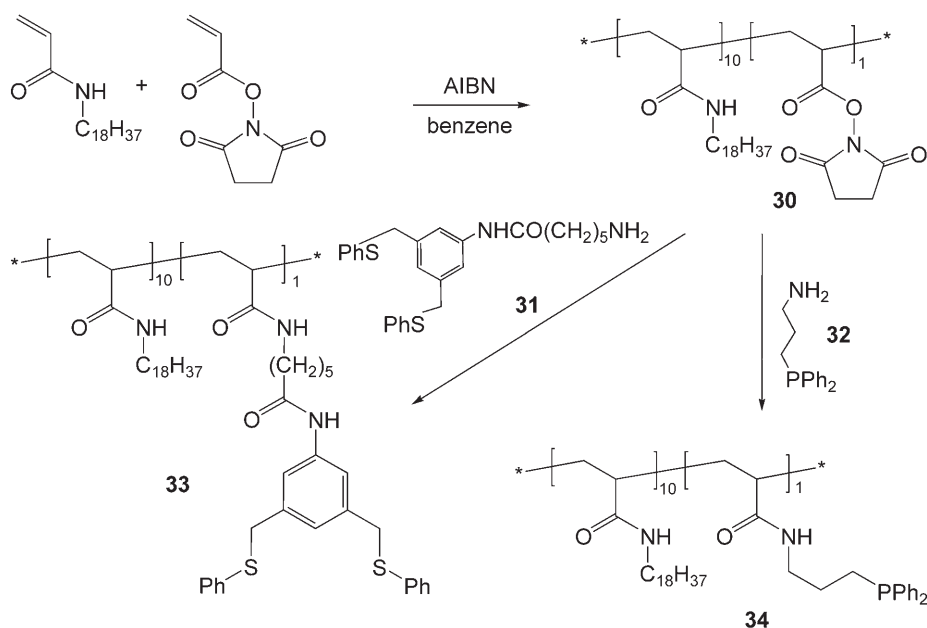
While polar soluble polymers can be used to separate and recover catalysts, the use of polar phase-selectively soluble polymer supports in thermomorphic or latent biphasic systems has some inherent problems. Polar soluble supports such as PNIPAM limit the synthetic scope to the preparation of non-polar products. Synthesis of a polar product would result in lower observed yields recovered from the non-polar heptane phase due to the predominant polar phase solubility of polar products. This is especially problematic since many specialty chemicals are polar products. Additionally, many reactions produce polar by-products (often salts) that can foul the polar phase of such a system. Continuous fouling over a number of cycles can result in a sufficient salt concentration to compromise the miscibilization step during which catalysis occurs. This is a potential problem in any biphasic Scheme that recycles the catalyst using a polar phase.

A recent report demonstrates how this problem affects separations and catalyst reuse. In the example, ligand **21** was used in thermomorphic in a solvent system composed of CH₃CN/Et₃N/*n*-heptane (5:2:5, vol%).^[66] This solvent mixture miscibilizes when heated above 80°C. In this instance, Et₃N in the system serves as the necessary base as well as a third solvent that serves to improve the miscibility of the CH₃CN and heptane mixture. In this system, palladium complexed by **21** was effective in coupling aryl iodides although it gave disappointing results with the less active aryl bromides. Recovery and reuse of the catalyst was achieved by cooling the system and sepa-

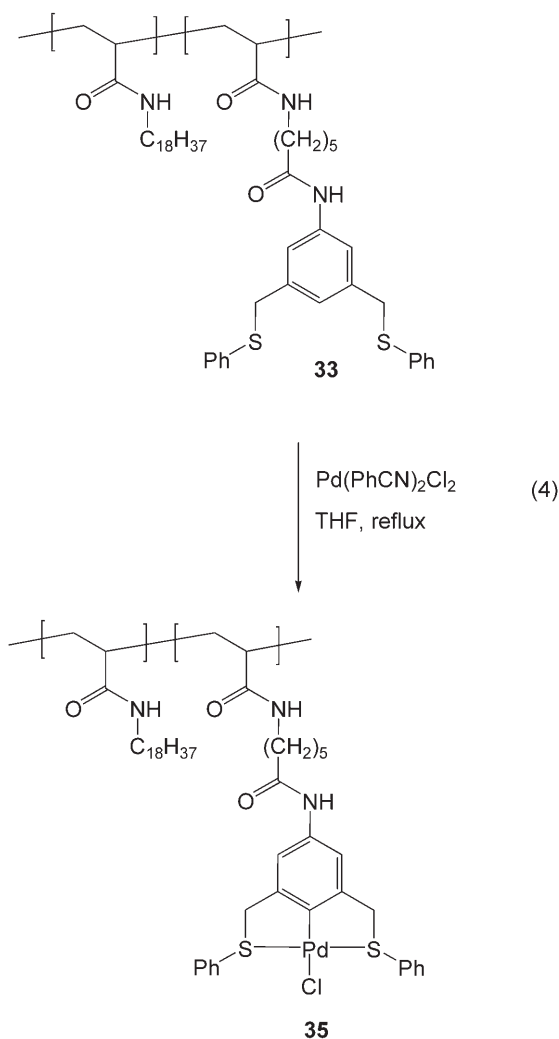
ration of the resultant biphasic systems. However, while palladium complexed by **21** in this solvent mixture was homogeneous on heating in the first cycle or first few cycles, accumulation of the by-product triethylammonium iodide in the polar phase of the system made miscibilization of the thermomorphic system become progressively more difficult throughout subsequent cycles of recycling experiments. This problem was vitiated by the addition of K₂CO₃ to the reaction mixture. This additional base effectively regenerated the Et₃N, forming solid KHCO₃ and KI which were easily removed from the reaction by filtration. This problem could, however, be more simply addressed by using a non-polar polymer support.

6.2 Application of Non-Polar Phase-Selectively Soluble Polymers

Poly(*N*-octadecylacrylamide) (PNODAM) is a lipophilic polymer that has heptane solubility. Copolymerization with the active ester, *N*-hydroxysuccinimide produces a copolymer (**30**) that has active ester groups. These groups readily react with primary amines. Attachment of an amine-containing ligand followed by catalyst ligation or direct attachment of an amine-containing catalyst, the amine-terminated catalysts or ligands like **31** or **32** for example, were efficiently and successfully attached to this PNODAM support to yield heptane-soluble PNODAM-supported SCS (**33**) and phosphine (**34**) ligands (Scheme 2). The SCS ligand could then be metalated with Pd-(PhCN)₂Cl₂ in THF at reflux to yield an SCS palladacycle that could, in turn, be used in the catalysis of



Scheme 2. Synthesis of PNODAM-supported SCS and phosphine ligands.



Heck reactions [Eq. (4)]. While later studies showed that this supported complex serves as a palladium pre-catalyst (probably forming Pd colloids), the catalytic reactions starting with **35** were successful in converting iodobenzene and acrylic acid into cinnamic acid for nine cycles in a heptane-dimethylacetamide thermomorphic mixture.^[87] A PNODAM-bound phosphine like **34** can also be used as a ligand for Pd(0), producing a non-polar analogue to the previously mentioned PNIPAM catalyst. This PNODAM-supported Pd(0) catalyst was utilized in an allylic sulfone synthesis in a heptane-90% ethanol thermomorphic system and could be recycled through 5 cycles before adventitious oxidation of the phosphine resulted in deactivation of the catalyst.^[16]

The success in recycling of these PNODAM-supported catalysts indicated that the design and attachment of catalysts to a soluble non-polar polymer support addressed the problems experienced with a polar polymer support. The preference of the polymer support for the non-polar phase of a thermomorphic

system allows synthesis of polar product molecules and also allows removal of any polar by-products at the conclusion of each cycle. This makes the support of catalysts or ligands on non-polar polymers more generally useful as most synthetically interesting molecules possess some polar character.

Polyethylene (PE) is a non-polar analogue of the popular and extensively used PEG supports. Previous work utilizing PE-supported materials has demonstrated the applicability of such materials as polymer supports for catalysis.^[90–93] However, PE is completely insoluble in any solvents below *ca.* 60 °C. The necessity to heat solutions to dissolve this polymer as well as the limited range of adequate solvents for this material (toluene, xylenes, mesitylene) restricts both the chemistry that can be used to modify these materials as well as the catalytic reactions that can be carried out with catalysts attached to this polymer.

Methylidene-terminated polyisobutylene (PIB) is an alternative. This readily available polyolefin is a structural isomer of PE that exhibits greatly improved solubility, readily dissolving in a variety of organic solvents including but not limited to dichloromethane, ether, THF, hexanes, and chloroform. Polyisobutylene has also been shown to have phase selective solubility in thermomorphic and latent biphasic systems that is sufficient to allow efficient recovery and recycling of a supported catalyst or reagent.^[15] Our group has thus developed the chemistry of polyisobutylene to make it into a useful, general soluble polymer support. Specific examples of ligands successfully attached to this polymer include PIB-SCS and PIB-phosphine species like **36** and **37** in thermomorphic and latent biphasic systems. Both ligands have also been used to prepare metal complexes that can be successfully used (Figure 12).

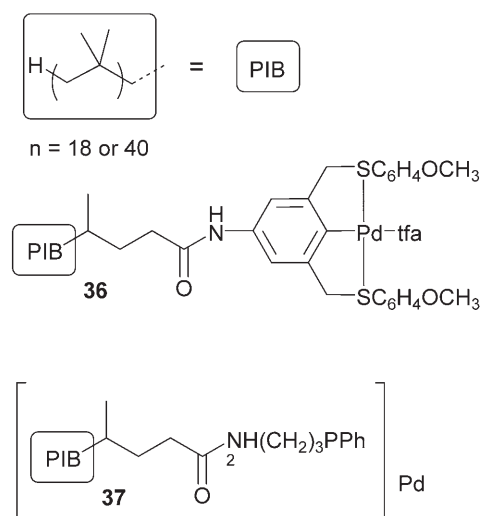


Figure 12. PIB-supported SCS and phosphine catalysts.

7 Conclusions

Liquid/liquid separations using gravity, a phase-selectively soluble polymer and two phases of different density are practical and viable ways to recover, separate and reuse soluble polymer-supported catalysts. Such polymer-supported catalysts can be used under either biphasic or monophasic conditions under aqueous/organic, fluorous/organic or other biphasic regimes. Alternatively, thermomorphic or latent biphasic conditions can be used so that reactions are monophasic. In either case, catalyst separation and recovery can be accomplished simply without the necessity of using significant quantities of additional solvent.

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