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The use of soluble polymers to effect homogeneous catalyst separation and reuse

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Abstract

The use of soluble polymeric ligands for homogeneous catalysts separation is reviewed with emphasis on work from the author's laboratory. Examples discussed include polyethylene-bound catalysts, poly(alkene oxide)-bound catalysts, poly(*N*-isopropylacrylamide)-bound catalysts, fluorous polymer-bound catalysts and amphoteric polymer-bound catalysts. The utility of these systems is also discussed in the broader context of polymer-supported catalysis and the advantages and limitations of soluble polymeric ligands are discussed in this context. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymers have been the subject of attention in connection with catalysis chemistry for many years. Much of this work began in the 1960s after the introduction of strongly acidic and strongly basic ion exchange resins for use in water purification and metal recovery. Later that decade after Merrifield's solid phase synthesis chemistry had been popularized, there was a surge of interest in polymer supports for homogeneous catalysts among both industrial and academic chemists [1,2]. At that time the thought was that insoluble polymer-supported catalysts would be a natural bridge between the areas of homogeneous and heterogeneous catalysis [3]. More recently there has been another upsurge of interest in polymer-supported chemistry in general and polymer-supported catalysis in particular. This renewed interest arises in part from the development of combinatorial chemistry and from the potential for combinatorial chemistry in catalyst development, optimization and testing [4–7]. This renewed interest is also a consequence of the interest in improving the efficiency of industrial chemical processes to minimize waste [8]. In this paper, I will discuss general strategies that use polymers to effect catalyst separation and reuse using examples of work from our group where appropriate.

The main roles of polymer supports in catalysis are in the areas of catalyst separation and reuse. This is the focus of this review. Separation is an often unappreciated but critical issue in nearly all chemical processes. It is typically the first experiment most students do in a sophomore organic laboratory. Presumably this is because phase separation is simple and because it is the easiest form of purification to understand and to effect. The phase difference between a heterogeneous catalyst and a soluble substrate and the consequent facile separation of catalyst/substrate/product is like-

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wise one of the main advantages of heterogeneous catalysis.

In conventional homogeneous catalysis, one usually has to forgo the advantages of phase separation in catalyst recovery and product purification for the sake of higher or more controllable catalyst activity and selectivity. As a result of the ligand/catalyst solubility, catalyst/product separations in homogeneous catalysis have to be accomplished by processes like distillation if the catalyst solution is to be simply recovered and reused. While this is a relatively simple operation when volatile products are being prepared, in other cases, product/catalyst separation requires more complicated steps and catalyst/ligand recovery may not lead to a recoverable reusable catalyst. Most conventional homogeneous catalysts operate in organic solvents and this can lead to a chemical waste problem, especially when post-reaction processing for catalyst/ligand recovery is required. One way to address this issue is to carry out homogeneous catalysis in other solvent systems – notably in water or in supercritical CO_2 media. These other solvent media have attracted recent attention since chemistry that employ these solvents is considered environmentally ‘friendlier’. Separation of catalysts and products in these latter cases presumably would produce less organic solvent waste.

Polymer-supported ligands were originally introduced as a way to make homogeneous catalysts separable without changing their reactivity [1–3]. The standard approach to effect catalyst/substrate phase separation in catalysis with a polymer is to use an insoluble crosslinked polymeric ligand to bind the catalyst. The most common polymer used in this regard is crosslinked polystyrene obtained from reaction of divinylbenzene and styrene or a styrene derivative [1,2]. Ligands can be attached to the resultant polymer before or after polymerization. Separation of such an insoluble polymer-bound transition metal catalyst and product is typically accomplished by filtration.

2. Experimental procedure

Experimental procedures for synthesis and use of the polymers described here have already been reported. Specific experimental procedures used in our synthesis and use of polyethylene-bound catalysts, poly(alkene oxide)-bound catalysts or substrates, poly(*N*-isopropylacrylamide)-bound catalysts or substrates, fluorous polymer-bound catalysts and substrates and amphoteric polymer-bound catalysts are cited in the discussion below.

3. Results and discussion

While crosslinked polystyrene systems remain a conceptually simple and elegant way to solve the problem of homogeneous catalyst/product separation, problems with catalyst leaching, catalyst or ligand characterization, reactivity and catalyst stability prompted us to look at other polymer systems [9]. Our first efforts in this regard involved the use of organic phase soluble polymers and our initial studies focused on polyethylene as the polymer support. Our interest in this polymer stemmed from our concurrent work on polyethylene surface functionalization [10]. Two features of polyethylene were of interest in its potential application in catalysis chemistry. First, polyethylene is relatively inert chemically. Thus, this polymer was unlikely to chemically interfere with a bound catalyst. Second and more importantly, we realized that polyethylene is a polymer whose solubility is profoundly affected by temperature. Specifically, polyethylene is completely insoluble in all solvents at room temperature but is quite soluble in a number of solvents at higher temperature. We reasoned that this sort of solubility change could be used effectively in catalysis if ligands and thus catalysts could easily be attached to polyethylene. Our expectation was that a polyethylene-bound catalyst would be insoluble at room temperature (and recoverable) but soluble (and active) at high temperature.

To insure that polyethylene’s solubility change with temperature would be retained in any catalyst, we chose to attach catalysts to terminally functionalized linear polymer chains. To insure that a useful amount of a homogeneous catalyst would be present in solution, we also chose to use polyethylene oligomers in place of high molecular weight linear polyethylene. Fortunately, linear polyethylene oligomers prepared by anionic polymerization have solubility like their high molecular weight analog and we were able to routinely prepare polyethylene oligomers whose poly-

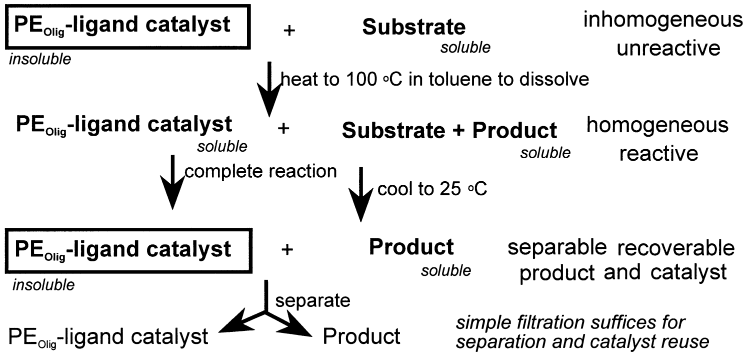


Fig. 1. Catalyst separation in organic systems with a polyethylene oligomer (PE_{Olig})-bound catalyst as a function of temperature.

ethylene portion had a M_n value of 2000 [11]. Such oligomers can be dissolved in hot toluene to produce solutions whose concentration of oligomer approaches 0.01 M – a concentration that is more than sufficient for a decently active homogeneous catalyst. Most importantly, such oligomers and the catalysts derived from them are insoluble at room temperature and soluble at elevated temperature.

The strategy we developed using polyethylene oligomers as ligands to separate, recover and reuse a homogenous catalyst is illustrated in Fig. 1. We have successfully used this strategy for a number of different catalysts [9,12–19]. Catalyst recovery is generally quantitative. Catalyst activity generally mirrors that of a low molecular weight analog so long as the polymer is soluble. However, this strategy does have some limitations. It requires relatively nonpolar organic solvents – toluene, dichlorobenzene and dibutyl ether. It requires elevated temperatures for ligand or catalyst dissolution and for the steps involved in synthesis of the ligand.

More recently, we have turned our attention to other soluble polymer supports. This decision to explore other polymer systems for homogeneous catalyst phase separation and reuse arose as a result of several issues. First, we had a desire to overcome the limitations of the polyethylene oligomer systems. Second, during the time we had been developing soluble polyethylene-bound catalysts, increasing attention had been focused on other solvent systems – notably water – where polyethylene oligomers were unlikely to be useful. Finally, we had developed an interest in combinatorial approaches to catalysis – chemistry we felt might be better addressed through synthesis of other soluble polymers with either terminal or pendant catalyst groups.

The use of water-soluble polymers for catalysis had attracted attention before our entry into the area [20,21]. However, while Nature has used water and biological polymeric catalysts including transition metal catalysts exclusively, there had been only sporadic work on water-soluble polymer-bound catalysts. This was not because water is incompatible with transition metal catalysis – aqueous homogeneous or biphasic catalysis in the form of the Rh(I)-catalyzed hydroformylation was well established [1,22]. Among the examples of polymer-supported transition metal catalysis in water we were aware of, the work of Steckhan in particular attracted our attention [21]. This work was noteworthy in that it served as an example of a water-soluble polymer-bound catalyst that did many of the things that we wanted to do with polymer-supported catalysts. This particular system used a poly(ethylene oxide)-bound rhodium(I) derivative as a cocatalyst to regenerate NADH from NAD in an enzymatic reduction. The polymer ligand in this case made the catalyst soluble in water and afforded a way to keep the rhodium(I) and enzyme apart. It afforded the catalyst water solubility with good catalyst activity. The polymeric ligand also made membrane separation of catalyst and products feasible.

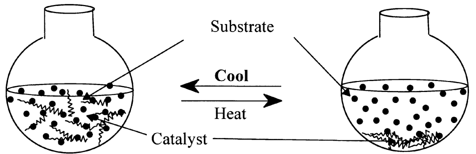
The results of Steckhan and the prior results from other groups where poly(ethylene glycol) or poly (ethylene oxide) derivatives were successfully used as polymer or oligomeric supports for homogeneous catalysts [20,21] suggested that these water-soluble polymers should generally be useful as catalyst supports. This premise is now well established. Indeed, recent work by Janda's group has shown that poly (ethylene oxide) supports may have especially good activity [23]. In their recent work, Janda's group has shown that poly(ethylene oxide) derivatives make excellent supports for very active asymmetric dihydroxylation catalysts. Separation in such cases can be affected by solvent precipitation or, presumably, by membrane filtration.

A general problem faced whenever polymers are used is what effect a polymer has on a bound catalyst's or substrate's reactivity. We thought that this could be a problem in the case of organic polymers in water and we therefore briefly studied the effect of polymer solubility on reactivity with several polymer-bound substrates [24]. In the case of PE_{Olig}, these effects were minimal in hydrocarbon solvents (e.g., toluene) at temperatures of 105°C (above the oligomer's dissolution temperature of 70–80°C). While polyethylene oligomers had little effect a bound substrate or catalyst's activity dissolution temperature, PE_{Olig}-bound catalysts were, however, inactive when they were insoluble. This suggested to us that there could be similar significant effects with other polymers under conditions where the polymer was not soluble or in poor solvents. To study this question, we examined the reactivity of a number of heterogeneous catalysts for reduction of substrates attached to the termini of poly(alkene oxide) polymers. We reasoned that changes in activity of a substrate would foretell those of a catalyst. We found that hydrogenations with Pt/C of terminal nitroaryl groups attached to the terminus of a PEG support were equally facile regardless of the size of the support so long as the reaction was carried out in a 'good' solvent for the polymer. Hydrogenation reaction rates were, however, markedly affected by polymer size if the polymer-solvent interactions were unfavorable.

The idea that a polymer could affect the reactivity of a bound species and our interests in using water-soluble poly(alkene oxide) polymer or poly(alkene oxide) oligomer supports to separate and recover catalysts led us to explore the idea of 'smart' catalysts [25–28]. This idea differed from what others had examined previously in that this is a very different potential advantage of these sorts of polymers.

Our earlier polyethylene oligomer support work had emphasized the utility of separating a polymeric catalysts from solvent and products by cooling, precipitation and filtering. In essence this work relied on what might be termed normal solubility. However, we were aware that polymers like poly(ethylene oxide) and suitable block copolymers of ethylene oxide and either propylene or butylene oxide have inverse temperature dependent solubility. Indeed, many water-soluble synthetic polymers precipitate or phase separate from water on heating [29,30]. This phenomenon is also common for other synthetic polymers including non-polar polymers in non polar solvents although it is often only seen above the boiling point of the solvent [31]. This solubility phenomenon is familiar to a lay person and is manifest in the behavior of proteins like egg albumin that precipitate from water on heating. However, most synthetic polymers including water-soluble synthetic polymers like poly(alkene oxide)s redissolve on cooling.

The ability to tailor the microstructure of polymers to affect the so-called Lower Critical Solution Temperature (LCST) at which the polymer separates from solution [29,30] and the fact that we had earlier found that catalyst and substrate activity is significantly affected by polymer solubility suggested a role for this process in catalysis chemistry. What we specifically did was to show that these temperature dependent solubility properties of polymers can be used to prepare 'smart' hydrogenation catalysts that regulate exothermic reactions and that can be recovered. In these cases, the reactivity of the catalyst is controlled through the temperature dependent phase separation of the polymeric ligand (Eq. (1)). At low temperatures, the catalyst is soluble and active because the polymer is in solution below its lower critical solution temperature (LCST). At elevated temperatures above the polymer's LCST, the polymer and the attached catalyst phase separates and the catalyst activity significantly decreases. Our initial work used a commercially available ethylene oxide – propylene oxide – ethylene oxide triblock copolymer surfactant (PEO–PPO–PEO) to prepare



Homogeneous active solution of catalyst, product and substrate at 33 °C

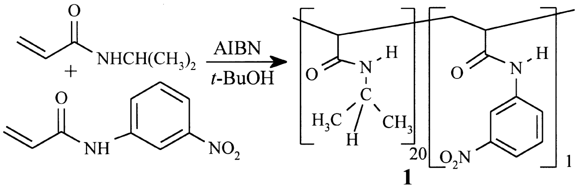
Heterogeneous inactive mixture of catalyst, substrate and product at 39 °C

(1)

chelating and monodentate alkyldiphenyl-phosphine ligands for cationic and neutral Rh(I) hydrogenation catalysts [25,26,32]. The resulting catalysts were active in hydrogenation of water-soluble substrates such as α,β-unsaturated carboxylic acids and allyl alcohol at 0°C. In the case of the cationic Rh(I) catalyst, this activity decreased >50-fold at 50°C (above the LCST point). Similar changes in reactivity were seen with a neutral Rh(I) catalyst but the change in catalytic activity occurred over a narrower temperature range (on at 0°C, off at 25°C) because the polymer had a lower LCST. Preliminary kinetic results showed that the catalytic activity gradually decreased as temperature increased [32].

While these PEO–PPO–PEO systems readily phase separate, this phase separation does not always lead to a cessation of catalytic activity. We speculated that this was due to the fact that this phase separation led to an oil-in-water emulsion. Indeed, although catalytic activity generally ceased and never increased as expected, a series of kinetic experiments to probe the how the activity of catalysts or substrates attached to PEO–PPO–PEO polymers around the polymers' LCST were not always very reproducible. We attributed these effects to the presence of an emulsion in which the polymeric catalysts or substrates could still be active.

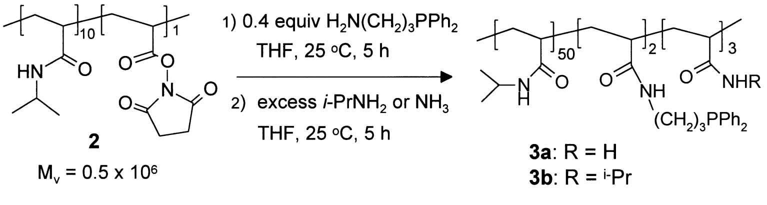
The irregular activity with temperature seen for the PEO–PPO–PEO systems led us to study other polymer supports that also exhibit critical phase behavior in water [27,28]. Poly(*N*-isopropyl acrylamide) (PNIPAM) has inverse temperature dependent solubility behavior in water with an LCST of ca. 31°C [29]. Derivatives of this polymer can serve as 'smart' substrates [27]. Our first demonstration of this was the use of a supported nitroarene attached to a random copolymer created by the radical copolymerization of *N*-isopropylacrylamide and the *m*-nitroaniline amide of acrylic acid (Eq. (2)). This substrate on hydrogenation with Pt/C at atmospheric pressure exhibited non-Arrhenius temperature dependent activity. This substrate was hydrogenated in EtOH and in water at a rate comparable to that of a low molecular weight analog, *m*-nitropropanilide, at 0°C. However, while the hydrogenation rate of **1** increased on heating in ethanol in the range 0–50°C, in water, the hydrogenation rate decreased 50-fold from 33°C to 39°C in water. This change in rate was correlated with a phase separation in aqueous solution at this same temperature range. The change in hydrogenation rate with temperature was fully reversible.



(2)

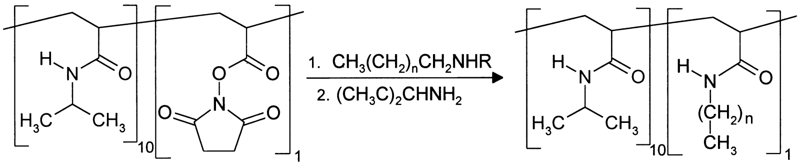
PNIPAM bound substrates proved to be a convenient way to test the inverse temperature dependent On/Off reactivity of these polymer-bound substrates. However, binding a substrate to a polymer is unlikely to be as practical a way to regulate a reaction as is binding a catalyst to a polymer. Fortunately Rh(I) hydrogenation catalysts attached to aminophosphine ligands attached to PNIPAM exhibit similar 'smart' behavior with their activity turning Off and On as the temperature is changed above and below the polymer's LCST [33].

While PEO–PPO–PEO block-copolymer supported catalysts and PNIPAM-supported catalysts all have the intriguing property of being able to regulate an exothermic reaction, these polymer supported catalysts and the PNIPAM-supported ligands also have the advantage of being readily separable. This is illustrated by the chemistry shown in Eq. (3) below where a water-soluble phosphine ligand **3a** is prepared [34]. This ligand was successfully used to prepare a



(3)

Pd(0) catalyst that was then used in an allylic substitution reaction in water. When the reaction was complete, the catalyst was separated and recovered by simply heating the solution to room temperature (the ligand-catalyst had an LCST <25°C). Alternatively, if a substrate that is not water-soluble were used, ligand **3b** Eq. (3) could be used in mixed water–ethanol or mixed water–acetonitrile media. In this second case, the ligand–catalyst complex could still be recovered by addition of a poor solvent for the polymer (e.g., diethyl ether). In either case, separation of the ligand–catalyst complex by centrifugation of filtration and redissolution of the polymer in fresh solvent could be used to repeat the reaction with fresh substrate.



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4a, n = 0, R = -CH$_3$
4b, n = 5, R = -H
4c, n = 17, R = -H

(4)

Soluble polymers like PNIPAM have the additional advantage of being easier to characterize. For example, if a polymer is soluble, UV-visible or fluorescence spectroscopy is facilitated. A more important issue for organic chemists is that NMR analysis of the polymer-bound ligands or substrates is more facile than would be the case with an insoluble polymer. Insoluble cross-linked polymers generally have broad NMR signals. While information can be gleaned from spectra of swollen gel-type polymers or with polymers containing graft spacer groups that facilitate NMR analysis of substrates, the large spacers involved necessarily lead to resins whose loading levels are reduced. Recent work from our group has shown that a soluble PNIPAM derivative requires only small spacer groups to significantly change a bound substrate's NMR spectroscopy behavior so that it resembles that of a small molecule [33]. For example, T_1 measurements for the terminal methyl group of a polymers like **4a**, **4b** and **4c** show that the relaxation time varies from 0.4 to 2.7 to 4.1 s. T_1 values for the terminal methyl group of hexylamine or octadecylamine under the same conditions are 6.8 and 4.6 s, respectively. Given that these values have errors of ±0.8 s, we estimate that a 10 atom chain should be sufficient to make terminal groups have dynamics and mobility like their low molecular weight analogs. Such changes in dynamics and mobility are also significant in that small-molecule NMR spectroscopic behavior likely will augur well for the catalytic activity of catalysts attached to soluble resins through similar spacers.

The three examples above of soluble polymers being used to effect phase separation of a catalyst have a common theme. Precipitation on cooling of the crystalline polyethylene, precipitation with a poor solvent (PEO or PNIPAM) and precipitation on heating (PNIPAM) all involve the general idea of using a polymer to dictate the solubility of a substituent. This general approach engineers solubility and separability into a catalyst by using the solubility and separability of the polymer support without significantly affecting the catalyst's activity. Two recent examples of fluorous phase polymer supports and of amphoteric polymer supports further illustrate this idea.

Fluorous phase chemistry is a very attractive idea [35–37]. It is a non-aqueous version of aqueous biphasic chemistry. The general idea is shown in Fig. 2 below. This chemistry requires fluorous phase soluble ligands or catalysts to be effective (Fig. 2). The fluorous biphasic approach to catalyst separation uses a hydrocarbon immiscible fluorocarbon solvent that dissolves a fluorous phase soluble catalysts (Cat). This mixture is then heated to achieve miscibility with an hydrocarbon phase containing substrate (S) or is shaken to form an emulsion. Cooling or standing at the end of the reaction leads to separation of the catalyst (Cat) and product (P).

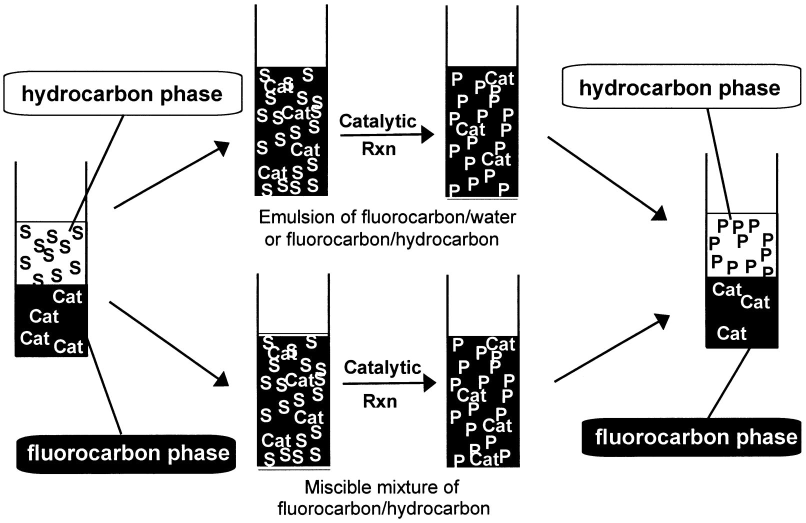
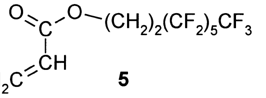


Fig. 2. Catalyst separation, use and recovery in fluorous–hydrocarbon biphasic systems wherein the catalyst is soluble only in the fluorous or mixed fluorous-hydrocarbon phase.

Our approach to this chemistry was to prepare a soluble fluorous phase polymer to which we could attach a variety of catalyst ligands. To this end, we prepared fluorinated copolymers from the fluoroacrylates **5**–**7** and *N*-acryloxysuccinimide. Then to show that these polymers



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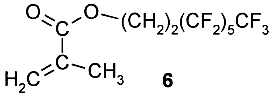

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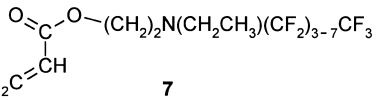

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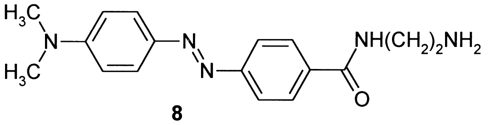
and species bound to them are reactive to hydrocarbon-soluble reagents but quantitatively and quickly separate from a hydrocarbon solvent, we attached a dye **8** via an amide bond. This



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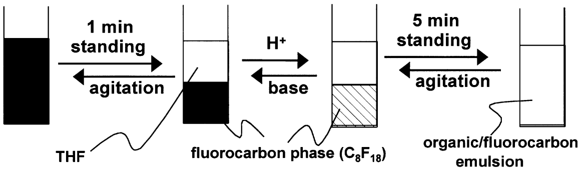
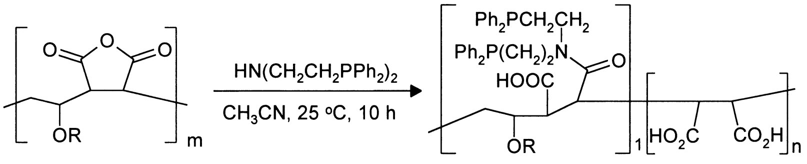
fluorous polymer-bound dye was then used in the reaction shown in Eq. (5)[38]. As shown, this fluorous polymer-bound dye reacts instantaneously with acid or base and is readily and quantitatively separated from the hydrocarbon solvent by standing and liquid/liquid extraction. We have then gone on to show that a dye attached to these polymers is reactive and fully separable from organic solvents.



(5)

Attachment of catalysts to copolymers derived from *N*-acryloxysuccinimide and the acrylates **5**–**7** was feasible when an aminophosphine ligand was used to introduce a phosphine group onto the fluorous phase soluble polymer [39]. These polymers represent a generally useful fluorous phase polymeric ligand that can engender fluorous phase solubility in many different substrates. It is also possible that these polymers can also be used as ligands in supercritical CO_2-systems given the precedent that fluoropolymers are highly soluble in this medium [40].

Polyelectrolytes are well known class of polymers. While there has been some application of these polymers as supports for catalysts, this work has generally focused on using the a polycarboxylate as an anionic ligand [41]. We recently reported another approach to use of polyelectrolyte polymers in separation in homogeneous catalysis [42]. In this approach, we used derivatives of a commercially available copolymer – Gantrez. Gantrez (**9**) is the tradename for a class of alternating copolymers of maleic anhydride with alkyl vinyl ethers and similar vinyl monomers. Due to the presence of the anhydride, **9** is a readily modified polymer. We reasoned that it should be possible to modify **9** by addition of a phosphine-containing amine, bis(diphenylphosphinoethyl)amine to the anhydride group to form an amic acid-containing polymer (**10**). This expectation has been realized (Eq. (6)), and we have found that we can prepare polymers **10** with varying loadings of phosphine (n=5, 10, 12, 15). In these polymers, the remaining anhydride groups are hydrolyzed to form amphoteric carboxylic acid groups that serve as a mechanism for recovery and dissolution of the catalysts. Use of the less reactive secondary aminophosphine in place of a primary amine (e.g., $H_2NCH_2CH_2CH_2PPh_2$) made it possible to control loading of the phosphine on the polymer **10**. Base-soluble rhodium(I) catalysts were made from these chelating, polymer-bound phosphine ligands. Survey experiments showed that catalysts made with **10c** seemed most active. Ligand **10a** was not used as it did not dissolve in aqueous base.



9 (Gantrez), R = $-CH_3$
m = 2200
M_n/M_w = 3.54

10a: n = 5
10b: n = 10
10c: n = 12
10d: n = 15

(6)

A cationic Rh(I) catalyst prepared from **10c** and 1 equiv of [Rh(COD)]+OTf was soluble in basic solutions (pH>7.5) at catalytically useful concentrations of ca. 1×10^{-3} M. Acidifying such solutions (CF_3SO_3H) produced an easily isolated yellow precipitate that readily redissolved when it is added to a fresh pH 7.5 solution. At higher pH values (>9), the catalyst was not stable, gradually forming what appears to be a black precipitate of rhodium metal. The catalytic activity of this Rh(I) catalyst was comparable to that of other water-soluble Rh(I) catalysts. Recycling catalyst from an organic (CH_3CN) solution was also feasible using solvent precipitation (addition into excess ether) to recover the polymer-bound catalyst at the reaction's end.

Horvath's original work on fluorous phase catalysts [35] and more recent work using poly(ethylene oxide)-substituted triphenylphosphines as thermoregulated phase transfer ligands [43] illustrates a final way in which catalyst separation and recovery could be effected beneficially with suitable polymers. While the work with fluorous phase chemistry described above generally used biphasic reaction conditions, Horvath noted that suitable pairs of hydrocarbon/ fluorocarbon solvent mixtures have temperature dependent miscibility (cf. Fig. 2 above). Likewise, while our published work to date on ligands with inverse temperature dependent solubility has emphasized their use as 'smart' ligands or has emphasized their recovery the thermal precipitation or solvent precipitation, Jin has recognized that polymers whose hydrophobicity changes with temperature can reversibly move from one phase to another as a function of temperature [43]. Both of these experiments are illustrative of a potentially useful new approach to catalyst separation where catalyst/product separation would occur at room temperature by liquid/liquid separation – a process that may, as Jin's work suggests, may be facilitated by the presence of a polymer.

4. Summary

The discussion above has illustrated the broad utility of soluble polymers in homogeneous catalysis and in separation and recovery of homogeneous catalysts. While we have focused our attention on polymers like polyethylene, poly(alkene oxide)s, poly(*N*-isopropylacrylamide)s, fluorous polymers and amphoteric polymers, other soluble polymers also merit more attention. The general idea that lightly loaded polymers or terminally functionalized polymers can confer on an attached ligand or catalyst the physiochemical properties of the polymer itself seems well established. There are also a number of other potential advantages of polymer supports that are likely to receive increasing attention. Multistep reactions, the use of a polymer to activate a catalysts, combinatorial catalyst synthesis, development and testing and catalyst control by polymers are all other opportunities where soluble (or insoluble) polymers can usefully impact the utility of homogeneous catalysis.

Acknowledgements

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