

Soluble polymer-supported organocatalysts*

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Abstract: Organocatalysts have been extensively studied for the past few decades as alternatives to transition-metal catalysts. Immobilizing organocatalysts on polymer supports allows easy recovery and simple product purification after a reaction. Select examples of recent reports that describe the potential advantages of using soluble polymers to prepare soluble polymer-supported organocatalysts useful in organic synthesis are reviewed.

Keywords: catalysts; green chemistry; organocatalysts; poly(ethylene glycol); polyisobutylene; polymers; polymer supports; polystyrene.

INTRODUCTION

In the past few decades, numerous important ligands, catalysts, and reagents have been developed to fulfill synthetic chemists' needs for reagents and/or catalysts for bond formation, functional group transformation, and the construction of complex organic frameworks. However, reuse of reagents or the separation, reuse, and recycling of catalysts remain unresolved issues in most cases. For example, although many ligand/catalyst combinations have been developed that demonstrate high activity and good selectivity with low catalyst loading, some concerns regarding the use of these reactions in industrial applications still remain as unresolved problems. These concerns include: (1) the high cost of many transition metals, (2) the high cost incurred in the synthesis and purification of ligands, and (3) the toxicity of ligands and catalysts. These economic, environmental, and safety concerns can pose problems in the application and use of these reagents and catalysts in industry. Therefore, studies that address the reuse and recovery of these ligands/catalysts/reagents have attracted much attention. In most cases, the strategies that have been developed to address these problems involve the use of supports to phase isolate a transition-metal catalyst after a reaction.

While there are many different types of transition-metal catalysts, organocatalysts have recently received heightened attention as alternatives to transition-metal catalysts because they avoid the use of expensive and sometimes toxic transition metals [1]. In many cases, their mode of action mimics catalysts nature uses. However, these catalysts often are used at high mol % loading. Thus, while their toxicity can be less than that of metal-containing catalysts, their separation, recovery, and reuse are still of interest [2–9]. Strategies that address this issue for organocatalysts are discussed below.

RESULTS AND DISCUSSION

Organocatalysts are currently of intense interest as metal-free alternatives to commonly used organometallic catalysts. Although many organocatalysts have the advantages of air- and moisture-stability, column chromatography typically has to be used to separate these catalysts from the products.

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Therefore, immobilization of organocatalysts on polymer supports to facilitate recovery and reuse of these catalysts is an attractive strategy since immobilization can more efficiently separate catalysts and can serve as a way to reuse these catalysts that often are used at relatively high mol % loadings. The potential economic and green chemistry advantages of this approach have led to many recent reports describing separable insoluble polymer-supported organocatalysts [2–20]. Selective examples of such catalysts are shown in Fig. 1. In this brief review, we will highlight select recent work describing an alternative strategy where organocatalysts are immobilized on soluble polymer supports.

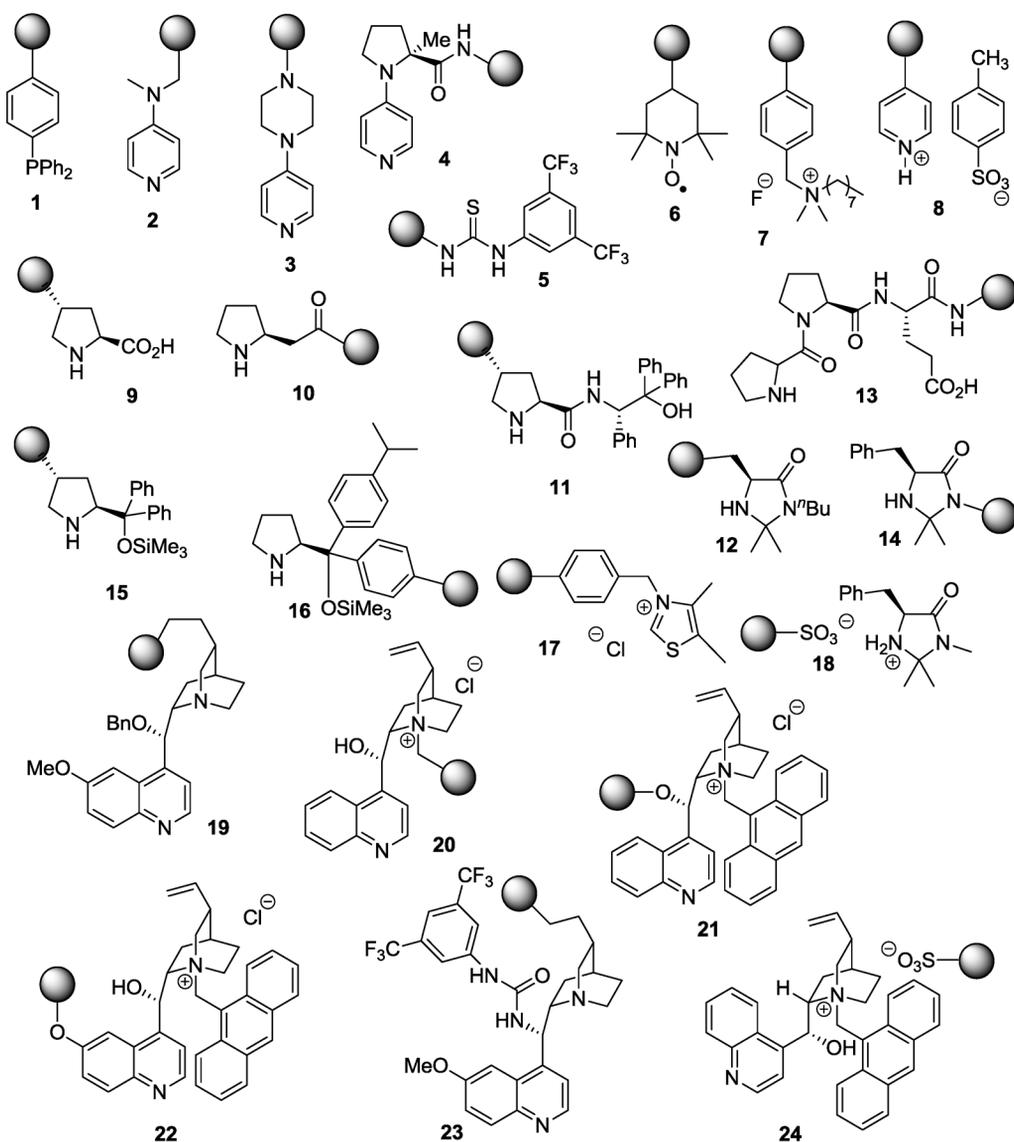


Fig. 1 Examples of insoluble polymer-supported organocatalysts.

The use of soluble polymers as polymeric supports as an alternative to the insoluble supports used to support catalysts like **1–24** has been receiving increasing attention in catalysis and has been a focus of work by our group [21,22]. The sorts of soluble polymer support used can vary widely and can

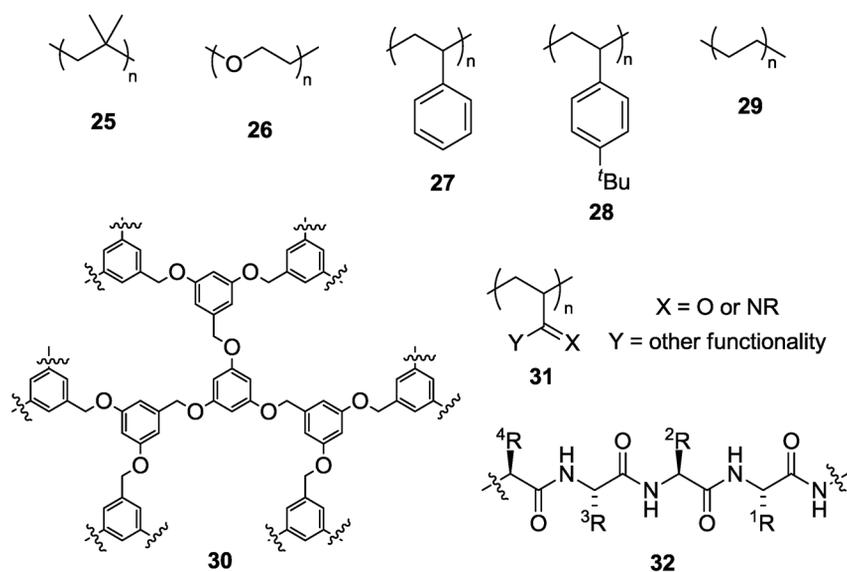


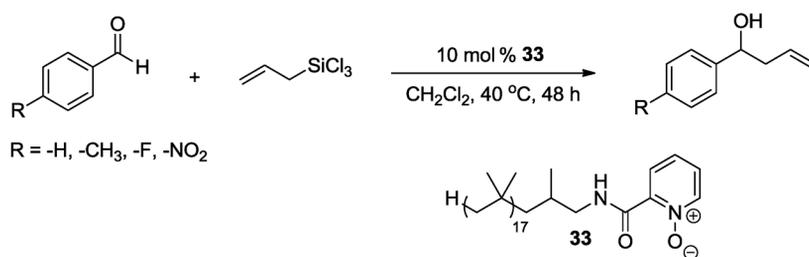
Fig. 2 Common soluble polymer supports.

involve both synthetic and bioderived polymer supports. Common examples of such supports include polyisobutylene (PIB) **25**, poly(ethylene glycol) (PEG) **26**, polystyrene **27**, alkylated polystyrene **28**, polyethylene **29**, dendrimer **30**, addition polymers with pendent groups **31**, and peptide **32** (Fig. 2).

Insoluble cross-linked polystyrene derivatives are polymeric supports that are insoluble before, during, and after a reaction. Separation after a reaction thus requires only a filtration or decantation that separates a solution from an insoluble solid to separate the catalyst and product. However, the insolubility of such supports before and during a reaction poses other problems in that catalyst characterization and catalyst reactivity can be affected by the support's insolubility.

Soluble polymer-bound catalysts can be designed to be easy to characterize by solution-state spectroscopy and can exhibit the same reactivity as their low-molecular-weight analogs. Soluble polymer-bound catalysts, however, usually require the solution of product and soluble polymer-bound catalyst to be separated other ways. For example, separations of a soluble polymer-bound species and a low-molecular-weight product can be effected on the basis of molecular size using permselective membranes [23]. However, this technique is still not widely used for recovery/reuse of soluble polymer-bound catalysts. More often a solution of a soluble polymer-bound catalyst is perturbed such that it becomes biphasic. Most commonly this involves a process that precipitates the polymer from the product solution. In some cases, this can be accomplished by cooling or heating. In other cases, this is accomplished by adding the solution of the soluble polymer and product to an excess of a poor solvent for the polymer. In successful cases, this leads to selective polymer precipitation. In either case, filtration or centrifugation serves to separate a solid polymer from the solution of product. The other alternative is to perturb a solution of the soluble polymer-bound catalyst and product so as to turn the solution into two liquid phases. If the product is soluble in one phase and the polymeric catalyst phase selectively soluble in the other, a gravity separation can be used to separate the product and catalysts and to recover the polymer-bound catalyst for use in a subsequent reaction.

The soluble polymers used to support organocatalysts can be classified as either polar or nonpolar supports. PIB **25** is an example of a nonpolar support our group has used extensively both for transition-metal catalysts and organocatalysts. For example, we have described a PIB-supported pyridine *N*-oxide catalyst **33** (Scheme 1) that was used in allylation of benzaldehydes [24]. After the reaction, the PIB-bound catalyst/product mixture was dissolved in a biphasic mixture of hexane/90 %



Scheme 1 PIB-pyridine *N*-oxide catalyzed allylation.

EtOH–H₂O. A gravity separation then isolated the hexane phase, which contained the PIB-bound catalyst **33**. In this case, the catalyst **33** could be isolated after hexane removal and reused in the following cycles. This catalyst was reused for five cycles with good conversions without significant loss of activity. This result suggests that hydrocarbon polymers like PIB should be generally useful as supports for recoverable organocatalysts.

Later in 2011, the Bergbreiter group reported syntheses of the PIB-bound alkyldiphenyl phosphine **34** and triaryl phosphine **35** shown in Fig. 3 [25]. These polymer-supported phosphines were used as recyclable organocatalysts in alkyne addition and allylic substitution reactions as shown in Scheme 2. In the alkyne addition reaction, the product mixture of the first run was obtained in 90 % combined yield with the ratio of *trans*:*cis*:*gem* products being 76:23:1. The same alkyne addition reaction carried out with a low-molecular-weight catalyst—*isobutyldiphenylphosphine*—that is electronically analogous to the PIB-bound alkyl diphenylphosphine **34**, afforded the same product mixture in 92 % combined yield with the ratio of *trans*:*cis*:*gem* products being 76:23:1. The phosphine catalyst **34** was recyclable and reusable, providing good yields of the product mixture through cycle 5. However, in cycle 6 a lower yield of the product mixture was obtained. The organocatalyst **35** was also used as a recyclable and reusable catalyst in the allylic substitution reaction shown in Scheme 2. This catalyst too afforded good yields of the product through five cycles. However, as was the case for alkyne addition catalyzed by **34**, increasing the number of cycles with **35** also led to lower yields of product. ³¹P NMR spectroscopy showed that these lower yields were a result of catalyst deactivation and formation of inactive phosphine oxide from **34** or **35**. This catalyst deactivation was attributed to adventitious oxidation of phosphines during exposure to air during a recycling step.

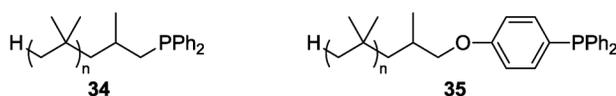
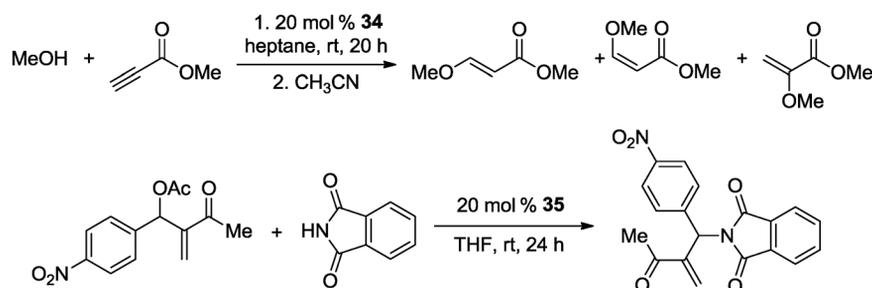


Fig. 3 PIB-bound phosphines **33** and **34**.



Scheme 2 Alkyne addition and allylic substitution reactions catalyzed by **34** and **35**.

While such oxidation could be presumably avoided with greater experimental care, we have also noted that the phosphine oxides resulting from this process can be easily converted back into a competent catalyst because the PIB group facilitates regeneration of these catalysts using trichlorosilane. This is a known reaction, but our experience is that its use often leads to difficult work-ups [26]. In our case, work-up and isolation of the regenerated phosphines **34** and **35** was simplified by the heptane solubility of the phosphines **34** and **35** and the heptane insolubility of all the siliceous by-products. The regenerated catalysts **34** and **35** as expected have the same activity as freshly prepared catalysts.

Since 2005 when Jørgensen [27,28] and Hayashi [29] independently reported diarylprolinol silyl ethers as effective organocatalysts for a variety of transformations, efforts have been made to immobilize these catalysts to prepare recyclable catalysts and to more simply separate these catalysts from the products. In 2010, Mager and Zeitler described how a PEG-supported Jørgensen–Hayashi catalyst **36** (Fig. 4) could be used for this purpose [30]. In this case, the catalyst was prepared through a copper-catalyzed Fokin–Huisgen reaction of a PEG-azide and a propargyl diarylprolinol silyl ether. The catalyst **36** so formed was then tested in asymmetric Michael addition of nitromethane to α,β -unsaturated aldehydes in methanol (Scheme 3). The yields and enantioselective excess (ee) of the products formed in these reactions were comparable to those of products prepared with low-molecular-weight catalysts. In these cases, the polymer-bound catalyst **36** could be precipitated and recovered by adding the reaction mixture into ether, separating a recoverable form of **36** from the products.

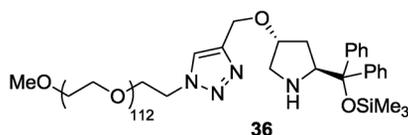
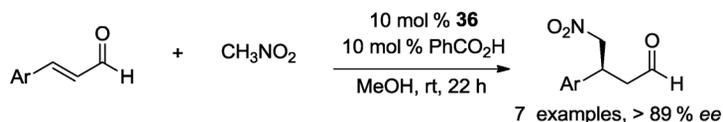


Fig. 4 PEG-supported Jørgensen–Hayashi catalyst **36**.



Scheme 3 Asymmetric Michael addition catalyzed by **36**.

To examine the recyclability of catalyst **36**, nitromethane and cinnamaldehyde were chosen as the substrates for an asymmetric Michael reaction. The catalyst was reused four times in this Michael reaction providing products with good enantioselectivity. However, the yields of the product were seen to decrease as the catalyst was recycled. In this instance, the catalyst deactivation was attributed to the formation of a catalyst-product adduct. The authors found that stirring of the recovered catalyst **36** with a solution of cinnamaldehyde (the substrate to be used for the following cycle) can restore the catalytic activity.

The common use of L-proline as an efficient organocatalyst has led to a significant number of other polymer-supported L-proline analogs that have been used as recyclable and reusable organocatalysts [8]. This is illustrated by work by Benaglia and Zhao who prepared the PEG-supported L-proline derivatives **37** and **38** shown in Fig. 5 as polymer-supported organocatalysts in aldol reactions and Mannich reactions (Scheme 4) [31,32]. When 4-nitrobenzaldehyde was used as the aldehyde substrate with dimethylsulfoxide (DMSO) as the solvent, the aldol product was isolated in 73 % yield with 62 % ee. An aldol reaction catalyzed by (2*S*,4*R*)-4-acetoxypoline as the low-molecular-weight catalyst under similar conditions afforded the aldol product with 70 % yield and 74 % ee [33]. Recyclability of the polymeric proline aldol catalyst **37** was examined using 4-nitrobenzaldehyde as the substrate and

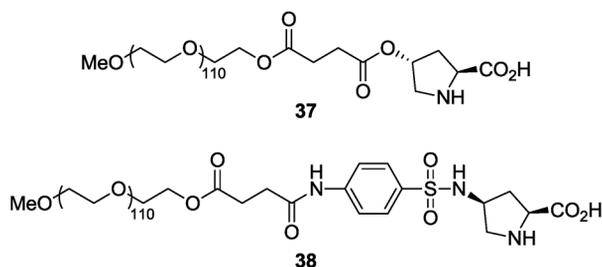
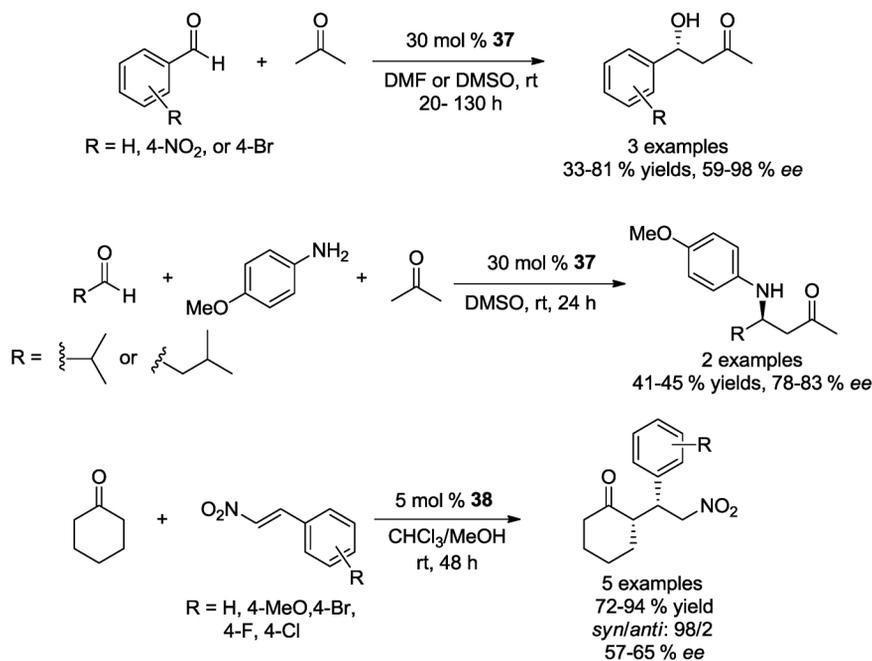


Fig. 5 PEG-supported L-proline derivatives.



Scheme 4 Asymmetric aldol, Mannich, and Michael addition reactions catalyzed by **37** and **38**.

dimethylformamide (DMF) as the solvent. The polymer-bound catalyst **37** was precipitated and recycled by adding the reaction mixture into ether. The catalyst **37** was recycled and reused for three times providing the aldol product with 77 % enantioselectivity but with yields that slightly decreased from 68 % in the first run to 51 % in the fourth run.

The polymer-bound L-proline **38** was used as a catalyst in a Michael addition reaction of cyclohexanone to nitrostyrene using MeOH as the solvent affording the product in 92 % yield with 46 % ee. The same reaction catalyzed by (2*S*,4*S*)-4-acetoxypoline as the low-molecular-weight catalyst under similar conditions afforded the product in 89 % yield and 40 % ee. Recycling experiments were carried out by using 4-nitrostyrene and cyclohexanone as the substrates. The PEG-bound catalyst **38** was collected by precipitation and filtration after adding the reaction mixture to ether. In this case, the PEG-bound catalyst **38** was recycled and reused three times. However, significant decreases in yield from 94 % in the first run to 24 % in the fourth run was seen along with a decrease in ee values from 60 % in the first run to <10 % in the fourth run.

Several reports have described polystyrene-supported organocatalysts. Toy reported a styrene copolymer **39** containing dimethylaminopyridine (DMAP) and piperazine moieties as shown in Fig. 6 [34]. In this report, the soluble polymer was designed to serve as a bifunctional catalyst. In the work reported, this polymer was used as an organocatalyst in Doebner–Knoevenagel reactions as shown in Scheme 5. A variety of substrates were examined in these condensation reactions, and in most cases good yields were obtained along with good *E/Z* selectivity. However, attempts to recover and reuse the organocatalyst **39** failed due to difficulty in precipitating **39** from the reaction mixtures. The inability to recover a pure catalyst precluded recycling.

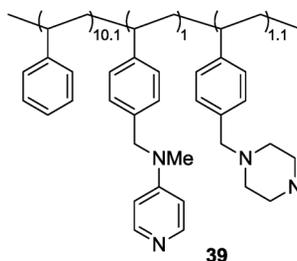
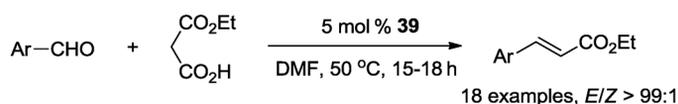


Fig. 6 Styrene copolymer **39** containing DMAP and piperazine moieties.



Scheme 5 Doebner–Knoevenagel condensation reactions catalyzed by **39**.

Toy [35] also synthesized the styrene copolymer **40** that contained trialkylamine and thiourea moieties as shown in Fig. 7. In this case, the soluble polymer was designed to serve as a bifunctional catalyst. The trialkylamine group on polymer can serve as a base for the nitroalkane or ylide precursor while the thiourea moiety can serve as a hydrogen-bonding activator for the nitroalkene group. This bifunctional polymer **40** was used as a catalyst in addition reactions of nitrostyrenes and sulfur ylides as shown in Scheme 6. These addition reactions proceeded in good yields with good *syn/anti* selectivity. In the addition reaction of sulfur ylides, a variety of cyclized products with moderate yields and good stereoselectivity were prepared [36]. However, recycling of **40** was not described.

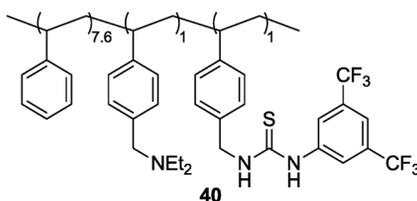
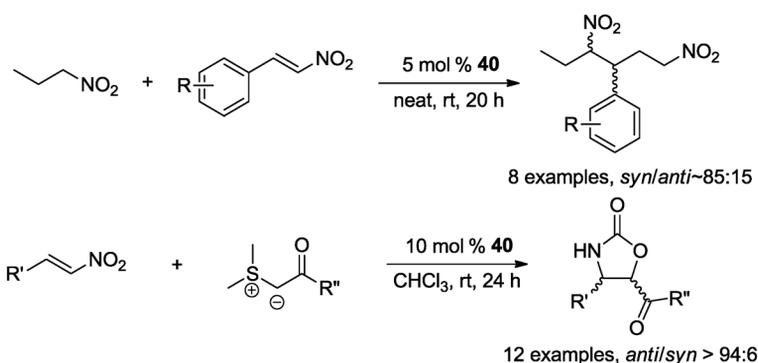
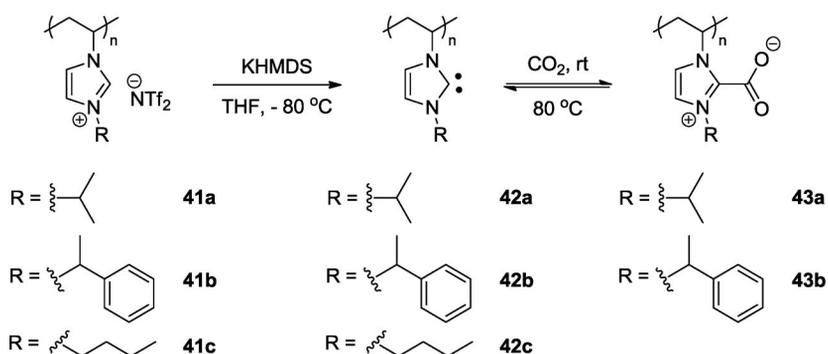


Fig. 7 Styrene copolymer **40** containing amine and thiourea moieties.

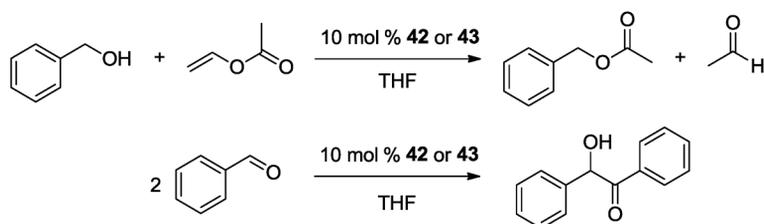


Scheme 6 Addition reactions catalyzed by **40**.

Linear polymers with polar pendant groups have also been used as soluble catalysts. For example, Pinaud and co-workers reported syntheses of poly(vinylimidazolium salt) **41** (Scheme 7) [37]. These imidazolium salts form corresponding *N*-heterocyclic carbenes (NHCs) **42** on deprotonation that lead in turn to CO₂ adducts **43** on exposure to CO₂. These CO₂ adducts are in equilibrium with the free carbenes, and the amount of free carbene present becomes significant on heating to 80 °C. Thus, on heating the polymers **43** could be used as organocatalysts in transesterification and benzoin condensation reactions as shown in Scheme 8. The free carbene **42** itself was also used as a polymer-bound catalyst. In this case, recycling the polymer-bound catalyst involved precipitating **42** by adding the reaction mixture to excess ether. In the case of **43**, the CO₂ adduct serves as a latent NHC catalyst that can be recovered at the end of a reaction by bubbling CO₂ through the cooled reaction mixture to reform the polymer-bound CO₂ adduct which precipitated. A simple filtration was used to recover the CO₂ adduct. This latter procedure has the advantage that it avoids the use of excess ether solvent.



Scheme 7 Polymer-bound imidazolium salts, NHCs, and CO₂ adducts.



Scheme 8 Benzoin condensation and transesterification reactions catalyzed by **42** and **43**.

While **42** and **43** can catalyze the transesterification providing the products in good yields in the first run, the product yields decreased significantly after the first run when the free carbene **42** was used. This could be due to the air and moisture sensitivity or dimerization of this NHC organocatalysts. Catalysis using the CO₂ adduct **43** showed better recyclability and **43b** was successfully recycled and reused for seven runs in the transesterification reaction providing an average yield of 76 % per run. In the benzoin condensation reaction, moderate-to-good yields were obtained with catalysts **42** and **43** in the first runs except for **42c**. However, recycling **42** and **43** were not successful as much lower yields of the product were obtained in the following cycles.

While polymers like PIB are achiral, polymers like polystyrene contain chiral centers. The general assumption with soluble polymer supports is the same as that with insoluble polystyrene supports and is that the chiral centers on polymer have little or no influence on an asymmetric catalytic reaction [38]. However, this assumption is not always true as shown by work by Miyake and co-workers who used cinchona alkaloid catalysts supported on poly(phenylacetylene)s (Fig. 8) as chiral catalysts in asymmetric synthesis [39]. In this instance, the chiral arylacetylene monomers were polymerized with a rhodium catalyst to form helical polymers **44** and **45**. These polyacetylene polymers have a chiral helical conformation, and the helical conformation of the support is believed to enhance enantioselectivity of Cinchona alkaloid catalysts compared to catalysts not attached to a helical polymer support. The catalytic activity of these polymer-supported cinchona alkaloids was studied in the Michael addition and Henry reactions shown in Scheme 9. In the Michael addition reactions, **44a** and **45a** were successful catalysts providing products with good yields with a modest ~30 % ee. In the case of **44a**, the organocatalyst can be recovered and reused twice affording products in similar yields and stereoselectivity in cycles 2 and 3. It is noteworthy in this case that the polymer served two roles—separation and enhancement of catalyst activity—since the low-molecular-weight catalyst was less stereoselective under similar conditions. In the Henry reactions, polymer-bound catalysts **44b** and **45b** were able to catalyze the reactions with moderate yields. However, only **44b** provided better enantioselectivity than its low-molecular-weight counterpart.

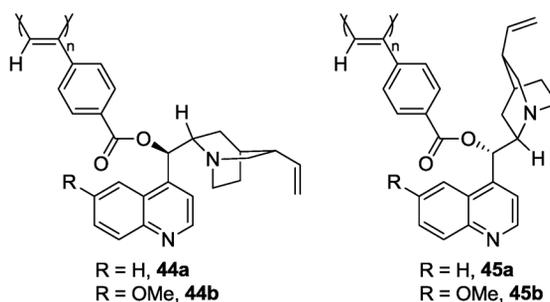
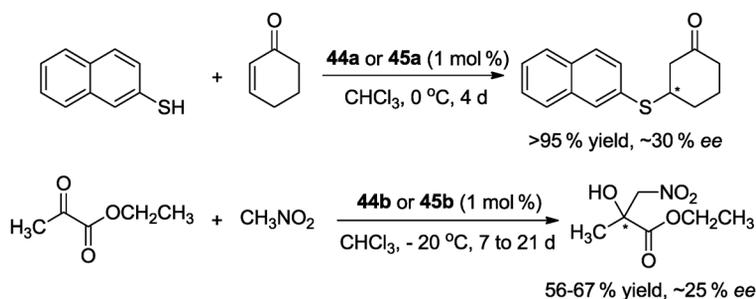


Fig. 8 Poly(phenylacetylene)-supported cinchona alkaloids.



Scheme 9 Asymmetric Michael and Henry reactions catalyzed by **44** or **45**.

Dendrimers are another class of functional soluble polymers that can be used as supports for catalysts and reagents [40]. This is illustrated by work by Bellis and Kokotos who prepared L-proline-modified poly(propyleneimine) dendrimers with five generations **46–50** (Fig. 9) [41]. These L-proline-modified dendrimers along with L-proline hydrochloride **51** were examined as catalyst precursors in the aldol reaction of acetone and 4-nitrobenzaldehyde (Scheme 10). Triethylamine was used as a base to generate proline moieties in situ. When L-proline hydrochloride **51** was used as a low-molecular-weight catalyst, the aldol product was isolated in 60 % yield with 63 % ee. Among the different generations of dendrimer-supported proline catalysts, the second-generation proline-modified dendrimer **47** showed the best results that the aldol product was isolated in 70 % yield with 53 % ee. Reactions using dendrimers with higher generations **48–50** with the same proline loading provided 60–68 % yields of the product but with lower enantioselectivity (21–41 % ee). Recycling of these dendrimer-supported prolines was not described.

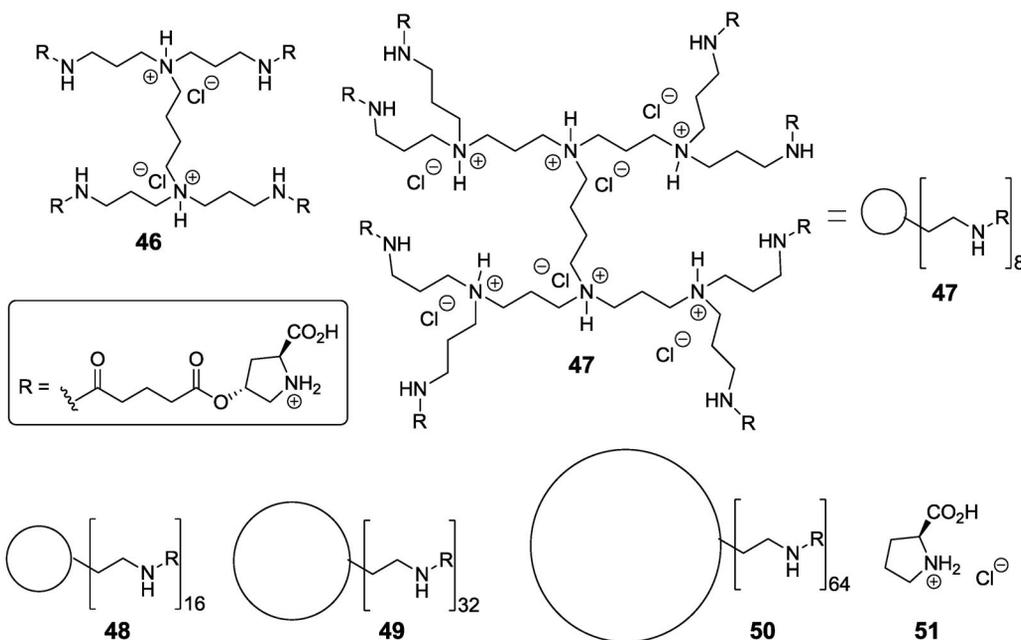
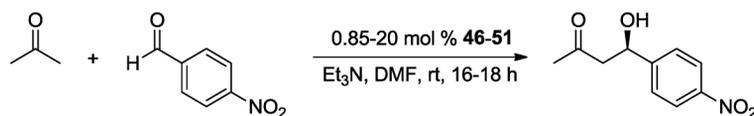


Fig. 9 Dendrimer-supported proline catalysts.



Scheme 10 Aldol reaction catalyzed by dendrimer-supported prolines.

In 2009, Lo and Chow reported synthesis of a series of pyrrolidines with different generations of aliphatic dendrons (Fig. 10) [42]. These authors used these dendrimer-supported diamino organocatalysts for aldol reactions and nitro-Michael reactions under emulsified reaction conditions (Scheme 11). In the aldol reactions, a mixture of products (four isomers) was obtained in moderate yields. In this chemistry, the *anti* products were the major products and were formed with good stereoselectivity (>85 % ee). In the nitro-Michael reactions, the *syn* products were the major products and were formed with moderate enantioselectivity. The authors found that the dendrimers **55** and **56** are

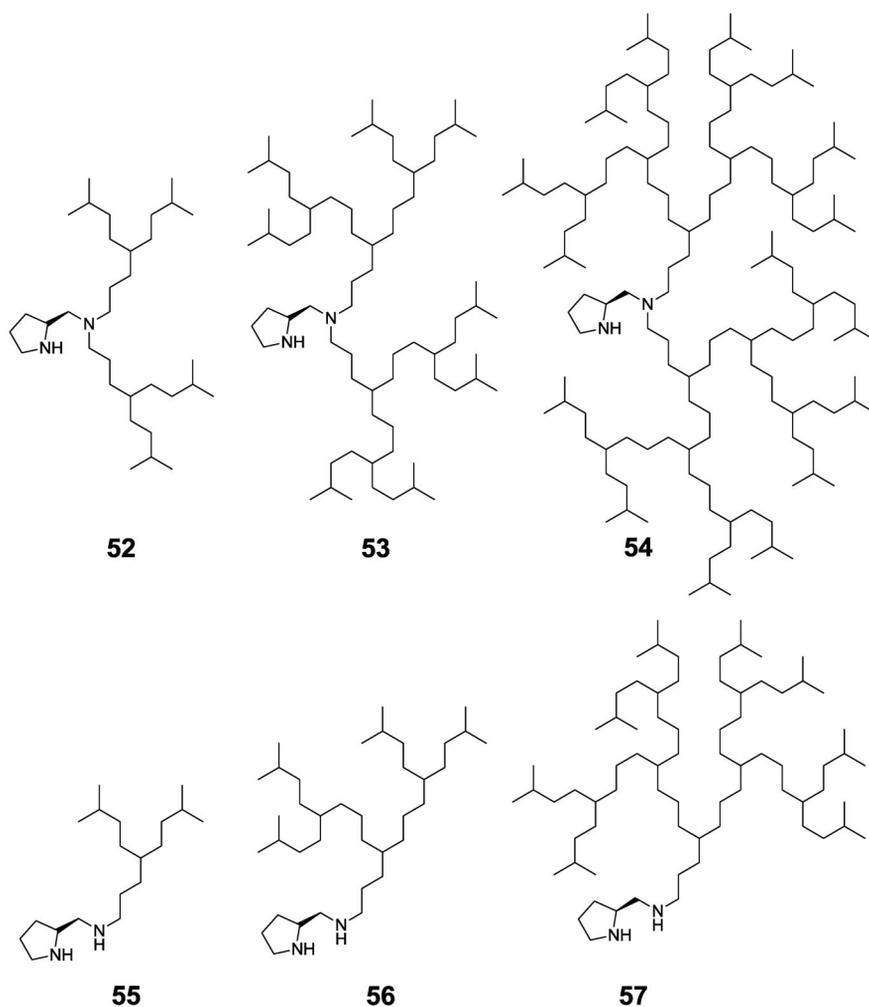
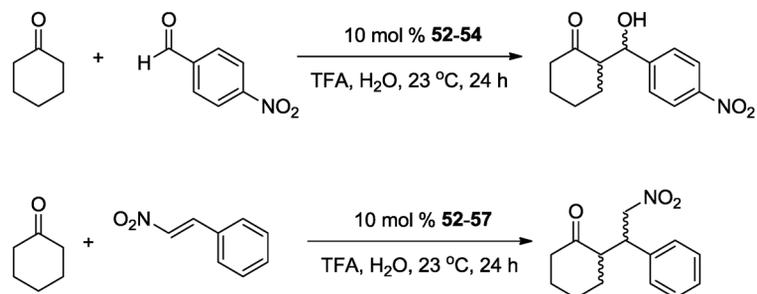


Fig. 10 Dendrimer-supported diamino organocatalysts.



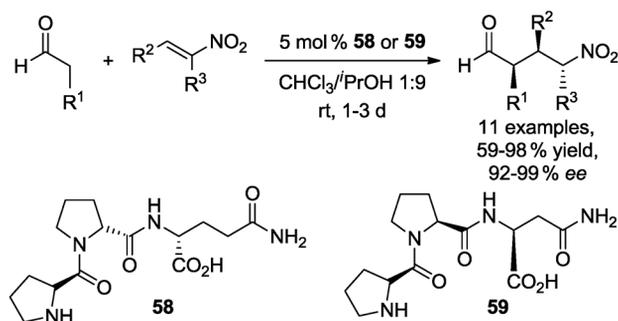
Scheme 11 Aldol and nitro-Michael reactions catalyzed by dendrimer-supported catalysts.

phase selectively soluble in heptane phase in a biphasic heptane/MeOH mixture. Therefore, recycling dendrimers **55** and **56** was possible in a nitro-Michael reaction in which the crude product mixture was dissolved in a mixture of heptane and MeOH and the catalyst was selectively soluble in the heptane

phase and the product mixture was selectively soluble in the MeOH phase. This group found that both **55** and **56** could be reused four times providing a mixture of products with similar yields and stereoselectivity comparable to that of the first cycle.

Catalysts **55** and **56** were also examined in aldol reactions. In these cases, similar yields and stereoselectivity were also observed in the product mixtures throughout five cycles.

Enzymes are polymers too and serve as useful soluble catalysts. While enzymes per se are outside the province of this review, it is worth noting that smaller soluble synthetic peptides can also be used as catalysts for asymmetric catalysis. While examples of such catalysts have been known for some time, the use of these types of soluble polymers as organocatalysts has received more attention recently [17,20,43,44]. For example, Duschmalé and Wennemers [45] reported success in using various tripeptides for asymmetric conjugate addition reactions of aldehydes to α,β -disubstituted nitroolefins. Among the screened tripeptides, **58** and **59** provided the best catalytic activity and stereoselectivity (Scheme 12). Recycling of **58** and **59** was not described.



Scheme 12 Addition reactions of aldehydes to α,β -disubstituted nitroolefins.

While the most common approach to immobilization of a catalyst on a polymer is via covalent bonds, ionically linked catalysts have also been studied. Several examples of this approach have been reported recently with soluble linear organic polymers. This is illustrated by work by Zlotin and co-workers who used poly(styrene sulfonate) salt as the support to ionically attach a Jørgensen–Hayashi catalyst to a polymer (Fig. 11) [46]. A low-molecular-weight analog was also prepared for comparison.

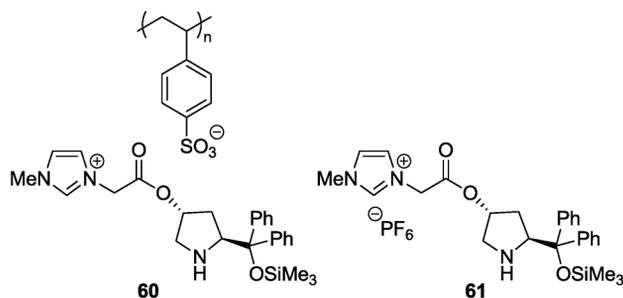
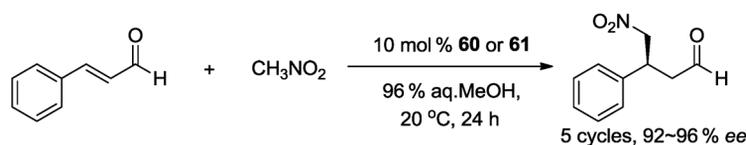


Fig. 11 Ionic Jørgensen–Hayashi catalysts.

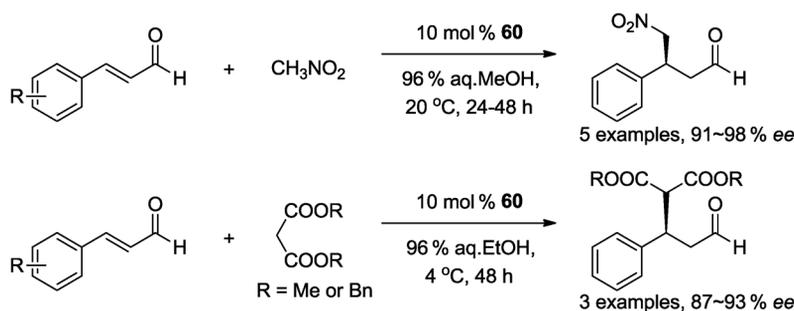
Polymer-bound ionically linked catalyst **60** was examined in a Michael addition reaction in which cinnamaldehyde and nitromethane were chosen as the substrates (Scheme 13) and compared with the non-polymeric Jørgensen–Hayashi catalyst **61**. Both of these catalysts catalyze the Michael reaction



Scheme 13 Michael addition reactions catalyzed by **60** or **61**.

with excellent conversions along with good enantioselectivity. Interestingly, both of the catalysts can be recovered at least four times by removal of the solvents and the product can be extracted by ether. In this case, decreasing conversion seen in the fourth and fifth runs was a more significant problem with **61**. This lowered conversion was attributed to physical losses of catalyst during work-up where **61**, which was recovered as an ionic liquid, lost ~20% of its original mass. In contrast, the ionically linked polymer-bound catalyst **61** had higher turnover number through five cycles with less than 5% loss of mass after five cycles.

The catalytic activity of polymer-supported catalyst **60** was also examined in asymmetric Michael additions with a variety of substrates (Scheme 14). By using similar reaction conditions, a variety of products were prepared with moderate-to-good yields and good enantioselectivity comparable to that of products prepared with **61**.



Scheme 14 Asymmetric Michael additions catalyzed by **60**.

Soluble polymeric organocatalysts can also be prepared by using the organocatalyst as a monomer in formation of supramolecular ionic polymers. While such supramolecular polymers are not assembled with covalent bonds between monomer units such material can exhibit many of the properties associated with polymers [47]. An example where such materials have been used as organocatalysts is seen in work by Itsuno and co-workers [48,49] who prepared several polymeric quaternary ammonium sulfonate supramolecular polymers **62** (Fig. 12). These polymers are insoluble in water and common organic solvents but are soluble in DMF and DMSO. Thus, these catalysts like other soluble polymer-bound catalysts can be characterized easily using conventional solution-state spectroscopic techniques.

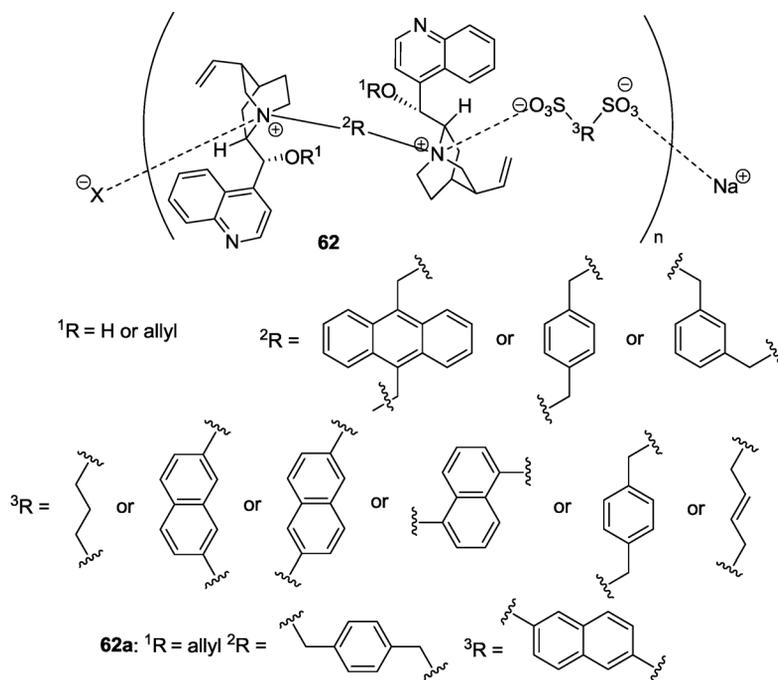
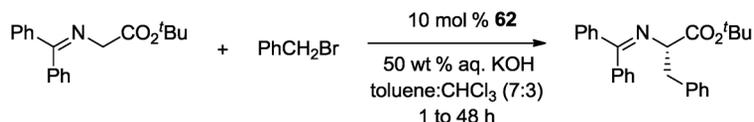


Fig. 12 Ionic polymer bearing chiral quaternary ammonium salts.

The catalytic activity of polymers **62** in an asymmetric benzylation of *N*-diphenylmethylene glycine *tert*-butyl ester is shown in Scheme 15. The reactions were carried out in a biphasic system consisting of an aqueous phase and an organic phase (a mixture of toluene and chloroform). While these polymers are soluble in polar organic solvents, polymers **62** were present as a solid suspension in this relatively nonpolar organic phase during the course of these phase-transfer catalyzed benzylation reactions. When the reactions were finished, the polymers were recovered by filtration. The polymer's stability was tested by analyzing the molecular weight of the recovered polymer, which did not show any change in intrinsic viscosity values. NMR spectroscopy was also used to show that the polymers' functionality was unchanged. One of the polymers, **62a**, was found to be reusable for three cycles giving the similar yields and ee values of the product.



Scheme 15 Asymmetric benzylation of *N*-diphenylmethylene glycine *tert*-butyl ester.

A MacMillan imidazolidinone catalyst was also ionically supported on similar polymers **63** by Haraguchi and co-workers [50] as shown in Fig. 13. These polymers have solubility properties like those of **62**, and their molecular weight distribution and degree of polymerization were analyzed by gel permeation chromatography (GPC). Both ionic polymers **63** and their low-molecular-weight analogs **64** were used in an asymmetric Diels–Alder reaction of cyclopentadiene and cinnamaldehyde (Scheme 16).

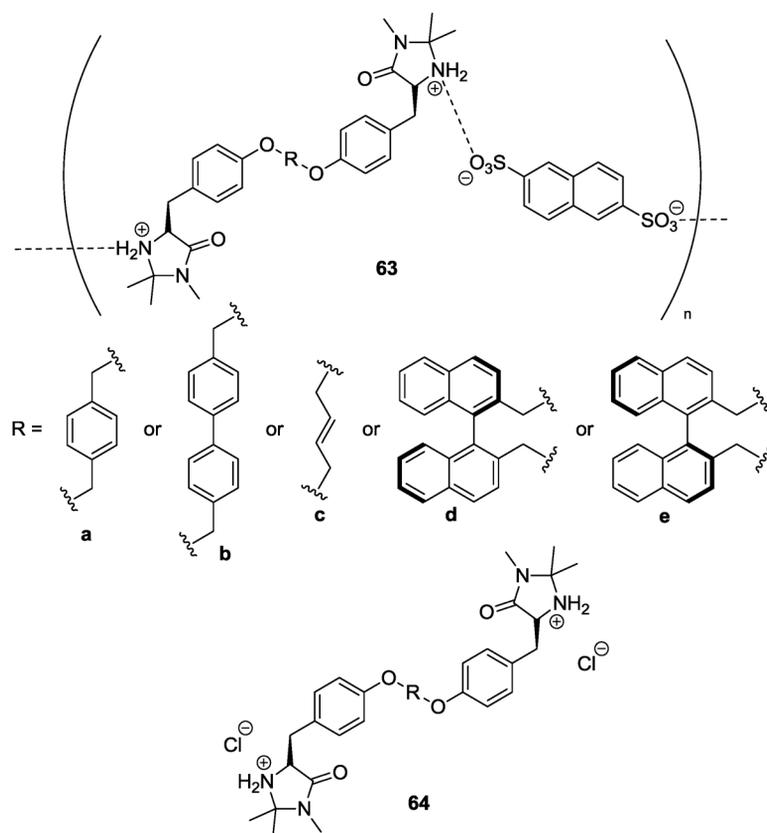
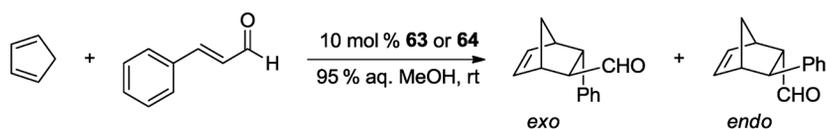


Fig. 13 Ionic polymers bearing imidazolium salts.



Scheme 16 Asymmetric Diels–Alder reaction.

The low-molecular-weight analog **64** was soluble in the reaction mixture and was able to catalyze the reaction to provide >90 % conversions with good ee values for the *endo* and *exo* product mixtures. When insoluble ionic polymers **63** were examined in the same reaction, longer reaction time was required to achieve good conversions, but the *exo/endo* ratios and ee values of the product mixtures were very similar to those of product mixtures obtained from **64**.

One ionic polymer **63c** was recovered and reused for two cycles. Although the *exo/endo* ratios and ee values of the product mixtures were very similar to those obtained in the first cycle, longer reaction times (two and three days for cycle two and three compared to one day for cycle one) were required with the recycled catalyst. While GPC analysis of the recovered **63c** after cycle three did not show significant change in terms of polydispersity index (PDI) and degree of polymerization, catalyst deactivation was still suggested as the reason for slower reactions with **63c**.

CONCLUSION

Recent reports using soluble polymer-supported organocatalysts including pyridine *N*-oxide, phosphines, NHCs, DMAP, thiourea, cinchona alkaloids, Jørgensen–Hayashi catalysts, MacMillan catalysts, peptides, and proline derivatives are discussed. Many of these catalysts can be recycled and reused giving similar conversion and selectivity of products compared to those prepared from non-supported catalysts, suggesting that strategies that efficiently and simply separate organocatalysts from products without catalyst deactivation could be a practical way to use organocatalysts that often are used at high mol % loadings.

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