Use of an Isotactic-Propylene/Hexene Copolymer as a New, Versatile, Soluble Support

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ABSTRACT: The use of isotactic-poly(propylene-*co*-hexene) (iPPH) as new polymeric scaffold for synthesis as well as a phase-selective, soluble polymer support for homogeneous catalysis is described. It was possible to functionalize olefin-terminated iPPH using standard organic transformations. Each derivative could be isolated and purified using typical precipitations into a minimum amount of polar solvent, negating the need for wasteful work up and chromatographic procedures. Furthermore, it was demonstrated that an iPPH-supported DMAP could serve as a recoverable, recyclable catalyst. Published 2013.† J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 600–605

KEYWORDS: green chemistry; organocatalysis; polymer-bound DMAP; polymer chemistry; polymer-supported catalysis; polyolefins; recyclable catalysts, supports; synthesis

INTRODUCTION The use of polymers as supports for homogeneous catalysts/reagents is still an important goal in synthetic chemistry as it allows for catalyst recovery and reuse. It also serves as an example of green chemistry as it reduces the amount of environmentally detrimental waste generated in catalytic processes. Some of the oldest examples utilized insoluble polymer supported-catalysts/reagents based off of cross-linked polystyrene (PS) resins.[1–3] Although this is a well-seasoned principle, it still sees use. Recently, Toy et al. has reported on a Rasta resin supported TBD as a recoverable catalyst for transesterifications.[4] Although catalyst recovery can be carried out using simple gravity filtration, the characterization of such insoluble, resin-supported catalysts can be difficult, as solution-state NMR spectroscopy cannot be used.

On the other hand, various soluble polymers have been used as supports for homogeneous catalysts. Bergbreiter et al. pioneered the use of polyethylene oligomers[1,2] as soluble supports, chemistry that is currently experiencing resurgence in the literature.[5–8] Numerous other types of polymer supports have been studied and most of them are typically recovered using either a solid/liquid or liquid/liquid technique.[1–10]

Although useful, many of the polymers used lack versatility; they are mostly limited to one type of recovery technique. For instance, since amorphous materials such as polyisobutylene[1,2,8] and atactic-polypropylene[11] cannot be precipitated, they are typically restricted to liquid/liquid separations, in which the supported catalyst/reagent and product are separated in two different solvent phases. Under special circumstances, however, solid/liquid techniques in which precipitation of the products away from the catalyst can occur,[4,12] although this self-separation is not typical. On the other hand, catalysts anchored to polymers such as poly(ethylene glycol), noncrosslinked PS, and ring-opening metathesis polymerization-based supports are almost always separated as solids using solvent precipitations. This is because such polymers typically lack the phase-selective solubility required for liquid/liquid separations.[1,2] Recently, though, Bergbreiter et al. have studied highly phase-selectively soluble linear PS derivatives.[10]

While liquid/liquid and solid/liquid separations each have their own advantages, in some cases, it may be desirable to use a more versatile polymer support that can be recovered using either system instead of relying on specifically engineered reaction conditions in which product precipitation occurs. We show herein that commercially-available,[13] isotactic-poly(propylene-*co*-hexene) (iPPH) can serve as a useful synthetic scaffold that can be transformed using standard, organic reactions to provide iPPH derivatives that can be easily isolated in good yield. Furthermore, these species require little purification (i.e., no column chromatography or wasteful workup procedures). We also demonstrate the prowess of this material to serve as a new, versatile polymer support through the preparation and use of a supported DMAP catalyst that can be recovered and recycled using both liquid/liquid and liquid/solid separations.

EXPERIMENTAL

General Experimental Procedures

Olefin-terminated samples of isotactic-poly(propylene-co-hexene) (iPPH) were donated by Baker Hughes. All other reagents were purchased from commercial suppliers (Aldrich, Alfa-Aesar, or VWR) and were used without further purification. ^{1}H and ^{13}C NMR spectra were obtained on an Agilent 400-MHz spectrometer operating at 399.7962 and 100.5288 MHz, respectively. All peaks are reported in ppm and are referenced to the residual $CHCl_3$ peak in $CDCl_3$. FTIR spectra were obtained on a Perkin Elmer Spectrum 100 spectrometer. The phase-selective solubility of **6** was determined using literature procedures[10,14] on a Photon Technology International fluorometer. Chromatographic purification of **10** was performed on a Grace Reveleris automated flash chromatography system equipped with simultaneous UV–vis and ELSD detection.

Hydroxy-Terminated iPPH (2)

To a 250-mL, round-bottomed flask, equipped with a magnetic stir bar and a rubber septum was added olefin-terminated iPPH **1** (4 g, 2 mmol) and THF (20 mL). While stirring at room temperature, $BH_3{\cdot}SMe_2$ (0.57 mL, 0.46 mmol) was added via syringe and the reaction mixture was allowed to stir for 1 h. At this time, an aqueous solution of NaOH (6 mL, 4 M) was added to the reaction mixture, followed by H_2O_2 (8 mL, 30%). The heterogeneous reaction mixture was allowed to stir for 1 h. At this time, THF (10 mL) was added to dissolve all of the material, which was then precipitated into MeOH (50 mL). The suspension was separated by vacuum filtration in which 3.6 g of **2** was isolated as a white powder in 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61–3.33 (m, 2H), 1.75–0.8 (m, 228H).

iPPH-Mesylate (3)

To a 25-mL, round-bottomed flask equipped with a magnetic stir bar and a rubber septum was added **2** (2.9 g, 1.45 mmol) followed by CH_2Cl_2 (42 mL). While stirring, the reaction mixture was charged with triethylamine (1.38 mL, 9.95 mmol) followed by methanesulfonylchloride (0.72 mL, 9.3 mmol). This reaction mixture was allowed to stir at room temperature for 45 min. Upon completion, the reaction mixture was precipitated into MeOH (30 mL). The suspension was separated by vacuum filtration in which 2.75 g of **3** was isolated as a white powder in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18–3.98 (m, 2H), 2.99 (s, 3H), 1.75–0.8 (m, 228H).

iPPH-Azide (4)

To a 25-mL, round-bottomed flask equipped with a magnetic stir bar, water-jacketed reflux condenser, and a rubber septum was added **3** (0.175 g, 0.088 mmol), KN_3 (0.036 g, 0.438 mmol), and a 1:1 mixture of toluene and DMF (2 mL). This mixture was placed on an oil bath regulated at 100 °C and was allowed to stir for 1 h. At this time, the reaction mixture was allowed to cool to room temperature and was then precipitated into MeOH (10 mL). The suspension was separated by vacuum filtration in which 0.155 g of **5** was isolated as a white powder in 89% yield.

FTIR (neat, cm^{-1}) 2954.63, 2917.52, 2871.51, 2098.29, 1458.18, 1376.47; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25–3.01 (m, 2H), 1.75–0.8 (m, 230H).

N-Ethyl-N-propargyl-dansyl (5)

To a 25-mL, round-bottomed flask equipped with a magnetic stir bar and a rubber septum was added dansyl chloride (0.5 g, 1.85 mmol), aminoethane (0.24 mL, 3.71 mmol), and CH_2Cl_2 (12 mL). This reaction mixture was allowed to stir at room temperature for 20 min. At this time, CH_2Cl_2 (30 mL) was added to this mixture and the organic layer was washed with three 25 mL portions of water, one 25 mL portion of brine, and then dried over Na_2SO_4 followed by filtration and removal of the solvent under reduced pressure to give 0.37 g of *N*-ethyl dansyl as a yellow solid in 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, $J = 8.5$ Hz, 1H), 8.30–8.24 (m, 2H), 7.60–7.50 (m, 2H), 7.19 (d, $J = 7.9$ Hz, 1H), 4.49 (t, $J = 6.1$ H, 1H), 2.95 (q, $J = 14.2$, 7.2 Hz, 2H), 2.89 (s, 6H), 1.03 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.07, 130.41, 129.69, 129.36, 123.18, 118.64, 115.15, 45.40, 38.37, 15.13, 0.03. This material was used without further purification.

To a 25-mL, round-bottomed flask equipped with a magnetic stir bar, a rubber septum, and a water-jacketed reflux condenser was added *N*-ethyl dansyl (0.2 g, 0.76 mmol), K_2CO_3 (0.99 g, 7.2 mmol), and DMF (4 mL). This mixture was allowed to stir at room temperature for 10 min. At this time, an 80% toluene solution of propargyl bromide (0.133 g, 0.9 mmol) was added and the flask was placed on an oil bath regulated at 75 °C and allowed to stir for 12 h. At this time, the reaction was allowed to cool to room temperature followed by the addition of ether and water. The organic layer was isolated and washed with three 25 mL portions of water, one 25 mL portion of brine, and then dried over Na_2SO_4 followed by filtration and removal of the solvent under reduced pressure to give 0.22 g of **5** as a yellow oil (that crystallized upon standing) in 80% yield, based on ^{1}H NMR analysis. **5** was used without any further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, $J = 8.6$ Hz, 1H), 8.32–8.19 (m, 2H), 7.59–7.47 (m, 2H), 7.21–7.14 (m, 1H), 4.29 (d, $J = 2.3$ Hz, 2H), 3.42 (q, $J = 14.5$, 7.4 Hz, 2H), 2.87 (s, 6H), 2.10 (t, $J = 2.4$ Hz, 1H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.7, 130.46, 128.15, 127.99, 123.19, 122.19, 119.63, 113.64, 115.16, 73.21, 45.49, 41.15, 38.47, 35.14, 15.18, 13.06.

General Procedure for CuAAC Reactions with iPPH-Azide (4)

To a 25-mL, two-necked, round-bottomed flask equipped with a magnetic stir bar, water-jacketed reflux condenser, and a rubber septum was added **4** (1 equiv), alkyne

(2 equiv), CuBr (10 mol %), and PMDETA (10 mol %). This flask was then charged with a 1:1 mixture of toluene and DMF and sparged with N_2 for 15 min. The reaction mixture was then placed on an oil bath regulated at 105 °C and was allowed to stir for 1 h. At this time, the reaction mixture was allowed to cool to room temperature and was then precipitated into MeOH (10 mL). The suspension was separated by vacuum filtration and the triazole product was isolated as a light brown or white powder.

Dansyl-Labeled iPPH (6)

Precipitation into methanol followed by isolation by vacuum filtration provided 0.072 g of **6** in 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, $J = 8.4$ Hz, 1H), 8.27 (d, $J = 8.7$ Hz, 1H), 8.18 (d, $J = 7.1$ Hz, 1H), 7.58–7.48 (m, 2H), 7.43 (s, 1H), 7.22–7.17 (m, 1H), 4.62 (s, 2H), 4.26–3.92 (m, 2H), 3.35 (q, $J = 14.2$, 7.5 Hz, 2H), 2.89 (s, 6H), 1.75–0.8 (m, 230H).

iPPH-Supported Pyridine (8)

Precipitation into methanol followed by isolation by vacuum filtration provided 0.18 g of **8** in 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.41 (d, $J = 7.8$ Hz, 2H), 6.4 (d, $J = 7.8$ Hz, 2H), 5.1 (s, 2H), 4.4–4.1 (m, 2H), 1.75–0.8 (m, 273H).

iPPH-Supported DMAP (11)

Precipitation into methanol followed by isolation by vacuum filtration provided **11** as a powder that was then dissolved in THF and passed through a short alumina plug to yield 0.18 g of **11** in 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (broad s, 3H), 6.59 (broad s, 2H), 4.64 (s, 2H), 4.29–3.98 (m, 2H), 3.1 (s, 3H), 1.75–0.8 (m, 273H).

4-(N-Methyl-N-propargylamino)pyridine (10)

To a 25-mL, round-bottomed flask, equipped with a magnetic stir bar and rubber septum was added MAP (1.0 g, 9.26 mmol) and THF (10 mL). This solution was cooled to −90 °C in an acetone/N_2 (l) bath. The cooled mixture was allowed to stir for 20 min. At this time, nBuLi (1.6 M, 6.6 mL, 10.56 mmol) was added via syringe and the reaction mixture was allowed to stir for 2 h while warming to −20 °C. Upon reaching this temperature, an 80% toluene solution of propargyl bromide (2.98 g, 13.9 mmol) was added via syringe and the reaction mixture was allowed to slowly warm to room temperature and was stirred for 24 h. At this time, the reaction was quenched by the addition of H_2O. The solvent was removed under reduced pressure followed by the addition of CH_2Cl_2 (50 mL). This organic layer was washed with three 25 mL portions of water and one 25-mL portion of brine. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure to give 0.85 g of **10** in 85% yield. **10** could be purified by automated flash column chromatography (0–100% ethyl acetate in hexane gradient), but, in most cases, was used without further purification.

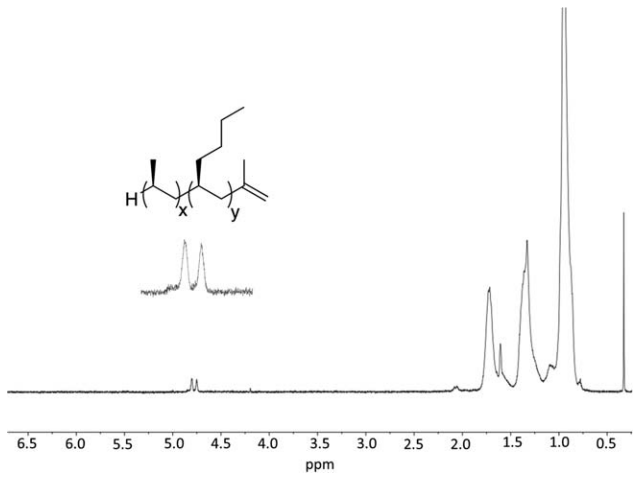
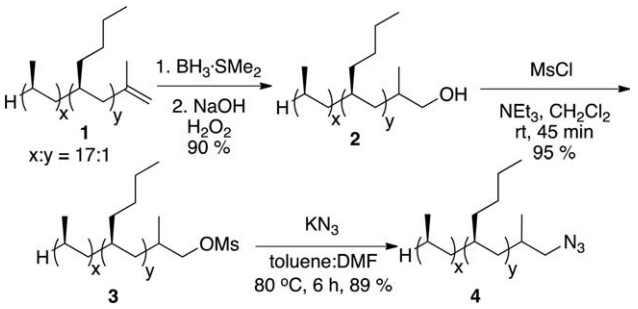


FIGURE 1 ^{1}H NMR spectrum of olefin-terminated 1 showing the signals corresponding to the terminal, disubstituted olefin.



SCHEME 1 Syntheses of iPPH derivatives.

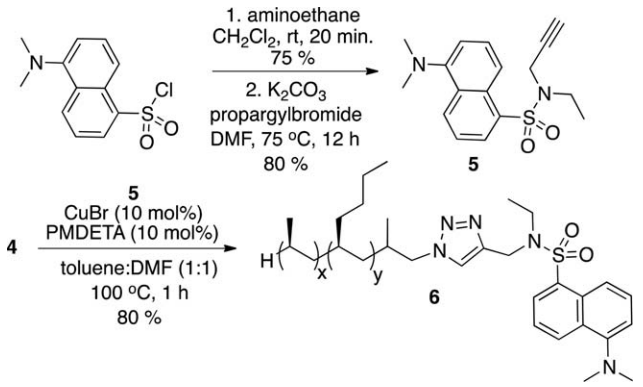
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.4 (d, $J = 6.6$ Hz, 2H), 6.6 (d, $J = 6.7$ Hz, 2H), 4.0 (d, $J = 2.4$ Hz, 2H), 3.0 (s, 3H), 2.2 (t, $J = 2.7$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154, 150, 107, 73, 40, 36.

Boc-Protection of 2,6-Dimethylphenol Catalyzed by 11 Using Solid/Liquid Separation for Catalyst Recovery

To a 5-mL, round-bottomed flask, equipped with a stir bar and a rubber septum was added **11** (0.1 g, 0.05 mmol), 2,6-dimethylphenol (0.122 g, 0.998 mmol), Boc_2O (0.23 g, 1 mmol), and THF (2 mL). This mixture was allowed to stir for 25 min followed by the addition of MeOH (10 mL), which caused **11** to precipitate. This suspension was subjected to centrifugation followed by decantation of the product-containing solvent phase. Pure product was isolated by removal of the solvent under reduced pressure while **11** was reused by the addition of fresh solvent and substrates. **11** could be reused four times with an average product yield of 94%. Product spectral data matched literature examples.[10]

Boc-Protection of 2,6-Dimethylphenol Catalyzed by 11 Using Liquid/Liquid Separation for Catalyst Recovery

To a 5-mL, round-bottomed flask, equipped with a stir bar and a rubber septum was added **11** (0.1 g, 0.05 mmol), 2,6-dimethylphenol (0.122 g, 0.998 mmol), Boc_2O (0.23 g, 1 mmol), and heptane (2 mL). This mixture was allowed to stir for 25 min followed by the addition of CH_3CN (2 mL),



SCHEME 2 Synthesis of dansyl-labeled iPPH 6.

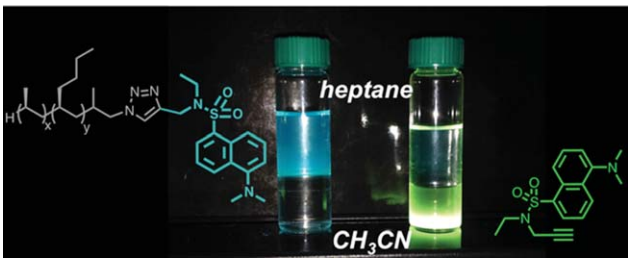


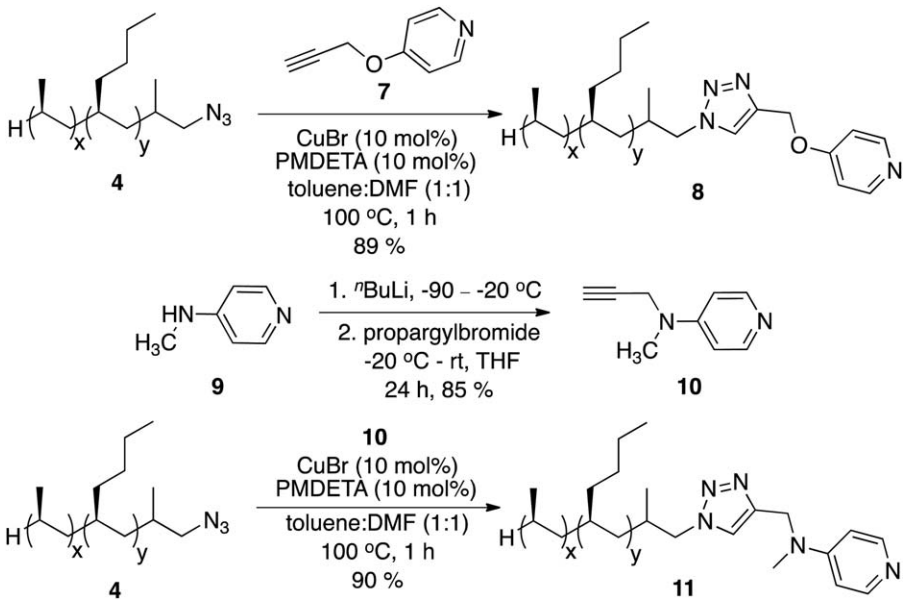
FIGURE 2 Photograph illustrating the phase-selective solubility of 6 (for heptane) compared to the selectivity of low molecular weight 5 (for acetonitrile) in a mixture of heptane and acetonitrile.

which resulted in a biphasic mixture. Pure product was isolated by removal of the polar solvent layer, followed by solvent removal under reduced pressure while **11** was reused by the addition of fresh substrates. **11** could be reused five times with an average product yield of 93%. Product spectral data matched literature examples.[10]

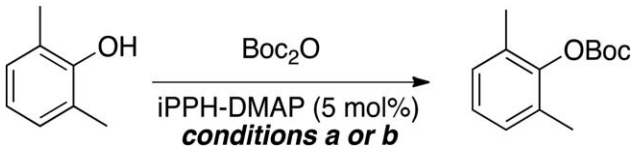
RESULTS AND DISCUSSION

iPPH oligomers (with a nominal M_n of 2000 and a statistical propylene/hexene ratio of ~17/1) are commercially available from Baker Hughes.[14] These species are soluble in a range of solvents (such as heptane, chloroform, THF, and toluene) which enables their characterization by solution state spectroscopic methods (i.e., ^{1}H NMR spectroscopy), like their amorphous counterparts.[11] Unlike these formless materials, iPPH exists as a semicrystalline solid, rendering its purification and isolation simpler (*vide infra*). This material contains, exclusively, an olefin terminus (Fig. 1) that can be converted into many other functional groups using standard organic transformations that are similar to existing procedures.[8,9,11,12,15,16,22]

Olefin terminated oligomer **1** could be transformed into alcohol **2** using typical hydroboration/oxidation conditions (Scheme 1). Analysis by ^{1}H NMR spectroscopy showed complete disappearance of the olefinic proton signals at 4.72 and 4.65 ppm and the appearance of a new multiplet at 3.6–3.3 ppm. Treatment of **2** with methanesulfonyl chloride in dichloromethane afforded mesylate **3** in quantitative conversion, as evidenced by the disappearance of the proton signals corresponding to **2** and the appearance of a multiplet and a singlet at 4.19–3.98 and 2.9 ppm, respectively, in the ^{1}H NMR spectrum. **3** served as a useful intermediate that could undergo a typical substitution reaction to provide azide **4**, as confirmed by the disappearance of the singlet at 2.9 ppm and an upfield shift of the multiplet from 4.19–3.98 to 3.28–3.05 ppm. **4** was further characterized by a peak at 2098 cm^{-1} corresponding to the azide stretch in the FTIR spectrum. It is important to note that each of these reactions proceeded to completion, as evidenced by ^{1}H NMR spectroscopy, but the yields are less than quantitative due to some mass loss occurring in the isolation/purification. Furthermore, the spectra obtained were similar to compounds previously reported.[17,18] Advantageously, these derivatives were all isolated as solids



SCHEME 3 Preparation of iPPH-supported pyridine 9 and DMAP 11.



SCHEME 4 Protection of 2,6-dimethylphenol with Boc_2O in the presence of 11. Conditions a: Boc_2O (1 mmol), phenol (0.99 mmol), 11 (0.05 mmol), THF (2 mL), catalyst separation: precipitation into methanol. Conditions b: Boc_2O (1 mmol), phenol (0.99 mmol), 11 (0.05 mmol), heptane (2 mL), catalyst separation: liquid/liquid extraction with acetonitrile (2 mL).

via precipitation into a minimum amount of methanol followed by filtration. This negates the need for wasteful gravity-based liquid/liquid work up procedures or chromatographic separations that are typically used.

A useful method for the determination of a polymer's phase selective solubility involves the use of catalyst/reagent surrogates that can be anchored to the polymer chain. The use of chromophores or fluorophores as surrogates allows for qualitative observation and quantitative measurement of this selectivity. A dansyl-labeled iPPH derivative was obtained through a copper-catalyzed azide/alkyne cycloaddition (CuAAC[19]) reaction between azide-terminated **4** and **5**. The preparation of **6** began with the synthesis of "clickable" dansyl **5** by first subjecting dansyl chloride to a reaction with aminoethane in CH_2Cl_2 for 20 min (Scheme 2). This was followed by a deprotonation with K_2CO_3 and reaction with propargyl bromide in DMF to provide alkyne **5** in good yield. The formation of **5** was confirmed by the appearance of a doublet at 4.19 ppm, a quartet at 3.42 ppm, a singlet at 2.87 ppm, and two triplets at 2.10 and 1.15 ppm in the ^{1}H NMR spectrum. Although this product was recovered from the reaction mixture in high yield, integration of the doublet at 4.19 ppm and the diminished triplet (corresponding to the amino proton of the intermediate sulfonamide) at 4.49 ppm in the ^{1}H NMR spectrum revealed an 80% conversion. Advantageously, this crude product could be used without any further purification in a click reaction between with **4** in the presence of CuBr and PMDETA. The formation of **6** was confirmed by the appearance of signals at 7.48 and 4.62 ppm and a shift in the signals from 3.28–3.05 ppm ($-CH_2-N_3$) to 4.26–3.92 ppm in the ^{1}H NMR spectrum and the disappearance of the azide stretch at 2098 cm^{-1} in the FTIR spectrum. Using literature procedures,[9,11] fluorescence spectroscopy showed that **6** has a phase selective solubility of >98%, suggesting a small amount of leaching of material into the polar phase. This selectivity can be observed in Figure 2. This indicated that iPPH has potential as a recoverable, polymer support in liquid/liquid separations.[1,2]

We next turned our attention to the development of functional iPPH derivatives. It was possible to use a "click" strategy, similar to that shown in Scheme 2, for the preparation of functionalized iPPH oligomers that have the potential to serve as recoverable reagents, ligands, or catalysts. Alkyne **7** (prepared using literature procedures[6]) could be clicked onto the end of **4** in the presence of CuBr and PMDETA to provide iPPH-pyridine derivative **8** (Scheme 3). However, since our goal in this report is the preparation and use of supported species that can act as recoverable reagents and organocatalysts, we became interested in the synthesis of an iPPH-supported DMAP. DMAP (and its derivatives) has been shown to be more nucleophilic than pyridine and can therefore be a more useful catalyst.[17,18,20]

DMAP derivative **11** was prepared using the atom economical, click strategy outlined in Scheme 3. First, 4-(*N*-methyl-*N*-propargylamino)pyridine **10** was prepared by a low-temperature deprotonation of 4-(*N*-methylamino)pyridine **9** with butyllithium at −90 °C. This mixture was allowed to warm to −20 °C at which point, propargyl bromide was added. Formation of **10** was confirmed by the appearance of doublets at 8.3, 6.6, and 4.0 ppm, a singlet at 3.0 ppm and a triplet at 2.3 ppm in the ^{1}H NMR spectrum. Although it was

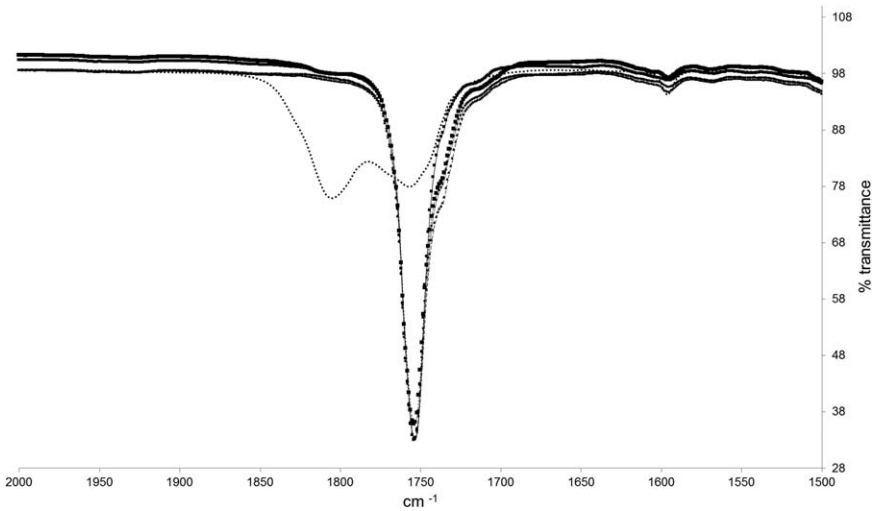


FIGURE 3 FTIR spectra for the Boc-protection of 2,6-dimethylphenol catalyzed by 11: cycle 1 (■ with solid line), cycle 2 (■ with dotted line), cycle 3 (◆ with dotted line), and cycle 4 (▲ with a dashed line), compared to the uncatalyzed reaction (dotted line).

possible to purify **10** using automated flash column chromatography, this was not necessary as it could be used in the next reaction with no further purification. Reaction of **10** with azide **4** in the presence of CuBr and PMDETA in a 1:1 mixture of toluene and DMF provided supported DMAP **11**, which was isolated and purified via precipitation into methanol followed by passing a THF solution of **11** through a short pad of alumina. Preparation of **11** was confirmed by the disappearance of the azide stretch at 2098 cm^{-1} in the FTIR spectrum. Furthermore, a shift in the proton signals from 3.28–3.05 to 4.29–3.98 ppm and the appearance of broad signals at 8.2, 6.6 ppm and singlets at 4.7, and 3.1 ppm in the ^1H NMR served as positive identification of **11**.

Nucleophilic organic bases such as DMAP have found wide use as organocatalysts for many different types of reactions. These include acylations,[17] esterifications,[18] and polymerizations.[21] As proof of principle, we were able to show that iPPH-DMAP **11** could be used as a recoverable catalyst for the Boc-protection of 2,6-dimethylphenol (Scheme 4). Furthermore, the versatility of this support allowed us to recover and reuse **11** under two different systems: (i) a classical solvent precipitation and (ii) a liquid/liquid extraction.

Using a precipitation method, **11**, Boc_2O, and 2,6-dimethylphenol were dissolved in THF and allowed to react at room temperature 25 min. At this time, excess methanol was added to the homogeneous reaction mixture, causing **11** to precipitate as a solid. This suspension was then subjected to centrifugation followed by decantation of the product-containing, methanol-rich solvent layer. Pure product was isolated by the removal of the solvent while the addition of fresh solvent and substrate to the recovered catalyst facilitated its reuse. Under these conditions, **11** was reused four times with an average yield of 94%.

To illustrate the flexibility of this support, we showed that it was also possible to run the same reaction under a liquid/liquid separation system by taking advantage of the high phase-selective solubility of iPPH. This first involved dissolution of **11**, Boc_2O, and 2,6-dimethyl phenol in heptane. This homogeneous reaction mixture was allowed to stir at room temperature for 25 min. At this time, the addition of acetonitrile resulted in a biphasic mixture in which **11** was isolated in the heptane phase while the product was isolated in the polar phase. To establish the effectiveness of supported DMAP **11** as a catalyst for this reaction, FTIR traces of the reaction mixture for each cycle compared to the uncatalyzed reaction (control) are shown in Figure 3. Removal of the polar phase (using a simple gravity separation), followed by addition of fresh substrates facilitated the reuse of **11**. Using this liquid/liquid scheme, **11** could be recycled four times with an average product yield of 93%.

CONCLUSIONS

In conclusion, we have shown that commercially available iPPH can serve as a new, useful synthetic scaffold for the preparation of a small library of derivatives using standard organic transformations. Using typical click chemistry, we were able to prepare an iPPH-supported DMAP that could be used as a recoverable catalyst whose versatility was illustrated by the fact that both liquid/solid and liquid/liquid separation strategies could be used for catalyst recovery and reuse.

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