JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Polyethylene as a Nonvolatile Solid Cosolvent Phase for Catalyst Separation and Recovery

Yanfei Yang, Nilusha Priyadarshani, Tatyana Khamatnurova, Jakkrit Suriboot, and David E. Bergbreiter*

Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012, United States

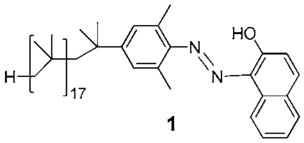
Ⓢ *Supporting Information*

ABSTRACT: The studies described here show that a relatively low molecular weight, narrow polydispersity polyethylene (PE) wax (Polywax) can serve as a nontoxic and nonvolatile alternative to alkane solvents in monophasic catalytic organic reactions where catalysts and products are separated under biphasic conditions. In this application, a polymer that is a solid at room temperature substitutes for a conventional alkane solvent at ca. 80 °C. In addition to the advantages of being a nonvolatile, nontoxic, reusable solvent, this hydrocarbon polymer solvent, like heptane, can sequester nonpolar soluble polymer-bound catalysts after a reaction and separate them from products. The extent of this separation and its generality were studied using polyisobutylene (PIB)- and poly(4-dodecylstyrene)-bound dyes and PE-bound Pd allylic substitution catalysts, PIB-bound Pd cross-coupling catalysts, and PE- and PIB-bound metathesis catalysts. Catalytic reactions were effected using single-phase reaction mixtures containing Polywax with toluene, THF, or THF/DMF at ca. 80 °C. These solutions either separate into two liquid phases on addition of a perturbing agent or separate as a solid/liquid mixture on cooling. The hydrocarbon polymer-bound dyes or catalysts either separate into the hot liquid Polywax phase or coprecipitate with Polywax and are subsequently isolated as a nonvolatile Polywax solid phase that contains the dye or the recyclable catalyst.

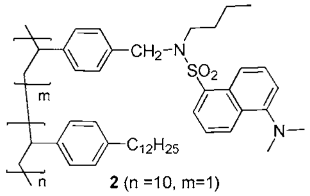
Replacement of organic solvents with benign media is a major problem in effecting "greener" reactions.[1−3] This interest is evident in the many studies using media such as water, supercritical carbon dioxide (scCO_2), or ionic liquids as alternative solvents or cosolvents.[4−8] Here we describe our initial studies that illustrate the potential of using inexpensive nonpolar low-melting polymers as solvents. The studies here show that relatively low molecular weight polyethylene (PE) waxes can take the place of volatile alkane solvents, both reducing use of volatile organic solvents and serving as a vehicle for catalyst recovery/reuse.

Although polymers such as poly(ethylene glycol) (PEG) have been used as solvents,[9−11] the use of polymers as solvents is relatively uncommon. There are only limited examples suggesting other polymers' use.[12−14] Moreover, in the cases where PEG has been used, the products are entrained in this polymer, leading to a need to extract the products from PEG with added organic solvent or with scCO_2. As we show here, hydrocarbon polymers can be used in simpler ways as alkane solvent replacements and can be recovered and separated from products using a biphasic separation. These approaches are modeled after other approaches where nonvolatile or nontoxic solvent phases such as ionic liquids, water, or carbon dioxide are used to recycle catalysts with biphasic separations and minimal use of volatile organic solvents.

Our group has also used biphasic thermomorphic and latent biphasic separations with alkane solvents and alkane phase-selectively soluble polymer-bound catalysts and reagents.[15,16] For example, we have shown that miscible solutions of heptane and ethanol can be perturbed by a perturbing agent (e.g., a change in temperature or physical addition of small amounts of water or salt) to form two phases. After this perturbation, nonpolar polymer-bound ligands, catalysts, and reagents that were soluble in the original miscible solvent mixture selectively partition into the heptane-rich phase, with products remaining in the polar solvent phase. For example, the nonpolar polyisobutylene (PIB)-bound azo dye **1**[17] and the nonpolar poly(4-dodecylstyrene)-bound fluorophore **2** are surrogates of polymer-bound catalysts and are both phase-selectively soluble in a heptane-rich phase after a water- or temperature-induced perturbation of a mixture of heptane and aqueous ethanol or heptane and DMF, respectively. This is illustrated visually for **1** in Figure 1.



1



2 (n =10, m=1)

These latent biphasic and thermomorphic separations are general and are useful ways to separate nonpolar soluble polymer-bound catalysts from polar solutions of products.[15] However, these strategies use heptane. We reasoned that we

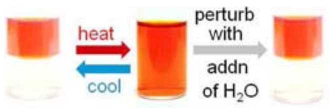


Figure 1. Photograph of reversible thermomorphic phase separation of **1** in a heptane/EtOH/H_2O mixture or irreversible phase perturbation after addition of an additional 10 vol% of H_2O.

Received: July 10, 2012
Published: August 28, 2012

dx.doi.org/10.1021/ja306719j | *J. Am. Chem. Soc.* 2012, 134, 14714−14717

might be able to improve this strategy further if we could replace all or part of the heptane solvent with a nonvolatile, nontoxic, and fully recyclable solvent. This proved to be the case using Polywax 400 (**3**), a commercially available low-molecular-weight unfunctionalized PE oligomer with a polydispersity index (PDI) of 1.08.[18] We first tested the efficiency of **3** as a solvent phase by dissolving 9.0 mg of **1** in 4 mL of a THF/DMF mixture (1/1 vol/vol). Next, 1.5 g of the solid solvent Polywax **3** was added to this homogeneous red solution. At 25 °C, **3** remained suspended in the solution. When **3** was removed from this suspension, it was visually evident that no **1** was sorbed. On heating to 80 °C, **3** dissolved to form a low-viscosity homogeneous red solution of THF, DMF, **1**, and **3**. When this miscible solution was perturbed by addition of 10–20 vol% water, a liquid/liquid biphasic mixture formed where the red dye **3** partitioned quantitatively into the hot liquid Polywax phase. Cooling this mixture formed a red solid wax that could be physically separated from the organic solvent phase (Figure 2). UV–visible spectroscopy analysis showed that <0.1% of the starting dye **1** was in solution.

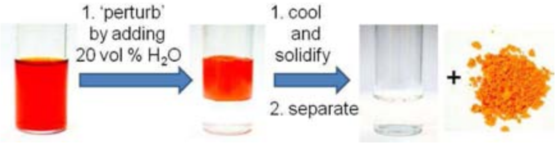
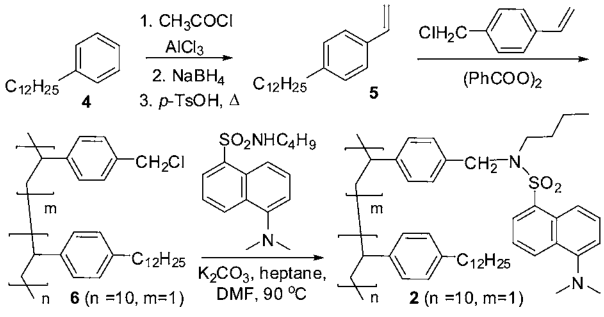


Figure 2. Polywax, THF, and DMF at 80 °C form a solution with the dye **1**. Subsequent perturbation of this solution produces a biphasic mixture consisting of a Polywax phase and a THF/DMF phase. This nonpolar soluble polymer-bound dye (as well as fluorophore **2**) partitions completely into the hydrocarbon phase which solidifies on cooling. Separation and drying leads to a **1**/Polywax mixture which redissolves in THF on heating.

A second experiment showed that sequestration of nonpolar polymer-bound species in Polywax is general for other nonpolar hydrocarbon-like polymers if the separation process includes a stage where two liquid phases are present. This was shown in an experiment with the alkane-soluble poly(4-dodecylstyrene)-bound dansyl dye **2**. In this experiment, a dansyl-labeled poly(4-dodecylstyrene) **2** was prepared as shown in Scheme 1.

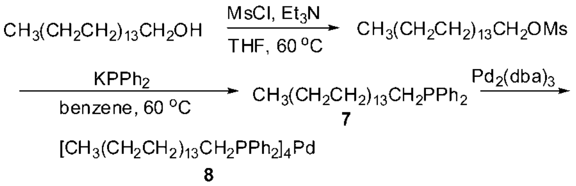
Scheme 1. Synthesis of Dansyl-Labeled Poly(4-dodecylstyrene) 2



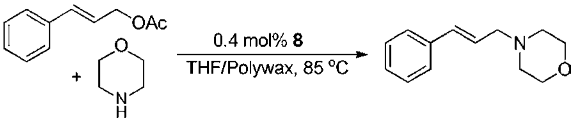
When a ca. 5 mN solution of **2** was prepared in Polywax and toluene at 70 °C and this homogeneous solution was simply cooled, the PE precipitated but did not entrap **2**. However, when a solution of **2** was prepared in Polywax and THF (1.5 g of Polywax, 5 mL of THF, 70 °C), perturbing the solution by addition of water generated a biphasic mixture of Polywax and THF/H_2O. Cooling the biphasic solution formed a solid wax phase that could be physically separated from the THF-rich phase. Fluorescence analysis showed that <0.01% of **2** remained in the THF-rich phase.

The miscibility of Polywax in hot organic cosolvents and the efficient separations seen with nonpolar polymer-bound dyes after a biphasic separation suggested that Polywax could substitute for heptane as a hydrocarbon phase for recovery and reuse of catalysts bound to hydrocarbon polymers. This was shown to be the case using three different types of catalysts. The first of these reactions used PE_{Olig}-bound diarylphosphine-ligated Pd(0) complexes that had previously been used to prepare PE_{Olig}-bound recyclable analogues of oxygen-sensitive Pd catalysts such as $Pd(P(PPh_3))_4$.[20] In this work, a phosphine-ligated Pd(0) molecular catalyst **8** was prepared using PE_{Olig}-PPh_2 ligands derived from commercially available functional PE oligomers that others had used in formation of PE_{Olig}-bound porphyrin polymerization catalysts.[21] The PE_{Olig}-PPh_2-bound Pd(0) catalyst prepared in Scheme 2 was then used as a recyclable and reusable analogue of tetrakis(triphenylphosphine) Pd(0) in a carefully degassed THF/Polywax system at 85 °C in the allylic substitution reaction shown in Scheme 3.

Scheme 2. Synthesis of a Polyethylene-Bound Pd(0) Catalyst



Scheme 3. Substitution of an Allyl Acetate in THF/Polywax Using 0.4 mol% of 8 as a Catalyst

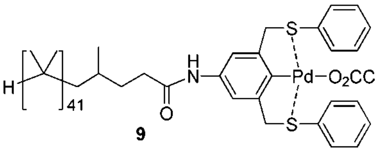


Formation of a Pd(0) catalyst that could be recycled was accomplished by reaction of excess PE_{Olig}-PPh_2 with $Pd_2(dba)_3$ in THF at elevated temperature or by reaction of excess PE_{Olig}-PPh_2 with $Pd(PPh_3)_4$. In either case, the $(PE_{Olig}\text{-}PPh_2)_4Pd$ complex was collected by cooling the mixture and rinsing several times with degassed THF at room temperature. In the latter case, several dissolution (heating)/precipitation (cooling) cycles were carried out to ensure complete exchange of the PPh_3 ligand.

Because of the air sensitivity of the $Pd(PE_{Olig}\text{-}PPh_2)_4$ catalyst, the allylic substitution reaction was performed in a septum-stoppered centrifuge tube under Ar using a mixture of 5 mL of THF and 1.5 g of Polywax that was degassed before heating. On heating to 85 °C, a low-viscosity homogeneous orange solution of THF, Polywax, and the Pd catalyst formed. The reaction was allowed to proceed overnight, after which a small portion of water was added. This perturbed the homogeneous reaction, producing a viscous less dense Polywax phase and a more dense THF-rich phase. This mixture was cooled and centrifuged for 20 min to separate the solid Polywax solvent phase. The THF phase containing the product was transferred by forced siphon under Ar using a cannula. The waxy mixture left in the tube was rinsed with one portion (10 mL) of degassed THF and dried under reduced pressure for 30 min before more THF and substrates were added. Heating then regenerated the solution of substrates and catalyst for a subsequent reaction cycle. When care was taken to avoid air exposure, the Polywax-containing Pd(0) phase was successfully recycled four times, with complete conversion of cinnamyl acetate to the cinnamylamine (average isolated yields of 83%/cycle). Pd leaching in the THF phase (using ICP-MS) after cycle 3 or 4 averaged 0.2% of the starting Pd.

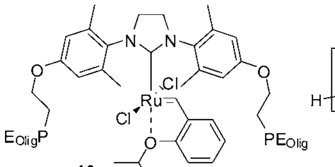
While solid Polywax-facilitated separation of **8** from the product allowed us to recycle **8**, Polywax did not protect **8** from air. Exposure of the solid Polywax phase containing **8** to air after the fifth cycle oxidized the phosphine ligands, leading to an incomplete reaction in the sixth reaction cycle. ^{31}P NMR spectroscopy confirmed that a phosphine oxide formed from PE_{Olig}-PPh_2 in this case, presumably because the polyethylene wax matrix, like polyethylene, is permeable to oxygen.[22]

Supported Pd species have been shown to be effective in cross-coupling chemistry as precatalysts that form some unspecified Pd(0) colloidal catalysts.[23−25] Since we had previously shown that polyolefin-bound SCS-Pd(II) pincer species serve in this manner, we examined Polywax as a medium for recycling the Pd catalyst formed from **9** in a Heck reaction. In this study, a PIB-bound SCS-Pd complex was synthesized according to a literature procedure.[26] We then examined coupling between iodoacetophenone and *n*-butylacrylate to evaluate Pd recycling with Polywax as a hydrocarbon phase. The reaction was conducted in a THF/DMF/Polywax (3/3/2 by wt) mixture using 2 mol% of SCS-Pd as the precatalyst at 85 °C in a capped vial. These reactions were allowed to run overnight because taking aliquots was experimentally inconvenient—removing an aliquot cooled the solution and produced a solid suspension. After an overnight reaction, 15 vol% of water was added, forming a biphasic mixture consisting of a THF/DMF/H_2O phase and a hot viscous Polywax phase. Cooling this biphasic mixture produced a solid Polywax phase and a solution of the product. The solid wax phase that contained the PIB-bound SCS ligand, any unreacted precatalyst, and the Pd(0) species that we believe is formed from this SCS-Pd complex was separated by suction filtration, and this solid could be used to carry out another reaction cycle. Complete conversion of substrate to product based on NMR spectroscopy was seen for eight cycles using the recovered Polywax phase. The average isolated yield is 92% per cycle. Pd leaching was 0.72 and 0.66% of the starting Pd based on ICP-MS analysis of the product solution from cycles 3 and 4, respectively.

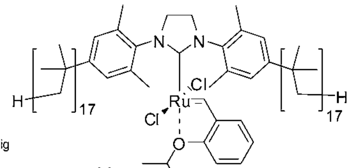


9

Finally, we examined the suitability of Polywax as a cosolvent in ring-closing metathesis (RCM) catalysis reactions using PE_{Olig}- and PIB-NHC-supported Ru catalysts **10** and **11**.[27,28] We first showed that we could entrap both **10** and **11** in Polywax. In the case of **10**, this involved preparing a solution of 30 mg of **10** and 1 g of Polywax in toluene and cooling the mixture to form the greenish powder shown in Figure 3b. This powder redissolved to form a green toluene solution similar to the initial solution of **10**/toluene/Polywax. A Polywax-entrapped form of **11** was prepared by dissolving 30 mg of **11** and 1 g of Polywax in hot THF. Perturbation of this mixture with water produced a biphasic solution, and cooling led to an isolable dispersion of **11**/Polywax that was similar in color to the **10**/Polywax solid.



10



11

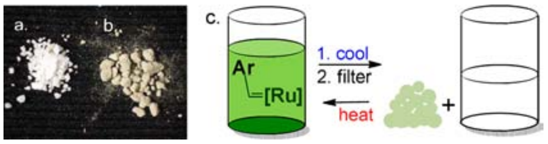


Figure 3. Photographs of (a) Polywax and (b) **10**/Polywax (30 mg of **10**/1 g of Polywax). (c) Schematic drawing of the greenish 80 °C solution of **10**, Polywax, and THF that forms a biphasic mixture consisting of a colorless THF phase and a greenish phase of hot liquid Polywax containing **10** on perturbation of the hot solution by addition of 20 vol% water. Cooling solidifies the Polywax phase, which on physical separation from the THF solution re-forms a solid wax phase like that in photograph (b).

We first tried an RCM reaction using a solvent mixture that contained 60% Polywax. Although this RCM reaction worked, cooling this hot toluene mixture led to a gel of Polywax and toluene that left little or no free toluene solvent, making it difficult to isolate the product. Thus, recycling was effected by first cooling the reaction mixture and then washing the gel with a minimum amount of toluene. As expected, conversion in this RCM reaction was complete. Centrifugation separated the **10**/Polywax from the toluene solution of the product. Subsequent reaction cycles involved addition of a fresh substrate to the recovered **10**/Polywax gel followed by heating. Five cycles afforded an average isolated yield of product of 86%/cycle with 0.19% Ru leaching in cycle 4, as measured by ICP-MS.

The Ru complex **11** in a hot solution of THF/Polywax also formed a competent catalyst for this same RCM reaction. However, recycling of this catalyst required perturbing the hot (80 °C) reaction mixture with water to generate a biphasic mixture in which the PIB-bound Ru catalyst that formed from **11** partitioned into a hot Polywax phase. While we achieved complete conversion of diethyl diallylmalonate to a cyclopentene derivative through three cycles, the reaction time increased in cycle 3, and yields decreased in subsequent cycles. Prior work has shown that the active methylidene species formed in RCM reactions of dienes can react with water.[29−31] While >70% of a relatively stable Grubbs−Hoveyda complex is recoverable after a week's exposure to water at ambient temperature,[31] it is not surprising that water addition could decompose the active Ru catalysts formed from **11** at 80 °C. In our case, partitioning of the PIB-bound Ru complex or unreacted **11** into a Polywax phase may partly protect the Ru species from decomposition. However, traces of water from earlier cycles and/or the 80 °C temperature required for the water-induced biphasic formation make this scheme for recovery of **11**/Polywax unsuitable. Other perturbation agents presumably could be developed for catalysts that react with water for reactions that use Polywax as a cosolvent with PIB-bound catalysts.

In summary, a relatively monodisperse low-molecular-weight polyethylene oligomer is a suitable nonvolatile and recoverable alternative to heptane. This solid wax serves as a polymeric solvent or cosolvent that is a direct substitute for heptane in recovering catalysts bound to both PIB and PE oligomer-bound ligands as solids at room temperature in biphasic separations at the end of a reaction. This hydrocarbon polymer solvent substitute is also a practical cosolvent for selective recovery of species on other suitably designed nonpolar polymers such as poly(4-dodecylstyrene). This oligomeric polyethylene solvent should have low toxicity and low volatility, like polyethylene. Presumably other polymers with low polydispersity, low molecular weight, and low viscosity as melts or in solution can also be used as media to partially substitute or fully substitute for other conventional volatile organic solvents. Studies of these possibilities are ongoing.

■ ASSOCIATED CONTENT

S Supporting Information

Experimental procedures for the synthesis of copolymer **2**; description of the fluorescence experiments; and details of the catalytic reactions, recycling, and ICP-MS analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

bergbreiter@tamu.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The generous gift of samples of Polywax and end-functionalized polyethylene oligomers by Dr. Paul K. Hanna of Baker-Hughes, assistance in ICP-MS analyses by Dr. Yun-Chin Yang, and support by the National Science Foundation (CHE-0952134) and the Robert A. Welch Foundation (Grant A-0639) are gratefully acknowledged.

■ REFERENCES

(1) Anastas, P. T. *ACS Symp. Ser.* **2002**, *819*, 1−9.

(2) Henderson, R. K.; Jimenez-Gonzalez, C.; Constable, D. J. C.; Alston, S. R.; Inglis, G. G. A.; Fisher, G.; Sherwood, J.; Binks, S. P.; Curzons, A. D. *Green Chem.* **2011**, *13*, 854−862.

(3) Clark, J. H.; Tavener, S. J. *Org. Process Res. Dev.* **2007**, *11*, 149−155.

(4) Pollet, P.; Hart, R. J.; Eckert, C. A.; Liotta, C. L. *Acc. Chem. Res.* **2010**, *43*, 1237−1245.

(5) Jessop, P. G.; Subramaniam, B. *Chem. Rev.* **2007**, *107*, 2666−2694.

(6) Jessop, P. G. *Green Chem.* **2011**, *13*, 1391−1398.

(7) Hallett, J. P.; Welton, T. *Chem. Rev.* **2011**, *111*, 322−353.

(8) Hagiwara, H. *Synlett* **2012**, *23*, 837−850.

(9) Heldebrant, D. J.; Jessop, P. G. *J. Am. Chem. Soc.* **2003**, *125*, 5600−5601.

(10) Chen, J.; Spear, S. K.; Huddleston, J. G.; Rogers, R. D. *Green Chem.* **2005**, *7*, 64−82.

(11) Karnakar, K.; Narayana, M. S.; Ramesh, K.; Satish, G.; Nanubolu, J. B.; Nageswar, Y. V. D. *Tetrahedron Lett.* **2012**, *53*, 2897−2903.

(12) Heldebrant, D. J.; Witt, H. N.; Walsh, S. M.; Ellis, T.; Rauscher, J.; Jessop, P. G. *Green Chem.* **2006**, *8*, 807−815.

(13) Molnar, L. K.; Buchwald, S. L.; Hatton, T. A. *Polym. Mater. Sci. Eng.* **1996**, *75*, 113−114.

(14) van den Ancker, T. R.; Cave, G. W. V.; Raston, C. L. *Green Chem.* **2006**, *8*, 50−53.

(15) Bergbreiter, D. E.; Tian, J.; Hongfa, C. *Chem. Rev.* **2009**, *109*, 530−582.

(16) *Recoverable and Recyclable Catalysts*; Benaglia, M., Ed.; John Wiley & Sons: Chichester, UK, 2009.

(17) Bergbreiter, D. E.; Priyadarshani, N. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1772−1783.

(18) Baker Hughes Inc. Polywax, http://www.bakerhughes.com/news-and-media/resources/technical-data-sheet/polywax-polyethylenes (accessed July 25, 2012).

(19) Bergbreiter, D. E.; Chen, Z.; Hu, H.-P. *Macromolecules* **1984**, *17*, 2111−2116.

(20) Bergbreiter, D. E.; Weatherford, D. A. *J. Org. Chem.* **1989**, *54*, 2726−2730.

(21) Older, C. M.; Dristjansdottir, S.; Ritter, J. C.; Tam, W.; Grady, M. C. *Chem. Ind.* **2009**, *123*, 319−328.

(22) Kanehashi, S.; Kusakabe, A.; Sato, S.; Nagai, K. *J. Membr. Sci.* **2012**, *365*, 40−51.

(23) Bergbreiter, D. E.; Osburn, P. L.; Frels, J. D. *Adv. Synth. Catal.* **2005**, *347*, 172−184.

(24) Yu, K.; Sommer, W.; Richardson, J. M.; Weck, M.; Jones, C. W. *Adv. Synth. Catal.* **2005**, *347*, 161−171.

(25) Crabtree, R. H. *Chem. Rev.* **2012**, *112*, 1536−1554.

(26) Bergbreiter, D. E.; Li, J. *Chem. Commun.* **2004**, 42−43.

(27) Hobbs, C.; Yang, Y.-C.; Ling, J.; Nicola, S.; Su, H.-L.; Bazzi, H. S.; Bergbreiter, D. E. *Org. Lett.* **2011**, *13*, 3904−3907.

(28) Hongfa, C.; Su, H.-L.; Bergbreiter, D. E.; Hassan, B. S. *Org. Lett.* **2009**, *11*, 665−667.

(29) Kirkland, T. A.; Lynn, D. M.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 9904−9909.

(30) Burtscher, D.; Grela, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 442−454.

(31) Hong, S. H.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 3508−3509.