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Introduction

Brønsted acid catalysts have been part of the repertoire of chemists for over 200 years. Sulfuric acid is a common example of such Brønsted catalysts. It is used in large scale processes like the isomerization of cyclohexanone oxime to caprolactam and in petroleum refining. Sulfuric acid is also used in organic chemistry as a catalyst for esterification, acetalization, ether formation, and dehydration reactions. In many cases, an inexpensive catalyst like sulfuric acid is not recycled. Nonetheless, though this acid catalyst is inexpensive, issues of recyclability, sustainability, and safety have led to the widespread use of solid inorganic or organic alternatives like polystyrene-bound sulfonic acids and Nafion as catalysts.^{1,2} These insoluble analogs of sulfuric acid allow for products to be separated from the acid catalysts by filtration and make catalyst reuse feasible. However, these heterogeneous catalysts can have drawbacks when compared to their homogeneous analogs. For instance, the activity of heterogeneous Brønsted acid catalysts can be limited by diffusion and recycling is not always as feasible as might be expected. While these catalysts are continuing to be improved,³⁻⁶ alternative systems remain of interest. One alternative to these recyclable heterogeneous acid catalysts would be a fully recyclable homogeneous catalyst. The problem in this case is in part how catalyst separation

Fully recyclable Brønsted acid catalyst systems†

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Homogeneous and heterogeneous sulfonic acid catalysts are some of the most common catalysts used in organic chemistry. This work explores an alternative scheme using a fully recyclable polymeric solvent (a poly- α -olefin (PAO)) and soluble PAO-anchored polyisobutylene (PIB)-bound sulfonic acid catalysts. This PAO solvent is nonvolatile and helps to exclude water by its nonpolar nature which in turn drives reactions without the need for distillation of water, avoiding the need for excess reagents. This highly nonpolar solvent system uses polyisobutylene (PIB) bound sulfonic acid catalysts that are phase-anchored in solvents like PAO. The effectivenes of these catalysts was demonstrated by their use in esterifications, acetalizations, and multicomponent condensations. These catalysts and the PAO solvent phase show excellent recyclability in schemes where products are efficiently separated. For example, this non-volatile polymeric solvent and the PIB-bound catalyst can be recycled quantitatively when volatile products are separated and purified by distillation. In other cases, product purification can be effected by product selfseparation or by extraction.

and reuse can be accomplished. In addition, a homogeneous Brønsted acid catalyst requires a solvent. Since the solvent is typically the majority of the mass of most reactions, it of particular concern in terms of sustainability and green chemistry.⁷

The issues associated with solvent use are well-recognized problems in green and sustainable chemistry.8-12 There have been many attempts to alleviate this problem. For example, there are now a range of more benign solvents which are less harmful as generated wastes.¹³ Since these solvents are bioderived, they produce no net greenhouse gas (GHG) in contrast to petroleum derived solvents if combustion is used for solvent disposal. However, regardless of the source for the carbons in the solvent, the best atom economic scenario for a solvent used in any reaction including a homogeneous Brønsted acid catalyzed process would be to use a solvent that is readily recyclable. Recycling not only minimizes GHG, it also reduces the need to remake more chemicals - another objective for green chemistry.¹⁴ Unfortunately, even when recycling is practiced, it most often involves an extra energy intensive distillation step to the overall process.

Our prior work has shown that $poly(\alpha$ -olefin)s (PAOs) have the potential to be highly recyclable polymeric solvents.^{15–17} These materials are commercially available on a large scale and are relatively inexpensive. PAOs have other advantages too. They have low toxicity, are nonvolatile, are reportedly biodegradable in some cases, and have higher flash points than conventional organic solvents.¹⁸ PAOs also have disadvantages in that they are simply alkanes and as alkanes they are poor solvents for polar catalysts, reactants, or substrates.



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Polymeric solvents like PAOs are not new.¹⁹ However, their recycling most often requires substantial additional solvent use or further purification. For example, the most common polymeric solvent, poly(ethylene glycol) (PEG), is commonly recycled by precipitation with excess ether. An alternative scheme would be to use distillation to separate products from a polymeric solvent and then to simply reuse the solvent in another reaction. However, while there is one report where products were separated from a polymeric propylene glycol solvent by distillation,²⁰ the solvent still had to be filtered before reuse and there was some evidence for solvent degradation.

The work here expands on the potential of soluble polymeric catalysts and polymeric solvents and addresses the green chemistry issues above in several ways. First, we show that a polyisobutylene (PIB)-bound alkyl- and arylsulfonic acid catalysts' high solubility in a PAO phase keeps them separate from a polar phase and makes them recyclable. This phase selective solubility requires a suitable $M_{\rm p}$ for the PIB phase anchor. Thus while a smaller PIB450-bound sulfonic acid might leach to a small extent into a polar extraction solvent like CH₃CN, an otherwise similar PIB₁₀₀₀-bound sulfonic acid has less than 0.2% leaching. Using a higher molecular weight PIB starting material requires using a more viscous PIB species in the synthesis of the catalyst (PIB₁₀₀₀ is highly viscous with a viscosity of ca. 190 cSt at 100 °C)^{21,22} the viscosity of the PIB species is irrelevant in the reactions since it is present at relatively low concentration. As a result, the viscosity of the reaction solution is essentially the same as the much lower viscosity of the PAO₄₃₂ (4.09 cSt at 100 °C).²³ PAO₄₃₂ was used because it has good balance of very low (<0.1 wt%) leaching and modest viscosity vis-à-vis PAOs of lower or higher molecular weight.¹⁶ Second, while added solvents can be used to extract products from a PAO phase, we show that the low volatility of a PAO solvent and the PIB-bound catalysts facilitates product isolation by distillation. Volatile products are typically purified by distillation anyway. Thus, separation by distillation of a volatile product from a nonvolatile polymeric solvent under reduced pressure is a simple but effective way to reuse a polymeric catalyst and polymeric solvent. Third, we show that these PAO solutions of recyclable Brønsted acid catalysts have general applicability in that they catalyze reactions such as acetal formation, a sulfonic acid catalyzed multicomponent condensation to form a 3,4-dihydropyrimidin-2-one, and esterifications. Finally, in the case of esterifications, we show that the self-removal of water from the PAO phase modestly shifts the predicted equilibrium to favor the ester product.

Results and discussion

Conventional strong organic acids such as *p*-toluenesulfonic acid and methanesulfonic acid have little to no solubility in PAOs. Thus, to explore PAOs as recyclable media for Brønsted acid catalysis, we had to first synthesize sulfonic acids that could be anchored and recycled in PAOs. Our initial attempts

involved synthesis of a PAO-soluble sulfonic acid from PIB that is commercially available as material derived from 100% renewable feedstock. These initial efforts to synthesize a polyisobutylene (PIB) bound arylsulfonic acid from alkenefunctionalized PIB *via* electrophilic aromatic substitution and then sulfonation failed due to depolymerization of the PIB in arene solvents.²⁴ Thus, we turned our attention to the synthesis of a PIB-bound alkylsulfonic acid. This methanesulfonic acid analog was synthesized in two steps *via* a thio-ene reaction followed by an oxidation. That process afforded the PIBbound sulfonic acid 2 in 47% yield (Scheme 1). The loading of the sulfonic acid on this analog of methanesulfonic acid was analyzed by titration and was shown to be 0.74 mmol of $-SO_3H$ per g of PIB, consistent with an M_n of the PIB-CH₂SO₃H 2 of 1400 Da.

We then turned to reexamine the problems of synthesis and sulfonation of an aryl functionalized PIB. While we were unable to develop a synthesis of a PIB analog of toluene sulfonic acid from alkene-terminated PIB, we were successful in sulfonating the more readily accessible anisole-terminated PIB that could be prepared by reaction of an alkene-terminated fully renewable PIB with anisole in the presence of catalytic sulfuric acid. Sulfonation of this PIB-bound anisole group with oleum afforded a 62% yield of the PIB-bound acid 3 (Scheme 1). The loading of the arylsulfonic acid was analyzed by titration and was shown to be 0.62 mmol of $-SO_3H$ per g of PIB, consistent with an M_n of the PIB-ArSO₃H 3 of 1600 Da.

The polymer products from both these syntheses have $M_{\rm p}$ values that are higher than that expected from the approximately 1000 Da starting material. We've noted this effect before in other chemistry modifying PIB groups to make catalysts.²⁵ We ascribe the increase in $M_{\rm p}$ of both of these products to fractionation of the PIB where in leaching of lower $M_{\rm n}$ polymers into extraction solvents occurs during the separations during this synthesis. The product sulfonic acids 2 and 3 are firmly phase anchored, are non-volatile, and do not leach to a measureable extent in other polar solvents. This phase selective solubility was noted too in prior work where these PIBbound sulfonic acids were used to solubilize silica nanoparticles in alkane solvents.²⁶ While they can be purified and isolated from low molecular weight solvents like heptane or THF during their synthesis, we have not attempted to and believe it would be difficult to separate them from PAO because of their phase selective solubility in PAO versus other solvents.

To further test the separability of the PIB-bound sulfonic acids 2 and 3 from a polar phase we carried out experiments



Scheme 1 Synthesis of PIB-bound alkyl- and arylsulfonic acids 2 and 3.

using biphasic solutions of methanol and PAO₄₃₂ that contained either a methanol-anchored azo dye or a PAO432anchored azo dye. In the first case, we use methanol containing the azo dye, *p*-methyl red 4a, and PAO_{432} . In the second case, we used a biphasic solution of methanol and PAO432 containing a PIB-bound p-methyl red dye 4b. The low molecular weight azo dye 4a either in the neutral or protonated form has no solubility in the 30-carbon PAO432 solvent. Likewise, the PIB-bound azo dye 4b has no solubility in methanol. To test the phase selective solubility of the PIB-bound sulfonic acids 2 and 3, we physically mixed a solution of 4a in methanol with a PAO₄₃₂ solution of 2 or 3. The resulting biphasic mixtures that formed showed that the dye in the methanol phase was not protonated by the PIB-bound acids (Fig. 1) based on the absence of any of the red protonated dye. We then added a similar PIB-bound azo dye (4b) that was soluble in heptane to PAO_{432} containing 2 or 3. In this case, the dye readily protonated. Then we added 4a to this second biphasic mixture. No protonation of 4a was seen under conditions where 4b was fully protonated by 2 or 3. The visual absence of leaching of the acids 2 and 3 into the methanol phase and the absence of protonation of 4a was confirmed by UV-visible analysis of the methanol phase which showed no detectable protonated 4a. Other experiments not shown in Fig. 1 showed that CH₃SO₃H did protonate 4a but that CH₃SO₃H did not protonate 4b dissolved in PAO₄₃₂. This shows that the PIB-bound sulfonic acids have the preferential solubility in PAO₄₃₂ necessary if they are to be used as recyclable Brønsted acid catalysts.

Next, the use of PAO as a solvent with both PIB-bound sulfonic acid catalysts 2 or 3 was explored using as an example the

4a R = H

Red $(\lambda_{max} = 514 \text{ nm})$

4b R = PIB₁₀₀

4a R = H

Yellow ($\lambda_{max} = 406 \text{ nm}$)

4b R = PIB₁₀₀₀





Scheme 2 Acetalization promoted by PIB-bound Brønsted acid catalysts PIB-SO₃H (2 or 3) in reactions that were recycled 10 times with average isolated yields of 91% and 90% respectively.

protection of benzyl alcohol with 3,4-dihydro-2H-pyran (DHP) (Scheme 2). Similar reactions have been carried out before with a heterogeneous Brønsted acid catalyst (Amberlyst 15) using the same 1:1.2 ratio of reactants, and 1 h reaction time at room temperature. Similar 93-98% yields were obtained using 10 mol% of a catalyst. Catalyst reuse was not described in this paper.²⁷ Using 2 or 3, we were able to show that this reaction could be carried out at ambient temperature using 1.2 mmol of DHP and 1.0 mmol of benzyl alcohol with 5 mol% of 2 or 3. After 1 h of stirring, the 10 mL of the PAO_{432} reaction mixture was shaken with 3 mL of acetonitrile and the resulting biphasic mixture was transferred to a centrifuge tube. After centrifugation, the bottom PAO₄₃₂ layer was removed with a pipette, charged with fresh substrates, and reused. This PAO phase containing 2 or 3 was also easily recycled. Ten cycles were carried out with no observable decrease in the volume of the PAO phase. The acetonitrile phases containing the product were combined and washed twice with 5 mL aliquots of heptane and the acetonitrile was then removed at reduced pressure to afford the product with 91% and 90% average isolated yield respectively for 2 and 3 over 10 cycles. The product THP ether was characterized by ¹H and ¹³C NMR spectroscopy and did not contain any detectable PAO₄₃₂, 2, or 3. This showed that the acid catalysts and PAO_{432} solvent system was recyclable when products were separated using a liquid/liquid extraction.

The recyclability of PIB-bound acids 2 and 3 was further tested by comparing the PIB-bound sulfonic acids 2 and 3 to a commercially available hydrocarbon soluble sulfonic acid, p-dodecylbenzenesulfonic acid 5 (Fig. 2). p-Dodecylbenzenesulfonic acid, like 2 and 3, was soluble in heptane, however 5 had limited solubility in PAO₄₃₂ presumably because it is not hydrophobic enough for this PAO solvent. Thus, our initial test to compare the recyclability of 2 and 3 versus 5 in the DHP protection of benzyl alcohol (Scheme 2) was studied in heptane to insure that we could use the catalysts 2, 3, and 5 at the same 5 mol% catalyst loading. The results in Fig. 2 show that over the course of five cycles, the conversion of benzyl alcohol to the THP ether was in the range of 90-100% for the PIB-bound acids. In contrast, the conversion of benzyl alcohol to THP ether decreased to ca. 10% after five cycles using 5. Similar results were seen using PAO432 though those studies required longer reaction times due to the diminished solubility of 5 in PAO₄₃₂ versus heptane. These studies using PAO₄₃₂ versus heptane showed catalysts 2 and 3 could be reused while the catalyst 5 leached into the acetonitrile solvent used to isolate the product. These studies also showed that some heptane was lost in each cycle while the PAO₄₃₂ was fully recoverable and



Fig. 2 Five cycles of a DHP protection of benzyl alcohol using three different acids; (from left to right) *p*-dodecylbenzenesulfonic acid **5**, the PIB-bound alkylsulfonic acid **2**, and the PIB-bound arylsulfonic acid **3**.

reusable over these 10 cycles. These results suggest that the PIB phase-anchor is required if these soluble sulfonic acid catalysts are to be effectively recyclable in an alkane solvent, and that PAO_{432} is a better choice than heptane as a recyclable solvent in these liquid/liquid separations.

A second example using 2 or 3 in PAO₄₃₂ involved a multicomponent reaction that forms a 3,4-dihydropyrimidin-2-one derivative (Scheme 3).²⁸ This reaction used 3 mmol of urea, 2 mmol of benzaldehyde, and 2 mmol of ethyl acetoacetate in 10 mL of PAO₄₃₂ and was carried out at 90 °C. In this case, we were able to effect a reaction even though one component was a highly polar substrate. The solubility of urea in PAO₄₃₂ was a concern since separate experiments showed that urea was essentially insoluble in PAO432 even at 90 °C. However, in the actual reaction, benzaldehyde and ethyl acetoacetate are present at concentrations of 0.2 M. In the event, we assume these compounds polarize the PAO phase enough to effect some urea solubilization in the PAO₄₃₂ solvent system allowing the reaction to occur. Regardless of the explanation, the result was that reaction proceeded to completion over 12 h. In this case, the product was insoluble in the PAO₄₃₂ solvent and precipitated as it formed. Thus, the product could be isolated by centrifugation. The remaining PAO₄₃₂ solution containing the catalyst 2 or 3 was decanted and reused in six more cycles with fresh substrates. The solids from the seven cycles were combined and purified by recrystallization from ethanol to remove



Scheme 3 Multicomponent condensation reaction that was recycled seven times with an average isolated yield of 82% and 81% per cycle using 2 and 3, respectively.

excess urea. The recrystallized product was then washed with two 5 mL portions of heptane to give a final product in 82% and 81% average isolated yield for reactions using 2 or 3, respectively. The final product was free of excess urea, PAO_{432} and the PIB sulfonic acids based on ¹H NMR spectroscopy. The use of a variety of heterogeneous Brønsted acids was explored in this case and Amberlyst 15 DRY, a heterogeneous acid Brønsted acid catalyst, was the most effective catalyst.²⁹ In these studies, this heterogeneous catalyst afforded products in a yield comparable to what we observed with 2 or 3 in PAO. However, unlike our system where the yields were comparable in cycles 1 and 7, yields in a reaction with a recycled heterogeneous catalysts decreased steadily through five recycling steps.

Esterifications were the third class of Brønsted acid catalyzed reactions studied. Esterifications were of particular interest to us because we hypothesized that they could highlight additional advantages of a PAO_{432} solvent. Specifically, esters are often volatile compounds. Thus, we thought that we could combine the separation of the ester products from a PAO_{432} solution of 2 or 3 with a purification of these products taking advantage of the nonvolatility of the PAO solvent and catalyst. This was accomplished removing the products from the reaction solution at reduced pressure after the equilibrium was established.

An additional feature of esterifications is that the reactant acid and alcohol are in equilibrium with the product ester and water. While the product ester and water are somewhat favored thermodynamically *versus* the reactant acid and alcohol, the equilibrium constants are not much different from one. Thus these reactions are typically driven to completion by using excess alcohol or by removing the water product as it forms using distillation and a Dean–Stark trap. In the case of PAO₄₃₂, we hypothesized that the immiscibility of water in PAO₄₃₂ and the nonpolar nature of the PAO₄₃₂ solvent might make these reactions more facile by self-separation of the water from the PAO₄₃₂ phase. This could allow us to carry out esterifications without excess reagents.

Our initial studies compared the reactivity of the sulfonic acids 2 and 3 in PAO₄₃₂ to a common sulfonic acid catalyst p-toluene-sulfonic (p-TsOH). Since p-TsOH does not dissolve in PAO₄₃₂, this comparison involved the reaction of propionic acid with benzyl alcohol in PAO432 with 2 or 3 or in toluene with p-TsOH. The results of this kinetic comparison are shown in Fig. 3. These data show that the acids 2 and 3 in PAO_{432} are kinetically comparable to a conventional p-TsOH catalyst in toluene in esterification chemistry suggesting that PIB-bound sulfonic acids have acidity like their low molecular weight counterparts, a result consistent with the results in Fig. 2 above. We also briefly explored the potential of quantifying the acidity of these PIB-bound sulfonic acids using Hammett indicator dyes30 or 31P NMR spectroscopy probes of Brønsted acidity.³¹ Unfortunately, the Hammett indicator dyes are insoluble in PAO and even a relatively hydrophobic trialkyl-phosphine oxide probe of Brønsted acidity - trioctylphosphine oxide - did not dissolve in PAO. Thus, we can only qualitatively compare 2 and 3 with other sulfonic acids (cf. Fig. 2 and 3).



Fig. 3 Comparison of esterification rates for reactions using PIB-bound acids 2 or 3 in PAO_{432} with a esterification using *p*-toluenesulfonic acid catalyst in toluene.

The conversion of acids to esters in a solution of PAO_{432} with catalysts 2 and 3 was then tested and compared with the theoretical values that could be calculated from NIST data (Tables 1 and 2).³² These calculations used the $\Delta H_{\text{formation}}$ for these materials as an approximation of the ΔG of the reaction. In these calculations we assume the entropy term should be small for a reaction of two substrate molecules forming two molecules of product. Thus, we assume that the ΔH value is roughly equal to the ΔG of the reaction. Using these assumptions, we calculated a theoretical equilibrium constant and theoretical conversion for reactions forming methyl and ethyl esters at 70 °C.

These reactions used 10 mmol of the carboxylic acid and 10 mmol of the alcohol with 1 mol% of catalysts 2 or 3 in

 Table 1
 Conversions of carboxylic acids to esters with various alcohols using catalyst 2 and a 1:1 molar ration of acid: alcohol as measured by ¹H NMR spectroscopy. Calculated conversions are shown in parentheses for the methyl and ethyl esters

Catalyst 3	Acetic acid	Hexanoic acid	Octanoic acid
Methanol	94% (84%)	91% (73%)	91% (55%)
Ethanol	89% (77%)	95% (78%)	84% (69%)
Propanol	86%	93%	80%
Benzyl alcohol	80%	87%	73%

Table 2Conversions of carboxylic acids to esters with various alcoholsusing catalyst 3 and a 1:1 molar ration of acid : alcohol as measured by¹H NMR spectroscopy. Calculated conversions are shown in parenthesesfor the methyl and ethyl esters

Catalyst 2	Acetic acid	Hexanoic acid	Octanoic acid
Methanol	94 (84%)	88% (73%)	89% (55%)
Ethanol	83% (77%)	97% (78%)	95% (69%)
Propanol	87%	80%	81%
Benzyl alcohol	77%	81%	65%



Scheme 4 Esterification of hexanoic acid using methanol. Recycled 10 times with 2 and 3 to give 80% and 81% averaged isolated yield respectively.

10 mL of PAO_{432} at 70 °C for 5 h. The results showed that the conversion of alcohol to ester under these conditions as measured by ¹H NMR is better than the calculated values in all cases. While the differences are modest for ethyl and methyl acetate, the observed conversions are much better than the predicted conversions for methyl and ethyl octanoate. The result of higher conversion in these PAO solvent systems is consistent with our hypothesis that the exclusion of water can help drive these reactions by Le Chatelier's Principle. The results also show that even relatively polar materials such as methanol and acetic acid can be used in a PAO solvent system to give good conversions to ester products without the use of excess reagents or a Dean–Stark apparatus.

The use of this system was then tested for its recyclability using the esterification of hexanoic acid with methanol with 2 and 3 (Scheme 4). The reaction was carried out in PAO_{432} using the same 1:1 mol ratio of the carboxylic acid: alcohol and 1 mol% of the PIB-bound catalyst in 10 mL of PAO_{432} .

The ester product was separated from the PAO_{432} solvent, the catalyst, and any unreacted acid by a distillation of the product at reduced pressure. Each additional cycle required only addition of fresh alcohol and carboxylic acid substrate. This reaction was carried out five times without any decrease in product yield for both acids **2** and **3**. The average isolated yield of methyl hexanoate was 80% and 81% for catalysts **2** and **3** respectively.

Esterifications have been catalyzed using the heterogeneous Brønsted acid catalyst Amberlyst 15 before.³³ However these reactions typically used excess alcohol (a 6 : 1 mole ratio of the alcohol to the carboxylic acid) to achieve yields like those in Table 1. The Amberlyst 15 catalyzed reactions also employed a slightly higher 80 °C reaction temperature and the catalyst was less recyclable.

Conclusions

Two PIB-bound sulfonic acids that were highly phase-selectively soluble in alkane solvents were synthesized. Both PIBbound alkyl- and arylsulfonic acids showed good catalytic activity in known sulfonic acid catalyzed reactions. The work presented here shows that a PAO₄₃₂ solvent system with these acids is effective in a variety of different reactions with an assortment of reagents and that these soluble acid catalysts and PAO₄₃₂ can be repeatedly recycled. This is an improvement on classical solvents such as heptane, because the PAOs do not suffer from leaching or evaporative losses. This PAO solvent system modestly facilitates the esterification reactions by expelling water due to its hydrophobicity. Finally, we show that polymeric solvents like these PAO solvent systems can not only be used in schemes where filtration and extraction are used to isolate products, but that they are also useful when volatile products are isolated and purified by distillation.

Experimental

General procedures

Alkene terminated PIB 1 (M_n = 1048 Da, M_w = 1886 Da, PDI = 1.8, 81% alpha vinylidene content, viscosity at 100 °C = 196 cSt) was obtained from the TPC group and used without purification.²¹ The PAO₄₃₂ used was obtained from Exxon-Mobil (viscosity at 100 °C = 4.09 cSt) and used without purification.²³ Acetonitrile (>99.9%), heptane (99%), azobisisobutyronitrile (98%), 3,4-dyhydro-2H-pyran (99%), toluene (99.8%), acetonitrile (99.5%) and ethyl acetoacetate (99%) were purchaced from Sigma-Aldrich. Tetrahydrofuran, methanol (99.8%), and urea were purchased from Fisher Chemical. Octanoic acid (98%), anisole (99%) were purchased from Tokyo Chemical Industry. 1-Propanol (99%), hydrogen peroxide (35 wt%) were purchased from Acros organics. Benzyl alcohol (98%), hexanoic acid (98%) were purchased from Merck. Dodecylbenzene sulfonic acid (97%) was purchased from spectrum chemical. Benzaldehyde (99%) and thioacetic acid (97%) were purchased from Alfa Aesar. Acetic acid (97%) was purchased from Millipore Sigma. Fuming sulfuric acid (20%) was purchased from Beantown Chemical. Propionic acid (99.9%) was purchased from Mallinckrodt. Formica acid (88%) was purchased from Aqua Solutions. Ethanol (200 proof) was purchased from Koptec. All reagents and solvents were used without further purification.

Synthesis of PIB-bound alkylsulfonic acid 2

Alkene terminated polyisobutylene 1 (10 g, 10 mmol) (M_w = 1000) was dissolved in a 50:50 mixture of heptane and ethanol (200 mL) in a 250 mL round-bottomed flask. To this was added azobisisobutyronitrile (0.165 g, 1 mmol) and thioacetic acid (2.15 mL, 30 mmol). The reaction mixture was then irradiated overnight with a 254 nm UV lamp. After stirring overnight, water (50 mL) was added to induce biphasic separation of this latent biphasic solvent mixture.³⁴ The aqueous phase was separated, and the organic phase was washed 3 times with 50 mL portions of 90% aqueous ethanol. The organic phase was then concentrated under reduced pressure and the resulting viscous residue was dissolved in 100 mL of THF in a 250 mL round-bottomed flask. This thioester was then hydrolyzed and oxidized using 35% hydrogen peroxide (3.7 mL) and 88% formic acid (23 mL). This reaction mixture was stirred overnight at 60 °C. After stirring overnight, the reaction mixture was concentrated under reduced pressure and the residue was dissolved in 100 mL of heptane. This heptane

solution was then washed 3 times with 50 mL portions of acetonitrile and concentrated to give 5.1 g of a viscous brown oil; ¹H NMR (400 MHz, CDCl₃) δ 5.67 (br, chemical shift is concentration dependent due to trace water), 3.23 (dd, J = 3.7, 14.2 Hz, 1H), 3.00 (dd, J = 8.9, 14.2 Hz, 1H), 2.18 (br, 1H), 0.84–1.6 (m).

Synthesis of PIB-bound arylsulfonic acid 3

Anisole-terminated PIB (10 g, 10 mmol) was prepared using a literature procedure.³⁵ The product of this synthesis was dissolved in dichloromethane (100 mL) in a 250 mL round-bottomed flask. The reaction flask was then charged with 20% fuming sulfuric acid (10 mL). This mixture was stirred overnight and then concentrated under reduced pressure. The viscous oily residue was dissolved in heptane (100 mL) and washed with 3 times with 50 mL portions of acetonitrile to remove residual sulfuric acid. The heptane phase was then concentrated under reduced pressure to give 7.4 g of a viscous purple oil. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 2.2 Hz, 1H), 7.59, 7.02 (dd, *J* = 8.8, 2.2 Hz, 2H), 3.82 (s, 3H), 3.76 (br, chemical shift is concentration dependent due to trace water), 1.80 (s, 2H), 0.84–1.6 (m).

Recycling of PAO/acid in the dyhydropyran protection of benzyl alcohol

Benzyl alcohol (108 mg, 1.0 mmol) and 3,4-dyhydro-2H-pyran (DHP) (101 mg, 1.2 mmol) were dissolved in PAO₄₃₂ (10 mL) containing 0.05 mmol of 2 or 3. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then placed into a test tube, and acetonitrile (3 mL) was added. The resultant biphasic mixture was then thoroughly mixed and then separated by centrifugation for 5 min at 1000 rpm. The acetonitrile and PAO₄₃₂ layers were then separated using a pipette. The PAO₄₃₂ phase containing the PIB-bound acid 2 or 3 was recycled by addition with fresh alcohol and DHP. This process was carried out 10 times with no measurable loss of the PAO solvent. The acetonitrile phases from these 10 cycles were then combined, washed twice with 5 mL portions of heptane, and then concentrated to give an average isolated yield of 91% and 89% for 2 and 3 respectively. ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.29 (m, 5H), 4.82 (d, J = 12 Hz, 1H), 4.72 (t, J = 3.4, 1H), 4.53 (d, J = 12 Hz, 1H), 4.00-3.92 (m, 1H), 3.63–3.55 (m, 1H), 1.94–1.54 (m, 6H).

Comparison of acid recyclability in the 3,4-dyhydro-2*H*-pyran protection of benzyl alcohol

Benzyl alcohol (108 mg, 1.0 mmol) and 3,4-dyhydro-2*H*-pyran (DHP) (101 mg, 1.2 mmol) were dissolved in 10 mL of heptane containing 0.05 mmol of 2, 3, or 5. This solution was stirred at room temperature for 1 h. After 1 h, a small aliquot of the heptane phase was dissolved in CDCl₃ and the conversion was determined by ¹H NMR spectroscopy. The remaining heptane was extracted with 5 mL of acetonitrile to separate the product, from heptane. The heptane phase containing the acid catalysts 2, 3, or 5 was charged with fresh alcohol and DHP and the process was repeated for 5 cycles.

Recycling of PAO/acid in a multicomponent synthesis of 3,4dihydropyrimidin-2-one

Benzaldehyde (212 mg, 2 mmol), ethyl acetoacetate (260 mg, 2 mmol), and urea (180 mg, 3 mmol) were dissolved in 10 mL of PAO₄₃₂ in a capped vial. Then 0.5 mmol of either 2 or 3 was added. The resulting mixture was then stirred at 90 °C for 12 h. Then the mixture was transferred to a centrifuge tube and centrifuged for 5 min at 1000 rpm. The PAO₄₃₂ and acid were then decanted and reused in a subsequent reaction cycle with fresh reagents. The solid product and excess urea were from all 7 cycles was combined and recrystallized from ethanol to remove excess urea. The recrystallized 3,4-dihydropyrimidin-2-one was then washed twice with 5 mL portions of heptane to remove any residual. The product was isolated in average isolated yield of 82% and 81% for 2 and 3 respectively. ¹H NMR (400 MHz, $CDCl_3$) δ 7.51 (br, chemical shift is concentration dependent, 1H), 7.35-7.29 (m, 5H), 5.53 (br, chemical shift is concentration dependent, 1H), 5.43 (dd, J = 2.5 Hz, 1H), 4.1 (dq, J = 2.5, 7.3 Hz, 2H), 2.38 (s, 3H), 1.19 (t, J = 7.3 Hz, 3H), mp = 201–203 °C.²⁸

Rate comparison for esterification of propionic acid with benzyl alcohol using 2, 3, and *p*-toluenesulfonic acid

Propionic acid (740 mg, 10 mmol) and 10 mmol of benzyl alcohol (1.08 g, 10 mmol) were dissolved in 10 mL of PAO_{432} (using 0.1 mmol of 2 or 3 as a catalyst) or in toluene (using 0.1 mmol of *p*-TsOH as a catalyst). The reaction was then stirred at 70 °C. Aliquots of the reaction were removed periodically and analyzed by ¹H NMR spectroscopy. The conversion percentage was determined from the integration ratio of the alcohol protons at 4.6 δ and the ester protons at 5.0 δ .

General esterification procedure

A carboxylic acid (10 mmol) and an alcohol (10 mmol) were added to a 20 mL vial and dissolved in PAO₄₃₂ (10 mL) containing 0.1 mmol of either 2 or 3. The vial was then capped, and the reaction mixture was heated to 70 °C and stirred for 5 h. After 5 h, an aliquot was taken, and dissolved in CDCl₃. The conversion of starting material to product was then determined by comparison of the integral of the alcohol for singlets at *ca.* 4.6 δ or 3.4 δ (benzyl alcohol and methanol, respectively), triplet at *ca.* 3.6 δ (propanol) and quartet at *ca.* 3.7 (ethanol) and the ester proton singlet at *ca.* 5.0 δ and 3.6 δ (benzyl esters and methyl esters, respectively), triplet at *ca.* 4.1 δ (propyl esters) and quartet at *ca.* 4.1 δ (ethyl esters) using ¹H NMR spectroscopy.

Recycling of PAO/acid in the esterification of hexanoic acid with methanol

Hexanoic acid (1.16 g, 10 mmol) and methanol (320 mg, 10 mmol) were dissolved in PAO_{432} (10 mL) in a 25 mL roundbottomed flask. Then 0.1 mmol of either 2 or 3 was added. The reaction was carried out at 70 °C for 5 h. After 5 h, the product was isolated and purified by vacuum distillation at reduced pressure. The remaining solution of PAO_{432} and the catalyst was charged with fresh hexanoic acid and methanol and the procedure was repeated. This process was repeated 5 times, affording methy hexanoate with an average isolated yield of 80% and 81% for 2 and 3, respectively. ¹H NMR (400 MHz, CDCl₃) δ 3.60 (s, 3H), 3.23 (t, *J* = 7.6 Hz, 2H), 1.59–1.52 (m, 2H), 1.3–1.19 (m, 4H), 0.83 (t, 3H).

Calculated conversion in esterifications using a 1:1 ratio of carboxylic acid/alcohol

The change in the Gibbs free energy was approximated as the heat of formation of the products minus the reactants with the assumption that the change in entropy should be minimal. Using the heats of formation from NIST (see ESI†) the equilibrium constant for the reaction was calculated and this equilibrium used to calculate the expected conversion at 70 °C.

Author contributions

Christopher B. Watson contributed to this work by conceptualization, formal analysis, investigation, methodology, visualization, and writing. Adrianna Kuechle contributed to this work by investigation. David E. Bergbreiter contributed to this work by con-ceptualization, funding acquisition, project administration, resources, supervision, and writing.

Conflicts of interest

There are no conflicts to declare.

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