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Fluoroacrylate-Bound Fluorous-Phase Soluble Hydrogenation Catalysts

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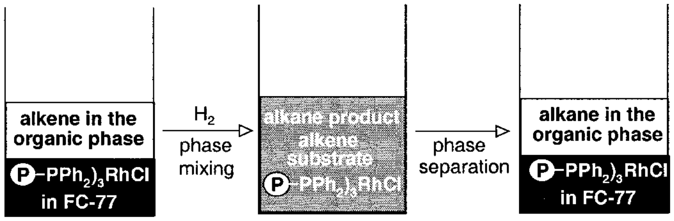
ABSTRACT



Fluoroacrylate polymer-bound hydrogenation catalysts are described. *N*-Acryloxysuccinimide-containing fluoroacrylate polymers were converted into phosphine ligands and subsequently into analogues of Wilkinson's catalyst by amidation of *N*-acryloxysuccinimide active ester residues and Rh exchange. The resulting catalysts have excellent activity and can be reused following fluorous biphasic liquid/liquid separation and extraction.

Fluorous biphasic chemistry is now well established. Since Horvath's original report in 1994,[1] it has become a useful strategy in both synthesis and catalysis.[2−8] Typically, fluorous-phase solubility (and separations) in such chemistry is the result of attachment of a so-called "Teflon pony-tail" [9] onto a catalyst, reagent, or substrate. Given the success in changing solubility of catalysts, reagents, and substrates generally with soluble polymers[10−14] and the availability of fluorinated monomers, we reasoned that soluble fluorinated supports could be used as a general sort of macromolecular "Teflon pony-tail". The hydrogenation catalysts described below supported on a fluorous-phase soluble fluoropolymer demonstrate this idea.

The fluoroacrylate polymers used in this work were prepared using the fluoroacrylate monomer **1** and *N*-acryloxysuccinimide (NASI, **2**). This monomer is available commercially from DuPont. The product fluoroacrylate

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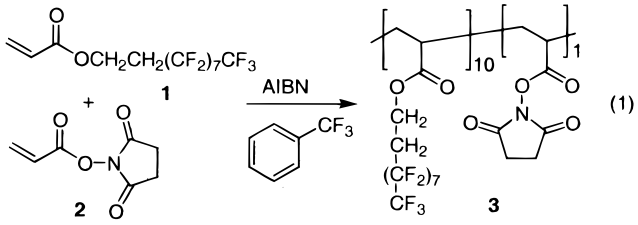
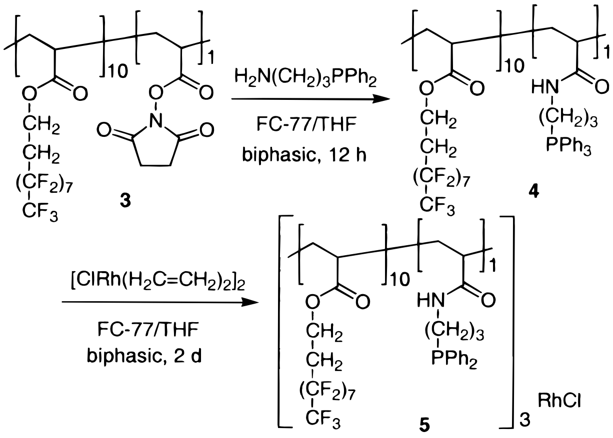
polymer **3** was prepared by a free radical polymerization (AIBN as initiator, 48 h) in benzotrifluoride as solvent at 100 °C (Scheme 1). The product fluoroacrylate copolymer was isolated by precipitation using methanol and was characterized using IR and ^{1}H NMR spectroscopy and elemental analysis.[15] When the fluoroacrylate monomer and NASI were present in a 12:1 feed ratio, the product polymer contained ca. 10 mol % of NASI. NMR analysis showed broad peaks due to the -OCH_2- peak of the fluoroacrylate at δ 4.5 and a peak at δ 2.9 corresponding to the two methylenes of the NASI group in a ratio of 5:1, respectively.

Scheme 1



In a prior report,[16] we have shown that a reactive ester-containing fluoropolymer such as **1** could be derivatized by reaction with an amine-containing dye. We were able to similarly attach diphenylphosphinopropylamine to **3** (Scheme 2). In this reaction, **3** was dissolved in FC-77[17] and allowed to react with an equivalent amount of diphenylphosphinopropylamine dissolved in THF. The two phases were stirred rapidly to form a white emulsion. When the reaction was complete, the two layers were easily separated. ^{1}H NMR and ^{31}P NMR spectroscopy were used to characterize the product. The ^{1}H NMR spectrum showed the loss of the NASI methylene peak at δ 2.9 and the presence of aromatic peaks between δ 7.2 and 7.8, from the diphenylphosphine. The ^{31}P NMR spectrum showed a peak at δ −16, for the product polymer, and a small peak at δ 35, for phosphine oxide. The amount of oxidized phosphine ligand varied but typically was <10%. The complete conversion of the NASI group to amide was also confirmed by comparing the integral for the aromatic protons of the phosphine ligand to the integral for the fluoroacrylate -OCH_2- group at δ 4.5, which showed the expected 10 mol % loading of phosphine.

Scheme 2



The rhodium catalyst **5** was prepared by the reaction of the phosphine-containing polymer **4** with μ-dichlorotetraethylene dirhodium ($[RhCl(CH_2CH_2)_2]_2$).[12] The resulting fluorous-phase soluble polymer-bound rhodium catalysts formed in these reactions were found by ^{31}P NMR spectroscopy to have a single broad signal centered at δ 32.8. This broad signal is presumably a result of phosphine−rhodium exchange and sequence and stereochemical heterogeneities in the polymer structure and is typical of broad signals seen with other soluble polymer-bound catalysts.[12,18] The 3:1 ratio of P:Rh in the product polymer was confirmed by elemental analysis (a 3.3:1 ratio was found). Other fluoroacrylate polymers, **6** and **7**, and similar Rh(I) catalysts, **8** and **9**, were also prepared using chemistry analogous to that used to prepare **5** (Figure 1).

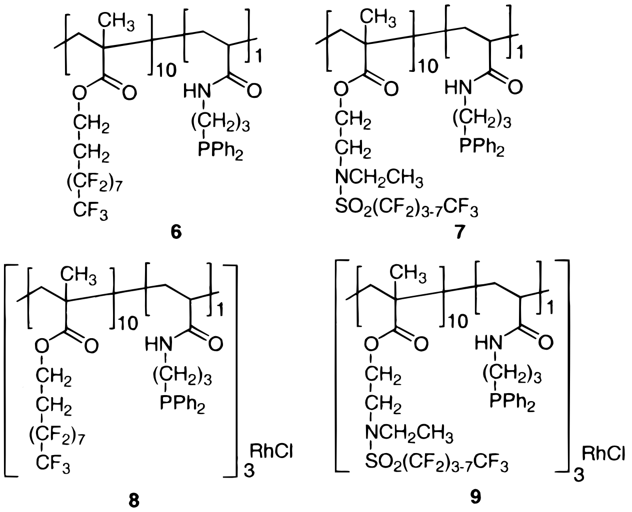


Figure 1.

Studies of rates and turnover numbers with these Rh(I) catalysts show that these fluorous-phase soluble polymer-bound hydrogenation catalysts are comparable to traditional hydrogenation catalysts. For example, the reported rate for hydrogenation of 1-octene in *p*-xylene at 100 ± 2 °C with

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Wilkinson's catalyst is 190 mmol of H_2/mmol of Rh/h while the reported rate for hydrogenation of cyclohexene in benzene with Wilkinson's catalyst is 75 mmol of H_2/mmol of Rh/h at 25 °C.[18] In comparison, rates for the hydrogenation of 1-octene, cyclohexene, and bicyclo[2.2.1]hept-2-ene with the fluorous polymer-bound catalyst **5** were 203, 78, and 65 mmol of H_2/mmol of Rh/h at 25 °C on the basis of the measured Rh loading of 0.013 mmol of Rh/g of polymer. These rates are comparable or better than those reported by us for other polymer-supported hydrogenation catalysts. In prior work, we reported that the hydrogenation rate for 1-octene at 100 °C with a polyethylene-bound Rh(I) catalyst was 99 mmol of H_2/mmol of Rh/h, that the rate of hydrogenation of this same alkene with a polystyrene-bound catalyst was ca. 5 mmol of H_2/mmol of Rh/h, and that the rate of hydrogenation of 1-octene with an amphoteric polymer-supported catalyst in CH_3CN at 25 °C was 14 mmol of H_2/mmol of Rh/h.[18,19] Rates measured with other similar fluorous polymer-bound Rh(I) catalysts were comparable. For example, **8** and **9** hydrogenated 1-octene, cyclohexene, and bicyclo[2.2.1]hept-2-ene with rates or 44, 17, 14 and 15, 20, and 56 mmol of H_2/mmol of Rh/h, respectively.

These soluble fluorous polymer-bound catalysts can be recycled several times. The only limitation we have found is the necessity of a strict inert atmosphere to prevent oxidation of the phosphine ligands. This recycling employed simple liquid/liquid-phase separation. In a typical procedure, turnover numbers measured for the fluorous polymer catalyst **5** through seven cycles were 21 700 mmol of alkene hydrogenated/mmol of Rh. Similar recyclability was seen for catalyst **8** through 10 use/reuse cycles (670 mmol of alkene hydrogenated/mmol of Rh/cycle, respectively). The catalysts could be recycled and reused without a loss in activity. In studying catalyst reuse, hydrogenations were carried out using a Parr apparatus at 30 psi. In a typical recycling experiment, a mixture of 5 mL of THF, containing 2 mmol of an alkene, and 5 mL of FC-77 containing a polymer-bound catalyst such as **5** was added to a Parr reactor under N_2. Flushing the reactor with H_2 and shaking then formed an emulsion, and hydrogenation commenced. When the hydrogenation was complete, the upper layer was removed and the lower layer was washed twice with fresh THF. Then a new upper layer containing another portion of the initial alkene (or another alkene) was added to the lower layer, the apparatus was flushed with hydrogen, and then the reaction was restarted.

In summary, fluoracrylates are useful supports for fluorous-phase soluble polymers whose activity and turnover numbers are comparable or superior to those of other fluorinated catalysts. Such polymers should also be a viable way to prepare other polymer-supported reagents and substrates that will be fluorous-phase soluble. Such product polymer-supported species can easily be separated from organic solutions but retain excellent reactivity as judged by the catalytic activity described above.

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Supporting Information Available: Experimental procedures for the formation of the copolymers **3**, **5**, and **6** along with spectra data, molecular weight data, and elemental analyses. This material is available free of charge via the Internet at http:pubs.acs.org.

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