Synthesis of New Functionalized Polymers and Their Use as Stabilizers of Pd, Pt, and Rh Nanoparticles. Preliminary Catalytic Studies

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ABSTRACT: Polymers **I-X** with functionalized main chain were synthesized from commercial polymers containing reactive groups, anhydride (for Gantrez), or carboxylate (for polyacrylates) moieties, to be used as stabilizers of metallic nanoparticles. ^1H HRMAS, ^{13}C MAS NMR, IR, and GPC techniques were applied to characterize the new polymers. Metal transition nanoparticles stabilized with these polymers were prepared in organic solvents (Pd and Pt) and also in water/ethanol medium (Rh), under hydrogen atmosphere. TEM analysis revealed the formation of small nanoparticles, in the range ~ 3–20 nm, depending on the solvent, metal precursor, metal concentration, and polymer nature. Preliminary catalytic applications, C—C couplings using palladium and hydrogenations using platinum and rhodium systems in organic and also aqueous medium, were tested. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2772–2782, 2007

Key words: functionalization of polymers; colloids; metal-organic catalysts; TEM

INTRODUCTION

The use of well-defined metal nanoparticles (size between 1 and 10 nm) for catalytic processes is a rapidly growing area.[1–8] Similarly to molecular complexes, metal nanoparticles have been proved to be efficient and selective catalysts for hydrogenation of olefins or C—C couplings, but also for reactions which are not or poorly catalyzed by molecular species such as hydrogenation of arenes.[6,7,9] However, despite impressive progresses in asymmetric catalysis, few colloidal systems have been found to display an interesting activity in this field, namely Pt(Pd)/cinchonidine for the hydrogenation of ethyl pyruvate,[10–13] Pd/BINAP for styrene hydrosilylation,[14] or Pd-catalyzed kinetic resolution of racemic substrates in allylic alkylation.[15] Metal nanocatalysts can be obtained by a variety of methods according to the organic or aqueous nature of the media and the stabilizers used.[16]

Poly(vinyl)pyrrolidone, PVP, has been the homopolymer most used as stabilizing agent of metallic nanoparticles.[17–32] Others like cellulose and polysaccharide,[33–35] polyvinylalcohol,[36–40] polystyrene,[41–44] polyacid[45] or poly(vinyl)formamide derivatives,[46] and copolymers[47–55] have been also applied for similar purposes.

We are particularly interested in side-chain functionalized polymers[46,56,57] for their applications as stabilizers of metallic nanoparticles, because the functional groups can interact with the metallic surface. The further utilization of these new materials in catalysis, mainly in enantioselective processes, leads to the introduction of chiral groups in polymeric chains. Essentially, three types of synthetic main chain chiral polymers have been used in asymmetric catalysis[58–60]: (i) polypeptides; (ii) polyesters and polyamides containing flexible chiral chains; and (iii) chiral conjugated polybinaphthyls involving rigid and sterically regular chiral chains.

From the best of our knowledge, this strategy has not been employed until now for the synthesis of
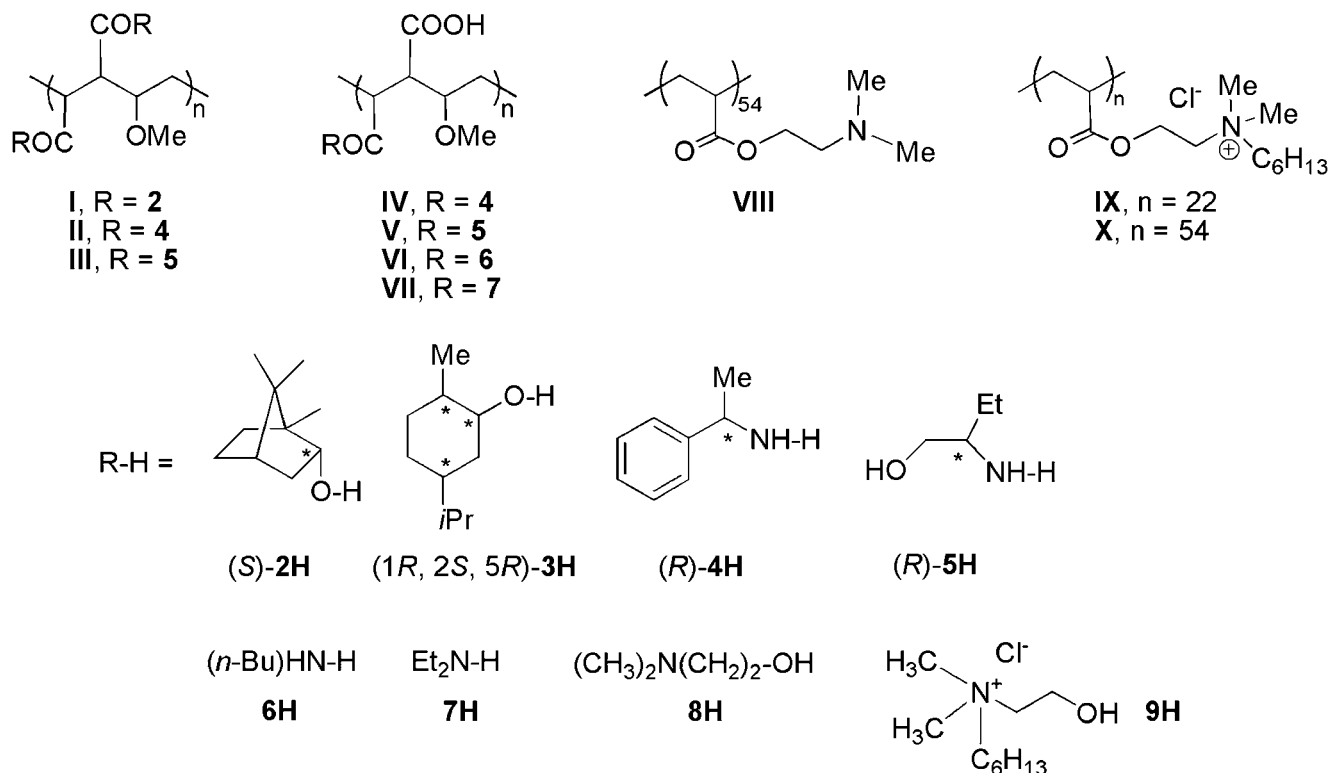

Figure 1 Functionalized polymers from Gantrez (I-VII, $n = 6928$) and sodium polyacrylates (VIII-X).

metallic nanoparticles as potential catalysts in selective organic transformations.

Looking for an available polymer easy to be functionalized, poly(methyl vinyl ether-*co*-maleic anhydride), i.e., Gantrez (registered trademark of GAF), seems to be appropriated because of the presence of anhydride groups in its structure (Chart 1).

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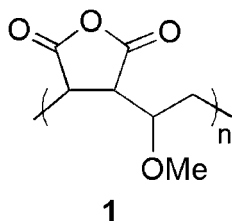
In the literature, numerous Gantrez derivatives have been reported, like ester,[61–68] amide,[69–76] and maleimine derivatives,[77,78] prepared by reaction of the polymer with alcohols and amines respectively. But only menthol has been used as chiral reagent.[79]

In addition, we have been also interested in preparing polyacrylate derivatives[80,81] to obtain hydrosoluble polymers, able to stabilize catalytic precursors in water.

Here we show our investigations concerning the preparation of new polymers containing stereo-controlled moieties by functionalization of commercially available random copolymer Gantrez AN-139 (**I-VII**, Fig. 1). Polyacrylates have been also prepared containing amino and ammonium groups to obtain water soluble polymers (**VIII-X**, Fig. 1). Some of these new polymers were used as stabilizers of palladium and platinum nanoparticles in organic solvent, and rhodium nanoparticles in aqueous medium. In this article, we describe also the preliminary investigations of these polymer-stabilized metallic nanoparticles for various catalytic processes both in organic and aqueous media.

EXPERIMENTAL

Materials

The solvents were purified by standard procedures and distilled under nitrogen atmosphere. Gantrez AN-139, poly(maleic anhydride)-*c*-poly(methyl vinyl ether) with absolute $M_w = 1080$ kg mol^{-1} and $M_w/M_n = 3.47$, was a gift of International specialty products (ISP) and was used as received. Sodium polyacrylate, $M_w = 5100$ g mol^{-1}, was purchased from Fluka. Pt$_2$(dba)$_3$ (dba = dibenzylidenacetone) was prepared following the methodology described in the literature.[82] NMR spectra were recorded on Varian Gemini 200, Mercury 400 (^{13}C MAS NMR), and Bruker 500 DMX (^{1}H HR MAS NMR). IR spectra were recorded on a Nicolet 520 and FTIR Nicolet

Impact 400. Elemental analyses were made with an Eager model 1108. The conversion of ethyl pyruvate and e.e. value of the final product were determined on a Fison GC 9000 with a FID detector equipped with a Lipodex-E column (25 m × 0.25 mm, 0.25 μm film) at 90°C. Samples for TEM analysis were prepared in a glovebox by slow evaporation of a drop of each crude colloidal solution deposited onto a holey carbon covered copper grid. TEM analysis for palladium and platinum nanoparticles were performed on a Hitachi H800 MT electron microscope operating at 200 kV. TEM analysis for rhodium nanoparticles were performed on a JEOL 200 CX-T electron microscope operating at 200 kV with a point resolution of 4.5 Å. The approximation of the particle mean size was made through a manual analysis of enlarged micrographs by measuring a number of particles on a given grid. Molecular weights were obtained by gel permeation chromatography combined with light scattering. Mobile phase was hexafluoro-2-propanol (HFIP) containing sodium trifluoroacetate (NaTFA) 0.05M and stationary phase was a styrene-divinylbenzene linear column. Chromatographic equipment was composed by a Waters 410 pump, a Waters U6K manual injector and two detectors in series: a mini Dawn scatterometer from Wyatt and an Optilab refractometer from Wyatt. Differential refractive indices increments was estimated assumed 100% mass recovery of every sample. Flux was 0.5 mL/min and 100 μL of a 2–4 mg/mL solution was injected. Recovered data were analyzed by Astra program from Wyatt.

Synthesis of polymers

I: 2.0 g of **1** (13 mmol of monomeric units), 31.0 mg of $Fe_2(SO_4)_3$ (0.08 mmol), 4.1 g of borneol (*S*)-**2H** (27.0 mmol), and few drops of concentrated H_2SO_4 (95–97%) in 30 cm^3 of toluene were stirred at 110°C for 3 days. The solvent was then eliminated under reduced pressure. The residue obtained was washed with water and dried under reduced pressure, giving a brown powder. Yield: 4 g (95%). M_p > 350°C. IR (KBr, cm^{-1}): 2950(C—H alkyl groups), 1735 (C=O), 1459, 1183, 1114. ^{13}C-NMR MAS (75.4 MHz): 172.8 (*CO*), 85–75 (*CH*—OCH$_3$, *CH*—OH), 60–10 (aliphatic carbons: CH, CH$_2$, CH$_3$) ppm. Anal. Found: C, 65.32, H, 10.18. Calc. for C$_{27}$H$_{42}$O$_5$·2.8 H$_2$O: C, 65.32, H, 9.60%.

II: 2.3 g of **1** (15 mmol of monomeric units), 6.5 g of α-methylbenzylamine (*R*)-**4H** (53.4 mmol) and 1.5 cm^3 of concentrated H_2SO_4 (95–97%) in 30 cm^3 of toluene were stirred at 70°C for 4 days. The solvent was then eliminated under reduced pressure. The residue obtained was washed consecutively with acetone and water, giving a white powder. Yield: 4.9 g (69%). Mp 240°C. IR (KBr, cm^{-1}): 2945, 2851, 2757, 2677(C—H alkyl groups) 1729, 1649, 1548(C=O),

1454, 1387, 1152, 1085, 1038, 762, 695, 608. ^{13}C-NMR MAS (75.4 MHz): 183.1 (*CO*), 130.1 (*CH* aromatic), 80–20 (aliphatic carbons: CH$_2$, CH, OCH$_3$), 17.4 (*CH$_3$*) ppm. Anal. Found: C, 57.12, H, 7.19, N, 5.98, S, 4.65. Calc. for C$_{23}$H$_{28}$O$_3$N$_2$·0.7H$_2$SO$_4$·1.9H$_2$O: C, 57.16, H, 6.88, N, 5.80, S, 4.64%.

III: 2 g of **1** (13 mmol of monomeric units), 1.5 cm^3 of H_2SO_4 and 6.5 g of 2-aminobutanol (*R*)-**5H** (73 mmol) in 30 cm^3 of toluene were stirred at 90°C for 4 days. The mixture was filtered off and the pale yellow solid was washed with CH$_2$Cl$_2$ to eliminate the excess of 2-aminobutanol and dried under reduced pressure. Yield 3.3 g (72%). M_p 245°C. IR (KBr, cm^{-1}): 2973(C—H alkyl groups) 1700, 1644, 1567 (C=O), 1398, 1117, 1068, 618. ^{1}H-NMR (50 MHz, D$_2$O, ppm): 3.4, 3.3, 2.9, 1.3, 0.6. ^{13}C-NMR MAS (75.4 MHz): 178.3 (*CO*), 78.4 (CH—OCH$_3$), 59.6 (CH$_2$O), 56.1 (CH$_3$O), 60–20 (aliphatic carbons: CH, CH$_2$), 21.4 (CH$_2$—CH$_3$), 9.22 (CH$_3$—CH$_2$) ppm. Anal. Found: C, 50.19, H, 8.97, N, 7.51, S, 1.40. Calc. for C$_{15}$H$_{28}$O$_5$N$_2$·0.15H$_2$SO$_4$·1.5 H$_2$O: C, 50.32, H, 8.75, N, 7.84, S, 1.34%.

IV: 2.2 g of **1** (14 mmol of monomeric units) and 3.9 g of α-methylbenzylamine (*R*)-**4H** (32 mmol) in 30 cm^3 of toluene were stirred at 70°C for 2 days. The solvent was then eliminated under reduced pressure. The product obtained was washed consecutively with dichloromethane and acetone to eliminate the amine excess. The solid was dried under reduced pressure, giving a white powder. Yield 3.9 g (93%). M_p 233°C. IR (KBr, cm^{-1}): 3410(OH), 3066, 2972, 2932 (C—H alkyl groups) 1716, 1642, 1561(C=O), 1380, 1232, 1092, 769, 702. ^{13}C-NMR MAS (75.4 MHz): 174.1 (*CO*), 128.2 (CH aromatics), 80.6 (CH—OCH$_3$), 70–10 (aliphatic carbons: CH$_3$, CH$_2$, CH; OCH$_3$) ppm. Anal. Found: C, 60.31, H, 7.36, N, 4.80. Calc. for C$_{15}$H$_{19}$O$_4$N.0.2-C$_7$H$_{10}$O$_5$.0.25C$_8$H$_{11}$N.1.6H$_2$O: C, 60.25, H, 7.33, N, 4.78%.

V: 2.2 g of **1** (14 mmol of monomeric units), 1.5 cm^3 of concentrated H_2SO_4 (95–97%) and 7 cm^3 of 2-aminobutanol (*R*)-**5H** (74 mmols) in 40 cm^3 of toluene were stirred at 100°C for 4 days. The solvent was then eliminated under reduced pressure. The product obtained was washed consecutively with water and acetone. The solid obtained was dried under reduced pressure, giving a white powder. Yield 3.4 g (64%). M_p > 350°C. IR (KBr, cm^{-1}): 3395(OH), 2972(C—H alkyl groups), 1689(C=O), 1555, 1467, 1372, 1192, 1091, 803. ^{13}C-NMR MAS (75.4 MHz): 178.8 (*CO*), 78.5 (CH—OCH$_3$), 61.5 (CH$_2$O), 57.4 (CH$_3$O), 60–20 (aliphatic carbons: CH, CH$_2$), 23.6 (CH$_2$—CH$_3$), 11.2 (CH$_3$—CH$_2$) ppm. Anal. Found: C, 48.56, H, 8.54, N, 5.10, S, 0.81. Calc. for C$_{11}$H$_{19}$O$_5$N 0.1H$_2$SO$_4$·1H$_2$O: C, 48.39, H, 7.77, N, 5.13, S, 1.17%.

VI: 1.5 g of **1** (10 mmol of monomeric units) and 4.1 g of butylamine **6H** (56 mmol) in 30 cm^3 of toluene were

stirred at 60°C for 4 days. The solvent was then eliminated under reduced pressure. The product obtained was washed consecutively with dichloromethane and acetone. The solid was dried under reduced pressure, giving a white powder. Yield 2.4 g (99%). M_p 220°C.IR (KBr, cm^{-1}): 3500(OH), 2959(C—H alkyl groups) 1723, 1649, 1568 (C=O) 1461, 1380, 1226, 1192, 1098. ^{13}C-NMR MAS (75.4 MHz): 176.8 (CO) ppm, 80.1 (CH—OCH$_3$), 60–20 (aliphatic carbons: CH$_2$, CH), 56.9 (OCH$_3$), 40.6 (CH$_2$—NH), 31.4 (CH$_2$—CH$_2$—NH), 20.9 (CH$_2$—CH$_3$), 14.3 (CH$_3$—CH$_2$) ppm. Anal. Found: C, 57.01, H, 9.65, N, 6.36. Calc. for C$_{11}$H$_{19}$O$_4$N: C, 57.64, H, 8.30, N, 6.11%.

VII: 1.5 g of **1** (10 mmol of monomeric units) and 4.3 g of diethylamine **7H** (59 mmol) in 30 cm^3 of toluene were stirred at 60°C for 4 days. The solvent was then eliminated under reduced pressure. The product obtained was washed consecutively with dichloromethane and acetone. The solid was dried under reduced pressure, giving a white powder. Yield 3.2 g (>99%). M_p > 350°C. IR (KBr, cm^{-1}): 3463(OH), 2985, 2932(C—H alkyl groups) 1716, 1635 (C=O) 1461, 1387, 1098, 803. ^{13}C-NMR MAS (75.4 MHz): 176.3 (CO), 80.6 (CH—OCH$_3$), 60–30 (CH$_2$, CH), 56.9 (CH$_3$O), 42.7 (CH$_2$—CH$_3$), 12.7 (CH$_3$) ppm. Anal. Found: C, 54.91, H, 9.47, N, 6.45. Calc. for C$_{11}$H$_{19}$O$_4$N 0.6H$_2$O: C, 55.05, H, 8.42, N, 5.84%.

Polyacryloyl chloride

2.8 g of sodium polyacrylate (29.7 mmol of monomeric units) were dissolved in 10 cm^3 of HCl 1M. After complete dissolution of the polymer, the water was evaporated under reduced pressure. The salts were removed by precipitation in EtOH, filtered off, and solvent evaporated under reduced pressure. Next SOCl$_2$ (30 cm^3) were added slowly (over 30 min) onto the polyacrylic acid, which was placed in an ice bath. The mixture was then heated at 40°C for 4 h. Thionyl chloride was then evaporated under reduced pressure. The product was obtained as white sticky solid. Yield 1.4 g (53%). IR (KBr, cm^{-1}): 2960 (C—H alkyl groups), 1755 (C=O), 1196, 1024.

VIII: 1.4 g of polyacryloyl chloride (15.5 mmol of monomeric units) were dissolved in 30 cm^3 of toluene and 1.4 g of aminoethanol **8H** (15.5 mmol) were added. The reaction was stirred overnight at 60°C. The solvent was removed and the solid obtained washed with toluene (3 × 10 cm^3). The solvent was then removed under reduced pressure. The product was obtained as yellow oil of high viscosity. Yield 1.7 g (87%). IR (KBr, cm^{-1}): 2960 (C—H alkyl groups), 1739 (C=O), 1578, 1465, 1165, 1078. ^{1}H-NMR (D$_2$O): 3.7 (CH$_2$), 3.1 (CH$_2$), 2.8 (CH$_3$), 2.5-1 (broad signal) ppm. ^{13}C-NMR (D$_2$O): 182 (COOR), 176 (COOH), 45 (CH), 35 (CH$_2$) ppm. Anal. Found:

C, 48.70, H, 9.35, N, 5.33. Calc. for C$_7$H$_{13}$O$_2$N$_1$.1.2-C$_3$H$_4$O$_2$.1.5H$_2$O: C, 49.60, H, 8.17, N, 5.46%.

IX: 0.7 g of polyacryloyl chloride (7.5 mmol of monomeric units) and 1.3 g of ammonium salt **9H** (7.5 mmol) in 30 cm^3 of toluene were stirred at 60°C overnight. The solvent was then removed and the residue washed with toluene and dried under reduced pressure. The product was obtained as yellow oil. Yield 0.7 g (40%). IR (KBr, cm^{-1}): 2954, 2927, 2864 (C—H alkyl groups), 1725 (C=O), 1473, 1160, 1087. ^{1}H-NMR (CDCl$_3$): 4.1 (CH$_2$O), 3.7 (CH$_2$N), 3.5 (CH$_2$N), 3.3 (N(CH$_3$)$_2$), 1.8 (CH$_2$ hexyl), 1.3 (CH$_2$)$_3$ hexyl), 0.90 (CH$_3$ hexyl) ppm. ^{13}C-NMR (CDCl$_3$): 183 (COOR), 65.9 and 65.7 (CH$_2$O, CH$_2$N), 56 (CH$_2$N), 52 (N(CH$_3$)$_2$), 26, 24, 23, 22, (CH$_2$), 14 (CH$_3$) ppm. Anal. Found: C, 51.46, H, 9.70, N, 4.42. Calc. for 1.1C$_{13}$H$_{26}$O$_2$NCl.0.23C$_3$H$_4$O$_2$.2.4H$_2$O: C, 51.45, H, 9.81, N, 4.40%.

X: 0.6 g of polyacryloyl chloride (6.6 mmol of monomeric units) and 1.5 g of ammonium salt **9H** (6.9 mmol) in 30 cm^3 of toluene were stirred at 60°C overnight. The solvent was then removed and the residue washed with toluene and dried under reduced pressure. The product was obtained as sticky oil. Yield 0.7 g (40%). IR (KBr, cm^{-1}): 2964, 2924, 2854 (C—H alkyl groups), 1732 (C=O), 1472, 1164, 1084. ^{1}H-NMR (CDCl$_3$): 4.1 (CH$_2$O), 3.7 (CH$_2$N), 3.4 (CH$_2$N, N(CH$_3$)$_2$), 1.7 (CH$_2$ hexyl), 1.3 (CH$_2$)$_3$ hexyl), 0.90 (CH$_3$ hexyl) ppm. ^{13}C-NMR (CDCl$_3$): 184 (COOR), 64.9 and 64.7 (CH$_2$O, CH$_2$N), 55 (CH$_2$N), 51 (N(CH$_3$)$_2$), 25, 22, 21, (CH$_2$), 13 (CH$_3$) ppm. Anal. Found: C, 46.11, H, 10.01, N, 5.54. Calc. for C$_{13}$H$_{26}$O$_2$NCl 1.9C$_8$H$_{18}$O$_1$NCl 0.3C$_3$H$_4$O$_2$.7.6H$_2$O: C, 45.77, H, 10.04, N, 5.32%.

Synthesis of metallic nanoparticles

Pd-III: To a solution of Pd$_2$(dba)$_3$ (10 mg, 0.011 mmol) in 50 cm^3 of distilled and degassed THF in a Fischer-Porter bottle, a solution of polymer **III** (139 mg, 0.44 mmol; monomer/palladium = 20) was added. The mixture was then pressurize at 3 bar of hydrogen at room temperature and stirred for 1 h. During this time the color solution changed from violet to black, with formation of colloidal suspension. The mixture was then depressurized under nitrogen atmosphere and the solvent removed under reduced pressure. The residue was then washed with hexane (6 × 15 cm^3) to eliminate dba and its reduced products (monitored by TLC). The black solid obtained was dried under reduced pressure. Anal. Found: C, 49.71, H, 9.15, N, 7.42, S, 1.47, Pd, 10.55%. Mean diameter (TEM, nm): 22.

Pt-III: To a solution of Pt$_2$(dba)$_3$ (120 mg, 0.11 mmol) in 50 cm^3 of distilled and degassed THF in a Fischer-Porter bottle, a solution of polymer **III** (140 mg, 0.44 mmol; monomer/platinum = 2) was added. The mixture was then pressurize at 3 bar of hydro-
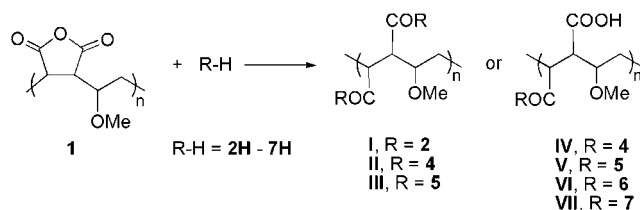
Scheme 1 Synthesis of functionalized polymers (**I-VII**) from Gantrez, 1.

gen at room temperature and stirred for 1 h. During this time the color solution changed from violet to black, with formation of colloidal suspension. The mixture was then depressurized under nitrogen atmosphere and the solvent removed under reduced pressure. The residue was then washed with hexane (6 × 15 cm³) to eliminate dba and its reduced products (monitored by TLC). The black solid obtained was dried under reduced pressure. Anal. Found: C, 47.70, H, 8.97, N, 7.14, S, 1.42, Pt, 9.44%. Mean diameter (TEM, nm): 100.

Catalysis

Catalytic C—C Suzuki coupling using phenylboronic acid

5 mg of **Pd-III** nanoparticles were mixed in a Schlenk vessel with 0.98 g (12 mmol) of NaOAc, 0.73 g (6 mmol) of phenylboronic acid and 0.31 g (2 mmol) of phenylbromide in 20 cm³ THF, during 14 h at reflux temperature. Organic products were extracted with diethyl ether, dried over anhydrous $MgSO_4$, filtered off, evaporated under reduced pressure and analyzed by ^{1}H-NMR.

Catalytic C—C Suzuki coupling using 2-methylnaphtyl-1-yl boronic acid

5 mg of **Pd-III** nanoparticles were mixed in a Schlenk vessel with 0.57 g (3 mmol) of $Ba(OH)_2 \cdot H_2O$, 0.37 g (2 mmol) of 2-methylnaphtyl-1-yl boronic acid and 0.41 g (mmol) of 1-bromonaphtalene in 12 cm³ of DME : H_2O (5/1), overnight at reflux temperature. Reaction was monitored by GC.

Catalytic hydrogenation of ethyl pyruvate with polymer-stabilized rhodium(0) nanoparticles.

0.95 mmol (25 eq) of monomeric units of polymer were dissolved in a water/ethanol (1/1) mixture and stirred for several days. Ten milligram of $RhCl_3 \cdot 3H_2O$ (0.038 mmol) were added and stirred for 30 min. The reaction mixture was hydrogenated under 30 bar during 1 h and turned into a black colloidal suspension. 440 mg of ethylpyruvate (3.8 mmol) was then added and the reaction mixture

was hydrogenated at room temperature under 10 bar H_2. Reaction was monitored by GC.

RESULTS AND DISCUSSION

Functionalized polymers

Gantrez derivatives

Ester (**I**) and amide (**II-VII**) polymers were prepared by reaction of **1** with **2H** and the appropriated amines (**4H–7H**), respectively. Both the alcoholysis and aminolysis processes led to a complete opening of the anhydride groups, except for menthol (**3H**) (in this case, a low percentage of anhydride functions reacted) (Scheme 1). Mono- (**IV-VII**) or difunctionalized (**I-III**) polymers were obtained depending on the nature of the nucleophilic agent (alcohol or amine) and the reaction conditions (see Supplementary information for detailed discussion at http://www.interscience.wiley.com/jpages/0021-8995/suppmat).

Polymers **I-VII** were characterized in solid state by elemental analysis, IR and NMR (^{13}C MAS NMR and ^{1}H HRMAS NMR) spectroscopies (IR and ^{13}C MAS NMR spectra for **I-VII** are collected in the Supplementary material).

In relation to the nature of the functional groups present in the polymers, IR spectroscopy was specifically useful in the 1900–1600 cm^{-1} distinctive region, which allows the comparative study of COR moieties (anhydrides, carboxylic acids, esters, and amides) (Table I). Gantrez shows two strong bands at 1871 and 1784 cm^{-1}, typical for five-membered cyclic anhydrides. The diesterified polymer **I** exhibits only one strong band at 1735 cm^{-1} corresponding to the stretching C=O; in addition, the two bands observed at 1183 and 1114 cm^{-1} were characteristic for the asymmetrical and symmetrical C—O stretching, respectively. In relation to amide derivatives, polymers **II-VII** show two strong bands at 1729–1689 and 1649–1555 cm^{-1}, typical for C=O and N—C=O symmetric stretching respectively. For polymers **IV-VII** containing carboxylic acid groups, a large absorption at ~ 3400 cm^{-1} is observed because of the COO—H stretching. For mono-amide/mono-acid derivatives (**IV-VII**) and for the diesterified

TABLE I
IR and ^{13}C NMR MAS Data for 1 and I-VII Polymers

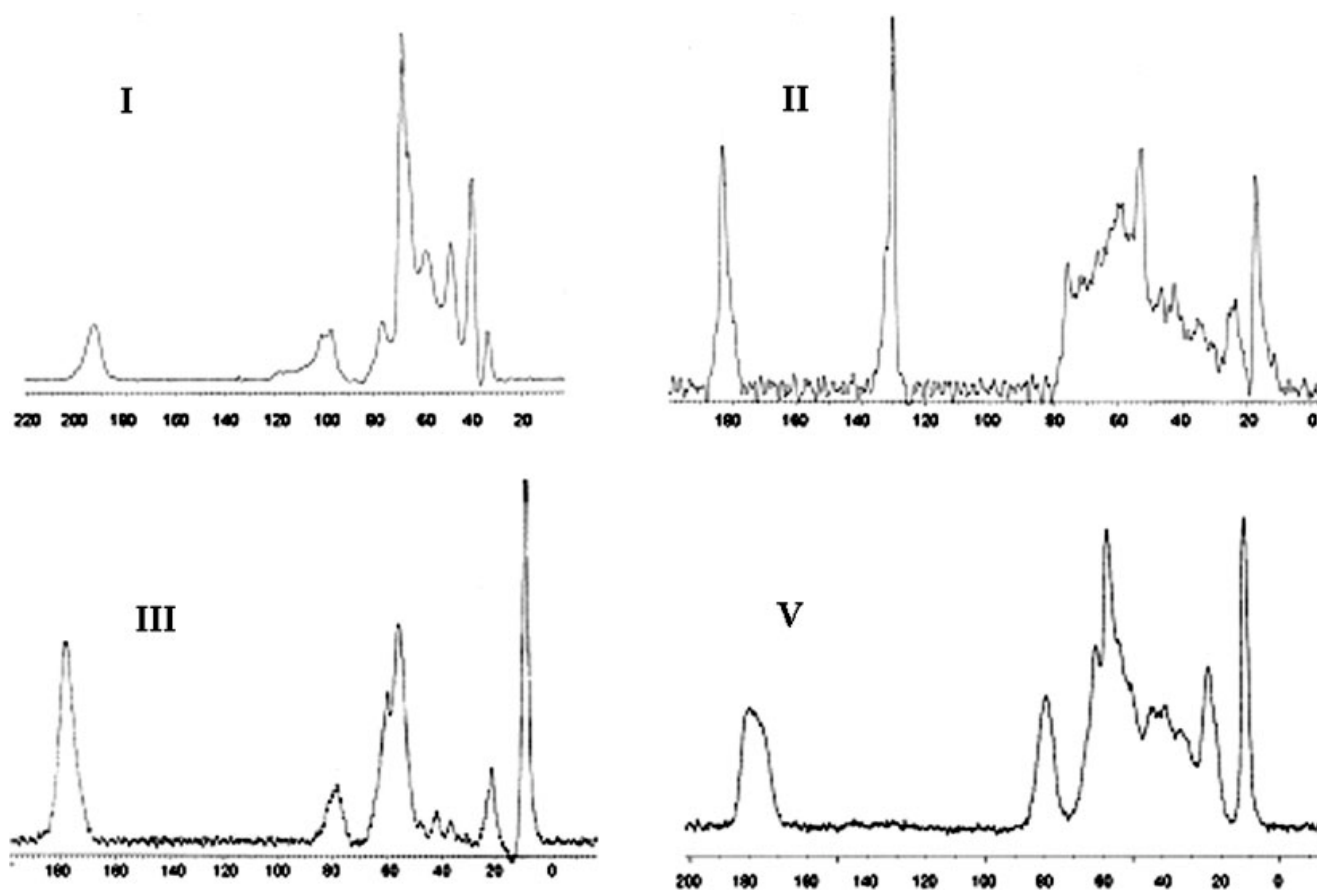| Polymer	v_{st}(COR) (cm^{-1})	δ(CO) (ppm)	δ(CH_2OH)(ppm)
1	1871; 1784	173.0	–
I	1735	172.8	–
II	1729; 1649	183.1	–
III	1700; 1644	178.3	59.6
IV	1716; 1642	176.4	–
V	1689; 1555	178.8	61.5
VI	1723; 1649	177.6	–
VII	1716; 1635	176.8	–

Figure 2 ^{13}C MAS NMR (75.4 MHz) spectra of I, II, III and V.

polymer **I**, one medium absorption is also detected at the region 1450–1480 cm^{-1} because of the O—C=O symmetrical stretching.

^{13}C MAS NMR spectra were recorded for all the polymers prepared, **I-VII**, the carbonyl region being the most useful zone (Fig. 2). In the case of the fully difunctionalized polymers, **I-III**, one symmetrical signal is observed for the quaternary carbonyl carbon atom (Table I). For the diester derivative **I**, the chemical shift is close to that of Gantrez (~ 173.0 ppm); while for the diamide polymers **II** and **III**, chemical shifts at lower fields are observed (~180 ppm). The monoacide-monoamide polymers, **IV-VII**, show in the carbonyl region one signal. Unfortunately, no differences can be detected between carboxylic acid and amide carbonyl groups. Other chemical shifts indicate the presence of alkyl substituents bonded to primary (17.4, 9.2, 14.3, 12.7 ppm for polymers **II**, **III**, **VI**, **VII**) or secondary carbon atoms (21.4, 20.9 ppm for polymers **III**, **VI**), and aromatic carbons (130.1 and 128.2 ppm for **II** and **IV** respectively). In this sense, the chemical shift corresponding to CH$_2$OH for polymer **III** (59.6 ppm) and **V** (61.5 ppm) points to the formation of amide and no ester bonds, which would be expected at lower field (~ 70 ppm for CH$_2$OOC group). In the case of

III, the chemical shift at 54 ppm corresponds to CH—NOC, excluding the ester formation (in this case, a chemical shift at ~ 40 ppm would be expected due to CH—NH$_2$ group).[83]

Unfortunately, full characterization in solution could not be carried out for all of them, because of their low solubility. Only **III** formed a gel in water, allowing us recording the ^{1}H HRMAS NMR spectrum (see below).

Polymer **III** in water swells up and gives a gelatinous mixture in contrast to the other synthesized polymers. ^{1}H HRMAS NMR spectrum in D$_2$O could be then recorded. Using a CPMG (Carr-Purcell-Meiboom-Gill) sequence, protons with significant differences in relaxation time T_2 can be differentiated. The protons close to the polymeric chain show more restricted mobility (in general, smaller T_2) in the medium than those placed in the lateral chains, and they can be cancelled. In Figure 3, both spectra, with a single pulse (a) and with a CPMG sequence (b) are represented. Two types of signals depending on the relative broadening are distinguished [Fig. 3(a)]. The larger signals are not almost detected when the CPMG sequence was applied [Fig. 3(b)], only observing the side chain protons. To prove that these signals are not because of free aminoalcohol,
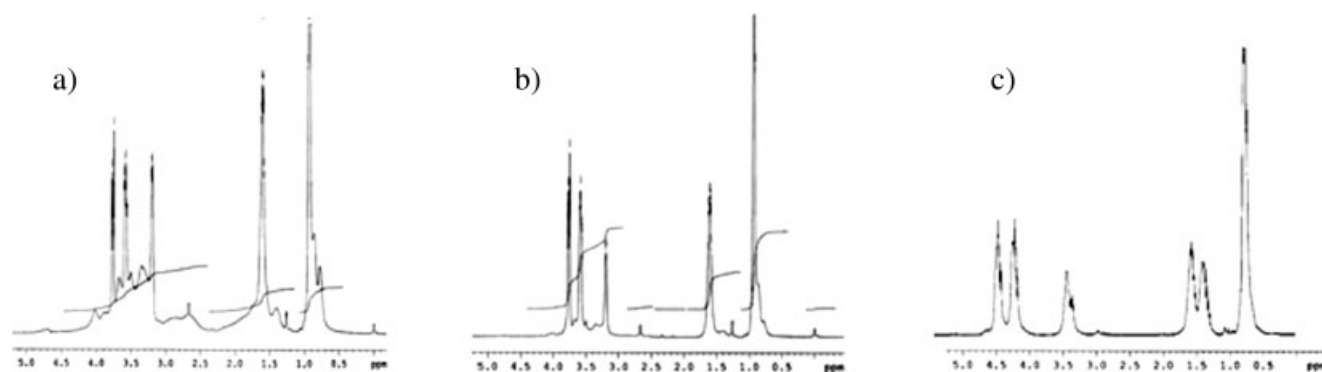
Figure 3 ^{1}H HRNMR MAS spectra (500 MHz, D$_2$O) for III: a) spectrum obtained with a single pulse; b) spectrum obtained with a CPMG sequence (total relaxation delay 40 ms); c) spectrum obtained with a CPMG sequence (spin echo total time 40 ms) after addition of 10% 5H.
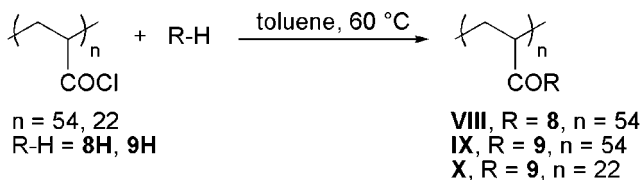
10% of **5H** was added [Fig. 3(c)]. The broadening and shifts of the signals point to the interaction between side chain groups and free aminoalcohol.

GPC-LS analyses were performed to determine the degree of functionalization of the synthesized polymers. The data obtained for the starting material **1** (M_w = 1350, M_n = 725 kg mol^{-1}) was in agreement with the commercial data for Gantrez AN-139 grade (M_w = 1080 kg mol^{-1}). Only polymer **IV**, which was completely soluble in hexafluoro-2-propanol, leads to compatible results with a total opening of the anhydride groups and a CONHR/COOH ratio 1/1 (M_w = 2470 kg mol^{-1} and M_n = 1165 kg mol^{-1}). For **I** and **II**, the molar masses obtained were higher than expected, probably due to their low solubility. Polymers **III** and **V** were not detected under these analytical conditions.

Polyacrylate derivatives

Amine (**VIII**) and ammonium derivatives (**IX** and **X**) were synthesized from commercial sodium polyacrylates (—(CH$_2$—CH(COONa))$_{22}$— and —(CH$_2$—CH(COONa))$_{54}$—). These polymers were water soluble and consequently could be used as stabilizers of metallic nanoparticles in aqueous solution (see below, rhodium nanoparticles).

Polymers **VIII-X** were prepared by reaction between the appropriated polyacryloyl chloride and N,N-dimethylethanolamine (**8H**) or its ammonium salt derivative (**9H**), as shown in Scheme 2. These

new compounds were also characterized by infrared spectroscopy, ^{1}H and ^{13}C-NMR spectroscopy, and elemental analysis (see Supplementary material for IR and NMR spectra). GPC (in THF) and mass spectrometry (MALDI and FAB) analysis were performed, but no concluding results could be deduced.

IR spectra evidenced ester and carboxylic acid groups as analogously described above for Gantrez derivatives. Concerning the functionalization degree of the main polymeric chain, the ratio ester/acid, determined by elemental analysis, was found 1/1.2, 1/0.2, and 1/0.3 for **VIII**, **IX** and **X** respectively, showing that ionic alcohol (**9H**) is more reactive than neutral one (**8H**). Both NMR spectra and elemental analysis pointed to the presence of free ammonium salt (**9H**) for **X**, in a monomer/ammonium ratio 1/1.5, which can justify its higher solubility in water and alcohols than that observed for **IX**.

Metal nanoparticles stabilized by functionalized polymers

Palladium and platinum nanoparticles containing polymer III

Platinum and palladium nanoparticles were prepared from the corresponding organometallic precursor, [M_2(dba)$_3$], in presence of polymer **III** under dihydrogen atmosphere in THF solution (Scheme 3), following the methodology described by Chaudret et al.[18]

Scheme 2 Synthesis of polyacrylate derivatives **VIII**, **IX** and **X**.

Scheme 3 Synthesis of Pt and Pd nanoparticles stabilized by polymer **III**, **Pt-III** and **Pd-III**.

Figure 4 TEM micrographs for: a) Pt-III (Φ_m = 21 nm); b) Pd-III (Φ_m = 22 nm).

Under these conditions, the polymer was soluble and a gray-black suspension of colloid was formed after few minutes (~15 min). The reaction was stirred for 1 h at room temperature. Dibenzylidenacetone (dba) decoordination is therefore favored; in addition, dba is partially reduced (dbaH) as observed by ^{1}H-NMR analysis of extracted fractions. To eliminate the organic by-products, the black residue was washed with hexane (monitored by TLC and ^{1}H-NMR).

The nanoparticles were characterized by IR spectroscopy, elemental analysis and transmission electronic microscopy (TEM). IR spectra (KBr pellets) of **Pt-III** and **Pd-III** showed the characteristic absorption bands corresponding to **III** (see above), without any shifting relative to the signals of the pure polymer; then no covalent strong interactions between polymer **III** and the corresponding metallic surfaces are established. The new materials contain ~ 10% of metal (determined by elemental analysis). Particles of size ~20 nm were observed (Fig. 4), showing an interparticle organization because of the polymer structure.

We have studied the influence of solvent, metal concentration and monomer/metal ratio, on the nanoparticles size. The results are summarized in Table II. We have used tetrahydrofuran and toluene as solvents, but in the case of toluene only agglomerate products were isolated. The metal concentration effect was significant for platinum compounds (entries 5 and 6, Table II) but no remarkable for palladium materials (entries 1-3, Table II), giving particles of the same average size, ~20 nm. Pt nanoparticles were also sensitive towards the relative proportion of polymer and metal (indicated by the ratio between repeated moiety of monomer and metal), obtaining small nanoparticles when low proportion of metal was present (for monomer/platinum ratio = 20, average size is ~ 20 nm, and for monomer/platinum ratio = 2, average size is ~ 60 nm; entry 6 vs. 7, Table II). However, this behavior was not observed for palladium systems (entry 2 vs. 4, Table II). In addition, the palladium allyl precursor, [Pd(μ-Cl)(η^3-C$_3$H$_5$)]$_2$, was tested under the same conditions described above (Scheme 3), using a monomer/Pd ratio 2.4 and a palladium concentration 1.2×10^{-3} mol L^{-1}, but only agglomerates were obtained.

Pd-III and **Pt-III** were tested as catalysts in C—C Suzuki couplings and ethyl pyruvate hydrogenation,

TABLE II
Mean Size for Pd-III and Pt-III Nanoparticles, in Relation to Metal Concentration and Monomer/Metal Ratio

Entry	[M_2(dba)$_3$]	[M] (mol L^{-1})	Monomer/ metal	Φ_m (nm)
1	[Pd$_2$(dba)$_3$]	2.2×10^{-3}	2.3	26
2	[Pd$_2$(dba)$_3$]	2.2×10^{-4}	2.3	18
3	[Pd$_2$(dba)$_3$]	2.2×10^{-5}	2.3	17
4	[Pd$_2$(dba)$_3$]	2.2×10^{-4}	20	22
5	[Pt$_2$(dba)$_3$]	6.9×10^{-3}	2.3	100
6	[Pt$_2$(dba)$_3$]	2.2×10^{-5}	2.3	61
7	[Pt$_2$(dba)$_3$]	2.2×10^{-5}	20	21

$$RhCl_3 \cdot 3H_2O \ + \ polymer \ \xrightarrow[\text{rt}]{\text{H}_2\text{O/EtOH} \\ \text{30 bar H}_2} \ [Rh/\textbf{polymer}]_{coll}$$

polymer: **VIII, IX, X**

Rh-VIII
Rh-IX
Rh-X

Scheme 4 Synthesis of Rh nanoparticles stabilized by polyacrylate derivatives, **Rh-VIII**, **Rh-IX**, and **Rh-X**.
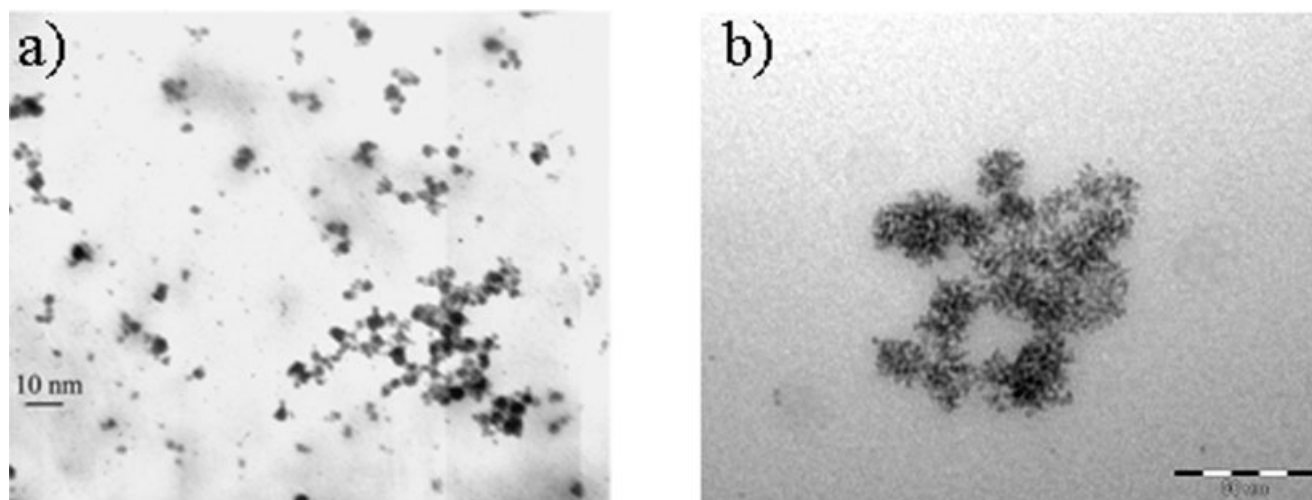
Figure 5 TEM micrographs for Rh-X: a) before catalysis ($\Phi_m = 3.5 \pm 0.5$ nm); (b) after catalysis.

respectively, (see Experimental section for details). But in any case, no activity was observed.

Rhodium nanoparticles containing water-soluble polymers, **VIII**, **IX**, and **X**

Rhodium nanoparticles were prepared by reduction of rhodium chloride salt in water under hydrogen pressure for 1 h, in the presence of the appropriated polyacrylate polymer previously dissolved in a water/ethanol mixture (Scheme 4).

Concerning the stabilization of rhodium nanoparticles, the amine polymer **VIII** and its corresponding ammonium derivative **X** prove to be quite good candidates as homogenous black colloidal suspensions, while a black solid was formed under the same reaction conditions with polymer **IX**. We could presume that the amine and ammonium functions were essential for the solubilization of the polymer in a hydroalcoholic media and that the polymer size (monomer number = 54 or 22) has an influence on the stabilization of colloidal systems, the best result being obtained with 54 monomers. Moreover, the presence of un-reacted ammonium salt (9H) in **X**, as described above, might be responsible for the better solubility of **X**, compared to **IX**, and therefore a better stabilization of metal colloids. Precisely, electrostatic and steric effects due respectively, to ionic and macromolecule parts in the polymer **X** were combined to efficiently stabilize the metallic nanoparticles in water. In this case, the significant steric repulsion associated with the ionic group provides relevant electrosterical stability towards nanocatalyst agglomeration in aqueous solution. For polymer **VIII**, the partial protonation of the dimethylamine group by the chlorhydric acid formed during the reduction process, could be proposed to justify the efficient

nanoparticles hydrosolubility. Rh colloids stabilized by **X** were analyzed by TEM [Fig. 5(a)].

The colloidal suspensions (**Rh-VIII** and **Rh-X**) and the heterogeneous catalyst (**Rh-IX**) were tested in the ethyl pyruvate hydrogenation (Table III). In the case of polymer-stabilized Rh-nanoparticles (entries 1 and 3), the substrate was totally converted into ethyl lactate in 1 h, whereas the reaction seems to be slower for the heterogeneous catalyst **Rh-IX** (entry 2). TEM micrographs of Rh-X show nanoparticles agglomeration after catalysis [Fig. 5(b)]. Nevertheless, no sedimentation of nanoparticles in bulk materials was observed after catalysis probably due to the efficient stabilizing effect of **X**. It is important to mention that no conversion is observed in the absence of catalyst, under the same conditions used in the presence of colloidal catalysts.

Moreover, we have performed the ethyl pyruvate hydrogenation in presence of cinchonidine, a chiral inducer introduced to the polymer-stabilized colloi-

TABLE III
Ethyl Pyruvate Hydrogenation Catalyzed by Rh Systems Containing Functionalized Polymers, I and VIII-X

Entry	Catalyst	Time (min)	Conv. (%)
1	**[Rh-VIII]**	60	100
2	**[Rh-IX]**	120	70
3	**[Rh-X]**	60	100
4[a]	**[Rh-X] + CD**	70	88
5	**[Rh-I]**	150	100

[a] 2 equivalents of cinchonidine (**CD**) related to rhodium were added to the catalytic system. No enantiomeric excess was detected (ee = 0%).

dal system, leading to a modified cinchonidine rhodium nanoparticles system (entry 4), approach previously reported with surfactant-stabilized platinum nanoparticles.[84] But, no asymmetric induction was observed.

For Rh system containing the water insoluble Gantrez derivative I, we observed a similar behavior like that described for Rh-IX, giving a low active heterogeneous catalyst (entry 5).

In conclusion, both types of main chain functionalized polymers, Gantrez and polyacrylate derivatives, have been obtained in satisfactory yields and mainly characterized by IR and NMR spectroscopies. These polymers have efficiently stabilized Pd, Pt and Rh nanoparticles (relative small size, less than 20 nm), by decomposition of organometallic compounds or metallic salts, under hydrogen atmosphere. The preliminary catalytic study discussed here shows their potential in hydrogenation processes in aqueous medium.

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