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Synthesis of Gold Nanoparticle Catalysts Based on a New Water-Soluble Ionic Polymer

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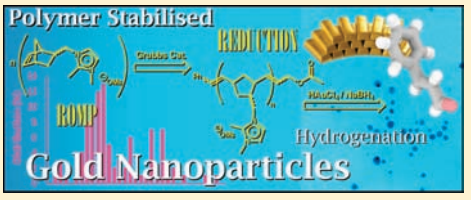
Supporting Information

ABSTRACT: A new water-soluble methyl-imidazolium-based ionic polymer was synthesized by ring-opening metathesis polymerization that was subsequently used to prepare aqueous gold nanoparticle solutions which were characterized by UV−vis spectroscopy and transmission electron microscopy (TEM). The aqueous gold nanoparticle solutions were employed as catalysts in the reduction of *p*-nitrophenol and in the hydrogenation of cinnamaldehyde and were found to exhibit excellent activity under mild conditions.



INTRODUCTION

Gold in the bulk metallic state is generally regarded to be inactive in heterogeneously catalyzed reactions.[1] In 1987, however, Haruta et al. discovered that small gold nanoparticles (GNPs <5 nm) immobilized on metal oxide supports are highly active catalysts for carbon monoxide oxidation at ambient temperatures.[2] This discovery led to considerable interest in gold catalysts,[3−5] and the range of successful catalytic applications of GNPs includes the selective oxidation of alkenes,[6−11] aldehydes,[12−17] alcohols,[18−27] and carbohydrates,[28−34] the water-gas shift reaction,[35−46] and the removal of atmospheric pollutants, such as nitrogen oxides, by reduction.[47,48] Because of the extremely small size associated with highly active GNPs, they are only kinetically stable and consequently stabilizers must be used to prevent agglomeration.[49] In aqueous solutions stabilizers providing steric protection like poly(vinyl-pyrrolidone), PVP, or poly(vinyl-alcohol), PVA, have been used for a wide range of applications.[25,26,50−55] Moreover, in the past few years polymers providing electrosteric stabilization, that is, ionic polymers, were also successfully employed as GNP stabilizers.[56,57]

This paper describes the design and synthesis of a new water-soluble ionic polymer using ring-opening metathesis polymerization (ROMP) and the role of the polymer in the stabilization of water-soluble GNPs. Their catalytic properties in the reduction of *p*-nitrophenol showed very high performance under mild conditions and in the hydrogenation of cinnamaldehyde they exhibited selectivity toward the C═O bond under certain conditions.

RESULTS AND DISCUSSION

It has previously been shown that imidazolium-containing cross-linked polymers can stabilize GNPs that, depending on the counteranion, effectively disperse in water.[57] An attractive feature of these imidazolium-containing polymers over other polymers such as PVP is that variation of the counteranion allows the physicochemical properties of the polymer to be varied in a facile manner. A limitation of this cross-linked polymer is that it has a poorly defined structure and therefore gives rise to GNPs with a wide size distributions and poorly defined shapes. We therefore decided to prepare imidazolium-containing polymer stabilizers via ROMP (see Scheme 1) using a similar synthetic methodology to that reported previously.[58]

The polymer, **2**, is generated in high yield from **1** using the commercially available second generation Grubbs Catalyst and subsequent end-capping using *cis*-1,4-diacetoxy-2-butene,[59] since the more commonly used vinylethylether was not efficient at decoupling the final ruthenium complex from the terminal end of the polymer. The polymer is insoluble in common organic solvents, and precipitates in CH_2Cl_2; thus the final capping reaction is more difficult. To ensure an efficient cross metathesis reaction between the polymer end chains and the *cis*-1,4-diacetoxy-2-butene capping agent, a small amount of degassed MeOH was added to the reaction medium. The polymer was then dissolved in water and the resulting uncoupled catalyst was extracted with CH_2Cl_2. The final purification of the polymer was performed by dialysis in water using a membrane tube with molecular weight cut off of 2000.

Synthesis and Characterization of the Polymer Stabilized GNPs. GNPs were prepared from $HAuCl_4$, the polymer, and $NaBH_4$ in water with the gold/polymer ratios indicated in Table 1. As soon as a freshly prepared aqueous solution of $NaBH_4$ was added to the solution containing $HAuCl_4$ and the polymer, the solutions turned from orange to red-brown, indicative of the formation of GNPs of <10 nm diameter.[60] GNP solutions in water usually feature a Surface Plasmon Band (SPB), that is, a broad absorption band in the visible region around 520 nm.[60] The UV−vis spectra (Supporting Information, Figure S1) of **GNP1**−**3** show a characteristic absorption at about 520 nm, consistent with a particle size below 10 nm, whereas in **GNP4** this absorption is absent suggesting the formation of GNPs with a core diameter of <4 nm;

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Scheme 1

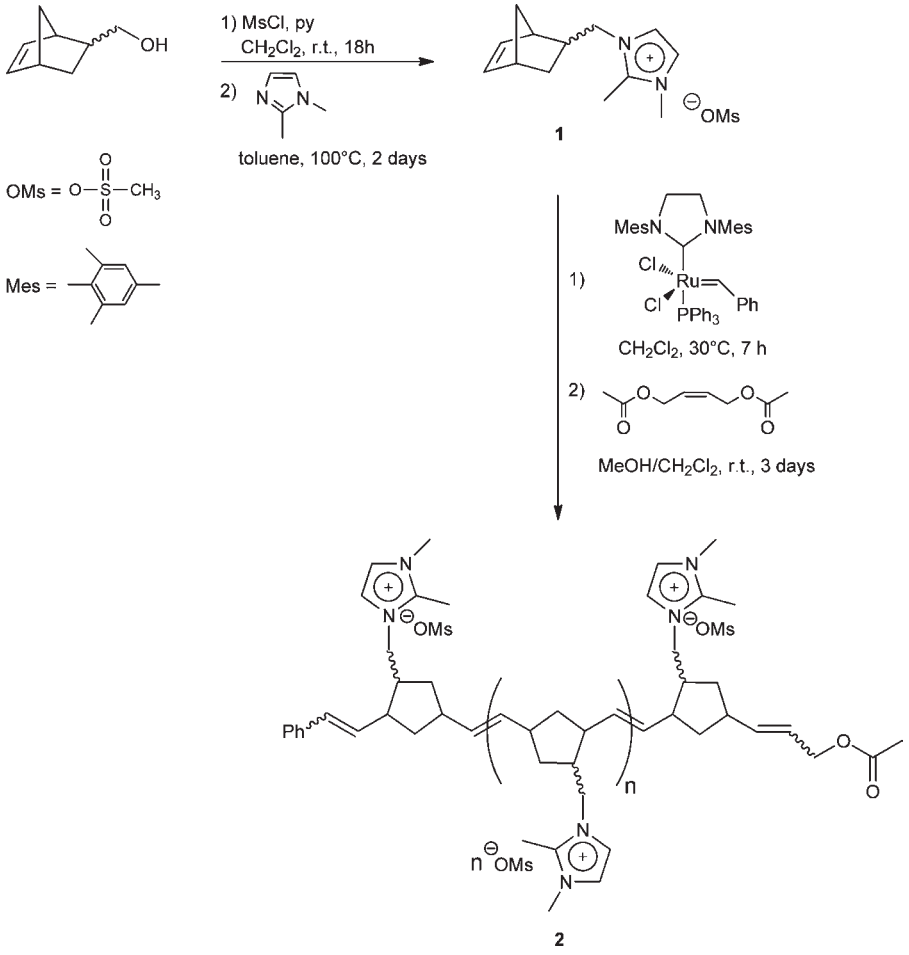

Table 1. Composition of the GNP Solutions Used in This Study[a]

solution	ratio of polymer/Au
GNP1	3:1
GNP2	5:1
GNP3	10:1
GNP4	50:1

[a] All solutions were prepared with a 1:1, w/w ratio of $NaBH_4$ to Au at a concentration of 100 mg L^{-1} of gold.

for such small particles, the sharpness of the SPB peak decreases because of the onset of quantum size effects.[60] The GNPs exhibit good stability although in the case of **GNP4** (Supporting Information, Figure S1) an absorption peak is observed after about 2 months indicating that aggregation of the GNPs has occurred; however, the diameters of the aggregates are <10 nm.

Confirmation of the GNP size and distribution was obtained from TEM. At lower polymer/Au ratio the particle size was found to be quite broad, whereas in the case of **GNP4**, which contains the highest polymer/gold ratio of 50:1, the GNPs showed a very narrow monodisperse distribution in the range of 1.8 to 2.8 nm (see Figure 1).

The size and dispersity of the GNPs appear to be directly correlated with the amount of polymer used in their preparation. Presumably the polymer layer adsorbed on the surface of GNPs serves as a barrier, resulting in diffusion-limited growth, which reduces the size distribution of the initial nuclei and, at high concentrations, leads to near monosized nanoparticles.[61]

Catalytic Reduction of *p*-Nitrophenol. The catalytic reduction of *p*-nitrophenol by GNPs using $NaBH_4$ in water is a well-known reaction which proceeds through an electrochemical mechanism, where the electron transfer occurs through the nanoparticle surface. The catalytic efficiency may be explained by the nanoparticle redox properties relating with the particle size and the nanoparticle potential, which has to be in the range of the potential of the reducing agent (the donor) and the substrate (the acceptor).[62]

The catalytic properties of **GNP1**−**4** were initially evaluated in the reduction of *p*-nitrophenol, chosen as a model system, as the reaction is easily monitored by UV−vis spectroscopy. The **GNP4** solution exhibited the best performance, presumably because of their small size and greater stability, emanating from the higher amount of polymer stabilizer present. It is also conceivable that the polymer facilitates diffusion of the substrate onto the NP surface which further enhances catalytic activity. Consequently, **GNP4** was further studied at different GNP/*p*-nitrophenol ratios (see Table 2); a large excess of $NaBH_4$ was used so that the kinetics could be evaluated with respect to *p*-nitrophenol consumption.

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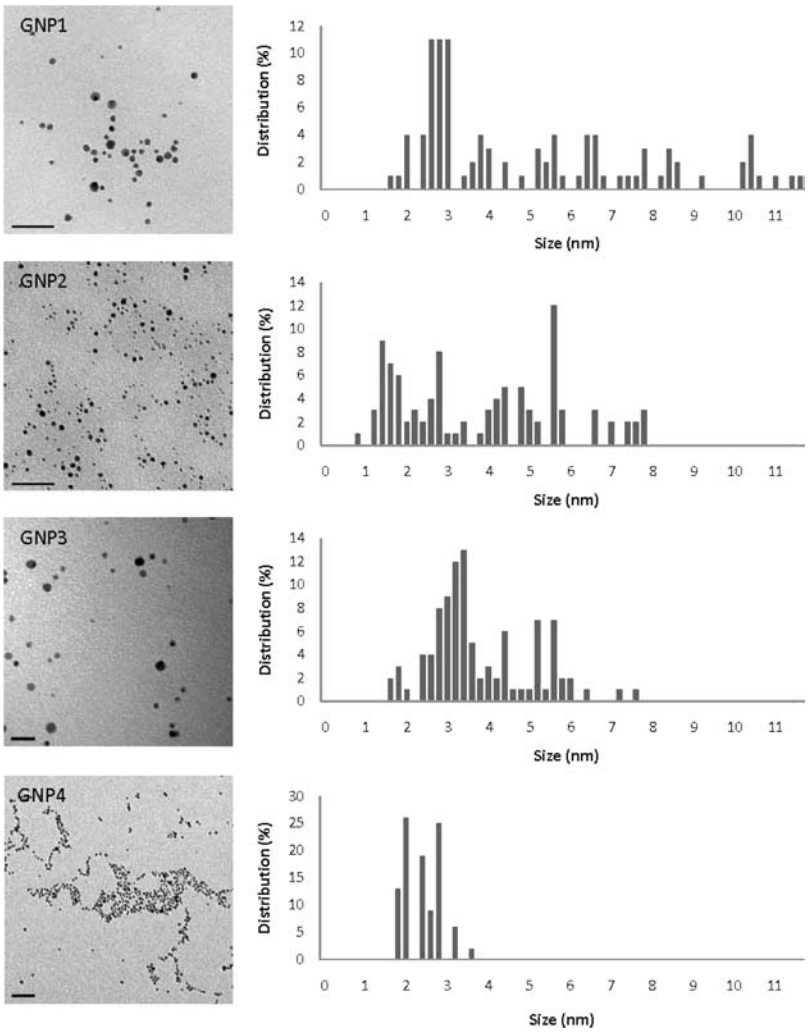

Figure 1. TEM images and size distribution histograms for **GNP1** (scale bar 50 nm), **GNP2** (scale bar 50 nm), **GNP3** (scale bar 20 nm), and **GNP4** (scale bar 20 nm).

Table 2. GNP4:*p*-Nitrophenol Ratios and Associated Rate Constants for the Reduction of *p*-Nitrophenol with $NaBH_4$[a]

entry	ratio of **GNP4**:*p*-nitrophenol	k (min^{-1})
1	1:5	1.9905
2	1:7	1.573
3	1:28	0.766
4	1:56	0.732
5	1:70	0.5485
6	1:90	0.5204
7	1:140	0.077

[a] *p*-Nitrophenol solution (0.048 mM), **GNP4** (0.5076 mM), $NaBH_4$ (10 mg); in all experiments $NaBH_4$/*p*-nitrophenol ratio is 88:1. Removal of oxygen from the reaction mixture is required to produce reproducible results.[62,63]

As confirmed by control experiments, in absence of **GNP4**, the reduction of *p*-nitrophenol with $NaBH_4$ did not take place, and the reaction mixture showed only an absorption peak at 400 nm in the UV−vis spectrum which corresponds to the formation of *p*-nitrophenate. The addition of **GNP4** to the reaction mixture caused the yellow solution to reduce in intensity with complete bleaching observed. The gradual disappearance of the absorption peak at 400 nm and the formation of a new peak at 300 nm indicated that the substrate had been consumed with the formation of *p*-aminophenol (Figure 2). The change of absorbance values at 400 nm over time and the consequent linear relationship between ln(absorbance) and time for the reactions are indicative of pseudo first-order kinetics with respect to *p*-nitrophenol consumption (Figure 3) allowing the apparent rate constants, k, to be estimated (Table 2), in agreement with related nanocatalysts.[63−69]

GNP4 exhibited high catalytic activity for the reduction of *p*-nitrophenol which reached completion within a few minutes. Although at the highest substrate/catalyst ratio (Table 2, entry 5), the dependence between the absorbance values at 400 nm and time is linear[62] (see Supporting Information, Figure S2) and the reduction is complete in <20 min. **GNP4** compares favorably with other GNP catalysts. For example, Haruta et al. found that the rate of GNPs, deposited on poly(methyl methacrylate), is 7.3×10^{-3} s^{-1} using a substrate/catalyst ratio of 1:15.[64] Liu reported GNPs that catalyzed the reduction of *p*-nitrophenol in 19 min at a substrate/GNP ratio of 1:10.[70] Pal et al. were able to obtain complete conversion in 4 min with GNP, but only using a

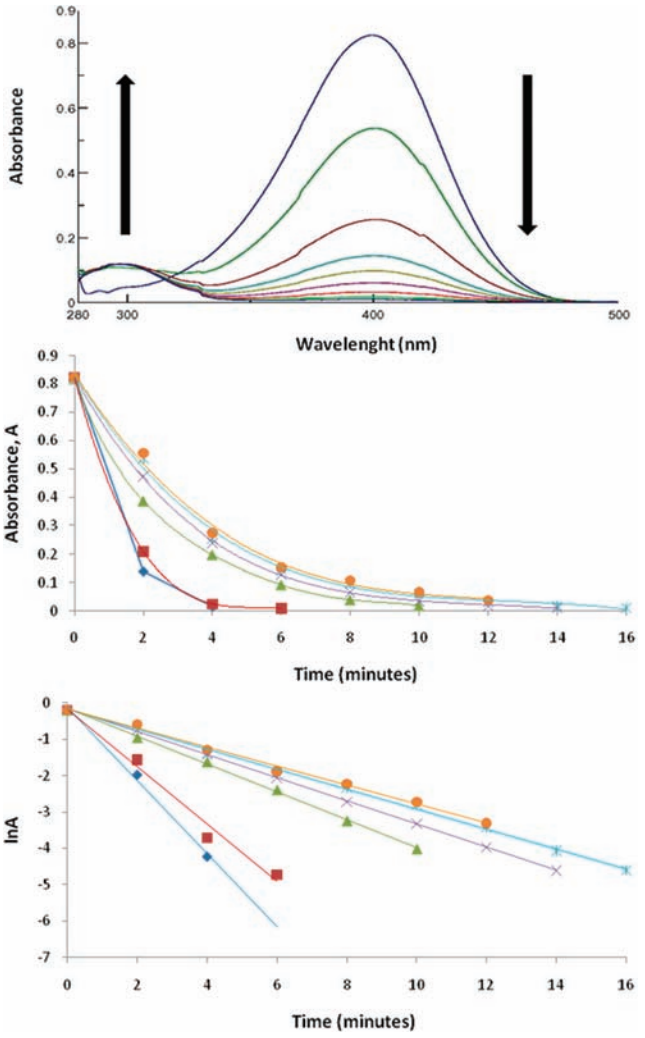

Figure 2. (top) Successive UV−vis spectra recorded every 2 min for *p*-nitrophenol reduction (**GNP4**/*p*-nitrophenol 1:70, entry 5 in Table 2); (middle) Kinetic curves for the reduction of *p*-nitrophenol with $NaBH_4$ in water using **GNP4** obtained by plotting the absorbance values against time: blue diamonds, 1; reddish brown squares, 2; light green triangles, 3 × 4; light blue asterisks, 5; yellow circles, 6. (bottom) Estimation of rate constants by plotting ln(absorbance) against time: blue diamonds, 1; reddish brown squares, 2; light green triangles, 3; purple circles, 4; light blue asterisks, 5; yellow circles, 6 (numbers refer to the entries in Table 2).

substrate/GNP ratio of 1:12 and a *p*-nitrophenol/$NaBH_4$ ratio of 1:500.[62]

Catalytic Hydrogenation of Cinnamaldehyde. Since **GNP4** is extremely active under mild conditions for the reduction of *p*-nitrophenol we decided to evaluate the GNP catalysts in the hydrogenation of cinnamaldehyde. The selective reduction of C═O bonds, when conjugated to a C═C bond, represents another important application of GNP catalysts. This type of hydrogenation reaction is of industrial interest as it provides access to different α,β-unsaturated alcohols that are commonly used as flavors and fragrances and are key intermediates in the synthesis of pharmaceuticals.[71] The selective reduction of C═O bonds is usually achieved by transfer hydrogenation,[72−76] or is performed with reducing agents such as $NaBH_4$, although the use of molecular hydrogen is more suitable for industrial applications.[77] However, the ability of a catalyst to selectively hydrogenate a C═O functionality when conjugated with a C═C double bond is a major challenge because the hydrogenation of a C═C double bond is kinetically and thermodynamically favored.[78,79] In recent years many supported GNP-based catalytic systems have been developed,[71,78−85] but studies on the hydrogenation of aldehydes and ketones show that the outcome of the reaction is strongly related to the support material used to immobilize the particles, making it difficult to distinguish the ability of the GNP catalysts to selectively hydrogenate the carbonyl group. The use of unsupported GNPs is more suitable to study their true catalytic activity; however, there are only a few reports on the selective hydrogenation of α,β-unsaturated aldehydes and ketones with unsupported GNPs. For example, De Vos and co-workers carried out the reaction on several α,β-unsaturated carbonylic compounds with polyvinylpirrolidone-stabilized GNPs in DMF,[86] and Jin and co-workers studied the selective hydrogenation of benzalacetone with thiolate-stabilized GNPs in a toluene-ethanol mixture,[87] but kinetic studies were not reported. Consequently, **GNP1−4** were screened as catalysts in the hydrogenation of cinnamaldehyde, a reaction that can result in the formation of three products, that is, cinnamyl alcohol from selective hydrogenation of the C═O group, hydrocinnamaldehyde from selective hydrogenation of the C═C double bond, and the fully hydrogenated product, hydrocinnamyl alcohol (see Scheme 2).

The **GNP4** solution showed promising activity and was further studied in situ by NMR spectroscopy, under a H_2 pressure of 100 bar in a sapphire NMR tube,[88] which allowed the reaction products to be continuously monitored. At 70 °C the highest selectivity is obtained after 40 min with a conversion of 30% (see Supporting Information). At 40 min the cinnamyl alcohol corresponds to 73% and the hydrocinnamaldehyde to 27% of the obtained products. Hydrocinnamyl alcohol is only observed after 1 h and while the concentration of cinnamyl alcohol increases rapidly during the first 4 h, the concentration of hydrocinnamaldehyde does not change after the first hour. Both of the partially reduced products start to decrease in concentration after 4 h, and by 14 h the hydrocinnamaldehyde is almost completely consumed.

Under the conditions described above the GNPs selectively reduce the C═O group at the initial stage of the reaction, when the conversion of cinnamaldehyde is relativity low, but at higher conversions hydrogenation of the C═C double bond is observed, although the resulting hydrocinnamaldehyde is proportionally smaller than the corresponding alcohols. Tsukuda[89] and co-workers demonstrated that GNPs interact (and activate) carbonyl groups preferentially over C═C bonds which presumably leads to the initial selectivity for the hydrogenation of the C═O bond. As the broad peak in the range 5.4−6.0 ppm, that corresponds to the C═C double bonds of the polymer, remains unchanged at the end of the reaction it would appear that they do not undergo hydrogenation (see Supporting Information, Figure S4), although it has been shown that polynorbornenes can be hydrogenated with molecular catalysts.[90−92]

The hydrogenation of cinnamyl alcohol and hydrocinnamaldehyde to hydrocinnamyl alcohol were performed separately under the same conditions, that is, 100 bar H_2 pressure at 70 °C (see Supporting Information), indicating why the selectivity of the reaction at 70 °C is not high. At elevated temperatures preferential interactions between the carbonyl group and the gold surface are presumably reduced, and indeed, at 60 °C the

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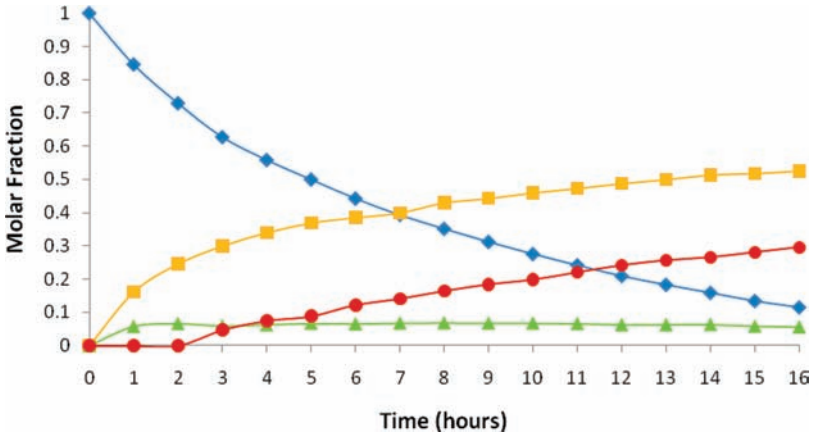
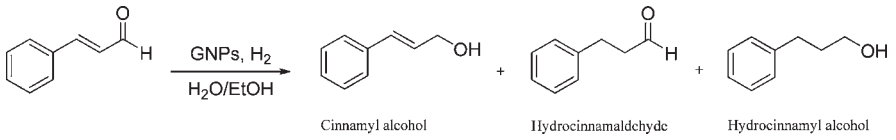


Figure 3. Kinetic curves for cinnamaldehyde hydrogenation at 60 °C and 100 bar H_2 using the **GNP4** solution: light blue diamonds, Cinnamaldehyde; yellow squares, Cinnamyl alcohol; light green triangles, Hydrocinnamaldehyde; red circles, Hydrocinnamyl alcohol.

Scheme 2



hydrogenation of cinnamaldehyde exhibits higher selectivity toward the cinnamyl alcohol product (78% after 2 h albeit at a conversion of only 27%). However, after 3 h the formation of hydrocinnamyl alcohol is also observed, although the overall selectivity toward cinnamyl alcohol remains essentially unchanged (Figure 3).

As shown from kinetic studies, the hydrogenation of cinnamaldehyde is a first order reaction with respect to the substrate consumption, and the estimation of rate constants equates to 0.52 h^{-1} and 0.12 h^{-1} for the hydrogenation performed at 70 and 60 °C, respectively (see Supporting Information for details).

The selectivity is not significantly improved at lower temperatures, and the rate of hydrogenation becomes very slow (after 40 h at 50 °C, 10% of the cinnamaldehyde starting material is present). The hydrogenation studies show that the selectivity for the reduction of the carbonyl group in cinnamaldehyde is possible, even if subsequent competitive hydrogenation of the C═C bond occurs, resulting in the saturated alcohol product. It is noteworthy that ruthenium[93] and palladium[94] NPs have been used for the hydrogenation of cinnamaldehyde under mild conditions, but both show a high selectivity for the C═C bond and hydrocinnamaldehyde is the main product. As expected, the larger GNPs are also less active (see Supporting Information), but the chemoselectivity does not change.

CONCLUSIONS

A new water-soluble ionic polymer has been prepared using ROMP, and its application as a NP stabilizer has been studied. At high polymer concentrations small well-defined GNPs were obtained that are stable against aggregation, even under catalytic conditions, and based on in situ spectroscopic studies there is no evidence to suggest that the polymer undergoes reaction during catalysis. Indeed, the GNPs were successfully employed as catalysts both in *p*-nitrophenol reduction with $NaBH_4$ and in the hydrogenation of cinnamaldehyde in aqueous solutions, demonstrating promising catalytic activity for both reactions.

EXPERIMENTAL SECTION

1,2-Dimethylimidazole was recrystallized from toluene before use. All the other chemicals were purchased from Aldrich or Acros Organics and used without further purification. Membrane dialysis tubes (MWCO 1000, MWCO 2000) were purchased from Spectrum Laboratories. Melting points were measured on a Stuart Melting Point Apparatus SMP3. ATR FT-IR spectra were recorded on a Perkin-Elmer Spectrum-One instrument using freshly ground samples pressed on top of a diamond anvil window. Sample preparation and spectral recording (in air) was performed within 2 min. Elemental microanalysis was obtained on a CE Instruments EA-1110 elemental analyzer. Mass spectra were recorded using nanoelectrospray ESI techniques using a ThermoFinnigan LCQ DECA XP Plus quadrupole ion trap instrument on samples diluted in acetone.[74] UV−vis spectra were recorded on a Jasco V-550 spectrometer. NMR spectra were measured on a Bruker DMX 400 using $SiMe_4$ as an external standard at 20 °C. For ICP-MS the samples were digested in concentrated nitric acid for 3 h and filled to a total volume of 8 mL with water. Indium was added as an internal standard at a concentration of 0.5 ppb. Determinations of total metal contents were achieved on an Elan DRC II ICP-MS instrument (Perkin-Elmer, Switzerland) equipped with a Meinhard nebulizer and a cyclonic spray chamber. The ICP-MS instrument was tuned using a solution provided by the manufacturer containing 1 ppb of each Mg, In, Ce, Ba, Pb and U. External standards were prepared gravimetrically in identical matrix to the samples (with regard to internal standard and nitric acid) with ruthenium standard obtained from CPI International (Amsterdam, The Netherlands).

Synthesis of 3-(Bicycle[2.2.1]hept-5-en-2-ylmethyl)-1,2-dimethyl-1*H*-imidazolium Methanesulfonate 1. To a solution of bicyclo[2.2.1]hept-5-en-2-ylmethyl methanesulfonate (13.96 g) in toluene (9 mL), a solution of 1,2-dimethylimidazole (6.76 g) in toluene (2 mL) was added, and the reaction mixture was vigorously stirred under

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reflux under N_2 for 2 days. After removal of the solvent under reduced pressure a dark brown viscous liquid was obtained. The product was precipitated by addition of Et_2O (300 mL) and filtered to afford a highly hygroscopic pale brown powder. Yield: 86% Mp 90−93 °C, ^{1}H NMR (25 °C, 400.1 MHz, $CDCl_3$), δ(ppm): 7.06 (m,C−H), 7.35 (m, 1H), 7.23 (m, 1H), 7.22 (m, 1H), 6.34 (m, CH═CH), 6.13 (m, CH═CH), 6.04 (m, CH═CH), 4.30−4.10 (m, 2H, CH_2O,) 3.97 (s, 3H, NCH_3), 3.88−3.77 (m, 5H), 2.94 (m, 1H), 2.88 (m, 1H), 2.79 (m, 1H), 2.74 (s, 3H), 2.71 (s, 3H), 2.69 (s, 3H), 2.55−2.50 (m, 1H), 1.98−1.84 (m, 1H), 1.54−1.26 (m, 2H), 0.67−0.64 (m, 1H). ^{13}C NMR (25 °C, 100.6 MHz, $CDCl_3$), δ(ppm): 144.09, 139.48, 137.71,135.64, 131.20, 123.17, 122.25, 121.46, 120.75, 118.75, 53.71, 52.56, 49.75, 45.11, 44.12, 42.43, 41.76, 39.52, 4, 35.70, 34.59, 30.92, 30.08, 10.99, 10.34. ESI-MS (25 °C, acetone), (m/z) positive mode: 204, 203, 97, 59; (m/z) negative mode 95, 62, 61, 60 [CH_3SO_3]. FT-IR (25 °C, solid), υ(cm^{-1}): 3123, 3098, 2975, 2951, 2875, 1534, 1538, 1459,1419,1379, 1327, 1287, 1251, 1204, 1126, 1038, 911, 767, 733, 681. Anal. Calc. for $C_{14}H_{22}N_2O_3S$ (298.4012) C, 56.35; H, 7.43; N, 9.34%. Found: C, 53.36; H, 8.03; N, 9.87%.

Synthesis of Poly-(3-((2,4-divinylcyclopentyl)methyl)-1,2-dimethyl-1*H*-imidazolium Methanesulfonate) 2. In a glovebox the monomer **1** (745 mg, 2.5 mmol) and $(IMesH_2(PCy_3))(Cl)_2Ru$=CHPh (85 mg, 0.1 mmol) were dissolved in dry CH_2Cl_2 (10 mL), and the solution was stirred at 30 °C. After 30 min a dark brown solid started to precipitate, and the solution was stirred for a further 7 h. After this time a degassed solution of *cis*-1,4-diacetoxy-2-butene (0.5 mL, 3.14 mmol) in methanol (2 mL) was added, and the reaction stirred at room temperature (RT) for 3 days. The solvents were then removed under reduced pressure, bidistilled water was added (100 mL), and after a few minutes the precipitation of a fine dark brown powder was observed. The solution was then transferred to a membrane dialysis tube (MWCO: 2000) and dialyzed for 1 week, after which the water was removed under reduced pressure and a brown solid was obtained. Yield: 80% ^{1}H NMR (25 °C, 400.1 MHz, D_2O) δ(ppm): 7.26, 5.52, 5.34, 4.71, 3.99, 3.83, 3.66, 3.15, 3.02, 2.70, 2.48, 2.15, 2.01, 1.72, 1.56, 1.14. FT-IR (25 °C, solid), υ(cm^{-1}): 3434, 3135, 2931, 1644, 1588, 1538, 1453, 1421, 1328, 1176, 1037, 978, 767, 700. Ru content <0.005% (w/w).

Synthesis of the GNPs. To an aqueous solution of $HAuCl_4$ (1 mg/mL, 3 mL, 7.62 μmol) an aqueous solution of **2** (22.86 μmol of **2** for **GNP1**, 38.1 μmol for **GNP2**, 76.2 μmol for **GNP3**, 381 μmol for **GNP4**) was added. Under vigorous stirring an aqueous $NaBH_4$ solution (0.5 mg/mL, 3 mL, 39.6 μmol) was rapidly added, and the color immediately turned from pale yellow to red-brown. After stirring the solution for 2 min, bidistilled water was added to obtain a final volume of 15 mL, and then the samples were dialyzed for 24 h (MWCO: 1000).

Catalytic Reduction of *p*-Nitrophenol. To a Schlenk flask (250 mL) an aqueous solution of *p*-nitrophenol (5 mL, 0.625 mM) was added diluted in water (65 mL), and the solution was degassed. $NaBH_4$ (10 mg) was added, and the solution immediately turned from pale to intense yellow. A 1.6 mL portion of this solution was transferred in a 2 mL quartz cuvette, **GNP4** (20 μL, 0.5076 mM of Au, in this case the GNP:substrate ratio is 1:7), and degassed water (30 μL) was added to keep the same *p*-nitrophenol concentration in all experiments. The course of the reaction was monitored by UV−vis spectroscopy recording a spectrum every 2 min. Experiments were repeated three times each to ensure reproducibility.

In Situ NMR Studies. In a typical experiment a freshly prepared GNP solution in D_2O (0.4 mL) and cinnamaldehyde (1.3 μL) in EtOH (20 μL) were mixed and transferred to a 10 mm sapphire NMR tube.[95] The mixture was pressurized to 100 bar and immediately introduced to the NMR spectrometer set at the appropriate temperature. Spectra were recorded every 10 min until the reaction neared completion. Note, as a H_2 pressure of 100 bar corresponds to an approximate H_2 concentration of 0.081 M dissolved in water,[96,97] a substrate:catalyst ratio of 50:1 was employed to ensure that the concentration of H_2 in the solution was in excess compared to the substrate. The samples were prepared as D_2O solutions with 8.4% EtOH included as a cosolvent to improve the solubility of the substrates.

TEM. **GNP1−3** (0.1 mL) was diluted in bidistilled water (0.5 mL) and immersed in a ultrasonic bath at 20 °C for 5 min. One drop of this solution was deposited on a carbon film copper grid (200 mesh) and dried under vacuum for 2 h prior to analysis. In the case of **GNP4**, the solution (1.0 mL) was reduced in volume (0.1 mL) and ultrasonicated for 5 min at 20 °C. One drop was deposited on a carbon film copper grid (200 mesh) and dried under vacuum for 12 h prior to analysis. TEM images were obtained on a PHILIPS/FEI CM20 transmission electron microscope (200 KeV) using Quantifoil Carbon film Cu grids on 200 mesh as specimen supports. The size distribution was estimated from 200 nanoparticles.

■ ASSOCIATED CONTENT

Supporting Information. Further details are given in Figures S1−S12. This material is available free of charge via the Internet at http://pubs.acs.org.

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