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## Gold Nanoparticles Incarcerated in Nanoporous Syndiotactic Polystyrene Matrices as New and Efficient Catalysts for Alcohol Oxidations

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Abstract: The controlled synthesis of gold nanoparticles (AuNPs), incarcerated in a semicrystalline nanoporous polymer matrix that consisted of a synpolystyrene-co-cis-1,4-polydiotactic butadiene multi-block copolymer is described. This catalyst was successfully tested in the oxidation of primary and secondary alcohols, in which we used dioxygen as the oxidant under mild conditions. Accordingly,  $(\pm)$ -1-phenylethanol was oxidised to acetophenone in high yields (96%) in 1 h, at 35°C, whereas benzyl alcohol was quantitatively oxidised to benzaldehyde with a selectivity of 96% in 6 h. The specific rate constants calculated from the corresponding kinetic plots were among the highest found for polymer-incarcerated AuNPs. Similar values in terms of reactivity and selectivity were found in the oxidation of primary alcohols, such as cinnamyl alcohol and 2-thiophenemethanol, and secondary alcohols, such as indanol and  $\alpha$ -tetralol. The remarkable catalytic properties of this system were attributed to the formation, under these reaction conditions, of the nano-

**Keywords:** alcohol oxidation • gold • heterogeneous catalysis • nanoparticles • nanoporous polymer matrix

porous  $\varepsilon$  crystalline form of syndiotactic polystyrene, which ensures facile and selective accessibility for the substrates to the gold catalyst incarcerated in the polymer matrix. Moreover, the polymeric crystalline domains produced reversible physical cross-links that resulted in reduced gold leaching and also allowed the recovery and reuse of the catalyst. A comparison of catalytic performance between AuNPs and annealed AuNPs suggested that multiple twinned defective nanoparticles of about 9 nm in diameter constituted the active catalyst in these oxidation reactions.

### Introduction

Gold nanoparticles (AuNPs) with controlled dimensions and a narrow dimensional distribution have found application in nanoscience<sup>[1a]</sup> and nanotechnology,<sup>[1]</sup> because of their peculiar electronic<sup>[2]</sup> and optical<sup>[3]</sup> properties. Remarkably, this "noble metal" was converted into a highly active redox catalyst when the particle size was reduced to 1–10 nm.<sup>[4]</sup> Actually, the AuNP-catalysed oxidation of alkanes,<sup>[5]</sup> alcohols,<sup>[6]</sup> and olefins to the corresponding carbonyl<sup>[7]</sup> compounds and epoxides;<sup>[8]</sup> the direct synthesis of hydrogen peroxide;<sup>[9]</sup> and the oxidation of carbon monoxide to carbon dioxide<sup>[10]</sup> under mild conditions and in the presence of air or dioxygen as the oxidising agent,<sup>[11]</sup> have been recently reported. One

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Dipartimento di Scienze Molecolari e Nanosistemi Università Ca' Foscari Venezia Via Torino 155/B, 30170 Venezia-Mestre (Italy) of the main targets in gold catalysis is to stabilise the AuNPs to prevent the aggregation of the nanoparticles without deactivating the active sites. For this purpose the AuNPs are typically supported on carbon or metal oxides, such as  $TiO_2$ ,  $CeO_2$ ,  $Al_2O_3$  and  $SiO_2$ .<sup>[5,6,12]</sup>

Relatively less studied are polymeric supports, even though their use could undoubtedly lead to a number of advantages:<sup>[13]</sup> The hydrophilic and -phobic properties of the polymer matrix can be tuned by appropriate functionalisation of the surface of the polymer particles; the presence of functional groups that contain donor atoms can covalently bind the metal nanoparticles and reduce their tendency to coalesce or leach from the support; and, last, the polymer morphology can control the accessibility to the catalytic metal nanoparticles that are embedded in the polymer matrix by the substrates.

Tsukuda et al. extensively studied the catalytic performance of AuNPs that were stabilised by poly(*N*-vinyl-2-pyrrolidone).<sup>[14]</sup> Recently, Kobayashi et al. reported the controlled synthesis of AuNPs of about 1 nm in diameter by the reduction of [AuCl(PPh<sub>3</sub>)] with NaBH<sub>4</sub> in the presence of stereoirregular random copolymers of styrene with *para*-substituted styrene monomers, which had pendant epoxy and alkoxy groups.<sup>[15]</sup> Notably, this incarcerated gold catalyst (PI-AuNPs) was successfully used in multiple alcohol oxidations with high efficiency.

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We extensively studied the synthesis and properties of syndiotactic polystyrene and copolymers of syndiotactic polystyrene with conjugated 1,3-dienes.<sup>[16]</sup> Syndiotactic polystyrene is a semicrystalline thermoplastic polymer characterised by a  $T_g$  value of 105 °C and a melting temperature of 270 °C; it is thermally stable and not reactive with strong oxidising chemicals and/or strong Brønsted–Lowry and Lewis acids or bases.<sup>[17a]</sup> Five crystalline forms, denoted as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\varepsilon$ , were described for this polymer.<sup>[17a,b]</sup> It is noteworthy that the last two crystalline forms were characterised by the presence of nanopores and -channels, respectively, where the diffusion of low-molecular-weight molecules was higher than in the amorphous phase, and thus, clathrate and intercalated co-crystalline forms were produced.<sup>[17]</sup>

We recently synthesised multi-block copolymers comprising segments of syndiotactic polystyrene and *cis*-1,4-polybutadiene (sPSB). The sPSB samples, which contained butadiene with a molar fraction higher than 0.15 were soluble in chloroform at room temperature.<sup>[16]</sup> When the average styrene block lengths were longer than nine units, the copolymers showed crystalline behaviour that was analogous to that observed for syndiotactic polystyrene. The sPSBs could be, thus, considered as novel examples of thermoplastic elastomers, in which the crystalline polystyrene domains acted as reversible physical cross-links.<sup>[16a]</sup>

### **Results and Discussion**

We initially obtained AuNPs incarcerated in a syndiotactic polystyrene matrix by swelling the polymer in THF (0.5 wt%) heated at reflux, followed by the addition of HAuCl<sub>4</sub> (0.6 mM) at room temperature and treatment with sodium triethylborohydride (B/Au molar ratio of 8) at 60 °C. The overall process produced a red slurry. Fast coagulation of the polymer in methanol yielded a colourless filtrate and a red polymer (1- $\delta$ ; Figure 1 and Table 1). The gold loading in 1- $\delta$  was assessed by atomic absorption spectroscopy (AAS) and a value of 2.0 wt% was found. Thus, the entrapment of the gold precursor in the syndiotactic polystyrene polymer matrix was quantitative and this yielded a heterogeneous catalyst that contained AuNPs in a predetermined concentration.

Table 1. Synthesis of AuNPs incarcerated in sPS and sPSB matrices.

Catalyst <sup>[a]</sup>	Polymer matrix	Thermal annealing	Solvent <sup>[b]</sup>	Crystal- linity <sup>[c]</sup> [%]	AuNP diameter [nm]
1-δ	sPS	_	_	58	6.1
<b>2</b> -δ	sPS <sub>87</sub> B	_	_	23	4.6
$2(t)$ - $\beta$	sPS <sub>87</sub> B	170°C, 5 h	_	21	9.5
$2(t)-\delta$	sPS <sub>87</sub> B	170°C, 5 h	H <sub>2</sub> O/toluene	-	9.5
<b>2</b> ( <i>t</i> )-ε	sPS <sub>87</sub> B	170°C, 5 h	H <sub>2</sub> O/CHCl <sub>3</sub>	31	9.5

[a] The symbol (*t*) stands for annealed samples; the Greek symbol indicates the crystalline form of the sPS domain. [b] Further treatment of the annealed catalyst with a mixture of solvents to effect transformation of the crystalline polymer phase. [c] Relative crystallinity of the sPS fraction estimated by differential scanning calorimetry (DSC), assuming a  $\Delta H_{\rm m}$  reference value of 53.2 Jg<sup>-1[17d]</sup> for highly crystalline sPS.

The wide-angle powder X-ray diffraction (WAXD) spectrum of  $1-\delta$  exhibited two patterns: one showing signals at  $2\theta = 8.6$  and 9.9°, which is diagnostic of the  $\delta$  co-crystalline form of syndiotactic polystyrene with THF,<sup>[17]</sup> and an additional pattern that exhibited characteristic broad signals at  $2\theta = 38.1, 44.4, 64.6$  and  $77.8^{\circ}$ , which were attributed to the (111), (200), (220) and (311) planes of the fcc crystalline lattice of nanocrystalline gold (Figure 2).<sup>[18]</sup> An average particle diameter of 6.1 nm was calculated by the Scherrer method.<sup>[19]</sup> The TEM micrograph of 1-δ showed AuNPs, apparently of tens of nanometers in diameter, homogeneously incarcerated in the polymer matrix (Figure 3a). High-resolution transmission electron microscopy (HRTEM) analysis, however, demonstrated that these AuNPs consisted of aggregates of primary particles (with diameters of a few nanometers), which shared crystalline faces (Figure 3b).

The sPSBs were more soluble in organic solvents than syndiotactic polystyrene; permitted milder conditions for the synthetic procedure. Copolymers with a styrene weight fraction of 87%, namely, sPS<sub>87</sub>B, were more appropriate and were thus utilised to prepare samples that had a gold weight fraction of 2% (2- $\delta$ ). The Scherrer method suggested an average diameter of 4.6 for the AuNPs. TEM analysis, which was carried out in several regions, gave an average diameter value for the AuNPs that was in agreement with the value predicted by the Scherrer method (Figure 3c and d); a limited number of very small AuNPs (of about 2 nm or less) were also detected in 2- $\delta$ .



Figure 1. Synthesis of the gold catalysts (Table 1).

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Figure 2. WAXD profiles showing the reflections of the crystalline syndiotactic polystyrene domains and those of the AuNPs in a) 1- $\delta$  THF clathrate form; b) 2- $\delta$  THF clathrate form; c) 2(*t*)- $\beta$ ; d) 2(*t*)- $\delta$ ; and e) 2(*t*)- $\epsilon$ .

In the synthetic route we followed, the polystyrene matrix strongly stabilised the AuNPs, probably through a strong interaction with the aromatic moieties of the polymer chains, without requiring additional ligands or stabilisers, as previously showed by Kobayashi et al. who used a similar polymer matrix.<sup>[15]</sup> Subsequently, sample 2- $\delta$  was heated for 5 h at 170 °C to test the thermal stability of these catalytic systems and, as a result, was converted into 2(t)- $\beta$ . Therefore, annealing effected a crystalline-phase change (from the  $\delta$  to the  $\beta$  form),<sup>[17]</sup> while the AuNP dimension increased from 4.6 to 9.5 nm (Table 1 and Figures 2 and 3c and f).

Remarkably, the morphology of the single-crystal AuNPs changed from cuboctahedral in **2**- $\delta$  (Figure 3d) into twinned and multiple-twinned nanoparticles (MTPs) in **2**(*t*)- $\beta$  (Figure 3 f), whereas isolated single-crystal AuNPs with icosahedral morphology were also observed. The SAED pattern of these nanoparticles is typical of that of crystalline gold (see Figure 3d).

AuNPs incarcerated in the sPSB polymer matrix were tested in the model reaction of the aerobic oxidation of  $(\pm)$ -1-phenylethanol to acetophenone, under the reaction conditions reported in reference [15] (1.25 mmol of 1-phenylethanol, 25 °C, oxygen fed at atmospheric pressure, with water or a mixture of water and chloroform 1:1 v/v as the solvent). In a preliminary screening, the oxidation reaction was carried out with KOH as the co-catalyst and water as the solvent to preserve the crystalline phase of the polymer matrix. The catalyst 2- $\delta$  was more active than 1- $\delta$  (compare entries 1 and 2 in Table 2) as was partly expected by the spherical morphology of isolated AuNPs found in 2- $\delta$  (versus the nanoparticle aggregates of 1- $\delta$ ).



Figure 3. a) TEM micrograph of 1- $\delta$ ; b) HRTEM micrograph of 1- $\delta$ ; c) TEM micrograph with the AuNP diameter distribution in 2- $\delta$ ; d) HRTEM and selected-area electron diffraction (SAED) micrographs of a typical cuboctahedral AuNP found in 2- $\delta$ ; e) TEM micrograph with the AuNP diameter distribution in 2(t)- $\varepsilon$ ; and f) HRTEM micrograph of a typical defective AuNP found in 2(t)- $\varepsilon$ .

The oxidation rate of 2(t)- $\beta$  (Table 2, entry 3) was higher than that of 2- $\delta$ , despite the fact that the average particle size was greater and the permeability of the crystalline polymer phase was lower<sup>[17]</sup> in 2(t)- $\beta$  than in 2- $\delta$  (see below), which showed that the annealing process enhanced the catalytic performance of AuNPs. Subsequently, sample 2(t)- $\delta$ (Table 2, entry 4) was tested under the same conditions to definitively confirm this finding and the role of the porous polymer phase, and it was found that the highest oxidation rates were achieved in water.

Chloroform was introduced into the reaction mixture to improve the diffusion of oxygen and the swelling of the polymer phase. Surprisingly, the conversion of 1-phenylethanol to acetophenone, in a solvent mixture of  $H_2O$  and CHCl<sub>3</sub> (1:1 v/v), was quantitative in 5 h (Table 2, entry 7). The kinetic profile of the 2(t)-catalysed oxidation of 1-phenylethanol, under these conditions and varying concentra-

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	Catalyst	Solvent	KOH/alcohol molar ratio	<i>t</i> [h]	Yield <sup>[b]</sup> [%]	
1	1-δ	H <sub>2</sub> O	1	24	30	
2	<b>2</b> -δ	$H_2O$	1	24	57	
3	$2(t)$ - $\beta$	$H_2O$	1	24	74	
4	$2(t)-\delta$	$H_2O$	1	24	84	
5	$2(t)$ - $\epsilon$	$H_2O$	1	7	83	
6	<b>2</b> -δ	H <sub>2</sub> O/CHCl <sub>3</sub>	1	24	70	
7	$2(t)$ - $\epsilon$	H <sub>2</sub> O/CHCl <sub>3</sub>	1	5	>99	
8	$2(t)$ - $\epsilon$	H <sub>2</sub> O/CHCl <sub>3</sub>	0.3	24	68	
9	$2(t)$ - $\epsilon$	H <sub>2</sub> O/CHCl <sub>3</sub>	0.5	24	88	
10	$2(t)$ - $\epsilon$	H <sub>2</sub> O/CHCl <sub>3</sub>	3	24	>99	
11 <sup>[c]</sup>	$2(t)-\varepsilon$	H <sub>2</sub> O/CHCl <sub>2</sub>	1	1	96	

[a] Reaction conditions: ( $\pm$ )-1-phenylethanol (1.25 mmol), solvent (15 mL), T=25 °C,  $PO_2=1$  bar. [b] Determined by GC analysis using anisole (1.25 mmol) as the internal standard. [c] T=35 °C.

tions of KOH (Table 2, entries 7–10), showed that the KOH/ alcohol molar ratio of 1:1 was optimal, and that after a partial induction time of about 30 min the reaction followed pseudo-first-order kinetics with  $k = (1.10 \pm 0.10) \text{ h}^{-1}$  (Figure 4a and b). This was one of the highest rate constant values observed for this reaction carried out at ambient temperature, and catalysed by polymer-incarcerated AuNPs. The increase of the reaction temperature to 35 °C resulted in the quantitative oxidation of 1-phenylethanol to acetophenone in only 60 min (Table 2, entry 11). Under these



Figure 4. a) Oxidation of 1-phenylethanol catalysed by 2(t)- $\varepsilon$  with variation of the KOH/1-phenylethanol molar ratio: 0.3 ( $\blacksquare$ ; Table 2, entry 8), 0.5 ( $\bullet$ ; Table 2, entry 9), 1.0 ( $\blacktriangle$ ; Table 2, entry 7), 3.0 ( $\triangledown$ ; Table 2, entry 10). b) Plot of  $\ln([A]/[A]_0)$  versus time ([A] is the molar concentration of 1-phenylethanol). c) Oxidation of benzyl alcohol catalysed by 2(t)- $\varepsilon$  (experimental conditions are those given in entry 1, Table 3). d) Plot of  $\ln([A]/[A]_0)$  versus time ([A] is the molar concentration of benzyl alcohol).

Despite the presence of simple physical cross-links, the catalyst 2(t) was repeatedly used at least six times without any observable loss of activity (>97% in 5 h). The inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of both the reaction solution and the catalyst at the end of the oxidation runs confirmed that there was no loss of gold from the polymer matrix. It was found that reactivation of the catalyst by thermal annealing or washing with acids or bases after each catalytic run was superfluous.<sup>[6, 15a]</sup>

Similarly, the oxidation of benzyl alcohol at  $35 \,^{\circ}$ C, with oxygen at atmospheric pressure as the oxidant, proceeded smoothly and exhibited high efficiency and selectivity (Table 3, entry 1, and Figure 4c and d). A conversion higher

Table 3. Alcohol oxidation catalysed by 2(t)- $\epsilon$ .<sup>[a]</sup>

	Substrate	Product <sup>[b]</sup>	t	Yield <sup>[b]</sup>	Selec-
			[h]	[%]	tivity <sup>[b]</sup>
					[%]
1	benzyl alcohol	benzaldehyde	6	>99	97
2 <sup>[c]</sup>	cinnamyl alcohol	cinnamaldehyde	6	>99	95
3	thiophene-2-methanol	2-formylthiophene	7	76	>99
4	1-indanol	1-indanone	1	>99	>99
5	α-tetralol	$\alpha$ -tetralone	6	86	>99
6	furfuryl alcohol	furfural	6	30	>99
7	geraniol	geranial	21	29	>99
8	1-butanol	-	24	-	-
9	1-hexanol	-	24	-	-
10	cyclohexanol	cyclohexanone	24	10	> 99

[a] Reaction conditions: alcohol = 0.507 mmol, catalyst = 0.200 g,  $solvent = H_2O/CHCl_3$  (1:1, total volume 6 mL), KOH = 0.507 mmol,  $T = 35^{\circ}C$ ,  $PO_2 = 1$  bar. [b] Determined by NMR spectroscopy or GC-MS analysis when using anisole as the internal standard. [c]  $T = 0^{\circ}C$ .

than 99 mol% with a selectivity of 97% in benzaldehyde was attained in 6 h. Initial reaction rates were higher (a conversion of about 84% was obtained in 2 h). At longer reaction times (>24 h), further oxidation of benzaldehyde was not observed. The reaction followed a pseudo-first-order rate law with a rate constant value of  $(0.55\pm0.04)$  h<sup>-1</sup> (calculated for a reaction time of 6 h). The performance and selectivity of 2(t) in benzyl alcohol oxidations was remarkable relative to other polymer-supported AuNP<sup>[14,15]</sup> catalysts, the use of which led to partial or complete overoxidation to benzoic acid. The mechanism of the overoxidation of benzyl alcohol to benzoic acid or benzylbenzoate via the formation of the gem-benzyldiol  $ArCH(OH)_2$  or the benzyl hemiacetal ArCH(OH)OBn intermediates, respectively, was thoroughly investigated.<sup>[5a,20]</sup> The reaction temperature, the solvent, the presence of a Brønsted-Lowry/Lewis base and the support were among the experimental conditions that significantly influenced the selectivity of the reaction. The source of high selectivity found with 2(t)- $\varepsilon$  could be explained by taking two significant factors into account: 1) the mild conditions employed (i.e., a reaction temperature of 35°C) hampered the oxidation of the diol or the hemiacetal produced by the reaction of benzaldehyde with benzyl alcohol under basic

conditions; and 2) the hydrophilic nature of the diol and the hemiacetal disfavoured their repartition in the fully hydrophobic nanoporous polymer phase swelled in chloroform, thus inhibiting their further oxidation.

The crystalline phase of sPS<sub>87</sub>B in 2(t) was thoroughly investigated by WAXD analysis after carrying out catalytic experiments in water/chloroform to investigate the beneficial role of the polymer host matrix and of chloroform in the catalytic performance of 2(t) (Figure 2). The  $\beta$  crystalline form of syndiotactic polystyrene, which resulted from annealing at 170 °C, was transformed in this solvent mixture into a crystalline phase that contained the nanoporous  $\varepsilon$  crystalline form 2(t)- $\varepsilon$ . The crystalline index of the polymer phase was estimated by DSC after calculating the heat of melting of the syndiotactic polystyrene domains at 243–247 °C (Figure 5) and using the limit value of 53.2 J g<sup>-1</sup> for



Figure 5. DSC traces of a)  $2-\delta$ , b)  $2(t)-\beta$  and c)  $2(t)-\epsilon$ .

the heat of melting of syndiotactic polystyrene.<sup>[17d]</sup> The crystallinity index increased from about 20% in **2**- $\delta$  and **2**(*t*)- $\beta$  to about 31% in **2**(*t*)- $\varepsilon$  after the catalytic run (Table 1).

Two aliquots of 2(t) were treated with toluene/water and chloroform/water to definitively confirm the role of the polymer host matrix; as a result,  $2(t)-\delta$  and  $2(t)-\varepsilon$  were produced, respectively, in which the AuNPs had the same thermal history and thus the same morphology. The results of the oxidation of 1-phenylethanol in water (Table 2, entries 4 and 5) unequivocally showed that the polymer phase of 2(t)- $\varepsilon$  was responsible for the highest catalytic activity. Two pieces of experimental evidence further confirmed this conclusion: The oxidation of 1-phenylethanol in water catalysed by preformed 2(t)- $\varepsilon$  was more extensive than that catalysed by  $2(t)-\delta$  (Table 2, entries 4 and 5). The oxidation of 1phenyl ethanol with PI-AuNPs, as reported by Kobayashi et al., was zero order with respect to the concentration of 1phenylethanol (the process was diffusion-controlled).<sup>[15c]</sup> The access of the substrate to the catalytic nanoparticles embedded in the polymer phase occurred only by slow diffusion through the polystyrenic amorphous phase. In our case, the reaction was first order with respect to the molar concentration of 1-phenylethanol, in agreement with the performance of AuNPs supported on metal oxides. This suggested a fast

diffusion of the alcohol toward the gold catalyst, a process which was probably favoured by the presence of the nanochannels of the polymer host phase. Notably, the kinetic plots reported by Kobayashi et al.<sup>[15c]</sup>, and in Figure 4, showed an induction time that needs to be further investigated in detail.<sup>[21]</sup>

SEM analysis of 2(t)- $\beta$  showed a compact polymer phase after annealing at 170 °C, whereas for 2(t)- $\epsilon$  (which resulted from the catalytic run in chloroform/water), it showed a higher specific surface area and the formation of a microporous polymer phase (Figure 6).



Figure 6. SEM micrographs of a)  $2(t)-\beta$  and b)  $2(t)-\epsilon$ .

A variety of primary and secondary alcohols were screened (Table 3) to get a deeper insight into the catalytic performance of 2(t). Cinnamyl alcohol and thiophene-2-methanol were oxidised with high selectivity in 6 h (Table 3, entries 2 and 3). Benzylic alcohols, such as 1-indanol and 1,2,3,4-tetrahydro-1-naphthol ( $\alpha$ -tetralol) were quantitatively and readily oxidised to the corresponding ketones in 1 and 6 h, respectively (Table 3, entries 4 and 5), whereas linear and cyclic aliphatic alcohols were slowly oxidised, if at all, under the same conditions (Table 3, entries 8–10).

### Conclusion

We have reported the controlled synthesis of naked AuNPs incarcerated in a fully hydrocarbon polymer matrix, which were characterised by a high  $T_{g}$  value and contained reversible high-melting physical cross-links of crystalline polymer domains. The cross-links still permit to the substrates to be accessible to the AuNPs and impart good stability toward gold leaching. The catalyst 2(t) was highly efficient in successive oxidations of 1-phenylethanol under mild conditions. Primary alcohols, such as benzyl alcohol, cinnamyl alcohol and thiophene-2-methanol, yielded the corresponding aldehydes in high yields and with high selectivity. Similar results were obtained in the oxidation of secondary alcohols, such as 1-indanol and a-tetralol. The formation of the nanoporous  $\varepsilon$  crystalline phase of the polymer matrix was proposed to rationalise catalyst performance. Additionally, WAXD and HRTEM analyses of 2(t) after six catalytic runs of 1phenylethanol oxidation revealed the presence of multitwinned and defective AuNPs of about 9 nm in diameter.

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Thus, the improved catalytic performance of 2(t) could also be ascribed to this AuNP morphology. It is noteworthy that, recently, Hutchings et al. showed that multi-twinned gold nanoparticles in Au–Pd/C samples, with predominantly icosa- and decahedral structures, exhibited higher catalytic activity than cuboctahedral single/double twinned particles of Au–Pd/TiO<sub>2</sub> samples in toluene oxidations.<sup>[5a]</sup> The findings reported herein seem to support this hypothesis. Moreover, the thermoplastic nanoporous matrix we described could allow us to successfully tackle the challenging problem of the selective oxidation of alcohols.

### **Experimental Section**

**General:** The manipulation of air- and moisture-sensitive compounds was performed under a nitrogen atmosphere using standard Schlenk techniques and an MBraun glovebox. Tetrachloroauric(III) acid, sodium triethylborohydride (1 m in THF), (±)-1-phenylethanol, benzyl alcohol, cinnamyl alcohol, 2-thiophenemethanol, 1-indanol, α-tetralol, furfuryl alcohol, geraniol, 1-butanol, 1-hexanol, cyclohexanol, anisole, potassium hydroxide, sulfuric acid and hydrogen peroxide were purchased from Sigma–Aldrich and used as received. Oxygen was purchased from Rivoira and used as received. CDCl<sub>3</sub>, and [D<sub>2</sub>]1,1,2,2-tetrachloethane (TCDE) were purchased from Euriso–Top and used as received. The gold(III) standard solution  $(1.000\pm0.002)\,gL^{-1}$  in water with HCl (2 wt%) used in AAS and ICP-OES analyses was purchased from Carlo Erba and used as received. Syndiotactic polystyrene (sPS) and sPSB multi-block copolymers were synthesised according to literature procedures.<sup>[16]</sup>

Instrumentation: NMR spectra were recorded by using a Bruker AVANCE 400 spectrometer (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C). WAXD spectra were obtained, in reflection, with an automatic Bruker D8 powder diffractometer using nickel-filtered  $Cu_{K\alpha}$  radiation. TEM analyses were carried out with a JEOL (JEM 3010) electron microscope operating at 300 kV, with a point-to-point resolution of 0.17 nm (at Scherzer defocus). Specimens for TEM analysis were sonicated in 2-propanol, or dissolved in chloroform, and then transferred (10 µL) onto a copper grid covered with a lacey carbon film supplied from Assing. SEM analyses were carried out with a scanning electron microscope (JEOL). AAS analysis was performed on a PerkinElmer AAnalyst 100 spectrophotometer using an Au hollow cathode lamp (Perkin-Elmer). ICP-OES was performed on a Perkin-Elmer Optima 7000 DV instrument. GC analyses were carried out with a Focus GC spectrometer (Thermo Electron Corporation) equipped with a FAMEWAX column (Crossbond PEG, 30 m, 0.32 mm ID) and a FID detector, and a GC-MS 7890A/ 5975C spectrometer (Agilent Technologies) equipped with an OPTIMA 17MS column (diphenylpolysiloxane/dimethylpolysiloxane, 1:1, 30 m, 0.25 mm ID) and a mass-selective detector. Thermal analyses were carried out on a TA Instrument DSC 2920 calorimeter (heating rate =  $10 \,{}^{\circ}\mathrm{C}\,\mathrm{min}^{-1}$ ).

**Synthesis of 1**: A 1 L round-bottomed three-necked flask equipped with a magnetic stirrer bar was charged with THF (300 mL) and finely ground syndiotactic polystyrene (1.47 g) was added. The suspension was stirred for 3 d at room temperature and then heated to reflux for 1 h to complete the swelling of the polymer. HAuCl<sub>4</sub> (0.060 g;  $1.52 \times 10^{-1}$  mmol) was added at room temperature and the resulting slurry was kept under agitation for 24 h, and was subsequently heated to reflux for 1 h. A solution of sodium triethylborohydride (1.9 mL, 1 M) in THF was then added at 60 °C. A rapid change of colour from pale yellow to red was observed. The polymer rapidly precipitated with the addition of methanol, was recovered by filtration, washed with fresh methanol and dried in vacuo at room temperature.

Synthesis of 2: A 1 L round-bottomed three-necked flask equipped with a magnetic stirrer bar was charged with THF (800 mL) and finely ground

sPS<sub>87</sub>B (4.90 g) was added. The mixture was stirred for 3 d at room temperature and then heated to reflux for 1 h to complete the swelling of the polymer. HAuCl<sub>4</sub> (0.200 g;  $5.08 \times 10^{-4}$  mol) was added at room temperature and the resulting slurry was kept under agitation for 24 h, and was subsequently heated to reflux for 1 h. A solution of sodium triethylborohydride (4.1 mL, 1 M) in THF was added at 40 °C, producing a rapid change of the colour from pale yellow to red. The polymer rapidly precipitated with the addition of methanol, was recovered by filtration, washed with fresh methanol and dried in vacuo at room temperature.

**Preparation of** 2(t)- $\beta$ , 2(t)- $\delta$  **and** 2(t)- $\varepsilon$ : Samples of 2 (2.0 g) were annealed on a hot plate at 170 °C for 5 h to effect the transition from the sPS- $\delta$  form to the  $\beta$  form (2(t)- $\beta$ ). Samples of 2(t)- $\beta$  (0.5 g) were stirred in a mixture of toluene and water (15 mL, 1:1 v/v) for 24 h to effect the transition from the sPS- $\beta$  form into the  $\delta$  form (2(t)- $\delta$ ). Samples of 2(t)- $\beta$  (0.5 g) were stirred in a mixture of chloroform and water (15 mL, 1:1 v/v) for 24 h to yield 2(t)- $\varepsilon$ . The crystalline phase of polymers was analysed by powder WAXD.

**Determination of the gold loading in 1 and 2**: The sample (50 mg) was acid digested in a Kjeldahl flask by treatment with concentrated  $H_2SO_4$  (2.5 mL, 98 wt%) at 250 °C for 30 min and then with  $H_2O_2$  (4.0 mL, 35 wt%) at room temperature. The resulting solution was heated at 250 °C until to produce a clear colourless solution. Aqua regia (1.5 mL) was added at room temperature and the solution was diluted with an aqueous solution of HCl (10 vol%) to a final volume of 10.0 mL. The resulting solution was analysed by AAS or ICP. Calibration was performed by analysing seven standard solutions of  $Au^{III}$  prepared by progressive dilution of a standard solution for AAS (( $1.000 \pm 0.002$ ) gL<sup>-1</sup> in water with 2 wt% of HCl) with water and an aqueous solution of HCl (10 wt%).

**Oxidation of alcohols catalysed by 2**: A 50 mL round-bottomed twonecked flask equipped with a magnetic stirrer bar was charged with KOH (0.070 g,  $1.25 \times 10^{-3}$  mol), H<sub>2</sub>O (7.5 mL), alcohol ( $1.25 \times 10^{-3}$  mol), CHCl<sub>3</sub> (7.5 mL), anisole (0.135 mL,  $1.25 \times 10^{-3}$  mol) and the catalyst (0.500 g, alcohol/Au molar ratio = 25). The mixture was stirred at 35 °C and O<sub>2</sub> was supplied at atmospheric pressure. An aliquot of the reaction mixture was precipitated in CD<sub>3</sub>OD or CD<sub>3</sub>CN and the filtrate was analysed by <sup>1</sup>H NMR spectroscopy and GC-MS. The reaction was terminated at the end of the run with an excess of methanol. The polymer was recovered by filtration and the filtrate analysed by GC-MS.

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- [21] On this issue, we acknowledged the suggestion of one referee and carried out preliminary investigations into the role of radical traps, such as 4-methoxyphenol, in the oxidation of benzyl alcohol. We found that the addition of 4-methoxyphenol at a 1:1 molar ratio relative to the alcohol totally inhibited the oxidation reaction, whereas at molar ratios of 0.2:1 and 0.3:1 partial inhibition of 61 and 77%, respectively, was observed. A deeper investigation is necessary to clarify whether a radical pathway was active in the oxidation reaction catalysed by 2(t)- $\varepsilon$ . In previous studies it was suggested that a hydride shift from the carbinolic carbon atom to the gold atom constituted the rate-determining step.<sup>[15b,6b]</sup>

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