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Gold-promoted styrene polymerization†

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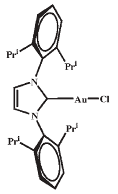
Styrene can be polymerized at room temperature in the presence of equimolar mixtures of the gold(III) complexes (NHC)AuBr$_3$ (NHC = *N*-heterocyclic carbene ligand) and NaBAr′$_4$, in the first example of a gold-induced olefin polymerization reaction.

The use of gold in homogeneous catalysis has considerably gained attention in the last few years and it is expanding rapidly. Simple salts or well-defined complexes of this noble metal, either in oxidation state +I or +III, can catalyze an increasing number of reactions.[1] A recent review by Hashmi and Hutchings[2] highlights this metal as being very effective both in heterogeneous and homogeneous conditions for a wide array of transformations. But to the best of our knowledge, there are no reports on the use of gold for olefin polymerization reactions under homogeneous conditions.

We have recently reported[3,4] the use of gold-based catalysts of composition (NHC)AuCl (NHC = *N*-heterocyclic carbene ligand) for the decomposition of ethyl diazoacetate (N$_2$CHCO$_2$Et, EDA) and the subsequent transfer of a :CHCO$_2$Et group to saturated and unsaturated substrates. When using styrene as the substrate, we detected minor amounts of polystyrene (1–2%) in the reaction mixture. To pursue on this early lead, we now report on the capabilities of NHC-containing Au(III) complexes of general formulae (NHC)AuBr$_3$ to polymerize styrene.



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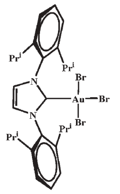

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In a first series of experiments, IPrAuCl (**1**) and IPrAuBr$_3$ (**2**)[5] (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) were employed in catalytic amounts in bulk polymerization reactions involving styrene. Under these conditions no detectable amounts of polystyrene were observed. The addition of one equiv. of NaBAr′$_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl)[6] as a halide scavenger to solutions of **1** or **2** in neat styrene (2 mL) induced a distinct response: the former reaction mixture remained unaltered whereas the latter proceeded in a highly exothermic process. Addition of methanol induced the precipitation of polymeric material that was identified as atactic polystyrene (PS) by NMR studies.[7] Blank experiments carried out with NaBAr′$_4$ revealed the need of **2** to initiate the polymerization. No reaction was observed when the NHC ligand was employed as the promoter, in absence of the metal. After those promising results, we carried out a series of experiments using equimolar mixtures of IPrAuBr$_3$ and NaBAr′$_4$, at room temperature.‡ The results are shown in Table 1. Bulk polymerization was observed at different metal concentrations (varying the volume of styrene), but the conversion did not surpass the 50% mark. However, the use of lower concentrations of the gold promoter improved the M_w, M_n and PDI (polydispersity index) values. The final conversions remained unaltered in experiments carried over the course of 2 to 24 h of stirring prior to workup, therefore gold-promoter lifetime issues appear to exist that preclude complete conversion. We thought that this could be related to the large excess of styrene employed in these experiments. Therefore we carried out several experiments where a co-solvent was added. The presence of toluene, chlorobenzene and methylene chloride in the reaction mixture clearly influenced this transformation. The reaction carried out in toluene : styrene (5 : 2 mL) led to a 60% yield, and a 1.7 PDI value. Chlorine-containing solvents dramatically increased the conversions up to 90–95%, although the polydispersity was also higher than in the case of both bulk or toluene-containing experiments. Interestingly, the addition of tetrahydrofuran, diethyl ether or acetononitrile completely inhibited the transformation, with no polymer being formed after 24 h.

In order to obtain control of the polymer properties, we designed a second series of experiments where toluene and methylene chloride were employed as the solvent in different

Table 1 Room temperature styrene polymerization[a] induced by IPrAuBr$_3$ and NaBAr′$_4$ (Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$)‡

Styrene/mL	Co-solvent	TON[b]	TOF/h^{-1}	M_w[c]	M_n[c]	PDI[c]
2	None	1629	6516	21 300	10 300	2.1
5	None	3636	14 546	27 300	14 600	1.9
10	None	4363	17 455	31 200	16 600	1.9
2	PhMe (5 mL)	1745	6982	12 300	7100	1.7
2	PhCl (5 mL)	2647	10 589	22 100	8100	2.7
2	CH$_2$Cl$_2$ (5 mL)	2763	1 1055	39 900	13 200	3.0
2	Thf (5 mL)	0	0	—	—	—
2	Et$_2$O (5 mL)	0	0	—	—	—
2	CH$_3$CN (5 mL)	0	0	—	—	—
2	PhMe (1 mL)	1745	6982	19 900	9700	2.0

[a] Equimolar mixtures of IPrAuBr$_3$ and NaBAr′$_4$ (6 × 10^{-3} mmol). [Styrene]/[Au] = 2900 when 2 mL of styrene were employed. [b] Isolated yield after precipitation with methanol. [c] Determined by GPC using polystyrene standards.

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Table 2 Effect of the solvent on the polymerization of styrene[a] at room temperature by $IPrAuBr_3$ and $NaBAr'_4$ ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$)‡

Co-solvent	Vol./mL	TON[b]	TOF/h^{-1}	M_w[c]	M_n[c]	PDI[c]
None	—	1629	6516	21 300	10 300	2.0
PhMe	1	1745	6982	19 800	9700	2.0
PhMe	5	1745	6982	12 300	7100	1.7
PhMe	10	640	2560	7000	4500	1.5
PhMe	20	203	814	5500	4100	1.3
CH_2Cl_2	5	2851	11 404	37 600	11 600	3.2
CH_2Cl_2	20	2560	10 240	19 700	8100	2.4
PhMe + CH_2Cl_2[d]	2.5 + 2.5	2676	10 706	18 500	9400	2.0
PhMe + CH_2Cl_2[d]	3.75 + 1.25	2152	8611	15 700	8700	1.8

[a] [b] [c] As in Table 1. Vol. of styrene: 2 mL [d] Mixture of toluene and dichloromethane.

ratios (Table 2). It appears that in both cases the use of larger amounts of solvent provokes a decrease both in the conversion (measured as isolated PS) as well as in the PDI. A 1.3 value for the latter was achieved when the reaction was carried out with 20 mL of toluene, although the obtained isolated yield was quite low, only 7%. Using a similar volume of CH_2Cl_2 gave 88% isolated yield of PS, the PDI increasing to 2.4. These opposite effects were successfully balanced out when using mixtures of solvents where conversion and molecular weight were optimized. A 1 : 1 mixture (v/v) of toluene and methylene chloride led to 92% yield and PDI = 2.0. Further improvement in the PDI to 1.8 was accompanied with a decrease in the conversion to 72%, although this is higher than any yield obtained with toluene as the sole solvent.

The results shown in Tables 1 and 2 are quite remarkable in that, as far as we know, they constitute the first example of a gold-promoted polymerization of an olefin, styrene in this case. Since it is also well-known that styrene undergoes rapid radical polymerization processes, we conducted an experiment with 2,6-di-*t*-butylhydroxytoluene (BHT) added as radical inhibitor: no substantial differences in the conversion nor in the polymer properties were observed when compared with the experiment carried out in the absence of such inhibitor. Thus, we believe that this specific reaction does not involve a radical polymerization transformation. To gain information that could shed light on the nature of this polymerization reaction, we monitored these transformations with time both in bulk and with methylene chloride as the co-solvent. Fig. 1 shows the variation of conversion with time and nicely shows the difference induced by the co-solvent that leads to complete conversion of styrene into polystyrene. In the case of the experiment carried out in bulk styrene, the maximum conversions obtained only reached 40%.

To test the scope of this system, we performed several experiments with *p*-substituted styrenes $X\text{–}C_6H_4CH{=}CH_2$ (X = OMe, Cl) and methyl acrylate. As shown in Table 3, the results are quite distinct depending on the olefin employed. The use of methyl acrylate resulted in no conversion at all whereas in the case of the styrenes, 4-vinylanisole gave quantitative conversions either in bulk or with toluene or dichloromethane as the co-solvent. On the other hand, *p*-chlorostyrene was polymerized in low to moderate yield in bulk or with methylene chloride, respectively but no reaction was observed with toluene as the co-solvent. The case of *p*-vinylanisole is worth further comment as it provides very high values of M_w and M_n in comparison with those previously presented for styrene. The lowest polydispersity (2.1) is given, in this case, by the transformation carried out in toluene as the co-solvent.

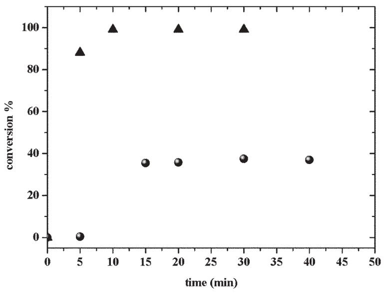


Fig. 1 Variation of conversions (%) *vs.* time in the styrene polymerization reaction induced by $IPrAuBr_3 + NaBAr'_4$ at room temperature: ● styrene as solvent; ▲ CH_2Cl_2 as co-solvent.

Table 3 Polymerization of other olefins[a] by $IPrAuBr_3$ and $NaBAr'_4$ ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$)‡

Monomer	Co-solvent	TON[b]	TOF/h^{-1}	M_w[c]	M_n[c]	PDI[c]
p-MeO–styrene	None	2879	11 517	158 000	30 000	5.2
p-MeO–styrene	PhMe	2879	11 517	830 000	40 000	2.1
p-MeO–styrene	CH_2Cl_2	2879	11 517	3 690 000	880 000	4.2
p-Cl–styrene	None	639	2559	6100	3850	1.6
p-Cl–styrene	PhMe	0	0	—	—	—
p-Cl–styrene	CH_2Cl_2	1599	6398	13 500	8000	1.7
Methyl acrylate	None	0	0	—	—	—

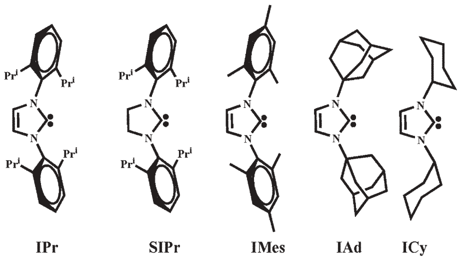
[a] [b] [c] As in Table 1. [olefin]/[Au] ratio of 2900. Vol. of the co-solvent: 10 mL

Table 4 Effect of the NHC ligand in the room temperature polymerization[a] of styrene by $(NHC)AuBr_3$ and $NaBAr'_4$‡

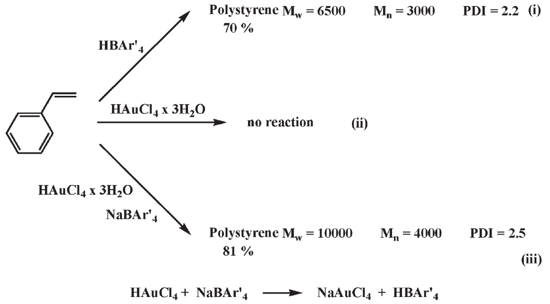
NHC ligand	TON[b]	TOF/h^{-1}	M_w[c]	M_n[c]	PDI[c]
IPr	3636	14 546	27 300	14 600	1.9
ICy	3272	13 091	28 000	12 750	2.2
SIPr	3636	14 546	31 400	17 300	1.8
IMes	4363	17 455	397 450	330 800	1.2
			17 300	7350	2.3
IAd	1090	4363	820 000	556 500	1.5
			24 000	13 500	1.8

[a] [b] [c] As in Table 1. Vol. of styrene: 5 mL. [Styrene]/[Au] = 7270.

We have also tested a series of $(NHC)AuBr_3$ complexes as polymerization promoters with addition to 1 equiv. of $NaBAr'_4$. As shown in Table 4, there is a substantial effect of this variable on the styrene polymerization reaction, with two different behaviours being observed. A first group formed by the complexes containing IPr, ICy and SIPr (Scheme 1) provided similar conversions (40–50%) as well as molecular weight and PDI values. However, the use of IMes or IAd ligands clearly performed in a different manner. The main feature of this different behaviour is the observation of bimodal distributions, with quite distinct M_w, M_n and PDI values. For example, in the case of IMes both distributions displayed PDIs of 1.2 and 2.3 and M_w values of 397 450 and 17 300, respectively. The conversion of 60% is in contrast with that of 15% measured for the ICy case. We believe that these experiments indicate that the "(NHC)Au(III)" core is not innocent in this process. For some reactions involving organo-transition metal complexes as initiator, it has been proposed that a proton is the actual catalytic species.[8,9] It could be thought that hydrolysis of the cationic metal species,[10] formed from $(NHC)AuBr_3 + NaBAr'_4$ (eqn (1)), with adventitious water would

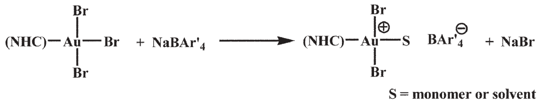


Scheme 1 Different NHC ligands employed in this work.



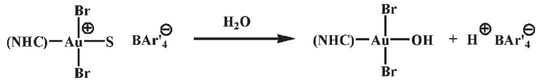
Scheme 2 Styrene polymerization with other promoters: $HAuCl_4$ + $NaBAr'_4$ or $HBAr'_4$.

produce protons (eqn (2)) that would induce the polymerization reaction. The real promoter would be, in the present case, the acid $HBAr'_4$.[6]



$$\mathrm{(NHC)-\underset{Br}{\overset{Br}{Au}}-Br + NaBAr'_4 \longrightarrow (NHC)-\underset{Br}{\overset{Br}{Au^{\oplus}}}-S\quad BAr'^{\ominus}_4 + NaBr} \tag{1}$$

S = monomer or solvent



$$\mathrm{(NHC)-\underset{Br}{\overset{Br}{Au^{\oplus}}}-S\quad BAr'^{\ominus}_4 \xrightarrow{H_2O} (NHC)-\underset{Br}{\overset{Br}{Au}}-OH + H^{\oplus}\,BAr'^{\ominus}_4} \tag{2}$$

Actually, in a separate experiment, the addition of this acid to styrene (2 mL) at room temperature induced the polymerization reaction in 70% after 2 h, although the isolated polystyrene displayed different molecular weight distributions as well as PDI values (Scheme 2, i) than those obtained with the gold complexes (Tables 1, 2 and 4). Interesting information has been obtained from experiments in which styrene was reacted with $HAuCl_4{\cdot}3H_2O$ in the absence and in the presence of 1 equiv. (with respect to Au) of $NaBAr'_4$. The former experiment gave no polymer (Scheme 2, ii), using styrene as the sole solvent (and with 3 equiv. of H_2O present), whereas in the latter case, an exothermic reaction took place after a few minutes. Workup of the reaction mixture gave polystyrene (Scheme 2, iii) in *ca.* 80% yield. It is worth pointing out that this polymer was similar to that obtained with $HBAr'_4$ as the promoter, a fact that we interpret to be as a consequence of the formation of such acid in the reaction mixture that contains both $HAuCl_4$ and $NaBAr'_4$.[11]

Experiments with *p*-substituted styrenes are evidence that cationic species could be involved in the transformation.[12] The lack of reactivity of methyl acrylate, that is known to be unreactive in cationic polymerization processes, also supports this hypothesis. Moreover, the presence of thf or acetonitrile in the reaction mixture also blocks this transformation (Table 1). Such inhibition not only takes place when using these nucleophiles as co-solvents. In a separate set of experiments, styrene was polymerized in bulk under the conditions shown in Table 1 in three minutes; at that time addition of thf stopped the polymerization of styrene.

In conclusion, we have found that styrene can be polymerized at room temperature in the presence of the gold(III) complexes $(NHC)AuBr_3$ and $NaBAr'_4$, in the first example, to the best of our knowledge, of a gold-induced olefin polymerization reaction. The data collected seem to indicate that the presence of the NHC ligand is crucial not only for the reaction to proceed but also defines the polymer properties whereas the role of the gold complex appears to exceed that of a mere initiator.

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Notes and references

‡ Polymerization procedure: in a 30 mL glass vial equipped with a magnetic stirring bar, 0.006 mmol of **1** were introduced along with one equiv. of $NaBAr'_4$. The co-solvent and/or the olefin were added *via* syringe and the mixture stirred at room temperature. Most of the reactions were finished after 15 min. Addition of 20 mL of methanol induced the precipitation of the polymer that was collected by filtration and washed with two portions of MeOH before being dried under vacuum.

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