

Electronic Supplementary Information for Gold-promoted styrene polymerization.

Juan Urbano, A. Jesús Hormigo, Pierre de Frémont, Steven P. Nolan, M. Mar Díaz-Requejo* and Pedro J. Pérez*

1- General.

The complexes (NHC)AuBr₃ and NaBAr'₄ (Ar' = 3,5-(CF₃)₂C₆H₃) were prepared according to literature methods. Olefins were purchased from Aldrich, and stabilizers were removed by filtration through alumina. Solvents were dried prior to use. NMR spectra were recorded in a Varian Mercury 400 MHz. Gel-permeation chromatography (GPC) of the polymers was conducted on a Waters 2414 Refractive Index Waters instrument equipped with a styragel HR 5E column using standard PS as the reference and THF as the eluent at 40°C.

2- Experimental procedure.

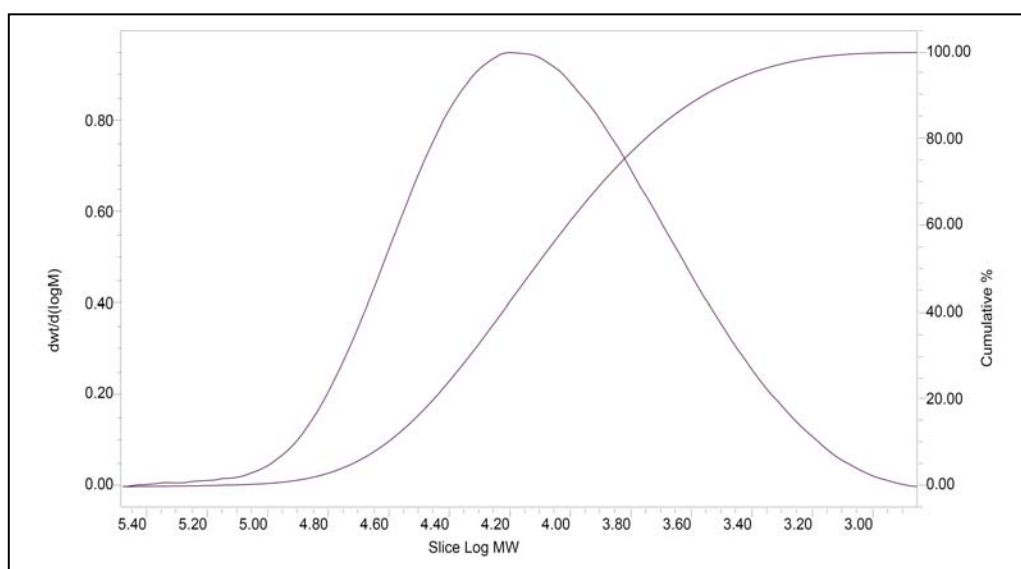
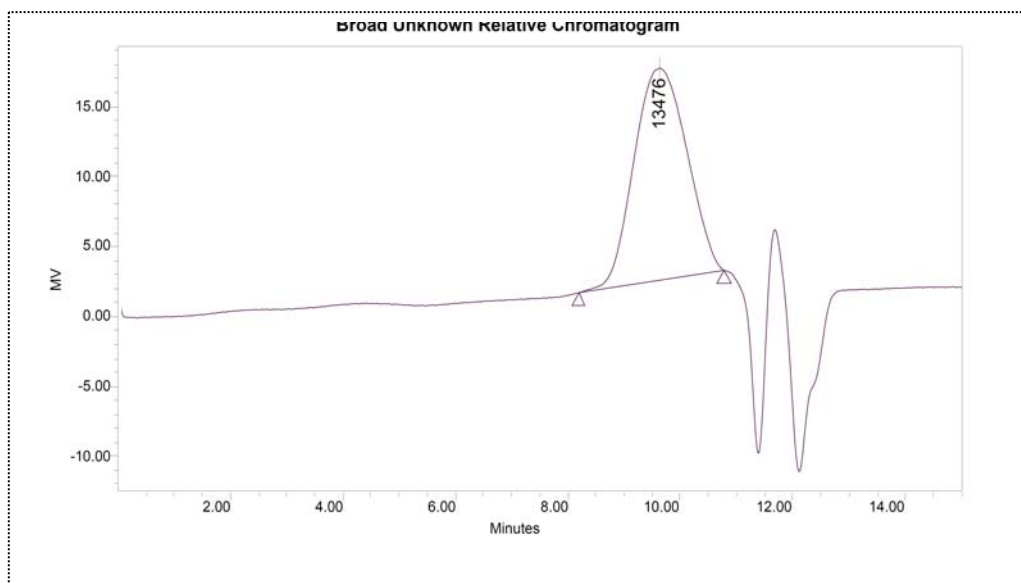
General polymerization procedure: In a new, not previously used 30 mL glass vial equipped with a magnetic stirring bar, 0.006 mmol of IPrAuBr₃ were introduced along with one equiv of NaBAr'₄. The co-solvent and/or the olefin were added via syringe and the mixture stirred at room temperature. The initial yellowish colour readily converted into a colourless mixture, at the same time that heating of the vial was observed. The increase of viscosity is also clearly observable in the stir bar movement. 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. After filtration, the polymer was dried first under vacuum and later in the oven at 100 °C for 12h before isolated yield was calculated.

GPC analyses.

A sample of 10 mg of PS was dissolved in 10 mL of thf, from which a 25 µL sample was injected in the GPC for analysis. Representative examples of the GPC chromatograms are given in the following pages.

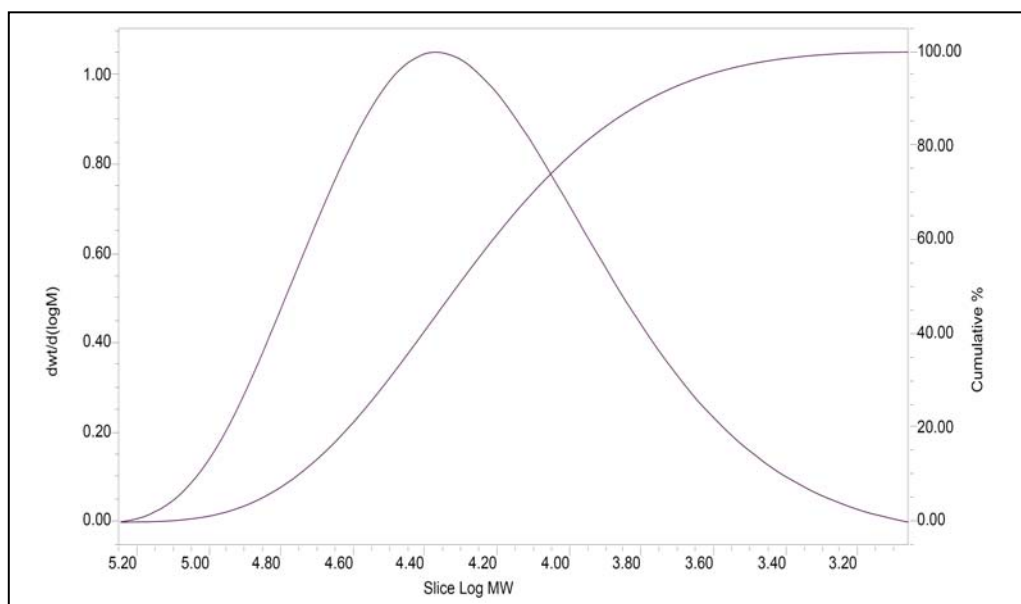
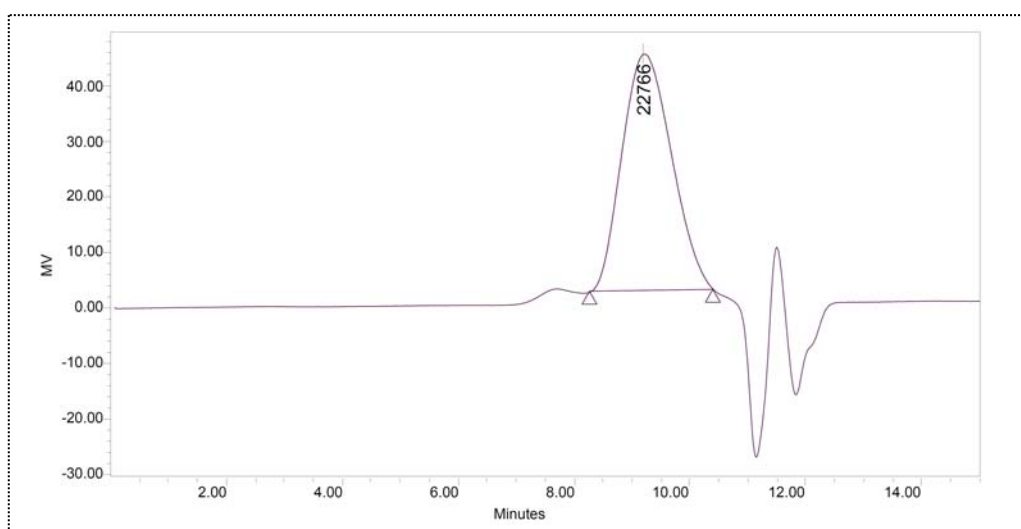
Entry 1 in Table 1 :

IPrAuBr ₃	NaBAR' ₄	Styrene	Co-solvent	Mw	Mn	PDI
0.006 mmol	0.006 mmol	2 ml	-	21300	10300	2.1



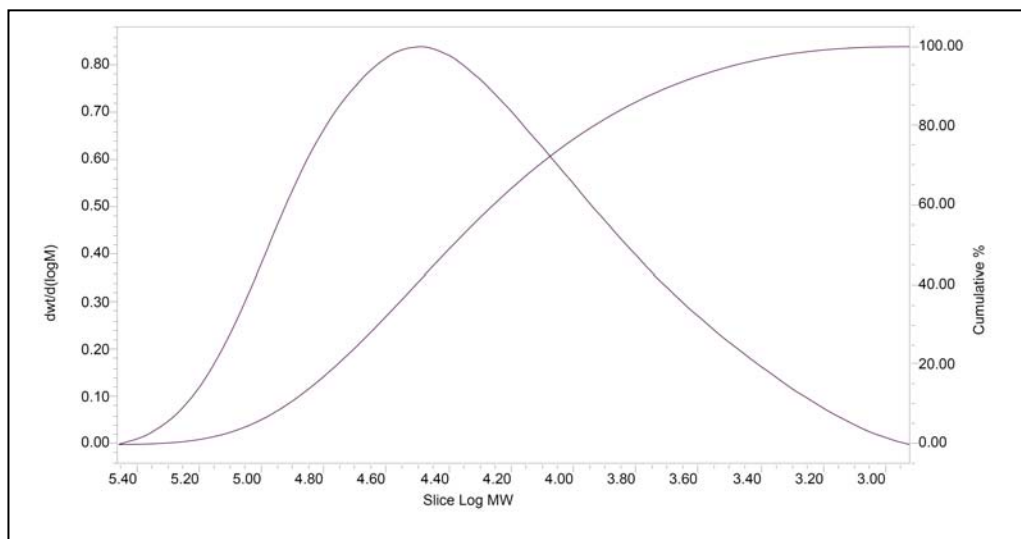
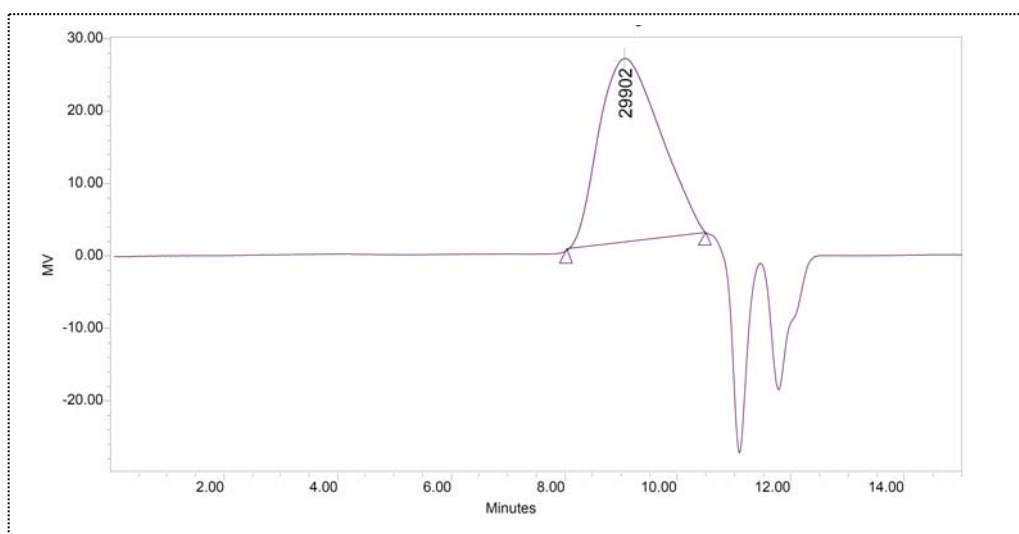
Entry 2 in Table 1

IPrAuBr ₃	NaBAR' ₄	Styrene	Co-solvent	Mw	Mn	PDI
0.006 mmol	0.006 mmol	5 ml	-	27300	14600	1.9



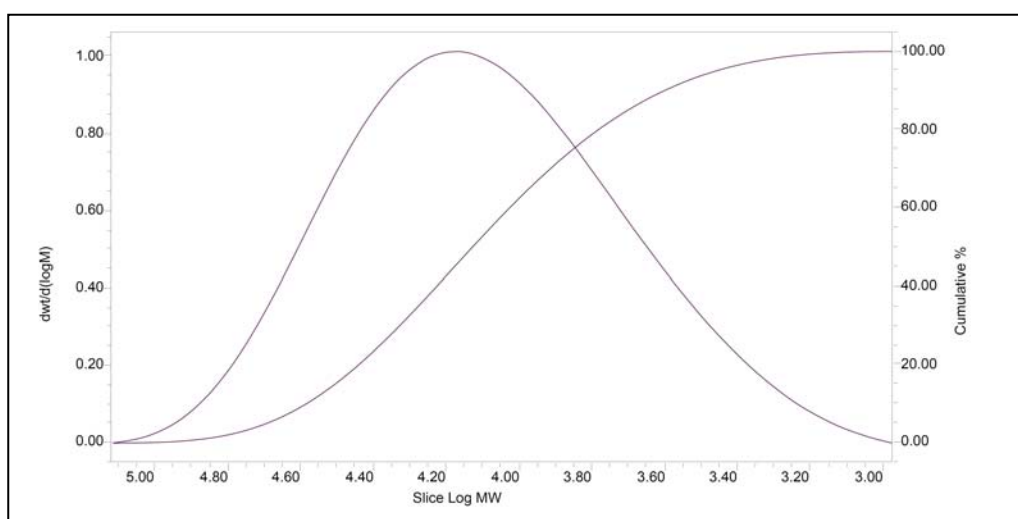
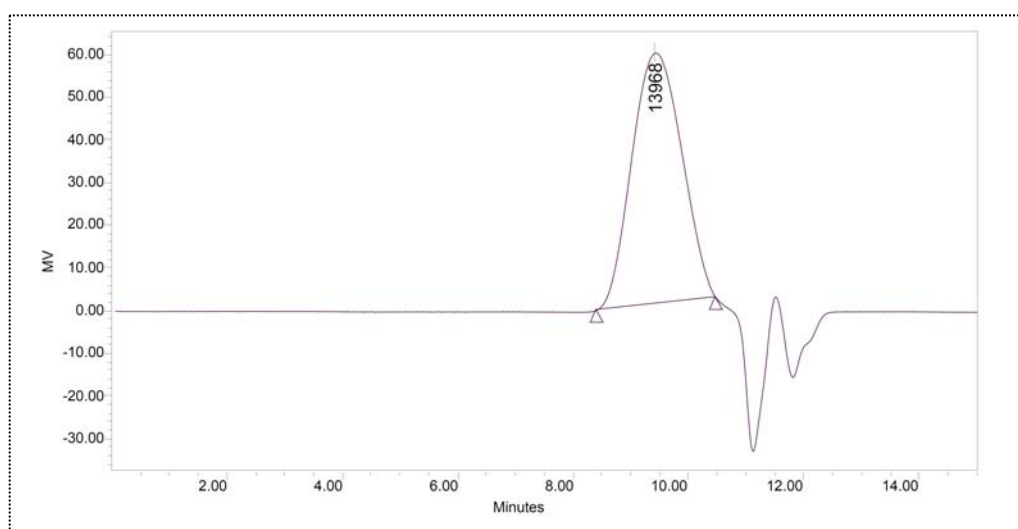
Entry 6 in Table 1:

IPrAuBr_3	NaBAR'_4	Styrene	Co-solvent	Mw	Mn	PDI
0.006 mmol	0.006 mmol	2 ml	5 mL DCM	39900	13150	3.0



Entry 9 in Table 2

IPrAuBr ₃	NaBAR' ₄	Styrene	Co-solvent	Mw	Mn	PDI
0.006 mmol	0.006 mmol	2 ml	2.5 ml DCM + 2.5 ml Tol.	18500	9400	1.96



Entry 4 in Table 4

IAdAuBr ₃	NaBAR' ₄	Styrene	Co-solvent	Mw	Mn	PDI
0.006 mmol	0.006 mmol	2 ml	---	1090	4363	820000 24000

