Supporting information

for

Indium(III) halides as exceptionally active, water-tolerant catalysts for cationic polymerization of styrenics

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I. Experimental section

1. General Methods and Materials

Styrene (St, 99%), α-methyl-styrene (*α*-MeSt, 98%), *p*-methylstyrene (*p*MeSt, 98%), indene (Ind, 95%), *p*-xylene (99%), 1-*p*-tolylethanol (98%), 1-indanol (99%), 1-bromophenethyl (99%), *tert*-butyl chloride (98%), diisopropylether ($i\mathrm{Pr_2O}$, 99%), indium(III) chloride (99.999%), and indium(III) bromide (99.999%) were purchased from Sigma-Aldrich, Acros or Strem chemicals and all used as received. The water content of the monomers and solvent was determined by the Karl-Fisher method and was in the ranges 150 ± 50 ppm for styrene, 100 ± 50 ppm for α-methyl-styrene, 90 ± 30 ppm for *p*-methylstyrene, 180 ± 50 ppm for indene and 100 ± 30 ppm for *p*-xylene; repeated controls indicated that these values did not change over the time period where investigations were carried out. All polymerization reactions were performed under air, in opened glass flasks.

2. Physical Methods

^{1}H and ^{13}C NMR spectra of polymers were recorded on Bruker AC-200, AC-300, and AM-500 spectrometers in 5 mm NMR tubes. ^{1}H and ^{13}C chemical shifts are reported in ppm versus $\mathrm{SiMe_4}$ and were determined by reference to the residual solvent resonances. Assignment of signals was carried out via multinuclear 1D (^{1}H, ^{13}C{^{1}H}) and 2D (^{1}H-^{1}H COSY, ^{1}H-^{13}C HMBC and HMQC) NMR experiments.

Gel Permeation chromatography (GPC) of polymers was performed independently on two apparatuses: (a) in THF (flow rate: 1.0 mL.min^{-1}) at 23 °C using a Polymer Laboratories PL50 apparatus equipped with PLgel 5 μm MIXED-C 300 × 7.5 mm columns, and combined RI and Dual angle LS (PL-LS 45/90°) detectors. (b) in THF (flow rate: 1.0 mL.min^{-1}) at 35 °C using a Polymer Laboratories PL50 apparatus equipped with four columns dedicated to lower molecular weight materials: 2 mixed D columns, one 100 Å column and one 50 Å column, and combined RI/UV detectors. In both cases, the number average molecular masses (M_n) and polydispersity index (M_w/M_n) of the polymers were calculated with reference to a universal calibration *vs*. polystyrene standards (M_w: 377,400; 188,700; 96,000; 46,500; 19,720; 9,920; 4,490; 2,360; 1,180; 580 and 162 g.mol^{-1}).

Differential scanning calorimetry (DSC) analyses were performed on a Mettler Toledo DSC1/700 or Setaram DSC 131 apparatus, under continuous flow of helium (25 mL.min^{-1}), using aluminum capsules. The thermograms were recorded according to the following cycle: −10 °C to +100 °C at 10 °C.min^{-1}; the T_g values are reported for the second cycle.

^{115}In NMR spectra were obtained with a Bruker Avance III 400 MHz spectrometer with a 5 mm BBOF probe operating at 87.7 MHz. The instrument was internally locked onto the deuterium resonance of D_2O introduced as a capillary in NMR tubes. All samples were studied as *ca*. 40 mmol.L^{-1} solutions (7 mg $InCl_3$ in *ca*. 0.8 mL O*i*Pr$_2$) at 23 °C. The experimental conditions were as follows: 2-14,000 scans, time domain: 32K, spectral window: −800 to +200 ppm; acquisition time: 0.18s, additional relaxation time: 0.2 s. Chemical shifts were externally referenced via the Bruker software to the resonance of $In(H_2O)_6^{3+}$.

3. General Procedure for Polymerization of Monomers

a) Polymerization of p-methylstyrene. In a typical experiment (Table 1, entry 4), $InBr_3$ (4.0 mg, 11.3 µmol), *p*MeSt (75 mL, 0.56 mol) and *p*-xylene (75 mL) were charged under air in a 250 mL round bottom flask containing a magnetic stir bar. *t*BuCl (2.6 mL, 28.2 mmol, 5 mol% *vs*. *p*MeSt) was added dropwise to the mixture and the vessel was heated in an oil bath preset at the required temperature (typically 60 °C) under stirring. The reaction was cooled to room temperature and quenched by addition of methanol (ca. 5 mL). The conversion was determined by ^{1}H NMR analysis of the crude solution mixture. The polymer was isolated as colorless gummy solid by evaporation of the solvent at 220 °C under vacuum with a Kugelrohr apparatus and was subsequently analyzed by NMR and GPC.

b) Co-polymerization of α-methylstyrene and styrene. In a typical experiment (Table 2, entry 21), styrene (0.97 mL, 8.5 mmol), *α*-MeSt (2.6 mL, 19.7 mmol) and *p*-xylene (2.5 mL) were charged under air in a glass flask equipped with a magnetic stir bar. Then, PhCHBrMe (19.3 µL, 0.14 mmol) was added to the mixture, followed by 1.0 mL of a solution prepared by dissolving $InBr_3$ (4.0 mg, 11.3 µmol) in a mixture of diisopropylether (200 µL) and *p*-xylene (19.8 mL) (*i.e.*, 0.2 mg, 0.556 µmol $InBr_3$). The resulting clear mixture was heated at 60 °C overnight by immerging the reaction vessel in an oil bath preset at the desired temperature. Aliquots of the solution were sampled to determine the conversion by ^{1}H NMR spectroscopy. After a given time period, the reaction was cooled to room temperature and quenched by adding solid calcium carbonate (*ca*. 0.5 g). The resultant mixture was filtered, the residue was washed with *p*-xylene and the clear solution was concentrated under vacuum at 220 °C under vacuum with a Kugelrohr apparatus to give a colorless gummy solid.

II. Representative kinetic and thermic monitoring of the co-polymerization of styrene and α-methylstyrene with the $InCl_3$/*t*BuCl system

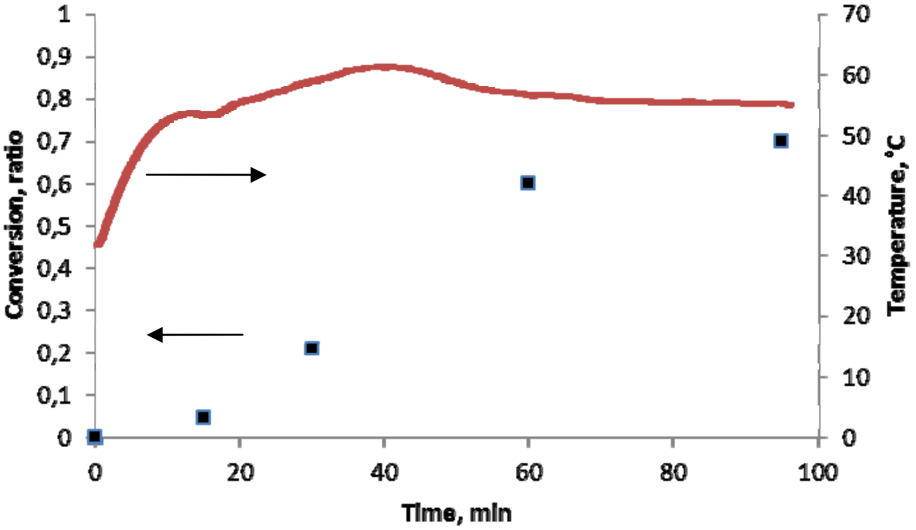


Figure S1. Representative kinetic and thermic monitoring of the co-polymerization of styrene and α-methylstyrene (Sty_{70}-α-$MeSty_{30}$) with the $InCl_3$/*t*BuCl system (100 ppm $InCl_3$, 1.0 mol% *t*BuCl, 60 °C) (Table 2, entry 26).

III. NMR characterization of oligostyrenes produced from the homopolymerization of styrene with the $InCl_3$/*t*BuCl system

Note: the oligostyrenes used for the NMR analyses shown hereafter were purposely produced for chain-end analysis, following protocols similar to those employed for the production of oligo(*p*-methylstyrene)s.

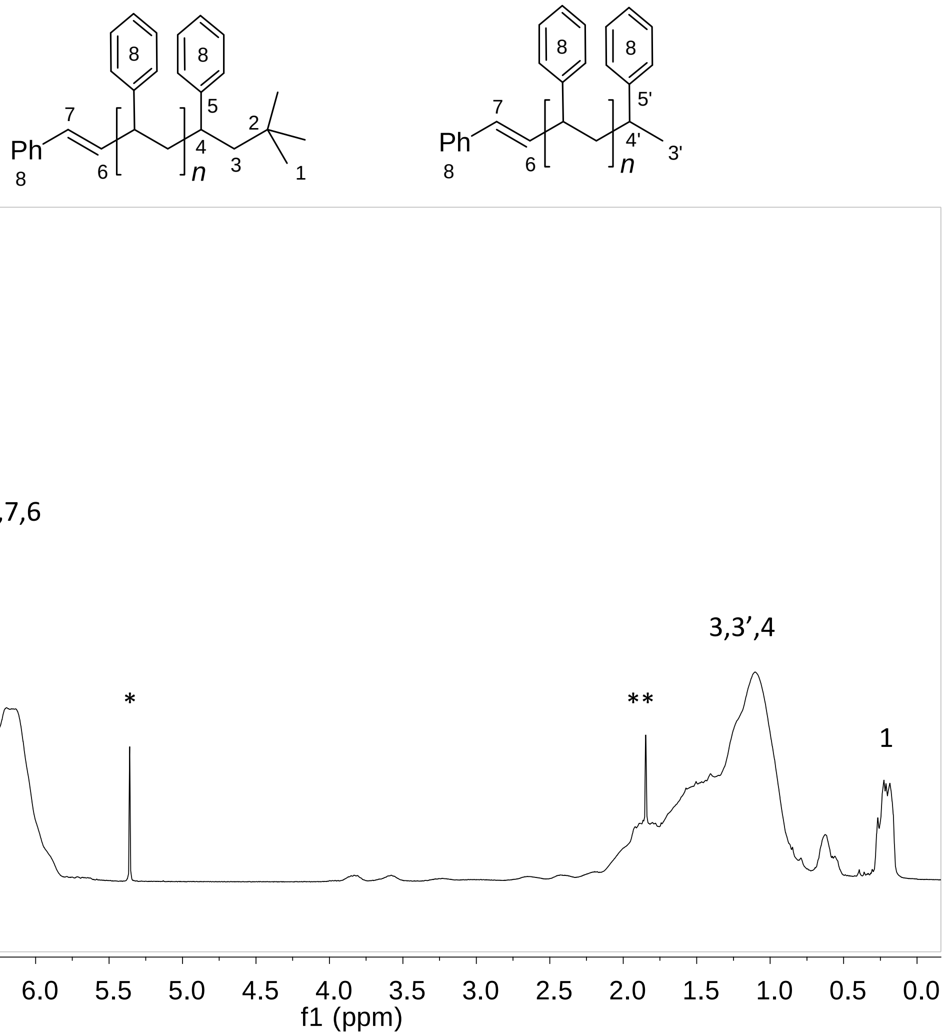


Figure S2. ^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 23 °C) of oligostyrenes produced from the homopolymerization of styrene with the $InCl_3$/*t*BuCl system (20 ppm In, 1 mol% *t*BuCl, 60 °C) (* and ** stand for the resonance of $C_2D_2Cl_4$ and residual *p*-xylene, respectively)

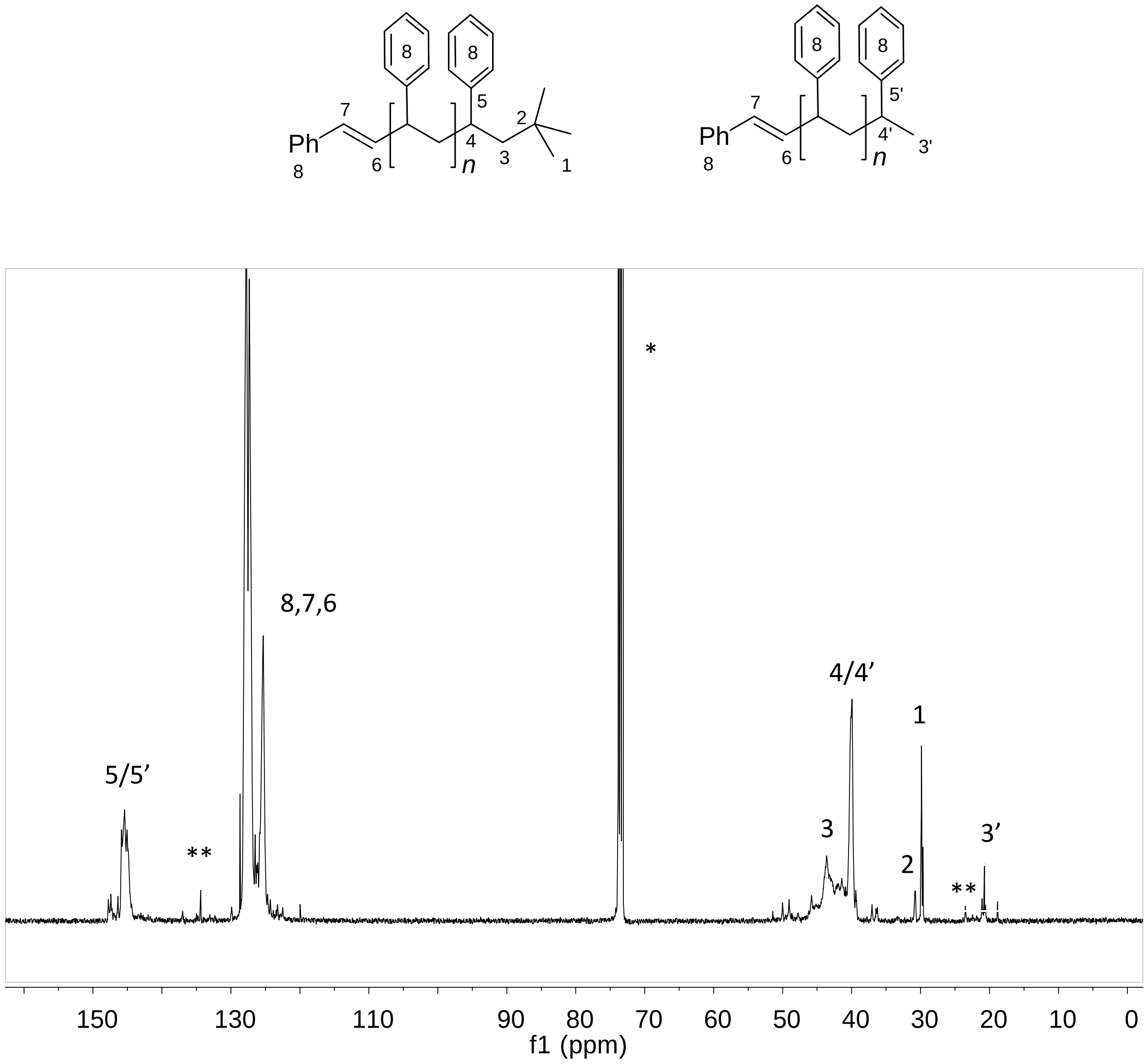
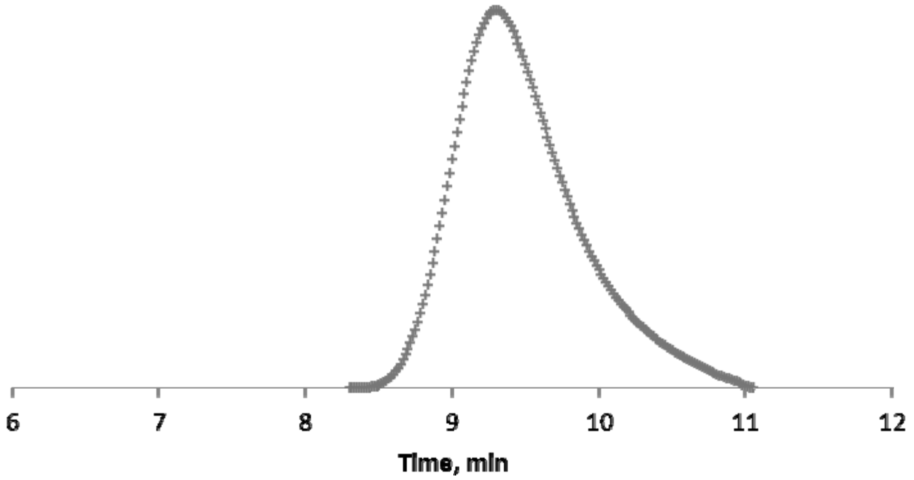


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (500 MHz, $C_2D_2Cl_4$, 23 °C) of oligostyrenes produced from the homopolymerization of styrene with the $InCl_3$/*t*BuCl system (20 ppm In, 1 mol% *t*BuCl, 60 °C) (* and ** stand for the resonance of $C_2D_2Cl_4$ and residual *p*-xylene, respectively)

IV. Representative GPC traces of oligomers



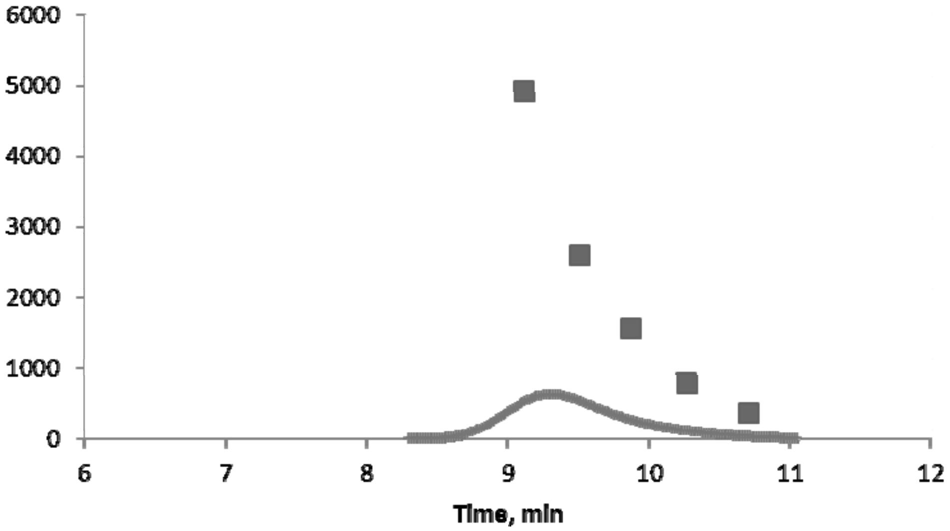


Figure S4. GPC traces (without and with the calibration curve) of a polyindene prepared from $InBr_3$ (100 ppm), 1.0 mol% PhCHBrMe, at 60 °C; $M_n = 2100$ g.mol^{-1}, $M_w/M_n = 1.7$ (Table 1, entry 12).

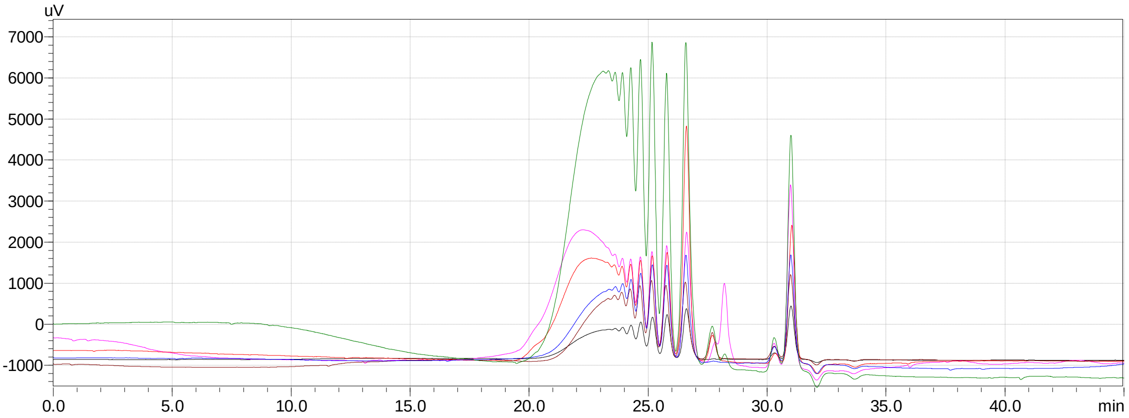


Figure S5. GPC traces of poly(styrene-*co*-α-methylstyrene) resins prepared from :

1: ref#M1: InCl$_3$ (100 ppm), 1 mol% *t*BuCl, Sty$_{70}$-α-MeSt$_{30}$, 60 °C (industrial grade reagents)

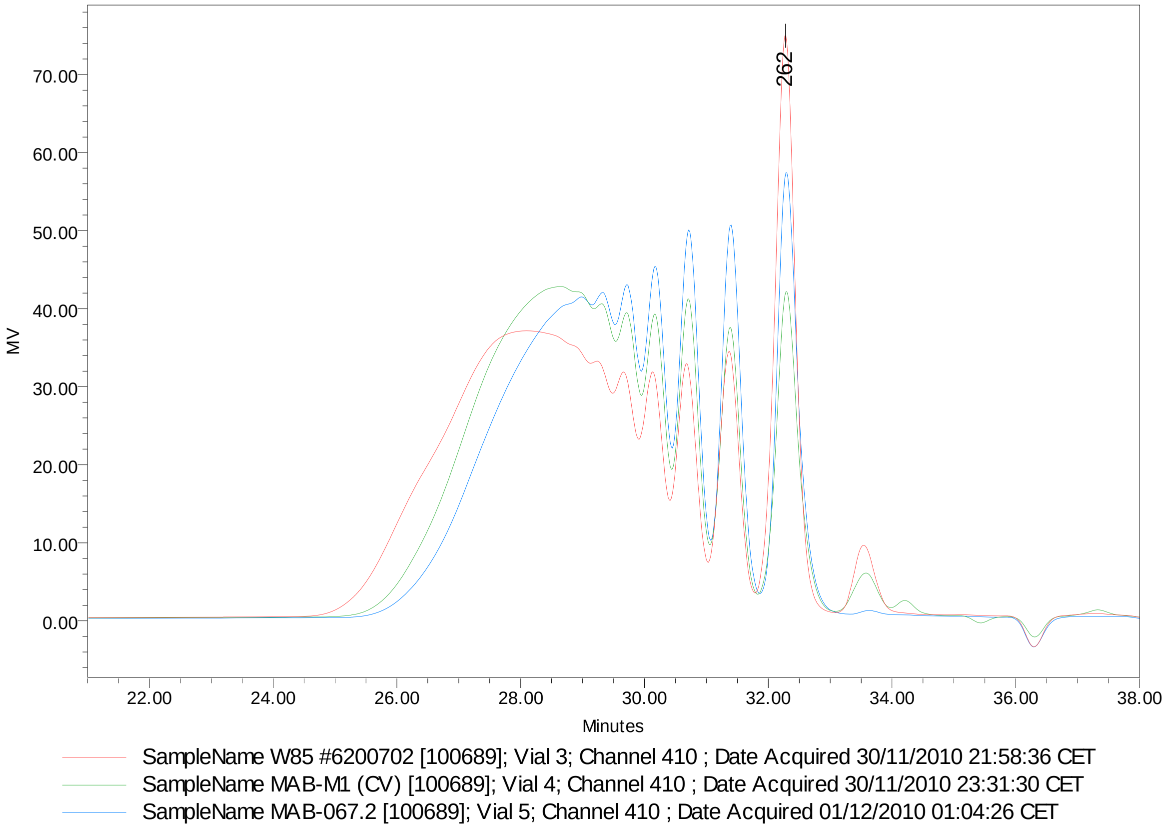
2: ref#67 1: InCl$_3$ (100 ppm), 1 mol% PhCHBrMe, Sty$_{50}$-α-MeSt$_{50}$, 45 °C (industrial grade reagents)

3: ref#67 2: InCl$_3$ (100 ppm), 1 mol% *t*BuCl, Sty$_{50}$-α-MeSt$_{50}$, 60 °C (industrial grade reagents)

4: ref#66 3: InCl$_3$ (100 ppm), 1 mol% *t*BuCl, Sty$_{40}$-α-MeSt$_{60}$, 60 °C (industrial grade reagents)

5: ref#68 4: InCl$_3$ (100 ppm), 1 mol% PhCHBrMe, Sty$_{70}$-α-MeSt$_{30}$, 45 °C (industrial grade reagents)

6: ref#w85: BF$_3$ (200-350 ppm) / H_2O (150 ppm), Sty$_{30}$-α-MeSt$_{70}$, 10 °C (industrial grade reagents)



Peak Results

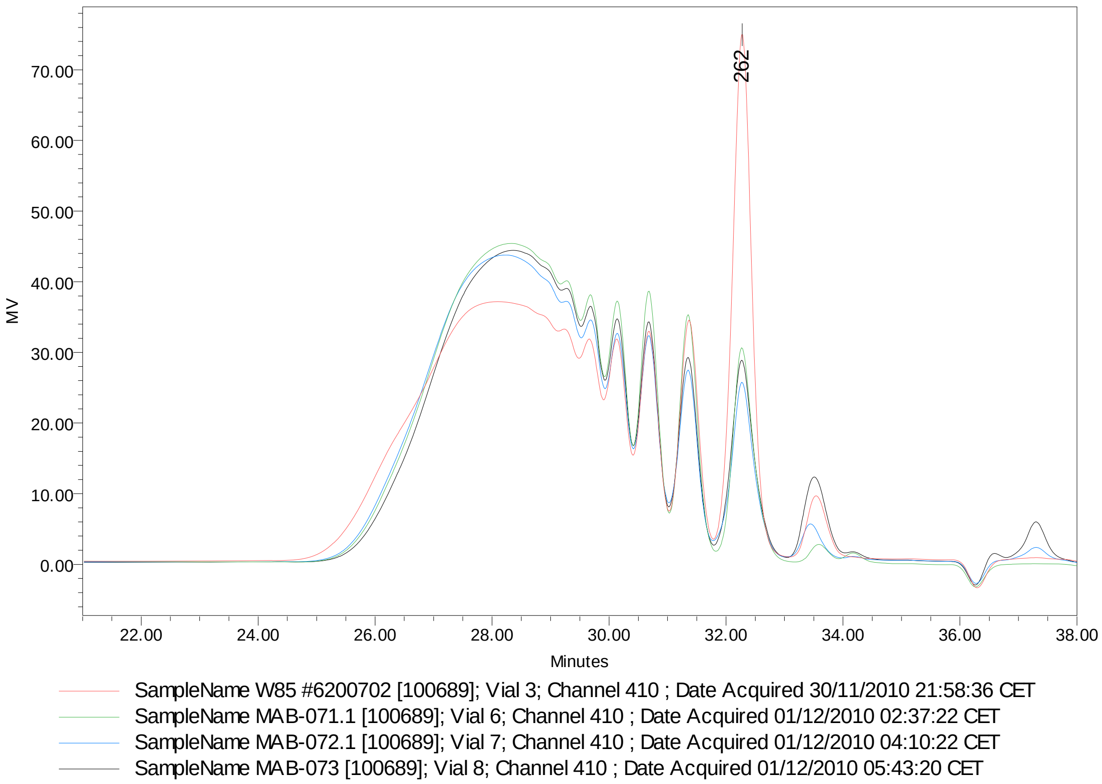
	SampleName	Mn	Mw	Mz	Poly dispersity	MP
1	MAB-067.2 [100689]	549	826	1265	1.50	261
2	MAB-M1 (CV) [100689]	602	962	1518	1.60	963
3	W85 #6200702 [100689]	588	1120	2044	1.91	262

Figure S6. Details of GPC traces of poly(styrene-*co*-α-methylstyrene) resins prepared from :

1: ref#M1: $InCl_3$ (100 ppm), 1 mol% *t*BuCl, Sty_{70}-*α*-$MeSt_{30}$, 60 °C (industrial grade reagents)

3: ref#67 2: $InCl_3$ (100 ppm), 1 mol% *t*BuCl, Sty_{50}-*α*-$MeSt_{50}$, 60 °C (industrial grade reagents)

6: ref#w85: BF_3 (200-350 ppm) / H_2O (150 ppm), Sty_{30}-*α*-$MeSt_{70}$, 10 °C (industrial grade reagents)



Peak Results

	SampleName	Mn	Mw	Mz	Poly dispersity	MP
1	MAB-071.1 [100689]	687	1100	1688	1.60	1108
2	MAB-072.1 [100689]	698	1139	1753	1.63	1166
3	MAB-073 [100689]	642	1061	1635	1.65	1090
4	W85 #6200702 [100689]	588	1120	2044	1.91	262

Figure S7. Reproducibility results: Details of GPC traces of poly(styrene-*co*-α-methylstyrene) resins prepared from :

1: ref#71.1: $InCl_3$ (100 ppm), 1 mol% *t*BuCl, Sty$_{60}$-*α*-MeSt$_{40}$, 50 °C (industrial grade reagents)

2: ref#72 1: $InCl_3$ (100 ppm), 1 mol% PhCHBrMe, Sty$_{60}$-*α*-MeSt$_{40}$, 50 °C (industrial grade reagents)

3: ref#73.1: $InCl_3$ (100 ppm), 1 mol% *t*BuCl, Sty$_{40}$-*α*-MeSt$_{60}$, 50 °C (industrial grade reagents)

4: ref#w85: BF_3 (200-350 ppm) / H_2O (150 ppm), Sty$_{30}$-*α*-MeSt$_{70}$, 10 °C (industrial grade reagents)

VI. ^{115}In NMR spectroscopy

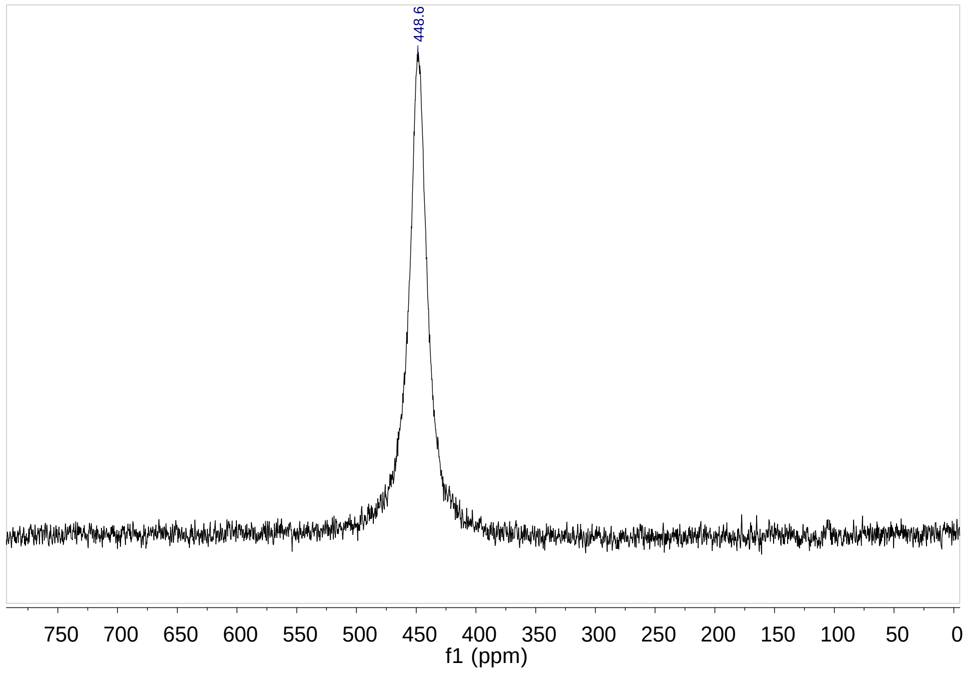


Figure S8. ^{115}In NMR spectrum (87.7 MHz, 23 °C) of a $InCl_4^-$ solution prepared from a 1:1 mixture of $InCl_3$ and HCl (2M in Et_2O) in *i*Pr_2O ([In] = 40 mmol.L^{-1}).

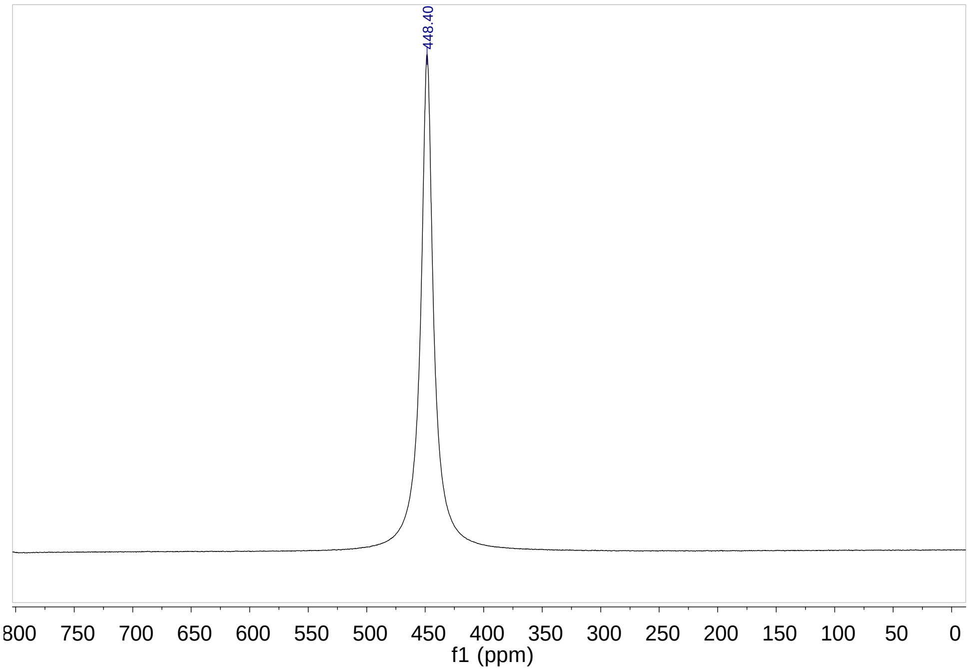


Figure S9. ^{115}In NMR spectrum (87.7 MHz, 23 °C) of a $InCl_4^-$ solution prepared from a 1:5 mixture of $InCl_3$ and HCl (2M in Et_2O) in *i*Pr_2O ([In] = 40 mmol.L^{-1}).

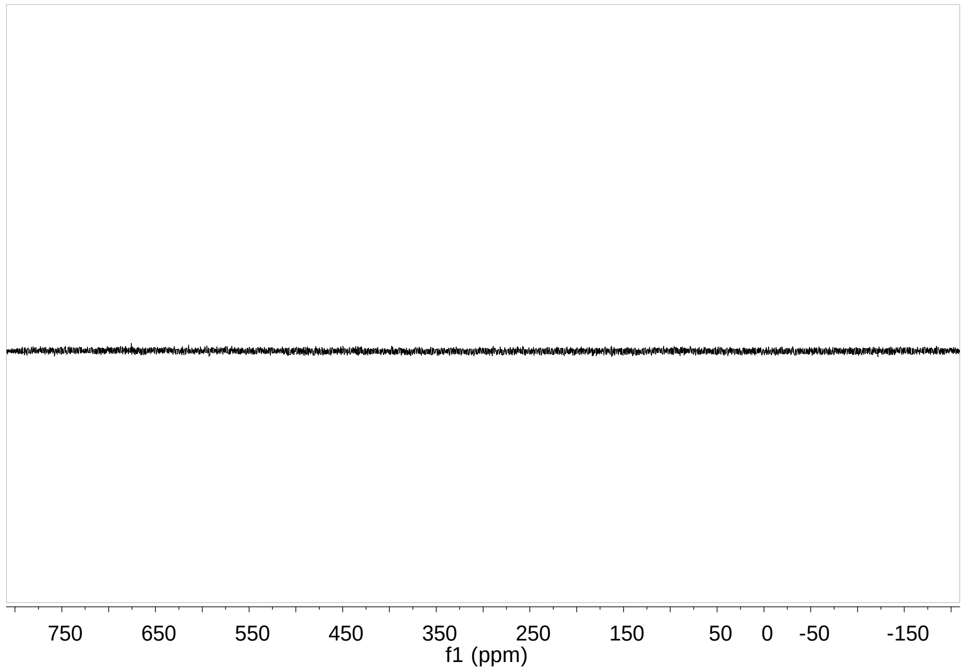


Figure S10. ^{115}In NMR spectrum (87.7 MHz, 23 °C) of a solution of $InBr_3$ in *i*Pr_2O ([In] = 40 mmol.L^{-1}).

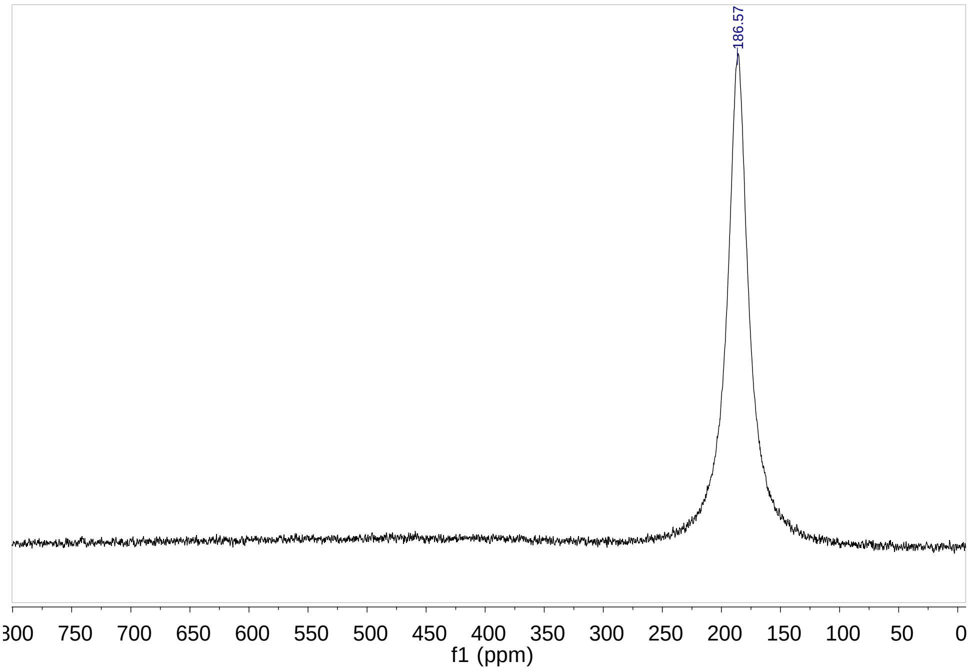


Figure S11. ^{115}In NMR spectrum (87.7 MHz, 23 °C) of a 1:1 mixture of $InBr_3$ and PhChBrMe in *i*Pr_2O ([In] = 40 mmol.L^{-1}) after 12 h at 23 °C.

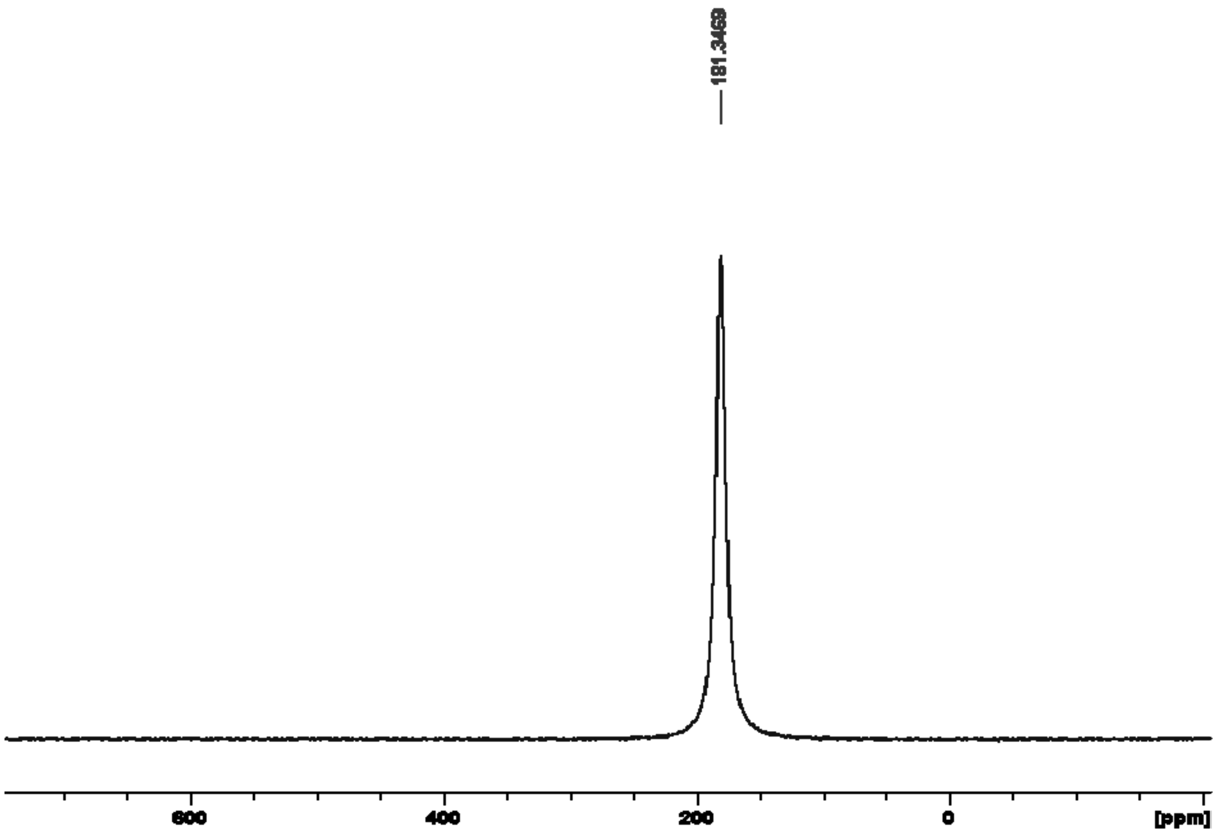


Figure S12. ^{115}In NMR spectrum (87.7 MHz, 23 °C) of a $InBr_4^-$ solution prepared from a 1:1 mixture of $InBr_3$ and HBr (20% aq) in *i*Pr_2O ([In] = 40 mmol.L^{-1}).