Supporting Information

Reusable and Environmentally Friend Catalyst of Ionic Trinuclear Iron Complex for Atom Transfer Radical Polymerization

Shota Niibayashi,[†] Hitoshi Hayakawa,[†] Ren-Hua Jin,[†] and Hideo Nagashima[‡*]

[†] *Central Research Laboratories, Dainippon Ink and Chemicals, Incorporated;*

[‡] *Institute for Materials Chemistry and Engineering, Kyushu University*

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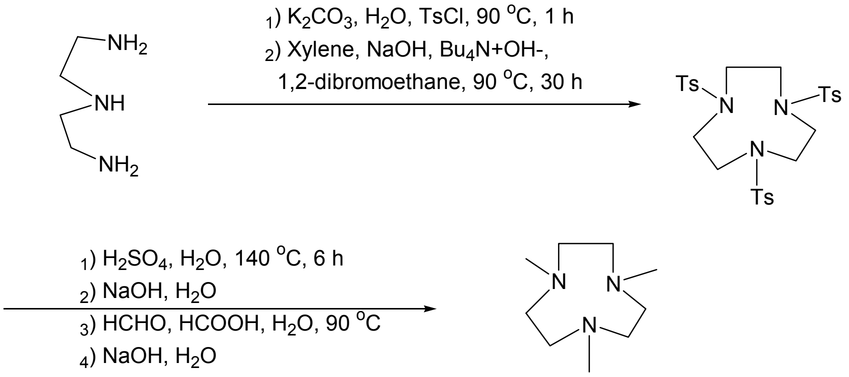
1) General Information

Commercially available MMA, styrene, and 1-chloroethylbenzene were dried over CaH_2, distilled under reduced pressure. Anhydrous solvents were purchased from commercially source and used without further purification. All of these chemicals were degassed just prior to use. Conversion of the monomer was determined by ^1H NMR spectroscopy. The NMR sample for the determination of the conversion was made in a nitrogen filled grove box (MBRAUN) in order to avoid aerobic oxidation of catalytically active Fe(II) species. The molecular weight and the molecular weight distribution were determined by SEC with Shodex KF-804L and KF805-L (elution: THF) at 40°C. The molecular weight was calibrated by Shodex STANDARD M-75（PMMA）、Shodex STANDARD SM-105（PSt）. NMR spectra were taken with a JEOL Lambda 400 or 600 spectrometer. Chemical shifts are given in ppm, relative to the solvent signal ($CDCl_3$-*d*, δ 7.24; CD_3CN, δ 1.93). UV-vis spectra were recorded on JASCO V520 spectrometer.

2) Preparation of 1,4,7-trimethyltriazacyclononane

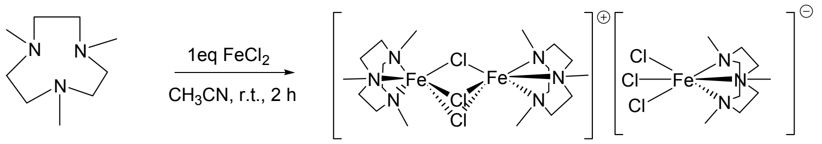


The trimethyl tacn ligand (1,4,7-trimethyltriazacyclononane) was prepared according to the method reported in a patent (WO94/00439). In a 2 L three necked flask, diethylenetriamine (5.5 g, 53 mmol) and p-toluenesulfonyl chloride (31 g, 160 mmol) were added to a solution of K_2CO_3 (24.3 g, 250 mmol) dissolved in distilled water (600 mL) with vigorous stirring. After the mixture was heated at 90°C for 1 h, xylene (240 mL), NaOH (19.15 g, 480 mmol), $Bu_4N^+OH^-$ (1 M, 8 mL, 8 mmol), and 1,2-dibromoethane (8 mL, 93 mmol) were added. The mixture was heated at 90°C with stirring for 30 h, during which. two portions of additional 1,2-dibromoethane (8 mL each, 93 mmol) were added at 4 h and 12 h after the first addition. The mixture was cooled to room temperature, and the formed precipitates were separated by filtration. Washing the white solids by water gave tritosylated tacn in 79 % yield (25 g).

In a 30 mL round bottomed flask, were placed tritosylated tacn (10.37 g, 18 mmol), water (2 mL), and conc. H_2SO_4 (10 mL). Heating the mixture at 140 °C with stirring resulted in formation of black solution, which was heated at this temperature for 6 h. The reaction mixture was cooled to room temperature. In a 500 mL two necked flask was placed a mixture of 50% (w/w) NaOH aq. (32 g) and water (13 mL), and the solution was cooled to 0 °C. To this solution, the reaction mixture described above was added dropwise with care. Addition of 37 % aqueous solution of formaldehyde (23 mL) and 85% formic acid (23 mL) was followed by heating the mixture at 90°C. Evolution of CO_2 gas was observed. After the gas evolution ceased, the mixture was cooled to room temperature. Addition of 50% (w/w) NaOH aq. (32 g) was followed by extraction with hexane gave the desired trimethyl tacn in 75% (2.25 g).

3) Preparation of the iron complex **1**

Ref. A. C. Moreland, T. B. Rauchfuss, *Inorg. Chem.* **2000**, *39*, 3029-3039



All manipulation was carried out under an inert gas atmosphere with a combination of Schlenk technique associated with a glove box. In a 100 mL Schlenk tube, Me_3TACN (0.50 mL, 2.58 mmol) was added to a suspension of $FeCl_2$ (0.317 g, 2.50 mmol) in MeCN (20 mL) with stirring. After 2 h, insoluble materials were filtered off, and the solution was concentrated to ca. 5 mL. Addition of ether (50 mL) resulted in precipitation of white solids. Recrystallization of the formed solids from a mixture of MeCN and ether afforded **1** as colorless crystals (664 mg, 89%).

^{1}H NMR chemical shifts in CD_3CN δ(ppm): δ= 120.61 (12H, CH_2, cation), 102.13 (24H, Me, cation, and CH_2, anion), 52.69 (12H, CH_2, cation), 46.21 (9H, Me, anion), 39.42 (6H, CH_2, anion).
cf. *Inorg. Chem.* 2000, *39*, 3029-3039: ^{1}H NMR chemical shifts in CD_3CN δ(ppm): δ= 121.6 (12H, CH_2, cation), 103.2 (24H, Me, cation, and CH_2, anion), 53.2 (12H, CH_2, cation), 46.2 (9H, Me, anion), 39.7 (6H, CH_2, anion).

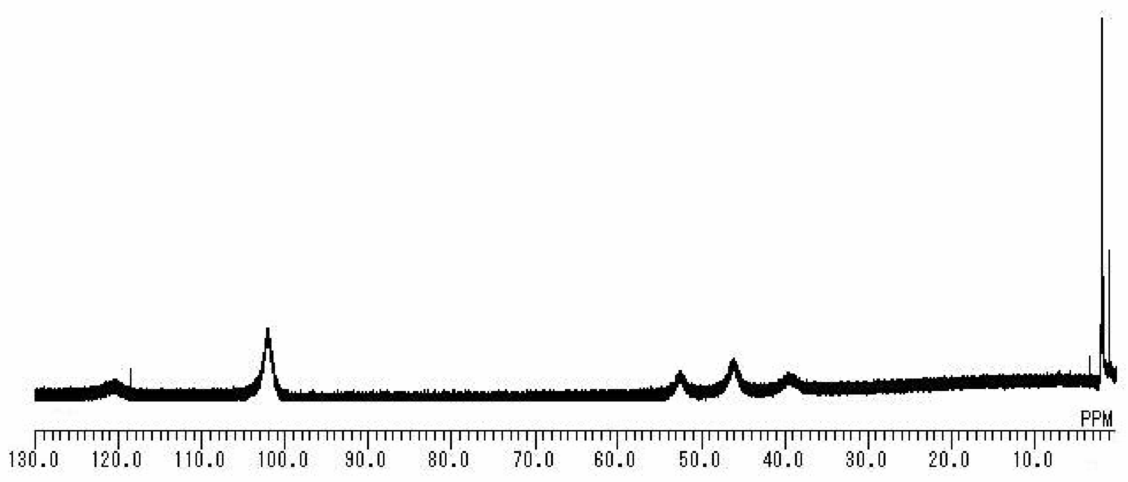


Figure ^{1}H NMR spectrum of iron complex **1**, CD_3CN, 600 MHz

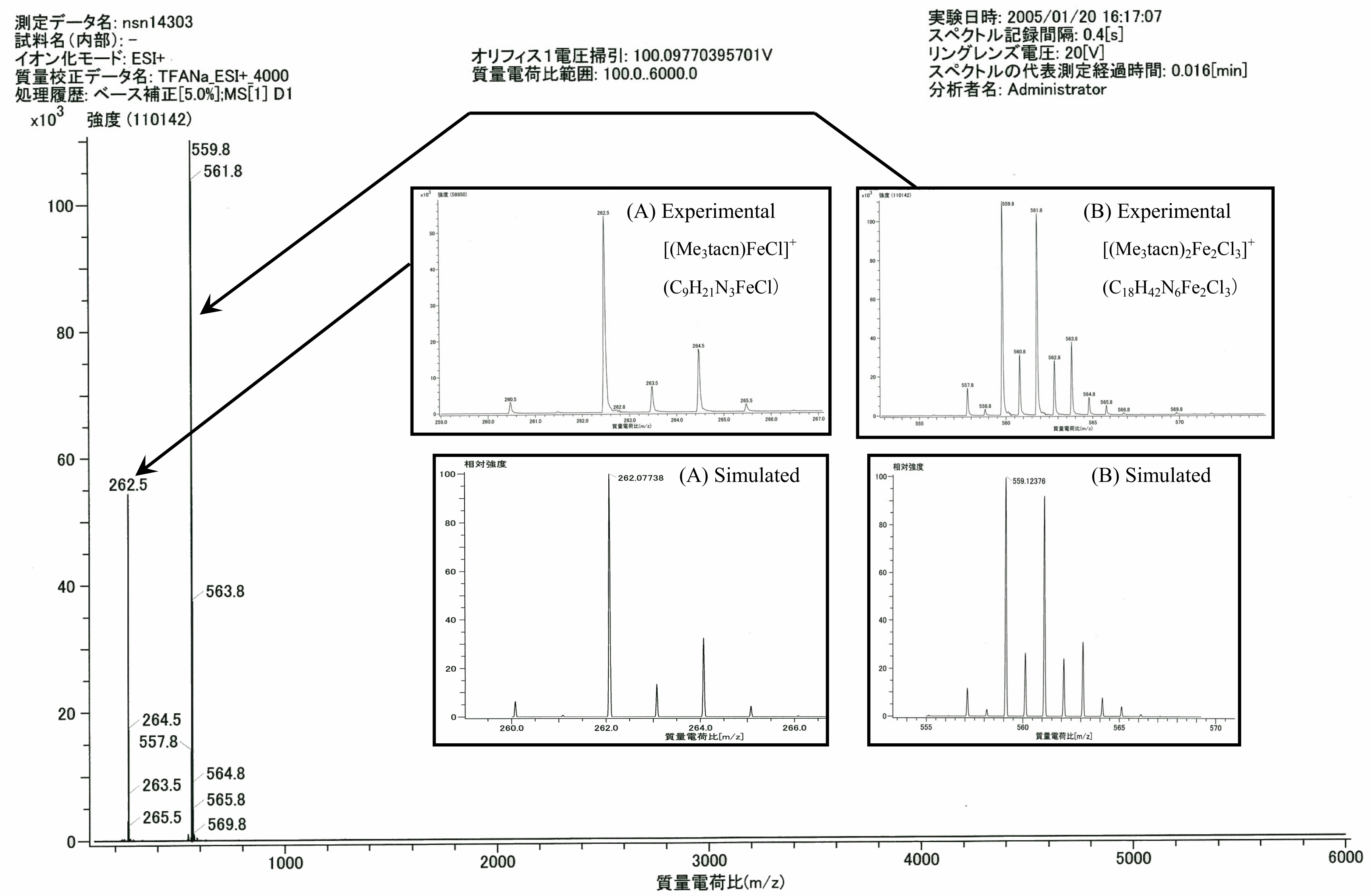
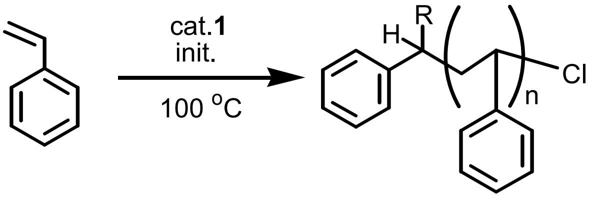


Figure ESI mass spectrum of complex **1** (JEOL JMS-T100CS; Solvent: acetonitrile; 0.01 mM)

4) Polymerization of styrene



In a glove box, a sitter chip and the catalyst were placed in a 15 mmϕ glass tube fitted with a tight cap. A solution of styrene and the initiator was added. The test tube was sealed by the cap, and heated at 100 °C with stirring. In order to investigate solvent effect, in several experiments in the table, toluene was added as a solvent. The polymerization was also performed in a glass tube flame-sealed in vacuum to experiment under a strict non-oxygen condition. The conversion was determined by ^{1}H NMR, whereas the yield was calculated from the gravity of the formed polymer after precipitation from methanol.

Time-conversion curve was prepared as follows: the reaction vessel was cooled to room temperature periodically, and a small portion of the mixture was separated and subjected to ^{1}H NMR and SEC analyses.

Table1. Time conversion plot of styrene polymerization (initiator = 1-chloro-ethylbenzene)

Time (h)	Conversion (%)	$M_{n(th)}$	$M_{n(exp)}$	PDI
0	0	0	0	0
4	15	8,000	11,000	1.7
9	30	15,000	15,000	1.6
20.5	48	24,000	23,000	1.3
70.5	82	41,000	44,000	1.2

Table Time conversion plot of styrene polymerization (initiator = chlorodiphenylmethane)

Time (h)	Conversion (%)	$M_{n(th)}$	$M_{n(exp)}$	PDI
0	0	0	0	0
4	4	2,000	7,000	1.6
9	10	5,000	11,000	1.4
20.5	22	11,000	22,000	1.2
70.5	74	37,000	66,000	1.2

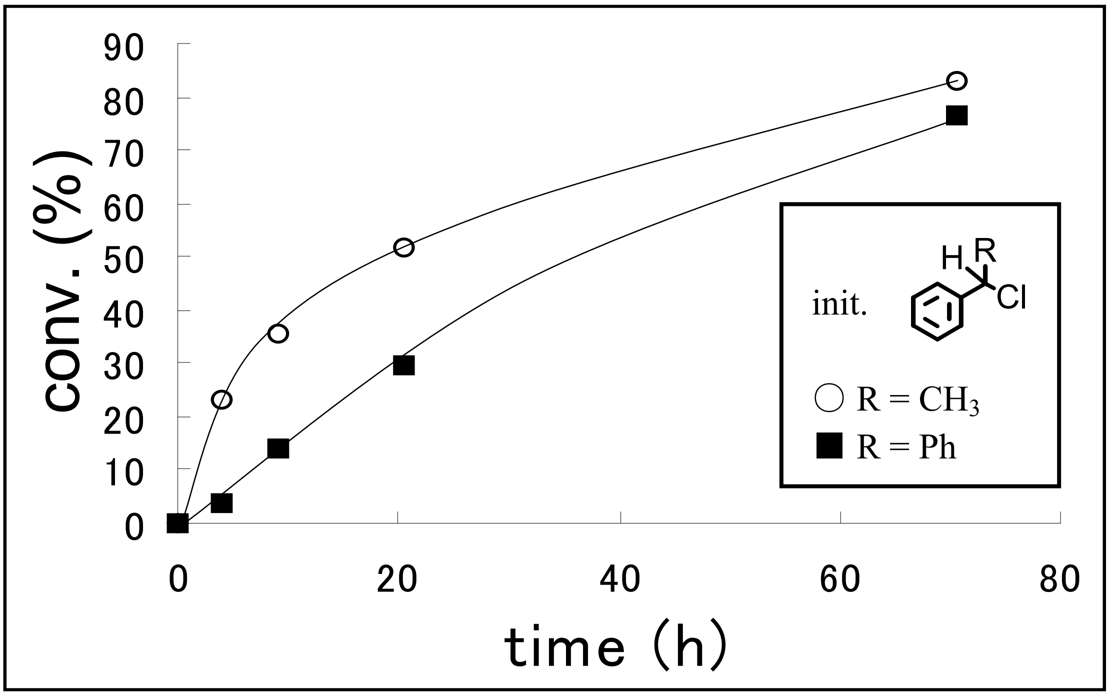


Figure Plots of reaction time vs conversion.

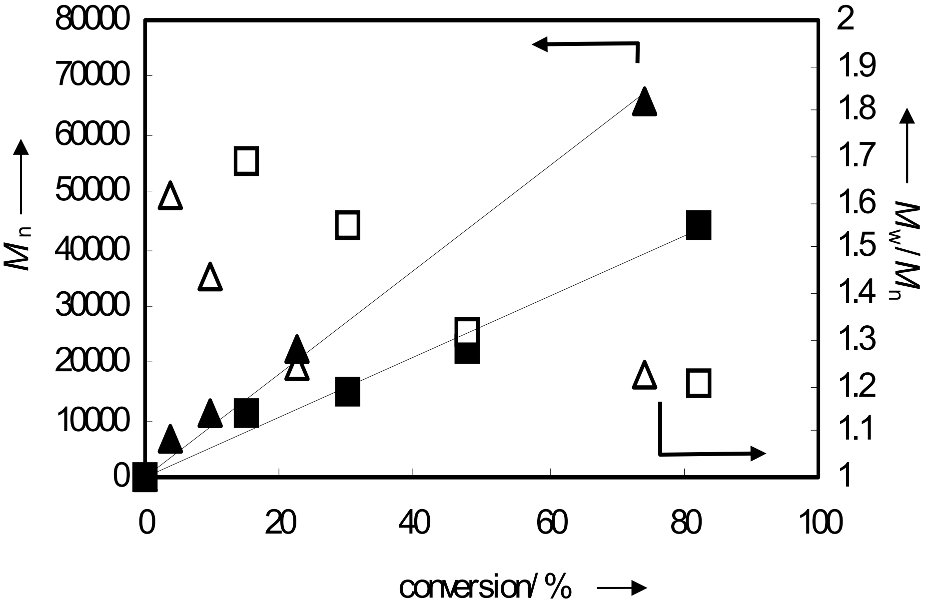


Figure Plots of M_n (■ and ▲) and M_w / M_n (□ and △) vs conversion. Initiator: 1-chloroethylbenzene (▲ and △) or diphenylchloromethane (■ and □). Temperature 100 °C. **1** / Initiator / St = 0.02 / 0.04 / 20 mmol,

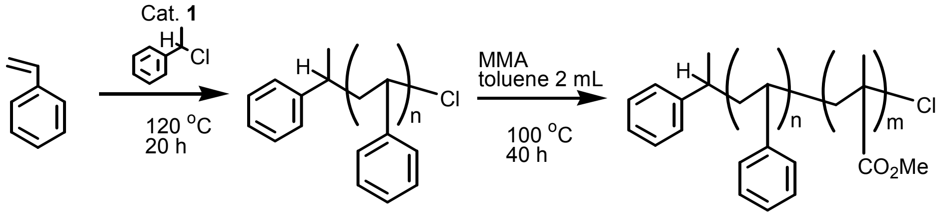
Table.

	conditions					results				
entry	Fe cat (mmol)	Initiator (mmol)	Styrene (mmol)	Toluene (mL)		Conv (%)	Mn(exp)	Mn(calc)	Mw/Mn	Initatpr efficiency
1	0.01	0.005	10	0	under N_2	95	377,300	197,600	1.74	0.52
2	0.01	0.01	10	0	under N_2	100	162,700	104,000	1.41	0.64
3	0.01	0.06	10	0	under N_2	100	37,700	17,300	1.23	0.46
4	0.01	0.2	10	0	under N_2	100	15,900	5,200	1.29	0.33
5	0.01	0.01	10	1	under N_2	65	129,300	67,800	1.34	0.52
6	0.01	0.02	10	1	under N_2	68	51,600	35,400	1.22	0.69
7	0.01	0.06	10	1	under N_2	76	28,400	13,100	1.16	0.46
8	0.01	0.2	10	1	under N_2	93	13,100	4,800	1.22	0.37
9	0.02	0.04	20	0	in vacuum	95	53,800	49,400	1.28	0.92
10	0.02	0.04	20	1	in vacuum	46	50,200	24,000	1.24	0.48
11	0.02	0.04	20	2	in vacuum	36	41,600	18,700	1.27	0.45
12	0.02	0.04	20	4	in vacuum	22	30,000	11,400	1.32	0.38

*Mn(calc) = ([St] /[init]) x (conv) x 104.15

*initEfic = Mn(calc)/Mn(exp)

5) Block Copolymerization of styrene with MMA



Polymerization of styrene was carried out according to a procedure described in section 3) with **1** (18 mg, 0.02 mmol), 1-chloroethylbenzene (5.5 μL, 0.04 mmol), and styrene (1.02 g, 10 mmol) at 120°C. After 20 h, the reaction vessel was moved to a glove box, and toluene (2 mL) was added. ^{1}H NMR and SEC measurements of this sample showed the conversion of the reaction and the molecular weight and the molecular weight distribution of the formed polymer to be 93%, Mn = 35,000, and PDI =1.3, respectively. MMA (1.0 g, 10 mmol) was added, and the mixture was heated at 100°C for 40 h. The conversion of the post polymerization was over 95%, and the molecular weight and the molecular weight distribution of the formed PSt-b-PMMA were Mn = 75,000 and PDI 1.4, respectively.

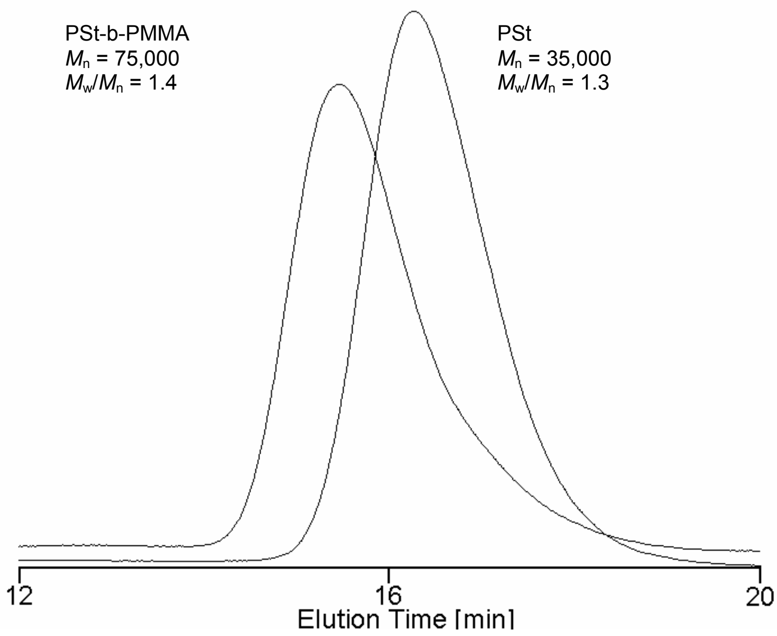
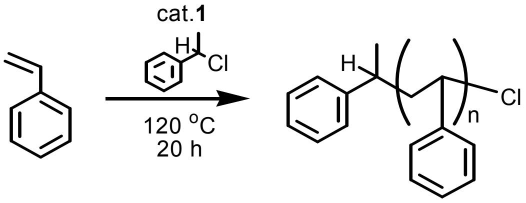


Figure block copolymerization

6) Reuse of the catalyst (polymerization of styrene)



Polymerization of styrene was carried out according to a procedure described in section 3) with **1** (18 mg, 0.02 mmol), 1-chloroethylbenzene (5.5 µL, 0.04 mmol), and styrene (1.02 g, 10 mmol) at 120 °C. After 20 h, the reaction vessel was opened under an inert gas atmosphere, and THF 4mL was added. The resulting THF solution was poured into methanol (30 mL) under an inert gas atmosphere, and the polystyrene precipitated was separated by filtration. The filtrate was concentrated to 5 mL in vacuum, and the formed polymer was separated by filtration. The resulting solution containing **1** was moved to the new reaction vessel, and the solvent was removed in vacuum. Styrene (1.02 g, 10mmol) and 1-chloroethylbenzene (5.5 µL, 0.04 mmol) was added, and the second run of polymerization was performed as described above. The sequence of polymerization followed by the catalyst recycle described above was repeated four times, and the results are summarized in the table below.

Table

	Conversion [%]	M_n(exp)[c]	M_n(calc)[d]	$M_\mathrm{w}/M_\mathrm{n}$
1st[a]	95	32,300	23,800	1.31
2nd[b]	93	29,000	23,300	1.33
3rd[b]	92	31,000	23,000	1.39
4th[b]	93	27,100	23,300	1.34

[a] The first run of polymerization was carried out at 120 °C for 20 h in the presence of **1** (the catalyst) and 1-chloroethylebenzene (the initiator) with the ratio of [**1**] / [I] / [St] = 0.02 / 0.04 / 10 mmol. [b] The 2nd, 3rd, and 4th polymerizations were carried out with the recovered catalyst by the method described in the text. Other conditions were the same as those of [a]. [c] Determined by size exclusion chromatography (SEC) with PSt calibration. [d] M_n(calc) is calculated from the conversion of monomer.

The recovered catalyst after the first run of styrene polymerization was subjected to ^{1}H NMR analysis. As shown below, the spectrum was identical with that of the complex **1**.

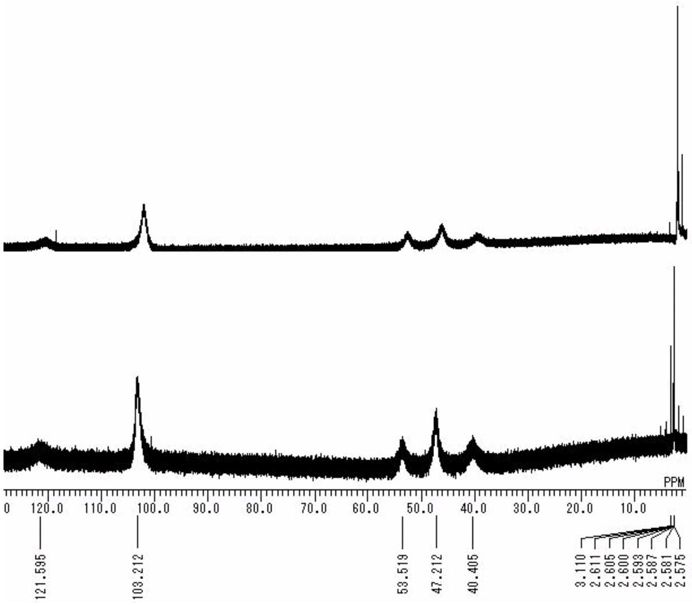
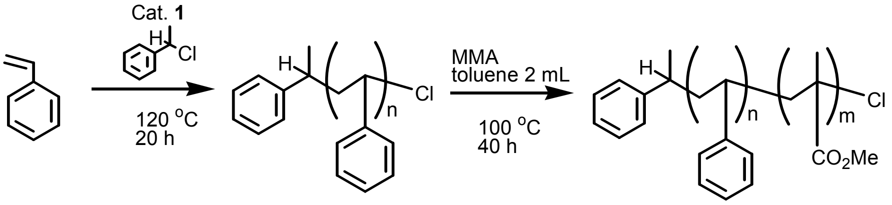


Figure. Comparison in ^{1}H resonances between the crude (above) and the purified (below) complex **1**.

1 (authentic sample): ^{1}H NMR chemical shifts in CD_3CN δ(ppm): δ= 120.61 (12H, CH_2, cation), 102.13 (24H, Me, cation, and CH_2, anion), 52.69 (12H, CH_2, cation), 46.21 (9H, Me, anion), 39.42 (6H, CH_2, anion)

1 (recovered from the polymerization of styrene): ^{1}H NMR chemical shifts in CD_3CN δ(ppm): δ= 121.60 (12H, CH_2, cation), 103.21 (24H, Me, cation, and CH_2, anion), 53.52 (12H, CH_2, cation), 47.21 (9H, Me, anion), 40.41 (6H, CH_2, anion)

7) Reuse of the catalyst (block copolymerization of styrene and MMA)



Cat.1 / init. / St / MMA = 0.02 / 0.04 / 10 / 10 (mmol)

Polymerization of styrene was carried out according to a procedure described in section 3 with **1** (18 mg, 0.02 mmol), 1-chloroethylbenzene (5.5 μL, 0.04 mmol), and styrene (1.02 g, 10 mmol) at 120°C. After 20 h, the reaction vessel was moved to a glove box, and toluene (2 mL) was added. ^{1}H NMR and SEC measurements of this sample showed the conversion of the reaction and the molecular weight and the molecular weight distribution of the formed polymer to be over 95%, M_n = 35,000, and PDI =1.2, respectively. MMA (1.0 g, 10 mmol) was added, and the mixture was heated at 100 °C for 40 h. The conversion of the post polymerization was over 95%, and the molecular weight and the molecular weight distribution of the formed PSt-b-PMMA were M_n = 77,000 and PDI 1.4, respectively.

The reaction vessel was opened under an inert gas atmosphere, and THF 8 mL was added. The resulting THF solution was poured into methanol (60 mL) under an inert gas atmosphere, and the block copolymer precipitated was separated by filtration. The filtrate was concentrated to 5 mL in vacuum, and the formed polymer was separated by filtration. The resulting solution containing **1** was moved to the new reaction vessel, and the solvent was removed in vacuum. Styrene (1.02 g, 10 mmol) and 1-chloroethylbenzene (5.5 μL, 0.04 mmol) was added, and the second run of polymerization (conversion >95%, M_n = 43,000、PDI 1.2) and post polymerization with MMA (conversion >95%, M_n = 116,000、PDI 1.7) was performed as described above.

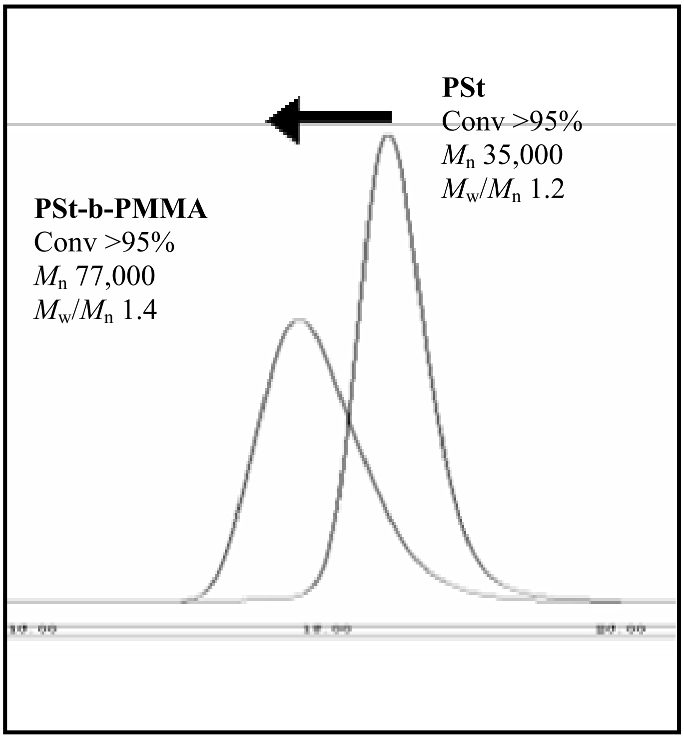


Figure GPC chart of 1st block copolymerization

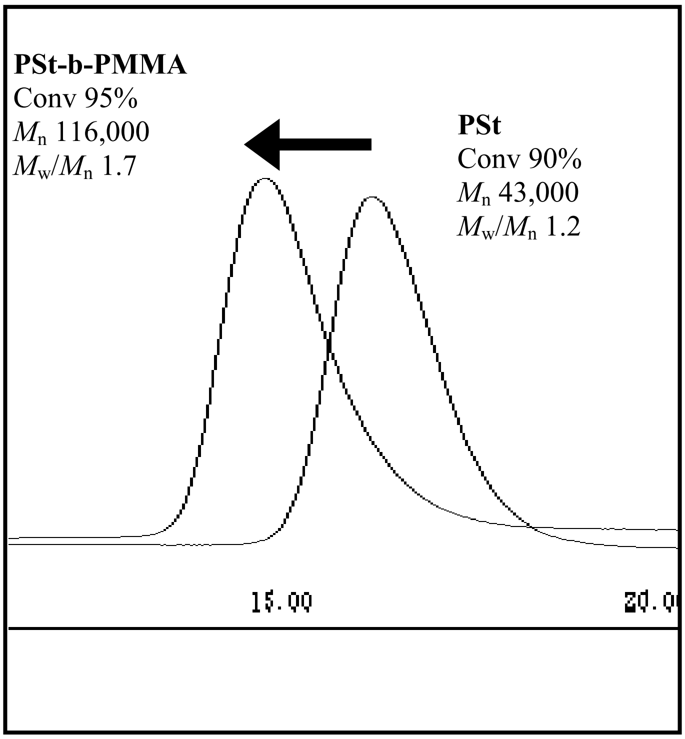


Figure GPC chart of 2nd block copolymerization

8) Analyses of the iron residues in polystyrene

ICP mass analysis. The weight of the polymer measured by precise micro balance. The sample was dissolved by microwave-assisted dissolution (Milestone General, MLS-1200MEGA) using HNO_3 and H_2SO_4. The sample was subjected to the ICP analysis (Perkin Elmer, Optima 3300DV). In typical examples, polystyrene (M_n 23,000, PDI 1.2) synthesized by the procedure described above contain 4,600ppm of iron, which was calculated from the weight of the iron catalyst used and that of the polymer formed. After precipitation from methanol twice (as described in section 5)), the iron content was reduced to 17 ppm. Similarly, polystyrene (M_n 44,000, PDI 1.2) which should contain 2300 ppm of iron was purified by precipitation from methanol twice; the iron content of the purified polystyrene was 14 ppm.

UV measurement. Polystyrene （M_n = 49,000, PDI = 1.39） was synthesized by the ATRP procedure mentioned at section 3 (polymerization conditions: cat **1** / init / styrene = 0.01 / 0.02 / 5 (mmol), 90 ^oC, 60 h, ethyl-2-bromoisobutyrate as initiator). . A part of the crude sample (300 mg) was separated, and dissolved in THF (2 mL) and precipitated from methanol (30 mL) to give purified polystyrene (277 mg, 92%). The crude polystyrene was pale yellow, whereas the purified polystyrene was colorless. UV measurement of a solution of the crude polystyrene (10 mg of polystyrene was dissolved in 3 mL of CH_2Cl_2) showed absorption at λ_{max} = 382 nm, whereas that of the purified sample showed no peak as shown below.