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Supporting Information

for

Synthesis of Well-Defined Halogenated Styrenic (Co)polymers: Polymerisation Catalyzed by

Half-Titanocenes and Their Post-Modification

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General experimental procedure, synthesis of ('BuC₅H₄)TiCl₂(O-2,6-^{*i*}Pr₂-4-SiEt₃-C₆H₂) (2), (1,2,4-Me₃C₅H₂)TiCl₂(O-2,6-^{*i*}Pr₂-4-SiEt₃-C₆H₂) (4).

All experiments involving air- and moisture sensitive compounds were conducted under a nitrogen atmosphere by using of a drybox or standard Schlenk techniques. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was stored over molecular sieves (mixture of 3 A 1/16 and 4 A 1/8, and 13X 1/16) in a drybox without further purification. Ethylene (polymerisation grade, purify >99.9 %, Sumitomo Seika Co., Ltd.) was used as received. p-Trimethylsilyl styrene (p-TMSSt) was prepared according to the published procedures^{1, 2} and stored over molecular sieves after passing through an alumina short column under nitrogen atmosphere. Commercially available methylaluminoxane (TMAO-S, Tosoh Finechem Co., Ltd., Al 9.5wt% toluene solution) was dried in vacuo in drybox at 50 °C (then at >100 °C for 1 h to completion) to remove toluene and AlMe3 and used as a white solid (d-MAO). ('BuC5H4)TiCl2(O-2,6-'Pr2-4-R-C6H3)^{3, 4}, (1,2,4-Me3C5H2)TiCl2(O-2,6-'Pr2-4-C6H3)⁵, $Cp*TiCl_2 (O-2,6-iPr_2-4-R-C_6H_2) [R = H (5)^{3,4}, Si^iPr_3 (6)^6], and (Me_3SiC_5H_4)CpTiCl_2(O-2,6-iPr_2-C_6H_3) (7).^7$ were prepared according to the reported procedure. All other reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. Measurement of ¹H and ¹³C NMR spectra were conducted on a Bruker AV500 spectrometer (500.13 MHz, ¹H; 125.77 MHz, ¹³C) or JEOL 400 spectrometer (400 MHz, ¹H; 100 MHz, ¹³C). The polymer samples for the NMR analysis prepared by dissolving in chloroform-d, 1,1,2,2-tetrachloroethane- d_2 , dichloromethane- d_2 . ¹³C NMR spectra of the resultant ethylene copolymers were measured at 110 °C with proton decoupling (pulse interval, 5.2 s, acquisition time, 0.8 s; pulse angle, 90°; number of the transients accumulated, ca. 6000). Elemental analyses were performed using a UNICUBE CHN/O/S elemental analyzer (UNICUBE, ELEMENTAR, Inc., Germany). The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the resultant polymers were measured by gel-permeation chromatography (GPC). HPLC grade THF (containing 0.03 wt% of 2,6-di-tert-butyl-p-cresol) or orthodichlorobenzene (containing 0.05 wt.% 2,6-di-tert-butyl-p-cresol) were chosen as a solvent. GPC analyses were performed on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF at 40 °C (GPC columns: ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm diameter, spherical porous gel made of styrene/ divinylbenzene copolymer, ranging from $<10^2$ to 2×10^7 MW, flow rate 1.0 mL/min) or a Tosoh HLC-8321GPC/HT using a RI-8022 detector in o-dichlorobenzene at 140 °C (GPC columns: TSKgel H_{HR} HT-RC, TSKgel GMH_{HR}-H(S) HT2 \times 3, 30 cm \times 7.8 mm diameter, MW ranging from $<10^2$ to $<2.8 \times 10^8$, flow rate 1.0 mL/min), respectively. Based on the calibration curve using standard polystyrene samples, the weight molecular weight and polydispersity index were calculated. Differential Scanning Calorimetric (DSC) thermograms for the resulted polymer were measured by using a Hitachi DSC-7000X instrument under nitrogen atmosphere. After preheating [30 to 150 °C or 325 °C (20 °C /min)], samples were firstly heated from -100 °C or 325 °C at 20 °C /min and then cooled at the 10 °C /min. By repeating twice of these heating and cooling cycles, T_m and T_g were chosen from the middle of the phase transition in the second heating scan. Wide-angle X-ray diffraction measurements were carried out at BL-6A in the Photon Factory of High Energy Accelerator Research

Organization. The diffraction angle was calibrated with a diffraction pattern of silver behenate. The diffraction angle was calibrated using the diffraction pattern of silver behenate. Diffraction data were obtained with a PILATUS 100 K detector (DECTRIS Ltd., Switzerland). Samples were placed between thin polyimide films with a 1 mm aluminum spacer.

Synthesis of (^{*i*}BuC₅H₄)TiCl₂(O-2,6-^{*i*}Pr₂-4-SiEt₃-C₆H₂) (2).

Into a dried diethyl ether (20 mL) solution containing ('BuC₅H₄)TiCl₃ (289 mg, 0.850 mmol), a driedndiethyl ether (5.0 mL) containing 2,6-^{*i*}Pr₂-4-SiEt₃-C₆H₂OH (292 mg, 1.00 mmol) and Et₃N (152 mg, 1.50 mmol) was added at -30 °C. The stirred reaction mixture was allowed to warm to room temperature and was stirred overnight. The resultant reaction mixture was filtered on a pad of celite, and the filtercake was washed by diethyl ether. Volatiles in the filtrate were removed *in vacuo*, and the resultant solids were recrystallized from *n*-hexane to give orange crystals (282 mg, 0.646 mmol, yield: 76%). ¹H NMR (500 MHz, CDCl₃): δ 7.20 (s, 2H), 6.82 (t, 2H, *J* = 2.8 Hz), 6.23 (t, 2H, *J* = 2.8 Hz), 3.30-3.22 (m, 2H), 1.44 (s, 9H), 1.23 (d, 12H, *J* = 6.9 H), 0.99 (t, 9H, *J* = 7.9 Hz), 0.78 (q, 6H, *J* = 7.9 Hz). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 165.2, 151.2, 137.0, 136.4, 133.2, 129.2, 119.1, 34.0, 30.9, 26.8, 23.7, 7.5, 3.6. Anal. Calcd for C₃₁H₅₂Cl₂OSiTi: C, 61.02; H, 8.34. Found: C, 60.69; H, 8.16.

Synthesis of (1,2,4-Me₃C₅H₂)TiCl₂(O-2,6-^{*i*}Pr₂-4-SiEt₃-C₆H₂) (4).

The procedure for synthesis of **4** was conducted by the similar procedure for **2** (327 mg, 0.638 mmol, yield: 75%). ¹H NMR (500 MHz, CDCl₃): δ 7.19 (s, 2H), 6.20 (s, 2H), 3.28-3.19 (m, 2H), 2.27 (s, 6H), 2.22 (s, 3H), 1.23 (d, 12H, J = 6.9 Hz), 0.99 (t, 9H, J = 7.9 Hz), 0.78 (q, 6H, J = 7.9 Hz). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 162.8, 137.5, 134.8, 134.7, 132.5, 129.1, 121.3, 26.7, 23.8, 16.3, 14.6, 7.5, 3.6. Anal. Calcd for C₂₆H₄₂Cl₂OSiTi: C, 60.35; H, 8.18. Found: C, 60.42; H, 8.03.

Syndiospecific Polymerisation of *p*-Trimethylsilylstyrene (*p*-TMSSt).

Synthesis of syndiotactic polymers were typically performed according to the following procedure: a prescribed amount of *p*-TMSSt and toluene, MAO (1.72 mmol, 100 mg), and were charged into the autoclave (20 mL, stainless steel) in the dry box. After an addition of a toluene solution containing titanium complex (2.0 μ mol/ mL in toluene) via a syringe, the reaction mixture was stirred magnetically for 10 min at room temperature or 50 °C. After reaction, the mixture was then poured into MeOH (150 mL) containing HCl (3 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried *in vacuo* (at 55 °C for several hours.). According to the establish procedure^{8,9}, the syndiotactic polymer was isolated as acetone-insoluble fraction, and then dried *in vacuo*.

Syndiospecific Copolymerisation of *p*-Trimethylsilylstyrenes (*p*-TMSSt) with Styrene.

A prescribed amount of MAO white solid, styrene and *p*-TMSSt were charged into the autoclave in the dry box, and the total volume of toluene and comonomer was set to 5.0 mL. After an addition of a toluene solution containing titanium complex (2.0 μ mol/ mL in toluene) via a syringe, and then the copolymerisation and purification were performed according to our reported procedure. The *p*-TMSSt contents were estimated based on ratio of the integration values of *p*-TMSSt versus styrene at each resonance in the ¹H NMR spectra.

Ethylene copolymerisation of *p*-trimethylsilylstyrenes (*p*-TMSSt).

In the dry box, d-MAO (174 mg, 3.00 mmol), p-TMSSt (prescribed amount) and toluene (total 9.0 mL) were added into a 100 mL stainless steel autoclave. The autoclave was then set in the lab hood with rapid stirring, and ethylene (1 atm) was then introduced after adjusting to a certain temperature. A toluene solution (1.0 mL) containing a titanium complex (prescribed amount) was then added into the autoclave at a prescribed temperature. Ethylene was immediately pressurized 3 atm (ethylene total 4 atm) by closing the valve, and the reaction mixture was magnetically stirred for 10 min. During the reaction, ethylene pressure was kept constant. After the reaction, remaining ethylene in the reactor was purged at 0 °C (ice bath), and the reaction mixture was poured into a mixed solution of MeOH (150 mL) and HCl (3 mL). The resultant precipitates were then collected through a vacuum filter and dried in *vacuo* for several hours. According to the previous procedure for poly(ethylene-co-styrene)s,⁵ the resultant polymer mixture was separated into three fractions, and atactic poly(p-TMSSt) which was prepared only by MAO was extracted with acetone. Poly(ethylene-co-p-TMSSt) was then extracted with THF (polyethylene and/or syndiotactic polystyrene as the by-products was separated as THF insoluble fraction), and the soluble fraction was dried in vacuo at 55 °C for several hours. The microstructure analyses in the resultant copolymers were estimated by the ¹³C NMR spectra of the copolymer, and each of the resonances were assigned by comparison with the previous reports.⁵ The *p*-TMSSt contents were estimated based on ratio of the total integration values of *p*-TMSSt versus ethylene at each resonance in the ¹H NMR spectra.

Iodination for the silylated polystyrenes.

In a nitrogen-filled glovebox, a cold solution of ICl (0.1 M, 4.38 mL, 0.438 mmol, 1.3 equiv.) in dry CH₂Cl₂ was added dropwise at room temperature to a cold solution of syndiotactic poly(styrene-*co-p*-TMSSt)s (*p*-TMSSt 20 mol%, 200 mg, 0.337 mmol of TMS groups) in 100 mL of dry CH₂Cl₂. After the addition was completed, the solution was stirred at room temperature. After being stirred for 24 h, methanol was added to precipitate the polymer. The resultant polymers were then collected through a vacuum filter and dried *in vacuo* for several hours. Iodination for ethylene copolymers were performed according to the same procedure.

Bromination for the silylated polystyrenes.

In a nitrogen-filled glovebox, *N*-bromosuccimide (NBS) (30 mg, 0.17 mmol, 5.0 equiv.) in THF was added dropwise at room temperature to a stirring solution of syndiotactic poly(styrene-*co-p*-TMSSt)s (*p*-TMSSt 20 mol%, 20 mg, 0.034 mmol of TMS groups) in 10 mL of dry CH₂Cl₂. After the addition was completed, the solution was stirred at room temperature. After being stirred for 24 h, methanol was added to precipitate the polymer. The resultant polymers were then collected through a vacuum filter and dried *in vacuo* for several hours. Bromination using bromine reagent was performed according to the similar procedure as that used for iodination.

Sonogashira coupling reaction for the iodinated polystyrenes.¹⁰

To a solution of syndiotactic poly(styrene-*co-p*-ISt)s (*p*-TMSSt 20 mol%, 20 mg, 0.030 mmol of Iodine groups) in dry THF (1.0 mL) were added 4-ethynyl-3-methylbenzene (9.6 mg, 0.060 mmol, 2.0 equiv.), Pd(PPh₃)₄ (1.7 mg, 0.0015 mmol, 5.0 mol%), CuI (0.50 mg, 0.0015 mmol, 5.0 mol%), ^{*i*}Pr₂NH (15.2 mg, 0.150 mmol 5.0 equiv.) in the drybox and the mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with CH₂Cl₂ (10 mL) and filtered on a celite pad. The filtrate was concentrated by evaporation and dissolved in 1.0 mL CH₂Cl₂, and MeOH was then added to precipitate the polymer. The precipitation process was repeated one more time to ensure complete removal of excess of the reagents trapped in the polymer. The cross-coupling reaction for ethylene copolymers were performed according to the same procedure.

Suzuki coupling reaction for the iodinated polystyrenes.¹¹

To a solution of syndiotactic poly(styrene-*co-p*-ISt)s (*p*-TMSSt 20 mol%, 20 mg, 0.030 mmol of Iodine groups) in dry THF (1.0 mL) were added 4-(Methoxycarbonyl)phenylboronic acid (16.2 mg, 0.090 mmol, 3.0 equiv.), Pd(dppf)Cl₂(1.1 mg, 0.0015 mmol, 5.0 mol%), K₂CO₃ (16.5 mg, 0.120 mmol, 4.0 equiv.) in the dry box and the mixture was stirred at 50 °C with the use of an oil bath for 24 h. The reaction mixture was poured into MeOH, and the precipitation process was repeated one more time to ensure complete removal of excess of the reagents trapped in the polymer.

Heck coupling reaction for the iodinated polystyrenes.¹⁰

To a solution of syndiotactic poly(styrene-*co-p*-ISt)s (*p*-TMSSt 20 mol%, 20 mg, 0.030 mmol of Iodine groups) in dry DMF (1.0 mL) were added methyl acrylate (25.8 mg, 0.30 mmol, 10.0 equiv.), Pd(dba)₂ (2.8 mg, 3.0 μ mol, 10 mol%), NaOAc (3.7 mg, 0.045 mmol, 1.5 equiv.) in the dry box and the mixture was stirred at 80 °C with the use of an oil bath for 24 h. The reaction mixture was poured into MeOH, and the precipitation process was repeated one more time to ensure complete removal of any small molecules trapped in the polymer.

Analysis of Tensile Properties, Elastic Properties and Healing tests.

Stress/strain experiments were performed at 20 mm/min (23 °C, humidity $50 \pm 10\%$) using a Shimadzu Universal Testing Instruments (Autograph AGS-10kNX) equipped with a load cell (cell capacity 500 N). Strain–Stress curves of 10 cycles (loaded and unloaded) were performed at strain 200 and 300% at room temperature at 200 mm/min equipped with a tensile tester from Acroedge Co. Ltd (Stency Series OZ918, load cell capacity max 50 N). At least three specimens of each sample were tested in all measurements (shown in Supporting Information). The copolymer sample sheets were cut to obtain the dumbbell-shaped tensile-test specimens. All test specimens showed 3 mm width of a parallel portion, 25-mm length, and thickness of 0.1 mm. The distance between grippers was 10 mm. For self-healing tests, the films were cut into two parts using razor blade, and then brought together at 23 °C for several days. The healed polymer films were then stretched following the same procedure to obtain the stress-strain curves.

Preparation of sample film for tensile analysis.

Solvent cast method. The sample films were prepared by mixing a solution of samples (ca. 120 mg) in toluene (2.0 mL). The mixed solution was then placed into PTFE petri dish (φ 50 mm) and prepare the film by removing solvent upon heating (on hot plate).

WAXD measurements.

The WAXD experiments were conducted using synchrotron radiation at beamline BL-6A of the Photon Factory at the Institute of Materials Structure Science of the High Energy Accelerator Research Organization in Tsukuba, Japan.41 Two-dimensional scattering images were collected using a PILATUS 100K detector. One-dimensional profiles were obtained by radial averaging of the two-dimensional images. The scattering angle was calibrated by using silver behenate having a periodical structure of 5.838 nm. The scattering vector was defined as $q = (4\pi/\lambda)\sin(\theta/2)$, where θ and λ are the scattering angle and the wavelength of the incident X-ray.



Figure S1. ¹H and ¹³C NMR spectra (chloroform-*d* at 25 °C) for (${}^{t}BuC_{5}H_{4}$)TiCl₂(O-2,6- ${}^{t}Pr_{2}$ -4-SiEt₃-C₆H₂) (2).



Figure S2. ¹H and ¹³C NMR spectra (chloroform-*d* at 25 °C) for $(1,2,4-Me_3C_5H_2)$ TiCl₂(O-2,6-^{*i*}Pr₂-4-SiEt₃-C₆H₂) (4).

2. Additional results in syndiospecific polymerisation of *p*-trimethylsilylstyrene (*p*-TMSSt).

(-6_{H_2}) [K - H (5), SI PI ₃ (6)] (Me ₃ SIC ₅ H ₄) IICl ₂ (0-2,0- PI ₂ -4-C ₆ H ₃) (7) catalyst-MAO system.										
run	cat.	[<i>p</i> -TMSSt] ₀ ^b / M	temp / °C	yield / mg	activity ^c	$M_n \times 10^{-4d}$	$M_w / {M_{ m n}}^d$	$T_{\rm m} (T_{\rm g}) / {}^{\rm o} { m C}^{e}$		
1	1	0.46	25	13.1	200	7.30	2.26			
S 1	1	0.46	50	113.6	1700	3.64	1.95			
2	1	0.83	25	38.6	580	9.07	2.30			
S2	1	0.83	50	225.3	3380	3.61	2.22	300.8 (123.2)		
3	1	1.40	25	72.1	1080	10.1	2.46			
4	1	2.15	25	161.5	2420	10.6	2.68	301.9 (122.9)		
5	1	2.15	50	404.8	6070	7.30	2.11	304.1 (123.8)		
6	2	2.15	50	343.0	5150	6.12	2.16	304.0 (124.9)		
7	3	2.15	50	356.9	5350	92.0	2.96	300.2 (128.3)		
8	4	2.15	50	85.9	1290	69.7	2.82	303.9 (127.0)		
9	5	2.15	50	122.3	1830	94.9	2.99			
10	6	2.15	50	89.8	1350	87.4	2.94	301.7 (128.2)		
11	7	2.15	25	1133.5	17000	31.1	2.83			
12	7	2.15	50	124.0	1860	11.6	2.82	303.6 (125.9)		

Table S1. Syndiospecific Polymerisation of *p*-TMSSt using (${}^{1}BuC_{5}H_{4}$)TiCl₂(O-2,6- ${}^{i}Pr_{2}$ -4-R-C₆H₂) [R = H (1), SiEt₃ (2)], (1,2,4-Me₃C₅H₂)TiCl₂(O-2,6- ${}^{i}Pr_{2}$ -4-R-C₆H₂) [R = H (3), SiEt₃ (4)], Cp*TiCl₂ (O-2,6- ${}^{i}Pr_{2}$ -4-R-C₆H₂) [R = H (5), Si ${}^{i}Pr_{3}$ (6)] (Me₃SiC₅H₄)TiCl₂(O-2,6- ${}^{i}Pr_{2}$ -4-C₆H₃) (7) catalyst-MAO system.^{*a*}

^{*a*}Conditions: *p*-trimethylsilylstyrene (*p*-TMSSt) 2.0 mL, Ti catalyst (0.4 μ mol, 2.0 μ mol/mL in toluene); MAO 1.72 mmol, 100 mg (Al/Ti = 4300 molar ratio). ^{*b*}Monomer concentration in mol/L; ^{*c*}Activity in kg- SPS/mol-Ti•h⁻¹, ^{*d*}GPC data in THF *vs* polystyrene standards; ^{*e*}By DSC thermogram.



Figure S3. Plots of the catalytic activity of 1 (after 10 min, kg- SPS/mol-Ti• h^{-1}) vs monomer concentration a) at 25 °C and b) 50 °C based on results shown in Tables 1, S3.

3. Additional results in syndiospecific copolymerisation of *p*-trimethylsilylstyrene (*p*-TMSSt) with styrene.

run	<i>p</i> -TMSSt/St feed / mol%	yield ^b / mg	activity ^b	$M_n imes 10^{-4d}$	M_w/M_n^d	cont. /mol% ^e	$T_{\rm g}(T_{\rm m})/{}^{\rm o}{ m C}^{f}$
1	5.0	308.4	4630	4.29	1.76	5.2	99.4 (225.9)
S 1	5.0	243.0	3640	4.37	1.83	5.8	100.2(241.4)
2	10.0	277.4	4160	3.59	1.92	10.1	101.4
3	15.0	219.3	3290	3.51	1.98	14.8	102.7
4	20.0	207.7	3120	3.59	2.04	20.0	105.9
S3	20.0	353.0	5290	5.33	2.21	20.1	104.1
$S4^g$	20.0	836.7	408	9.86	2.36	20.0	104.1
5	30.0	193.5	2900	3.13	2.51	30.0	107.5
S5	30.0	158.3	2370	3.28	2.75	29.9	104.6
6	40.0	144.0	2160	4.35	2.54	40.2	109.1
S6	40.0	170.0	2550	6.72	2.07	39.8	

Table S2. Syndiospecific copolymerisation of *p*-TMSSt with styrene by $({}^{t}BuC_{5}H_{4})TiCl_{2}(O-2,6-{}^{i}Pr_{2}-C_{6}H_{3})$ (1)-MAO catalyst systems.

^{*a*}Conditions: *p*-TMSSt + St + toluene = 5.0 mL, cat.1 (0.4 µmol, 2.0 µmol/mL in toluene), MAO, 1.72 mmol, 100 mg (Al/Ti = 4300 molar ratio), at 50 °C, 10 min. ^{*b*}Isolated yield as acetone insoluble fraction. ^{*c*}Activity:Kg-SPS /mol-Ti•h⁻¹. ^{*d*}GPC data in THF *vs* polystyrene standards. ^{*e*}*p*-TMSSt content (mol%) estimated by ¹H NMR spectra. ^{*f*}By DSC thermogram. ^{*g*}cat.1 (4.0 µmol, 20.0 µmol/mL in toluene), 30 min.

4. Additional results in ethylene copolymerisation with *p*-trimethylsilylstyrene (*p*-TMSSt).

$[R = H (5), Si'Pr_3 (6)], (Me_3S_1C_5H_4)T_1Cl_2(O-2,6-'Pr_2-4-C_6H_3) (7) \text{ catalyst-MAO system."}$										
	cat.	ethylene	$[p-TMSSt]_0^b$	temp.	yield		$M_n{}^d$	M_w	cont. ^e	$T_{\rm g}(T_{\rm m})^{f}$
run	(µmol)	/ atm	/ M	/ °C	/ mg	activity	/ × 10 ⁻⁴	$/M_n^d$	/ mol%	/ °C
1 (P3)	1 (0.25)	4	0.50	25	145.0	3480	32.9	2.27	20.3	21.4
S 1	1 (0.25)	4	0.50	25	133.3	3200	29.0	2.28	18.5	18.7
2	1 (0.50)	4	0.50	25	250.2	3000	23.0	2.36	20.6	21.9
S2	1 (0.50)	4	0.50	25	241.5	2900	27.6	2.30	20.5	23.5
S3	1 (0.50)	4	0.50	25	228.3	2740	17.4	2.21	20.5	21.9
S4	1 (1.00)	4	0.50	25	440.6	2640	13.1	2.22	20.0	21.5
S5	1 (0.25)	4	0.50	50	160.8	3860	11.5	2.20	21.9	25.9
S 6	1 (0.25)	4	0.50	50	154.2	3700	8.57	2.47		
S 7	1 (0.10)	6	0.76	25	75.5	4530	35.7	2.33	20.1	21.6
S 8	1 (0.10)	6	0.76	25	70.9	4250	27.6	2.25		
S9	1 (0.25)	4	1.26	25	115.5	2770	18.6	2.22	35.6	51.1
S10	1 (0.25)	4	1.26	25	102.9	2470	14.4	2.02		
3 (P1)	2 (0.25)	4	0.25	25	230.4	5530	29.2	2.27	10.7	-4.0 (50.0)
S11	2 (0.25)	4	0.25	25	217.2	5100	36.2	2.36		-0.2 (47.2)
S12	2 (0.10)	4	0.50	25	36.4	2180	26.5	2.27	19.0	18.4
4	2 (0.25)	4	0.50	25	156.9	3770	24.6	2.18	20.3	20.9
5	2 (0.25)	4	0.50	50	205.3	4930	9.65	2.46	21.5	24.1
S13	2 (0.25)	4	0.50	50	187.7	4500	8.45	2.29		
6	2 (0.25)	2	0.50	25	40.8	980	8.83	1.89	32.5	43.6
S14	2 (0.25)	2	0.50	25	36.5	880	8.50	1.86		
S15 (P2)	2 (0.10)	6	0.50	25	102.5	6160	43.6	2.21	15.0	6.2
S16	2 (0.10)	6	0.50	25	96.1	5770	41.9	2.14	14.1	5.0
7	2 (0.25)	6	0.50	25	258.1	6190	38.7	2.33	13.6	3.8
S17	2 (0.25)	6	0.50	25	264.2	6340	34.5	2.36	14.1	5.0
8 (P4)	2 (0.25)	4	0.76	25	118.6	2840	21.6	2.45	25.3	36.2
S18	2 (0.25)	4	0.76	25	103.0	2710	21.5	2.27	26.2	36.3
9	2 (0.25)	4	0.76	50	171.7	4120	9.00	2.18	26.2	37.0
S19	2 (0.25)	4	0.76	50	188.3	4520	7.59	2.37		
10	2 (0.25)	4	1.00	25	103.3	2480	16.6	2.31	32.0	44.0
S20 (P5)	2 (0.25)	4	1.00	25	129.3	3100	15.7	2.20	32.4	46.8
11	2 (0.25)	4	1.00	50	148.7	3570	5.73	2.34	36.8	53.3
S21	2 (0.25)	4	1.00	50	138.7	3310	5.63	2.16		
12	2 (0.25)	2	1.00	25	26.7	640	6.80	1.83	50.0	69.2

Table S3. Ethylene copolymerisation with *p*-TMSSt using (${}^{t}BuC_{5}H_{4}$)TiCl₂(O-2,6- ${}^{i}Pr_{2}$ -4-R-C₆H₂) [R = H (1), SiEt₃ (2)], (1,2,4-Me₃C₅H₂)TiCl₂(O-2,6- ${}^{i}Pr_{2}$ -4-R-C₆H₂) [R = H (3), SiEt₃ (4)], Cp*TiCl₂ (O-2,6- ${}^{i}Pr_{2}$ -4-R-C₆H₂) [R = H (5), Si ${}^{i}Pr_{3}$ (6)], (Me₃SiC₅H₄)TiCl₂(O-2,6- ${}^{i}Pr_{2}$ -4-C₆H₃) (7) catalyst-MAO system.^{*a*}

Table S3. (Continued.)										
run	cat.	ethylene	<i>p</i> -TMSSt ^b	temp.	yield	activity	$M_n{}^d$	M_w	cont. ^e	$T_{\rm g}(T_{\rm m})^{f}$
1 UII	(µmol)	/ atm	/ M	/ °C	/ mg	activity	/ × 10 ⁻⁴	$/M_n^d$	/ mol%	/ °C
13	2 (0.25)	2	1.50	25	21.5	520	6.70	1.80	52.2	75.7
$S22^{g}$	2 (0.25)	4	0.50	25	74.1	1780	9.69	2.14	19.8	19.8
S23 ^{<i>h</i>}	2 (0.25)	4	0.50	25	34.1	820	4.13	1.85	19.1	19.3
14	3 (0.25)	4	0.50	25	130.3	3130	37.4	2.38	19.2	19.7
S24	3 (0.25)	4	0.50	25	140.8	3380	38.9	2.48		
S25	3 (0.25)	4	0.50	50	110.6	2650	15.5	2.46	20.7	21.8
S26	3(0.25)	4	0.50	50	88.4	1890	13.9	2.40	20.4	10.4
S27	3(0.50)	4	0.50	50	251.1	3010	13.3	2.46	20.4	19.4
S28	3 (0.50) 4 (0.25)	4	0.50	50 25	230.6	2770	21.5	2 10	20.2	20.0
15	4 (0.25) 4 (0.50)	4	0.50	25 25	97.6	2340	31.5	2.18	20.3	20.9
529 520	4 (0.50)	4	0.50	25	160.0	1990	28.1	2.10	18.3	17.3
S30 S31	4(0.30)	4	0.50	23 50	100.8	2420	12.2	2.20	20.8	22.1
S31 S32	4(0.23)	+ 1	0.50	50	100.8	2420	12.2	2.30	20.8	22.1
S32	4 (0.23)	- - -	0.50	50	189.3	2470	12.7	2.71	20.2	197
S34	4 (0.50) 4 (0.50)	4	0.50	50	181.8	2180	12.3	2.29	20.2	17.7
551	• (0.50)		0.20	20	101.0	2100				-6.4
16	5 (0.25)	4	0.50	25	30.4	730	18.4	1.73	9.4	(56.8)
S35	5 (0.25)	4	0.50	25	32.7	780	13.5	1.78		()
S 36	5 (0.50)	4	0.50	25	98.9	1190	27.8	1 57	96	-7.4
550	0 (0.00)	•	0.00	20	2012	1170	27.0	110 /	2.0	(55.3)
S37	5 (0.50)	4	0.50	50	91.3	1100	12.4	1.81	11.4	-5.5
529	5 (0, 50)	4	0.50	50	80.7	070	11.0	1.90		(58.1)
330	3 (0.30)	4	0.50	30	80.7	970	11.0	1.60		-4.5
S39	5 (1.00)	4	0.50	50	137.4	820	9.60	1.70	12.5	(56.9)
S40	5 (1.00)	4	0.50	50	135.8	810	9.30	1.70		(00.5)
17	(0.25)	4	0.50	25	26.4	620	14.0	1.40	0.1	-4.5
17	0(0.23)	4	0.50	23	20.4	030	14.9	1.49	9.1	(56.7)
S41	6 (0,50)	4	0.50	25	68 7	820	19.2	1 71	97	-5.7
511	0(0.50)	I	0.50	23	00.7	020	17.2	1.71	<i>J</i> .1	(54.5)
S42	6 (0.50)	4	0.50	25	50.8	610	15.9	1.58		
S43	6 (1.00)	4	0.50	25	164.5	990	21.5	1.56	11.4	-5.5
S44	6 (1.00)	4	0.50	25	150.3	900				(32.3)
S15	6 (0.50)	Λ	0.50	50	00 1	1100	0.10	1 72	126	-4.0
543	0(0.30)	4	0.30	50	96.1	1180	9.10	1./2	12.0	(56.9)
S46	6 (0.50)	4	0.50	50	87.4	1050	9.15	1.75		
S47	6 (1.00)	4	0.50	50	160.9	970	7.74	1.64	13.3	-4.1
										(03.3)

Table S3. (Continued.)

S48

6 (1.00)

164.0

980

7.76

1.56

50

0.50

4

Table S3. (Continued.)										
m110	cat.	ethylene	<i>p</i> -TMSSt ^b	temp.	yield	octivity	$M_n{}^d$	M_w	cont. ^e	$T_{\rm g}(T_{\rm m})^{f}$
Tull	(µmol)	/ atm	/ M	/ °C	/ mg	activity	/ × 10 ⁻⁴	$/M_n^d$	/ mol%	/ °C
18	7 (0.25)	4	0.50	25	202.1	4850	15.4	2.21	21.6	22.6
S49	7 (0.25)	4	0.50	25	192.6	4620	15.3	2.02		
$S50^{g}$	7 (0.25)	4	0.50	25	103.3	2480	6.12	2.18	21.0	22.7
S51 ^g	7 (0.25)	4	0.50	25	98.1	2350				
$S52^h$	7 (0.25)	4	0.50	25	148.0	3550	10.6	2.50	20.9	23.3
$S53^h$	7 (0.25)	4	0.50	25	155.2	3720				
19	7 (0.25)	4	0.50	50	86.9	2090	4.92	2.29	25.6	32.0
S54	7 (0.25)	4	0.50	50	80.0	1920	4.60	2.30		
S55	7 (0.50)	4	0.50	50	122.1	1470	4.06	2.26	25.4	32.8
$S56^h$	7 (0.25)	4	0.50	50	106.8	2560	5.72	2.03	22.3	29.6
$S57^h$	7 (0.25)	4	0.50	50	90.2	2160				
S58	7 (0.25)	4	0.76	25	182.4	4380	14.8	1.96	28.1	39.2
S59	7 (0.25)	4	0.76	25	187.8	4500	16.4	2.20	28.1	36.8
20	7 (0.25)	4	1.00	25	151.9	3650	10.1	2.09	34.0	47.3
S60	7 (0.25)	4	1.00	25	160.3	3850	9.21	2.42		
21	7 (0.25)	2	1.26	25	78.1	1870	7.85	1.85	47.3	69.9
22	7 (0.25)	2	1.50	25	98.9	2370	7.38	1.88	50.7	73.0

^{*a*}Conditions: *p*-trimethylsilylstyrene (*p*-TMSSt) + toluene total volume 10.0 mL, MAO 3.0 mmol, 10 min, ^{*b*}Comonomer concentration in mol/L. ^{*c*}Activity in kg-polymer/mol-Ti·h. ^{*d*}Determined by GPC in THF *vs* polystyrene standards. ^{*e*}Estimated by ¹H NMR spectra. ^{*f*}By DSC thermogram. ^{*g*}MAO 1.0 mmol. ^{*h*}MAO 2.0 mmol.

5. Selected NMR spectra in the silylated polymers.



Figure S4. ¹H and ¹³CNMR spectra (chloroform-*d* at 25 °C) for syndiotactic poly(*p*-TMSSt) (**SPS-TMS**) prepared by **1**-MAO catalyst system at 50 °C (Table 1, run 5).



Figure S5. ¹H NMR spectrum (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-TMSSt) (**SPS-TMS**) prepared by **1**-MAO catalyst system at 50 °C (Table 2, run 1, *p*-TMSSt 5.2 mol%).



Figure S6. ¹H and ¹³C NMR spectra (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-TMSSt) (**SPS-TMS**) prepared by 1-MAO catalyst system at 50 °C (Table 2, run 2, *p*-TMSSt 10.1 mol%).





Figure S8. ¹H and ¹³C NMR spectra (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-TMSSt) (**SPS-TMS**) prepared by **1**-MAO catalyst system at 50 °C (Table 2, run 4, *p*-TMSSt 20.0 mol%).



Figure S9. ¹H and ¹³C NMR spectra (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-TMSSt) (**SPS-TMS**) prepared by 1-MAO catalyst system at 50 °C (Table 2, run 5, *p*-TMSSt 30.0 mol%).





Figure S11. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/***p***-TMSSt)** prepared by **1**-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 1, *p*-TMSSt 20.3 mol%).



Figure S12. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/***p***-TMSSt)** prepared by **2**-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 4, *p*-TMSSt 20.3 mol%).



Figure S13. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/***p***-TMSSt)** prepared by **3**-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 14, *p*-TMSSt 19.7 mol%).



Figure S14. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/p-TMSSt**) prepared by **4**-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 15, *p*-TMSSt 20.9 mol%).



Figure S15. ¹H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/p-TMSSt)** prepared by **5**-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 16, *p*-TMSSt 9.4 mol%).



Figure S16. ¹H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C for poly(ethylene-*co-p*-TMSSt) **poly(E/***p***-TMSSt)** prepared by **6**-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 17, *p*-TMSSt 9.1 mol%).



Figure S17. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/p-TMSSt**) prepared by 7-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 18, *p*-TMSSt 21.6 mol%).



Figure S18. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/p-TMSSt)** prepared by 1-MAO catalyst system at 50 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table S3, run S5, *p*-TMSSt 21.9 mol%).



Figure S19. ¹H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/p-TMSSt)** prepared by **2**-MAO catalyst system at 50 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 5, *p*-TMSSt 21.5 mol%).



Figure S20. ¹H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for poly(ethylene-*co-p*-TMSSt) poly(E/*p*-TMSSt) prepared by 3-MAO catalyst system at 50 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table S3, run S25, *p*-TMSSt 20.7 mol%).



Figure S21. ¹H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/p-TMSSt)** prepared by **4**-MAO catalyst system at 50 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run S33, *p*-TMSSt 20.2 mol%).



Figure S22. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/p-TMSSt)** prepared by **5**-MAO catalyst system at 50 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run S37, *p*-TMSSt 11.4 mol%).



Figure S23. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/***p***-TMSSt)** prepared by **6**-MAO catalyst system at 50 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table S3, run S45, *p*-TMSSt 12.6 mol%).



Figure S24. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/***p***-TMSSt)** prepared by 7-MAO catalyst system at 50 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 19, *p*-TMSSt 25.6 mol%).



Figure S25. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/***p***-TMSSt)** prepared by **2**-MAO catalyst system at 25 °C, *p*-TMSSt 1.00 M, ethylene 2 atm (Table 3, run 12, *p*-TMSSt 50.0 mol%).



Figure S26. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 25 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/***p***-TMSSt)** prepared by 7-MAO catalyst system at 25 °C, *p*-TMSSt 1.50 M, ethylene 2 atm (Table 3, run 22, *p*-TMSSt 50.7 mol%).



Figure S27. (a) ¹³C NMR and (b) dept spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*cop*-TMSSt) **poly(E/***p***-TMSSt)** prepared by 1-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 2, *p*-TMSSt 20.6 mol%, $M_n = 23.0 \times 10^4$, $M_w/M_n = 2.36$, $T_g = 21.9$ °C).



Figure S28. (a) ¹³C NMR and (b) dept spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/***p***-TMSSt)** prepared by 4-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 15, *p*-TMSSt 20.3 mol%, $M_n = 31.5 \times 10^4$, $M_w/M_n = 2.18$, $T_g = 20.9$ °C).



Figure S29. ¹³C NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/p-TMSSt)** prepared by 1-MAO catalyst system at 25 °C, *p*-TMSSt 1.26 M, ethylene 4 atm (Table S3, run S9, *p*-TMSSt 35.6 mol%, $M_n = 18.6 \times 10^4$, $M_w/M_n = 2.22$, $T_g = 51.1$ °C).



Figure S30. ¹³C NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/p-TMSSt)** prepared by **2**-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table 3, run 3, *p*-TMSSt 10.7 mol%, $M_n = 29.2 \times 10^4$, $M_w/M_n = 2.27$, $T_g = -4.0$, $T_m = 50.0$ °C).



Figure S31. ¹³C NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co-p*-TMSSt) **poly(E/p-TMSSt)** prepared by **5**-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table S3, run 16, *p*-TMSSt 9.4 mol%, $M_n = 18.4 \times 10^4$, $M_w/M_n = 1.73$, $T_g = -6.4$ °C, $T_m = 56.8$ °C).



Figure S32. ¹³C NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co-p*-TMSSt) prepared by **6**-MAO catalyst system at 25 °C, *p*-TMSSt 0.50 M, ethylene 4 atm (Table S3, run S41, *p*-TMSSt 9.7 mol%, $M_n = 19.2 \times 10^4$, $M_w/M_n = 1.71$, $T_g = -5.7$ °C, $T_m = 54.5$ °C).



Figure S33. ¹³C NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co-p*-TMSSt) prepared by 7-MAO catalyst system at 25 °C, *p*-TMSSt 1.50 M, ethylene 2 atm (Table 3, run 22, *p*-TMSSt 50.7 mol%, $M_n = 7.38 \times 10^4$, $M_w/M_n = 1.88$, $T_g = 73.0$ °C).



6. Selected NMR and IR spectra in the halogenated polymers.

Figure S34. ²⁹Si NMR spectra (dichloromethane-*d*₂, 25 °C) for (a) poly(styrene-*co-p*-TMSSt) (*p*-TMSSt 20.0 mol%), (b) with ICl, (c) with Br₂ reagent.



Figure S35. ¹H NMR spectra (dichloromethane- d_2 , 25 °C) for (a) poly(styrene-*co-p*-TMSSt) (*p*-TMSSt 20.0 mol%), (b) with ICl, (c) with Br₂ reagents.



Figure S36. ¹H NMR spectrum (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-ISt) prepared by ICl (Table 4, run 1, *p*-ISt 4.8 mol%).



Figure S37. ¹H NMR spectrum (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-ISt) prepared by ICl (Table 4, run 2, *p*-ISt 10.0 mol%).



Figure S38. ¹H and ¹³C NMR spectra (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-ISt) prepared by ICl (Table 4, run 3, *p*-ISt 20.0 mol%).


Figure S39. ¹H and ¹³C NMR spectra (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-ISt) prepared by ICl (Table 4, run 4, *p*-ISt 29.8 mol%).



Figure S40. ¹H and ¹³C NMR spectra (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-ISt) prepared by ICl (Table 4, run 5, *p*-ISt 40.0 mol%).





Figure S42. ¹H and ¹³C NMR spectra (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-BrSt) prepared by NBS (Table 4, run 13, *p*-BrSt 20.0 mol%).





Figure S44. ¹H and ¹³C NMR spectra (chloroform-*d* at 25 °C) for syndiotactic poly(styrene-*co-p*-BrSt) prepared by NBS (Table 4, run 16, *p*-BrSt 40.1 mol%).



Figure S45. ¹³C NMR spectra of syndiotactic poly(ethylene-*co-p*-ISt)s.



Figure S46. ¹³C NMR spectra of syndiotactic poly(ethylene-*co-p*-BrSt)s.



Figure S47. ¹H and ¹³C NMR spectra (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for poly(ethylene-*co-p*-ISt) prepared by ICl (Table 4, run 8, *p*-ISt 20.3 mol%).



Figure S48. ¹H and ¹³C NMR spectra (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for poly(ethylene-*co-p*-ISt) prepared by ICl (Table 4, run 9, *p*-ISt 28.1 mol%).





prepared by ICl (Table 4, run 11, *p*-ISt 50.7 mol%).



Figure S51. ¹H and ¹³C NMR spectra (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for poly(ethylene-*co-p*-BrSt) prepared by NBS (Table 4, run 18, *p*-BrSt 20.3 mol%).



Figure S52. ¹H and ¹³C NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for poly(ethylene-*co-p*-BrSt) prepared by NBS (Table 4, run 21, *p*-BrSt 28.1 mol%).





Figure S54. ¹H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for poly(ethylene-*co-p*-BrSt) prepared by Br₂ (Table 4, run 14, *p*-BrSt 20.6 mol%).



Figure S55. ¹H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for poly(ethylene-*co-p*-BrSt) prepared by Br₂ (Table 4, run 19, *p*-BrSt 20.3 mol%).



Figure S56. FT-IR spectra for syndiotactic polystyrenes.

7. Selected NMR spectra in the cross-coupled polymers.



Figure S57. ¹H and ¹³C NMR spectrum (chloroform-*d* at 25 °C) for the cross-coupled polymer with methyl 4ethynylbenzoate (98% yield, quant. functionalization, $M_n = 95400$, $M_w/M_n = 2.24$) prepared from syndiotactic poly(styrene-*co-p*-ISt) (*p*-ISt 20.0 mol%, $M_n = 91700$, $M_w/M_n = 2.37$) via Sonogashira coupling reaction.



Figure S58. ¹H and ¹³C NMR spectrum (chloroform-*d* at 25 °C) for the cross-coupled polymer with methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (85% yield, 91% functionalization, Insoluble for GPC analysis) prepared from syndiotactic poly(styrene-*co-p*-ISt) (*p*-ISt 20.0 mol%, $M_n = 91700$, $M_w/M_n = 2.37$) via Suzuki coupling reaction.



Figure S59. ¹H and ¹³C NMR spectrum (chloroform-*d* at 25 °C) for the cross-coupled polymer with methyl acrylate (86% yield, 85% functionalization, $M_n = 91900$, $M_w/M_n = 2.34$) prepared from syndiotactic poly(styreneco-p-ISt) (p-ISt 20.0 mol%, $M_n = 91700$, $M_w/M_n = 2.37$) via Heck coupling reaction.



Scheme S1. Transformations of the syndiotactic polysilylstyrene via iodination and Sonogashira coupling reaction.



Figure S60. ¹H NMR spectra (chloroform-*d* at 25 °C) for the syndiotactic polysilylstyrene and syndiotactic cross-coupled polymer (93% yield, quant functionalization, prepared from syndiotactic polyiodostyrene via Sonogashira coupling reaction.



Figure S61. ¹H, ¹³C NMR and dept spectra (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for the cross-coupled polymer with methyl 4-ethynylbenzoate (98% yield, quant. functionalization, $M_n = 358000$, $M_w/M_n = 2.27$) prepared from poly(ethylene-*co-p*-ISt) (*p*-ISt 20.3 mol%, $M_n = 326000$, $M_w/M_n = 2.33$) via Sonogashira coupling reaction.



Figure S62. ¹H and ¹³C NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for the cross-coupled polymer with pyrene moiety (99% yield, quant. functionalization, $M_n = 357000$, $M_w/M_n = 1.90$) prepared from poly(ethylene-*co-p*-ISt) (*p*-ISt 20.3 mol%, $M_n = 326000$, $M_w/M_n = 2.33$) via Sonogashira coupling reaction.



Figure S63. ¹H and ¹³C NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for the cross-coupled polymer with pyrene moiety (99% yield, quant. functionalization, $M_n = 258000$, $M_w/M_n = 2.20$) prepared from iodinated sample of poly(ethylene-*co-p*-TMSSt) (*p*-TMSSt 10.7 mol%, $M_n = 243000$, $M_w/M_n = 1.68$) via Sonogashira coupling reaction.



Figure S64. ¹H and ¹³C NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 25 °C) for the cross-coupled polymer (85% yield, 85% functionalization, insoluble for GPC analysis) prepared from poly(ethylene-*co-p*-ISt) (*p*-ISt 20.3 mol%) via Suzuki coupling reaction.

8. Selected GPC in the resultant polymers.



Figure S65. Selected GPC traces for a) syndiotactic poly(styrene-co-p-XSt), b and c) poly(ethylene-co-p-XSt).



Figure S66. Selected GPC traces for the cross-coupled polymers.



9. Selected DSC thermograms in the resultant polymers

Figure S67. (a) DSC thermograms for resultant polymers in syndiospecific polymerisation of *p*-trimethylsilylstyrene (*p*-TMSSt) by **1-7**–MAO catalyst systems at 50 °C. The detailed data are shown in Table 1 (runs 5, 7, 10, 12, Table 1). (b) Expanded view of Figure S67(a).



Figure S68. DSC thermograms (up to 320 °C) for resultant polymers in syndiospecific polymerisation of *p*-TMSSt) with styrene by **1**-MAO catalyst systems at 50 °C. The detailed data are shown in Table 2 (runs 4,5, Table 2).



Figure S69. DSC thermograms for resultant polymers in ethylene copolymerisation of *p*-TMSSt by **1**,**2**–MAO catalyst systems at different comonomer concentration. The detailed data are shown in Table 3 (runs 1,2,4,5,9,11).



Figure S70. DSC thermograms for resultant polymers in ethylene copolymerisation of *p*-TMSSt by **2**–MAO catalyst systems at different comonomer concentration. The detailed data are shown in Table 3 (runs 4,8,10).



Figure S71. DSC thermograms for resultant polymers in ethylene copolymerisation of *p*-TMSSt by **2**–MAO catalyst systems at different ethylene pressure. The detailed data are shown in Table 3 (runs 4,6,7).



Figure S72. DSC thermograms for resultant polymers in ethylene copolymerisation of *p*-TMSSt by 7–MAO catalyst systems. The detailed data are shown in Table 3 (runs 18-20,22).



Figure S73. DSC thermograms for resultant polymers in ethylene copolymerisation of *p*-TMSSt by **5**,**6**- MAO catalyst systems at 25 °C. The detailed data are shown in Table 3 (runs 16,17,S36,S41).



Figure S74. Selected DSC thermograms for syndiotactic poly(styrene-*co-p*-XSt) (*p*-XSt 20.0 mol%, R = TMS, I, Br)



Figure S75. Selected DSC thermograms for syndiotactic poly(styrene-*co-p*-XSt) (*p*-XSt 30.0 mol%, R = TMS, I, Br)



Figure S76. Selected DSC thermograms for poly(ethylene-co-p-XSt) (p-XSt 20.3 mol%, R = TMS, I, Br)



Figure S77. Selected DSC thermograms for poly(ethylene-*co-p*-XSt) (*p*-XSt 28.1 mol%, X = TMS, I, Br).



Figure S78. DSC thermograms for the cross-coupled polymers in post-modification of poly(styrene-*co-p*-ISt) through Suzuki, Sonogashira and Heck coupling reaction.



Figure S79. DSC thermograms for the cross-coupled polymers in post-modification of poly(ethylene-*co-p*-ISt) through Suzuki and Sonogashira coupling reaction.



10. Summary of tensile and elastic properties for poly(ethylene-co-p-XSt)s.

Figure S80. Reproducibility of stress-strain curves measured in a speed of 20 mm/min. Samples for *p*-TMSSt contents: (a) 10.7 mol% (P1, run 3, Table 3), (b) 15.0 mol% (P2, run S15, Table S3), (c) 20.3 mol% (P3, run 1, Table S3), (d) 25.3 mol% (P4, run 8, Table S3), (e) 32.4 mol% (P5, run S20, Table S3).



Figure S81. Reproducibility of stress-strain curves measured in a speed of 20 mm/min. Samples for p-XSt contents: (a) p-ISt 20.3 mol% (P6, run 8, Table 4), (b) p-ISt 32.4 mol% (P7, run 10, Table 4), (c) Pyrene 10.7 mol% (P8), (d) Pyrene 20.3 mol% (P9).



Figure S82. Reproducibility of stress-strain curves measured in a speed of 20 mm/min. Samples for St contents: (a) 21.5 mol% (P10), (b) 24.8 mol% (P11), (c) 36.0 mol% (P12).

Sample	<i>p</i> -XSt	$M_{ m n}{}^b$	$M_{ m w}$	tensile strength	elongation at break	Toughness
	cont./ mol%	×10 ⁻⁴	$/M_n^b$	/ MPa	/ %	$/J/m^3$
P1	<i>p</i> -TMSSt, 10.7	29.2	2.27	31 (±2)	390 (±30)	4000 (±400)
P2	<i>p</i> -TMSSt,15.0	35.9	2.57	10 (±2)	340 (±30)	1500 (±80)
P3	<i>p</i> -TMSSt, 20.3	32.9	2.27	33 (±3)	260 (±10)	4400 (±200)
P4	<i>p</i> -TMSSt, 25.3	21.6	2.45	34 (±2)	110 (±10)	2800 (±100)
P5	<i>p</i> -TMSSt, 32.4	15.7	2.20	34 (±4)	40 (±30)	1500 (±800)
P6	<i>p</i> -ISt, 20.3	32.6	2.33	14 (±1)	330 (±30)	2000 (±200)
P7	<i>p</i> -ISt, 32.4	15.3	2.48	23 (±1)	130 (±10)	2300 (±100)
P8	Pyrene, 10.7	25.8	1.68	46.2(±6)	64(±10)	2044(±500)
P9	Pyrene, 20.3	35.7	1.90	24 (±1)	130 (±10)	1500 (±300)
P10	St, 21.5	31.7	2.39	14 (±2)	430 (±20)	2300 (±300)
P11	St, 24.8	11.4	1.67	8.7 (±0.3)	370 (±30)	1700 (±100)
P12	St, 36.0	15.3	1.80	17 (±2)	278 (±2)	1600 (±200)

Table S4. Summary of the tensile property of poly(ethylene-*co-p*-XSt) P1-P11 measured at a speed of 20 mm/min^a.

^{*a*}Stress/strain experiments were performed at room temperature using a Shimadzu Universal Testing Instruments (Autograph AGS-10kNX) equipped with load cell (cell capacity 500 N). The test specimens had the following dimensions: width 0.3 cm, length 0.1 cm and thickness mm. ^{*b*}GPC data in THF vs polystyrene standards.



Figure S83. Plots of hysteresis experiments of 10 cycles at a strain of 300 % for poly(ethylene-*co-p*-TMMSt) (measured at a speed of 200 mm/min). (a) *p*-TMSSt 10.7 mol% (**P1**), (b) *p*-TMSSt 15.0 mol% (**P2**), (c) *p*-TMSSt 20.3 mol% (**P3**). d) The photographs of a sample **P1** after 10 times of 300% elongation and recovery (right) and its original form (left).


Figure S84. Plots of hysteresis experiments of 10 cycles at a strain of 300 % for poly(ethylene-*co-p*-TMMSt) (measured at a speed of 200 mm/min). (a) *p*-ISt 20.3 mol% (P6), (b) St 21.5 mol% (P10), (c) St 36.0 mol% (P12).

Table S5. Summary of the strain recovery at a strain of 300 % for poly(ethylene-co-p-XSt)s.

Sample	<i>p</i> -XSt cont./ mol%	1st cycle recovery / %	2 st cycle recovery /%	3 st cycle recovery / %
P1	<i>p</i> -TMSSt, 10.7	84.7	83.8	82.2
P2	<i>p</i> -TMSSt,15.0	91.6	84.7	81.8
P3	<i>p</i> -TMSSt, 20.3	-	-	-
P6	<i>p</i> -ISt, 20.3	92.2	91.0	90.4
P10	St, 21.5	84.8	94.8	83.2
P12	St, 36.0	-	-	-

^{*a*}Stress/strain experiments were performed at room temperature using a Shimadzu Universal Testing Instruments (Autograph AGS-10kNX) equipped with load cell (cell capacity 500 N). The test specimens had the following dimensions: width 0.3 cm, length 0.1 cm and thickness mm.



Figure S85. Plots of hysteresis experiments of 10 cycles at a strain of 200 % for poly(ethylene-*co-p*-TMMSt) (measured at a speed of 200 mm/min). (a) *p*-TMSSt 10.7 mol% (**P1**), (b) *p*-TMSSt 15.0 mol% (**P2**), (c) *p*-TMSSt 20.3 mol% (**P3**).



Figure S86. Plots of hysteresis experiments of 10 cycles at a strain of 200 % for poly(ethylene-*co-p*-TMMSt) (measured at a speed of 200 mm/min). (a) *p*-ISt 20.3 mol% (P6), (b) St 21.5 mol% (P10), (c) St 36.0 mol% (P12).

Sample	<i>p</i> -XSt cont./ mol%	1st cycle recovery / %	2 st cycle recovery / %	3 st cycle recovery /%
P1	<i>p</i> -TMSSt, 10.7	99.7	99.2	89.1
P2	<i>p</i> -TMSSt,15.0	82.0	84.0	81.0
P3	<i>p</i> -TMSSt, 20.3	20.0	21.4	25.0
P4	<i>p</i> -TMSSt, 25.3	-	-	-
P6	<i>p</i> -ISt, 20.3	92.2	91.0	90.4
P10	St, 21.5	99.3	94.5	93.8
P12	St, 36.0	74.5	69.0	69.9

Table S6. Summary of the strain recovery at a strain of 200 % for poly(ethylene-*co-p*-XSt)s.

^{*a*}Stress/strain experiments were performed at room temperature using a Shimadzu Universal Testing Instruments (Autograph AGS-10kNX) equipped with load cell (cell capacity 500 N). The test specimens had the following dimensions: width 0.3 cm, length 0.1 cm and thickness mm. ^{*b*}GPC data in THF vs polystyrene standards.



Figure S87. Wide-angle X-ray (WAXD) spectra of samples P1, P3, P4, P10 in the film.

11. Self-healing and shape memory property.



Figure S88. Self-healing phenomenon of a film of poly(ethylene-*co-p*-XSt)s at room temperature (23.0 °C).



Figure S89. Self-healing tests for series of poly(ethylene-co-p-XSt)s (measured at a speed of 20 mm/min).

	Original				Repaired		
Sample	<i>p</i> -XSt cont./ mol%	tensile strength / MPa	elongation at break / %	Toughness / J/m ³	tensile strength / MPa	elongation at break /%	Toughness / J/m ³
P1	<i>p</i> -TMSSt, 10.7	31(±2)	390(±30)	4000(±400)	33.2	348	3928
P2	<i>p</i> -TMSSt, 15.0	10(±2)	340(±30)	1500(±80)	8.6	280	845
P3	<i>p</i> -TMSSt, 20.3	33(±3)	260(±10)	4400(±200)	14.9	162	1354
P4	<i>p</i> -TMSSt, 25.3	34 (±2)	110 (±10)	2800 (±100)	-	-	-
P6	<i>p</i> -ISt, 20.3	14(±1)	330(±30)	2000(±200)	4.5	14	411

Table S7. Summary of self-healing properties of poly(ethylene-co-p-XSt)s.

^aHysteresis experiments of 10 cycles at a strain 300 % using a compact high performance tensile test by Acroedge Co. Ltd (Stency Series OZ918, load cell capacity max 50 N). The test specimens had the following dimensions: width 1.0 cm, length 2.5 cm and thickness 0.1 mm.



Figure S90. a) Absorption spectra for **P8** in chloroform (0.5 mg/mL). (b) Normalized fluorescence spectra for **P8** in chloroform and in the solid state (film) with excitation wavelength at 380 nm, and Photographs of the THF solution and the film taken during photoirradiation, UV lamp (365 nm).

12. References

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