# Installation of Superacidic Carbon Acid Moieties into Polymer Materials via PostPolymerization Modification

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## SUPPORTING INFORMATION

#### Experimental

#### Materials

The reagent  $2FPy^+-CH_2-C^-Tf_2$  was synthesized according to the previous report.<sup>1</sup> The monomer 4acetoxystyrene was purchased from Tosoh Finechem Corporation. Prior to polymerization, the monomers styrene and 4-acetoxystyrene were passed through basic aluminum oxide to remove the inhibitor. AIBN was purchased from FUJIFILM Wako Pure Chemical Co., Ltd. and used after recrystallization from methanol. 2 mol·L<sup>-1</sup> HCl in ethanol was purchased from Kokusan Chemical Co., Ltd. The polyethylene-polypropylene fabric was purchased from Kurashiki Textile Manufacturing Co., Ltd. All other chemical are commercially available used as received unless otherwise noted.

#### Instruments

All the <sup>1</sup>H and <sup>19</sup>F NMR spectra in deuterated solvents were recorded on JEOL 400 and Brucker 500 MHz FT-NMR spectrometers, and the chemical shifts ( $\delta$ ) are given in ppm with either the solvent peak or tetramethylsilane as the internal standard. The <sup>19</sup>F NMR spectra were calibrated using C<sub>6</sub>F<sub>6</sub> as an internal standard [ $\delta$ (C<sub>6</sub>F<sub>6</sub>) = 0 ppm]. The SEC measurements were performed at 40 °C and a flow rate of 0.35 mL·min<sup>-1</sup> in dimethylformamide (DMF) containing 10 mmol·L<sup>-1</sup> LiCl on a Waters gel permeation chromatography e2695 system embedded with a column (4.6 × 150 mm Tosoh TSKgel SuperMultiporeHZ-M). The  $M_n$  and D values of the polymers were calculated with polystyrene calibration. The standard IR spectra were recorded using an Agilent Cary 630 spectrometer equipped with an ATR unit. Optical images were taken as JPEG by using Panasonic Lumix DC-G100 equipped with LUMIX G VARIO 12-32 mm/F3.5-5.6 ASPH./MEGA O.I.S.. Scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDX) measurement was performed with SSX-550 and SEDX-500 (SHIMADZU Co., Ltd.). For the SEM(-EDX) measurements, the sample was attached to the holder with carbon tape and coated with OsO<sub>4</sub>.

#### Synthesis

Synthesis of  $P(St_{0.8}-co-StOAc_{0.2})$ : A 1,4-dioxane solution (18.8 mL) of AIBN (123 mg, 0.75 mmol), styrene (6.23 g, 60 mmol), and 4-acetoxystyrene (2.45 g, 15 mmol) was degassed under argon for 15 min. The degassed solution was stirred at 70 °C for 18 h. The solution was exposed to air to quench the polymerization. The crude product was purified by precipitation into methanol to afford the target polymer P(St\_{0.8}-co-StOAc\_{0.2}).

Yield : 5.99 g (67.8 %, monomer conv. :84.4 %).  $M_n$  (SEC, DMF): 29.8 kg mol<sup>-1</sup>; D: 1.56.

Synthesis of  $P(St_{0.8}-co-StOH_{0.2})$ : A THF (3.0 mL) solution of  $P(St_{0.8}-co-StOAc_{0.2})$  (600 mg,  $[OAc]_0 = 1.04$  mol) and TBA-OH (6.58 mL, 2.08 mmol) was stirred for 3.5 h at room temperature. After the reaction completion, 5.2 mL of 2 mol·L-1 HCl in ethanol was added to the reaction mixture and the obtained mixture was further stirred for 1.5 h at room temperature. The crude product was purified by precipitation into methanol to afford the target polymer  $P(St_{0.8}-co-StOH_{0.2})$ .

Yield : 493 mg (88.7 %).;  $M_n$  (SEC, DMF): 49.9 kg mol<sup>-1</sup>; *D*: 1.49.

Typical procedure for the post-polymerization modification reaction of P(St-*co*-StOH) with  $2FPy^+-CH_2-C^-Tf_2$ .: In a vial, P(St<sub>0.8</sub>-*co*-StOH<sub>0.2</sub>) (300 mg, [PhOH]<sub>0</sub> = 0.559 mmol) and 2-(2-Fluoropyridium-1-lum-1-yl)-1,1-bis(trifluoromethylsulfonyl)ethan-1-ide (326 mg, 0.839 mmol) were solubilized in 3.0 mL of chloroform and 1.5 mL of acetonitrile. The reaction mixture was stirred at room temperature for 24 h. The crude product was purified by dialysis in methanol to afford the target polymer P(St<sub>0.8</sub>-*co*-StOH-CH<sub>2</sub>CTf<sub>2</sub>H<sub>0.2</sub>).

Yield: 448 mg (94.9 %); M<sub>n</sub> (SEC, DMF): 248 kg mol<sup>-1</sup>; D: 1.40.

Graft Polymerization of PE/PP with styrene and 4-acetoxystyrene and the subsequent acetyl deprotection (PE/PP-g-P(St-co-StOH)): The PE/PP was cut into roughly  $1.4 \times 2.8$  cm square pieces. The prepared PE/PP fabric were irradiated with electron beams at a dose of 200 kGy under air-free conditions to generate radicals on the PE/PP surface for the further graft polymerization. Styrene (2.58

mL, 22.5 mmol) and 4-acetoxystyrene (3.41 mL, 22.5 mmol) were added into a glass tube and the mixture was purged with Ar for 20 minutes. An irradiated PE fabric (22.0 mg) was rapidly immersed into the reaction tube and allowed to be purged with Ar for additional 2 min. The reaction mixture was heated at 60 °C for 3 hours. The grafted fabric was removed and washed two times with acetone and three times with methanol. Finally, the obtained fabric was dried under vacuum to afford PE/PP-g-P(St-co-StOAc) with the weight of 73.3 mg and GD of 233 %. Next, PE/PP-g-P(St-co-StAOc) was immersed in the solution containing TBA-OH (1.14 mL, [TBA-OH]<sub>0</sub> = 0.36 mmol) and MeOH (4.86 mL), and the mixture was stirred at room temperature for 5 h. Then, the reacted fabric was transferred and immersed into 6 mL of 2M HCl in ethanol ([HCl] = 12 mmol) and stirred at room temperature for 2 hours. The fabric was washed three times with methanol. Finally, the obtained fabric at room temperature for 2 hours. The afford PE/PP-g-P(St-co-StOH) with the weight of 67.3 mg.

The surface modification of PE/PP-g-P(St-co-StOH) with 2FPy<sup>+</sup>-CH<sub>2</sub>-C<sup>-</sup>Tf<sub>2</sub>: 2FPy<sup>+</sup>-CH<sub>2</sub>-C<sup>-</sup>Tf<sub>2</sub> (500 mg, 1.28 mmol) was dissolved in 3.5 mL MeCN and 2.5 mL CHCl<sub>3</sub>. PE/PP-g-P(St-co-StOH) was immersed in the solution and stated at room temperature for 24 hours. The fabric was washed two times with CHCl<sub>3</sub>/MeCN (v/v = 1/1) and three times with methanol. Finally, the obtained PE/PP-g-P(St-co-StOH-CH<sub>2</sub>CTf<sub>2</sub>H) was dried under vacuum.

PE/PP-g-P(St-co-StOH-CH<sub>2</sub>CTf<sub>2</sub>H) weight : 114 mg

Typical procedure for the organocatalytic Mulaiyama aldol reaction catalyzed by PE/PP-g-P(Stco-StOH-CH<sub>2</sub>CTf<sub>2</sub>H): To a solution of 2-methylcyclohexanone (57.3 mg, 0.511 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL), PE/PP-g-P(St-co-StOH-CH<sub>2</sub>CTf<sub>2</sub>H (6.7 mg, 2 mol% as the CTf<sub>2</sub>H moiety) and *tert*-butyl((1ethoxyvinyl)oxy)dimethylsilane (152 mg, 0.751 mmol) were added at room temperature. After being stirred for 1 h at the same temperature, the reaction mixture was filtrated through a glass filter to remove the immobilized organocatalyst, which was reused for the next run after washing with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated under reduced pressure. Thus obtained residue was purified by column chromatography on silica gel to give ethyl  $2-((1S^*, 2S^*)-1-((tert-butyldimethylsilyl)oxy)-2-$  methylcyclohexyl)acetate in 75% yield (121.0 mg, 0.385 mmol). The NMR data of this product were identical with those of authentic sample.<sup>2</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.16-4.03 (2H, m), 2.77 (1H, d, J = 12.8 Hz), 2.35 (1H, d, J = 12.8 Hz), 1.78 -1.27 (8H, m), 1.24 (3H, t, J = 7.1 Hz), 1.24-1.16 (1H, m), 0.89 (9H, s), 0.93-0.87 (3H, m), 0.10 (3H, s), 0.08 (3H, s); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.8, 76.3, 60.1, 46.4, 38.8, 37.7, 30.5, 26.0, 25.9, 21.8, 18.8, 15.6, 14.2, -1.8, -2.2.



*Figure S-1*. SEM-EDX spectra of the PE/PP-*g*-P(St-*co*-StOHCH<sub>2</sub>CTf<sub>2</sub>H). (The symbol \* refers to the base Al plate)



*Figure S-2.* SEM-EDX atom mapping of the PE/PP-*g*-P(St-*co*-StOHCH<sub>2</sub>CTf<sub>2</sub>H).

### References

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