ELECTRONIC SUPPLEMENTARY INFORMATION

Post-modification of polypentafluorostyrene: a versatile "click" method to create well-defined multifunctional graft copolymers

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EXPERIMENTAL INFORMATION

Materials

2,3,4,5,6-Pentafluorostyrene was obtained from Fluorochem Ltd. and styrene from Sigma-Aldrich. Both monomers were purified by column chromatography (basic AlOx) before usage. Amino-functionalized poly(ethylene glycol) (Shearwater Polymers, Inc.) and 5-aminopentanol (Fluka) were utilized as received from the suppliers. *L*-Lactide was recrystallized from toluene and OEGMA 474 was treated with an inhibitor-remover (Aldrich) before usage.

Synthesis and characterization of the polymers

(**1**) **Terpyridine-functionalized poly(pentafluorostyrene)** (]-$PPFS_{30}$)
The initiator (180 mg, 3.1×10^{-4} mol was dissolved in purified 2,3,4,5,6-pentafluorostyrene (4.1 g, 0.02 mol, M/I = 70). Three freeze-pump-thaw cycles were applied for removal of oxygen before the reaction vessels were immersed in an oilbath of 120 °C for 5 hours. The polymer was precipitated twice from CH_2Cl_2 into cold methanol.
^{1}H-NMR (CD_2Cl_2): δ = 8.68 (m, 2 H; $H_{6:6"}$), 8.65 (m, 2 H; $H_{3:3"}$), 8.13 (m, 2 H; $H_{3':5'}$), 7.89 (m, 2 H; $H_{4:4"}$), 7.45-6.95 (m, 11 H; $H_{aromatic}$, $H_{5,5"}$), 5.30-5.20 (m, 2 H; tpyOC*H*$_2$),4.78 (m, 1 H; *H*C-ON, both diastereomers), 3.54-3.20 (m, 1 H; ON-C*H*, major & minor), 3.09-1.70 (m, 91 H; $H_{PPFS\ backbone}$, CH_3CHCH_3 major), 1.60-0.15 (m, 18 H; C(C*H*$_3$)$_3$; CH_3CHCH_3 minor, C*H*$_3$CHC*H*$_3$; C*H*$_3$CH-ON).

(**2**) **Terpyridine-functionalized poly(pentafluorostyrene-*b*-styrene)** (]-$PPFS_{30}$-*b*-PS_{73})
The poly(pentafluorostyrene) macroinitiator **1** (250 mg, 3.9×10^{-5} mol, M_n = 6,400 g/mol) was dissolved in purified styrene (700 mg, 6.7 mmol, M/I = 170). Three freeze-pump-thaw cycles were applied, and the reaction mixture was heated for 3 hours at 120 °C. The block copolymer was precipitated twice from dichloromethane into methanol. The precipitate was collected and dried under vacuum to yield the desired block copolymer.
^{1}H-NMR (CD_2Cl_2): δ = 8.68 (m, 2 H; $H_{6:6"}$), 8.65 (m, 2 H; $H_{3:3"}$), 8.13 (m, 2 H; $H_{3':5'}$), 7.89 (m, 2 H; $H_{4:4"}$), 7.45-6.30 (m, 376 H; $H_{PS\ backbone}$, $H_{aromatic}$, $H_{5,5"}$), 5.30-5.20 (m, 2 H; tpyOC*H*$_2$),4.78 (m, 1 H; *H*C-ON, both diastereomers), 3.54-3.20 (m, 1 H; ON-C*H*, major & minor), 2.90-0.10 (m, 328 H; $H_{PPFS\ \&\ PS\ backbone}$, CH_3CHCH_3 major, C(C*H*$_3$)$_3$; CH_3CHCH_3 minor, C*H*$_3$CHC*H*$_3$; C*H*$_3$CH-ON).

General procedure of the post-modification reaction by microwave irradiation
The polymer (**1** or **2)** and the corresponding amine-functionalized compound were dissolved in *N*-methylpyrrolidone (NMP). The mixture was heated for 20 min at 95 ºC in a sealed microwave vial.

(3) Terpyridine-functionalized poly(pentafluorostyrene-*g*-ethylene glycol) (]-$PPFS_{30}$-*g*-$(PEG_{75})_9$)
Polymer **1** (100 mg) and NH_2-functionalized poly(ethylene glycol) (600 mg, M_w = 3,400 g/mol) were dissolved in 0.7 mL NMP. The polymer was purified by preparative SEC and precipitation into ice-cold diethyl ether.
^{1}H-NMR (CD_2Cl_2): δ = 8.68 (m, 2 H; $H_{6:6"}$), 8.65 (m, 2 H; $H_{3:3"}$), 8.13 (m, 2 H; $H_{3':5'}$), 7.89 (m, 2 H; $H_{4:4"}$), 7.45-6.95 (m, 11 H; $H_{aromatic}$, $H_{5,5"}$), 5.30-5.20 (m, 2 H; tpyOCH_2),4.78 (m, 1 H; *H*C-ON, both diastereomers), 4.20-3.20 (m, 2701 H; O$CH_{2\ PEG\ backbone}$, ON-C*H*, major & minor), 3.09-1.70 (m, 91 H; $H_{PPFS\ backbone}$, CH_3CHCH_3 major), 1.60-0.15 (m, 18 H; C(CH_3)$_3$; CH_3CHCH_3 minor, CH_3CHCH_3; CH_3CH-ON).

(4) Terpyridine-functionalized poly(pentafluorostyrene-*g*-pentanol) (]-$PPFS_{30}$-*g*-$(AP)_9$)
Polymer **1** (100 mg) and NH_2-pentanol (17 mg, M_n = 103 g/mol) were dissolved in 0.5 mL NMP. The polymer was precipitated into cold methanol.
^{1}H-NMR ($CDCl_3$): δ = 8.80 (m, 4 H; $H_{6:6"}$ & $H_{3:3"}$), 8.24 (m, 2 H; $H_{3':5'}$), 8.02 (m, 2 H; $H_{4:4"}$), 7.65-6.89 (m, 11 H; $H_{aromatic}$, $H_{5,5"}$), 5.47-5.24 (m, 2 H; tpyOCH_2), 4.64 (m, 1 H; *H*C-ON, both diastereomers), 3.67 (m, 18 H; CH_2OH) 3.54-3.20 (m, 19 H; CH_2NH, ON-C*H*, major & minor), 3.09-1.70 (m, 109 H; $H_{PPFS\ backbone}$, CH_3CHCH_3 major, CH_2NH, CH_2OH), 1.69-0.15 (m, 72 H; C(CH_3)$_3$; CH_3CHCH_3 minor, CH_3CHCH_3; CH_3CH-ON, $(CH_2)_3CH_2OH$).

(5) Terpyridine-functionalized poly(pentafluorostyrene-*g*-lactide) (]-$PPFS_{30}$-*g*-$(PLA_{11})_9$)
Polymer **4** (40 mg), *L*-lactide (150 mg, M_n = 144 g/mol) and 0.4 mL dry toluene were added to a polymerization tube and stirred at 100 ºC for 10 minutes. Subsequently, the polymerization was started by adding three drops of the catalyst stannous octoate. The desired graft copolymer was purified from residual monomer by precipitation into cold hexane.
^{1}H-NMR ($CDCl_3$): δ = 8.60 (m, 4 H; $H_{6:6"}$ & $H_{3:3"}$), 8.05 (m, 2 H; $H_{3':5'}$), 7.82 (m, 2 H; $H_{4:4"}$), 7.40-6.85 (m, 11 H; $H_{aromatic}$, $H_{5,5"}$), 5.47-5.24 (m, 2 H; tpyOCH_2), 5.19-4.99 (m, 200 H, lactide C*H*(CH_3)O), 4.64 (m, 1 H; *H*C-ON, both diastereomers), 4.26 (m, 11 H; lactide-endgroup C*H*(CH_3)OH), 3.67 (m, 18 H; CH_2O-lac) 3.54-3.20 (m, 19 H; CH_2NH, ON-C*H*, major & minor), 3.09-0.30 (m, 736 H; $H_{PPFS\ backbone}$, CH_3CHCH_3 major, CH_2NH, CH (CH_3)O, C(CH_3)$_3$; CH_3CHCH_3 minor, CH_3CHCH_3; CH_3CH-ON, CH_2CH_2OH).

(6) Terpyridine-functionalized poly((pentafluorostyrene-*g*-pentanol)-*b*-styrene)
(]-$PPFS_{30}$-*g*-$(AP)_7$-*b*-PS_{73})
Polymer **2** (200 mg) and NH_2-pentanol (15 mg, M_n = 103 g/mol) were dissolved in 0.5 mL NMP. The polymer was precipitated into cold methanol.
^{1}H-NMR (CD_2Cl_2): δ = 8.69 (m, 2 H; $H_{6:6"}$), 8.66 (m, 2 H; $H_{3:3"}$), 8.13 (m, 2 H; $H_{3':5'}$), 7.89 (m, 2 H; $H_{4:4"}$), 7.60-6.30 (m, 376 H; $H_{PS\ backbone}$, $H_{aromatic}$, $H_{5,5"}$), 5.30-5.20 (m, 2 H; tpyOCH_2),4.78 (m, 1 H; *H*C-ON, both diastereomers), 3.98-3.56 (m, 14 H; CH_2OH), 3.54-3.20 (m, 15 H; CH_2NH, ON-C*H*, major & minor), 2.90-0.32 (m, 384 H; $H_{PPFS\ \&\ PS\ backbone}$, CH_3CHCH_3 major, C(CH_3)$_3$; CH_3CHCH_3 minor, CH_3CHCH_3; CH_3CH-ON, CH_2NH, CH_2OH, $(CH_2)_3CH_2OH$).

(7) Terpyridine-functionalized poly((pentafluorostyrene-*g*-Br)-*b*-styrene)
(]-$PPFS_{30}$-*g*-$(Br)_7$-*b*-PS_{73})
Polymer **6** (100 mg) was dissolved in 2 mL of methylene chloride (DCM). Triethylamine (37 mg, M_n = 101 g/mol) was added to the mixture. Afterwards 2-bromoisobutyryl bromide (90 mg, M_n = 230

g/mol) diluted in 1 mL methylene chloride was added dropwise to the mixture and was stirred at room temperature for 24 hours. The polymer was purified by precipitation into methanol.
^{1}H-NMR ($CDCl_3$): δ = 8.73 (m, 4 H; $H_{6:6"}$ & $H_{3:3"}$), 8.18 (m, 2 H; $H_{3':5'}$), 7.92 (m, 2 H; $H_{4:4"}$), 7.55-6.28 (m, 376 H; $H_{aromatic}$, $H_{5,5"}$), 5.43-5.18 (m, 2 H; tpyOCH_2), 4.64 (m, 1 H; *H*C-ON, both diastereomers), 4.28-4.07 (m, 14 H; CH_2O-CO) 3.65-3.20 (m, 15 H; CH_2NH, ON-C*H*, major & minor), 3.13-0.26 (m, 419 H; $H_{PPFS\ \&\ PS\ backbone}$, CH_3CHCH_3 major, C(CH_3)$_3$; CH_3CHCH_3 minor, CH_3CHCH_3; CH_3CH-ON, CH_2NH, $(CH_2)_3CH_2O$, CO-CBr(CH_3)$_2$).

(8) Terpyridine-functionalized poly((pentafluorostyrene-*g*-OEGMA)-*b*-styrene)
(]-$PPFS_{30}$-*g*-$(POEGMA_{10})_7$-*b*-PS_{73})
Polymer **7** (60 mg) and OEGMA (800 mg, M_n = 475 g/mol) were dissolved in 4 mL dry toluene and deoxygenated by bubbeling argon though the polymer solution for 5 minutes. In a different vial, a mixture of PMDETA (6.6 mg, M_n = 173 g/mol), CuBr (5 mg, M_n = 143 g/mol) and toluene were also deoxygenated in the same way. Afterwards, the polymer solution was transferred to the catalyst solution and heated to 70 ºC for 5 h. The solution was filtered over basic aluminium oxide, the excess solvent was removed and the polymer was precipitated twice into ice-cold hexane.
^{1}H-NMR (CD_2Cl_2): δ = 8.69 (m, 2 H; $H_{6:6"}$), 8.66 (m, 2 H; $H_{3:3"}$), 8.13 (m, 2 H; $H_{3':5'}$), 7.89 (m, 2 H; $H_{4:4"}$), 7.60-6.30 (m, 376 H; $H_{PS\ backbone}$, $H_{aromatic}$, $H_{5,5"}$), 5.43-5.18 (m, 2 H; tpyOCH_2), 4.64 (m, 1 H; *H*C-ON, both diastereomers), 4.25-3.95 (m, 140 H; CH_2O-CO), 3.90-3.20 (m, 2535 H; $H_{OEGMA\ backbone}$, CH_2NH, ON-C*H*, major & minor), 3.10-0.30 (m, 769 H; $H_{PPFS\ \&\ PS\ backbone}$, $H_{OEGMA\ aliph.\ backbone}$, CH_3CHCH_3 major, C(CH_3)$_3$; CH_3CHCH_3 minor, CH_3CHCH_3; CH_3CH-ON, CH_2NH, $(CH_2)_3CH_2O$, CO-C(CH_3)$_2$).

Characterization techniques

Gel permeation chromatographic measurements (GPC) of the polymers were performed on a Shimadzu system with a SCL-10A system controller, a LC-10AD pump, a RID-6A refractive index detector and a Polymer Laboratories PLgel 5 μm Mixed-D column. DMA (with 2.1 g/L LiCl) was used as an eluent at a flow rate of 1 mL/min. Molecular weights were calculated against polystyrene standards.

Proton nuclear magnetic resonance spectra (^{1}H-NMR) were recorded on a Varian Gemini 400 MHz spectrometer at room temperature using deuterated chloroform ($CDCl_3$) and methylene chloride (CD_2Cl_2).