Supporting Information

Synthesis of molecularly tunable, dual-reactive poly(4-hydroxystyrene)-based photoresists *via* anionic polymerization, sequential deprotection, and reprotection reactions

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Materials, characterization methods and experimental section

1. Materials

The monomer 4-*tert*-butoxystyrene (BSt, 98%, TCI Co.) and initiator *sec*-butyllithium (*s*-BuLi, 1.4 M in cyclohexane, Aldrich Co.) were used for anionic polymerization. The purification procedures for all reagents used in the polymerization are described in detail in our previous publication.[64]

Hydrochloric acid (HCl, 35.0–37.0%, Samchun Co.) was used as received for the acid-catalyzed deprotection of *tert*-butoxy and acetal groups. Hydrazine monohydrate ($N_2H4{\cdot}H_2O$, 50–60%, Aldrich Co.) was used for base-mediated deprotection of acetoxy groups without further purification. Ethanol (EtOH, 99.5%, Samchun Co.) was used in combination with tetrahydrofuran (THF) as a cosolvent in acid- and base-deprotection reactions.

For the protection of hydroxy groups in PHSt, acetyl chloride (AcCl, 98.0%, Samchun Co.), ethyl vinyl ether (EVE, 99%, Aldrich Co.), and 3,4-dihydro-*2H*-pyran (DHP 97%, TCI Co.) were purified *via* alumina column chromatography before use. A mixed solvent of acetonitrile (ACN, 99.5%, Samchun Co.) and THF was used as the reaction medium for protection steps. Triethylamine (Et_3N, 99.5%, Aldrich Co.) and pyridinium *p*-toluenesulfonate (PPTS, 98.0%, TCI Co.) were used as catalysts without further purification.

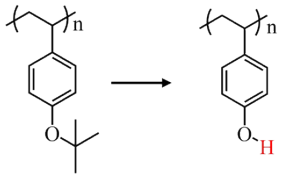
For ^{1}H-NMR spectroscopy, deuterated solvents including chloroform-d ($CDCl_3$, 99.8%, Aldrich Co.), dimethyl sulfoxide-d_6 (DMSO-d_6, 99.9%, Aldrich Co.), and acetone-d_6 (99.9%, Aldrich Co.) were used as appropriate for each sample.

2. Characterization methods

^{1}H NMR Spectra were recorded on a Bruker Avance 500 MHz spectrometer. $CDCl_3$, DMSO-d_6, and acetone-d_6 were used as NMR solvents. The M_n, M_w, and dispersity ($Đ = M_w/M_n$) of the polymers were determined by HPLC using a JASCO LC-4000 Series system. The JASCO HPLC system was equipped with two columns (target molecular weight range = 100–50,000 g/mol and 100–300,000 g/mol), which were eluted with THF at 40 °C at a flow rate of 1.0 mL/min, and calibrated using monodisperse polystyrene standards. T_g were measured using differential scanning calorimetry (DSC, Discovery 250, TA Instruments). All T_g values were obtained from the second heating scan after eliminating the thermal history from the first scan, unless otherwise noted. The heating and cooling rates for the second scan were both 20 °C/min, unless specified otherwise in the polymerization tables.

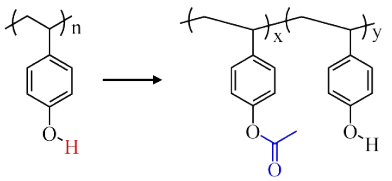
3. Experimental section

3.1 Deprotection of PBSt



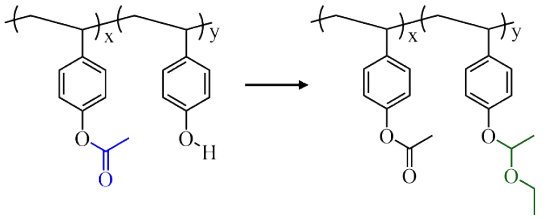
The anionic polymerization of BSt in the presence of *n*-Bu_2Mg was conducted following procedures previously reported by Shin et al. in 2024.[64] For deprotection, PBSt (141.8 mmol) was dissolved in a mixture of THF (140 mL) and EtOH (70 mL) in a 250 mL two-neck round-bottom flask under a nitrogen atmosphere. HCl (150 mmol) was added dropwise at 50 °C, and the reaction mixture was stirred for 24 h. After completion, the reaction mixture was concentrated under reduced pressure at 25 °C and precipitated using deionized water (300 mL). The precipitation and concentration steps were repeated twice to thoroughly remove residual HCl. The resulting polymer was dried under vacuum at 40 °C in the presence of P_2O_5 for 24 h to afford PHSt (140 mmol) as a white powder with a yield of 98 mol%.

3.2 Partial acetylation of ***(1)-2***



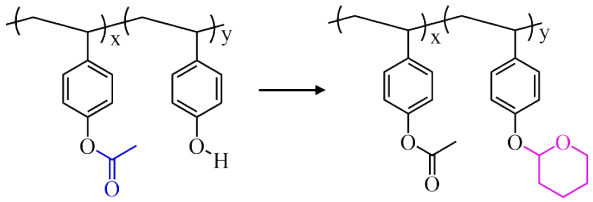
The acetylation of PHSt (130 mmol) was performed in a 250 mL two-neck round-bottom flask under nitrogen. PHSt was dissolved in a mixed solvent of THF (80 mL) and ACN (80 mL), followed by the addition of Et_3N (260 mmol). AcCl (93.6 mmol, corresponding to 72 mol% of the hydroxy groups) was added dropwise at 25 °C. The reaction mixture was stirred for 24 h, concentrated under reduced pressure at room temperature, and precipitated with deionized water (300 mL). The precipitation and concentration steps were repeated twice. The final polymer was dried under vacuum at 40 °C in the presence of P_2O_5 for 24 h to yield **(2)-7** (129 mmol) in 99 mol% yield.

3.3 Synthesis of ***(3)*** *via hydroxy group protection of* ***(2)-7***



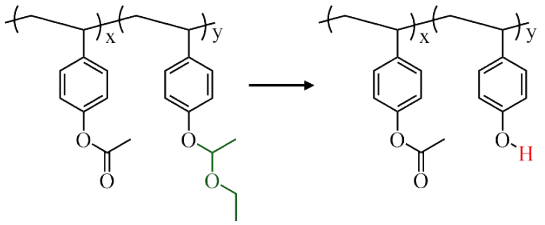
To protect the remaining hydroxy groups in **(2)-7** with EVE, **(2)-7** (0.113 mmol, OH content: 1.87 mmol) and PPTS (0.4 mmol) were charged sequentially into a 250 mL two-neck flask under nitrogen. The mixture was dissolved in a mixed solvent of THF (10 mL) and ACN (10 mL), and the solution was cooled in an ice bath (0 °C). EVE (66.6 mmol, 35.6 equivalents relative to residual OH) was added, and the reaction mixture was allowed to warm to room temperature and stirred for 24 h. The solution was concentrated and precipitated with deionized water (20 mL). The polymer was dried under vacuum at 40 °C in the presence of P_2O_5 for 24 h to yield (3), with complete protection of the hydroxy groups as EE groups, in 97 mol% yield (6.5 mmol).

3.4 Synthesis of (4) via hydroxy group protection of ***(2)-7***



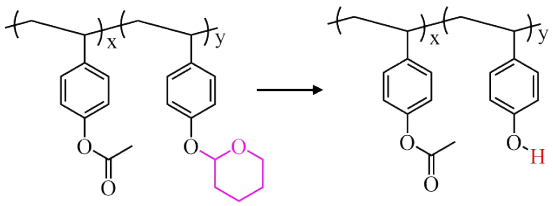
For tetrahydropyranyl (THP) protection of the hydroxy groups, **(2)-7** (0.113 mmol, OH content: 1.87 mmol) and PPTS (0.4 mmol) were added to a 250 mL two-neck flask under nitrogen. The polymer and catalyst were dissolved in THF (10 mL) and ACN (10 mL), and the mixture was stirred at 25 °C. DHP (66.6 mmol, 35.6 equivalents relative to OH) was added, and the reaction proceeded at 25 °C for 24 h. The reaction mixture was concentrated under reduced pressure and precipitated using deionized water (20 mL). The product was dried under vacuum at 40 °C in the presence of P_2O_5 for 24 h to afford (4), with full THP protection, in 96 mol% yield (6.4 mmol).

*3.5 Selective deprotection of **(3)** under acidic conditions*



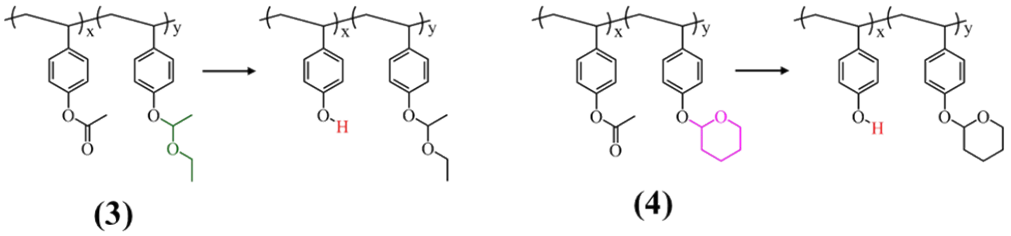
To selectively remove the EE groups from **(3)**, **(3)** (0.029 mmol, EE content: 0.48 mmol) was dissolved in a mixture of THF (10 mL) and EtOH (10 mL) in a 250 mL two-neck flask under nitrogen. HCl (2.1 mmol, 4.4 equivalents relative to EE) was added at room temperature, and the reaction was stirred for 24 h. The reaction mixture was concentrated and precipitated with deionized water (20 mL). The polymer was dried under vacuum at 40 °C in the presence of P_2O_5 for 24 h to obtain **(5)**, in which the EE groups were completely removed.

*3.6 Selective deprotection of **(4)** under acidic conditions*



The selective deprotection of THP groups in **(4)** was performed as used for **(3)**, except for the acid addition step. After identical pretreatment, HCl (3.5 mmol, 7.3 equivalents relative to THP groups) was added at 40 °C, and the reaction was stirred for 2 h. The reaction mixture was concentrated and precipitated with deionized water. The precipitate was dried under vacuum at 40 °C in the presence of P_2O_5 for 24 h to obtain **(7)**, with complete removal of THP groups.

*3.7 Selective deprotection of **(3)** or **(4)** under basic conditions*



(3) **(4)**

To selectively remove Ac groups from **(3)** or **(4)**, the copolymer (0.029 mmol, Ac content: 1.23 mmol) was dissolved in a mixture of THF (10 mL) and EtOH (10 mL) under nitrogen in a 250 mL two-neck flask. Hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 2.1 mmol, 1.70 equivalents relative to Ac groups) was added at 25 °C, and the reaction was continued for 24 h. After completion, the solution was concentrated and precipitated with deionized water (20 mL). The polymer was dried under vacuum at 40 °C in the presence of P_2O_5 for 24 h to afford **(6)** or **(8)**, in which only the Ac groups were selectively removed.

4. Additional information

The GPC results for PHSt **(1)-1** obtained from PBSt-1 and those of the subsequent acetylated polymers are shown in Fig. S1.

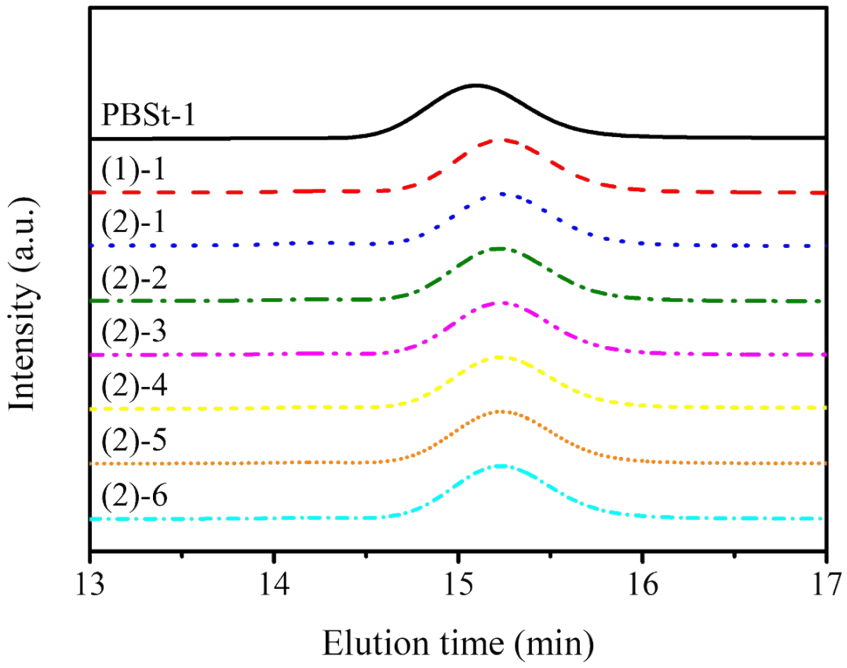


Fig. S1 GPC results for PBSt-1 and P(AcOSt-*co*-HSt) **(2)-1** through **(2)-6**.