

ATRP copolymerization of 4-methoxymethyl styrene with styrene using 2,2'-bipyridine (bipy). A 25 mL Schlenk flask was loaded with 2.00 mL (17.4 mmol) of distilled styrene, 15 mol % of 4-methoxymethyl styrene (0.445 g, 3.00 mmol), 20.0 μ L of 1-phenylethyl bromide (0.171 mmol), 23.9 mg of CuBr (0.167 mmol), and 71.2 mg of 2,2'-bipyridine (0.450 mmol). The flask was fitted with a glass stopper, and the solution was degassed by three freeze-pump-thaw degas cycles. The flask was placed in an oil bath thermostatted at 110 °C for 17 h. Afterwards, the contents were dissolved in THF and precipitated using CH₃OH. The precipitate was filtered and volatile materials were removed under vacuum yielding 1.04 g (46 %) of a colorless solid. SEC (THF): $M_n = 4.00 \times 10^3$, $M_w / M_n = 1.20$ ($M_n^{calc} = 3,050$). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.1 (br, aromatic ring H's), 6.5 (br - 2 maxima signal, aromatic ring H's), 4.4 (br, -CH₂- of methoxymethyl unit), 3.3 (br, -CH₃ of methoxymethyl unit), 1.8 (br, backbone H's), 1.4 (br, backbone H's); ¹³C {¹H} NMR (75 MHz, CDCl₃): δ (ppm) 145.9, 128.0 (broad signal), 126.3, 75.3 (small signal, -CH₂OCH₃), 58.6 (small signal, -CH₂OCH₃), 46.6 - 41.0 (broad multiline signal); IR (neat): ν (cm⁻¹) 1240 (ν C-O).

ATRP copolymerization of 4-methoxymethyl styrene with styrene using 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbipy). Similar procedure as in Reference 12. Quantities 10.0 mL (87.0 mmol) of distilled styrene, 17 mol % of 4-methoxymethyl styrene (2.75 mL, 18.4 mmol), 0.100 mL of 1-phenylethyl bromide (0.74 mmol), 0.112 mg of CuBr (0.780 mmol), 0.750 g of 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbipy) (18.2 mmol), and 3.00 mL of *p*-xylene. After 18 h the yield was 6.72 g (57 %) of a colorless solid. SEC (THF): $M_n = 8.90 \times 10^3$, $M_w / M_n = 1.08$ ($M_n^{calc} = 9,080$). ^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.1 (br, aromatic ring H's), 6.5 (br - 2 maxima signal, aromatic ring H's), 4.4 (br, $-\text{CH}_2-$ of methoxymethyl unit), 3.3 (br, $-\text{CH}_3$ of methoxymethyl unit), 1.8 (br, backbone H's), 1.4 (br, backbone H's); ^{13}C { ^1H } NMR (75 MHz, CDCl_3): δ (ppm) 145.9, 128.0 (broad signal), 126.3, 75.3 (small signal, $-\text{CH}_2\text{OCH}_3$), 58.6 (small signal, $-\text{CH}_2\text{OCH}_3$), 46.6 - 41.0 (broad multiline signal); IR (neat): ν (cm^{-1}) 1240 (ν C-O).

Conversion of the 4-methoxymethyl styrene-containing copolymer to the bromomethyl-containing copolymer. In a 50 mL round bottom flask with stir bar and West condenser, 2.13 g of the 4-methoxymethyl styrene / styrene copolymer (dNbipy prep) and 0.113 g of Aliquat 336 were dissolved in 20 mL of toluene. To this solution 20 mL of conc. HBr was added, and the solution was stirred and heated at 70 °C. After 48 h, the toluene layer was separated and added to 50 mL of CH₃OH. The colorless precipitate was filtered and volatile materials were removed under vacuum yielding 1.87 g (88 %) of a colorless solid. SEC (THF): $M_n = 9.00 \times 10^3$, $M_w / M_n = 1.08$. ¹H NMR (CDCl₃): δ (ppm) 7.1 (br, aromatic ring H's), 6.5 (br - 2 maxima signal, aromatic ring H's), 4.4 (br, -CH₂- of bromomethyl unit), 1.8 (br, backbone H's), 1.4 (br, backbone H's); ¹³C {¹H} NMR (75 MHz, CDCl₃): δ (ppm) 145.3, 129 - 128 (broad signal) 125.9, 46 - 40 (broad multiline signal), 34.3 (small signal, -CH₂Br); IR (neat): ν (cm⁻¹) ν O-H absent.

Procedure for the graft polymerization of styrene from a macroinitiator. A 25 mL Schlenk flask was charged with 0.534 g of the bromomethyl-containing macroinitiator (from methoxymethyl group-containing parent copolymer, 0.770 mmol of initiator sites), 0.117 g (0.810 mmol) of CuBr and 0.766 g (1.85 mmol) of dNbipy (see Table 1 for concentrations). Next, 1.50 mL of xylene and 5.0 mL (6.70 mmol) of styrene were added, and the mixture was degassed by three cycles of freezing, evacuation, thawing, and backfilling with nitrogen. The flask was immersed in an oil bath at $110 \pm 1^\circ\text{C}$, and a time = 0 data point was taken immediately. At timed intervals, a 0.500 mL sample of the solution was withdrawn using a purged syringe and added to 5.00 mL of THF. The THF solutions were injected into the GC, and percent conversions were calculated relative to the time = 0 data points and using the xylene signal as an internal standard. The samples were then filtered through a small column of neutral alumina and precipitated using methanol. Each sample was freeze-dried from benzene. The samples were dissolved in 5.00 mL of THF, passed through a 0.2 micron filter, and then injected into the GPC for analysis.