Alkyne-Functional Polymers through Sonogashira Coupling to Poly(4-bromostyrene)

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ABSTRACT: Alkyne-functional polymers and block copolymers were synthesized by postpolymerization modification of poly(4-bromostyrene) (PBrS) via palladium-catalyzed coupling with terminal alkynes. Several coupling methods, most notably bis(benzonitrile)palladium dichloride/tris-*tert*-butylphosphine catalyst systems at room temperature, were examined on well-defined polymers and copolymers of 4-bromostyrene prepared by nitroxide-mediated polymerization (NMP) with TEMPO. High conversions to alkyne-functional repeat units were obtained with low molecular weight homopolymers of PBrS (8−15 kg/mol) to afford alkyne-rich random copolymers of poly[(4-phenylethynyl)styrene]-*co*-poly(4-bromostyrene) and poly[(4-hexynyl)styrene]-*co*-poly-(4-bromostyrene). Coupling reactions run on higher molecular weight polymers (70 kg/mol) or multiblock copolymers also gave high conversions to poly[(4-phenylethynyl)styrene], while coupling reactions with 1-hexyne suffered from side reactions. ^{1}H NMR analysis of the coupled products suggests that up to 80% of terminal TEMPO groups are lost under standard coupling conditions. The polymers were purified from residual catalyst by treatment with tetrakis(hydroxymethyl)phosphonium chloride.

Introduction

Postpolymerization modification of functional polymers has proven to be a general route to materials that might otherwise be difficult or impossible to make by direct polymerization routes.[1−6] General classes of postpolymerization modification reactions include main-chain modification, for example chlorination of natural rubber and polybutadiene to yield nonflammable materials; side-group modification, for example hydrolysis of poly(vinyl acetate) to poly(vinyl alcohol); and cross-linking reactions, for example vulcanization of rubber.[1]

The specific reactivity of alkyne functional groups, which can be added to polymer systems by postpolymerization side-group modification reactions, allows the preparation of a broad range of polymer-based materials. Addition of thiols, silanes, or aluminum hydrides to alkyne-functional polymers has been shown to lead to new polymers with alkenyl sulfide, alkenylsilane, or alkene moieties.[7] Alkyne groups have been used in cycloaddition reactions to generate low dielectric constant materials for microprocessor and other semiconductor devices.[8,9] The application of highly efficient “click” reactions for post-polymerization modification of pendant or end-group alkynes by cyclization reactions with azides has enabled the preparation of a range of functional polymers.[10−15] Alkyne-containing polymers have also been employed as anchors for selective incorporation of metallic species through alkyne-specific reactions with inorganic species such as dicobalt octacarbonyl.[16] Such cobalt−polymer adducts have been used as redox-active species[17] or as precursors to ceramics,[18] lithographic resists,[19,20] cobalt nanoparticles,[20,21] and micron-sized carbon−cobalt particles.[22]

One general strategy for the preparation of alkyne-functional polymers involves the palladium-mediated cross-coupling (commonly known as Sonogashira coupling) of terminal alkynes with polymer-bound halogenated sp^2 carbons.[23−25] Conjugated polymers made by this cross-coupling method have been studied for light-emitting applications,[26,27] and polymers resulting from the coupling of alkynes to brominated polyphenylenes or poly(bromostyrene)s have been employed as fire-retardant thermosetting materials.[28,29]

While direct polymerization of styrenic monomers containing pendant alkynes has also been shown under certain conditions to be a facile route to alkyne-functional polymers, difficulties stemming from effects of the triple bond have been found with both anionic and radical polymerization methods. With anionic polymerization, living polymerizations have been achieved with 4-(phenylethynyl)styrene (PES), but the range of multiblock copolymers that can be prepared by this method is limited by inefficient crossover to polystyrene blocks.[30] Monomers such as 4-hexynylstyrene (HS), with acidic protons on methylene groups adjacent to the alkyne groups, undergo nonliving polymerization due to the occurrence of termination and transfer side reactions.[30] While conventional radical polymerization of alkyne-functional monomers has been carried out,[29,31] the broad molecular weight distributions and undefined end groups of the resulting chains limit their utility for preparation of more complex polymer architectures and make characterization of side reactions difficult. Nitroxide-mediated radical polymerization (NMP) allows polymerization of a range of alkyne-functional monomers to moderate conversions but suffers from loss of control at higher conversions due to side reactions of nitroxides with alkyne groups.[32]

Because these issues with the direct polymerization of alkyne-functional monomers ultimately limit the placement of alkyne-functional polymers within more complicated polymer structures, we have undertaken a further examination of postpolymerization side-group modification of poly(4-bromostyrene) with alkynes via Sonogashira coupling as an alternative route to these polymers. Previous efforts at conducting Sonogashira coupling reactions on brominated polystyrene derivatives have met with difficulty. Coupling of phenylacetylene and trimethylsilylacetylene to poly(4-bromostyrene) of low molecular weight (M_n = 6.8 kg/mol; M_w/M_n = 1.9; prepared by conventional radical

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polymerization) with $PdCl_2(Ph_3P)/CuI/Et_3N$ catalyst systems has been reported to result in polymer degradation accompanied by broadened molecular weight distributions, most likely due to the high reaction temperature (120 °C) and time (72 h) used.[29] The related coupling of phenylacetylene to poly(dibromostyrene) conducted at a lower temperature (89 °C) was shown to be relatively successful, but complete functionalization with alkyne groups was not achievable.[33] To enable a better understanding of the stability of polymers to coupling conditions and to allow the preparation of functional block copolymers, several coupling protocols were studied on poly(4-bromostyrene) with well-defined end groups, narrow molecular weight distributions, and molecular weights as high as 70 kg/mol made by NMP. Coupling to triblock copolymers containing a poly(4-bromostyrene) block was also studied in order to demonstrate the utility of this technique in the presence of other functional blocks.

Experimental Section

Materials. Phenylacetylene (98%), 1-hexyne (97%) (both from Aldrich), styrene (99%), pyrrolidine (99+%), and triethylamine (99%) (all from Acros) were purified by passage through basic alumina (0.05−0.15 mm, Fluka). 2-Vinylpyridine (97%, Acros) was distilled from calcium hydride. Benzoyl peroxide (BPO, 97%), diisopropylamine (≥99.5%), 1,4-dioxane (99.8%), tetrakis(hydroxymethyl)phosphonium chloride (80% aqueous solution), 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO, 98%) (all from Aldrich), copper(I) iodide (98%, Alfa Aesar), tri-*tert*-butylphosphine (10 wt % solution in hexane), bis(benzonitrile)palladium dichloride (99%), bis(triphenylphosphine)palladium dichloride (99%), and cobalt carbonyl (stabilized with 1−5% hexane) (all from Strem) were used without further purification. Solvents were dried by passage through basic alumina under N_2 purge.[34]

Instrumentation. Molecular weights and molecular weight distributions were estimated by size exclusion chromatography (SEC) with tetrahydrofuran as eluent at 40 °C at a flow rate of 1.0 mL/min on a set of two PLgel 5 μm Mixed-D columns and a PL-ELS 1000 evaporative light scattering detector (Polymer Laboratories). Data were analyzed with Cirrus GPC software (Polymer Laboratories) based upon polystyrene standards (EasiCal PS-2, Polymer Laboratories). Block copolymer composition was estimated by NMR spectroscopy (Varian Unityplus-500; $CDCl_3$). Elemental analyses for C, H, N, and Br as well as Cu and Pd were performed at Schwarzkopf Microanalytical Laboratory (Woodside, NY). IR spectroscopy was carried out on neat samples using a Nicolet Avatar 330-FT-IR with ATR capabilities. Differential scanning calorimetry (DSC) was performed at heating and cooling rates of 10 °C/min on a 100Q differential scanning calorimeter (TA Instruments).

Synthesis. Poly(2-vinylpyridine)-*b*-polystyrene (PVP−PS−TEMPO)[35] and 4-bromostyrene[36] were made by literature procedures. Directly polymerized samples of PPES and PHS for comparison of T_gs were made by reversible addition fragmentation chain transfer (RAFT) polymerization using benzhydryl dithiobenzoate as a chain transfer agent.[37]

Poly(4-bromostyrene) (PBrS).[38] 4-Bromostyrene (15.28 g, 83.5 mmol), TEMPO (0.238 g, 1.52 mmol), and BPO (0.181 g, 0.75 mmol) were added to a 50 mL Schlenk tube. This reaction mixture was degassed by three freeze−pump−thaw cycles, sealed under N_2, and heated at 125 °C with stirring for 21 h. The viscous, pale-yellow reaction mixture was dissolved in dichloromethane (40 mL), precipitated into hexanes (800 mL), and isolated by vacuum filtration. Drying under vacuum afforded the polymer as a white powder (12.67 g, 83%). SEC (vs polystyrene standards): M_n = 7.6 kg/mol, M_w/M_n = 1.09. ^{1}H NMR ($CDCl_3$): δ 7.9 (br, s, 2H, *o*-$C_6H_5CO_2$−), 7.7−6.0 (br, m, 4H per BrS repeat unit, Ar*H*; 3H, *m-/p*-$C_6H_5CO_2$−), 2.2−0.8 (br, m, 3H per BrS repeat unit, −C*H*$_2$C*H*Ar−; 6H, TEMPO −(C*H*$_2$)−; 3H, TEMPO −C*H*$_3$), 0.3 (s, 3H, TEMPO −C*H*$_3$), 0.1 (s, 6H, TEMPO −C*H*$_3$). Anal. Calcd for $PhCO_2$−$PBrS_{45}$−TEMPO: C, 53.04; H, 4.00; N, 0.16, Br, 42.23. Found: C, 53.47; H, 4.03; N, 0.12; Br, 42.17.

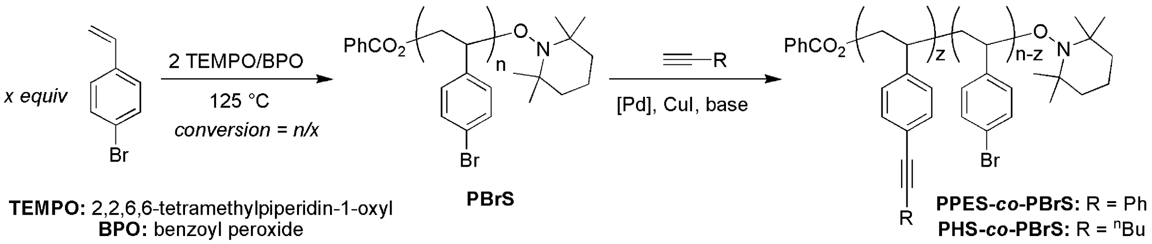
Poly(2-vinylpyridine)-*block*-poly(styrene)-*block*-poly(4-bromostyrene) (PVP-*b*-PS-*b*-PBrS) Synthesis. PVP−PS−TEMPO [M_n(NMR) = 46.0 kg/mol, M_w/M_n(SEC) = 1.35; 2.98 g, 0.0648 mmol] was loaded into a 100 mL Schlenk tube along with 4-bromostyrene (1.54 g, 8.41 mmol) and toluene (14 mL). This reaction mixture was degassed by three freeze−pump−thaw cycles, sealed under N_2, and heated at 125 °C with stirring for 26 h. The viscous, yellow reaction mixture was dissolved in dichloromethane (25 mL), precipitated into hexanes (800 mL), and isolated by vacuum filtration. Drying under vacuum afforded the polymer as a beige powder (3.03 g, 81%). SEC (vs polystyrene standards): M_n = 39.7 kg/mol, M_w/M_n = 1.34, slight tail to low MW. M_n (estimated by ^{1}H NMR by comparison of peak integration values to those of the parent PVP−PS−TEMPO diblock copolymer) = 57.7 kg/mol. ^{1}H NMR ($CDCl_3$): δ 8.5−8.0 (br, m, 1H per vinylpyridine repeat unit), 7.4−6.1 (br, m, ArH), 2.4−1.2 (br, m, 3H per repeat unit, −C*H*$_2$C*H*Ar−). Anal. Calcd for $PhCO_2$−PVP_{144}−PS_{297}−$PBrS_{45}$−TEMPO: C, 80.92; H, 6.69; N, 3.50, Br, 8.81. Found: C, 80.48; H, 6.95; N, 3.88; Br, 8.96.

Representative Procedures for Coupling Reactions. *Coupling Method I.* A solution of poly(4-bromostyrene) (1.73 g, 8.8 mmol of bromostyrene repeat units, M_n = 8.8 kg/mol, M_w/M_n = 1.12), bis(triphenylphosphine)palladium(II) chloride (0.265 g, 0.378 mmol), and copper(I) iodide (0.100 g, 0.525 mmol) in dry tetrahydrofuran (15 mL) was placed in a 100 mL two-neck round-bottom flask equipped with a condenser. Diisopropylamine (4.2 mL, 30.0 mmol) and phenylacetylene (3.3 mL, 30.3 mmol) were loaded into a separate 50 mL flask. Both solutions were sparged with N_2 for at least 15 min. The phenylacetylene solution was then added dropwise over 1 min to the poly(4-bromostyrene) solution with stirring to afford a dark brown reaction mixture after 2 min. The reaction was heated at 60 °C under N_2 for 95 h. After cooling, 100 mL of distilled water was added to the reaction mixture, and the resulting solution was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with saturated ammonium chloride (3 × 60 mL). The dichloromethane solution was evaporated to 10 mL and precipitated into methanol. The light brown polymer was dried under vacuum (1.65 g, 57% based on 100% conversion). SEC: M_n ≈ 10.3 kg/mol, M_w/M_n ≈ 1.15. ^{1}H NMR ($CDCl_3$): δ 7.9 (br, s, 2H, *o*-$C_6H_5CO_2$−), 7.8−6.1 (br, m, 9H per PES repeat unit, Ar*H*; 3H, *m-/p*-$C_6H_5CO_2$−), 2.2−0.8 (br, m, 3H per BrS repeat unit, −C*H*$_2$C*H*Ar−; 6H, TEMPO −(C*H*$_2$)−; 3H, TEMPO −C*H*$_3$), 0.3 (s, 3H, TEMPO −C*H*$_3$), 0.1 (s, 6H, TEMPO −C*H*$_3$). Anal. Calcd for $PBrS_2$-*co*-$PPES_{43}$: C, 91.73; H, 5.91; N, 0.15, Br, 1.70. Found: C, 91.42; H, 5.97; N, <0.15; Br 1.49.

Coupling Method II. A solution of poly(4-bromostyrene) (1.36 g, 7.0 mmol of bromostyrene repeat units, M_n = 8.8 kg/mol, M_w/M_n = 1.12), bis(triphenylphosphine)palladium(II) chloride (0.184 g, 0.262 mmol), and copper(I) iodide (0.077 g, 0.40 mmol) in 15 mL of dry tetrahydrofuran was placed in a 50 mL two-neck round-bottom flask equipped with a condenser. Pyrrolidine (10 mL, 120 mmol) and phenylacetylene (2.5 mL, 23 mmol) were loaded into a separate 25 mL flask. Both solutions were sparged with N_2 for at least 15 min. The phenylacetylene solution was then added dropwise under N_2 to the poly(4-bromostyrene) solution while stirring, turning the reaction mixture dark brown. The reaction mixture was heated at 60 °C under N_2 for 13.5 h. The workup was the same as for coupling method I. The light brown polymer was dried under vacuum (1.08 g, 75% based on 49% conversion). SEC: M_n ≈ 9.3 kg/mol, M_w/M_n ≈ 1.14. ^{1}H NMR peak locations identical to those for product of coupling method I. Anal. Calcd for $PBrS_{23}$-*co*-$PPES_{22}$: C, 73.82; H, 5.03; N, 0.16, Br, 20.46. Found: C, 72.67; H, 5.11; N, 0.26; Br, 20.31.

Coupling Method III. In a 50 mL Schlenk flask, copper(I) iodide (0.037 g, 0.19 mmol) was combined with 1.5 mL of dioxane and degassed using three freeze−pump−thaw cycles. In a N_2-filled glovebox, bis(benzonitrile)palladium(II) chloride (0.080 g, 0.21 mmol)and tri-*tert*-butylphosphine (0.96 mL, 0.386 mmol, 10 wt % solution in hexane) were added to the Schlenk flask. In a separate flask, a solution of poly(4-bromostyrene) (1.00 g, 5.11 mmol of bromostyrene repeat units, M_n ≈ 8.8 kg/mol, M_w/M_n ≈ 1.12) and

Scheme 1



phenylacetylene (1.0 mL, 9.1 mmol) in dioxane (6.5 mL) was sparged with N_2 for at least 15 min. The Schlenk flask was removed from the glovebox, the poly(4-bromostyrene) solution and diisopropylamine (1.2 mL, 8.6 mmol) were added sequentially under N_2, and the reaction mixture was stirred at room temperature for 96 h. The workup was the same as in coupling method I. The light brown polymer was dried under vacuum (1.0 g, 88% based on 100% conversion). SEC: $M_n \approx 10.1$ kg/mol, $M_w/M_n \approx 1.11$. ^{1}H NMR peak locations identical to those for product of coupling method I. ^{13}C NMR: ($CDCl_3$, 125 MHz): δ 145.0 (Ar, C1), 131.2−131.8 (Ar, *C*2, C3), 128.5 (Ar′, C3), 128.2 (Ar′, C4), 127.7 (Ar, *C*2), 123.6 (Ar′, C1), 120.9 (Ar, C4), 89.8 (Ph−C≡*C*), 89.2 (Ph−*C*≡C), 40.6−44.0 (CH_2CH). Anal. Calcd for $PBrS_4$-*co*-$PPES_{41}$: C, 90.10; H, 5.83; N, 0.15, Br, 3.41. Found: C, 90.48; H, 5.77; N, <0.10; Br, 3.05.

Postcoupling Purification from Residual Catalyst. After coupling and precipitation, elemental analysis showed polymers typically contained residual palladium in the range from 0.5 to 3.0 mass % and residual copper in the range from 0.1 to 0.3 mass %. To a solution of the polymer in a minimal amount of toluene or dichloromethane, 25 equiv (relative to an assumed value of 3 wt % residual palladium) of tetrakis(hydroxymethyl)phosphonium chloride (80 vol % in water), 50 equiv of triethylamine, and 1 mL of methanol were added, and the resulting solution was stirred for at least 1 h until it became lighter in color. The solution was washed several times with water to remove complexed palladium; then the organic fraction was concentrated and precipitated into methanol (or hexanes for triblock copolymers), and the resulting polymer was isolated by vacuum filtration. For higher molecular weight polymers ($M_n > 70$ kg/mol) or triblock copolymers, the organic fraction was stirred over silica gel and filtered through Celite and a syringe filter (0.45 μm pores) prior to precipitation. All tested samples showed residual palladium amounts of less than 0.08 mass % (with values as low as 200 ppm observed) and residual copper amounts of less than 0.06 mass % (with values as low as 30 ppm observed) by elemental analysis. Recovered yields after purification are typically around 90%.

Polymer−Cobalt Adduct. In a N_2-filled glovebox, $PPES_{337}$-*co*-$PBrS_{53}$ (25.3 mg; 0.109 mmol of PES repeat units) was dissolved in toluene (1 mL), and a solution of dicobalt octacarbonyl (38.4 mg, 0.113 mmol) in toluene (1.5 mL) was added with stirring. The resulting mixture was stirred for 1 h at room temperature, and then the solvent was removed under vacuum. The resulting adduct was removed from the glovebox, redissolved in dichloromethane (1 mL), and precipitated into methanol (20 mL). The adduct was isolated as a brown powder (44.0 mg, 76%) by vacuum filtration. ^{1}H NMR (CD_2Cl_2): δ 7.8−5.9 (mult, br), 2.4−0.8 (mult, br). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 199.8 (Co−*C*≡O), 138.7, 129.5, 129.2, 128.3, 110.3 (Ar), 92.3 (br, Ph−*C*≡C, PhC≡*C*), 30.1 (br, CH_2CH). IR: 3056, 3023, 2929, 2087 (s), 2050 (vs), 2013 (vs), 1675, 1597, 1495, 1442, 1408, 1177, 1072, 1012, 886, 832, 758, 717, 691 cm^{-1}. Anal. Found: C, 52.83; H, 2.86; Br, 2.91; Co, 22.06. Calcd for $PPES_{337}$-$[Co_2(CO)_6]_{330}$-*co*-$PBrS_{53}$ (composition based upon best fit to found % C while keeping % Co within 0.4% of found value): C, 54.18; H, 2.58; Br, 2.45; Co, 22.46.

Results and Discussion

Sonogashira coupling of phenylacetylene and 1-hexyne as representative terminal alkynes to poly(4-bromostyrene) was investigated as a route to alkyne-functional polymers (Scheme 1). Polymers of 4-bromostyrene submitted to cross-coupling reactions were prepared by nitroxide-mediated polymerization so that changes in molecular weight or molecular weight distribution resulting from the chosen coupling conditions could be easily observed. Nitroxide-mediated polymerization also allowed the preparation of block copolymers with poly(4-bromostyrene) blocks for evaluation of coupling conditions on more complex polymer architectures.

Table 1. TEMPO-Mediated Polymerization of 4-Bromostyrene[a]

entry	BrS/ TEMPO[b]	TEMPO/ BPO[c]	*t* (h)	M_n[d] (kg/mol)	M_w/M_n[d]	DP[e]
A	55	2	20[f]	8.8	1.12	48
B	56	2	21	8.3	1.07	45
C	55	2[g]	20.5[f]	14.6	1.18	80
D	500	2	20	71.4	1.12	390
E	95[h]	*g*	26	57.7[i]	1.34	64[i]

[a] All polymerizations run at 125 °C unless otherwise specified. [b] BrS = 4-bromostyrene; TEMPO = 2,2,6,6-tetramethylpiperidin-1-yloxy. [c] BPO = benzoyl peroxide. [d] Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) calculated by size-exclusion chromatography vs polystyrene standards. [e] Average degree of polymerization (DP) of repeat units of 4-bromostyrene per polymer chain calculated from SEC unless otherwise specified. [f] The first 2 h of the polymerization was run at 95 °C (see text). [g] Polymerization run in the presence of 1 wt % acetic anhydride. [h] Ratio of BrS to diblock copolymer PVP−PS−TEMPO (M_n(SEC) = 33.8 kg/mol, M_w/M_n = 1.35; M_n(NMR) = 46.0 kg/mol; 33 wt % PVP) used as a macroinitiator. Polymerization run in toluene (3 mL per gram of reagents). [i] Values calculated from ^{1}H NMR by comparison to PVP−PS−TEMPO macroinitiator. For block copolymer E, M_n(SEC) = 39.7 kg/mol.

Polymerization of 4-Bromostyrene. Controlled polymerization of 4-bromostyrene by NMP has previously been accomplished with 4-methoxy-2,2,6,6-tetramethylpiperidin-1-oxyl (MTEMPO) as a mediating radical in a bimolecular initiating system with benzoyl peroxide (BPO).[38] MTEMPO-mediated NMP of 4-bromostyrene was found to be faster than that of styrene due to the facile C−O homolysis in the dormant alkoxyamine polymer, encouraged by stabilization of the bromostyryl radical from electron withdrawal by the *para* bromide.[38]

Following these conditions with the less-expensive TEMPO substituted for MTEMPO, a bimolecular initiating system employing 2 equiv of TEMPO relative to BPO was used for polymerization of 4-bromostyrene at 125 °C in bulk. PBrS samples with narrow molecular weight distributions resulted from polymerization with 2 equiv of TEMPO to BPO (Table 1, entries A, B, D). Though the previous studies with MTEMPO used a two-stage heating procedure (3.5 h at 95 °C, then 48 h at 125 °C),[38] similar molecular weights were obtained with these TEMPO-based systems whether a preheating period at 95 °C was used or not (Table 1, entries A, B), as has been observed with TEMPO-mediated polymerization of styrene.[39] Relatively high molecular weight PBrS (~70 kg/mol) was also made without difficulty (Table 1, entry D). Synthesis of higher molecular weight polymers was not attempted as thermal

Table 2. Coupling Conditions for PBrS and PVP-*b*-PS-*b*-PBrS[a]

entry	alkyne/ BrS[b]	amine/ BrS[c]	Pd catalyst	solvent[d]	*T* (°C)
I	3	3	$(PPh_3)_2PdCl_2$	THF	60
II	3	22[e]	$(PPh_3)_2PdCl_2$	THF	60
III	1.5	1.5	$(PhCN)_2PdCl_2$[f]	dioxane[f]	rt

[a] All systems involved use of 3−5 mol % of palladium catalyst and 3−5 mol % of copper(I) iodide. [b] Equivalents of phenylacetylene or 1-hexyne per BrS repeat unit. [c] Equivalents of base to BrS repeat units. Diisopropylamine was used as a base unless otherwise specified. [d] Solvent was added such that the concentration of BrS repeat units was from 0.5 to 1.0 M for homopolymers and 0.1 M for triblock copolymers. [e] Pyrrolidine was used instead of diisopropylamine. [f] Tri-*tert*-butylphosphine (7 mol %) as a solution in hexane was also added, resulting in 8−10 vol % hexane as a cosolvent in the reaction mixture for homopolymer coupling reactions and 2 vol % hexane as a cosolvent for coupling reactions with triblock copolymers. For several runs, dioxane was replaced with benzene or toluene (see Table 3).

autoinitiation of styrenic monomers is known to result in broadening of polymer molecular weight distributions.[40,41]

Acetic anhydride is often employed in NMP to increase the rate of polymerization by decreasing the concentration of TEMPO through acylation of free TEMPO.[42−45] Here it was found to lead to a higher molecular weight than predicted (Table 1, entry C), possibly as the result of a slight decrease in the number of propagating polymer chains occurring as a consequence of the increase of chain−chain termination that should result from the anhydride-increased concentration of propagating radicals. The SEC trace of this polymer showed a unimodal distribution and low polydispersity index despite the higher than expected molecular weight.

To allow exploration of coupling conditions in the presence of other blocks, a triblock copolymer of poly(2-vinylpyridine)-*block*-polystyrene-*block*-poly(4-bromostyrene) (PVP−PS−PBS) was made by solution polymerization of 4-bromostyrene from a macroinitiator of TEMPO-capped PVP−PS[35] in toluene (Table 1, entry E). Conversion to the triblock copolymer proceeded smoothly to yield a PVP−PS−PBS triblock copolymer with no broadening of the molecular weight distribution (triblock copolymer $M_w/M_n = 1.34$ vs diblock copolymer $M_w/M_n = 1.35$).

Sonogashira Coupling to Poly(4-bromostyrene). Adaptation of Sonogashira coupling conditions that are successful for small organic molecules requires the consideration of two specific issues. As polymers are typically soluble in a narrower range of solvents than small molecules, changes in reaction solvent are often necessary. With reactions such as Sonogashira cross-couplings that are particularly sensitive to substrate and reaction conditions,[25] these changes in solvent often necessitate further changes in other reaction components (i.e., catalyst, added ligands, base, copper salt). We have investigated three coupling methods in an effort to efficiently prepare alkyne-functional homopolymers and block copolymers from poly(4-bromostyrene) precursors (Table 2).

Method I. PBrS homopolymers were submitted to Sonogashira coupling conditions previously shown to be effective for coupling to brominated polyphenylenes with bis(triphenylphosphine)palladium dichloride and copper iodide as a catalyst system and a 3-fold excess of alkyne and diisopropylamine relative to aryl halide in THF at 60 °C (Table 2, entry I).[28] With phenylacetylene, long reaction times were required to achieve high conversions (95% at 96 h) to PPES-*co*-PBrS copolymers (Table 3, entries 1, 2), but in contrast to previous studies at higher temperatures,[29] no evidence of polymer degradation was seen at this temperature. The coupled polymer product with 1-hexyne under the same reaction conditions presented a bimodal molecular weight distribution by SEC analysis (Table 3, entry 11). This distribution can perhaps be attributed to the extended reaction times at elevated temperatures allowing cross-linking between the polymer chains, an occurrence which seems more likely for the less sterically hindered PHS than for PPES. Palladium-mediated dimerization or oligomerization of alkynes is one possible pathway to cross-linking in these systems.[46,47]

Table 3. Coupling Reactions of PBrS and PVP-*b*-PS-*b*-PBrS

entry	starting polymer[a]	method[b]	*t* (h)	% conv[c]	M_n(SEC)[d] (kg/mol)	M_w/M_n[d]
			Phenylacetylene			
1	A	I	68	71	12.2	1.05
2	B	I	95	96	10.3	1.15
3	B	II	13.5	49	9.3	1.14
4	B	III	96	91	10.1	1.11
5	C	III	7	83	15.6	1.26
6	C	III	96	99	17.9	1.18
7	D	III	7	87	96.2	1.08
8	E	III	48	27	53.0	1.18
9	E	III[e]	45	100	54.3	1.20
10	E	III[f]	45	100	51.6	1.26
			1-Hexyne			
11	B	I	96		25.4/11.9	bimodal
12	C	I[g]	96	76	22.2	1.24
13	B	II	13.5	71	10.2	1.10
14	B	III	96	89	10.8	1.13
15	D	III	7	47	95.7	1.12
16	D	III[f]	26	63	96.6	1.27

[a] See Table 1 for polymer (A−D) and copolymer (E) characteristics. [b] See Table 2 for descriptions of coupling conditions. [c] Percent conversion of PBrS repeat units to alkyne repeat units calculated by elemental analysis for bromine. [d] Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) calculated by size-exclusion chromatography vs polystyrene standards. [e] Dioxane replaced with toluene as reaction solvent. [f] Dioxane replaced with benzene as reaction solvent. [g] Reaction run in the presence of 5 mol % BHT.

Inclusion of the radical inhibitor and antioxidant 2,6-di-*tert*-butyl-*p*-cresol (BHT, 0.5 mol %) under identical coupling conditions with 1-hexyne led to unimodal molecular weight distributions and reasonably high conversions (77%) at equivalent reaction times (Table 3, entry 12). While radical inhibitors have previously been used in Sonogashira reactions to prevent homocoupling of terminal alkynes, it is not clear exactly what role BHT is playing in this case.[48] While the occurrence of alkyne homocoupling would reduce the rate of coupling by lowering the concentration of alkynes, it would not lead directly to cross-linking, only to the formation of low molecular weight diyne contaminants that would be removed during purification of the resulting polymers by precipitation. BHT may prevent cross-linking through the cyclotrimerization of polymer-bound alkynes,[49] or it might also serve to retard radical polymerization of the conjugated species that might result from alkyne oligomerization.[46,47] Given these problems and the general understanding that the most effective conditions for a given Sonogashira reaction are extremely dependent upon the substrate,[25,50] modified coupling conditions were investigated.

Method II. Highly efficient coupling of alkynes to aryl bromides with pyrrolidine as both the base and the solvent has been reported by Linstrumelle and co-workers.[51] In an adaptation of these conditions, a second set of couplings with $(PPh_3)_2PdCl_2$, CuI, and a 3-fold excess of alkyne was run in mixtures of pyrrolidine (22 equiv per bromostyrene repeat unit) with enough THF to solubilize the polymer (Table 2, entry II). While these reaction conditions led to more rapid coupling than did method I, incomplete conversions with both phenylacetylene and 1-hexyne were reached after 13.5 h (Table 3, entries 3, 13). As small shoulders could already be seen in the SEC traces of the product polymers resulting from coupling with 1-hexyne (Table

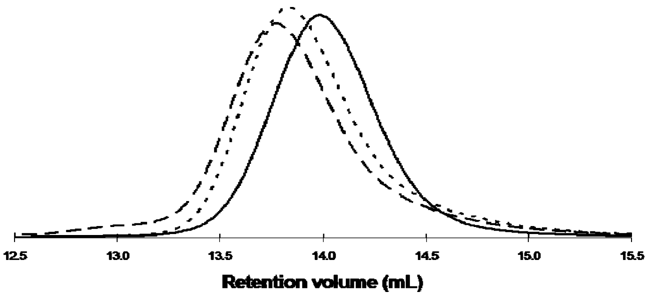


Figure 1. Molecular weight distributions for starting PBrS (—; Table 1, entry B) and coupled product polymers, PHS$_{40}$-*co*-PBrS$_5$ (— —; Table 3, entry 14) and PPES$_{41}$-*co*-PBrS$_4$ (- - -; Table 3, entry 4).

3, entry 13), longer reaction times were not investigated. As THF is typically found to accelerate Sonogashira coupling reactions,[52] it is likely that this specific combination of conditions facilitates the competitive occurrence of side reactions with 1-hexyne. While this method is likely to be effective for efficient coupling of phenylacetylene to pBrS, more general conditions were sought for coupling of both phenylacetylene and 1-hexyne with high conversions.

Method III. As a third method, conditions reported by Fu, Buchwald, and co-workers[53] for Sonogashira coupling at room temperature were applied (Table 2, entry III). These systems comprise bis(benzonitrile)palladium dichloride as the catalyst, copper iodide as a cocatalyst, and tris-*tert*-butylphosphine as a bulky electron-donating ligand to activate the palladium center toward reductive elimination of the product reaction at ambient temperatures. With 1.5 equiv of alkyne per 4-bromostyrene repeat unit, these coupling conditions gave high conversions for both phenylacetylene and 1-hexyne with the lower molecular weight PBrS samples (8−15 kg/mol; Table 1, entries B, C) to yield the desired alkyne-functional polymers (Table 3, entries 4, 5, 14). For the low molecular weight polymers examined, shorter reaction times (7 h) resulted in high conversions (>80%) with phenylacetylene (Table 3, entry 5), but extended reaction times (>95 h) were required to approach complete conversion with phenylacetylene (Table 3, entry 6) and high conversions (>85%) with 1-hexyne (Table 3, entry 14). Importantly, no multimodal molecular weight distributions were seen, and SEC traces of the polymer products did not show significant broadening of molecular weight distributions compared to the starting polymers, though very small high molecular weight shoulders could be seen in the product molecular weight distributions at high conversions in coupling reactions with 1-hexyne (Figure 1). The initial article on this coupling method reports slower coupling with a terminal alkyne (1-octyne, 5 h, 70% yield) than with phenylacetylene (0.5 h, 94% yield),[53] so the slower coupling with 1-hexyne here is not surprising.

Method III with a higher molecular weight polymer (71.4 kg/mol; Table 1, entry D) at these shorter reaction times (7 h) was also found to afford high conversions (>85%) with phenylacetylene (Table 3, entry 7), but only moderate conversions (47%) with 1-hexyne (Table 3, entry 15). Longer reaction times (96 h) with 1-hexyne and the higher molecular weight PBrS in dioxane led to cross-linking as indicated by visible gelation of the reaction mixture. One possible explanation for the lack of success of these reaction conditions with the higher molecular weight polymer relies on a combination of solvent and molecular weight effects—as coupling conversion increases and the polymers become less polar as a result of hexyne functionalization, the lower molecular weight polymers still remain sufficiently solvated for the reaction to continue, while the miscibility of the higher molecular weight polymer with the reaction mixture decreases to the extent that the rate of further coupling is lowered relative to the rate of cross-linking side reactions.

In efforts to promote the coupling rate with 1-hexyne by increasing the accessibility of the polymer-bound aryl bromides to active catalyst, the solvent was changed from dioxane to benzene with the rationale that an aromatic solvent might more effectively solvate the aromatic polymer side chains. Coupling reactions with 1-hexyne in benzene under these room temperature conditions still only yielded moderate levels of functionalization with 1-hexyne after 26 h, and the formation of a small amount of a black tarlike residue, a subnormal isolated yield (∼44%), and product SEC traces with high molecular weight shoulders again suggested the occurrence of cross-linking side reactions (Table 3, entry 16), as did the presence of small peaks resulting from unidentified side reactions at 5.5−6.0 ppm in the ^{1}H NMR spectrum of the product. These peaks suggest the possibility of competitive coupling of alkynes to form enynes that might be leading to the observed cross-linking. Addition of BHT (0.5 mol % to BrS repeat units) to these coupling reactions did not appear to be helpful in preventing these problems in this case as, though conversion values were comparable, extraneous peaks around 5.5−6.0 ppm were again visible in the ^{1}H NMR spectra of the products.

Sonogashira Coupling to Poly(2-vinylpyridine)-*b*-polystyrene-*b*-poly(4-bromostyrene). Coupling method III (Table 2) was applied to poly(2-vinylpyridine)-*b*-polystyrene-*b*-poly(4-bromostyrene) (PVP−PS−PBrS) triblock copolymers to test the efficacy of this method in the presence of the basic coordinating polymer PVP. Coupling in dioxane led only to low conversion of bromostyrene moieties to phenylethynylstyrene repeat units after 48 h (Table 3, entry 8). Use of benzene or toluene as a reaction solvent led to high conversions with phenylacetylene in 45 h (Table 3, entries 9 and 10). For effective coupling to these polymers, the choice of a solvent system that effectively solvates the polymer chains and enables reagent access to the polymeric aryl halides is apparently very important for high conversion in these reactions. With PVP−PS−PBrS, 1-hexyne coupling was again problematic, as coupling efficiencies were very low and a low molecular weight shoulder was present in the SEC trace of the product polymer, suggesting either polymer decomposition or hexyne oligomerization.

Polymer Purification. For many applications, including those in which alkyne-functional polymers are to be used as precursors to inorganic materials such as cobalt or other metallic nanoparticles,[16,21] it is desirable to minimize the level of contamination of these polymers by residual palladium and copper. In an adaptation of work from Maynard and Grubbs in which ruthenium residues are effectively removed from cross-metathesis reactions by treatment of crude reaction mixtures with water-soluble phosphines,[54] polymers were treated with a water-soluble phosphine postcoupling to allow removal of metal catalyst residues, typically 0.5−3.0 mass % Pd and 0.1−0.3 mass % Cu (elemental analysis), by washing with water.[55] At least one published patent suggests that this strategy is also useful for removal of palladium residues.[55] Crude polymers were dissolved in toluene or dichloromethane and stirred with tetrakis(hydroxymethyl)phosphonium chloride and triethylamine to generate tris(hydroxymethyl)phosphine in situ as a water-soluble ligand. After washing these solutions with water and isolating polymers by precipitation, all tested samples showed residual palladium amounts of less than 0.08 mass % (with values as low as 200 ppm observed) and residual copper amounts of less than 0.06 mass % (with values as low as 30 ppm observed) by

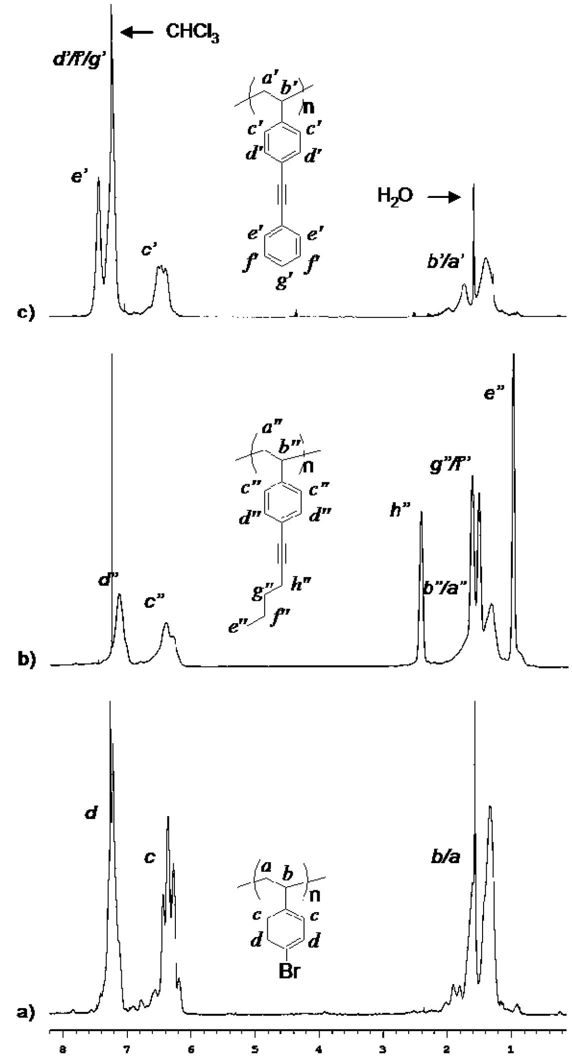


Figure 2. ^{1}H NMR spectra (CDCl$_3$, 500 MHz) of (a) PBrS (Table 1, entry B) and coupled products (b) PHS$_{40}$-*co*-PBrS$_5$ (Table 3, entry 14) and (c) PPES$_{41}$-*co*-PBrS$_4$ (Table 3, entry 4). For spectra of copolymers (b) and (c), only peaks corresponding to protons on alkyne-functional repeat units are labeled.

elemental analysis. These values are comparable to previous results for polymer purification with tris(hydroxymethyl)-phosphine and similar phosphines.[54,56–59] For higher molecular weight polymers as well as multiblock copolymers, an additional step of stirring the purification solution over silica gel[54] followed by filtration through Celite and a syringe filter with 0.45 μm pores was needed to give palladium and copper residues less than 0.1 mass %.

Coupled Polymer Characterization. The success of coupling as determined by elemental analysis was corroborated by structural analysis of the polymer products. ^{13}C NMR spectroscopy verified the presence of alkyne groups by the appearance of peaks at 89.8 and 89.2 ppm for PPES-*co*-PBrS and at 89.8 and 80.6 ppm for PHS-*co*-PBrS, though analysis of the randomness of the distribution of alkyne groups along the polymer backbone was not carried out. IR spectra of the coupled polymers also confirmed the presence of alkyne groups by showing alkyne stretch absorptions at 2220 cm^{-1} for PPES and 2228 cm^{-1} for PHS. ^{1}H NMR spectra of the coupled polymers show peaks at characteristic chemical shifts (7.6 ppm for PES and 2.4, 1.6, 1.5, and 0.8 ppm for HS) not seen in the starting PBrS that correspond to the coupled aryl protons in phenylethynylstyrene repeat units or the alkyl protons in hexynylstyrene repeat units (Figure 2).

Table 4. Alkoxyamine End-Group Retention in Alkyne Coupling to Poly(4-bromostyrene)

entry^a	method^b	polymer	t (h)	T (°C)	% end groups remaining^c
1	I	PPES	68	60	22
11	I	PHS	96	60	67
3	II	PPES	13.5	60	100
4	III	PPES	96	rt	40
14	III	PHS	96	rt	30

^{a} See Table 3 for polymer details. ^{b} See Table 2 for description of coupling methods. ^{c} Estimation of residual end groups was done by comparison of the integration of a peak at 0.2 ppm that represents 6 H on TEMPO methyl groups with integration of the region between 2.6 and 1.0 ppm that represents 3 H on the polymer backbone—other TEMPO methyl and methylene groups in this region were neglected from calculations.

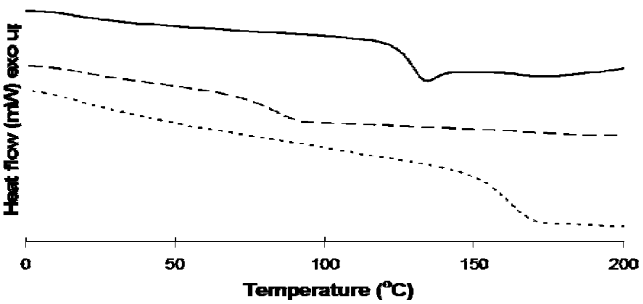


Figure 3. DSC traces for (a) PBrS (—; Table 1, entry B), (b) PHS$_{40}$-*co*-PBrS$_5$ (— —; Table 3, entry 14), and (c) PPES$_{41}$-*co*-PBrS$_4$ (- - -; Table 3, entry 4). Heating rate of 10 °C/min; T_g measured on the third cycle of a heat/cool/heat experiment.

While peaks in the ^{1}H NMR spectra corresponding to two benzoate end-group protons (7.85 ppm) and TEMPO protons (0.8, 0.3, and 0.2 ppm) are visible after coupling reactions, calculations based upon the relative integrations of these peaks suggest loss of TEMPO end groups at longer reaction times (Table 4). Though the ratio of monomer units to end groups might be expected to increase slightly due to fractionation upon precipitation, there is considerably more TEMPO loss than can be accounted for by this effect. Comparison of *ortho* protons on the benzoate end group to the TEMPO protons suggested the same amount of TEMPO loss as comparison of TEMPO protons to monomer backbone protons. Even in couplings run at room temperature (method iii), 60–70% of terminal TEMPO groups appear to have been lost after 96 h (Table 4, entries 4, 14). While some homolysis of alkoxyamine end groups at 60 °C to give free TEMPO, which could lead to formation of TEMPO–Pd(II) complexes, might be expected,[60,61] no literature precedent for end-group loss at room temperature on these time scales could be found, suggesting that some component of the catalytic system is playing a role in decomposition of the terminal alkoxyamine groups. Further efforts are underway to determine whether this composition occurs by transfer hydrogenation or some alternative mechanism and to identify the structure of the new end groups that result.

DSC demonstrated changes in the thermal properties of the products from the starting materials (Figure 3). While PBrS (Table 1, entry B) has a glass transition temperature (T_g) of 130 °C, PHS$_{40}$-*co*-PBrS$_5$ (Table 3, entry 14) and PPES$_{41}$-*co*-PBrS$_4$ (Table 3, entry 4) have T_g values of 84 and 162 °C, respectively. For comparison, homopolymers of PHS and PPES with similar molecular weights made by direct polymerization (reversible addition–fragmentation chain transfer polymerization:[37] PHS with $M_n = 9.9$ kg/mol, $M_w/M_n = 1.15$; PPES with $M_n = 10.5$ kg/mol, $M_w/M_n = 1.04$) have T_g values of 70 and

162 °C. While the Fox equation ($1/T_g = M_1/T_{g1} + M_2/T_{g2}$, where M is the weight fraction of a given polymer)[62] reasonably predicts a T_g of 159 °C for PPES$_{41}$-*co*-PBrS$_4$, the low prediction of a T_g of 76 °C for PHS$_{40}$-*co*-PBrS$_5$ may fit with the elevated T_g that might result from the occurrence of a low extent of cross-linking side reactions in the hexyne couplings.

Coupled Polymer−Cobalt Adduct. The application of the coupled products in the formation of polymer−cobalt composite materials was demonstrated by stirring the polymer PPES$_{337}$-*co*-PBrS$_{53}$ (Table 3, entry 7) with 1 equiv of dicobalt octacarbonyl per alkyne repeat unit in toluene for an hour at room temperature in inert atmosphere to yield the polymer−cobalt carbonyl adduct. The conversion of alkyne groups to cobalt carbonyl adducts was calculated to be ~97% on the basis of fitting elemental analysis data to possible compositions; however, the found carbon content was lower than predicted by >1%, suggesting that other reactions could be occurring. The incorporation of cobalt carbonyl was further supported by the presence of ^{13}C NMR peaks at 92.3 ppm for the Co-bound alkyne carbons and at 199.8 ppm for the CO ligands. CO stretches were visible in the IR spectra at 2087, 2050, and 2013 cm^{-1}. These results correspond to those from our previous studies of polymer−cobalt composites.[21]

Conclusions

The utility of Sonogashira coupling to polymer-bound aryl bromide groups to yield alkyne-containing polymers has been verified on well-defined polymer systems. Room temperature coupling conditions on homopolymers of poly(4-bromostyrene) as well as multiblock copolymer systems are effective with phenylacetylene and 1-hexyne, but there are some difficulties with cross-linking side reactions with the latter alkyne. Purification from catalyst residues was accomplished by treatment of crude polymers with tetrakis(hydroxymethyl)phosphonium chloride. Further application of the coupled products was demonstrated by incorporation of dicobalt octacarbonyl to form polymer−cobalt composite materials.

By variation of the alkyne and the extent of functionalization, a range of different polymers can be made from the same parent polymer. We have focused upon coupling of poly(4-bromostyrene) (PBrS) homopolymers and blocks with phenylacetylene and 1-hexyne as representative alkynes to generate copolymers of poly[(4-phenylethynyl)styrene] (PPES) and poly[(4-hexynyl)-styrene] (PHS), but successful coupling with other terminal alkynes should be possible under appropriate conditions. This coupling protocol should allow for synthesis of copolymers with a broader range of compositions than those attainable through direct nitroxide-mediated polymerization of alkyne-functional monomers. Use of these procedures for the preparation of alkyne-functional multiblock copolymer precursors to cobalt and other metal nanoparticles is in progress.

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