Alkyne-Functional Homopolymers and Block Copolymers through Nitroxide-Mediated Free Radical Polymerization of 4-(Phenylethynyl)styrene

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ABSTRACT: Nitroxide-mediated polymerization of the alkyne-functional monomer 4-(phenylethynyl)styrene allows the preparation of homopolymers and block copolymers with narrow molecular weight distributions. At higher conversions, side reactions, including addition of mediating nitroxides to alkyne groups, lead to broader molecular weight distributions. While differential scanning calorimetry suggests that poly((4-phenylethynyl)styrene) blocks of moderate molecular weight have a fair degree of miscibility with polystyrene, reaction of the pendant alkyne groups of these copolymers with dicobalt octacarbonyl leads to microphase-segregated cobalt-functional materials.

While alkene-functional polymers are readily obtained through a range of chain polymerization techniques (including radical/anionic/cationic polymerization of dienes and ring-opening or acyclic diene metathesis polymerizations), polymers containing alkyne groups are not as easily prepared. This is unfortunate, as alkyne-functional polymers and oligomers have proven useful in a variety of applications. The propensity of carbon-carbon triple bonds to form aromatic rings through thermal cyclization has allowed their use in thermosetting systems (e.g., SiLK).1,2 Linear and branched arylacetylene-based polymers have been prepared by stepwise growth processes and have been shown to have interesting electronic, conformational, and photoluminescent properties.^{3,4} Metal-catalyzed condensation processes have yielded related high polymers.^{5,6} With the recent interest in the use of facile azide-alkyne [3+2] cycloaddition reactions as a means to easily prepare a range of compounds, alkynefunctional polymers are being investigated as polymeric precursors to a variety of functional materials.⁷

Alkynes also might serve as a convenient means by which to prepare polymers containing transition metals, as a number of metal species are known to form complexes with alkynes. As inorganic–organic hybrid polymers are of great current interest,^{8–11} development of controlled routes to well-defined polymers and copolymers containing pendant alkynes should lead to novel organic–inorganic hybrid systems. Selective reaction of alkyne groups with a metal complex (e.g., $Co_2(CO)_8)^{12}$ will lead to self-assembled block copolymers containing metallic species in specific microphase-separated domains.¹³ Similar cobalt–alkyne complexes prepared from hyperbranched polymers have been utilized as precursors to soft ferromagnetic materials.⁴

Well-defined alkyne-functional polymers have previously been prepared by living anionic polymerization of a range of alkyne-functional monomers, including styrenic monomers such as 4-(phenylethynyl)styrene (PES, 1), though the preparation of block copolymers is limited by the inability of the poly(PES) anion to effectively initiate polymerization of styrene and isoprene.¹⁴ Conventional radical polymerization of such monomers has also been carried out,¹⁵ though the uncontrolled nature of these processes makes predictions about the potential for controlled polymerization of these monomers difficult.

To prepare polymeric materials that simultaneously contain both cobalt and a second metal, we are ultimately interested in the preparation of ABC triblock copolymers such as poly(2-vinylpyridine)-block-polystyrene-block-poly(alkyne-functional monomer) that are difficult, if not impossible, to prepare by sequential anionic polymerization starting from either terminus. Polymerization of styrene from living poly(vinylpyridyl) anion is plagued by the formation of graft copolymers via termination at pyridyl rings.¹⁶ Conversely, the crossover from PES to styrene is reported to proceed with about 10% efficiency to give a mixture of homopolymer and diblock copolymer with a broad, multimodal molecular weight distribution.¹⁴ Thus, to extend the useful range of these monomers and to allow their incorporation in a range of copolymer architectures, we have undertaken a study of their nitroxide-mediated free radical polymerization.

Experimental Section

Materials. Styrene (Aldrich, 99%) and phenylacetylene (Aldrich, 98%) were purified by passage through basic aluminum oxide for chromatography (0.05–0.15 mm, Fluka). 4-Bromostyrene (96%), benzoyl peroxide (97%, BPO), 2,2,6,6-tetramethylpiperidin-1-yloxyl (98%, TEMPO), and acetic anhydride (99+%) (all from Aldrich) were used without further purification. Solvents were of analytical grade. 1-Phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (PhEt-TEMPO),¹⁷ TEMPO-terminal polystyrene (PS-TEMPO),¹⁸ 4-(phenylethy-nyl)styrene (PES),¹⁴ and 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (PhEt-TIPNO)¹⁹ were prepared according to literature procedures.

Instrumentation. Size exclusion chromatography (SEC) was carried out at 25 or 40 °C with THF as eluent at a flow rate of 1.0 mL/min on a system consisting of a K-501 pump

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(Knauer), a K-3800 Basic autosampler (Marathon), a set of two PLgel 5 μ m Mixed-D columns (300 \times 7.5 mm, rated for linear separations for polymer molecular weights from 200 to 400 000 g/mol, Polymer Laboratories), and a PL-ELS 1000 evaporative light scattering detector (Polymer Laboratories). Data were acquired through a PL Datastream unit (Polymer Laboratories) and analyzed with Cirrus GPC software (Polymer Laboratories) based upon a calibration curve built upon polystyrene standards with peak molecular weights ranging from 580 to 400 000 g/mol (EasiCal PS-2, Polymer Laboratories). The composition of the block copolymers was ascertained by means of NMR (Varian Unity 500; CDCl₃) and IR (Perkin-Elmer 1600) spectroscopies. Thermal analysis was carried out on a Q100 differential scanning calorimeter (TA Instruments) under nitrogen calibrated with an indium reference standard. Samples were analyzed with a heat/cool/heat cycle between 40 and 180 °C at a heating/cooling rate of 10 °C/min. Glass transition temperatures (half- ΔC_p) were recorded during the second heating cycle. Elemental analysis was carried out by Schwartzkopf Microanalytical (Woodside, NY). TEM images were obtained using a JEOL 2000FX analytical electron microscope operating at 80 or 100 kV. Copolymer TEM samples were prepared by ultramicrotomy (Sorvall MT-1) at room temperature of epoxy-embedded bulk samples. Cobaltalkyne domains appear darker due to the higher electron density afforded by the metal atoms.

PPES. In a representative procedure, PES (0.497 g, 2.44 mmol), PhEt-TEMPO (0.008 g, 0.0316 mmol), and acetic anhydride (0.005 g, 0.053 mmol, 1% w/w) were degassed with three freeze-pump-thaw cycles, sealed under nitrogen, and heated at 95 °C for 7 h. The resulting polymer was dissolved in dichloromethane and precipitated into hexanes to yield PPES as a white powder (0.145 g, 34%). SEC (THF, vs PS standards): $M_n = 13.3$ kg/mol, $M_w/M_n = 1.34$. ¹H NMR (500 MHz, CDCl₃): δ 6.2-7.7 (br m, 9H per repeat unit, ArH), 1.0-2.2 (br m, overlapping polymer backbone protons, 3H per repeat unit, and TEMPO -CH2-, 6H), 0.9 (br s, 3H, TEMPO CH_3), 0.4 (br s, 3H, TEMPO CH_3), 0.25 (br s, 6H, TEMPO CH_3). ¹³C NMR (125 MHz, CDCl₃): δ 40-44 (CH₂CH), 89.2 (Ph-C≡C), 89.8 (Ph-C≡C), 121.0 (Ar, C4), 123.7 (Ar', C1), 127.7 (Ar, C2), 128.4(Ar', C4), 128.8 (Ar', C3), 129.2 (Ar', C2), 131.6 (Ar, C3), 132.2 (Ar, C2), 145.1 (Ar, C1). IR (KBr powder): ν_{CH} 3053, ν_{CH_2} 2925, ν_{CH_2} 2849, $\nu_{\text{C}=\text{C}}$ 2216 w, $\sigma_{\text{CH(overtone)}}$ 1948, $\sigma_{CH(overtone)}$ 1908, $\sigma_{CH(overtone)}$ 1800, $\sigma_{CH(overtone)}$ 1720, $\sigma_{CH(o-1)}$ vertone) 1670, v_{C=C} 1596, v_{C=C} 1507, v_{C=C} 1441, v_{C=C} 1411, σ_{CH} 1177, $\sigma_{\rm CH}$ 1105, $\sigma_{\rm CH}$ 1066, $\sigma_{\rm CH}$ 1018, $\sigma_{\rm CH}$ 911, $\sigma_{\rm CH}$ 833, $\sigma_{\rm CH}$ 755, $\sigma_{\rm CH}$ 689, $\sigma_{\rm C=C}$ 566, and $\sigma_{\rm C=C}$ 525 cm⁻¹.

Polymerization of PES from PS-TEMPO.¹³ In a typical polymerization, an air free tube was loaded with PS-TEMPO (1.20 g, 62.4 $\mu \mathrm{mol}, M_\mathrm{n} \approx 19.2$ kg/mol, $M_\mathrm{w}/M_\mathrm{n} \approx 1.08),$ 4-(phenylethynyl)styrene (2.29 g, 11.2 mmol), and toluene (11.6 mL). The reaction mixture was degassed by three freeze-pumpthaw cycles, sealed under N₂, and heated at 125 °C for 16.5 h (30% conversion by ¹H NMR) to afford a pale yellow, slightly opaque viscous liquid. CH₂Cl₂ (1 mL) was added, and the resulting solution was precipitated into hexanes (800 mL), filtered, washed with hexanes, and dried under vacuum to give PS₁₈₁-PPES₅₆ (1.46 g, 77% based upon conversion). ¹H NMR (500 MHz, CDCl₃): $\bar{\delta}$ 1.45 (br, CH₂); 1.85 (br, CH); 2.12 (br, CH); 6.53 (br, ArH); 7.08 (br, ArH); 7.25 (br, ArH); 7.48 (br, ArH). ¹³C NMR (125 MHz, CDCl₃): δ 40-44 (br, CH₂CH); 89.1 (Ph-C≡C-); 89.8 (Ph-C≡C-); 120.9, 123.6, 125.7, 125.8, 127.5-128.5, 131.8, and 145.3. M_n(¹H NMR): 30.3 kg/mol; 37 wt % PPES. SEC: $M_w/M_n = 1.16$. IR (NaCl): ν_{CH} 3080, ν_{CH} $3062, \ \nu_{\rm CH} \ \ 3025, \ \nu_{\rm CH_2} \ \ 2926, \ \nu_{\rm CH_2} \ \ 2855, \ \nu_{\rm C=C} \ \ 2225w, \ \nu_{\rm C=C}$ 1601, $\nu_{C=C}$ 1513, $\nu_{C=C}$ 1492, $\nu_{C=C}$ 1454, σ_{CH} 1030, σ_{CH} 832, $\sigma_{\rm CH}$ 755, and $\sigma_{\rm CH}$ 700 cm $^{-1}.$ Anal. Calcd for $(C_7H_5O_2)\text{--}$ PS₁₈₁PPES₅₆(C₉H₁₈NO): C, 92.71; H, 7.08; N, 0.05. Found: C, 92.77; H, 7.21; N, 0.17.

Model Reaction of PhEtTEMPO with Diphenylacetylene. In a Schlenk tube, diphenylacetylene (DPA) (0.818 g, 4.59 mmol) and PhEt-TEMPO (1.20 g, 4.58 mmol) were dissolved in *m*-xylene (4.0 mL). The resulting solution was degassed, sealed under nitrogen, and heated at 125 °C for 24 h to give a red solution. The mixture was separated by column



chromatography (SiO₂, 5:1 hexanes/EtOAc, mixed fractions further purified with 8:1 hexanes/EtOAc or 4:1 hexanes/EtOAc) to give a mixture of products identified by ¹H NMR, including styrene (23 mg, 4.8%), PhEt–TEMPO (548 mg, 46%), diphenylacetylene (631 mg, 77%), 1,2-diphenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-ethanone (2)²⁰ (129 mg, 8.9%), benzil (*CAUTION*: strong irritant!) (39 mg, 4.1%), and benzyl phenyl ketone (62 mg, 6.9%) and other incompletely characterized products, including aromatic compounds and paramagnetic compounds.

Reaction of PS-PPES with Co₂(CO)₈.¹³ In a representative procedure, a solution of PS_{173} -PPES₆₇ (0.298 g, 9.27 μ mol, $M_{\rm n}$ (NMR) = 32.2 kg/mol; $M_{\rm w}/M_{\rm n}$ = 1.17) in dry toluene (12 mL) was treated with Co₂(CO)₈ (0.212 g, 0.621 mmol) in toluene (5.0 mL) in a N2-filled glovebox. The dark brown reaction mixture was heated at reflux under N2 for 1 h followed by removal of the volatiles under vacuum. The dark brown solid residue was dissolved in CH_2Cl_2 (~2 mL) and precipitated in dry hexanes (200 mL). The supernatant was decanted, and the polymer was washed with hexanes and dried under vacuum to give PS₁₇₃PPES₆₇[Co₂(CO)₆]₆₁ (composition estimated by elemental analysis by fitting found % Co) as a dark brown powder (0.379 g, 85%). ¹H NMR (500 MHz, CDCl₃): δ 1.43 (br); 1.87 (br); 2.05 (br); 6.47 (br), 7.06 (br); 7.1 (br), 7.27 (br); 7.47 (br). 13 C NMR (125 MHz, CDCl₃): δ 40–41 (CH₂CH); 92.1 (Ph-C=C, Ph-C=C); 125.6, 125.9, 127.4-128.4, 129.0, 129.3, and 145.6 (Ar); 199.4 (Co-C=O). Anal. Calcd for complete reaction with $Co_2(CO)_8$, $(C_7H_5O_2)PS_{173}PPES_{67}$ -(Co₂(CO)₆)₆₇(C₉H₁₈NO): C, 67.47; H, 4.37; N, 0.03; Co, 15.45. Anal. Calcd for (C7H5O2)PS173PPES67(Co2(CO)6)61(C9H18NO): C, 68.96; H, 4.52; N, 0.03; Co, 14.55. Found: C, 68.61; H, 4.68; N, <0.10; Co, 14.50. IR (NaCl): v_{CH} 3047, v_{CH} 3015, v_{CH2} 2916, $\nu_{\rm CH_2}$ 2839, $\nu_{\rm CO}$ 2083, $\nu_{\rm CH}$ 2048, $\nu_{\rm CH}$ 2015, $\sigma_{\rm CH(overtone)}$ 1871, $\nu_{\rm C\equiv C/Co}$ 1600, $\nu_{C=C}$ 1493, $\nu_{C=C}$ 1449, σ_{CH} 751, and σ_{CH} 695 cm⁻¹.

Results and Discussion

4-(Phenylethynyl)styrene (PES, 1) was prepared in high yield by Sonogashira coupling of 4-bromostyrene with phenylacetylene.¹⁴ Nitroxide-mediated preparation of homopolymers of PES was carried out with three initiating systems: benzoyl peroxide/TEMPO, PhEt-TEMPO, and PhEt-TIPNO (Scheme 1). Typical high temperatures (125 °C) used for the TEMPO-mediated polymerization of styrene led to rapid polymerization of PES (50% conversion in 1 h) to afford poly(4phenylethynylstyrene) (PPES) with multimodal molecular weight distributions and, at longer reaction times, cross-linked material. Polymerizations run at 95 °C afforded PPES with narrow, unimodal molecular weight distributions and controllable molecular weights (Table 1). Both ¹³C NMR (δ 89.2, 89.8) and IR spectroscopy (C=C stretch at 2216 cm⁻¹) support the presence of alkyne groups in the resulting PPES.

Decreasing the ratio of TEMPO to BPO from 1.5 to 1 led to an increase in polymerization rate with an apparent decrease in control as evidenced by increasing polydispersity index (Table 1: entries 1-3). The inclu-

	[PES]/[TEMPO] ^a	[TEMPO]/[BPO] ^a	$egin{array}{c} { m Ac}_2 { m O}^b \ (\% \ { m w/w}) \end{array}$	PhMe ^c (mL/g)	$t^{d}\left(\mathbf{h} ight)$	% conv ^e	$M_{ m n}^f$ (kg/mol)	$M_{ m n,calcd}^{ m g}$ (kg/mol)	$M_{ m w}/M_{ m n}^f$	
1	60	1.5	1	0	8	31	6.7	3.8^h	1.22	
2	60	1.3	1	0	8	48	11.3	5.9^h	1.31	
3	60	1	1	0	8	63	12.4	7.8	1.49	
4	60	1	0	0	8	25	4.1	3.1	1.24	
5	60	1	1	2	22	33	3.9	4.0	1.20	
6	60	1	1	2	48	67	6.1	8.2	1.37	
7	60	1	1	2	72	79	10.2	9.7	1.36	
8	100	1	1	2	48	60	14.1	12.2	1.19	
9	200	1	1	2	48	53	19.5	21.6	1.18	

Table 1. Polymerization of PES with BPO and TEMPO^a

^{*a*} All polymerizations run at 95 °C under N₂ for specified time. PES = 4-phenylethynylstyrene; TEMPO = 2,2,6,6-tetramethylpiperidin-1-yloxy; BPO = benzoyl peroxide. ^{*b*} Ac₂O = acetic anhydride. ^{*c*} PhMe = toluene. ^{*d*} t = time in hours. ^{*e*} Percent conversion (% conv) was estimated from ¹H NMR spectroscopy (CDCl₃) by comparison of integrated areas under residual PES terminal vinyl proton peaks (δ : 5.38, 5.86) to integrated areas under PPES backbone methylene (δ : 1.30–1.77) and methine (δ : 1.77–2.25) proton peaks. ^{*f*} Numberaverage molecular weight (M_n) and polydispersity index (M_w/M_n) calculated by size-exclusion chromatography vs polystyrene standards. ^{*g*} M_n based on calculated percent conversion. ^{*h*} Value calculated based upon the assumption that one chain results per TEMPO molecule.

Table 2. Polymerization of PES from Unimolecular Initiators PhEt-TEMPO and PhEt-TIPNO^a

	[PES]/[initiator] ^a	initiator PhEt $-X^a$	$\mathrm{Ac_2O^b}\ (\% \mathrm{w/w})$	PhMe ^c (mL/g)	$\mathbf{t}^{d}\left(\mathbf{h}\right)$	% conv ^e	$M_{\mathrm{n}}^{f}(\mathrm{kg/mol})$	$M_{ m n,calcd}^{ m g}$ (kg/mol)	$M_{ m w}/M_{ m n}{}^f$
1	60	TEMPO	1	0	8	28	5.4	3.4	1.25
2	60	TEMPO	0	0	8	21	4.7	2.6	1.19
3	60	TEMPO	1	2	48	49	4.9	6.0	1.11
4	60	TEMPO	1	2	72	60	5.6	7.3	1.11
5	100	TEMPO	1	2	48	51	8.5	10.4	1.08
6	200	TEMPO	1	2	48	49	13.4	20.0	1.11
7	60	TIPNO	1	0	8	69	9.5	8.4	1.21
8	60	TIPNO	0	0	8	42	5.4	5.1	1.16
9	60	TIPNO	1	2	48	83	10.0	10.2	1.15
10	60	TIPNO	1	2	72	85	10.8	10.4	1.17

^{*a*} All polymerizations run at 95 °C under N₂ for specified time. See Scheme 1 for abbreviations. ^{*b*} Ac₂O = acetic anhydride. ^{*c*} PhMe = toluene. ^{*d*} t = time in hours. ^{*e*} Percent conversion (% conv) was estimated from ¹H NMR spectroscopy (CDCl₃) by comparison of integrated areas under residual PES terminal vinyl proton peaks (δ : 5.38, 5.86) to integrated areas under PPES backbone methylene (δ : 1.30–1.77) and methine (δ : 1.77–2.25) proton peaks. ^{*f*} Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) calculated by size-exclusion chromatography vs polystyrene standards. ^{*g*} M_n based on calculated percent conversion.

sion of acetic anhydride (1% w/w) gave well-controlled polymerizations with a marked increase in polymerization rate (Table 1: entries 3 and 4).²¹ Polymerizations run in toluene (2 mL toluene per g of reactants) are also effective, if slower than those run in bulk (Table 1: entries 3 and 5), and show a smooth increase in M_n and an accompanying increase in M_w/M_n with time (Table 1: entries 5–7). For example, polymerization of 200 equiv of PES (relative to TEMPO) from a 1:1 mixture of TEMPO and BPO goes to 53% conversion after 48 h and results in a polymer with a calculated M_n of 21.6 kg/mol and a narrow molecular weight distribution $(M_w/M_n = 1.18; Table 1: entry 9).$

In agreement with previous reports for the nitroxidemediated polymerization of styrenic monomers,¹⁷ use of a unimolecular initiator such as PhEt-TIPNO or PhEt-TEMPO at 95 °C gives polymers with narrower molecular weight distributions than those resulting from TEMPO/BPO initiating systems (Table 2). While PhEt-TEMPO leads to a slower apparent polymerization rate than BPO/TEMPO, PhEt-TIPNO leads to a faster apparent polymerization, even in the absence of acetic anhydride. For example, while polymerization of 60 equiv of PES from PhEt-TEMPO in toluene for 48 h results in 49% conversion of PES (Table 2: entry 3), polymerization of 60 equiv of PES from PhEt-TIPNO under identical conditions results in 83% conversion (Table 2: entry 9). Unimolecular initiators appear to give narrower molecular weight distributions when low molecular weight PPES is desired (Table 2).

Conversion of PES to PPES over time was followed by SEC and NMR. Typical plots of apparent $M_{\rm n}$ (by SEC) against conversion (by ¹H NMR) show the linearity expected of living polymerization processes over a relatively large conversion window. Kinetic plots, assuming the polymerization rate is first order in PES, tend to show deviations from linearity at times corresponding to conversions from 50 to 65%. At longer reaction times and higher conversions, the rate of monomer loss decreases, and broader molecular weight distributions with visible high molecular weight shoulders become evident in both the TEMPO-mediated polymerizations and in the otherwise better-behaved TIPNO-based systems (Tables 1 and 2). For example, polymerization of 60 equiv of PES from PhEt-TIPNO shows a linear relationship between apparent $M_{\rm n}$ and conversion through 80% conversion, but the polymerization kinetics begin to deviate from first-order behavior between 65 and 80% conversion (Figure 1).

Elimination of dialkylhydroxylamines from chain ends to yield "dead" alkene-terminal polymer chains is a known side reaction in many nitroxide-mediated polymerizations.²² The additional deleterious effect of diarylalkynes, such as diphenylacetylene, upon TEMPOmediated free radical polymerization has been reported, though the mechanism behind this effect has not been studied.²³ The origins of the observed deviations from living behavior in the polymerization of PES can in part be tentatively ascribed to side reactions involving addition of the mediating nitroxide to the alkyne moiety of the monomer. While the reaction of TEMPO with



Figure 1. (a) Evolution of apparent number-average molecular weight, M_n (as estimated by size exclusion chromatography vs polystyrene standards), as a function of conversion (measured by ¹H NMR spectroscopy) for the TEMPO-mediated polymerization of 4-phenylethynylstyrene (PES). (b) First-order kinetic plot (conversion p measured by ¹H NMR spectroscopy). Polymerization conditions: [PES]/[PhEt-TIPNO] = 60, 1% w/w Ac₂O, 2 mL of toluene/g of reactants, 95 °C, 72 h. Final polymer: $M_n = 10.8$ kg/mol, $M_w/M_n = 1.17$ (see Table 2, entry 10).

cycloalkynes has been reported to be very slow at ambient temperatures,²⁴ the much higher temperature at which these polymerizations are conducted might promote slow addition of the nitroxide to the alkyne.

Model studies were carried out by heating diphenylacetylene in the presence of PhEt-TEMPO. Oxidized products resulting from reaction of TEMPO with the alkyne moiety were observed in every case. For example, equimolar amounts of diphenylacetylene and PhEt-TEMPO were heated in xylenes at 125 °C for 24 h. A majority (77%) of the initial charge of diphenylacetylene was recovered, as was 46% of the starting PhEt-TEMPO. The remainder of the product mixture consisted of oxidized products including 1,2-diphenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethanone (2, 4.9% relative to DPA), benzyl phenyl ketone (3, 6.2% relative to DPA), benzil (4, trace; *CAUTION*! strong irritant), and other incompletely characterized products. Styrene was also observed to be present, suggesting that much of the PhEt-TEMPO had decomposed to styrene and *N*-hydroxy-2,2,6,6-tetramethylpiperidine under these conditions.



Compound 2 is known to decompose to ketone 3 by radical pathways and to ketone 4 by ionic pathways.²⁰ Presumably, ketone 2 results from the decomposition of unstable compound 5 by a related pathway. Further studies of these side reactions are in progress, and other controlled free radical polymerization methods that do not use nitroxides and that can proceed at lower temperatures, such as RAFT and ATRP, are being examined for the polymerization of PES and other alkyne-functional monomers.

Small changes in nitroxide concentrations are known to have drastic effects on the course of a given nitroxidemediated radical polymerization. As these side reactions occur with concomitant loss of TEMPO from the polymerization mixture, the resulting propagating radicals are free to undergo termination and transfer reactions, the occurrence of which would explain the loss of control observed at higher conversions. Branching and the accompanying broadening of molecular weight distribution can result from incorporation of active initiating species such as $\mathbf{2}$ in the PPES backbone.

Despite the difficulties involved in polymerization of PES, diblock copolymers in a range of compositions with narrow molecular weight distributions ($M_w/M_n < 1.2$) can be prepared by polymerization of PES from TEMPO-terminal PS (Table 3). For example, heating PS-TEMPO ($M_n = 18.4$ kg/mol) with PPES (170 equiv) in toluene from 3 to 17 h results in PS-PPES block copolymers with PPES conversions up to 43% and narrow molecular weight distributions ($M_w/M_n < 1.2$). In contrast to the homopolymerization of PES, controlled polymerization of PES from PS-TEMPO was observed at 125 °C,

-1 and 0 . Characterization of 1.0 , 1.1 by Dividen Cobolynics Collained by the Lorine leadout of 1 by Hom 1.0, -1 by the	Table 3. Characterization of	of PS-PPES Diblock Copoly	mers Obtained by the Pol	vmerization of PES from PS	-TEMPO
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	$\begin{array}{l} \text{PS-TEMPO} \\ M_{\text{n}} \ (\text{kg/mol})^{b} \end{array}$	[PS]/[PES]	PhMe ^c (mL/g)	$\mathbf{t}^{d}\left(\mathbf{h} ight)$	% conv ^e (NMR)	$M_{\rm n}^{f}$ (NMR)	$M_{\rm w}/M_{\rm n}^{g}$ (SEC)	$\mathrm{wt}~\% \ \mathrm{PPES}^h$	$\mathrm{PS-PPES}_{\mathrm{composition}^h}$
1	11.0	85	3.0	6	16.4	13.9	1.06	21	$PS_{103}PPES_{14}$
2			3.0	12	28.2	15.9	1.08	31	$PS_{103}PPES_{24}$
3	18.4	170	3.3	3	9.4	21.6	1.09	15	$PS_{173}PPES_{16}$
4			3.3	6	24.1	26.7	1.1	31	$PS_{173}PPES_{41}$
5			3.3	17	39.4	32.2	1.17	43	$PS_{173}PPES_{67}$
6	19.2	180	3.3	3	9.4	22.7	1.09	15	$PS_{181}PPES_{17}$
7			3.3	6	16.1	25.1	1.12	23	$PS_{181}PPES_{29}$
8			3.3	16	36.6	32.7	1.19	41	$PS_{181}PPES_{66}$

^{*a*} All polymerizations run at 125 °C for specified time under N₂. See Scheme 1 for abbreviations. ^{*b*} PS–TEMPO number-average molecular weight (M_n) determined by size-exclusion chromatography (SEC) vs polystyrene (PS) standards; $M_w/M_n \approx 1.1$ for all samples. ^{*c*} PhMe = toluene. ^{*d*} t = time in hours. ^{*e*} Percent conversion (% conv) was estimated from ¹H NMR spectroscopy (CDCl₃) by comparison of integrated areas under residual PES terminal vinyl proton peaks (δ : 5.38, 5.86) to integrated areas under PPES backbone methylene (δ : 1.30–1.77) and methine (δ : 1.77–2.25) proton peaks. ^{*f*} M_n based on calculated % conversion. ^{*g*} Polydispersity index (M_w/M_n) measured by SEC vs PS standards. ^{*h*} Wt % PPES and composition (subscripts represent number-average degree of polymerization in each block) based upon integration of ¹H NMR spectra.



Figure 2. (a) Evolution of apparent number-average molecular weight, M_n (as estimated by size exclusion chromatography vs polystyrene standards), as a function of conversion (measured by ¹H NMR spectroscopy) for the polymerization of PES (85 equiv) from TEMPO-terminated polystyrene (PS-TEMPO; open circle, $M_n = 11.0 \text{ kg/mol}, M_w/M_n = 1.07$). (b) First-order kinetic plot (conversion *p* measured by ¹H NMR spectroscopy).

presumably due to the combination of dilution and viscosity effects afforded by the macroinitiator. As with homopolymerization of alkyne-functional monomers, polymerization from PS macroinitiators is well-behaved, as evidenced by a linear relationship between M_n and conversion, and first order in monomer up to moderate conversions (Figure 2).

Miscibility of PPES with PS was probed by DSC studies of blends and block copolymers (Figure 3). Glass transition temperatures were measured on a second heating scan from 40 to 180 °C; the initial DSC heating scan showed no evidence of the occurrence of any thermal cross-linking reactions in this temperature window, and high-temperature DTA of the model compound diphenylacetylene showed no side reactions at temperatures under 300 °C.²⁵ Blends of a sample of PS $(T_{\rm g} = 92 \text{ °C}; M_{\rm n} = 18.8 \text{ kg/mol})$ with a sample of PPES $(T_{\rm g} = 154 \text{ °C}; M_{\rm n} = 10 \text{ kg/mol})$ over a range of compositions were examined. Blends at low PPES compositions show a single $T_{\rm g}$ of increasing value (up to 114 °C) as the relative amount of PPES is increased (Figure 3: traces a-c). At higher PPES compositions, two $T_{\rm g}$ s are evident: one at 114 °C corresponding to the PS/PPES blend and one corresponding to pure PPES at 154 °C (Figure 3: traces c and e). Comiscibility of PS and PPES is also apparent from DSC studies of block copolymers-for example, a PS-PPES diblock copolymer $(M_n = 32.3 \text{ kg/mol}; 38 \text{ wt } \% \text{ PPES})$ shows a single glass transition at 114 °C corresponding to a mixture of the two blocks (Figure 3: trace d). The approximate composition of the combined PS-PPES phase is confirmed by the Fox equation $(1/T_{g,mix} = w_{PS}/T_{g,PS} + w_{PPES}/T_{g,PPES}; w_X = weight fraction of component X), which suggests$



Figure 3. Comparative differential scanning calorimetry (DSC) traces (heating rate = 10 °C/min, N₂ atmosphere, second heating scan shown) of (a) polystyrene (PS; glass transition temperature, $T_g = 92$ °C), (b) 88:12 by weight blend of PS and poly(4-phenylethynylstyrene) (PPES; $T_g = 97$ °C), (c) 62:38 by weight blend of PS and PPES ($T_g = 114$, 154 °C), (d) polystyrene-*block*-poly(4-phenylethynylstyrene) (PS-PPES; 38 wt % PPES; $T_g = 114$ °C), (e) 78:22 by weight blend of PS-PPES and PS ($T_g = 114$, 154 °C), (f) PPES ($T_g = 154$ °C). Sample molecular weights: PS: $M_n = 32.3$ kg/mol; PPES: $M_n = 10$ kg/mol; PS-PPES: $M_n = 32.3$ kg/mol (38 wt % PPES).



Figure 4. Transmission electron micrograph of a microtomed section of bulk PS_{181} -PPES₅₆[Co₂(CO)₆]₅₀ prepared by solvent-casting from toluene.

that a $T_{\rm g}$ of 114 °C corresponds to a mixture with 39 wt % PPES.²⁶ These data point to a significant degree of miscibility for these two aromatic polymers in the molecular weight regime under examination.

To examine the utility of PS-PPES block copolymers for localization of cobalt-containing moieties through microphase separation of the two blocks, PS-PPES was treated with dicobalt octacarbonyl in refluxing toluene, purified by precipitation into hexanes, and solvent cast from toluene. The dried bulk composite was embedded in epoxy, microtomed, and examined by TEM. A representative TEM image (Figure 4) shows microphase separation of the block copolymer into dark cobaltalkyne domains and lighter polystyrene domains. Further experiments probing the use of these composite materials for the preparation of cobalt-copolymer composites are under way.¹³

Conclusions

Nitroxide-mediated polymerization of 4-(phenylethynyl)styrene exhibits living characteristics up to moderate conversions due to the occurrence of side reactions involving the alkyne group of the monomer. Further investigation of these side reactions through preparation of model compounds and polymerization of other alkynefunctional monomers is underway. DSC studies indicate that PPES exhibits a relatively high degree of miscibility with polystyrene; however, addition of dicobalt carbonyl leads to sufficient differentiation of the two blocks to allow microphase separation as evidenced by electron microscopy. Further studies of these and related copolymer systems and their utility for the preparation of hybrid organic-inorganic systems are in progress.

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