Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 3249–3255 **3249**
DOI: 10.1021/ma1001657

Synthesis of End-Functionalized Polystyrene by Direct Nucleophilic Addition of Polystyryllithium to Bipyridine or Terpyridine

Ian M. Henderson and Ryan C. Hayward*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Received August 26, 2009; Revised Manuscript Received February 23, 2010

ABSTRACT: We describe a new approach to synthesize 2,2′-bipyridine- or 2,2′:6′,2″-terpyridine-terminated polystyrene that relies on anionic polymerization and direct end-capping with the desired pyridyl species. End-functionalization occurs by nucleophilic addition of the living polystyryllithium chain to the 6-position of the pyridine ring, followed by termination and oxidative rearomatization. By using an excess of the pyridyl species to avoid coupling of two living chains through addition to the same bipyridine or terpyridine unit, this technique yielded samples consisting of 77−93% singly end-functionalized chains. The functionality of the polymers was determined by nuclear magnetic resonance spectroscopy and chromatographic separation, while molecular weight and polydipersity were determined by size exclusion chromatography. The crude products were easily purified to near-quantitative functionalization by short column chromatography, and the excess pyridyl species could be efficiently recovered and reused. Even though the addition of the polystyrene chain to the 6-position provides some steric hindrance to the ability of pyridyl end-caps to serve as ligands, the terpyridine-functionalized products were found to form bis complexes readily upon addition of 0.5 equiv of iron(II) chloride to a solution of the polymers, as determined by ultraviolet−visible spectrophotometry and nuclear magnetic resonance spectroscopy.

Introduction

Polymers bearing ligands with the ability to complex transition metals are a continued subject of interest due to their ability to form tunable and reversible supramolecular structures.[1−3] In particular, metal−bipyridyl and −terpyridyl complexes have received much attention since they provide strong noncovalent associations for which the kinetics and thermodynamics of binding can be tuned through the choice of metal ion and because the behavior of these complexes is well characterized for small molecule systems.[2,4,5] Polymer-bound bipyridyl and terpyridyl complexes of metals such as Zn, Fe, Ni, Co, Cu, and Ru have been used to construct supramolecular step-growth polymers,[6] block copolymers,[7,8] amphiphilic polymer assemblies,[9] star polymers,[10−14] micelles,[15] tunable self-assembled structures,[16] polymeric chromophores,[17,18] and polymers for self-healing materials.[19] These constructs make use of two main classes of polypyridyl-functionalized polymers: side-chain functionalized polymers and end-functionalized polymers. Here, we focus on the latter.

End-functionalization of polymers with terpyridine and bipyridine can be approached by incorporation of the pyridyl species either pre- or postpolymerization. Prefunctionalization has been accomplished using a polypyridine-bearing initiator for nitroxide-mediated polymerization (NMP) of polystyrene, polyisoprene, poly(*N*,*N*-dimethylacrylamide), poly(butyl acrylate), poly(2-vinylpyridine), and poly(4-vinylpyridine) with polydispersities in the range of 1.1−1.3.[20] Polypyridyl initiators have also been used to prepare polystyrene bearing bipyridine−ruthenium complexes via atom-transfer radial polymerization (ATRP) from a complexed bipyridyl initiator.[10,14,21] Similar complexes have also been used to initiate the anionic ring-opening polymerization of 2-ethyl-2-oxazoline, ethylenimine, ethylene oxide, and lactic acid.[11−13,22] In addition to the aforementioned techniques, reversible addition−fragmentation chain transfer polymerization (RAFT) has been used to accomplish similar goals with vinyl monomers.[23−26]

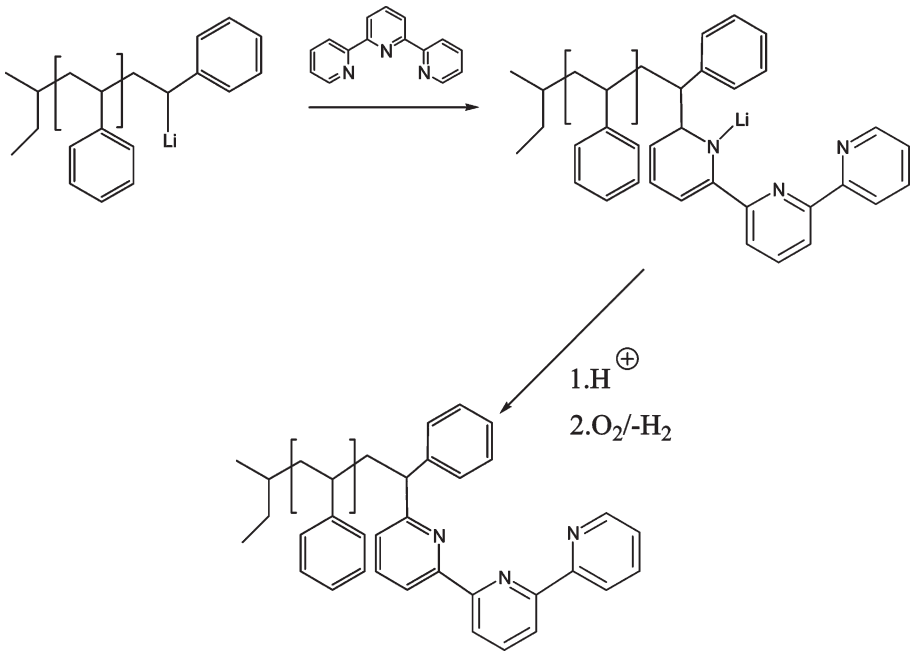
While effective, prefunctionalization methods suffer from the drawback that an involved synthesis is needed to obtain the appropriately functionalized initiators. Postfunctionalization approaches, on the other hand, have most commonly focused on the reaction of hydroxyl-terminated polymers with 4′-chloro-2,2′:6′,2″-terpyridine (chloroterpyridine) under basic conditions, leading to nucleophilic attack of the alkoxide at the 4′-position and displacement of chloride. This approach has been successfully employed for end-functionalization of polystyrene,[27] poly(ethylene oxide),[28] and poly(ethylene-*co*-butylene).[8]

The application of living anionic polymerization, which remains the method of choice for obtaining narrow molecular weight distributions, to polypyridyl-functionalized polymers has so far been constrained by the issue of side reactions with pyridine rings. The nucleophilic aromatic addition of alkyllithium reagents to pyridine[29−31] and bipyridine[32] at the 2- or 6-positions to create 1,2- or 1,6-dihydropyridines, followed by oxidation to form alkyl-substituted pyridines, is well documented. This nucleophilic addition has also been employed in the addition of polystyryllithium and polyisoprenyllithium to poly(2-vinylpyridine) to form comblike graft copolymers.[33] However, in most cases this reaction is undesirable; for example, avoiding attack of the living anion on pyridine motivates the use of polar solvents at low temperature as commonly employed for anionic polymerization of 2- and 4-vinylpyridine.[34] In preparing terpyridine end-functionalized polymers, one route that has been taken to circumvent this reaction is to end-cap the living anionic chains with ethylene oxide, followed by coupling of the hydroxyl-terminated chains with chloroterpyridine as described above for polystyrene and poly(ethylene-*co*-butylene).[8] An alternative method is to end-cap or copolymerize polystyrene with

*Corresponding author. E-mail: rhayward@mail.pse.umass.edu.

Published on Web 03/05/2010

Scheme 1. End-Capping of Polystyryllithium with Terpyridine



1,1-diphenylethylene. As described by Schubert and co-workers, the diphenylethylene anion is not sufficiently reactive to add to the 6-positions; thus, it reacts selectively with the 4′-position of chloroterpyridine.[35,36] While both of these approaches provide effective routes to end-functionalized polymers, they require the purification and addition of an intermediate end-capping agent before reaction with chloroterpyridine, increasing the number of steps in the synthesis.

Here, rather than seeking to reduce the reactivity of the anionic chain end, we exploit the direct nucleophilic addition of polystyryllithium to bipyridine and terpyridine to provide a simple route to end-functionalized polymers. To avoid coupling by addition of two living chains to the same pyridyl unit, we employ a large excess of purified bipyridine or terpyridine, resulting in predominantly singly substituted 6-polystyrylpolypyridine species upon rearomatization, as shown in Scheme 1. We show that this approach allows us to take advantage of the fast reaction times, quantitative conversions, and low-polydispersity products afforded by anionic polymerization to yield polypyridyl end-functionalized polymers without the need for an intermediate end-capping agent. The primary disadvantage of this approach is the need to use an excess of bipyridine and terpyridine; however, the excess quantities can easily be separated and reused. While the addition of polystyrene to the 6-position might be expected to introduce significant steric hindrance to the ability of the pyridyl end-functionalities to serve as ligands for metal salts, the terpyridine-terminated polymers synthesized here are shown to form bis-complexes in 2:1 mixtures with iron(II) chloride, a behavior well-known to occur with terpyridine-functionalized polymers prepared by other techniques.[34]

Experimental Section

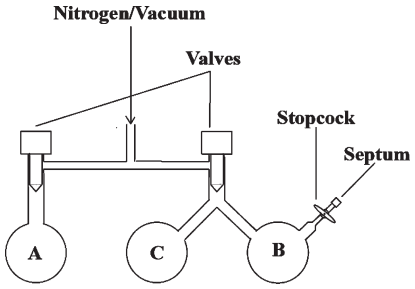
Materials. Styrene (90−100%) was purchased from Mallinckrodt-Baker and stored over calcium hydride (Acros, 92%). 2,2′-Bipyridine (99%) was purchased from Sigma-Aldrich and sublimated twice at 110 °C before being stored at 50 °C under vacuum until use. 2,2′:6,2″-Terpyridine, obtained partially from Strem Chemicals (98%) and partially from the Tew Research Group at the University of Massachusetts, Amherst, was purified by sublimation at 130 °C followed by recrystallization from methanol. As with bipyridine, terpyridine was stored under vacuum at 50 °C until use (and at least overnight) to maintain dryness. *sec*-Butyllithium (1.3 M in 92:8 cyclohexane/hexane) and dibutylmagnesium (0.5 M in heptane) were obtained from Acros Organics and used as received. The *sec*-butyllithium was titrated periodically to confirm concentration using previously developed techniques.[32] Silica gel (0.032−0.063 mm particle size, 60 Å pore size) was purchased from MP Biomedicals and activated by stirring in methanol followed by heating to 115 °C for 12 h prior to use. Deuterated chloroform (99.8% D) and ferrous chloride tetrahydrate (99%) were purchased from Acros Organics and used without further purification. Ethanol (95%) was purchased from Pharmco-Aaper and used without further purification, tetrahydrofuran (THF) was purchased from Fisher Scientific (99.9%), and benzene (99.5%) was purchased from TCI America.

Instrumentation. All ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in deuteriochloroform ($CDCl_3$) and referenced to tetramethylsilane. UV−vis spectra were recorded on a Hitachi U-2010 spectrophotometer with optical glass cuvettes obtained from Buck Scientific. Size exclusion chromatography (SEC) was conducted using a Polymer Laboratories GPC-50 with THF as the solvent and a Polymer Laboratories mixed-C guard column, one Polymer Laboratories mixed D column (5 μm pore size, 0.2−40 kg/mol range), and two Polymer Laboratories mixed C (5 μm pore size, 0.2−2000 kg/mol range) columns at 50 °C and 1 mL/min flow rate. Signal was generated by an RI detector, and molecular weight was determined against polystyrene standards.

Anionic Polymer Synthesis. Anionic synthesis was carried out using a modified version of a previously described apparatus,[37] as shown in Scheme 2. All glassware and stir bars were heated in an oven to 115 °C for at least 2 h prior to use and assembled quickly while hot. Flask C (300 mL RBF) was charged with either 5.0 g of bipyridine or 7.0 g of terpyridine (25- and 23-fold molar excesses to the initiator, respectively). Vacuum (60−80 mTorr) was pulled inside of the setup while the outside of the glassware was heated via hand torch for further drying. Following the heating of the glassware under vacuum, the setup was evacuated and backfilled three times with dry, deoxygenated nitrogen gas, and all glassware joints were fitted with paraffin wrap.

Following the vacuum/backfill steps, the desired amount of styrene was transferred to flask A (250 mL of RBF) accompanied

Scheme 2. Apparatus Used for Anionic Polymerization[a]



[a] Solvent and monomer were distilled from flask A, polymerization was carried out in flask B, and the living polymers were transferred to flask C for end-functionalization.

by 2 mL of dibutylmagnesium solution. The mixture was allowed to stir at 70 °C for 30 min while the rest of the setup was exposed to vacuum. At the end of this time, flask B (300 mL RBF) was cooled to −196 °C, and flask A was exposed to vacuum briefly to remove residual atmosphere. The nitrogen/vacuum valve on the Schlenk line was then closed, and the vacuum transfer of styrene was completed.

After the vacuum transfer of styrene into flask B, flask A was placed under nitrogen flow and charged with 200 mL of solvent (benzene or THF) accompanied by 5 mL of styrene. A drying polymerization was initiated by adding 0.5 mL of 1.3 M *sec*-butyllithium in 92:8 cyclohexane/hexane. During the 10 min that the drying reaction was allowed to proceed, the entire setup was subjected to vacuum and flask B was cooled with liquid nitrogen. After 200 mL of solvent was vacuum transferred to flask B, the process was repeated to transfer 50−100 mL of solvent into flask C. Once the vacuum transfers were completed, three freeze/pump/thaw cycles were undertaken on flasks B and C simultaneously.

Polymerization of styrene was initiated by addition of 1.0 mL of 1.3 M s*ec*-butyllithium solution under a positive pressure of nitrogen in flask B. The s*ec*-butyllithium was added through the septum shown in Scheme 2 with a long needle that reached completely through the stem. After the initiator was added, the resulting orange color indicated initiation of the polymerization. The stopcock on flask B was then closed in order to isolate the punctured septum, and the reaction was allowed to proceed for 1 h at room temperature in the case of benzene (−78 °C in the case of THF). After the allotted time was over, the entire setup was tilted so that all but about 10−30 mL of the reaction mixture was decanted from flask B into flask C, resulting in a dark red color for bipyridine or a dark green color for terpyridine. The end-capping reaction was allowed to proceed for an additional hour at room temperature (−78 °C in THF) before the polymer was quickly poured into 400 mL of ethanol to both terminate and precipitate the polymer. Unfunctionalized polymer remaining in flask B was simultaneously terminated and precipitated separately by quickly pouring the reaction mixture into methanol.

Following synthesis, the functionalized polymer was filtered, dissolved in acetone, and reprecipitated into ethanol twice more. All ethanol fractions were saved, the solvent was removed *in vacuo*, and the bipyridine and terpyridine were recovered and repurified for use in future polymerizations. A typical recovery of the unconsumed end-capping material was greater than 95%.

Chromatographic Separation. The crude end-functionalized polystyrene (15−30 mg) was weighed into a tared vial and dissolved into 20 mL of chloroform. A fritted glass filter (100 mL) mounted on a vacuum flask with a rubber adaptor was filled to within 2 cm of the top with silica before the polymer solution was poured into the filter. Vacuum was pulled on the flask, and 300 mL of chloroform was poured through the filter. Functionalized polymer was retained in the column due to the strong adsorption of terpyridine onto silica gel; this was confirmed by concentrating the eluent *in vacuo* and characterizing by TLC in chloroform. In the event that TLC showed material at the baseline (indicating the presence of functionalized polymer), the polymer solution was pulled through (fresh) silica a second time. A control experiment using nonfunctionalized polystyrene was conducted to verify that the nonfunctionalized side products did not adhere to the column and could be quantitatively recovered from the eluent.

The resulting solution, which contained only nonfunctionalized chains, was then evaporated to dryness in a tared vial using a rotary evaporator, and the residual polymer weighed to determine the weight-average percent functionality of the crude polymer sample. Neat triethylamine (300 mL) was then introduced into the column to displace the functionalized chains from the silica; the resulting solution was then collected and concentrated *in vacuo* before being precipitated in methanol and filtered to afford the purified functionalized product.

Ultraviolet−Visible Spectrophotometry (UV−vis) Characterization of Chain Ends. An optical glass cuvette fitted with a septum was charged with 2.5 mL of dried THF and 0.2 mL of styrene. The polymerization was then initiated by 0.1 mL of 1.3 M *sec*-butyllithium, and the UV−vis spectrum was immediately measured. After the spectrum was recorded, an excess of dried, sublimated bipyridine was added to the reaction, and the UV−vis spectrum of the resulting dark red solution was recorded. An analogous experiment was conducted with terpyridine.

MALDI-TOF Characterization of Sample 5. The MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight mass spectrometry) spectrum of sample 5 was recorded on a Bruker Daltonics Reflex III MALDI-TOF with a 337 nm pulsed laser. The spectrum was recorded in reflectron mode, and positive ions were used as the detection species. The MALDI-TOF spectrometer was calibrated using equine cytochrome *c*, bovine insulin, and oxidized bovine insulin chain B (Sigma-Aldrich). To prepare polymer/matrix mixtures, 5 μL of a saturated solution of dithranol (MP Biomedicals, 99%) in THF was mixed with 5 μL of a 1 mg/mL polymer solution in THF. To this solution was added 1 μL of a saturated solution of silver(I) trifluoroacetate (Alfa Aesar, 98%) in THF. Approximately 0.5 μL of this solution was dropped onto the target, and the solvent was allowed to evaporate before the spectrum was recorded. The number of laser shots was generally 200−300 at 75% intensity.

UV−vis Titration of Sample 1. Purified, functionalized sample **1** (38.8 mg) was dissolved in 100 mL of chloroform and allowed to stir continuously. After recording a baseline, a solution of $FeCl_2 \cdot 4H_2O$ in methanol (16 mM) was added in 0.1 mL quantities, allowing 5−10 min between the addition of iron and the removal of 3 mL aliquots for spectral observation. Absorption values for each portion were taken for the peak at 325 nm, after which the aliquot was reintroduced into the reaction vessel.

NMR Characterization of the Iron Complex of Sample 5. Functionalized sample **5** (50.7 mg) was dissolved in 1 mL of deuterated chloroform (0.39 mM) containing 0.02 vol % TMS (Acros Organics). A stock solution of iron(II) chloride was made by dissolving 79.0 mg of $FeCl_2 \cdot 4H_2O$ in 2 mL of methanol for a concentration of 0.195 M. An aliquot (10 μL) of the iron solution was added to the polystyrene solution to give a molar ratio of 2:1 PS/iron. An NMR spectrum of this solution was taken and compared with the NMR spectrum of a 0.39 mM solution of noncomplexed functionalized sample **5** in deuterated chloroform.

Results and Discussion

Our approach to prepare end-functionalized polystyrene relies on end-capping of living anionic chains using an excess of the appropriate pyridyl species. Evidence for successful nucleophilic addition of the living chains to bipyridine or terpyridine was provided by a change in color from orange for the polystyryl

anion to dark red or dark green, respectively. To further characterize this process, we performed UV−vis absorption measurements on each of the anionic chain-end species (Figure 1). The spectrum of polystyryllithium shows no features at wavelengths above 375 nm, in clear contrast to the spectrum of the PS-bipyridyl anion, which shows an absorption peak around 425 nm, and that of the PS-terpyridyl anion, which shows a small absorption peak at around 410 nm and an intense broad peak centered at 615 nm, the latter giving rise to the intense dark green color. Since bipyridine and terpyridine on their own do not show any absorption in this region, these spectral changes strongly suggest the formation of anionic pyridyl chain ends. We note that the concentrations of polystyryllithium and pyridyl species used in this experiment were too high for reliable data to be obtained below 375 nm, thus preventing observation of the polystyryllithium peak at 334 nm.

Having obtained spectroscopic evidence for reaction of anionic polystyrene chains with terpyridine and bipyridine, we used this method to synthesize a range of end-functionalized polymer chains with molecular weights of 2−13 kg/mol, as summarized in Table 1. In addition to carrying out polymerizations in benzene at room temperature, we prepared sample **2** to verify that the approach also worked for polymerizations in THF at −78 °C. The efficiency of end-functionalization for each sample was calculated in two ways: by NMR spectroscopy and by gravimetric analysis of chromatographically separated polymer chains. Calculation of efficiency by NMR for bipyridine-terminated samples was performed by comparing the integrated intensity of the singlet at 8.62 ppm from the remaining 6′ hydrogen on bipyridine (see Figure 2) to that of the multiplet at 0.69 ppm arising from the two methyl groups on the initiator.

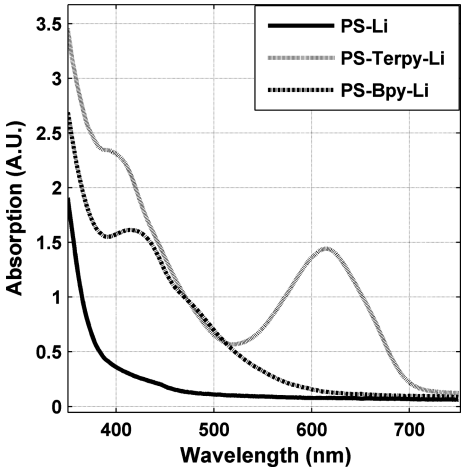


Figure 1. Ultraviolet−visible spectrophotometry absorption spectra of polystyryllithium (solid line), polystyryllithium with terpyridine (gray line), and polystyryllithium with bipyridine (dashed line). No absorption from free bipyridine or terpyridine occurs at these wavelengths; thus, the spectral changes result from addition of polystyryllithium to the pyridyl species to form anionic intermediates.

In the case of terpyridine, it was not possible to resolve peaks from individual pyridyl protons, thus we used the integrated intensity of the peaks between 7.9 and 8.7 ppm, corresponding to the six terpyridyl protons not obscured by the polystyrene aromatic peaks (the 3, 3′, 4′, 5′, 3″, and 6″ protons). Functionalities determined by NMR ranged from 83 to 93% and were generally very close to the values determined by chromatographic separation, which ranged from 77 to 93%. We note that the dihydropyridyl species formed initially upon termination of the pyridyl anions were never observed by NMR, suggesting that oxidative rearomatization to the substituted bipyridine or terpyridine occurs very rapidly under ambient conditions.

Further evidence for the successful functionalization of polystyrene by this approach is given by comparing the molecular weights of chains end-capped with bipyridine or terpyridine to those determined for the small quantity of polymer from each reaction where polystyryllithium was directly terminated with methanol. As summarized in Table 1, most samples showed only a slight change in M_n as determined by SEC, consistent with the addition of a single polypyridyl unit to the end of each chain. (Sample **6** yielded a slightly *greater* molecular weight for the nonfunctional polymer compared to its functionalized counterpart, likely indicating that the conversion of styrene had not reached 100% when the majority of the polymer was transferred to the flask containing terpyridine.) A slight increase in polydispersity also occurred between the functionalized and nonfunctionalized polymers for each sample synthesized in benzene, predominantly reflecting a small quantity of double-molecular-weight chains in the functionalized samples, as described below. MALDI-TOF mass spectrometry was used to definitively establish terpyridine end-capping of the purified functionalized polymer **5** by examining the specific mass peaks (Figure 3). The spacing of peaks in the spectrum corresponds to the molecular weight of styrene (104.15 g/mol), and the central peak shows a

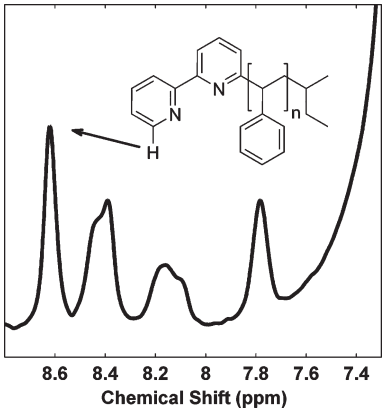


Figure 2. ^{1}H nuclear magnetic resonance spectrum of functionalized sample **4** in deuteriochloroform showing the bipyridyl shifts in detail. The integrated intensity of the peak at 8.62 ppm was compared to the methyl peaks from the initiator (0.69 ppm) to determine the degree of end-functionalization.

Table 1. Properties of Bipyridine and Terpyridine End-Functionalized Polymers

	M_n (PDI) by SEC		end-functionality (%)			
sample no.	nonfunctionalized	functionalized	NMR	chromatography	solvent/temperature	terminating species
1	2100 (1.11)	2250 (1.13)	88.5	85.9	benzene/rt	terpyridine
2	2560 (1.13)	2790 (1.13)	91.2	93.4	THF/−78 °C	bipyridine
3	4400 (1.07)	4500 (1.08)	91.4	93.3	benzene/rt	bipyridine
4	a	6300 (1.09)	92.4	89.7	benzene/rt	bipyridine
5	11250 (1.06)	11170 (1.07)	87.3	84.2	benzene/rt	terpyridine
6	13460 (1.09)	12865 (1.13)	82.8	77.0	benzene/rt	bipyridine

[a] Data not collected.

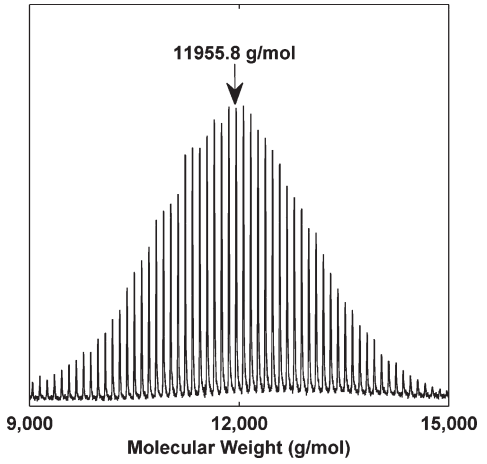


Figure 3. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectrum of terpyridine-functionalized, purified sample **5** in reflectron mode using dithranol as a matrix and silver(I) trifluoroacetate as a cationization agent. The molecular weight of the labeled peak (11955.8 g/mol) corresponds to a polymer with 111 styrene repeat units and a terpyridyl group, confirming successful end-functionalization of this sample. The number-average molecular weight calculated from this spectrum was 11.6 kg/mol, in good agreement with the value of 11.3 kg/mol from SEC.

molecular weight of 11 955.8 g/mol. This represents 111 styrene repeat units, the *sec*-butyl group from the initiator (57.1 g/mol), terpyridine minus a hydrogen atom (232.3 g/mol), and the silver cationation agent (107.9 g/mol), totaling 11 958.0 g/mol. The small discrepancy of 2.2 g/mol from the measured value is reasonable for MALDI-TOF spectra of polymers in this weight range. The number-average molecular weight determined by MALDI-TOF, M_n = 11.6 kg/mol, is also in good agreement with that from SEC, M_n = 11.3 kg/mol.

Although the efficiency of end-functionalization was less than 100%, leading to a significant fraction of nonfunctionalized polymers in the crude reaction products (Table 1), samples could easily be purified to higher purity by short column chromatography. The affinity of terpyridine and bipyridine for the silica gel column packing means that end-functionalized polymers show little movement on the column unless a competing base is introduced into the eluent, while nonfunctional chains can be washed out of the column. Specifically, we used chloroform as the eluent in all cases, followed by the addition of neat triethylamine to displace the functionalized chains. The purities of the resulting materials, as characterized by NMR, are shown in Table 2 for three samples. In all cases the percentage of functional chains was increased to above 96%, significantly greater than that for the crude reaction products described in Table 1. In the most extreme case, sample **5**, the functionality was increased from 87% to greater than 99% by this separation.

Coupling of PS Chains through Addition to Polypyridine Units. The main shortcoming of our approach, and the reason that large excesses of pyridyl species were used for end-capping, is that each bipyridine or terpyridine contains two reactive 6-positions, and thus two living polymer chains may couple during functionalization to yield a double-molecular-weight species with a polypyridyl moiety at its midpoint. With a 23−25-fold excess of polypyridyl species, the occurrence of double-weight species, as determined by SEC, was fairly low in all samples, ranging from undetectable to 4.8% of polymer chains in the worst case of sample **3** (Figure 4). In contrast, polymers synthesized with stoichiometric amounts of bipyridine and terpyridine contained ~15% by number of double-weight chains (Supporting Information). We note that these values may also

Table 2. End-Functionalities after Purification by Short-Column Chromatography

sample no.	end-functionality, % (NMR)
1	99.7
4	96.5
5	99.3

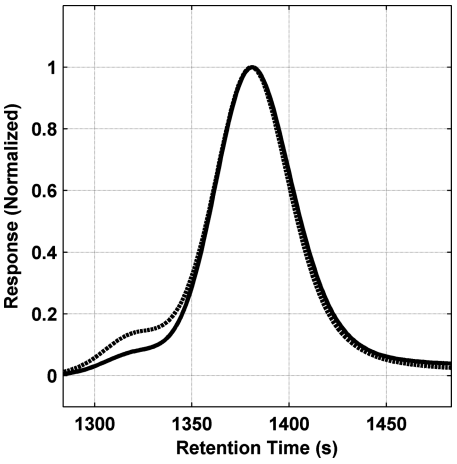


Figure 4. Size exclusion chromatographs of end-functionalized sample **3** before (dashed line) and after (solid line) purification by short column chromatography reveal a decrease in the proportion of double-molecular-weight chains.

reflect any polymer chains coupled through the inclusion of oxygen[38,39] into the sample. Thus, to unambiguously establish that the dominant coupling process occurred through addition to polypyridine units, a detailed characterization of the side products for sample **4** was undertaken (see Supporting Information for details), which revealed that greater than 75% of the double-weight species for this sample were bipyridine-centered.

On the basis of a simple model of equal reactivity of both reactive positions on each polypyridine (Supporting Information), one would expect that a stoichiometric amount of bifunctional terminating agent would yield 33% by number of double-weight chains, substantially greater than actually observed. By contrast, a 25-fold excess would be expected to yield 1% double-weight chains, less than typically observed in our experiments. These observations suggest that the process of coupling through a polypyridine unit is more complicated than independent reactivity of each reactive 6-position; we note that several factors, including steric effects, electrostatic interactions, and the tendency of living anionic polymer chains to aggregate in nonpolar solvents,[40] may all influence the efficiency of coupling. Further study is required to better understand this process and find suitable conditions to minimize (or enhance) its occurrence. In practice, however, it is straightforward to keep the proportion of mid-functionalized double-weight chains acceptably low by using a sufficiently large excess of pyridyl species during end-capping. Even in the worst case of sample **3**, following purification by column chromatography, double-weight chains made up only 1.6% of the sample (Figure 4).

Finally, we note that the presence of double-weight polymers introduces some complications into our determination of percent functionality. In terms of chromatographic separation, TLC analyses suggest that the double-weight chains show a decreased affinity for the silica gel due to steric hindrance at the polypyridyl center, and thus they move on the column at a rate intermediate between the

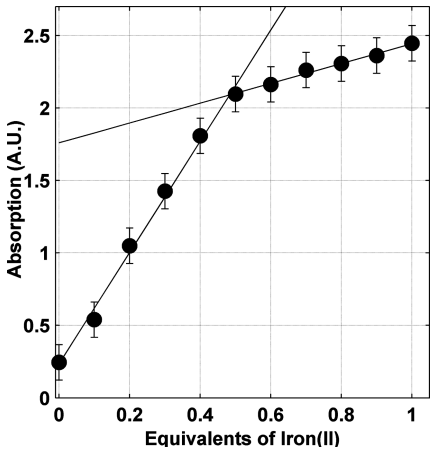


Figure 5. Ultraviolet−visible spectrophotometry (absorption at 329 nm) of a 0.17 mM solution of terpyridine-functionalized sample **1** titrated with iron(II) chloride hexahydrate. The change in slope of the line at 0.5 equiv of iron indicates nearly quantitative formation of a bis(tepyridyl)iron complex, despite the presence of polystyrene chains on the 6-position of each terpyridine ligand.

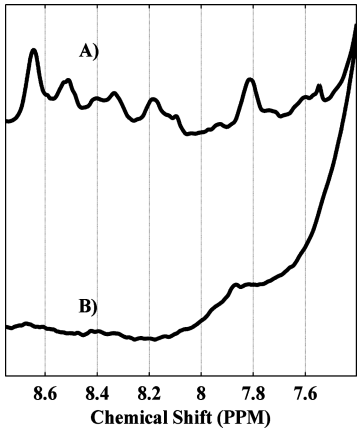


Figure 6. ^{1}H nuclear magnetic resonance spectra of the pyridyl regions of (A) terpyridine-functionalized sample **5** in deuteriochloroform and (B) a 2:1 mixture of functionalized sample **5** with iron(II) chloride in deuteriochloroform. The complete disappearance of the terpyridyl peaks at 0.5 equiv of iron further supports the near quantitative formation of a bis-complex.

end-functionalized chains and the nonfunctionalized chains. Since there is significant uncertainty in the extent to which these species are reflected in the chromatographic yield calculations, the reported values overestimate slightly the percentage of end-functionalized chains. Similarly, our NMR analyses overestimate the percentage of terpyridine end-functionalized chains, since one double-weight chain is counted as 5/6 of a functionalized chain due to the remaining contributions of the 3, 3′, 4′, 5′, and 3″ positions of mid-functional terpyridine moieties to the NMR spectrum. For bipyridine, the values determined by NMR accurately reflect the fraction of end-functional chains, as the 6′ proton used to identify bipyridine is absent in the case of the double-weight polymers. However, in all cases the errors introduced are several percent or less due to the relatively small proportion of double-weight chains, and thus we have not attempted to correct for these complications.

Steric Effects and Formation of Supramolecular Complexes. An important distinction between the end-functionalized polymers produced here and those prepared via other routes lies in the attachment of polystyrene at the 6-position of the pyridine ring, *ortho* to the nitrogen atom, compared to the typical 4′ (or 4)-position, *para* to the nitrogen. This positioning of the polystyrene chain may be expected to impose steric limitations on the ability of the polypyridyl species to serve as a ligand for metal ions. Indeed, as described above, we suspect that such steric effects are responsible for the reduced affinity of the mid-functional double-molecular-weight polymers for silica gel. To establish that the end-functionalized polymers prepared here were nonetheless capable of forming supramolecular complexes, we performed a UV−vis titration of terpyridine-capped polymer **1** with $FeCl_2 \cdot 4H_2O$ in chloroform (Figure 5). The absorption at 325 nm shows a linear increase with the concentration of iron(II) until 0.5 equiv, where a transition to a smaller slope occurs. This titration curve is a clear indication of essentially quantitative formation of a bis-complex until greater than 0.5 equiv of iron is added, as typically observed for nonsterically hindered terpyridine moieties.[35] In addition to the peak at 325 nm from which the titration was recorded, a metal-to-ligand charge-transfer band was observed at 563 nm; both are consistent with the values reported by Schubert and co-workers as distinguishing characteristics of the iron−terpyridine bis-complex.[35]

Further indication of bis-complex formation was provided by an NMR spectrum taken of sample **5** in the presence of 0.5 equiv of iron(II) (Figure 6). While the spectrum of sample **5** in the absence of iron clearly shows terpyridine peaks in the aromatic region, the spectrum of the 2:1 mixture of sample **5**: iron(II) shows no such peaks, which suggests the formation of a paramagnetic high-spin iron(II) complex. This is likely the result of a lengthened Fe−N bond brought about by steric hindrance due to substitution of terpyridine at the 6-position with polystyrene, an effect that has been previously reported for iron(II) complexes of 6,6″-substituted terpyridines.[41] Thus, while the steric hindrance provided by functionalization at the 6-position does influence the complexation behavior, it is not sufficient to prevent formation of a bis-complex. It is notable that no Knight shift protons were observed in the NMR spectrum from $\delta = -600$ to $+600$ ppm, as protons with large upfield or downfield shifts are expected from paramagnetic compounds.[42] The absence of Knight shift protons in paramagnetic terpyridine-functionalized polymer complexes has been reported previously for aqueous PEO-bound $[terpy]_2Co(II)$ systems,[7] though the reason for this behavior remains under investigation.

Conclusions

In this work we have shown that bipyridine- and terpyridine-terminated polystyrenes can be effectively synthesized via anionic polymerization and end-capping by direct nucleophilic attack of polystyryllithium on the desired polypyridine species, followed by oxidative rearomatization. Lower molecular weight polymers showed high efficiencies of functionalization (around 90%) by NMR and chromatographic separation, while higher molecular weight samples showed a slightly decreased yield. While the degree of functionalization of the crude products is somewhat lower than for a previously reported approach to terpyridine-functionalized anionically polymerized polystyrenes that yielded 91−100% functionality when conducted in toluene,[35] the current approach does not require the addition of an intermediate end-capper to the polymer chain. Further, when conducted in THF (sample **2**), the present approach yielded 91% functionalization with bipyridine, which is a considerably better than terpyridine-capped polymers synthesized in THF in the previous study (59−66%).[35] Additionally, we have shown that it is relatively straightforward to purify samples to obtain highly enriched (> 96%) end-functionalized polymer. The ability of the purified

terpyridine-functionalized polymers to form bis-complexes with an iron(II) salt was confirmed by UV−vis. This process has advantages over existing procedures, namely rapid reactions, low PDI, and the absence of synthetically demanding initiators or intermediate end-capping agents. The main disadvantage to this process is the large excess of terpyridine and bipyridine needed to minimize the fraction of chains that couple through addition to a single pyridyl unit; however, the excess bipyridine and terpyridine can be easily separated from the polymer and purified for later reuse. This technique may also be applicable to the functionalization of dienes and other monomers suitable for anionic polymerization and further raises the possibility to intentionally prepare homopolymers or block copolymers containing a single terpyridine- or bipyridine mid-chain functionality by allowing the end-functionalized polymers to react with the live anion of a second polymer.

Acknowledgment. We thank E. Bryan Coughlin, Gunjan Gadodia, Stephen Eyles, and Weiguo Hu for advice and discussion, the Tew research group for providing materials, Charles Bauer and Thomas Mouray of the Eastman Kodak Company for discussions and advice regarding chromatography, and A. Novey, D. Wrublewski, J. Zimberlin, and S. Eastman for their suggestions on the manuscript. Support for this work was provided by the Eastman Kodak Company in the form of a Kodak Fellowship for I.M.H. and by the ACS Petroleum Research Fund through Grant 48858-DNI7. NMR and mass spectra were recorded in facilities supported by the NSF MRSEC at UMass (DMR-0820506).

Supporting Information Available: Results of using a stoichiometric amount of terpyridine, a more detailed analysis of the side products of the reaction, an equal-reactivity model for pyridyl-centered chain coupling, and more detailed synthetic procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Burnworth, M.; Knapton, D.; Rowan, S. J.; Weder, C. *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 91–103.
(2) Schubert, U.; Hofmeier, H.; Newkome, G. *Modern Terpyridine Chemistry*; Wiley-VCH: Weinheim, 2006.
(3) Friese, V. A.; Kurth, D. G. *Curr. Opin. Colloid Interface Sci.* **2009**, *14*, 81–93.
(4) Constable, E. *Chem. Soc. Rev.* **2007**, *36*, 246–253.
(5) Thompson, A. M. W. C. *Coord. Chem. Rev.* **1997**, *160*, 1–52.
(6) Chiper, M.; Meier, M. A. R.; Wouters, D.; Hoeppener, S.; Fustin, C. A.; Gohy, J. F.; Schubert, U. S. *Macromol. Chem. Phys.* **2007**, *208*, 679–689.
(7) Chiper, M.; Meier, M. A. R.; Wouters, D.; Hoeppener, S.; Fustin, C. A.; Gohy, J. F.; Schubert, U. S. *Macromolecules* **2008**, *41*, 2771–2777.
(8) Lohmeijer, B. G. G.; Schubert, U. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3835–3829.
(9) Guillet, P.; Fustin, C. A.; Wouters, D.; Hoeppener, S.; Schubert, U. S.; Gohy, J. F. *Soft Matter* **2009**, *5*, 1460–1465.
(10) Wu, X.; Fraser, C. L. *Macromolecules* **2000**, *33*, 4053–4060.
(11) Fiore, G. J.; Klinkenburg, J. L.; Fraser, C. L. *Macromolecules* **2008**, *41*, 9397–9405.
(12) Fiore, G. L.; Edwards, J. M.; Payne, S. J.; Klinkenberg, J. L.; Gioeli, D. G.; Demas, J. N.; Fraser, C. L. *Biomacromolecules* **2007**, *8*, 2829–2835.
(13) Lamda, J. J. L.; Fraser, C. L. *J. Am. Chem. Soc.* **1997**, *119*, 1801–1802.
(14) Wu, X. F.; Collings, J. E.; McAlvin, J. E.; Cutts, R. W.; Fraser, C. L. *Macromolecules* **2001**, *34*, 2812–2821.
(15) Guillet, P.; Fustin, C. A.; Mugemana, C.; Ott, C.; Schubert, U. S.; Gohy, J. F. *Soft Matter* **2008**, *4*, 2278–2282.
(16) Aamer, K.; de Jeu, W.; Tew, G. N. *Macromolecules* **2008**, *41*, 2022–2029.
(17) Shunmugam, R.; Tew, G. N. *Polym. Adv. Technol.* **2007**, *18*, 940–945.
(18) Shunmugam, R.; Tew, G. N. *Polym. Adv. Technol.* **2008**, *19*, 596–601.
(19) El-ghayoury, A.; Hofmeier, H.; de Ruiter, B.; Schubert, U. S. *Macromolecules* **2003**, *36*, 3955–3959.
(20) Lohmeijer, B. G. G.; Schubert, U. S. *J. Polym. Sci., Polym. Chem.* **2005**, *43*, 6331–6344.
(21) Fraser, C. L.; Smith, A. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 4704–4716.
(22) McAlvin, J. E.; Fraser, C. L. *Macromolecules* **1999**, *32*, 6925–6932.
(23) Zhou, G. C.; Harruna, I. I. *Macromolecules* **2004**, *37*, 7132–7139.
(24) Zhou, G. C.; He, J. B.; Harruna, I. I. *J. Polym. Sci., Polym. Chem.* **2007**, *45*, 4225–4239.
(25) Zhou, G. C.; Harruna, I. I.; Ingram, C. W. *Polymer* **2005**, *46*, 10672–10677.
(26) Zhang, L.; Zhang, Y.; Chen, Y. *Eur. Polym. J.* **2006**, *42*, 2398–2406.
(27) Lohmeijer, B. G. G.; Schubert, U. S. *Polym. Mater. Sci. Eng.* **2001**, *85*, 460.
(28) Hien, O.; Eschbaumer, C.; Schubert, U. S. *Macromol. Rapid Commun.* **2000**, *21*, 1156–1161.
(29) Ziegler, K.; Zeiser, H. *Liebigs Ann.* **1931**, *485*, 174–192.
(30) Ziegler, K.; Zeiser, H. *Chem. Ber.* **1930**, *63*, 1847.
(31) Barr, D.; Snaith, R.; Mulvey, R. E.; Reed, R. F. *Polyhedron* **1988**, *8*, 665–668.
(32) Ireland, R. E.; Meissner, R. S. *J. Org. Chem.* **1991**, *56*, 4566–4568.
(33) Gosnell, A. B.; Gervasi, J. A.; Woods, D. K.; Stannet, V. *J. Polym. Sci., Part C: Polym. Symp.* **1969**, *22*, 611–620.
(34) Quirk, R. P.; Corona-Galvan, S. *Macromolecules* **2001**, *34*, 1192–1197.
(35) Guerrero-Sanchez, C. A.; Lohmeijer, B. G. G.; Meier, M. A. R.; Schubert, U. S. *Macromolecules* **2005**, *38*, 10388–10396.
(36) Ott, C.; Pavlov, G. M.; Guerrero-Sanchez, C. A.; Schubert, U. S. *J. Polym. Sci., Polym. Chem.* **2009**, *47*, 3691–3701.
(37) Ndoni, S.; Papadakis, C. M.; Bates, F. S.; Almdal, K. *Rev. Sci. Instrum.* **1995**, *66*, 1090–1095.
(38) Fetters, L. J.; Firer, E. M. *Polymer* **1977**, *18*, 306–307.
(39) Quirk, R. P.; Chen, W. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2993–3000.
(40) Morton, M.; Fetters, L. J. *J. Polym. Sci., Part A* **1964**, *2*, 3311–3326.
(41) Constable, E. C.; Baum, G.; Bill, E.; Dyson, R.; van Eldik, R.; Fenske, D.; Kaderli, S.; Morris, D.; Neubrand, A.; Neuburger, M.; Smith, D. R.; Wieghardt, K.; Zehnder, M.; Zuberbuhler, A. D. *Chem.—Eur. J.* **1999**, *5*, 498–508.
(42) Bertini, I.; Luchinat, C. *Coord. Chem. Rev.* **1996**, *150*, 1–296.