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Synthesis of Terpyridine-Terminated Polymers by Anionic Polymerization

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ABSTRACT: The synthesis of terpyridine-functionalized polystyrene was achieved by reacting 4′-chloro-2,2′:6′,2″-terpyridine (terminating agent) with "living" polymeric carbanions synthesized by anionic polymerization. The obtained polymers were characterized by gel permeation chromatography, nuclear magnetic resonance, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, elemental analysis, and ultraviolet−visible absorption spectroscopy. The conversion of the polystyryllithium species into the corresponding 1,1-diphenylalkyllithium chain ends by reaction with 1,1-diphenylethylene (DPE) was a necessary step in order to promote an efficient chain-end functionalization and to avoid undesired side reactions (coupling) between the polymer chains due to the high reactivity of the polystyryl anion. Moreover, the obtained well-defined terpyridine-terminated polystyrenes were used for the synthesis of self-assembled metallo-supramolecular block copolymers.

Introduction

Metal-containing polymers have been the topic of great attention in recent years due to their wide range of potential applications. These materials have shown interesting properties such as optical activity, electrical conductivity, luminescence, and photorefractivity.[1] Metal-containing polymers have also opened a new avenue for the formation of novel supramolecular structures: double helicates, dendrimers, ordered architectures on surfaces, and self-assembled block copolymers.[2] Incorporation of suitable metal-complexing ligands into the polymer chains is a critical step for the formation of well-defined materials. Bipyridine and terpyridine ligands are among the most frequently used compounds to act as metal-complexing ligands in polymer architectures.[3] Terpyridine ligands self-assemble with different transition-metal ions in low oxidation states (Mn, Fe, Ru, Os, Co, Ir, Ni, Pt, Cu, Ag, Zn, Cd, and Hg) into octahedral complexes.[4] For this purpose, the outer rings cooperatively rotate along the central C−C bonds connecting the rings to create a stable binding site through the lone pairs of three nitrogen atoms.[5] Didentate ligands, such as bipyridine or phenanthroline, on the other hand, give rise to two different conformations (fac and mer stereoisomers) around an octahedral metal ion,[6] which are not so easy to selectively control.[7] Several synthetic strategies for the incorporation of terpyridine ligands into the polymer chains have been reported: end-group modification, copolymerization of terpyridine-modified monomers, functionalized initiators, and end-cappers.[2d,e] For the end-group modification strategy hydroxy-terminated polymers have been employed as precursors using etherification and urethane-formation reactions. For implementing terpyridine moieties into the polymer chains via copolymerization, terpyridine-containing monomers have been utilized, e.g., applying free-radical polymerization methods.[8] Finally, functionalized initiators have been applied successfully in cationic ring-opening polymerization, atom transfer radical polymerization (ATRP), and nitroxide-mediated radical polymerization (NMP).[2d] However, all these procedures show some drawbacks, from rather demanding organic synthesis procedures for the initiators or monomers to several purification steps of the obtained polymers.

Nowadays, perfect control over molecular architecture is one of the most important goals in polymer science because this determines to a large extent the final material properties. In this context controlled/living polymerization techniques offer the synthesis of polymers with tunable chain length and low polydispersity indices as well as the possibility to build well-defined block copolymers. Even though some of the modern controlled/living polymerization strategies have been applied for the incorporation of metal-complexing ligands into polymer chains, up to now living anionic polymerizations have never been used for this purpose. Living anionic polymerizations offer important advantages over other polymerization techniques:[9] short reaction time, good control over the molecular weight, low polydispersity indices, and straightforward synthesis of block copolymers and complex polymeric architectures. It is also well known from the literature that living anionic polymerization is a suitable, efficient, and straightforward technique to synthesize functionalized polymers.[10] Moreover, it has been found that the conversion of the polymeric organolithium chain ends to 1,1-diphenylalkyllithium chain ends (by reaction with 1,1-diphenylethylene) promotes an efficient chain-end functionalization for several systems.[10b] Among the examples of functionalized polymers via anionic polymerization are the synthesis of 1,2-dicarboxyethyl,[11] nitroxide,[12] dimethylamino,[13] and 2-bromoisobutyryl[14] terminated polymers. However, the main "drawback" of living anionic polymerization is the requirement of stringent reaction conditions (moisture- and oxygen-free atmosphere) to proceed in a proper way.[15]

In this contribution, the synthesis of terpyridine-terminated polystyrenes via anionic polymerization is investigated. This approach opens alternative routes for

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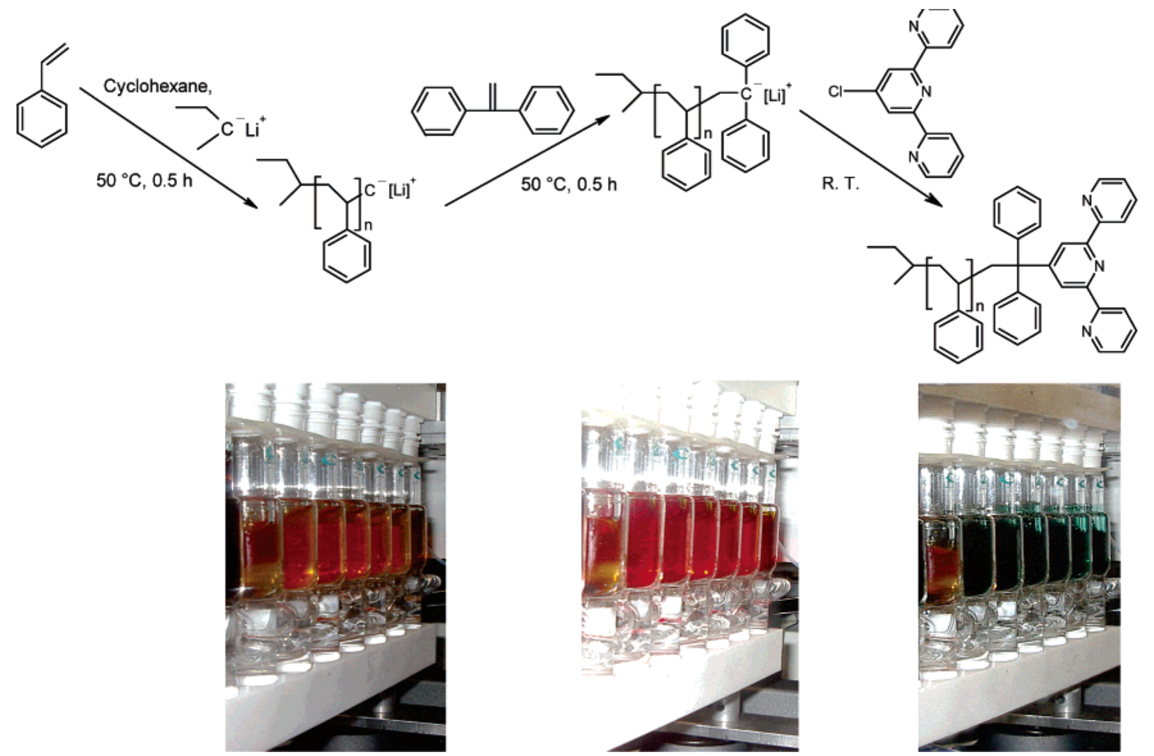
Scheme 1. Reaction Scheme for the Synthesis of Terpyridine-Terminated Polystyrene via Anionic Polymerization as Well as the Corresponding Visual Impression of the Reaction Steps in a Chemspeed ASW2000 Automated Synthesizer



an efficient synthesis of terpyridine-functionalized polymers because the obtained materials have no ether/urethane linkages (present in other synthetic procedures), which may improve the chemical stability of the polymer chains. The characterization of the materials by GPC, ^{1}H NMR, elemental analysis, MALDI-TOF-MS, and UV−vis spectroscopy is described in detail. Finally, the formation of metallo-supramolecular block copolymers using the functionalized polymers is discussed.

Experimental Section

Reagents and Solvents. All solvents and monomers were distilled after the corresponding drying procedure and stored under argon.[15] Cyclohexane and toluene (Biosolve) were distilled from polystyryllithium oligomers. Tetrahydrofuran (Biosolve) was refluxed and distilled from a deep purple sodium−benzophenone complex solution. 1,1-Diphenylethylene (Aldrich) was dried over *sec*-butyllithium and distilled under vacuum. Styrene (Acros Organics) was refluxed over calcium hydride (Aldrich) for 24 h, distilled under reduced pressure, and stored at −25 °C. *sec*-Butyllithium (1.4 M) in cyclohexane (Aldrich) was used as received. 4′-Chloro-2,2′:6′,2″-terpyridine was purified by repeated sublimation. Methanol (Biosolve) was degassed with argon for 15 min just prior to use. *N,N*-Dimethylformamide (anhydrous Biosolve) and *N,N*-dimethylacetamide (anhydrous Aldrich) were dried over molecular sieves and degassed with argon for 15 min just prior to use. All other solvents and reagents were used as received: chloroform (Biosolve), ruthenium(III) chloride ($RuCl_3$) (anhydrous Aldrich), iron(II) chloride ($FeCl_2$) (anhydrous Aldrich), and silver tetrafluoroborate ($AgBF_4$) (Aldrich).

Polymerization and Functionalization. Anionic polymerizations were performed in a Chemspeed ASW2000 synthesizer, comprising up to 20 glass reactors of 75 mL or 80 glass reactors of 13 mL equipped with heating/cooling jacket, a glovebox for inert atmosphere, vortex stirring system (0−1400 rpm), heating/cooling system (−90 to 150 °C), and a fully automated liquid handling system. The use of this synthesizer enables carrying out the experiments under the same reactions conditions (same sort of reactors, same inert atmosphere, same experimental error, etc.), and therefore the obtained results are easily comparable and reproducible.[16] In a typical procedure the anionic synthesis of polystyrenes and their functionalization with terpyridine units was performed as follows: a predetermined amount of styrene was added into the reactors of the synthesizer containing a predetermined amount of cyclohexane at 50 °C and 450 rpm of vortexing under an argon atmosphere. Addition of *sec*-butyllithium into the reactors started the polymerization yielding the characteristic orange-yellow color of the polystyryl anion. After 0.5 h of reaction, 1.25 molar excess (with respect to *sec*-butyllithium) of 1,1-diphenylethylene was introduced into the reaction media, turning the solution red. An intermediate step at this stage consisted in withdrawing an aliquot of the reaction media for GPC characterization of the unfunctionalized polystyrene. After another 0.5 h, a predetermined volume (1.25 molar excess with respect to *sec*-butyllithium) of a solution of 4′-chloro-2,2′:6′,2″-terpyridine in tetrahydrofuran or toluene was added into the reactor. Immediately the reaction showed a deep blue color. Subsequently, the reaction mixtures were kept under an argon atmosphere overnight at room temperature. Methanol was added into the reactors to finish the reaction (the blue color of the mixture disappeared with the addition of methanol). A reaction scheme of the functionalization process is shown in Scheme 1 as well as a view of the Chemspeed ASW2000 automated synthesizer during the different stages of the process. Purification of the polymers was performed with three cycles of dissolution−precipitation steps (chloroform/methanol) to remove the unreacted 4′-chloro-2,2′:6′,2″-terpyridine. The obtained materials were dried at 50 °C under vacuum for 24 h and subsequently characterized.

Synthesis of Metallo-supramolecular Block Copolymers. Complexation experiments for the synthesized terpyridine-terminated polystyrenes were performed as follows. Ru(III) monocomplexes were obtained by heating a solution of $RuCl_3$ in *N,N*-dimethylacetamide at 130 °C in an oil bath with magnetic stirring followed by the dropwise addition of a solution of terpyridine-terminated polystyrene in *N,N*-dimethylacetamide to obtain a 2-fold molar excess of $RuCl_3$ with

Table 1. GPC Results for Different Terpyridine-Terminated Polystyrenes Synthesized via Anionic Polymerization (4′-Chloro-2,2′:6′,2″-terpyridine Dissolved in Toluene and in Tetrahydrofuran)

expt	M_n (reference polystyrene)	PDI	end-capping with 1,1-diphenylethylene	solvent for 4′-chloro-2,2′:6′,2″-terpyridine	M_n (terpyridine-terminated polystyrene)	PDI
1	1500	1.16	yes	tetrahydrofuran	1800	1.11
2	2200	1.16	yes	tetrahydrofuran	2300	1.15
3	2700	1.12	yes	tetrahydrofuran	2800	1.17
4	3500	1.12	yes	tetrahydrofuran	3700	1.14
5	5100	1.11	yes	tetrahydrofuran	5300	1.15
6	8500	1.09	yes	tetrahydrofuran	8800	1.13
7	7500	1.06	yes	toluene	7800	1.09
8	7500	1.06	yes	toluene	7700	1.09
9	10600	1.07	yes	toluene	11000	1.10
10	10600	1.07	yes	toluene	11400	1.10
11	18700	1.11	yes	toluene	20600	1.13
12	18700	1.11	yes	toluene	20500	1.12
13	10600	1.07	No	toluene	17000	1.32

respect to the polymer. Bis-complexation: a solution of $RuCl_3$ monocomplex terpyridine-terminated poly(ethylene oxide) (M_n = 3100 g/mol)[17] in *N,N*-dimethylformamide was heated at 130 °C in an oil bath with magnetic stirring in the presence of 3 equiv of $AgBF_4$. Subsequently, a solution of terpyridine-terminated polystyrene (in *N,N*-dimethylformamide) was added dropwise to obtain a 1.2-fold molar excess of terpyridine-terminated polystyrene. For both, mono- and bis-complexation experiments, the concentration of the polymer was 10 wt % and the reaction time was 6 h.

Characterization Techniques. GPC measurements were performed on a Shimadzu system with an SCL-10A system controller, an LC-10AD pump, an RID-6A refractive index detector, and a Polymer Laboratories Plgel 5 μm Mixed-D column. A solution of 4% triethylamine and 2% 2-propanol in chloroform was used as an eluent at a flow rate of 1 mL/min. Molecular weights were calculated against polystyrene standards. For GPC characterization, aliquots from the reactors of the synthesizer were withdrawn[16] before and after the addition of 4′-chloro-2,2′:6′,2″-terpyridine solutions into the reaction mixtures of "living" polystyryl anions. All protonated polystyrenes (reference samples, before functionalization) showed a single narrow peak (polydispersity indices varied between 1.06 and 1.16). The calculated molecular weights (according to the used monomer/initiator ratio) of the synthesized polystyrenes were in agreement with the obtained values from GPC. Experimental molecular weight values of the different synthesized polystyrenes varied from 1500 to 18 700 g/mol. A summary of the GPC results of the experiments (reference polystyrene and the corresponding terpyridine-terminated polystyrene) is given in Table 1. An additional GPC system (Waters) equipped with photodiode array and refractive index detectors was used for the characterization of the metal-containing supramolecular polymeric complexes.[18] A solution of 5 mM NH_4PF_6 in *N,N*-dimethylformamide was used as an eluent at a flow rate of 0.5 mL/min with 50 °C column temperature (polystyrene/divinylbenzene cross-linked beads). ^1H NMR spectra were recorded on a Varian Gemini 400 spectometer using deuterated chloroform (Cambridge Isotopes Laboratories) at room temperature. MALDI-TOF-MS analysis was performed on a Voyager-DE PRO Biospectrometry workstation (Applied Biosystems) in linear operation mode. Spectra were obtained in positive ion mode, and ionization was performed with a 337 nm pulsed nitrogen laser. Data were processed using the Data Explorer software package (Applied Biosystems). UV−vis analysis was carried out on a Perkin-Elmer Lambda 45 UV−vis spectrometer using quartz cuvettes (1 cm path length). For UV−vis titrations, solutions of different terpyridine-terminated polystyrenes in chloroform were titrated with a solution of $FeCl_2$ in methanol of known concentration and followed by UV−vis spectroscopy (see Supporting Information for details of this method). Elemental analyses were recorded on a Euro elemental analyzer from EuroVector. Efficiency of functionalization of the different synthesized terpyridine-terminated polystyrenes was determined from the nitrogen content obtained from elemental analysis or from the complex formation process during UV−vis titrations and the molecular weights as determined by GPC or MALDI-TOF-MS.

Results and Discussion

Functionalization Process. During the experiments of the synthesis of terpyridine-terminated polystyrenes via anionic polymerization, three main parameters were investigated: (I) use of 1,1-diphenylethylene as an end-capper of the polystyryl anion, (II) use of tetrahydrofuran for dissolving 4′-chloro-2,2′:6′,2″-terpyridine, and (III) use of toluene for dissolving 4′-chloro-2,2′:6′,2″-terpyridine. Other experimental parameters with less relevance for the functionalization procedure of polystyrene, such as the length of the polymer chains, were also investigated. However, no significant influence on the synthetic approach was observed. Therefore, the discussion of experimental results is mainly focused on the variation of those three main parameters mentioned above.

The starting point to achieve the synthesis of terpyridine-terminated polystyrenes via anionic polymerization was the investigation of the reaction between the anionically synthesized polystyryllithium moieties and 4′-chloro-2,2′:6′,2″-terpyridine (dissolved in toluene). For this reaction, one can expect a direct electrophilic attack of 4′-chloro-2,2′:6′,2″-terpyridine to the living polymeric carbanion in order to yield the corresponding terpyridine-terminated polymer and the chloride salt (here lithium chloride). Figure 1a (experiment 13 of Table 1) shows that the obtained polymer revealed two distributions in the GPC trace (gray line). One of these peaks appears at the same position of the unfunctionalized polystyrene (methanol-terminated polystyryllithium, black line), and the other one arises at a lower elution time (with about the double number-average molecular weight of the protonated polystyryllithium). This finding suggests the presence of undesired coupling reactions between "living" polystyrene chains. Moreover, ^1H NMR characterization of these polymers revealed only signals for the aromatic protons of polystyrene (region from 6.2 to 7.4 ppm) and the absence of the signals corresponding to the terpyridine moiety (region from 7.4 to 8.7 ppm), as is shown in Figure 2a (experiment 13 of Table 1). Similar experiments were performed using tetrahydrofuran instead of toluene for dissolving 4′-chloro-2,2′:6′,2″-terpyridine in order to investigate potential solvent effects. However, GPC and ^1H NMR results showed qualitatively the same behavior (two signals in the GPC traces and no signals for the terpyridine moiety in the ^1H NMR spectra). According to these results, one can conclude that this synthetic approach is far away from

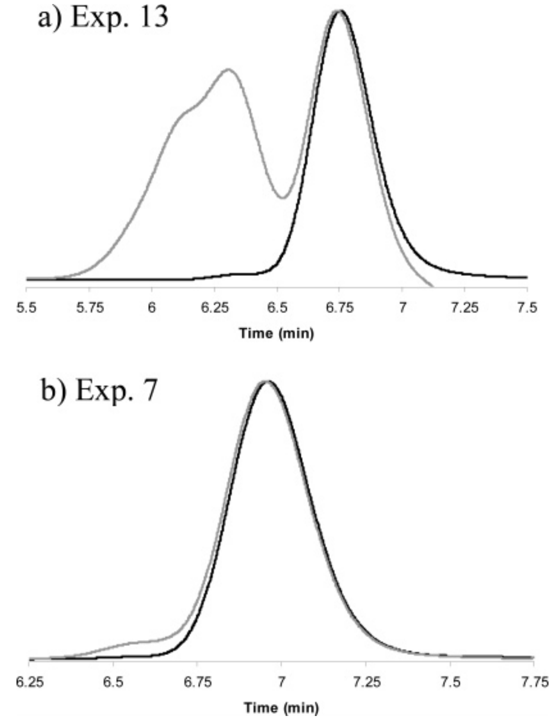


Figure 1. Normalized GPC traces (eluent 4% triethylamine and 2% 2-propanol in chloroform) for diferent polystyrenes. (a) Protonated (black line) and 4′-chloro-2,2′:6′,2″-terpyridine-terminated (gray line) polystyryllithium of experiment 13 of Table 1 (no end-capping with 1,1-diphenylethylene used). (b) Protonated (black line) and 4′-chloro-2,2′:6′,2″-terpyridine-terminated (gray line) polystyryllithium of experiment 7 of Table 1 (end-capping with 1,1-diphenylethylene used).

representing an efficient procedure to obtain well-defined terpyridine-terminated polystyrenes via anionic polymerization.

The conversion of polymeric organolithium chain ends to the corresponding 1,1-diphenylalkyllithium chain ends by reaction with 1,1-diphenylethylene is known to reduce effectively the reactivity of the chain ends.[10b] It is reported that the steric hindrance provided by the addition of 1,1-diphenylethylene to the highly reactive polystyryllithium anions avoids the broadening of the molecular weight distribution caused by the undesired coupling reactions between the "living" polymer chains.[11] Therefore, the next step toward the synthesis of well-defined terpyridine-terminated polystyrenes was the use of 1,1-diphenylethylene as a protective agent of the polystyryl anion in order to reduce its reactivity and to promote an efficient functionalization reaction. The approach is displayed in Scheme 1. GPC results revealed that for the case when the 1,1-diphenylethylene is used for end-capping the polystyryl anions the obtained polymers revealed narrow molecular weight distributions (single peaks), and their elution time was almost the same with respect to the reference (protonated) polystyrenes. A characteristic example of this is shown in Figure 1b (experiment 7 of Table 1).

The effect of 1,1-diphenylethylene as end-capper for the polystyryl anions during the functionalization procedure can be also seen in the ^{1}H NMR spectra of the isolated products . Parts b and c of Figure 2 show the ^{1}H NMR spectra of the obtained polymers from experiments 7 and 12 of Table 1, respectively. When using the 1,1-diphenylethylene end-capping approach, besides the signals of the aromatic protons of polystyrene (region from 6.2 to 7.4 ppm), in the ^{1}H NMR spectra four signals related to the aromatic protons of the terpyridine moiety arose in the region from 7.4 to 8.7 ppm. A tiny shoulder of the fifth signal corresponding to the terpyridine part at 7.3 ppm can be also observed; however, it is overlapped with the aromatic signals of the polystyrene part and chloroform. It is also worth mentioning that the ^{1}H NMR signals of the terpyridine part become less intense as the molecular weight of the polymers increases for the different synthesized polystyrenes. For example, for one of the highest molecular weight samples (Figure 2c, experiment 12 of Table 1), the signals for the terpyridine part are still visible in the ^{1}H NMR spectrum. This is not the case when 1,1-diphenylethylene was not used as end-capper and the undesired coupling reaction occurred (Figure 2a, experiment 13 of Table 1), even though the final molecular weight of this sample was smaller than the one of the experiment 12 of Table 1. The ^{1}H NMR spectra were also used to estimate the molecular weight of the polymers by integration of the terpyridine signals and

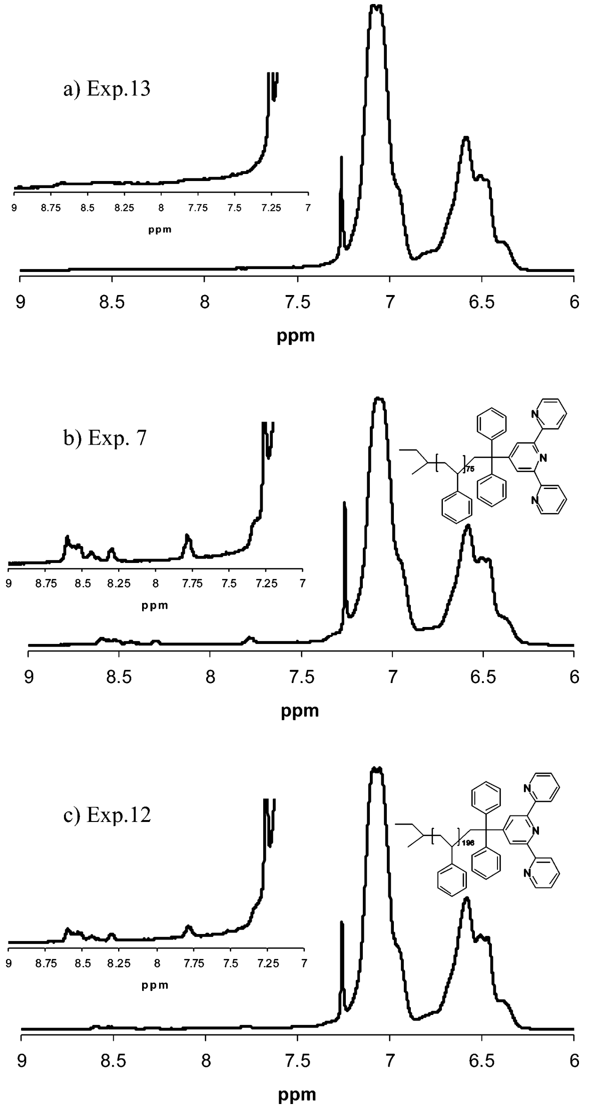


Figure 2. ^{1}H NMR spectra for some of the synthesized terpyridine-terminated polystyrenes in $CDCl_3$ at room temperature: (a) Polymer from the reaction of polystyryllithium with 4′-chloro-2,2′:6′,2″-terpyridine (experiment 13 of Table 1, no end-capping with 1,1-diphenylethylene used). (b) Experiment 7 of Table 1 and (c) experiment 12 of Table 1 (polymers from the reaction of 1,1-diphenylethylene end-capped polystyryllithium with 4′-chloro-2,2′:6′,2″-terpyridine).

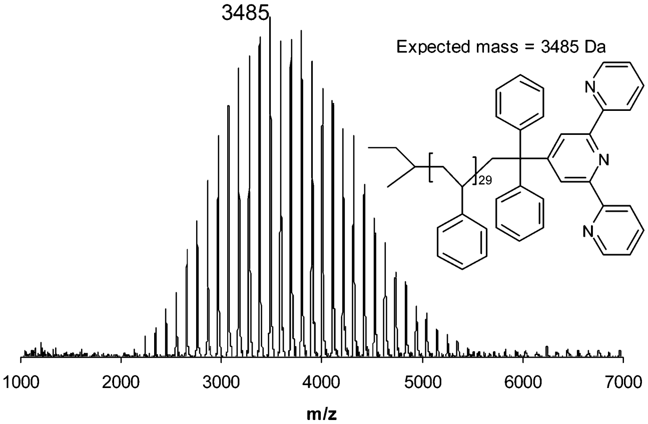


Figure 3. MALDI-TOF-MS spectrum for one of the synthesized terpyridine-terminated polystyrenes via anionic polymerization (experiment 3 of Table 1).

the aromatic signals of polystyrene. Calculations of the molecular weights by this method were in good agreement with those obtained by GPC (Table 1).

MALDI-TOF-MS is a suitable technique to perform end-group analysis of polymers and to determine their absolute molecular weight.[19,20] Figure 3 shows the MALDI-TOF-MS spectrum of the polymer of experiment 3 of Table 1. The spectrum clearly reveals chemical species matching with the mass of different terpyridine-terminated polystyrene chains (only one distribution series can be seen). The distance between the peaks of the spectrum corresponds to the mass of styrene (104 Da). Moreover, the expected mass of a terpyridine-functionalized polystyrene with 29 styrenic units is 3485 Da, which was experimentally found in the MALDI-TOF-MS spectrum of the polymer of Figure 3. This finding clearly proves that the synthesis of terpyridine-terminated polystyrene by anionic polymerization is feasible. Moreover, the molecular weights of the polymers found by MALDI-TOF-MS were again in good agreement with those found by GPC (Table 1) and ^{1}H NMR.

For all synthesized terpyridine-terminated polystyrenes (except the one from experiment 13 of Table 1 when the undesirable coupling reaction occurred), the content of nitrogen was determined by elemental analysis; therefore, the efficiency of the functionalization can be quantified using these data (see Supporting Information for a detailed explanation). Calculation of the expected content of nitrogen in the polymers (theoretical value) was performed utilizing the molecular weight (M_n) found by GPC (terpyridine-terminated polystyrene values of Table 1). For example, for the polymer of experiment 3 the M_n found by GPC was 2800 g/mol; the closest molecular weight to this value corresponds to a terpyridine-terminated polystyrene (final compound in Scheme 1) with 22 styrenic units (molecular weight of 2761 g/mol), and therefore the expected nitrogen content is 1.52%. Figures 4 and 5 show the efficiency of the functionalization process for the case when tetrahydrofuran was used for dissolving 4′-chloro-2,2′:6′,2″-terpyridine (experiments 1−6 of Table 1) and for the case when toluene was used for dissolving 4′-chloro-2,2′:6′,2″-terpyridine (experiments 7−12 of Table 1), respectively. Figure 4 reveals that the use of tetrahydrofuran for dissolving 4′-chloro-2,2′:6′,2″-terpyridine has an influence in the efficiency of the functionalization (60−70% efficiency). Even though tetrahydrofuran was purified with the standard procedure reported in the literature (distilled from a deep purple sodium−benzophenone complex solution), it is difficult to conclude whether the lower efficiency in this case is due to the high polarity of the THF (chemical effect) or due to impurity traces in the solvent. Further experiments are required to allow a final conclusion regarding this effect. However, when 4′-chloro-2,2′:6′,2″-terpyridine is dissolved in a less polar solvent, such as toluene, the efficiency of the functionalization process is considerably increased up to values close to 100%, as can be seen in Figure 5.

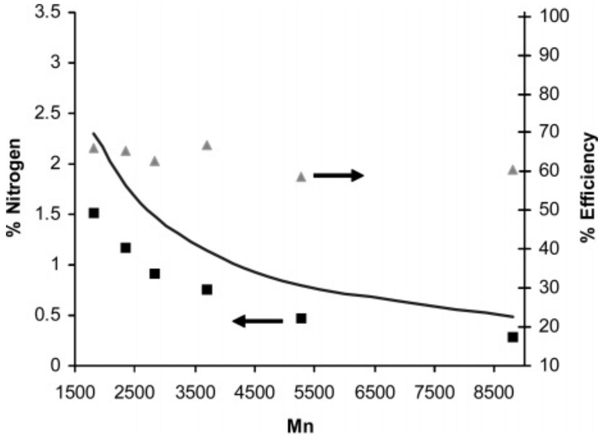


Figure 4. Efficiency of the synthesis of terpyridine-functionalized polystyrenes via anionic polymerization (when tetrahydrofuran is used for dissolving 4′-chloro-2,2′:6′,2″-terpyridine) determined by elemental analysis and GPC data from Table 1. Theoretical values for the content of nitrogen in the polymers in % (solid line), experimental values for the content of nitrogen in the polymers in % (black squares), and obtained values of the efficiency of the functionalization process (gray triangles).

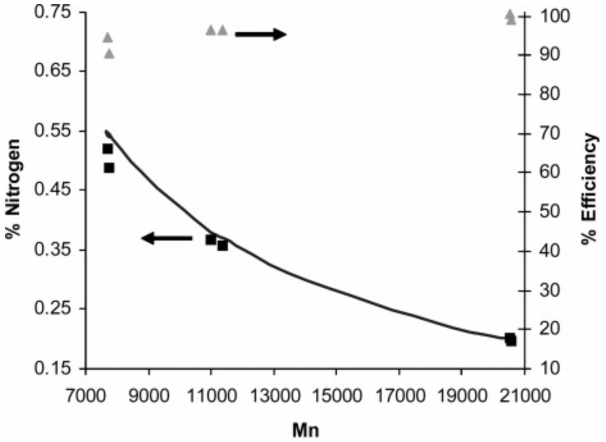


Figure 5. Efficiency of the synthesis of terpyridine-functionalized polystyrenes via anionic polymerization (when toluene is used for dissolving 4′-chloro-2,2′:6′,2″-terpyridine) determined by elemental analysis and GPC data from Table 1. Theoretical values for the content of nitrogen in the polymers in % (solid line), experimental values for the content of nitrogen in the polymers in % (black squares), and obtained values of the efficiency of the functionalization process (gray triangles).

UV−vis titration analysis represents an additional technique to characterize and quantify the degree of terpyridine modification.[21] For this purpose, the obtained terpyridine-terminated polystyrenes were titrated with $FeCl_2$. An increase of the metal-to-ligand charge-transfer (MLCT) band of the iron(II) complex at 565 nm was observed, which is typical for these experiments (Figure 6, titration of the polymer from experiment 7 of Table 1). For this analysis, the titration

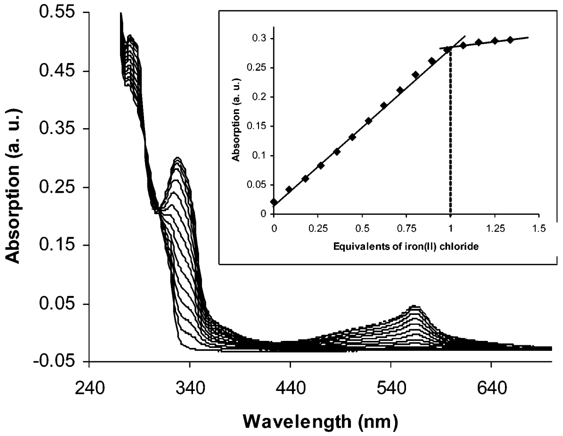


Figure 6. UV−vis titration for a terpydine-terminated polystyrene (experiment 7 of Table 1) with $FeCl_2$.

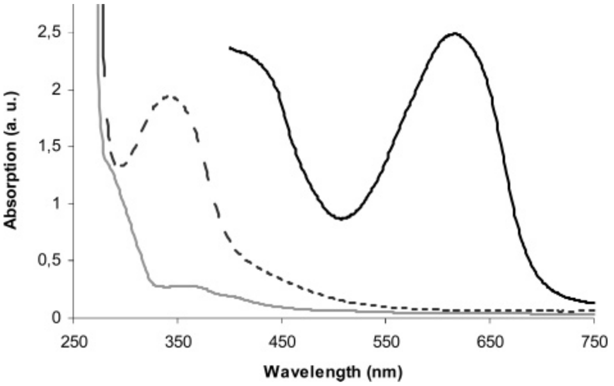


Figure 7. UV−vis spectra for different chemical species present during the synthesis procedure of terpyridine-terminated polystyrene via anionic polymerization. Polystyryllithium (dashed line), polystyryllithium reacting with 4′-chloro-2,2′:6′,2″-terpyridine (black line) (both samples taken directly from the inert reaction media (cyclohexane)), and isolated polystyrene after functionalization (chloroform) (gray line).

process can be also monitored following the appearance of the signal at 329 nm. A plateau was reached after a linear increase with the addition of $FeCl_2$, indicating the complete complexation of the material as shown in the inset in Figure 6. The equivalence point was approximately observed at a ligand-to-metal ratio of 2:1, indicating quantitative complexation (see Supporting Information for details of this technique). Utilizing the results of theses experiments, it is also possible to calculate the efficiency of the functionalization process in a similar way as discussed for the elemental analysis results. Calculation of the efficiency for the obtained terpyridine-terminated polystyrenes with the UV−vis titration data resulted in similar findings as those obtained by the elemental analysis data. These results are additional proof that the efficiency of the functionalization was around 70% when tetrahydrofuran was used for dissolving 4′-chloro-2,2′:6′,2″-terpyridine and was around 100% for the case of toluene.

The change of color of the reaction mixtures during the synthesis of terpyridine-terminated polystyrenes via anionic polymerization is also worth mentioning (Scheme 1). This effect was studied by UV−vis spectroscopy. Figure 7 shows the change in the absorption spectra for some of the different stages during the synthesis procedure. The characteristic peak of polystyryllithium appears at 338 nm (orange-yellow color solutions in Scheme 1).[22] Immediately after the addition of 4′-chloro-2,2′:6′,2″-terpyridine (in solution) into the reaction mixture, a new band appeared at 617 nm (deep blue solutions in Scheme 1) vanishing the preceding peaks corresponding to the polystyryllithium and the 1,1-diphenylalkyllithium chain end (red solutions in Scheme 1, not shown in Figure 7). The UV−vis spectrum for the recovered terpyridine-terminated polystyrene in chloroform is also shown in Figure 7. The observed deep blue color in the reaction media may have originated from the electrophilic attack of 4′-chloro-2,2′:6′,2″-terpyridine to the anionic polymer chain ends. This color appeared also in the reaction mixtures where 1,1-diphenylethylene was not used as end-capper of the polystyryl anion (experiment 13 of Table 1 (Figures 1a and 2a)).

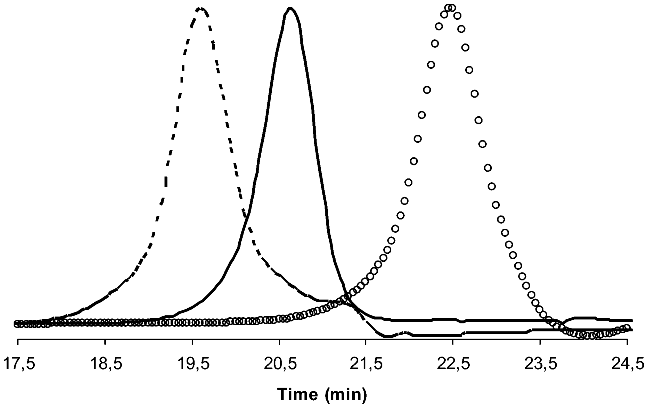
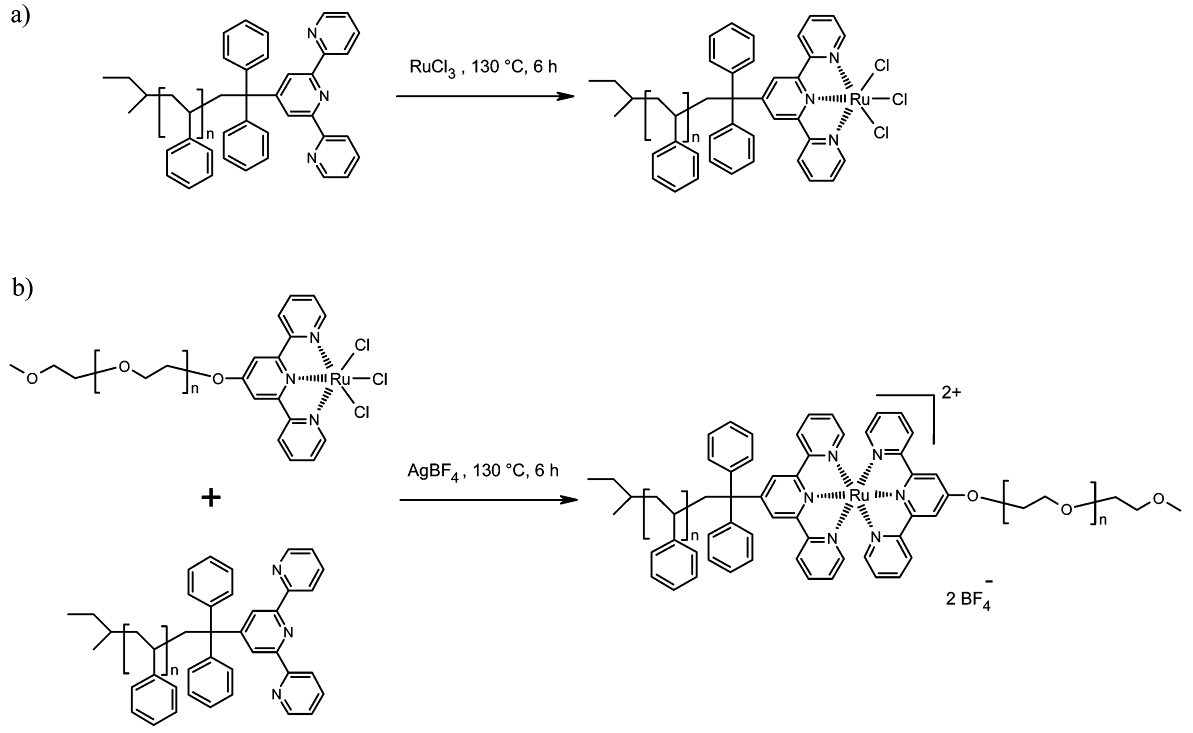


Figure 8. Normalized GPC traces (eluent; 5 mM NH_4PF_6 in *N,N*-dimethylformamide) of a self-assembled metallo-supramolecular block copolymer polystyrene-*b*-poly(ethylene oxide) after purification by preparative size exclusion chromatography (dashed line) and its precursors terpyridine-terminated polystyrene (open circles, experiment 8 of Table 1) and $RuCl_3$ monocomplex of terpyridine-terminated poly(ethylene oxide)[17] (solid line).

Formation of Metallo-supramolecular Polymeric Complexes. The main objective of the following discussion concerning the synthesis of metallo-supramolecular polymeric complexes is to provide additional characterization as well as application possibilities of the synthesized terpyridine modified polymers in order to demonstrate that these materials have comparable properties to those obtained by other synthetic approaches. Since the scope of this contribution is, mainly, to establish an alternative route for the synthesis of terpyridine-functionalized polymers via anionic polymerization, a detailed description regarding the characteristics of metallo-supramolecular polymeric complexes[21] (stability, synthesis, purification procedures, characterization, etc.) will not be discussed here in detail. The terpyridine-terminated polystyrenes described within this contribution could be useful materials for the formation of novel block copolymer libraries.[23] Therefore, their ability to form bis(terpyridine)Ru(II) complexes with other polymeric building blocks was investigated. The synthetic procedure of the metallo-supramolecular polymeric mono- and bis-complexes with $RuCl_3$ described in this section was mentioned in the Experimental Section (Scheme 2). The formation of self-assembled metallo-supramolecular block copolymers was achieved reacting one of the terpyridine-terminated polystyrenes with a $RuCl_3$ monocomplex of terpyridine-terminated poly(ethylene oxide) (M_n = 3100 g/mol).[17] Figure 8 shows the GPC traces of the obtained self-assembled metallo-supramolecular block copolymer af-

Scheme 2. Schematic Synthesis of Metallo-supramolecular Polymeric Complexes: (a) Polystyrene $RuCl_3$ Monocomplex; (b) Polystyrene-*b*-poly(ethylene oxide) Bis-Complex (Self-Assembled Metallo-supramolecular Block Copolymer)



ter purification by preparative size exclusion chromatography.[21] Purification is a necessary step in order to remove unreacted precursor monocomplexes and/or homopolymers during the preparation of the diblock copolymers. The traces of the precursor homopolymers ($RuCl_3$ monocomplex of terpyridine-terminated poly(ethylene oxide) and terpyridine-terminated polystyrene) are also included in Figure 8. The difference in the elution times of the GPC traces of the $RuCl_3$ monocomplex of terpyridine-terminated poly(ethylene oxide) and terpyridine-terminated polystyrene precursors shown in Figure 8 can be explained by their hydrodynamic volumes in the *N,N*-dimethylformamide GPC eluent. This GPC system does for instance show lower retention times for polystyrene standards than for poly(ethylene oxide) standards of the same molecular weight due to the smaller hydrodynamic volume of polystyrene in *N,N*-dimethylformamide if compared to poly(ethylene oxide). From the ^1H NMR spectra of the obtained self-assembled metallo-supramolecular block copolymer (polystyrene-*b*-poly(ethylene oxide)) (Figure 9) the block copolymer composition can be determined with respect to the terpyridine signals (7.5−8.5 ppm) and/or the signals of the backbones of each block (aromatic protons of the styrenic block arising between 6.5 and 7.5 ppm and the $O-CH_2$ group of the poly(ethylene oxide) around 3.7 ppm). For this case, the block copolymer composition revealed a content of 46% of poly(ethylene oxide) and a degree of polymerization in acceptable agreement with the expected value. Notice that Figure 9 also shows a shifting of the terpyridine signals in the region of 7.5−8.5 ppm with respect to those presented in Figure 2 where no complexes have been formed. This effect is also an indication for the successful complex formation as reported in the literature.[21] Additionally, UV−vis measurements of the obtained polymeric complexes were recorded and are shown in Figure 10. The spectrum for the $RuCl_3$ monocomplex reveals a band at 400 nm, whereas this latter band disappeared in the spectrum of the Ru(II) bis-complex and a new one arose at 485 nm.

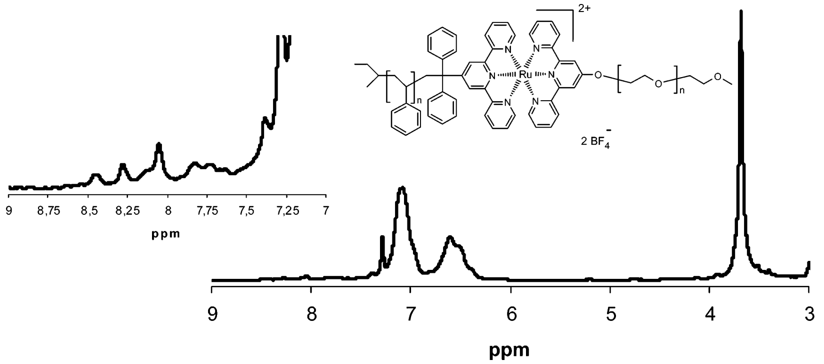


Figure 9. ^1H NMR spectra in $CDCl_3$ at room temperature of an obtained self-assembled metallo-supramolecular block copolymer polystyrene-*b*-poly(ethylene oxide) after purification by preparative size exclusion chromatography (precursors: terpyridine-terminated polystyrene (experiment 8 of Table 1) and $RuCl_3$ monocomplex of terpyridine-terminated poly(ethylene oxide)[17]).

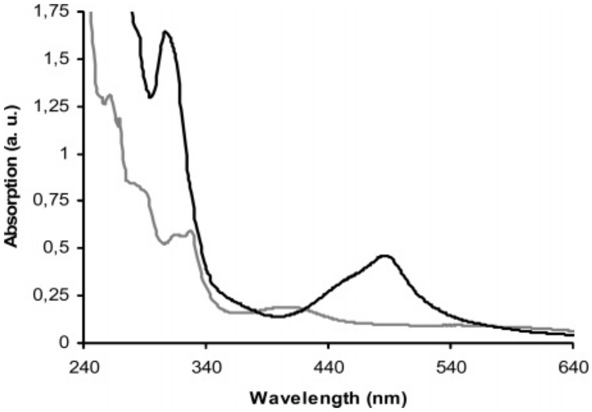


Figure 10. UV−vis measurements for the formation of Ru complexes of some of the synthesized terpyridine-terminated polystyrenes via anionic polymerization: Ru(III) mono-complex of the polymer from experiment 7 of Table 1 (gray line) and Ru(II) bis-complex of the polymer from experiment 8 of Table 1 with poly(ethylene oxide) Ru(III) monocomplex (black line, polystyrene-*b*-poly(ethylene oxide) block copolymer).

Conclusions and Outlook

In the present work an alternative synthetic route for obtaining well-defined terpyridine-functionalized polymers is described. Starting from a conventional synthesis of "living" polystyrene via anionic polymerization in cyclohexane, an intermediate step of end-capping of the polystyryl anion with 1,1-diphenylethylene was found to be necessary to promote an efficient terpyridine functionalization process of the polymer chain and to avoid undesired coupling reactions. Moreover, the process revealed to be highly efficient when toluene was used as a solvent for 4′-chloro-2,2′:6′,2″-terpyridine during the functionalization procedure. The functionalized polymers were fully characterized by the means of GPC, ^{1}H NMR, elemental analysis, MALDI-TOF-MS, and UV−vis spectroscopy. The obtained materials displayed the typical characteristics of terpyridine-containing polymers reported in the literature (i.e., formation of metal complexes and self-assembled block copolymers). Furthermore, the formation of polymeric ruthenium complexes and metallo-supramolecular block copolymers was also achieved using the functionalized polymers. This synthetic route offers some advantages in comparison with the existing routes (i.e., direct functionalization, short reaction times, full control over the chain length of the polymers with low polydispersity index, high efficiency of functionalization) and can be easily scaled up since anionic polymerization is a well-established industrial process. The prepared materials will be used in the future to connect them to a whole range of terpyridine-modified poly(ethylene oxides). Preliminary experimental results have shown the possibility to synthesize also terpyridine-terminated polyisoprene by this route, which will be discussed in the future. Moreover, this route can be an alternative for the synthesis of terpyridine-functionalized polymers such as polybutadiene, polyisoprene, and poly(methyl methacrylate), which are unstable under some reported reaction conditions of other routes.[2d] Furthermore, an outlook for this synthetic procedure may include the direct synthesis of terpyridine-terminated block copolymers (covalent linked) and terpyridine telechelics by using bifunctional anionic initiators such as those reported in the literature.[24]

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Supporting Information Available: Description of GPC as an alternative characterization technique for metallo-supramolecular polymeric complexes, determination of efficiency of functionalized terpyridine-terminated polymers by elemental analysis, and UV−vis titration analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Cho, Y. S.; Lee, H. K.; Lee, J. S. *Macromol. Chem. Phys.* **2002**, *203*, 2495. (b) Juris, A.; Balazani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1998**, *84*, 85. (c) Yu, S. C.; Gong, X.; Chan, W. K. *Macromolecules* **1998**, *31*, 5639. (d) Aoki, A.; Miyashita, T. *Chem. Lett.* **1996**, 563. (e) Kimura, M.; Horai, T.; Hanabusa, K.; Shirai, H. *Adv. Mater.* **1998**, *10*, 549. (f) Gong, X.; Ng, P. K.; Chan, W. K. *Adv. Mater.* **1999**, *11*, 459. (g) Wong, C. T.; Chan, W. K. *Adv. Mater.* **1999**, *11*, 455. (h) Zhu, S. S.; Swager, T. M. *Adv. Mater.* **1996**, *8*, 497.
(2) (a) Lehn, J. M. *Supramolecular Chemistry, Concepts and Perspectives*, VCH: Weinheim, 1995. (b) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689. (c) Salditt, T.; An, Q. R.; Plech, A.; Eschbaumer, C.; Schubert, U. S. *Chem. Commun.* **1998**, 2371. (d) Lohmeijer, B. G. G.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 413. (e) Aamer, K. A.; Tew, G. N. *Macromolecules* **2004**, *37*, 1990.
(3) (a) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373. (b) Newkome, G. R.; Patri, A. K.; Holder, E.; Schubert, U. S. *Eur. J. Org. Chem.* **2004**, 235.
(4) Constable, E. C. *Adv. Inorg. Chem. Radiochem.* **1986**, 69.
(5) Schubert, U. S.; Eschbaumer, C.; Andres, P.; Hofmeier, H.; Weidl, C. H.; Herdtweck, E.; Dulkeith, E.; Morteani, A.; Hecker, N. E.; Feldmann, J. *Synth. Met.* **2001**, *121*, 1249.
(6) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Thomson, A. J. *Inorg. Chim. Acta* **1982**, *64*, L25.
(7) Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chim. Acta* **1986**, *118*, 73.
(8) (a) Schubert, U. S.; Hofmeier, H. *Macromol. Rapid Commun.* **2002**, *23*, 561. (b) Calzia, K. J.; Tew, G. N. *Macromolecules* **2002**, *35*, 6090.
(9) (a) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Dekker: New York, 1996. (b) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747.
(10) (a) Jagur-Grodzinski, J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2116. (b) Quirk, R. P.; Yoo, T.; Lee, Y.; Kim, J.; Lee, B. *Adv. Polym. Sci.* **2000**, *153*, 67.
(11) Zhong, X. F.; Eisenberg, A. *Macromolecules* **1994**, *27*, 4914.
(12) Kobatake, S.; Harwood, H. J.; Quirk, R. P.; Priddy, D. B. *Macromolecules* **1999**, *32*, 10.
(13) Pispas, S, Hadjichristidis, N.; Mays, J. W. *Polymer* **1996**, *37*, 3989.
(14) Acar, M. H.; Matyjaszewski, K. *Macromol. Chem. Phys.* **1999**, *200*, 1094.
(15) (a) Ndoni, S.; Papadakis, C. M.; Bates, F. S.; Almdal, K. *Rev. Sci. Instrum.* **1995**, *66*, 1090. (b) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.
(16) Guerrero-Sanchez, C.; Abeln, C. H.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4151.
(17) Gohy, J. F.; Lohmeijer, B. G. G.; Varshney, S. K.; Schubert, U. S. *Macromolecules* **2002**, *35*, 7427.
(18) Meier, M. A. R.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Rapid Commun.* **2003**, *24*, 852.
(19) Nielen, M. W. F. *Mass Spectrom. Rev.* **1999**, *18*, 309.
(20) Pasch, H.; Schrepp, W. *MALDI-TOF Mass Spectrometry of Synthetic Polymers*; Springer: Berlin, 2003.
(21) Lohmeijer, B. G. G. Playing LEGO with macromolecules: connecting polymer chains using terpyridine metal complexes. Dissertation thesis, Technische Universiteit Eindhoven, Eindhoven, 2004.

(22) Bywater, S.; Johnson, A. F.; Worsfold, D. J. *Can. J. Chem.* **1964**, *42*, 1255.

(23) Lohmeijer, B. G. G.; Wouters, D.; Yin, Z.; Schubert, U. S. *Chem. Commun.* **2004**, 2886.

(24) (a) Yu, J. M.; Dubois, Ph.; Teyssié, Ph.; Jeromé, R. *Macromolecules* **1996**, *29*, 6090. (b) Quirk, R. P.; Ma, J. J. *Polym. Int.* **1991**, *24*, 197.

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