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Incorporation of terpyridine into the side chain of copolymers to create multi-functional materials

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Abstract

Polymer architectures containing metal–ligands in their side chain represent a diverse approach to generating multi-functional materials. The ability to define a versatile synthetic platform will enable many chemistries and architectures to be studied. This report describes our latest efforts to prepare these unique polymers by either a direct polymerization of functionalized monomers or a post-polymerization attachment. Random and block copolymers have been successfully prepared. Subsequent functionalization with metal ions leads to a variety of properties including metal induced gelation and solvochromic sensors.

Keywords: Supramolecular; Terpyridine; Block copolymer

1. Introduction

Hybrid materials are formed by integrating organic and inorganic components into the same molecular backbone leading to a wide variety of advanced properties and applications [1]. This increase in structural complexity can give rise to new properties not foreseen from the single constituting moieties [2]. One such approach is the synthesis of macromolecules containing metal–ligand complexes [3–13]. These complexes impart properties such as luminescence, electro- and photo-chemistry, catalysis, charge, magnetism, and thermochromism [14]. Polymers containing poly pyridyl metal–ligands in their side chain have included polyoxazolines that gelled in the presence of transition metal ions and were thermal reversibility [15–17] and copolymers based on 4′-vinyl-2,2′:6′,2″-terpyridinyl [18–21].

The preparation of polymeric systems containing terpyridine (terpy) in the side chain has been limited mainly due to limited emission properties from transition metal complexes [22,23]. Interestingly, terpy binds a range of lanthanide ions resulting in excellent luminescence which we have studied [24]. As a result there has been increased interest in such polymeric materials, a little more than two years ago our lab and Schubert's reported methylmethacrylate (MMA) polymers containing terpy in the side chain [22,23]. These initial reports only covered random copolymers until our recent work on block–random copolymers which localized the metal ligand to one segment of a block copolymer for the first time [25]. The ability to generate block copolymer architectures with metal–ligands confined to one block will have important applications in the field of supramolecular polymer science.

Access to block copolymers required the application of controlled or living polymerization techniques which are compatible with many functional groups. Our approach has focused on living controlled radical polymerization (CRP) methods including atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMP), and reversible addition-fragmentation chain transfer polymerization (RAFT). In addition to these synthetic methods, a direct approach that involves the polymerization of vinyl functionalized terpy as well as an indirect approach which focuses on the polymerization of active ester monomers and subsequent conversion to incorporate terpy after polymerization was studied. For this indirect method, the *N*-methacryloxysuccinimide (OSu) ester was selected since these esters provide an excellent way to attach functionality after polymerization. In addition, to the best of our knowledge, the controlled polymerization of OSu

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monomer has only been reported twice for the copolymerization of acrylate based polymers [26,27]. Our work extends the use of this monomer to random copolymers with methyl methacrylate (MMA), *n*-butyl methacrylate (*n*BMA), poly ethylene glycol methacrylate (PEGMA), and styrene (S) as well as very well defined block copolymers with monomodal size exclusion chromatography (SEC) curves and narrow PDI [24].

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), *n*-butyl methymethacrylate (*n*BMA) and styrene (S) were vacuum-distilled and stored in an air free flask in the freezer. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and stored in the freezer. Poly(ethylene glycol) methyl ether methacrylate macromonomer (PEGMA); (M_n=480) was obtained from Aldrich and purified by passing through a neutral alumina. 4′-Chloro-2,2′:6′,2″-terpyridine was purchased from Lancaster and all other chemicals were used as received from Aldrich. Reagent grade DMF was for GPC. All other solvents were used as received. CuBr (98%) was obtained from Fischer Scientifics, PMDETA (99%), ethyl 2-bromoisobutyrate (2-EiBBr, 98%), and anisole (99.7%) were obtained from Aldrich and used without further purification. PMMA macroinitiator and terpyridine amine were synthesized following the procedure as reported earlier [23–25]. Following ATRP synthesis, polymers were checked for the presence of residual copper by elemental analysis and no copper was detected. This is important considering the complexation studies that were performed.

2.2. Measurements

^{1}H NMR spectra were obtained at 300 MHz with a Bruker DPX-300 NMR spectrometer in $CDCl_3$. The mole percent incorporation of terpyridine into the copolymer was calculated by normalizing the integration values of the OCH_2 from the terpyridine functions, and OCH_3, from MMA. Gel permeation chromatography (GPC) was performed in dimethylformamide (DMF) or tetrahydrofuran (THF) at room temperature using a PL LC 1120 pump, a Waters R403 differential refractometer, and three PLgel columns (105, 104, and 103 Å) and calibrated with narrow molecular weight poly (methyl methacrylate) standards. UV–vis spectra were obtained using a Perkin–Elmer Lambda 2 series spectrophotometer with PECSS software. Fluorescence spectra were obtained using a Perkin–Elmer LS 55 luminescence spectrometer. IR spectra were obtained using a Bio-Rad FTS 3000 Excalibur Series.

2.3. Synthesis

2.3.1. Synthesis of poly(styrene-ran-sty$_{terpy}$) copolymer

A mixture of the alkoxyamine initiator (5.0 mg, 0.0151 mmol), styrene (608 mg, 5.82 mmol), and sty$_{yerpy}$ (300 mg, 0.65 mmol) were degassed by three freeze/thaw cycles, sealed under Nitrogen, and heated at 125 °C under nitrogen for 10 h 25 min. The viscous reaction mixture was then dissolved in dichloromethane (10 ml) and precipitated (2×) into methanol (400 ml). The white precipitate was collected and dried under vacuum at 100 °C to give the desired copolymer as a white precipitate (0.69 g, 66% yield), M_n=32.1 k, PD=1.33. ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.60–8.62 ppm (dd, broad), 8.10 ppm (s, broad), 8.00–8.08 ppm (m, broad), 7.87 ppm (m, broad), 6.8–7.6 ppm (m, broad), 6.1–6.8 ppm (m, broad), 4.0–4.4 ppm (m, broad), 3.2–3.6 ppm (m, broad). Elemental analysis, Calculated based on 10 mol% sty$_{terpy}$: Calculated: C% (86.34), H% (7.12), N% (3.99), Found: C% (86.23), H% (7.37), N% (4.03).

2.3.2. Synthesis of poly(styrene-b-(styrene-ran-sty$_{terpy}$)) copolymer

A mixture of the alkoxyamine initiator, sty$_{terpy}$ (10 mg, 0.0307 mmol), styrene (1.531 g, 14.651 mmol), and acetic anhydride (0.626 mg, 0.00613 mmol) were degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 125 °C under nitrogen for 7 h. The colorless solid was dissolved in dichloromethane (15 ml) and precipitated (2×) in methanol (400 ml). The white precipitate was dried under vacuum to give the desired polystyrene macroinitiator (1.166 g, 76%), M_n=44,350, PDI=1.13. The polystyrene, 6, Starting block (271.8 mg, 0.00613 mmol), sty$_{terpy}$ (272.4 mg, 0.59 mmol) were dissolved in styrene (0.513 g, 2.452 mmol). The mixture was degassed by three freeze/thaw cycles, sealed under nitrogen and heated at 125 °C for 16 h 30 min. the solidified reaction mixture was dissolved in dichloromethane and precipitated (2×) in methanol (500 ml). The white precipitate was dried under vacuum at 100 °C to give the desired copolymer (590 mg, 56% yield) M_n=67,200, PDI=1.4. ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.603 ppm (s, broad), 8.091 ppm (s, broad), 7.793 ppm (s, broad), 7.040 ppm (s, broad), 6.8–6.0 ppm (m, broad), 4.162 (s, broad), 3.470 ppm (s, broad), 2.41–1.00 ppm (m, broad). Elemental analysis, calculated based on 7.5 mol% sty$_{terpy}$: calculated: C% (87.47), H% (7.23), N% (3.19), Found: C% (87.14), H% (7.37), N% (3.19).

2.3.3. General procedure for copolymerization of OSu

Table 1 summarizes experimental conditions, molecular weights and MWDs for these random copolymers. In a typical experiment, a dry vial equipped with a stir bar was charged with CuBr (4.3 mg, 0.033 mmol) under a flowing stream of nitrogen. To this, specified amounts of PMDETA (8.5 mg, 0.049 mmol), 2-EiBBr (8.6 mg, 0.044 mmol), and anisole (0.3 ml) were added. After this, MMA (85 mg,

Table 1
Conditions and results for the random copolymerization of active ester monomer with various comonomers in anisole

No	Polymer	OSu:R:EiBBr:-Cu:PMDETA	Ratio (^{1}H NMR)	T (°C)	Time (h)	M_n Obs	PDI
1	p(OSu-*r*-MMA)	50:50:1:1:2	47:53	90	10 min	11,300	1.23
2	p(OSu-*r*-MMA)	35:65:1:1:2	35:65	90	2	10,000	1.23
3	p(OSu-*r*-nBMA)	50:50:1:1:2	42:58	90	2	9700	1.12
4	p(OSu-*r*-PEG)	50:50:1:1:2	49:51	90	2	10,400	1.20
5	p(OSu-*r*-S)	30:70:1:1:2	34:66	90	6	3500	1.16

R = MMA, *n*BMA, PEG and S.

0.82 mmol) and OSu (150 mg, 0.819 mmol) were added. The reaction mixture was purged well with the stream of nitrogen to remove the dissolved oxygen. Finally, copolymerization was carried out by immersing the reaction vial in an oil bath maintained at 90 °C. After 10 min the reaction mixture was cooled and then the crude polymeric product was dissolved by the addition of DMF (1 ml). This solution was slowly added to a stirred solution of methanol–water mixture (60:40) to precipitate the polymer as a white solid (69%).

2.3.4. *General procedure for synthesis block copolymerization*

A known quantity of previously synthesized and purified macroinitiator (110 mg, 0.601 mmol) was dissolved in anisole (0.5 ml). The specified volume of this solution (0.5 ml) was introduced to the glass vial, which contained CuBr (9.1 mg, 0.063 mmol), PMDETA (20 mg, 0.12 mmol) and OSu (400 mg, 2.2 mmol) under a nitrogen flow. After stirring to generate homogeneous solutions, the reaction mixture was placed in an oil bath at 90 °C. Following polymerization, typically 2 h, the resulting crude polymeric product was dissolved by the addition of DMF (1 ml). This solution was slowly added to a stirred solution of methanol–water mixture (60:40) to precipitate polymer as a white solid (71%). The conversion was calculated by weighing the polymer after precipitation and through drying. The same procedure was followed to obtain p(MMA-*b*-OSu) block copolymers.

2.3.5. *Procedure for post polymer modification to attach terpy*

A 2 ml vial was charged with copolymer (60 mg, 0.21 mmol), amine functionalized terpy [25] (120 mg, 0.32 mmol) and a magnetic stirring bar. The vial was sealed with a septum and purged with nitrogen. Anhydrous DMSO (0.3 ml) was injected and the reaction mixture stirred until it became homogeneous. TEA (25 μL, 0.24 mmol) was then added under nitrogen and the vial was placed in an oil bath at 60 °C for 3 h. The polymeric product was isolated by precipitation with acetone. Yield: 96% ^{1}H NMR ($CDCl_3$, ppm): 8.69 (br, 2H, pyridine H), 8.62 (br, 2H, pyridine H), 8.00 (br, 2H, pyridine H), 7.85 (br, 2H, pyridine), 7.32 (br, 2H, pyridine H), 4.15 (br, 2H, OCH_2), 3.95 (br, 2H, OCH_2), 3.60 (br, 3H, OCH_3), 1.95 (s, 2H, CH_2), 1.84 (br, 2H, CH_2), 1.50 (br, 4H, CH_2), 1.33 (br, 6H, CH_2), 1.00–0.88 (br, 3H, CH_3).

3. Results and discussion

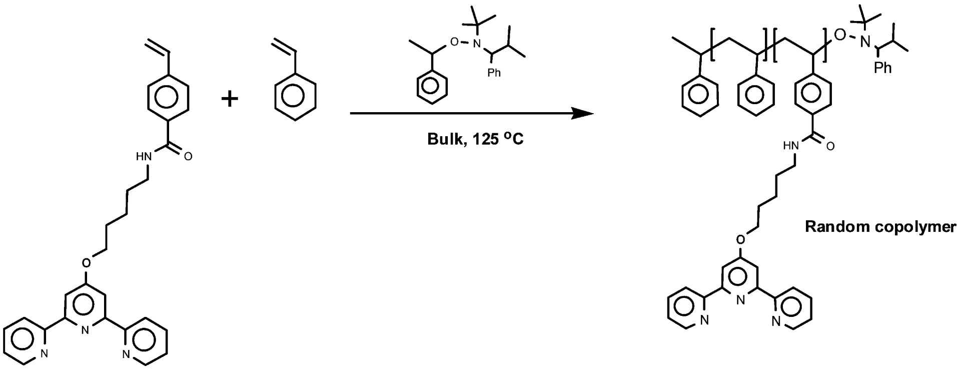
3.1. *Direct method*

3.1.1. *Random copolymers*

Scheme 1 shows the synthesis of a random copolymer with molecular weight (M_w) of 32.2 kDa composed of styrene and terpyridine functionalized styrene (sty_{terpy}). Elemental analysis and ^{1}H NMR integration of the copolymer indicates 10 mol% sty_{terpy} was successfully incorporated. The ^{1}H NMR spectra for the copolymer contains the terpy proton signature in the aromatic region between 6 and 9 ppm. The GPC curve shown in Fig. 1 yields a monomodal peak with molecular weight distribution (MWD) of 1.3. This MWD is reasonable for the copolymer but may in fact be even lower. It is well documented that poly(vinylpyridines) adhere to the stationary phase broadening the distribution. Terpy is expected to be even worse and several groups have reported SEC complications. If the sample of the copolymer is significantly diluted (≤0.5 mg/ml), the MWD decreases to 1.20. Correspondingly, increasing the copolymer concentration (2–3 mg/ml) broaden the MWD to above 1.40. Addition of triethylamine (TEA) to the GPC had a smaller influence but also decreased the MWD to 1.33. To summarize, NMP provides easy access to random copolymers via vinyl functional terpy monomers.

3.1.2. *Block–random copolymer*

Following successful synthesis of the random copolymer, block copolymer architectures were pursued. Using NMP techniques, block–random copolymers were successfully produced as outlined in Scheme 2. Starting from a polystyrene macroinitiator, the addition of styrene (90 mol%), and sty_{terpy} (10 mol%) at 125 °C afforded the copolymer in reasonable efficiency. The ability of the macroinitiator to reinitiate sty_{terpy} is evidenced from the overlaid GPC chromatograms in Fig. 2 which shows both the macroinitiator and copolymer. The presence of the terpy



Scheme 1. Synthesis of poly(sty-*ran*-sty$_{\mathrm{Terpy}}$) via NMP.

causes broadening of the peak, which is consistent with the above observations on random copolymers. The tailing of the block copolymer in Fig. 2 may result from incomplete initiation or autopolymerization, but it is most likely the result of interactions between terpy units and the GPC stationary phase. ^{1}H NMR confirms the structure with the terpy protons appearing in the aromatic region shown in Fig. 3. These results show NMP allows block architectures, based on styrene, to be prepared in which the terpy unit is confined to one segment.

3.1.3. Block–block

These block–random architectures are enabled by the CRP technique; however, the ability to synthesize traditional diblock copolymers remained attractive because of their remarkable microphase separation properties which promote ordering of the two dissimilar blocks into different morphologies. The incorporation of terpy in one of these blocks is very tempting since the terpy block can be functionalized with various metal ions to gain additional functionality. In this case, the alkoxyamine end functionalized polystyrene macroinitiator was used to grow a second block of sty$_{\mathrm{terpy}}$ in diglyme at 125 °C in the presence of a catalytic amount of acetic anhydride as shown in Scheme 3.

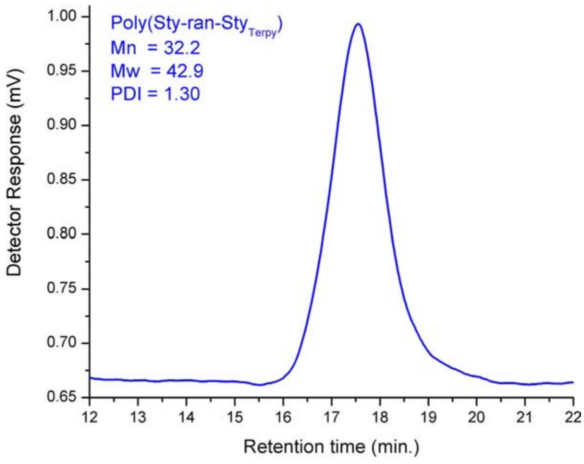


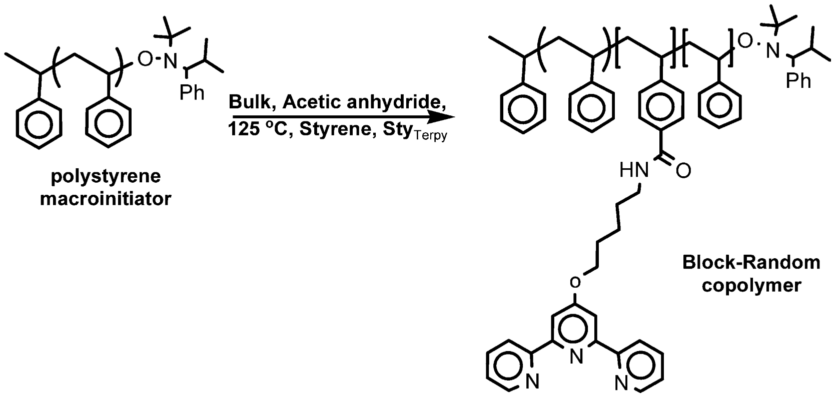
Fig. 1. GPC trace of poly(styrene-*ran*-sty$_{\mathrm{Terpy}}$) synthesized via NMP in THF as mobile phase.

Based on elemental analysis of the nitrogen content, the mol% of sty$_{\mathrm{terpy}}$ is 27. Along with the NMR spectrum shown in Fig. 4, there is good evidence showing polymerization of the second block. However, neither of these two techniques confirms covalent connectivity. SEC of this polymer containing such a high terpy percentage proved impossible with the conditions available to us. However, these chromatograms did confirm absence of the poly(S) macroinitiator. All attempts to remove the terpy function including treating the polymer with refluxing methanol/NaOH and transamidation with benzylamine in the presence of Sc(OTf)$_3$ and toluene at 90 °C failed. In an effort to confirm diblock copolymer formation, we utilized optical microscopy techniques. The material was spun onto a silicon wafer, annealed for 3 days at 170 °C under nitrogen and examined. Inspection of the film showed a clear material suggesting the absence of macrophase separation that would be expected if two homopolymers were present. As shown in Fig. 5, the optical birefringent micrograph of the diblock at the film edge shows discrete color changes which are consistent with microphase separated domains; although it does not provide any information about the presence of residual homo polystyrene from the macroinitiator. This technique is commonly used as a first approximation for microphase separated copolymers in which the difference in refractive indices for each domain generates refraction and the observable color changes.

3.2. Indirect method

3.2.1. Random copolymer synthesis

Given the difficulty in characterizing this simple diblock copolymer prepared from the direct approach, we considered an alternative strategy for generating these copolymers. A post-polymerization approach might allow easy characterization of the pre-polymer by traditional methods like SEC while convenient monitoring of the reaction to incorporate terpy could be followed by another technique. This approach also overcomes batch to batch differences that occur in polymerization reactions including monomer sequence heterogeneity and tacticity. Generating



Scheme 2. Synthesis of and poly(styrene-*b*-(styrene-*ran*-sty$_{Terpy}$)), synthesized via NMP.

reactive polymers for subsequent modification has been studied extensively [28] but the use of activated ester monomers has gained favor recently due to their chemical versatility [26,27]. We have focused on *N*-methacryloxysuccinimide (OSu) since these esters are more hydrolytically stable than other commonly used active esters and the conversion can easily be followed by IR. We developed optimized ATRP conditions for the homopolymerization of OSu in nonpolar solvent [24].

Having established that the OSu monomer undergoes well-behaved ATRP polymerization with CuBr/PMDETA systems [24], we examined the generation of AB random and diblock copolymers. A distinctive advantage of ATRP is that the random copolymers of OSu with MMA, *n*BMA, PEGMA and S can be achieved with controlled molecular weights and narrow MWDs. In addition, because of the living nature of the polymerization, minimal compositional differences in each copolymer chain are expected within a single sample [21]. Random copolymers of OSu and MMA with narrow MWD were synthesized successfully using the optimized copper catalyst system as shown in Table 1, entry 1. It was observed that when both the monomer concentrations were equal, the polymerization became extremely viscous in only 10 min and gave well controlled polydispersity as well as monomer incorporation very close to the starting feed ratio. When the MMA feed ratio was increased, the significant viscosity increase, or gelation, was delayed until 2 h because of the improved solubility of the copolymer due to the larger composition of MMA. These conditions still generated copolymers with composition similar to the feed ratios.

Based on the successful polymerization of OSu and MMA, we examined the copolymerization with other monomers to generate copolymers with controlled properties. Copolymerization of an equimolar mixture of OSu and *n*BMA gave copolymers with controlled molecular weights and relatively narrow MWDs as shown in Table 1, entry 3. These conditions also produced controlled random copolymerization of OSu and PEGMA with narrow MWD (Table 1; entry 4). Further, it was possible to prepare styrene-based random copolymers in a well controlled manner as shown by entry 5 in Table 1. The copolymers are more soluble in organic solvents than the OSu

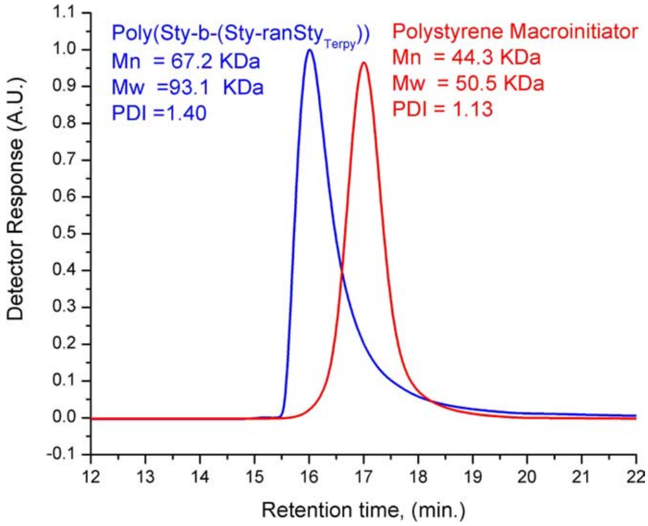


Fig. 2. Overlaid GPC trace of polystyrene macroinitiator end capped with the alkoxyamine, and poly(styrene-*b*-(styrene-*ran*-sty$_{Terpy}$)), synthesized via NMP in THF as mobile phase.

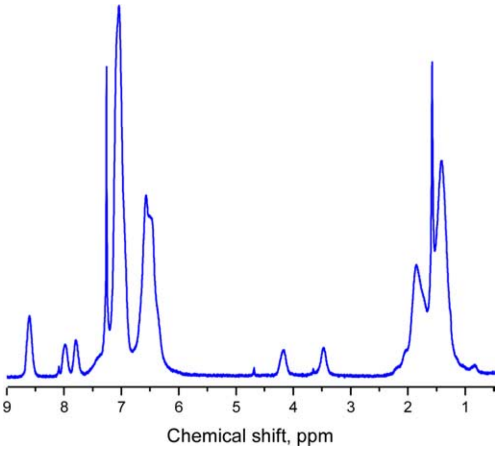
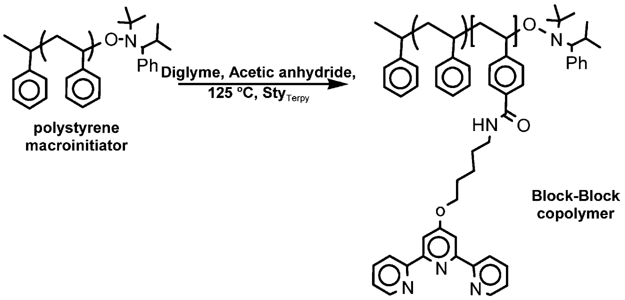


Fig. 3. ^{1}H NMR of poly(sty-*b*-(sty-*ran*-sty$_{Terpy}$)) in CDCl$_3$.



Scheme 3. Synthesis of poly(sty-*b*-sty$_{Terpy}$) via NMP.

homopolymer including $CHCl_3$ and THF. The copolymer of OSu and PEGMA is also water soluble.

3.2.2. Block copolymer synthesis

Using macroinitiators of MMA or stryene (S), block copolymers of OSu were prepared by optimized ATRP conditions as illustrated for p(MMA-*b*-OSu) in Scheme 4. Formation of the diblock copolymers was confirmed by NMR, IR and overlaying SEC traces of the macroinitiator and resulting copolymer. A typical example of the SEC is shown in Fig. 6 for a PMMA macroinitiator and p(MMA-*b*-OSu) block copolymer. All block copolymers showed monomodal Gaussian-shaped SEC peaks suggesting very good chain extension from the macroinitiator. The process appears to work well regardless of whether the macroinitiator belongs to the same monomer class (methacrylate) or not. A macroinitiator was used to polymerize OSu leading to very good block copolymer formation which is an improvement over an earlier report in which a macroinitiator based on OSu was used to generate poly(OSu-*b*-MMA) copolymers [26]. These workers reported less efficient initiation based on a substantial macroinitiator peak present after copolymer formation. This is an interesting comparison and further work is necessary to understand if the monomer order or differences in chemistry control good initiation.

After block copolymer formation, the active ester functions were converted to terpy. The conversion was easily accomplished by reacting an amine functionalized terpy with the polymer in anhydrous DMSO and triethylamine at 60 °C for 3 h as shown in Scheme 4. ^{1}H NMR and IR spectroscopy indicated the reaction proceeds quantitatively. Covalent attachment of terpy to the polymer backbone is supported by the shift in the methylene protons adjacent to the amine. In terpy, these protons come at 2.6 ppm but shift to 3.3 ppm when bound to the polymer backbone while the methylene protons adjacent to oxygen have the same integration as those at 3.3 ppm indicating that all signals from terpy are associated with backbone attachment. In agreement with these observations, the complete disappearance of the signal at 2.8 ppm, corresponding to the methylene protons of the succinamide ring, was observed. The active ester has characteristic IR stretches at 1808, 1781, and 1672 cm^{-1} which disappear completely upon reaction, suggesting high conversion of the active esters.

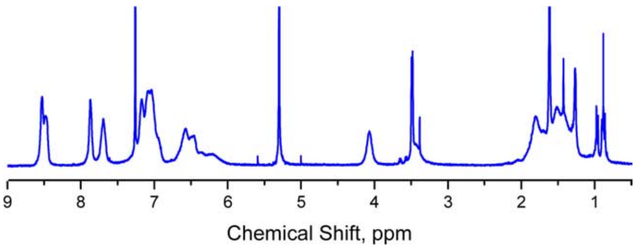


Fig. 4. ^{1}H NMR spectrum of poly(sty-*b*-sty$_{Terpy}$) in $CDCl_3$.

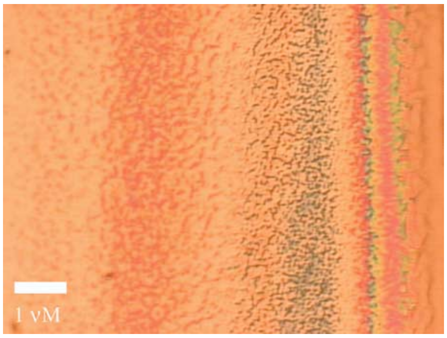
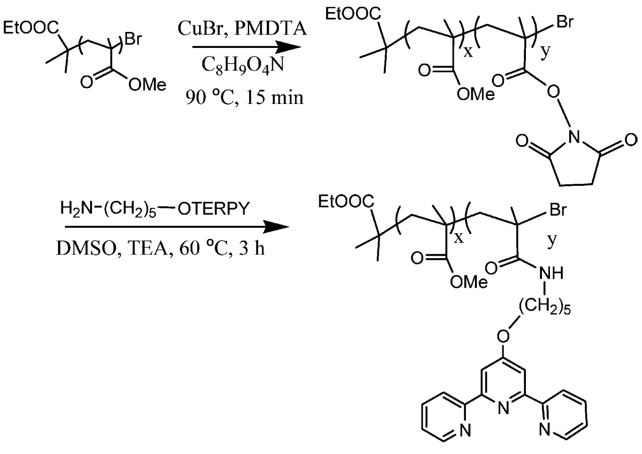


Fig. 5. Optical micrograph of annealed diblock film on oxidized surface of silicon wafer.

3.3. Intramolecular cross-linking

A solution of polymer was monitored at a single concentration as Cu(II) ions (copper nitrate) were added to determine the presence of intermolecular cross-links. For the experiments represented in Fig. 7, a polymer solution of 4 mg/ml (0.35 wt%) in 1:1 $CHCl_3$:MeOH was used for both polymers, terpy copolymer and p(MMA) homopolymer. As seen in this figure, there is a clear difference in the response of the terpy copolymer and p(MMA) homopolymer to metal ion addition. As more metal is added, the viscosity of the



Scheme 4. Active ester block copolymer formation and subsequent conversion to incorporate terpy.

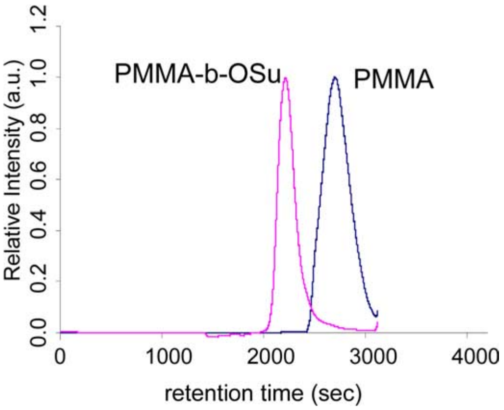


Fig. 6. SEC chromatograms of a p(MMA) macroinitiator, centered at 2750 s, and p(MMA-*b*-OSu) block copolymer, centered at 2200 s. These SEC curves were collected in DMF.

copolymer increases rapidly while the homopolymer remains flat. Such an increase in viscosity is consistent with increased polymer molecular weight, suggesting intermolecular cross-links are formed. The curve does not increase further after the last data point. Finally, the addition of PMDETA to the viscous solution resulted in the immediate decrease in viscosity as shown by the red triangle.

A single, low concentration of polymer was used in these experiments to determine the response to metal ions. In fact, the initial concentration of polymer in the solution does not detectably change the viscosity of the solvent. In contrast, if the experiment is repeated with a significantly higher concentration of terpy functionlized polymer then a solid precipitates upon metal ion addition as shown in Fig. 8 [23]. This blue solid is insoluble in any solvent, including DMF which usually dissolves both the apo-polymer (no metal ion) and metal complexed polymer. This insolubility suggests the precipitate is highly cross-linked by the metal–ligand complexes.

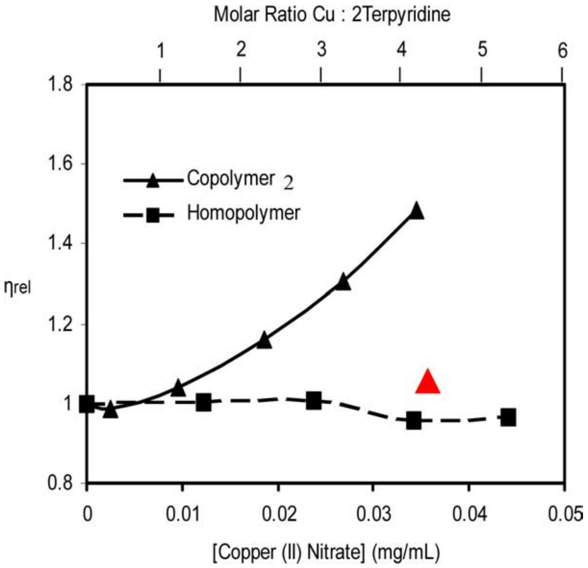


Fig. 7. The change in relative viscosity as Cu(II) ions are added to the solution. Only the terpyridine containing polymer, **2** from Table 1, shows an increase in viscosity, while the PMMA homopolymer remains essentially unchanged. At the end point, a better ligand, PMDETA, is added and the viscosity decreases as shown with the larger red triangle (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3.4. Polymer based sensors

The incorporation of metal-complexes into macromolecular architectures produces multi-functional materials. Beyond the use of these interactions to drive polymerizations and reversible cross-links, applications in sensors should be enabled. Toward this end, we are exploring these systems for sensing of other metal ions, solvent, temperature, and chemical agents. We have already reported thermochromic materials based on lanthanides and recently discovered Hg(II) selective sensors. Here, we report on Co(II) films that serve as solvent sensors based on observable solvochroism from green to brown. Fig. 9 shows polymer samples from a Co(II) complexed macromolecule based on PMMA. When these films are prepared at room temperature, they are green in color; however, upon exposure to methanol and water they change to gold within 100 s. The color returns to green upon removal of the agent and the process is completely repeatable. The overall time scale to sense and return to the initial green color is temperature dependent, but approximately 2 min.

4. Conclusions

Creating hybrid materials by integrating metal ligand complexes into polymer architectures, including block copolymers, is a versatile approach to novel supramolecular materials. Extensive work at this early stage needs to focus on synthetic methods that provide access to a wide variety of polymer chemistries and architectures. This report describes significant advances toward block copolymers using CRP methods combined with a direct or indirect approach to ligand incorporation. Each approach, direct or

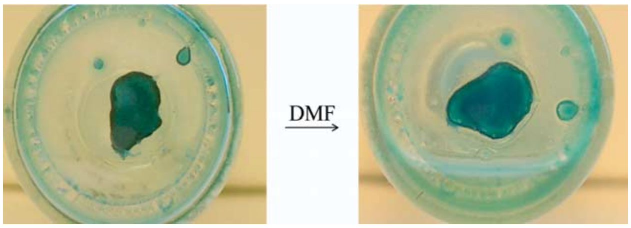


Fig. 8. Picture of a highly cross-linked gel produced by adding Cu(II) ions to a more concentrated polymer solution of **2** from Table 1. The addition of DMF, a good solvent for the apo- and metal-containing polymer, swells but does not dissolve the sample.

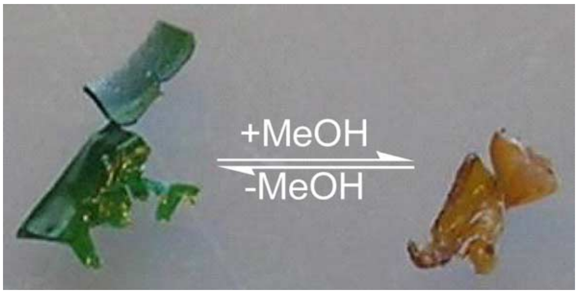


Fig. 9. A polymer film of **1** from Table 1 containing Co(II) ions (left) before and (right) after exposure to methanol. The color change is rapid and reversible.

indirect, has advantages; however, the indirect approach allows access to well characterized polymers with high terpy content. Until the problems of SEC chromatography are solved, this indirect approach remains the top choice in our laboratory. Preliminary results demonstrate the array of properties that will be realized from these unique macromolecules. Applications in areas such as sensors, 'smart,' and self-healing materials are expected.

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