Methacrylate Polymers Containing Metal Binding Ligands for Use in Supramolecular Materials: Random Copolymers Containing Terpyridines

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Supramolecular materials represent an important area of current research.[1] There are many interactions used to self-assemble molecules into supramolecular materials including hydrogen and metal bonds, $\pi-\pi$ and donor−acceptor associations, electrostatics, hydrophilic−hydrophobic, and van der Waals forces.[2] Of these, metal−ligand bonds exhibit both strong and directional interactions where the selection of metal ion and ligand dictate association strength. The incorporation of metal ligand interactions into organic molecules imparts new and potentially useful properties to the final material including luminescence, magnetism, and thermochromism.[3−5] To this end, we have begun a program to incorporate metal binding ligands into polymers and copolymers in an effort to create new materials with tunable properties. An initial example of this work is reported here where we synthesized methacrylate random copolymers containing terpyridine (terpy) units as the minor comonomer and examined their properties in the presence and absence of metal ions.

Metal-induced self-assembling systems include helicates, dendrimers, hyperbranched, star, telechelate, and coordination polymers.[6] Fraser and Schubert report elegant systems focused on metal-centered polymers.[7−12] In some of these systems, ligands are coordinated around metal centers followed by outward radial growth of the polymer chain.[8,9] In other cases, the metal ligand is used to initiate polymerization, placing the supramolecular function at the chain end. Subsequent introduction of metal ions initiates self-assembly between two or three polymer chains, resulting in an increase in molecular weight.[9,12] The reversible nature of the metal−ligand interaction was demonstrated in both cases. Chujo and co-workers published preliminary experiments suggesting metal-induced gelation of polyoxazolines containing bipyridyl units.[13−15] They assumed network formation based on observation of a solid after metal addition. Upon further dilution in water, the solid swells and then dissolves. It was suggested the solid dissolved because intermolecular bonds were replaced with intramolecular ones.[15]

Alternatively, supramolecular networks based on hydrogen bond formation have been reported in apolar polymers like polybutadiene and polyolefin.[16−20] Recent work in this area incorporated ureidopyrimidinone functions into amorphous polyolefin.[20] It was shown that the solution viscosity increased much more rapidly with increased polymer concentration compared to the unfunctionalized homopolymer, In addition, elastomeric properties were produced as a result of the supramolecular network. It is known that polar environments significantly compete with the desired hydrogen bonding, eliminating its association. This effect was observed in the polyolefin system when solvents like THF and chloroform ($CHCl_3$) were added to the polymer.[20] In this paper, we report the synthesis of methacrylate random copolymers containing multiple metal ligands per chain. The addition of transition metal ions forms coordination complexes which influence the polymers properties even in polar solvents.

The synthesis of the desired metal−ligand monomer for radical polymerization was achieved by reacting 4′-chloro-2,2′:6′,2”-terpy with 1,8-octanediol, as shown in Figure 1. Free radical polymerization produced several random copolymers of **2** with different compositions which are summarized in Figure 1. ^{1}H NMR spectra, shown in Figure 2, of **1** and **4** confirm the incorporation of terpy into the polymer backbone. The aromatic signals are essentially identical in both monomer and copolymer. Further, the methylenes adjacent to oxygen in the terpy units of the copolymer are observed clearly in the polymer spectra (Figure 2b). UV−vis spectroscopy also supports terpy incorporation into the polymer. The absorption spectra shown in Figure 3a for **1** and copolymer **4** have similar primary $\pi-\pi^*$ transition bands at λ_{max} of 290 and 292 nm, respectively.

In addition, UV−vis spectroscopy was used to investigate metal−ligand complex formation. Complexes were formed in 50:50 $CHCl_3$:MeOH solvent mixtures by Cu(II) addition. After stirring for 2 h, a solid was isolated upon solvent removal, and Figure 3b shows the spectra for complexed compound, **1**, and **4**. These spectra are superimposable and consistent with Cu(II)-terpy$_2$ formation, suggesting metal−ligand complexes are formed in the macromolecular system. The polymers here are significantly different from traditional systems in which metal ions produce cross-linked materials through ill-defined association with functional groups like carboxylates, sulfonates, and amides.[21] However, the observation of metal−ligand bonds in the polymer by UV−vis spectroscopy does not indicate if inter- or intramolecular bonds are formed. Therefore, solution viscosity was measured to investigate the formation of interchain cross-links. A solution of **4** was monitored at a single concentration as Cu(II) ions were added. For the experiments represented in Figure 4, a polymer solution of 4 mg/mL (0.35 wt %) in 50:50 $CHCl_3$:MeOH was used for both polymers, copolymer **4** and methyl methacrylate homopolymer. Polymer solutions were stirred for 30 min after each addition of metal ions. As seen in Figure 4, there is a clear difference between copolymer **4** and homopolymer in viscosity response to metal ion addition. As more metal is added to the system, the viscosity of the copolymer increases rapidly while the homopolymer remains essentially flat. Such an increase in viscosity is consistent with increased polymer molecular weight, suggesting intermolecular cross-links between chains are formed upon metal ion addition. The copolymer curve continues to increase after the calculated saturation value of Cu(II) ion has been reached (~0.01 mg/mL $Cu(NO_3)_2$). This continued increase in viscosity after the calculated saturation point is still under investigation but may be related to the

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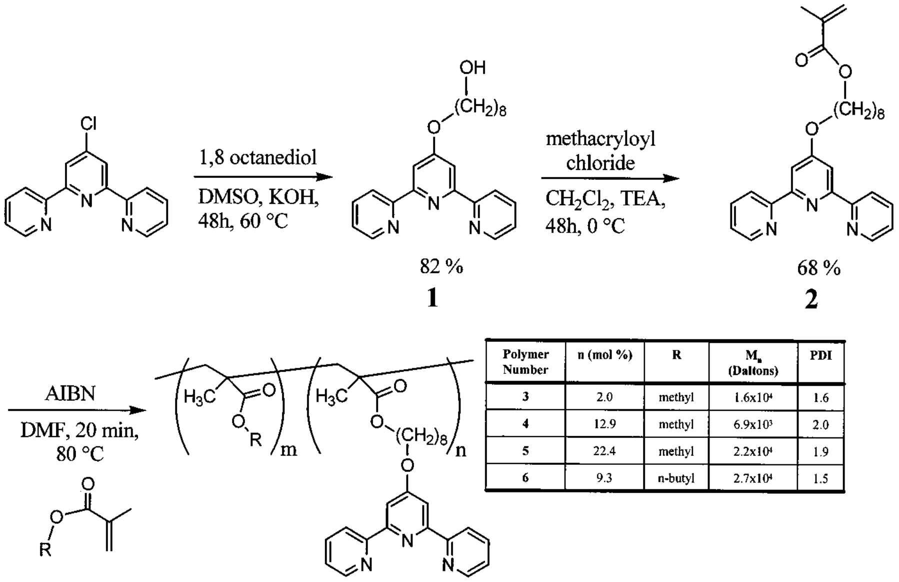

Polymer Number	n (mol %)	R	M_n (Daltons)	PDI
3	2.0	methyl	1.6×10^4	1.6
4	12.9	methyl	6.9×10^3	2.0
5	22.4	methyl	2.2×10^4	1.9
6	9.3	n-butyl	2.7×10^4	1.5

Figure 1. Synthetic outline for the preparation of monomer and copolymers. A series of different compositions have been prepared including methyl and *n*-butyl methacrylate materials. Copolymerization was chosen over post-polymer modification to yield more homogeneous samples.

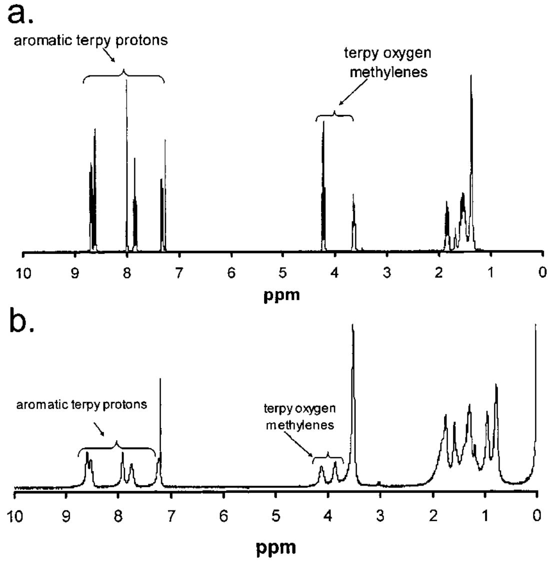

Figure 2. ^{1}H NMR spectra for (a) **1** and (b) **4** are shown. Comparison between the two spectra indicates terpy incorporation into the polymer backbone. The key resonances are the aromatic signals and methylenes adjacent to the oxygen atoms.

kinetics of metal–ligand bond formation.[22] When the final solution was allowed to stand for an extended period (>2 days), the viscosity remained constant (near 1.5), suggesting the intermolecular interactions in this systems are stable. Similar observations were not reported by Chujo and co-workers and may be related to the use of terpy ligands in this work or the use of water as a solvent in their work. A single, low concentration of polymer was used in these experiments to determine the response to metal ions. In fact, the concentration of homopolymer does not detectably change the viscosity of the solvent. Interestingly, Coates observed no difference in relative viscosity between supramolecular polymer and homopolymer at 4 mg/mL concentrations.[20]

We report a new random copolymer system containing metal ligands for subsequent metal-induced supramolecular association. These polymers are based on methacrylate monomers, and metal–ligand bond formation is observed by UV–vis spectroscopy. This bond affects the solution viscosity of the copolymer even at very low concentrations and polar solvents. Important experiments to address network formation are needed including higher polymer concentration and molecular weight. However, the current data are supportive of intermolecular bond formation driven by metal ion addition. The incorporation of metal–ligand interactions into polymer side chains will create new and unique supramolecular systems.[23]

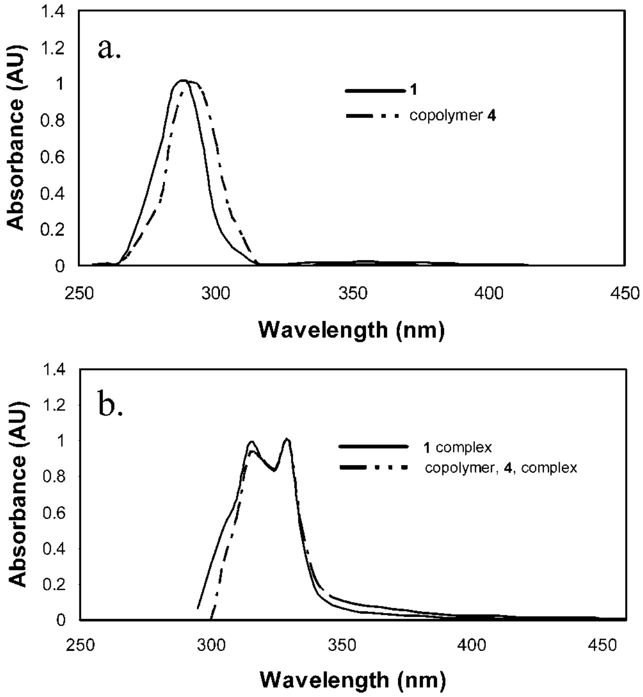

Figure 3. UV–vis spectra are shown for **1** and **4** (a) before and (b) after metal complexation.

Experimental Section. 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

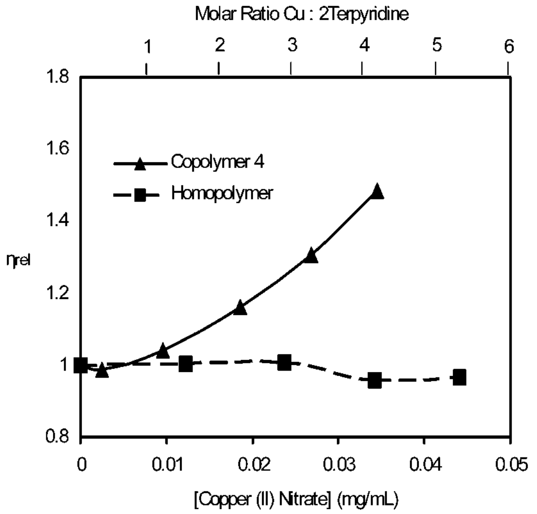

Figure 4. Solution viscosity data are reported relative to 50:50 $CHCl_3$:MeOH. As metal is added to the solution, there is an increase in viscosity of **4** while no increase is observed for the homopolymer. The solution concentration for each polymer is 4 mg/mL (0.35 wt %), and the molecular weight of the homopolymer is $M_n = 16\,000$.

calculated by normalizing the integration values of the OCH_2 and OCH_3 units in **4** and MMA, respectively. Gel permeation chromatography (GPC) was performed in tetrahydrofuran (THF) at room temperature using a PL LC 1120 pump, a Waters R403 differential refractometer, and three PLgel columns (10^5, 10^4, and 10^3 Å) and calibrated with narrow molecular weight poly(methyl methacrylate) standards. Thin-layer chromatography (TLC) and column chromatography were done using neutral alumina (150 mesh, 60 Å). UV−vis spectra were obtained using a Perkin-Elmer Lambda 2 series spectrophotometer with PECSS software. All samples were diluted in 50:50 chloroform:methanol to give absorption peaks less than 1.0 AU. Capillary viscosity measurements were taken in 50:50 chloroform:methanol with a polymer concentration of 4.0 mg/mL. The viscometer was kept in a stirred water bath at 26.5 °C, and three time readings per data point were taken using a stopwatch. $Cu(NO_3)_2{\cdot}2.5H_2O$ was added to the solutions in an Erlenmeyer flask with stirring and allowed to complex for 20−30 min before new viscometry readings were taken.

Materials. Methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA) were vacuum-distilled and stored in an airfree flask in the freezer. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and stored in the freezer. 4′-Chloro-2,2′:6′,2″-terpyridine and all other chemicals were used as received from Aldrich. Reagent grade THF was distilled under nitrogen from sodium benzophenone and used for GPC. All other solvents were used as received.

Procedure for Synthesis of Terpyridine Alcohol (1). 1,8-Octanediol (4.000 g, 27.41 mmol), potassium hydroxide (KOH) (0.672 g, 11.92 mmol), and DMSO (10 mL) were added to a round-bottom flask (RBF) with stirring and heated to 60 °C for several minutes. 4′-Chloro-2,2′:6′,2″-terpyridine (0.800 g, 2.988 mmol) was added, and the reaction was left to stir for 48 h. The mixture was removed from the heat, poured into ice-cold water, and neutralized to pH 7. The solid was collected and recrystallized in methanol to give a white fluffy solid with 82% yield. ^{1}H NMR ($CDCl_3$) δ: 8.69 (d, 2H, pyridine H), 8.62 (d, 2H, pyridine H), 8.00 (s, 2H, pyridine H), 7.83 (t, 2H, pyridine), 7.33 (dd, 2H, pyridine H), 7.26 (s, 1H, $CHCl_3$), 4.22 (t, 2H, OCH_2), 3.64 (t, 2H, OCH_2), 1.85 (m, 2H, CH_2), 1.51 (m, 4H, CH_2), 1.37 (m, 6H, CH_2). UV−vis (50:50 chloroform:methanol): λ_{max} (290 nm).

Procedure for Synthesis of Terpyridine Monomer (2). The terpyridine alcohol, **1** (0.2550 g, 0.6764 mmol), and triethylamine (TEA) (0.4107 g, 4.0584 mmol) were added to a 250 mL round-bottom flask along with 80 mL of dichloromethane. The flask was purged with nitrogen and stirred for 20 min before cooling to 0 °C and adding methacryloyl chloride (0.2828 g, 2.7056 mmol). The reaction was stirred for 22 h and turned a pale yellow as it slowly warmed to room temperature over that time. The solution was transferred to a separatory funnel and rinsed three times with 1 wt % aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$ and filtered before removing the solvent by vacuum. No heat was applied when concentrating the product under vacuum to prevent polymerization. A yellow oil was collected and passed through a column of neutral alumina with 80:20 hexane:ethyl acetate. The product containing fractions were collected and concentrated under vacuum to give a clear oil with a yield of 68%. The oil became a white solid upon cooling in the freezer and could be returned to an oil by heating in the hands. ^{1}H NMR ($CDCl_3$) δ: 8.69 (d, 2H, pyridine H), 8.62 (d, 2H, pyridine H), 8.00 (s, 2H, pyridine H), 7.83 (t, 2H, pyridine), 7.33 (dd, 2H, pyridine H), 7.27 (s, 1H, $CHCl_3$), 6.10 (s, 1H, alkene H), 5.54 (s, 1H, alkene H), 4.22 (t, 2H, OCH_2), 4.15 (t, 2H, OCH_2), 1.84 (m, 2H, CH_2), 1.50 (m, 4H, CH_2), 1.39 (m, 6H, CH_2), 1.20−0.88 (m, 3H, CH_3).

Procedure for Copolymerization (3−6). MMA or *n*-butyl MA (0.8975 g, 8.9760 mmol) was added to a nitrogen purged test tube filled with 10 mL of dimethylformamide (DMF) followed by **2** (0.1988 g, 0.4488 mmol), which was dissolved in a minimal amount of DMF. AIBN (0.0141 g, 0.0898 mmol) was dissolved in a minimal amount of DMF and was added to the mixture. The test tube was placed immediately in an 80 °C oil bath and stirred for 20 min. The test tube was removed from the oil bath and cooled before precipitating the copolymer into cold, stirred water and filtering to remove the DMF. A white solid was collected, redissolved in THF, and precipitated in stirred hexane. This was done to remove any unpolymerized terpyridine monomer. The product was filtered with a fine filter collecting a white solid. The same procedure was followed for copolymerization with BMA, but the product was a clear oil and the solvent had to be removed by vacuum. ^{1}H NMR ($CDCl_3$) δ: 8.69 (d, 2H, pyridine H), 8.62 (d, 2H, pyridine H), 8.00 (s, 2H, pyridine H), 7.85 (t, 2H, pyridine), 7.32 (dd, 2H, pyridine H), 7.26 (s, IH, $CHCl_3$), 4.15 (t, 2H, OCH_2), 3.95 (t, 2H, OCH_2), 3.60 (s, 3H, OCH_3), 1.95 (s, 2H, CH_2), 1.84 (m, 2H, CH_2), 1.50 (m, 4H, CH_2), 1.33 (m, 6H, CH_2), 1.00−0.88 (m, 3H, CH_3).

Complex Formation for UV−vis Experiments. Terpyridine copolymer (0.0098 g, 0.0014 mmol) was dissolved in 5 mL of chloroform in a round-bottom flask. Approximately 5 times excess $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.0001 g, 0.0004 mmol) was dissolved in 2.5 mL of methanol, and 2.5 mL of acetone and was added to the copolymer solution. The reaction mixture was stirred at room temperature for 2 h before removing the solvent by vacuum leaving a blue solid.

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