Polymers Containing Metals in the Side Chains: Impact on Self Assembly and Properties

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Introduction

Supramolecular chemistry has evolved into a powerful strategy for the creation of new materials [1]. There are many interactions that can be used to self-assemble molecules including hydrogen and metal bonds, π-π and donor-acceptor interactions, electrostatics, hydrophilic-hydrophobic, and van der Waals [2]. Of these, metal-ligand bonds exhibit both strong and directional interactions in which the selection of metal ion and ligand can guide the strength of the association. The incorporation of metal-ligand interactions into organic molecules imparts new and potentially useful properties to the material. 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 [3, 4]. We have focused on blocky architectures prepared by controlled/living radical polymerization techniques.

Metal induced self-assembling systems include helicates, dendrimers, hyperbranched, star, telechelate and coordination polymers. Chujo and co-workers published preliminary experiments suggesting the metal induced gelation of polyoxazolines containing bipyridyl units [5]. More recently, Fraser and Schubert have reported elegant systems focused on metal centered polymers including multi-armed star polymers [6, 7]. These systems assemble ligands around a metal center followed by radially outward growth of the polymer chain. In other cases, the metal ligand is used to initiate polymerization which places the supramolecular function at the chain end. Subsequent introduction of metal ions initiates self-assembly between two polymer chains resulting in an increase in molecular weight. In this paper, we report the synthesis of methacrylate copolymers containing multiple metal ligands per chain.

Results and discussion

Given the difficulty in characterizing this simple diblock copolymer prepared from the direct approach [3], 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 reactive polymers for subsequent modification has been studied extensively [10] but the use of activated ester monomers has gained favor recently due to their chemical versatility [11, 12]. 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 [13, 14].

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 Figure 1. Formation of the diblock copolymers was confirmed by NMR, IR and overlaying SEC traces of the macroinitiator and resulting 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 [11]. 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 Figure 1. ^{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.

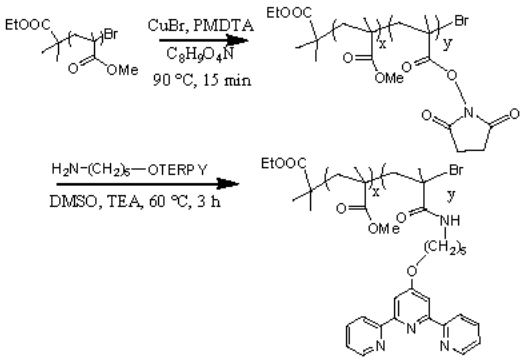

Figure 1. Synthesis of terpy containing block copolymer.

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 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.

References

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