

Polymeric Nanoscale All-Solid State Battery

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ABSTRACT

The advent of polymer electrolytes has provided a promising route to an all solid-state polymer battery. Such a battery would have greater safety, without potential discharge of liquid or gel electrolyte. Current battery configurations typically involve a metal anode, a solvent-plasticized polyelectrolyte, such as poly (ethylene oxide) (PEO), and a composite cathode. We have synthesized an A/B/C triblock copolymer which could have potential use as an all-solid state nanoscale polymer lithium battery. The polymeric battery was synthesized with an anode, electrolyte and cathode by synthesizing an A/B/C triblock copolymer whose microphase separation would form lamellar domains. These nanodomains contain cobalt oxide, a derivative of PEO synthesized by ring opening metathesis polymerization, and a spinel phase LiMn_2O_4 as the anode, electrolyte and cathode material, respectively. The first block contains cobalt oxide that stores lithium ion in a novel electrochemical reaction that allows use in a battery configuration. The second block is polyethylene oxide derived from an unsaturated crown ether, and is used for its high ionic conductivity. The third block contains LiMn_2O_4 , which is currently being investigated as a potential cathode material because of its low toxicity and ease of preparation. The nanometer size domains in the battery can be used in unique applications in microelectronics. In addition, such size scale allows use of the battery in discrete circuits, reducing the amount of wiring necessary in conventional battery configurations.

INTRODUCTION

In recent years, the interest in polymeric batteries has increased dramatically. With the advent of lithium batteries used in cell phones and laptop computers, the search for an all solid-state battery has continued. Research on polymeric materials for batteries has focused primarily on polyelectrolytes [1,2]. Current configurations have a liquid or gel electrolyte between the anode and cathode. This leads to problems with electrolyte loss and decreased performance over time. There are certain benefits for all polymer devices as the anode and cathode materials. For instance, processability of polymers can allow fabrication of batteries in a sheet configuration. One method of synthesizing anode and cathode materials in polymer systems is block copolymers in which metals and metal oxides are confined within microphase-separated domains. The goal of this research is to synthesize A/B/C triblock copolymer self- assembled nanocomposites and evaluate their electrical properties for the fabrication of solid-state batteries. The nanoscale polymer battery would exhibit a lamellar microphase separation. Several research groups have used block copolymers with self-assembled domains as a template for loading metals. [3-5]. Our work uses an A/B/C triblock copolymer that functions as the anode, electrolyte and cathode, as "A", "B" and "C" respectively.

EXPERIMENTAL

The "A" block synthesis begins with a Diels-Alder reaction between cyclopentadiene and dimethyl fumarate to produce norbornene-5,6 dimethyl ester. The dimethyl ester is reduced with LiAlH_4 to form 2-norbornene di-methyl alcohol. The dialcohol is protected from further reaction with *p*-toluenesulfonyl chloride. The toluenesulfonyl chloride is displaced by *t*-butyl amine to allow for chelation with Li. *n*-butyl Lithium is reacted with the *t*-butyl amine to form a lithium amido end-capped norbornene monomer. The Li capped monomer is reacted with cobalt chloride. The monomer is then polymerized with Schrock's catalyst.

The "B" block acts as a polymer electrolyte to transmit ions to the cathode block. "B" block synthesis starts with allyl bromide, sodium hydride and triethylene glycol. The middle block consists of polyethylene oxide (PEO) derived from a ring closing metathesis (RCM) reaction using Grubb's catalyst to form an unsaturated crown ether analog. The compound is a 12,4 crown ether with a double bond at the carbon (1) position. A reaction to remove Grubb's catalyst from the ring-closed species purifies the monomer, allowing polymerization [6].

The "C" block of the copolymer acts as the cathode in the electrochemical chain. The monomer used in this block is norbornene-5,6 dicarboxylic trimethylsilyl ester, which is then hydrolyzed with acid. This polymer can be dissolved in THF with MnCl_2 and LiCl and the metal salts are hydrolyzed and oxidized with water to form LiMn_2O_4 .

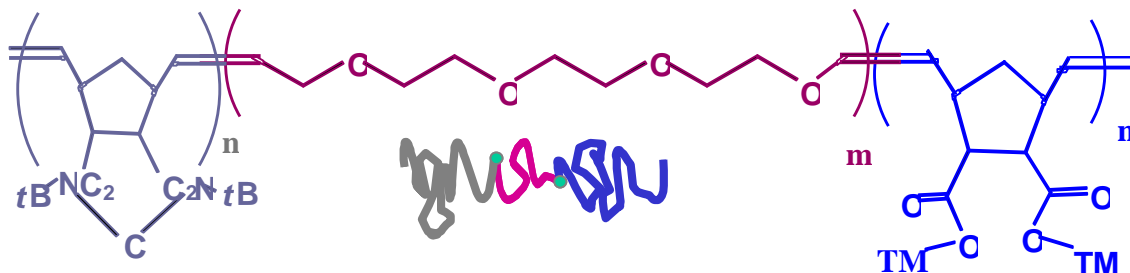


Figure 1. ABC Triblock copolymer structure

NMR and Gel permeation chromatography (GPC) were performed to characterize the homopolymers of the individual monomers. A Bruker AC-300 NMR operating at 300 MHz with C_6D_6 as the solvent and tetramethylsilane as the reference peak at 0 ppm was used to obtain the spectra. GPC was performed with a Waters GPC 2000 with a series of Waters Styragel columns in conjunction with a Waters RI detector. The mobile phase was THF with a flow rate of 1.0 mL/min. The GPC columns were calibrated with polystyrene standards (Polymer Laboratories).

DISCUSSION

The polymerization of the monomers to form homopolymers has been completed. A ^1H NMR spectra was performed to determine if polymerization of the cobalt containing monomer had occurred (see Figure 2). The shift in the spectra from 6 ppm to 5.5 ppm indicates the ring opening of the monomer has occurred and polymer is being formed.

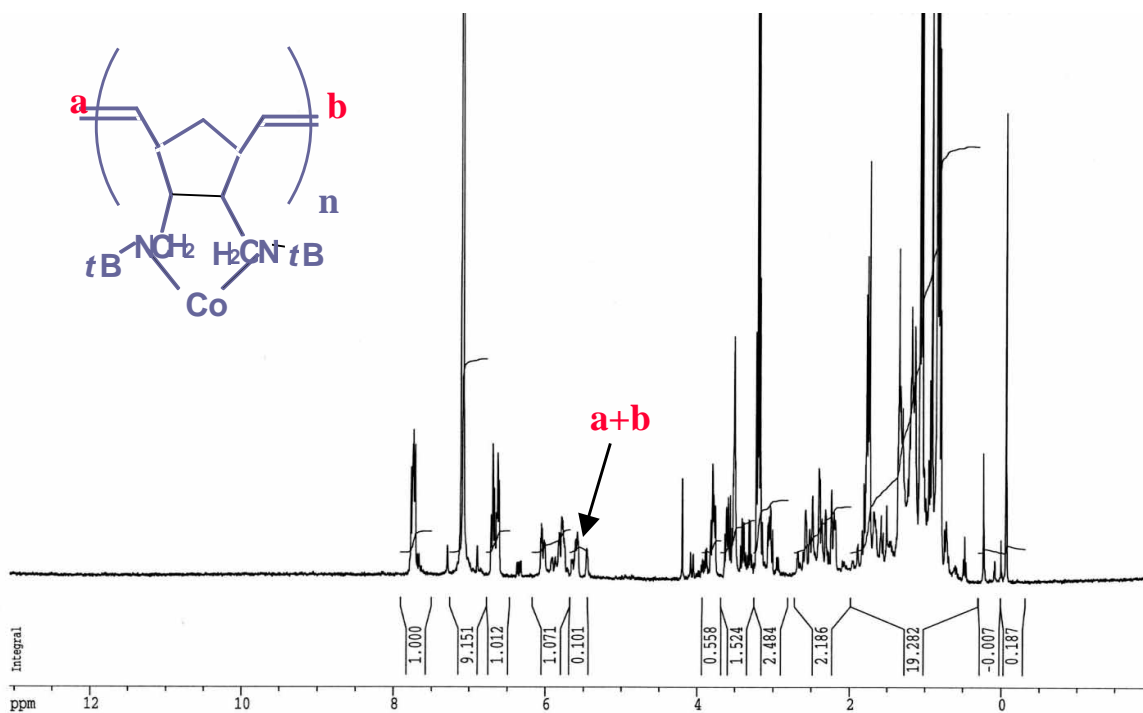


Figure 2. ^1H NMR of norbornene amidocobalt homopolymer.

The remaining homopolymers were characterized with GPC. The second block, the homopolymer of unsaturated PEO was incompatible with the THF mobile phase and GPC could not be performed. GPC of the homopolymer of the norbornene dicarboxylic trimethylsilylester is shown in Figure 3. The molecular weight was referenced to polystyrene standards and the PDI index was 1.64.

The triblock as synthesized is an air sensitive compound, and degradation of the polymer would occur in the columns of the GPC. This makes conventional GPC analysis unsuitable to characterize the polymer. Light scattering will be used to determine the molecular weight and polydispersity of the triblock.

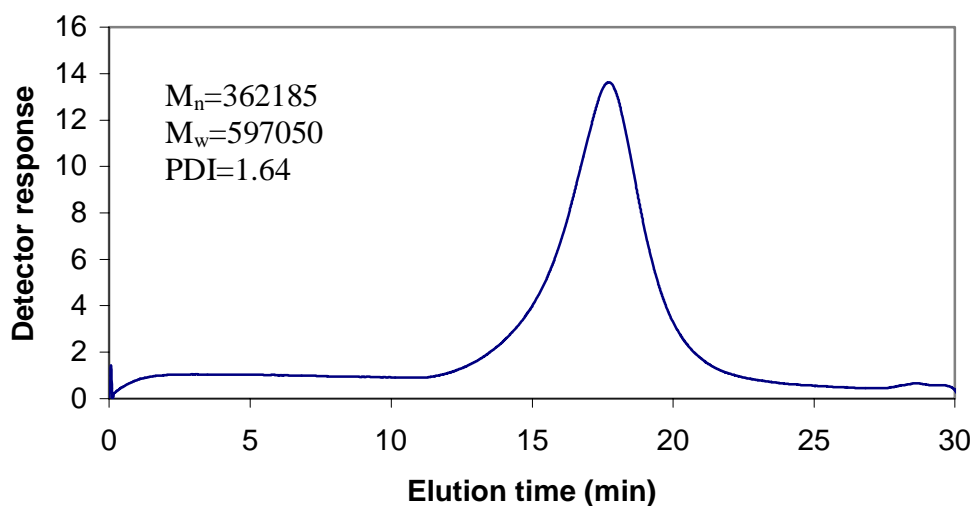


Figure 3. GPC of poly[NORCOOTMS]

CONCLUSIONS

The synthesis of polymeric candidates for nanoscale battery applications was discussed. Polymers for anode, electrolytes and cathode systems were synthesized and characterized with NMR and GPC. Metal and metal oxide clusters can be introduced into the cathode block of the triblock to form the cathode material. The potential to create an all-polymer nanoscale battery is both exciting and of great benefit to device miniaturization. A solid-state polymeric electrolyte will not leak toxic liquid electrolyte and would allow the production of a thin film nanoscale battery that could be wound into coils or processed as sheets.

ACKNOWLEDGEMENTS

This research is supported by ONR Grant # N000140010039. The authors would like to thank Dr. A. Snow of the Naval Research Laboratory for helpful discussions of the synthesis work.

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