Polyelectrolytes for Battery Applications: Synthetic Approaches and Properties

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The goal of our research is to develop a new class of anionic polymer electrolytes for use in organic solid state batteries. The resulting devices are expected to be lightweight and non-toxic with applications in energy storage and power supply for the human exploration and development of space, as well as for communications devices on Earth. Critical characteristics for successful ion-conducting materials are high cation mobility, electrochemical/chemical stability, and high charge density. Here we report synthetic progress toward ionic polyelectrolytes which incorporate these requirements into their structures.

The polyelectrolyte design includes a semi-rigid polymer backbone, connected using a flexible chain to pendent anions. The key feature is the identity of the charged groups, which affect the mobility of counterions. We have selected boron clusters, initially $CB_{11}H_{12}^{-1}$, in hopes of synthesizing the first example of a polyelectrolyte with non-nucleophilic charged groups (pK_a of conjugate acid < -10). In carboranes, the single negative charge is delocalized over the entire spherical cluster, providing an extensive electrostatic field to stabilize nearby positive charges, but not react with them. The electrostatic properties of $CB_{11}H_{11}^{-}$ are dramatically different than those of the common electrolyte RSO_3^{-}, which concentrates electron density on oxygen, and the pendent carboranes potentially will promote higher mobility of cations (especially Li^+). Carboranes have the added advantages of low toxicity, insensitivity to pH, good chemical and electrochemical stability, and ease of functionalization at carbon.[1] The linking groups are oligoethylene glycol chains, which are hydrophilic, and promote conductivity of ions.[2] To simplify polymer purification and processing, the polymers or copolymers should have a narrow distribution of molecular weights and the polymerization conditions should be tolerant of charged groups. Given these restrictions, an obvious choice for the polymerization method is ring opening metathesis polymerization (ROMP). ROMP of 7-oxabicyclo[2.2.1]hept-2-ene derivatives such as *exo*-5,6-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**1a**) may be carried out in aqueous solutions, and results in low polydispersity, stable polymers with semi-rigid backbone structures.[3] Ease of synthetic access to **1a** and derivatives, established ROMP methodology to form **poly(1a)** and derivatives,[3] as well as some understanding of the resulting polymer microstructure, make this backbone structure ideal for our purposes. Appropriate derivatives of **poly(1)** have the potential to be a water-soluble, non-toxic, stable polymers with a variety of charged groups, and are expected to be good candidates for battery materials.

Literature procedures were used to obtain 5-*exo*-hydroxymethyl-6-*exo*-methoxymethyl-7-oxa-bicyclo[2.2.1]hept-2-ene (**2**).[4] Under Williamson ether synthesis conditions, $ClCH_2CH_2$-$(OCH_2CH_2)_2OTs$ was reacted with **2** to give 5-*exo*-2-[2-(2-chloroethyl)ethoxy]ethoxymethyl-6-*exo*-methoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene (**1b**).[5] Tetraethylene glycol ditosylate[6] or -dibromide gave mixtures of products which were difficult to separate. Treatment of **1b** with $Li(Et_3N)CB_{11}H_{11}^{2-}$ resulted in the carbaundecaborate derivative (**1c**). Chloride **1b** also reacted readily with trimethylamine to give a cationic monomer with a pendent trimethylammonium (**1d**).[5]

Although the monomers investigated thus far have not been soluble in water, all polymerizations were carried out in water solutions containing recycled $RuCl_3$ catalyst. For simplification of the nomenclature for the polymers, the structure of the polymers will be assumed for the remainder of

the discussion to be **backbone-X**, where X includes the linking group, and is defined for each structure as a reminder.

The thermal properties of **poly(1a)** (X=Me), **poly(1b)** (X= -$(CH_2CH_2O)_2CH_2CH_2Cl$), **poly(1c)** (X= -$(CH_2CH_2O)_2CH_2CH_2NMe_3^+Cl^-$), and neutral copolymers were investigated.[5] **Poly(1d)** (X= -$(CH_2CH_2O)_2CH_2CH_2NMe_3^+Cl^-$) had a T_g at 192 °C and T_d at 309 °C. The thermal properties of **poly(1c)** (X= -$(CH_2CH_2O)_2CH_2CH_2CB_{11}H_{11}^-$) are expected to be comparable to those of **poly(1d)** (X= -$(CH_2CH_2O)_2CH_2CH_2NMe_3^+Cl^-$). However, isolation and purification of the carborane polymers are likely to be more difficult due to the high solubility of boron clusters in organic and aqueous media. Copolymers of **1a** (X=Me) and **1b** (X= -$(CH_2CH_2O)_2CH_2CH_2Cl$) decomposed between 274 and 294 °C. No T_g was observed for ratios of 1: 0.5, 2, and 3 of **1a** and **1b**, but at a 1:1 ratio, a T_m was observed at 195 °C. The molecular weights of these copolymers ranged from 2.6-37 x 10^5 with narrow polydispersities.[5]

The synthetic phase of the research is well underway and we are currently investigating the properties of the new ionic polymers.

References

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