



~~~~ Polymer Physics Seminar ~~~~

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301 Steidle Bldg.

Synthesis and characterization of polyurethane ionomers

Applications such as lithium ion batteries and actuator membranes of ion-conducting polymers usually require both mechanical strength and ionic conductivity simultaneously. In my project, PEO-based polyurethane ionomers are explored for achieving both good mechanical strength and high ionic conductivity. Polyurethane is an interesting material that it can have coexisting a mechanically strong hard phase and a fast relaxing soft phase, which can potentially have high conductivity. Anionic groups like carboxylate and sulfonate groups are attached on the polyurethane chain either in the hard segment or soft segment to prepare single-ion conducting polyurethane ionomers that allow only cations to move under an applied electric field. Morphology, mechanical strength, ionic conductivity, thermal and dielectric properties are characterized to develop the structure-property relationships of these polyurethane ionomers.

Carboxylate-based polyurethane ionomers are prepared by attaching carboxylate groups in the hard segment. The effect of the counterions, from small sodium ions to large ionic liquid type counterions, is studied. It is found that with ionic groups in the hard segment, polyurethane ionomers do not microphase separate into hard and soft phases even with a 40wt% hard segment content. The glass transition temperature T_g decreases with increasing cations size because the distance between cation and anion increases and the Coulombic

force decreases. The ionomers with lower T_g show a much higher ionic conductivity (up to 5 orders of magnitude) and the ionic conductivity is strongly coupled to polymer segmental relaxation. However, the modulus is also reduced because these ionomers do not microphase separate and it is also found that more than 50% of the counterions are trapped in the hard segment.

Polyurethane ionomers with sulfonate groups in the center of the soft segment are also synthesized. It is found that with sulfonate groups in the soft segment and long enough PEG spacer ($M_w > 600$), the product polyurethane ionomers can microphase separate if there is more than 23wt% of hard segment, achieved by incorporating butane diol chain extender. The microphase separated ionomers are solids with modulus \sim MPa up to 200°C. A lower soft phase T_g (\sim 5°C independent of hard segment content) and higher ionic conductivity are also detected compared to ionomers with carboxylate groups in the hard segment. The ionic conductivity is again found to strongly couple with polymer segmental relaxation. By placing the ionic groups in the soft segment, the problem of many ions being trapped in the hard segment is solved and all ions can respond to electric field and contribute to ionic conductivity. Overall, the best ionomer obtained has shear modulus of 4 MPa and ionic conductivity of 2×10^{-5} S/cm at 150 °C.