Thermomechanical Properties of Poly(ethylene glycol)-based Segmented Ionenes with two structurally different hard segments

Jae Sang Lee,[a] Mehrnoosh Taghavimehr,[b] Reza Montazami,[b]* and Matthew D. Green[a]*

[a] Chemical Engineering, School for Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ 85287, USA

[b] Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA

Ionenes are ion-containing polymers that have charges in their backbone rather than on pendant sites. Segmented ionenes behave like an elastomer, similar to elastomeric polyurethane, by having alternating hard and soft segments along the backbone. This work described the influence of structural difference of hard segments, linear and heterocyclic aliphatic amines, as well as the weight fraction of soft segments on the thermomechanical properties, elasticity, and microphase separation of poly(ethylene glycol) (PEG)-based ionenes. Step-growth polymerization via the Menshutkin reaction of aliphatic and aromatic ditertiary amines with dihalides afforded the synthesis of PEG-based ionene random block copolymers. ^{1}H NMR spectroscopy confirmed the successful synthesis of PEG-2k dibromide oligomers and segmented ionenes. DSC and XRD revealed that DABCO-based ionenes have higher purity of PEG crystallites compared to aliphatic ionenes, and 75 wt% of soft segment triggered soft-hard mixing in both aliphatic and DABCO hard segments. TGA showed that both aliphatic and DABCO-based ionenes were thermally stable up to 250 °C and the possible crosslinking of DABCO upon exposure to elevated temperatures for DABCO-based ionenes. DMA revealed that DABCO-based ionenes possess superior elastomeric behavior compared to aliphatic ionenes at all weight fractions, possibly due to the better ionic aggregation and microphase separation. AFM confirmed the presence of microphase separated morphology with both aliphatic and DABCO-based ionenes having 25 wt% of the soft segment, which showed a better degree of phase separation among different weight fractions. Uniaxial tensile analysis showed that the elongation of PEG-based ionenes is highly dependent on the melting temperature of the PEG crystallites. Thus, these findings improve our understanding of microphase separated segmented ionene elastomers for a diverse set of applications.

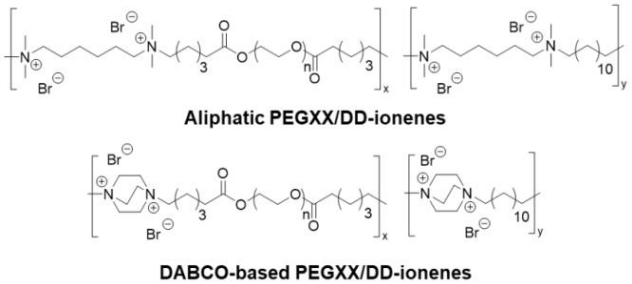

Figure 1. Structures of poly(ethylene glycol)-based segmented ionenes with aliphatic and DABCO hard segments. XX refers to 25, 50, and 75 which are corresponding to the overall weight fractions of the soft segment.