Effects of Salts on the Miscibility between Polymers

Prof. Zhen-Gang Wang
Division of Chemistry and Chemical Engineering
California Institute of Technology

Friday, November 5, 2010
3pm, refreshments at 2:45
66-110

There is much current interest in ion-containing polymers as materials for energy applications. For example, a promising system for rechargeable battery applications consists of diblock copolymers of an ion-dissolving block, typically polyethylene oxide (PEO) and a nonconducting block such as polystyrene. The addition of lithium salts has been shown to significantly alter the order-order and order-disorder transition temperatures, which reflects a change in the miscibility between the two polymer blocks. In this talk, I discuss some simple theoretical ideas for explaining and predicting the change in polymer miscibility due to the addition of salt ions. A key effect is the solvation energy of the ions by the polymers, which we approximate using the Born solvation model. The difference in the Born energy of the ions between different polymers provides a driving force towards phase separation, whereas the translational entropy of the ions favors keeping the polymers mixed. We find that when the dielectric constants of the two polymers are both low, adding salt decreases the miscibility, while when the dielectric constants of the polymers are both high, the addition of salt enhances the miscibility. The effect can be significant at ion concentrations corresponding to an order of one ion per polymer chain. The magnitude of the miscibility change predicted by our theory is within the same order of magnitude of the experimental values, without using adjustable parameters. Furthermore, for lithium salts with different anions, we predict that the effect should weaken with increasing ion size, in agreement with experiments.