The Impact of Solutes on other Aqueous Polymerizations

From previous disclosures on this website we have seen that the inclusion of hydrophilic solutes to aqueous cationic polymerizations can affect the outcome of reaction in some interesting ways. High salt content water is readily available in the form of desalination reject water in addition to waste water generated from various manufacturing processes. Use of *such waste streams* as polymerization diluents for suspension and emulsion type polymerization processes offers a *sustainable alternative* to traditional processes based water of higher purity. Such a strategy not only reduces waste streams but also decreases the overall demand placed upon limited supplies of fresh water. High salt content aqueous media might also be of benefit for polymerizations conducted at decreased reaction T as they have depressed freezing points. This could be of value since the MWs of polymers produced by both radical, and most especially cationic, methodologies are inversely related to reaction T. Lewis has demonstrated in the past that such eutectic mixtures allow for the production of high MW polymers of IB. *In a similar manner it should be feasible to make very high MW grades of polymers that are typically formed via a free radical mechanism in aqueous media (e.g., styrene-butadiene rubber) by the inclusion of hydrophilic solutes and use of cryogenic reaction T coupled with low T free radical initiators.* It should be obvious that the depressed freezing point of such aqueous diluents would allow for stronger cooling of the polymerization reactor and thus more efficient heat transfer without fear of solidification of the aqueous phase. This could provide an avenue for better overall control of aqueous polymerizations.

The inclusion of **hydrophobic solutes might also provide some unusual benefits to the polymerization of water soluble monomers** {e.g., acrylamide, acrylic acids and their salts (e.g., methacrylic acid, sodium acrylate)}. Usually such monomers are polymerized via "inverse" free radical suspension or emulsion techniques in which the polar monomer is suspended in a hydrocarbon nonsolvent to which is added a hydrophilic free radical initiator. Such monomers might be polymerized in water containing a high concentration of salts *as the presence of such hydrophilic solutes could potentially force the water soluble monomer to undergo phase separation from the aqueous layer and thus undergo heterophase polymerization in aqueous media*, something which is impossible in water that contains a low solute content. The presence of hydrophilic solutes could *also potentially be useful for controlling the initiation* process of suspension and emulsion polymerizations of vinyl monomers. For example, the presence of hydrophilic solutes could in theory be used to push free radical initiators into the organic (i.e., monomer containing) phase, even if the initiator itself has somewhat hydrophilic characteristics. *This could dramatically boost initiator efficiency in heterophase free radical polymerizations.*