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Polyelectrolytes and ionomers

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Since the advent of ionomers ca. 25 years ago, the problem has existed of defining the differences between ionomers on the one hand, and polyelectrolytes on the other. Currently, ionomers are defined as polymers containing a relatively low ion-content (up to ca. 10 to 15 mole %) while polyelectrolytes are defined as materials containing a very high ion-content, to the point of being water soluble.

The above definitions satisfy many requirements; however, we feel that they do not address the heart of the problem, which is the fact that some materials can behave both as polyelectrolytes in aqueous solution, as well as ionomers in the absence of water.

In this note, we would like to propose definitions which do not approach the problem from the materials point of view but rather a phenomological point of view. Thus, we would like to define ionomers as polymers in which the bulk properties are governed by ionic interactions in discrete regions of the material (the ionic aggregates). In these materials, for example, the bulk viscosity would be expected to increase as the ion concentration increases, the glass transition would be expected to increase as the ion-concentration increases etc. By this definition, all the materials which behave as ionomers would be defined as ionomers, independent of the ion content. Surlyn^{R}, copolymers of styrene and sodium methacrylate, etc. would obviously be included. Polyelectrolytes on the other hand would be defined as polymers in which solution properties in solvents of high dielectric constants are governed by electrostatic interactions over distances larger than typical molecular dimensions. Thus, one would expect the intrinsic viscosity to go up as the monovalent salt content of the solution goes down. Similarly the radii of gyration will be expected to increase as the salt content goes down or as polymer concentration goes down. Again, all the materials which we think of as polyelectrolytes now would fit into this framework, but so would styrene containing ca. 10 mol % of ionic grups in a solvent of high dielectric constant. Polyelectrolytes could, of course, be crosslinked or gelled and still be polyelectrolytes. While one could not measure the intrinsic viscosity of the gel or the unperturbed coil dimensions, the distances between crossolinks are certainly governed by electrostatic interactions.

These definitions could be supplemented by materials related descriptions. For example, for polyelectrolytes, one could add that these are generally polymers with a high ion content soluble in solvents of a high dielectric constant, while ionomers are, in general, polymers with a low ion contents.

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