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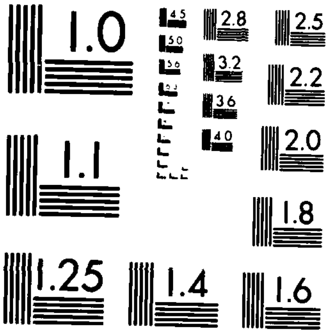

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Final Report

to

Office of Naval Research

Macromolecular Interactions
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We have conducted systematic investigations of the kinetic evolution of cluster size distributions of polymerizing macromolecules as the reaction proceeds toward the sol-gel transition. Using a resistive pulse analyzer we have been able to determine experimentally the mathematical form and time evolution of the number of monomers, dimmers, trimmers, quadrimers, etc., in a model system of polyfunctional antigens crosslinked by antibody. These results have been interpreted using the Smoluchowski equation originally developed for colloidal aggregates. According to our analysis the observed temporal evolution of the cluster size distribution is a direct reflection of the structure of the bimolecular reaction rate coefficients which enter as matrix elements of the Smoluchowski equation. We have shown that the expected form of these matrix elements is consistent with binding between molecules on the surface of the clusters. Our data provides perhaps the most complete experimental characterization of the kinetics of aggregating systems: a subject which is now experiencing intense theoretical study.

We have also conducted measurements of the temporal evolution of the second moment and mean number of bonds in an A_3-B_2 polymerizing system. In our case A_3 are three functional aziridine molecules and B_2 is sebacic acid. Using a specially constructed small angle light scattering system we have examined the temporal evolution of the first and second moments of the polymer size distribution from t=0 to the gel point. We are interpreting these results using the scaling properties of the Smoluchowski equation.

It was discovered that a polymer gel undergoes a discontinuous volume transition upon applying a small electric field across the gel[1]. A copolymer gel of acrylamide and sodium acrylate gel immersed in an acetone-water mixture was placed between two platinum electrode. A voltage of several hundred millivolts was applied on the gel develops an electrostatic stress gradient along the electric field. There is a critical stress over which the gel collapses and below which it is swollen gel can be several hundred times larger than the collapsed gel, but the volume ratio can be controlled by the amount of ionizable group of sodium acrylate. The phenomenon has opened the door to a variety of possible applications of gels as switches, memories, sensors, display units or mechanochemical transducers and artificial muscles.

We have "doped" acrylamide gels containing the ester N-acryloxysuccinimide; subsequent hydrolysis of the ester alone yielded gels of varying network ionization. After incubation in acetone-water mixtures, these gels displayed a swelling behavior qualitatively similar to that obtained from time-dependent hydrolysis of pure acrylamide gels. These results confirm that the network ionization plays a crucial role in the phase transition of these ionic gels.

We have also conducted thorough experiments on the salt effects on the phase transition in the ionic gels[4]. An ionized acrylamide gel is found to undergo a discrete phase transition in equilibrium volume upon varying the salt concentration in the solution. The salt concentration required for the transition depends strongly on the valency of the positive salt ion added to the solution. In certain cases the concentration at the transition is many thousand times larger for monovalent ions than for divalent ions. A simple theoretical consideration of the osmotic pressure of the ions can explain the phenomenon.

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Publications Made Possible by ONR Grant

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