5.2 RADIATION POLYMERIZATION

Ionizing radiation can be used for understanding mechanism of polymerization reaction as well as for initiation of the polymerization process. Some of the advantages of the radiation initiated polymerization over conventional methods are: (i) absence of foreign matter, like initiator, catalyst, etc., (ii) polymerization at low temperature or in solid state, (iii) rate of the initiation step can easily be controlled by varying dose rate and (iv) the initiating radicals can be produced uniformly by γ-irradiation. The kinetics of polymerization of a variety of monomers was extensively studied which led to better understanding of the mechanism of polymerization reactions. Using the technique of pulse radiolysis, the rate constants of the various initial steps, initiation and a few propagation steps, were evaluated and correlated with the structures of the transients formed by initiation with H, OH, and eaq species. The different intermediates in the polymerization reactions were also characterized by absorption spectra, pKₐ, redox behaviour, their decay and formation kinetics, etc., which further helped in understanding the polymerization process.

Radiation Synthesis of Polyaniline

Polyaniline (PAni) is an important conducting polymer, with wide range of applications. PAni was synthesized, for the first time, by radiation polymerization method. It was characterized by optical absorption, TEM and light scattering techniques. The light scattering study indicated formation of PAni particles of average sizes 160 and 200 nm, with low polydispersity, in aqueous medium, without any stabilizer. TEM picture showed presence of spherical particles of about 100 nm size, along with long fibers of similar diameter, in the dry sample.

Metal Nanoparticles in Hydrogel Matrix

Metal nanoparticles in hydrogels have many advantages over the conventional sols, e.g., smaller size, higher stability, easy accessibility and separation from reaction mixtures, etc. During
the formation process, the aggregation of nanoparticles is very much restricted and once formed, these do not coagulate or settle down in a hydrogel matrix. Thus, nanoparticles of non-noble metals, like Cu and Cd, could also be stabilized in a hydrogel matrix for a few hours, which otherwise are stable only for a few seconds in aqueous medium in the presence of air. Most of the reactants/products can diffuse easily in a hydrogel network, thus having easy access to well-separated nanoparticles for any catalytic application. Separation of nanoparticles of a catalyst from reaction mixtures generally requires tedious ultrafiltration or centrifugation processes, whereas nanoparticles in the hydrogel matrix can be easily separated from the reaction mixture, after completion of the reaction.

PVA is a major component of hydrogel wound dressings and an efficient stabilizer for Ag nanoparticles (prevents aggregation). Silver is a well known disinfectant. Thus, PVA hydrogel wound dressings containing Ag nanoparticles, would be highly desirable for treatment of infected wounds. Ag clusters have been radiolytically produced in the PVA hydrogel matrix, using AgNO₃ and AgCl. Viscosity, absorption spectra and swelling studies indicated that on radiolysis, Ag⁺ ion reduction is followed by crosslinking of PVA chains in the presence of AgNO₃.

While restricted availability of Ag⁺ ions, in case of AgCl, helps in simultaneous radiolytic formation of Ag nanoparticle, along with crosslinking of PVA chains. Ag clusters of sizes smaller than the pore size of the hydrogel matrix (~ 2 to 20 nm) have been produced. The swollen hydrogel containing two different concentrations of silver nanoparticles is shown in figure.

**Hydrogel Resins for Removal of Toxic Metals from Aqueous Waste**

Organic pollutants can be decomposed/oxidized by various methods, but metal ions have to be removed from waste water, otherwise they accumulate, enter into the food chain and never get destroyed by natural processes. Study on the development
of a hydrogel-based resin to remove metal ions from polluted water was carried out. A hydrogel resin containing about 80% water, with capacity greater than 220 mg/g for cobalt adsorption, has been synthesized by radiation-induced method.

It has shown efficient extraction of Co^{2+} and Cu^{2+} ions from aqueous solutions and could be recycled without any loss of capacity.

**Superabsorbents**

Superabsorbents are materials which can absorb about 100 gm or more of solvent per gram. These are extensively used in medical, chemical and agriculture industries. An acrylic acid–carrageenan based superabsorbent hydrogel, with high Equilibrium Degree of Swelling (EDS) of about 800 g/g, was prepared by γ-irradiation method. It was found to be sensitive to pH and ionic strength of the medium and can have applications in concentrating many natural extracts and drug formulations by absorption/removal of water.

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**Solid/Liquid Phase Extraction of Radionuclides**

The solid/liquid phase extraction of U(VI), Pu(IV), Am(III) and some fission products from aqueous nitrate solutions, using extractant immobilized PVA/acryl amide copolymer gel, was carried out in collaboration with FRD. More than 90% extraction, under optimized conditions, of U(VI), Pu(IV) and Am(III) was obtained, while extraction of Cs and Sr was negligible. Radiation modification of polymeric films and fibers to attach suitable extractant groups was also carried out. The loading capacity, extraction and elution efficiency were evaluated for both the systems and were found to remain nearly the same, even after three to four cycles of extraction and elution. These modified polymers could selectively extract ~ 90% U/Th from nitric acid medium, in the presence of Cs, Bi, Ph, Tl, etc.

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