Development of Polymers for Various Applications

Juby K. Ajish

Preamble:

This article summarises the evolution of polymer research in Chemistry Group which started from around 1970. In the initial years work was mainly oriented towards the pulse and gamma radiolytic effects of methacrylates and other similar monomers. The research was later extended towards fabrication of hydrogels and nanoparticles radiolytically. From 2010 onwards, research in the polymer chemistry was focused on developing materials for departmental benefits, like polymeric resins for radionuclide extraction, targeted drug delivery and toxic as well as precious metal extraction. A brief description of all these activities have been given in this article including the recent work in the area of radiation detection, gallium extraction from Bayer's liquor, glycopolymers etc.

Introduction:

Polymer science has always been an important area of research for enhancing the quality of life and showcasing the role of science and technology in human welfare. The polymer research in Chemistry Group has played a key role in its formative years where a number of projects of departmental relevance were carried out, to take it to a level of technology transfer, patents and MoU with industries. Some of the activities in polymer laboratory involved radiation induced synthesis of polymeric materials for various applications, pulse radiolysis studies, synthesis of extractant encapsulated beads for extraction of toxic metals and radionuclides. The research was further extended to fabrication of hydrogels, antibacterial materials, bacterial detection and also self assembly of polymeric materials. Various biomedical and separation science based applications of polymers have been explored using synthetic and natural polymers.

As the application of polymers is vast in various fields, the journey which started from radiolytic synthesis of polymeric materials has now expanded to wide areas including radiation detection and neutron dosimetry. In addition, polymer beads synthesized in-house have been utilized for the separation of gallium from Bayer's liquor which is a major programme relevant to DAE. A brief outline of the work and major milestones are given in the following pages.

Radiation induced polymerization of various monomers

This was the major area of polymer chemistry research in the early 1970s in Chemistry Group. Both gamma as well as pulse radiolysis set up was utilized to study the reactions. Some important works include gamma ray induced polymerization of trioxane which is a cyclic ether having commercial importance. Polymerization of trioxane was investigated by both in-source and post –polymerization techniques. The purification strategy for trioxane and its polymerization procedure was successfully developed for a 10 Kg batch in 1975. Interactions of hydrated electrons with various monomers like ethylene, styrene, vinyl acetate, vinyl benzoate, methyl acrylate, methyl methacrylate etc were studied extensively. In radiation induced anionic polymerization, addition of an electron to the monomer molecule leads to the formation of the anionic initiating species. Rate constants of the reaction of solvated electrons with various monomers were investigated using flash photolysis technique. It was observed that styrene with ethylenic bond in conjugation with benzene ring is more reactive towards electrons compared to ethylene itself.

The late 1970s marked the beginning of applied radiation chemistry research of polymers in Chemistry Group. Grafting of vinyl monomers using radiation onto synthetic fibres and suppression of their homopolymerization was widely explored. The scavengers used while grafting vinyl based monomers onto synthetic fibres in aqueous solution are ferrous ammonium sulphate for acrylic acid and copper sulphate for methacrylic acid and acrylamide. The radiation induced grafting was taken up as a major research area where a lot of work like grafting of styrene, methylmethacrylate, acrylic acid and methacrylic acid on synthetic fibres like polypropylene (PP) fibres, wool etc were carried out.

Radiation induced polymerization of various monomers like vinylidene chloride and effect of solvents such as chloroform, bromoform and benzene on the same was studied extensively. In addition, copolymerization studies using vinyl monomers like vinylidene chloride and acrylonitrile as well as methyl methacrylate were also an area of investigation.

Polymer based sealants for nuclear industry:

Sealant materials used in nuclear industry should be durable, radiation resistant, ensure leak tightness and allow movement of all joints that undergo thermal expansion and contraction cycles. For nuclear applications polysulfide sealants were a material of choice, because of their superior extensibility, durability and bonding characteristics and also water, chemical and heat resistance. Polysulfide sealants consist of a blend of polysulfide resin and plasticizer. A final composition which is suitable for use in a reactor building was chosen and about 100 kg of the material was produced.

Polymer based biomedical devices:

The polymer research was not only confined to studying radiation polymerization but also to the development of various biomedical devices. In 1980, hemodialyzers namely BA-60 were developed, which showed good efficiency for urea clearance under simulated conditions and it was one of the most compact and efficient hemodialyzers during that period.

Another device named “Oral Artificial Kidney” capable of removing metabolic toxins through gut walls when taken orally was developed during the period 1977-80. This was made using oxidized cellulose composites, hydrogels and ion-exchange resins. In addition, a new method of fabricating microcapsules as well as a hemodialysis alternative was designed in the same time period. These developments facilitated detection of bilirubin in urine for early diagnosis of hepatitis.

Liquid extractant encapsulated polymeric beads for the extraction of toxic metals and radionuclides:

Numerous methods/technologies have been developed over the years, to treat industrial wastes. Among the different separation methods for metals, liquid-liquid extraction (LLE) is widely used in industry for bulk separation. LLE can overcome many of the problems associated with the solvent extraction techniques like third phase formation, excessive organic waste generation and complexity in handling. Solid–liquid mode of separation is more efficient and green technique for dilute aqueous water management. Further new sorbent composites, with tuned selectivity and high capacity can be developed for the solid - liquid method. Extractant encapsulated polymeric beads (EEPBs) have been synthesized for separation of metals from different aqueous wastes which is more advantageous than other polymeric extractants as their metal uptake capacity can be improved by increasing the extractant concentration of the composite material. Fig. 1A depicts the Di-(2-Ethyl Hexyl) Phosphoric Acid (D2EHPA)-encapsulated polymeric beads for sorption of uranyl ions. The porous polymeric beads encapsulating liquid extractant such as; D2EHPA encapsulated polymeric beads, Benzodioxodiamide (BenzoDODA) encapsulated polymeric beads, 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (PC88A)encapsulated polymeric beads, TBPencapsulated polymeric beads and N,N,N′,N′-tetra-(2-ethylhexyl)-dithiodiglycolamide (DTDGA) encapsulated polymeric beads were synthesized for the extraction of various metal ions from aqueous waste streams. These synthesized beads exhibited very good radiation stability upto 60 MRad and good extraction capacity for multiple extraction/stripping experiments which points towards its recyclability in treating radioactive waste.

Many types of inorganic sorbent polymer composite beads were also synthesized, which could overcome many of the shortcomings of conventional inorganic sorbents. The fine morphology and gel like nature of inorganic sorbents leads to many practical difficulties like excessive pressure drop across the bed and low hydraulic conductivity. Fig. 1B shows the photographs of various beads synthesized in this category. A method of synthesizing resol beads with good control over particle size have been developed and has been patented (Patent no: 3986/MUM/2013) (Fig. 1C).

Radiation induced synthesis of hydrogels and glycopolymers for bio-medical applications:

Radiation processing technology is being increasingly used to produce better materials which cannot be obtained by any other means. One such material with wide range of applicability and possibilities is the hydrogel. High energy radiation can generate highly reactive radicals or ions on the irradiated substrate in any phase and at any temperature. The hydrogels resemble living tissues because of their relatively high water content which facilitates the diffusion of small molecules like metabolites, oxygen and nutrients, making them ideal materials for controlled release of drugs and other active agents. Hydrogels find application in burn and wound materials as they protect the wound from microbial contamination, prevent loss of body fluids and permits free diffusion of oxygen in to the wound thereby accelerating the healing process.

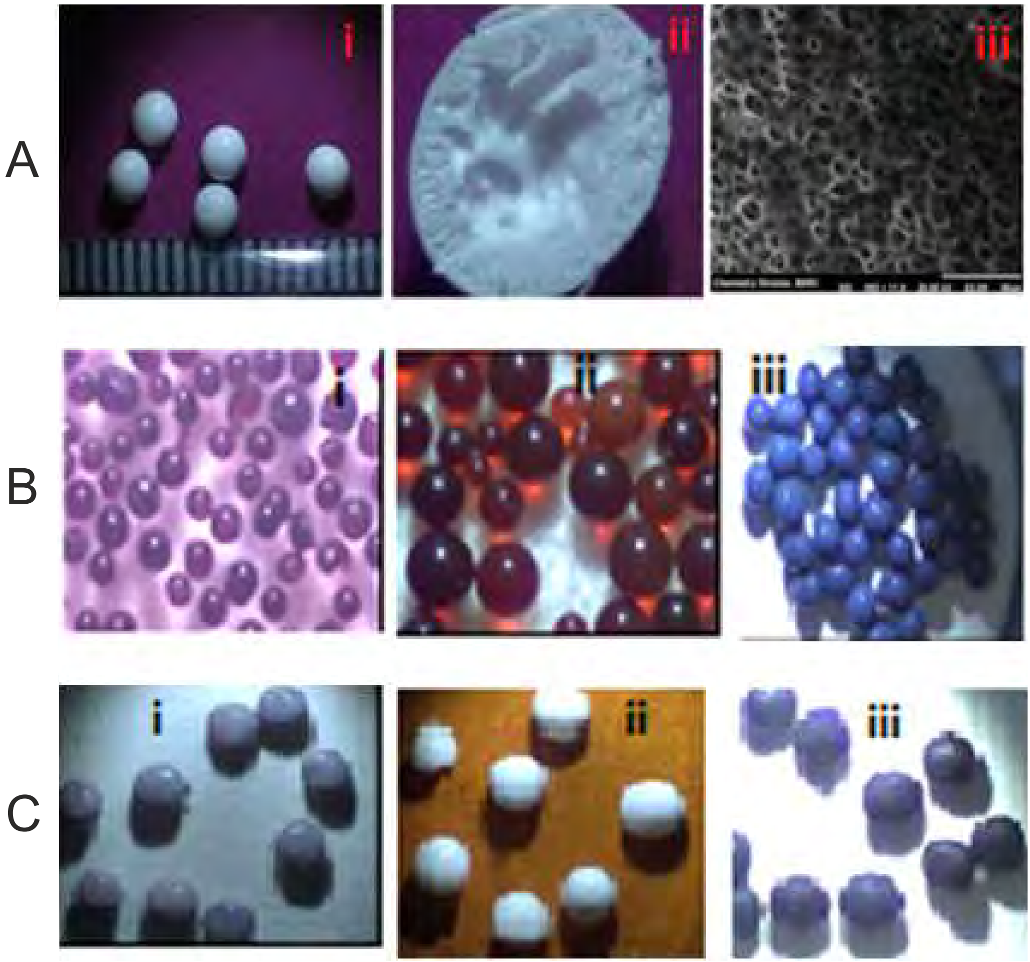

Fig. 1: (A) (i) Optical image of D2EHPA-encapsulated polymeric beads for sorption uranyl ions (ii) crossectional view of the bead (iii) SEM image of the bead (B) Optical images of inorganic sorbent polymer composite beads (i) Resorcinol formaldehyde (RF) bead (patented) (ii) RF-XAD bead (iii) KCoHCF-Gel bead (C) Optical images of inorganic sorbent polysulphone (PS) beads (i) CuHCF-PS composite beads (ii) TiO_2-PS composite beads (iii) MnO_2-PS composite beads

High energy radiation is the most suitable and a green tool for the synthesis of hydrogels due to easy process control and facile synthesis along with sterilization in one step. Even though the radiation induced synthesis of hydrogels is one of the most successful applications of radiation chemistry; it cannot be generalized for all types of hydrogel systems. Only certain monomer/polymer systems, with high cross linking G values are capable of forming sufficiently stronger hydrogels for different biomedical applications.

Some limitations of radiation induce polymerization include lack of selectivity as it reacts equally with all bonds in the material unlike chemical or photo initiated reactions and it induces degradation of materials. Relatively large power requirements (accelerators) and the shielding requirements (radioactive sources) makes the radiation induced techniques less affordable. But all these limitations never outweigh the greener and clean nature of radiation processes.

In most of these studies, irradiation of pure polymers in aqueous solution without using any monomers or crosslinking agents were used. This provides the ease to control the reaction also, reduces the number of unwanted processes like homo-polymerization and grafting of monomer on a base polymer chain. The hydrogels formed at a dose of 25 KGy or higher, are sterile and can be used directly without any further purification. Given below are highlights of the work on hydrogels synthesized by radiation induced technique.

One of the outstanding contributions in the field of bio-medical polymer research in Chemistry Group was technology development for radiation processed hydrogel useful for burn and injury dressing. Applying radiation technology, one pot synthesis of a poly vinylalcohol (PVA) based hydrogel was achieved devoid of any synthetic additives unlike chemical synthesis. The extensive clinical trials conducted in collaboration with various reputed hospitals in Mumbai which confirmed effectiveness of the hydrogel in treating burns, wounds as well as non-healing ulcers like leprosy ulcers. The technology was then transferred to private firms and is commercialized with the brand name ‘Hizel’.

Radiation induced synthesis of superabsorbent hydrogels:

Superabsorbent polymers can absorb and retain very large volume of water upto many hundred times than their dry weight even under pressure. They find application in agriculture, personal hygiene products, and other specialized areas, like controlled drug delivery systems. Superabsorbent polymers include synthetic, semi-synthetic, or natural polymers in which water soluble polymers are made insoluble by crosslinking.

Carrageenan is a viscosity enhancing polysaccharide commercially extracted from certain species of red seaweeds. A combination of acrylic acid and carrageenan was used to make hydrogels with superabsorbent properties.

Radiolytic synthesis of Ag clusters in aqueous PVA solution and hydrogel matrix

Silver and gold nanoparticles are the most studied ones among the different metal nanoparticles. Radiolytic synthesis of metal nanoparticles is more environment friendly because it does not employ any chemical reducing agents. The influence of Ag^{+} ions on the radiation-induced crosslinking of PVA chains was studied which revealed that the Ag^{+} ions could be efficiently reduced to form the Ag clusters, by gamma irradiation, in both PVA solution and hydrogel matrix.

Syntheses of biocompatible hydrogels from natural polymers like polysaccharides are more advantageous than that from synthetic polymers. Gum Acacia is a natural polysaccharide which cannot be crosslinked whereas PVA can be crosslinked, by gamma as well as electron irradiation, to form hydrogels. Both gum acacia and PVA are highly biocompatible, economical and environmental friendly and hence were utilized to make silver nanoparticles (AgNPs) loaded hydrogel matrix, with antimicrobial property. The release of silver from the polymeric matrix to the pathogenic environment, governed the antibacterial activity of these hydrogels.

Fabrication of biocompatible glycopolymeric hydrogels:

Glycopolymers are a new class of biodegradable and biocompatible materials containing sugar moieties as pendants, which has received great attention in the scientific community. This is attributed to their wide range of applications, in the field of synthesis of macromolecular drugs, matrices for cell culture, model biological systems, surface modifiers, chromatographic purposes and so on. The carbohydrate pendants in these polymers have glycotargeting ability which helps in recognizing the carbohydrate binding proteins called lectins present on the cell surface and this makes them a unique class of materials for targeted drug delivery applications. Radiation induced synthesis of glycopolymeric hydrogels from in house synthesized monomers and crosslinkers were carried out and was investigated for targeted anticancer drug delivery applications.

Radiation induced polymerization has started receiving wide spread public acceptance and there is growing interest in the area of radiation based manufacturing techniques. Radiation chemistry has indeed played a major role in understanding the reaction mechanisms and chemical kinetics for exploring the use of high energy radiation in many more systems.

Separation of precious metals using polymeric systems:

Extraction of gallium from Bayer's liquor:

The work regarding the recovery of gallium(Ga) from Bayer's liquor was initiated as a part of the MoU signed between NALCO and BARC. The primary material for the process, i. e., a chelating polymeric resin, which is synthesized inhouse, is capable of selectively extracting Ga from large background of aluminium from a highly alkaline medium of the Bayer's liquor. To serve this purpose, a crosslinked polyacrylonitrile based chelating resin (Fig.2) was developed, which not only showed an excellent stability in the high alkaline medium but also exhibited a good capacity for selective Ga uptake, in the batch mode. The synthesis of this developed resin was scaled up to from ~5g/batch to 20 kg/batch level, in collaboration with ChED, BARC. About 100 kg of this resin was synthesised to perform the pilot scale column experiments at Heavy Water Board (HWB) facility, RCF, Chembur. The developed resin showed excellent reusability up to 20 cycles (in batch mode) and up to 10 cycles (in pilot scale column mode) using both acidic and alkaline eluting agent. The elute solution containing gallium generated in pilot scale column mode of operation, is given for downstream process to obtain metallic gallium.

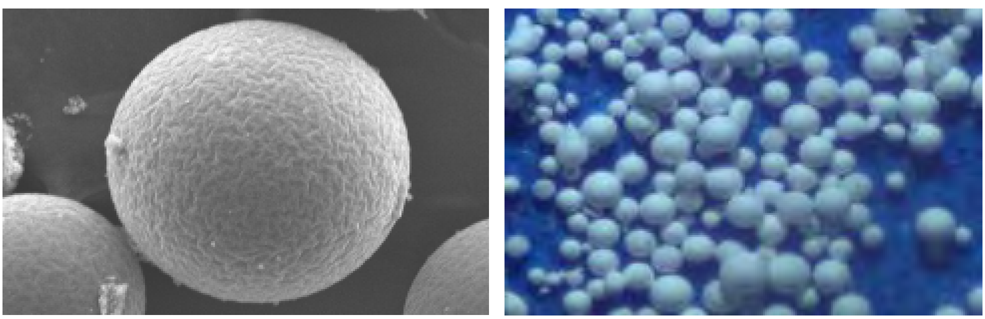

Fig. 2: Polyacrylonitrile based chelating resin for gallium extraction from Bayer's liquor

Based upon the experience gained during the pilot scale column operation using the developed resin beads, a demonstration plant for gallium recovery process is proposed to be set up at NALCO site Damanjodi, Odisha.

Polymeric materials for radiation detection:

Organic scintillators,mainly the solid plastic materials have long been an inexpensive source of radiation detector material. In addition to their low cost, easy production in large sizes and variable shapes, fast response time, ruggedness, etc, makes these most suitable for applications, such as portal monitoring, limb monitoring, cargo scanning, physics research, etc. Presently, Radiation Safety Systems Division (RSSD), Nuclear Physics Division (NPD), BARC and ECIL, Hyderabad, are importing a large quantity of plastic scintillators, in different shapes and sizes, for making such devices.

In this context, work on the development of plastic scintillators, was initiated and cylindrical shape 2 inch dia plastic scintillator samples of different heights were successfully made. These scintillators are produced by controlled polymerization of monomers, such as styrene and its derivatives, in the presence of organic fluorescence additives and suitable polymerization initiators. These synthesized plastic scintillators were tested in a working model of portable hand-held radiation monitor at RSSD, BARC. The performance of the developed monitor was found to be better than that of the imported ones, as tested with sources like ^{137}Cs. The developed radiation monitor can be employed for different radiation detection applications. Work is also in progress for fabrication of CR-39 films for personal neutron monitoring.

Some recent activities and way forward:

There are many areas where work is still ongoing which involves development radiation grafted polyacrylic acid-polyurethane foam co-polymer for efficient toxic metal removal from aqueous waste, treatment of low-level radioactive wastewater containing cesium ions by using cobalt hexacyanoferrate-sand composite, synthesis and characterization of magnetite/go/potassium copper hexacyanoferrate nanocomposite for removal of radioactive cesium ions, facile synthesis of two-dimensional materials for fabrication of photoelectrodes in photoelectrochemical catalytic processes, modification of sulfur cathode by polymerization in Li-S battery. In addition stimuli responsive self assembled glycopolymers have been synthesized, a reusable column based on glycopolymeric resins for bacterial capture and detection have been developed.

The way ahead will be dedicated to the polymeric materials relevant to the departmental applications and of societal benefit. Tailoring the properties of polymers for very specific needs of the nuclear industry and import substitutes will be the main focus of the future activities. In addition, studies on the emerging polymerization and characterization techniques will be pursued as an integral part of the R & D activities. This research area is vast and it will continue to have a big impact on various activities of the department for the foreseeable future.