2.1. Chemical reagents

All reagents were of high purity and used as received. Prior to use, glassware was cleaned with aqua regia (volume ratio HNO₃/HCl = 1 : 3) and thoroughly rinsed with nano pure water. Aqueous solutions were prepared using nano pure water (resistivity =18 MΩ cm). AgNO₃ and ascorbic acid obtained from M/s Sarabhai Chemicals, Vadodara, India, hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, 99.99%) from MV laboratories, o-phenylenediamine (o-PDA), horseradish peroxidase (HRP) (300 units/mg), hydrogen peroxide and poly(N-vinyl-2-pyrrolidone)s (PVPs) of molecular weights 40,000; 1,60,000 and 3,60,000 Da from Aldrich, isopropyl alcohol, acetone, sodium hydroxide, citric acid, sodium citrate, potassium dihydrogen phosphate and sodium hydrogen diphosphate from S. D. Fine Chemicals Ltd., Mumbai, India, guar gum from Sigma, cetyl trimethyl ammonium bromide (> 99%) from Fluka and methacrylic acid from CDH laboratories, Mumbai, India, dopamine hydrochloride (98%) from HiMedia Laboratories, Mumbai, India were used as received. A 0.125mg/10ml aqueous solution of horseradish peroxidase (HRP) was prepared for further use. High pure N₂ gas was used for saturating the reaction mixture before subjecting to gamma irradiation.

2.2. Gamma irradiator and dosimetry aspects

2.2.1. Gamma irradiator

A Gamma irradiation source, Gamma Chamber- 5000, supplied by the Board of Radiation & Isotope Technology (BRIT), Mumbai, INDIA was used for irradiation of reaction mixture solutions. Figure 2.1 shows the layout of gamma chamber used in these studies. Gamma chambers mainly consist of a set of stationary Cobalt-60 (⁶⁰Co) source placed in a cylindrical cage surrounded by a lead shield. The shield is provided around the source to keep external radiation field well within the permissible limits. The material for irradiation is placed in an irradiation chamber located in the vertical drawer inside the lead flask. The drawer can be moved up and down with the help of a system of motorized drive, which enables precise
positioning of the irradiation chamber at the center of the radiation field. $^{60}\text{Co}$ radioisotope emits two $\gamma$ rays of energy 1.33 and 1.17 MeV.

Figure 2.1: Layout of Gamma chamber 5000

2.2.2. Radiation dosimetry

To quantify the physical, chemical or biological changes produced by ionizing radiation, the knowledge of the amount of energy absorbed per unit mass and distribution of the absorbed energy in the absorbing material is necessary. Radiation dosimetry constitutes determination of these quantities.
(i). **Absorbed dose**: The absorbed dose is the amount of energy absorbed per unit mass of the irradiated material. The SI unit for the absorbed dose is Joules/kilogram (J kg$^{-1}$), which is known as gray (Gy) [122]. The old unit is rad (1 rad = 0.01 Gy) [123].

(ii). **Absorbed dose rate**: The absorbed dose rate is the absorbed dose per unit time. The unit for the absorbed dose rate is Gy s$^{-1}$.

(iii). **Absorbed dose in samples**

The absorbed dose measured by the dosimeter will represent the dose absorbed by the sample only when the following conditions are satisfied: (i) the dosimeter as well as the sample are both homogeneous, (ii) both have same size, density and atomic composition, and (iii) both are irradiated under same conditions. The simple and widely used method to achieve these conditions is to use equal volumes of dilute solutions of both sample and dosimeter, and irradiated them in turn using the same container at the same position in the radiation field. Therefore, experimental conditions must be suitably controlled for accurate measurement of the absorbed dose in the sample. However, these conditions do not match very often and in such cases a calculation must be carried out to obtain the absorbed dose in the sample using the Equations 2.1. For electromagnetic radiation like $^{60}$Co γ-rays, the absorbed dose in the dosimeter ($D_d$) and sample ($D_s$) are related by equation (1.11).

$$D_s = \frac{D_d \times (Z/A)_s}{(Z/A)_d} \quad (2.1)$$

Where, $Z/A$ is the ratio of the atomic number ($Z$) to the atomic weight ($A$) for an element and the ratio of the sum of the atomic numbers of the element present to the molecular weight for a compound.

(iv). **Primary and secondary dosimeters**

Dosimeters can be classified into two categories viz. primary dosimeters and secondary dosimeters. Primary dosimeters utilize a physical measurement such as temperature rise in a calorimeter, ionization produced in a gas or the charge carried by a beam of charged particles of known energy [123,124]. Secondary dosimeters are those dosimeters whose response to radiation has to be calibrated against a primary dosimeter. These include Fricke dosimeter, nylon film dosimeter, solutions of various dyes, perspex dosimeters [125]. The choice of a dosimeter for a particular application depends on many factors namely, (i) state of the system, (ii) dose range to be monitored and (iii) nature of radiation.
2.2.3. Dosimetry of gamma chamber

The dose rate delivered by gamma chamber 5000 was measured by Fricke dosimetry before carrying out any experiment. The oxidation of ferrous ions to the ferric ions in acidic aqueous solutions in presence of oxygen and under influence of radiation is the basic principle of Fricke dosimeter [126–129]. The standard Fricke dosimeter consists of an aerated solution of 1.0 x 10\(^{-3}\) mol dm\(^{-3}\) ferrous ammonium sulphate, 1.0 x 10\(^{-3}\) mol dm\(^{-3}\) NaCl and 0.4 mol dm\(^{-3}\) sulphuric acid (pH= 0.46). The reaction involved in the Fricke dosimeter is the radiation-induced oxidation of ferrous ion to ferric ion at low pH and in the presence of oxygen in accordance with the series of reactions (2.2) – (2.8).

\[
\begin{align*}
H_2O & \xrightarrow{\text{e}_{aq}^-} e_{aq}^- & H^- & \cdot \text{OH}, H_2, H_2O_2, H_3O^+ \quad (2.2) \\
e_{aq}^- + H^+ & \rightarrow H^+ \quad (2.3) \\
H^- + O_2 & \rightarrow HO_2^- \quad (2.4) \\
Fe^{2+} + \cdot \text{OH} & \rightarrow Fe^{3+} + OH^- \quad (2.5) \\
Fe^{2+} + HO_2^- & \rightarrow Fe^{3+} + HO_2^- \quad (2.6) \\
HO_2^- + H^+ & \rightarrow H_2O_2 \quad (2.7) \\
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + OH^- + \cdot \text{OH} \quad (2.8)
\end{align*}
\]

The yield of ferric ion is related to the primary radical and molecular yields by Equation (2.9)

\[
G_{Fe^{3+}} = 2G_{H_2O_2} + 3 \left[ G_{e_{aq}^-} + G_{H^+} \right] + G_{\cdot \text{OH}} \quad (2.9)
\]

Since each molecule of hydrogen peroxide oxidizes two ferrous ions by reactions (2.8) and (2.5), while the reducing radicals each oxidize three ferrous ions by sequential reactions involving HO\(_2^\cdot\), H\(_2\)O\(_2\) and \(\cdot\)OH respectively. The number of moles of Fe\(^{3+}\) ions (M) produced upon irradiation is determined by absorption spectrophotometry employing Beer's law (\(\Delta A = \Delta \epsilon c l\)) at 304 nm with \(\epsilon_{Fe^{3+}} = 2205 \pm 3\) dm\(^{-3}\) mol\(^{-1}\) cm\(^{-1}\) and \(\epsilon_{Fe^{2+}} = 1\) dm\(^{-3}\) mol\(^{-1}\) cm\(^{-1}\) at 25\(^\circ\)C. The \(G_{Fe^{3+}}\) value accepted for electron and photon radiation in the range 1 to 30 MeV is 15.5 (or, 1.606 x 10\(^{-6}\) mol dm\(^{-3}\) J\(^{-1}\)) at 25\(^\circ\)C and the density of Fricke dosimeter solution (\(\rho\)) is 1.024 gm ml\(^{-1}\). The absorbed dose (D) is derived by following expression (2.10)

\[
D = \frac{100 \times 1.602 \times 10^{-19} N_A M}{\rho G} G_Y
\]

\[
\Rightarrow D = \frac{9.647 \times 10^8 \nabla A}{\rho G \nabla \epsilon} G_Y
\]

30
\[ D = 277 \times \frac{\nabla A}{l} \text{ Gy} \quad (2.10) \]

Where \( N_A \) is Avogadro’s number and \( l \) is the path length in centimeters.

The Fricke dosimeter can be used to accurately determine dose only up to 400 Gy. Because of depletion of oxygen in the system beyond this dose \( G_{(Fe^{3+})} \) does not remain constant. Fricke dosimeter is independent of dose rate between 0.2 to 2.0 \( \times 10^6 \) Gy s\(^{-1}\). A modified version of Fricke dosimeter, also called as super Fricke dosimeter, containing \( 10^{-2} \) mol dm\(^{-3}\) ferrous ions, oxygenated but without any sodium chloride, is dose rate independent up to absorbed dose rates of the order of \( 10^8 \) Gy s\(^{-1}\). The upper limit of absorbed dose that can be measured using a super Fricke dosimeter is 2.0 kGy. Lead attenuators of suitable thickness were used for reducing the dose rates.

### 2.3. Characterization techniques

#### 2.3.1. Ubbelohde viscometer

Viscosity measurement studies were carried out using an Ubbelohde viscometer from M/s Scam India having a flow time of 62 s for double-distilled water at 25 °C. The molecular weight of polymer was determined with the viscosity method from Mark-Houwink equation,

\[ \eta = \kappa M_0^\alpha \quad (2.11) \]

Where, \( \eta \) is the intrinsic viscosity, \( M_0 \) is the viscosity-average molecular weight, and \( \kappa \) and \( \alpha \) are constants, whose values can be found from literature [130].

#### 2.3.2. UV-visible spectrophotometer

The absorption spectra of aqueous silver nanoparticles in guar gum and short aspect ratio gold nanorods in CTAB were recorded on a Shimazu model 4600 recording spectrophotometer in the wavelength region 250–900 nm. In all other cases the absorption spectra of gold nanoparticles were recorded on a Thermoelectron - Evolution 300 uv-visible spectrophotometer in the wavelength region of 250-900 nm.

#### 2.3.3. TEM instrument

Transmission electron microscopy (TEM) of silver nanoparticles was performed on a Model JEOL 2000 FX transmission electron microscope with an accelerating voltage of 160 kV. Transmission Electron Microscopy (TEM) was of gold nanorod solution in CTAB
performed on Libra 120 Zeiss cryoelectron microscope from TIFR with an accelerating voltage of 160 kV. Transmission Electron Microscopy (TEM) of other anisotropic gold nanoparticles in CTAB and gold nanoparticles in PVP were performed on a Model JEOL 2000 FX transmission electron microscope with an accelerating voltage of 120 kV. For the measurement of TEM a drop of dilute gold nanoparticle solution was placed on a carbon coated copper grid and dried before it was observed under the microscope. The solution of spherical nanoparticles in polymer was directly placed on a carbon coated copper grid allowing the water to evaporate at room temperature and then the grid was analyzed under TEM instrument. In case of anisotropic nanoparticle in surfactant solution the TEM sample was prepared by centrifuging the sample of nanorod twice at 15,000 rpm for 15 minutes in order to remove excess surfactant. Precipitates were collected and redispersed in a small amount of nanopure water, and 50 µl of the suspension was placed on a carbon coated copper grid and allowing the water to evaporate at room temperature.

2.3.4. FTIR spectrophotometer

Fourier transformed infrared spectroscopy (FTIR) measurements were performed on a FTIR spectrophotometer, FT/IR-610 from JASCO, Japan. Solid samples of metal-polymer were thoroughly ground at liquid nitrogen temperature and mixed with KBr. The mixture was compressed to prepare disc for FTIR analysis. In case of liquid samples, like Ag/polymethacrylate, one drop of each sample solution was spread evenly on the ATR crystals window. The samples were air dried for water evaporation, the holder was mounted in the sample window of the spectrometer and the sampling window was scanned. FTIR spectra were recorded in the range from 400 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) and averaged over 25 scans.

2.3.5. X-ray diffractometer

The X-ray diffraction (XRD) patterns of powdered metal-polymer were recorded on a Philips XRD spectrophotometer (model PW 1729) in the range 2\(\theta\) = 20\(^{\circ}\)-70\(^{\circ}\). The size of metal nanoparticles were calculated from Debye- Scherrer equation,

\[
d = \frac{K\lambda}{\beta \cos \theta}
\]

(2.12)

where \(K\) is the shape factor (0.9), \(\lambda\) is the x-ray wavelength (1.5 A\(^{\circ}\) for Cu k\(_{\alpha}\)), \(\beta\) is the line broadening at half the maximum intensity (FWHM) in radians, and \(\theta\) is the Bragg angle.
2.3.6. Thermo gravimetric instrument

Thermo gravimetric experiments were carried out under a N\textsubscript{2} flow with a TGA Mettler 3000 instrument at a heating rate of 10 °C/minute. The thermal stability of virgin polymer is different from metal nanoparticle incorporated polymer due to high thermal conductivity of metal.

2.3.7. Powder sample preparation

Powdered samples of Ag nanoparticles in guar gum for TG, XRD and FTIR analysis were prepared as follows. Ag/guar gum nanocomposite was precipitated by adding excess acetone to aqueous guar gum solution containing Ag nanoparticle. The precipitate was finally washed with acetone and then dried in a laboratory oven at 50 °C for 5 hrs under vacuum. The dried sample was grounded to fine powder by using a mortar and pestle.