CHAPTER-2

Experimental
EXPERIMENTAL

This chapter contains details of the materials used, preparation and characterization of the samples through various techniques.

2.1 Materials

2.1.1 Monomers

Acrylamide (AM) extra pure: Analytical grade, Molecular weight = 71.08 g/mol; bp = 125 °C; mp = 82-86 °C; Source: Aldrich, Sigma.

2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA): Molecular weight = 207.25 g/mol; mp = 195 °C; Source: Aldrich, Sigma.

N,N'-methylenebisacrylamide (N MBA): Extra pure AR, molecular weight = 154.17 g/mol; Source: SRL (India).

2.1.2 Surfactants

Sodium bis (2-ethylhexyl) sulfosuccinate or Dioctyl sulfosuccinate sodium salt (AOT): Molecular weight = 444.56 g/mol; mp = 173-179 °C; Source: Aldrich, Sigma.

Span-80 Grade (Sorbitane monooleate): Molecular weight = 428.62 g/mol; density = 0.994; Source: Aldrich, Sigma.
2.1.3 Initiator

**2.2-azobisisobutyronitrile (AIBN):** Molecular weight = 164.20 g/mol; mp = 97-102 °C; 
Source: Spectrochem Private Ltd. (India).

2.1.4 Filler

**Silicon dioxide (SiO$_2$):** Molecular weight = 60.09 g/mol; BET surface area = 590-690 m$^2$/g; Size = 10 nm; bp = 2230 °C; Source: Aldrich, Sigma.

2.1.5 Other Chemicals

**Toluene:** AR grade, Molecular weight = 92.14 g/mol; boiling range = 110-111 °C; 
Source: SRL (India).

**Methanol:** Extra pure AR, molecular weight = 32.04 g/mol; boiling range = 64-65 °C; 
Source: SRL (India).

**Acetone:** Molecular weight = 58.08 g/mol; boiling range = 55.5-56.5 °C; Source: Central Drug House (P) Ltd, N. Delhi (India).

**Sodium hydroxide pellets purified:** Source: Sd fine (India).

Toluene and methanol were distilled prior to use while other materials were used directly without further purification. Double distilled water drawn from a Millipore purification system was used.

2.2 Preparation of the Sample

The aqueous phase of microemulsion system was obtained by dissolving desired amount of monomer(s) in water. For PAM composites and copolymer composites, SiO$_2$ was added to above prepared aqueous solution of monomer(s). This suspension was stirred by a
magnetic stirrer at 1000 rpm in a 100 ml single neck round-bottom flask for 2 h to attain proper dispersion of silicon dioxide nanoparticles in the solution of monomer(s). The dispersion medium of microemulsion was made by dissolving AOT in toluene in a 250 ml conical flask. Now the above prepared aqueous solution of monomer(s) (containing dispersed SiO₂ in case of PAM composites and copolymer composites) were added drop wise to surfactant solution to form W/O microemulsion. This microemulsion was transferred to 250 ml, 2 neck round bottom flask fitted with a condenser and a nitrogen gas inlet. It was stirred on magnetic stirrer at 1000 rpm for 6 h. AIBN and NMBA (each 1 wt % of monomers) was added to initiate the polymerization and for crosslinking. The microemulsion was then purged with nitrogen gas for 30 min. The polymerization mixture was then heated in a constant temperature water bath at 50 °C for copolymer and copolymer composites while at 62 °C for PAM nanogels and PAM composites till complete conversion. After polymerization the mixture was cooled to room temperature and acetone / methanol was added to precipitate the polymerized product. The precipitates were separated and washed several times through centrifugation first with CH₃OH to remove residual monomer and then with toluene to remove AOT. The precipitates were then dried in vacuum oven at 50 °C until constant weight is obtained.

2.3 Characterization

Several techniques are available under the broad umbrella of characterization which may be used to study nanomaterials in one way or the other. The characterization methods used in the analysis of the chemical structure, microstructure and morphology, as well as the physical properties, of the nanogels / composites are varied. Although the techniques
to be used would depend upon the type of material, however the common parameters which are of interest for determination are size, shape, morphology, composition, thermal stability etc. The techniques employed for characterization of prepared nanogels and nano size composites are mentioned below-

2.3.1 Dynamic Light Scattering (DLS)
The particle size measured by DLS instrument is the hydrodynamic diameter \( D_h \) of the sphere that diffuses at the same speed as the particle being measured.

A Malvern Zetasizer Nano Series ZEN 1600 (Malvern Instruments Limited, U. K.) was used to measure the size of the reverse micelle of microemulsion droplet, nanogels and composites. DLS measurements were performed at 25 °C in a square glass cuvette with round aperture at a fixed angle of 173°. The value of dispersant refractive index and viscosity of toluene were taken 1.491, 0.5500 cP respectively.

2.3.2 Fourier Transform Infrared Spectrophotometer (FTIR)
The FTIR spectra were collected on SHIMADZU Japan FTIR-8700 Fourier transform infrared spectrophotometer. Samples of isolated particles of prepared nanogels and composites were mixed with KBr, homogenized and converted into pellets under a pressure of 8 ton and the spectra (Absorbance with wave number) were taken thereafter. The FTIR spectra of the prepared nanogels and composites were then interpreted.

2.3.3 \(^1\)H-Nuclear magnetic resonance spectrometer (\(^1\)H-NMR)
\(^1\)H-NMR spectrum of poly(AM-co-AMPSA) nanogels were recorded using Bruker DRX400 MHz spectrometer. Tetramethylsilane (TMS) was used as the reference and deuterated water (D\(_2\)O) as the solvent.
2.3.4 Elemental Analysis

The percentage of elements in the copolymer nanogels were determined by Vario EL III CHNS analyzer, Germany.

2.3.5 Thermogravimetric Analyzer (TGA)

The TGA analysis of nanogels and composites were performed using a Perkin-Elmer TGA7 Thermobalance. About 2-4 mg of the dried sample in a nitrogen atmosphere was subjected to TGA analysis in the temperature range of 50 °C to 800 °C at scanning rate of 20 °C/min.

2.3.6 Differential Scanning Calorimeter (DSC)

Differential scanning calorimeter (DSC Q10, TA Instruments, USA) was used to study the glass transition temperature of nanogels and nanocomposites. About 2-2.5 mg of the sample was sealed in an aluminium DSC pan and heated from 50 °C to 350 °C at a heating rate of 10 °C/min under nitrogen purge flow (50 ml/min).

2.3.7 Scanning Electron Microscope (SEM)

The surface morphology of the dried nanogels and nanocomposites were studied by using scanning electron microscope (LEO 435VP) operated at 15 Kv. Coating was carried out under reduced pressure in an inert argon gas atmosphere (Agar Sputter Coater P7340).

2.3.8 Transmission Electron Microscope (TEM)

A transmission electron microscope (Morgagni 268D TEM, The Netherlands) with a 70 kV accelerating voltage was used to measure the size of the prepared nano size composites. The aqueous dispersions of composite particles were sonicated at 25 °C then dried onto carbon-coated 400 mesh copper grids.

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