ABSTRACT

The piperazinium cationic polyelectrolytes were synthesized from four different piperazine derivatives (methyl, ethyl, benzyl and hydroxyethyl) and eight different counter ions (chloride, bromide, sulfate, nitrate, phosphate, perchlorate, fluoborate and fluorophosphate). Acryloyl piperazine derivatives methyl, ethyl and benzyl were synthesized from corresponding piperazine derivatives and acryloyl chloride in THF at 0°C. The preparation of N-acryloyl-N’-(2-hydroxyethyl)piperazine in the same manner became difficult due to the formation of mixture of mono and bis acryloyl products. To overcome this problem, the hydroxyethyl piperazine was converted to bis acryloyl-hydroxyethyl piperazine with one mole of hydroxyethyl piperazine and two moles of acryloyl chloride and the bis product was selectively hydrolysed at the hydroxyl end to get the acryloylhydroxyethyl piperazine.

The acryloyl derivatives were quaternized with mineral acids to get the corresponding piperazinium salts. The quaternization was carried out by the slow addition of mineral acids in stoichiometric quantity to the THF solution of acryloylpiperazine derivatives. The quaternary salts were hygroscopic in nature except for the four salts viz., ABPN, ABPPC, ABPFB and ABPFP in benzyl series.

The resulting piperazinium salts were polymerized in water using potassium peroxydisulfate as free radical initiator at 60-70°C. In some cases where the salts are not soluble in water, 50:50 mixture of water/DMF was used as solvent. High molecular weight polymers were precipitated in acetone and the low molecular weight polymers were precipitated in methanol. The
polymers were hygroscopic in nature except perchlorate polymers among all the four series and four polymers in benzyl series. All are freely soluble in water except four polymers in benzyl series.

The acryloyl derivatives, piperazinium salts and piperazinium polymers were characterized by IR, $^1$H-NMR and $^{13}$C-NMR spectral studies. IR spectrum of acryloyl derivatives showed absorption around 1640 cm$^{-1}$ corresponding to carbonyl group. Absorption around 1600 – 1610 cm$^{-1}$ corresponds to vinylic CH and peaks around 2940 cm$^{-1}$ showed the presence of CH stretching. Piperazinium salts showed strong absorption around 1640 cm$^{-1}$, which corresponds to carbonyl group. It also showed strong absorption around 3420 – 3450 cm$^{-1}$ which showed the presence of NH. Polymers also showed strong absorption around 1640 and 3440 cm$^{-1}$ corresponding to carbonyl and NH stretching frequencies, respectively.

$^1$H and $^{13}$C-NMR spectra of acryloyl piperazine derivatives clearly showed the proton and carbon orientation of the compounds. But the NMR spectra of piperazinium salts and polymers did not show well resolved peaks because of the quaternization of the piperazine moiety.

In the proton NMR spectrum of acryloylethylpiperazine compound methyl protons appeared as triplet at 1.01 δ because of the methylene group adjacent to the methyl group. Ring methylene protons attached to NCO appeared as a singlet around 3.6 δ. Allylic protons showed three peaks, one quartet and two doublets for CH and CH$_2$ protons, respectively.

The polymers were also characterized by thermal (TGA and DSC) and GPC techniques to ascertain the thermal stability and the molecular weight
of the polymers, respectively. Polymers with halogen counter ions were found to be thermally more stable compared to other counter ions. Also, the first degradation temperature of the polymers reveal that counter ion gets detached first from the polymer backbone in some cases. Weight average molecular weights were determined for representative samples and found that the molecular weight was in the range of 20,000 to 2,00,000.

The dilute solution viscosity of water soluble polymers was studied by Ubbelohde viscometer at 30°C. The reduced viscosity behaviour of these cationic polyelectrolyte shows typical polyelectrolytic behaviour in aqueous medium, which increase on dilution unlike normal polymers. In normal polymers, reduced viscosity will decrease on dilution of the solutions. The addition of simple electrolytes to the dilute solutions of polyelectrolytes will decrease the reduced viscosity of the solutions drastically to larger extent because of the charge neutralization of cationic sites by the excess anionic charges of the added salts. Hence intrinsic viscosity is decreased to a larger extent. After the addition of certain amount of salt, the polymeric solution started to behave like normal polymers because of the complete neutralization of the charges on the backbone of the polymer.

Flocculation efficiency of the twenty eight water soluble polymers synthesized were determined by flocculation studies using bentonite suspension. The flocculation performance was examined by turbidity measurement of the supernatant solution after flocculation. Interestingly all the polymers showed good flocculation results. In some cases like PAMPC, PAMPN, PAMPPC and PAEPC excellent flocculation results were obtained.