SUMMARY

The thesis entitled "Synthesis and Studies of Low Band Gap Squaraine Polymers and Their Model Compounds Derived from Pyrrole End-Capped Conjugated Monomers" describes the synthesis of a series of nonconventional conjugated polymers based on a novel class of organic dyes with interesting optical and electronic properties. A new and simple strategy for the designing of near infrared absorbing polysquaraines that has extremely low band gap and high intrinsic semiconductivity is described. The strategy involves the synthesis of pyrrole end-capped conjugated systems, which undergo facile polycondensation with squaric acid resulting in the formation of a series of low band gap polymers 6a-g. The optical properties and conductivity of these polymers are strongly influenced by the solubility inducing alkyl side chains, which underline their role in controlling the molecular packing. The optical band gaps and intrinsic conductivities of these polymers could be considerably modulated by changing the length of the hydrocarbon side chains.

The soluble polysquaraines 6d-g under investigation showed inherent tendency to form molecular assemblies in solvents such as chloroform, dichloromethane and toluene. Addition of polar solvents such as water and DMSO caused considerable blue shift and changes in the ratio of the intensities of the various absorption bands. On the other hand, model squaraine dyes 7a and 7g with extended conjugation showed characteristics of H-type aggregation in binary solvent mixtures, which are sensitive to solvent compositions, temperature and concentration. Based on the available data, it has been proposed that the polysquaraines form ordered assembly in less polar solvents and "frustrated" aggregates in polar solvent mixtures. The strong electrostatic interactions of the rigid, planar and extensively conjugated zwitterionic polymer backbone facilitate the formation of ordered aggregates in less polar solvents. Addition of polar solvents discourages the inter polymer electrostatic interactions and encourages the collapse of the hydrocarbon side chains to form...
disordered aggregates. The solvophobically driven order-disorder phenomena of polysquaraines are unique and different from the aggregation behavior of other conventional \( \pi \)-conjugated polymers.

The role of the alkyl side chains in controlling the solution and solid-state aggregation of polysquaraines has been established by the detailed studies of the squaraine dyes 11\(\text{a} \), 11\(\text{b} \), 17 and 21. In these cases, the formation of H-type and J-type aggregates was confirmed by solvent, temperature and concentration dependent changes in the electronic absorption spectra. In the case of 11\(\text{b} \), the aggregation phenomena were found to be time dependent. Solid-state aggregation of these squaraine dyes showed considerable difference in the colour of the films and their UV-vis-NIR absorption spectra thereby establishing the role of the alkyl side chains in controlling the molecular ordering. The formation of highly ordered molecular assembly is clear from the sharp and intense diffraction peaks observed in the X-ray diffraction patterns. In summary, the present study is a systematic and detailed effort towards the designing of low optical band gap polymers and investigation on their structure-property relationship.