Synopsis of the thesis entitled:

Novel Hydrophobically Modified Polymers using Hydrophobes derived from Renewable Resource Materials: Synthesis, Characterization and Rheology

Introduction:

Water-soluble polymers (WSPs) are an important class of materials to both society and industry due to their specific properties in thickeners, flocculants, dispersants or emulsifiers in aqueous based media. In the context of water becoming as absolute requirement in specific fields like food, pharmaceuticals and personal care applications WSPs are gaining more and more importance. Secondly, due to environmental hazardous issues, water-based formulations are replacing organic ones in important areas such as drilling fluids, cosmetics and paints. Despite their importance, conventional WSPs suffer from drawbacks in that their aqueous solution properties are adversely affected by external working conditions such as temperature, pH, shear and the presence of salt.

In order to overcome these problems, associating polymers (APs) or also known as hydrophobically modified polymers (HMPs) have emerged as frontier materials. Basically, APs are hydrophilic water-soluble polymers that contain a small amount (typically < 2-5 mole-%) of hydrophobic groups (such as alkyl, perfluoroalkyl or aromatic) Above a certain polymer concentration, the hydrophobic groups self-associate into micelles-like structures to minimize their exposure to water. The polymer backbone forms bridges between the micelles leading to the formation of transient network, which results into several fold increase in viscosity as compared to the unmodified polymer.

These hydrophobic groups called “stickers” in APs can be incorporated into hydrophilic backbone chain randomly, in a blocky fashion or at the terminal chain ends (telechelic). Therefore, the architectural richness of the associating polymers (i. e. random, block or hydrophobically end-capped) gives diverse physico-chemical properties. In aqueous solutions, these polymers exhibit both intra-molecular and intermolecular interactions depending on the concentrations of the solution. The synthesis of APS/HMPs together with their self-assembling properties in aqueous medium in semi-dilute regime, have been widely reported during the 90’s and have found industrial
developments. For example, with Hydrophobic Ethoxylated Urethanes (HEUR) and Hydrophobically Modified Alkali-swellable Emulsions (HASE).

**Two methodologies could be adopted to synthesize APs/HMPs:**

Copolymerization of hydrophilic and hydrophobic monomers using micellar polymerization. Functionalization of hydrophilic polymers using hydrophobic compounds. Different hydrophobic compounds, such as long chain alkyl amines, alkyl halides, alkyl isocyanates and alkyl anhydrides have been used for the hydrophobic modification of both synthetic and natural water-soluble polymers such as poly (acrylic acid) [PAA], polyethylene glycols [PEGs], carboxy methyl cellulose [CMC], and chitosan [CS]. Despite many reports on the study of APs in the scientific literature, their industrial development has not really taken place and only a small number of polymers are commercially available. Therefore, there is a need to design and develop newer APs aiming at specific end-applications.

The main objective of the research was to design and synthesize novel hydrophobically modified associating polymers using hydrophobic compounds derived /synthesized from renewable resource materials. The renewable resource materials used were cashew nut-shell liquid (CNSL) and gallic acid (GA) which are the byproducts of cashew processing industry and leather processing industry and leather industry, respectively.

**The thesis has been divided into following chapters:**

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**Chapter-1: Introduction and Literature Review**

The introductory chapter gives a comprehensive review of the literature on hydrophobically associating polymers [APs] covering, types of APs, synthetic methodologies for APs, rheological properties etc. The molecular architectures such as random, block and end-capping has been discussed in terms of their structure-property relationships and applications. The techniques like viscometry, rheometry and light scattering which was used for understanding the association behavior are discussed. An
interesting phenomenon of shear thickening in polymeric solutions and molecular origin for shear thickening along with its implication is also described.

**Chapter-2: Scope and objective.**

This chapter highlights the objective and scope of the present work.

Objectives of the present thesis:

- To synthesize hydrophobic compounds from renewable resource materials such as CNSL and Gallic acid.
- To synthesize novel hydrophobically associating polymers using the prepared hydrophobic compounds.
- To characterize novel hydrophobically associating polymers in terms of their structure.
- To study various physico-chemical aspects, which include coordinated studies of self-assembly and viscoelastic properties.
- To understand and correlate the structural attributes which are responsible for exhibiting the shear induced thickening in associating polymers.

**Chapter-3: Synthesis and Characterization of hydrophobic compounds**

In this chapter, synthesis of new hydrophobic compounds from renewable resource materials such as CNSL (3-PDP) and Gallic acid (3, 4, 5-trihydroxy benzoic acid) is described. The hydrophobic compounds namely, 3-pentadecyl cyclohexyl amine, 3, 4, 5-tris octyloxy benzoate (MGC₈), 3, 4, 5-tris dodecyloxy benzoate (MGC₁₂) and 3-pentadecyl cyclohexane carbaldehyde (3-PDCAl) were synthesized and characterized in terms of their structure by FT-IR and NMR spectroscopy. We synthesized hydrophobic compounds namely, 3-pentadecyl cyclohexyl amine [3-PDCA], C₈, C₁₂ alkoxy substituted methyl gallates and 3-pentadecyl cyclohexane carbaldehyde. The structural characterization of these hydrophobic compounds were performed using FT-IR and NMR spectroscopy. Subsequently, these hydrophobic compounds were utilized to synthesize novel hydrophobically modified associating polymers taking water soluble polymers, poly (vinyl alcohol), copolymers of N, N-dimethyl acryl amide-co-acrylic acid and chitosan. The novel
hydrophobically associating polymers were characterized in terms of their structure by FT-IR and NMR spectroscopy and their rheological properties in solution were studied using the state-of-the-art rheometers.

**Chapter-4: Hydrophobically modified poly (vinyl alcohol): Synthesis, characterization and Rheology**

This chapter describes the synthesis of hydrophobically modified poly (vinyl alcohol) [HMPVA] using the hydrophobic compounds namely, 3, 4, 5-tris octyloxy benzoate [MGC₈] and 3, 4, 5-tris dodecyloxy benzoate [MGC₁₂] prepared in our laboratory. The incorporation of hydrophobic compounds in PVA was confirmed by NMR spectroscopy. The formation of transient network structure as a result of the association of hydrophobic groups was largely manifested in macroscopic property of viscosity. The rheological behavior of HMPVA in aqueous solutions was studied in the dilute, semi-dilute and concentrated regime. Oscillatory experiments on concentrated solutions exhibited a gel-like soft-solid behavior and the nature of the soft-solids was probed by the strain-rate frequency superposition. (SRFS)

**Chapter-5: Hydrophobically modified poly (NN'-dimethyl acryl amide-co-acrylic acid): Synthesis, characterization and Rheology**

This chapter deals with the synthesis and characterization of hydrophobically modified poly (NN'-dimethyl acryl amide-co-acrylic acid) which exhibited both shear induced thickening and thinning in aqueous solutions. This has been explained on the basis of shear-induced structure formation (shear thickening) at low shear rates and shear induced structure breakage (shear thinning) at high shear rates. Steady shear experiments with polymer solutions of different concentrations indicated that the critical shear rate ($\gamma_{cni}$) at which the shear thickening occurs depends strongly on the concentration of the polymer. The shear thickening behavior observed in our system has been explained on the basis of shear induced transformation of intramolecular hydrophobic associations into intermolecular hydrophobic associations. Furthermore, the kinetics of gelation was investigated by performing creep and recovery measurements.
Chapter 6: Hydrophobically Modified Chitosan: Synthesis, Characterization and Rheology

This chapter describes the synthesis of hydrophobically modified chitosan [HMC] using a hydrophobic compound namely, 3-pentadecyl cyclohexane carbaldehyde which was prepared in our laboratory. The extent of hydrophobe content in HMC was varied from 3-7 mole-% and the evidence for the incorporation of hydrophobe into chitosan was obtained from $^1$H NMR spectroscopy. The solution behavior of HMC was studied using rheology and light scattering measurements.

Chapter 7: Summary and Conclusions

This chapter summarizes the important conclusions of the work.

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