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## Abstract

Gel forming materials have extended much consideration over the last few decades because of their ability to form supramolecular architectures as well as their potential applications in various fields from biomedical research to advanced functional materials. Thrust is more on stimuli induced gelation and multi stimuli responsive gels for functional applications. Most of the gelators were discovered through serendipity and their structural requirements are somewhat ambiguous. This is due, in part, to the fact that the supramolecular gelation phenomenon is not yet fully understood, though many structural classes have been found to be excellent organogelators. The aim of this thesis was to develop new thermoreversible organogelators (materials which can form gels in organic solvent upon stimulation), both low molecular weight compounds and polymers. The study also includes investigations on the gelation mechanism, structure-property relationship of the gels and their potential applications.

To begin with, we have synthesized a novel class of aromatic bis(*acyl*-semicarbazides) carrying aromatic core and alkyl side chains of varying length. The compounds were exhibiting thermoreversible gelation at concentrations below 10 mg/mL in common organic solvents. The effect of the chain length variation of fatty acid units on gel properties like gelation concentration, gelation time and gel melting temperatures were studied. In addition, when the gelator-solvent mixture was subjected to sonication, they underwent gelation. A high degree of inter-molecular H-bonding existed in the gel state between the semicarbazide moieties as confirmed by IR and XRD (WAXS) studies. Gelator with a specific spacer length was chosen to study the effect of stimuli (i.e. heat and ultrasound) on gel strength, mode of interaction and morphology. DSC, dynamic oscillatory studies, FT-IR and XRD revealed a difference in the modes of aggregation in the two cases. The gels could be tuned in the presence of anions at different concentrations – addition of 5 equivalents of F<sup>-</sup> and AcO<sup>-</sup> induced gel-sol transition. In addition, these organogels adsorbed dyes such as crystal violet and rhodamine-B from water very effectively.

As a next step, gelators carrying cycloaliphatic moiety in the core (instead of aromatic group) and hydrophobic side chains of varying length (C<sub>8</sub>-C<sub>18</sub>) were synthesized. The gelation occurred in the organic solvents with both heat and ultrasound as stimulus. The gels exhibited thermoreversibility and could be tuned in the presence of anions at different concentrations. IR

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and WAXS studies were carried out to propose a suitable mode of aggregation and mechanism of gelation. Experimental and computational studies on these gels revealed that the balance between two non-covalent interactions, viz., hydrogen bonding between the amide groups in *acyl*-semicarbazide moieties and Van der Waals forces between long hydrocarbon tails, is found to be the determining factor for self-assembly and hence organogelation and both intermolecular and intramolecular hydrogen bonding stabilize the aggregate structures. Viscoelastic properties of the gels were investigated by rheological studies and dependence of gel strength on length of alkyl substitutes/ concentrations of gel were also explained.

In the next phase, polymeric gelators were developed by incorporating LMWG aromatic and cycloaliphatic moieties in the polyurethane backbone. Segmented poly(urethane *acyl*-semicarbazides) carrying aromatic groups in the hard segments were synthesized by two step polymerization technique using polypropylene glycol ( $M_n \sim 1000$  and  $2000$ ), hexamethylene diisocyanate and terephthalic dihydrazide. The resulting polymers with specific ratios of NCO/OH were found to gel organic solvents like dimethylformamide, dimethylacetamide and N-methylpyrrolidone at a concentration of  $170 \text{ mg/mL}$  and their corresponding gels were thermoreversible. Tuning of the gelation behaviour and gel properties have been achieved by varying the polyol molecular weight ( $M_n 1000$  and  $2000$ ) and NCO/OH ratio. Films of xerogels reflected a network kind of structure due to physical crosslinks in the self-assembled state in SEM analysis and PPG<sub>1000</sub> based polymers exhibited higher tensile strength but lower elongation than PPG<sub>2000</sub> based systems. Viscoelastic nature of the supramolecular elastomeric gels was confirmed by dynamic oscillatory studies and stability of the gel was found to increase with increase in hard segment content. H-bonding between the urethane moieties and hydrophobic interactions between the PPG units in the soft segments lead to a phase separated structure. A phase separation induced gelation mechanism has been proposed and supported by SEM images and SAXS data. Both the gelators and xerogels had capability of adsorbing crystal violet from their aqueous solutions and desorbing in organic solvents like acetone and methanol.

To investigate polymers carrying cycloaliphatic moieties in the backbone, linear segmented poly(urethane *acyl*semicarbazides) of different compositions were synthesized from polypropylene glycol ( $M_n \sim 1000$  and  $2000$ ), hexamethylene diisocyanate and cyclohexanedicarboxylic acid-1,4-dihydrazide. The polymers exhibited thermoreversible gelation at a minimum gelation concentration of  $25 \text{ mg/mL}$  in DMSO in about 25 minutes.

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Among the compositions of varying NCO/OH ratios, PPG<sub>1000</sub> based polyurethanes with NCO/OH ~ 2.5 and 3 and PPG<sub>2000</sub> based systems with NCO/OH ~ 3.0 and 3.5 exhibited gelation. IR studies on the solutions and gels (in DMSO) revealed the extensive H-bonding between the chains in gel state. Scanning electron micrographs of the xerogel exhibited a 3D-network structure wherein higher hard segment content (P<sub>1000</sub>-1:3.5) led to a fibrous morphology and lower hard segment content (P<sub>2000</sub>-1:3) led to a microsphere like architecture. The phase separation induced gelation mechanism of self-assembly and effect of the stoichiometry on the morphology were explained based on the correlation between DSC, WAXS and FE-SEM data. The xerogels of the self-assembled polymers described in this work demonstrated a remarkable ability to remove dye molecules selectively, rapidly and efficiently. The xerogels retained their original structure and performance even after they are recycled several times.