

ABSTRACT

Adsorption is the most efficient, affordable, and environmentally beneficial approach for dye removal. Polymeric materials are developing as a new class of effective adsorbents. Natural and synthetic glycopolymers have been extensively researched to generate diverse architectures, including linear chain polymers and crosslinked gels. The compelling properties of D-galactose and its ability of protection-deprotection makes it attractive towards the synthesis of organic solvent-soluble polymers, as well as organogel and hydrogel utilizing the same monomeric unit. Although crosslinking of hydroxyl groups using diisocyanates have been reported earlier, its utility in hydrogel synthesis has been less explored.

Apart from glycopolymers, aliphatic polyesters, such as poly(lactic acid) (PLA), poly(ϵ -caprolactone) (PCL) and poly(butylene succinate) (PBS) are well established biodegradable polyesters utilized in biomedical sector. However, these hydrophobic polyesters lack reactive sites, limiting their biodegradability and so their use in few of the biomedical applications. Enhancing their hydrophilicity can improve biodegradation and widen their scope for use. Several literatures have reported on biodegradable polymers with pendant functionalities like hydroxyl, amino, carboxyl etc., they still suffer from longer degradation time. Thus, it is necessary to design and produce biodegradable polymers that degrade faster. Although incorporating ionomeric moieties as pendant units to accelerate degradation has been reported, their influence on the polymer backbone has been less explored, including cationic aliphatic polyesters as an interesting area of current research. The unique biological and physicochemical properties of piperazine moiety along with its stimuli-responsive pH sensitivity and its capability to impart antibacterial properties, provides it a huge potential as a precursor for the development of antimicrobial polyesters with enhanced biodegradability.

Therefore, this research focuses on development of biocompatible D-galactose based crosslinked polymers exploring dye sequestration, phase-selective organogelation, and drug

release applications. Additionally, a series of biodegradable piperazine-derived polyesters and copolyesters has been developed to overcome the degradability challenge.

In the first section, D-galactose has been utilized to synthesize acrylate-based monomer (**MAIpGal**) bearing isopropylidene moieties that led to organic solvent solubility. Based on the optimized parameters for linear polymer, the novel chemically crosslinked polymers (**OG10**, **OG15** and **OG20**) were prepared in good yields by varying the crosslinker amount as 10, 15 and 20 wt%, respectively, to evaluate the effect of crosslinker content on structural properties. The materials were designed with the objective of toxic dye sequestration and phase-selective organogelation from organic-aqueous solvent mixtures. The polymeric gel marked its capability to selectively adsorb cationic dyes, like ~85% of RhB dye from a mixture of RhB/MO from the water within 6 h. Also, **OG10** was found to be a suitable polymeric material for selective removal of organic solvents from their oil/water mixture by phase-selective organogelation, and showed nearly 100% absorption of toluene and chloroform from water.

In the next section, the same monomer was also utilized to develop a glutaraldehyde-free strategy to produce the novel glycomeric hydrogels. The pendant hydroxyl groups were condensed with different ratio of diisocyanate to produce macroporous novel crosslinked polymers (**HG5**, **HG2.5** and **HG1**) in good yields, utilizing 5, 2.5 and 1 wt% crosslinker content respectively. The swelling and morphological studies revealed the formation of macropores in the polymer matrix with 16-20 μm pore size and maximum swelling up to 526% in **HG1**. Due to their tunable porosity and cytocompatibility with the cells, the material was evaluated for drug load and release studies. The drug release took place through a simple diffusion mechanism and the trend correlates well with the decreased crosslinking density, larger pore size and thereby, comparatively faster drug release through **HG1** matrix (~92% in 72 h).

In the subsequent sections of this work, aliphatic polyesters and copolyesters were synthesized from piperazine-derived diester utilizing step polycondensation method. In the first part, polymers were synthesized using dimethyl 2,2'-(piperazin-1,4-diyl)diacetate (**M1**) with a series of alkane diols (C4 to C10) and characterized. An N-alkylation and protonation approach were adopted to tune their crystallinity and hydrophilicity so as to enhance the biodegradability. Significant changes in structural and thermal properties were observed after quaternization with methyl iodide, including reduced crystallinity and improved hydrophilicity. The T_g of polyesters varied from -19.3 to 30.4 °C, which decreased with alkyl chain length and increased with protonation/N-alkylation. Furthermore, the hydrolytic and microbial degradation studies were conducted to evaluate the biodegradability of the synthesized polyesters. In the second part, the incorporation of charged units utilizing the feasible copolymerization approach was carried out, to broaden the scope of hydrophobic polymers and achieve materials with tailored properties. A series of synthesized copolyesters own tunable hydrophilicity and crystallinity by charge modulation at N-atoms. Zeta potential measurements showed the pH-responsiveness of the polyesters and copolyesters. Further, the cytocompatibility with U2OS cells and antibacterial studies were performed against *E. coli* and *S. aureus* bacterial strains, to establish their suitability as potential antibacterial agents.