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CONTROLLED SYNTHESIS OF MULTI-ARM STAR BRANCHED POLYMERS AND COPOLYMERS OF L-LACTIC ACID : STRUCTURE AND PROPERTIES

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Poly (L-lactic acid) (PLA) is the quintessential bio-derived, bio-renewable, bio-degradable and bio-compatible polymer with a unique set of properties unmatched by any other polymer in its class. It is, therefore, not surprising that it has elicited wide spread attention from, both, academic researchers and industry. Derived from the simplest of self polymerizable AB monomers, namely, L-lactic acid, PLA possesses attractive physical properties, such as, high melting temperature, high strength, high modulus and optical clarity. However the polymer has significant weaknesses, namely, poor impact properties, low elongation at break, poor melt viscosity, low heat deflection temperature and slow rates of crystallization. These drawbacks limit the range of applications accessible to PLA. Consequently, substantial research efforts have been invested in devising methods to improve these properties.

We have pursued multiple strategies for improving the properties of PLA using the principles of macromolecular engineering.

We have explored the possibility of improving the viscoelastic properties of PLA melt by incorporating ionic groups on the polymer. For this purpose, we synthesized star telechelic PLA anionomers by a three-step procedure involving synthesis of star PLA, converting the hydroxyl end groups into carboxylic acid end groups, and finally converting these into ionic groups. Rheology data showed dramatic increase in the elasticity of the star telechelic ionomer melts relative to the star PLA melts.

Recently, synthesis of well-defined multi-arm star branched polymers and copolymer of L-lactide, ϵ -caprolactone and other cyclic ester monomers have attracted considerable attention. Star shaped polymers are characterized by low melt viscosity, lower T_g , are less crystalline and more compact in size compared to a linear polymer of similar molecular weight. We have examined the efficacy of multi-arm star branched random and block copolymers of ϵ -caprolactone with L-lactide as additives for enhancing the toughness of PLA's. We synthesized a series of well-defined star branched random and block copolymers with controlled molecular weights, narrow molecular weight distribution and well defined number of arms and explored their utility as an additive for improving the toughness of PLA's using a melt blending approach. The unique molecular architecture of star branched copolymers confer useful properties such as improved segmental miscibility resulting in two fold increase in toughness with no loss of modulus of rigidity.

Carbohydrates are a class of naturally occurring organic molecules which are polyfunctional useful as a biodegradable core for the synthesis of branched polymers. However, sugars pose a challenge to synthesis. Sugars are insoluble in organic solvents and, therefore, incompatible with ROP which are conducted in homogeneous solutions. Consequently, sugars have not been studied as a core in the ROP of L-Lactide. We report the first unequivocal synthesis of five arm star PLLA and PLGA polymers using D (+) glucose as the core and using an "arm first" approach and Click Chemistry. The fidelity of the arm structures is expected to be far better controlled in the "arm first" approach compared to the "core first" approach.