

I. Diamino Telechelic Polybutadienes: Synthesis, Characterization
and Melt Coupling

II. Poly(ϵ -caprolactone)-*b*-poly(ethylene glycol) Polymeric
Nanoparticles for Drug Delivery

III. Zirconia Based Cellulosic HPLC Chiral Stationary Phase for
Enantioseparations

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Abstract

This thesis is comprised of three parts under the theme of functional specialty polymers. The first project involves the synthesis, characterization and melt coupling of diamino telechelic polybutadienes. The second part describes the preparation of PCL-PEG polymeric nanoparticles for drug delivery. The third project focuses on the preparation of cellulosic HPLC chiral stationary phases for enantioseparations.

Styrene-butadiene-styrene (SBS) block copolymers (BCPs) containing central polybutadiene (PB) blocks of high molecular weight are particularly attractive in their potential use in pressure sensitive adhesives. However, premade SBS BCPs are difficult to process due to their high order-disorder transition temperature and high viscosity. An attractive strategy for approaching this problem is the use of reactive coupling between diamino telechelic PB (TPB) and anhydride-terminated polystyrene (PS-anh) to generate SBS BCPs *in situ* during melt processing. A series of diamino TPBs were successfully synthesized by ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene using 1,8-dicyano-4-octene as a chain transfer agent, followed by lithium aluminum hydride reduction. A ^{19}F NMR method was developed to quantify the primary amine functionality for polymers, especially for polymers with high molecular weight, large PDI, and multi-amino groups. Melt coupling of diamino TPB and PS-anh in a mini-max mixer at 120-180 °C resulted in formation of SBS triblock copolymers, and ~80% conversion of PS-anh was achieved in 30 sec. Morphology study of the coupling mixture by SAXS confirmed the formation of SBS triblock copolymer.

Maleimide terminated poly(ϵ -caprolactone)-*b*-poly(ethylene glycol) (PCL-PEG-MAL) nanoparticles are of special interest in potential biomedical applications. However, the synthesis of PCL-PEG-MAL with high maleimide functionality is difficult. Carboxylic acid functionalized poly(ϵ -caprolactone)s (PCL-COOHs) with narrow polydispersity

were prepared by ring-opening polymerization of ϵ -caprolactone using a carboxylic acid as initiator followed by fractionation using THF/methanol cosolvent. Three poly(ϵ -caprolactone)-*b*-poly(ethylene glycol) (PCL-PEG-OH) copolymers were synthesized by reactive coupling of excess HO-PEG-OH with three different molecular weight PCL-COCl. The block copolymer formation was confirmed by ^1H NMR and MALDI-TOF MS analyses. The hydroxyl end-groups were then transferred to maleimide groups to afford maleimide terminated PCL-PEG (PCL-PEG-MAL) with >90% functionality. Nanoparticles with maleimide functionality on surfaces were prepared by impingement mixing of a stream of PCL-PEG-MAL and non-functional PCL-PEG copolymers in THF and a stream of water in a confined impinging jet (CIJ) mixer. Particle sizes and size distributions were determined by dynamic light scattering (DLS). The amount of accessible maleimide on the surfaces was measured using Ellman's reagent and ~51-67% conjugation was obtained.

Chemical modification of hydroxyl groups of celluloses leads to the production of high value-added materials. 3,5-Dimethylphenyl isocyanate was used to derivatize cellulose to afford carbamate celluloses. Phosphonic acid, carboxylic acid, and methacrylate functionalized carbamate celluloses were synthesized through direct alkylation of carbamate celluloses. These functionalized carbamate celluloses were then deposited on zirconia particles through either Lewis acid-base interaction or covalent bonding, which were used as chiral stationary phases for HPLC. The separation and retention factors of columns packed by cellulose coated zirconia were evaluated on thirteen pairs of racemates. Columns packed by phosphonic acid functionalized carbamate celluloses were stable under test conditions and had better separation factors than columns from carboxylic acid and acrylate functionalized celluloses. The retention time is proportional to the amount of cellulose loading, and the higher the cellulose loading, the longer the retention time. The results were also compared with the results of a commercial cellulosic silica column under same test conditions. These zirconia-based columns had relatively smaller separation factors.