

The Synthesis of Biopolymers in the Macromolecular Complex Systems Group

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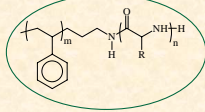
Current/Active User Projects

CNMS2004-025

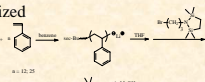
PI: Patrick Guenou

Synthesis of Diblock copolymers Containing Peptides as a Tool for Designing Biomineralization Strategies

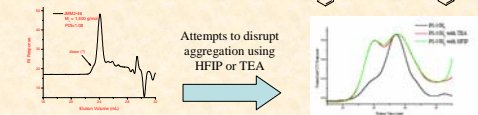
Polystyrene-polypeptide chimeras



Synthesis of primary amine-functionalized oligomeric polystyrene (PS-NH₂)

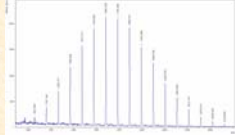


SEC (THF) Analysis of PS-NH₂



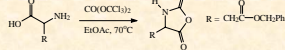
Due to aggregation of PS-NH₂ in SEC (THF) analysis, MALDI TOF MS was used to demonstrate that PS-NH₂ is monomodal that functionalization is quantitative

PS-NH₂: M_n = 1670 g/mol, PDI = 1.04



Monomer Synthesis:

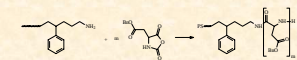
L-aspartic acid-β-benzyl ester-N-carboxyanhydride (NCA)



Purification of NCA is performed in apparatus under high vacuum: 3 consecutive "recrystallizations"

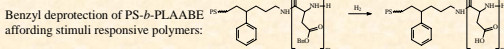
Aliferis, T.; Iatrou, H.; Hadjichristidis, N. *Biomacromolecules* **2003**, *5*, 1653-1656

Polymerization of NCA initiated with PS-NH₂

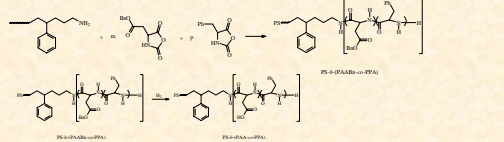


PS-*b*-PLAABE becomes insoluble in DMF at high conversion. As a result, different solvent systems are being employed to maintain copolymer solubility.

Intended direction of project:



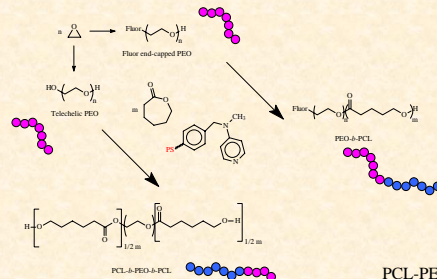
Chimeras consisting of copolypeptide segments:



CNMS2005-056

PI: Todd Giorgio

Synthesis of Biocompatible Block Copolymers for Medical Imaging and Drug Delivery Applications

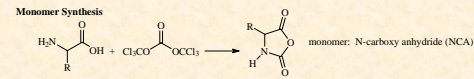


PCL-PEO block copolymers will be synthesized to encapsulate FeOx nanocrystals to examine the PCL biodegradation kinetics, products and effects of FeOx properties and characteristics, including drug release efficacy and toxicity.

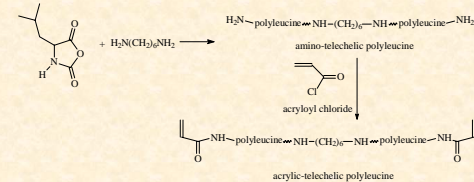
CNMS2005-113

PI: Nayer Eradat

Synthesis of Biocompatible Macromonomers



Polymerization of Leucine-NCA and Acrylate Derivatization

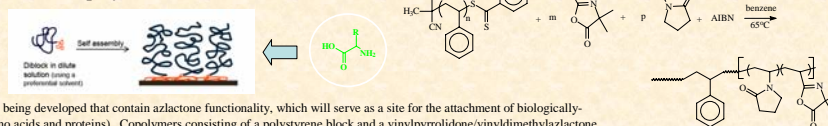


Polypeptides based on glycine or leucine are being developed as biocompatible macromonomers as candidates for tissue engineering using two-photon polymerization. Control of end-groups will facilitate the synthesis of a biocompatible, photopolymerizable glue, which is expected to form hydrogels upon irradiation in the presence of suitable photoinitiators.

CNMS2005-024

PI: Mike Kilbey

Synthesis of Novel Block Copolymers for Well-defined Bio-interfaces



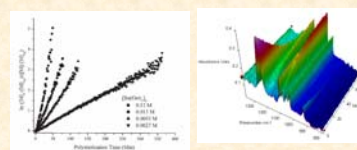
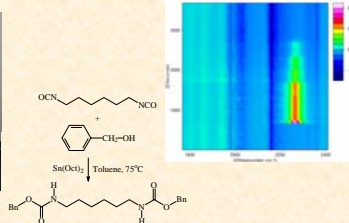
Novel block copolymers are being developed that contain azlactone functionality, which will serve as a site for the attachment of biologically-relevant materials (e.g., amino acids and proteins). Copolymers consisting of a polystyrene block and a vinylpyrrolidone/vinylidimethylazlactone block are currently being synthesized and characterized at CNMS. Subsequently, these materials will be assembled at submicellar concentrations into polymer brushes. In-situ phase modulated ellipsometry measurements will be conducted to determine kinetics of assembly as well as to monitor the post assembly swelling of the layer as they are functionalized by various amino acids.

Reaction Monitoring Using In-Situ Mid-IR Spectroscopy

Bruker Optics IRCube and PAT Probe

Monitoring Isocyanate Consumption

Evaluating Polymerization Kinetics



First order kinetic plots of rac-lactide polymerizations initiated with $\text{PROH}/\text{Sn}(\text{Oct})_2$, showing the effect of initial $[\text{Sn}(\text{Oct})_2]_0$, where $[\text{rac-lactide}]_0 = 1.0 \text{ M}$ and $[\text{PROH}]_0 = 0.019 \text{ M}$.

Messman, J.M. and Storey, R.F. *J. Polym. Sci. Part A* **2004**, *42*, 6238-6247.

Recent Synthetic Projects

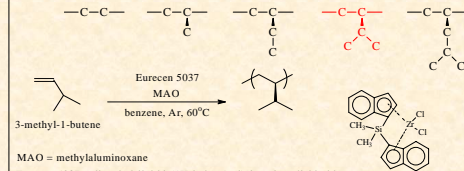
Synthesis of Isotactic-Poly-3-Methyl-1-Butene (*i*-P3M1B)

i-P3M1B was synthesized to evaluate its side-chain structure factor as derived from WAXD measurements. *i*-P3M1B was chosen to complete the data set for the various olefinic structures shown below.



ORNL Scientist Anton Habenschuss has determined/acquired:

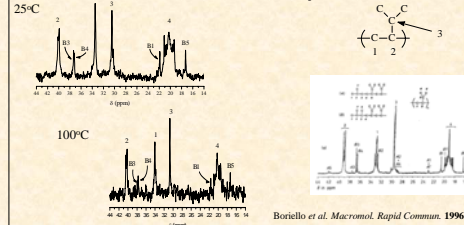
- "Pre-peak" appears below main chain diffraction peak in the carbon-carbon structure factor
- Data obtained for PE, *i*-PP, *i*-PIB, *i*-P4M1P
- Theoretical calculations (Polymer Reference Interaction Site Model-PRISM) *i*-P3M1B does not fit the model



MAO = methylaluminoxane

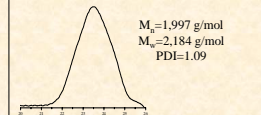
EURECEN 5037 = dimethylsilyl-bis(1H-inden-1-yl)zirconium dichloride

¹³C NMR Analysis of Product



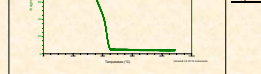
SEC Analysis

Trichlorobenzene at 140°C; PE standards

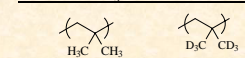


M_n = 1,997 g/mol
M_w = 2,184 g/mol
PDI = 1.09

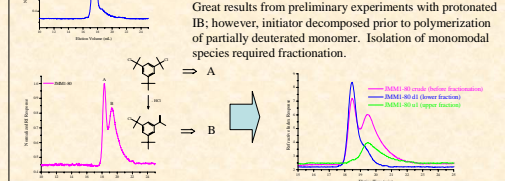
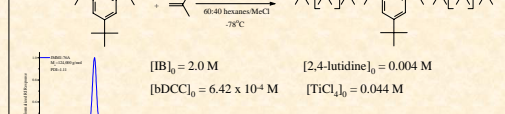
TGA Analysis demonstrating thermal decomposition (heating rate, 10°C/min)



Synthesis of Polyisobutylene (PIB) and Partially-deuterated PIB



Pseudo-living carbocationic polymerization of isobutylene



Great results from preliminary experiments with protonated IB; however, initiator decomposed prior to polymerization of partially deuterated monomer. Isolation of monomodal species required fractionation.



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