Stereoselective Cationic Polymerization of 3,6-disubstituded-*N*-vinylcarbazole Derivatives

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Introduction to Stereoselective Polymerization

What is Tacticity?

Relative stereochemistry

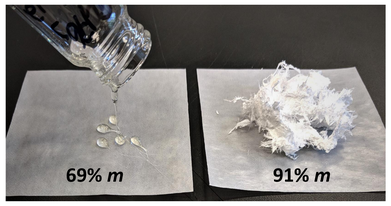
Meso Diad (*m*)

Meso Triad (*mm*)

Isotactic

Atactic (random)

Stereoselective polymerization alters polymer properties



Atactic Poly(vinyl ether)

- Lower Melting Point
- less crystalline
- more elastic

Isotactic poly(vinyl ether)

- Higher Melting Point
- More crystalline
- Stronger

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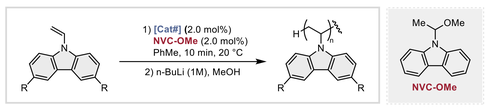
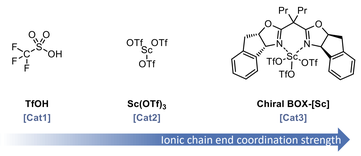
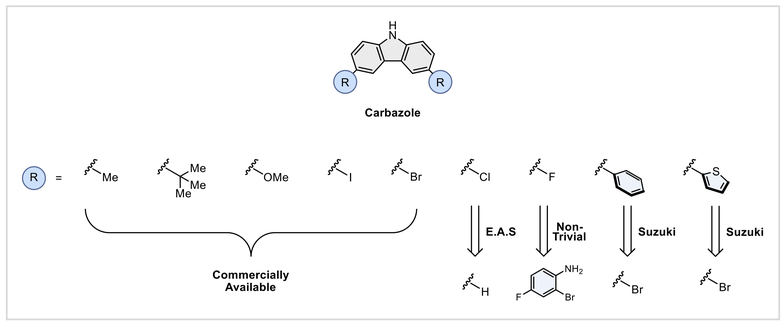
Polymerization of *N*-Vinylcarbazole

3,6-disubstituded-N-Vinylcarbazole Polymerization

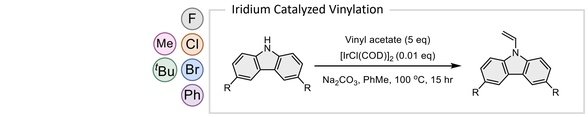


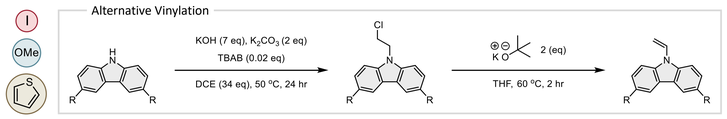


3,6-derivatization of Carbazole



3,6-disubstituded Carbazole Monomer Synthesis





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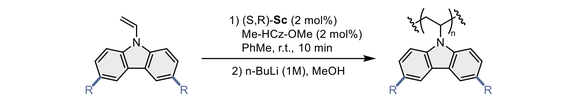
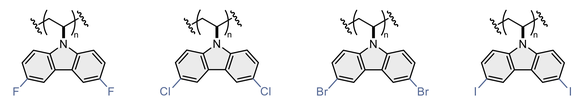
3,6-disubsituted-*N*-Vinylcarbazole Derivatives

Tacticity data for 3,6-disubsituted –*N*-Vinylcarbazole Derivatives



Halogen Series



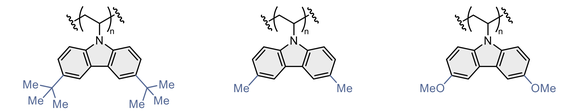
P-F — 79% *mm*

P-Cl — 94% *mm*

P-Br — 91% *mm*

P-I — 83% *mm*

Mechanistic Probes

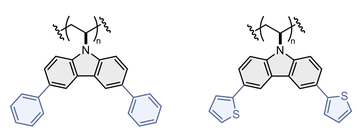


P-^{t}Bu — Atactic

P-Me — 91% *mm*

P-OMe — xx% *mm*

Aryl Containing Substituents

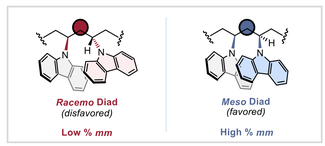


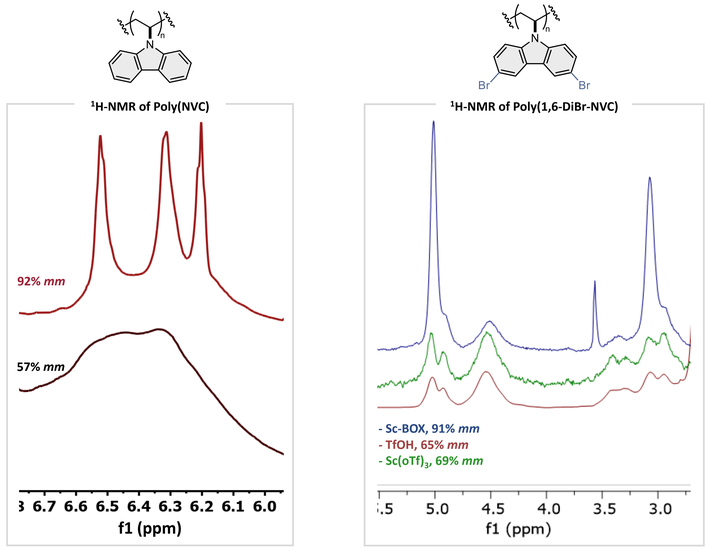
P-Ph — 91% *mm*

P-Thi — [a]74% *mm*

[a]*Sub. PhMe for PhCl*

How to Characterize Tactility





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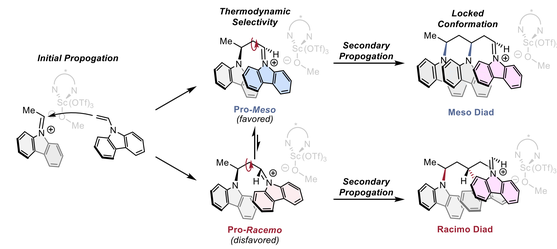
Mechanistic Insight for *N*-Vinylcarbazole Polymerization

Proposed Stereoselective Mechanism

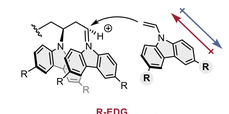


Our Rationale

Monomer size and electronegativity influence the tacticity of Poly(*N*-vinylcarbazole)

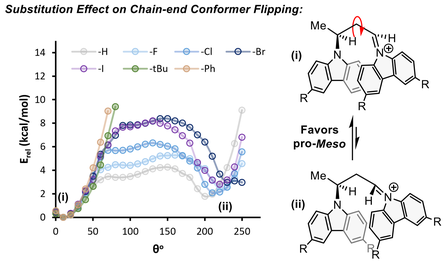
Monomer Size

Electronegativity



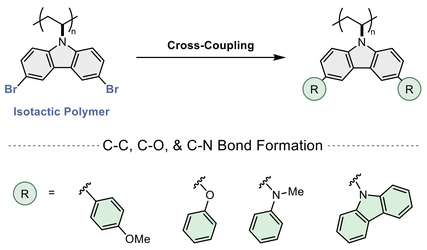
Density Functional Theory Data

Substitution Effect on Chain-end Conformer Flipping:



Future Work

Post-functionalization Cross Coupling of Poly(3,6-Dibromo-N-vinylcarbazole)



Benefits of Proposed work

- Can be used to access previously inaccessible materials
- Make materials with higher % *mm* compared to polymerization
- Change material properties

Acknowledgements

The UNC Department of Chemistry's NMR Core Laboratory provided instrumentation that enabled this study. This study was made in possible by Sorensen, C. C.; Leibfarth, F. A. *JACS* **2022**, *144*, 8487–8492, as well as supported by the findings of A.J. Teator, F.A. Leibfarth. Science, 363 (**2019**), pp. 1439-1443.