Selectively Activated Crosslinkers for Sequential Functionalization of Polymers

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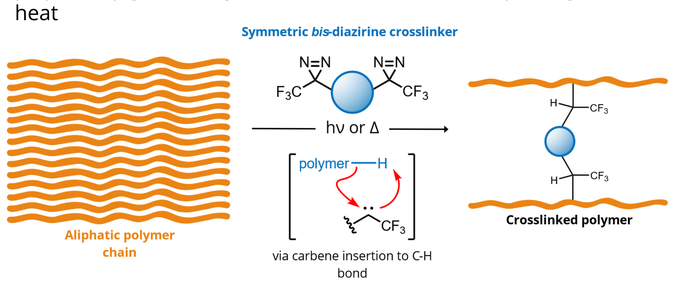
Introduction

Crosslinking is the process of forming new covalent bonds between polymer chains

→ ***Increases mechanical strength***
→ ***Improves temperature performance***

Traditional crosslinkers require specific technology and functionality for each polymer

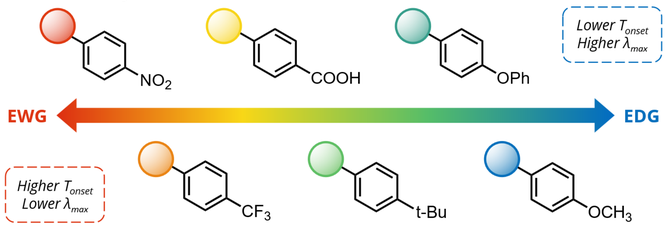
Diazirines provide a method to crosslink virtually any aliphatic polymer by generating a carbene when activated by UV light or heat



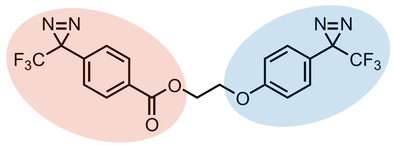
Lepage, M. L.; Musolino, S. F.; Wulff, J. E. Design, Exploitation, and Rational Improvements of Diazirine-Based Universal Polymer Crosslinkers. *Accounts of Chemical Research* **2024**.

Crosslinker Design

Activation temperature and wavelength can be tuned with different aryl substituents



Asymmetric *bis*-diazirine crosslinker:



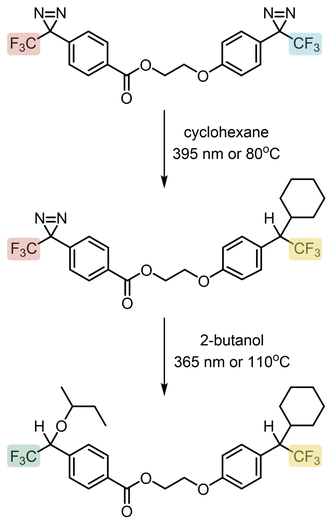
Electron-poor diazirine:
T_{onset} = 110°C
λ_{max} = 365 nm

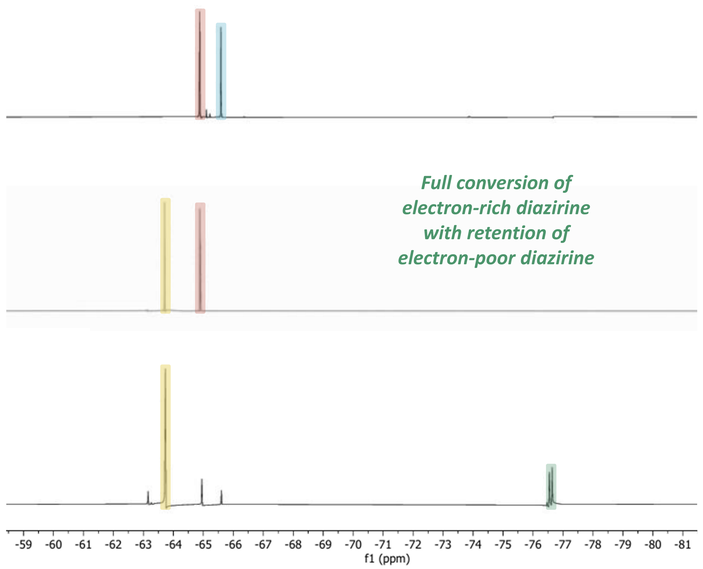
Electron-rich diazirine:
T_{onset} = 80°C
λ_{max} = 395 nm

Musolino, S. F.; Pei, Z.; Bi, L.; DiLabio, G. A.; Wulff, J. E. Structure–Function Relationships in Aryl Diazirines Reveal Optimal Design Features to Maximize C–H Insertion. *Chemical Science* **2021**.

Proof of Concept – Sequential Insertion Reactions in Solution

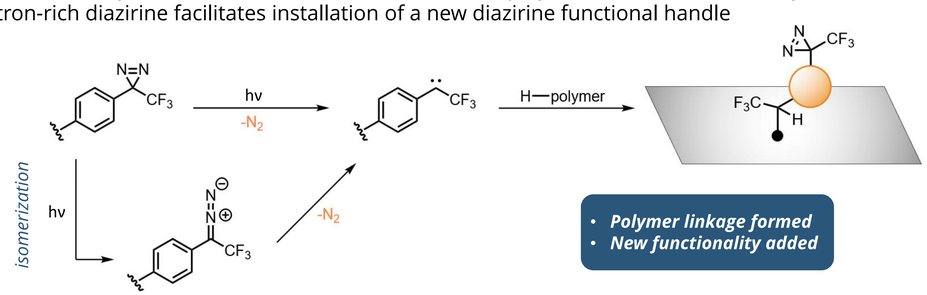
The progress of sequential insertion reactions can be tracked by ^{19}F NMR





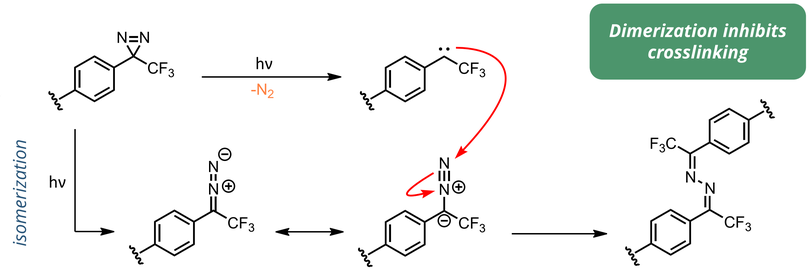
Surface Functionalization

Application of asymmetric crosslinker to the surface of a polymer substrate followed by activation of the electron-rich diazirine facilitates installation of a new diazirine functional handle



- ***Polymer linkage formed***
- ***New functionality added***

Dimerization is observed when the crosslinker is poorly miscible in the substrate



Dimerization inhibits crosslinking

Substrate Compatibility

- Several polymer substrates were tested for compatibility with the asymmetric crosslinker
- Washing the surface with ethyl acetate after irradiation removes any dimerized crosslinker
- The success of the insertion reaction was determined by the weight of crosslinker remaining after washing

substrate	mass untreated substrate (mg)	crosslinker loading (mg)	mass crosslinker treated substrate (mg)	mass substrate after wash (mg)	estimated crosslinker remaining after wash (mg)
UHMWPE	140.2	17.9	155.7	140.2	0.0
film-coated PE	192.3	22.4	204.0	192.7	0.4
silicone	2085.6	46.1	2088.1	2083.9	4.2
PVC	1871.7	38.2	1875.2	1871.8	0.1
nylon	2035.1	40.5	2037.3	2034.6	0.0
PMMA	1783.4	37.1	1786.1	1780.8	1.4

Nazir, R.; Musolino, S. F.; MacFarlane, M. A.; Wulff, J. E. Surface Modification and Dyeing of Ultrahigh-Molecular-Weight Polyethylene Fabrics Using Diazirine-Based Polymers. *ACS Applied Polymer Materials* **2024**.

Conclusions + Future work

- Solution experiments prove that the asymmetric crosslinker can undergo sequential insertion reactions
- Surface experiments show that the structure is not optimized for compatibility with many solids
- Further experimentation is needed to determine the scope of compatible substrates and optimize the structure and electronics of the asymmetric crosslinker

Acknowledgements

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