Phosphate Triesters as Catch Bonds in Dynamic Covalent Networks

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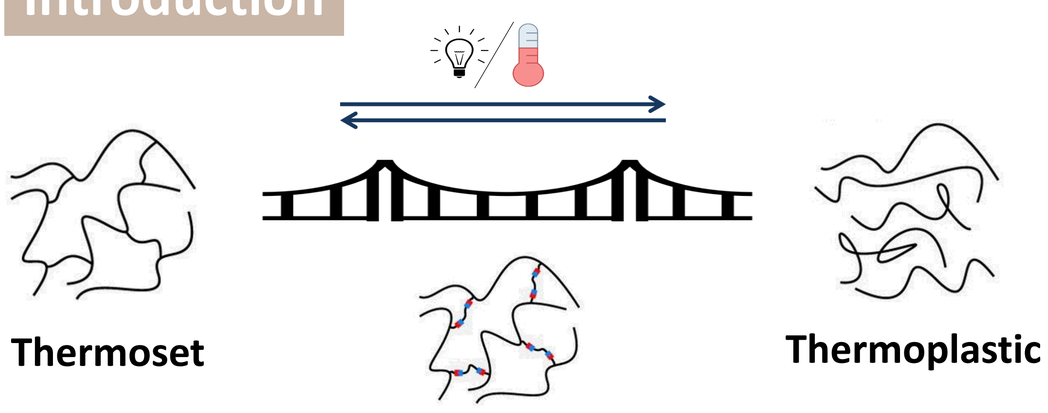
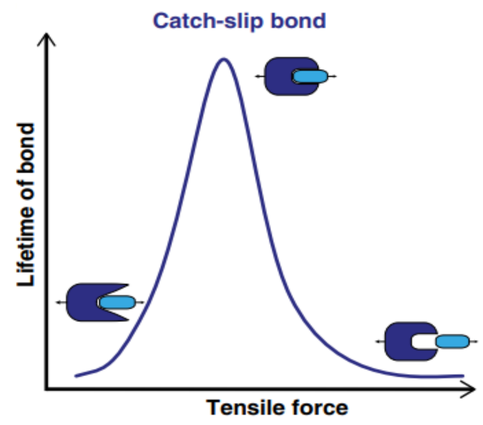
Introduction

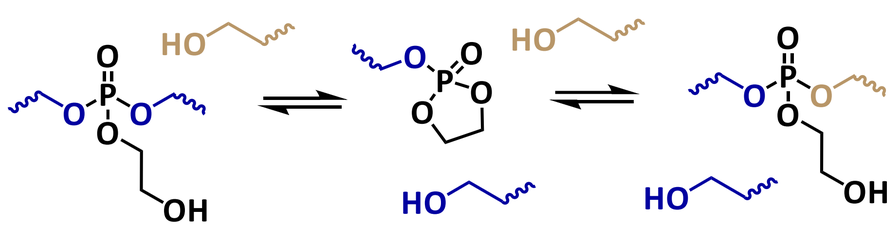




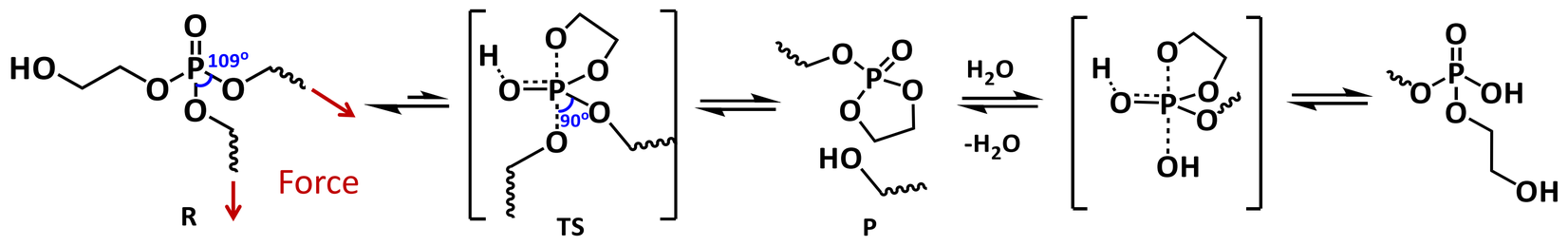
Catch bonds gain a lifetime on applying force, delaying mechanical failure under load. However, a slip bond character is obtained beyond a certain force.

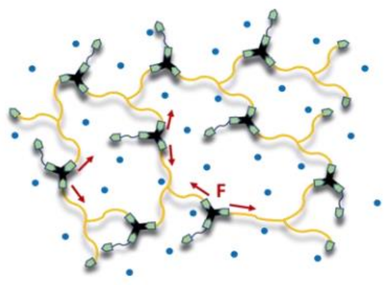
G. Helms et al. FEBS Letters, 2016

Concept



Transesterification-mediated rearrangement in phosphate triester dynamic covalent networks via a dissociative mechanism. Under force, neighboring group participation from β-hydroxyl is disfavored. Therefore, high osmotic stress is expected to cause less degradation, indicating catch bond character.

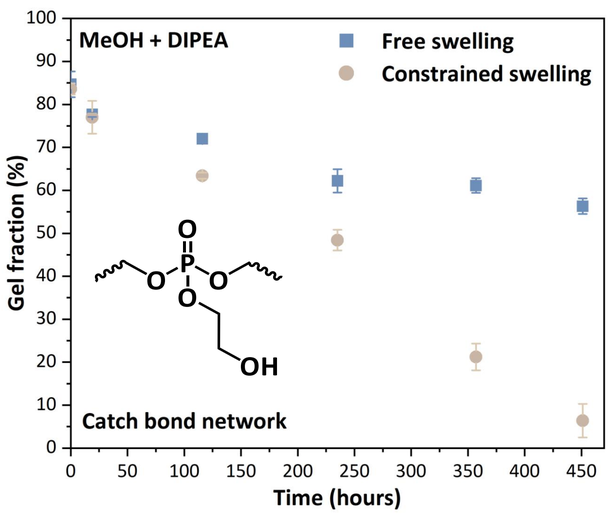




Osmotic stress in swollen network

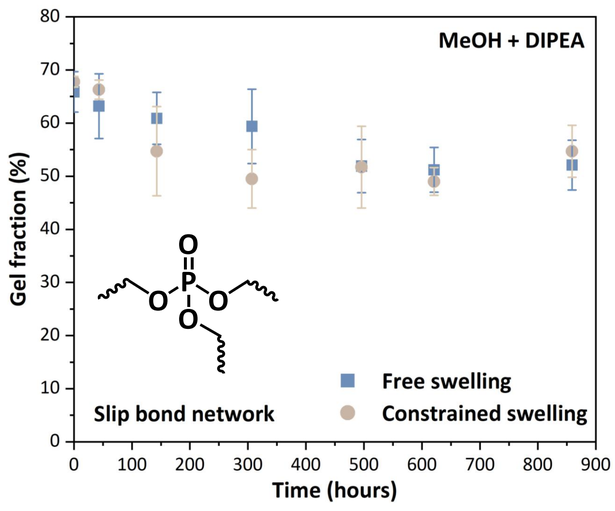
Results: Degradation Studies

Catch bond network



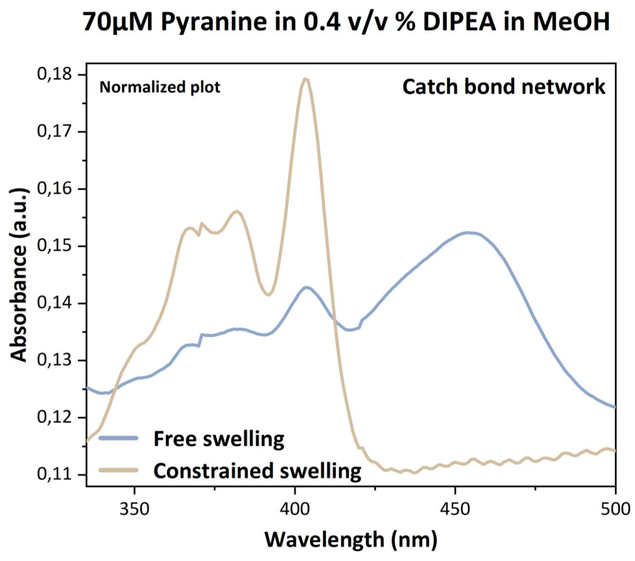
Freely swollen networks degrade slowly

Slip bond network



Degradation unaffected by swelling state

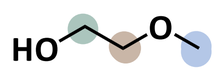
Catch bond network

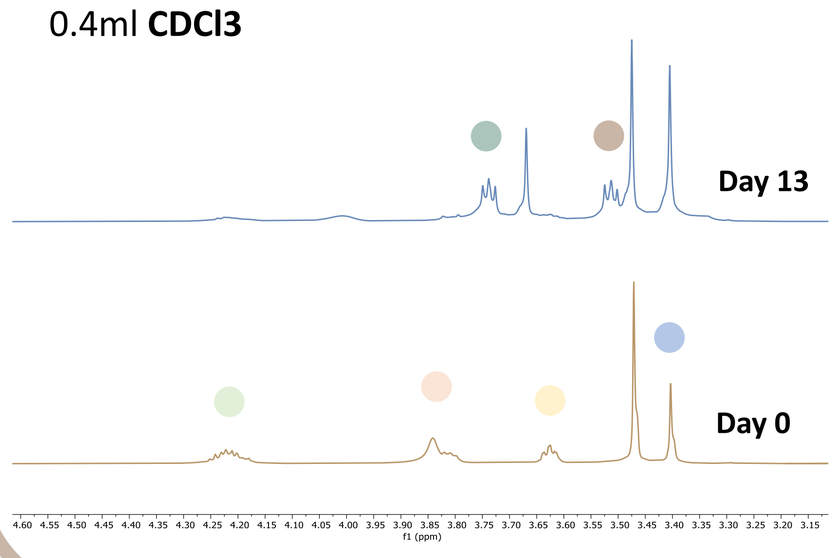


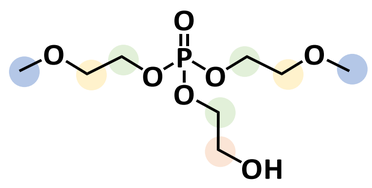
Constrained samples show reduced pH

^{1}H NMR: Model system degradation studies

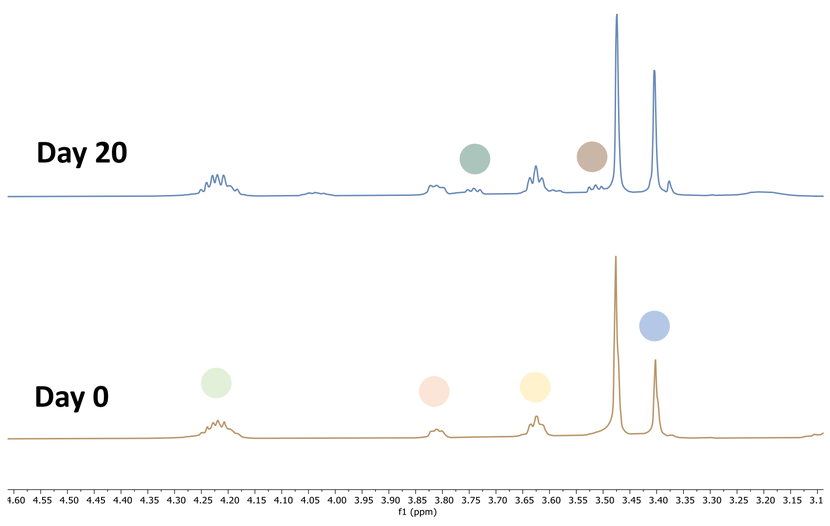
1 eq **Acetic acid**
4 eq **CH3OH**
0.4ml **CDCl3**

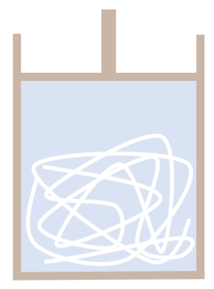






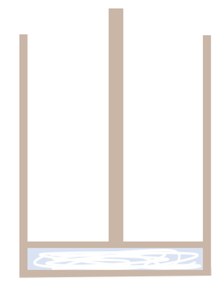
1 eq **DIPEA**
4 eq **CH3OH**
0.4ml **CDCl3**





Free Swelling

High Osmotic Stress



Constrained Swelling

Low Osmotic Stress

Conclusion & Outlook

Faster degradation of the catch bond network under constrained swelling suggests catch bond behavior. However, ^{1}H NMR of the model system shows accelerated cleavage of 2-methoxy ethanol groups under acidic conditions compared to basic, and constrained samples exhibit reduced pH (24 h, 40 °C). Therefore, the enhanced degradation may result from restricted diffusion and local accumulation of acidic by-products. Further analysis is required to distinguish pH-driven effects from true catch bond contributions.

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