RAFT SUMI: polymers from the bottom-up

Karen Hakobyan, Jiangtao Xu
University of New South Wales (UNSW)
Intro: polymer sequence control

How well does organic chemistry translate to polymers?

Iterative monomer additions: the middle ground.

*Polym. Chem.*, 2022, 13, 5431-5446

**Intro: challenges of controlling sequence of vinyl polymers**

*Practical challenge:* lower yield/turnover with more purification steps.

*Conceptual challenge:* find monomers only adding once at a time.


Balance single-addition vs polymerisation & termination.

Intro: solid-phase RAFT single unit monomer insertion (SUMI)

Addressed the practical challenge with solid-phase synthesis.

Brief: Operationally simple & versatile
Oxygen-tolerant PET-RAFT SUMI

Dithiocarbonyl: a “radical protecting group”.

ZnTPP gives oxygen tolerance.

Indefinite additions by alternating radical polarity

References:
Chem. Asian J. 2018, 13, 3611 – 3622
Polym. Chem., 2023, 14, 4116-4125
PET RAFT SUMI on resin: summary of previous work

1) Piperidine, DMF, r.t., 30 min
2) HO₂C-NC-S-SC₁₂H₂₅
   DIC, Oxyma, DMF, r.t., 3 h

Side reactions:
Phenylmaleimide double additions, disproportionation

Why not just try different monomers?

Polym. Chem., 2023, 14, 4116-4125
Fumaronitrile does not undergo double additions in trithiocarbonate-driven RAFT SUMI... but couldn’t even do single additions after a while.

Solid-phase SUMI of fumaronitrile-indene
Solid-phase SUMI of fumaronitrile–indene

Counts / a.u.

No double addition.
Remaining sequence error is incomplete addition

Addition or PET considered rate-limiting.

Penultimate unit effects?
Unlikely to be steric
Maybe electronics…

Manuscript in preparation
Penultimate unit effects and pyrazole carbodithiolates

Pyrazole carbodithiolates as "universal RAFT agents".

Sped up basic fumaronitrile SUMI

Rotatable bond mitigated CN–CN strain

Unconventional SUMI was possible with pyrazole carbodithiolates

Penultimate unit effects promoted pyrazole carbodithiolate SUMI!
Substrate scope

FUMARONITRILE TERMINAL UNIT
- IPN-FCN-PCDT
- IPN-FCN-(Cl)PCDT
- IPN-Ind-FCN-PCDT
- PhMeCH-FCN-PCDT
- IPN-FCN-Ind-FCN-PCDT
- PhMeCH-FCN-Ind-FCN-PCDT

STYRENIC TERMINAL UNIT
- IPN-St-PCDT
- IPN-Ind-PCDT
- IPN-Ind-(Cl)PCDT
- PhMeCH-FCN-Ind-PCDT
- IPN-FCN-Ind-PCDT

OTHER TERMINAL UNIT
- IPN-IBVE-PCDT
- IPN-CCN-PCDT
- PhMeCH-DiMeFum-PCDT

UNSUCCESSFUL ADDITIONS

Manuscript in preparation
Substrate scope (cinnamonnitrile)
Substrate scope (cinnamonicnitrile)

1,2/1,3-dinitrile strain vs terminal unit polarity match

3:1 regioisomer ratio

Reaction not feasible with trithiocarbonate “Z-group” or methylbenzyl “R-group”
Miscellaneous substrates (vinyl ether)

\[
\begin{align*}
\text{NC} & \quad \text{S} \quad \text{S} \quad \text{N} \quad \text{=O} \\
\text{S} \quad \text{S} \quad \text{N} \quad \text{=O} & \quad \text{ZnTPP, DMSO} \\
& \quad \text{hv, r.t.}
\end{align*}
\]

\[
\begin{align*}
\text{CDCl}_3
\end{align*}
\]

Manuscript in preparation
Alternating copolymerisation

More conventional RAFT behaviour in copolymerisation.
Conclusions

Practical challenge of scaling SUMI to multiple iterations has been addressed.

Theoretical challenge of ideal monomer combinations remains elusive yet instructive.

Pyrazole carbodiithiolates can expand the scope of SUMI to new sequences and monomer units.

Radical addition is not the main determining factor of RAFT SUMI

Principles of SUMI and alternating copolymerisation aren’t always transferable.
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See poster #11 tonight! (…and #42 and #53)