Seminar

Recent Advances in Switchable Group Transfer Radical Polymerization (GTRP)

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Prof. Dr. Junliang ZHANG (张俊良)

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Content

1. **Background**

2. **Key strategies in GTRP**

   2.1 1,4-Cyano migration

   2.2 1,5-Hydrogen/group migration

   2.3 Smiles rearrangement

3. **Conclusion & Outlook**

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Brief history of radical polymerization

Conventional
1950s - 1960s

Controlled
1980s - 1990s

Cutting-edge
2020s - Today

1956 Szwarc
Landmark proposal of
living polymerization

1st-order kinetics: $\ln\left(\frac{[M]_0}{[M]_t}\right) = k_{obs}t$

State-of-the-art

- Photo-regulated polymerization
- Enzyme-catalyzed ATRP
- O_2-initiation by novel initiators

Living radical polymerization

1982 Otsu
Iniferter

1993 Georges
SFRP (NMP)

1995
ATRP & RATRP

1998 Rizzardo
RAFT

✓ Tolerance of H_2O/impurities

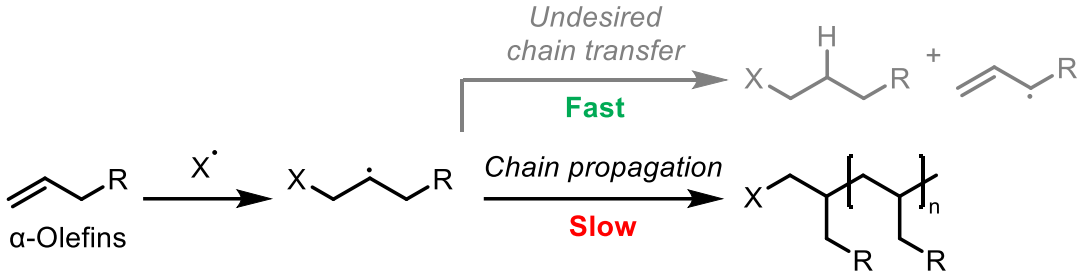
✓ Various monomers

✓ Controllable molecular weight

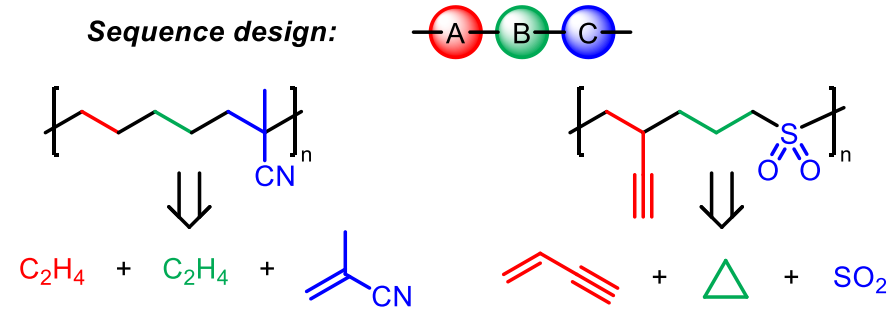
✓ High degree of polymerization

Colombani, D. *Prog. Polym. Sci.* **1997**, *22*, 1649-1720. 丘坤元. *大学化学* **2006**, *21*, 11-14.
Moad, G.; Solomon, D. H. *The Chemistry of Radical Polymerization* (Elsevier Oxford, ed. 2) **2006**, 1-9.

Why & what is GTRP?

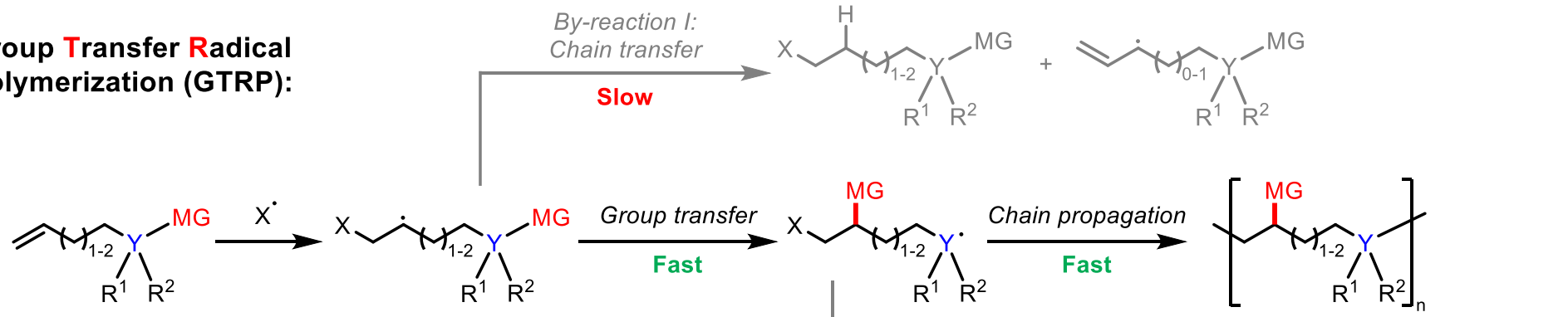


Challenge I: *limited degree of polymerization due to chain transfer*



Challenge II: *precise synthesis of sequence-regulated polymer*

Group Transfer Radical Polymerization (GTRP):

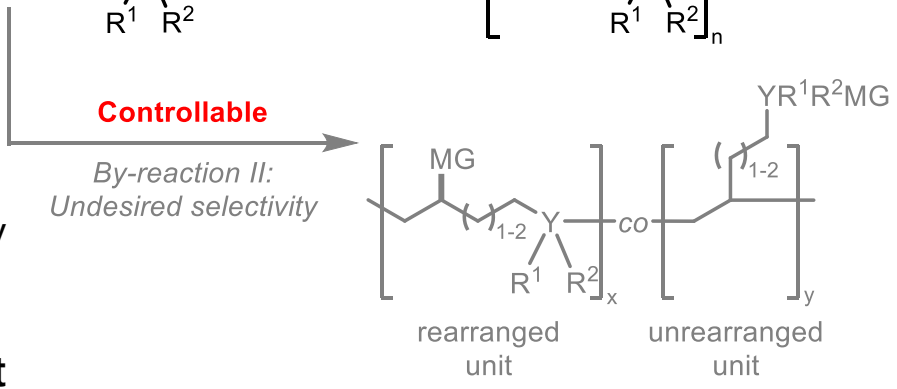


Rational design for switchability:

MG: inhibiting chain transfer

R^1/R^2: facilitating chain propagation by tuning radical polarity

Chain length: common ring intermediates

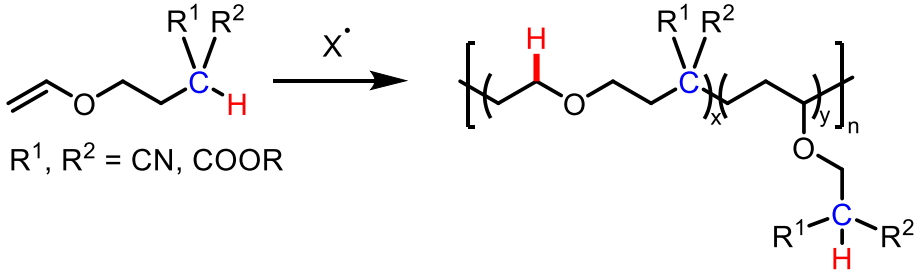


Today's focus: Substrate design & Mechanism insight

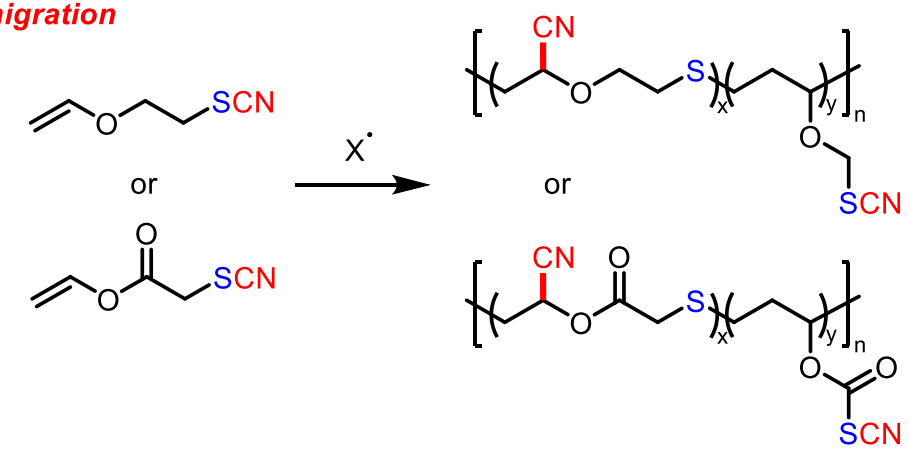
Zhu, C.; *et al*. *Sci. Adv.* **2024**, *10*, eadp7385.

Early researches before GTRP proposal

Sato, 1988-1996
1,5-H migration



Sato, 1999-2002
1,5-CN migration



	Previous reports (1988-2002)	Recent progresses (2024-2026)
Catalyst	None, only initiator needed	
Monomer	Terminal olefin	
Migration position	1,5-	1,4- / multi-step rearrangement
Migration type	C-H activation C-S cleavage	C-C cleavage
Polymer chain	Heteroatom-containing	Carbon-backbone
Chain length	Low M.W. (<10,000) Low n (<30)	Higher M.W. (>40,000) Higher n (>100)
Polymerization selectivity	Relatively non-uniform	Uniform (x/y > 20/1)

Sato, T.; *et al*. *J. Polym. Sci. Polym. Chem. ED.* **1988**, *26*, 2839-2847. Sato, T.; *et al*. *Macromolecules* **1991**, *24*, 2963-2967. Sato, T.; *et al*. *Eur. Polym. J.* **1996**, *32*, 827-835.
Sato, T.; *et al*. *Macromolecules* **1999**, *32*, 4166-4172. Sato, T.; *et al*. *J. Polym. Sci. A Polym. Chem.* **2002**, *40*, 573-582.

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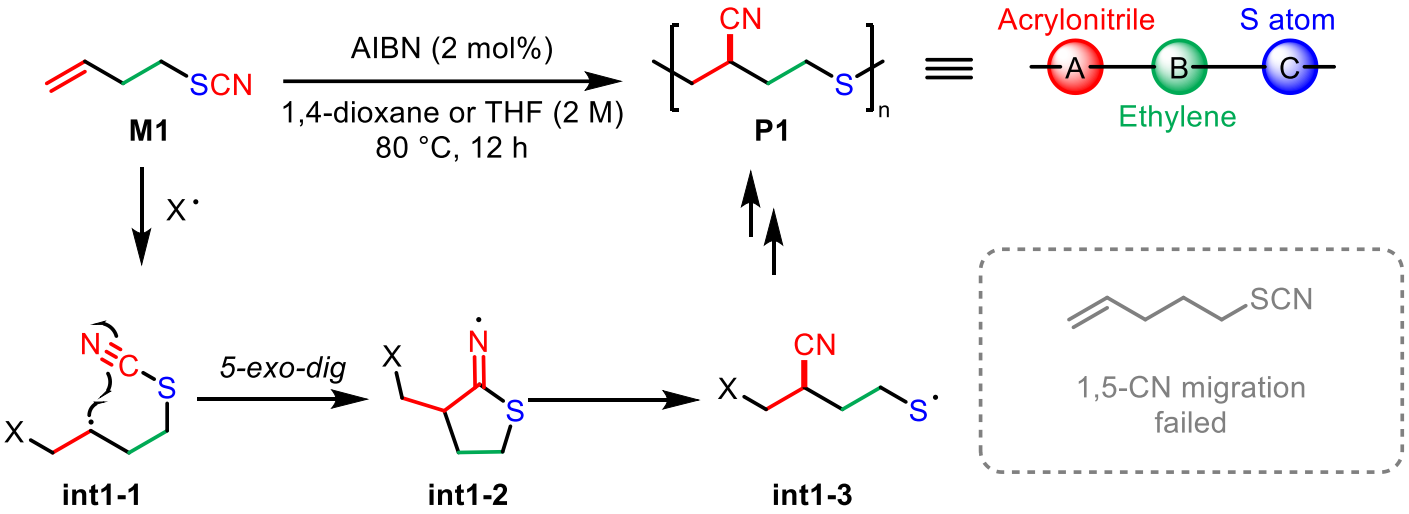
1,4-Cyano migration

Li, 2024



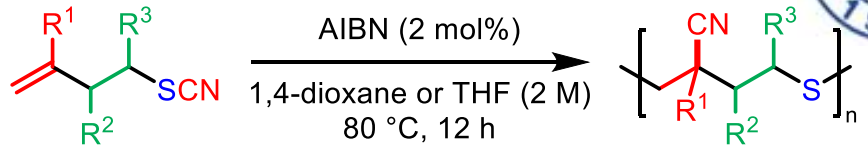
Key species: cyclic imine radical via 5-exo-dig radical addition

Innovation:

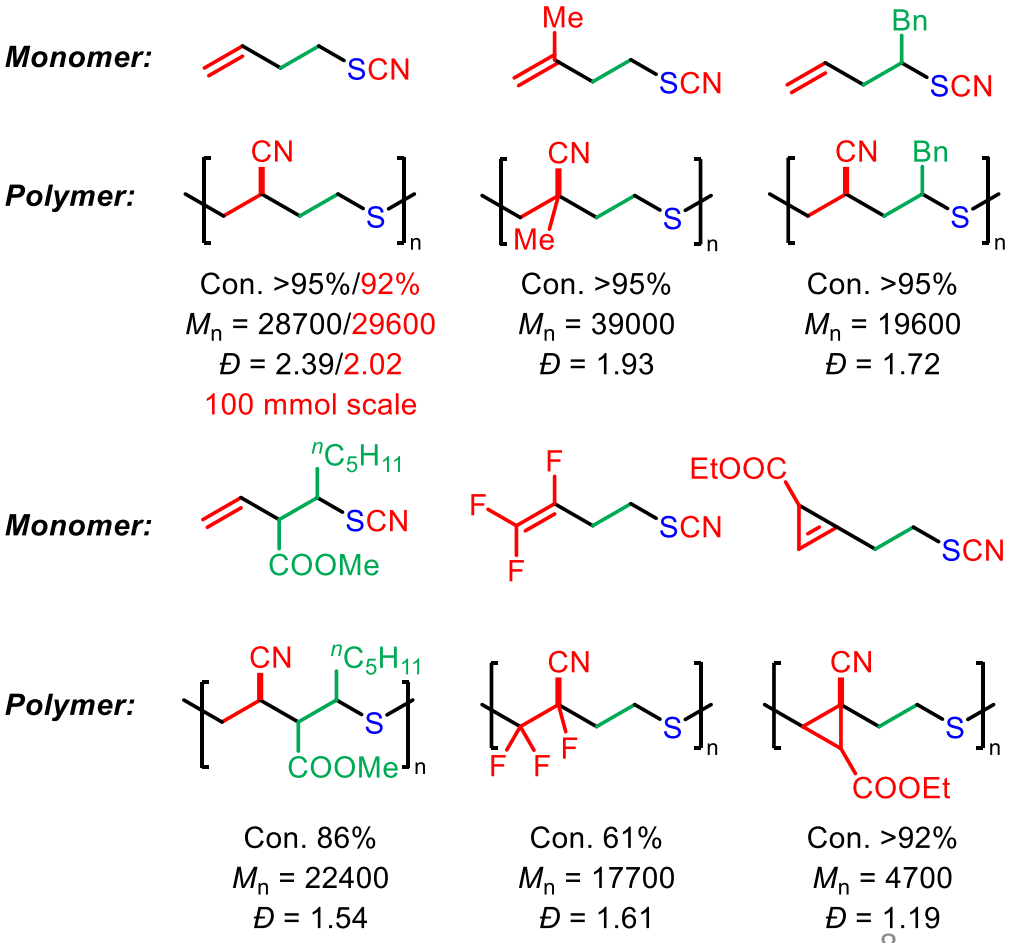
1,4-CN migration instead of 1,5-CN migration

Higher degree of polymerization

Tolerance of different substitution groups on monomer

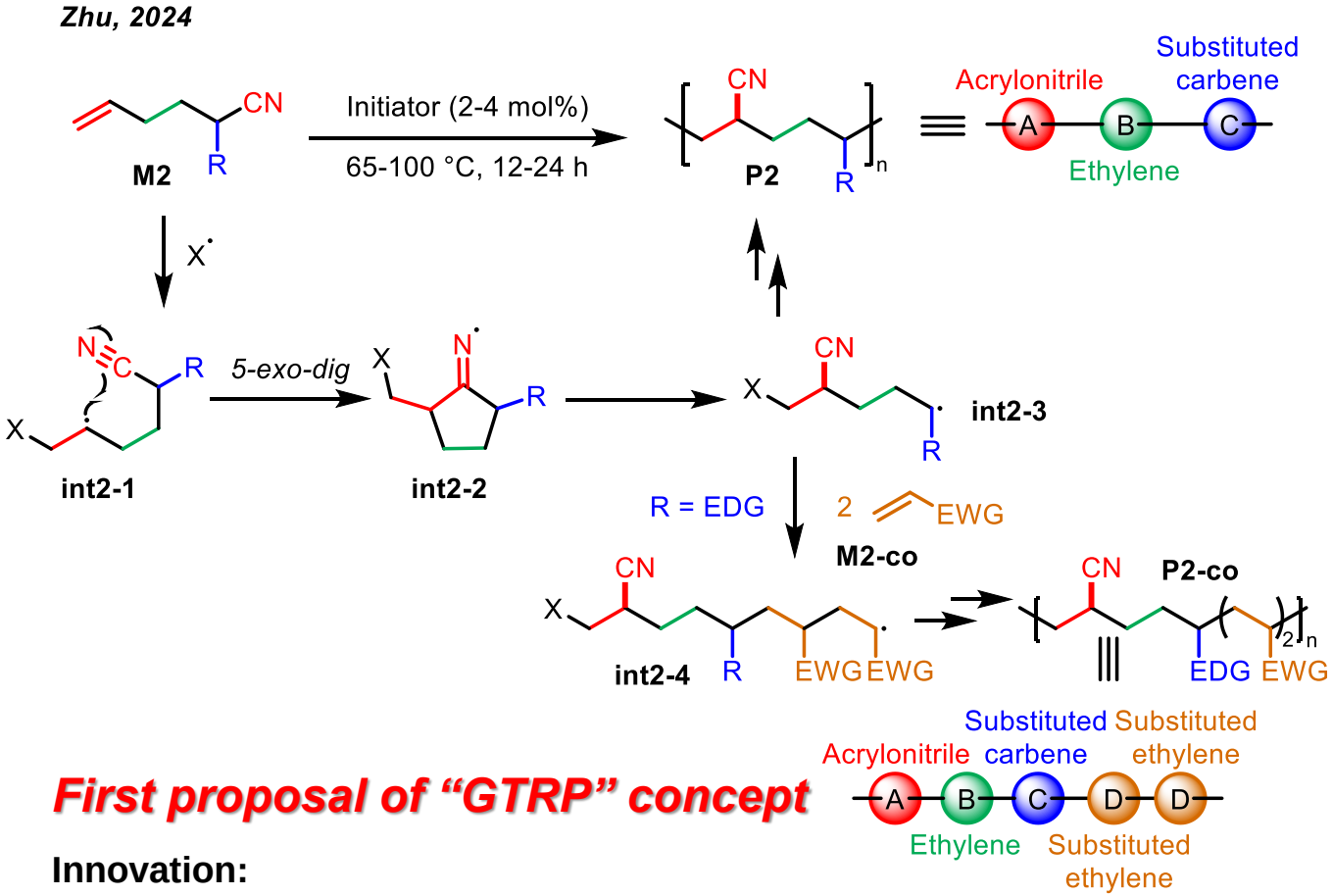


Representative examples (2 mmol scale)



Li, Y.; *et al*. *Angew. Chem. Int. Ed.* **2024**, *63*, e202402511.

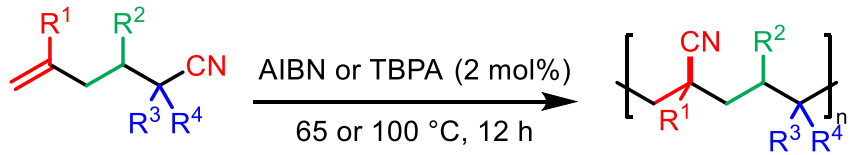
1,4-Cyano migration



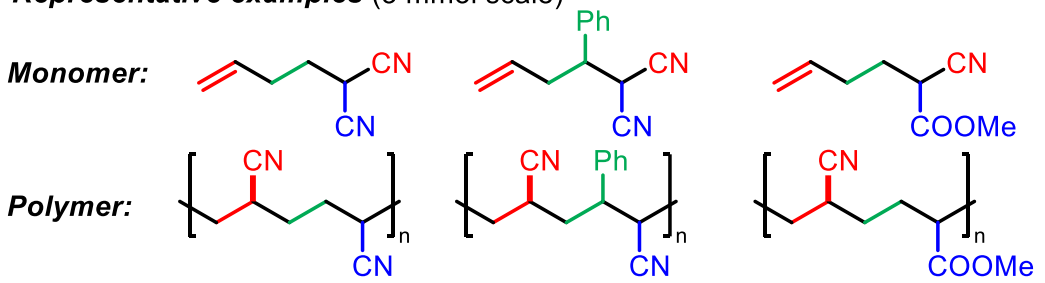
First proposal of "GTRP" concept

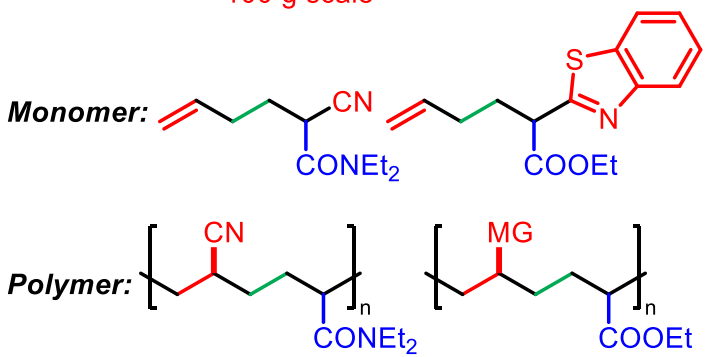
Innovation:

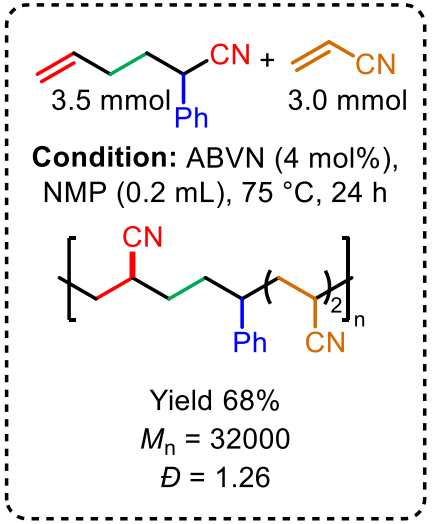
- C-C cleavage-induced radical migration
- Co-polymerization for complex polyolefin-type chain



Representative examples (3 mmol scale)



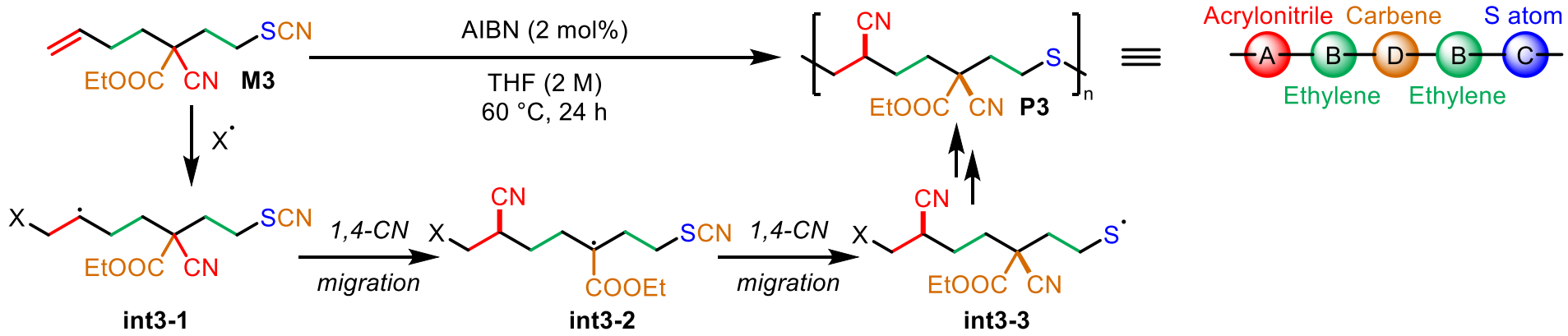




Zhu, C.; *et al*. *Sci. Adv.* **2024**, *10*, eadp7385.

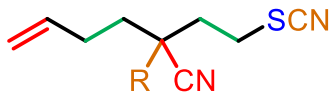
Dual 1,4-cyano migration

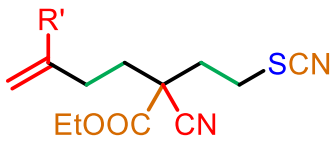
Li, 2026

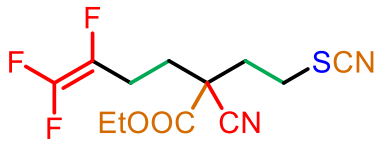


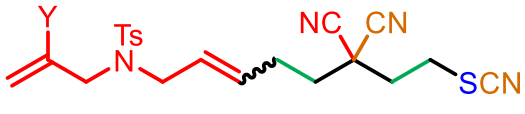
Substrate scope (0.7 mmol scale)

Monomer:

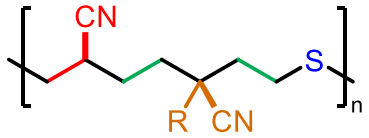


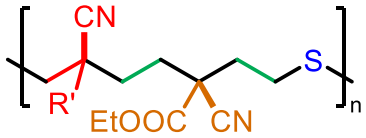


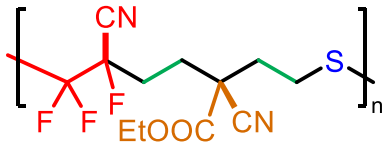


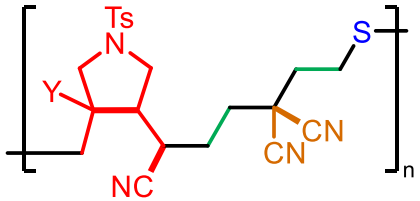


Polymer:









R= COOEt, Con. >95%, M_n = 46900, $Đ$ = 4.49
R= COOMe, Con. >95%, M_n = 10600, $Đ$ = 3.51
R= CN, Con. >79%, M_n = 28400, $Đ$ = 7.32

R'= Me, Con. >95%, M_n = 45000, $Đ$ = 2.47
R'= Ph, Con. >95%, M_n = 9500, $Đ$ = 1.66

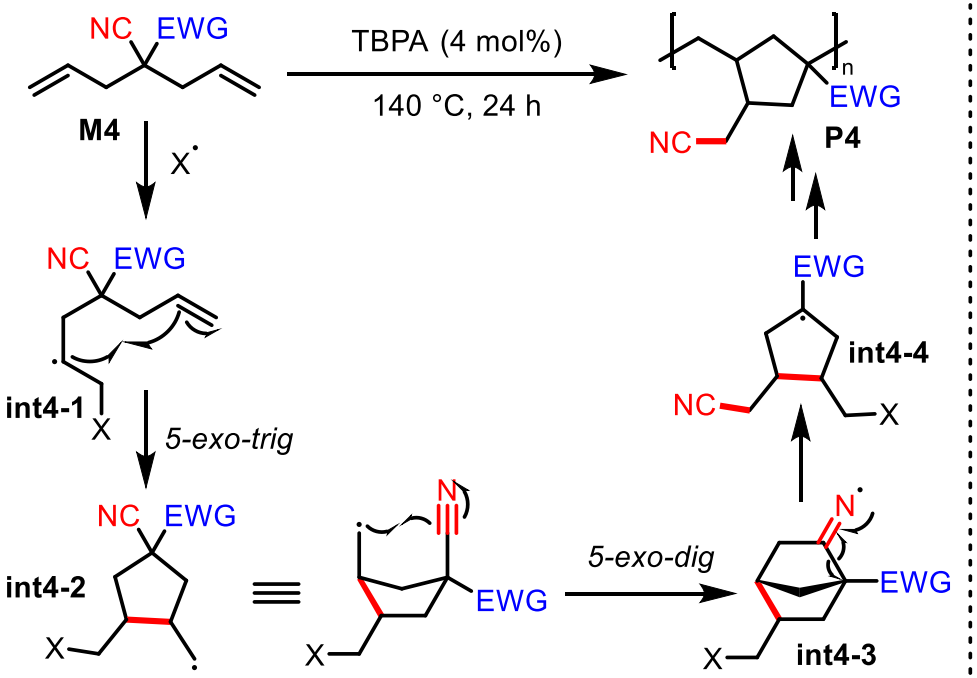
Con. 65%
M_n = 8800
$Đ$ = 1.57

Y = H, Con. 52%, M_n = 16100, $Đ$ = 2.26
Y = Me, Con. 56%, M_n = 19000, $Đ$ = 2.15
Y = Ph, Con. 76%, M_n = 33500, $Đ$ = 4.94

Li, Y.; *et al*. *Macromolecules* **2026**, *59*, 418-425.

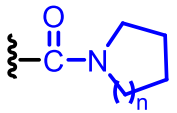
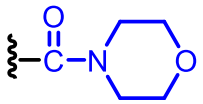
Ring introduction in polymer chain

Zhu, 2025



EWG tolerance (5 mmol scale)

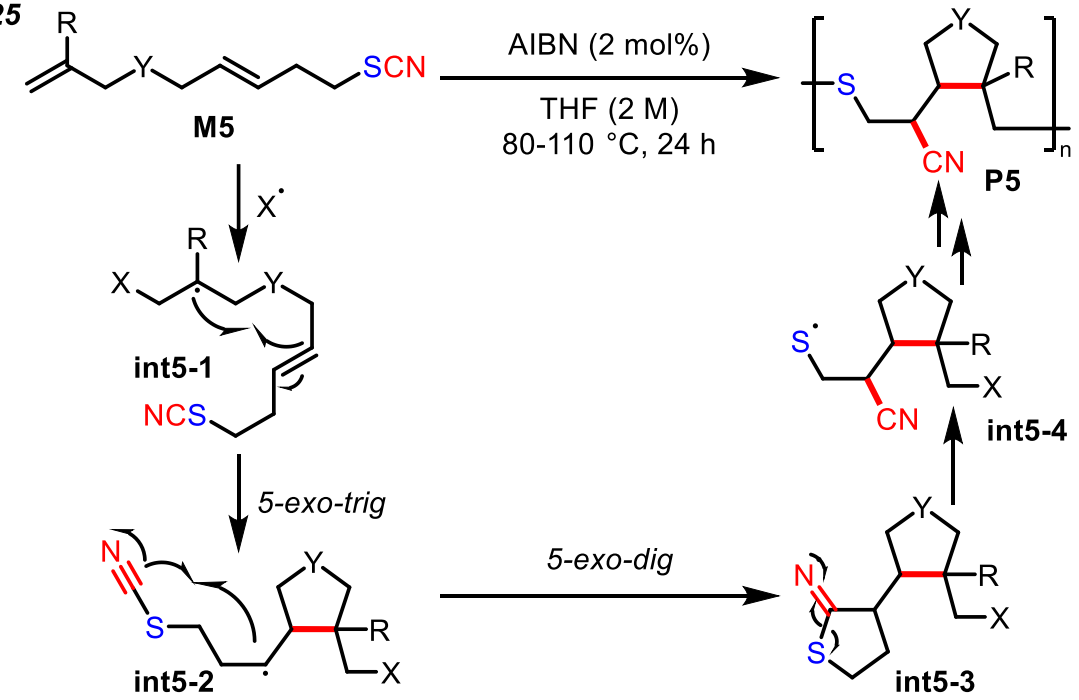
EWG	Con.(%)	M_n	Đ
CN	92	29100	1.70
$P(O)(OEt)_2$	73	20400	1.19
SO_2Ph	70	16400	1.12
SO_2Me	73	20400	1.13
COOEt	67	25000	1.38
$CONEt_2$	43	23100	1.30

EWG		Con.(%)	M_n	Đ
	n = 1	70	22500	1.38
	n = 2	44	20300	1.26
		71	30100	1.36

Zhu, C.; *et al*. *Angew. Chem. Int. Ed.* **2025**, *64*, e202507557.

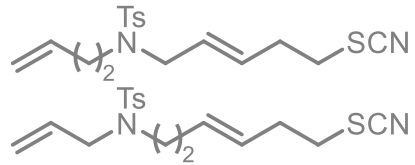
Ring introduction in polymer chain

Li, 2025

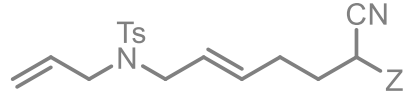


Substrate scope (0.4 mmol scale)

Y	R	Con.(%)	M_n	Đ
NTs	H	91	12100	1.36
	Me	>95	21900	1.56
	Ph	>95	24400	1.70
	COOEt	>95	14200	1.96
$C(COOEt)_2$	COOEt	>95	27000	1.42



1,7-diene via *6-exo-trig* ring closure failed



R = CN, COOEt C-C cleavage failed

Copolymerization attempt
(0.4 mmol scale)
M5 Y = NTs, R = COOEt

Co-monomer	M5/co-m.	$Con._{M5}$(%)	$Con._{co\text{-}m.}$(%)	M_n	Đ	$f_{M5}/f_{co\text{-}m.}$
Ph	1/1	>95	93	10300	1.81	-
COO^tBu	1/1	>95	>95	13900	1.59	55/45
OAc	1/1	>95	<5	9700	1.63	-
	1/1	>95	23	8300	1.84	98/2
	1/5	>95	-	4600	1.67	81/19

Li, Y.; *et al*. *Macromolecules* **2025**, *58*, 7406-7413.

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1,5-Hydrogen migration

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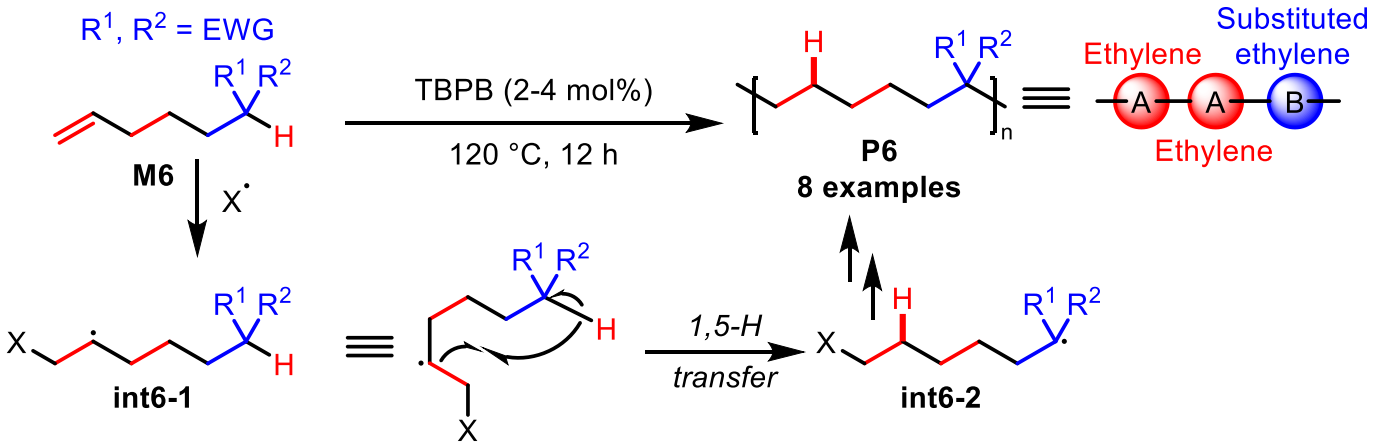
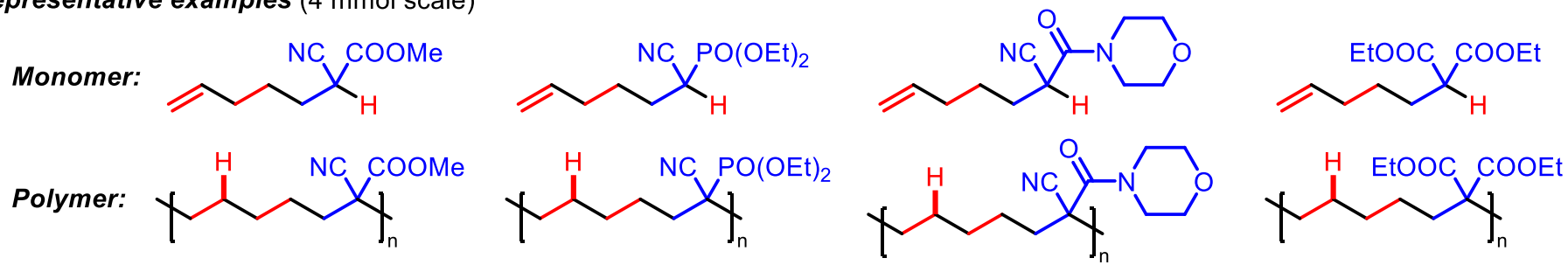


Representative examples (4 mmol scale)



Yield 95%/93%
M_n = 18600
$Đ$ = 1.96
100 gram scale

Yield 51%
M_n = 4300
$Đ$ = 1.62

Yield 37%
M_n = 6200
$Đ$ = 1.37

Yield 82%
M_n = 12200
$Đ$ = 1.62

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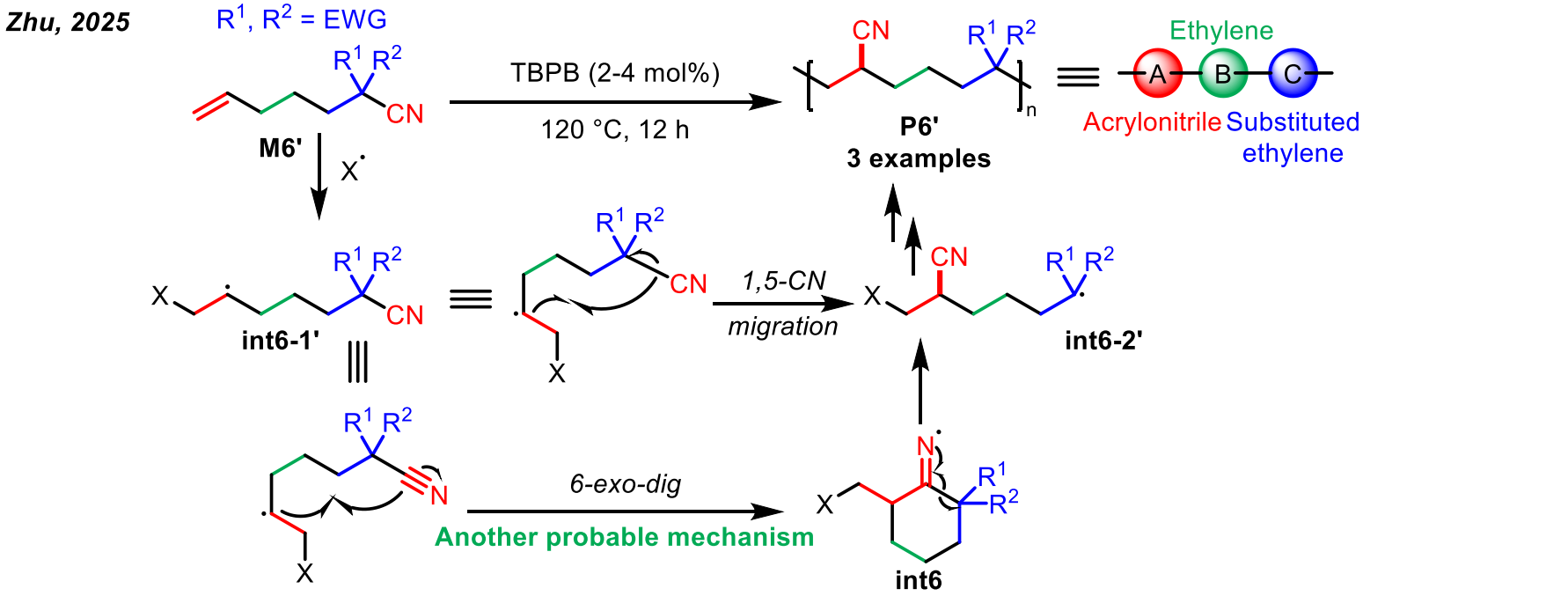
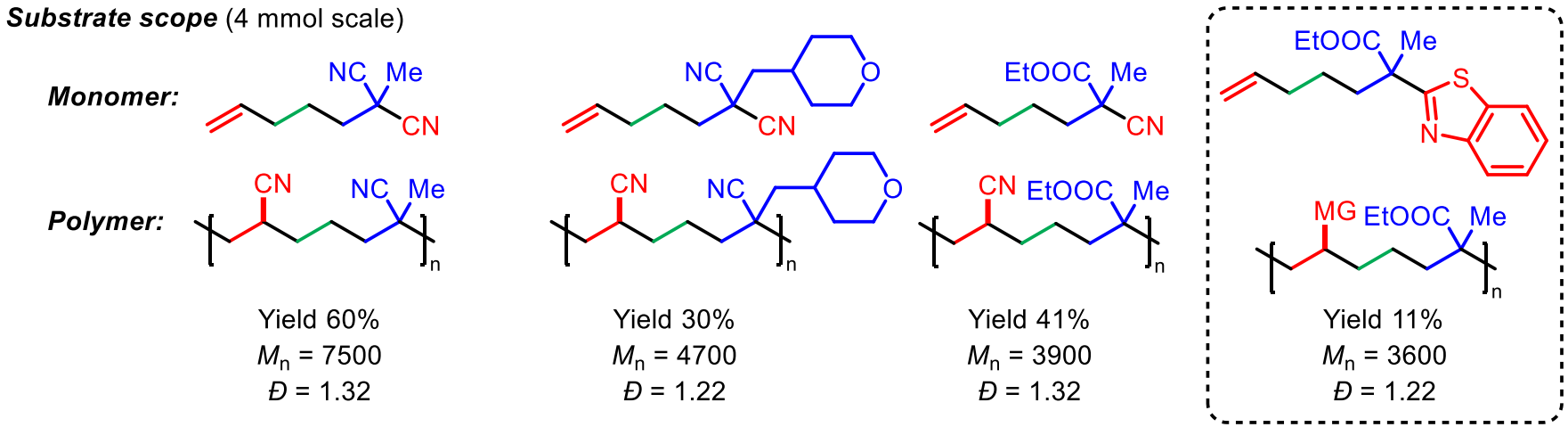
1,5-Cyano migration





Zhu, C.; *et al*. *Angew. Chem. Int. Ed.* **2025**, *64*, e202418350.

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Smiles rearrangement

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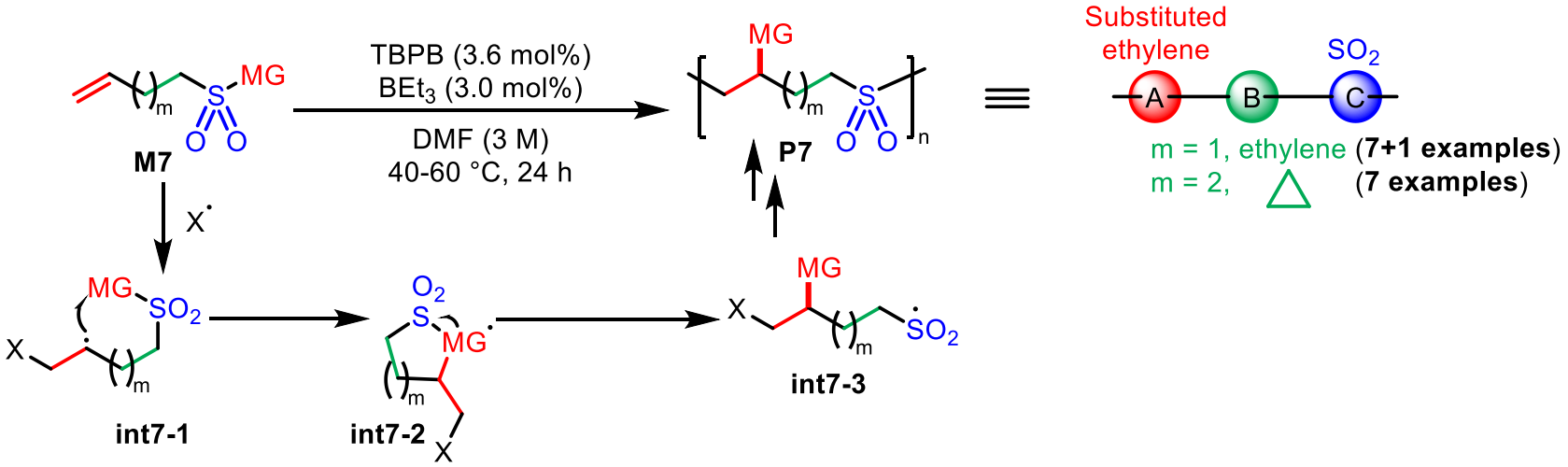
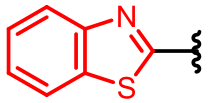
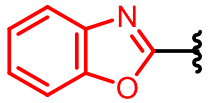


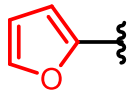
MG tolerance (0.6 mmol scale)



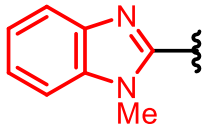
m = 1, Con. >95%, M_n = 82300, $Đ$ = 1.96
m = 2, Con. >95%, M_n = 91700, $Đ$ = 1.61



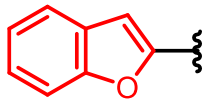
m = 1, Con. >95%, M_n = 58800, $Đ$ = 1.29
m = 2, Con. >95%, M_n = 49000, $Đ$ = 1.34



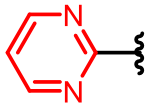
Con. >95%
M_n = 101800
$Đ$ = 2.64
m = 1



m = 1, Con. 77%, M_n = 45900, $Đ$ = 1.60
m = 2, Con. >95%, M_n = 199200, $Đ$ = 1.63



m = 1, Con. >95%, M_n = 168000, $Đ$ = 1.61
m = 2, Con. 64%, M_n = 30300, $Đ$ = 1.57



Con. 94%
M_n = 55300
$Đ$ = 1.42
m = 2

m = 1, Con. >95%, M_n = 24500, $Đ$ = 1.59
m = 2, Con. 75%, M_n = 13800, $Đ$ = 1.20

m = 1, Con. >95%, M_n = 27400, $Đ$ = 1.54
m = 2, Con. 58%, M_n = 9100, $Đ$ = 1.29

Zhu, C.; *et al*. *Angew. Chem. Int. Ed.* **2025**, *64*, e202500153.

Content

1. Background

2. Key strategies in GTRP

2.1 1,4-Cyano migration

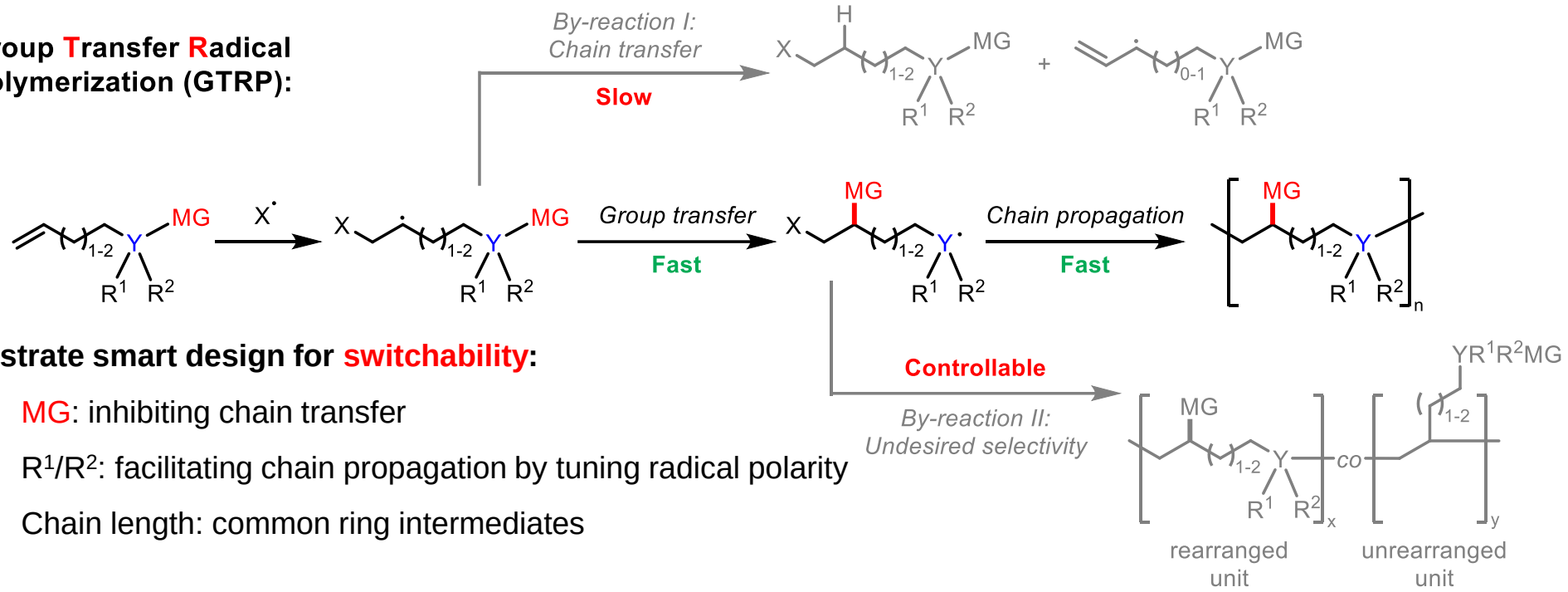
2.2 1,5-Hydrogen/group migration

2.3 Smiles rearrangement

3. Conclusion & Outlook

Conclusion & Outlook: Switchable GTRP

Group Transfer Radical Polymerization (GTRP):



Substrate smart design for switchability:

MG: inhibiting chain transfer

R^1/R^2: facilitating chain propagation by tuning radical polarity

Chain length: common ring intermediates

Current status

- **Reaction:** 1,4-CN, 1,5-H/CN, Smiles rearrangement
- **MG:** -CN, -H, -heteroaryl

Future prospects

- **New reaction:** based on small molecules' chemistry
- **MG library**

Thanks for attention!