Chain Shuffling: A Synthetic Pathway to Multiblock Copolymers

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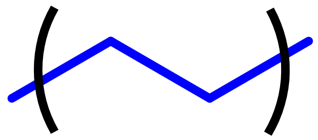
Tuesday, April 18, 2023

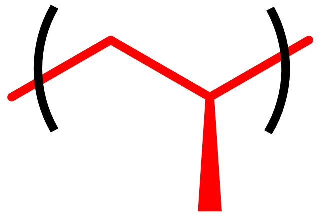
The University of Akron

Abundance of PE/iPP

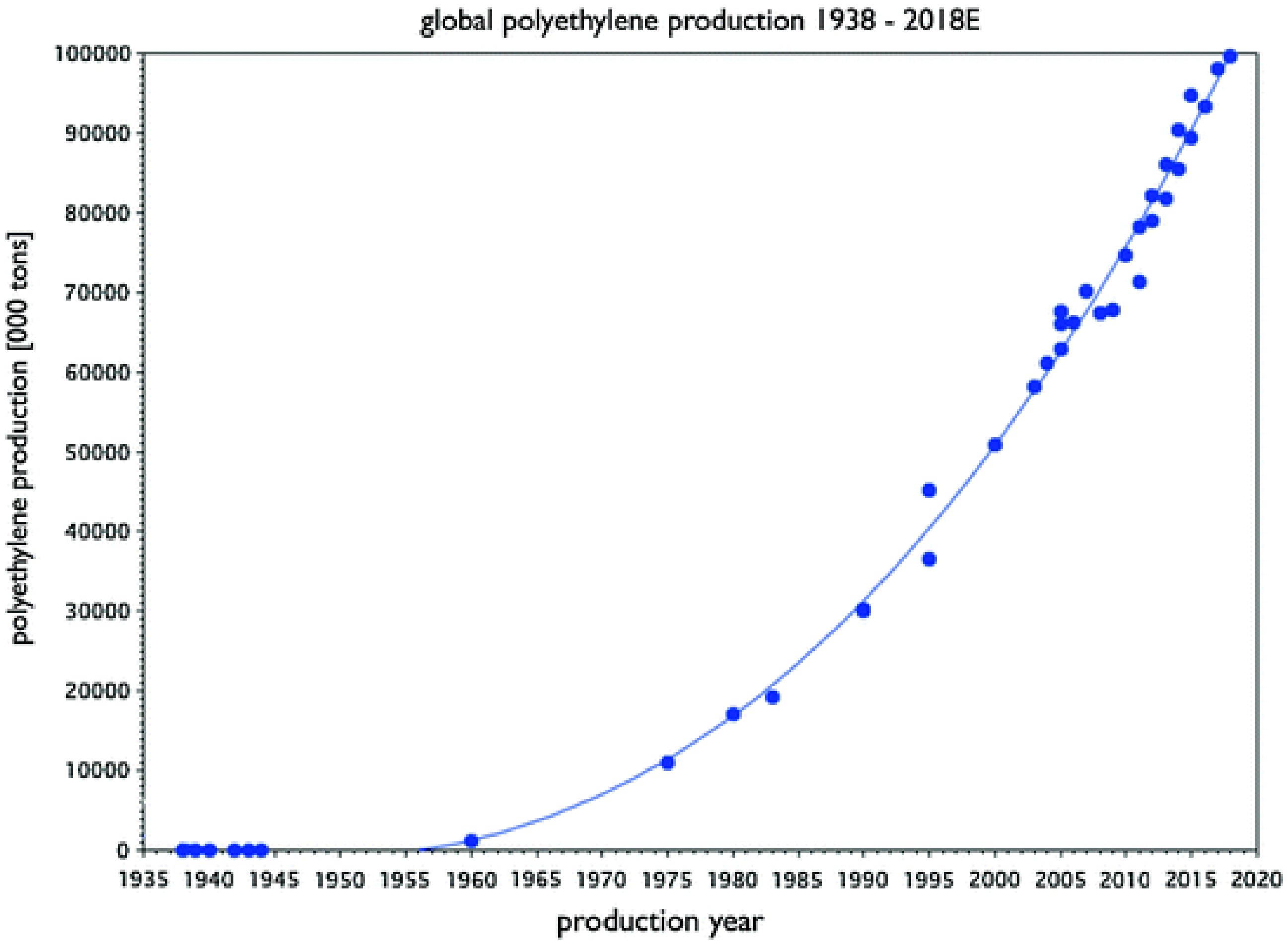
top two polymers



polyethylene

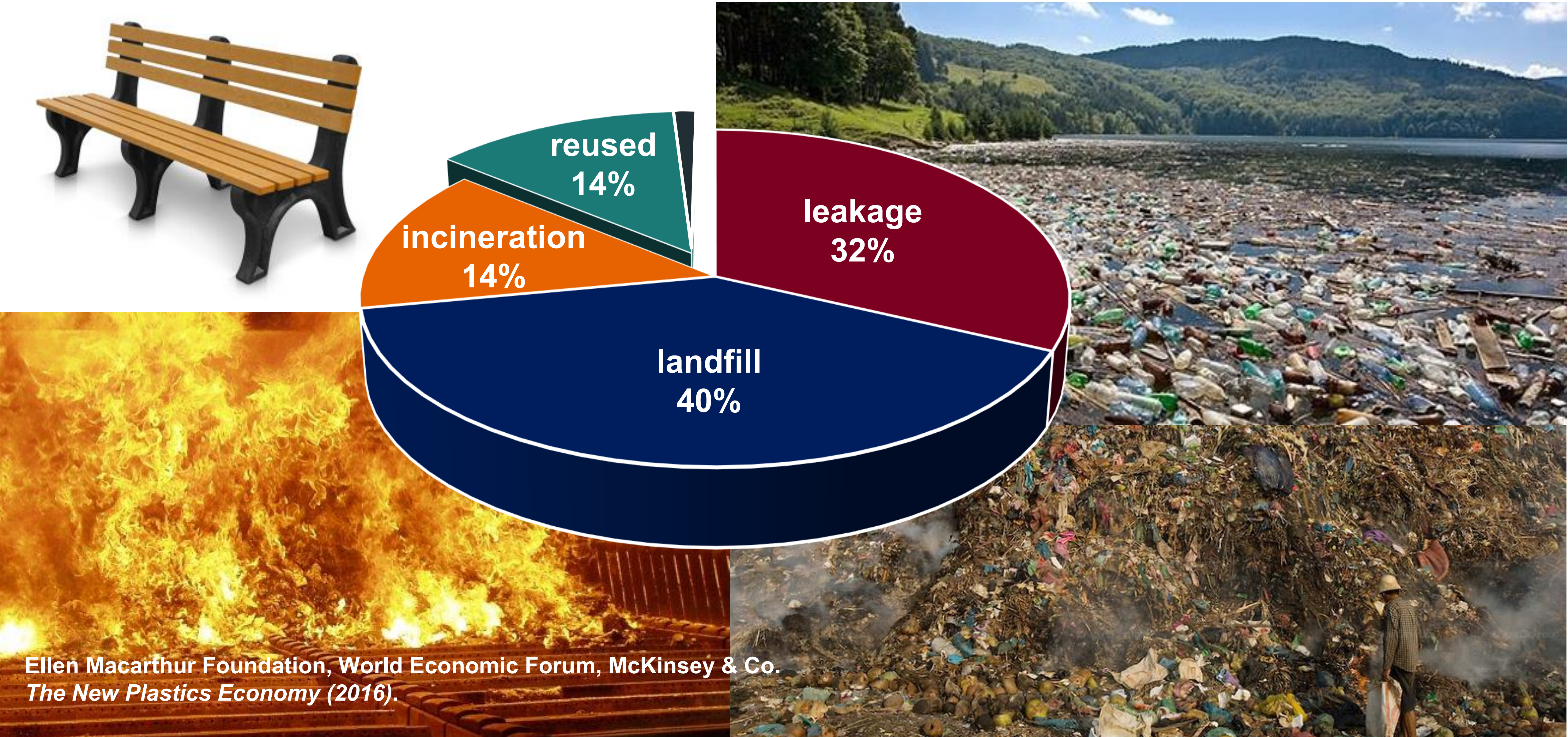


isotactic polypropylene



 T. J. Hutley, M. Ouederni. *Polyolefins – the History and Economic Impact.* **2015**, Springer Series on Polymer and Composite Materials.

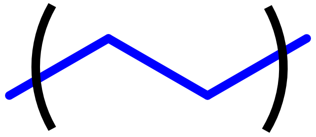
Recycling



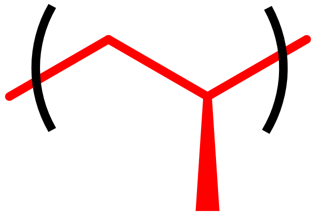
Ellen Macarthur Foundation, World Economic Forum, McKinsey & Co.
The New Plastics Economy (2016).

The Challenge

top two polymers



polyethylene

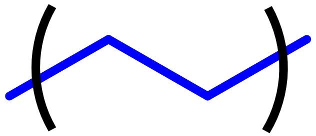


isotactic polypropylene

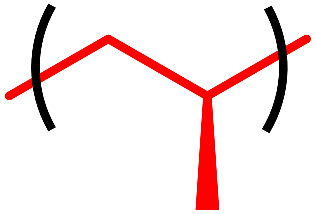
over 120 million tons produced annually

The Challenge

top two polymers

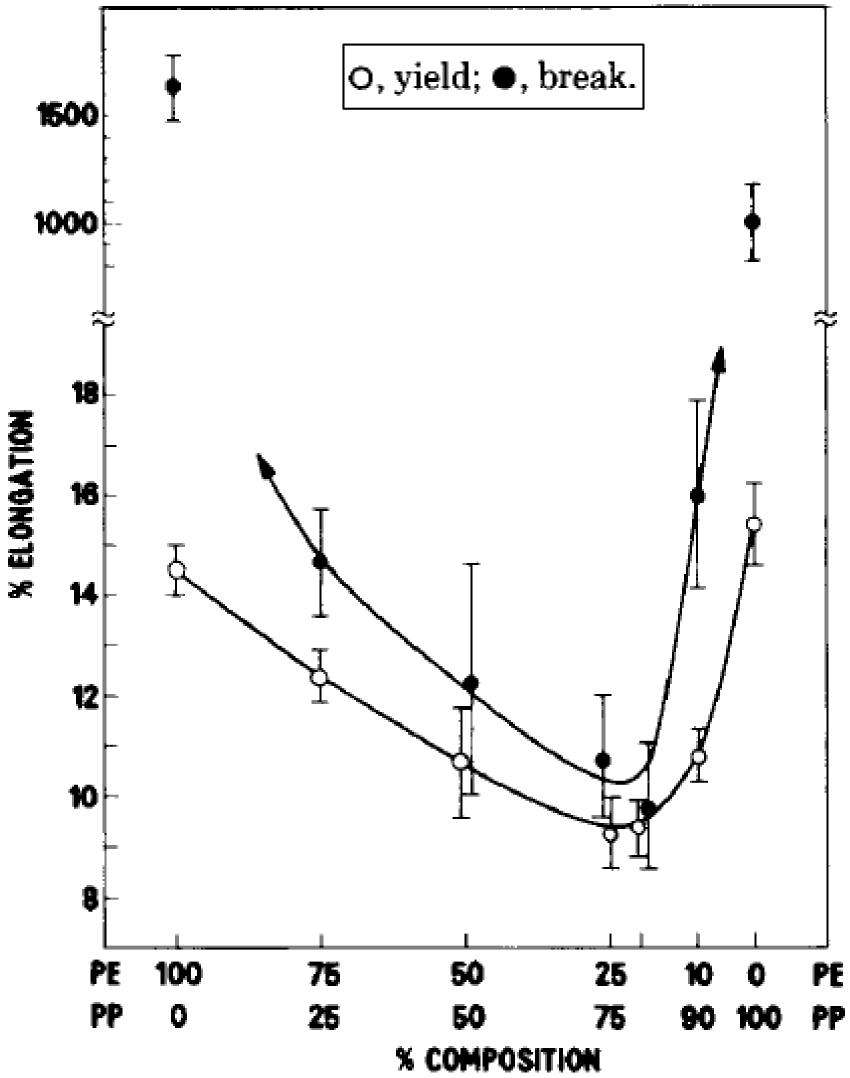


polyethylene



isotactic polypropylene

over 120 million tons produced annually

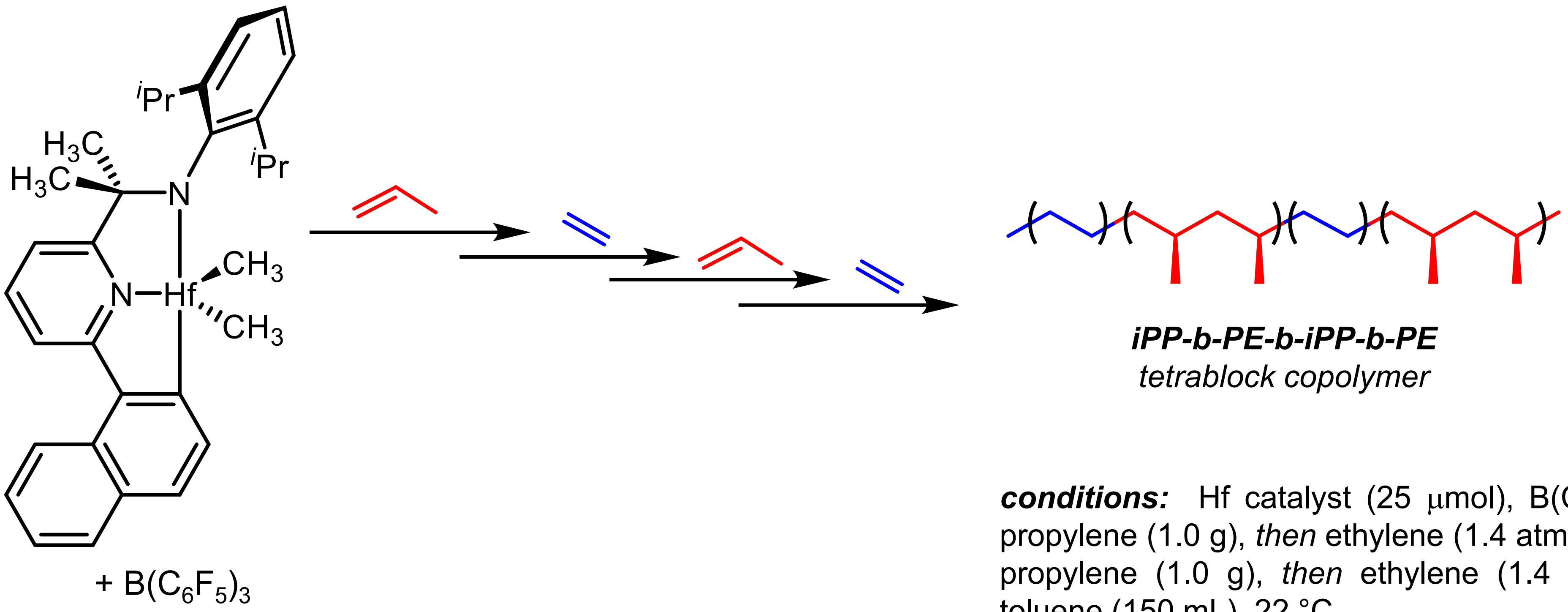


- Virgin PE and virgin iPP have high % elongations
- The addition of even a slight minor component drastically reduces % elongation

J. Appl. Polym. Sci. **1980**, *25*, 1703 –1713.

Tetrablock Copolymers

Pyridyl amidohafnium catalysts enable multiblock architectures

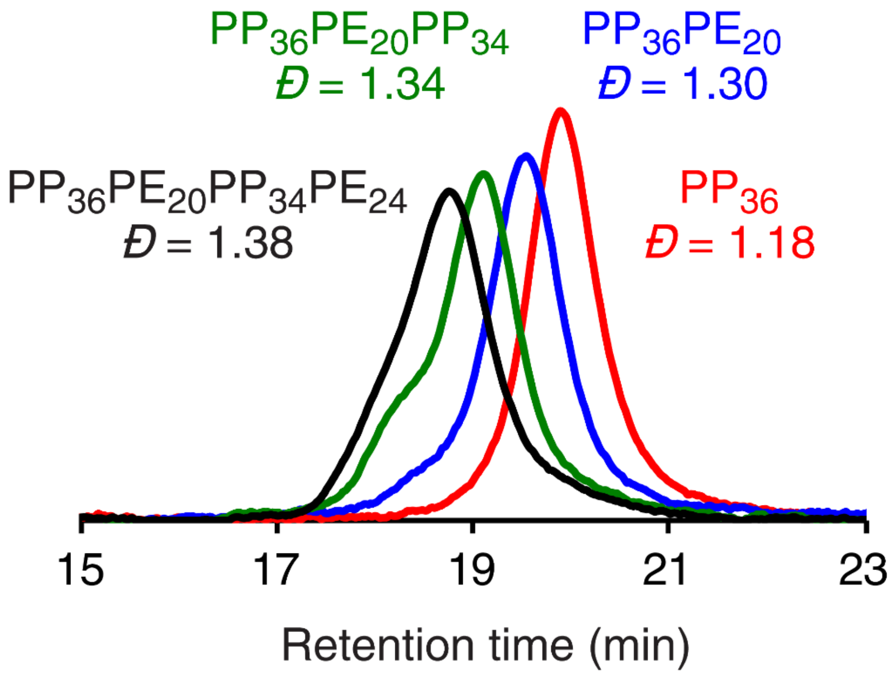


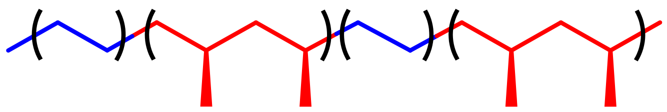
iPP-b-PE-b-iPP-b-PE
tetrablock copolymer

conditions: Hf catalyst (25 μmol), $B(C_6F_5)_3$ (25 μmol), propylene (1.0 g), *then* ethylene (1.4 atm), 4 minutes, *then* propylene (1.0 g), *then* ethylene (1.4 atm), 4 minutes, toluene (150 mL), 22 °C.

Science, **2017**, *355*, 814–816.

Tetrablock Copolymers



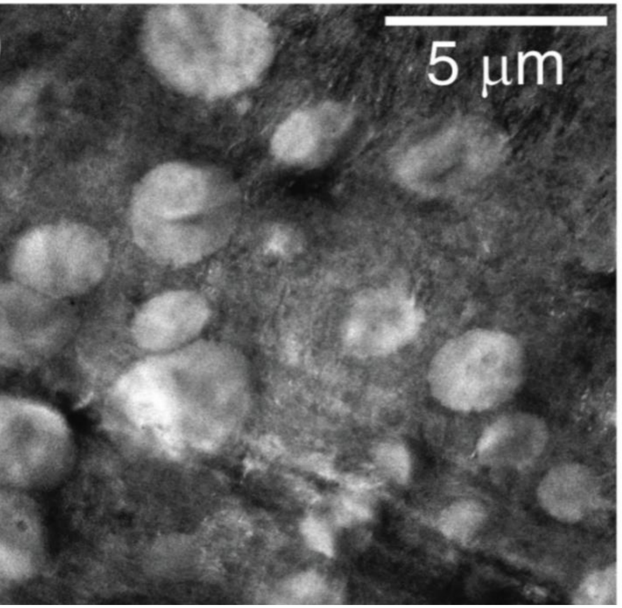


iPP-b-PE-b-iPP-b-PE
tetrablock copolymer

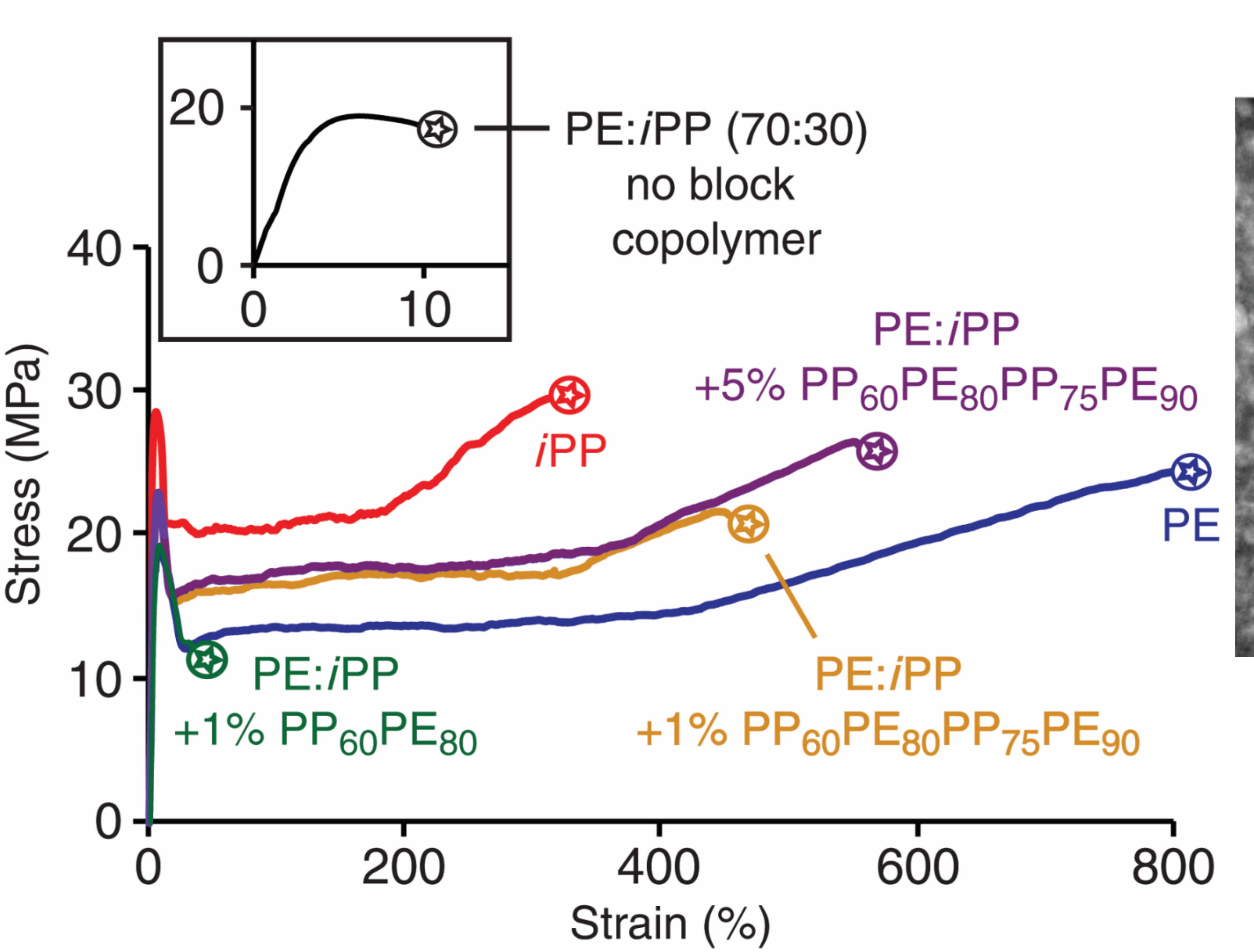
conditions: Hf catalyst (25 μmol), $B(C_6F_5)_3$ (25 μmol), propylene (1.0 g), *then* ethylene (1.4 atm), 4 minutes, *then* propylene (1.0 g), *then* ethylene (1.4 atm), 4 minutes, toluene (150 mL), 22 °C.

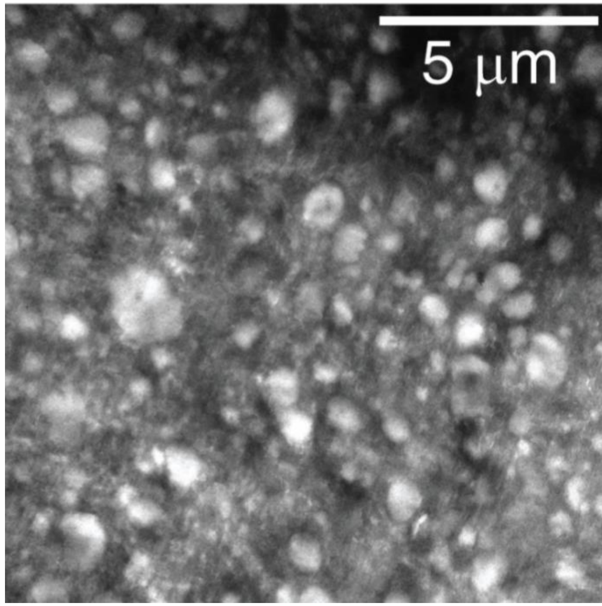
Science, **2017**, *355*, 814–816.

Tensile Properties



d_{av} = 2.16 µm

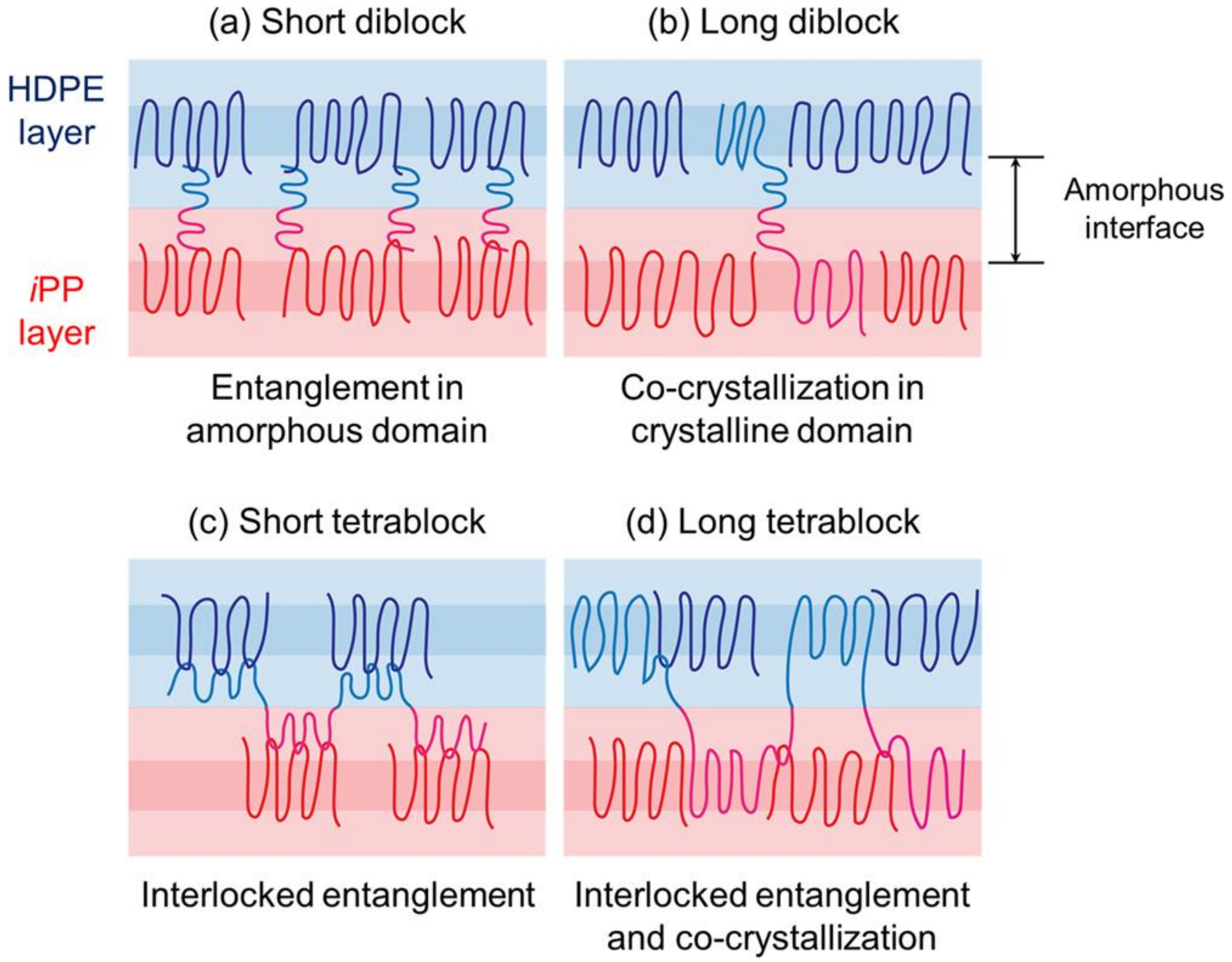




d_{av} = 0.55 µm

A) J. M. Eagan, et al. *Science*. **2017**, *355*, 814–816.
B) J. M. Eagan, G. W. Coates, A. M. LaPointe. WO2017205774A1. **2017**.

Advantages of Multi-blocks



Diblocks:

- Long diblocks co-crystallize in the crystalline domain
- Entanglements are relatively easy to dissociate

Tetrablocks:

- Tetrablocks exhibit trapped entanglements
- Dissociating entanglements requires greater force than bulk failure of the PE matrix

Living Catalysts for iPP-BCP

Living & isospecific catalyst

iPP

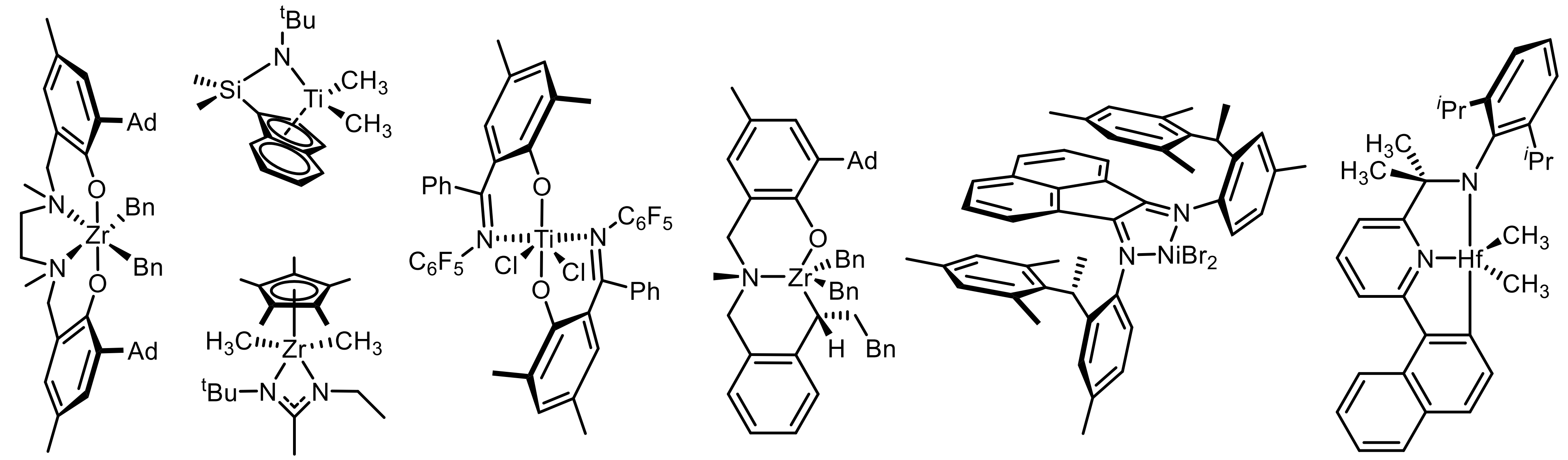
iPP-block copolymer

Living Polymerization

- Excellent MW control
- Narrow dispersities

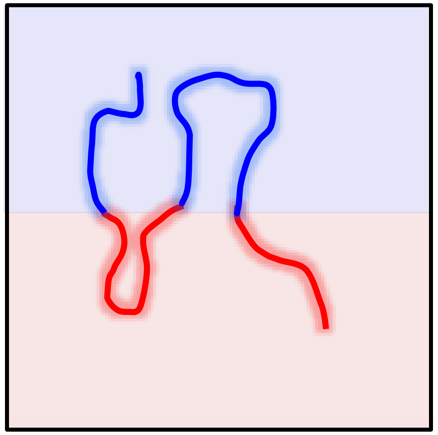
- Tacticity is challenging
- Comonomers are limited
- Not scalable

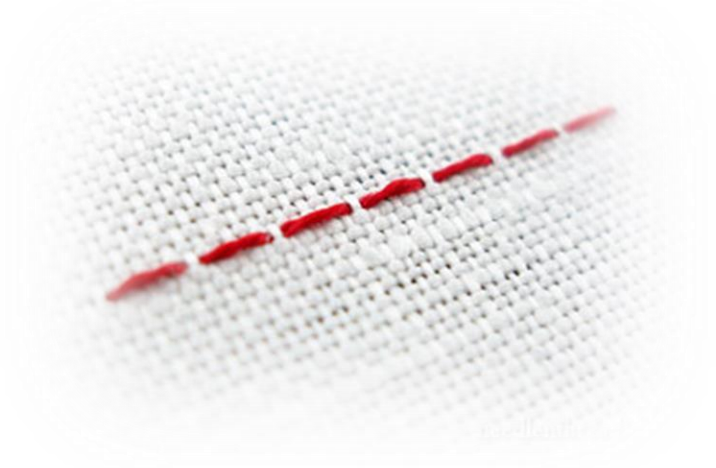
Examples of Living & Isospecific Catalysts



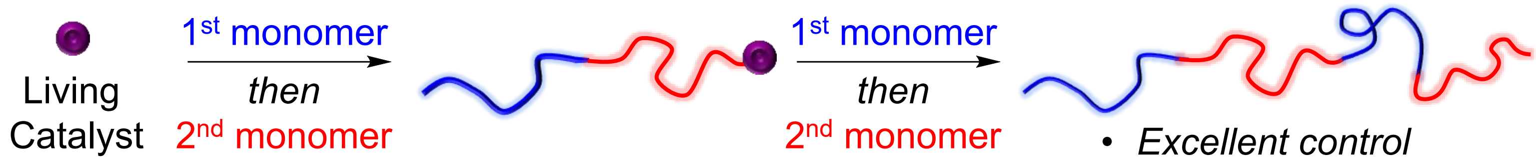
Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30.

Limits of the System





Living/Controlled Polymerization



- *Excellent control*
- *1 chain per catalyst*
- *Similar comonomers*

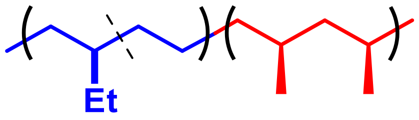
1) Too much catalyst

100m tons PE / *1 year*	*2,000 tons MBCP* / *1m ton PE*	*2 mol Hf* / *1,000 kg MBCP*
(annual PE)	*(0.2 wt%)*	*(500 kDa)*

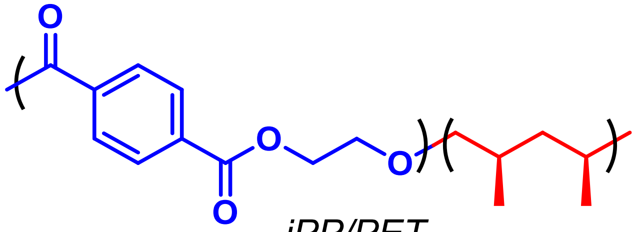
= 400 mol Hf/year = ***71 tons Hf/year***

Global production = 70 tons Hf/year

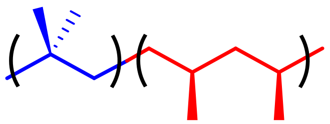
2) Compositionally limited



iPP/LLDPE



iPP/PET

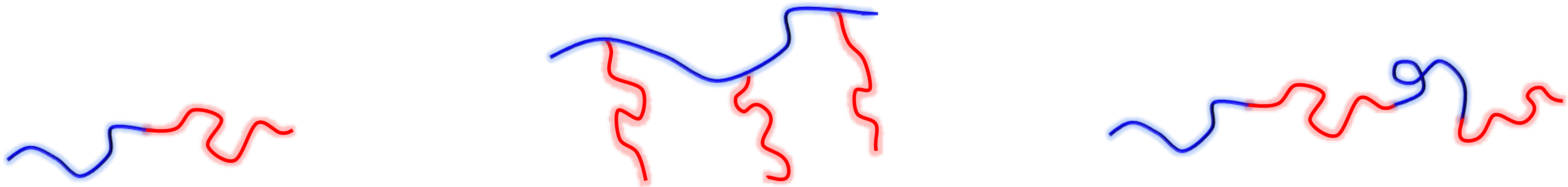


iPP/PIB

C. Ellison and coworkers. *ACS Appl. Mater. Interfaces* **2020**, *12*, 9726–9735

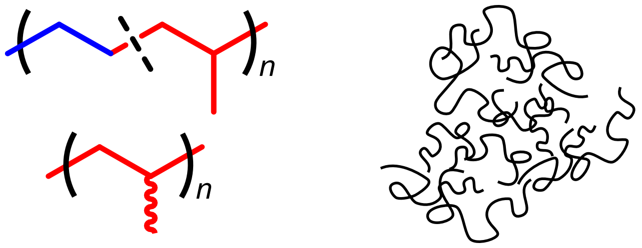
Polypropylene Block Copolymers

Architecture

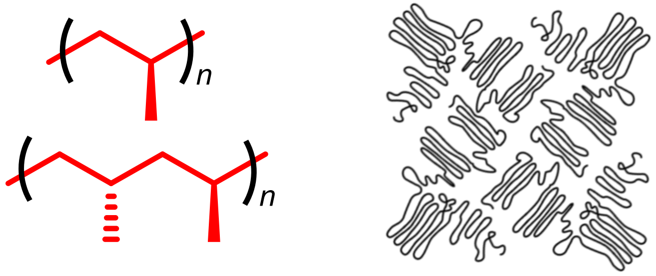


Linear *Branched* *Linear multiblocks*

Crystallinity/Modulus



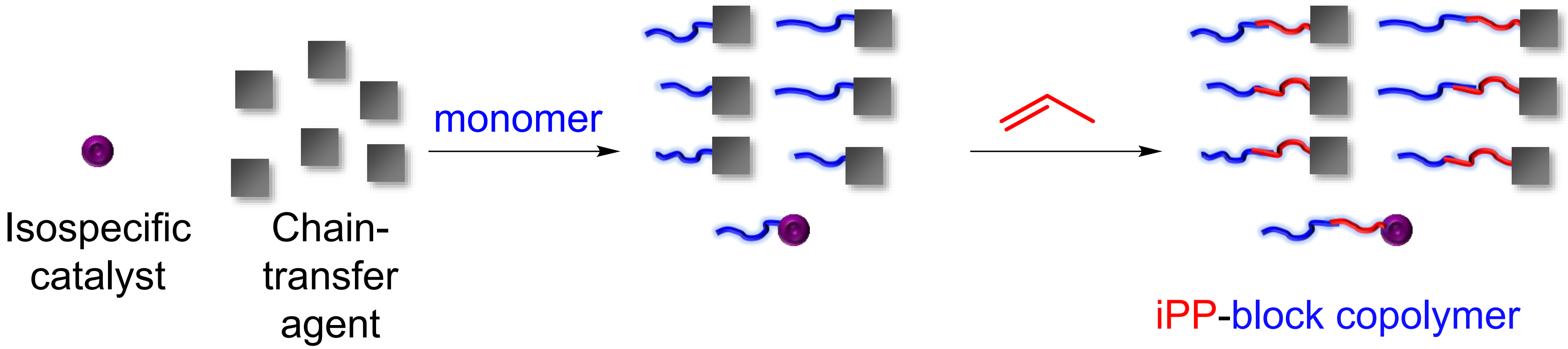
elastomeric polypropylenes



crystalline polypropylenes

C. Ellison and coworkers. *ACS Appl. Mater. Interfaces* **2020**, *12*, 9726–9735

Non-living ***CCTP***



Chain-Transfer Polymerization

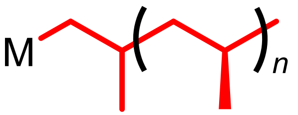
- Commercially scalable
- End-functionalization

- Termination in iPP
- Tacticity/reversibility is a challenge
- Comonomers are limited

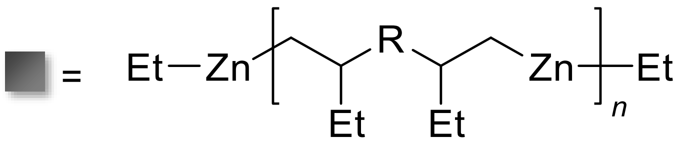
Selected Examples of CCTP (iPP)

Intune™ olefin block copolymers by Dow

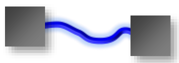
Infuse™ olefin block copolymers by Dow



M = Zn–iPP
B–$(iPP)_2$
SiH_2Ph



Multifunctional CTAs enable telechelic *polyethylenes*



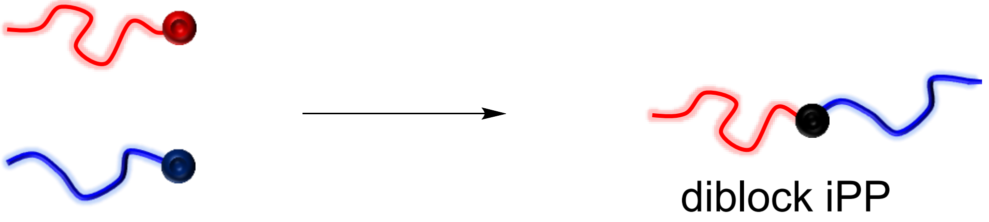
Additional PP-CCTP references:

Science, **2006**, *312*, 714.
J. Am. Chem. Soc. **2008**, *130*, 442.
Macromolecules **2000,** *33*, 9192.
Macromolecules **2007**, *40,* 7736.
J. Am. Chem. Soc. **2004**, *126*, 10701.
Macromol. Chem. Phys. **2006**, *207*, 295.
ACS Catal. **2021**, *11*, 10170.

1) S. B. Amin, T. J. Marks. *Angew. Chem. Int. Ed.* **2008**, *47*, 2006–2025; 2) Images from Dow.com

Macromolecular Engineering with iPP

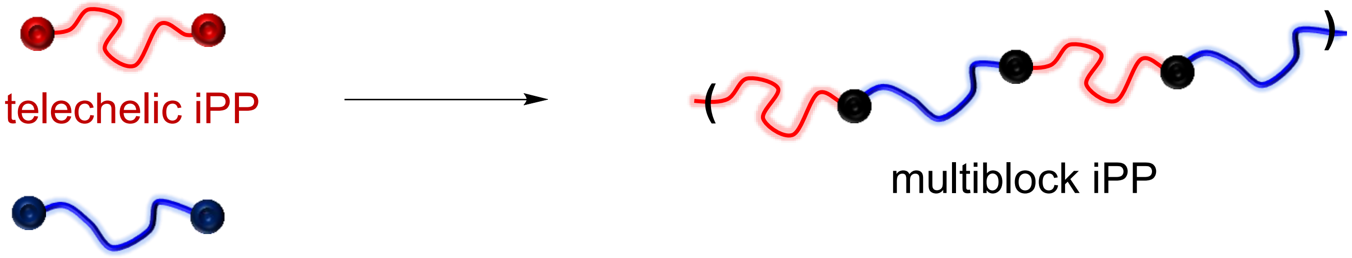
Diblock coupling



End-Functionalized iPP

- Non-living method
- Versatile comonomers
- Independent tuning of crystallinity

Multiblock Step-Growth



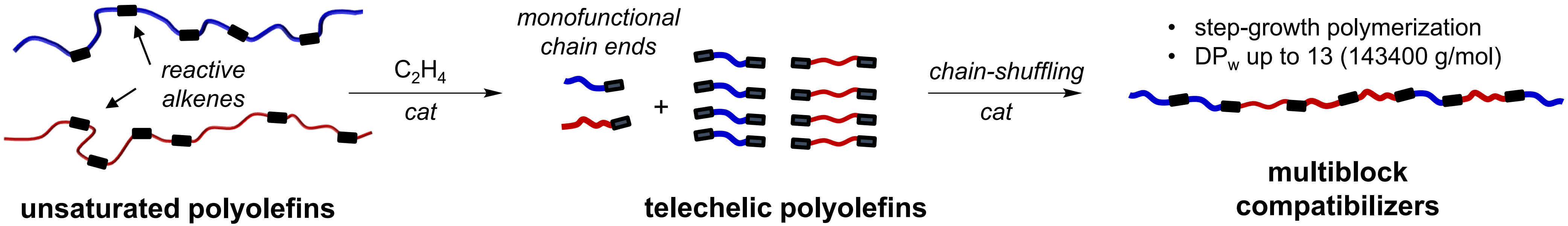
This work

Telechelic iPP

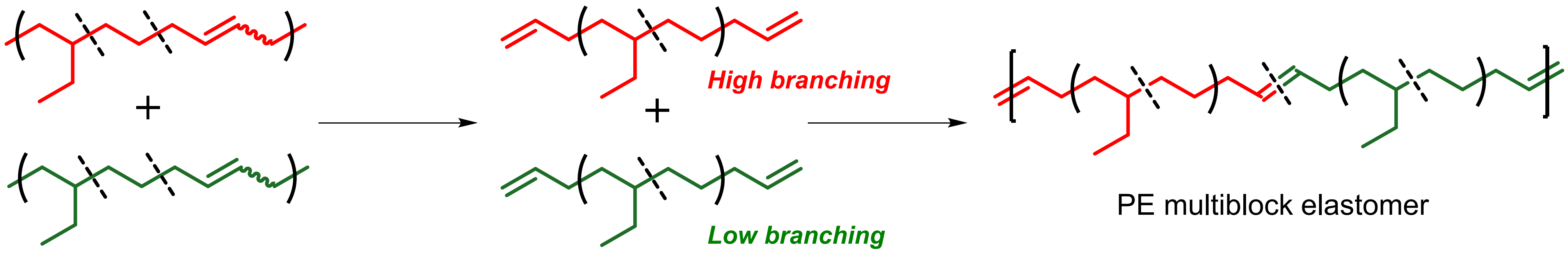
- Architecture control
- Difficult to maintain T_m, M_w, and scalability

For urethane linked PE/PP diblocks see: J. Appl. Polym. Sci, **2007**, *104*, 2766–2773.

Reactive Hydrocarbon Approach



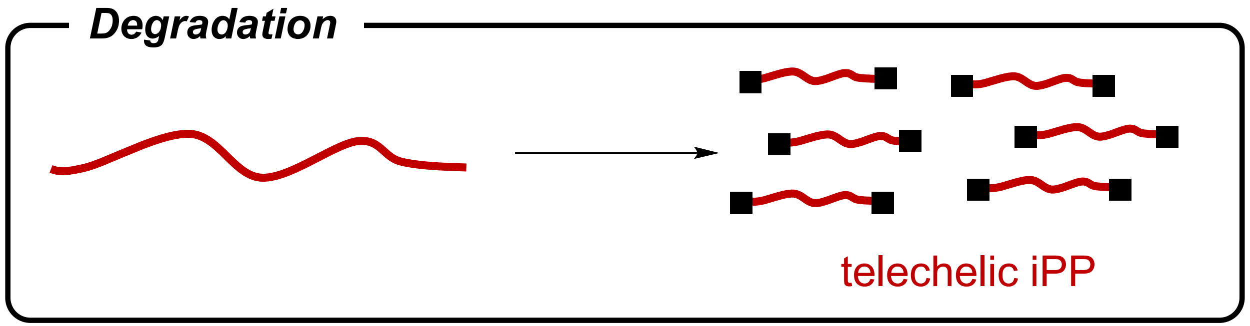
Inspiration: Fredrickson & Bazan



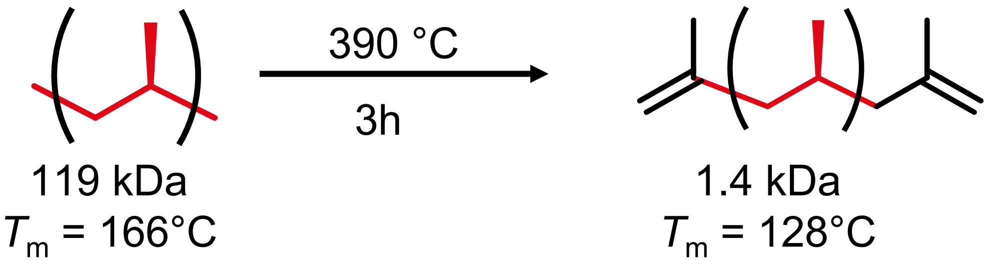
Chem. Commun., **2016**, 52, 2237–2240

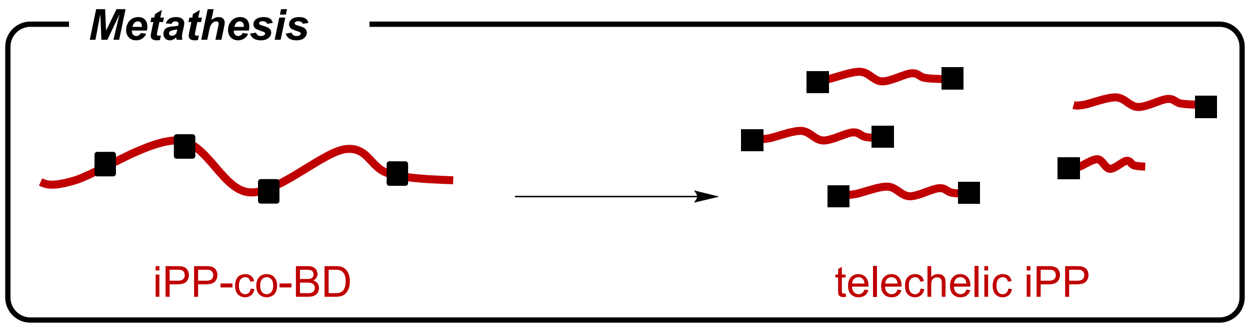
For urethane linked PE/PP diblocks see: J. Appl. Polym. Sci, **2007**, *104*, 2766–2773.

Methods for Telechelic iPP

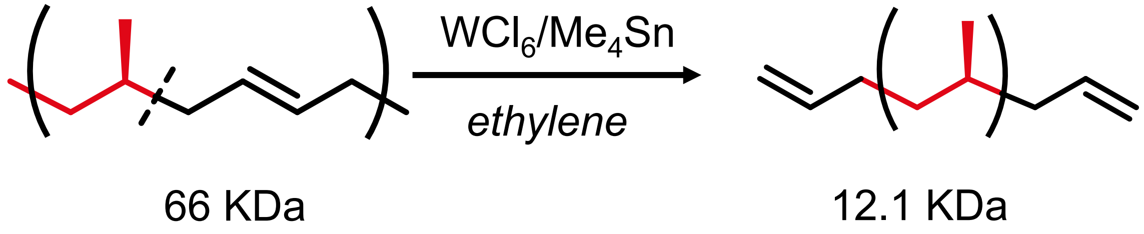


Sawaguchi and coworkers
Macromolecules **1995**, *28,* 7973–7978.

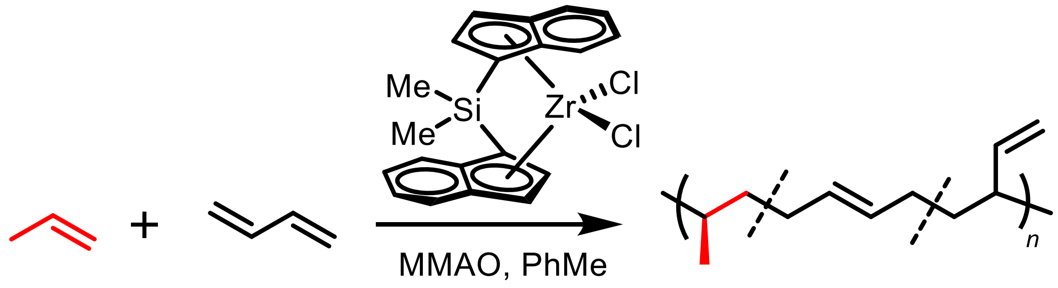




Shiono and coworkers
Macromolecules **2003**, *36*, 9675–9677.

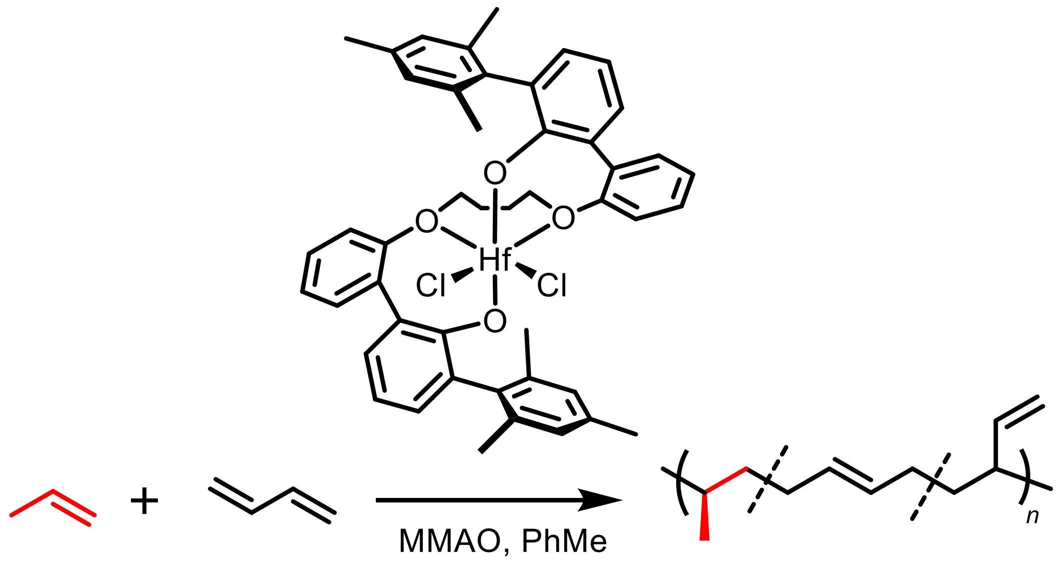


Synthesis of Unsaturated iPP



Shiono and coworkers
Macromolecules **2003**, *36*, 9675–9677.

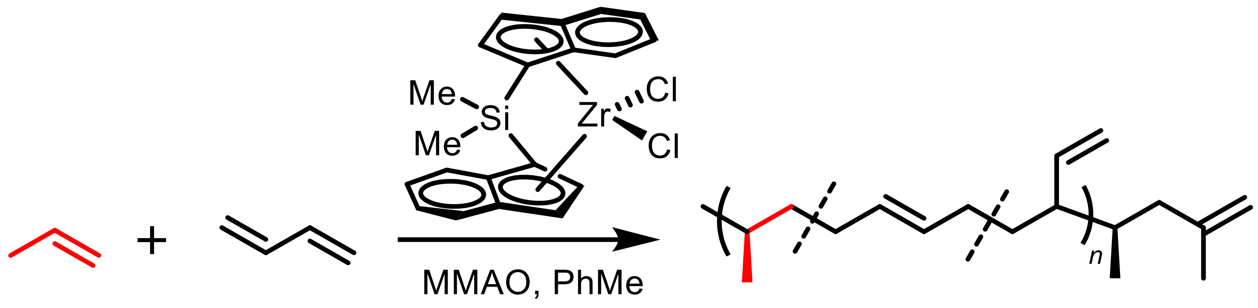
- Butadiene slows polymerization
- Yields < 2.5g
- T_m = 97 °C — 150 °C
- %1,4 = 0.23% — 5.38%



Coates and coworkers
J. Am. Chem. Soc. **2022**, *144*, 12613−12618.

- Cyclization of dienes
- T_m < 100 °C
- %1,4 = 0.26% — 1.18%

Scalable Unsaturated iPP Synthesis

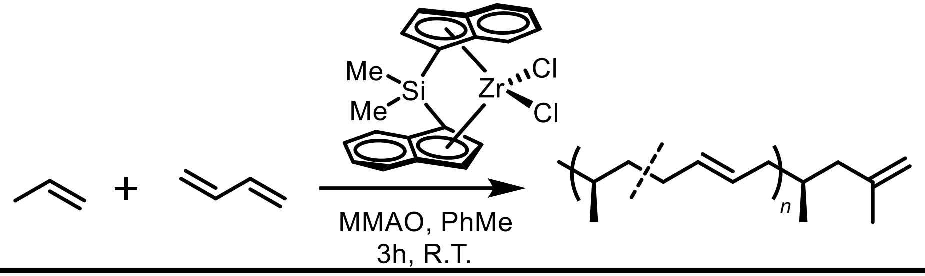


Entry (#)	Cat. conc. (μmol)	Initial C_3H_6 (mmol)	Final C_3H_6 (mmol)	Initial BD (mmol)	Aluminoxane (mmol)	T_{rxn} (°C)	Time (h)	Yield (g)	M_n (kg/mol	#1,2 BD (per chain)	#1,4 BD (per chain)	T_m (°C)
1	10	118.8	286.6	38.3	MMAO(1000)	25	6	2.28	26.4	1.63	6.07	139.3
2	20	118.8	413.0	74.0	MMAO(1000)	25	3	1.95	35.2	4.99	13.15	128.0
3	20	393.8	539.5	79.3	PMAO(4000)	25	3	6.13	31.3	3.10	10.83	130.9
4	20	558.4	665.3	74.5	PMAO(4000)	0	3	4.50	49.7	2.06	4.68	148.2

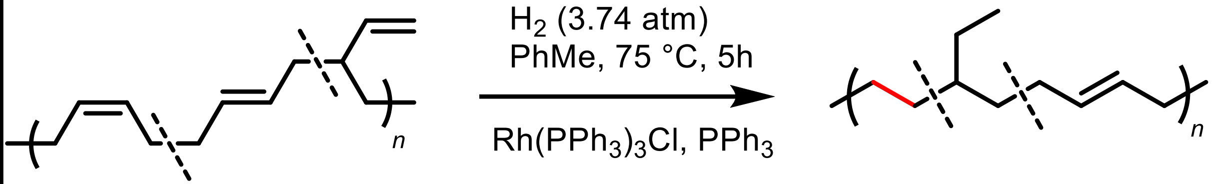
Nouryon's PMAO-IP improves the productivity of propene/1,3-butadiene polymerization using conventional isospecific metallocenes

Scalable Telechelic Polyolefin Synthesis

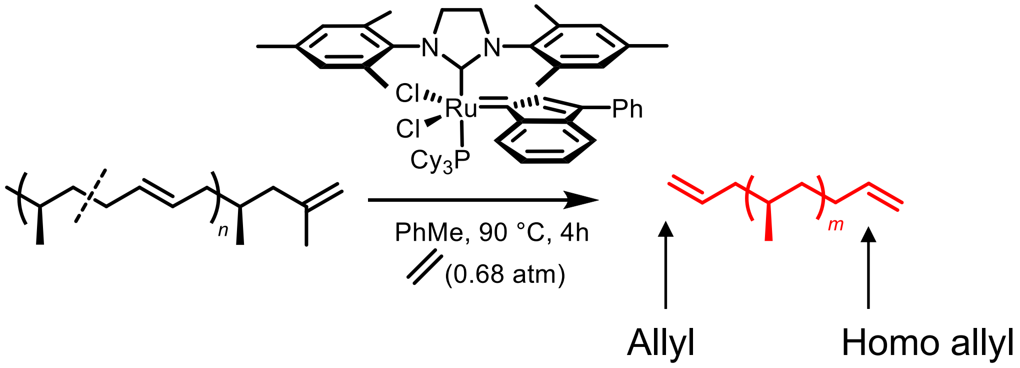
Unsaturated iPP



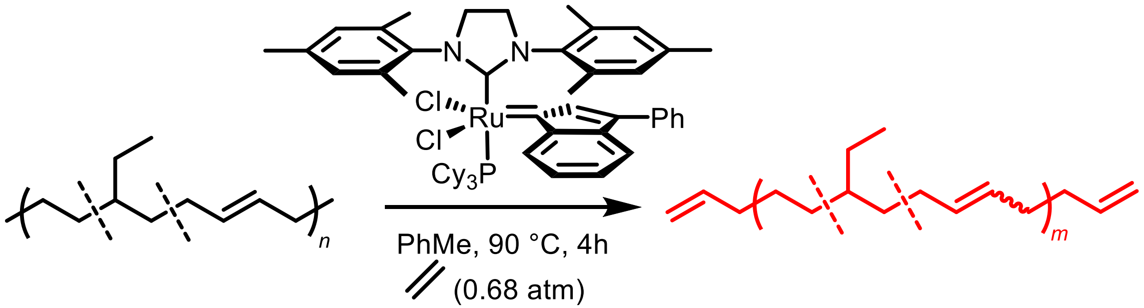
Unsaturated LLDPE



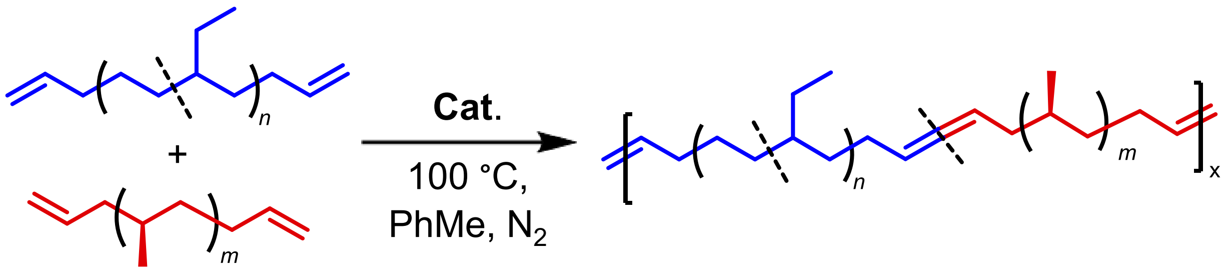
Telechelic allyl iPP



Telechelic allyl LLDPE



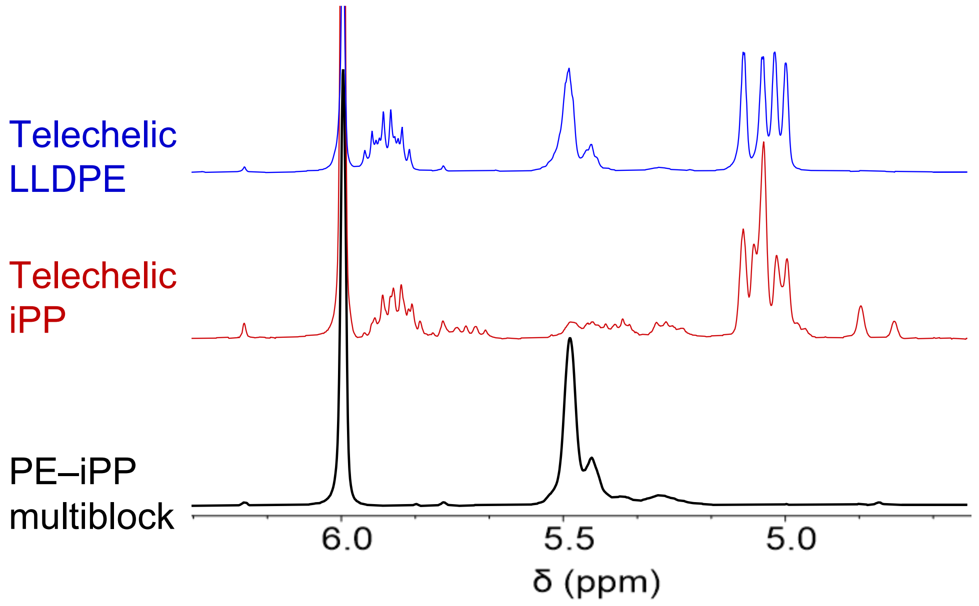
LLDPE-ran-iPP Multiblock Copolymer

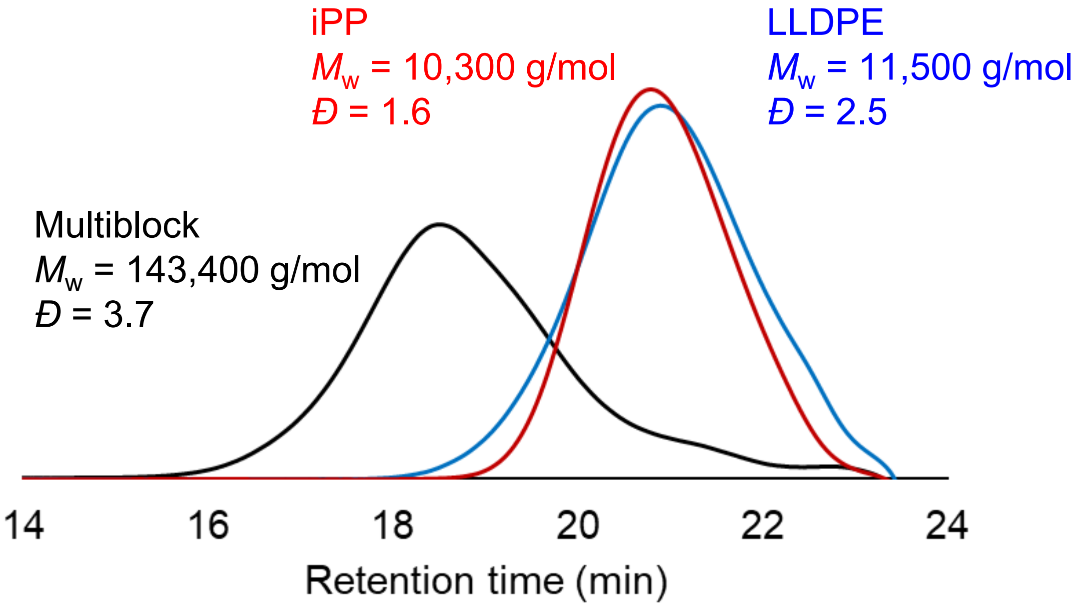


M_W = 143,400 g/mol (GPC)

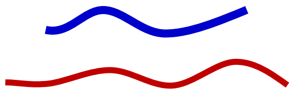
PP:PE = 1:1 (wt ratio)

DP_{avg} = 13

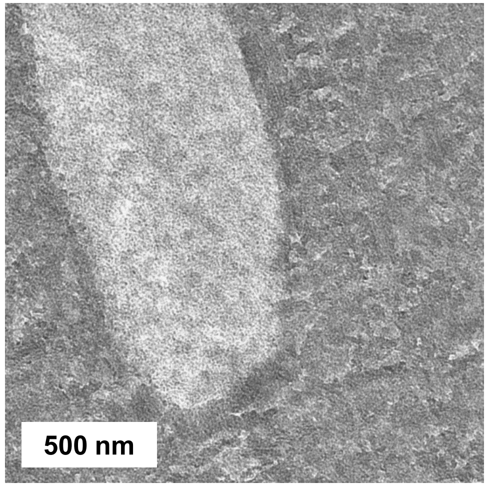




Morphology and Crystallization

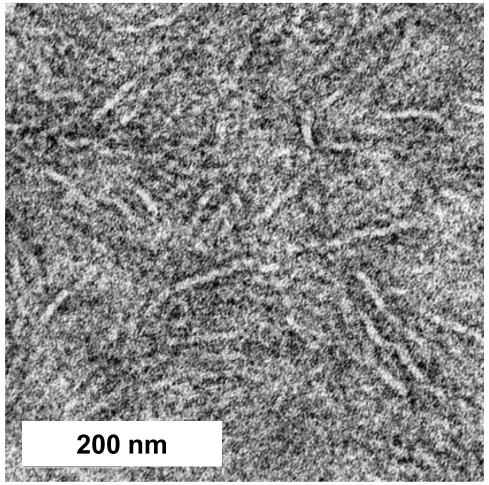


Commercial LLDPE:iPP blend



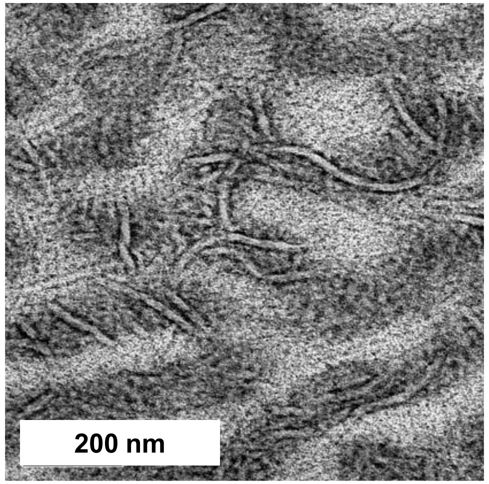
- Macro phase separation
- **High crystallinity / modulus**
- Poor mechanical properties

Dow Infuse OBC (multiblocks)



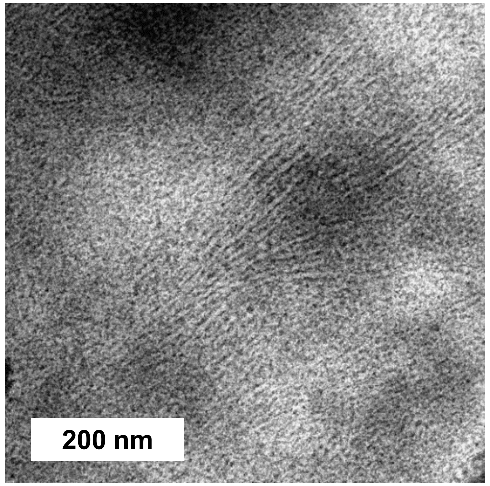
- **Homogeneous phase**
- Low crystallinity / modulus
- Elastomeric properties

Dow INTUNE (PE-PP diblocks)



- Micro phase separation
- **High crystallinity / modulus**
- **Compatibilizer**

Multiblock (shuffling)



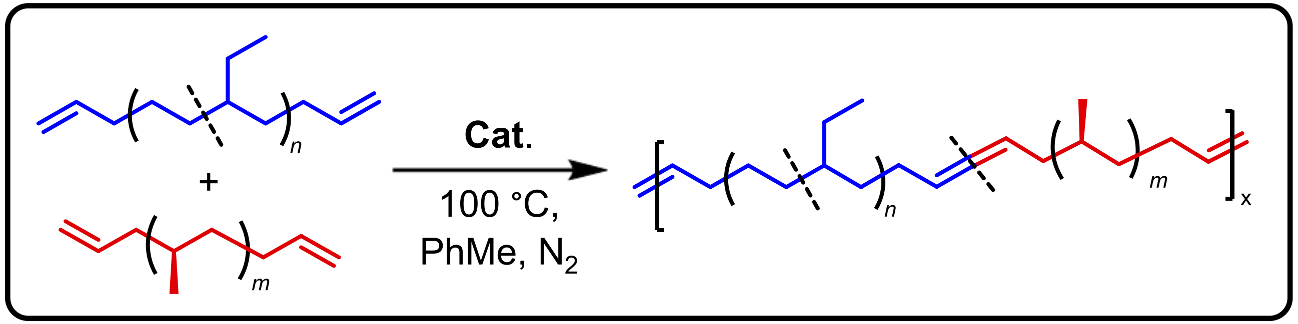
- **Homogeneous phase**
- **High crystallinity / modulus**
- **Compatibilizer**

TEM images of Dow materials from:
Munro, J.; Hu, Y.; Laakso, R.; Madenjian, L.; Vervoort, S.; Werner, S.; Marchand, G.
Polypropylene-Rich Blends with Ethylene/α-Olefin Copolymers Compatibilized with INTUNE™ Propylene-Olefin Block Copolymers.

Infuse chemistry: Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T., *Science* **2006**, *312*, 714–719.

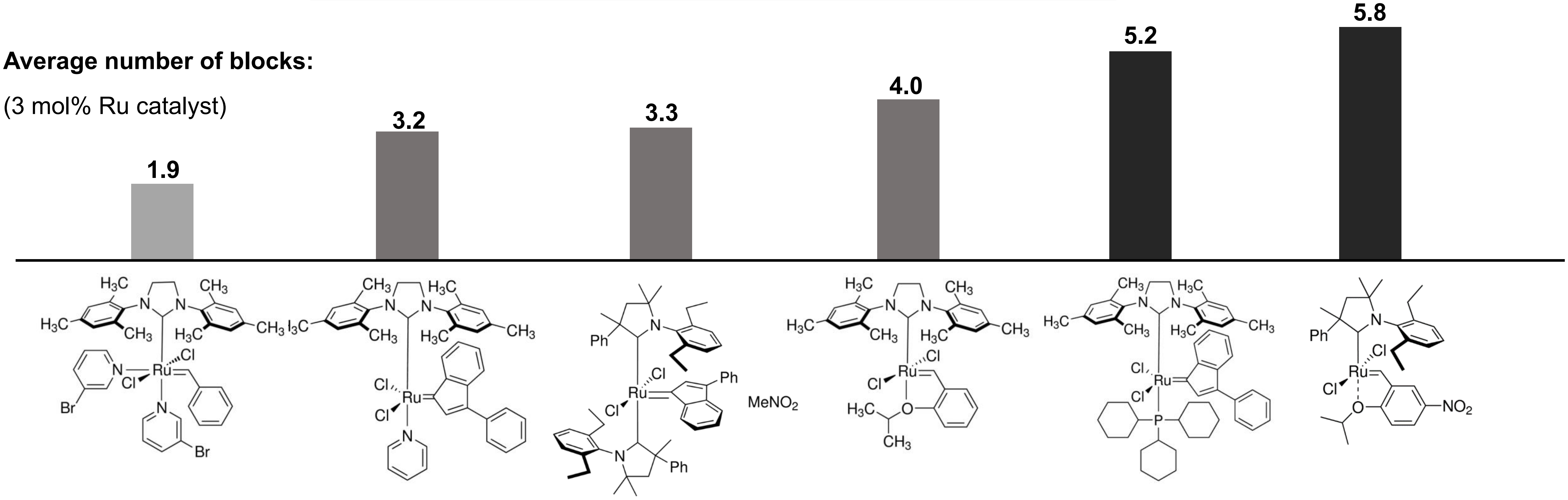
TEM results from Prof. Shin Horiuchi

Shuffling Catalyst Selection



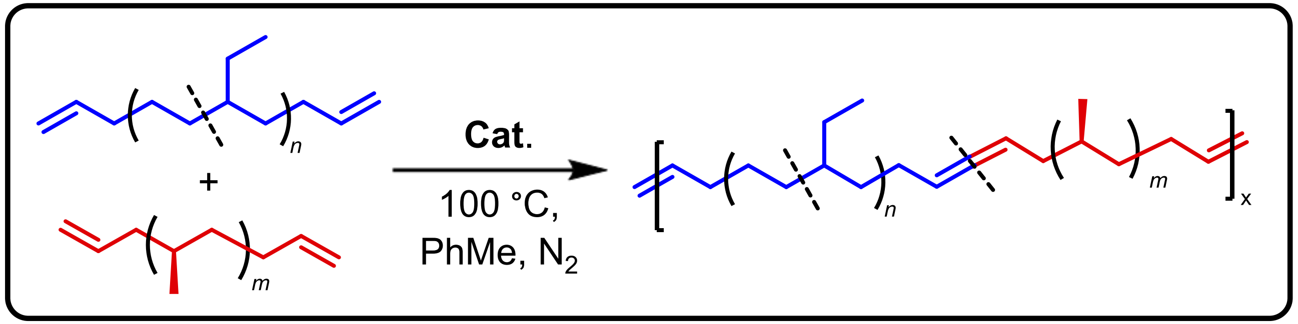
Average number of blocks:

(3 mol% Ru catalyst)



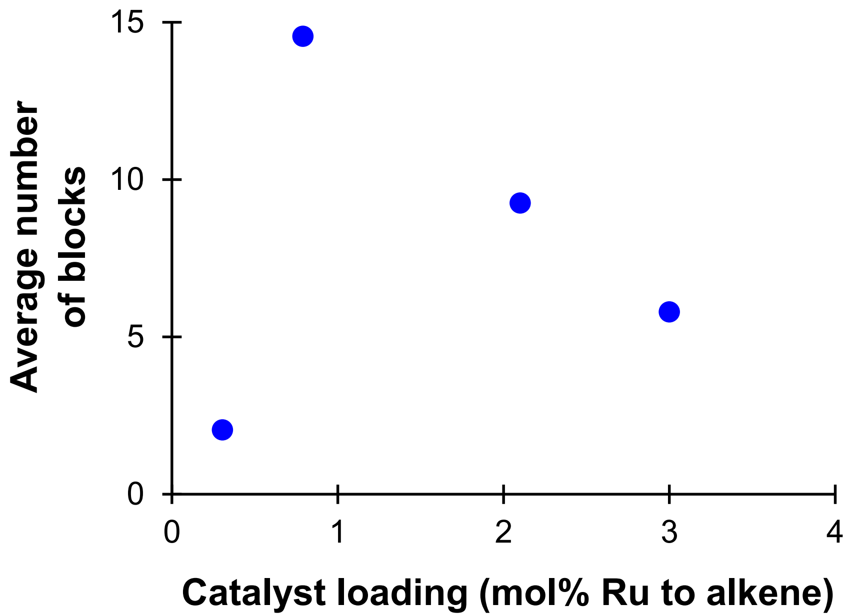
For metathesis catalyst design and stability to ethylene/temperature see: Fogg and coworkers. *J. Am. Chem. Soc.* **2019**, *141*, 10626–10631.

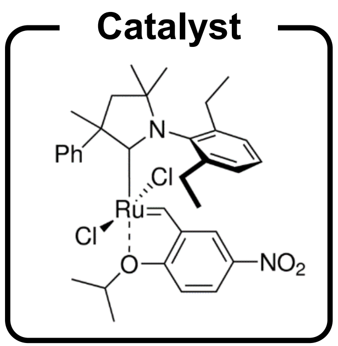
Shuffling Catalyst Selection



Key Catalyst Findings:

- Bulky cyclic alkyl amino carbenes improve thermal and ethylene stability
- Monofunctional Ru alkylidene limits molecular weight
- Sufficient catalyst activity is required for reactivity



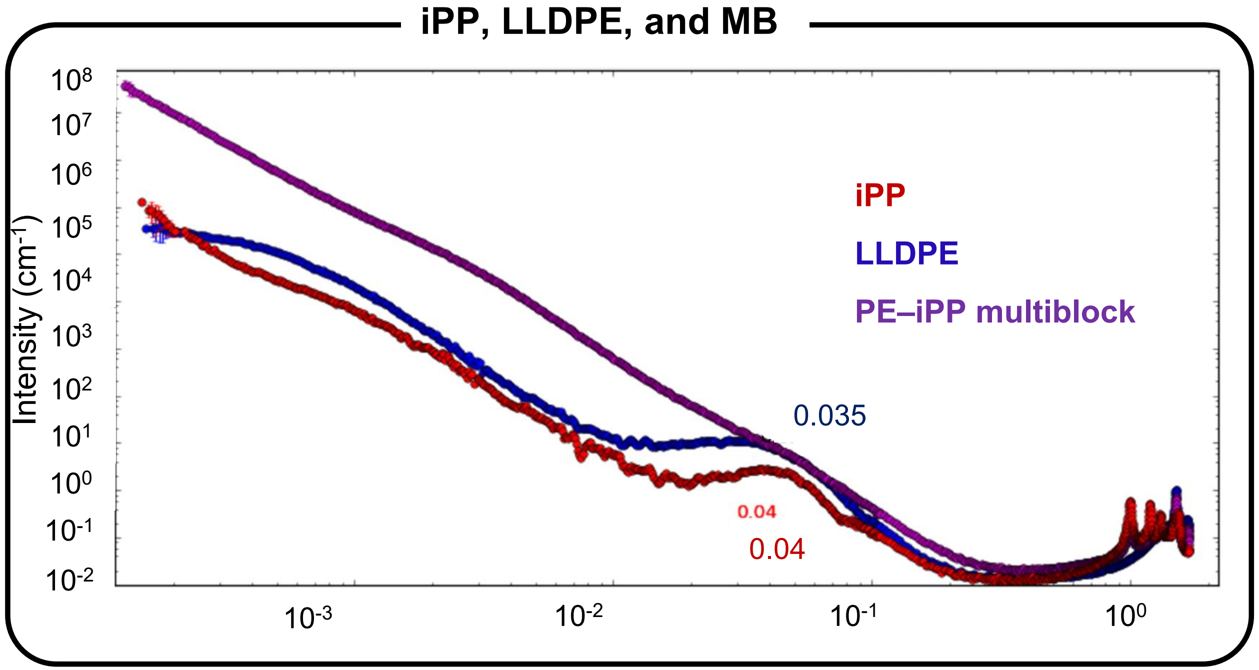


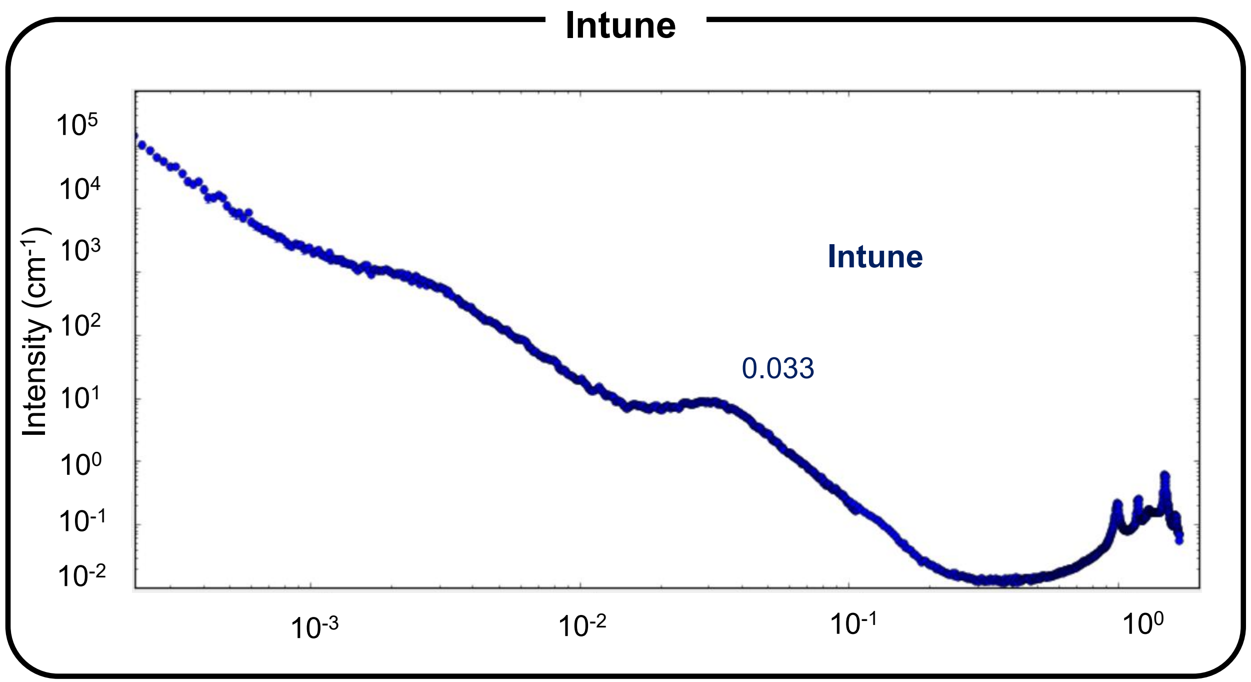
T_1 Relaxation Studies

Sample	T_1 (ms)	
	PP	PE
iPP/PE (Blend)	792	1921
Intune (Diblock)	658	667
iPP–PE (Multiblock) (Sample 1)	765	851

Covalently linked segments exhibit similar relaxation times

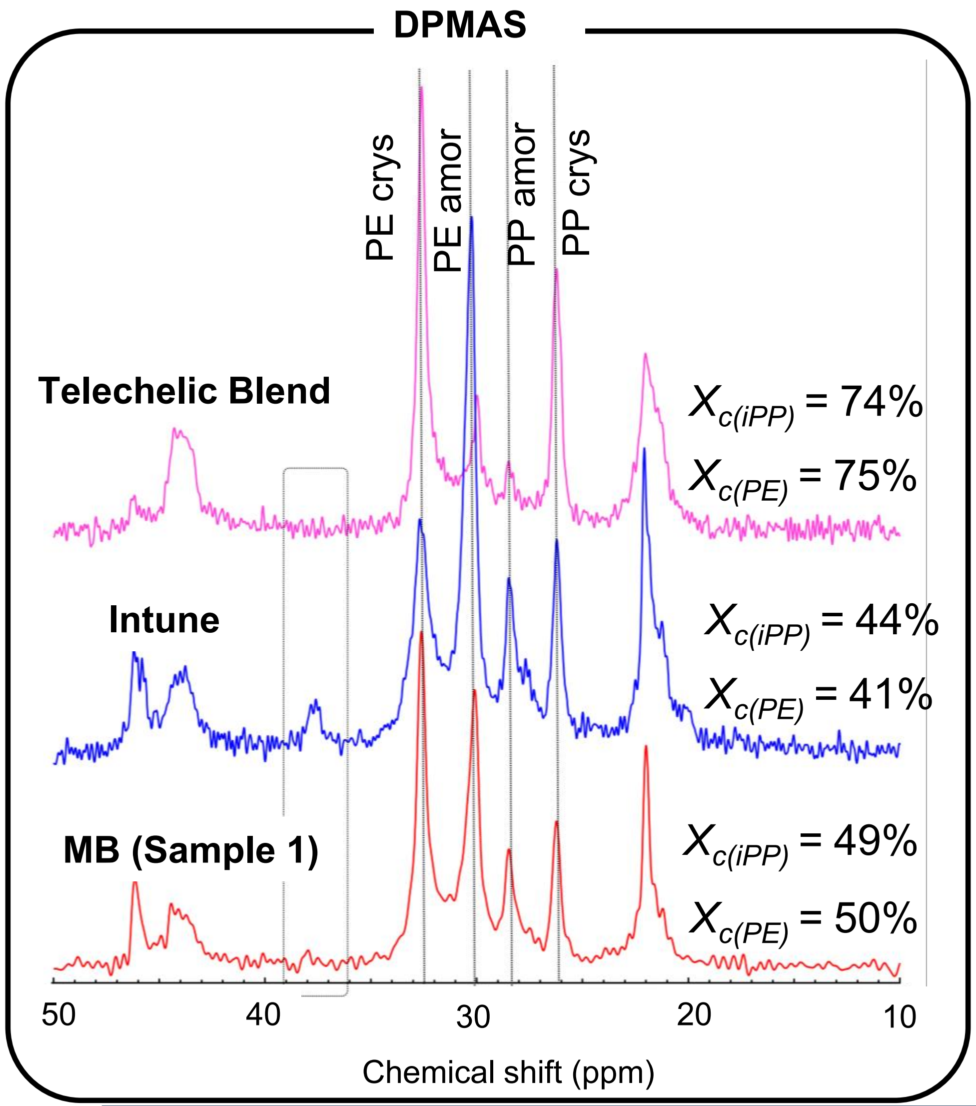
SAXS of Multiblock Product

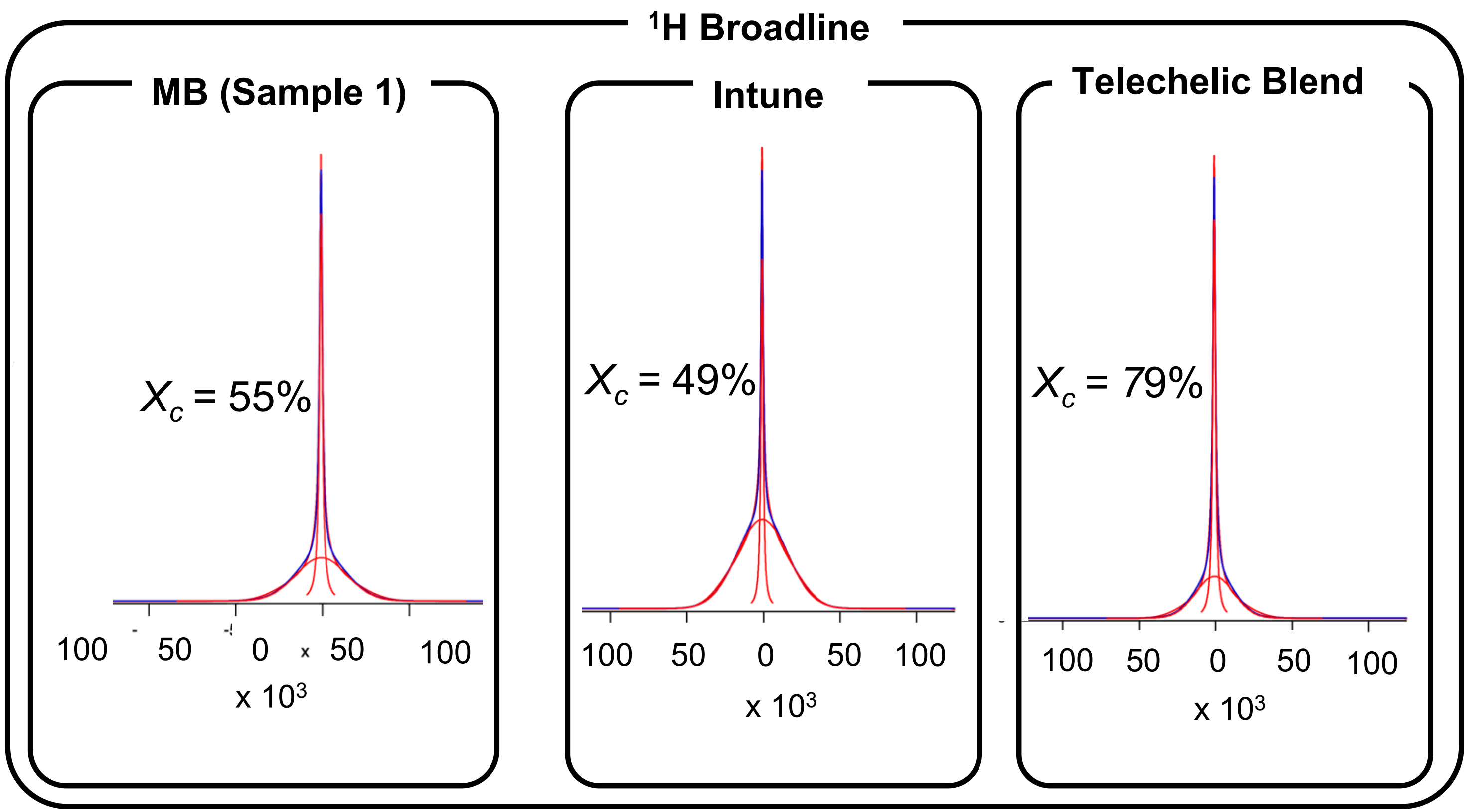




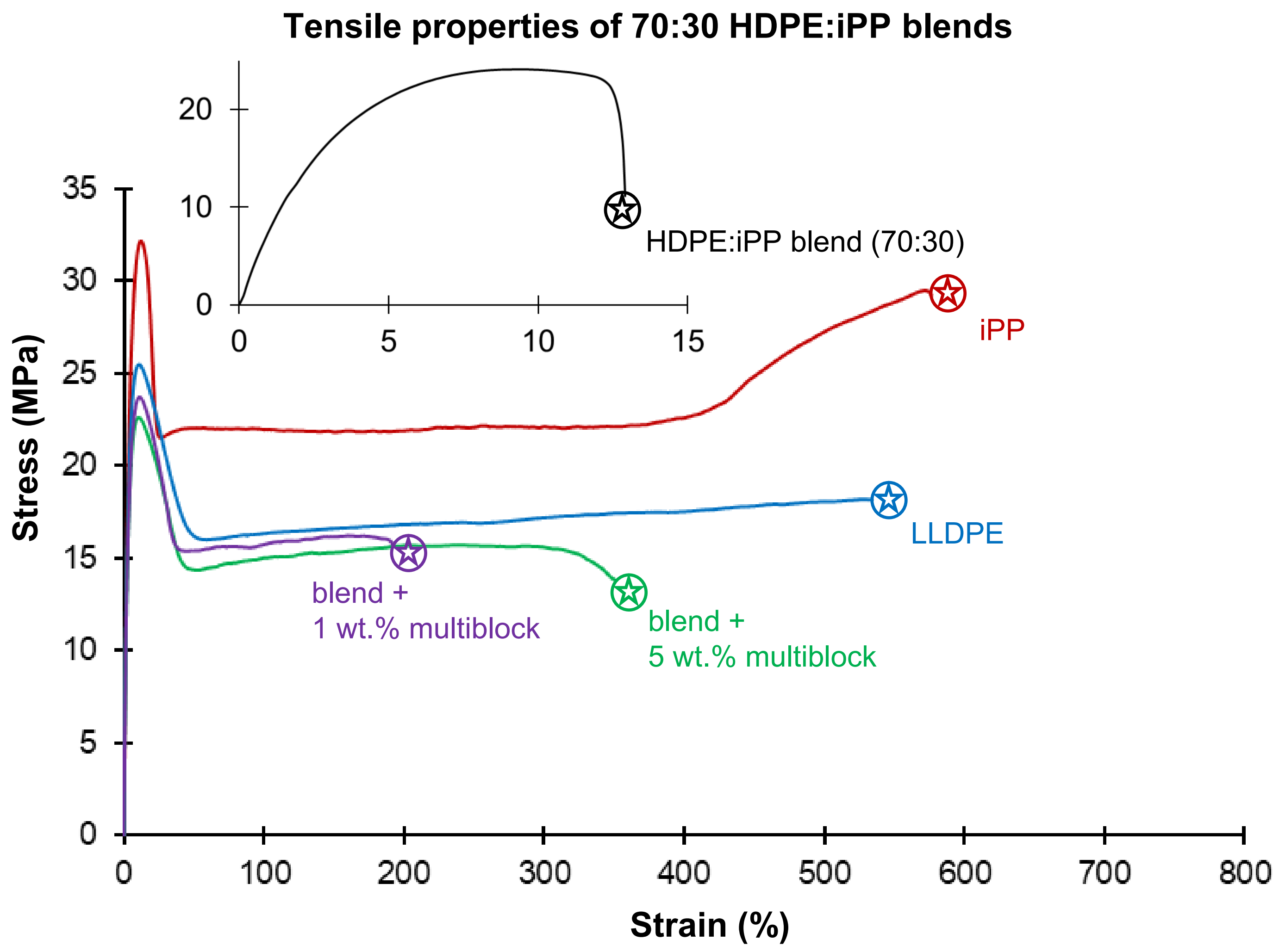
- Scattering invariant increases for the multiblock sample.
- Greater number of domains leads to more interfaces, which leads to more scattering intensity

Crystallinity Studies of Multiblock Product

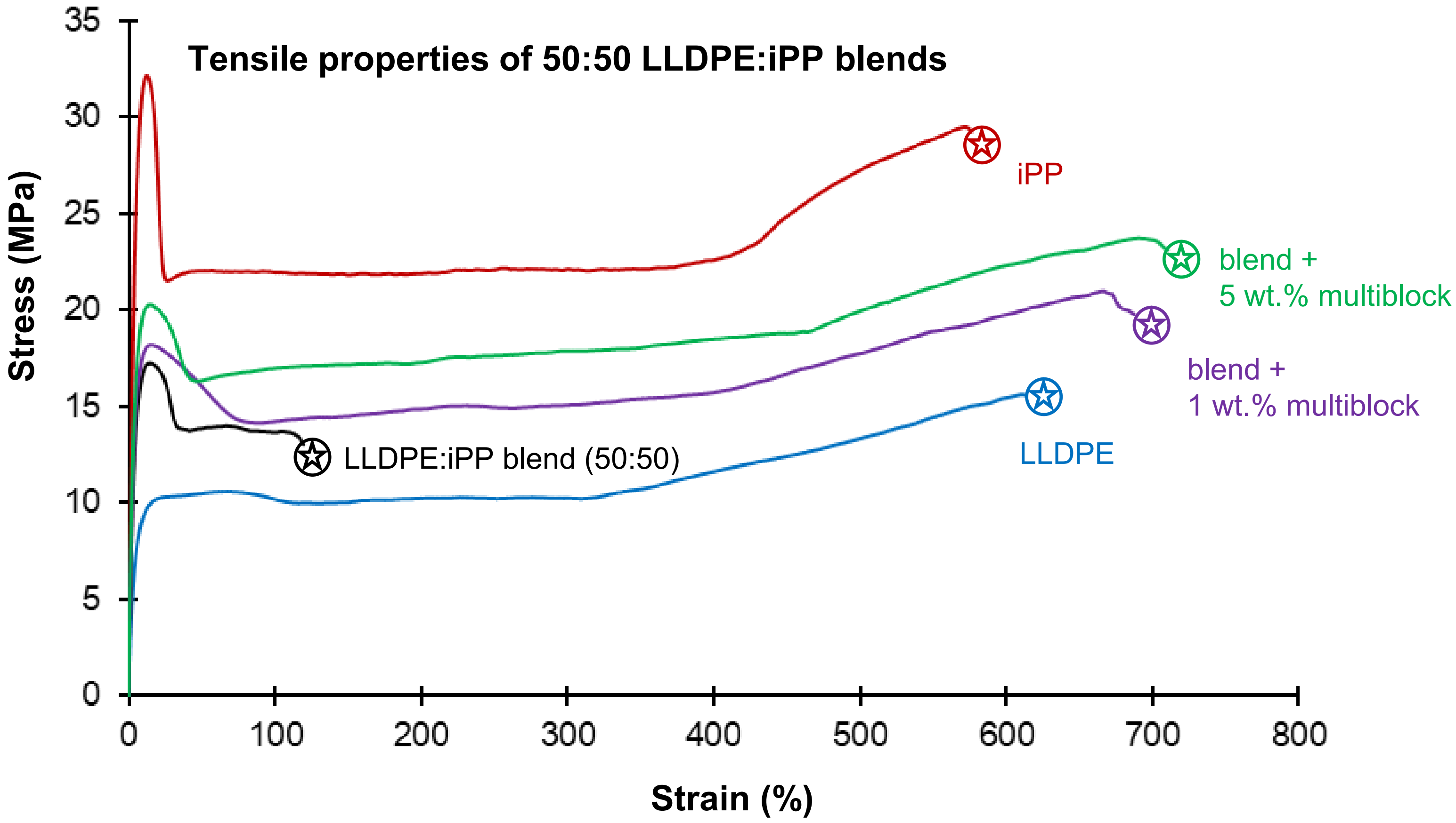




Compatibilization Efficiency



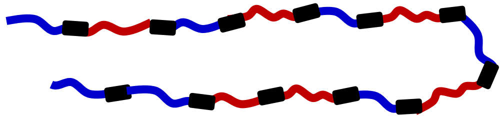
Compatibilization Efficiency



Molecular Weight Effects of MBCP

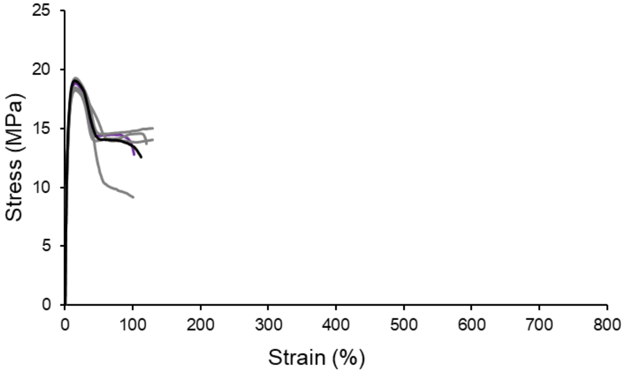
Multiblock DP = 4

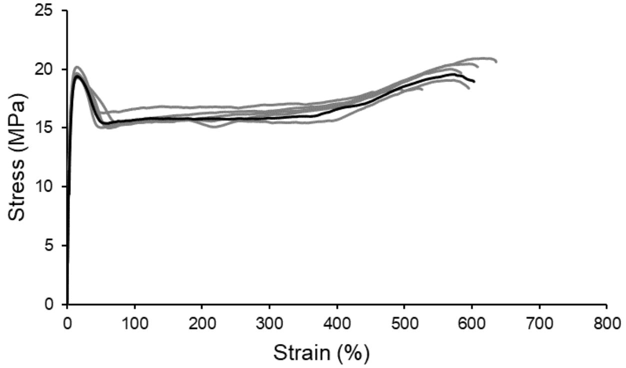
Multiblock DP = 8

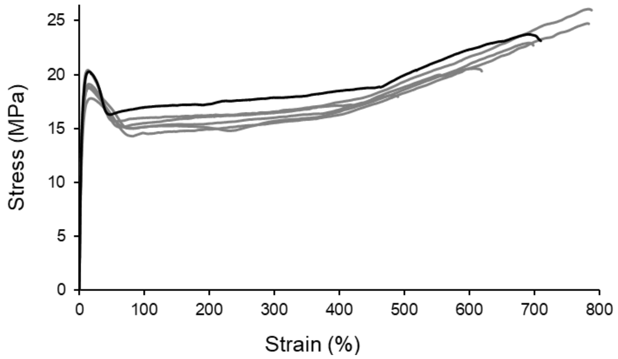


Multiblock DP = 13

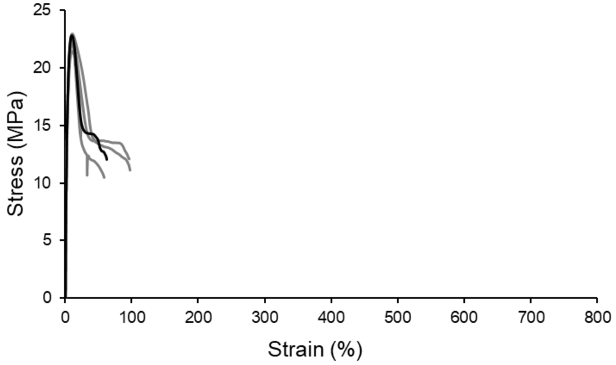
50:50 LLDPE:iPP blends
+ 5% compatibilizer

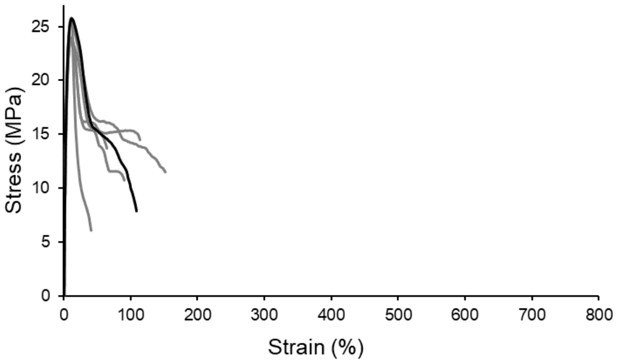


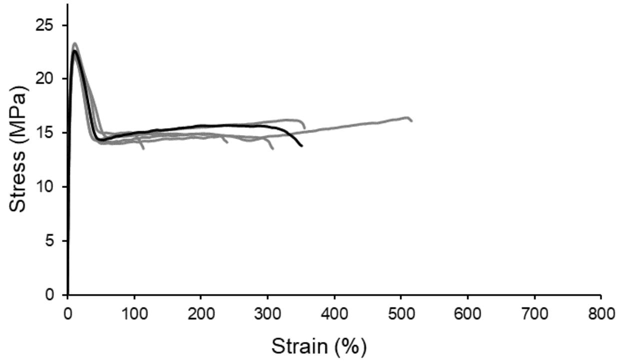




70:30 HDPE:iPP blends
+ 5% compatibilizer

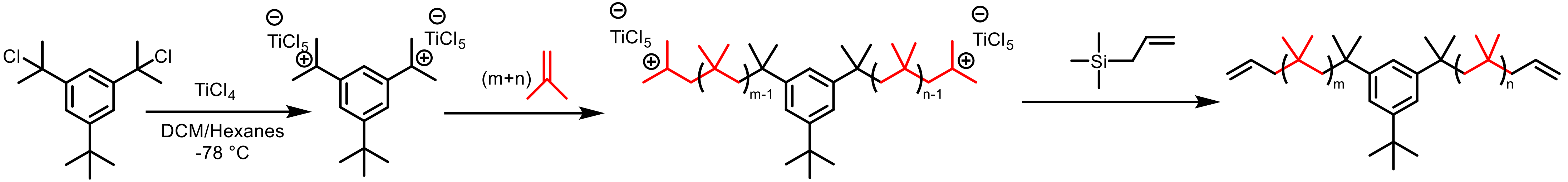




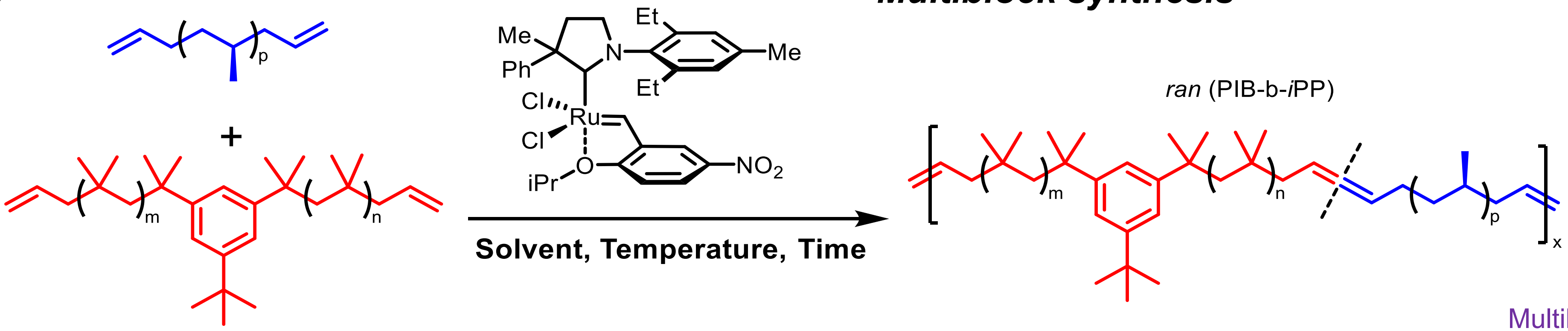


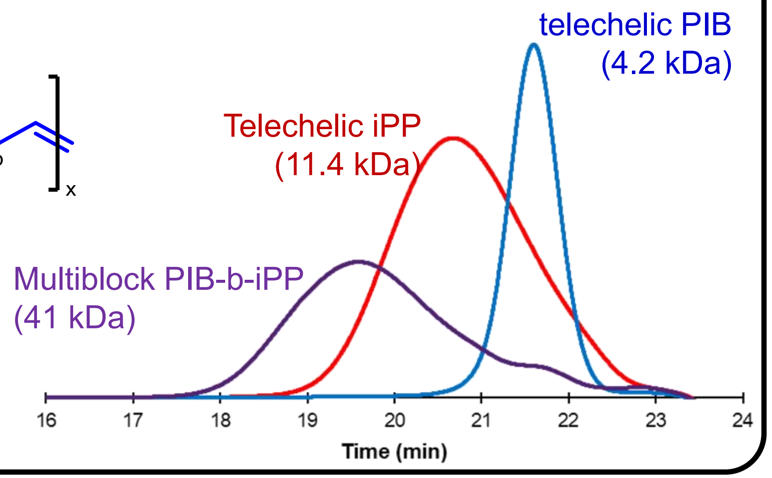
Future Work (In Progress)

Tel PIB synthesis



Multiblock synthesis





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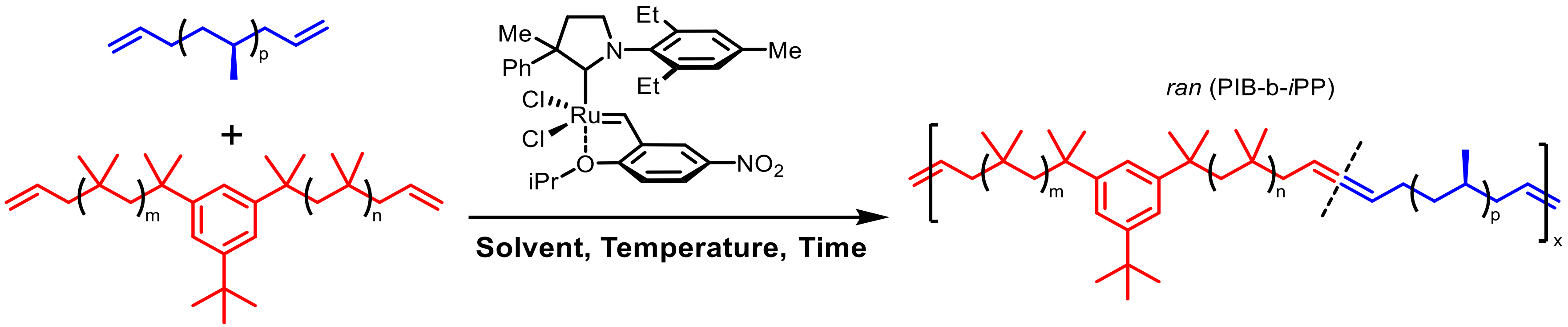
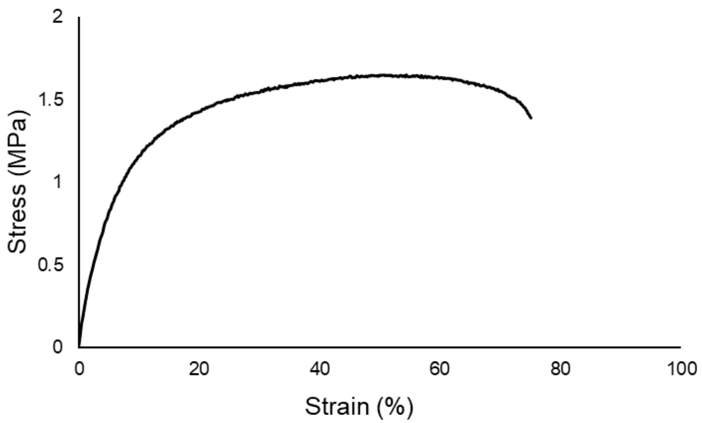
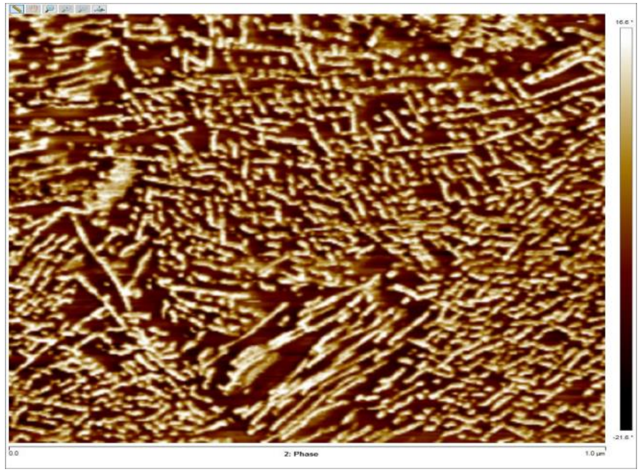


Yuliana Ospina-Yepes

Baseline multiblock properties

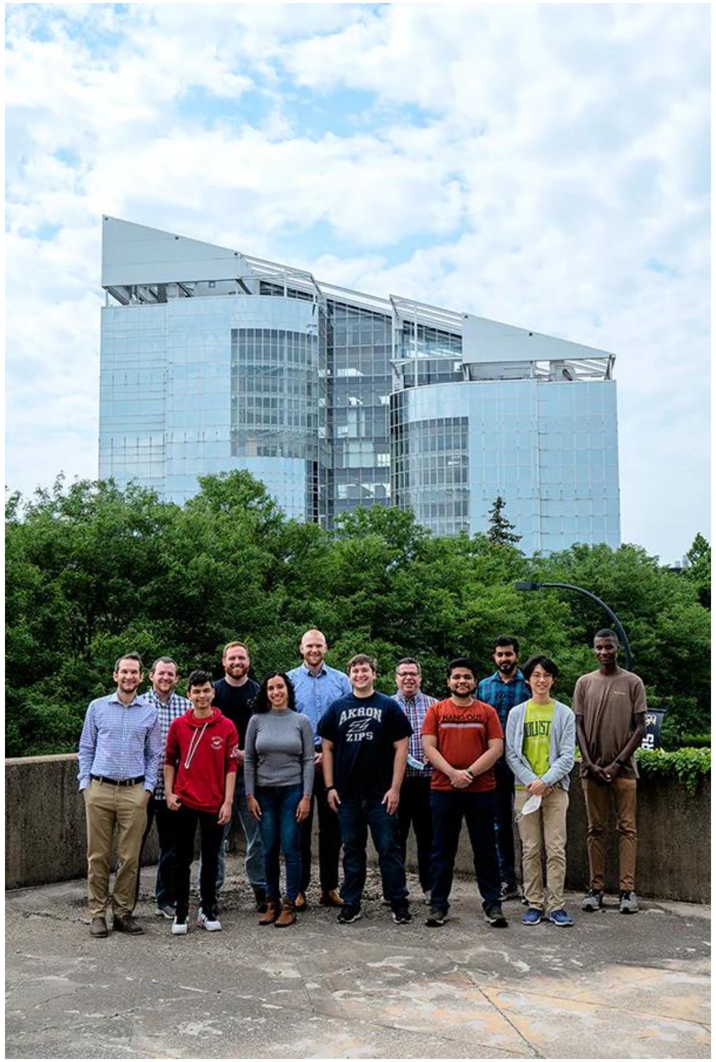




1x1 μm, T= 115 °C, t= 24 Hrs

$T_m \approx 130$ °C
$T_c \approx 100$ °C

Acknowledgements



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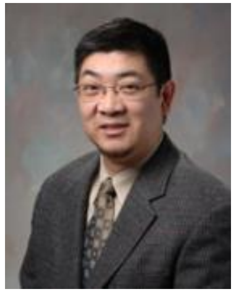

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Dr. Tohi Miyoshi

Argonne NATIONAL LABORATORY

Materials and Samples:

Dow · Braskem · Nouryon