Lubrication Polymers and Where to Find Them

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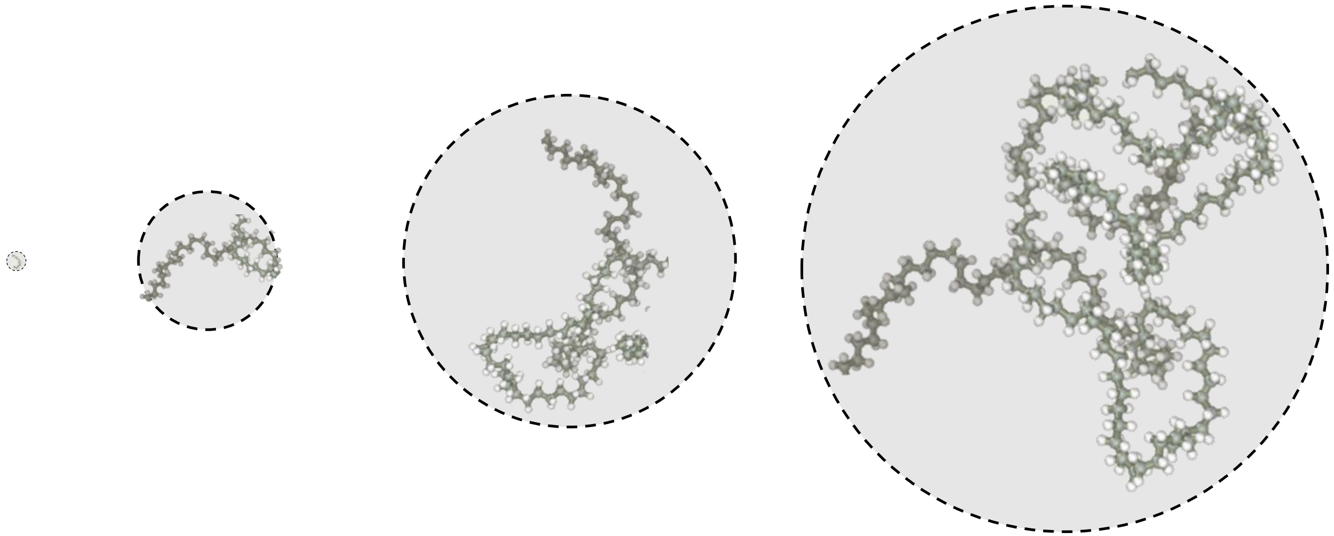
Outline

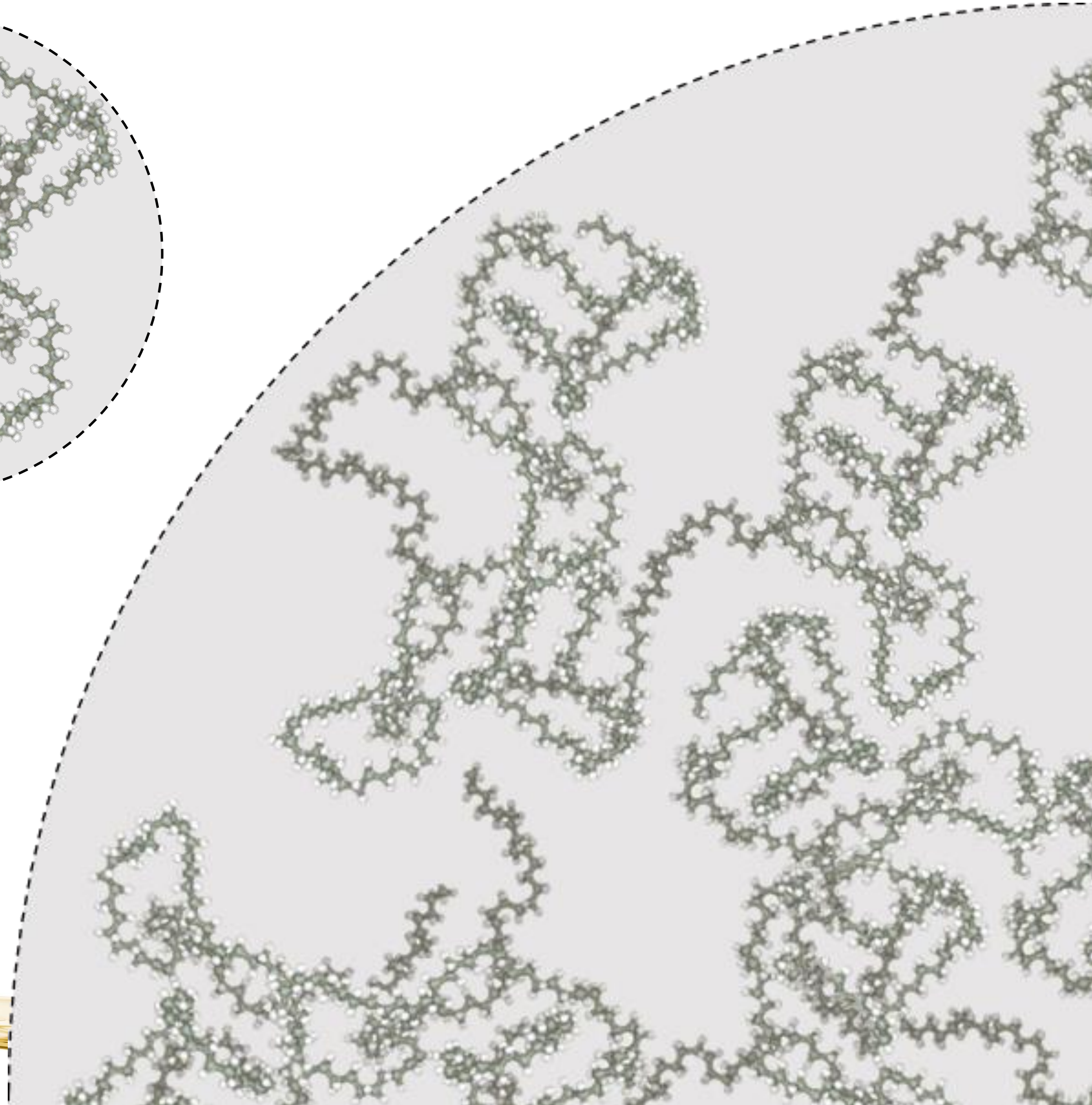
- Polymers, from small to big to enormous
  - Polymer base stocks
  - Olefin copolymers
  - Polymethacrylates
  - Tackifiers

"Structure vs. Properties"

- The key theme of material science
  - Chemical Structure – how the atoms are bonded, which atoms
  - Properties – how the material behaves by itself or when blended
  - Performance – effects of several properties in combination that humans measure and care about
- We'll look at where polymers are found in lubes and greases and how their structure and properties make them suitable for that use

Sense of Scale



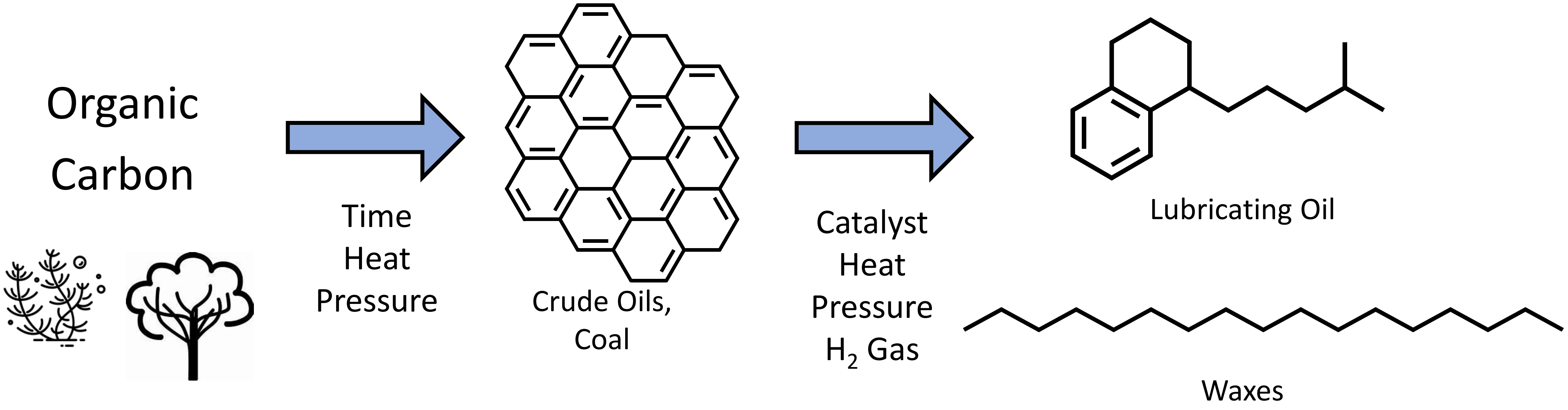


Material	MW	# of Carbons
Petroleum Oil	200 - 700	10 - 50
Polymer Base Oils	1K – 20K	150 – 3K
Polymethacrylates	20K – 100K	3K – 15K
Olefin Copolymers	100K – 200K	15K – 30K
Tackifiers	500K – 6M	71K – 858K

Scaled by molecular radius, approx. $(\text{\# carbon})^{0.5}$

Petroleum Oil (for reference)

- 85% of industrial lubricants
- 67% of automotive lubricants (significant shift to III/VI)
- 87% of grease



Viscosity

- Petroleum oils have some size and typically some wax or polar attraction creating resistance to flow – viscosity
- Lubricants demand certain viscosities to maintain fluid film thickness
  - Stribeck curve
- Target viscosity is met by thickening an oil

Blending

- To meet a certain target viscosity you have two options:

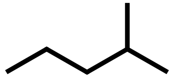
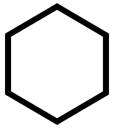
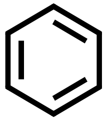
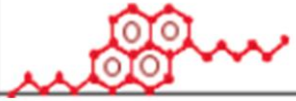
1. Use a straight cut – 300N Group II to make an ISO 68 way oil

2. 'Dumb bell blend' – mix a lighter oil and a heavier thickener

    - 150N Group II + Bright Stock to make an ISO 68

        - The lighter the oil or heavier the thickener makes a better product for low temp fluidity but more volatile

Petroleum Composition

	Molecule	Structure	VI	Pour point	Oxidation	Solubility	Toxicity
	*n*-paraffin		Excellent	Poor	Excellent	Poor	Low
	Single-ring naphthenic		Good	Good	Good	Good	Low
	Polycyclic aromatic		Poor	Poor	Very poor	Good	Very high

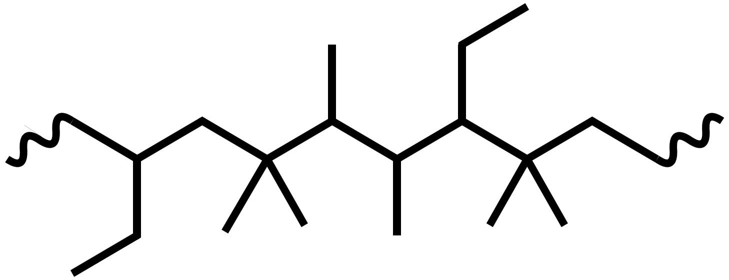
- After refining out the ring content we have limited viscosity options (4/6/8)
- Wouldn’t it be nice to get the properties of paraffins (and iso-paraffins) directly? Without all the petroleum refining?

Table edited from “Chapter 2: Lubricant Base Stock Production and Application”, Table 2.5

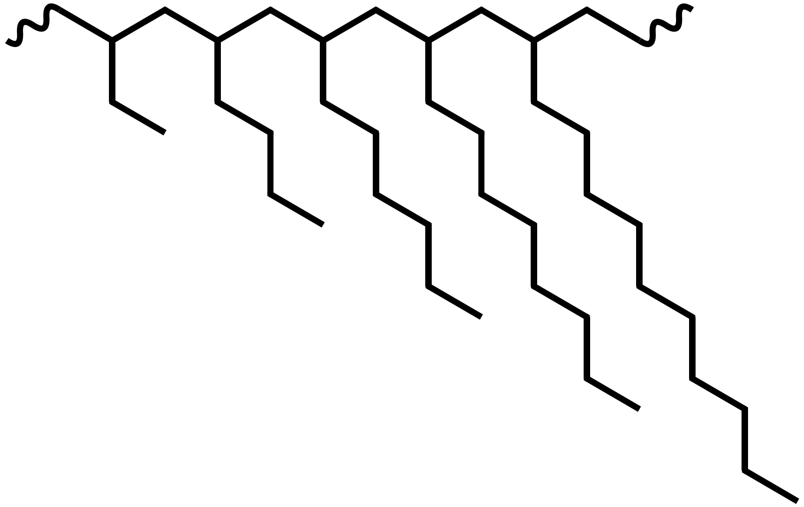
High Viscosity Synthetic Base Stocks

- Polymer liquids with MW from 1K – 20K
- Viscosities typically ISO 1000 to ISO 40,000

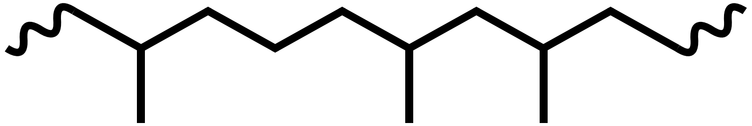
PB



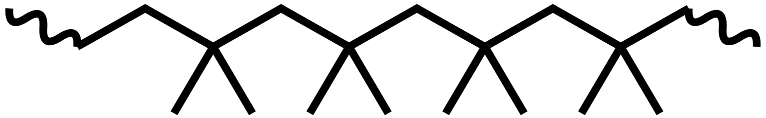
mPAO



EPO



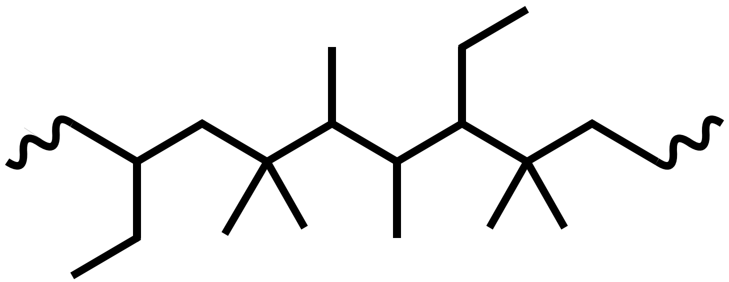
PIB



We'll cover what "metallocene" is later.

PB vs. mPAO

- Short branch vs. long branch

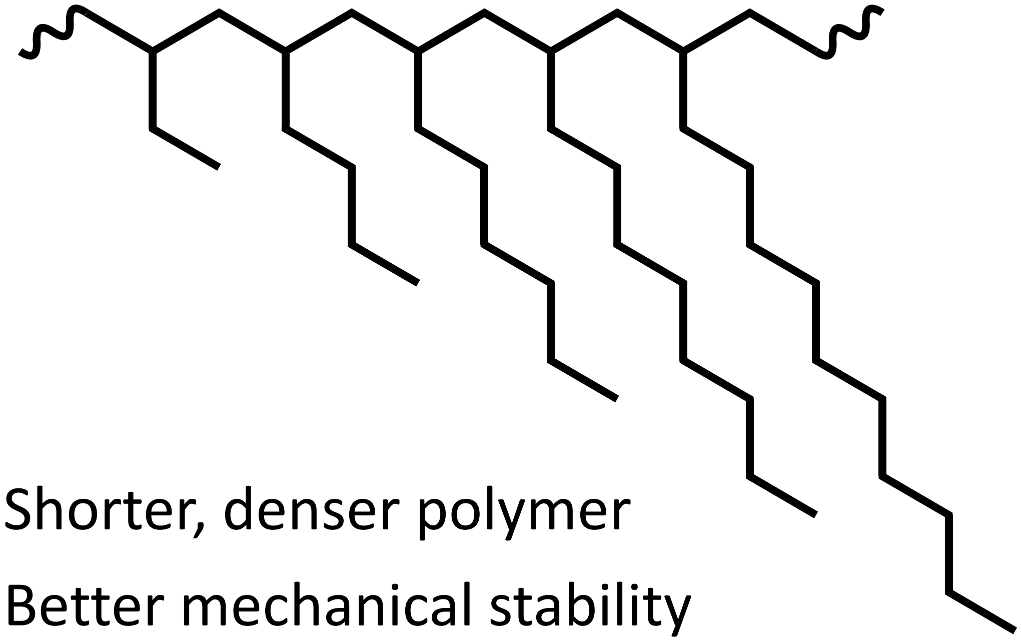


Longer polymer (for same MW)

Higher thickening efficiency

Lower treat

But… a lot of long polymer can affect low temperature flow



Shorter, denser polymer

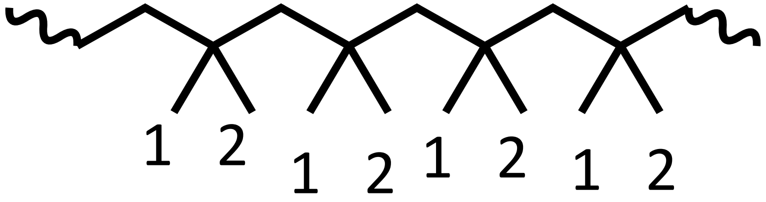
Better mechanical stability

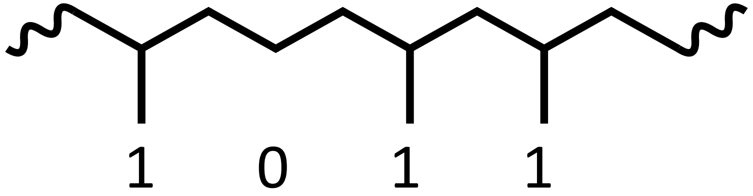
Flows better at low temperature

But… higher treat and worse solubility

PIB vs. EPO

- 2 methyl groups per carbon (PIB) vs. 0-1 methyl groups (EPO)





Lots of methyl groups nearby compete for space

Stresses the backbone, thermally falls apart

But… difficult for oxygen to get close and attack

Low varnish, burns clean, color fast

Spaced out methyl groups

More thermally stable

Difficult to volatilize (highest f.p.)

But… can form varnish and resins

“Polyisobutylene: A Most Unusual Polymer”, Kunal, Puskas, Sokolov et. al. (2008)

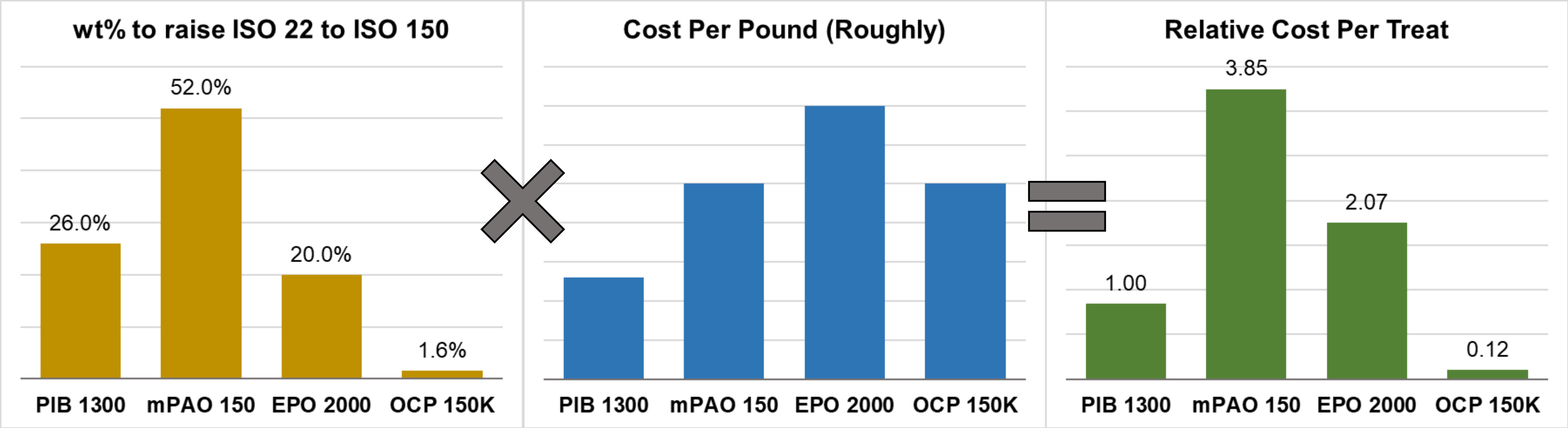
What Advantages from Syn Base Stocks?

- 8 cSt Group III is ISO 46, PAO10 is ISO 68 – how do we make an ISO 460?
- Much better low temperature fluidity than heavy oil cuts
  - Adding the right polymer to a light oil behaves like a light oil at low T
- Increased viscosity index and flatter temp. vs. viscosity profile (multigrade)
- But pricey
  - And possibly overengineered for some uses – what else can be done?

We'll discuss "viscosity index" later.

MW vs. Treat Rate vs. Cost

- If we keep increasing MW beyond a liquid then we need less, spend less
- Compare *relative cost* if we try a 150,000 MW ethylene-propylene polymer



Ethylene-Propylene Polymers

Polyethylene

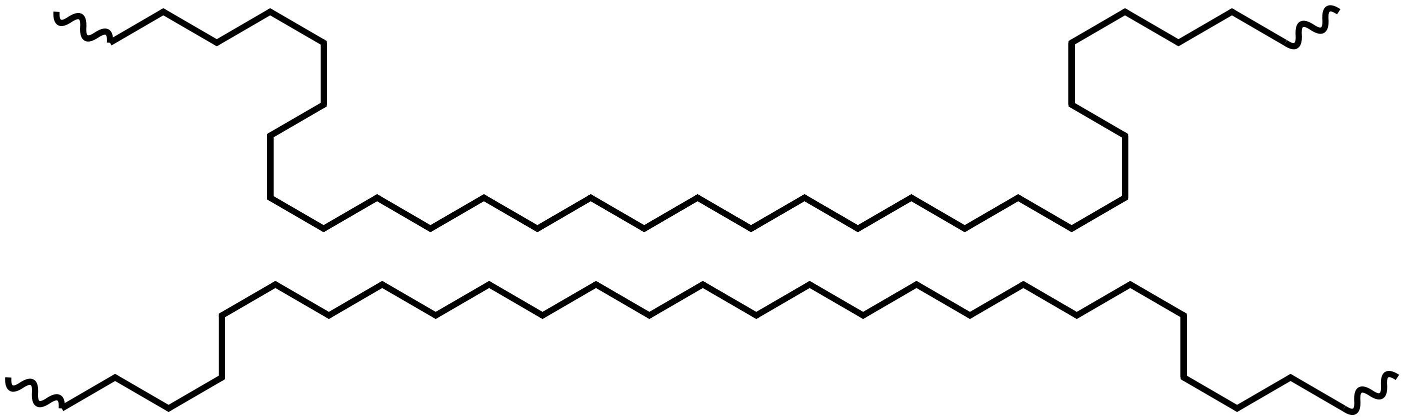
Polypropylene

- How are people making lubricants with this?

Crystallinity from Ethylene

- Long runs of ethylene (wax) form crystals

  - Same for polyethylene

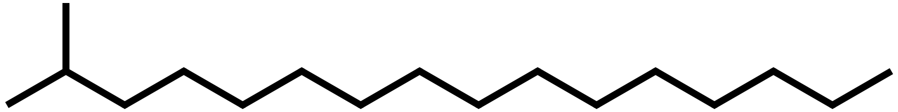


Branching Effect

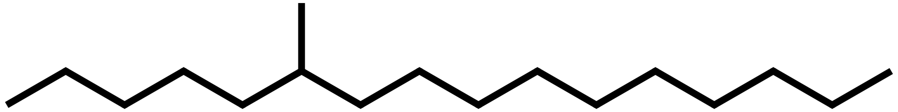
- Much like isomerizing wax in oil…

m.p. 18°C/64°F

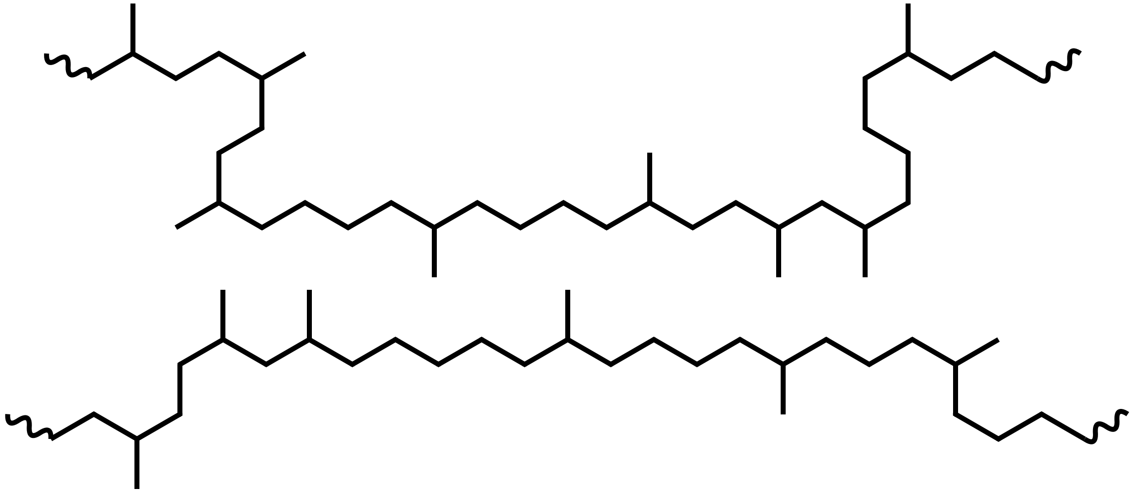
m.p. -10°C/14°F



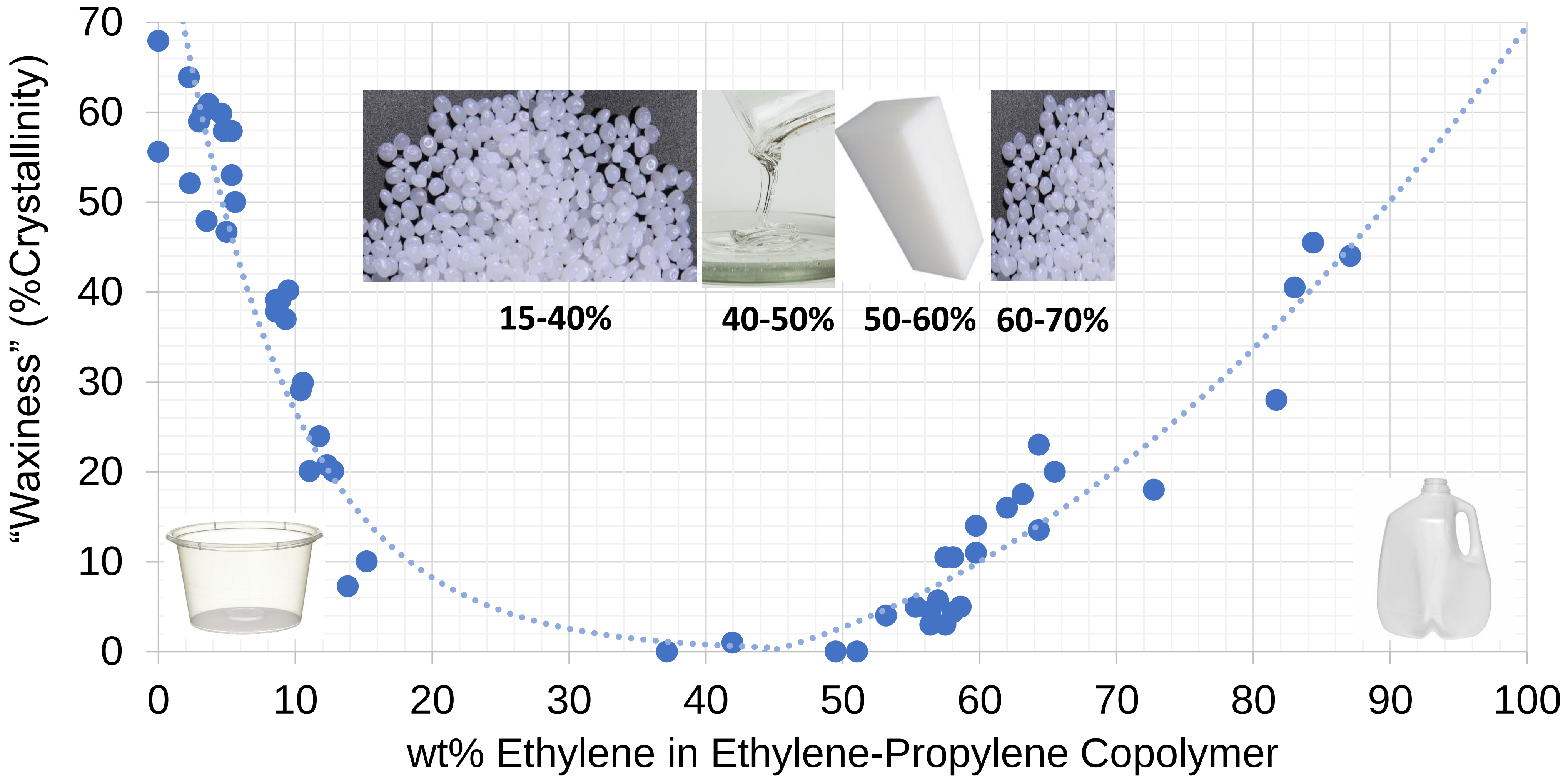
m.p. -32°C/-26°F



- Combining ethylene and propylene into one “co-polymer” removes wax



Propylene-Ethylene Balance



53 datapoints from six academic studies; shown for older E-P polymer production methods

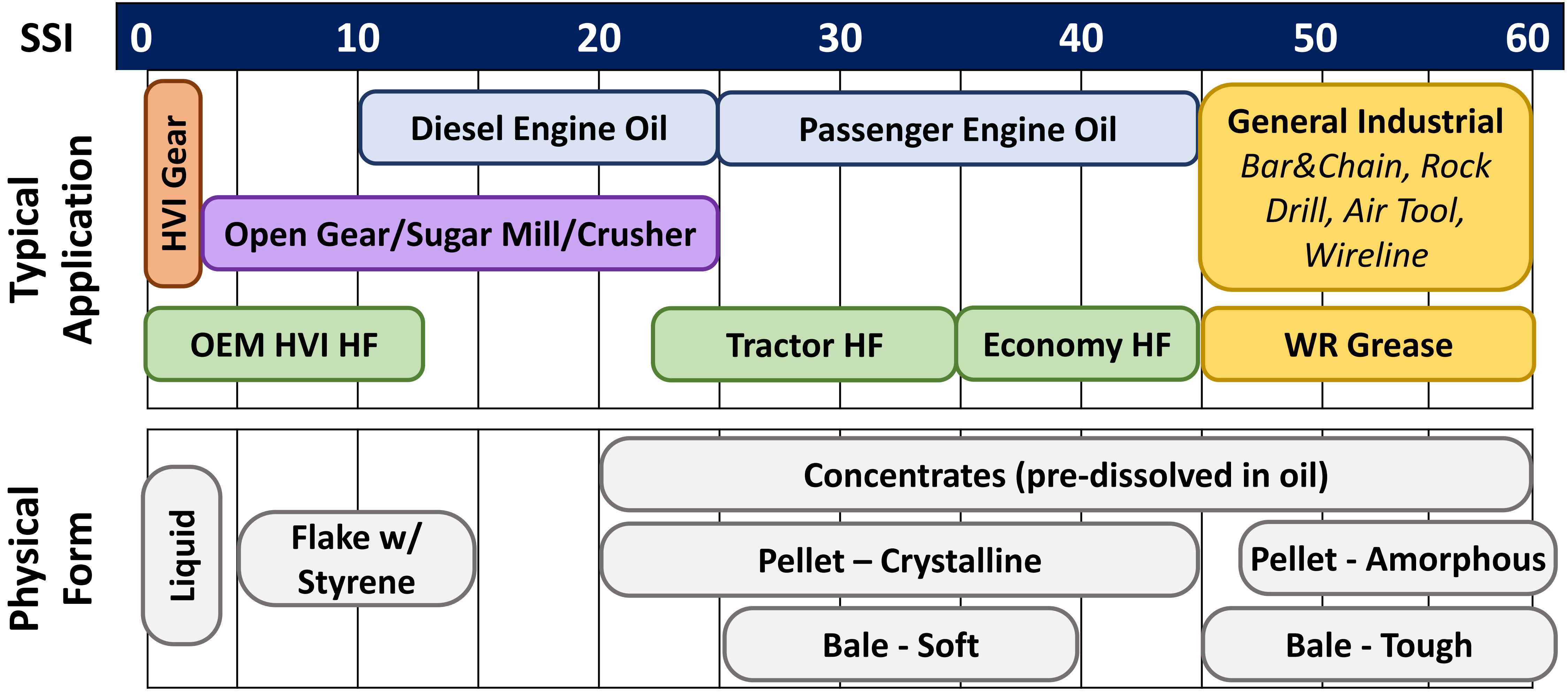
Comparing OCPs

- Fairly commodity – two main things

1. Shear stability index or "SSI" or "P-SSI"
    - Lower is lower MW, more shear-resistant, more premium
    - % viscosity added by the polymer lost in D6278 diesel injector shear

2. Form
    - Bale, pellet, flake
    - Typically a result of %ethylene (how amorphous or crystalline)

Typical SSI of VM by Use (and Typical Form)



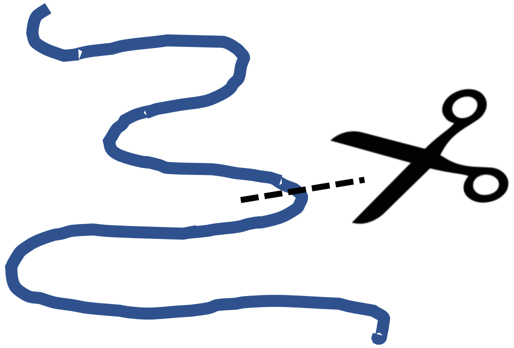
Challenges with OCP

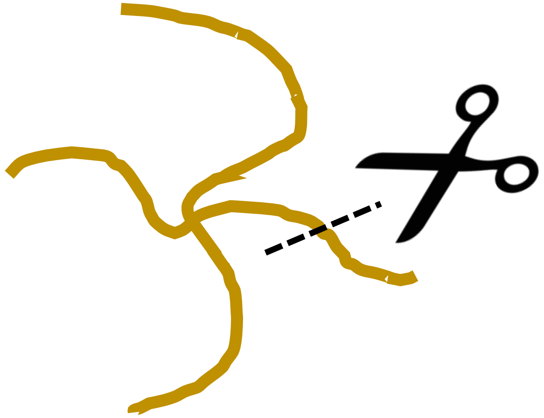
- Physical challenges
  - Medium MW grades are very difficult to process (viscous block)
  - Pellet grades can solve that but high ethylene causes haze and wax
  - Liquid VMs (solid polymer cut in oil) can be dilute

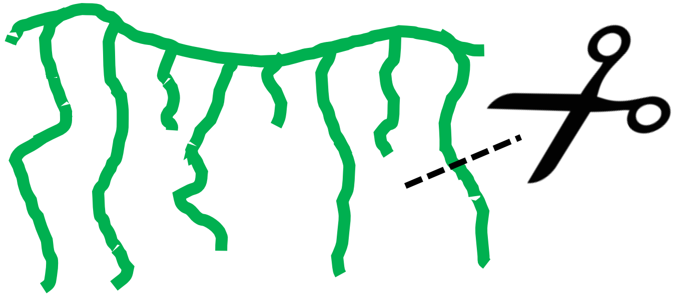
- Technical challenges:
  - Linear structure of the polymer is prone to mechanical damage (shear)
  - Hard to source lower SSI grades for more premium applications

  - *What else is out there?*

A Better Shape for Shear



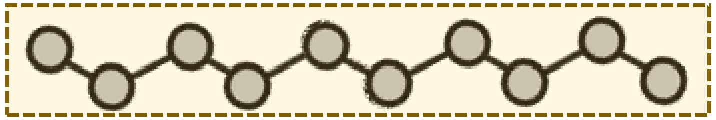




Branching into PMAs

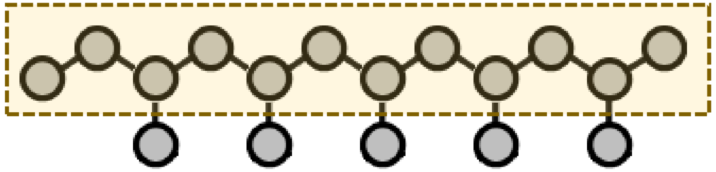
- **Polyethylene**

  100% of carbons on backbone



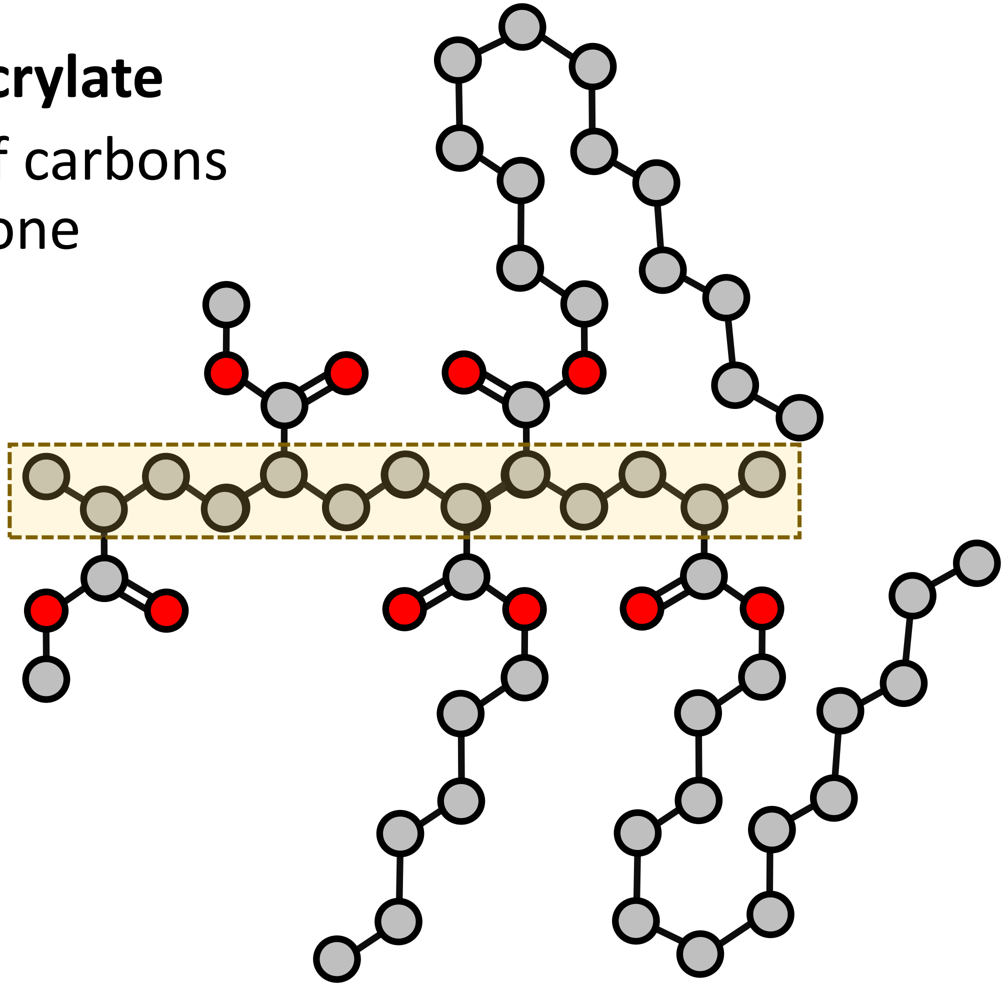
- **Polypropylene**

  67% of carbons on backbone



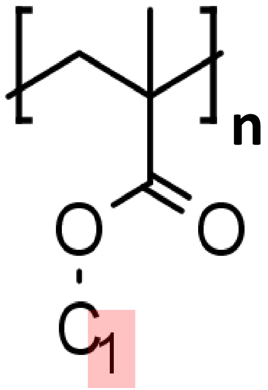
- **Polymethacrylate**

  10-20% of carbons on backbone



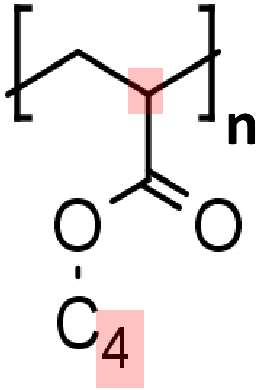
More Diversity Than OCP

Methyl

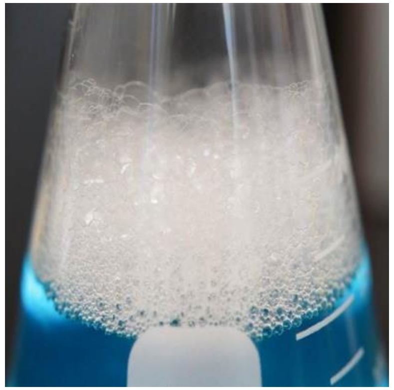


Plexiglass

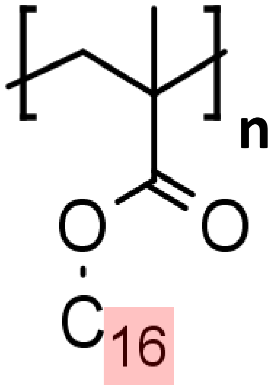
Butyl



Defoamer

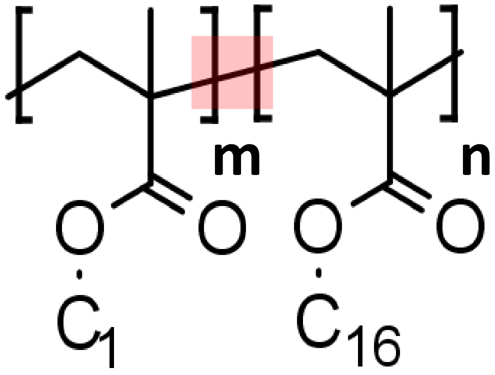


Cetyl



Cold Flow Improver

Methyl + Cetyl

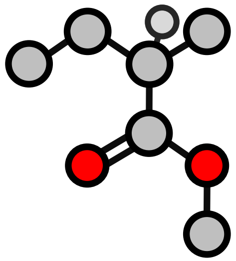


Viscosity Index Improver

Tuning Monomer Selection

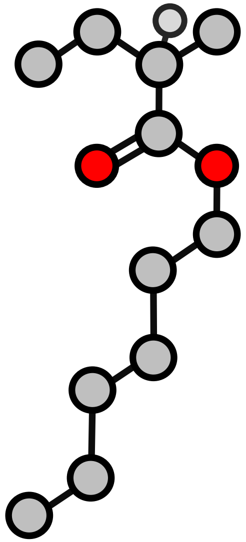
- Aside from simply tuning MW we have many options to combine:

“Short”
C1 – C5



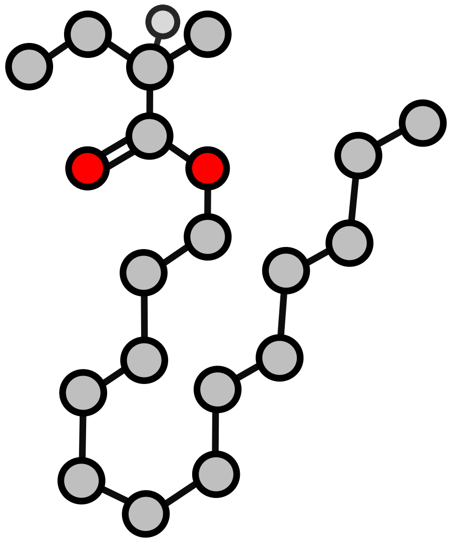
Improves Viscosity Index

“Medium”
C6 – C11



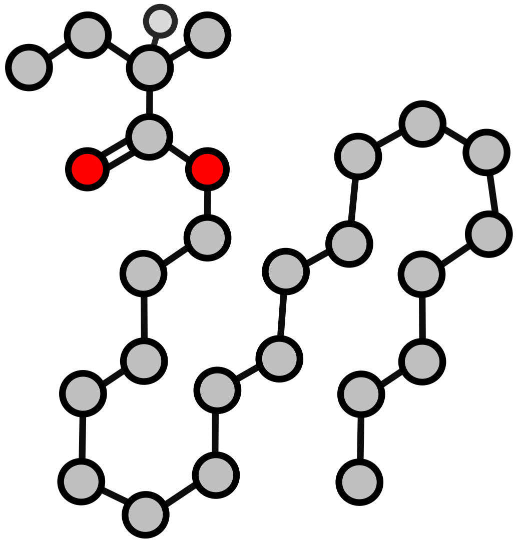
Thickening Efficiency

“Long”
C12 – C17



Oil Solubility, Wax Suppression

“Very Long”
C18+

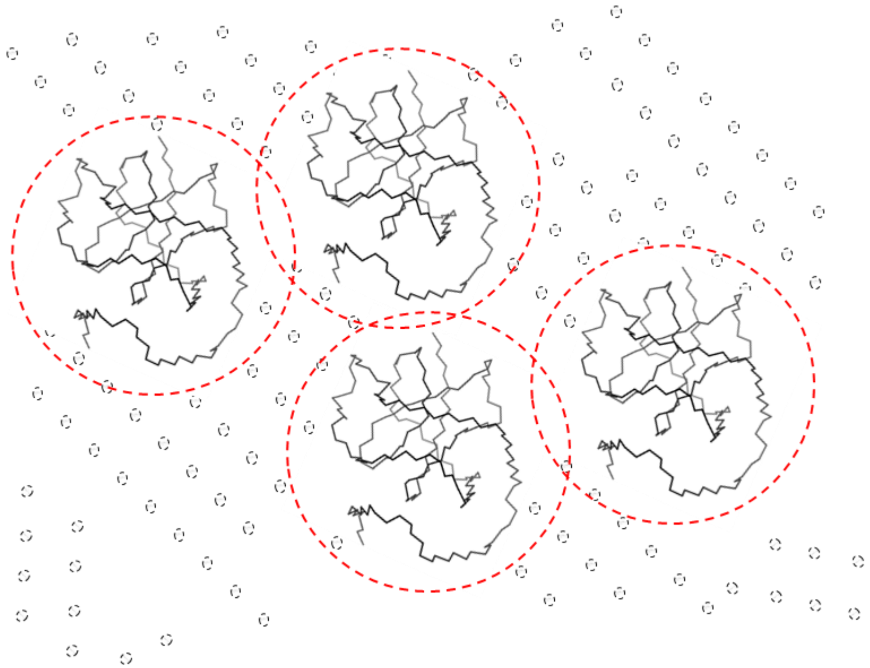


Wax Suppression

Florea, M., Catrinoiu, D., Luca, P. & Balliu, S. Lubr. Sci. 12, 31–44 (1999).

Tackifiers

- Ultrahigh molecular polymers soluble in the base fluid
- Meshed network of big polymers (chain link fence)
  - Slows the responsiveness of oil, motion makes it act like a solid



Levin; Stepan; Leonov. Evaluating Tackiness of Polymer Containing Lubricants by Open-Siphon Method. 2007
Rudnick, L. R. Lubricant Additives: Chemistry and Applications: Chapter 13, Second Edition. (CRC Press, 2009)

Tack in Action

- Useful in reducing fling-off, drippage, and misting in many applications:
  - Bar & chain
  - Chain or conveyor oil
  - Pneumatics – air tool and rock drill oils
  - Slideway lubricants
  - Metalworking fluids
  - Textile lubricants
  - Grease and rust preventatives

- "Non-Newtonian"
  - Motion-based and speed dependent effect
    - Better to show than tell – we'll finish this talk with *two videos*

Rod Climbing Behavior

- Tackified lubricant acts as a solid when struck at high speed

- “Hoop stress” around the rod creates net lift upwards

https://youtu.be/I-wO4weZ8is (FPI ‘Tack in Action’ video, ILMA 2021): start at 3:42

Anti Mist Behavior

- Increased surface tension from very high MW polymer

- Coalesces mist into larger droplets and strings

https://youtu.be/I-wO4weZ8is (FPI 'Tack in Action' video, ILMA 2021): start at 5:05

Conclusions

- Polymers used to add unique behaviors and performance to lubricants
- Chemical structure influences properties
- Those properties determine performance and which one you should pick
- Variety of factors affect structure and properties:
  - Monomers and ratios (E-P %)
  - Molecular weight (SSI)
  - Architecture (linear vs. branched)

Thank you
Pittsburgh STLE Chapter!

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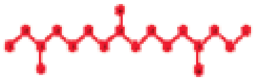
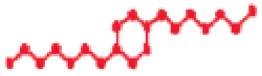
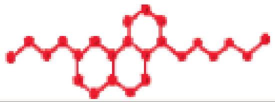
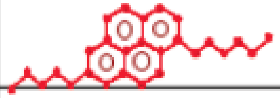
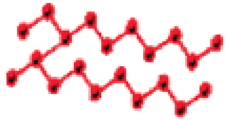
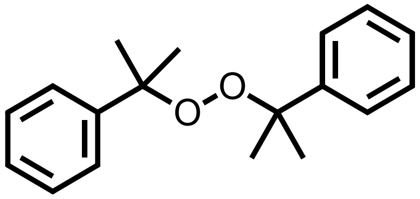
Extras: Full Carbon Type Table

Molecule	Structure	VI	Pour point	Oxidation	Solubility	Toxicity
n-paraffin		Excellent	Poor	Excellent	Poor	Low
Isoparaffin		Good/ excellent	Good	Excellent	Good	Low
Single-ring naphthenic		Good	Good	Good	Good	Low
Multiring naphthenic		Poor	Excellent	Good	Excellent	Low
Alkylbenzene		Good	Excellent	Good	Excellent	Moderate
Polycyclic aromatic		Poor	Poor	Very poor	Good	Very high
Polyalphaolefin		Excellent	Excellent	Excellent	Good/ poor	Low

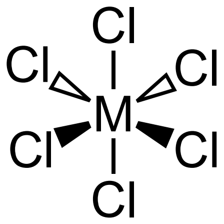
"Chapter 2: Lubricant Base Stock Production and Application", Table 2.5

Extras: OCPs – “Metallocene”

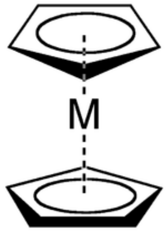
- Many ways of reacting ethylene and propylene (or other alpha-olefins) together
    - Free radical initiator (1940’s)
        - Initiator splits into radicals which set off chain reaction
        - Wide spec low quality LDPE



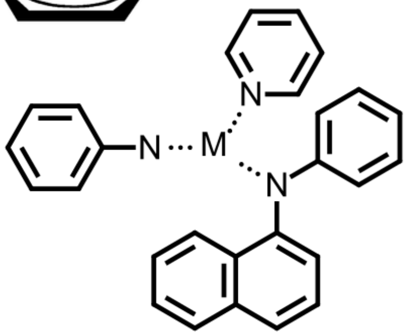
    - Ziegler-Natta catalyst (1960’s)
        - Olefins react freely on the surface of powdered metal chlorides
        - HDPE, LLDPE



    - Metallocene catalyst (1990’s)
        - Olefins assembled by soluble zirconium-ferrocene complexes
        - Very high control over finished product – high end polymers

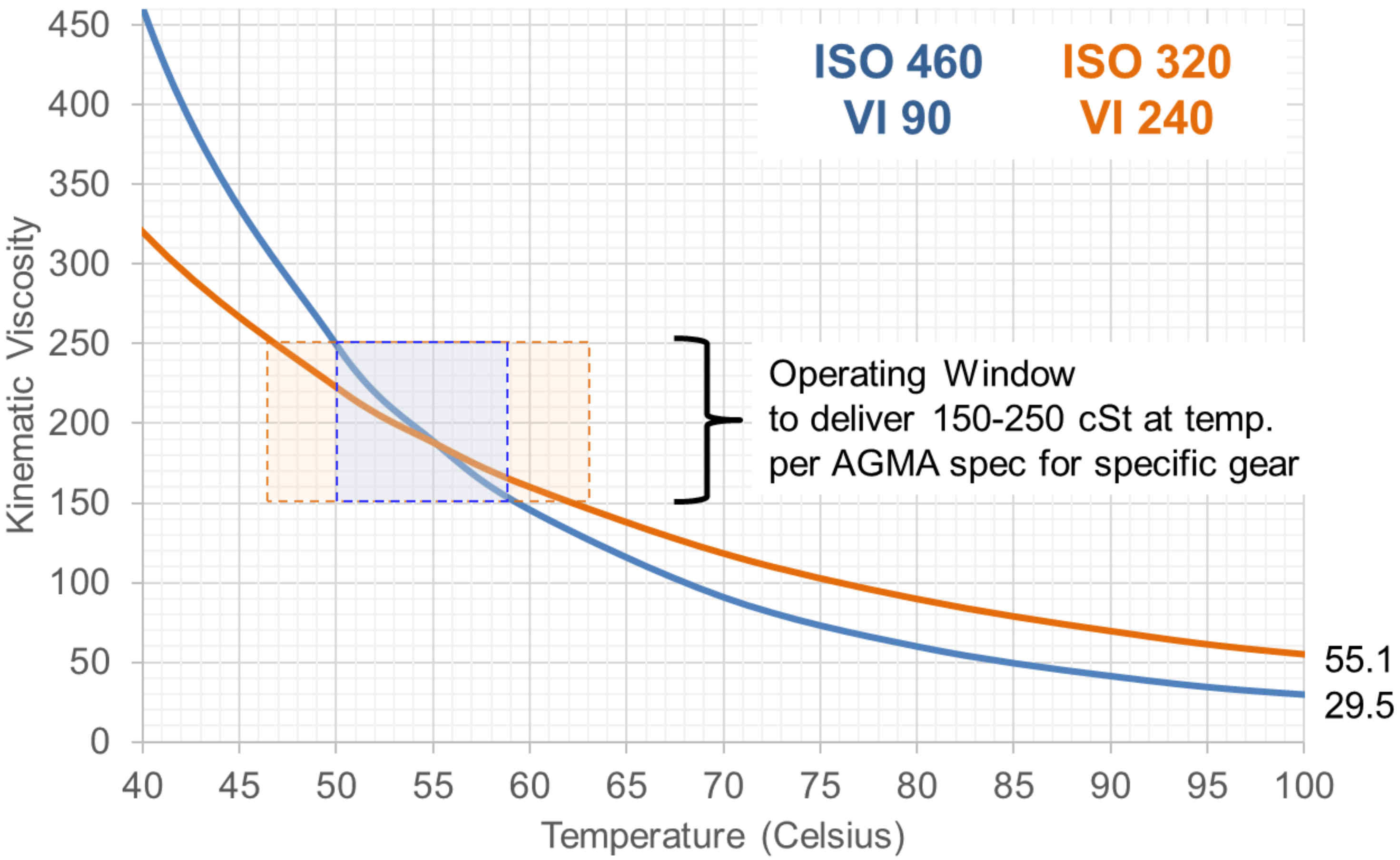


    - Post-Metallocene catalyst (2000’s)
        - Soluble metal complexes of aniline or PANA like structures



Extras: VI and "Multigrade"

- Wider operating temperature window for equipment
  - "All Season", "Multi-Grade", "High VI"



ANSI/AGMA 9005-F16. Example: gear with pitchline velocity of 1.8 m/s (35mm dia. at 1000 rpm)

Extras: Tackifier Effects Required by Industry

Behaviors Removed By Tackifier ("Anti-__")			**Behavior Added By Tackifier**		
Fling Off	*Drip*	*Misting*	*Adhesion*	*Wicking / Wetting*	*Cohesion*
Bar & Chain High Speed Couplings Gear Drilling	Oven Chain Conveyor Textile Assembly Lube Way Oil	MWF HF Open Gear	Chain Oil Rock Drill Bearings Dust Suppressant	Wire Rope Textile MWF Cutting Oil	Grease Rust Preventative