Investigation of High Temperature Stability of Tackifiers

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Outline

- Polymer Introduction
- Tackifier Basics
- Base Oil Impurity Study
- Tack Preservative Study

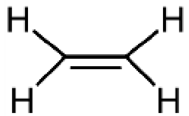
Polymers

Very long chains derived from many individual repeat units

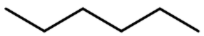
Size, shape, and repeat unit (monomer) affect polymer properties

Small Molecules

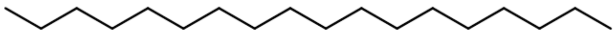
Ethylene (1 unit, monomer) - gas



Hexane (3 units) - liquid

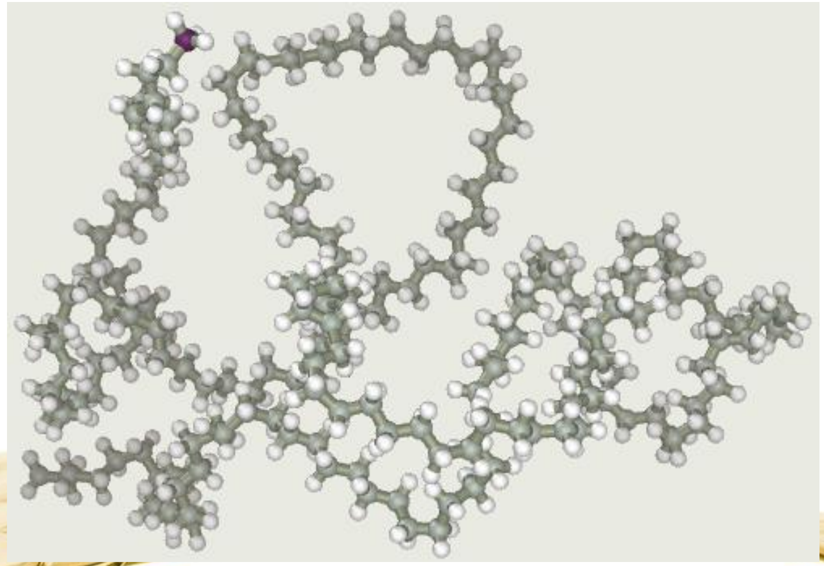


Octadecane (9 units) - wax



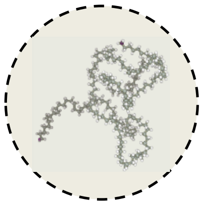
"Small" Polymer

6000 MW Polyethylene
(~200 ethylene units)



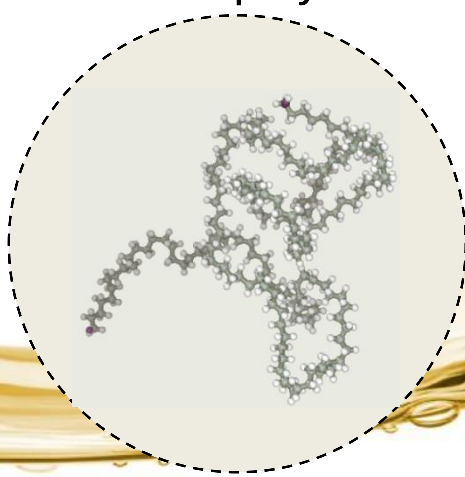
Polymers for Oil/Grease Additives

M_n ~ 100 – 10,000
Synthetic base oils
0 – 100wt%polymer in oil

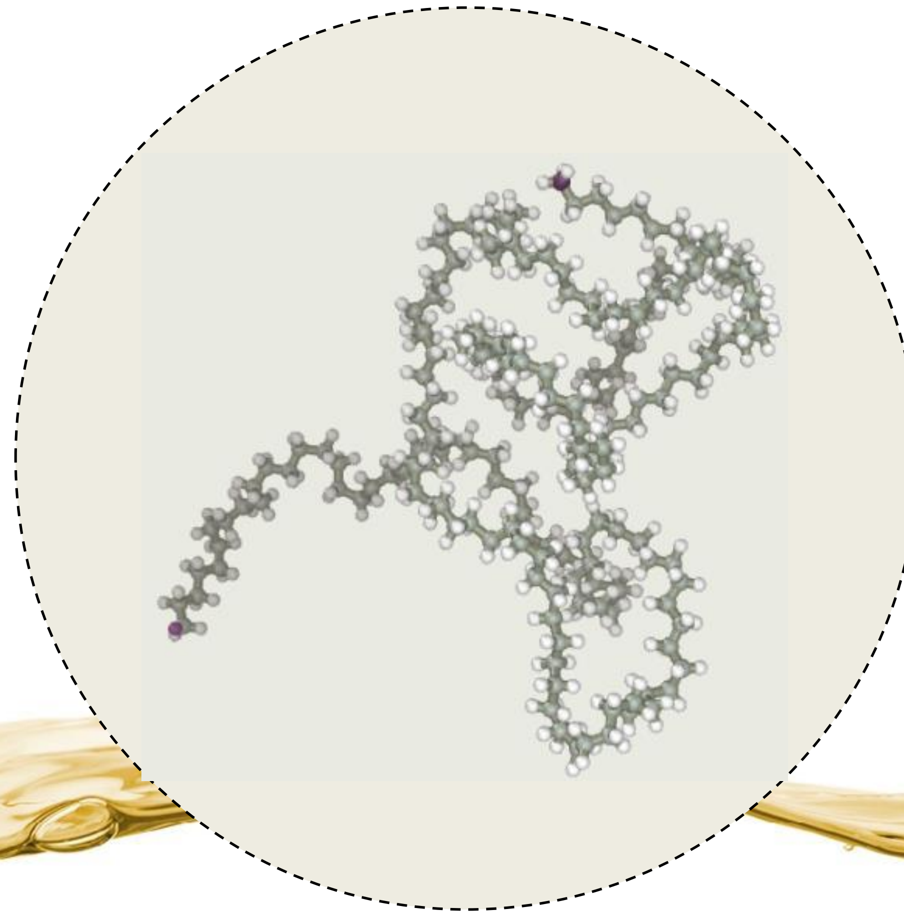


C15-30
oil
(for scale)

M_n ~ 10,000 – 200,000
Viscosity modifiers, pour point
0 – 10 wt% polymer in oil



M_n ~ 200,000 to >1M
Tackifiers
0 – 1 wt% polymer in oil



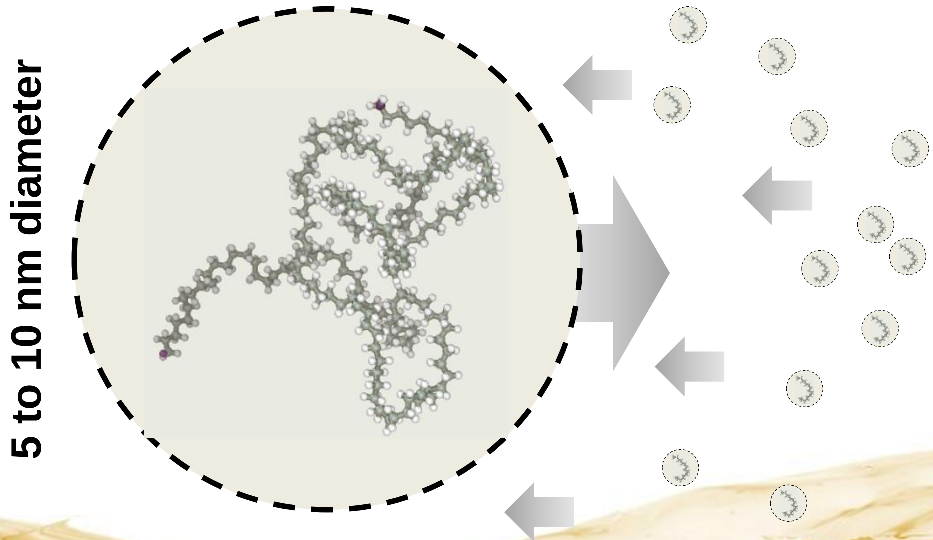
Polymer Solutions are Complex Liquids

Dissolve polymers are obstacles, slow the responsiveness of oil (viscosity)

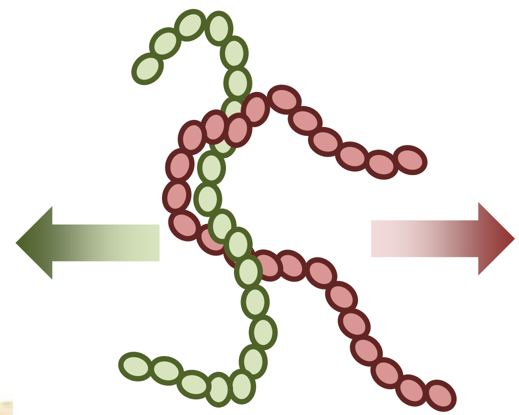
Solutions react to physical phenomena over **seconds**

Two major effects contribute to viscosity:

Polymer-Solvent Collisions (Hydrodynamic Drag)



Polymer-Polymer Entanglement



Non-Newtonian Behavior

Very long polymers (>100,000 MW) exhibit unique properties in solution

Oil-polymer behaves more like a solid when poured or sheared

Solutions produce temporary strings of oil and adhere to moving surfaces

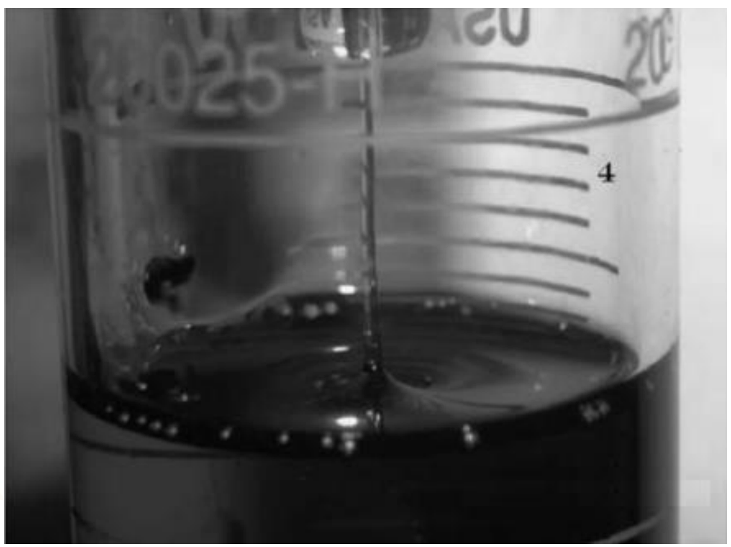
“Weissenberg Effect”

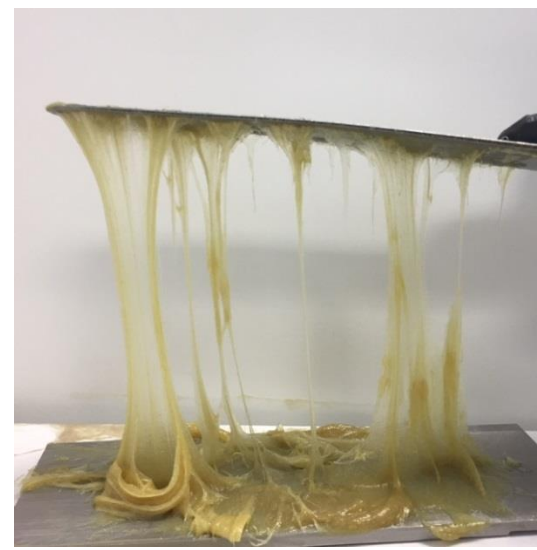
Weissenberg Effect – Screw Climb (MIT)

Tackifiers

Tackifiers are polymer-oil additives that contribute non-Newtonian behavior

- Tack and stringiness (greases)
- Adherence to moving parts for lower oil loss (gears, saws)
- Better feed through system (break-in oil, assembly lube)
- Anti-misting for improved safety (cutting oils)





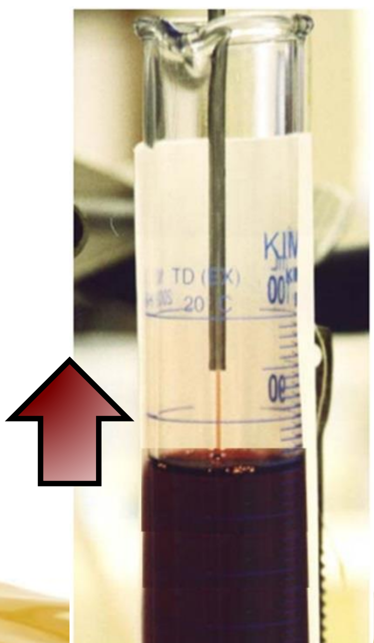
Rudnick, CRC 2009
Functional Products, “Additives for Grease”

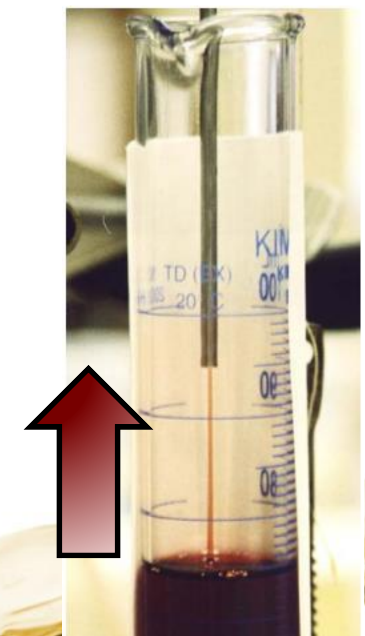
Measuring Tack via "Ductless Siphon" Method

Quantitative and reproducible measure of tack, no 'finger test'

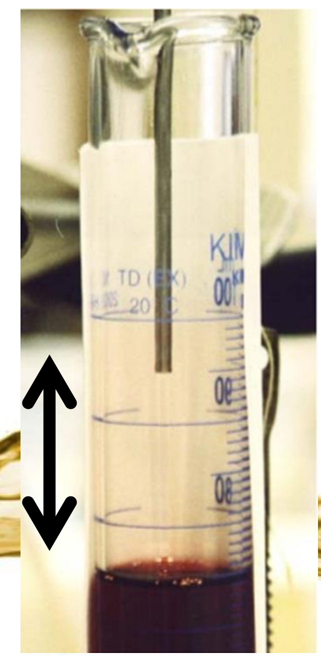
Vacuum tube used to drain tackified oil sample by pulling an oil string

Liquid level drops as sample withdrawn by string under vacuum





"String length" = Length of oil string at point of break

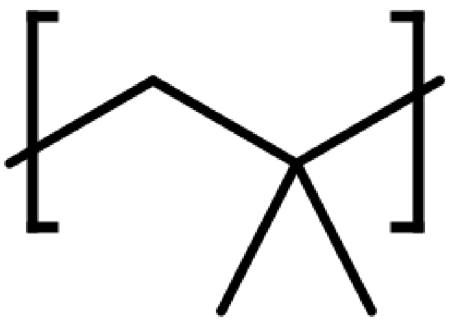


Selecting a Tackifier Polymer

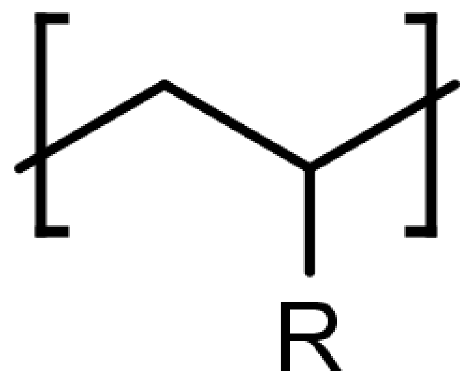
- Soluble in base fluid (aqueous, mineral oil, ester)
- Sufficiently large polymer M_n > 100,000 or M_v > 1M
- Effective at very low wt% in oil or grease – rubber or elastomers

Two major tackifier chemistries for <u>petroleum oil/grease</u>:

Polyisobutylene (PIB)



Polyolefin Copolymer (OCP)

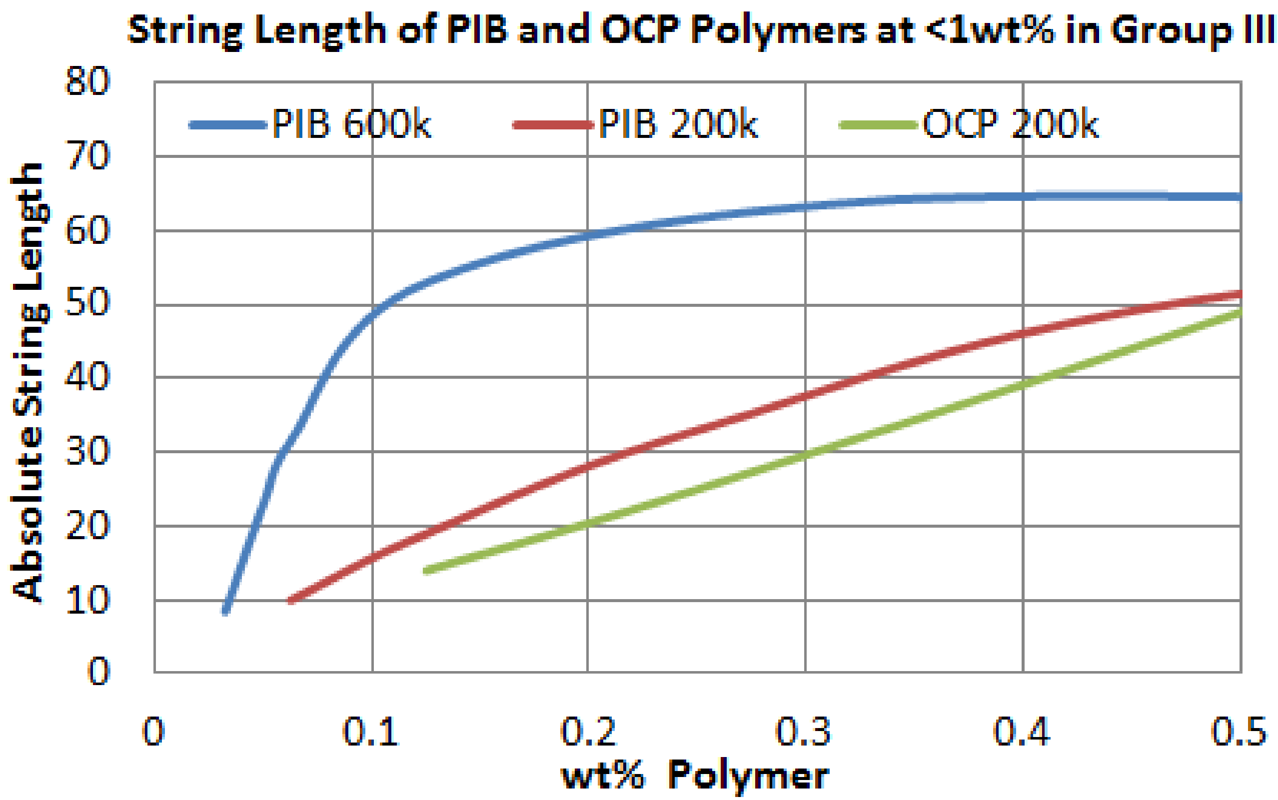


R = H, C1 – C8

PIB and OCP Tackifiers

- PIB has better tack than an equivalent OCP due to its structure
- Rubber industry maintains a stable supply of very long PIB

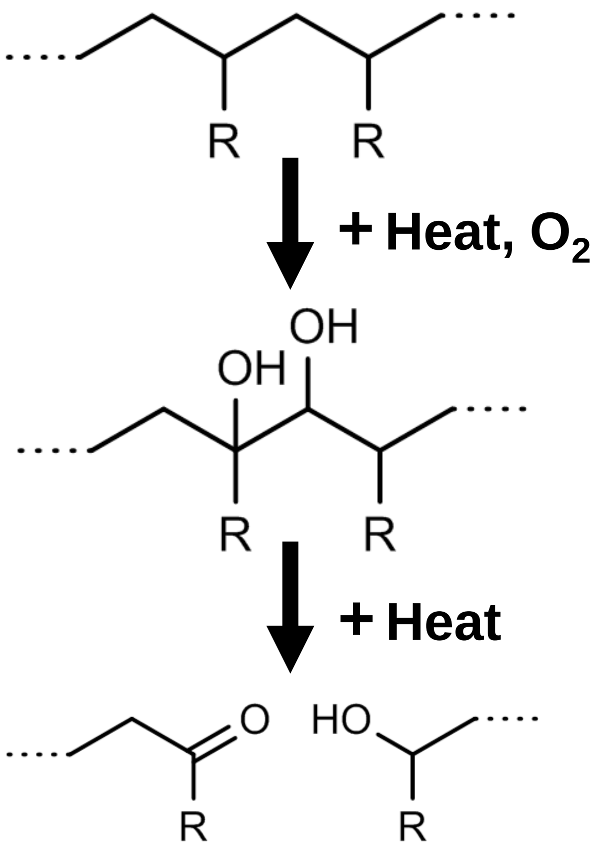
- Major drawback is the higher temperature sensitivity of PIB
  - We will focus on understanding and improving this sensitivity



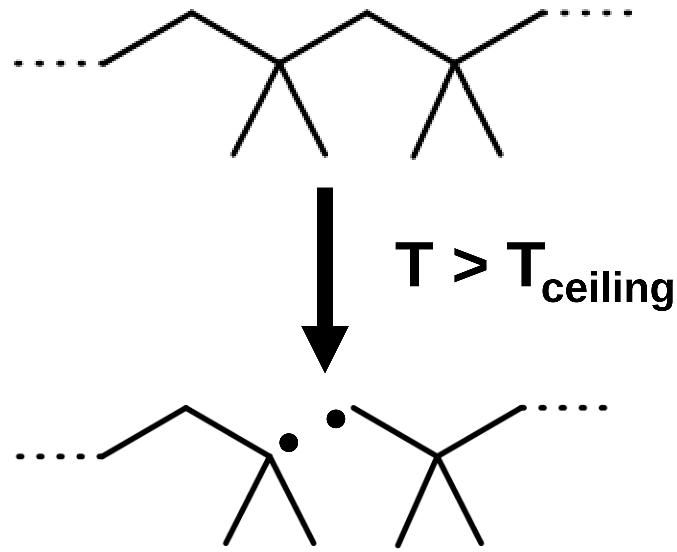
Thermal Stability of Tackifiers

- Oxidation and temperature ceiling effects limit tackifier stability at high T

Oxidation (OCP)



Temperature Ceiling (PIB)

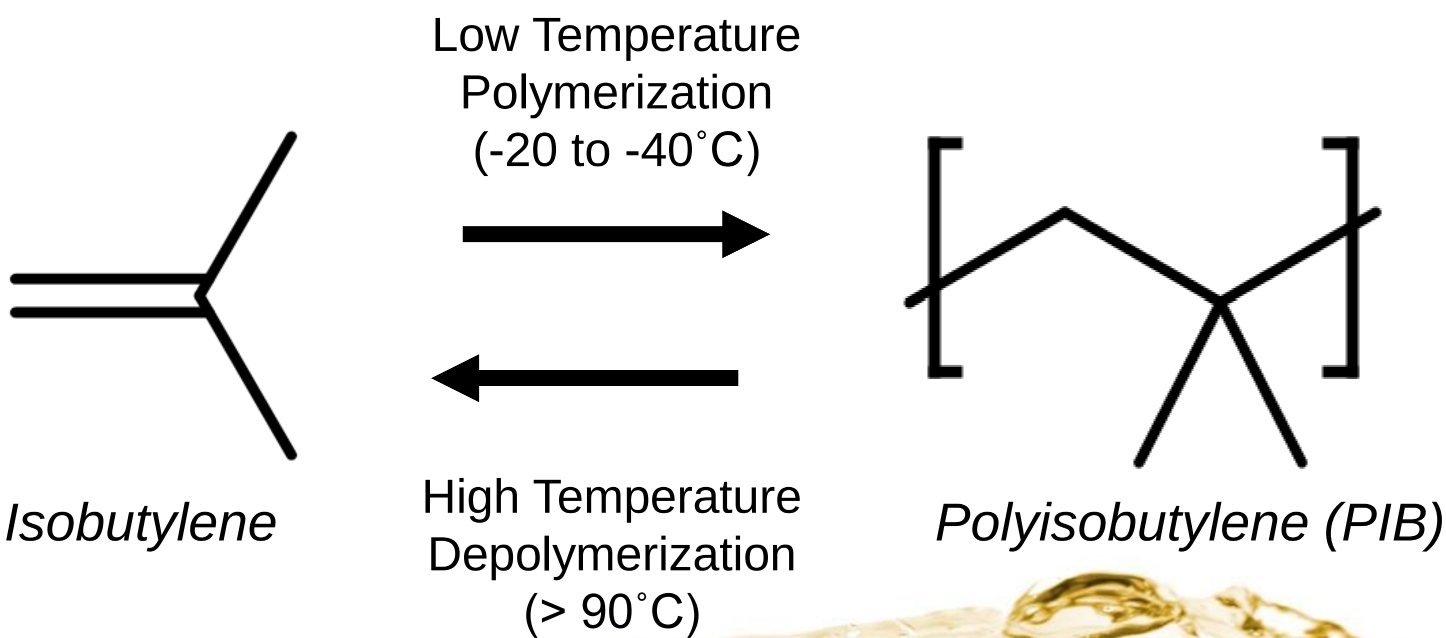


WHY?

PIB Thermal Stability

"Ceiling temperature" is a thermodynamic limit (entropy vs. enthalpy)

Usually > 300˚C but two methyl groups strain the PIB molecule (T ~ 90˚C)



High Temperature Oven Testing

To probe high temperature stability we need a controlled test

Oven tests are common in evaluating temperature effects

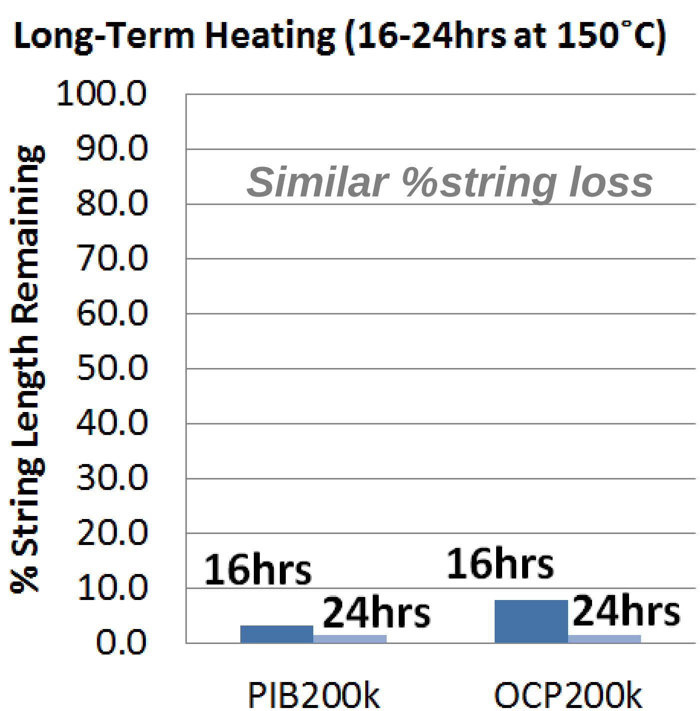
Two temperature/time settings found to produce sufficient tack loss

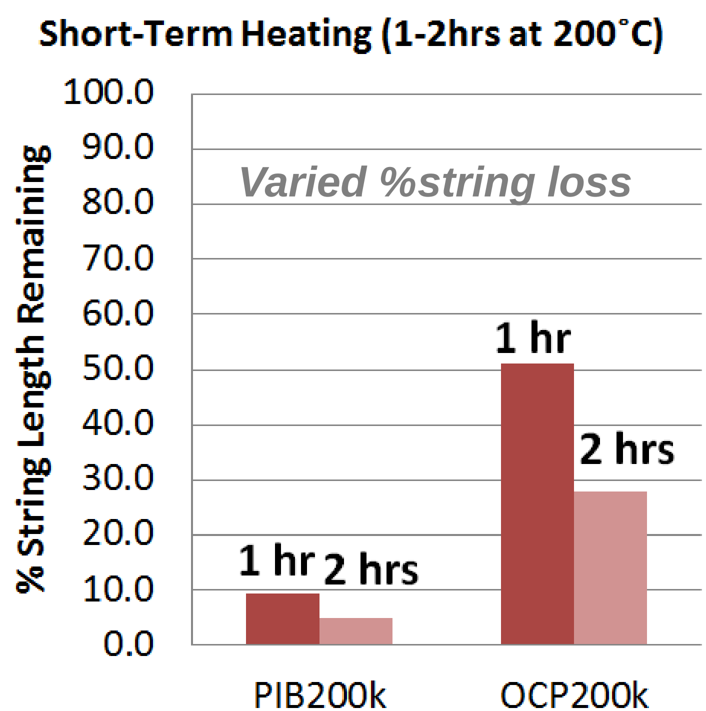
- <u>"Long-term high temperature testing"</u>: 16 – 24hrs @ 150˚C
- <u>"Higher temperature, short-term"</u>: 1 – 2hrs @ 200˚C

String length measured before and after heat treatment (% loss)

Comparing PIB and OCP String Length Stability

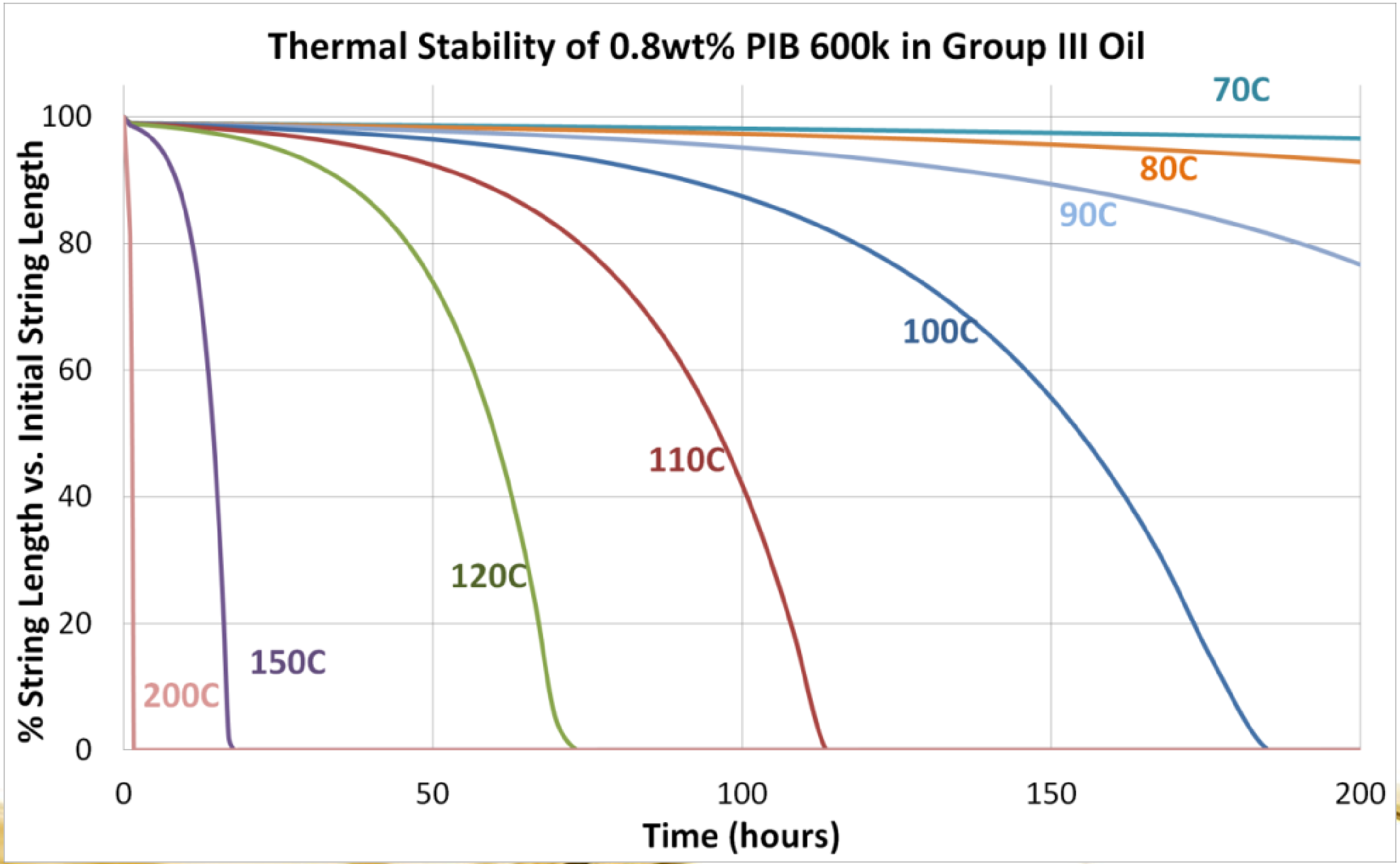
- Both OCP and PIB degrade almost completely with 24hrs at 150˚C
- OCP has much better stability than PIB at 200˚C
  - Oxidation slower than ceiling temperature effect





PIB "Shelf Life" at High Temperature

- From oven testing we can estimate tackifier shelf life at high T



Simple two-component polymer-oil, no antioxidant

2004 High Temperature Tackifier paper

Today's talk follows up on several key points from 2004

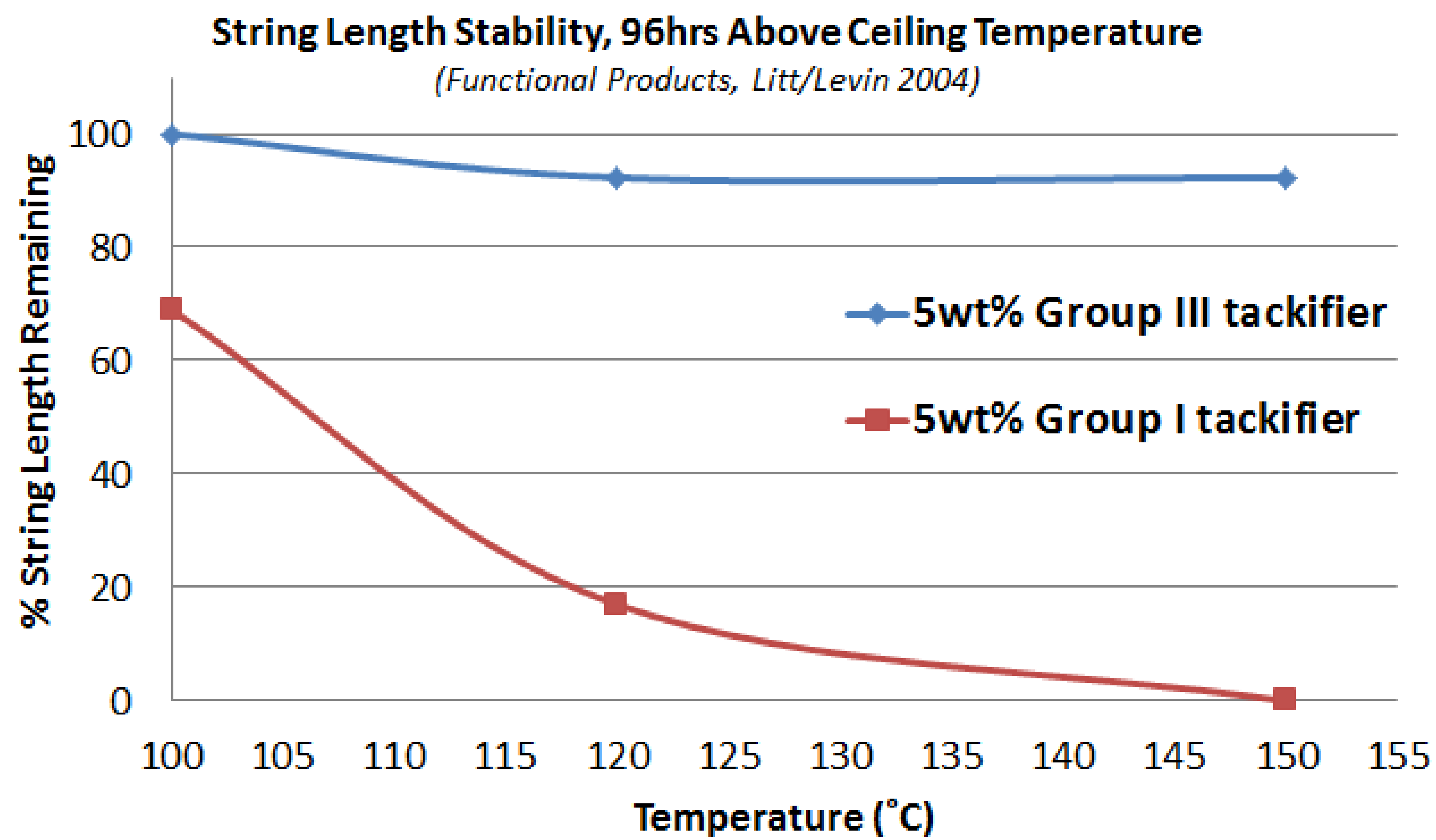
- Better PIB temperature stability in Group III and IV oil
- No benefit when using a Group I tackifier in a Group III base oil
- **Oil from Group I oil additives accelerates PIB tack loss in Group III**
    - *Group III lubricants need Group III additives*

Levin, V. & Litt, F. Tackifiers for high temperature lubricants. *Functional Products Inc.* (2004)

Base Oil Impurity Study

Mixing Group I and III Oils

- Implications for base oil suppliers and additive formulators

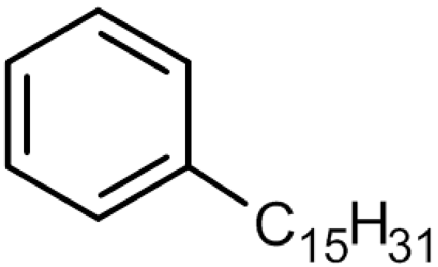


Base Oil Impurity Investigation

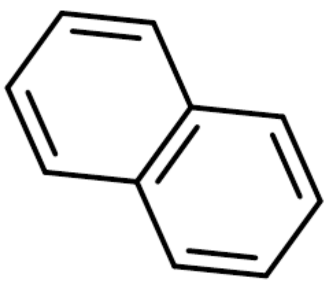
“What components of Group I oil are affecting tackifier stability?”

- Four classes of components identified: one representative per class
- Group III tackifiers prepared with impurity and heat treated

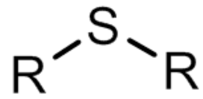
Monocyclic Aromatics



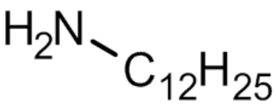
Polycyclic Aromatics



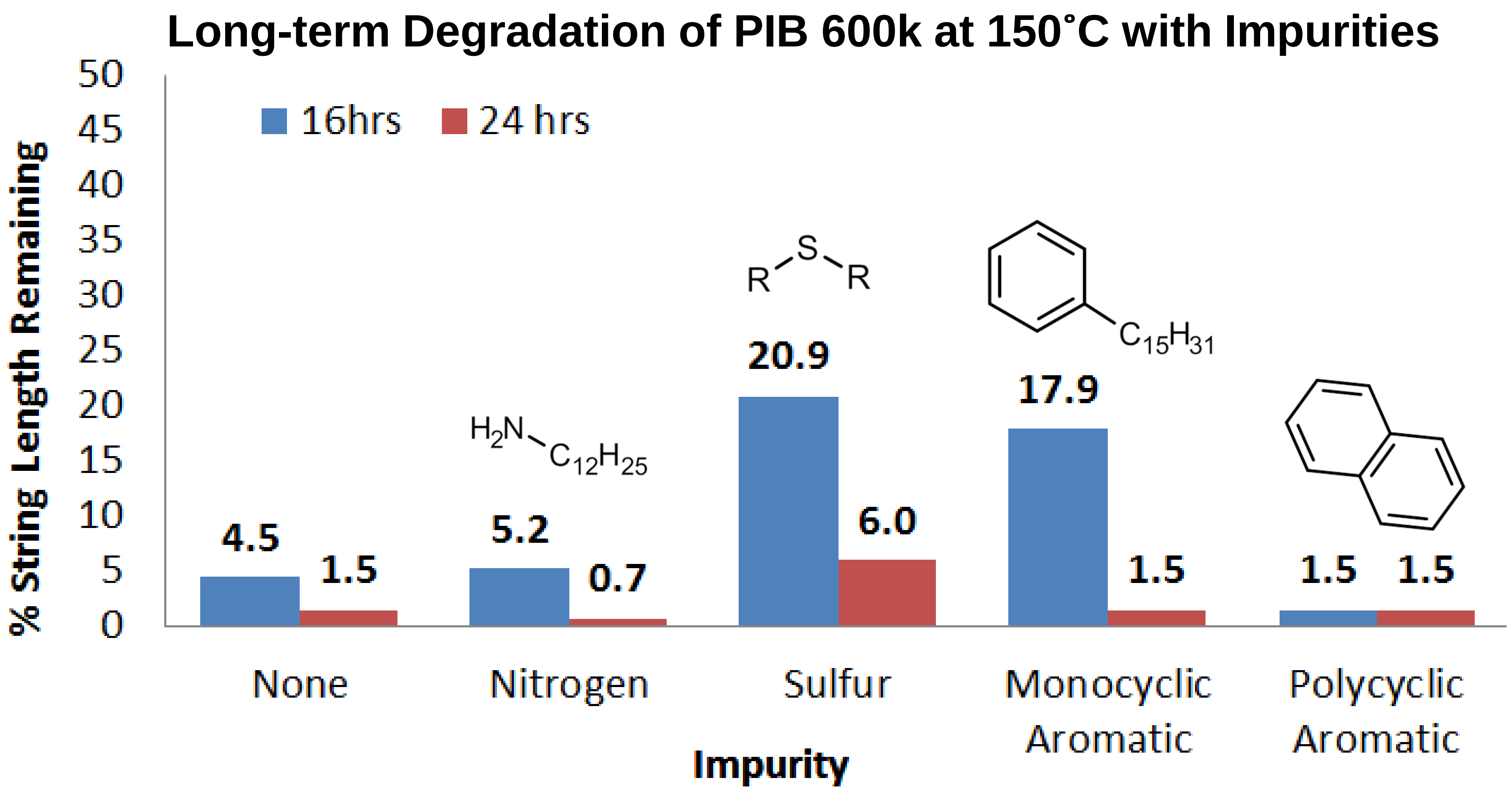
Sulfur



Nitrogen



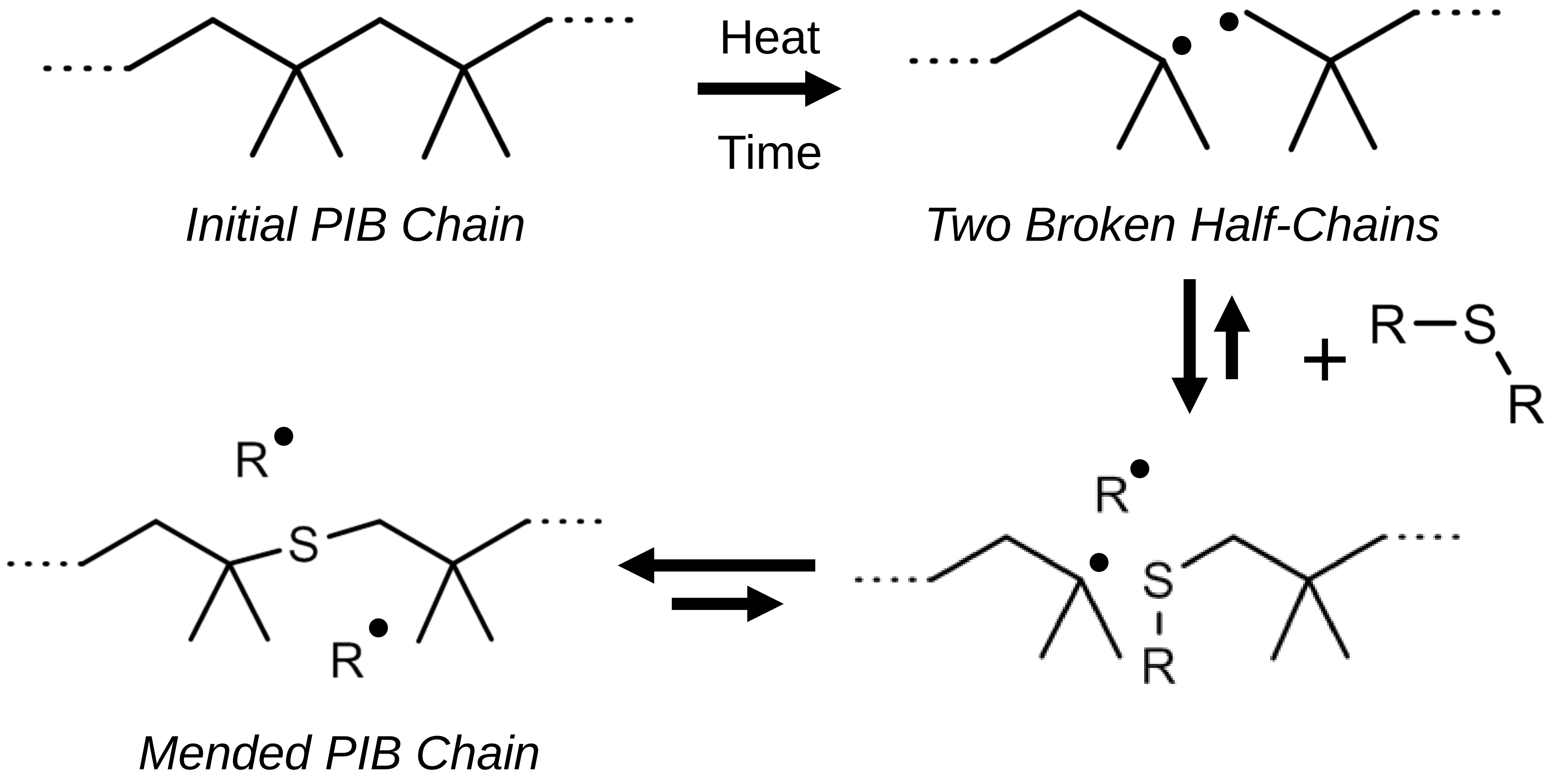
Tackifier with Impurities



Sulfur Mechanism?

Prior art in addition of two or more radicals – RAFT chemistry (1990-2000)

Radicals add to sulfur, displace alkyl groups

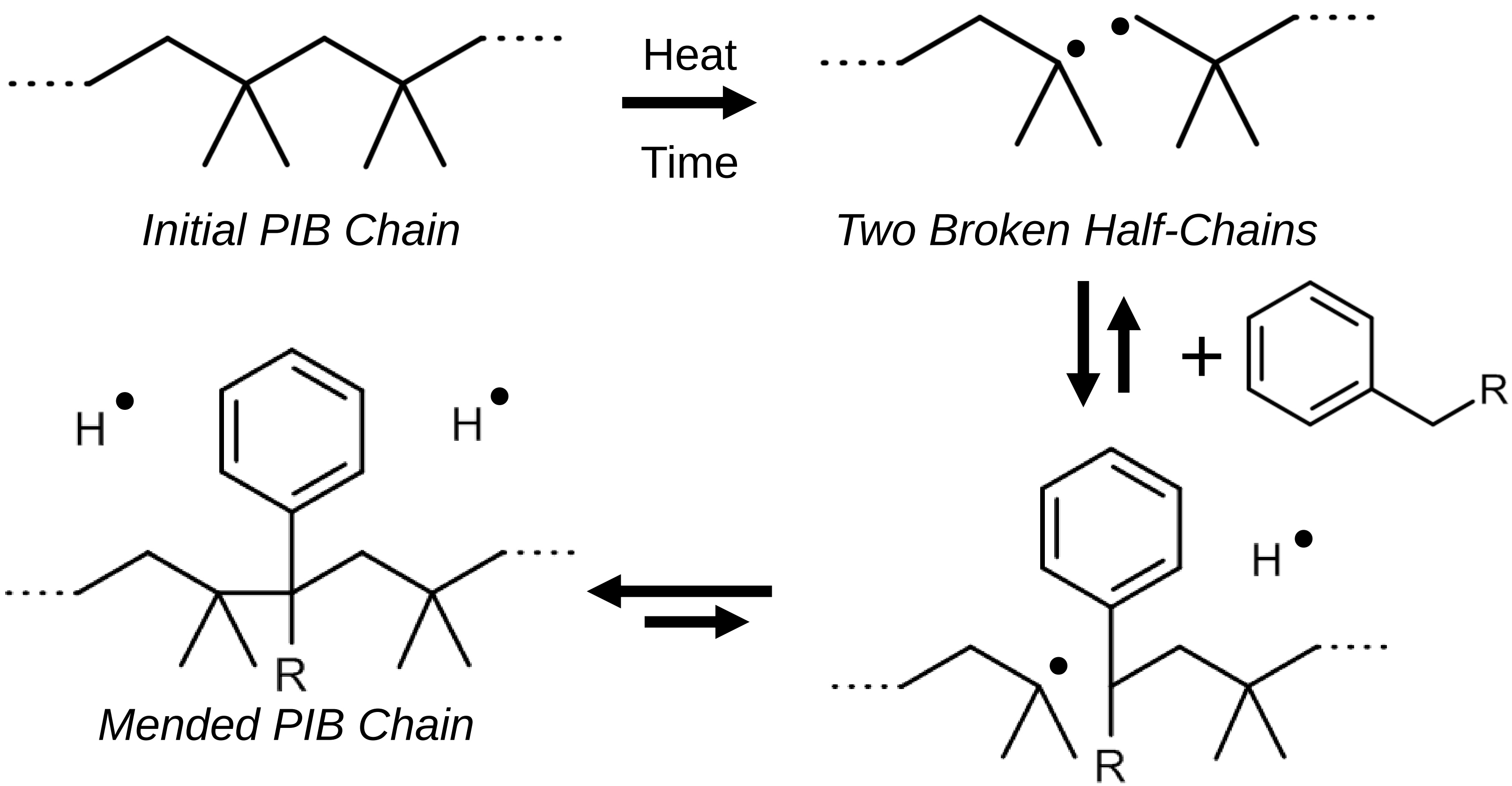


Moad; Rizzardo. *Aust. J. Chem.* **2006**

Monocyclic Aromatic Mechanism?

Prior art in chain transfer agents used to quench radical polymerizations

Radicals add to alkyl groups on aromatics



Odian, "*Principles of Polymerization*" **1981**

Base Oil Impurity Results

Impurities have a complex relationship at 0.1wt% - not always bad

PIB 600k tackifier showed benefit from added sulfur, monocyclic aromatics

Impurity Group	Representative	Effect on PIB 600k String Length
None	None	Loss of tack
Monocyclic Aromatics	Alkyl Benzene	**Reduced Loss**
Polycyclic Aromatics	Naphthalene	No Change
Sulfur	Thiosulfate	**Reduced Loss**
Nitrogen	Alkyl Amine	**Increased Loss**

Base Oil Impurity Summary

Findings

- Impurities can improve stability of tack, are not always ‘bad actors’
- Relationship is complex
  - Sulfur helps short (200k) and long (600k) PIB
  - Monocyclic aromatics help PIB 600k, polycyclics help PIB 200k

New Questions

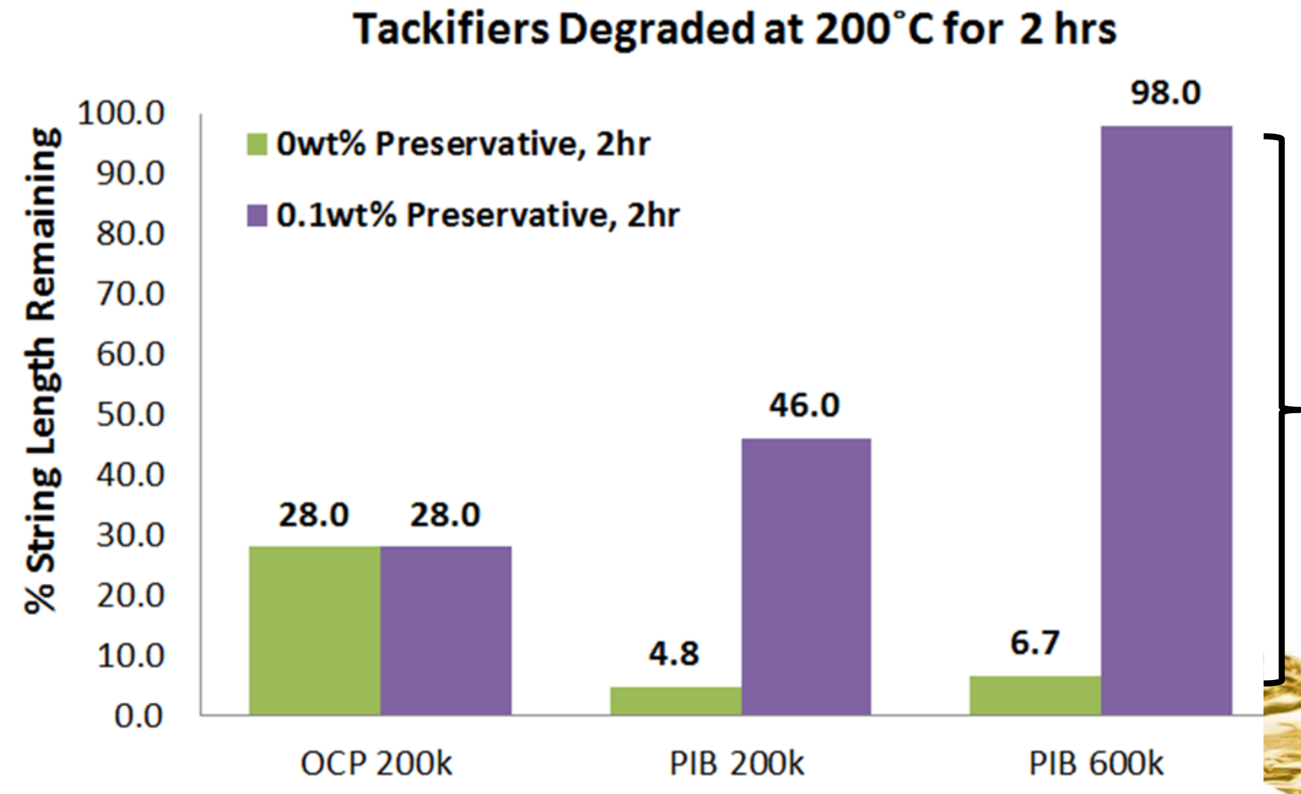
- How do combinations of classes (i.e. aromatic nitrogen) behave?
- Do the effects change above or below 0.1wt% impurity?
- *Do commercial additives act as impurities at high temperature?*

Tack Preservative Study

Tack Preservative for PIB-based Tackifiers

"Impurities can preserve tack" initiated a new survey of compounds

A novel 'tack preservative' was found using previous discussion/lessons



Best synergy with the longer PIB 600k

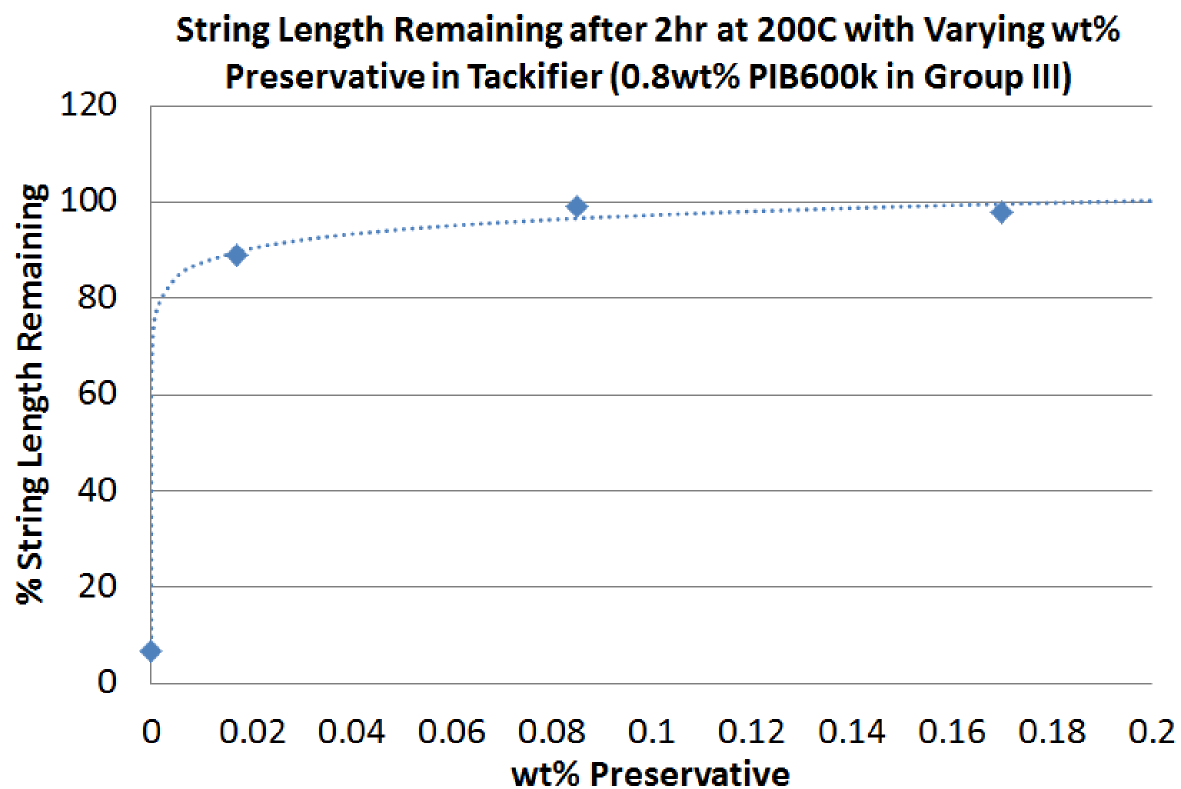
Only 2% loss

Determining Effective Treat Levels

Tackifiers are diluted into lubricants at < 5wt%

Does the preservative work when diluted?

Yes, effective over a broad treat level in simple PIB/oil solution



Tack Preservative Diluted in Lubricant

So far we discussed the preservative in a tackifier (0.8wt% polymer)

Does it continue to work in a simple lubricant (< 0.1wt%)?

Yes, final product with 20-25 cSt @ 100˚C and no string loss

- Preservative works with Group II oil and OCP from VI improver

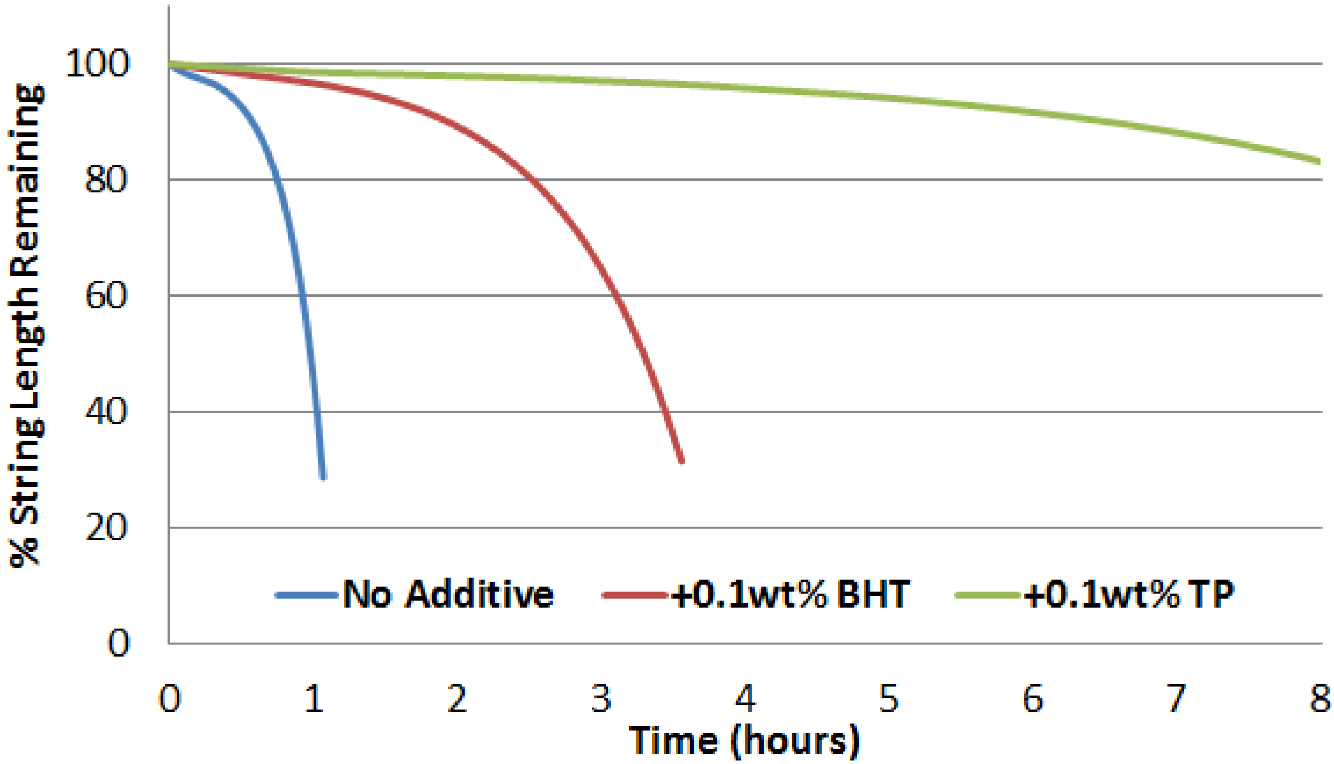
Sample	A0	A1	A2	B0	B1	B2
Note	1x PIB Control	1x PIB 1x TP	1x PIB 10x TP	2x PIB Control	2x PIB 1x TP	2x PIB 10x TP
wt% PIB 600k	0.08	0.08	0.08	0.17	0.17	0.17
wt% OCP VII	25.00	25.00	25.00	25.00	25.00	25.00
wt% Preservative	0.00	0.02	0.17	0.00	0.02	0.17
wt% Group III Oil	74.92	74.90	74.75	74.83	74.82	74.67
% String, 1hr at 200˚C	90	82	100	91	100	**100**
% String, 2hr at 200˚C	71	82	60	81	94	**100**

Tack Preservative

Tack preservative greatly extends string length stability at 200˚C

Better 200˚C stability = much better stability below 200

No observable tack loss after long-term treatment at 150˚C for 24hrs



Tack Preservative Summary

Findings

- A novel tack preservative was identified from base oil impurity study
- Effective from 0.001wt% (10 ppm) to 0.05wt%
- Able to eliminate string length loss during 2hr, 200˚C degradation test

New Questions

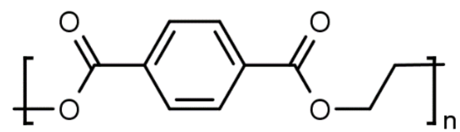
- Is a RAFT or chain transfer process reassembling broken chains?
    - GPC should be conclusive
- Can it work as a generic PIB preservative for PIB VI improvers?
- Applicable in grease?

Future Work – High Temperature Polymers

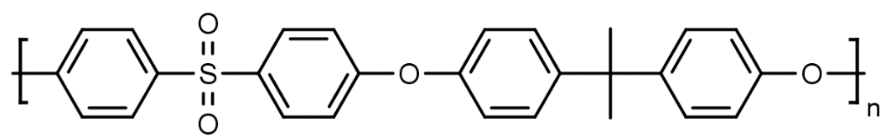
Engineering and high performance polymer chemistries operate at >200˚C

C-N / C=C / C-O bonds are stronger than C-C

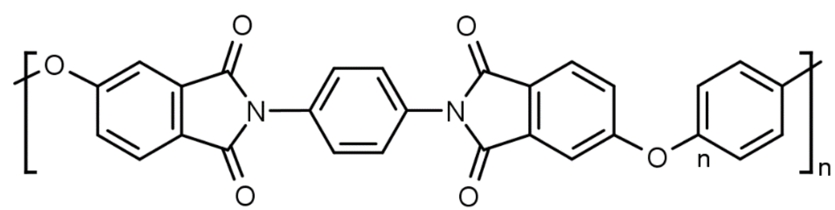
Polyethylene Terephthalate (PET)



Polysulfone (PSU)



Polyetherimide (PEI)



Thank you for your attention!

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