Viscometric and Low Temperature Behavior of Lubricants with Blended VI Improvers

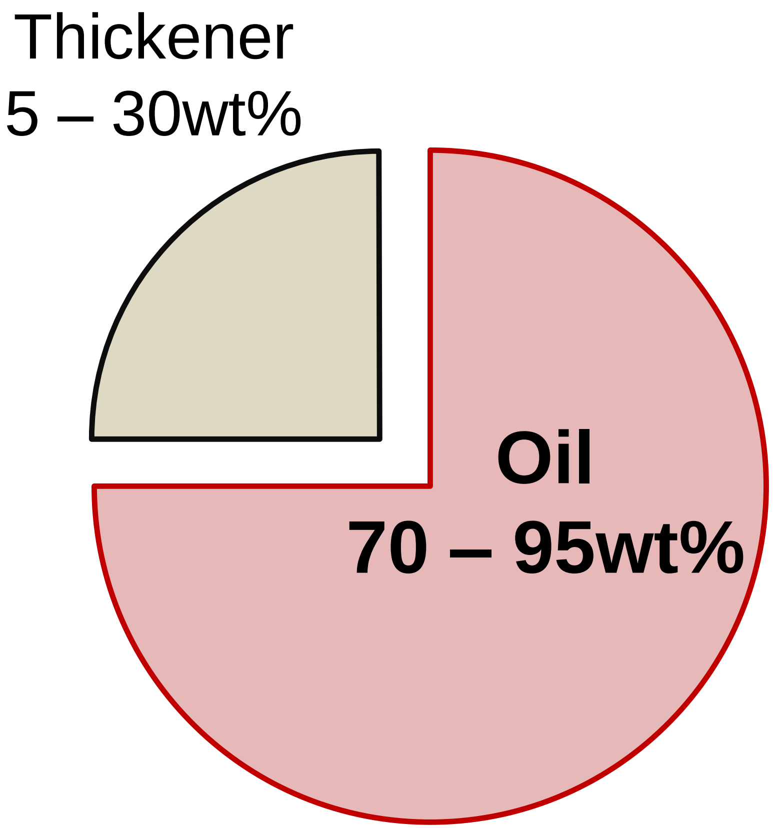
Functional Products Inc.

NLGI 85th Annual Meeting
Development Author Award Winner

Outline

- Lubrication Fundamentals
- VII Blending Study
- Interpretation of observed trends
- Summary, future work

What About Grease?



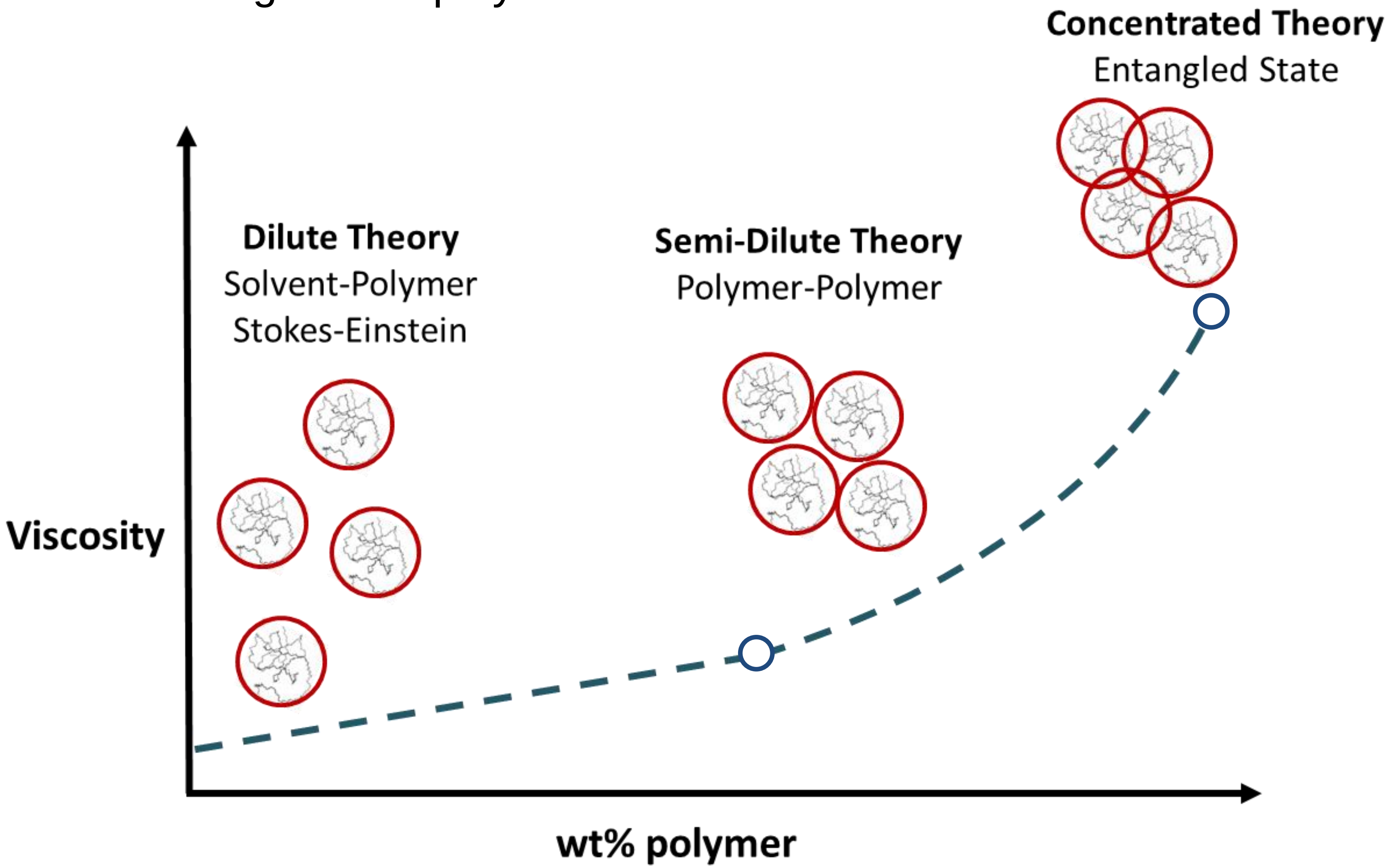
Gr. I/II + Naph.
Paraffinic: VI 80-90, p.p. >-12˚C
Naphthenic: VI 50, p.p. >-26˚C

Synthetics
High VI, low p.p.
Polymeric or use thickener

Natural / Synthetic Bio
VI vs. p.p. vs. oxidation
Low viscosity requires thickener

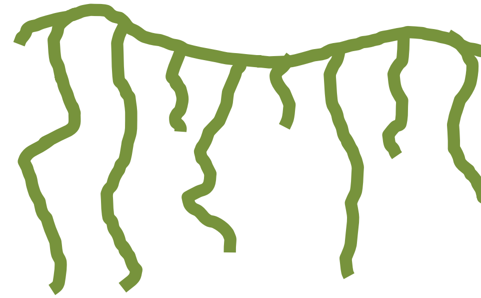
Viscosity From Polymers

- **Polymers** are dissolved into oil to increase viscosity
  - Three regimes of polymer solutions



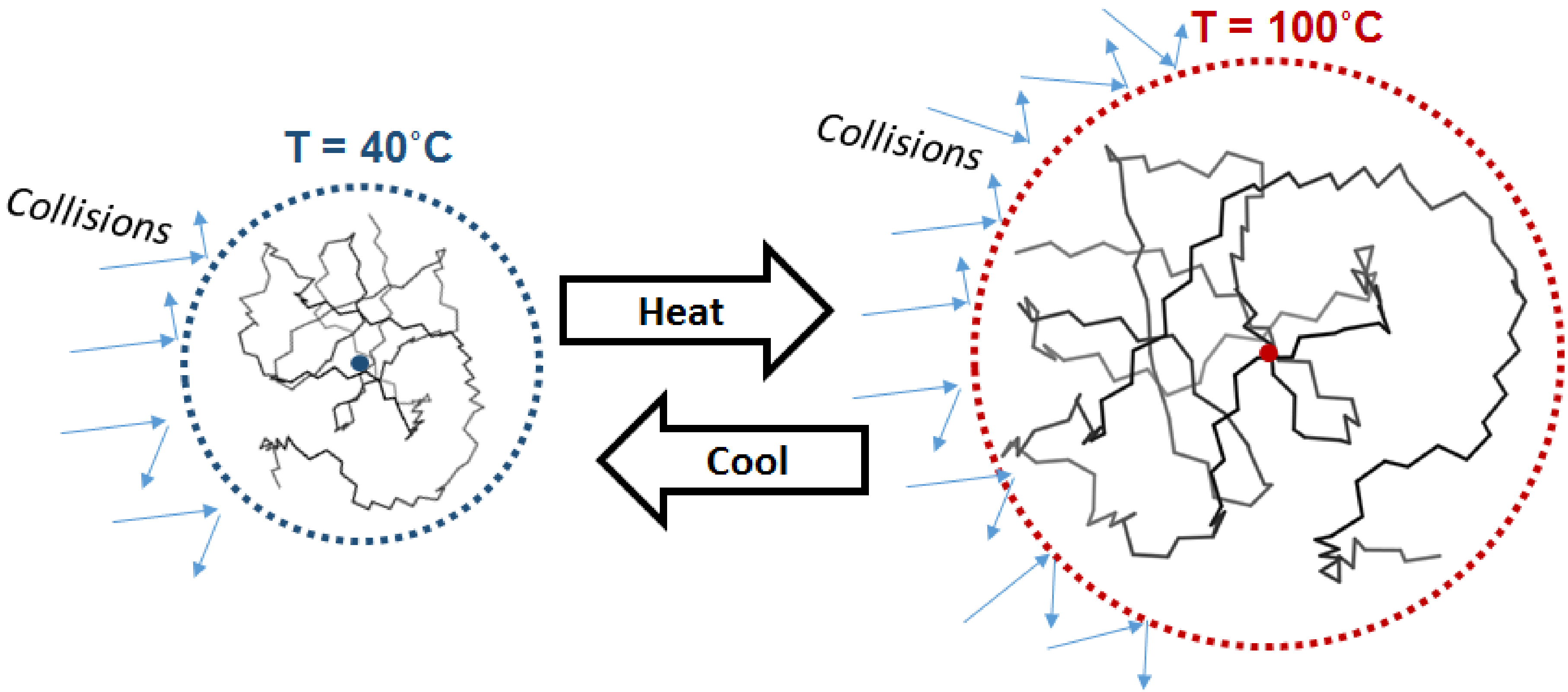
Properties of Polymers

ORGANIZATIONAL + CHEMICAL STRUCTURE



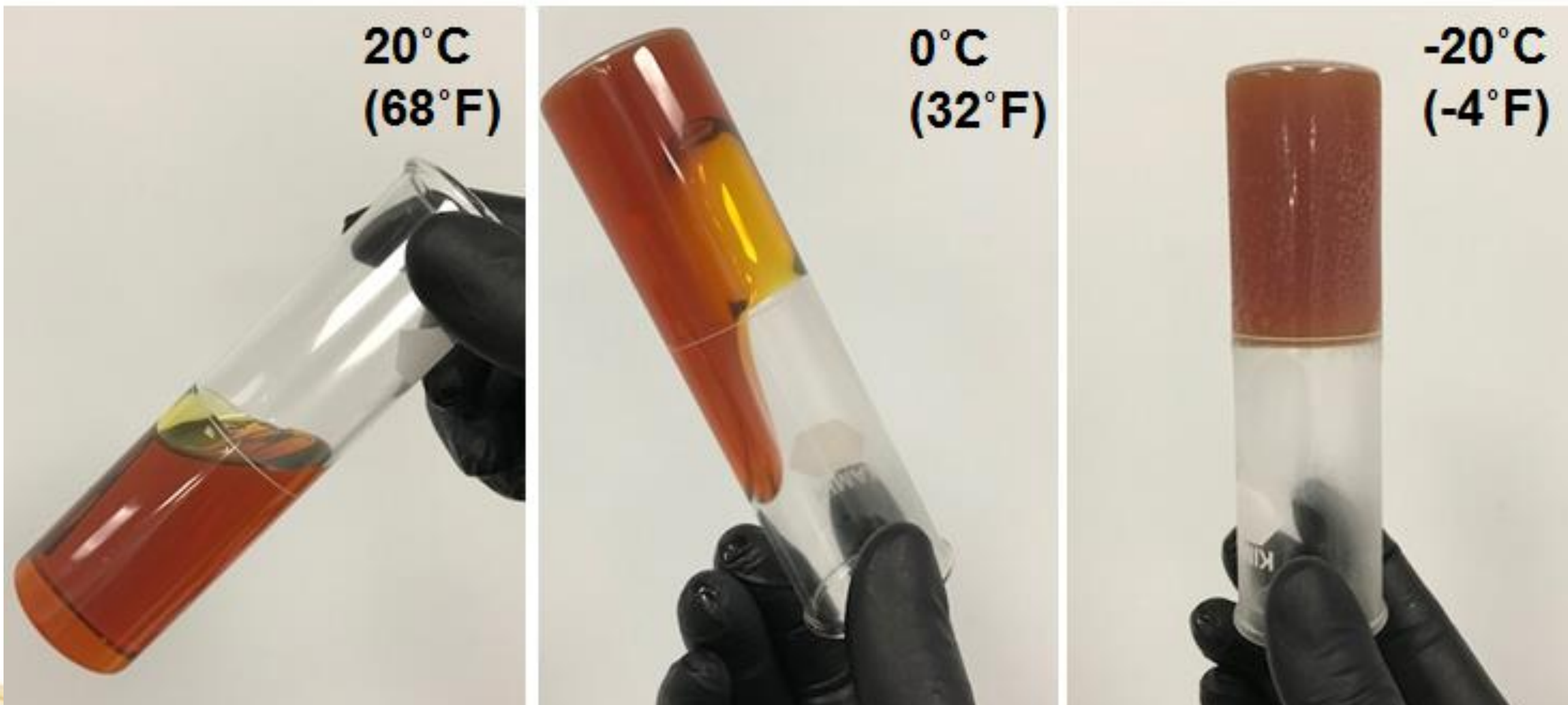
Viscosity Index

- Polymer coils dissolved in oil expand, compensate for thinning
- Ratio of KV100 to KV40, roughly (ASTM D2270)



Pour Point

- Temperature at which oil will not flow under its own weight
- Manual tilt test pour point (ASTM D97)



Approach to Blending

3 VI improver chemistries blended together at 5/10/20 wt%

VII	Chemistry	%Polymer wt%	MW (g/mol)	PSSI ASTM D6278	KV100 cSt	Application
"PB"	Polybutene	100%	2,000 – 3,000	0%	4000	Gear
"PMA"	Polymethacrylate	50 - 80%	10,000 – 30,000	1%	1100	Hydraulic
"OCP"	Olefin Copolymer	5 – 20%	50,000 – 100,000	22%	3500	Crankcase

Three base oils tested (0.2wt% PPD in Gr. II/III)

Oil	API Group	KV40 cSt	KV100 cSt	Viscosity Index	Pour Point, °C No PPD	Pour Point, °C 0.2wt% PPD
"Group II"	II	31.9	5	113	-18	-39
"Group III"	III	19.6	4	122	-15	-42
"PAO"	IV	30.2	6	137	-61	N/A

Blend then look at trends in VI, p.p.

Results Overview

- Formulations – simple premise
  - See Appendix A in technical paper for data

- Trends in VI and p.p. behavior – complex results
  - VI, p.p. varies as a function of wt% and VI improver type
  - wt% coincides with transitions in polymer solution theory
  - Why?

Findings - Formulations

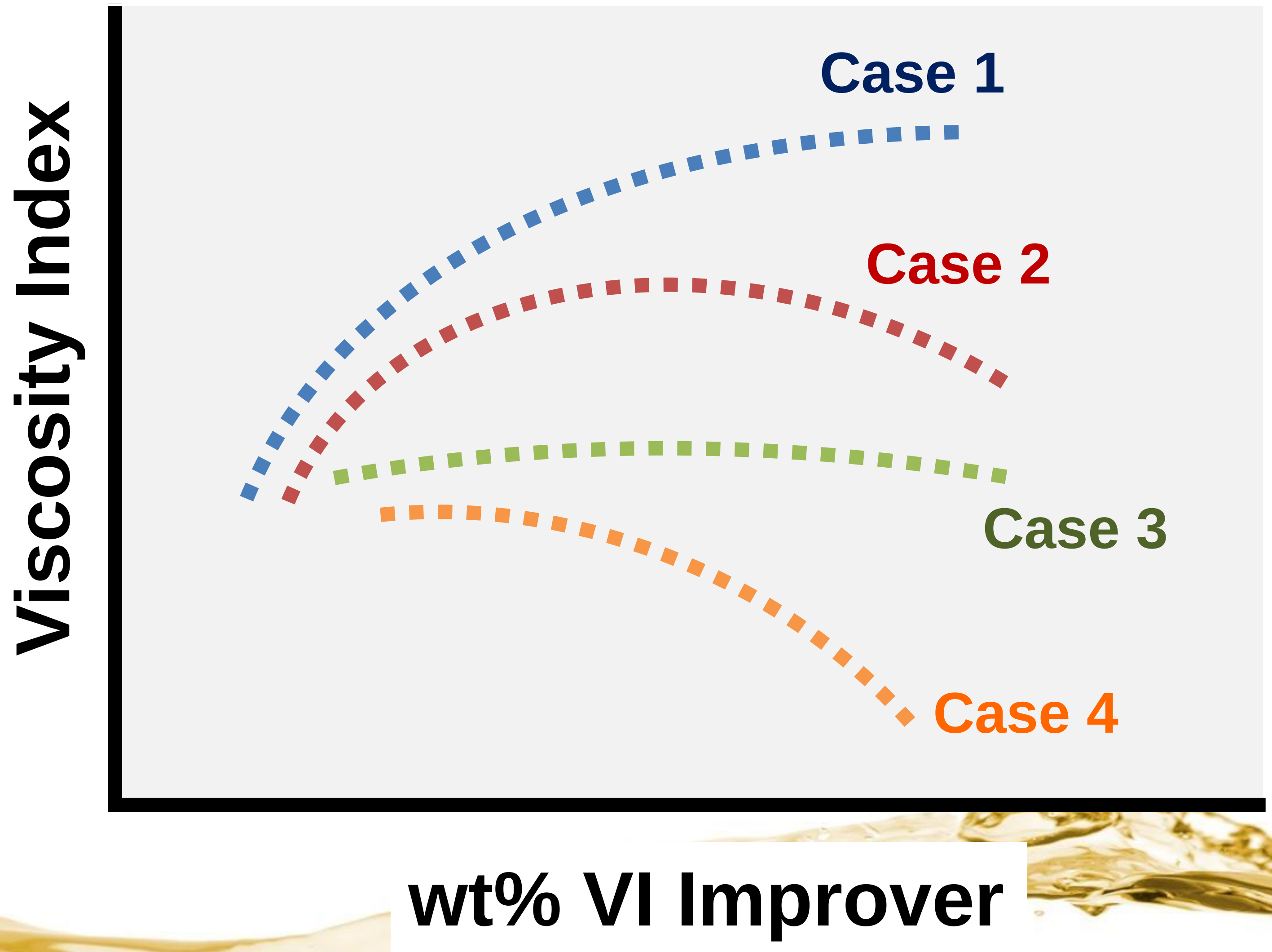
- 81 formulations tested using mixed VII
- Wide range of ISO/AGMA and SAE viscosity grades

Visc. Grade	#	Visc. Grade	#	Visc. Grade	#
ISO 46 / AGMA 1	2	**SAE 20**	2	**SAE 80**	5
ISO 68 / AGMA 2	8	**SAE 30**	13	**SAE 85**	11
ISO 100 / AGMA 3	7	**SAE 40**	13	**SAE 90**	12
ISO 150 / AGMA 4	2	**SAE 50**	12	**SAE 110**	13
ISO 220 / AGMA 5	6	**SAE 60**	4	**SAE 140**	10
ISO 320 / AGMA 6	6			**SAE 190**	9
ISO 460 / AGMA 7	2			**SAE 250**	2
ISO 680 / AGMA 8	0				
Total:	32		44		63
% of Samples:	40.7%		54.3%		77.8%

Appendix A – By Pour Point

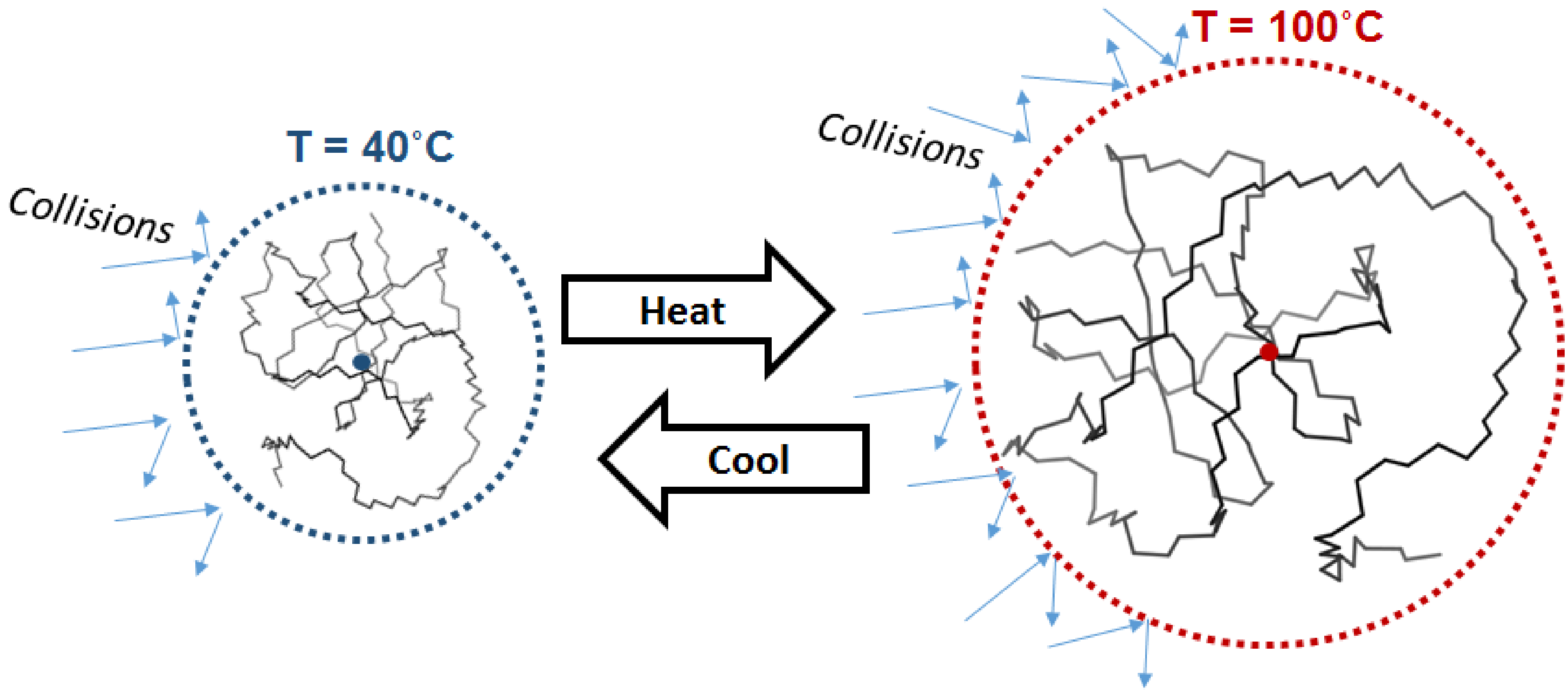
Base Oil	PPD wt%	PMA wt%	OCP wt%	KV40	KV100	VI	p.p., C	ISO VG	AGMA	SAE Eng.	SAE Gear
150N Gr. II	0.2	20	10	223.5	29.8	174	-27	220	5		140
150N Gr. II	0.2	20	5	133.7	20.2	174	-30			50	110
150N Gr. II	0.2	10	20	317.3	39.9	179	-33	320	6		190
100N Gr. III	0.2	20	5	82	15.8	206	-33			40	90
100N Gr. III	0.2	10	5	50	10.7	211	-39	46	1	30	85
100N Gr. III	0.2	10	10	80	15.4	205	-39			40	90
100N Gr. III	0.2	10	20	194.3	29.8	195	-39				140
150N Gr. II	0.2	5	5	62.8	10.6	159	-42	68	2	30	85
150N Gr. II	0.2	5	10	92.6	15	171	-42	100	3	40	90
150N Gr. II	0.2	5	20	104	16.2	168	-42	100	3	40	90
150N Gr. II	0.2	10	10	127.7	19.7	176	-42			50	110
100N Gr. III	0.2	5	5	40.6	8.3	186	-42			20	80
100N Gr. III	0.2	5	10	66.9	12.8	195	-42	68	2	40	85
100N Gr. III	0.2	5	20	182.7	28.4	195	-42				140
PAO 6		5	20	246.2	33.5	182	-44				190
150N Gr. II	0.2	10	5	66.5	11.7	173	-45	68	2	30	85
PAO 6		10	10	105.1	17.5	184	-50	100	3	50	110
PAO 6		10	5	77.1	13.3	176	-51			40	90
PAO 6		5	5	61.2	10.8	169	-52			30	85
PAO 6		5	10	91.5	15.1	174	-52	100	3	40	90

Findings - 4 VI Trends



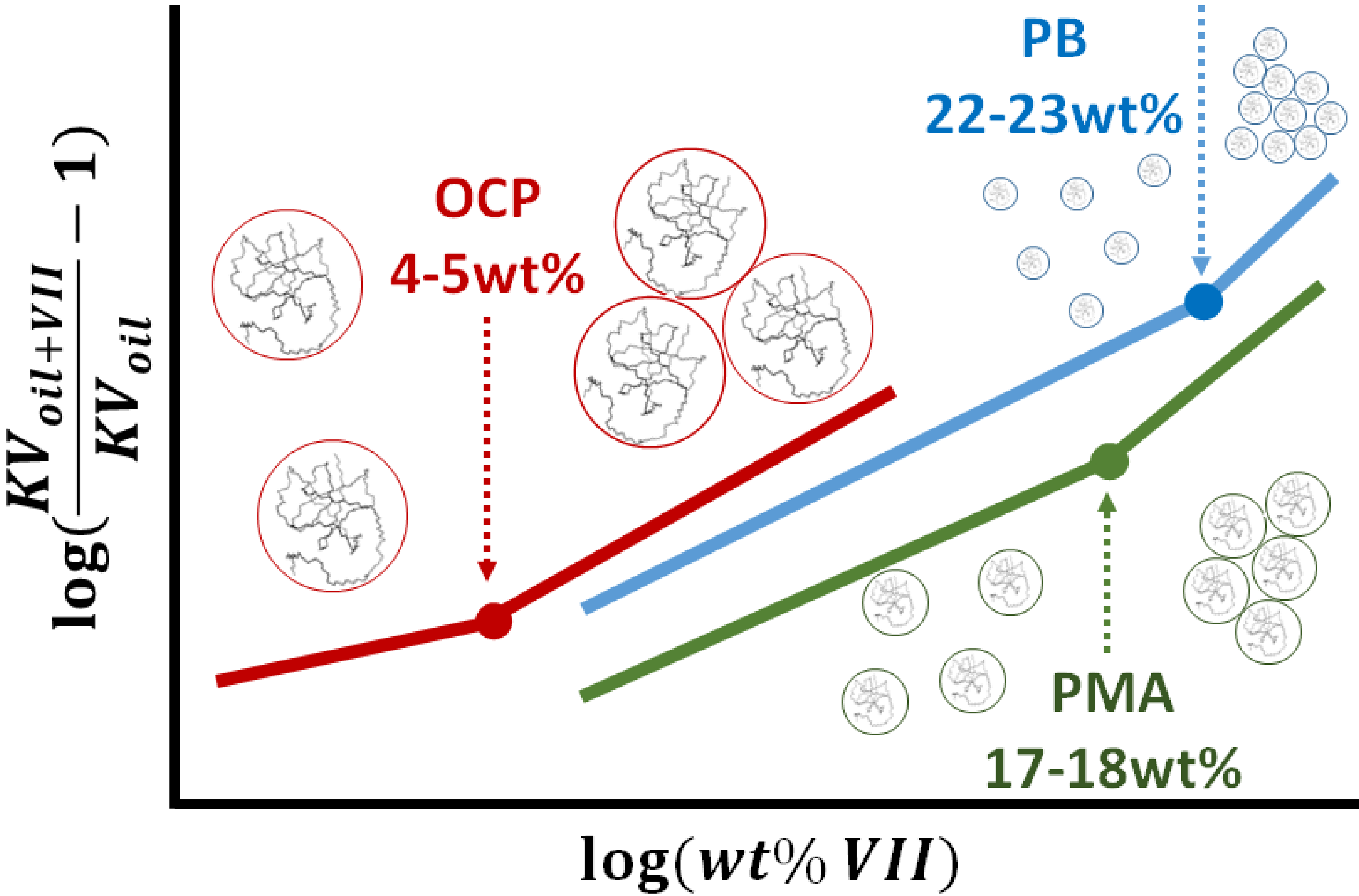
VI Trend – Case 1

- Textbook depiction of VI improvement



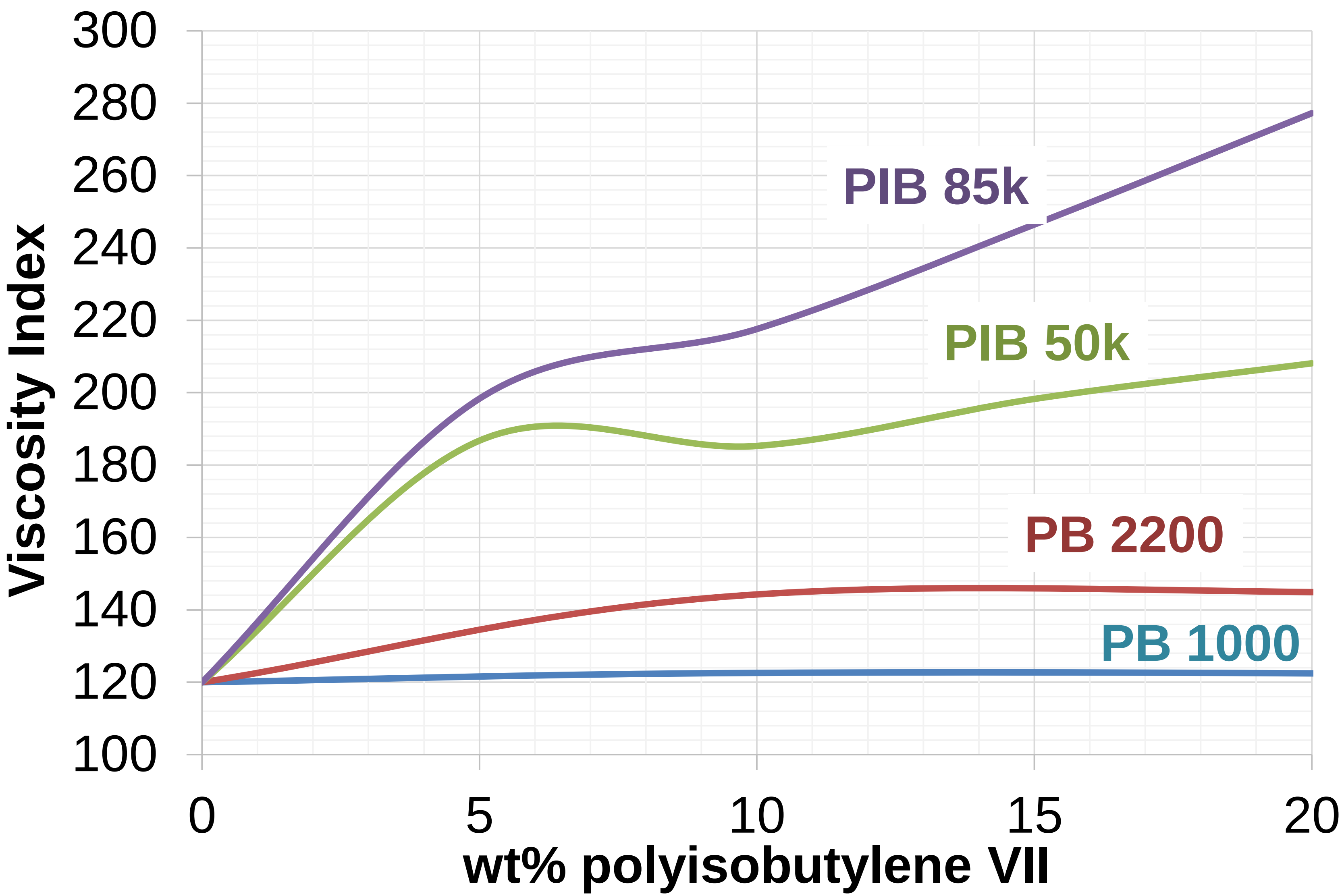
VI Trend – Case 2

- Dilute to semi-dilute transition



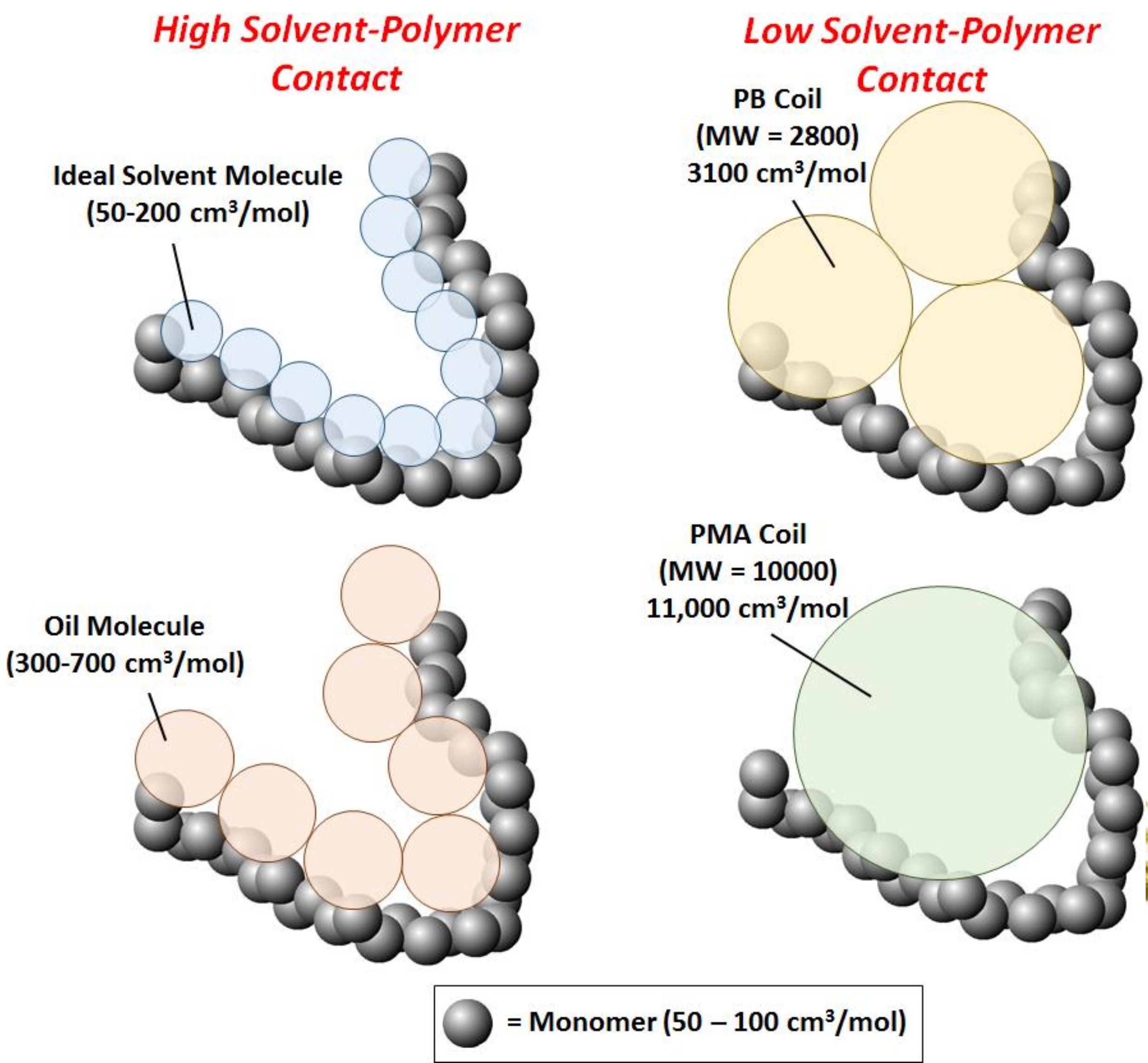
VI Trend – Case 3

- Small polymers don't improve VI – MW drives expansion

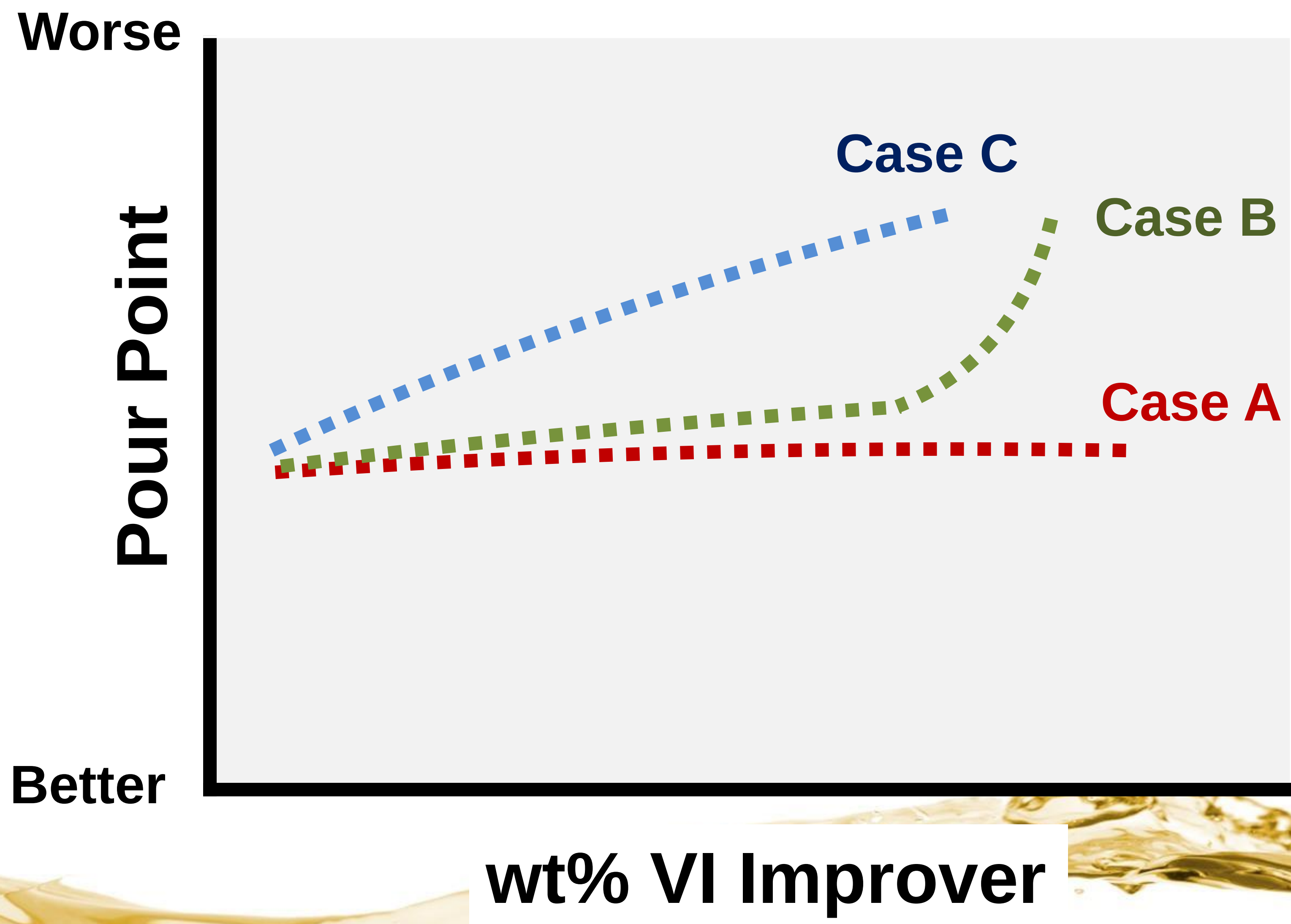


VI Trend – Case 4

- High concentration of low MW polymer replaces solvent



Findings – 3 Pour Point Trends



Relation b/w VI and PP Cases

- Frequency table of VI trend (case 1-4) vs. p.p. trend (case A-C)
- Coincidence suggests similar mechanism

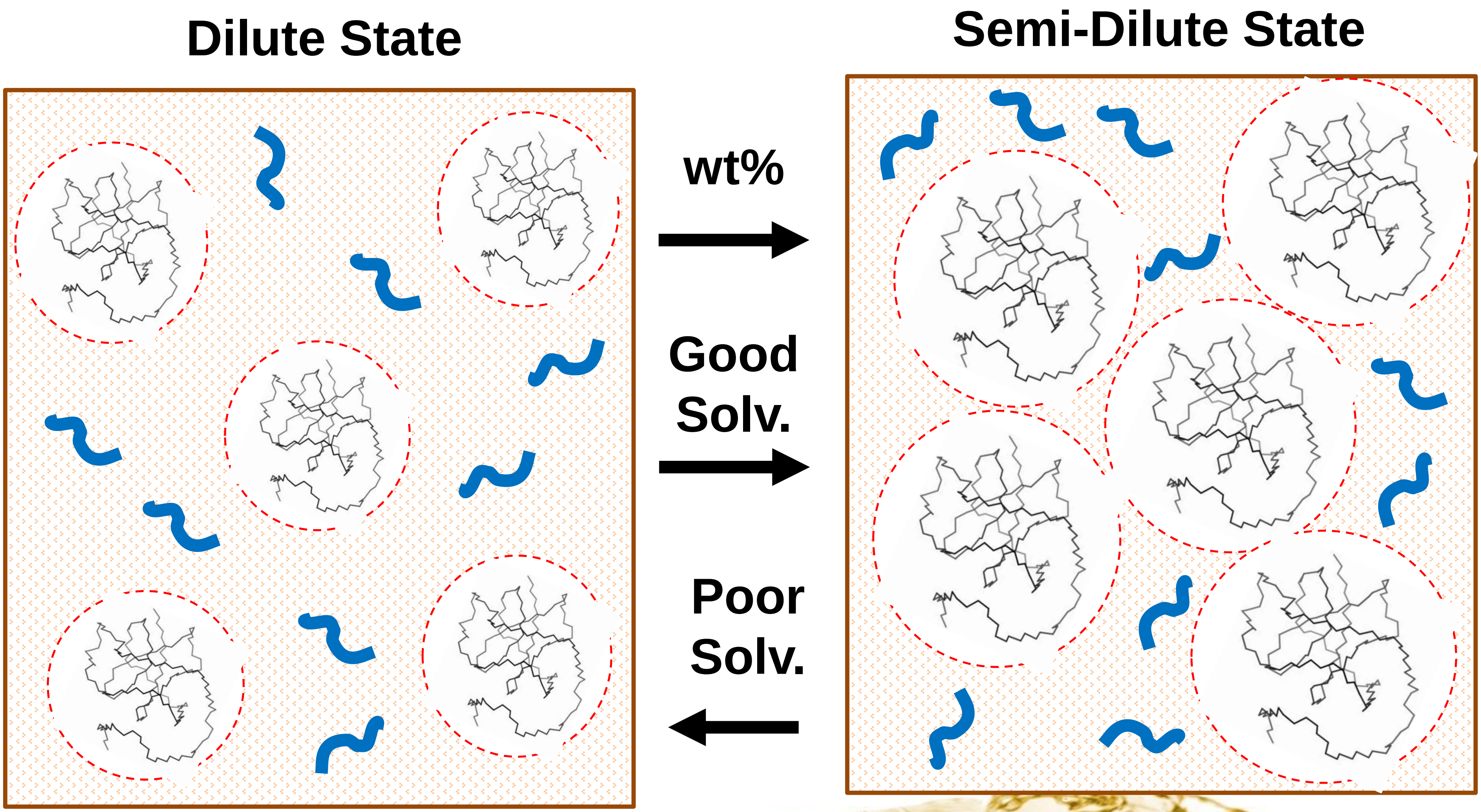
p.p. Case \ VI Case	1	2	3	4
A	2	4	3	<u>9</u>
B	4	4	2	2
C	2	<u>8</u>	1	2

Correlating Case A4 and C2

Summarize what we know:

- Case 4 – decrease in VI with treat
  - Poor solubility, high KV40
- Case A – no change in p.p. with treat (ideal)
- Case 2 – VI increases then decreases with treat
  - Dilute to semi-dilute transition (coil-coil contact)
- Case C – decrease in p.p. with treat

Coil and Wax Networks?



Summary of Findings

- Formulations – simple premise
  - Starting point formulations for Group II / III/ PAO with VI up to 200 and p.p. to -52˚C
- Trends in VI behavior – complex results
  - VI / ;p.p. trends coincide with key transitions in polymer solution theory
  - Transitions occur at wt% dependent on MW of VII
  - Further study at dilute/semi-dilute transition is needed

Conclusions

- Blending VII in Gr. II/III/PAO created wide data for analysis
  - Something for everyone
  - *Appendix A in technical paper*

- VI and p.p. behavior are complex
  - Simplified by grouping into qualitative trends
  - Trends explainable by fundamental principles

- ‘Semi-dilute’ condition responsible for loss of performance
  - Polymer coils in contact lose VI, worsen p.p.
  - How to avoid or mitigate this?

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Suggestions for Better VI

	Trend	Explanation	Suggested Improvements
Case 1	VI increases continuously from low to high treat	Polymer coils expand at high temperature to increase KV100; higher KV100 per KV40 means VI improves	N/A
Case 2	VI increases at low/medium treat; VI decreases or remains constant at high treat	Polymer coil concentration is sufficient for coil-coil interference (semi-dilute behavior)	Replace some wt% of VII with higher viscosity base oil
Case 3	VI unaffected by additive wt%	Polymer expansion is too small to compensate for base oil thinning at high temperature	Use higher MW VII and/or increase initial base oil VI
Case 4	VI decreases continuously	Polymer coils collapse due to high polymer content and/or low oil solvency	Replace some wt% of VII with higher viscosity base oil Increase base oil solvency with low viscosity ester/AN

Suggestions for Better p.p.

	Trend	Explanation	Suggested Improvement
Case A	Pour point unaffected by VII treat level	PB + OCP - Dilution of waxes by PB and polymer wt% is in dilute concentration PB + PMA – collapse of polymer chains prevents polymer coils from accelerating wax formation	N/A
Case B	Pour point worsens at high treat	Similar to Case A; wax from diluent oil in VII at high treat increases total wax content of oil	Use VII with higher wt% polymer or more refined oil Reduce VII use by increasing base oil viscosity
Case C	Pour point continuously worsens from low to high treat	High MW polymer coils begin to form a network in oil (semi-dilute condition) which helps the wax network form at low temperature	Reduce wt% or MW of VII to avoid semi-dilute condition Replace some VII with high viscosity base oil