Viscosity Modifiers: A Fundamental Study

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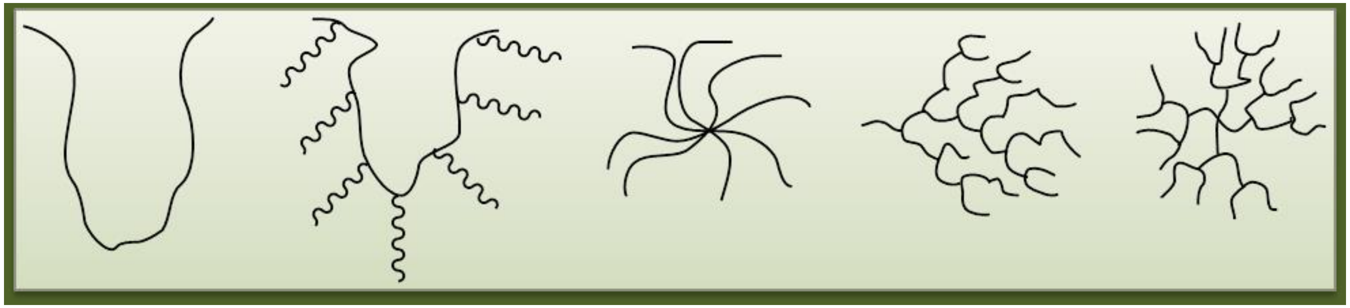
Viscosity Index Improvers and Polymer Architectures



Linear | Comb | Multi-star | Hyper-branch | Dendrimer

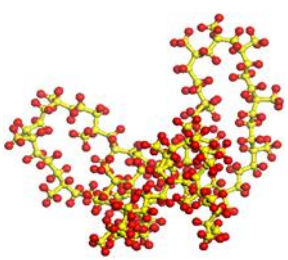
Increasing Viscosity Influence ⟷ Increasing Shear Stability

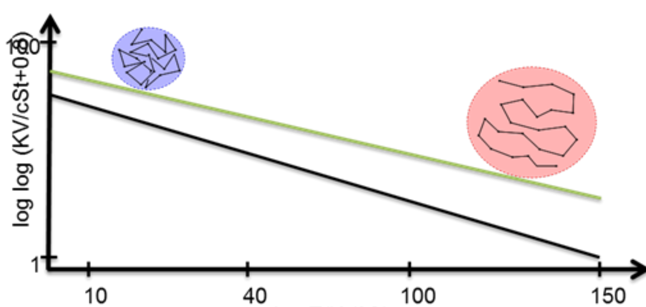
Fact

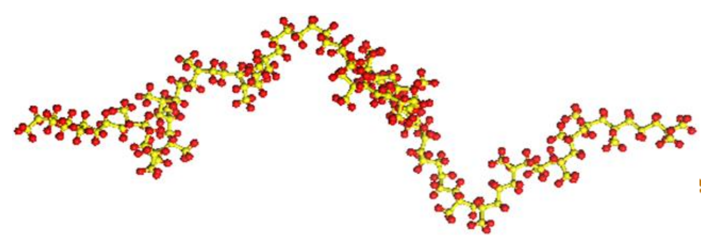
- VMs/VIIs are additives that minimize the change of fluid viscosity with temperature

Popular/empirical belief

- Change in size (Rg, Rh) is the mechanism







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Probing the Mechanism

- Methods used to probe the expansion mechanisms
  - Direct methods
    - Small angle neutron scattering (SANS)
    - Dynamic light scattering (DLS)
    - Triple detection size exclusion chromatography (SEC)
  - Indirect Methods
    - Flory-Fox Equation (change in coil size is directly proportional to change in the intrinsic viscosity)
  - Molecular dynamic simulations (MDS)
    - Simulation structures are created by placing one model VI polymer in an alkane solvent

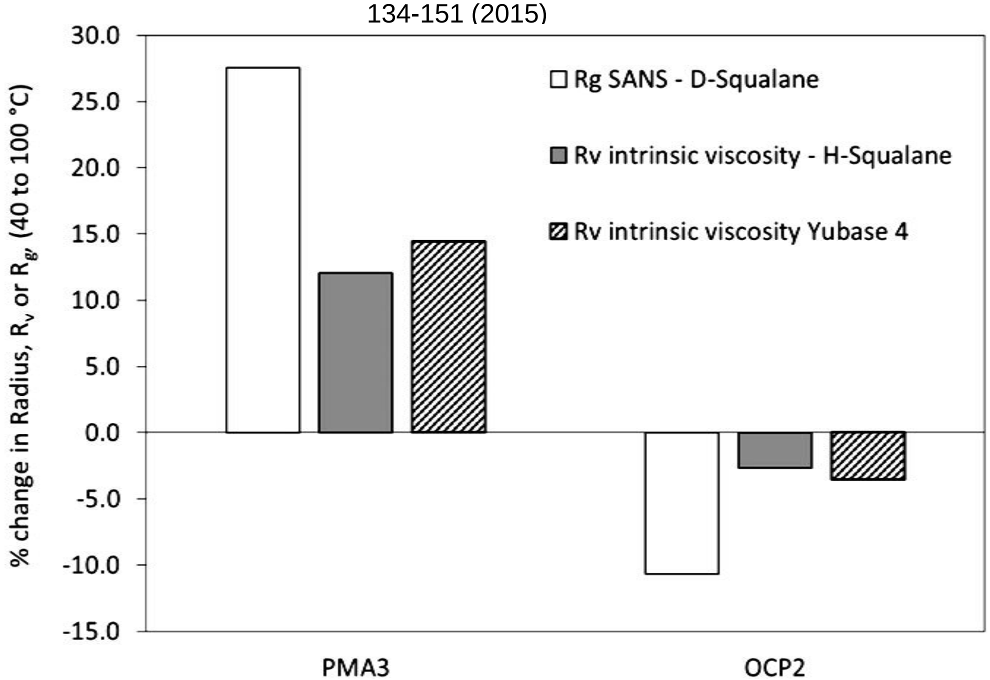
- Requirement: measurements/simulation must be run at 40 and 100 ^{o}C
- Viscosity Index is a measure of the change of fluid viscosity with temperature (based on KV40 and KV100)
- Can we predict VIs with any of the methods?

Prior Studies

Rg data from SANS Experiments

Polymer	Radius of Gyration / nm			
	Dodecane 40^0C	Dodecane 100^0C	Xylene 40^0C	Xylene 100^0C
OCP1	12.4	11.1	11.9	12.4
PMA1	12.8	13.6	12.9	13.4
PMA2	15.5	17.3	17.5	18.1

M.J. Covitch, K.J. Trickett, Advances in Chemical Engineering and Science, (5), 134-151 (2015)



Conclusions

- PAMA aka PMA polymers suggest a coil expansion mechanism
- OCP is actually shrinking upon heating

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DLS studies (PNNL)

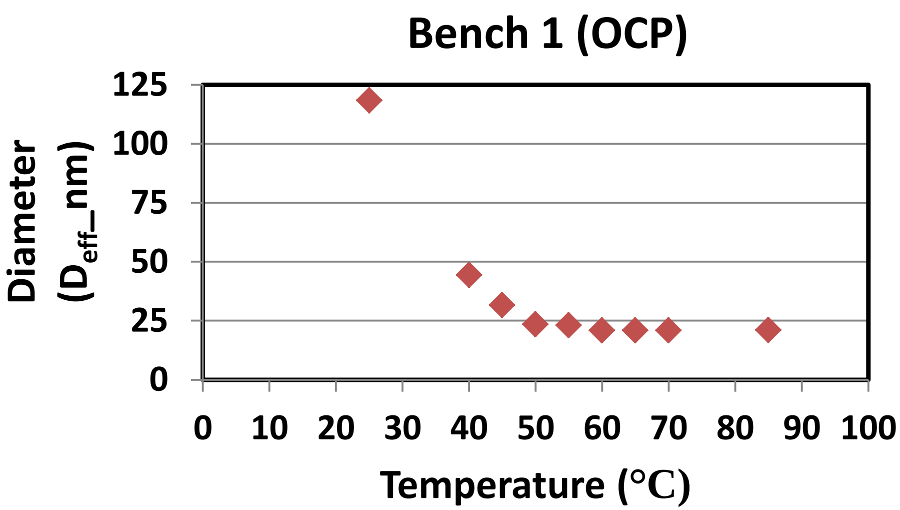
- Polymers were dissolved in hexadecane at 0.5% and then centrifuged to remove large aggregates (6000 nm diameter) to improve the autocorrelation function (ACF)

- The average diameters were determined with temperature corrected solvent viscosities

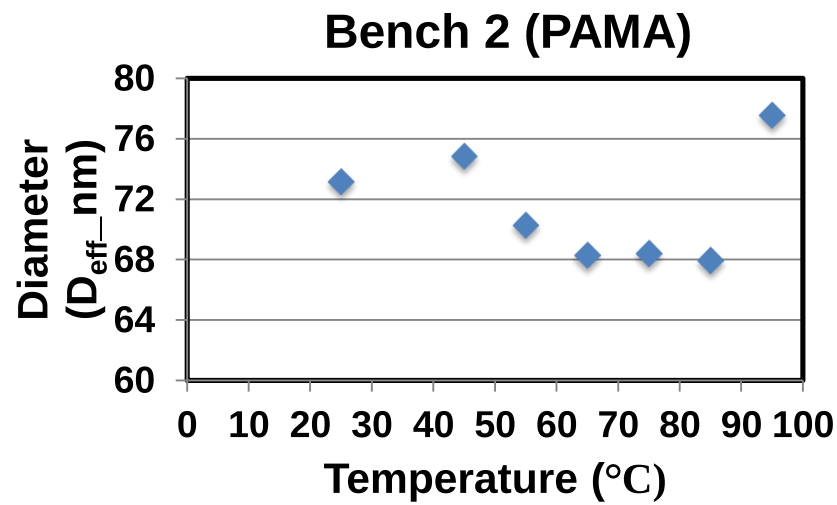
- Temperature sweep from RT to ~90 ^{o}C (software limitation)

- A measurement was taken every 5-10 ^{o}C

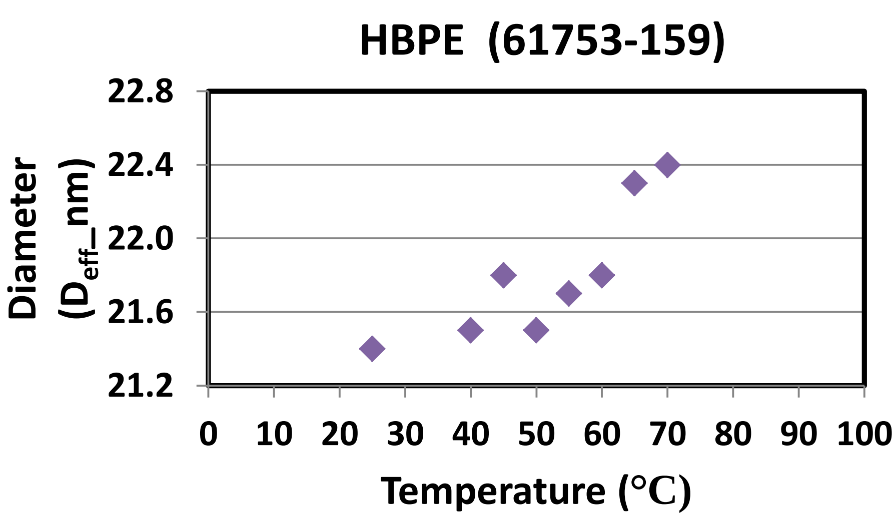
DLS Data



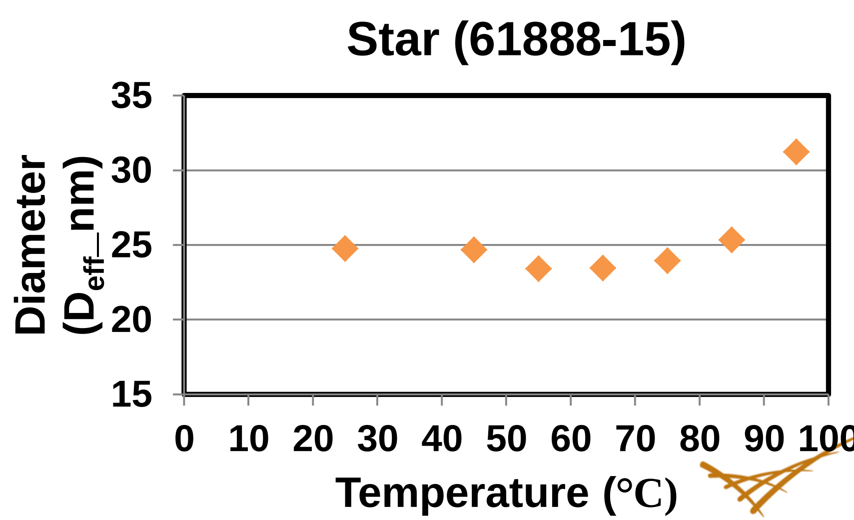
Bench 1 (OCP)
Diameter
(Deff_nm)
125
100
75
50
25
0
0 10 20 30 40 50 60 70 80 90 100
Temperature (°C)



Bench 2 (PAMA)
Diameter
(Deff_nm)
80
76
72
68
64
60
0 10 20 30 40 50 60 70 80 90 100
Temperature (°C)



HBPE (61753-159)
Diameter
(Deff_nm)
22.8
22.4
22.0
21.6
21.2
0 10 20 30 40 50 60 70 80 90 100
Temperature (°C)



Star (61888-15)
Diameter
(Deff_nm)
35
30
25
20
15
0 10 20 30 40 50 60 70 80 90 100
Temperature (°C)

DLS Results

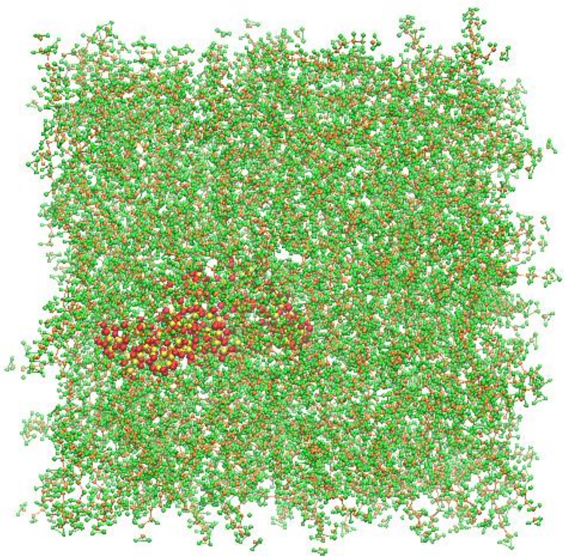
Sample	Diameter low T (nm)	Diameter high T (nm)	Percent change	
Bench 1 (OCP)	118.37 (25°C)	21 (85°C) 20.98 (70°C)	-82.25% -82.27%	VI=188
Bench 2 (PAMA)	73.17 (25°C)	77.58 (95°C) 68.43 (70°C)	+6.03% -6.47%	VI=238
HBPE 61753-159	21.4 (25°C)	22.4 (70°C)	+4.67%	VI=185
Star 61888-15	24.75 (25°C)	31.227 (95°C) 23.94 (70°C)	+26.16% -3.27%	VI=204

- Positive/Negative percent indicates size increases/decreases at higher temperatures
- Bench 1 (OCP) shows large decrease in size throughout the temperature range tested
- Bench 2 (PAMA) shows a moderate decrease in size throughout the temperature range tested, with a slight increase at the highest T
- HBPE shows negligible change with a slight increase in size from low to high T
- Star polymer shows a high increase in size from low T to high T

Molecular Dynamic Simulations (UC Merced)

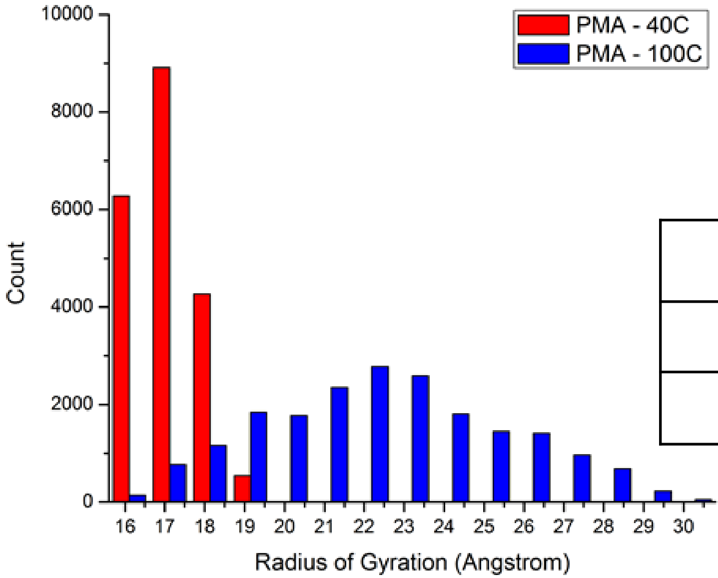
- Individual polymers are placed in dodecane (solvent mimic for oil)
- Characterization simulation at 40 and 100 ^oC
- Radius of gyration (R_g) information is collected for 100ns of simulation time
- Frequency histograms are plotted with the collected R_g data
- %change is estimated using the following equation:

$$\%\text{change} = \frac{(\text{mean\_R}_{g}\text{\_}100^{0}\text{C} - \text{mean\_R}_{g}\text{\_}40^{0}\text{C})}{\text{mean\_R}_{g}\text{\_}40^{0}\text{C}}$$



OCP in dodecane

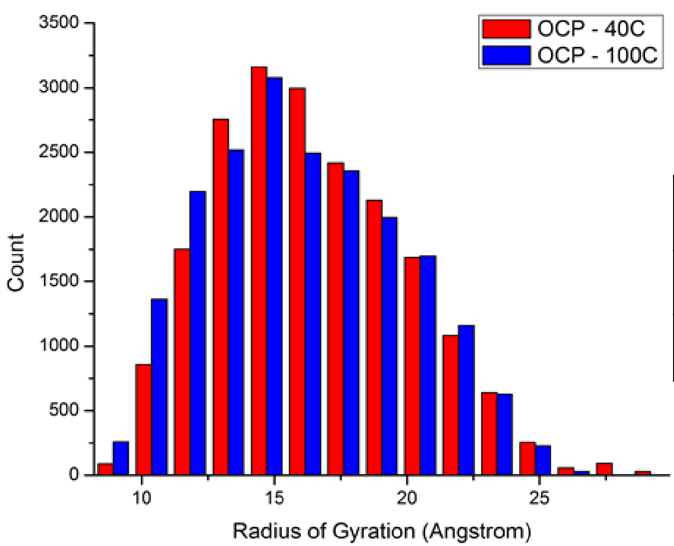
Rg Distribution for Various Structures



PAMA	Mean	Stdev
40 ºC	17.1	0.7
100 ºC	22.5	3.0

Agrees with DLS

↑ Significant size increase with temperature

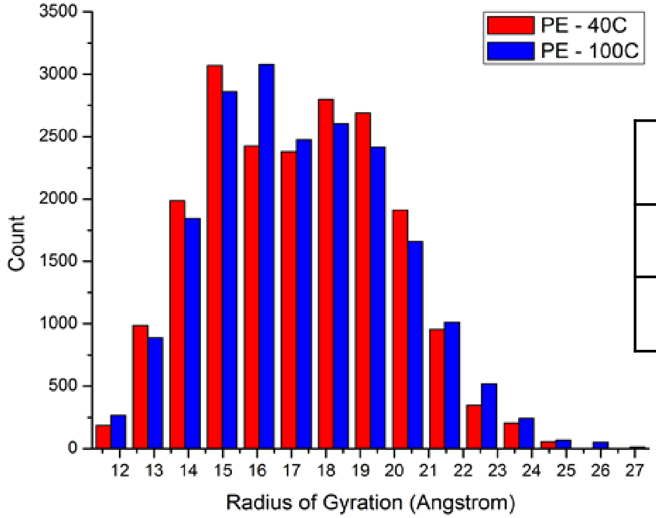


OCP	Mean	Stdev
40 ºC	16.5	3.6
100 ºC	16.1	3.7

No agreement with DLS

↓ Marginal size decrease

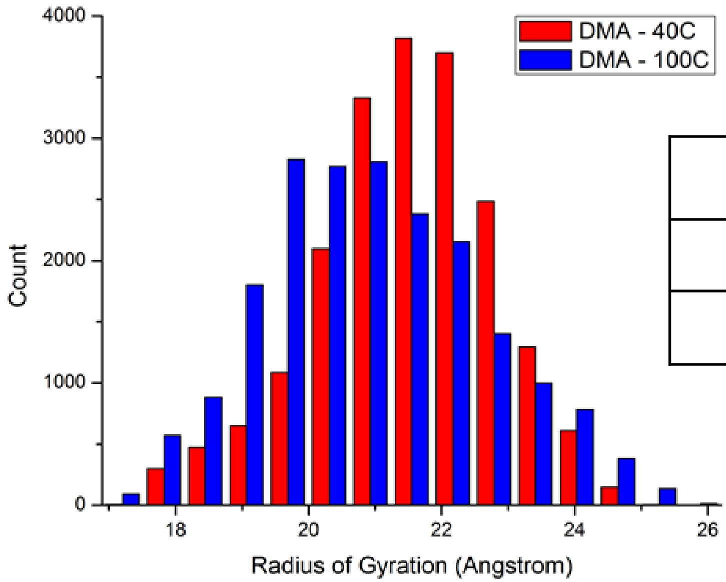
Rg Distribution for Various Structures



HBPE	Mean	Stdev
40 ºC	17.2	2.6
100 ºC	17.3	2.7

= No change in size with increasing temperature

Agrees with DLS



Star	Mean	Stdev
40 ºC	21.5	1.3
100 ºC	21.0	1.6

Slight decrease in size with increasing temperature

No agreement with DLS

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MD Simulations Summary

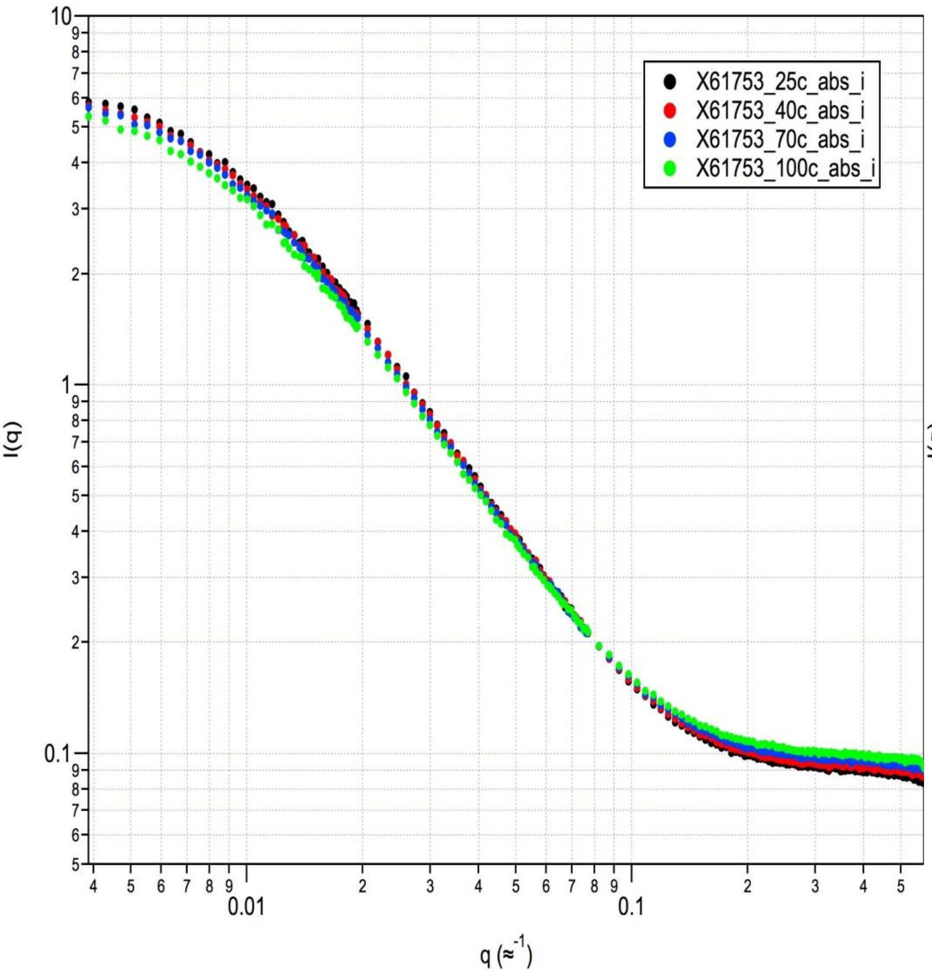
- PAMA shows a significant increase in Rg with temperature
- OCP and Star show a marginal decrease in Rg
- HBPE remains the same

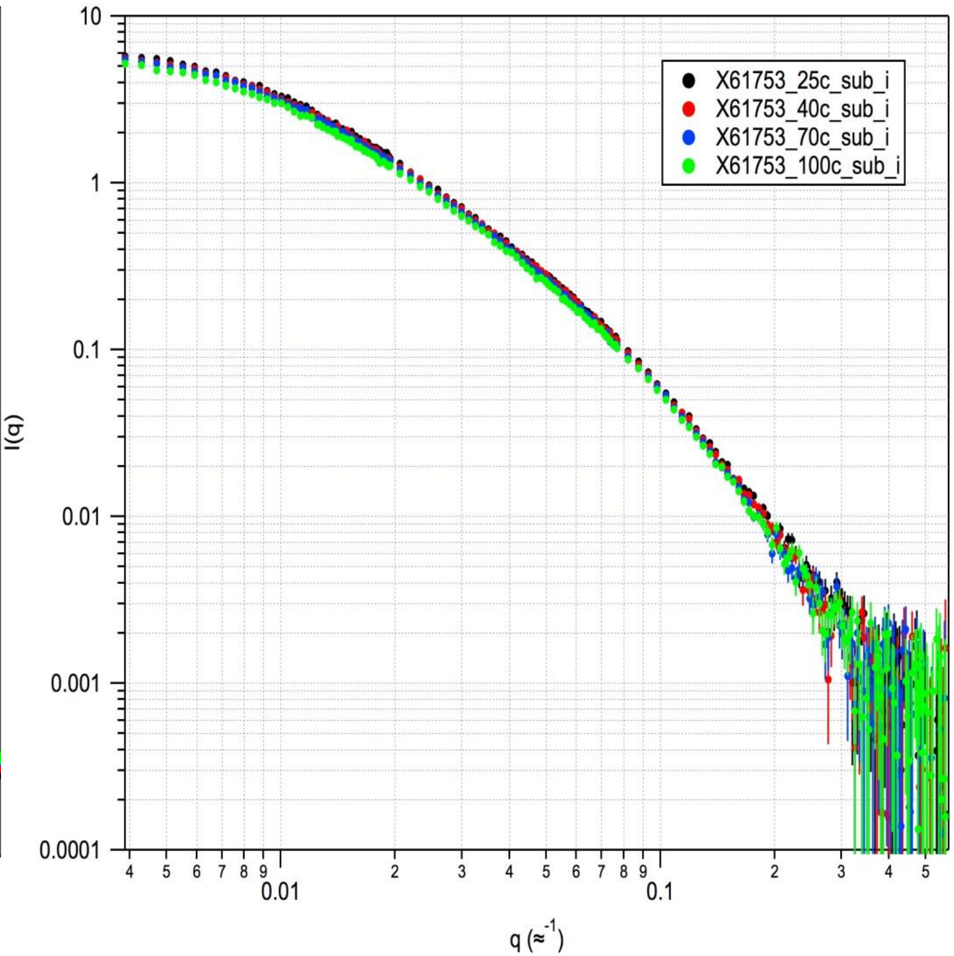
Mean	PAMA	OCP	HBPE	Star
40 ℃	17.1	16.5	17.2	21.5
100 ℃	22.5	16.1	17.3	21.0
% Change	31.5	-2.2	0.18	-2.4

SANS Measurements (NIST)

- NG-7 -- 30-m SANS instrument
- Temperature sweep: 25, 40, 70 and 100 ^{o}C
- Samples ran in deuterated hexadecane-d_{34} (good base oil mimic)
- Analogs: Bench 1 (OCP), Bench 2 (PAMA), 61888 (Star), 61753 (HBPE-hyperbranched)
- Constant concentration of 0.5% (w/w) for all
- SANS profile plots generated: scattering vector Q, versus scattering intensity I(Q)
- Fit the data to established models (Porod exponent, n)

SANS Raw Data for HBPE





Example of fitting curves for HBPE at 25 ^oC

Fit to PolymerExclVol, 12/3/15, 11:34:01 AM

Data file: X61753_25c_abs

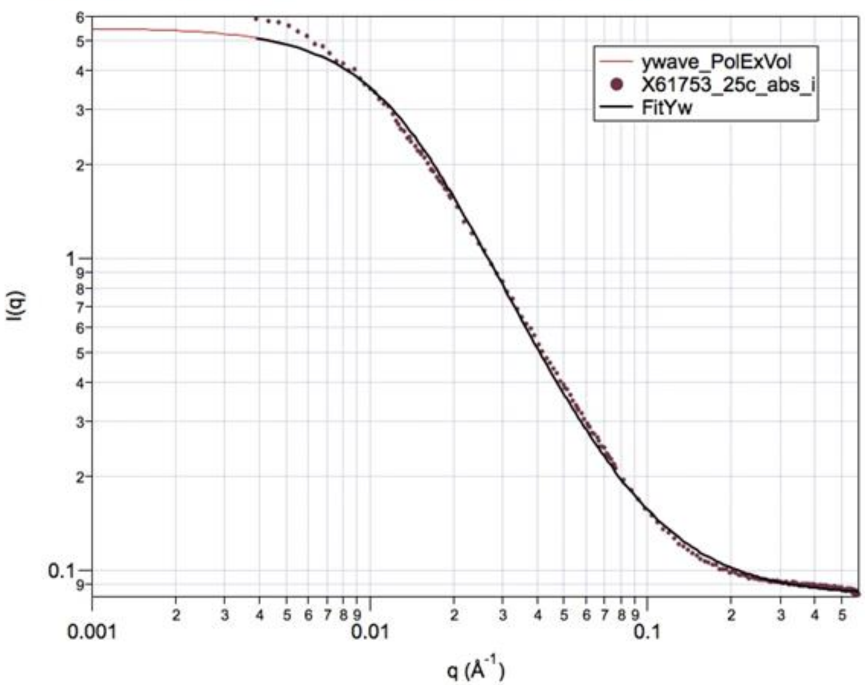
Scale Factor I0 =	5.39162	±	0.0287683
radius of gyration Rg [A] =	123.584	±	0.533071
Porod exponent m =	1.97578	±	0.00323221
Incoh Bgd (cm-1) =	0.0828205	±	8.12604e-05
Incoh Bgd (cm-1) =	0.08	±	0

chisq = 3542.88

Npnts = 202 Sqrt(X^2/N) = 4.18796

Fitted range = [0,201] = 0.003887 < Q < 0.5754

FitError = No Error **FitQuitReason = No Error**



Fit to CorrLength, 12/3/15, 4:19:20 PM

Data file: X61753_25c_abs

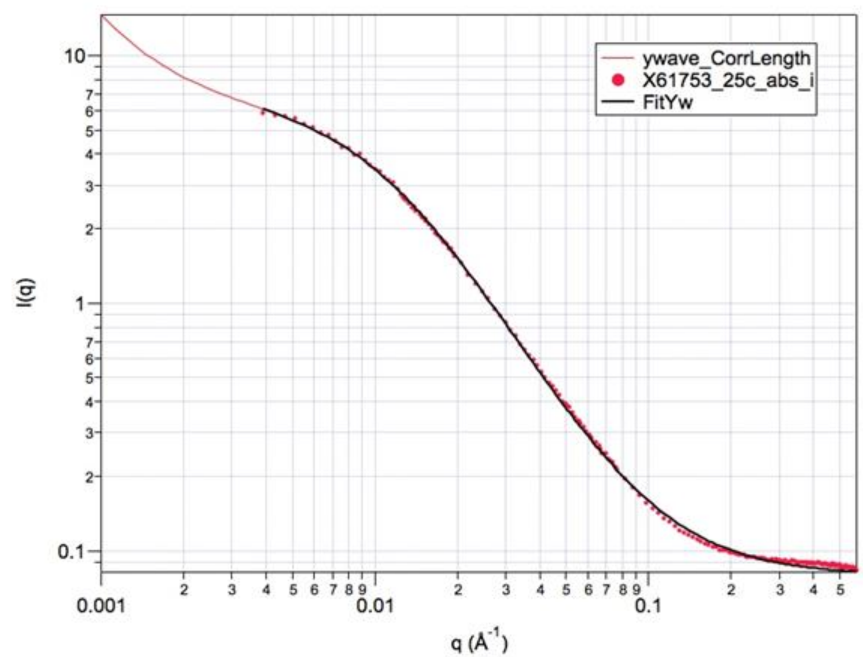
Porod Scale =	1.14454e-05	±	0.000242497
Porod Exponent =	1.95558	±	3.54575
Lorentzian Scale =	6.1567	±	1.20991
Lor Screening Length [A] =	92.6952	±	5.78919
Lorentzian Exponent =	1.95461	±	0.0435962
Bgd [1/cm] =	0.08	±	0

chisq = 4191.13

Npnts = 202 Sqrt(X^2/N) = 4.55501

Fitted range = [0,201] = 0.003887 < Q < 0.5754

FitError = No Error **FitQuitReason = No Error**



SANS - Radius of Gyration Values

- Polymer excluded volume fitting function
- Good fit for Bench 1 (OCP) and Bench 2 (PAMA)
- Porod exponent = 3, would mean collapsed polymer coil

Sample	Rg	Porod
bench1_25c.abs	**143**	**1.75**
bench1_100c.abs	**135**	**1.71**
HBPE_25c.abs	**124**	**1.98**
HBPE_100c.abs	**126**	**1.93**
Star_25c.abs	**95**	**2.0**
Star_100c.abs	**105**	**1.9**
bench2_25c.abs	**290**	**1.85**
bench2_100c.abs	**258**	**1.72**

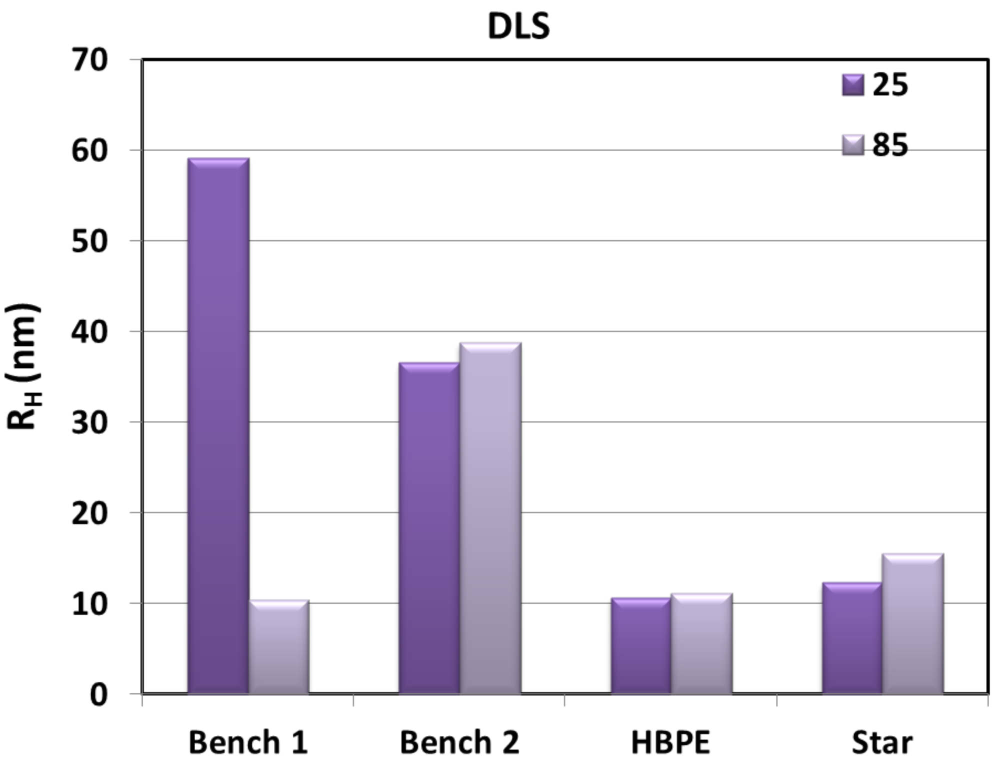
OCP ↓

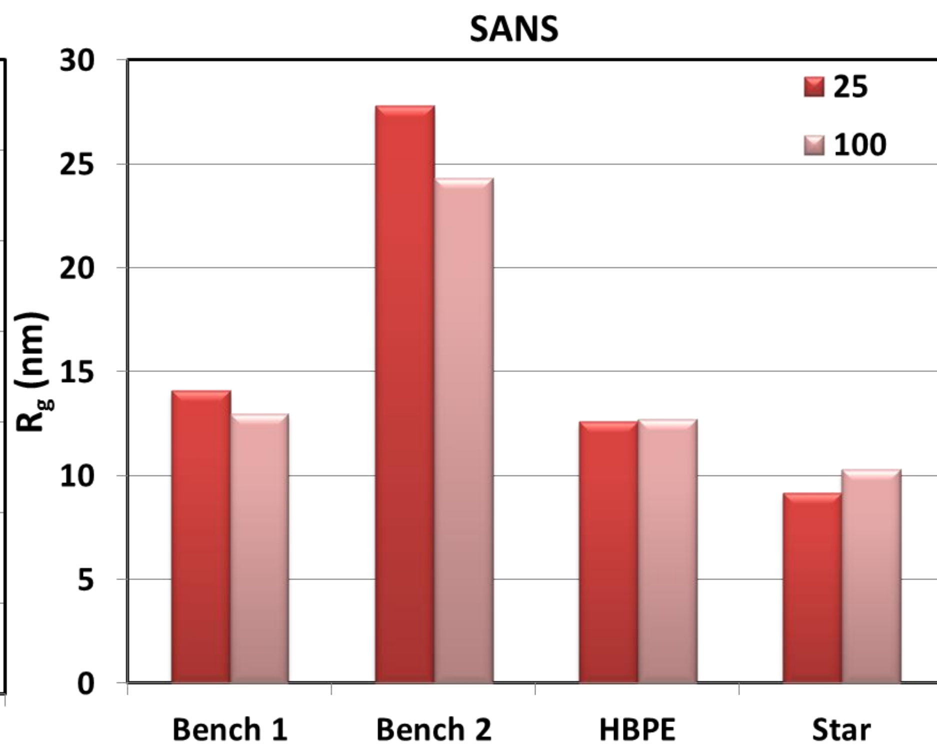
HBPE ↑ =

Star ↑

PAMA ↓

SANS and DLS comparison





- Bench 1 (OCP), star and hyperbranched show same trend
  - OCP first point may be an outlier
- Bench 2 - PAMA shows opposite trends
  - Anomalous behavior in the range studied

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Summary- Temperature Effects on Polymer Size

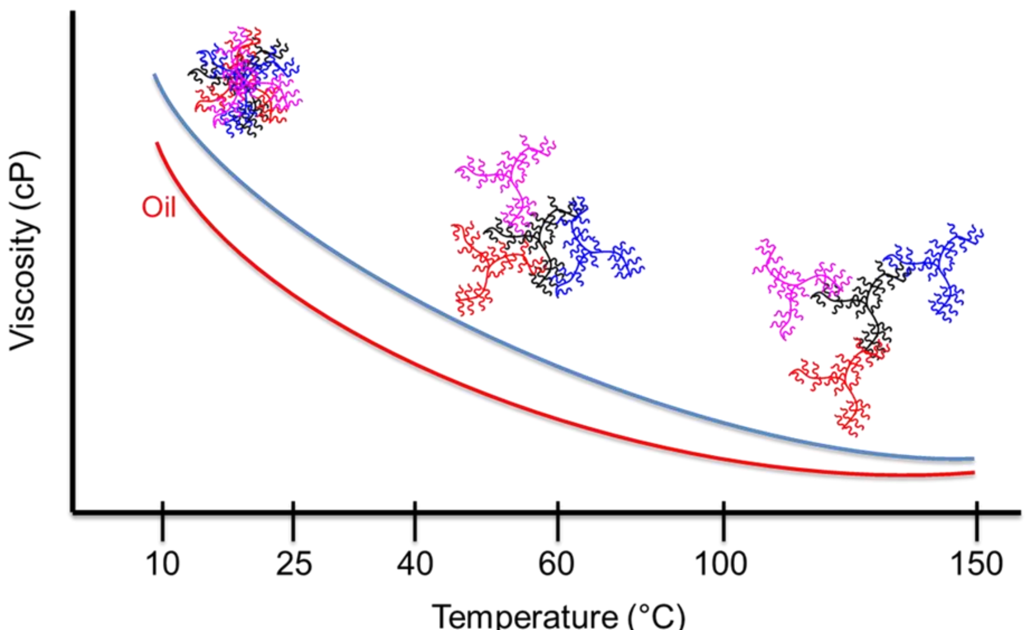
- Not all methods agree
- Experimental methods (DLS and SANS) agree with exception of PAMA

Method	PAMA	OCP	HBPE	Star
SANS (Rg)	−	−	=	+
DLS (Rh)	+	−	=	+
MD (Rg)	+	− Marginal	=	− Marginal

	VI=238	VI=188	VI=185	VI=204

Conclusions

- Can we predict polymer behavior (VI) with SANS, DLS, MD?
- The short answer is NO, at least not fully
- Due to more complex interactions and effects
  - Inter and intra-molecular interactions not accounted for
  - Shear resistance
  - Polarity
  - Molecular weight (huge influence on viscosity)
  - Topology and architecture



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Conclusions Cont'd

If multiple methods point in the same direction, size changes with temperature of can be predicted

However, VI cannot be predicted

OCP data agrees with literature

PAMA data is in disagreement

Acknowledgements

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  - DOE: Kevin Stork
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- UC Merced
  - Dr. Ashlie Martini
  - Uma Shantini Ramasamy
- Evonik
  - David Gray, JoRuetta Ellington
- Afton Chemical
  - Dr. Jeff Guevremont

Extra data

- Fit correlations for analogs with Porod exponent ~2

Sample	Corr Leng	Porod	Bgnd
61753_25c.abs	93	1.96	.08
61753_100c.abs	93	1.94	0.09
61888_25c.abs	56	2.0	.08
61888_100c.abs	68	2.0	.09

SANS Data

Sample	Scale Fact	Rg	Porod	Bgnd
bench1_25c.abs	3.1	**143**	1.75	.09
bench1_100c.abs	2.7	**135**	1.71	.1
bench1_25c.sub	2.9	141	1.83	-.001
bench1_100c.sub	2.5	130	1.85	-.001
61753_25c.abs	5.4	**124**	1.98	.08
61753_100c.abs	4.9	**126**	1.93	.09
61753_25c.sub	5.3	126	2.0	-.004
61753_100c.sub	4.8	127	1.98	-.004
61888_25c.abs	5.0	**95**	2.0	.08
61888_100c.abs	4.5	**105**	1.9	.09
61888_25c.sub	4.7	92	2.1	-.004
61888_100c.sub	4.2	103	2.0	-.004
bench2_25c.abs	47	**290**	1.85	.09
bench2_100c.abs	22	**258**	1.72	.1
bench2_25c.sub	45	278	1.9	-.004
bench2_100c.sub	20	243	1.8	-.004