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Unraveling Convoluted Structural Effects on Slow Crack Grow (SCG) Resistance using the Primary Structure Parameter (*PSP2*)

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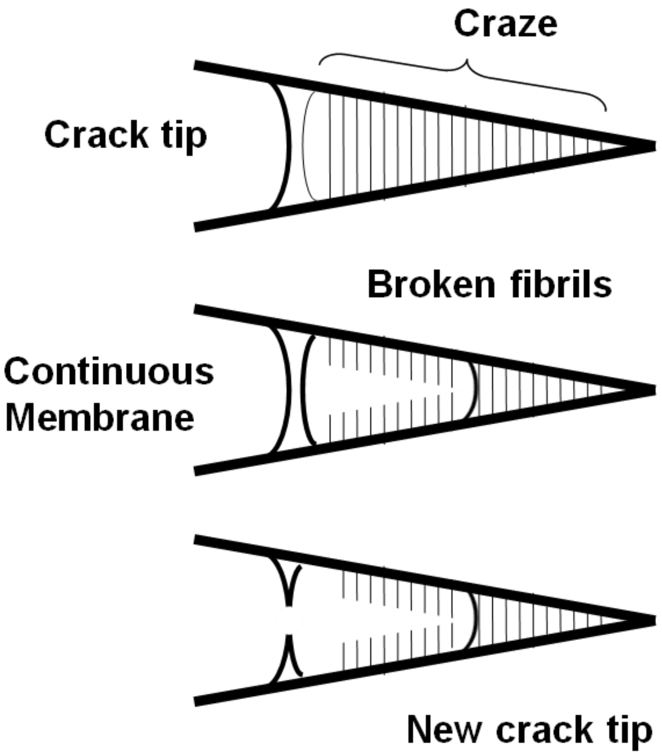
Presentation Overview

- Outline a general research approach and describe a method that estimates SCG resistance from a single primary structural parameter (*PSP2*)
- Illustrate how various structural changes affect SCG using *PSP2* values as a proxy for SCG resistance and digital MWD and SCB data
- Give summary/highlights

What is stress crack growth?

Three major events in stress crack failure

- **Visco-elastic creep**
  - Irreversible stretching of molecular structure
- **Crack initiation**
  - Molecular disentanglement and/or chain breaking
- **Crack propagation**
  - Initially has a 'brittle' characteristic
  - May transition to 'ductile' mode as crack grows



Simplified resin testing cycle

Polymer microstructure and crystallinity

Small scale resin tests

Tensile Tests
- Natural Draw Ratio (NDR)
- Strain Hardening Modulus <G_p>

ESCR
PENT
SP-NCTL

Large scale pipe tests

Notched pipe test (NPT)
Cone testing, etc.

Field performance

Research approach

Primary structure
Chemical composition
MW, MWD
Topology

model →

Tertiary structure (morphology)

↓ ***Correlate using a single value (PSP2)***

Stress Crack Growth resistance as estimated by short term resin tests

Proxy for SCG resistance of fabricated articles (e.g., pipe, bottles, etc.)

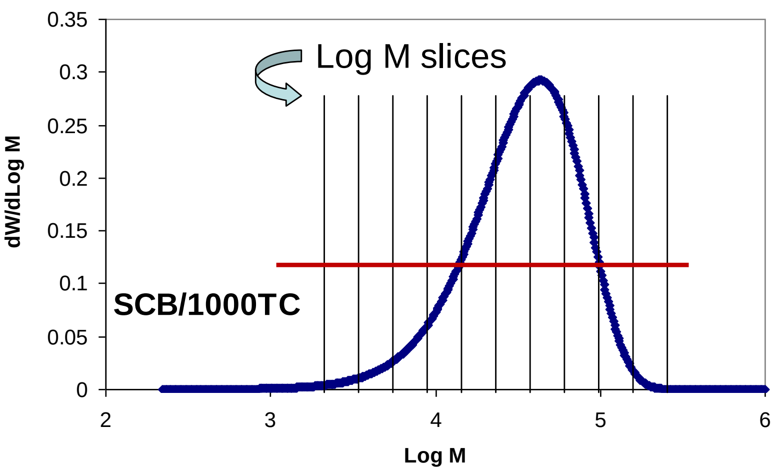
Density (slow cooled) from MWD and SCBD data

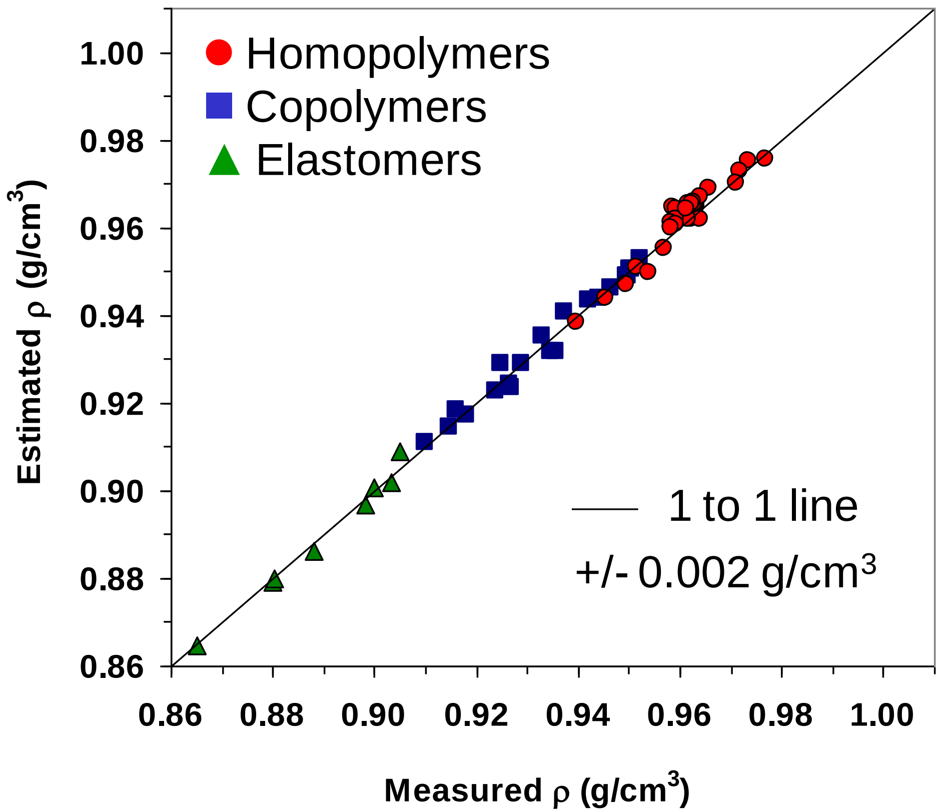
(DesLauriers & Rohlfing , Advances in Polyolefins 2009)

Correlations developed from homopolymer and copolymer samples…

$$1/\rho = 1/\rho_H + \Delta\rho_{SCB}$$

$$1/\rho = \sum (w_i / \rho_i) = \int \frac{1}{\rho}\left(\frac{dw}{dLogM}\right) dLogM$$



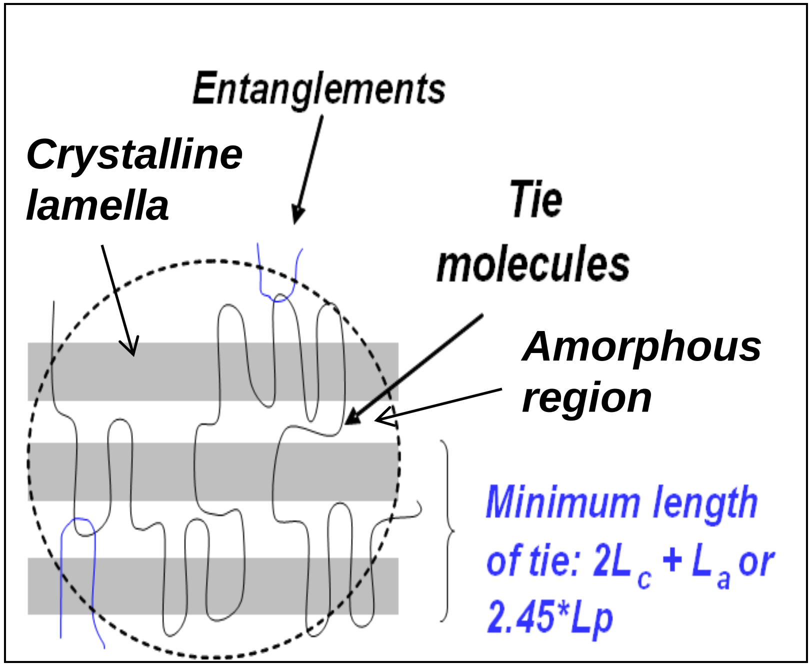


…density on a slice by slice basis added up to obtain whole polymer density

Other estimations used to calculate PSP2 via MWD integral methods

Estimate the following changes per MW slice….

1. Density (slow cooled sample)
2. Incorporate the concept of tie molecules



**Y. L. Huang & N. Brown, J. Mat. Sci., 1988, 23, 3648*

Other estimations used to calculate PSP2 via MWD integral methods

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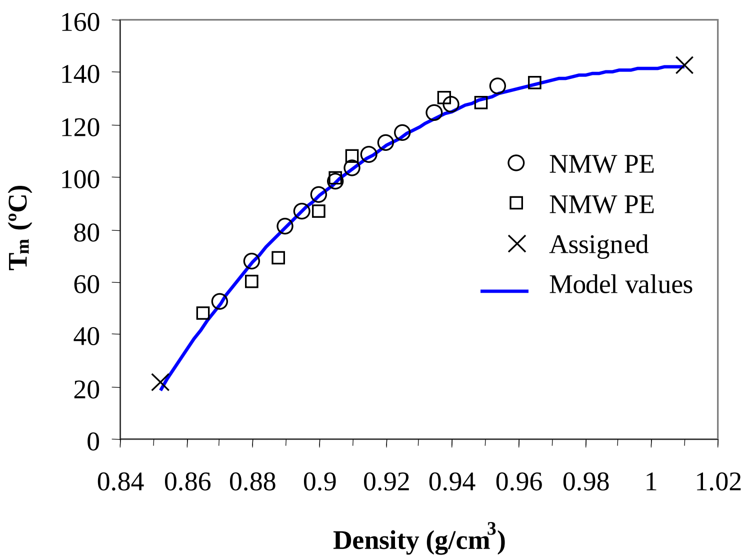
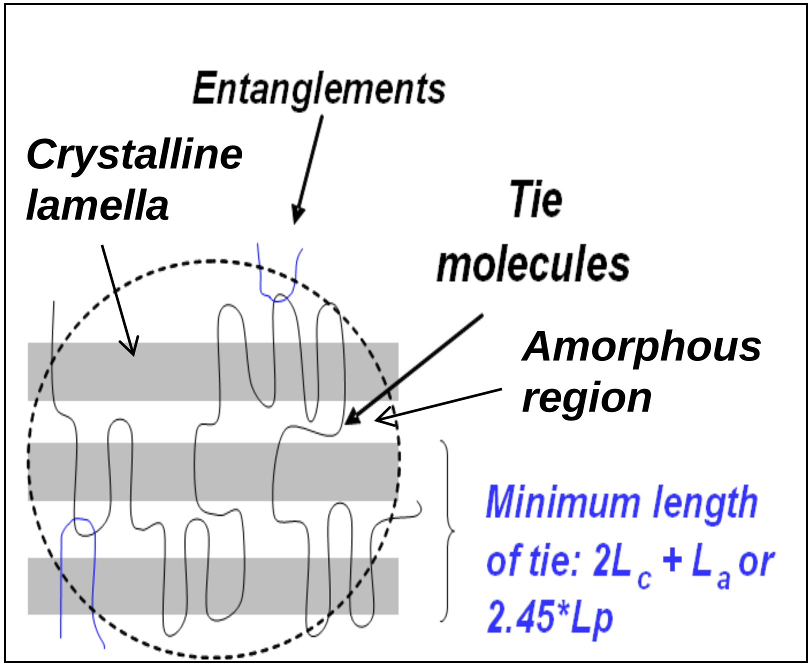
Estimate the following changes per MW slice….

1. Density (slow cooled sample)

2. Incorporate the concept of tie molecules
   a) T_m (°C) from density





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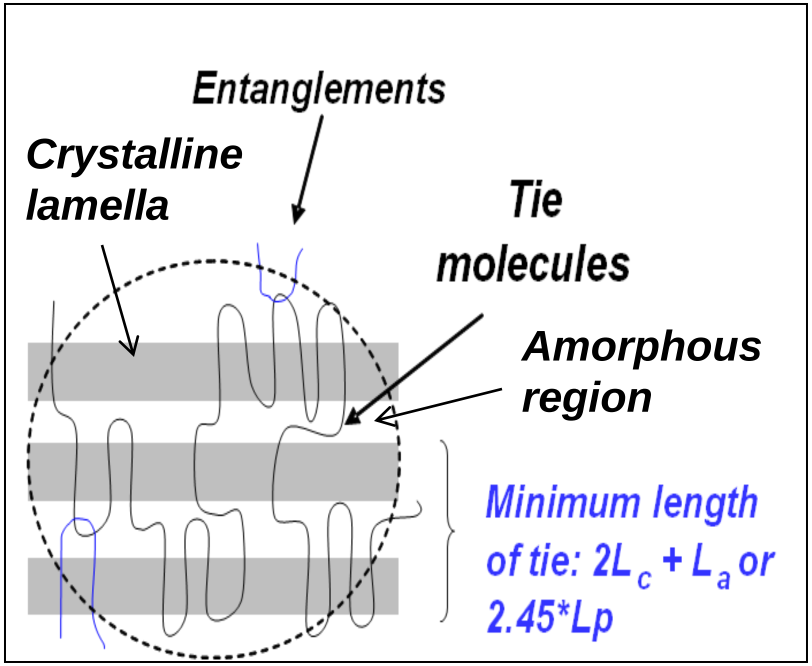
Other estimations used to calculate PSP2 via MWD integral methods

Estimate the following changes per MW slice….

1. Density (slow cooled sample)

2. Incorporate the concept of tie molecules
   a) T_m (^oC) from density
   b) $2L_c + L_a$ (from known eqs.)
   c) Probability of tie molecules *(P_{TM})* formation*

3. Account for weight fraction effects (both MWD and SCBD)



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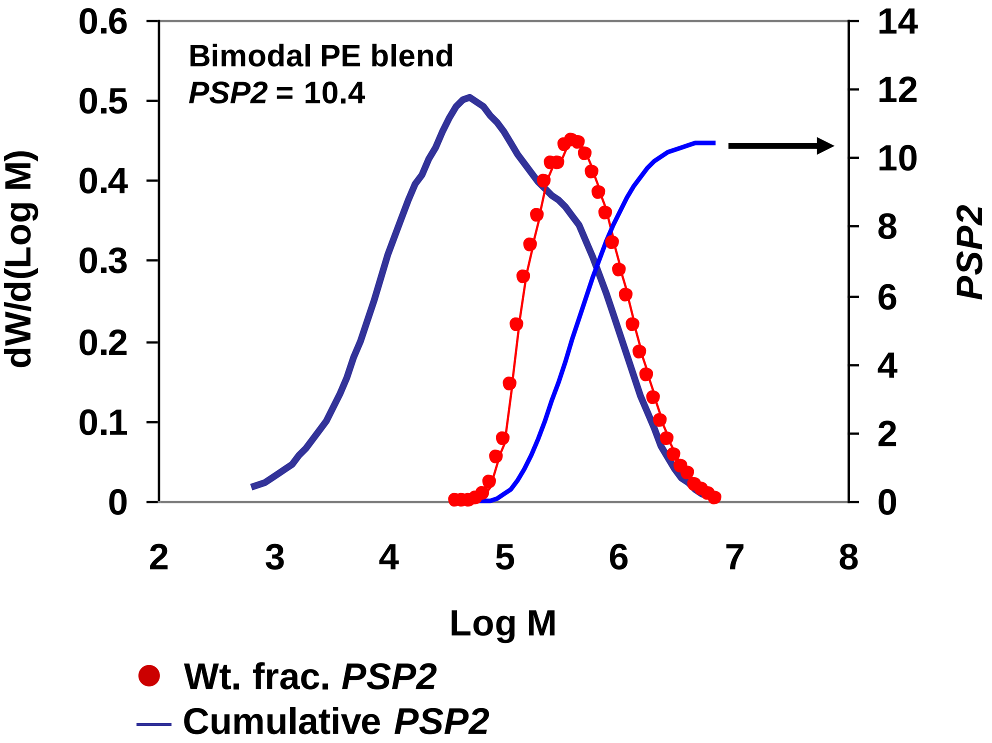
PSP2 calculations and reported values

(DesLauriers & Rohlfing, Macromolecular Symposia Volume 282, Issue 1, pages 136–149, August 2009)

The quantity (dW/dlog M * P_{TM}*100) vs. Log M summed over the MWD *defines the PSP2 value …*



*Tie Molecule Probability**

$$P = \frac{1}{3}\frac{\int_L^\infty r^2 \exp(-b^2r^2)dr}{\int_0^\infty r^2 \exp(-b^2r^2)dr}$$

Where:

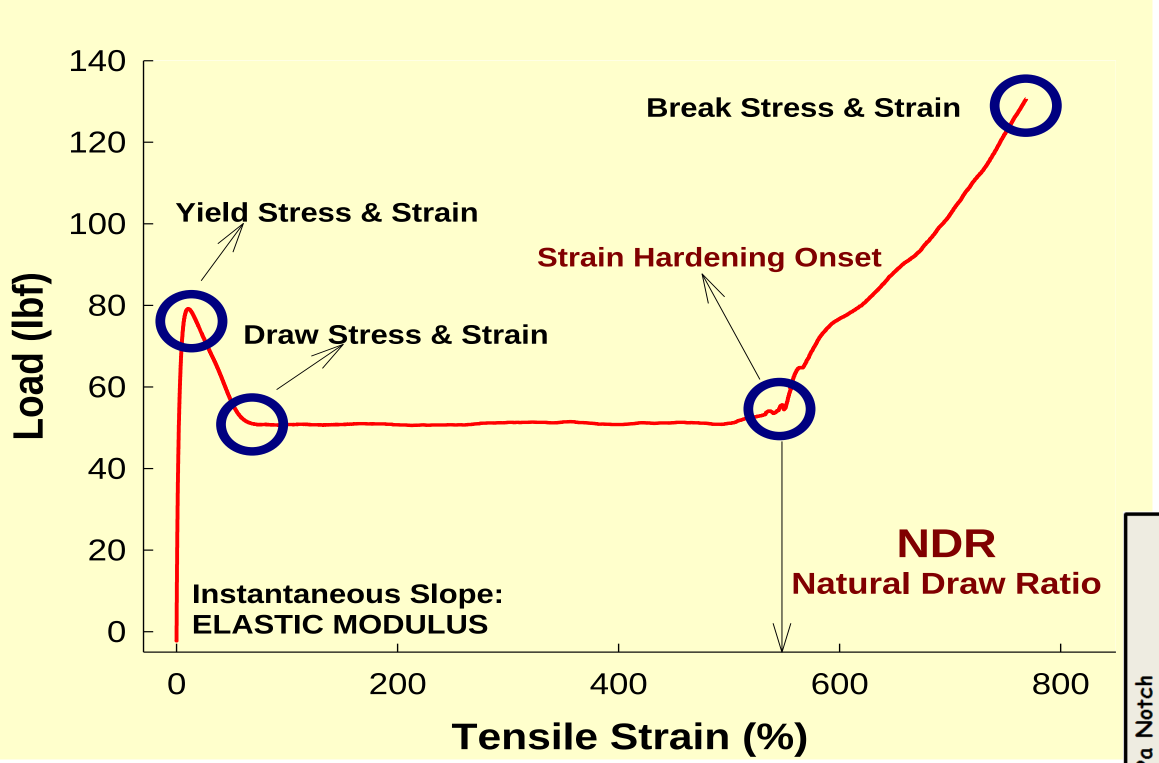
$$b^2 = \frac{3}{2\bar{r}^2}$$

$$\bar{r}^2 = 0.159\left(\frac{M}{14}\right)$$

$$P_{TM} = \frac{1}{3}\left(1 - \frac{4b^3}{\sqrt{\pi}}\int_0^L r^2 \exp(-b^2r^2)dr\right)$$

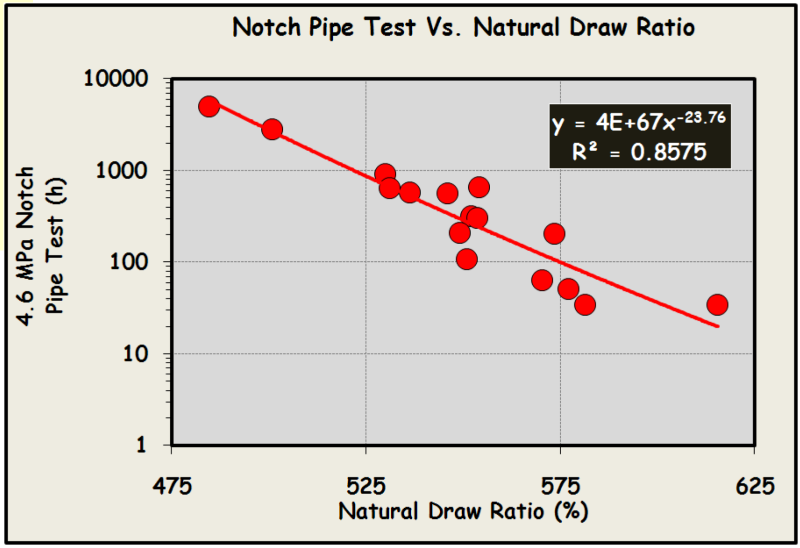
***R. M. Patel, K. Sehanobish,P. Jain, S. P. Chum, G. W. Knight, J. Appl. Poly. Sci. 1996, 60, 749.**

Small-scale resin tests



Tensile NDR

*Relationship between Notched Pipe Test and NDR**

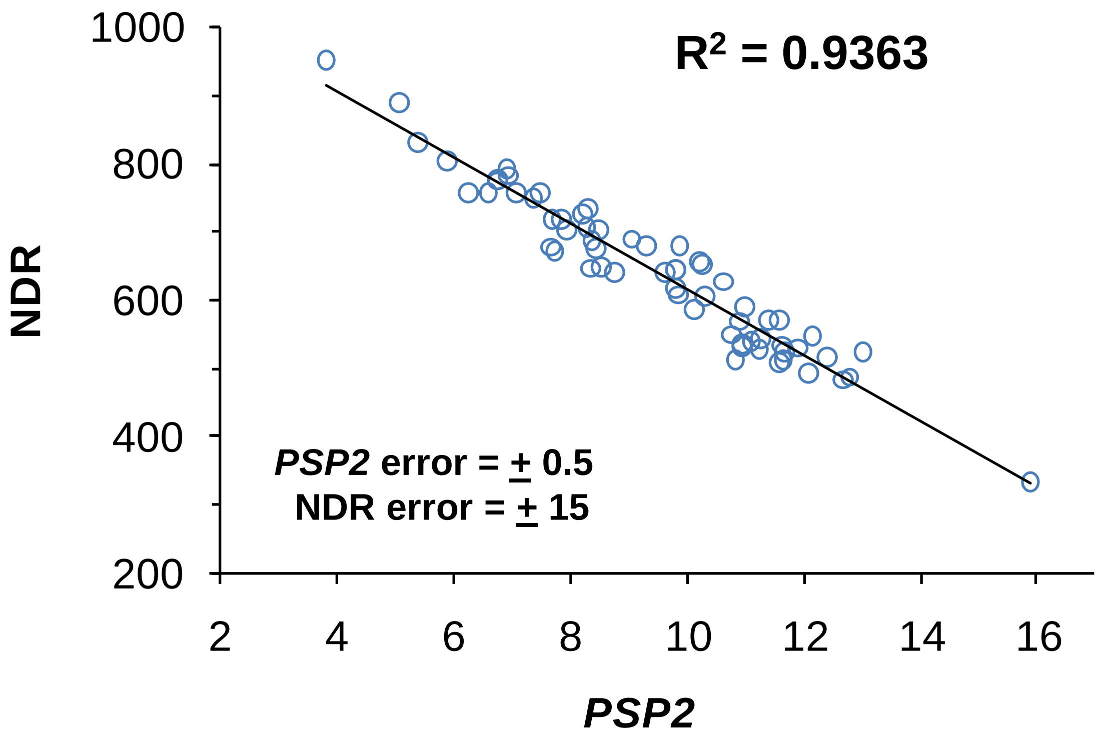


**Data from Sukhadia et. al., Proceeding of Plastics Pipes XV Conference. Vancouver, Canada, Sept. 2010*

Relationship between NDR* (i.e., onset of strain hardening) and PSP2

- **65 resins measured**
  - M_w 80 - 550 kg/mol
  - 2.1 – 50 PDI
  - 0.916 - 0.965 g/cm^3
  - monomodal and bimodal samples

- **Similar correlations found in other SCG resin tests**
  - PENT
  - SP-NCTL
  - ESCR



*Natural Draw Ratio

Limitations & Capabilities of PSP2 method to estimate SCG process

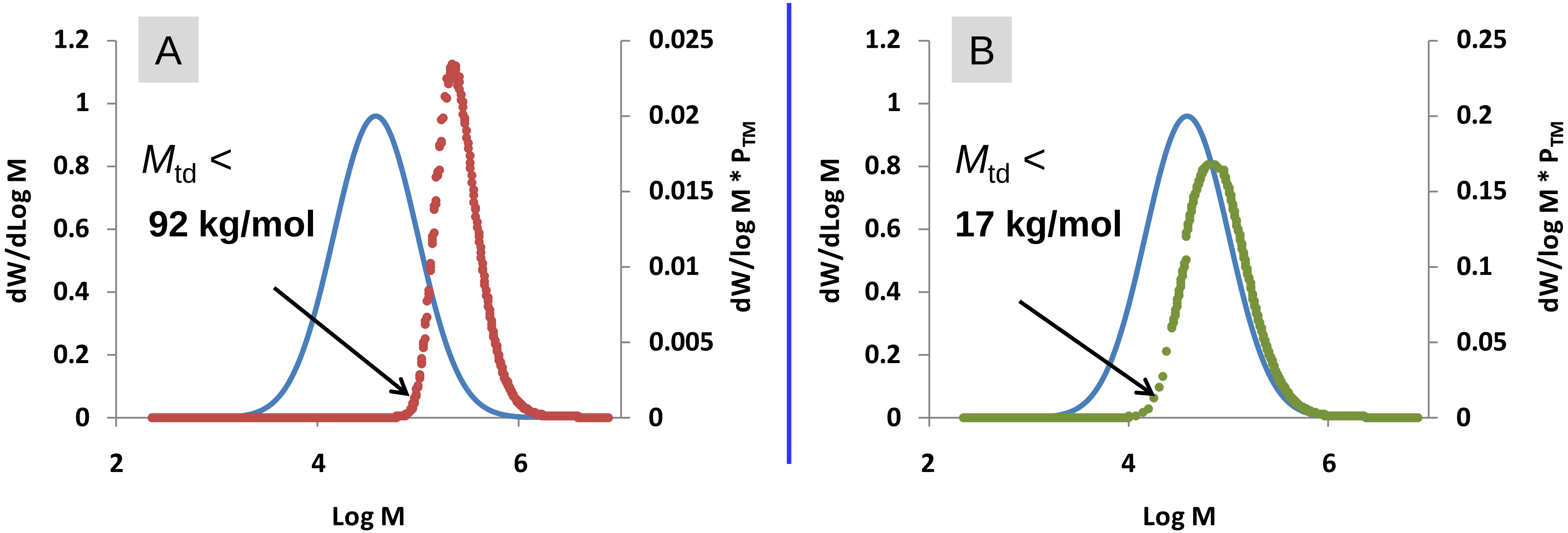
Limitations

- First approximation for MW effects on density (i.e., ends of MWD)
- Simplified two phase model used for semi-crystalline PE
- Entanglements partially captured
- Average values used for SCB, T_m, etc. per MW slice
- Branch type, lamellar orientation and process conditions not considered

Capabilities

- Captures MW, SCB, MWD and SCBD effects
- Qualitatively consistent with known structure/property trends
- Good correlations to SCG via small scale resin tests
- Can be used to estimate SCG for any type of PE resin with $\rho > 0.90$ g/cm^3 (experimental **or digital**)

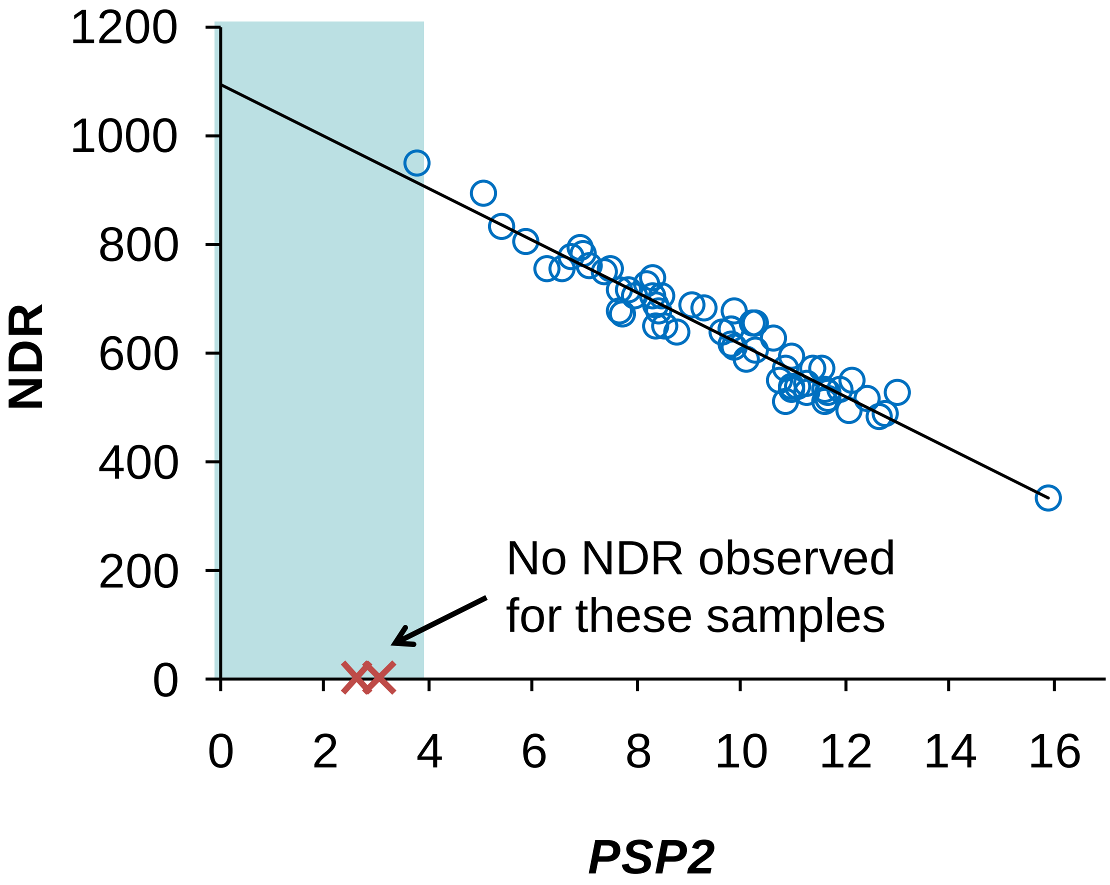
A critical MW (M_{td}) is needed before tie molecule formation is detected in a resin using this method



	M_w (kg/mol)	PDI	Density (g/cm^3)	*PSP2*
A	60	2.5	0.964	1.6
B	60	2.5	0.900	12.6

M_{td} is density dependent and can be considered a detection limit value (M_{td} at 5% PKHT shown)

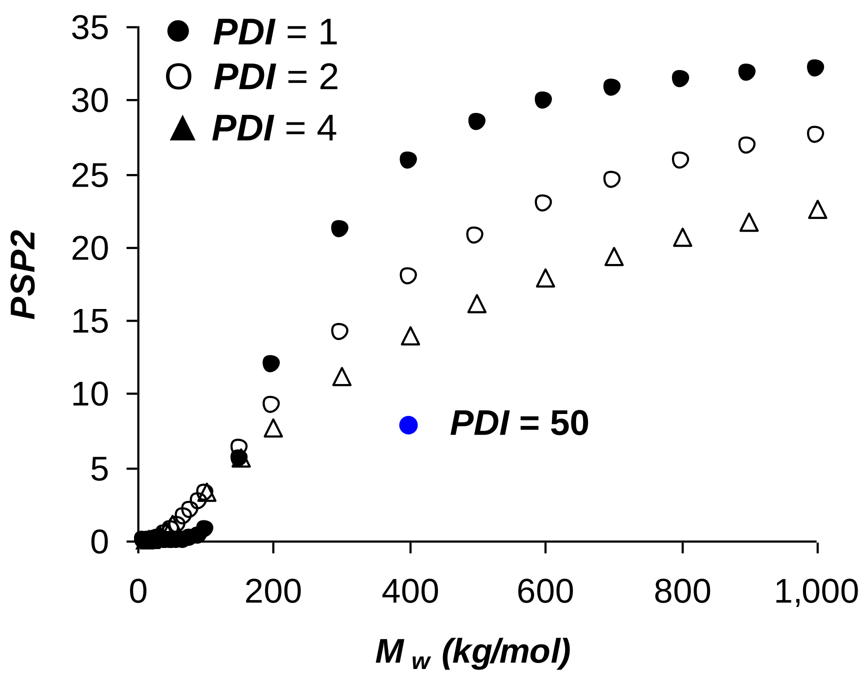
Critical M_w needed before SCG resistance is exhibited (sufficient level of tie molecules present)

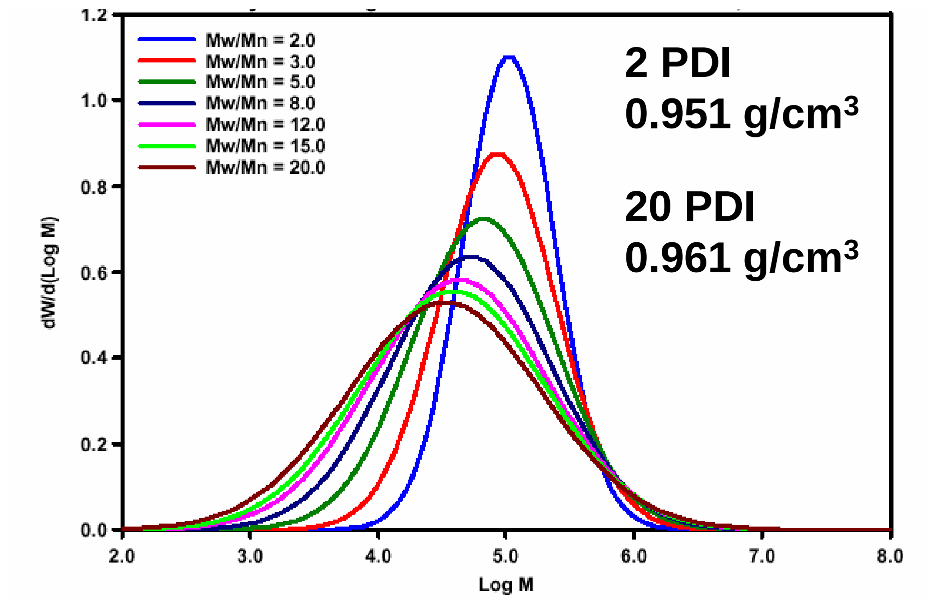


- Samples with PSP2 values < 4 indicate no functional connectivity between lamella
- *PSP2* increases with M_w at a set PDI; e.g., mPE (2.5 PDI)
  - 60 kg/mol; 0.964 g/cm^3 *PSP2* = 1.6
  - 125 kg/mol; 0.957 g/cm^3 *PSP2* = 4.3
  - 250 kg/mol; 0.949 g/cm^3 *PSP2* = 11.0

General effects of MWD on SCG resistance

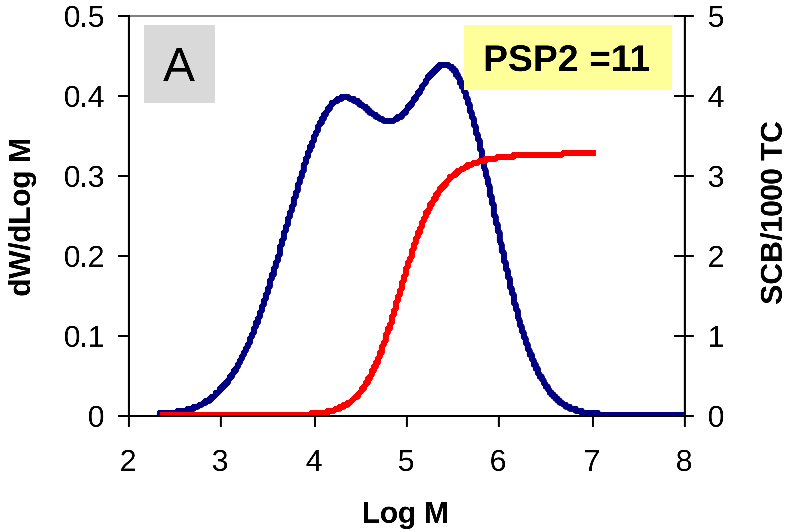
Increasing polydispersity (i.e., Mw/Mn) at a set Mw deceases PSP2 values for homopolymer like structures

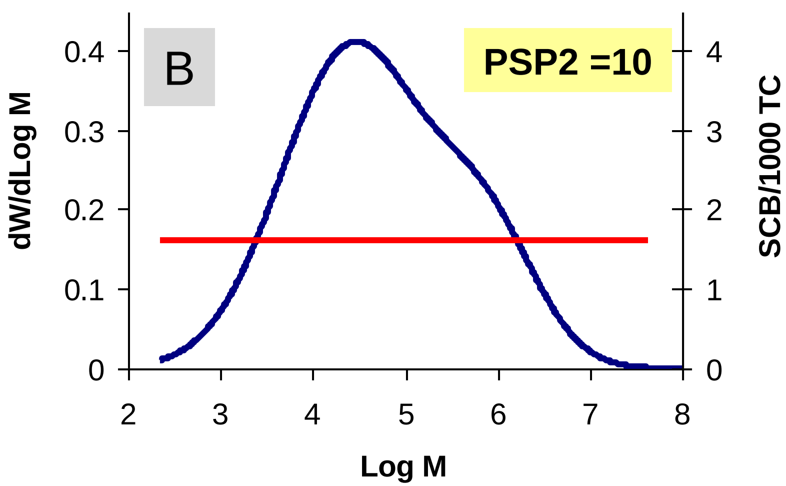


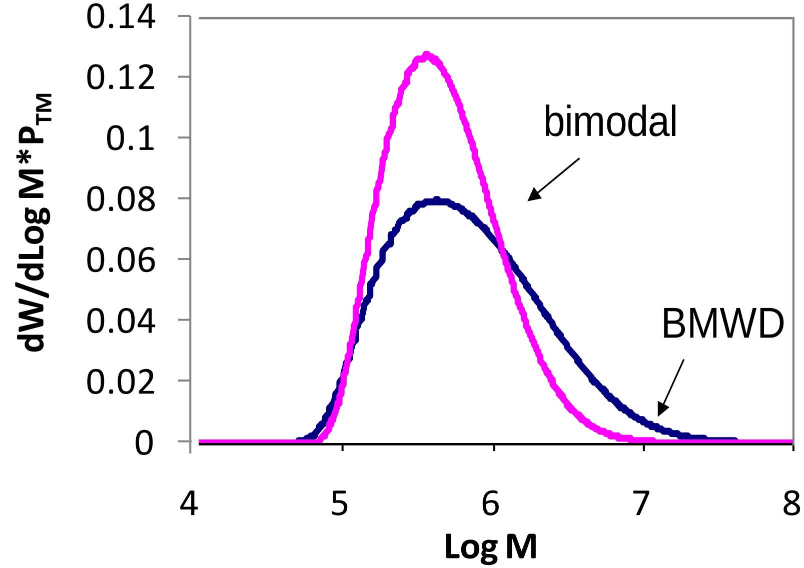


* Density calculated for digital Gaussian MWD peaks, M_w = 150,000 g/mol

Comparison of bimodal (A) and broad MWD (B) type samples (densities = 0.950 g/cm³)







Experimental data

Resin Type	Density (g/cm^3)	M_w (kg/mol)	*PSP2*	NDR
A	0.951	270	12.7	483
B	0.950	480	11.2	532

Use PSP2 method to investigate specific structural conditions

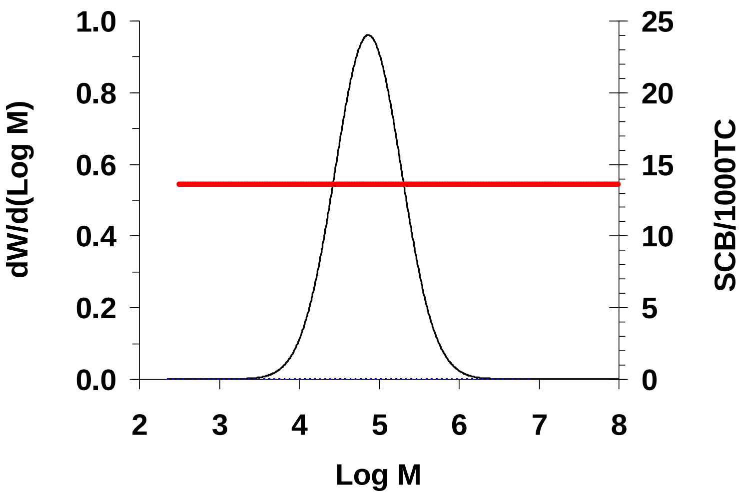
1. Use Gaussian curves for MWD
2. Keep MW and MWD of each component constant
3. Keep blend density constant
4. Use $\Delta\rho$ vs. SCB level calibration curve
5. Vary SCB level and wt fraction of HMW component

Sample	Wt frac. HMW	SCB HMW	Mw (kg/mol)	MWD	Density (g/cm^3)	*PSP2*	Est. NDR
D1	0.25	16.1	163	16.5	0.953	8.1	632
D2	0.27	12.5	174	17.1	0.953	8.4	621
D3	0.32	6.7	201	18.4	0.953	9.3	595
D4	0.45	3.5	218	19.0	0.953	9.8	581
D5	0.42	2.0	248	19.7	0.953	10.5	559
D6	0.50	0.6	290	20.0	0.953	11.4	532
D7	0.66	0.0	369	17.9	0.953	12.3	506

LMW homopolymer density = 0.972 g/cm^3

Multivariable statistical analysis: Effects of MW and SCB on PSP2 values

Constructed 3 level DOE of digital MWDs (Gaussian curves; PDI = 2.5) and SCB levels, assigned replicate error (± 0.002 for density)



Run	M_w (kg/mol)	SCB /1000 TC	Density (g/cm^3)	*PSP2*
1	100	0	0.959	3.3
2		3	0.940	8.0
3		6	0.933	10.1
4	500	0	0.942	19.0
5		3	0.924	25.1
6		6	0.916	26.8
7	1000	0	0.935	25.9
8		3	0.916	29.7
9		6	0.909	30.5
R5	500	3	0.922	25.5
R5	500	3	0.926	24.4

Multivariable statistical analysis: Effects of MW and SCB on PSP2 values

$$PSP2 = c_0 + c_1\, MW^2 + c_2\, SCB^2 + c_3\, MW*SCB + c_4\, MW + c_5\, SCB$$

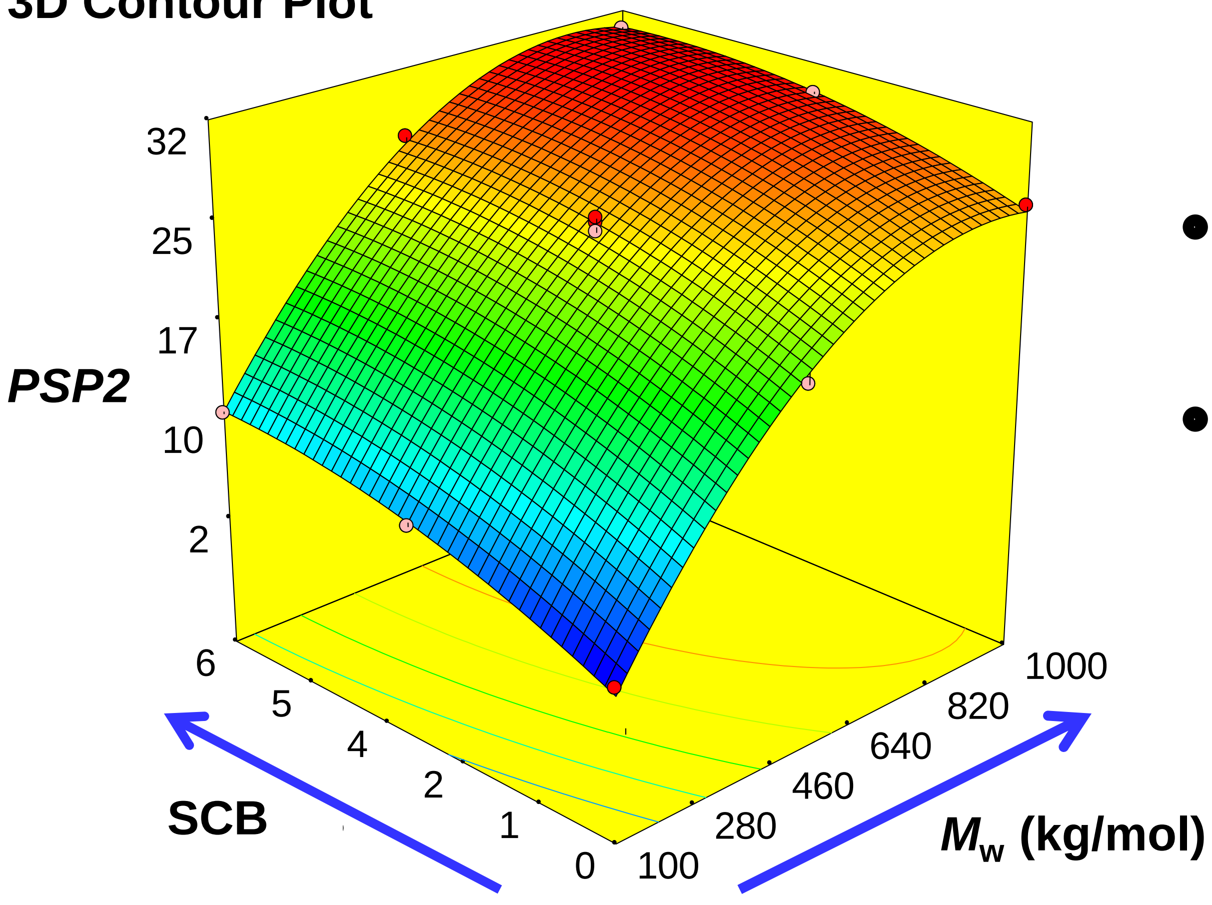
Coded coefficients: $c_4 = 10.77$; $c_1 = -7.08$; $c_5 = 3.18$; $c_2 = -1.71$

ANOVA Table

	Sum of		Mean	F	p-value		
Source	Squares	df	Square	Value	Prob > F		
Model	872.6419	5	174.528389	390.06929	< 0.0001	significant	
A-Mw	695.9574	1	695.9574	1555.4582	< 0.0001		
B-SCB	60.35149	1	60.3514911	134.88501	< 0.0001		
AB	1.403282	1	1.403282104	3.1363222	0.1368		
A^2	123.1309	1	123.1308723	275.19633	< 0.0001		
B^2	7.435105	1	7.435105263	16.61739	0.0096		
Residual	2.237146	5	0.447429193				
Lack of Fit	1.692679	3	0.564226433	2.0725839	0.3419	not significant	
Pure Error	0.544467	2	0.272233333				
Cor Total	874.8791	10					

Multivariable statistical analysis: Effects of MW and SCB on PSP2 values

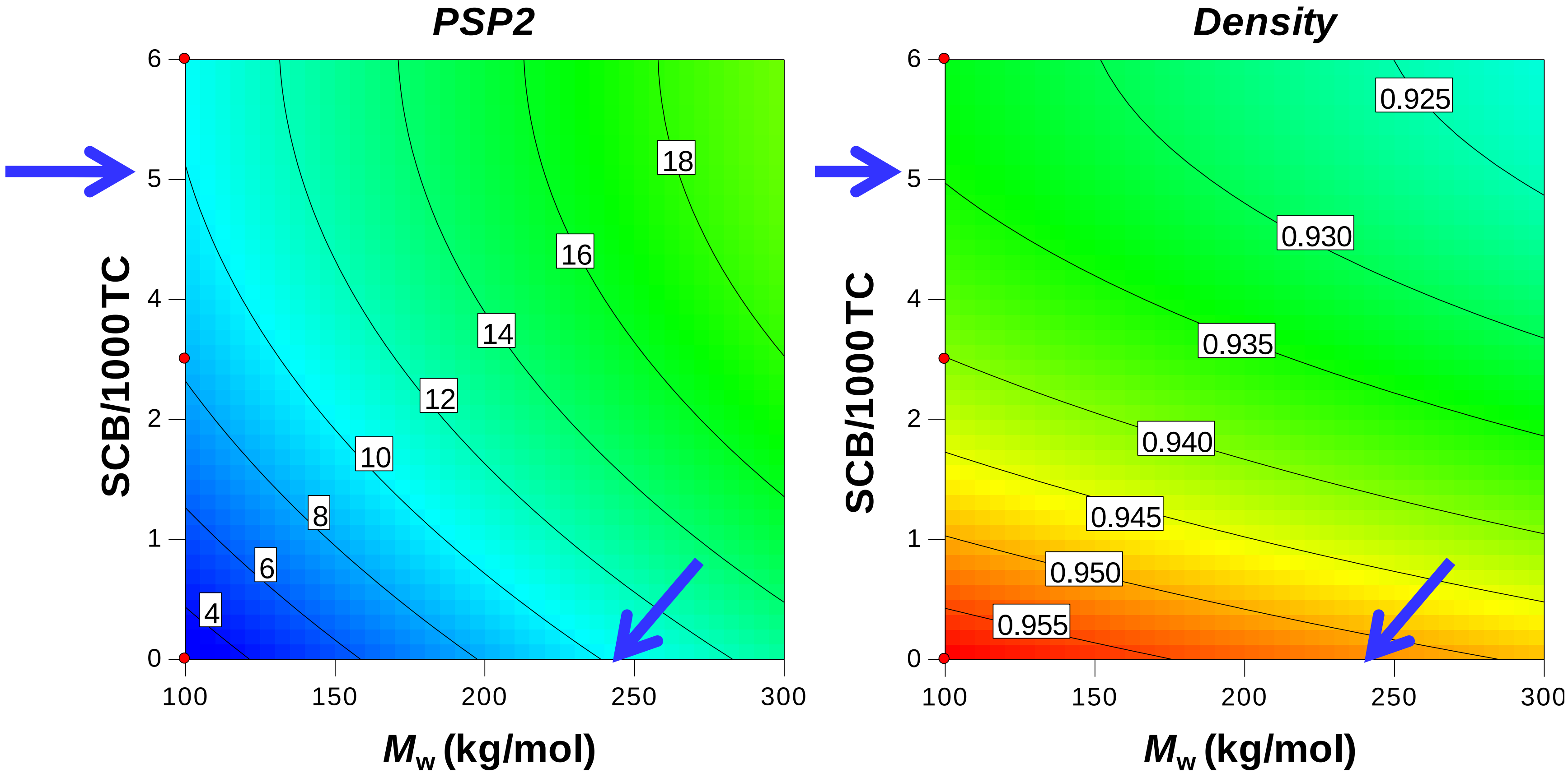
3D Contour Plot



- Mw has greater effect on *PSP2* than SCB
- *PSP2* plateaus at HMW

Multivariable statistical analysis for the effects of MW and SCB on PSP2 values

Same PSP2 values achieved with various resin structures…



Similar results reported in literature…

Reference	Catalyst Type	Mw (kg/mol)	PDI	SCB /1000 TC	Density (g/cm^3)	P_{TM}
Polymer -A*	Cr	223	13.2	6.8	0.934	0.13
Polymer -F*	mPE	118	6.3	11.5	0.924	0.14
Guassian 1		223	13.2	6.8	0.934	0.12
Guassian 2		118	6.3	11.5	0.924	0.12

***Data from Janimak & Stevens J. Material Sci. 36(2001) 1879-1884**

Inter-relationships between molecular characteristics and tie molecule formation is capture by PSP2 method

Summary/Highlights

- MW, MWD, SCB & SCBD variations that influence SCG (as determined by small scale resin tests) are adequately captured in a single structural parameter, *PSP2*
  - method uses familiar resin attributes (MWD and SCBD profiles)
  - results consistent with previous observations
  - allows for understanding of complex interrelationships
  - provides a base line from which deviations can be assessed
- Powerful tool for product design concepts when coupled with other statistical tools, models and experimental blend studies
- The use and further development of the *PSP2* method is expected to help better understand the SCG failure mechanisms in PE resins while improving the cost and effectiveness of product design

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