Low Temperature Cure of PBO Films on Wafers

Custom Polymer Design

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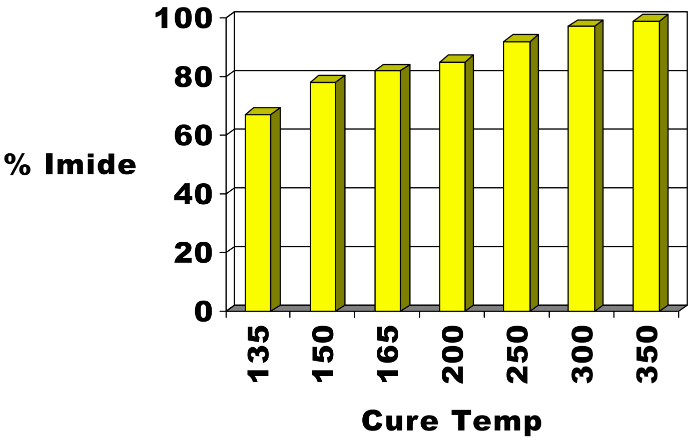
Designing a Low-Temp Polymer

- ☐ Increasing interest in low temperatures
  - **Moving to lower temperature sensitive devices (<200C)**
  - **Need lower thermal budget for wafers & packages**
  - **Need the same film properties (high Tg, elongation, etc.)**
  - **Low stress and tailored mechanical properties**
- ☐ Recent progress
  - **150-200ºC polyimides (10th Symposium on Polymers)**
  - **Lowered stress epoxies and silicones 2005**
- ☐ Polybenzoxazoles (PBO) wafer films
  - **Water processed**
  - **Mechanical properties similar to polyimides**

Limits to Convection Curing

- Lower temperature curing compromises film properties



PI-2525

- Polyimide convection limit appears to be around 250ºC
- PBO convection limit appears to be 250-330ºC
- Variable Frequency Microwave curing even lower

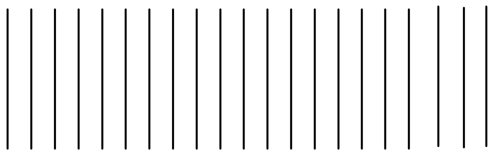
Hubbard 2006

Characteristics of VFM

- Multiple frequencies excite a large number of modes resulting in a uniform energy distribution
- Rapid frequency sweeping eliminates conditions that can cause arcing on metal components
- Agile control and feedback for fast response
- Benign process to semiconductors
    - 90 nm SRAM, DRAM, microprocessors, analog
    - No change to device parameters or dopants

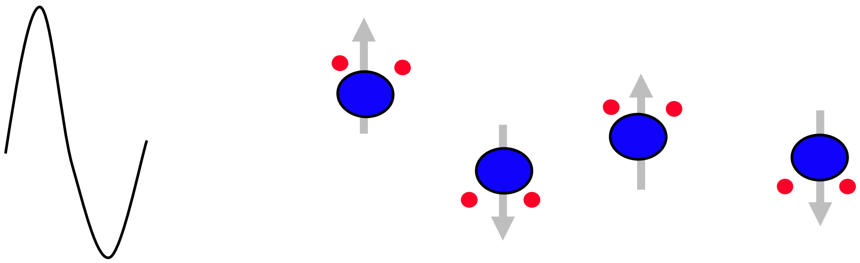
Variable Frequency Microwaves

- Multiple scanned frequencies
  - **4096 frequencies, each 260 Hz wide, for only 25 µs each**



C-band: 5.85-7.0 GHz
X-band: 7.9-8.7 GHz

- Dielectric relaxation causes dipole rotation



-
  - **Dipoles in uncured polymers cause whole chains to rotate**
  - **Rotation of dipoles causes very efficient heating in bulk**

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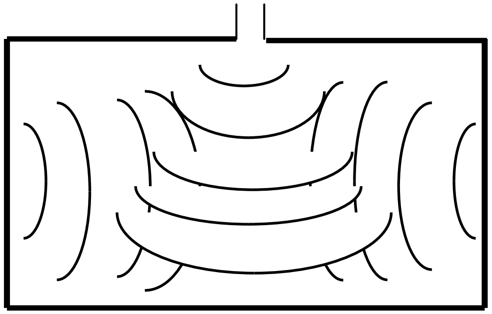
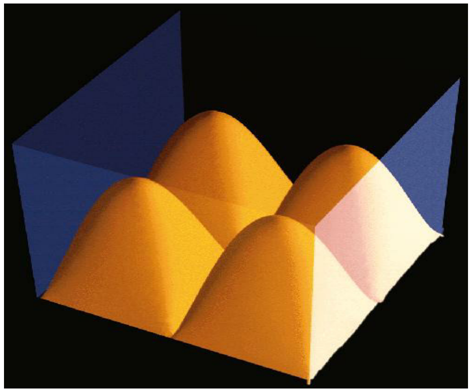
Compared with Fixed Microwave

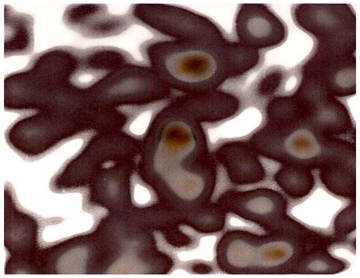
Fixed Modes Create Hot Spots vs. Uniform Heating

Fixed Frequency

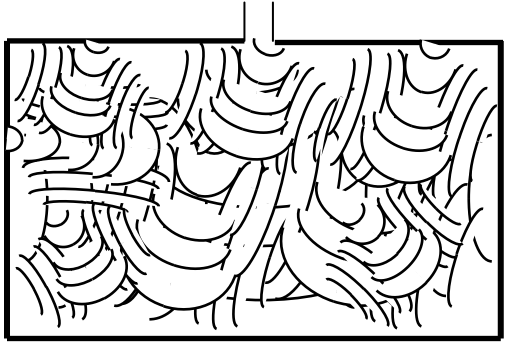


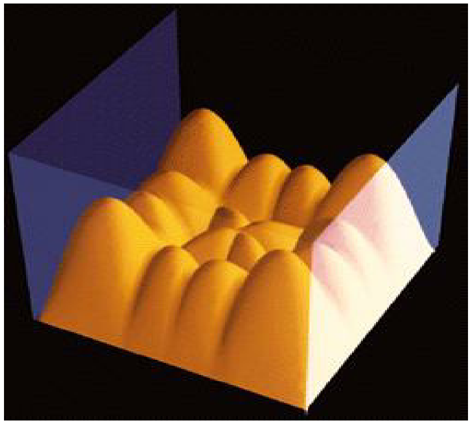


Actual Results



VFM





Actual Results

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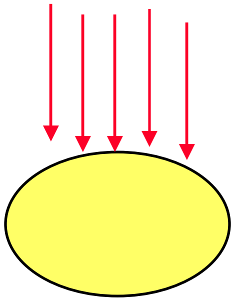
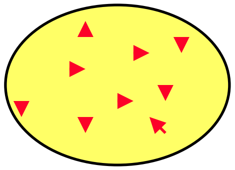
Microwave Heating

- Generates heat at the molecular level by forced oscillation of local molecular dipoles
- A material’s ability to absorb microwave depends on:
  - -Each materials dielectric property
  - -Frequency of microwave energy
  - -Temperature of material
- Heating is volumetric, throughout the material, as compared with external thermal transfer in convection heat

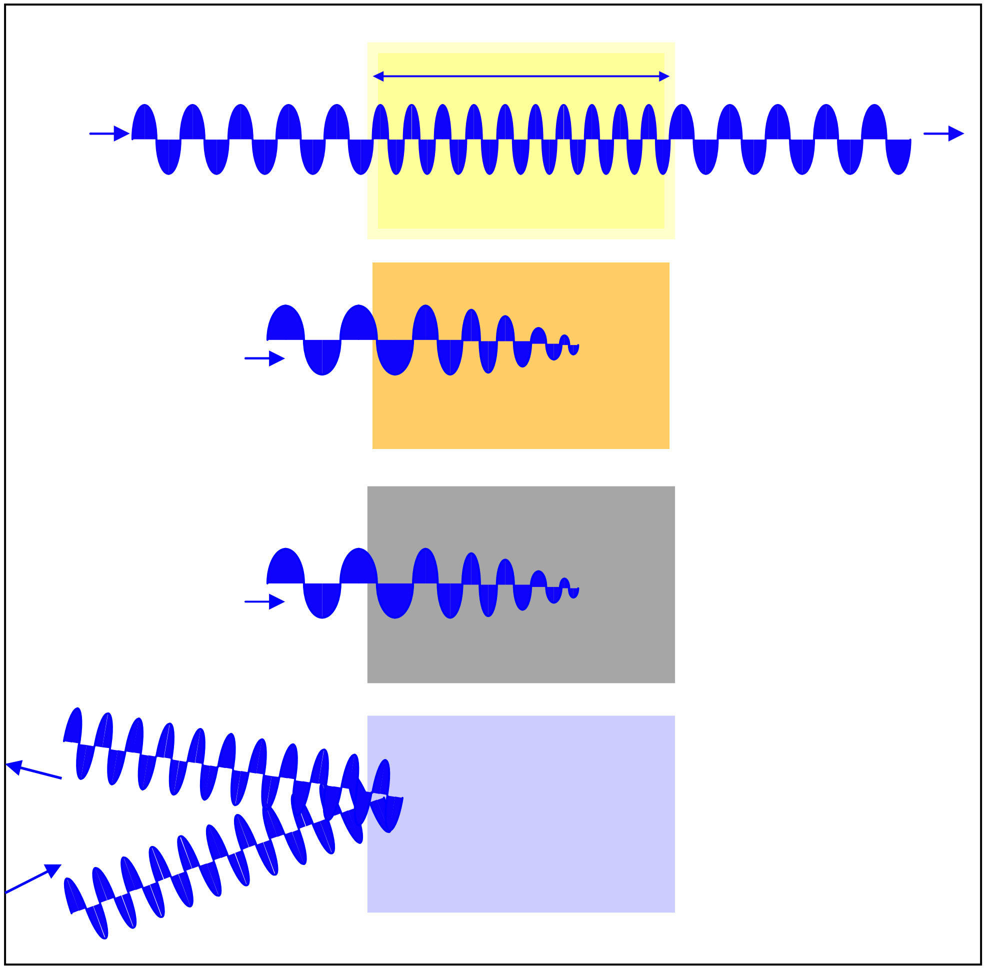
Convection Heat
-Outside - In



Microwave Heat
-Molecular level



Material Interactions



☐	**Glass & Ceramics**	**Dp ~2 to 20 m**
☐	**Polymer resins**	**Dp ~0.1 to 2 m**
☐	**Silicon**	**Dp ~0.01 to 0.2 m**
☐	**Metals**	**Dp ~2-50 µm**

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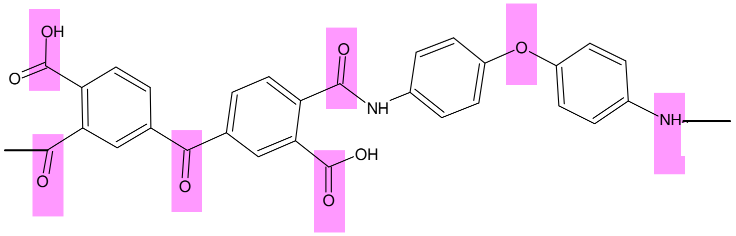
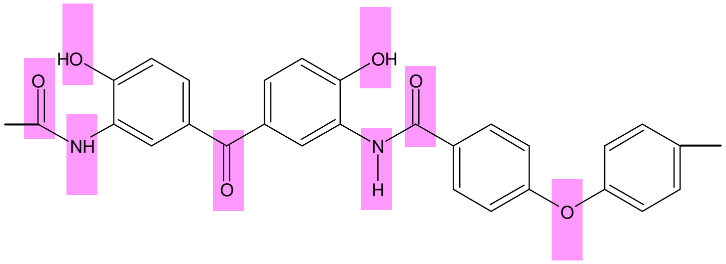
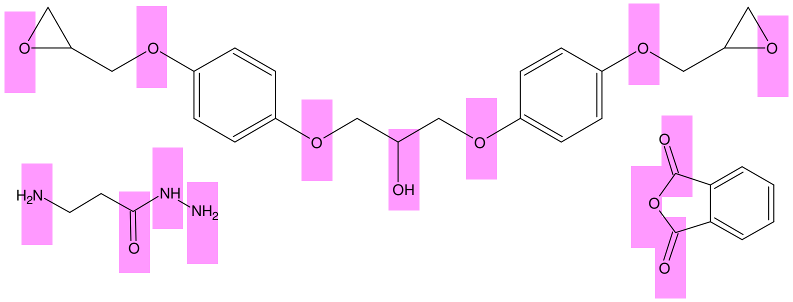
Dipoles in Polymer Resins



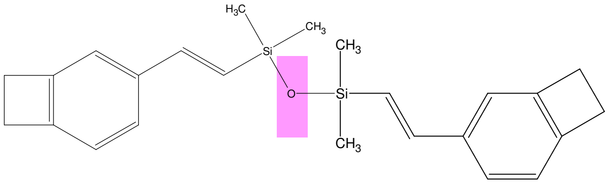
PI



PBO



Epoxies



BCB

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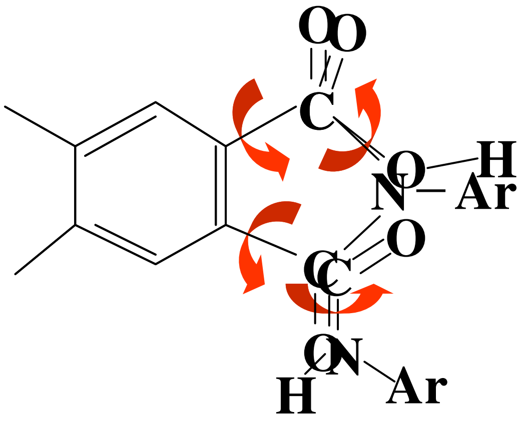
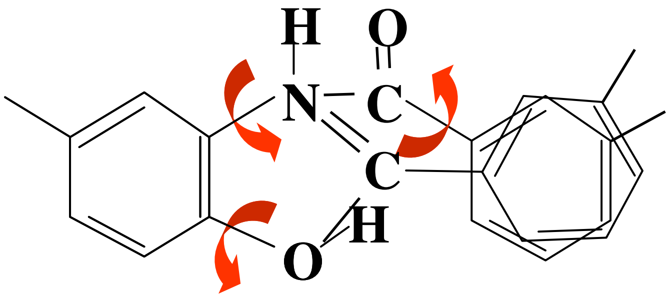
Polymerization Mechanisms

- **VFM ring closure reaction rate increase**



polyimides (PI)



polybenzoxazoles (PBO)

- **Faster, lower temperature polymerizations, cross-linking**

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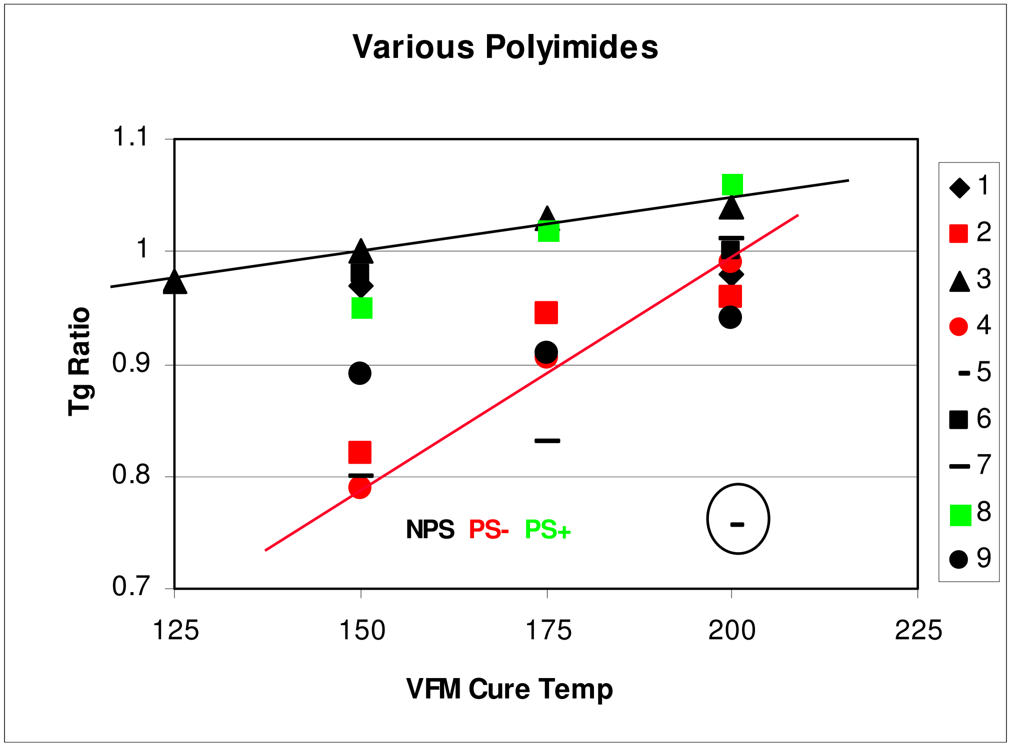
Previous Polyimide Results

- A measure of microwave cure efficiency is the comparison of the final film Tg as cured conventionally and by VFM.
- Example: convection cure at 4 hrs at 350ºC for Tg = 320ºC
  VFM cure at 1.5 hrs at 150ºC for Tg = 310ºC

Tg Ratio = 0.97



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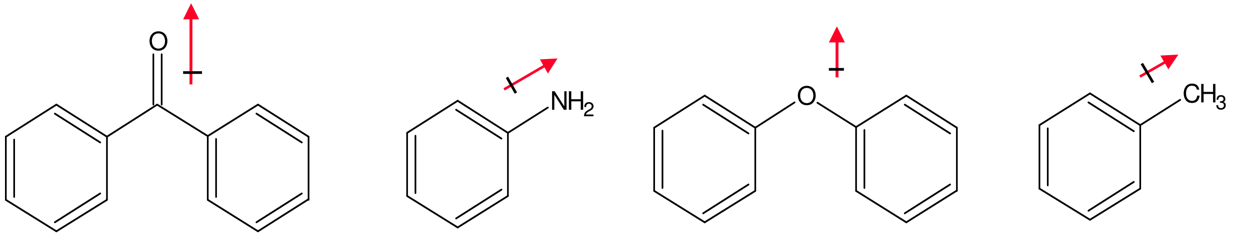
Electronic Correlations

- ❑ While the dipoles involved in curing are absorbing microwave energy, there may be additional dipoles that are heating the molecule as well.



- ❑ It is possible to calculate the total effective polarization of each structure by the matrix addition of the mean of each dipole contribution in each axis.

$$v1 = c11v1^* + c21v2^* + c31v3^* + p11$$
$$v2 = c12v1^* + c22v2^* + c32v3^* + p12$$
$$v3 = c13v1^* + c23v2^* + c33v3^* + p13$$

> where each dipole is represented by vectors in the longitudinal (v1), transverse (v2), and vertical (v3) axes

> where C11 represents the cosine of the angle between each longitudinal vectors, for example

> where p11 represents the distance between the Cartesian coordinates of each vector

Electronic Correlations

- Dipole vectors used:

Bond	Context	b_L	b_T	b_V
C-H	Alkane	0.65	0.65	0.65
C-C	Alkane	0.97	0.26	0.26
C-C	Cyclopropane			
C-C	Cyclobutane			
C=C	Alkene	2.80	0.73	0.77
C=C	Alkyne	3.79	1.26	1.26
Ar-Ar	Biphenyl			
C-F	MeF	1.2	0.4	0.4
C-CI	Mea	3.18	2.2	2.2
C-CI	*t-BuCI*	3.94	1.81	1.81
C-CI	PhCI	4.2	1.9	1.5
C-Br	MeBr	4.65	3.1	3.1
C-Br	t-BuBr	5.98	2.6	2.6
C-Br	PhBr	6.4	2.4	2.2
C-I	Mel	6.7	4.8	4.8
C-I	t-Bul	9.2	3.7	3.7
C-I	PhI	9.1	5.3	3.3
c-o	Ether	0.9	0.46	0.46
c-o	Acetal			
C=O	Ketone	2.3	1.4	0.5
N-H	Ammonia	0.5	0.83	0.83
C-N	Amine	0.57	0.7	0.7
N-N	Hydrazine			
N=N	Azo			
C=N	Imine			
C=N	Cyanide			
C-S	Sulphide	1.9	1.7	1.7
C-CN	*t-BuCN*	4.0	1.5	1.5
S-S	Disulfide			

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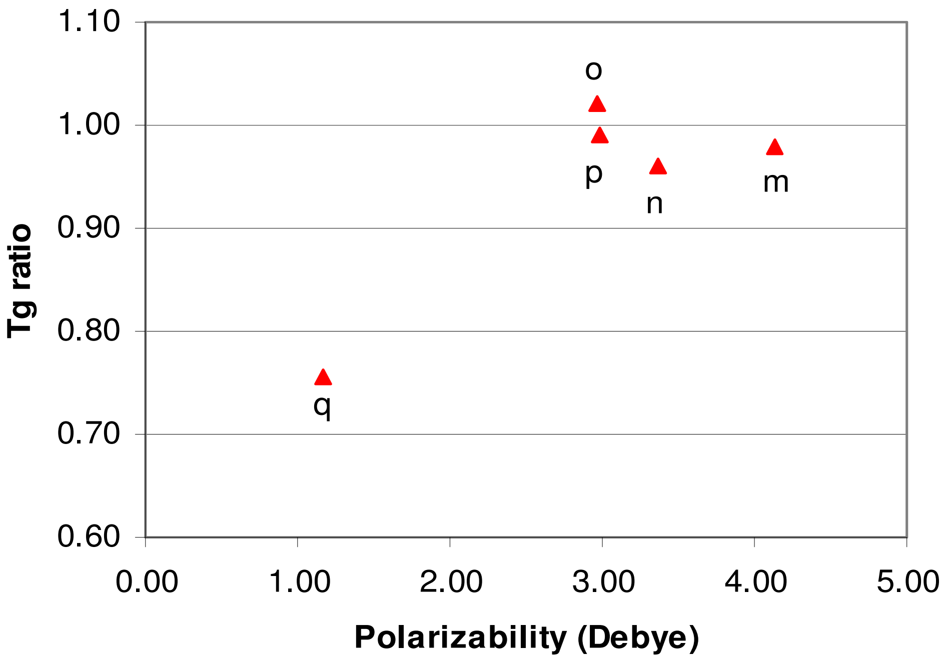
Electronic Corellations

- The molecular polarizabilities can be compared to the Tg just as other physical and optical properties are.



- More examples are being added to clarify the relationship

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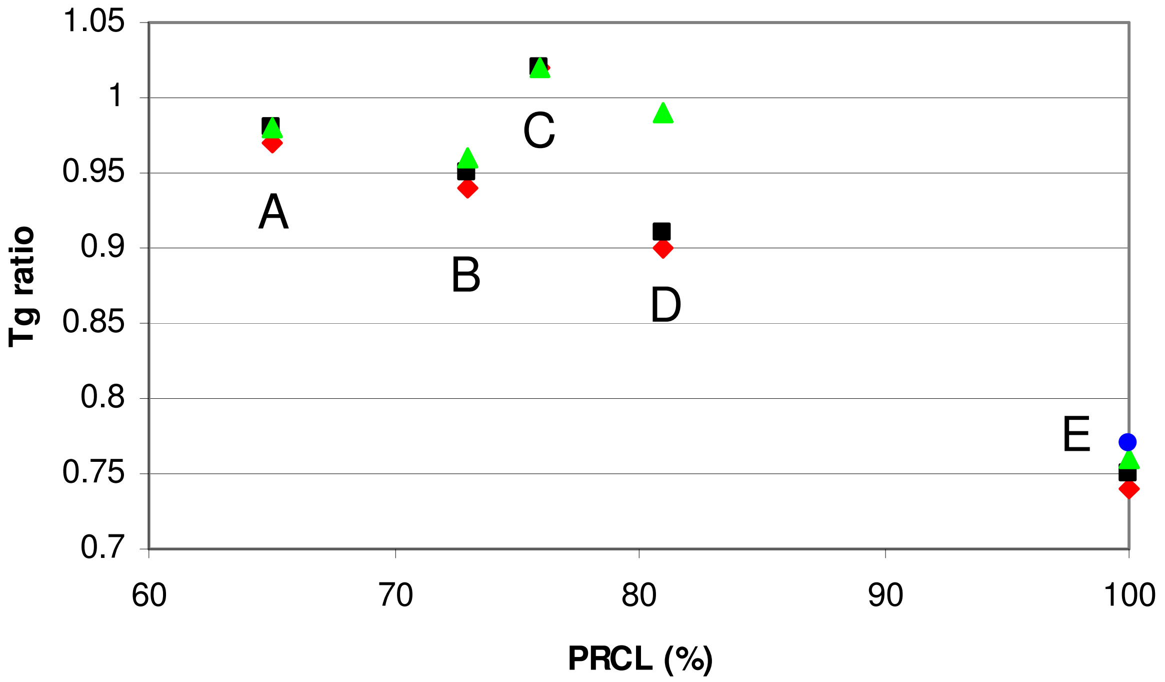
Structural Correlations

- There is a well known correlation between a polymer's "percent rigid chain length" (PRCL) and its physical properties including Tg.
- The rigidity of a polymer resin backbone will inhibit its cure efficiency when exposed to microwave energy.



- Apparently, there are additional factors

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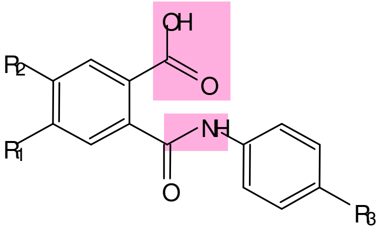
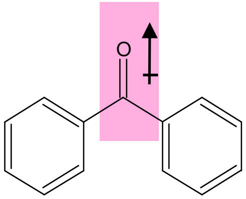
Electronic and Structural Effects

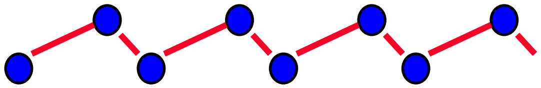
- **Efficiency of microwave heating depends on:**
  - Number of dipoles available for microwave heating
    - Dipoles involved in curing reactions



    - Dipoles elsewhere in the molecules



  - Structural flexibility (mobility of chain sections)



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Custom Design of PBOs

- Crosslinking more complex than linear PI
- Design options:
  - **Backbone:** aromatic or alicyclic
  - **Chain endcap:** dipole strength
  - **Cyclization promoter:** yes or no
  - **Crosslinker:** dipole strength
  - **Crosslinker:** amount
- Process options:
  - **Temperature of soak:** 170-200ºC
  - **Time of soak:** 1-2 hrs**.**
  - **Ramp rate up to soak:** 0.2-1.0 deg/s
  - **Solvent:** NMP or GBL
- Design Matrix (DOE)
  - **Newly synthesized molecules**
  - **Eight variables; 16 trials (2^{8-5}) with four center points**
  - **Dipole strengths are not exact center points**
- Confirmation experiments and photolithography

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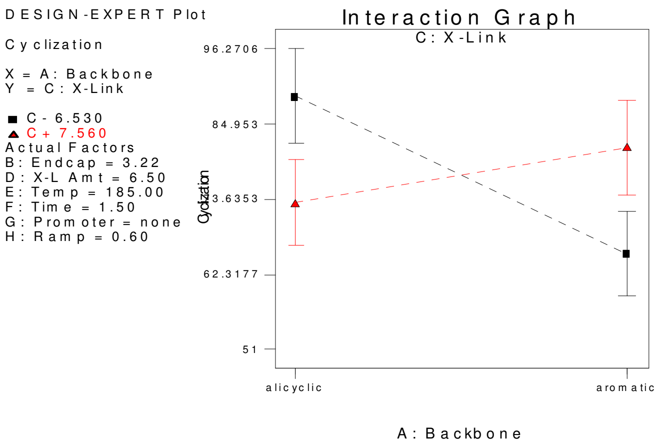
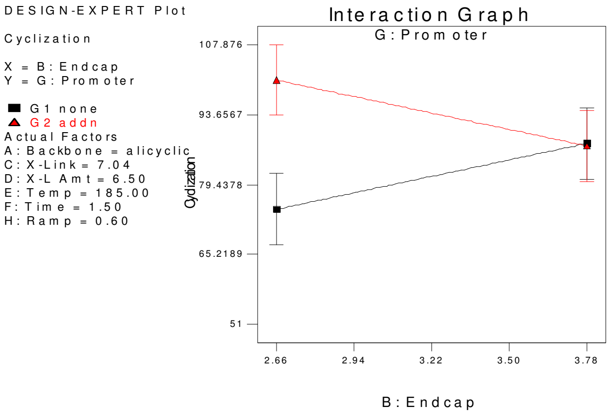
Cyclization Results

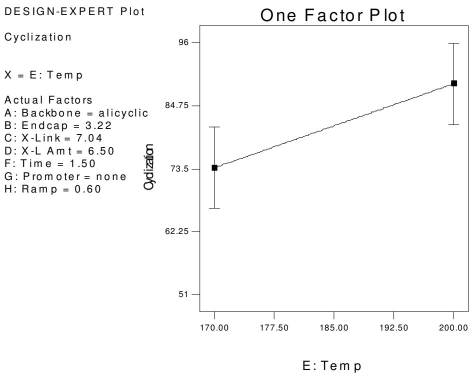
- ❑ Model
  - %Cycl. = 83.72 + 8.03 *AC + 7.46 *E + 6.69 *BG + 6.43 *G – 4.05 *D + 3.88 *DG – 3.83 *A
- ❑ Backbone – Crosslinker Dipole interaction:



- ❑ Endcap – Promoter interaction



- ❑ Temperature



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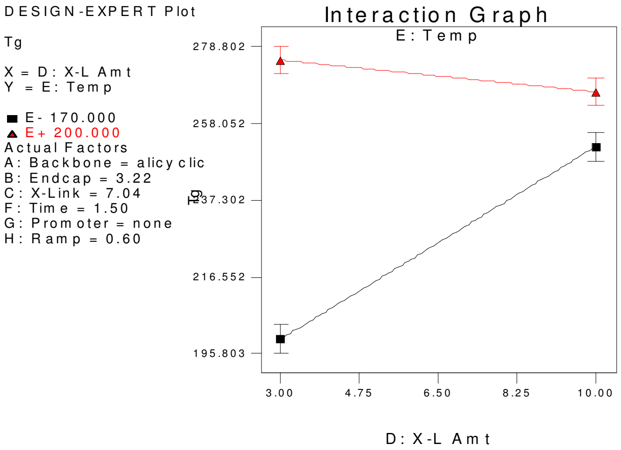
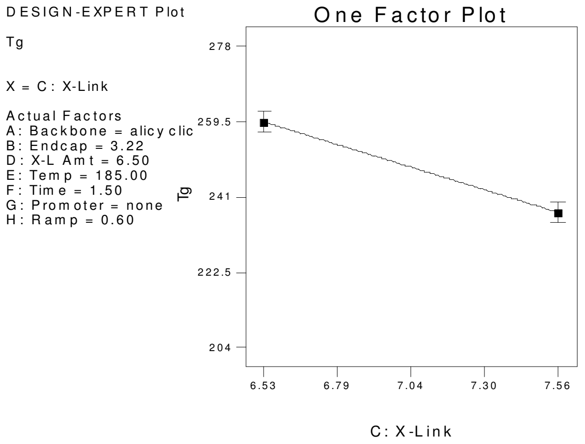
Tg Results

- Model
  - Tg = 251.84 + 22.58 *E – 15.18 *DE – 11.10 *C + 10.89 *D + 6.94 *B - 5.33 *F + 4.92 *H + 3.44 *G

- Temperature – Crosslink Amount interaction:

- Crosslink dipole





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Other Properties

- ❑ Residuals: Td(5%)
  - Td5% = +381.48 +11.35 * A +41.57 * E +24.19 * G -23.08 * A * D +17.64 * B * G
  - Backbone – Crosslink Amt interaction; Temperature; Promoter – Endcap interaction
- ❑ Modulus
  - Modulus = +2.58 +0.080 * A +0.35 * C -0.26 * E -0.22 * G -0.19 * A * C +0.21 * B * C
  - Backbone – Crosslink Dipole interaction; Endcap – Crosslink Dipole interaction; Promoter; Temperature
- ❑ CTE
  - CTE = +63.41 -2.54 * A -1.33 * B -4.19 * D +2.98 * E +1.24 * G +2.72 * A * B
  - Backbone – Endcap interaction; Crosslink Amt; Temperature
- ❑ Elongation
  - Elongation = +14.26 -9.27 * B +11.26 * E +8.73 * G -10.53 * H -7.37 * B * G
  - Promoter – Endcap interaction; Temperature; Ramp Rate
- ❑ Tensile Strength
  - TS = +105.92 +8.08 * A -11.33 * B -7.36 * C -14.21 * E +21.52 * F +18.07 * G +5.77 * H -9.66 * A * B
  - Backbone – Endcap interaction; Temperature; Time; Promoter

Solvent Effects

- ☐ NMP (N-methyl pyrolidone) was used for the primary experiment
- ☐ GBL (γ-butyrolactone) was used for a selected set of trials

	Cycl %	elong	TS	Mod	Td5	Tg	CTE
GBL	53	8	127	2.98	257	257	57
(σ)	3	1	7	0.14	2	2	2
NMP	89	11	110	2.57	421	280	57
(σ)	3	1	11	0.19	32	2	5

- ☐ Clearly NMP provides the highest cyclization, Tg, and lowest residuals.

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Molecular Design

- ☐ If the primary goals are highest cyclization and highest Tg:
  - **Use an alicyclic backbone and a crosslinking agent with a low dipole moment**
    - **If an aromatic backbone is preferred, then use a high dipole agent**
  - **Use a cyclization promoter and a low dipole endcap**
    - **If a high dipole encap is used, the promoter doesn't matter**
  - **Use NMP solvent rather than GBL**

- ☐ To decrease the residual solvents and water in the film
  - **For an alicyclic backbone use 3% crosslinking agent**
  - **For an aromatic backbone use 10% crosslinking agent**
  - **Use a high dipole endcap with promoter**
    - **OR a low dipole endcap with/without promoter**

- ☐ Note that Time and Temperature are relatively unimportant!

Confirmation Runs

- ❑ Results suggest confirmation runs:

	Backbone	**Crosslink dipole**	**Crosslink amt.**	**Endcap dipole**	**Promoter**
1	Alicyclic	6.53	3%	2.66	addn
2	Aromatic	7.56	3%	2.66	addn
3	Aromatic	7.56	10%	2.66	addn

- ❑ Predicted results from the models:

Mtl-Temp	Cycl. %	Tg	Td5%
1-170°C	101.4	286.3	312.0
1-185°C	108.9	248.6	353.6
1-200°C	116.3	210.8	395.2
2-170°C	93.7	264.1	380.9
2-185°C	101.2	226.3	422.5
2-200°C	108.7	188.6	464.0
3-170°C	93.4	255.5	334.7
3-185°C	100.9	248.1	376.3
3-200°C	108.3	240.7	417.9

- ❑ **Eighteen patterned wafers to determine effect on via slope (5 & 7 μm)**

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Summary

- PBO polymers can be custom synthesized for:
  - **Low temperature curing with VFM**
  - **Unique mechanical properties**
    - **As a result of the low temperature – fast cure**
    - **As a result of the uniform bulk cure of VFM**

- Next steps
  - **Analysis of confirmation/photolithography runs**
  - **Further refinement and selection of structures**
  - **Feedback from users of PBO films for passivation and WLP**
  - **Investigation of epoxy materials in progress**