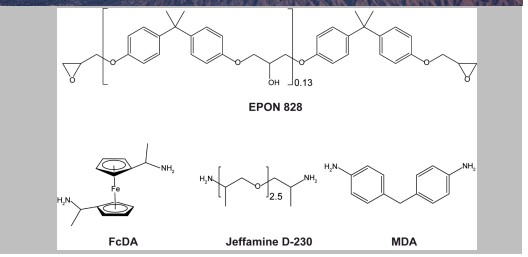
SAND2017-2895C

Double Quantum ^{1}H NMR to Investigate the Dynamics of Highly Crosslinked Thermoset Polymers



Todd M. Alam[1]

Sandia National Laboratories, Albuquerque, NM 87185

Brad H. Jones[1], Hayden T. Black[1,a]
[1]Department of Electronic, Organic Material Science Department
[a]Current Address: Illumina Inc. San Diego, CA

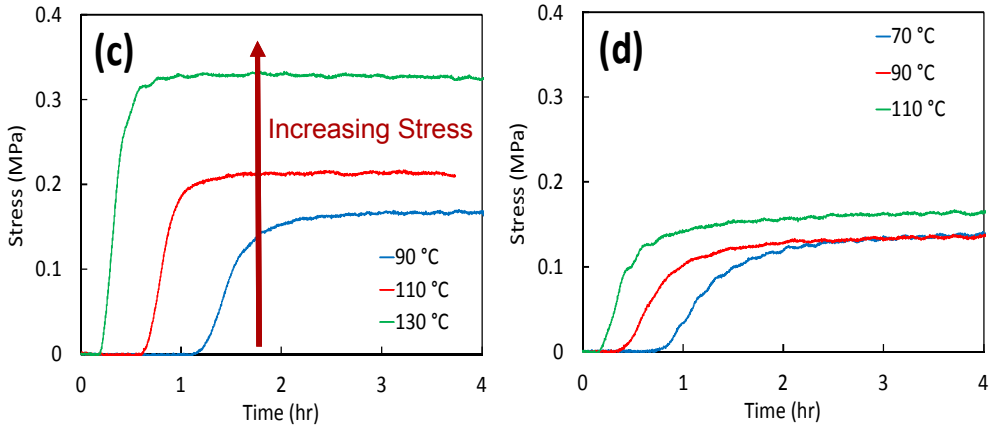
Work Presented at 58th Annual Experimental Nuclear Magnetic Resonance Conference (ENC), March 26-31st 2017, Asilomar, CA USA

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND2017-0625C

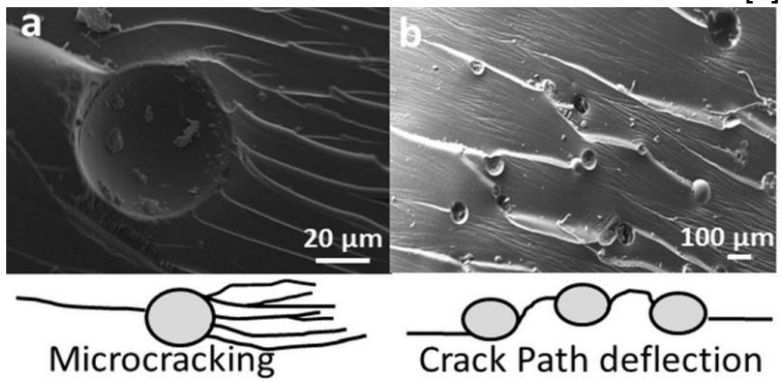
Motivation: Stress Relief in Thermoset Polymers

Cure Stress Variation

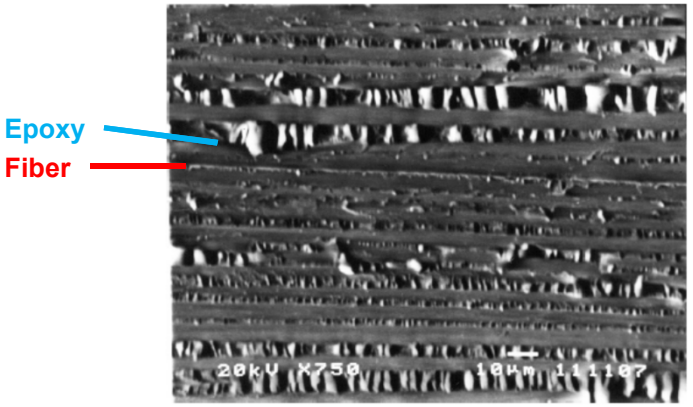
Epon 828 + MDA (C, methylenedianaline) or IPD (D, isophorene diamine) [1]



[2]



[3]



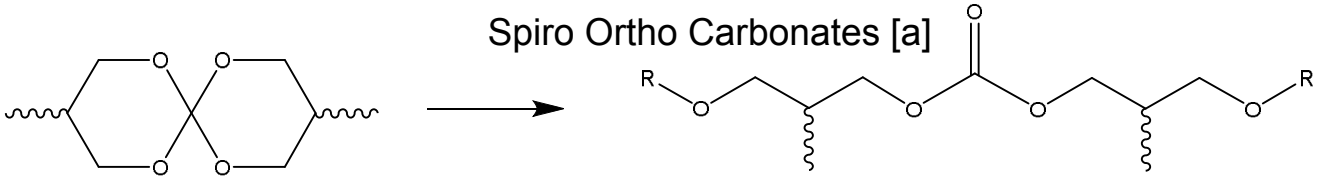
- **Cure stress due to polymerization shrinkage.**
- **Crosslinks prevent terminal viscoelastic behavior (flow).**
- **Stress formation a function of cure temperature.**
- **Stress formation a function of the curing agent.**

1. Jones, B. H.; Wheeler, D. R.; Stavig, M. E.; Black, H. T.; Sawyer, P. S.; Giron, N. H.; Celina, M. C.; Alam, T. M., Stress Relaxation in Highly Crosslinked Epoxy Thermosets via a Ferrocene-Based Curing Agent. Submitted 2017.
2. S. Chaudhary, S. Parthasarathy, C. Rajagopal, P. Roy, D. Kumar "Simple toughening of epoxy thermosets by preformed thermoplastics", Plastics Research Online (2014) http://www.4spepro.org/view.php?article=005409-2014-04-09&category=Polymer+Modifiers
3. Yayla, P., Fracture Surface Morphology of Delamination Failure of Polymer Fiber Composites Under Different Failure Modes. Journal of Failure Analysis and Prevention 2016, 16 (2), 264-270.

Alternative Chemistries For Stress Mediation (Self Repair)

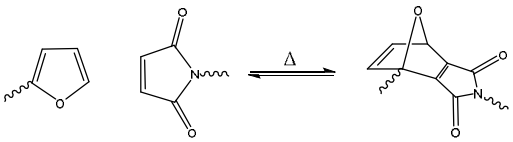
Volume Expandable

Spiro Ortho Carbonates [a]

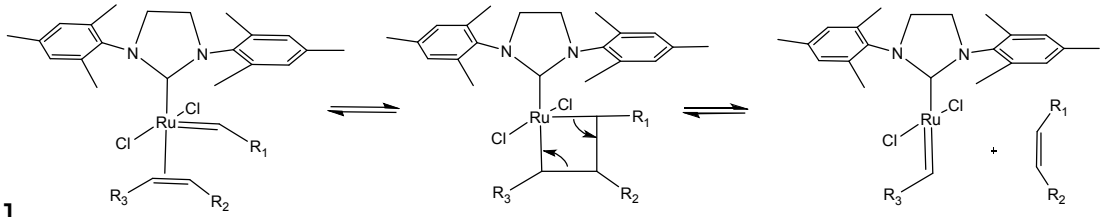


Covalent Adaptable Network (CAN)

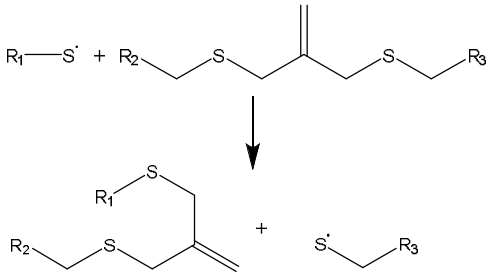
Diels-Alder [1]



Catalyzed Olefin Metathesis [5]



Addition-Fragmentation Chain Transfer [2,3,4]



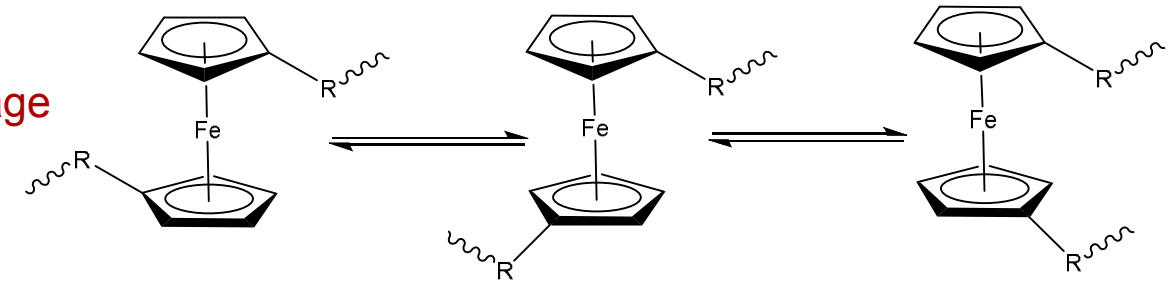
- Oxetane Ring Opening [6]
- Chain Exchange Reaction [7]
- Transesterfication [8]
- Transcarbamoylation
- Transamination
- Transalkylation

[a] Bailey, W. J., Matrices that expand on curing for high strength composites and adhesives. Materials Science and Engineering: A 1990, 126 (1–2), 271-279.; Alcoutlabi, M.; McKenna, G. B.; Simon, S. L., Analysis of the development of isotropic residual stresses in a bismaleimide/spiro orthocarbonate thermosetting resin for composite materials. Journal of Applied Polymer Science 2003, 88 (1), 227-244. [1] Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F., A Thermally Re-mendable Cross-Linked Polymeric Material. Science 2002, 295 (5560), 1698-1702. [**2**] Scott, T. F.; Schneider, A. D.; Cook, W. D.; Bowman, C. N., Photoinduced Plasticity in Cross-Linked Polymers. Science 2005, 308 (5728), 1615-1617. [3] Kloxin, C. J.; Scott, T. F.; Bowman, C. N., Stress Relaxation via Addition−Fragmentation Chain Transfer in a Thiol-ene Photopolymerization. Macromolecules 2009, 42 (7), 2551-2556. [4] Nicolaÿ, R.; Kamada, J.; Van Wassen, A.; Matyjaszewski, K., Responsive Gels Based on a Dynamic Covalent Trithiocarbonate Cross-Linker. Macromolecules 2010, 43 (9), 4355-4361. [5] Lu, Y.-X.; Tournilhac, F.; Leibler, L.; Guan, Z., Making Insoluble Polymer Networks Malleable via Olefin Metathesis. Journal of the American Chemical Society 2012, 134 (20), 8424-8427. [6] Ghosh, B.; Urban, M. W., Self-Repairing Oxetane-Substituted Chitosan Polyurethane Networks. Science 2009, 323 (5920), 1458-1460. [7] Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L., Silica-Like Malleable Materials from Permanent Organic Networks. Science 2011, 334 (6058), 965-968.[8] Capelot, M.; Montarnal, D.; Tournilhac, F.; Leibler, L., Metal-Catalyzed Transesterification for Healing and Assembling of Thermosets. Journal of the American Chemical Society 2012, 134 (18), 7664-7667.

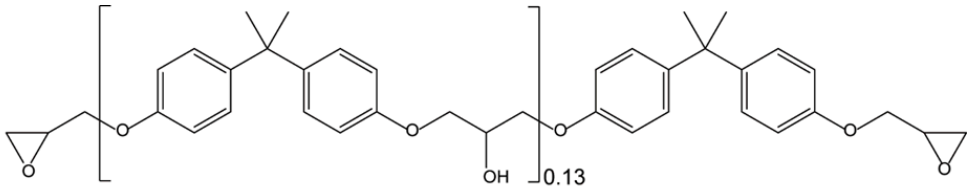
Metallocene Curing Agents for Stress Relief

Ferrocene Fluxional Mechanism

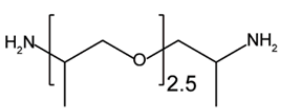
No bond breakage



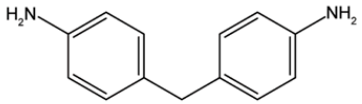
Linkages on both Ferrocene rings



EPON 828



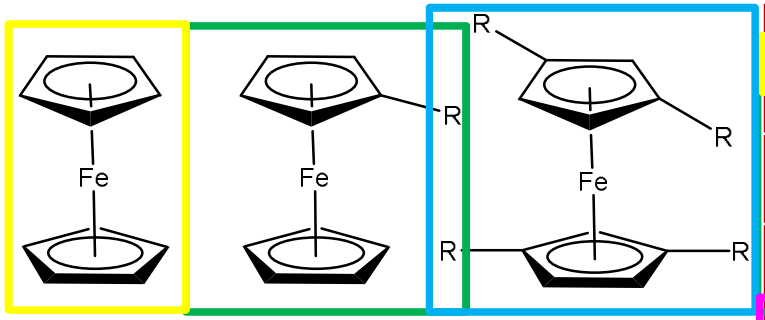
Jeffamine D-230

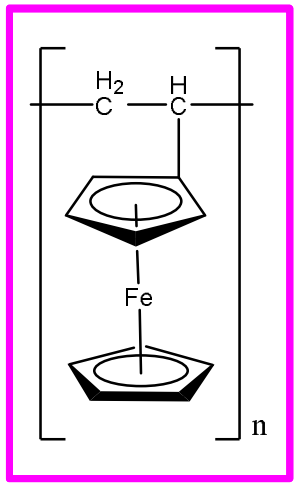


MDA

1. Jones, B. H.; Wheeler, D. R.; Stavig, M. E.; Black, H. T.; Sawyer, P. S.; Giron, N. H.; Celina, M. C.; Alam, T. M., Stress Relaxation in Highly Crosslinked Epoxy Thermosets via a Ferrocene-Based Curing Agent. Submitted 2017.

Rotation Barriers in Ferrocene Derivatives





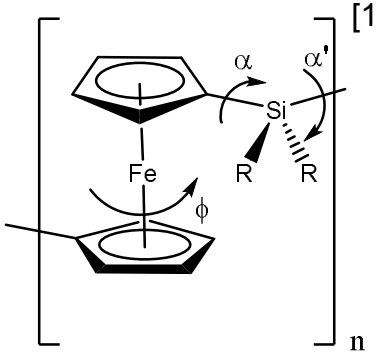
"Fe ball bearing"

Compound	$\Delta G^{\dagger}$ [E_a] kJ mol^{-1}	Ref.
$Fe(\eta^5\text{-}C_5H_5)_2$	4.4,5.4,7.5	
$Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CHO)$	15.2	[1]
$Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CMe_2Et)$	10.2 15.2	[2]
$Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Bu^n)$	8.0 11.7	[2]
PVFc	9.6	[3]
$Fe(\eta^5\text{-}C_5H_3(t\text{-}Bu)_4)$	55.6, 54.8	[4]
$Fe(\eta^5\text{-}C_5H_3(t\text{-}Pentyl)_4)$	56.7	[4]
$Fe(\eta^5\text{-}C_5H_2(TMS)_6)$	46.0	[4]
$Ru(\eta^5\text{-}C_5H_5)_2$	9.6	[5]
$Ru(\eta^5\text{-}C_5H_3(t\text{-}Pentyl)_2)$	45.7	[4]
$Ni(\eta^5\text{-}C_5H_5)_2$	7.5	[6]
$Co(\eta^5\text{-}C_5H_5)_2$	7.5	[6]
$Cr(\eta^5\text{-}C_5H_5)_2$	7.5	[6]

1. Pazur, R.J., et al., *Proton spin-lattice relaxation time studies and atom–atom non-bonded potential calculations on ferrocenecarbaldehyde (η^5-C_5H_5)Fe(η^5-C_5H_4CHO).* Canadian Journal of Chemistry, 1987. **65**(8): p. 1940-1944.
2. Mann, B.E., et al., *A determination of the activation energy of cyclopentadienyl group rotation and molecular tumbling in [Fe(h^5-C_5H_5)(h^5-C_5H_4R)](R = CMe_2Et or Bu^n) using carbon-13 nuclear magnetic resonance relaxation measurements.* Journal of the Chemical Society, Dalton Transactions, 1984(9): p. 2027-2028.
3. Appel, M.A., *Ring Rotation in Ferrocene and Ferrocene-Containing Polymers.* 2015, Technische Universität: Darmstadt, Germany. p. 137.
4. Abel, E.W., et al., *Dynamic NMR studies of ring rotation in substituted ferrocenes and ruthenocenes.* Journal of Organometallic Chemistry, 1991. **403**(1–2): p. 195-208.
5. Holm, C.H. and J.A. Ibers, *NMR Study of Ferrocene, Ruthenocene, and Titanocene Dichloride.* J. Chem. Phys., 1959. **30**(4): p. 885-888.
6. Luke, W.D. and A. Streitwieser, *Barriers to Ring Rotation in 1,1',4,4'-Tetra-tert-butyluranocene and 1,1',3,3'-tetra-tert-butylferrocene.* J. Am. Chem. Soc., 1981. **103**(12): p. 3241-3243.

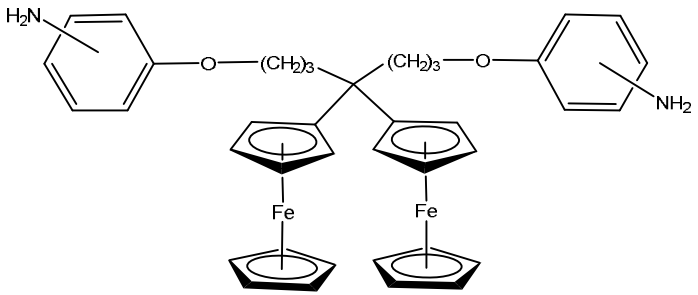
Ferrocene in Polymers (Including Epoxies)

[1,2]

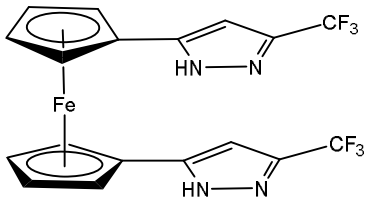


R = CH_3, OCH_3, OC_6H_{13}

[3]

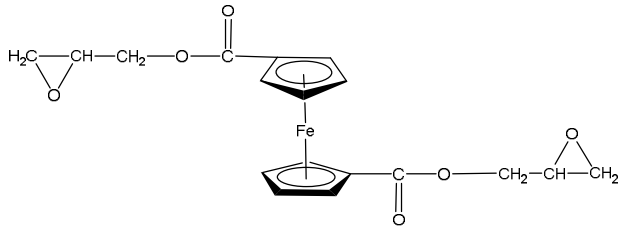


[4]

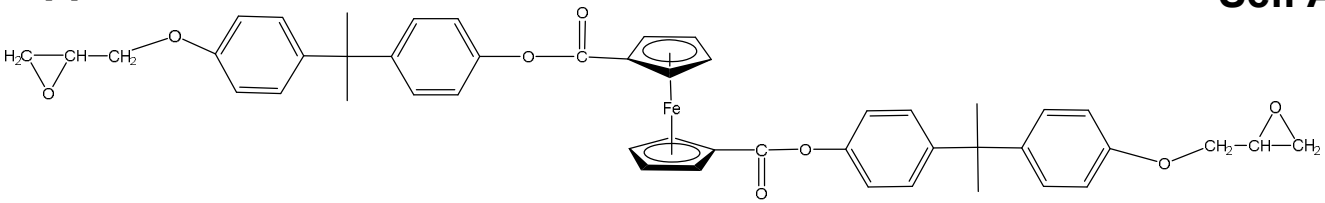


- **Propellent Burn Rate Catalyst**
- **Conductivity**
- **Electrochemical**
- **Magnetic Ceramics**
- **Refractive Index**
- **Electron Beam Resistance**
- **Self Assembly (fluxional impact)**

[5]

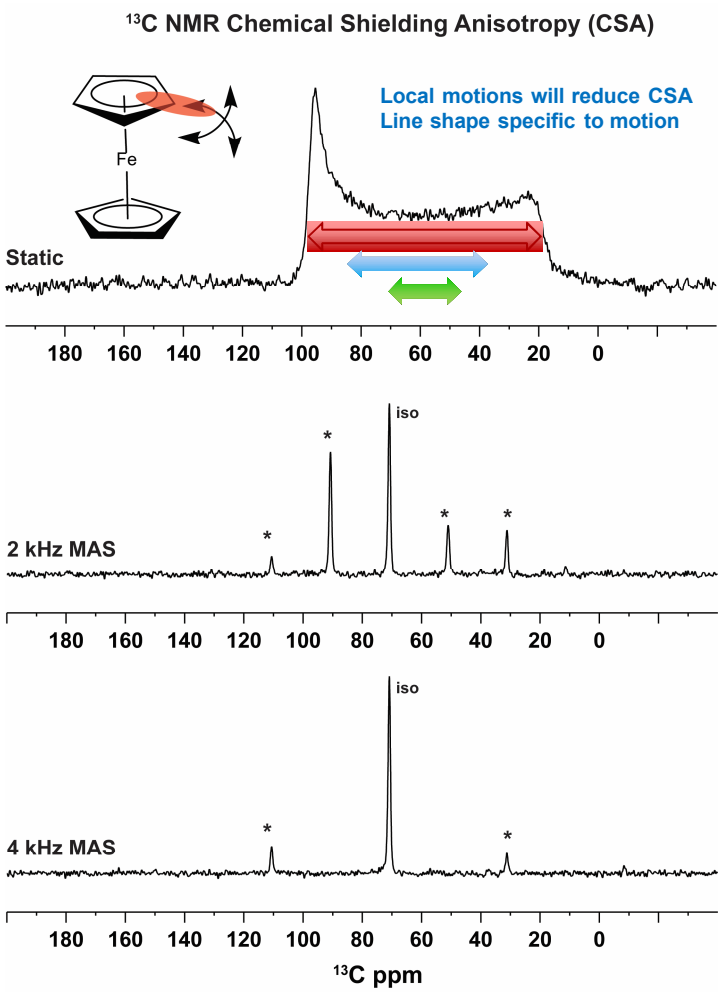


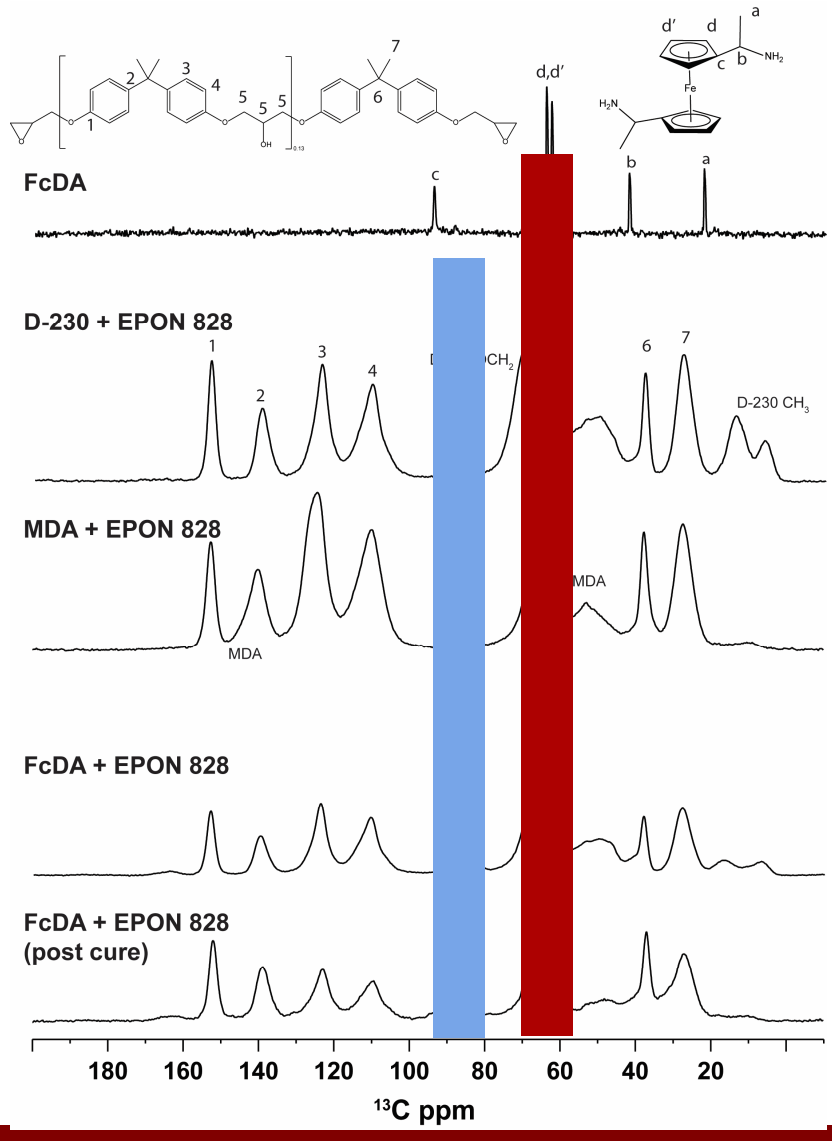
[6]



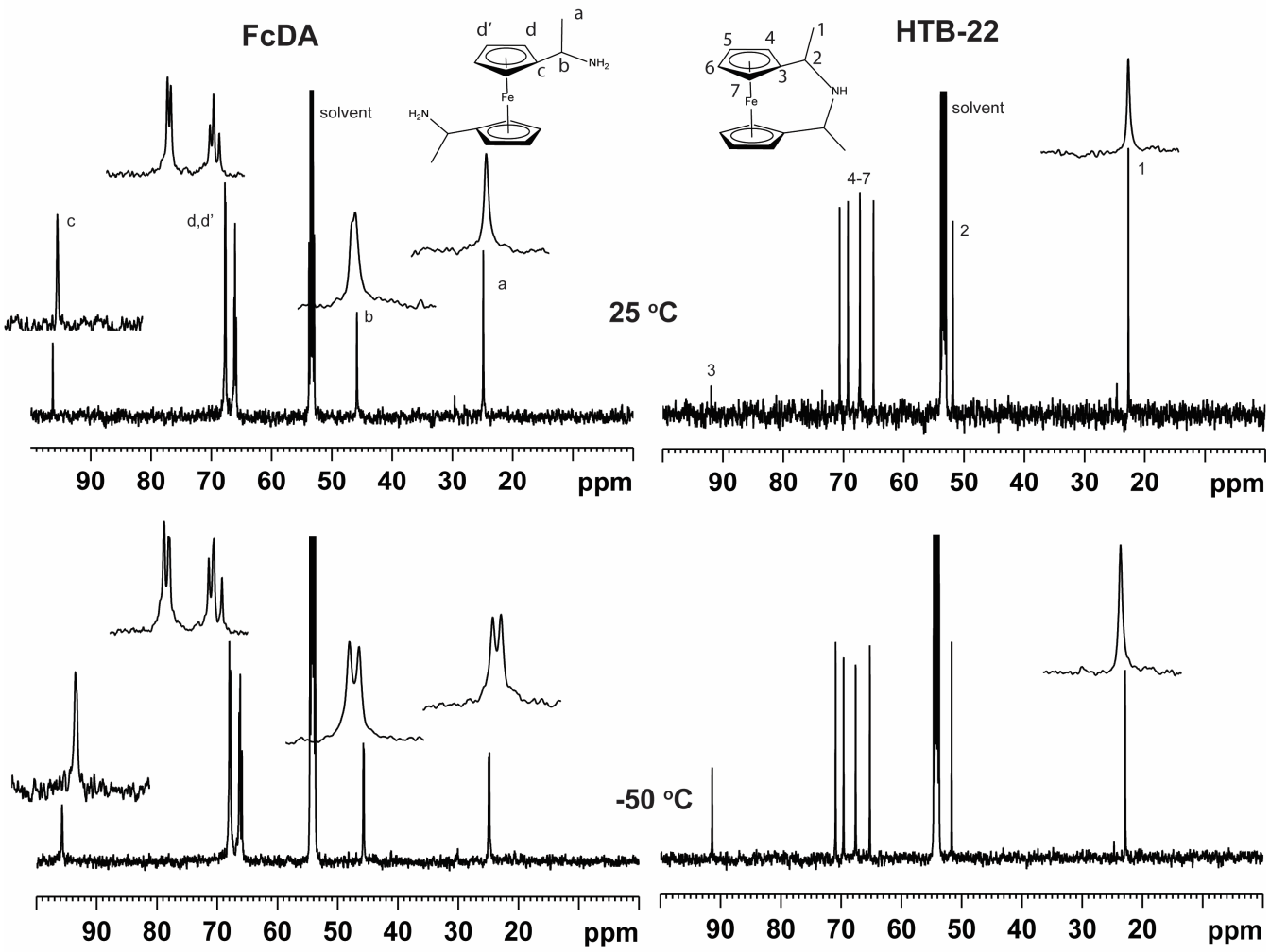
[1] Kulbaba, K.; Macdonald, P. M.; Manners, I., Molecular Motions in Poly(ferrocenes): Solid-State Deuterium NMR Studies of Poly(ferrocenylsilanes) near Their Glass Transition Temperature. Macromolecules 1999, 32 (4), 1321-1324. [2] Kulbaba, K.; Manners, I.; Macdonald, P. M., Molecular Motions in Metal-Containing Polymers: Solid-State Deuterium NMR Studies of Polyferrocenylsilanes near Their Glass Transition Temperature. Macromolecules 2002, 35 (27), 10014-10025. [3] Wright, M. E.; Laub, J.; Stafford, P. R.; Norris, W. P., Synthesis of new ferrocene containing diamines and their use in epoxy resins. Journal of Organometallic Chemistry 2001, 637–639, 837-840. [4] Veronelli, M.; Dechert, S.; Demeshko, S.; Meyer, F., 1,1′-Bis(pyrazol-3-yl)ferrocene: A Clip Ligand That Forms Supramolecular Aggregates and Prismatic Hexanuclear Coinage Metal Complexes. Inorganic Chemistry 2015, 54 (14), 6917-6927. [5] Yu, H.; Wang, L.; Huo, J.; Ding, J.; Tan, Q., Synthesis and Curing Behavior of a Novel Ferrocene-Based Epoxy Compound. J. Appl. Polymer Sci. 2008, 110, 1594-1599. [6] Yu, H.; Wang, L.; Huo, J.; Li, C.; Tan, Q., Synthesis of Glycidyl Ether of Poly(bisphenol-A-1,1'-ferrocene dicarboxylate) and Its Electrochemical Behavior. Designed Monomers and Polymers 2009, 12, 305-313.

^{13}C MAS NMR - Looking for Dynamics…

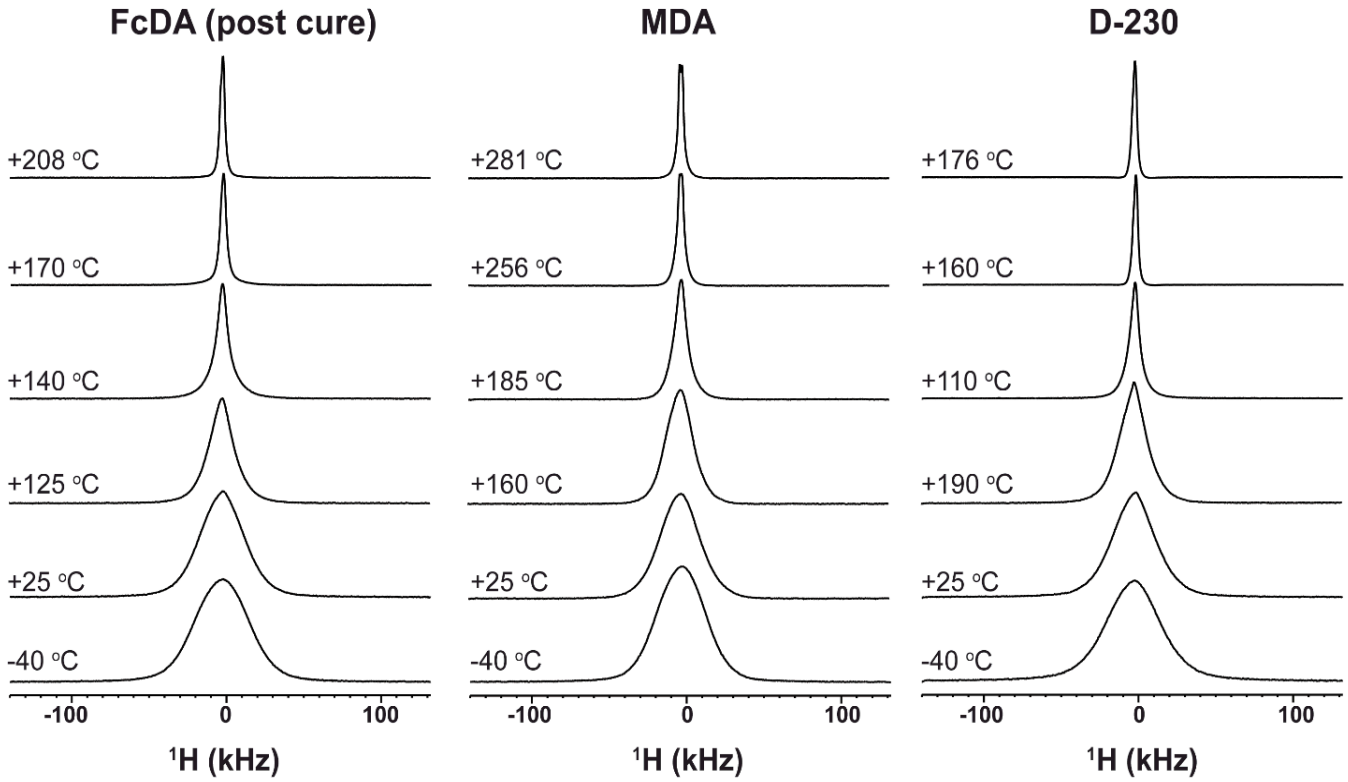




Solution ^{13}C NMR Reveals Multiple Conformers



Static ^{1}H NMR – Temperature Variations

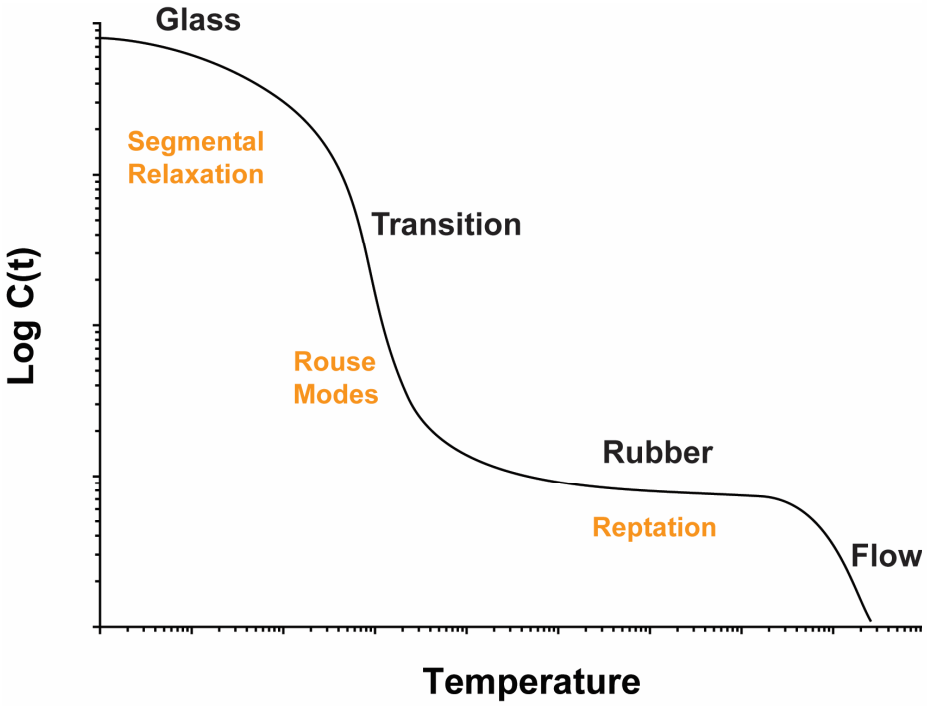


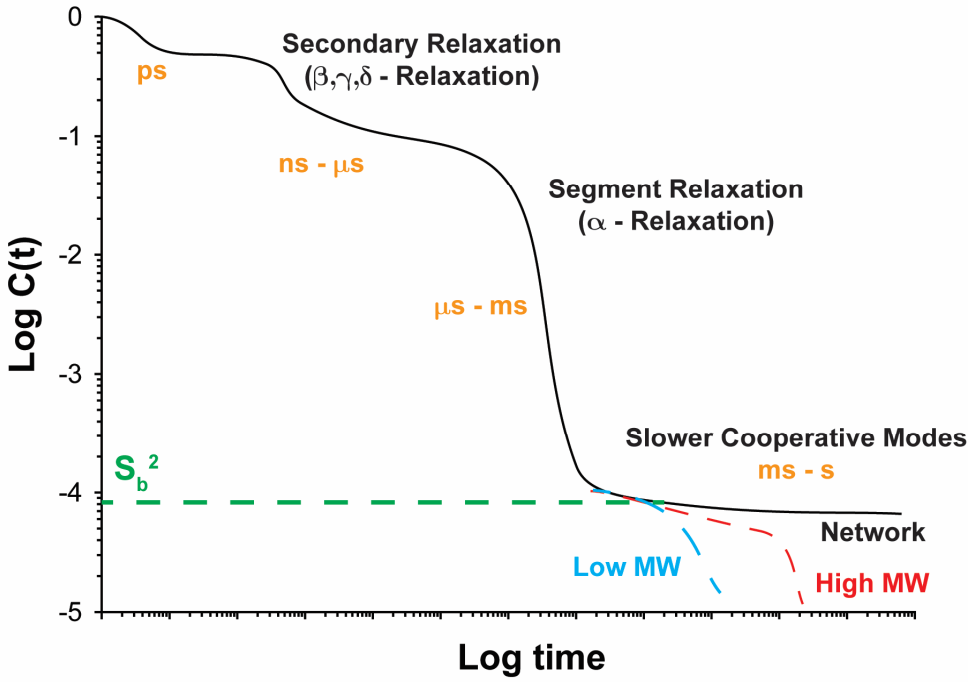
Dipolar Coupling and Motional Averaging

$$\omega_D^{ij} = \sqrt{\frac{3}{2}}\left[\frac{\mu_0 \gamma_I^2 \hbar}{4\pi r_{ij}^3}\right]\left(3\cos^2\theta - 1\right)$$

$$\left\langle \omega_D^{ij} \right\rangle = \sqrt{\frac{3}{2}}\left[\frac{\mu_0 \gamma_I^2 \hbar}{4\pi r_{ij}^3}\right]\left(3\cos^2\theta' - 1\right)\left\langle 3\cos^2\beta - 1\right\rangle \rightarrow \sqrt{\frac{3}{2}}\left[\frac{\mu_0 \gamma_I^2 \hbar}{4\pi r_{ij}^3}\right]\left(3\cos^2\theta' - 1\right) S_b$$

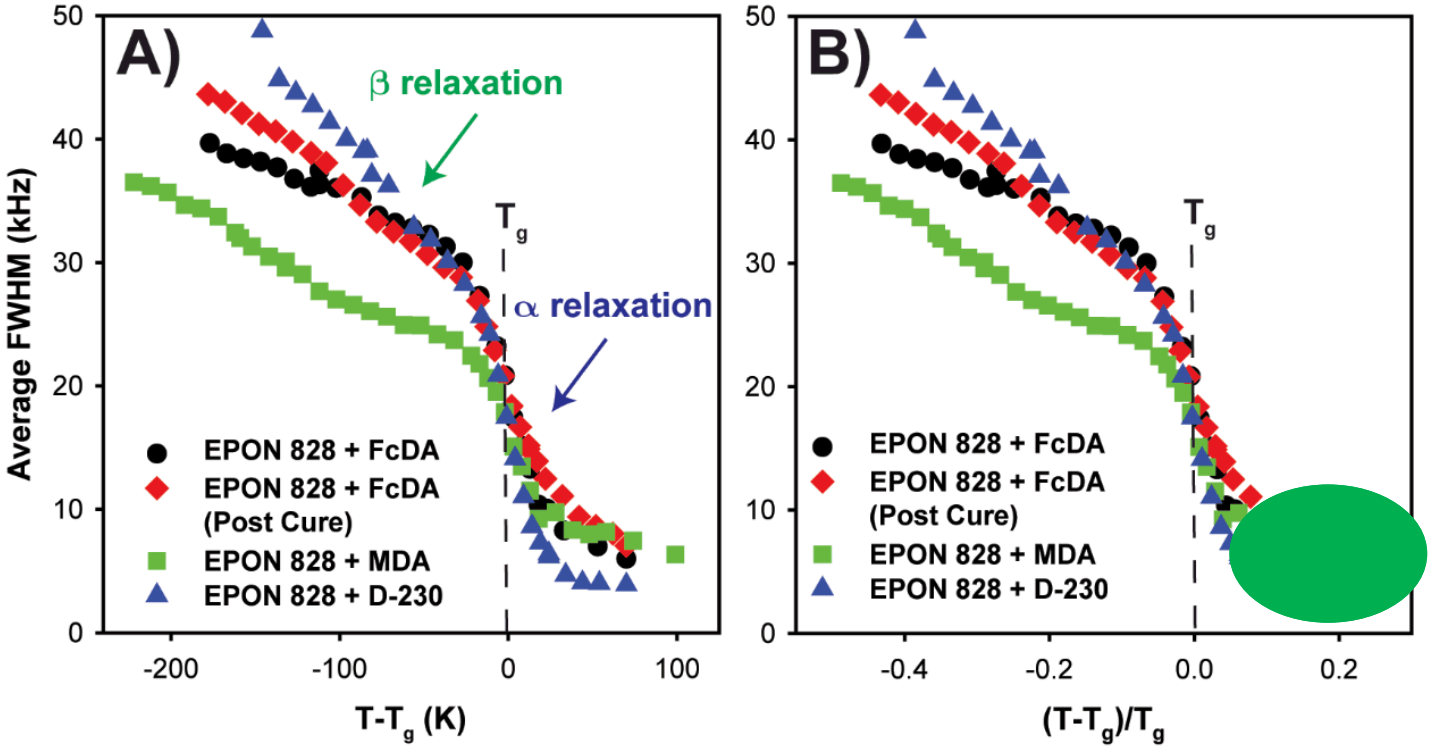
^{1}H NMR – Mapping Internal Polymer Motions





Leads to Concept of Time-Temperature Superposition

Static ^{1}H NMR Line Width - Dynamics



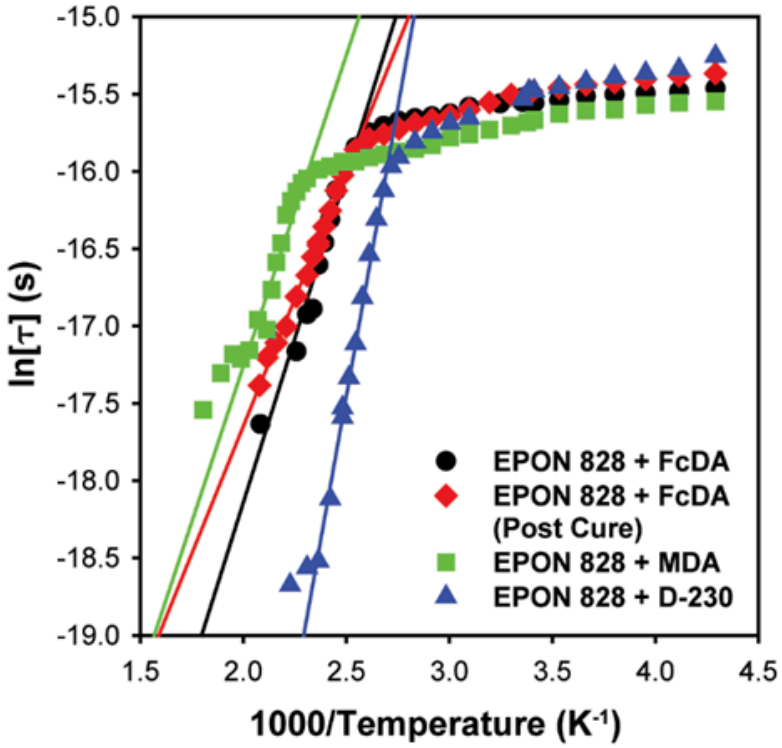
Reduced Temperature

$$\frac{T-T_g}{T_g}=\frac{\Delta T}{T_g}=\frac{T_g}{T}-1=\frac{1}{T_g}-\frac{1}{T}$$

$$\tau_i=\frac{1}{W_i}\tan\left[\frac{\pi}{2}\frac{W_i^2-\langle W\rangle^2}{W_0^2-\langle W\rangle^2}\right]$$

Structural Investigations by Means of Nuclear Magnetism. II. Hindered Rotation in Solids, H. S. Gutowsky and G. E. Pake, The Journal of Chemical Physics 18, 162 (1950); doi: 10.1063/1.1747580

Static ^{1}H NMR – Dynamics From Line Width



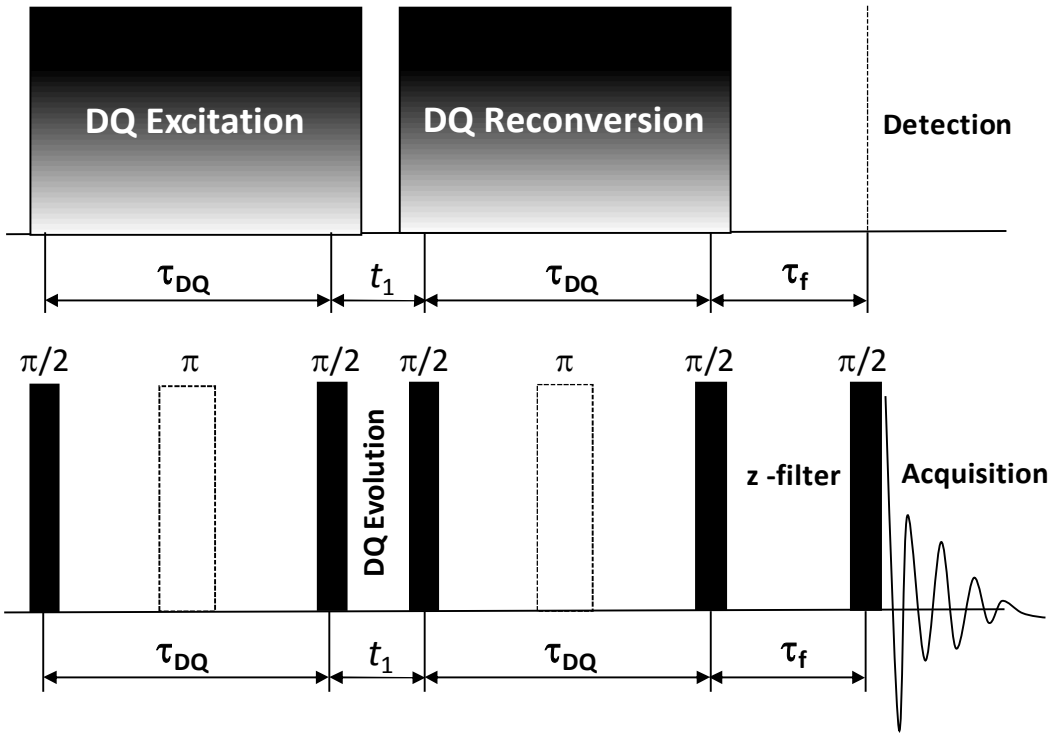
Temperature dependence of this molecular correlation time can be used to estimate T_g activation energy.

$$\tau_i = \tau_0 \exp\left[E_a / RT\right]$$

Epoxy Sample	T_g DSC (°C)	T_g NMR (°C)[a]	b[a]	T_g E_a (kJ/mol)[b]	Sub T_g E_a' (kJ/mol)[c]
EPON 828 + MDA	180	182	-11.1	33.5	2.8
EPON 828 + D230	90	106	-9.6	62.1	2.9
EPON 828 + FcDA	125	137	-13.8	35.3	1.8
EPON 828 + FcDA (postcure)	113	138	-15.6		2.0

*

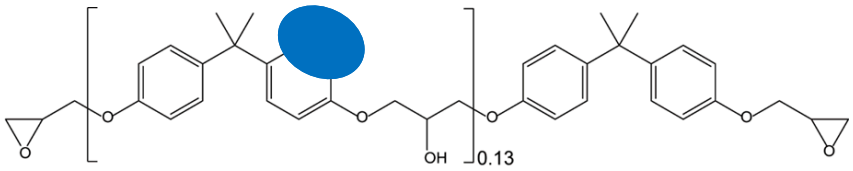
^{1}H NMR – Double Quantum (DQ) NMR



- 5 –pulse DQ sequence (Pines).
- π pulses for refocusing.
- Variation on τ_{DQ} for buildups.
- Not increased cycle number.
- Used extensively in rubbers for motions in the ms range.
- Cross link density in rubbers (industry – e.g. tires).

$$\omega_D^{ij} = \sqrt{\frac{3}{2}}\left[\frac{\mu_0 \gamma_I^2 \hbar}{4\pi r_{ij}^3}\right]\left(3\cos^2\theta - 1\right)$$

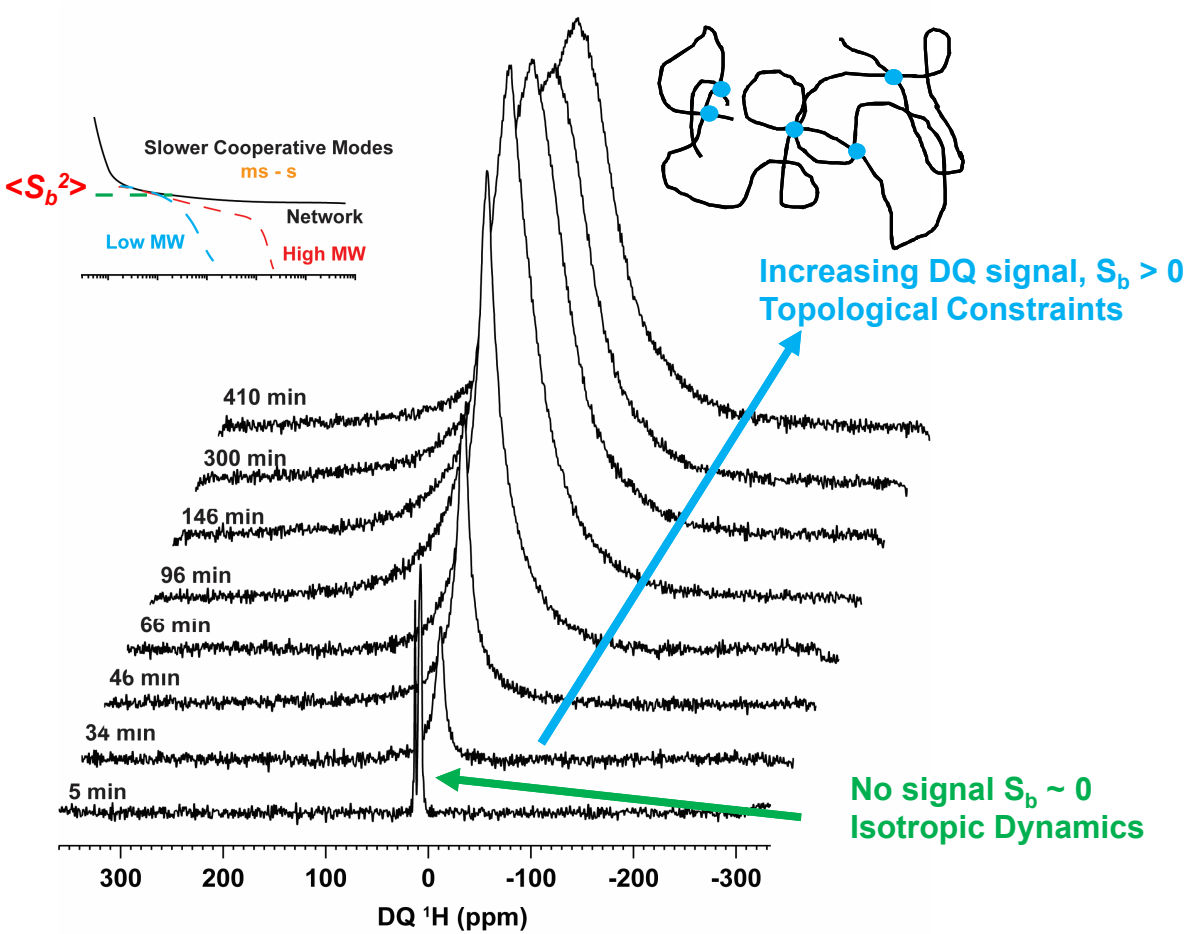
$$I_{nDQ} = \frac{I_{DQ}}{I_{DQ} + I_{ref} - B\exp\left[-2\tau_{DQ}/T_2\right]}$$

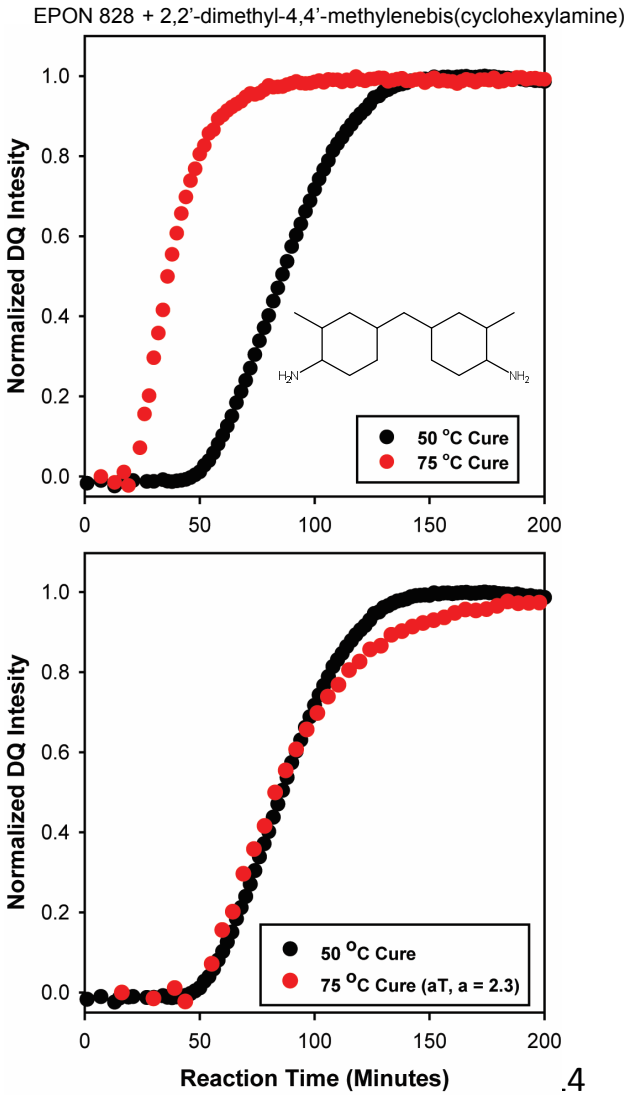


EPON 828

^{1}H NMR – DQ NMR During Cure

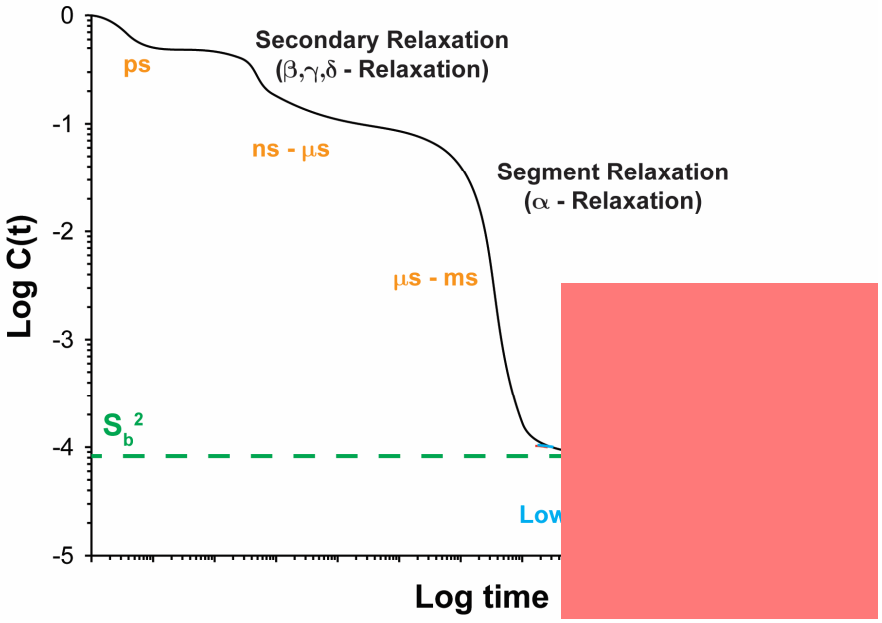
Cure Kinetics Followed by Segmental Topology

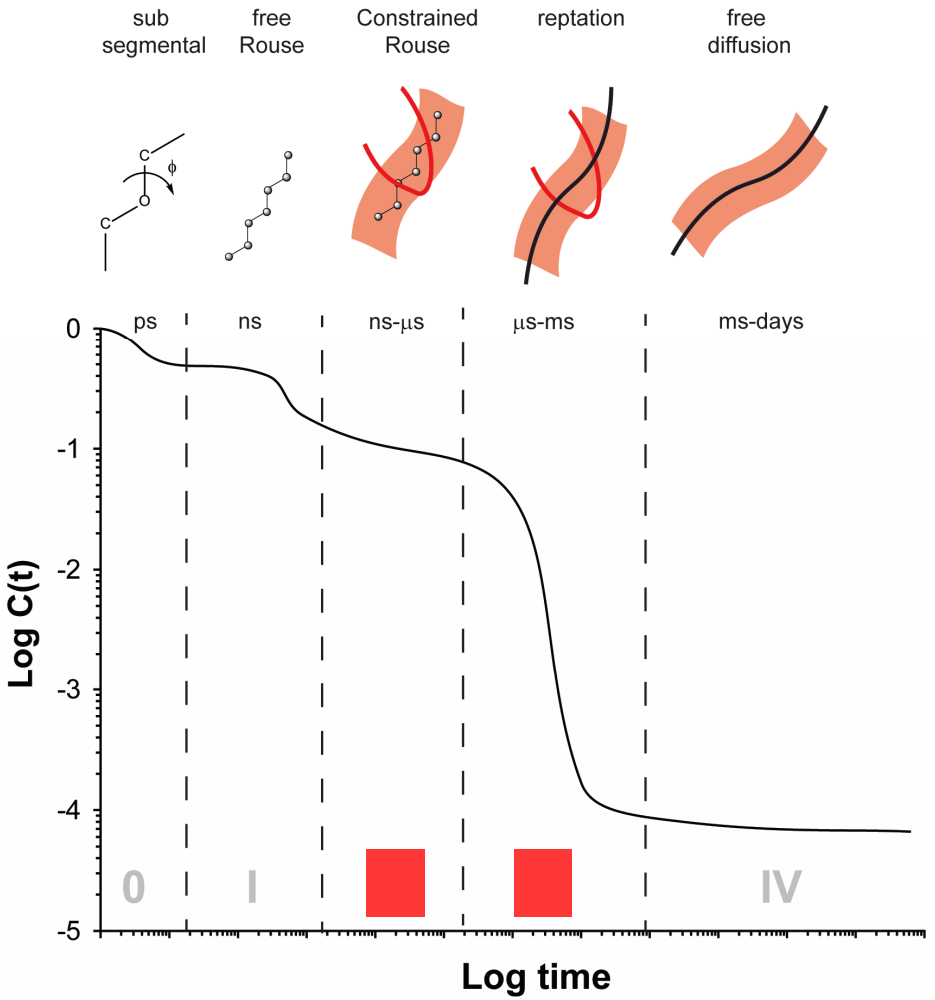




Martin-Gallego, M.; González-Jiménez, A.; Verdejo, R.; Lopez-Manchado, M. A.; Valentin, J. L., Epoxy resin curing reaction studied by proton multiple-quantum NMR. Journal of Polymer Science Part B: Polymer Physics 2015, 53 (18), 1324-1332.

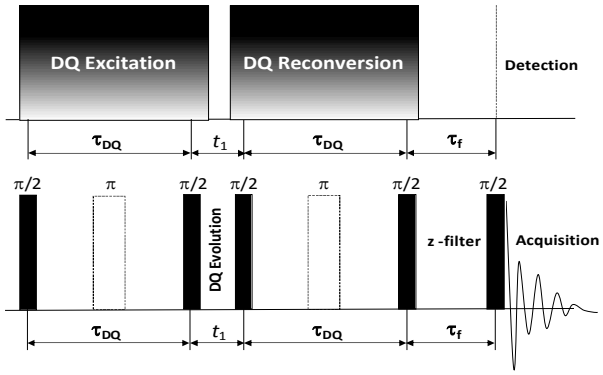
^{1}H NMR – DQ NMR Fully Cure



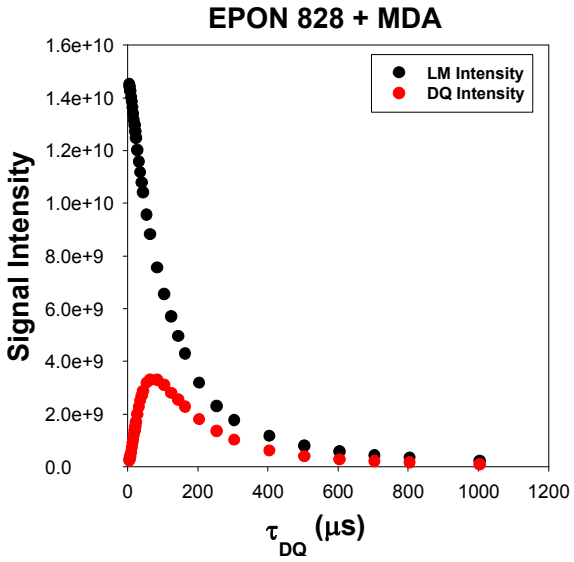


High temperature region $T > T_g$
DQ NMR directly measures S_b

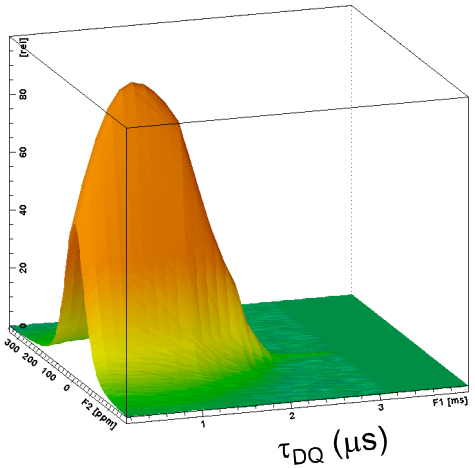
^{1}H NMR – DQ NMR Fully Cure



$$I_{nDQ} = \frac{I_{DQ}}{I_{DQ} + I_{ref} - B\exp\left[-2\tau_{DQ}/T_2\right]}$$

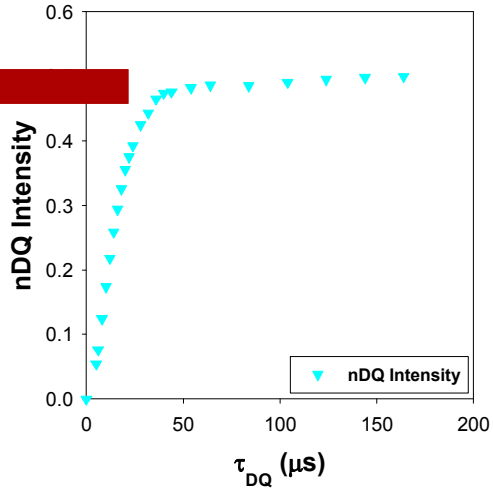


Raw DQ Data



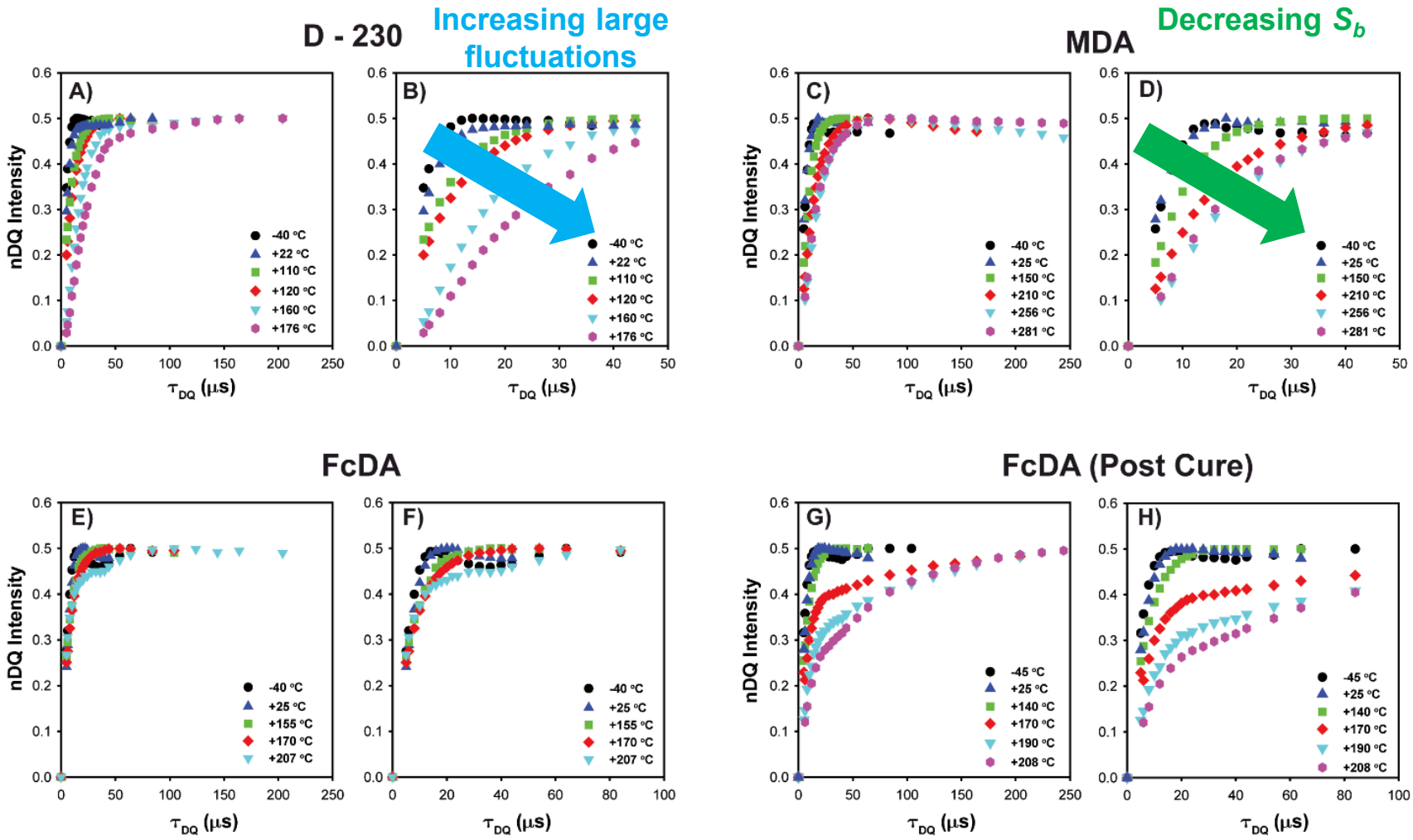
$$I_{nDQ} \rightarrow D_{res}$$

$$S_b = \frac{D_{res}}{D_{Static}}$$

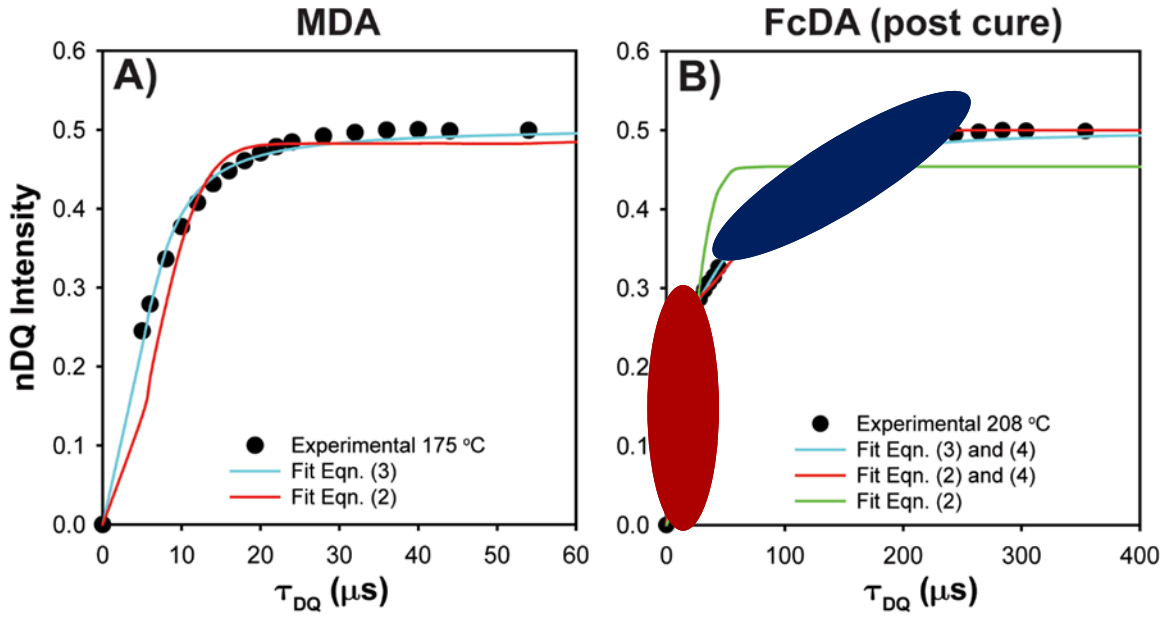


Normalized DQ Data

DQ ^{1}H NMR – Fully Cure Epoxy Normalized DQ Buildups



DQ ^{1}H NMR
Extraction of Effective Dipolar Coupling



Gaussian Buildup

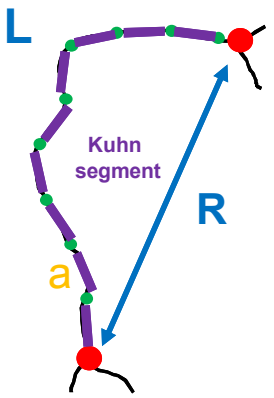
$$I_{nDQ}\left(D_{res}\right)=\frac{1}{2}\left(1-\exp\left\{-\frac{2}{5}\,\tau_{DQ}^{2}\right\}\right)$$

Gaussian-Distributed Buildup

$$I_{nDQ}\left(\bar{D}_{res},\sigma_D\right)=\frac{1}{2}\left(1-\exp\left\{-\frac{\tau_{DQ}^{2}}{1+\frac{4}{5}\sigma_D^2\tau_{DQ}^2}\right\}\left[1+\frac{4}{5}\sigma_D^2\tau_{DQ}^2\right]^{-1/2}\right)$$

$$I_{nDQ}\left(D_{res}^{(1)},D_{res}^{(2)},f\right)=f\,I_{nDQ}\left(D_{res}^{(1)}\right)+\left(1-f\right)I_{nDQ}\left(D_{res}^{(2)}\right)$$

So What….
How is this Related to Polymer Physics?



$$S_b = \left\langle P_2\left(\cos\theta_t\right)\right\rangle_t = k\frac{D_{res}}{D_{stat}}\frac{1}{\left\langle P_2\left(\cos\alpha\right)\right\rangle} = \frac{3}{5}\frac{\boldsymbol{R}^2}{L^2}$$

Freely Jointed Chain (FJC) Model

Scaling to N Kuhn segments of Length a
Follow Gaussian Statistics
Used to get cross link densities
Connects to Flory Constant C_∞
Connects to Freely Rotating Chain (FRC) and Hindered Rotation Models (HRC)

$$N_M l_M \longrightarrow Na$$

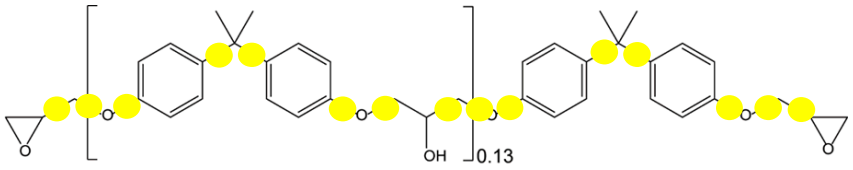
$$\boldsymbol{R}^2 = Na^2;\ L = Na;\ r = \boldsymbol{R}/\boldsymbol{R}_0$$

Has been used to measure cross-link densities

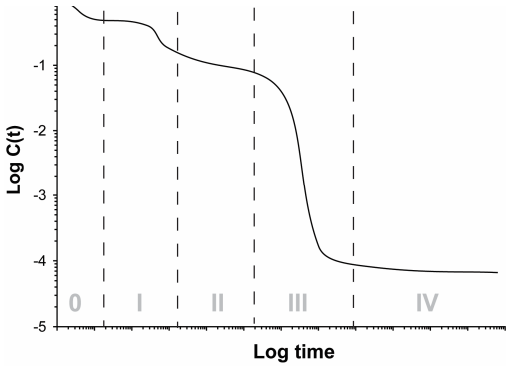
$$S_b = \frac{3}{5}\frac{\boldsymbol{R}^2}{L^2} = \frac{3}{5}\frac{r^2}{N}$$

$$\left\langle \boldsymbol{R}^2 \right\rangle \sim C_n n l^2 \quad \left(Flexible\ Chain\right)$$

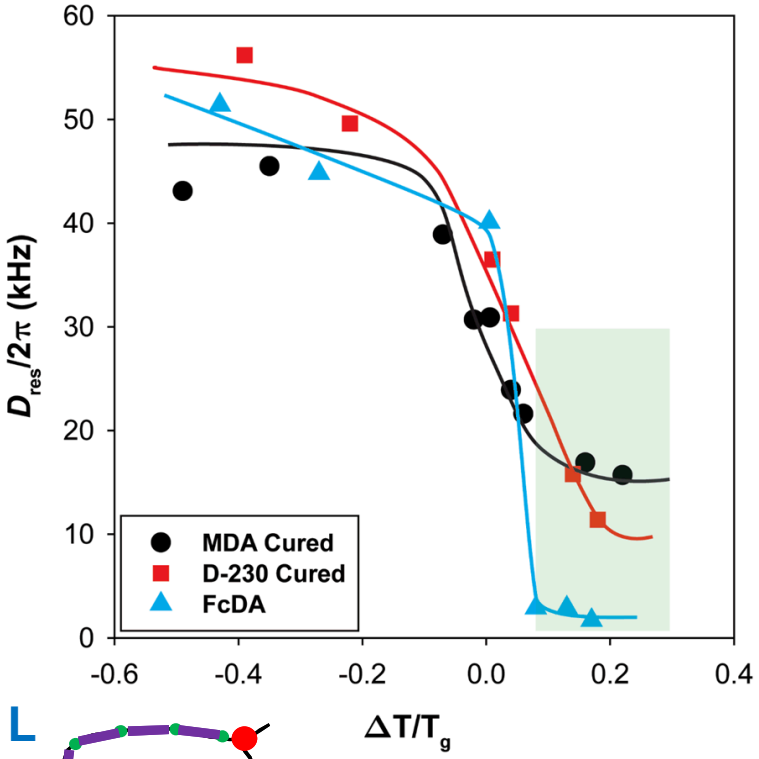
$$C_\infty = \lim_{N\to\infty} \boldsymbol{R}^2 / N_M l_M^2$$

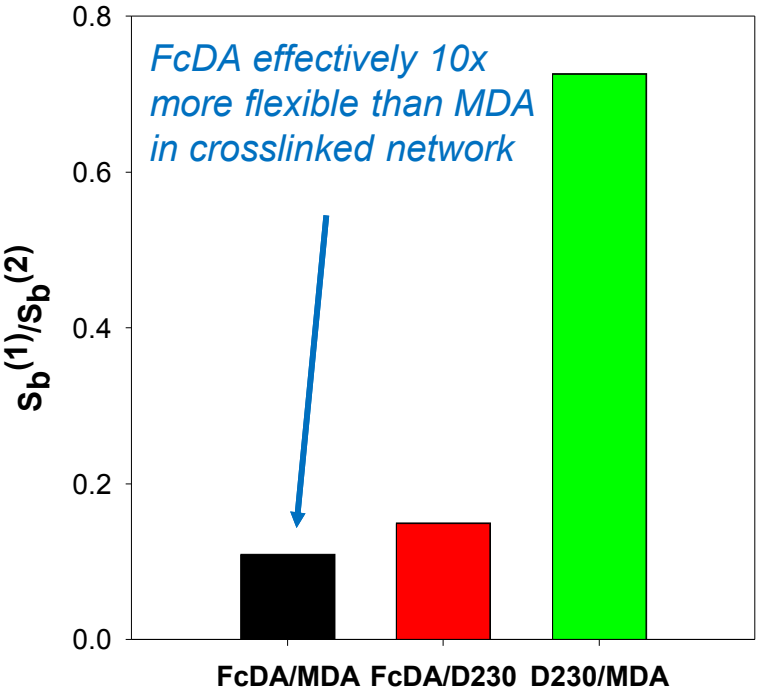


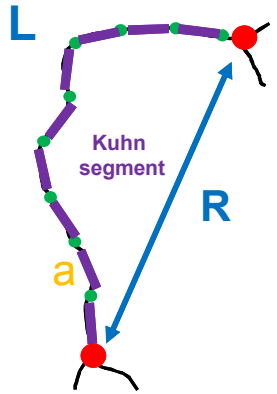
EPON 828



DQ ^{1}H NMR Derived Order Parameters







$$\frac{S_b^{(1)}}{S_b^{(2)}} = k\frac{D_{res}^{(1)}}{D_{stat}}\frac{1}{\left\langle P_2(\cos\alpha)\right\rangle} \Big/ k\frac{D_{res}^{(2)}}{D_{stat}}\frac{1}{\left\langle P_2(\cos\alpha)\right\rangle} \approx \frac{D_{res}^{(1)}}{D_{res}^{(2)}}$$

$$\frac{S_b^{(1)}}{S_b^{(2)}} \approx \frac{D_{res}^{(1)}}{D_{res}^{(2)}} = \left\{\frac{3}{5}\frac{r^2}{N^{(1)}}\right\} \Big/ \left\{\frac{3}{5}\frac{r^2}{N^{(2)}}\right\} = \frac{N^{(2)}}{N^{(1)}} = \frac{n^{(2)}C_\infty^{(1)}}{n^{(1)}C_\infty^{(2)}}$$

DQ ^{1}H NMR Distribution of D_{res}

Fredholm Integral Equation

Experimental DQ buildups

Distribution of D_{res}

$$\text{[red]} = \int_0^\infty K\left[D_{res}, \tau_{DQ}\right] \text{[blue]}\, dD_{res}$$

Kernel

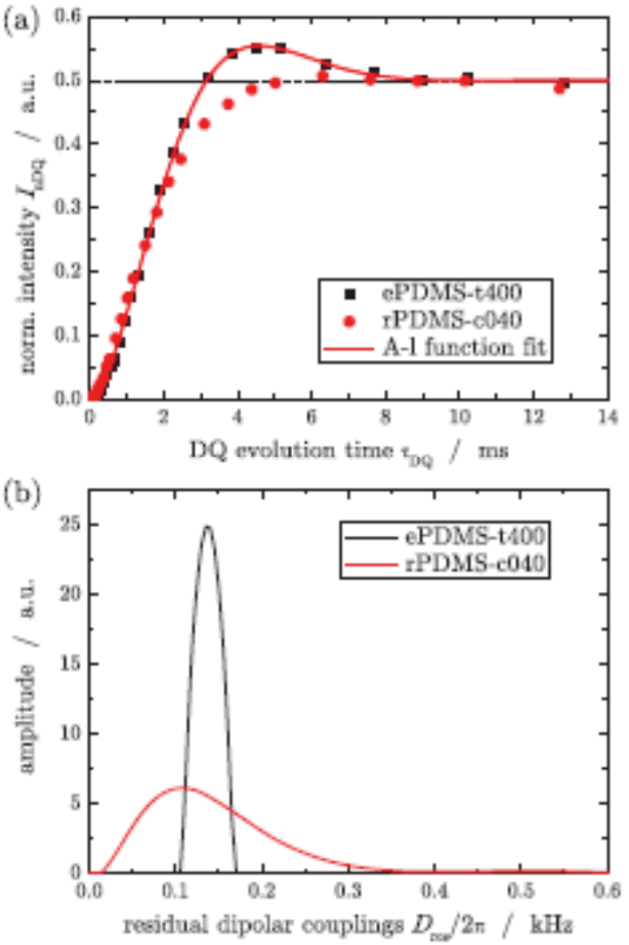
$$K\left[D_{res}, \tau_{DQ}\right]$$

Gaussian Buildup Kernal

$$I_{nDQ}\left(D_{res}\right) = \frac{1}{2}\left(1 - \exp\left\{-\frac{2}{5} D_{res} \tau_{DQ}^2\right\}\right)$$

"Abragam-like" (A-1) Kernel

$$I_{nDQ}\left(\tau_{DQ}, D_{res}\right) = \frac{1}{2}\left(1 - \exp\left\{-\left(0.378 D_{res} \tau_{DQ}\right)^{1.5}\right\}\right) \times \cos\left[0.583\right] D_{res} \tau_{DQ}$$



Chassé, W.; Valentín, J. L.; Genesky, G. D.; Cohen, C.; Saalwächter, K., Precise dipolar coupling constant distribution analysis in proton multiple-quantum NMR of elastomers. *The Journal of Chemical Physics* **2011,** *134* (4), 044907.

Conclusions

- ^{1}H NMR line width variation used to probe local polymer dynamics as a function of temperature.
- Allows evaluation of E_a for segmental motions at glass transition.
- DQ 1H NMR can be used to look at epoxy curing from purely segmental motion viewpoint (S_b).
- For $T >> T_g$ the DQ build up curves allow the order parameter S_b in the rubber plateau to be measured.
- The FcDA cured epoxy shows a heterogeneous cross-link (dynamic) environment.
- Order parameters can be related to polymer models and crosslink properties.
- Examples are an average over all ^{1}H and most likely includes distributions in segmental contributions.

Thank You for Your Attention!