



Probing the origins of ductility in amorphous polymers

Ashish Lele

Complex Fluids and Polymer Engineering Group

National Chemical Laboratory, India 411 008

ak.lele@ncl.res.in

Team Effort

- **Team NCL**

- Ashish Lele, Ajith Kumar, P R Rajamohanan, Renny Mathew, Neelima Bulakh, Kalyani Chikhalikar, Anurag Pandey, Nathan Noual.

- **Team GE/Sabic IP**

- Gautam Chatterjee, Satish Gaggar, Dibakar Dhara, Arun Sikder, C. Seetharaman, Sanjay Charati.

- **Acknowledgement**

- GE Plastics/SABIC-IP
- Bibhuti Das (IISc), Detlef Riechert (Univ Halle)

Origin and Motivation

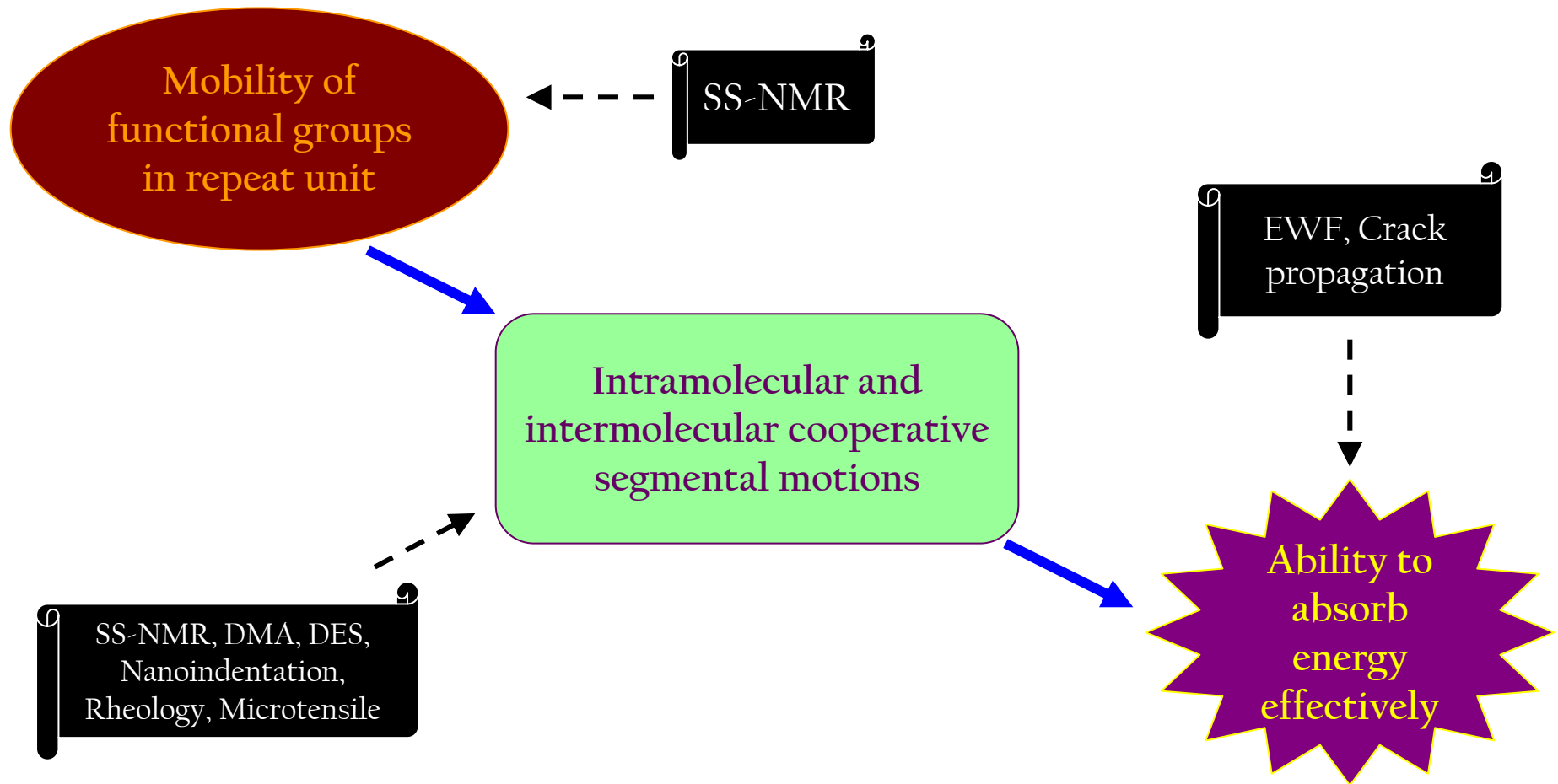
- Improved polycarbonates via copolymerization/blending.
- Ranking using micro-scale testing techniques.
- Understanding of molecular origins of ductility.

Approaches

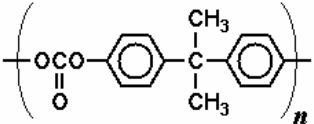
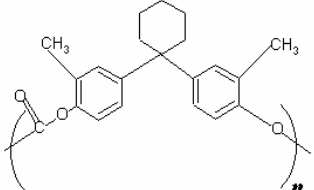
- Fracture Mechanics

- Molecular Mobility

Rationale and Approach



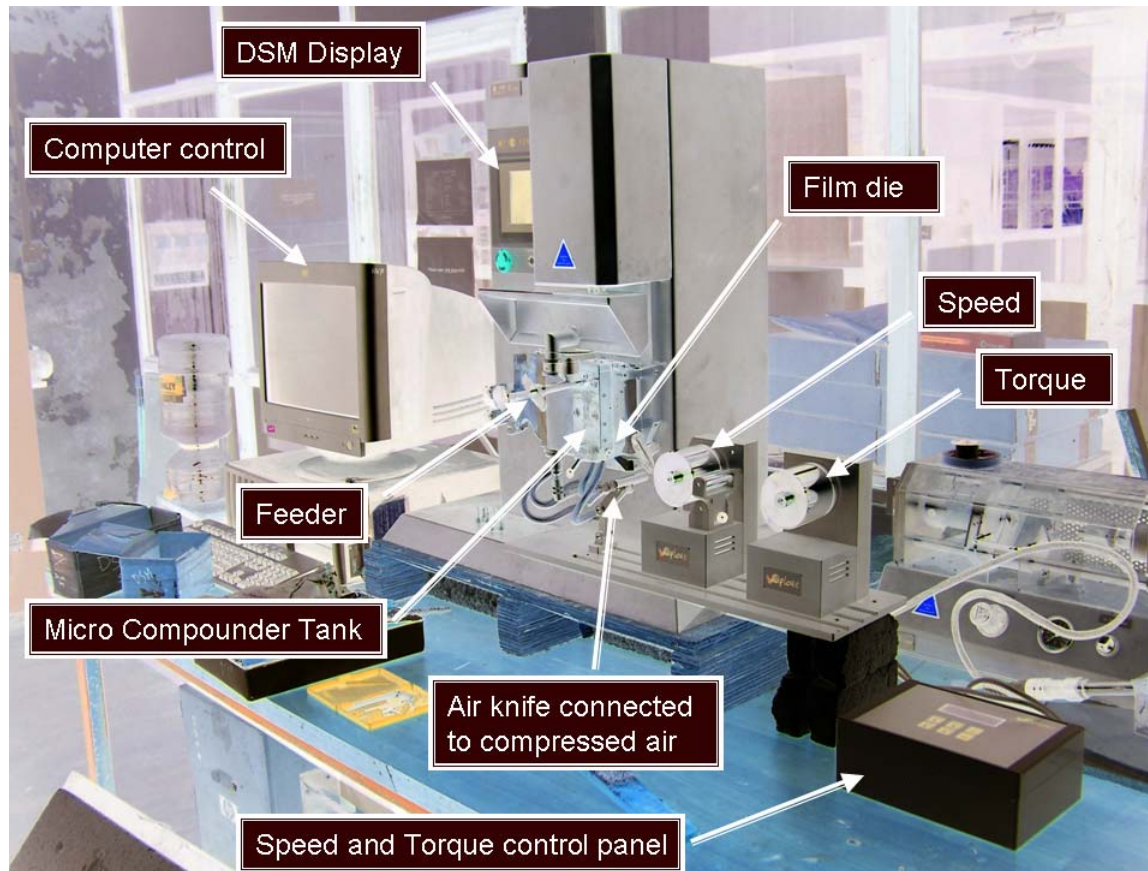
Materials

Polymer	Structure of repeat unit	Mn (kg/mol)	Mw (kg/mol)	PDI	Tg (°C)
BPA-polycarbonate		26.5	48.5	1.8	149
DMBPC-polycarbonate		23.0	43.0	1.9	140

Bisphenol-A Polycarbonate (BPA-PC)

Dimethyl bisphenolcyclohexane Polycarbonate (DMBPC)

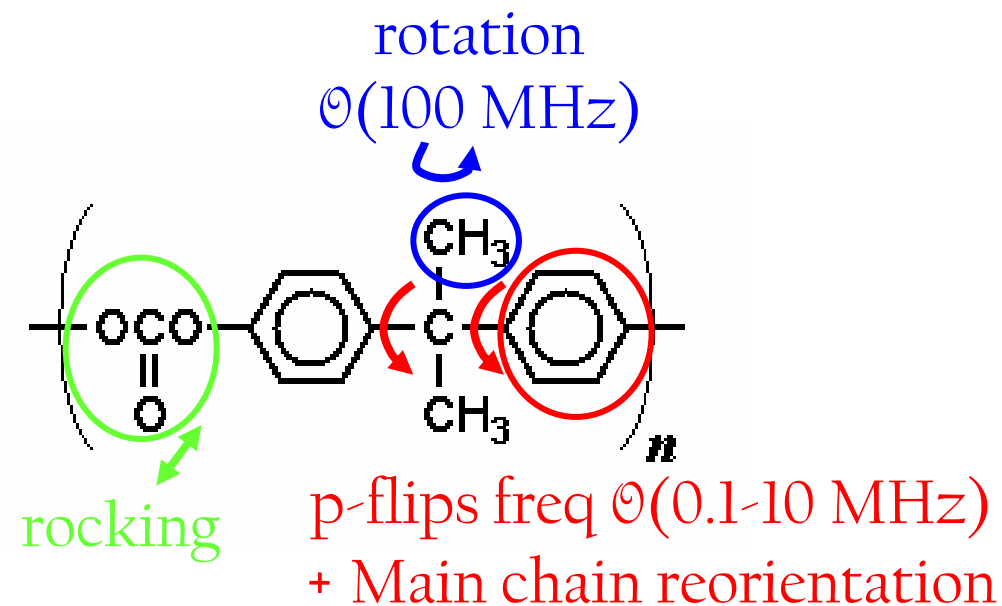
Sample Preparation



Outline

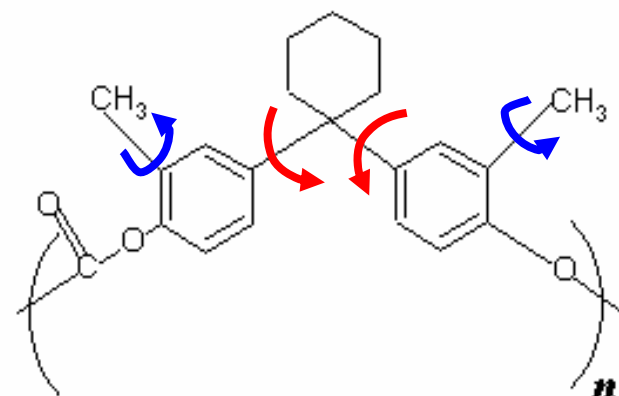
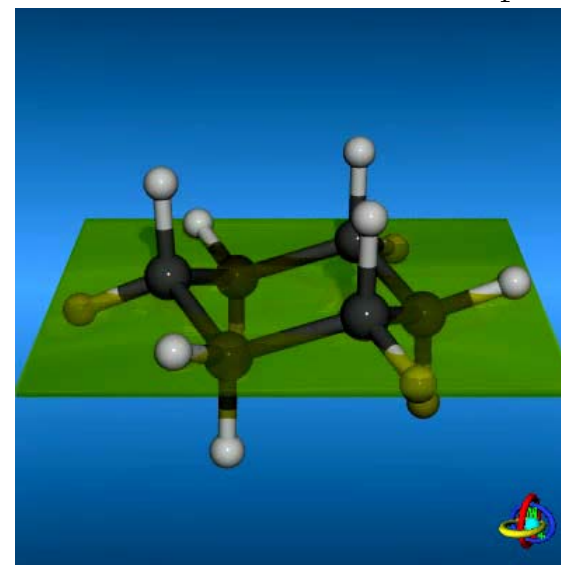
- Functional group mobility: SS-NMR (300 MHz)
- Segmental mobility: SS-NMR, DMA (Tensile-mode)
- Entanglements: Rheology (SAOS)
- Ductility: Nano-indentation and Microtensile
- Concluding remarks (homopolymers) and future work
- Copolymers

Functional Group Motions



At ambient temperature

Wikipedia



NMR: Basics

- Nuclear precession about B_0 .
- Angular momentum, magnetic moment and energy in field

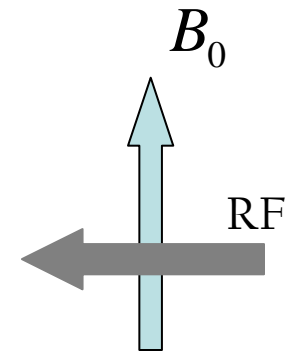
$$I_z = m\hbar \quad \text{and} \quad \mu_z = \gamma I_z = m\gamma\hbar \quad (m = -l \text{ to } +l \text{ in integral steps})$$
$$E = \mu_z B_0 = m\gamma\hbar B_0$$

- Energy states, population distribution and resonance

For ^1H and ^{13}C nuclei $m = -1/2$ and $+1/2$ $\therefore \Delta E = \gamma\hbar B_0$

$$\omega = \frac{\Delta E}{\hbar} = \gamma B_0 \quad \longrightarrow \quad \text{Radiofrequency range}$$

- Shielding and chemical shifts



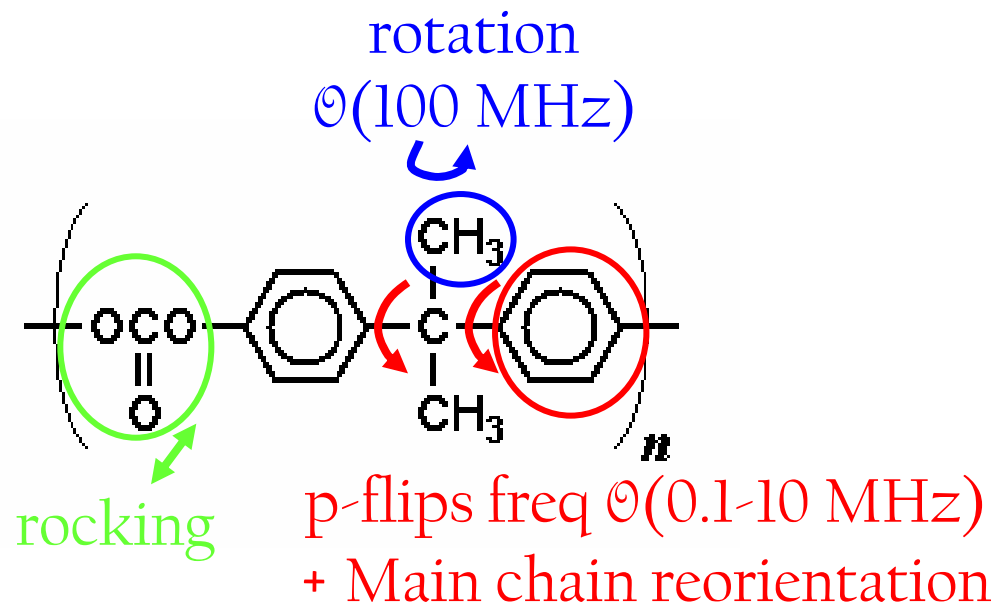
NMR: Spin-Lattice Relaxation

- Relaxation of the z-magnetic moment after a pulse perturbation.

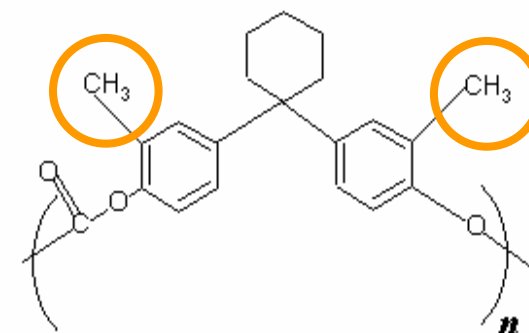
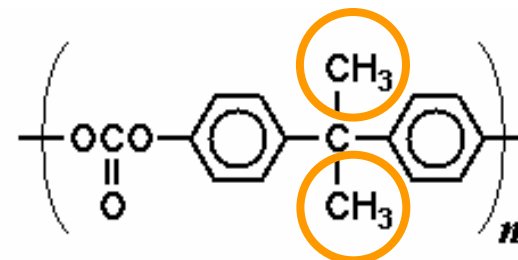
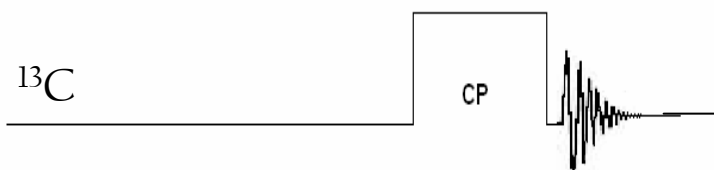
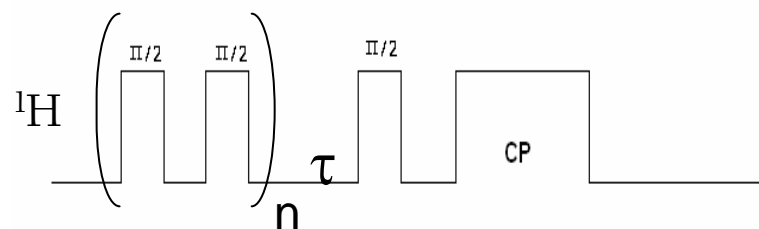
$$M_z = M_{z,eq} - [M_{z,eq} - M_z(0)] e^{-t/T_1}$$

- Exchange of nuclear spins with the surrounding (lattice)
- Driven by motions of the order of the applied NMR frequency.

NMR: Spin-Lattice Relaxation



^1H T_1 Relaxation Results



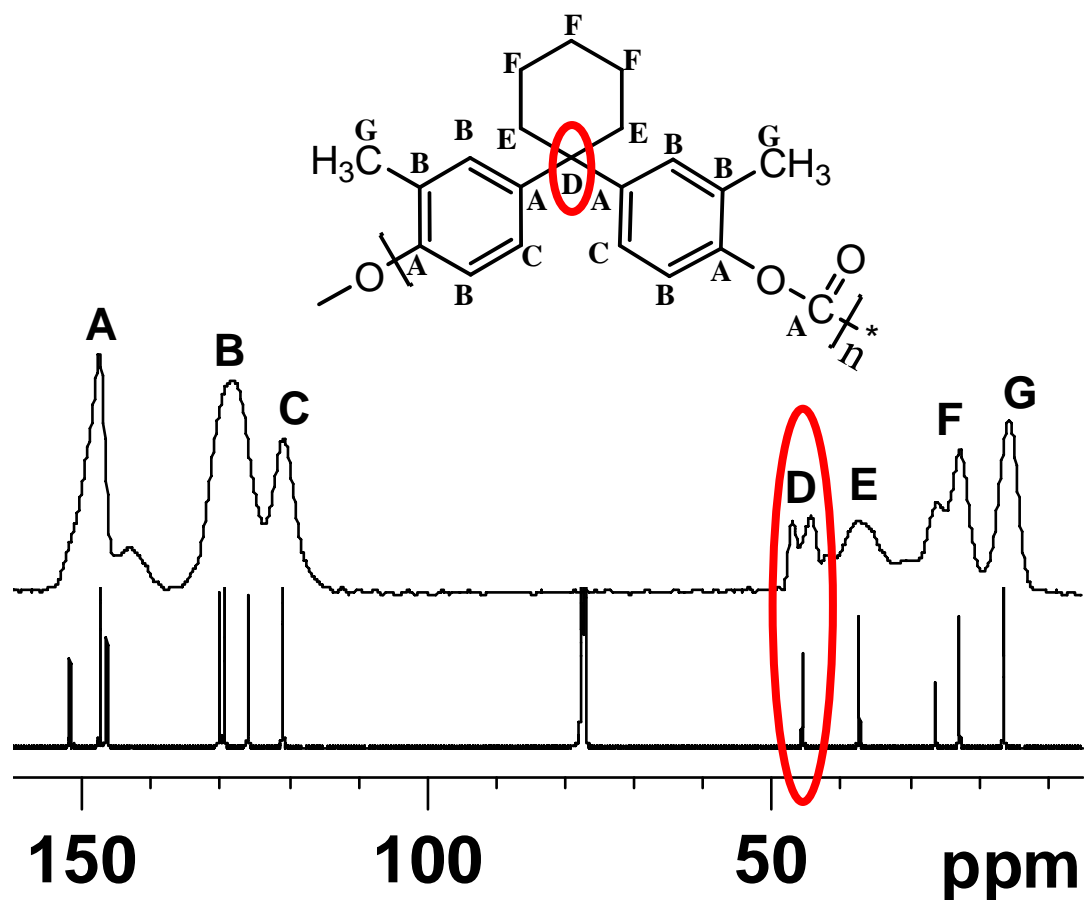
^1H Spin-Lattice (T_1) relaxation

Material	Average ^1H T_1 (ms)
BPA/DMBPC	
H-100/0	325.3
H-0/100	933.0

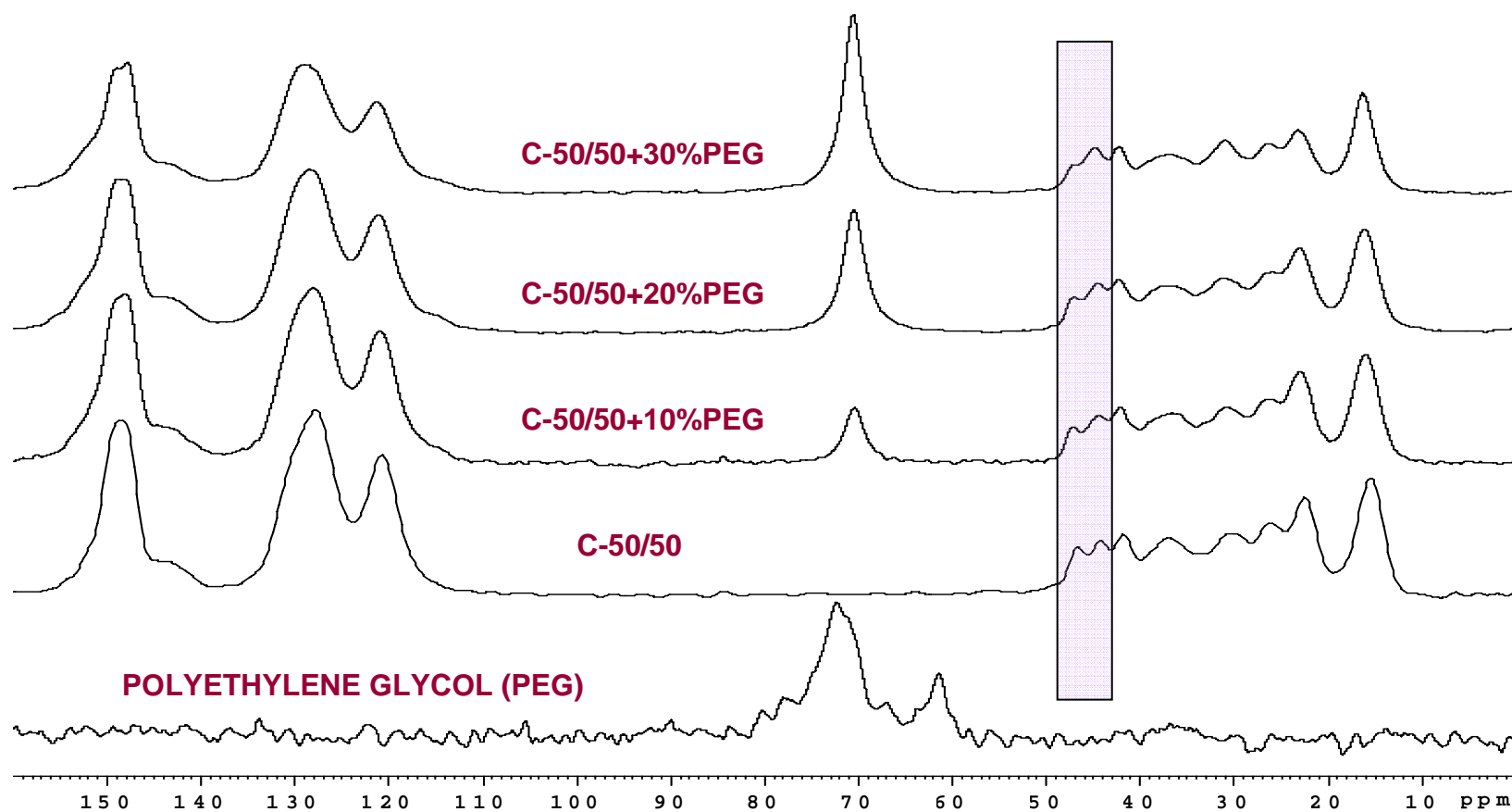
NMR: Inter-nuclear Coupling

- Two types: homonuclear and heteronuclear. ^1H - ^1H coupling is strong due to 100% abundance and high γ . Comparitively, ^{13}C - ^{13}C coupling is weaker due to low abundance and lower γ .
- High mobility in liquids averages the internuclear coupling to zero. In solids, this is not the case, and this causes broadening of signals. ^{13}C SS-NMR is better.
- MAS at $\theta_m = \cos^{-1}(1/\sqrt{3}) = 54.7^\circ$ averages internuclear dipolar coupling to zero resulting in narrower signals. MAS also removes effects of CSA.
- CP reintroduces heteronuclear coupling by transferring the magnetization from abundant ^1H to less abundant ^{13}C nuclei. This improves ^{13}C signals.

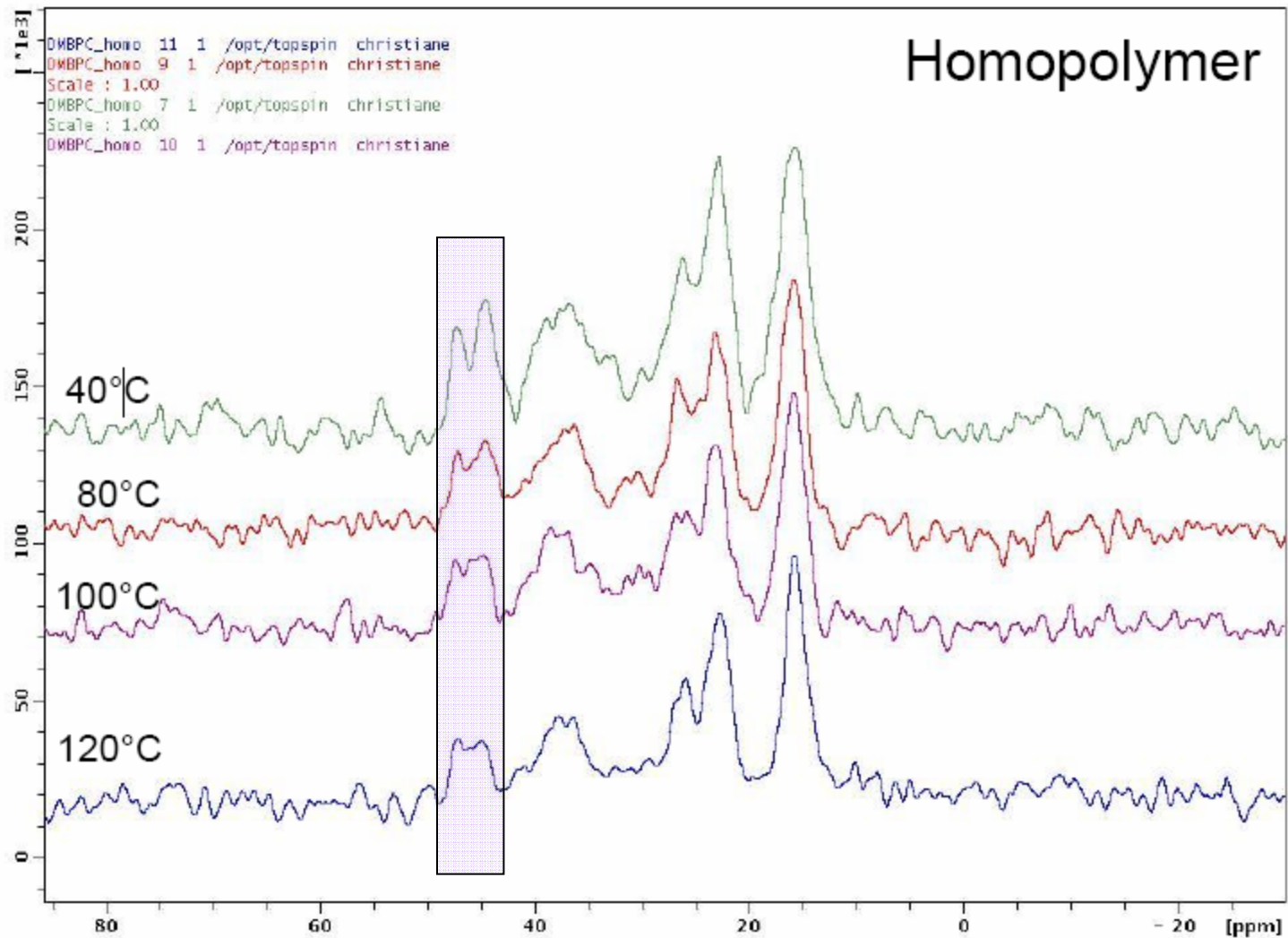
^{13}C CPMAS of DMBPC



^{13}C CPMAS of DMBPC

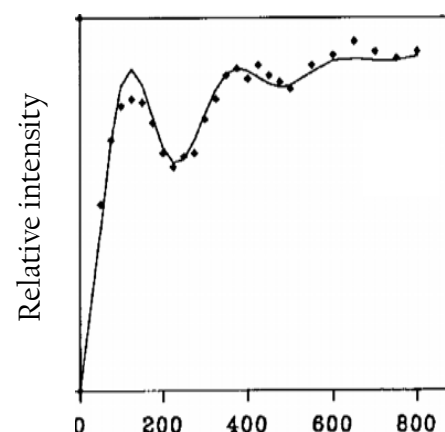
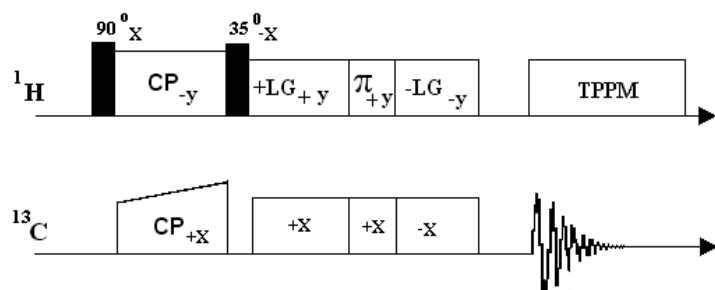


^{13}C CPMAS of DMBPC



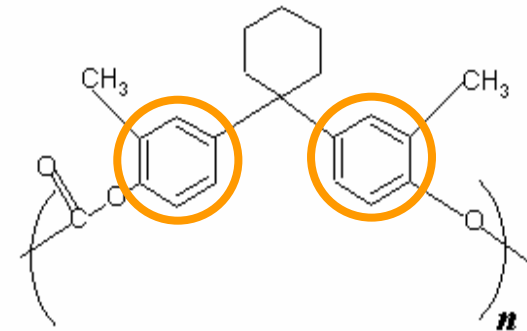
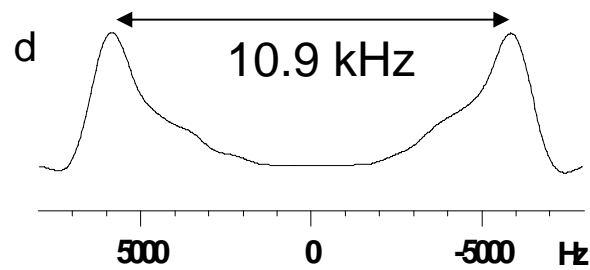
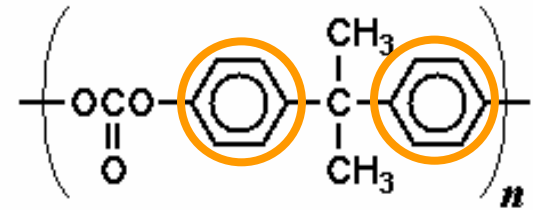
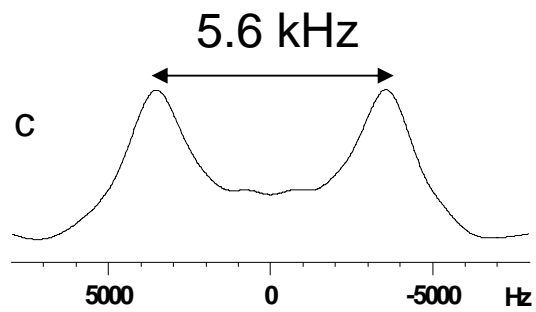
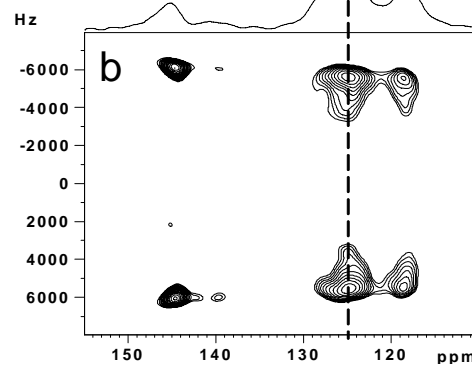
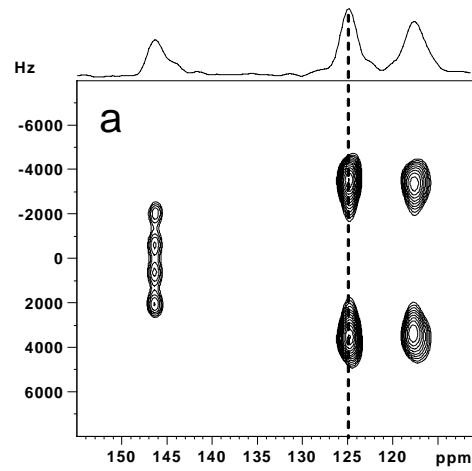
NMR: SLF Experiment

- SLF is a CP experiment in which the RF field is used to couple the magnetization of ^{13}C with that of ^1H for controlled intervals of time.

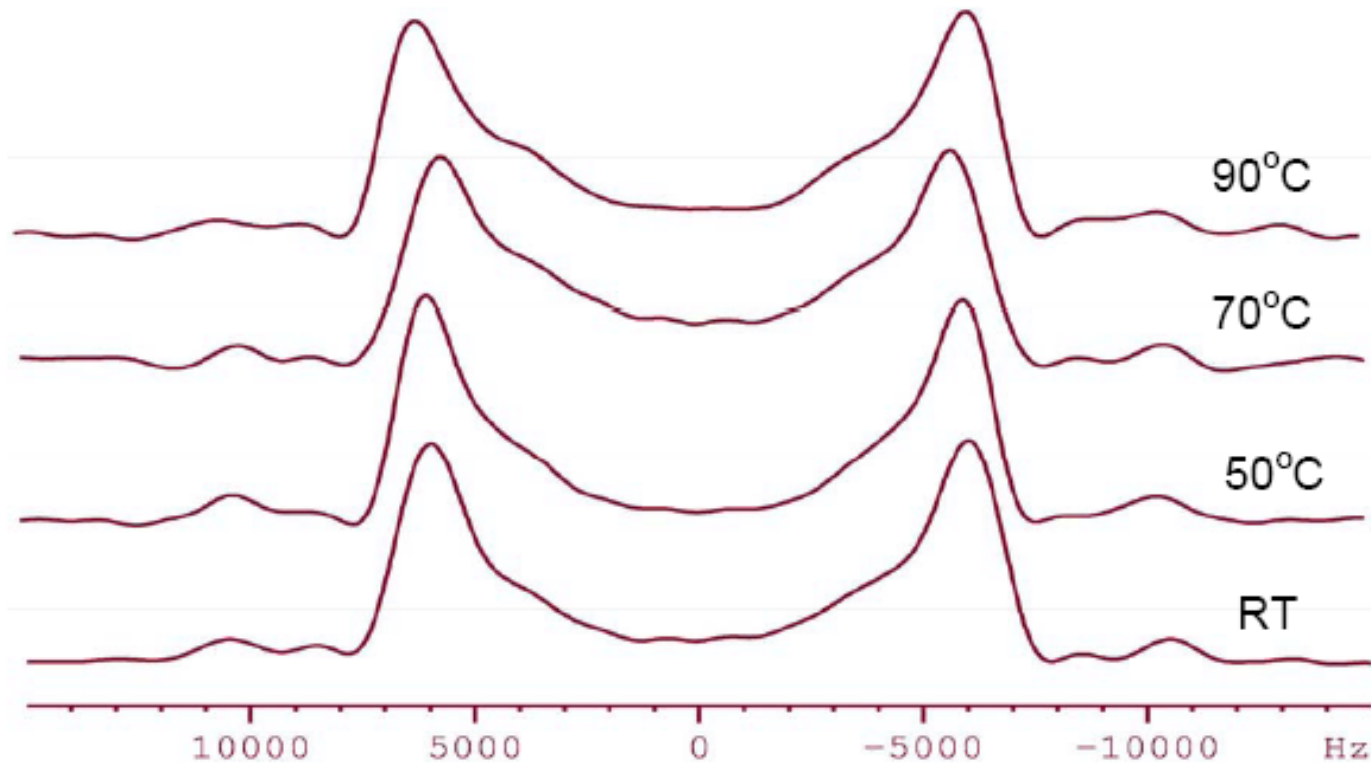


- The transfer of magnetization is a coherent process. The measured ^{13}C magnetization shows damped oscillations with a characteristic frequency.
- The frequency depends on the strength of the ^{13}C - ^1H heteronuclear coupling.
- Nuclei on immobile groups couple strongly than those on mobile groups. This provides for a way to measure mobility of functional groups.

SLF Results



SLF Results



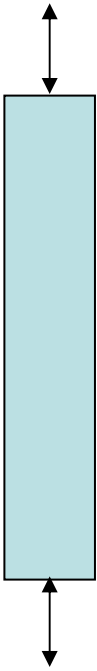
Functional Grp Motions: Summary

- Motions of functional groups in DMBPC (methyl rotation, cyclohexyl conformations and phenyl flips) are severely hindered. Functional groups in BPA-PC are highly mobile.
- Dimethyl substitution on phenyl rings hinder π -flips and chair-chair conformations of cyclohexyl.
- DMBPC monomer is a motionally rigid unit.

Outline

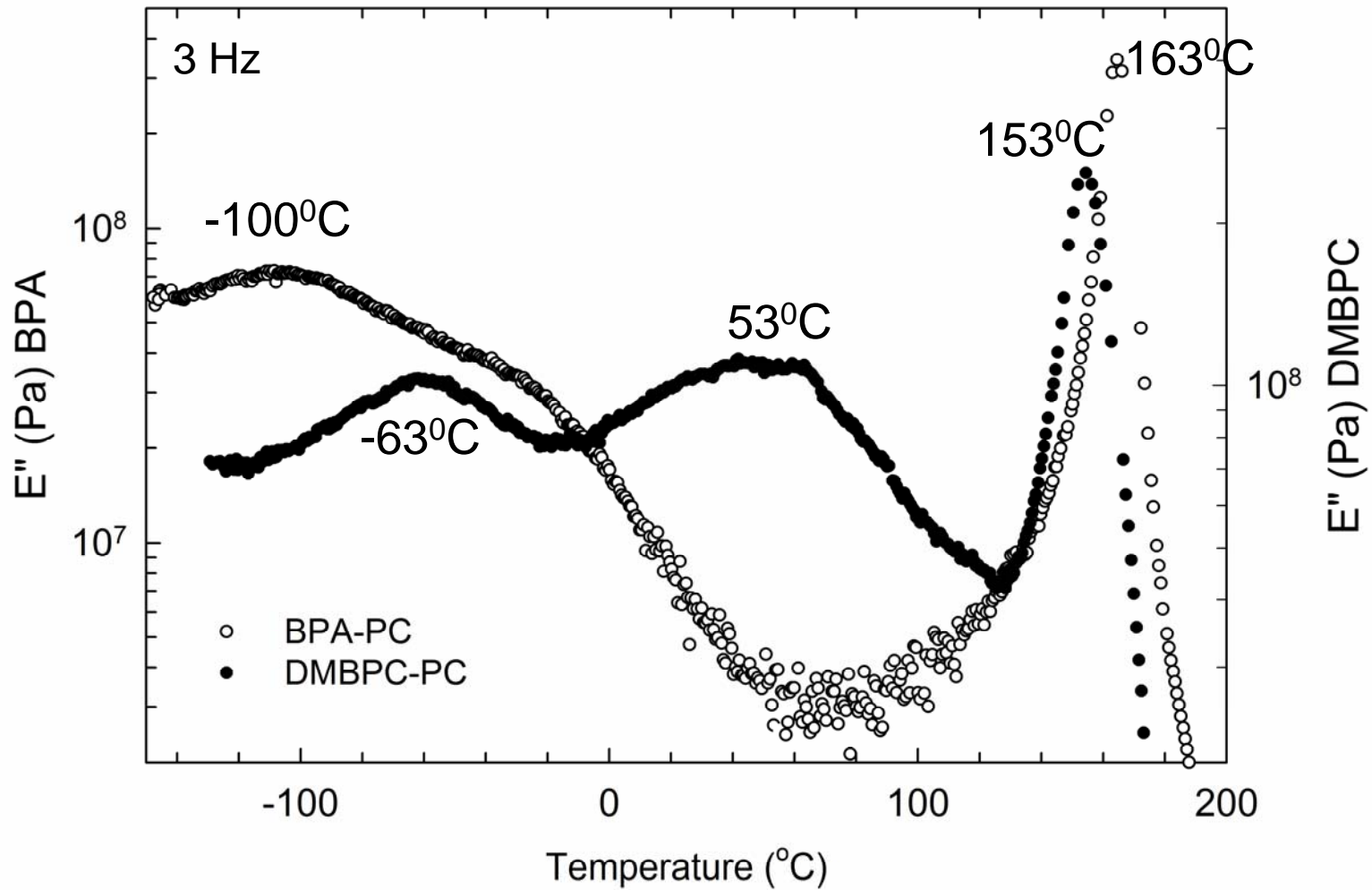
- ✓ ● Functional group mobility: SS-NMR (300 MHz)
- Segmental mobility: DMA (Tensile-mode), SS-NMR
- Entanglements: Rheology (SAOS)
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- Copolymers

DMA

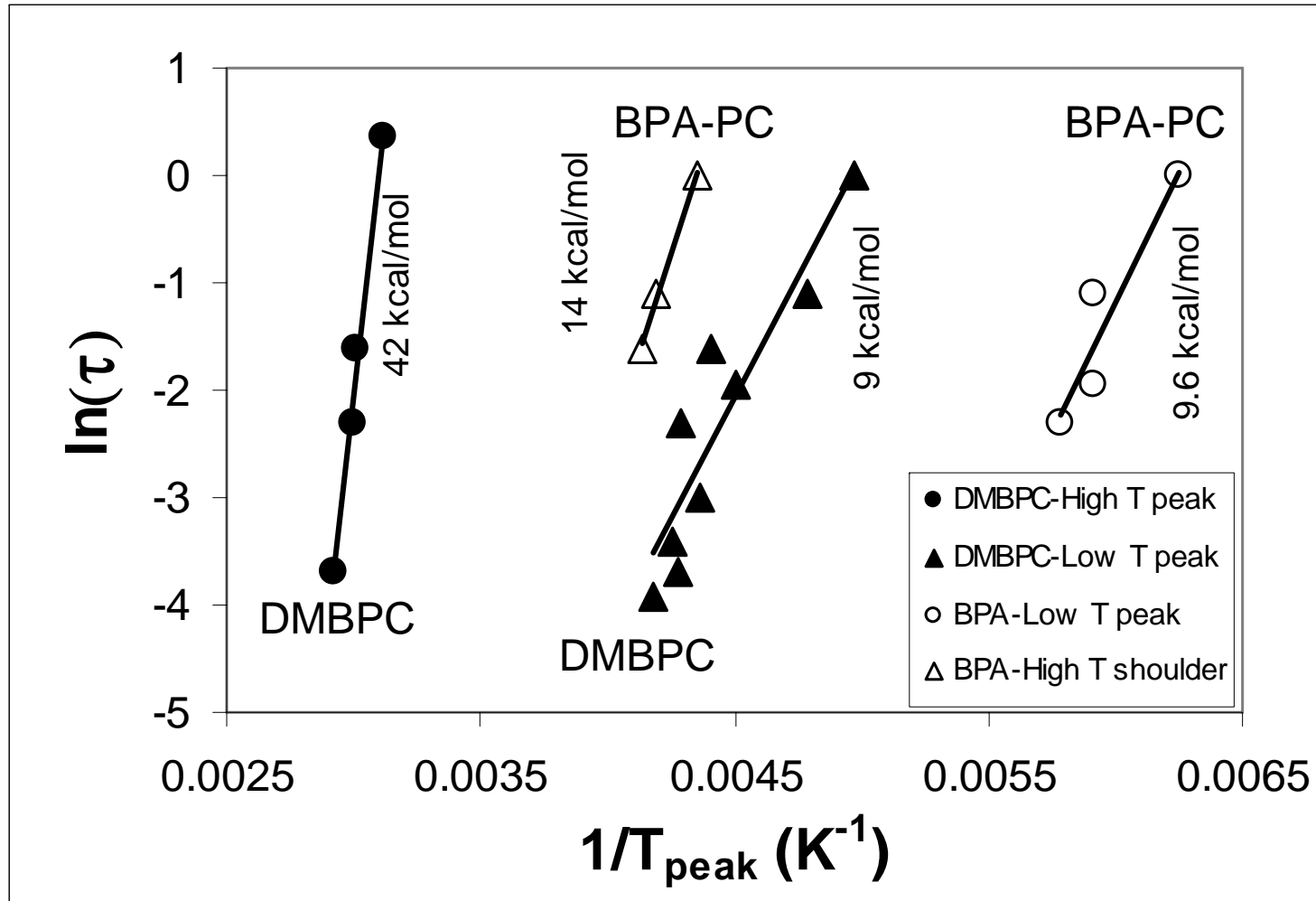


- Film samples prepared by extrusion casting/compression molding
- SAOT deformation to measure dynamic moduli. Peaks observed in loss moduli signify segmental relaxations.
- Equipment: Rheometrics DMTA IIIE
- Isochronal temperature ramp: -110°C to 200°C , 0.04% strain
- Frequency range: 1 – 50 Hz

DMA: Results

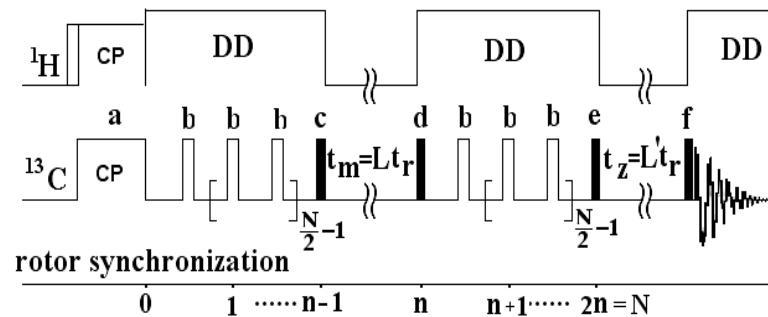


DMA: Analysis



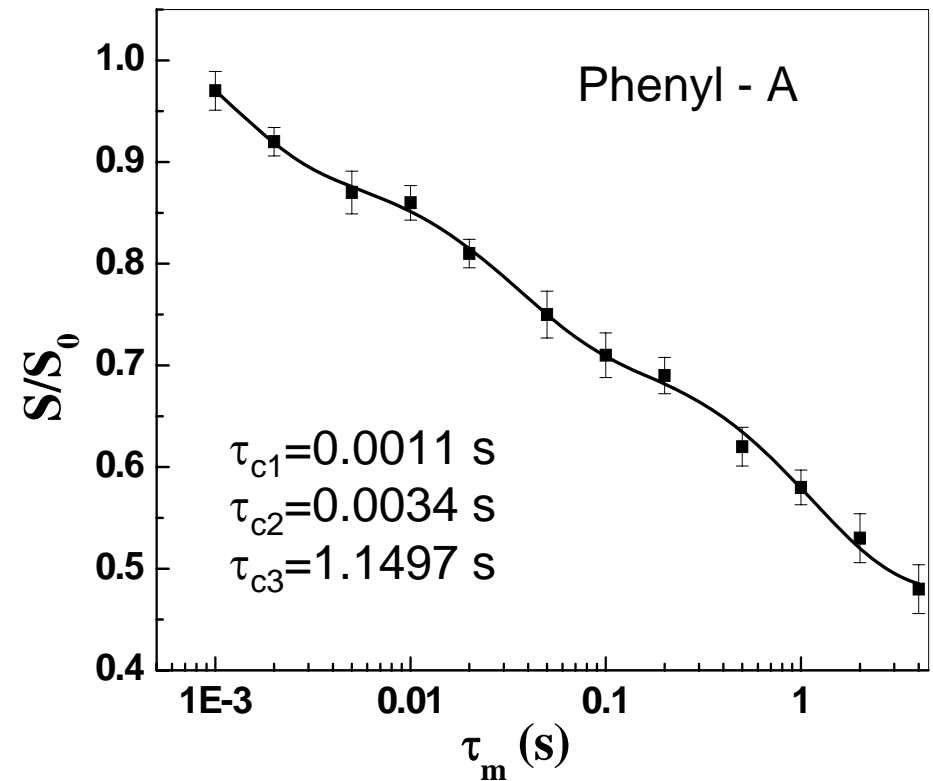
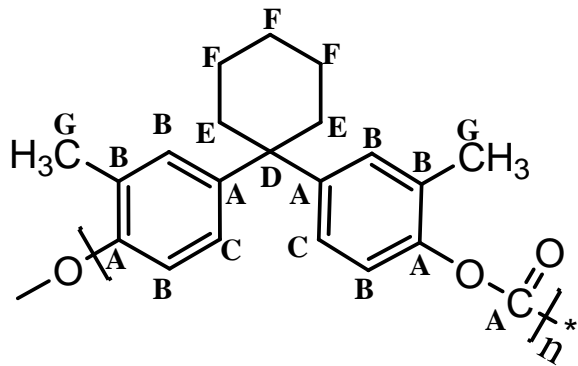
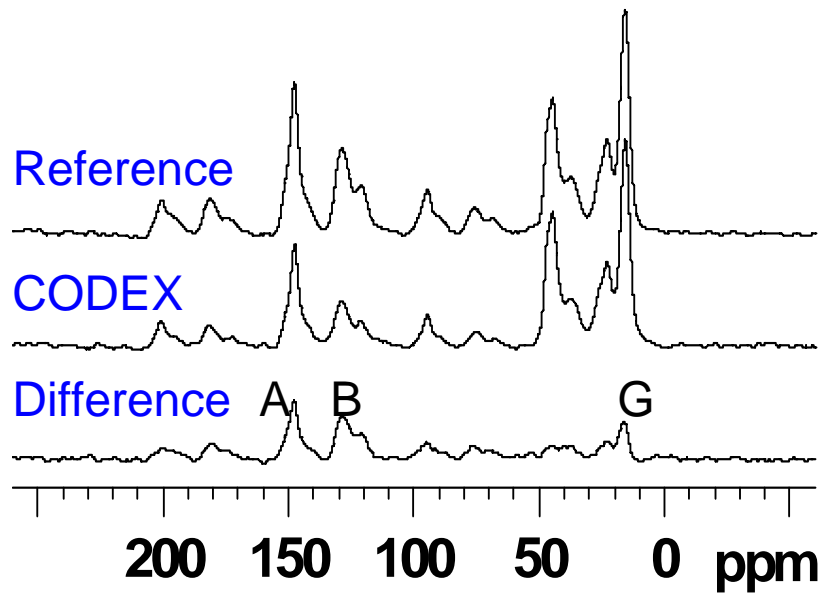
SS-NMR: CODEX

- CODEX is a CPMAS experiment in which a specific pulse sequence is used to reintroduce and measure CSA in ^{13}C nuclei.

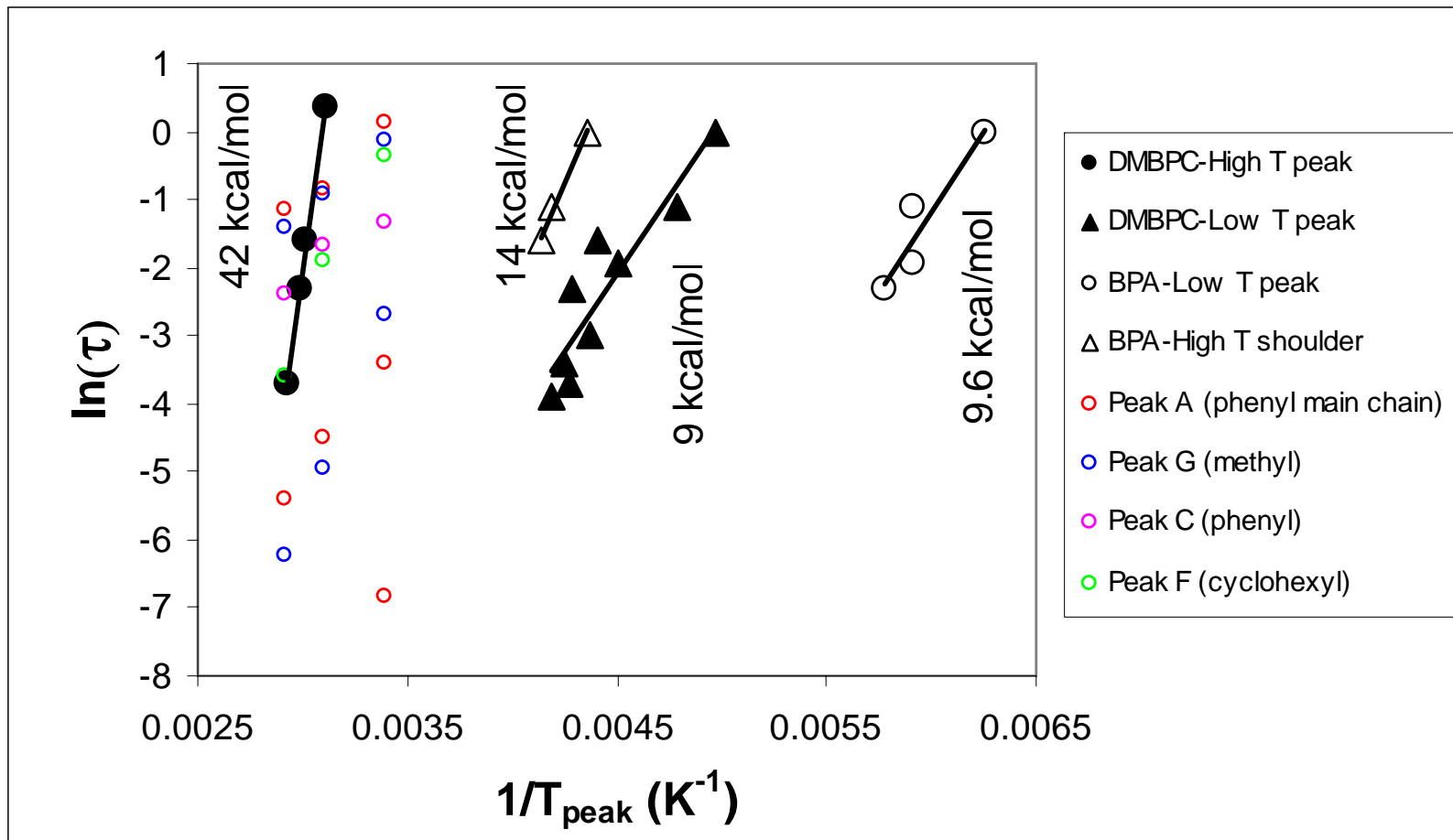


- After a controlled ‘mixing time’ the same pulse sequence is imposed to remeasure the CSA. If molecular reorientation occurs during mixing time, the CSA measured in the two pulse sequences will be different.
- CODEX allows for measurement of slow segmental motions ($\sim \mathcal{O}(\tau_m)$). Very fast and very slow motions do not respond in CODEX.

CODEX: Results



DMA and CODEX



Segmental Motions: Summary

- Compared to BPA-PC the segmental motions in DMBPC are slower (high peak temperatures in DMA), require higher activation energy, and are less cooperative (narrower peaks).
- CODEX shows that the β -transition in DMBPC involves backbone motions driven by phenyl flips and methyl rotations [and carbonyl rocking (by DES)]. Cyclohexyl group is motionally too rigid to contribute.
- Segmental motions involve multiple relaxations.

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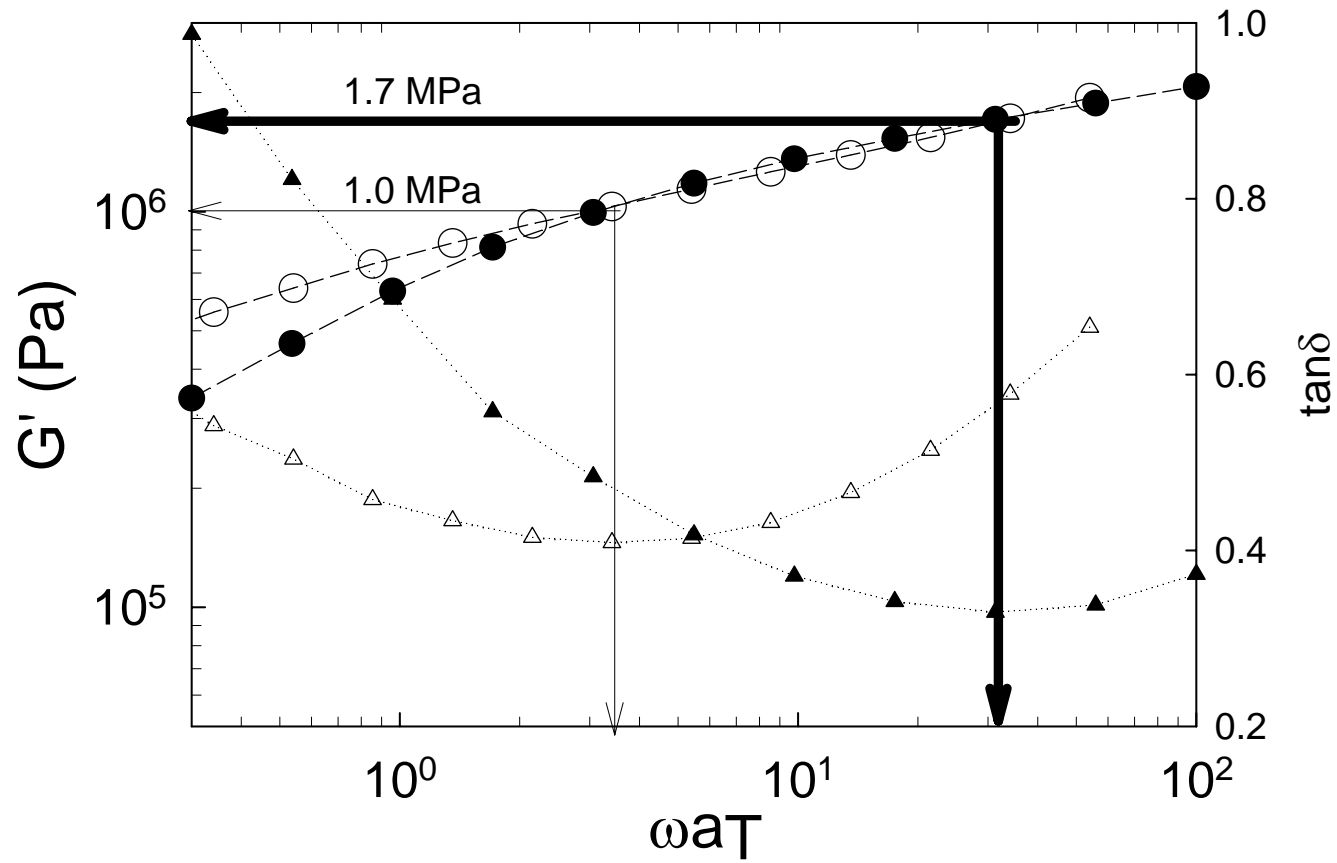
Rheology



- SAOS @ 0.1 – 100 rad/s, strain in LVE range, 170°C to 290°C.
- 25 mm parallel plate fixture, 0.5 mm gap
- Time-temperature superposition

Rheology: Results

170°C



Rheology: Analysis

Parameter	BPA-PC	DMBPC
M_e (g/gmol)	2812	4800
V_e (nm ³)	4.1	7.0
p (Å)	2.1	2.5
$\langle R^2 \rangle_0 / M$ (Å ² gmol/g)	0.69	0.41
a (nm)	4.4	5.3

$$M_e = \frac{\rho RT}{G_N^0}$$

$$V_e = \frac{M_e}{\rho N_{AV}}$$

$$p \cong \left[\frac{\exp(-T / 635) RT}{200 G_N^0} \right]^{1/3}$$

$$\frac{\langle R^2 \rangle_0}{M} = \frac{1}{p \rho N_{AV}}$$

Rheology: Summary

- Compared to BPA-PC chain the DMBPC polymer chain in the molten state is relatively stiffer and has a smaller mean square end-to-end distance.
- It is also relatively less entangled in the melt.
- As the polymer solidifies from melt into the glassy state, the entanglement density is expected to be largely retained. We may expect that glassy DMBPC has lower entanglement density than glassy BPA-PC.
- Lower entanglement density → lesser ability to delocalize imposed stress state.

Outline

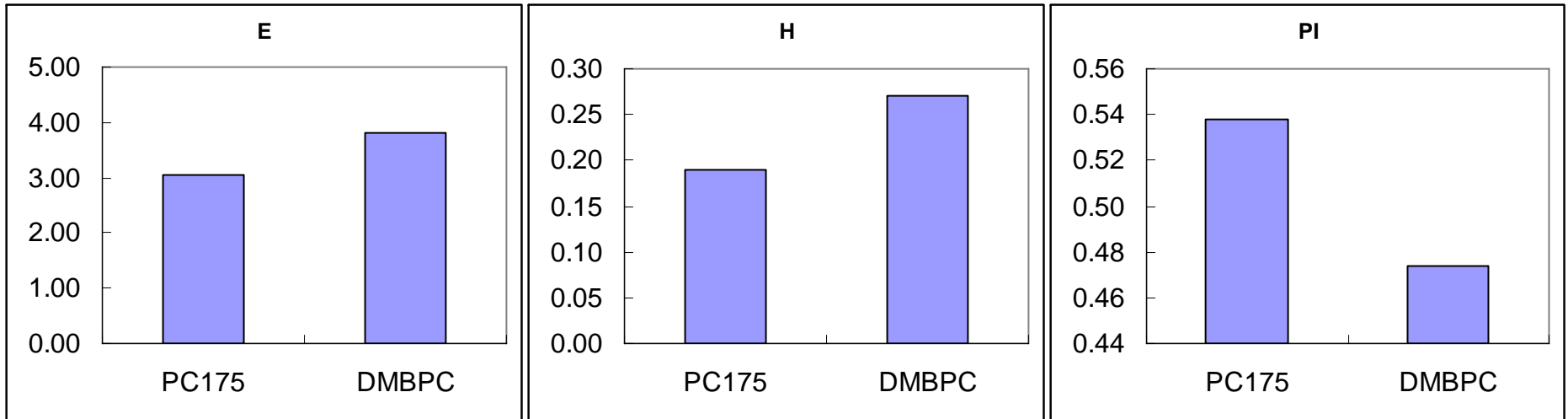
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Nanoindentation

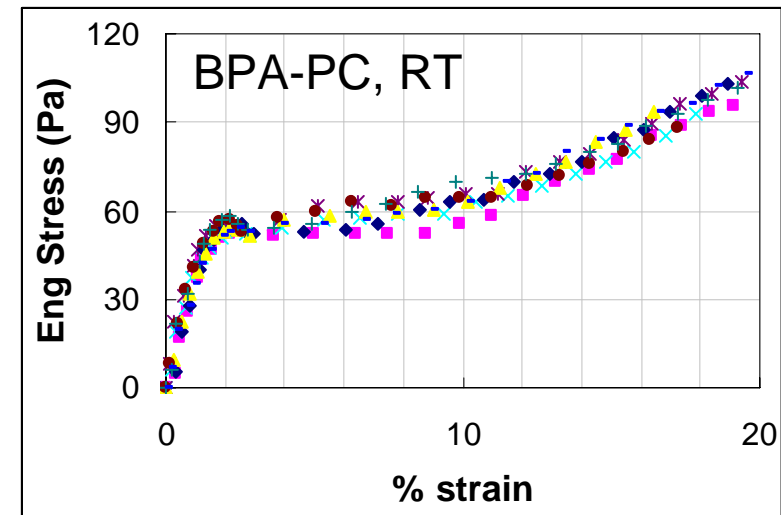
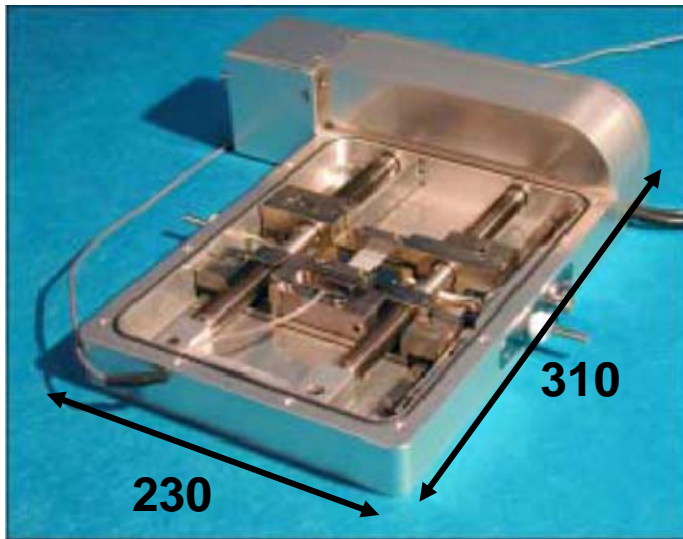
- Nano Indenter[®] XP (MTS System Corporation, Oak Ridge, TN) with a three-sided Berkovich-shaped diamond indenter.
- Extrusion cast films of ~ 100 μm (t) x 30 mm (W) x 60 mm (L) mounted on thickn glass slides.
- Continuous stiffness measurement technique used to generate load-displacement data. Contact depth of 500 nm was employed.
- Plasticity Index (PI) was calculated from data

$$PI = \frac{\text{Work of plastic deformation}}{\text{Total (elastic + plastic) work of deformation}}$$

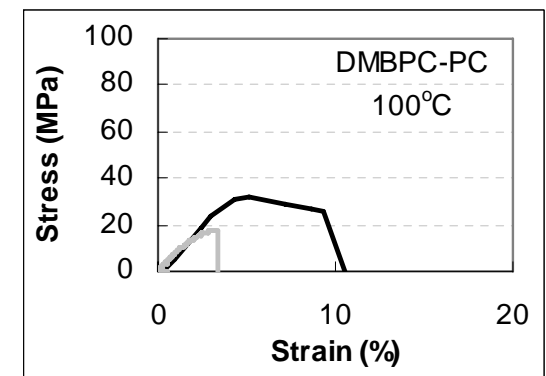
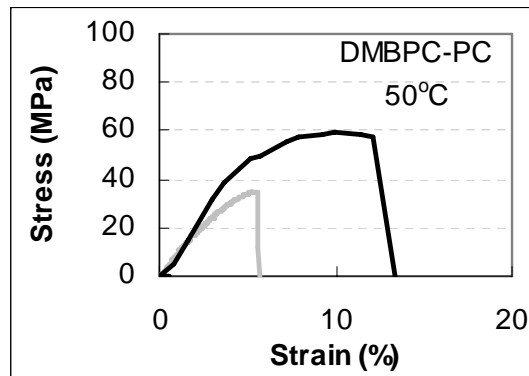
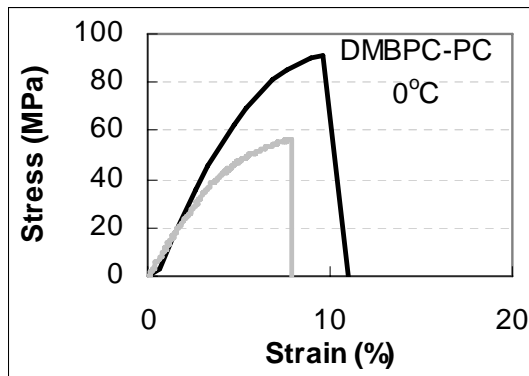
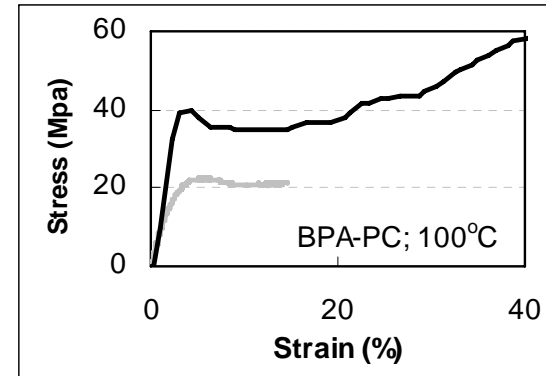
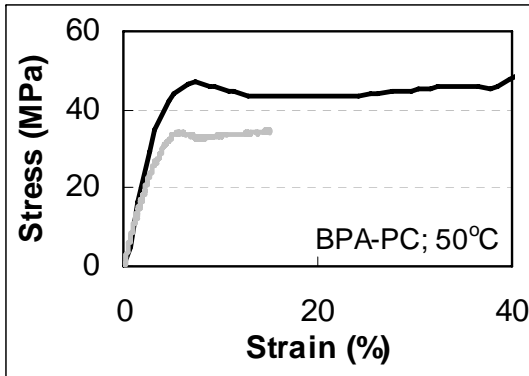
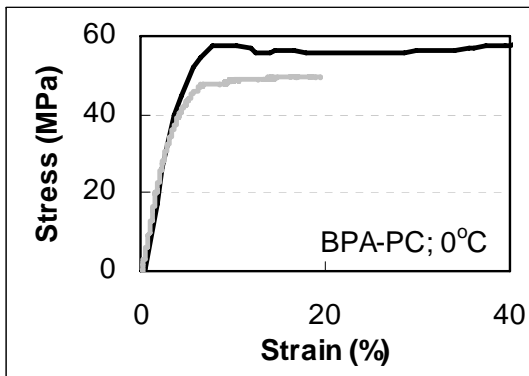
Nanoindentation: Results



Microtensile



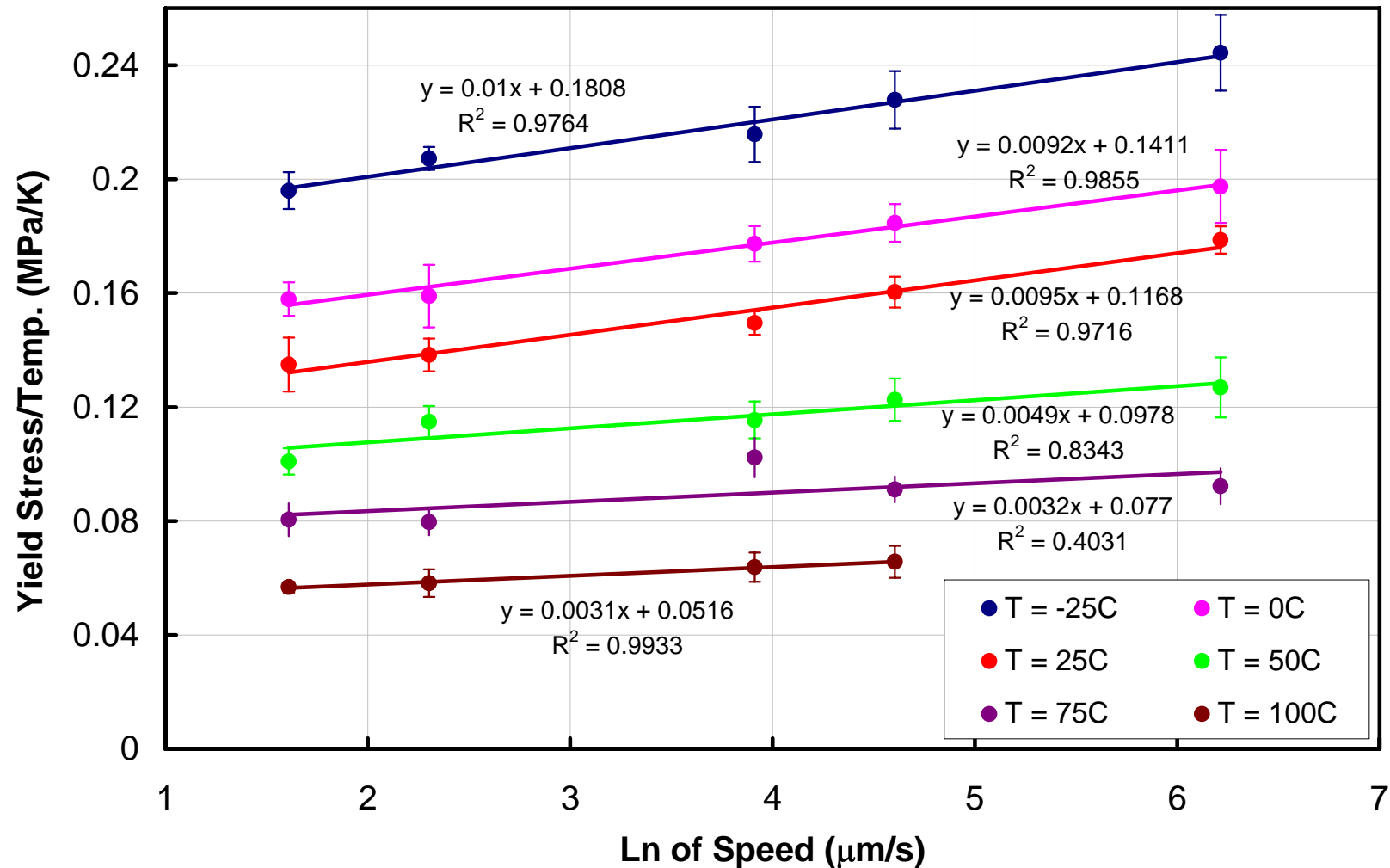
Microtensile: Results



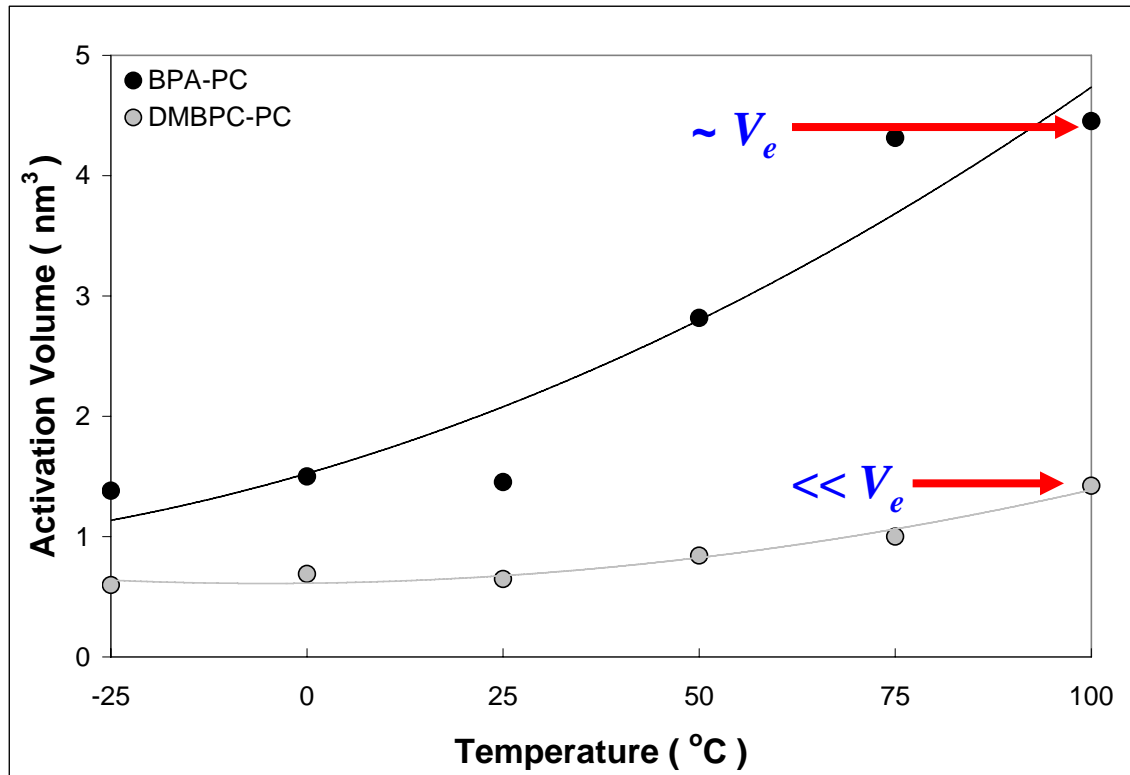
$$\frac{\sigma_y}{T} = \frac{\Delta H}{\nu T} + \frac{R}{\nu} \ln \frac{2\dot{\epsilon}}{\dot{\epsilon}_0}$$

Microtensile: Results

BPA-PC Eyring Plot



Microtensile: Results



Mechanical Studies: Summary

- At length scales probed by nanoindentation (~ 100 – 500 nm) the DMBPC is stiffer, harder and has lower plasticity index.
- Microtensile measurements show significantly lower elongation to break for DMBPC compared to BPA-PC at any given test speed and temperature.
- Eyring analysis shows that the activation volume of BPA-PC is higher than those of DMBPC at any given temperature, thereby indicating a larger extent of inter/intra-chain cooperative segmental mobility for BPA-PC than for DMBPC.
- The activation volume of BPA-PC is of the same order as the entanglement volume, indicating that the length scale involved in cooperative motions is of the order as the average entanglement spacing. For DMBPC the length scale of cooperative motion is much lower than the entanglement spacing.

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- Copolymers

Concluding Remarks

- *Monomer length scale* ($10^{-7} - 10^{-5}$ s): the motions of functional groups in DMBPC monomer are severely hindered.
- *Molecular length scale* ($10^{-3} - 1$ s): Segmental motions in DMBPC are hindered, they exhibit poor cooperativity and have high activation energy. Further, DMBPC has lower entanglement density in the melt state (consequently in the glassy state also).
- *Meso length scale*: DMBPC is stiffer, harder and shows lower plasticity index at meso-length scale,
- *Macroscopic length scale* ($10 - 10^3$ s): The elongation to break of DMBPC is lower, the activation volume is lower (and hence the inter- and intra-chain cooperativity)

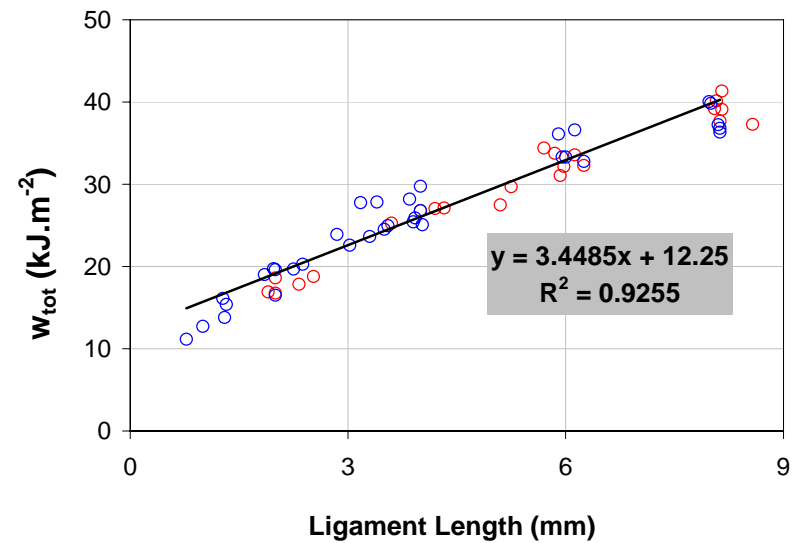
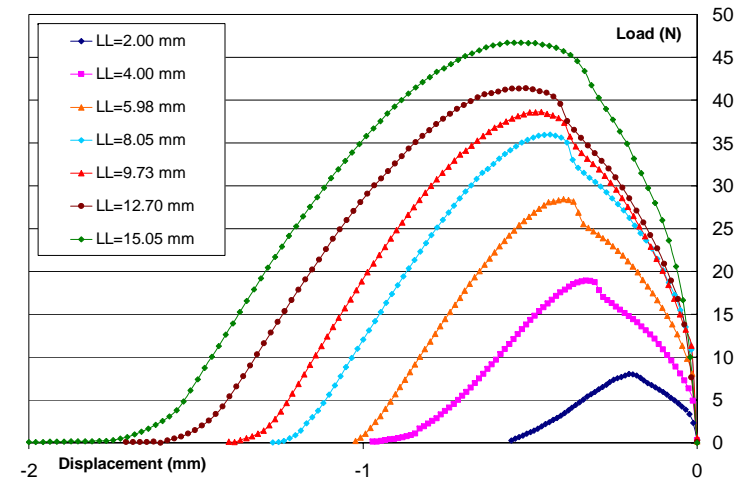
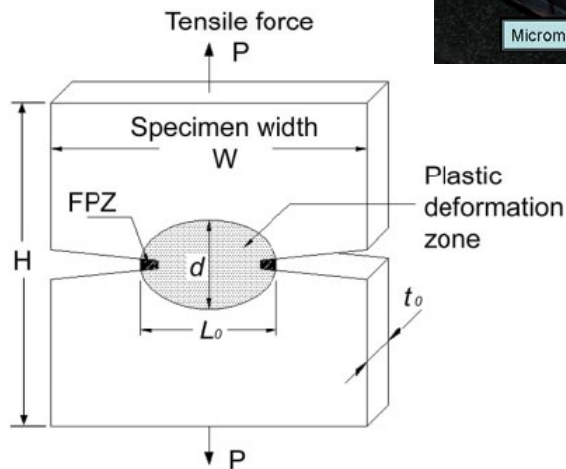
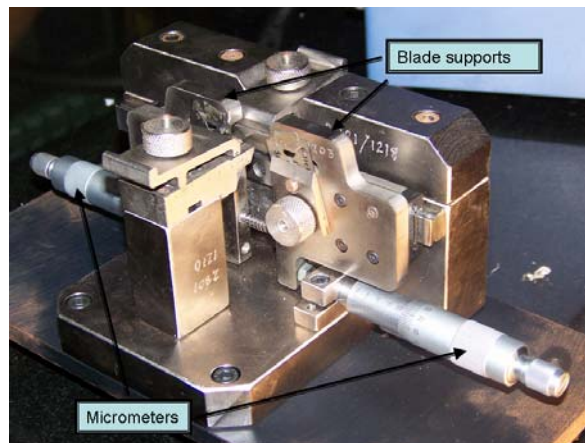
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Future Work

Essential Work of Fracture – Plane Stress

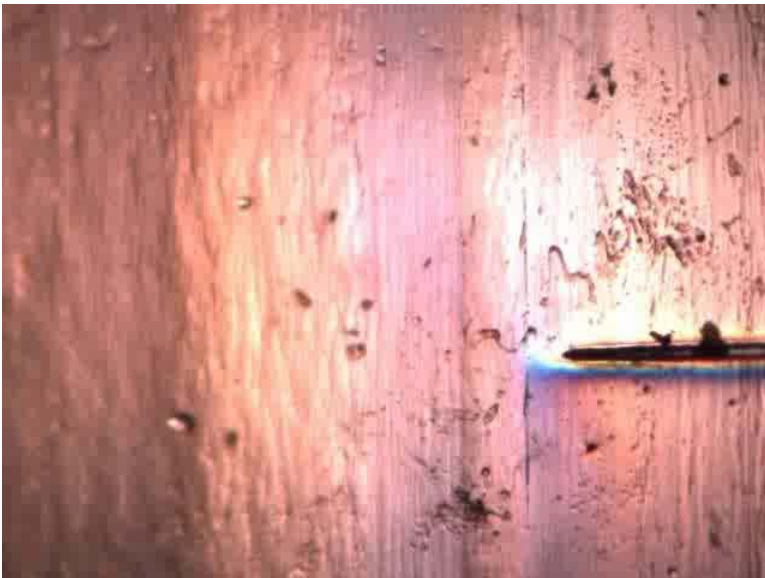
$$w_{tot} = \beta w_p \times L_o + w_e$$



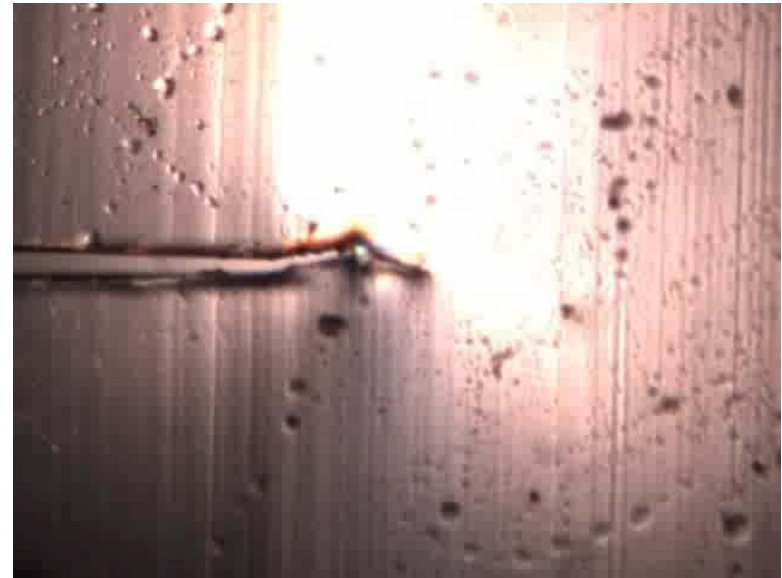
Future Work

Microtensile, 25°C, 50 $\mu\text{m/s}$

BPA-PC



DMBPC



Outline

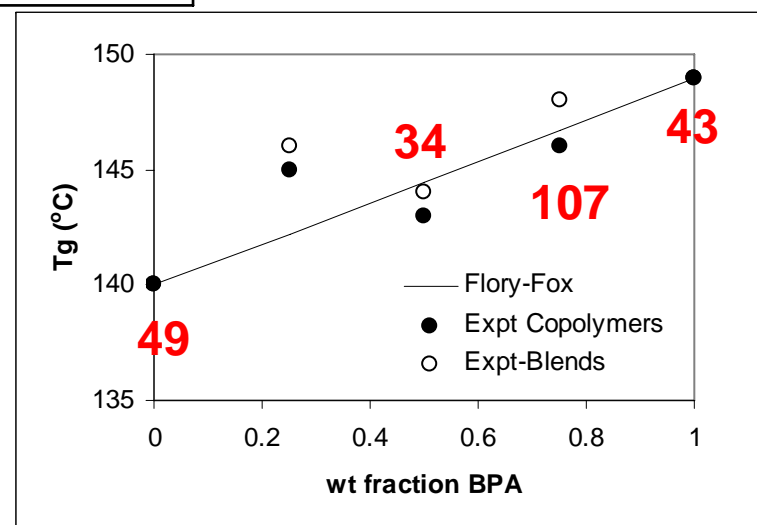
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● Copolymers

Copolymers: Composition

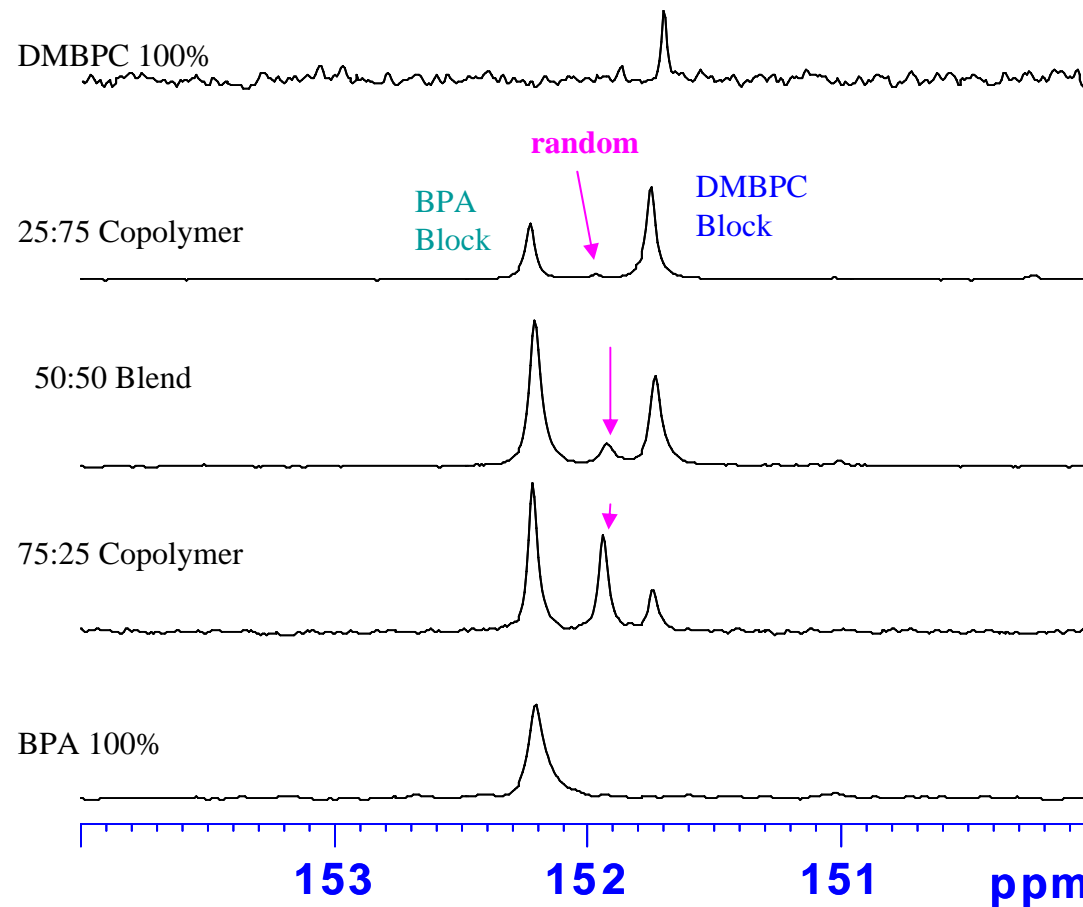
Comparison of ^1H and ^{13}C Values

Sl. No.	Sample Name (BPA:DMBPC)	Proton (%)		Carbon(%)	
		M_{BPA}	M_{DMBPC}	M_{BPA}	M_{DMBPC}
1	100:0	100	00	100	00
2	75:25 Copolymer	75	25	76	24
3	50:50 Copolymer	54	46	55	45
4	25: 75 Copolymer	26	74	25	75
5	0:100	00	100	0	100



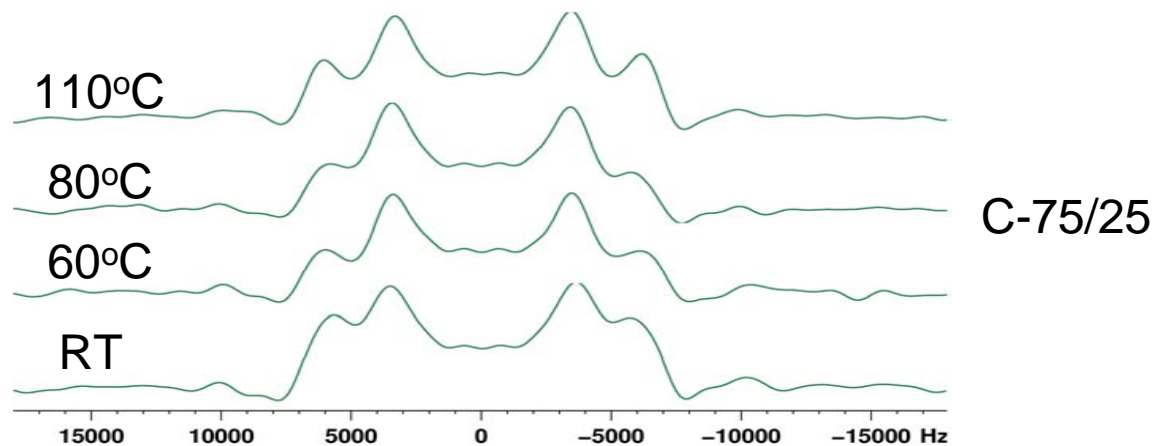
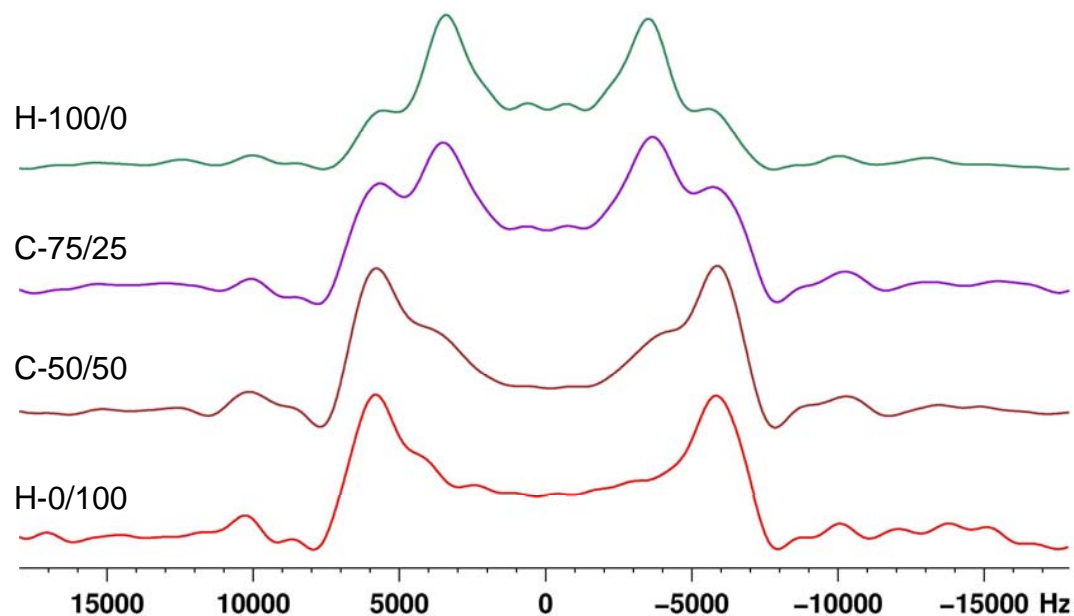
Copolymers: Randomness

Expanded ^{13}C Spectra :Carbonate region

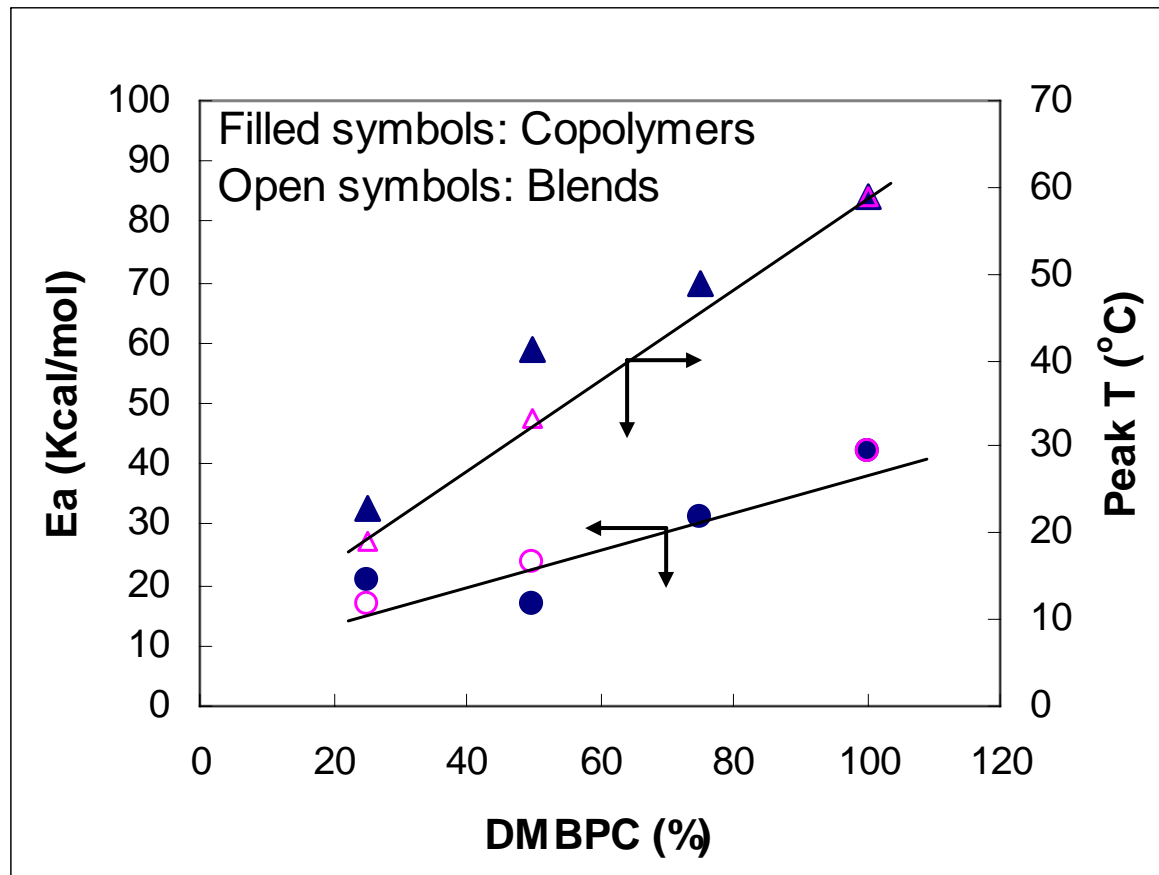


Copolymers: SS-NMR

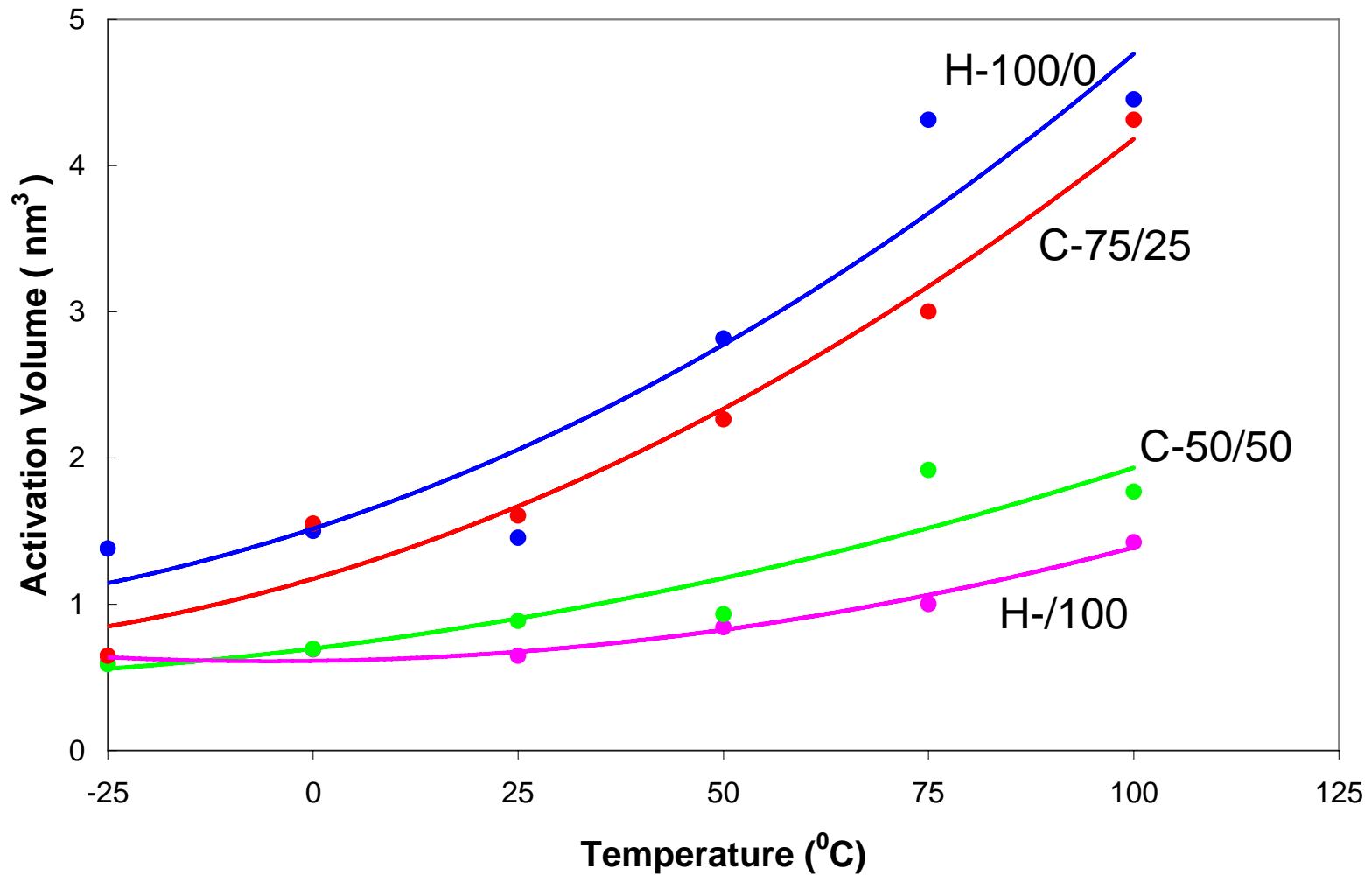
Material BPA/DMBPC	Average ^1H T_1 (ms)
H-100/0	325.3
C-75/25	428.9
C-50/50	638.1
H-0/100	933.0



Copolymers: DMA



Copolymers: Tensile



Copolymers: Remarks

- Rigidity in methyl rotation and phenyl flip motions increases with increase in DMBPC content.
- Segmental motions become increasingly difficult (higher activation energy and increase in peak temperature) with increase in DMBPC content.
- At a given temperature the activation volume decreases with increase in DMBPC content. The decrease in activation volume is highest between 75/25 and 50/50 BPC/DMBPC compositions.

Thank you
