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Introduction:

Hallmark of Polycarbonate (PC) is low haze, high glass transition temperature ($T_g \sim 150$ C) and remarkable toughness. Properties of PC can be improved via copolymerization but many times at the cost of ductility.

Motivation:

- Ranking using micro-scale testing techniques
- Understanding of molecular origins of ductility

Objective:

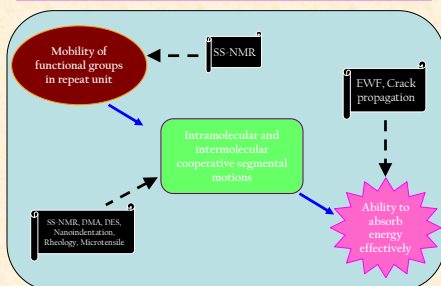
- To study model system of Bisphenol-A polycarbonate (BPA-PC) and dimethyl bisphenolcyclohexane polycarbonate (DMBPC)

Scope :



To use techniques such as

- SS-NMR: Functional group and segmental mobility
- DMA: Segmental mobility
- Rheology: Entanglement density
- Nano-indentation and Microtensile: Ductility

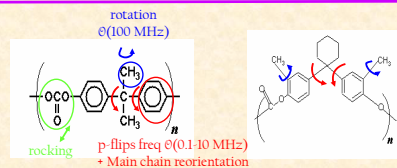
Rationale and Approach



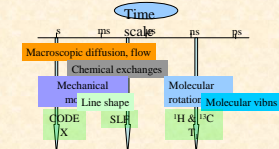
Details of polycarbonate samples used in this work

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

Functional Group Motions At ambient temperature



Time scales of NMR motions



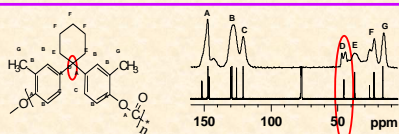
¹H T1 (Spin-lattice) Relaxation Results

¹H Spin-Lattice (T1) relaxation

Material	Average ¹ H T1 (ms)
H-100/0	325.3
H-0/100	933.0

the methyl rotation in the DMBPC is slower relative to that of BPA.

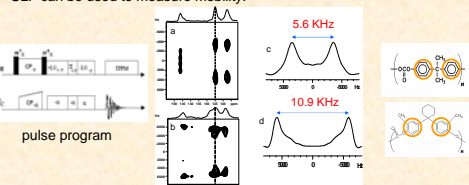
¹³C CPMAS of DMBPC (cross polarization magic angle spinning)



The solution spectrum shows a single peak for the cyclohexyl carbon labelled 'D' due to rapid configurational motions of cyclohexyl ring. The solid state spectrum shows a doublet indicating frozen/slow configurational states.

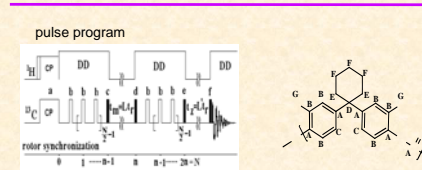
SLF (separated local field) Experiment

SLF measures the strength of carbon-proton dipolar coupling. Motion averages the coupling thereby decreasing its strength. Thus, SLF can be used to measure mobility.

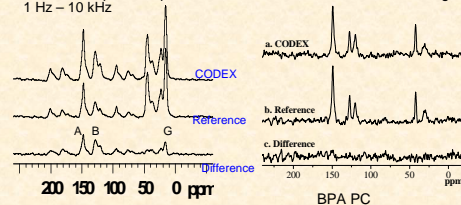


(a) shows the aromatic region from the two-dimensional spectra of the SLF experiment on BPA and (b) of DMBPC. (c) shows the slice of the 2D spectra of BPA at 125ppm which corresponds to one of the phenyl carbons and (d) shows the corresponding spectrum for DMBPC

Centre-band Only Detection of EXchange (CODEX)

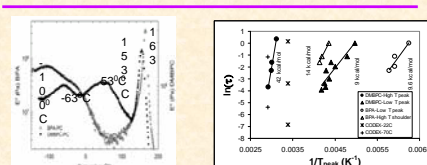


CODEX is a pulse sequence that measures slow motions in the range 1 Hz – 10 kHz



Peak	τ_c at RT	τ_c at 70 °C
A	$\tau c1 = 0.001$ $\tau c2 = 0.033$ $\tau c3 = 1.149$	$\tau c1 = 0.005$ $\tau c2 = 0.319$
C	$\tau c1 = 0.259$	$\tau c1 = 0.093$
F	$\tau c1 = 0.689$	$\tau c1 = 0.027$
G	$\tau c1 = 0.867$ $\tau c2 = 0.068$	$\tau c1 = 0.243$ $\tau c2 = 0.002$

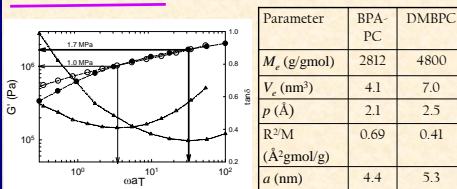
Dynamic Mechanical Analysis: Results



Temperature ramp DMA data at 3 Hz for BPA- and DMBPC

Frequency dependence of peak temperatures for subTg relaxations in BPA- and DMBPC polycarbonates.

Rheology



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.

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

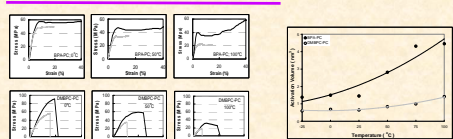
$$M_e = \frac{\rho RT}{G_e}$$

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

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

$$\left(\frac{R^2}{M} \right) = \frac{1}{\rho N_{AV}}$$

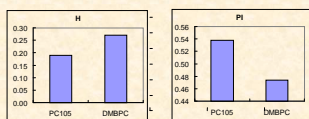
Microtensile: Results



(a) BPA-PC and (b) DMBPC at three different temperatures 0C, 50 C, 100 C, and at two different speeds 5 and 500 mm/s.

Comparison of activation volumes for BPA and DMBPC polycarbonates.

Nanoindentation: Results



Conclusions:

Monomer length scale ($10^{-7} - 10^{-5}$ s): the motions of functional groups (cyclohexyl conformational transition, phenyl flips) in DMBPC repeat unit are severely hindered.

Molecular length scale ($10^{-3} - 1$ s): Segmental motions in DMBPC are slow, 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 – 103 s): The elongation to break of DMBPC is lower, the activation volume is lower (and hence the inter- and intra-chain cooperativity)