High Flux Backscattering Spectrometer

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Typical Scans on HFBS I: Elastic Scan



Typical Scans on HFBS II: Dynamic scan



2011



Small Molecules and Biology....



Free volume and mobility in glass formers

250

Proto-type glass former Glycerol



Kilburn et al in Applied Physics Letters 92, 033109 (2008)



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200

T (K)

PALS is sensitive to available free volume and preferentially probes these regions

Higher free volume in the confined glycerol and the lower molecular mobility!

70 Å pores

Bulk

150

2.5

2.0

.5

1.0

 τ_{o-Ps} (ns)

Available free volume to drive the

molecular motions and relaxations

Temperature

Free volume

at Ta

Volume

Total volume

Occupied volume







Confined water in silica



Fragile-to-Strong transition at around 222K in relaxation time of water!

Liu et al., J. Phys: Cond. Matter 18, S2261 (2006)





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Hydration water enables dynamic transition.



• Larger amplitude of motions, $\langle r^2 \rangle_{Wet} - \langle r^2 \rangle_{Dry}$, in tRNA than in lysozyme.

Roh J. H., et al. *PRL* **2005**, *95*, 038101. Roh J. H., et al. *Biophysical J.* **2009**, *96*, 2755.





- Weaker temperature dependence of faster relaxation time in protein
- Contradicts the concept of "solvent-slaved" dynamics

Khodadadi S., et al. Biophysical J. 2010, 98, 1321.





 Electrostatic stabilization seems to play an important role in facilitating the coupled dynamics of biological macromolecules and hydration water.

Roh J. H., Tyagi M. To be submitted



Polymers....





Conductivity measurements

40

40

60

60

Temperature (°C)

20

20

1.E-02

1.E-03

1.E-04 S/cn

1.E-05

1.E-07

1.E-08

1.E-09

1.E-10

1.E-02

1.E-03

1.E-04

1.E-05

1.E-06

1.E-07

1.E-08

1.E-10

crystalline

PEO

0

S/cm)

vitv

vity 1.E-06 PEO based solid electrolytes (with $LiClO_4$)

- •PEO crystallization generally lowers the conductivity at temperature of interest.
- •At 50C, a partially crystalline shows, max conductivity despite being less mobile!
- Ionic conductivity and polymer segmental dynamics are decoupled!

max conductivity at 50C ~ 10⁻⁵ S/cm

1

0.9

0.8

0.7

0.4

0.3

0.1

0 0.1

Amorphous 0.2

PEO

+ LICIO,

(1'b) 0.5



Combined HFBS and DCS data



Fullerton-Shirey, Macromolecules 42, 2142 (2009)

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Water

14:1

4-1 1st heat

A-4-1 cool

----- 10:1 cool

80

- 8:1 1st heat

-- 8:1 2nd heat 10:1 1st heat

+--- 10:1 2nd heat

14-1 1st heat

14:1 2nd heat

30:1 1st heat

· 30:1 2nd heat

100:1 1st heat

100

nnnnnn

Crystalline PEO

PEO LICIO

PEO LICIO

100:1 cool 100:1 2nd hea

80

14:1 cool

- 30:1 cool

100

10

100

Time (ps)

alert Eleitertertet

Segmental

relaxation

4:1

Rotation

1000

10000

Pure PEO



Move to a different kind of PEO > hyper-branched PEO



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linear PEO Lee et al, Accepted in Chemistry of Materials









Overall Picture

Tyagi, Macromolecules, **39** (2008)



Q-dependent σ!





...even inelastic neutron scattering...



Low-T dynamics of confined CH₃I molecule



Dimeo et al., Phys. Rev. B 63, 014301 (2000)

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Recent examples of Tunneling and Rotational motions probed by HFBS

....Thank you!

