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#### Polymer properties change under nanoscale confinement

*Polymers experience confinement in nanocomposites* 



The change in the D is related to a confinement parameter,  $ID/2R_{g}^{-1}$ 

The randomness of the nanoparticle distribution creates a variety of confinement lengthscales and orientations making other confined properties difficult to measure.

*Cylindrical pores create a controlled system for studying polymer behavior in confinement* 



All chains experience similar confinement and domains are aligned so anisotropic effects can be measured.

Previous simulations show properties deviate more strongly as pore radius decreases, similar to the behavior observed in nanocomposites.

<sup>1</sup>Lin, et al., *Macromol.*, **2013**, 46; <sup>2</sup>Sussman, et al., *Macromol.*, **2014**, 47; <sup>3</sup>Tung, et al., *Macromol.*, **2015**, 48



# Polymer Behavior Under Rigid Symmetric Confinement

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#### **Polymer Conformation**



The average R<sub>g</sub> increases slightly in the unconfined direction, with a greater increase for larger chain lengths.

In the confined direction, the average R<sub>g</sub> asymptotes to a maximum value of  $r_{pore}/2$ . This value is equivalent to the radius of gyration of the pore cross-section.

## *Relative Shape Anisotropy,* $\kappa^2$

$$\kappa^{2} = \frac{3}{2} \frac{\lambda_{x}^{4} + \lambda_{y}^{4} + \lambda_{z}^{4}}{\left(\lambda_{x}^{2} + \lambda_{y}^{2} + \lambda_{z}^{2}\right)^{2}} - \frac{1}{2} \begin{bmatrix} \sum_{x \neq 0.6}^{N} & r = 7\sigma \\ 0.6 & r = 5\sigma \\ r = 3.5\sigma \\ r = 2.5\sigma \end{bmatrix}$$

- points are spherically  $\kappa^2 = 0$ symmetric
- $\kappa^2 = 1$  points lie on a line



 $\lambda_x$ ,  $\lambda_y$ ,  $\lambda_z$  are the x, y (confined) and z (unconfined) components of the average R<sub>g</sub>.

Relative shape anisotropy as a function of confinement ratio collapses to a single line, suggesting confined chain conformation can be fully described by the confinement ratio.

## **Experimental Methods**

- 290 kg mol<sup>-1</sup> polystyrene (PS) matrix polymer
- 100-800 kg mol<sup>-1</sup> deuterated PS (dPS) tracer polymer
- 15 nm radius anodic aluminum oxide (AAO) pores
- Phenyl-capped pore walls for athermal interactions
- 160 °C annealing temperature











Unlike conformation polymer diffusion in confinement is not fully described by a confinement parameter.

Apparent behavior in D as pore size decreases suggests two competing forces, most likely chain disentanglement (increased diffusivity) and polymer wall friction (decreased diffusivity).

#### Experimental



Elastic Recoil Detection (ERD) is used to measure the depth profile of the tracer dPS.

A Fickian diffusion profile, convoluted with a Gaussian beam resolution is used to fit the depth profile and extract a diffusion coefficient.

## Conclusions

In the confining dimension the average R<sub>g</sub> asymptotes, with increasing polymer size, to a maximum value of  $r_{pore}/2$ .

Confined chain conformation is dependent on the ratio between the confining length and the polymer size.

Polymer diffusion appears to exhibit a non-monotonic behavior in confinement, suggesting competing forces, most likely chain disentanglement and polymer-wall friction.

Experimental studies are underway to determine if the same trends observed in simulations occur experimentally.

