

Dynamics in Polymer Nanocomposite Melts with Small, Attractive Nanoparticles

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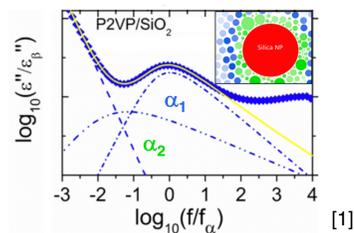


Dynamics in Nanocomposites with Large NPs

Investigations of nanoparticle (NP) diffusion in polymer melts are important for drug delivery, properties and processing of polymer nanocomposites, and many other related fields.

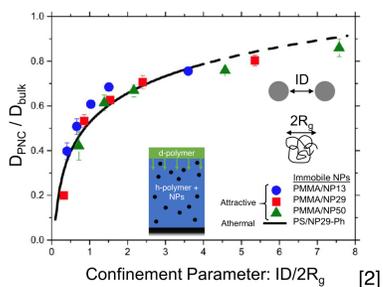
Polymer Segmental Dynamics:

- Segmental relaxations near the surface of a NP are slow relative to bulk.
- Segmental relaxations far from a NP surface remain bulk-like.



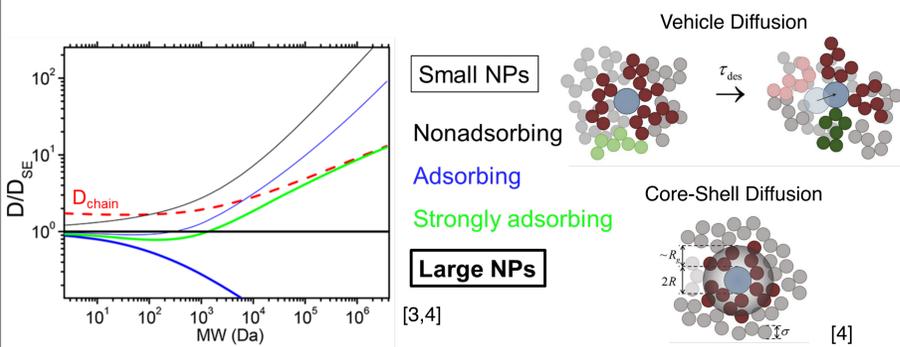
Polymer Diffusion:

- The polymer tracer diffusion into PNCs with immobile NPs is slowed relative to bulk.
- The reduced polymer diffusion coefficient depends primarily on the confinement parameter, which is related to the chain size, NP size, and NP concentration.



Nanoparticle (NP) Dynamics:

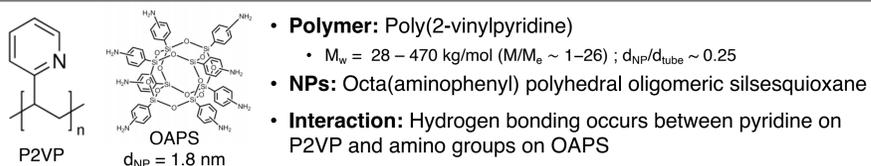
- The Stokes-Einstein relation is known to describe NP diffusion but often breaks down in polymer melts and other complex fluids.
- Vehicle diffusion ($D > D_{SE}$) is predicted for small, adsorbing, mobile NPs.
- Core-shell diffusion ($D < D_{SE}$) is predicted for large, adsorbing NPs.



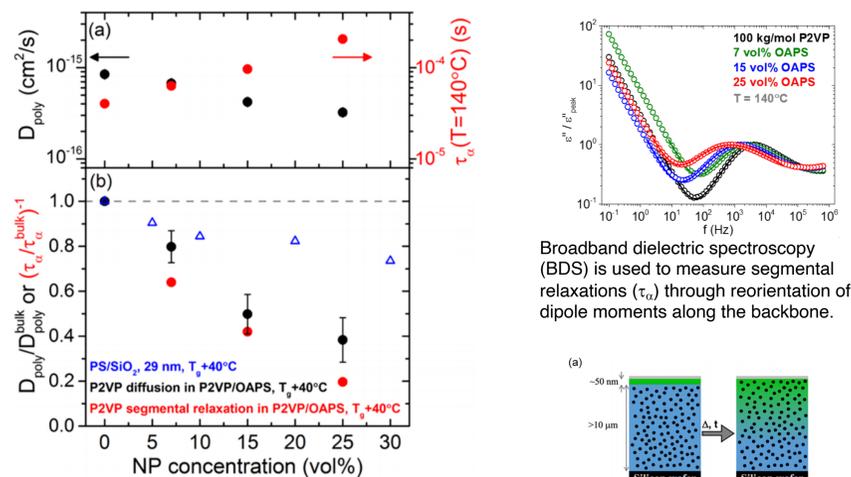
Experimental Question

How do polymer and NP dynamics in PNCs with small ($R_{NP} \ll R_g$), attractive NPs in entangled polymer melts differ from traditional PNCs with larger NPs ($R_{NP} \geq R_g$)?

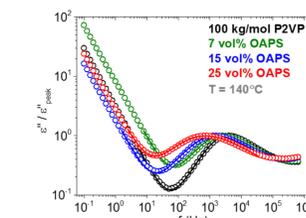
Nanocomposite Material System



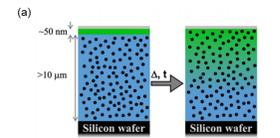
Polymer Dynamics in P2VP/OAPS



- Segmental dynamics are slightly more perturbed than chain-scale dynamics, likely due to changes in entanglement density.
- The perturbation to chain-scale motion is larger for small attractive NPs than large athermal NPs.

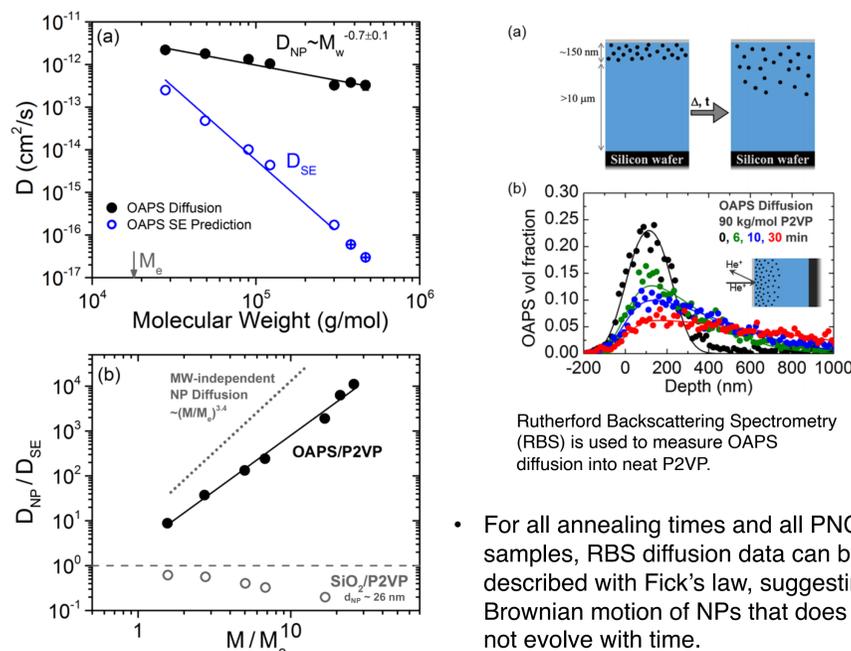


Broadband dielectric spectroscopy (BDS) is used to measure segmental relaxations (τ_c) through reorientation of dipole moments along the backbone.



Elastic Recoil Detection (ERD) is used to characterize the tracer diffusion coefficient (D_{poly}) into P2VP/OAPS PNCs.

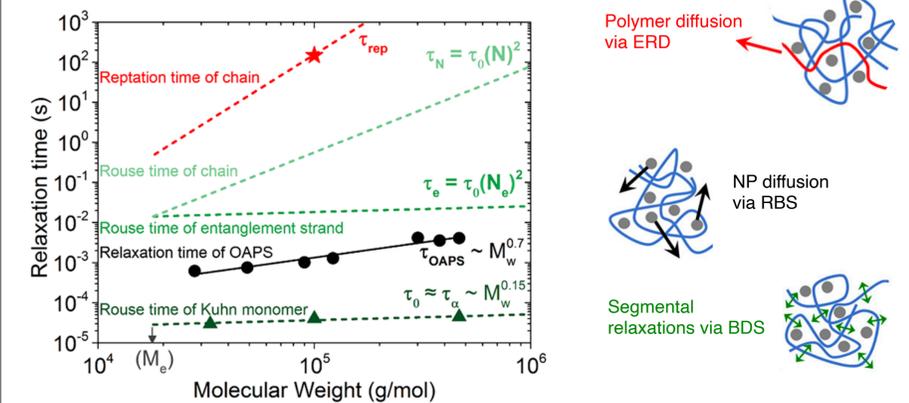
OAPS Diffusion in P2VP



- For all annealing times and all PNC samples, RBS diffusion data can be described with Fick's law, suggesting Brownian motion of NPs that does not evolve with time.

- D_{NP} scales weakly with $M_w^{-0.7}$, in agreement with theoretical predictions.
- $D_{NP} > D_{SE}$ is observed for all M_w and D_{NP}/D_{SE} reaches up to 10^4 at largest M_w .
- Decreasing NP size by a factor of ~ 14 changes D_{NP}/D_{SE} by more than four orders of magnitude in well-entangled polymer melts.

The Hierarchy of Dynamics in P2VP/OAPS



- NP relaxations fall between relaxations of segments and entanglement strand, all of which are significantly faster than chain relaxations.
- NPs diffuse with chain segments, desorb while chains undergo longer relaxations, and diffuse rapidly, all in agreement with the predicted vehicle mechanism.^[3,4]

Conclusions and Future Work

Conclusions:

- Polymer dynamics are homogeneously slowed by the addition of small, attractive NPs at the segment and chain-scale.
- For small, attractive NPs, $D_{NP} \sim M_w^{-0.7}$ and D_{NP}/D_{SE} reaches $\sim 10^4$ in large molecular weight polymer melts.
- NPs relax synergistically with polymer segments but desorb while chains undergo longer-range motion, as predicted in vehicle diffusion.

Future Work:

- Can NP diffusion and polymer dynamics be controlled by altering NP-polymer interaction? (via NP size, NP surface chemistry, etc.)

Acknowledgements

ERD and RBS measurements were made at the Nanoscale Characterization Facility at Penn and we thank Doug Yates and Jamie Ford for assistance. We acknowledge funding from NSF-CBET #1706014, NSF-DGE #1321851, and NSF-ECCS-1542153. **This work was published in Macromolecules, 52, pp 2181-2188 (2019).**

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