Aging Effects on Polymer-Grafted Nanoparticle Membranes

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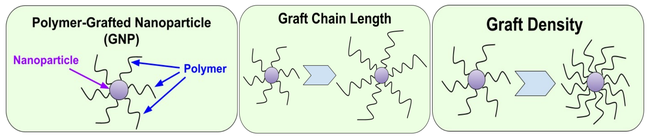
Introduction

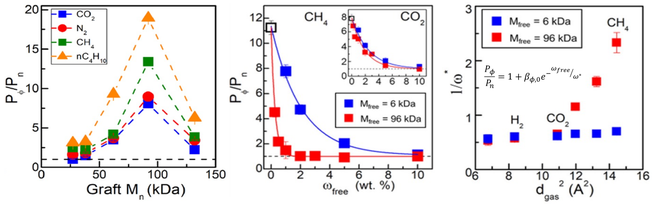
- Membrane-based separation can be used to capture greenhouse gases.
- Compared to distillation, membrane-based separation saves money, energy, and space.
- ✨The Dream✨: To create a polymer membrane that achieves high permeability and high selectivity of gases.
- Kumar Group uses polymer-grafted nanoparticles (GNPs) to make membranes.
- Today, we are studying how aging effects, specifically temperature and the addition of free homopolymers, change the structural properties of the GNP membranes, by using in-situ annealing in the SAXS.

Key Definitions



Background

- The degree of enhancement increases as the graft chain length increases to around 90 kDa [1].
- Different gas sizes are sensitive to different molecular weights of free polymers [2].

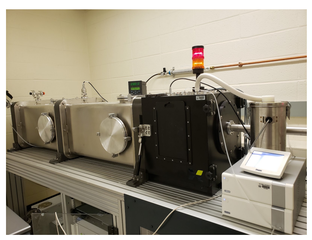


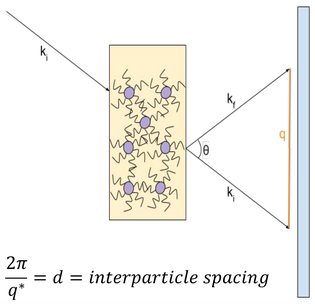
Method

1. First, 1 wt.%, 5 wt.%, and 10 wt.% of 6kDa free homopolymer were mixed with a pure GNP of 0.52 ch/nm^2 125 kDa. This step was repeated for the 96kDa. These mixtures are called blends.
2. Next, the pure GNP and the solutions were cast in Teflon molds, and were fast-evaporated.
3. When the membranes formed, a portion of each as-cast sample was put into the SAXS for in-situ annealing, using the Linkam Stage.

What is the SAXS?

Small Angle X-Ray Scattering

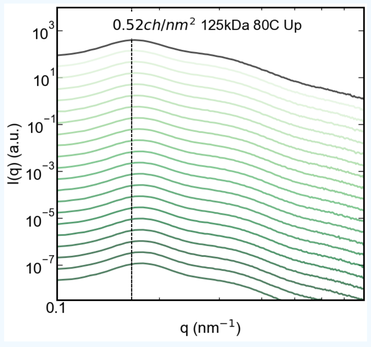


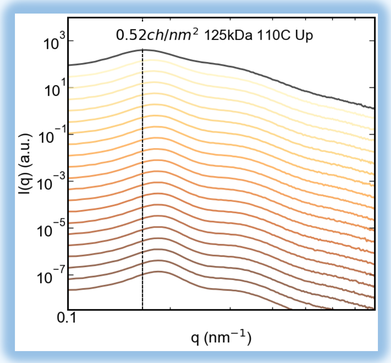


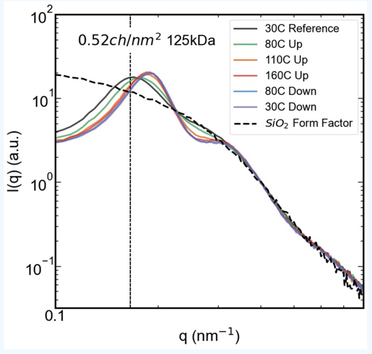
$$\frac{2\pi}{q^*} = d = interparticle\ spacing$$

Results

- As **time increases**, the **structure equilibrates** at the **set temperature**.
- As the **temperature increases**, the peaks narrow, and the **membrane structure is more well-defined**.
  - Look at the graph outlined in blue. See how the peak becomes narrow and shifts right as the colors darken?
  - Darker color = Higher temperature. The colored curves represent the structure. The structure changes over time.
- Structure is defined by the highest temperature it sees.

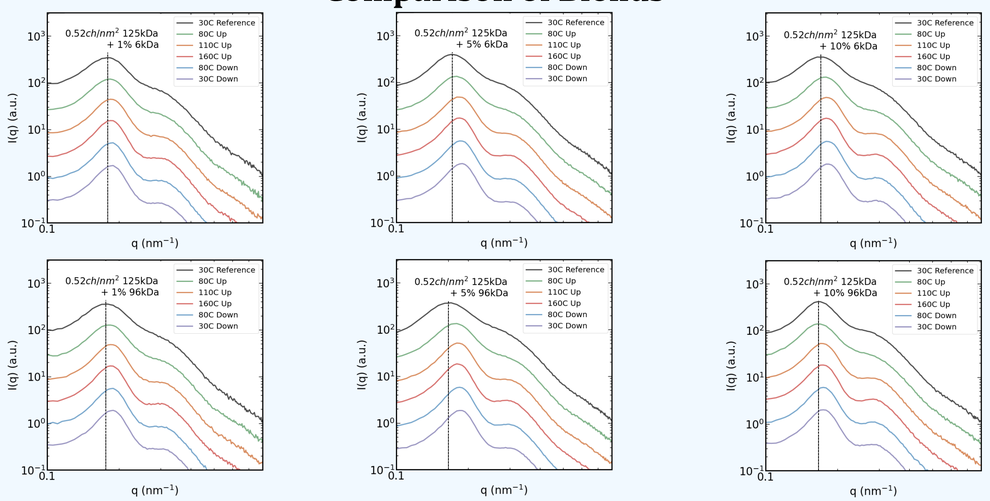






- These graphs contain continuous data for the same Pure GNP sample.
- The black curve at the top of the left and middle graphs is the same curve. It is the 30°C Reference curve recorded before any temperature changes.
- The vertical dotted line indicates where the 30°C Reference peak is relative to the x-axis.
- The graph on the right normalizes the last curve of the designated temperatures.

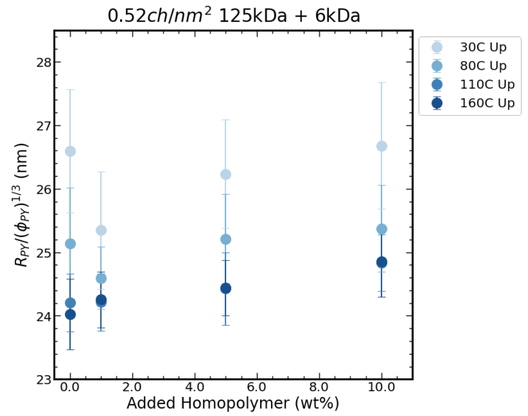
Comparison of Blends

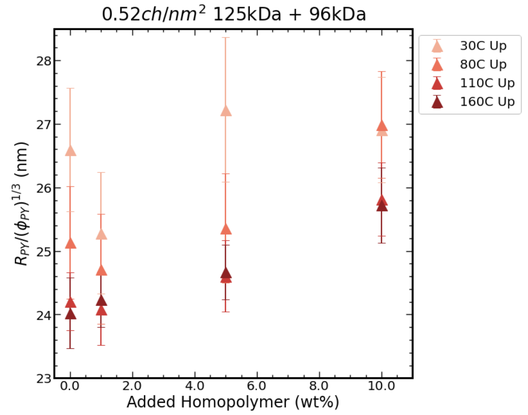


- These rainbow plots collect the last curve of every temperature up plot and every temperature down plot for each weight percent of every blend.
- This makes it easier to visualize how the structure is different during the final moments of each temperature range.

Interparticle Spacings

- The 1-D SAXS patterns are fit to Percus-Yevick Hard Sphere Model to determine the effective radii and volume fractions.
- $R_{PY}/\phi_{PY}^{1/3}$ ~ Total Interparticle Spacing





Conclusions

- Higher temperatures cause closer packing in the blends.
- Small wt.% decrease packing while larger wt.% swell.
- High temperature has a smaller impact on the high wt.% large molecular weight free homopolymers.
- Based on gas transport, it is possible a low wt.% of chain scission occurs in a pure GNP with a high MW_{graft} at 110°C.
- Structurally, this would make the membrane similar to a blend with a low wt.% at 80°C (of the same magnitude chain length).
- Further analysis is needed to understand the structural impact on blends at temperatures >160°C.

References

[1] Bilchak, C. R. et al. *Macromolecules* 50, 7111–7120 (2017)
[2] Bilchak, C. R. et al. *ACS Nano* 14, 12, 17174–17183 (2020)

Acknowledgements

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