The morphological effects of inserting nanoparticles into polymer matrices

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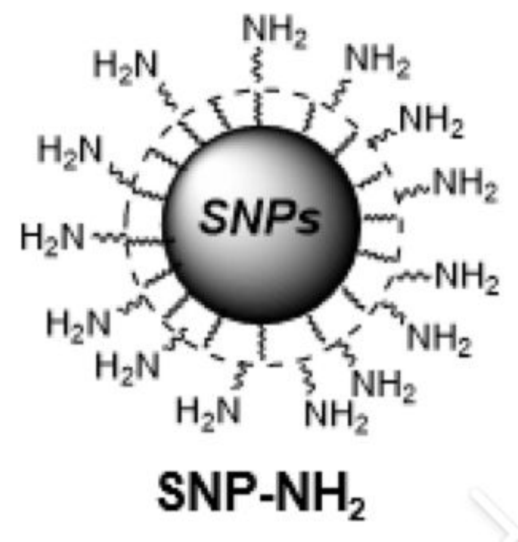
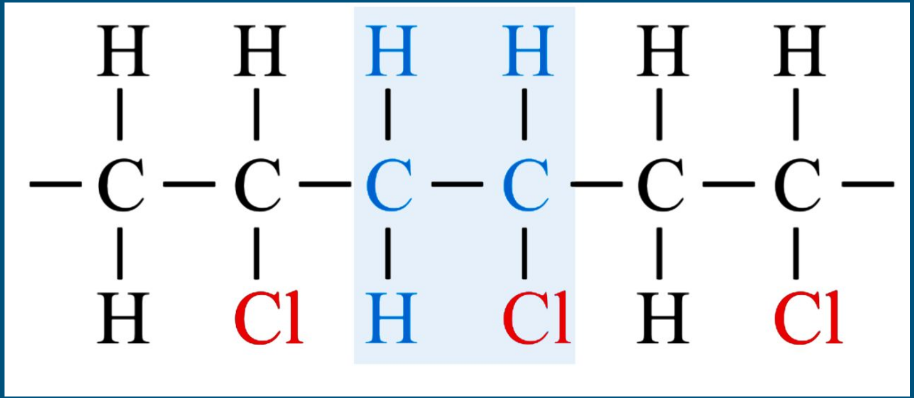
How do we make them?



Nanoparticle with nucleophilic amine substituents

+

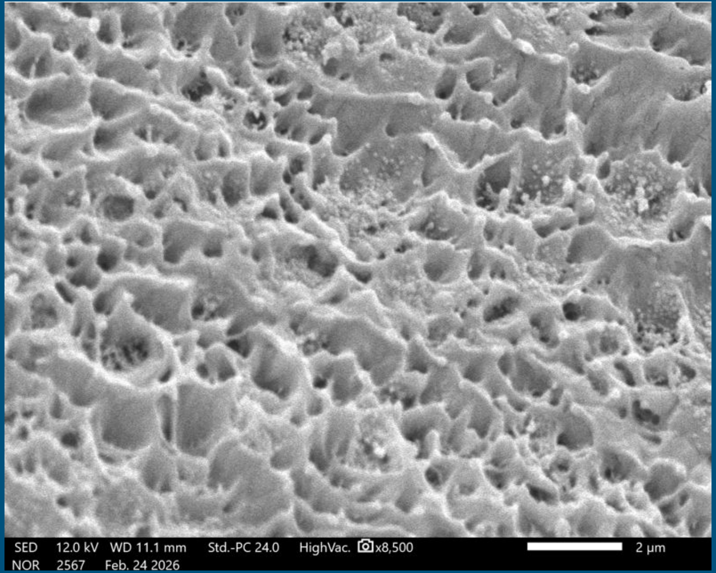


$$-CH_2-CHCl-CH_2-CHCl-CH_2-CHCl-$$

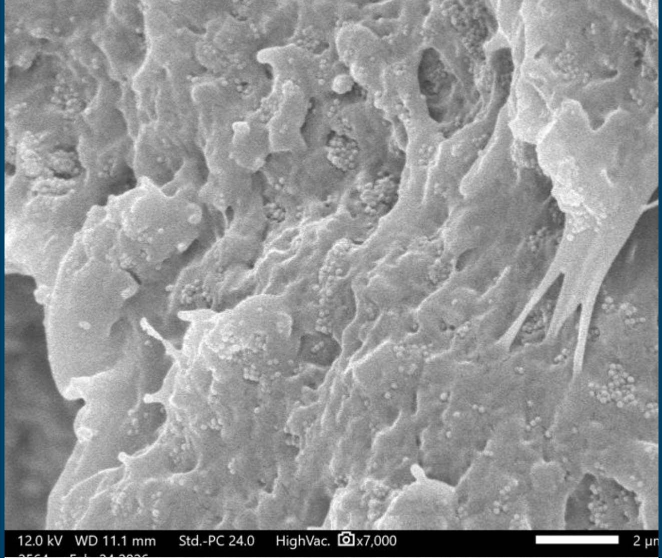
Polymer containing repeating units with good leaving groups

How do we determine the internal behavior of these nanoparticles?

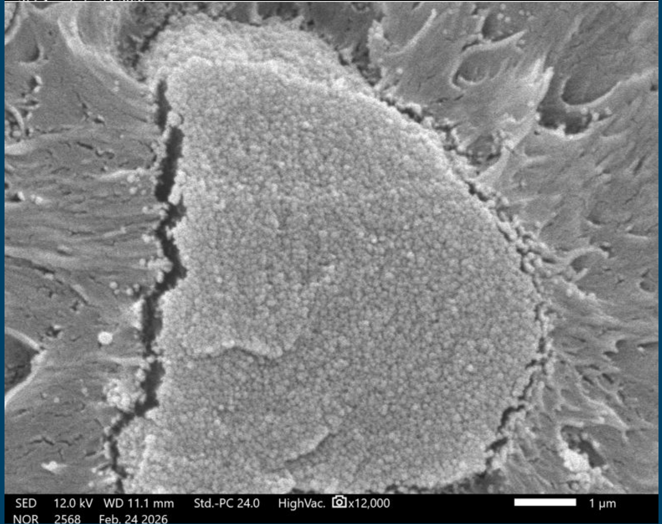
Scanning Electron Microscope
- We want to determine if the nanoparticles form clusters or disperse



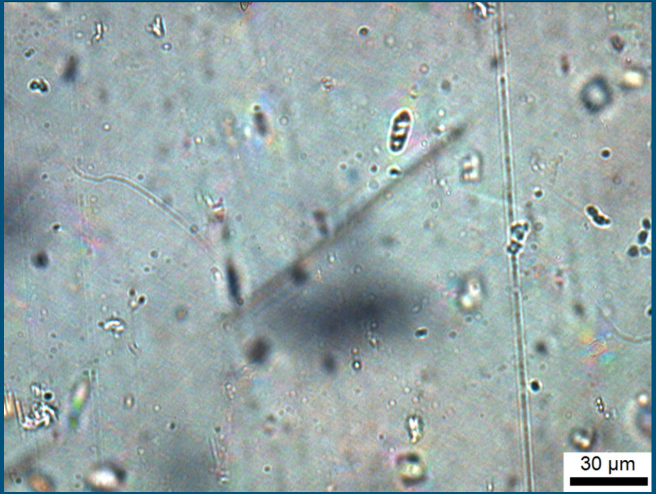
70 nanometer particles



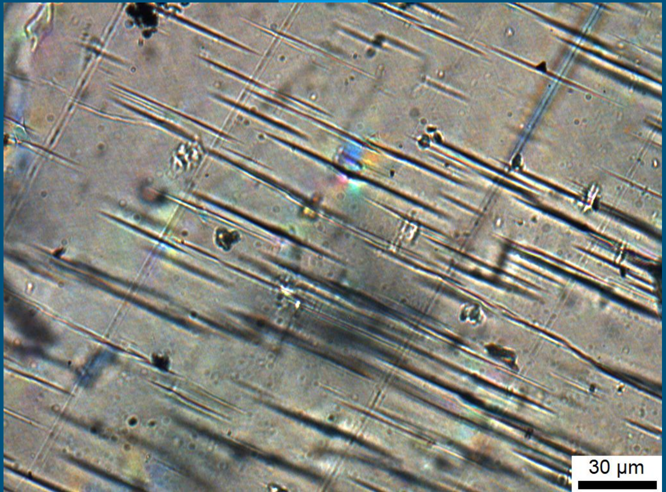
40 nanometer particles



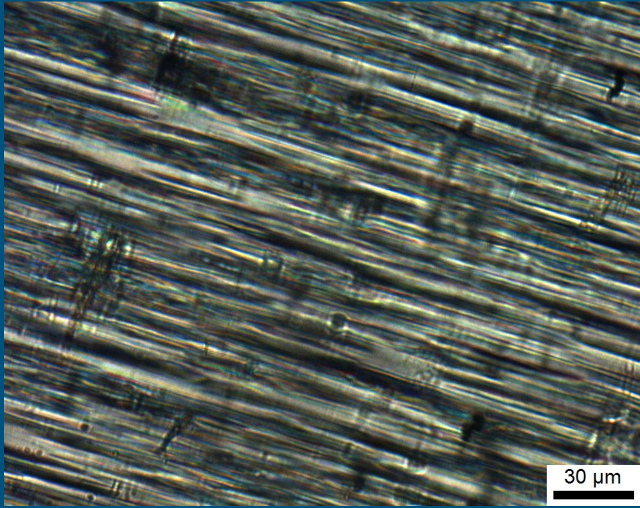
Polarized Optical Microscopy



- Mostly amorphous/ little crystallinity
- Lots of debris or contaminants



- Moderate crystallinity
- Some contamination



- Mostly crystallized
- Very few contaminants

What are some quantitative analysis methods?

So far, the methods described have only provided us with qualitative data.

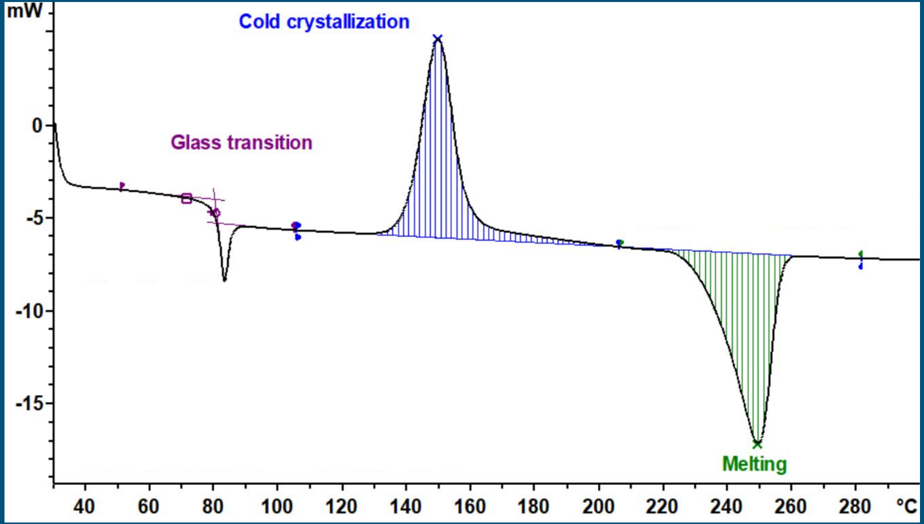
- We could <u>see</u> the behavior of the nanoparticles
- We could <u>see</u> the relative amounts of crystallinity

However, we need to put numbers to our observations. We need to quantify the physical/morphological effects

Quantifying Crystallinity: MDSC

MDSC = Modulated Differential Scanning Calorimetry
→ Allows us to quantify the enthalpy terms associated with different processes that occur while heating a polymer sample (i.e. melting, temperature change, crystal perfection, glass transition)

- Crystallinity affects properties like melting point.
- The process of melting polymers has an enthalpy value associated with it. Therefore, we can compare the enthalpy values of our sample to the enthalpy values of a sample with no crystallization to determine the effect and extent of initial crystallinity.



Q: What if we want to characterize the physical properties of the polymers?
A: We use G’ and G” modulus

What are the G’ and G” moduli you might ask? It’s this simple integral expression:

$$\sigma(t) = \int_{-\infty}^{t} G(t-t')\,\frac{d\gamma(t')}{dt'}\,dt'$$

Let $\tau = t - t'$:

$$\sigma(t) = \int_0^\infty G(\tau)\,\dot\gamma(t-\tau)\,d\tau$$

$$\sigma(t) = \int_0^\infty G(\tau)\,i\omega\gamma_0 e^{i\omega(t-\tau)}\,d\tau$$

$$G^*(\omega) = i\omega\int_0^\infty G(\tau)e^{-i\omega\tau}\,d\tau$$

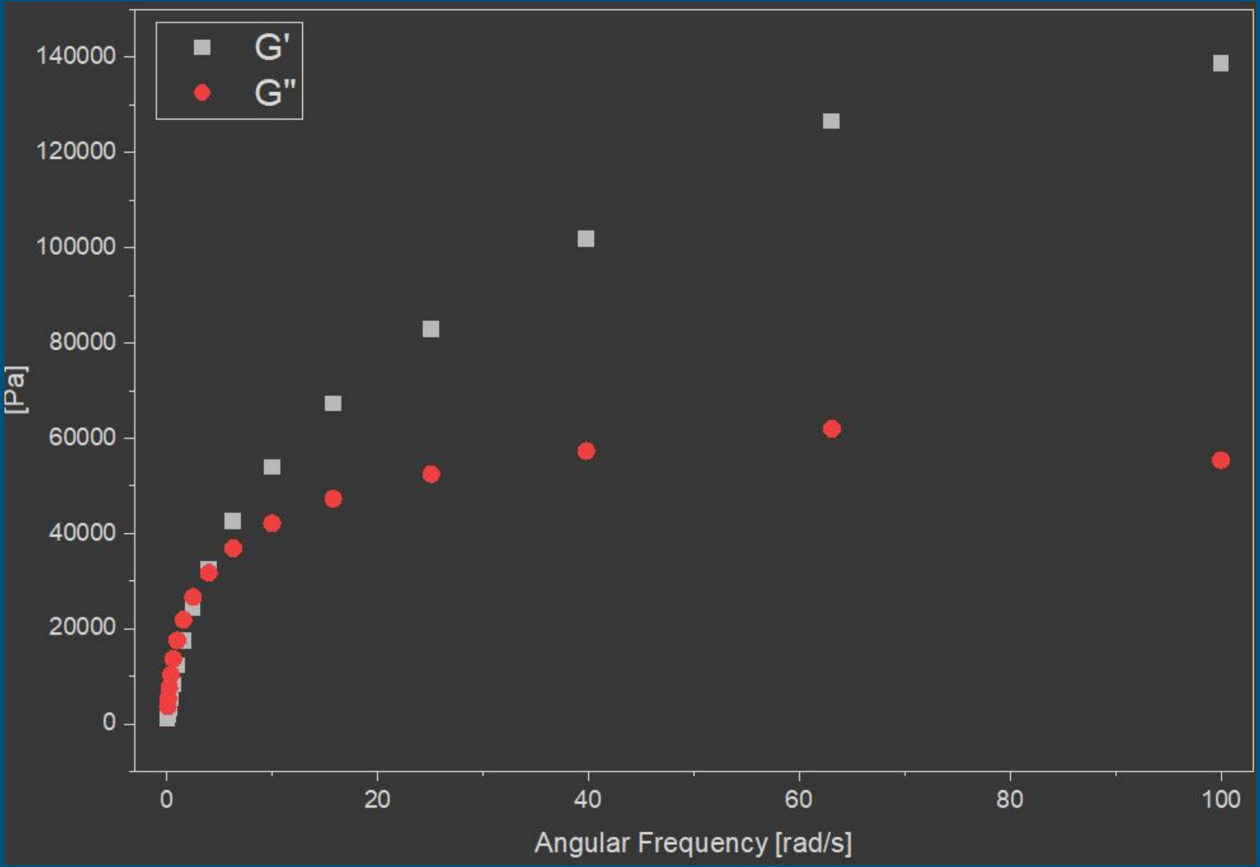
$$G^*(\omega) = i\omega\,\hat{G}(\omega)$$

$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

$$G'(\omega) = \omega\int_0^\infty G(\tau)\,\sin(\omega\tau)\,d\tau$$

$$G''(\omega) = \omega\int_0^\infty G(\tau)\,\cos(\omega\tau)\,d\tau$$

Although the formula looks complicated, G’ and G” boil down to much more intuitive measurement.



G’ = Solid-like component of the polymer.

G” = Liquid-like component of the polymer.

Thank you for your time

- Any questions may be discussed after class