Production and Analysis of Highly Monodisperse Oligomeric Poly(Ethylene Oxide)

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Adam Raegen

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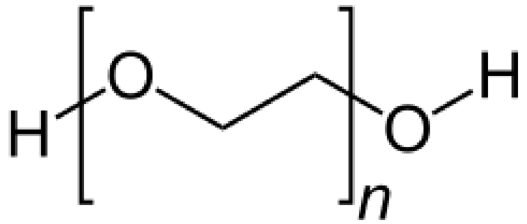
UNIVERSITY OF WATERLOO

PERIMETER INSTITUTE

Outline

Introduction	PEO and sample information
	Review of PEO crystallization
Technique and Products	Production technique
	MALDI-TOF results of products
Analysis on Crystallization	DSC measurements
	Crystal growth rates
Conclusions	Work done
	Future work

Introduction



Poly(Ethylene Oxide) (PEO) structure

linear structure

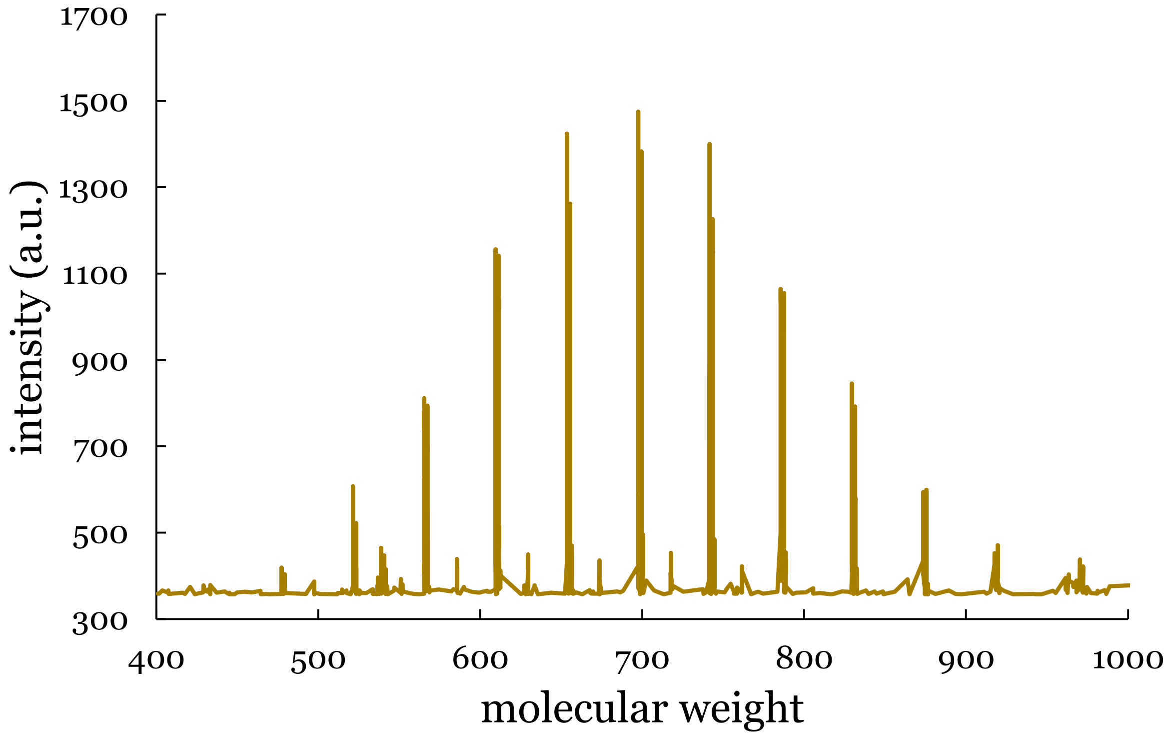
↓

easily crystallizes

How does N affect crystallization behaviours?

MALDI spectrum of neat sample

(Matrix-Assisted Laser Desorption/Ionization - Time Of Flight mass spectrometry)

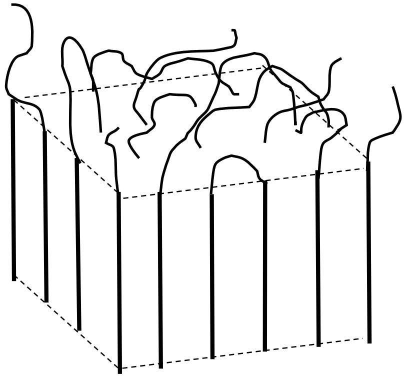


M_n=587.7 M_w=606.3 PDI=1.032

Review of PEO Crystallization

polymer crystallization

Folded chain model



lamella structure

Gibbs Thomson relation

$$T_m = T_m^{\infty}(1 - \frac{2\sigma_e}{l\Delta h})$$

σ_e: interfacial energy between amorphous and crystalline phases

T_m^{∞} = 342K for PEO

Review of PEO Crystallization

polymer crystallization

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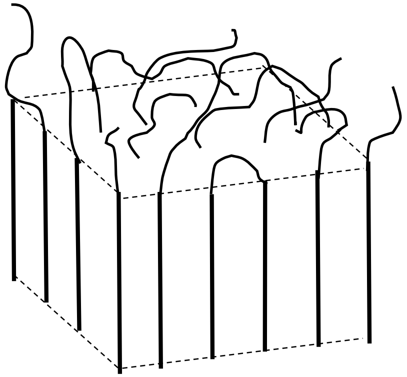

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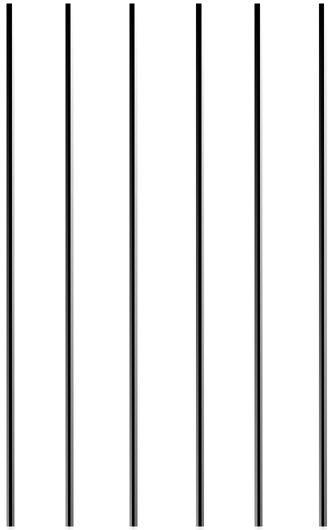

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$$T_m = T_m^{\infty}(1 - \frac{2\sigma_e}{l\Delta h})$$

ideal: $T_m = T_m^{\infty}$

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Review of PEO Crystallization

Makromol. Chem. 185,1559- 1563 (1984)

polymer crystallization

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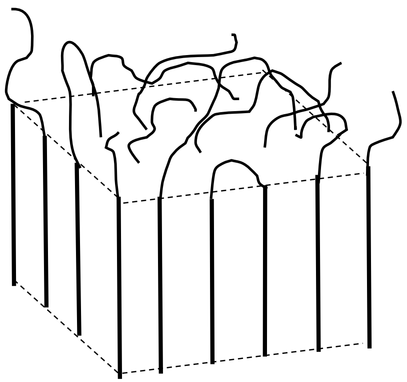

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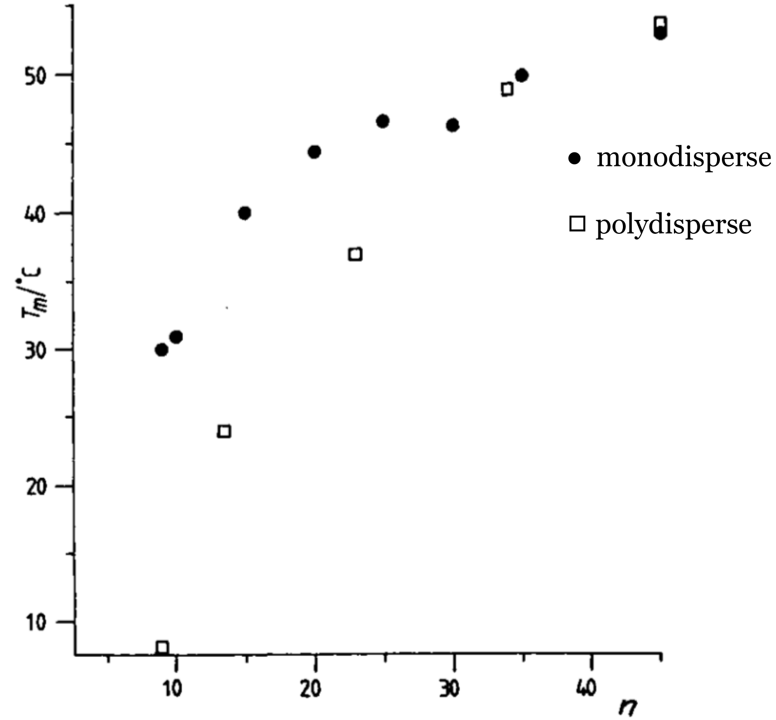

T_m vs N for PEO oligomers.

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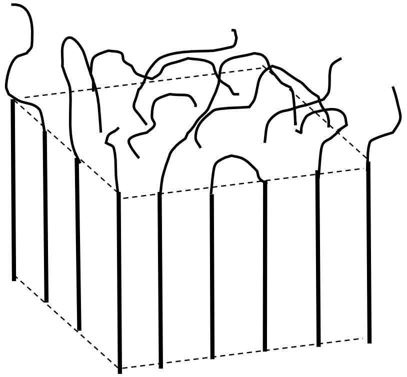
Review of PEO Crystallization

J. POLYMER SCI.: Symposium No. 50, 283-325 (1975)

polymer crystallization

Folded chain model



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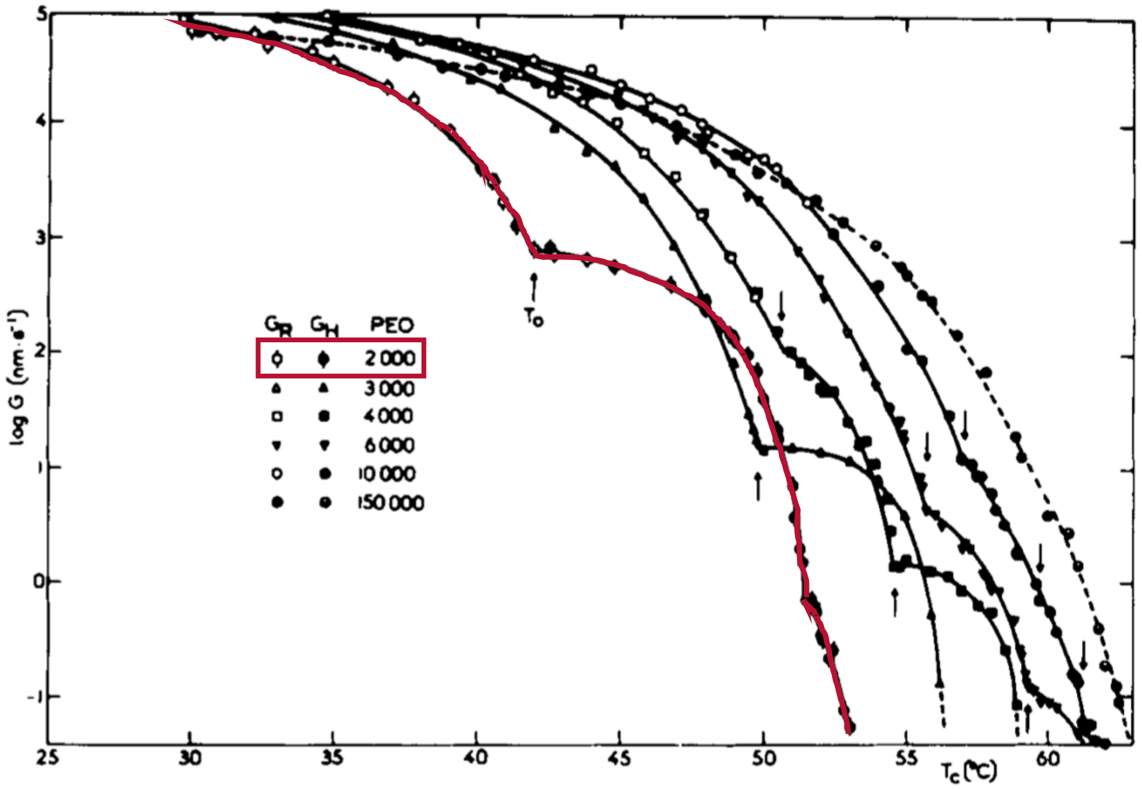

Crystal growth rates vs T_c and MW.

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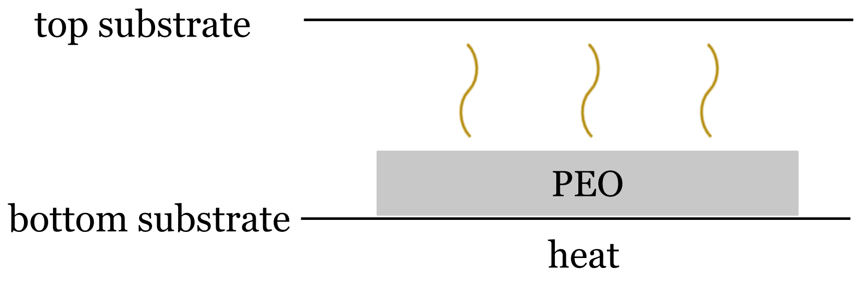
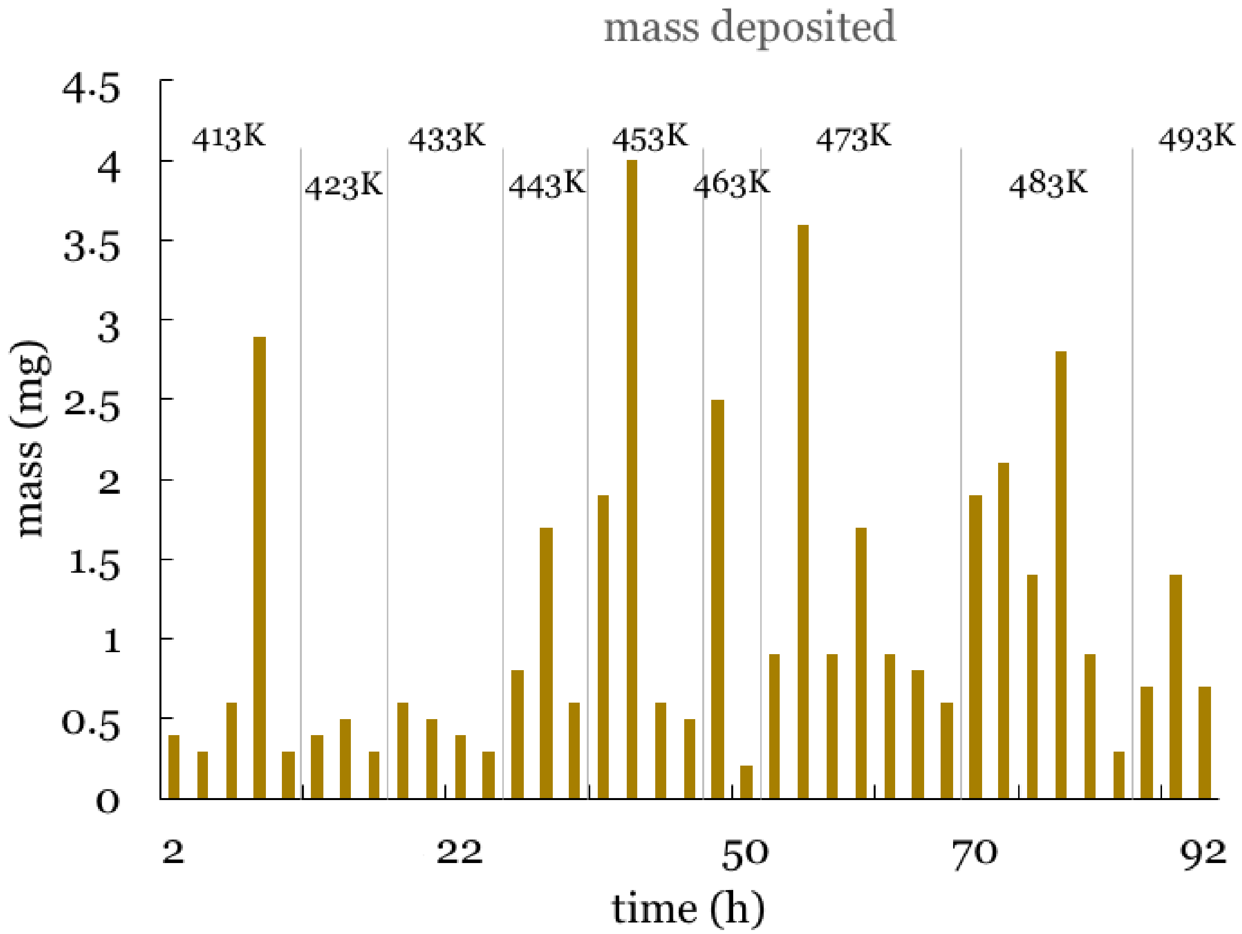
Production Technique



in N_2
P ~ 847 mbar



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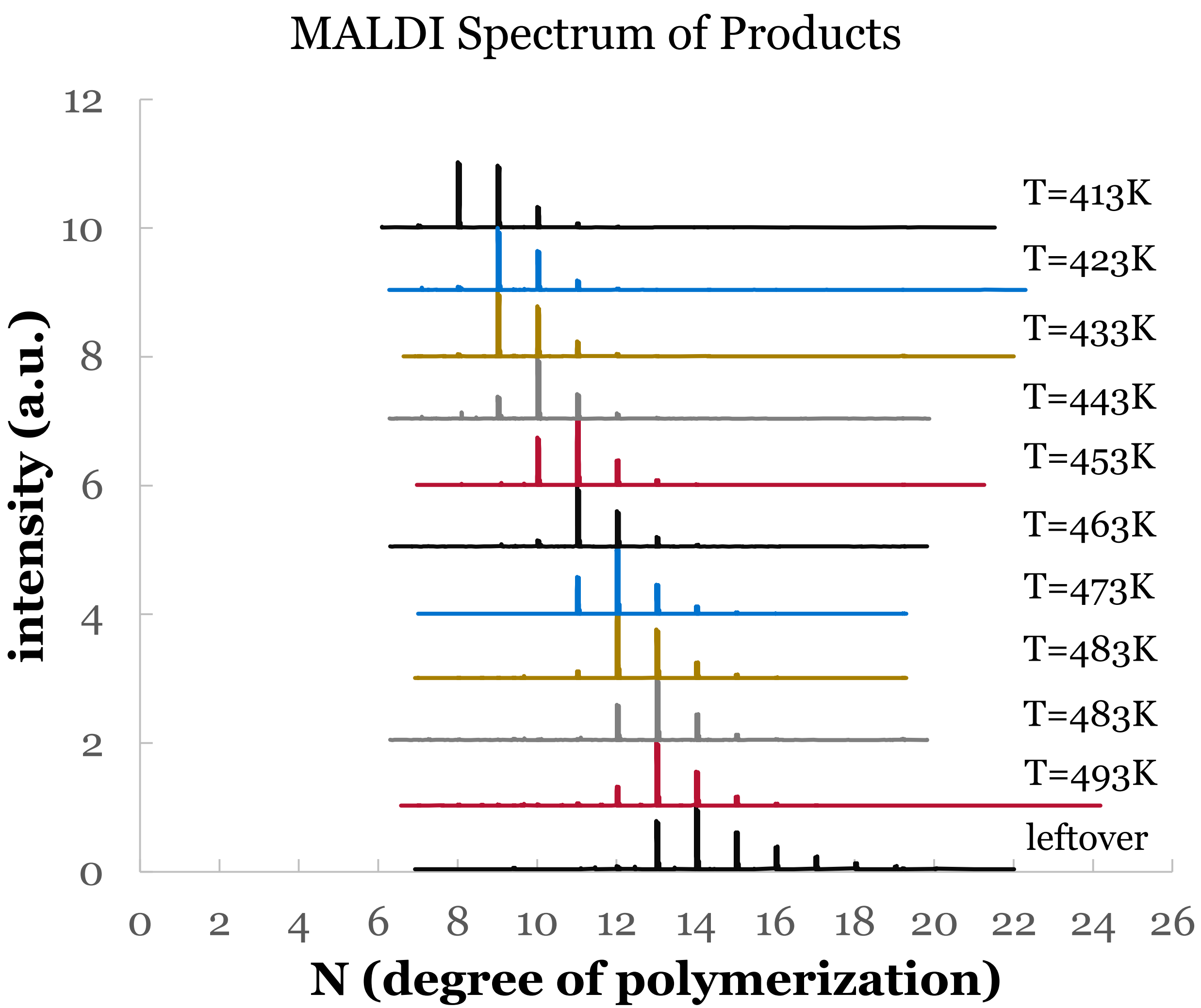
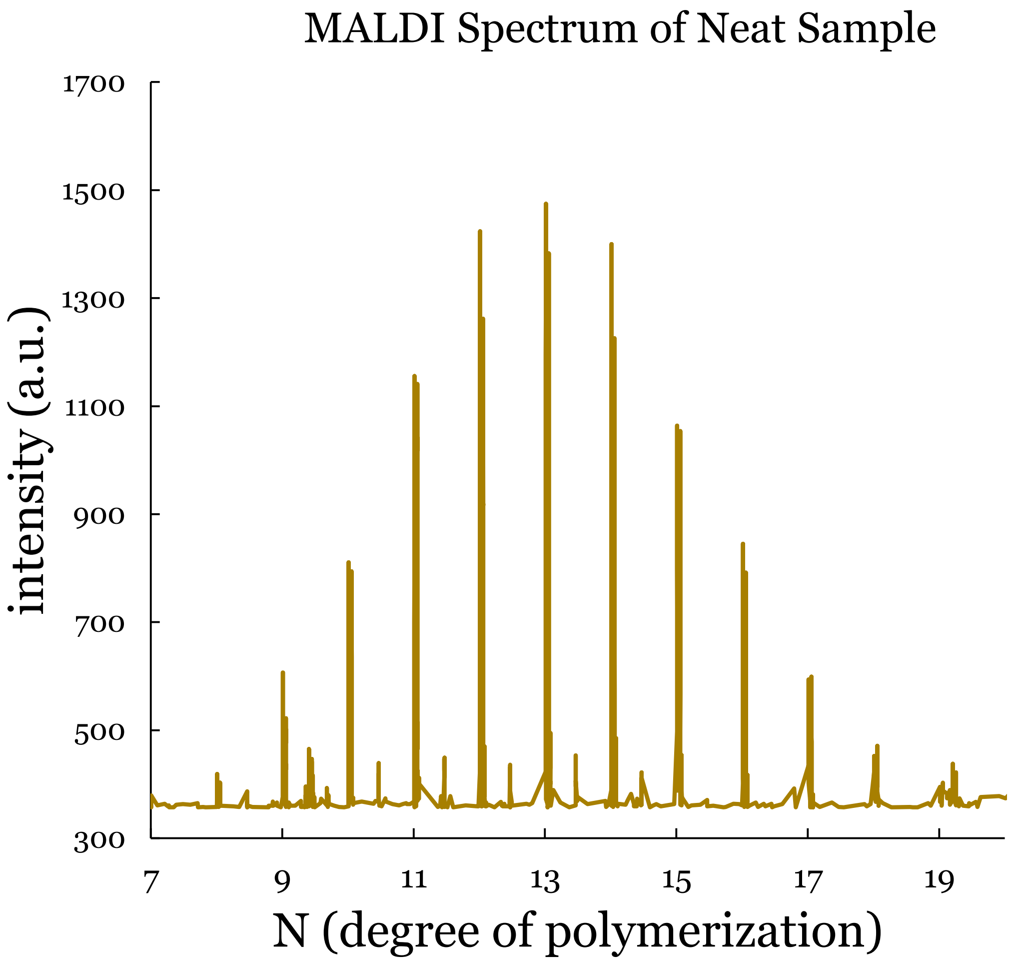
MALDI-TOF Results





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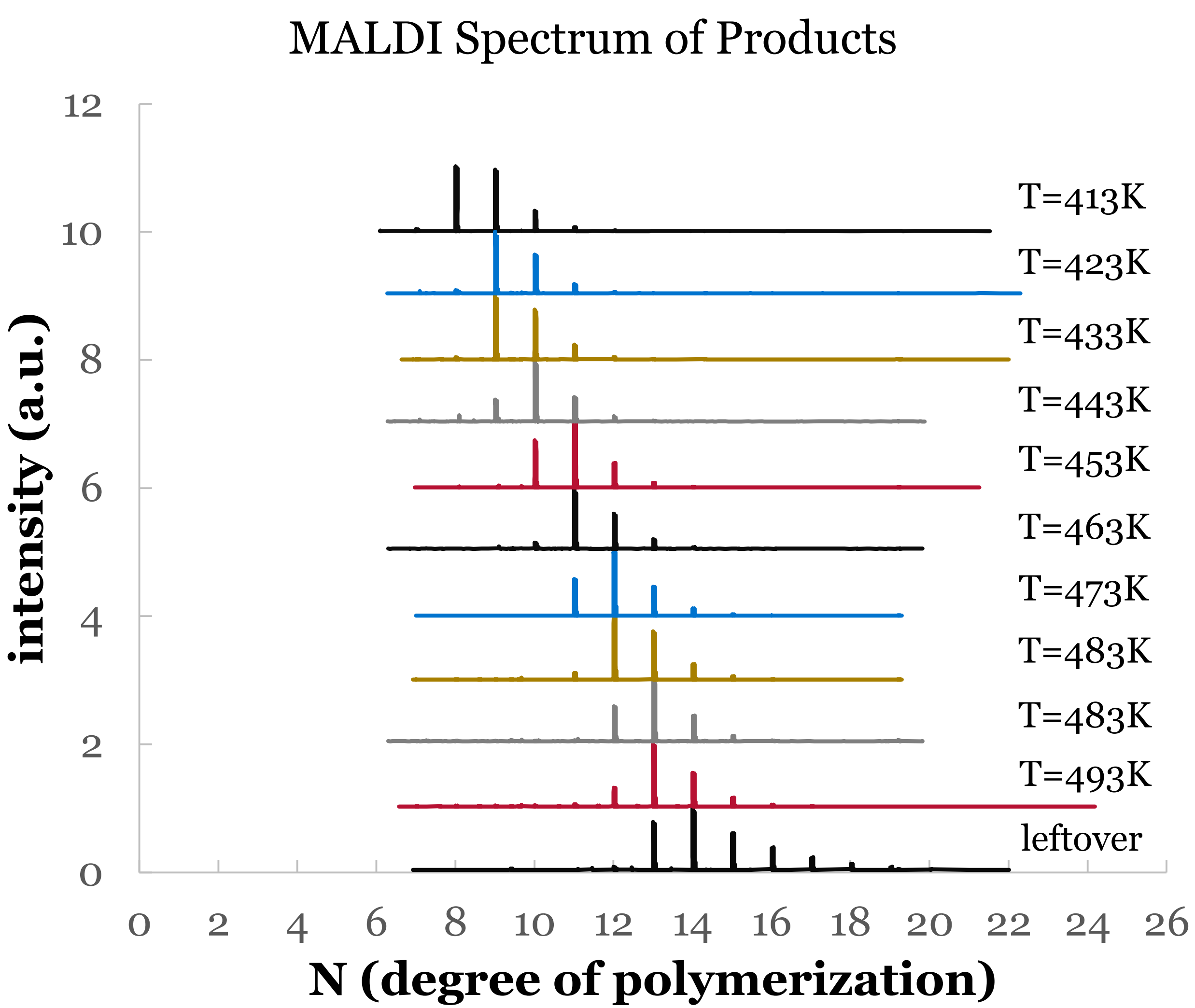

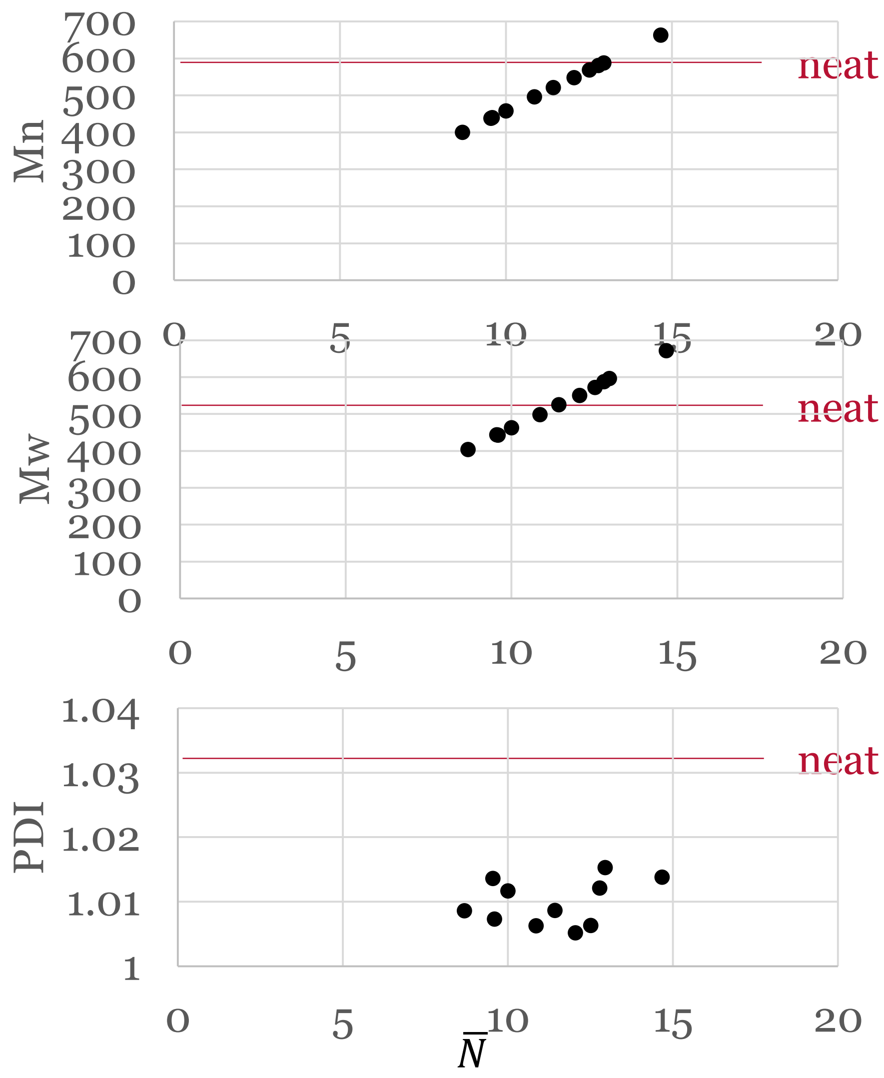

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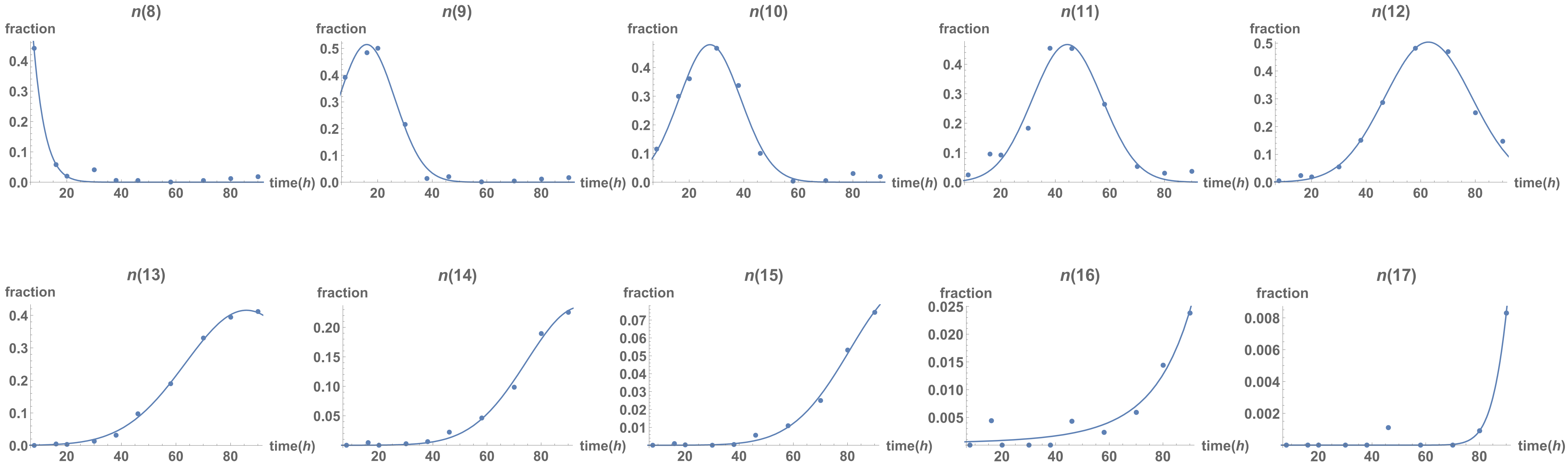
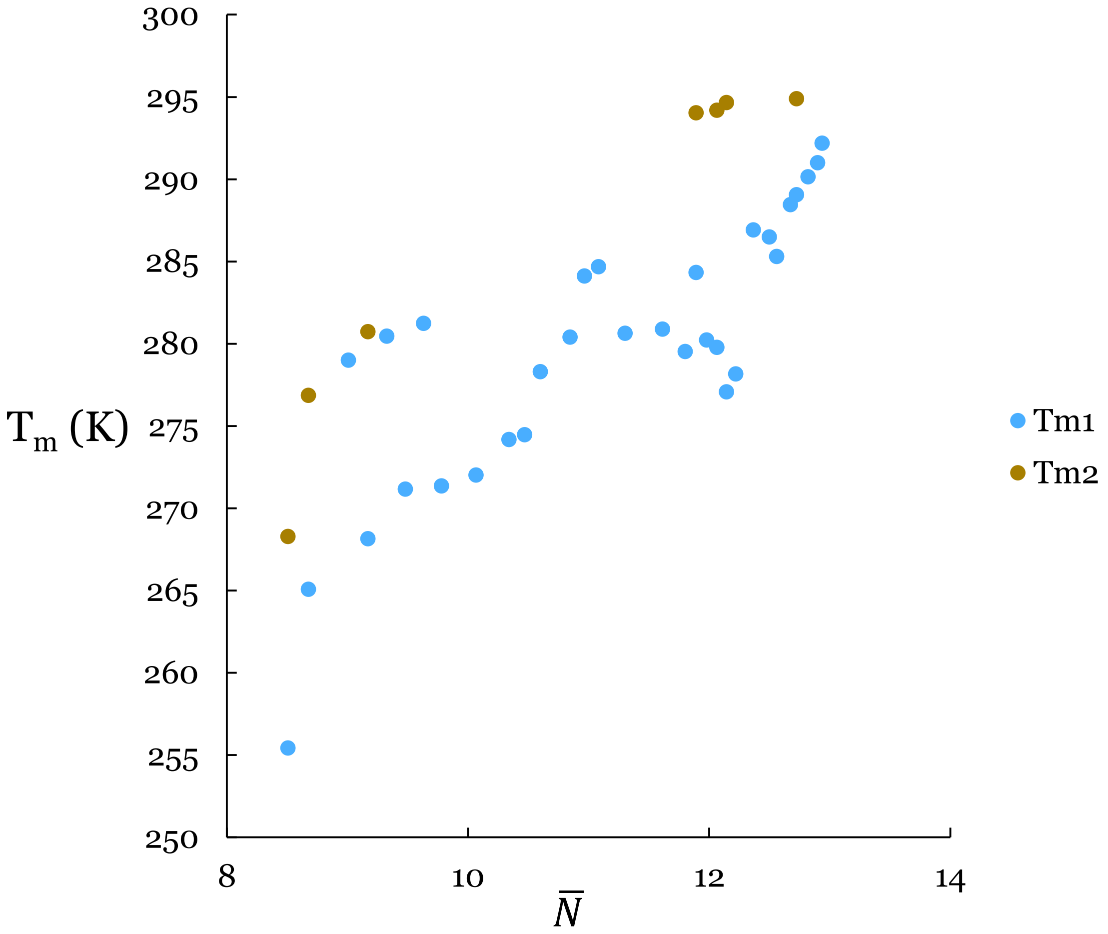
MALDI-TOF Results

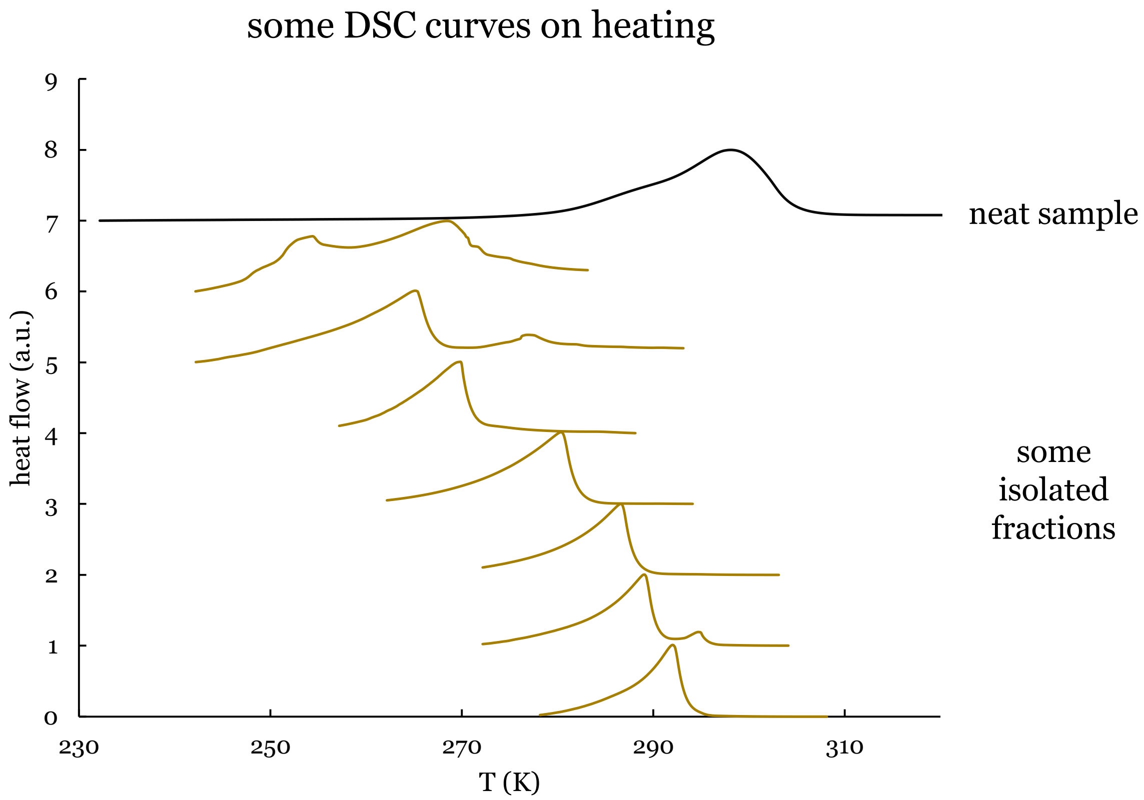


Evolution of n(N) with respect of evaporation time

DSC Measurements

(Differential Scanning Calorimetry)





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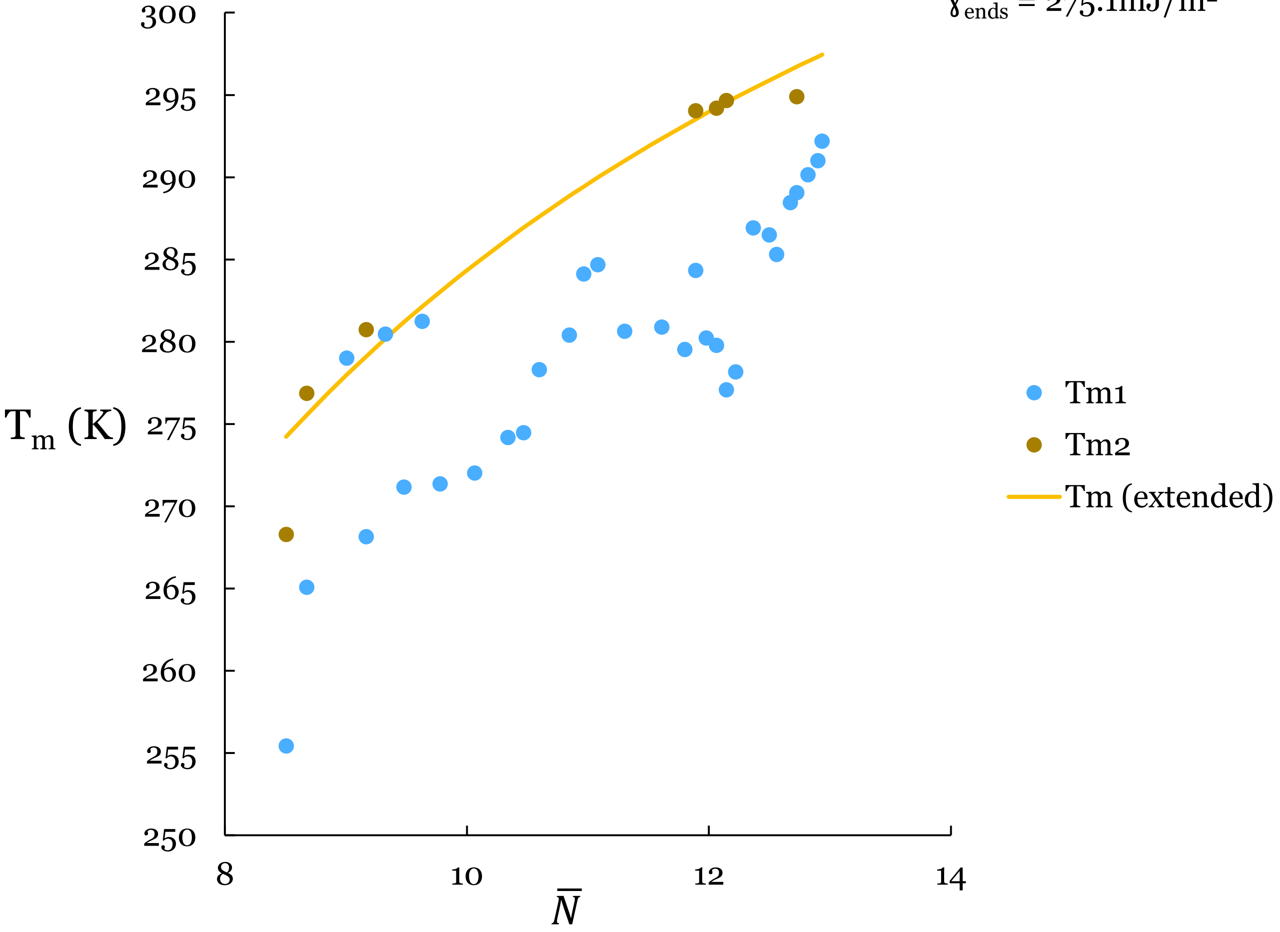
Colloid and Polymer Science, *254*(8), 695-715
Blaine, R. L. (2002). *Texas Instruments*.
European Polymer Journal, *44*(12), 4146-4150

DSC Measurements

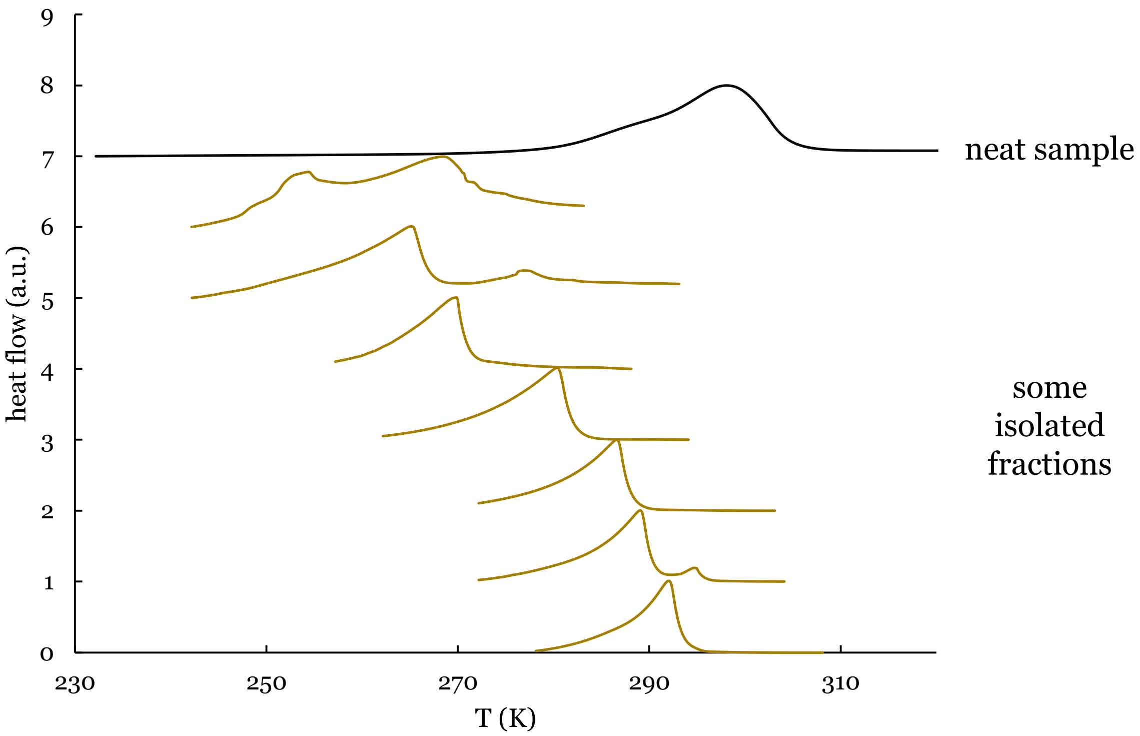
(Differential Scanning Calorimetry)

(γ_{amo} = 98.4mJ/m²)

γ_{ends} = 275.1mJ/m²



some DSC curves on heating



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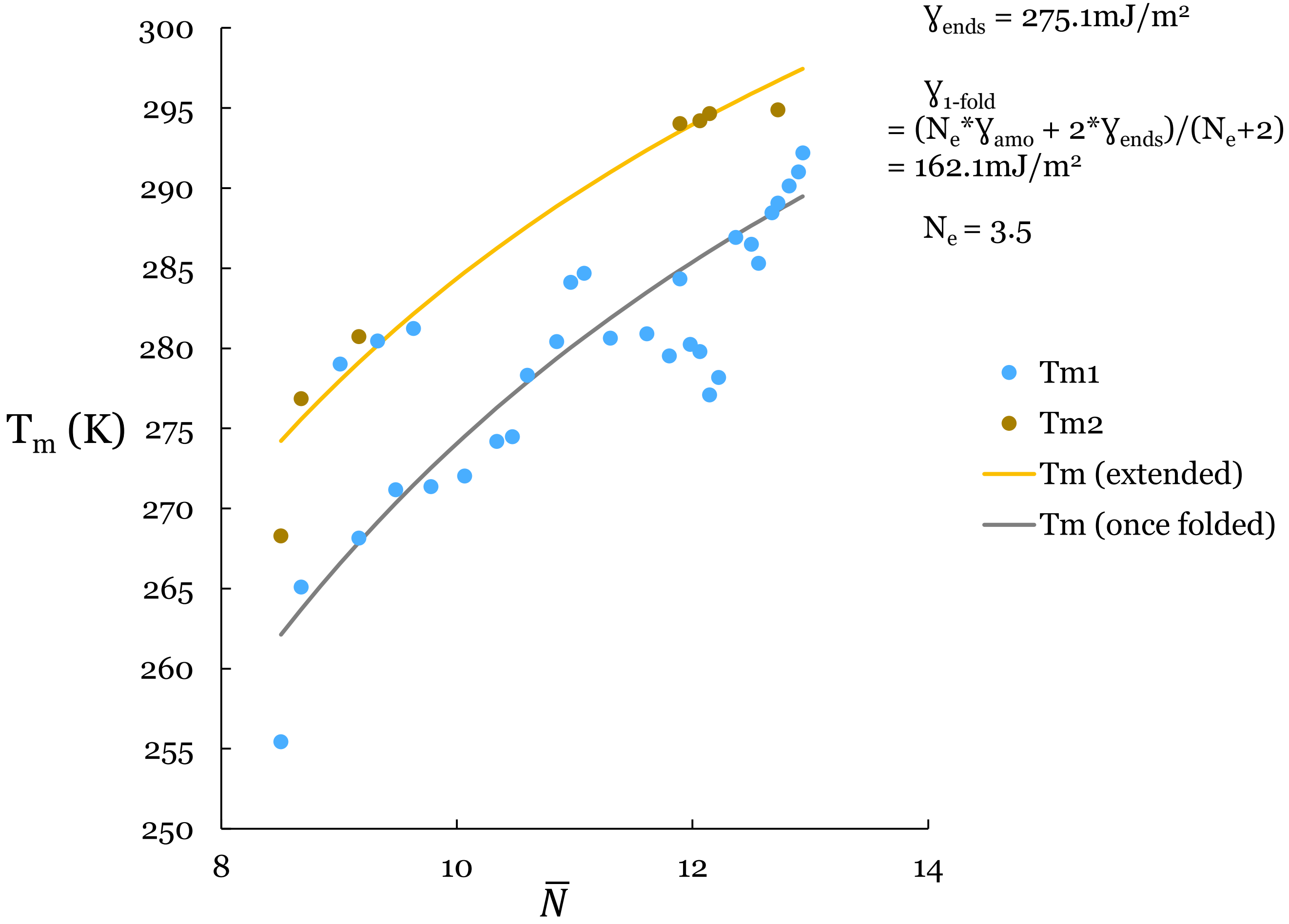
(Differential Scanning Calorimetry)

(γ_{amo} = 98.4mJ/m²)

γ_{ends} = 275.1mJ/m²

$\gamma_{1\text{-fold}}$
= $(N_e{*}\gamma_{amo} + 2{*}\gamma_{ends})/(N_e+2)$
= 162.1mJ/m²

N_e = 3.5



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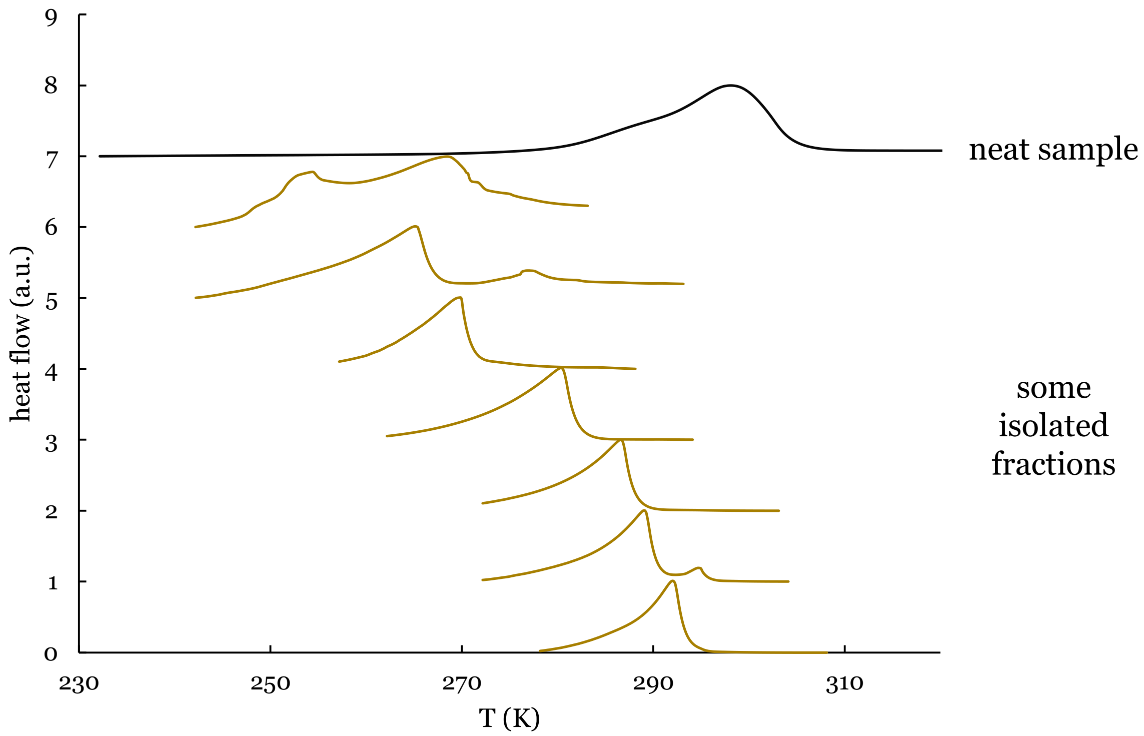

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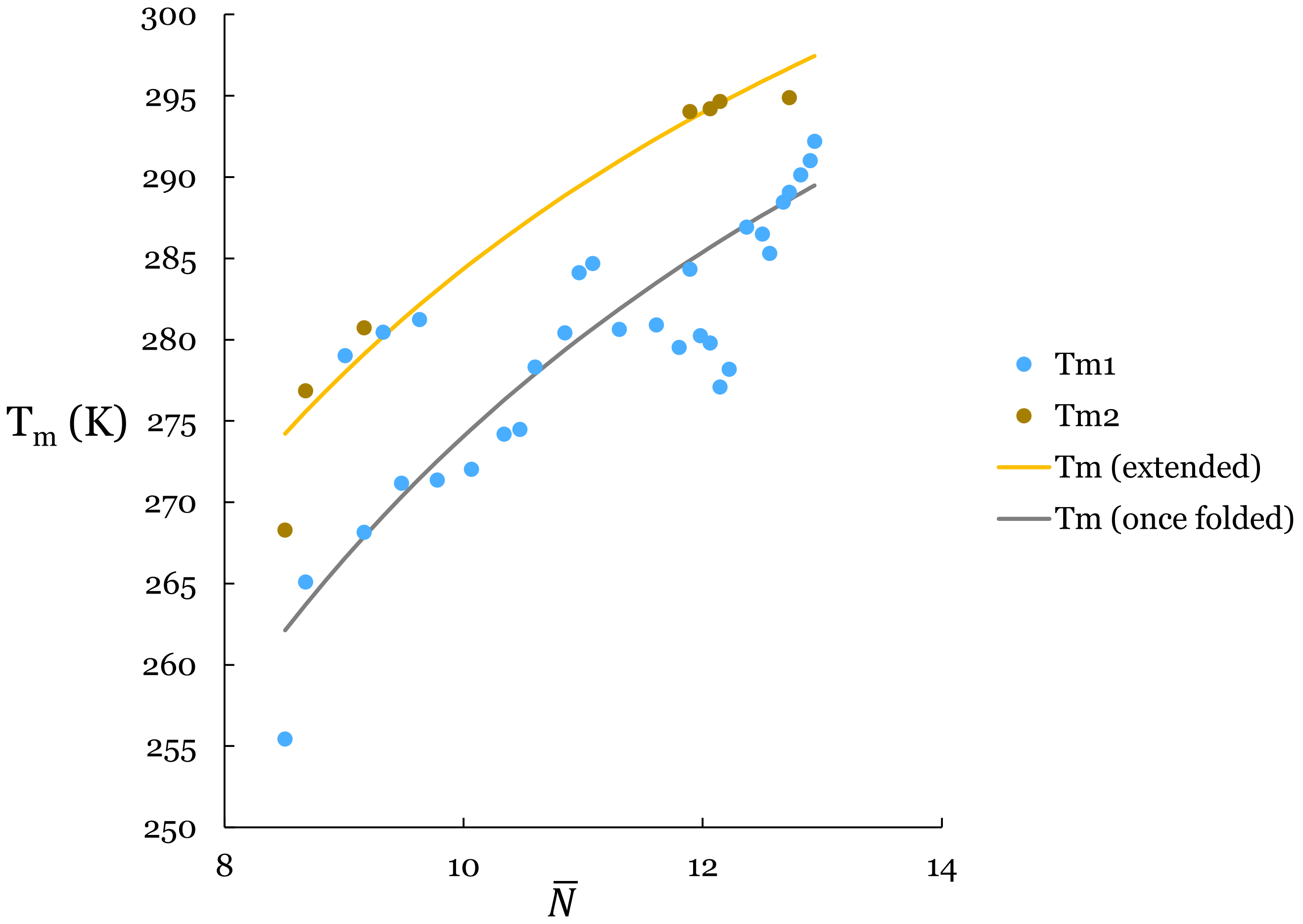
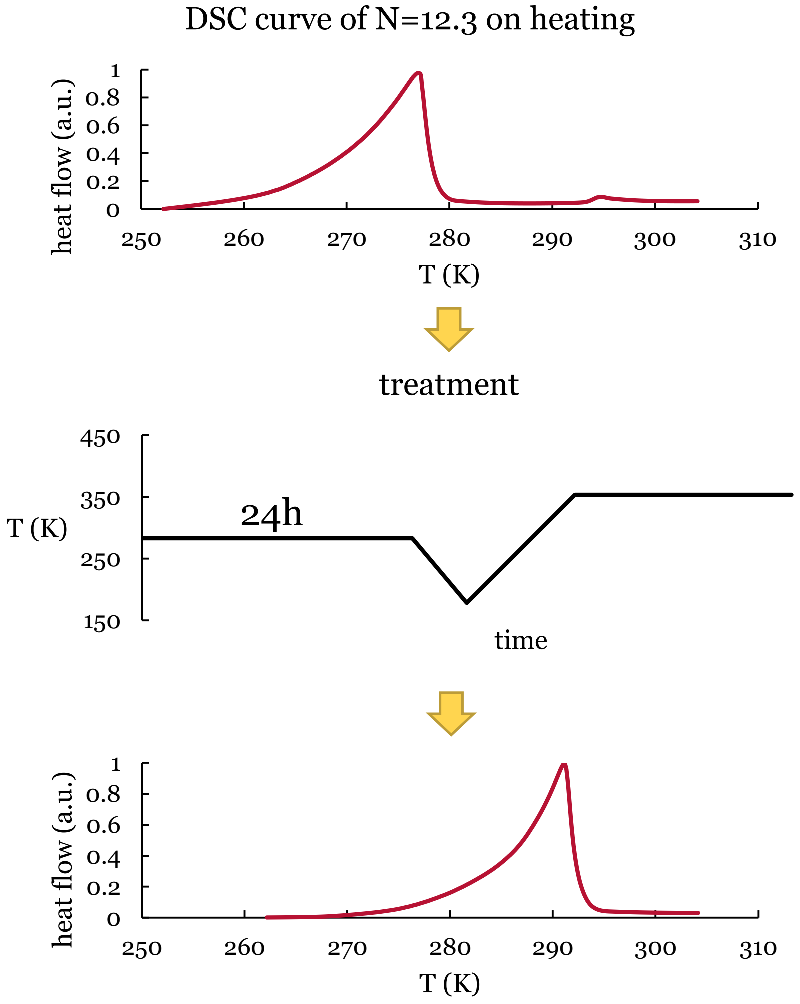


lamella thickening?



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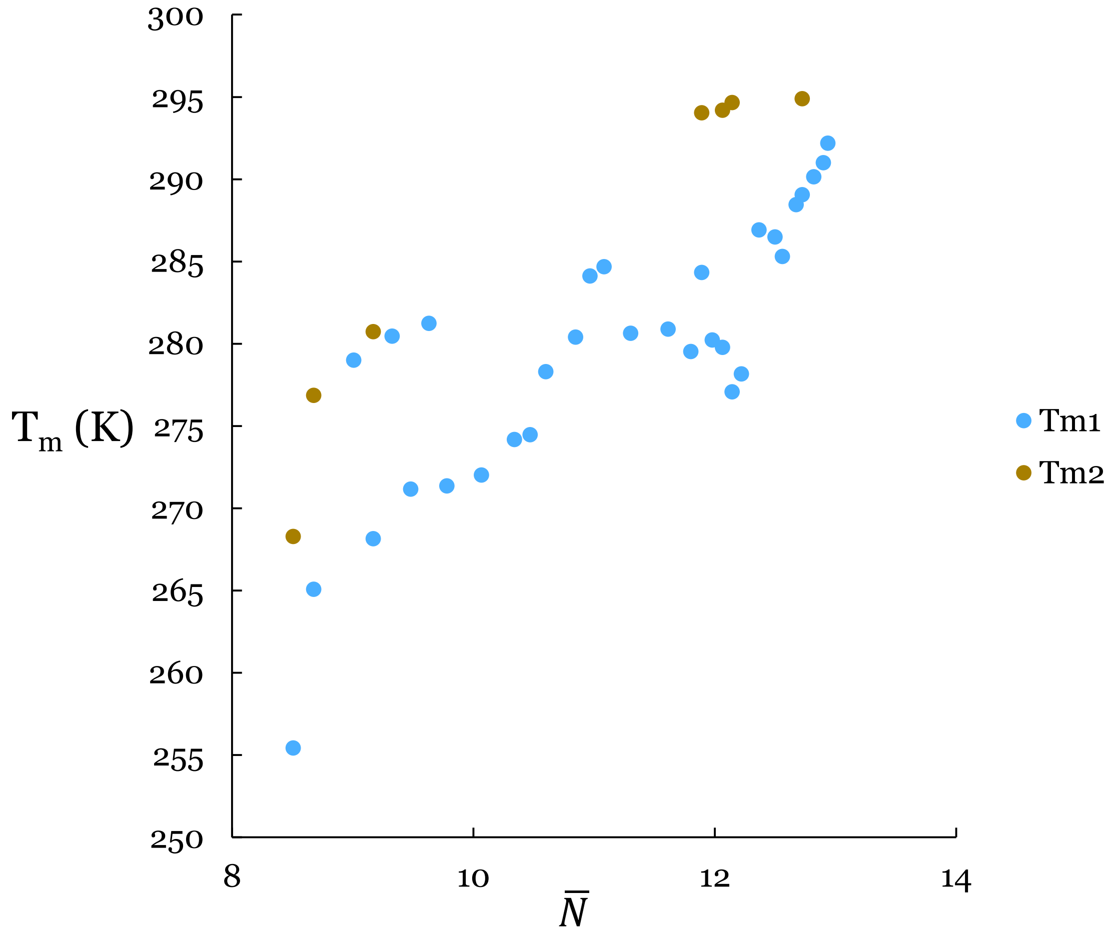
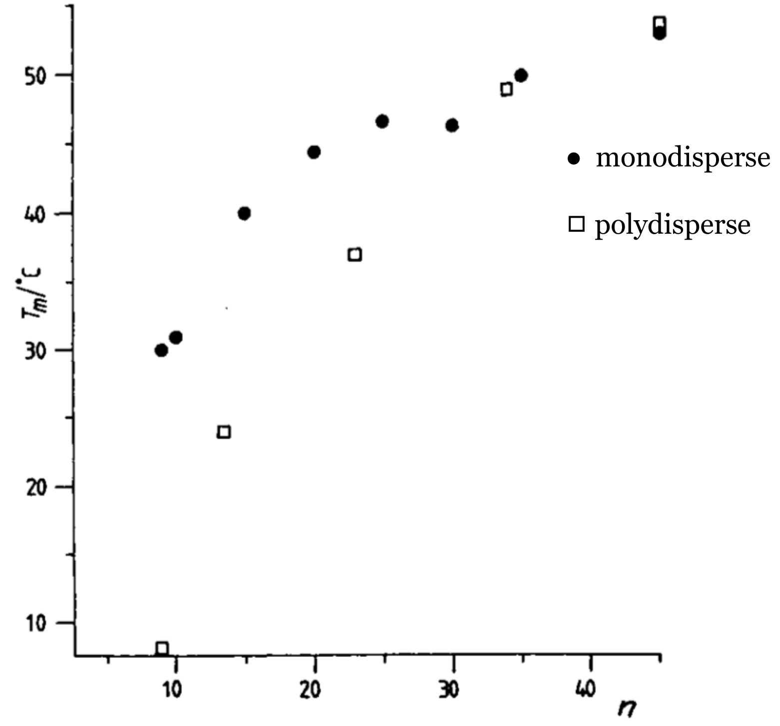
Makromol. Chem. 185,1559- 1563 (1984)





T_m vs N for PEO oligomers.

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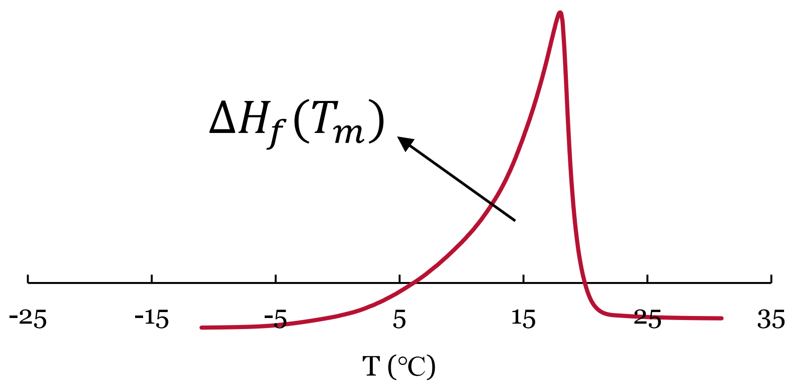
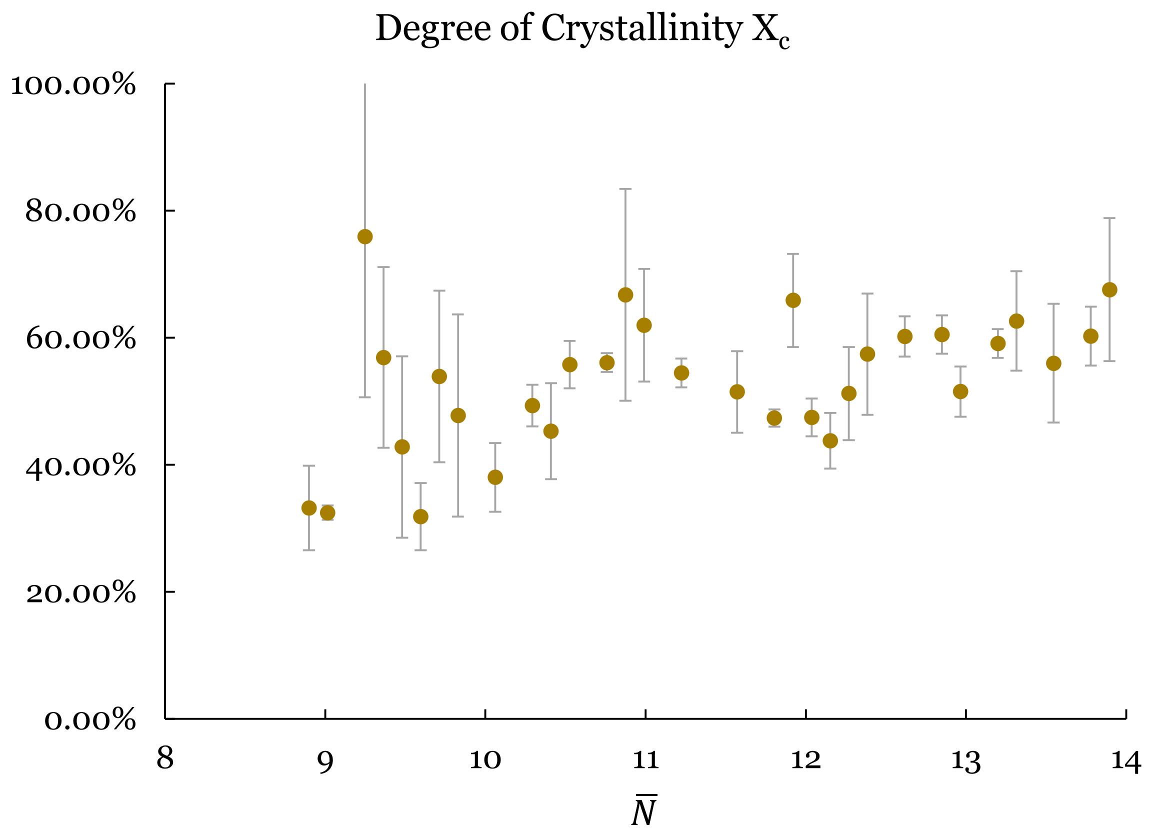
Blaine, R. L. (2002). *Texas Instruments*.

European Polymer Journal, *39*(8), 1721-1727.



$$X_C = \frac{\Delta H_f(T_m)}{\Delta H_f^{\infty}(T_m)}$$

$\Delta H_f^{\infty}(T_m)$ = 197J/g,
enthalpy of melting of PEO with 100% crystallinity



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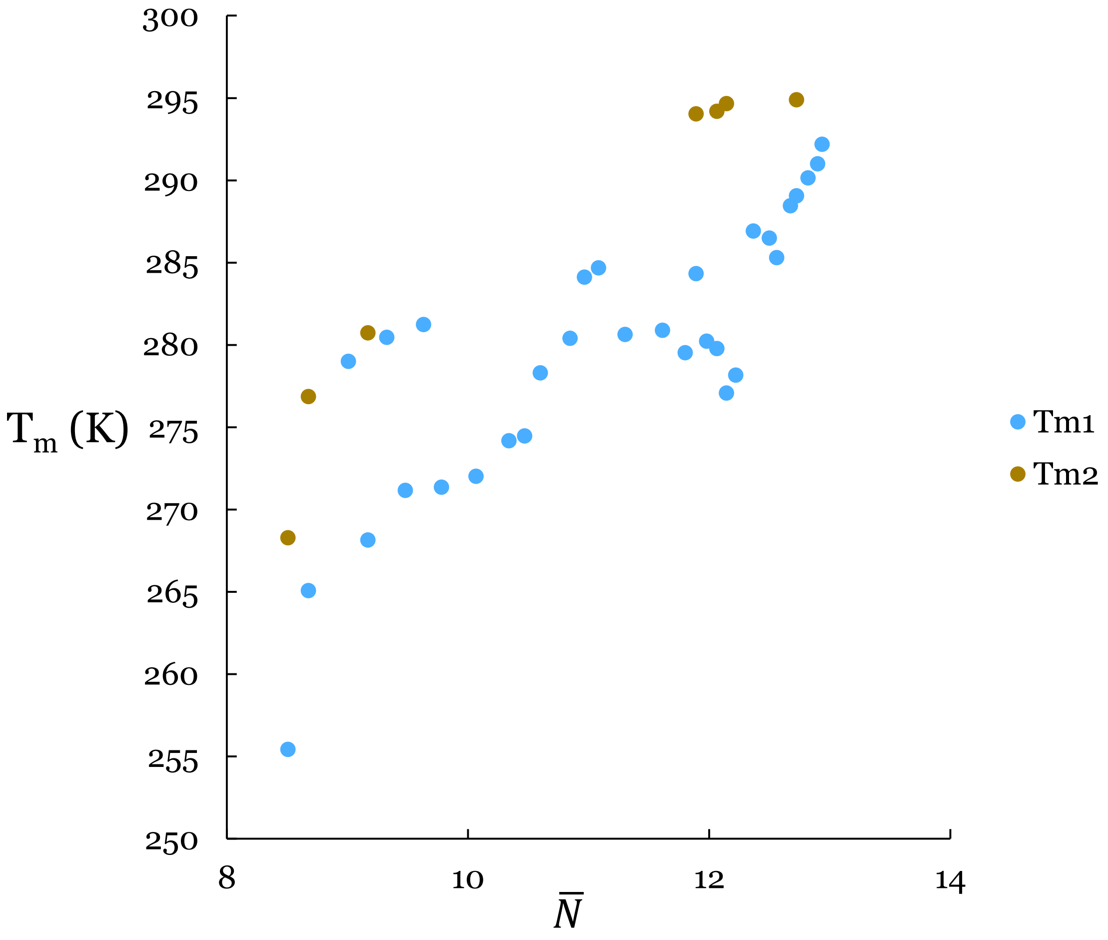
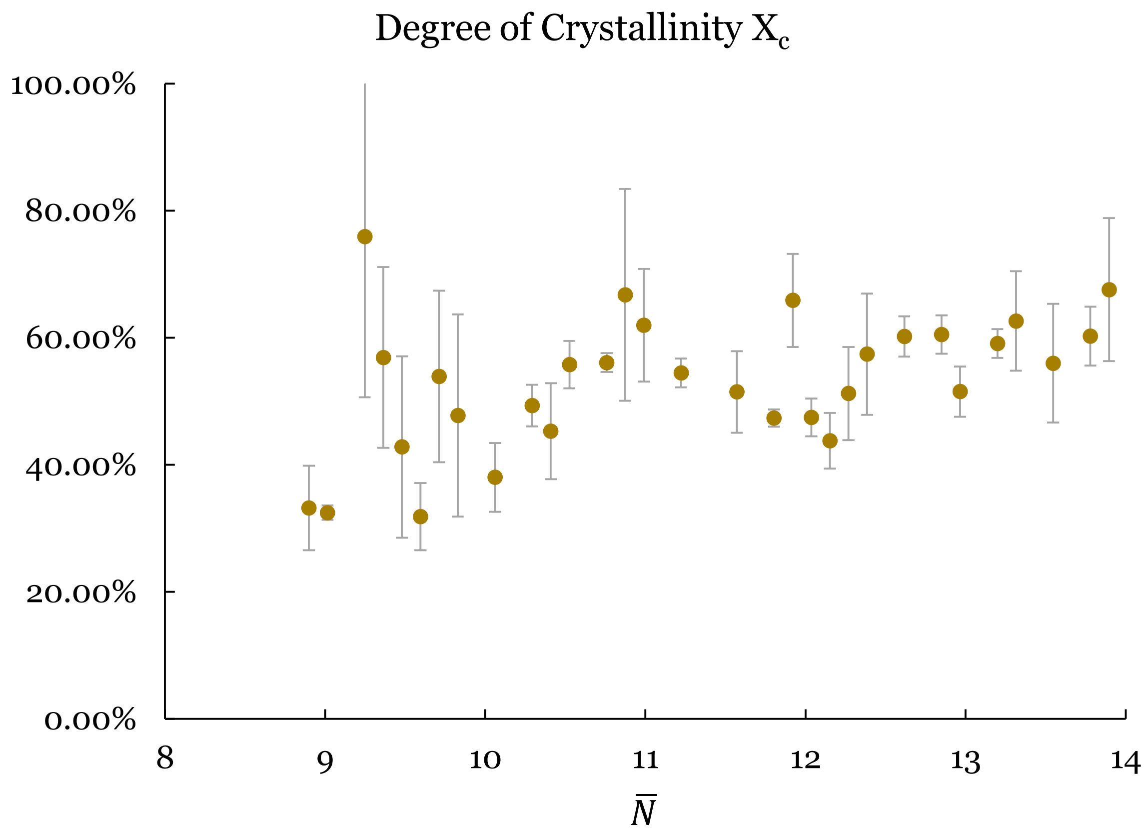
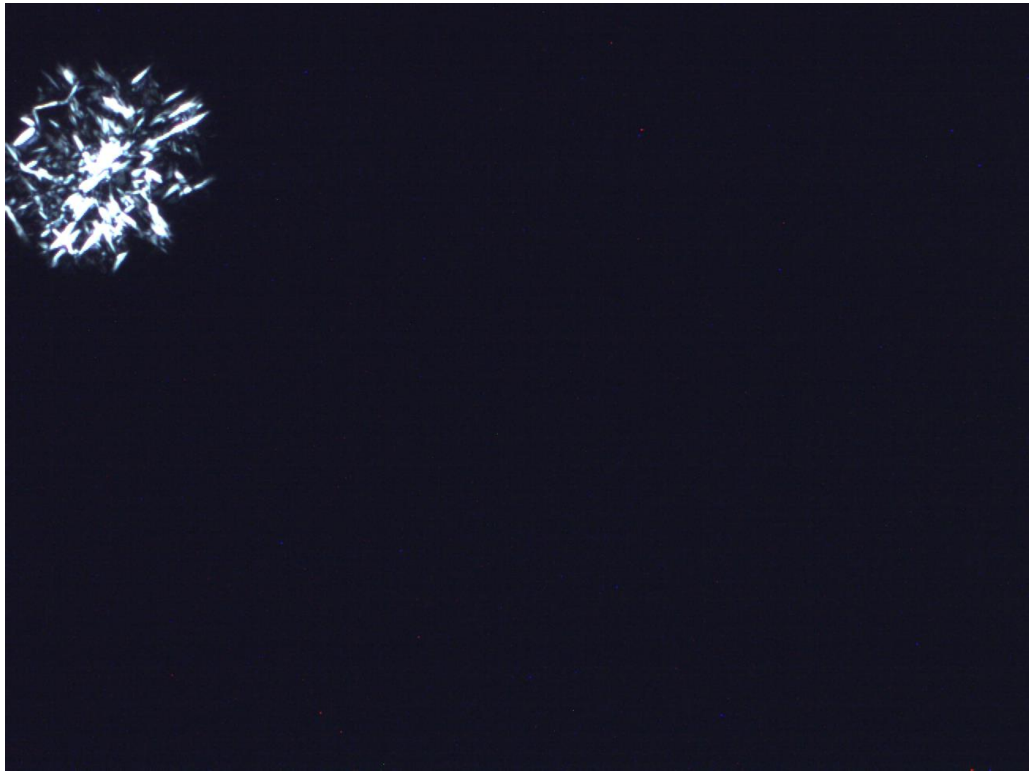




Crystal Growth



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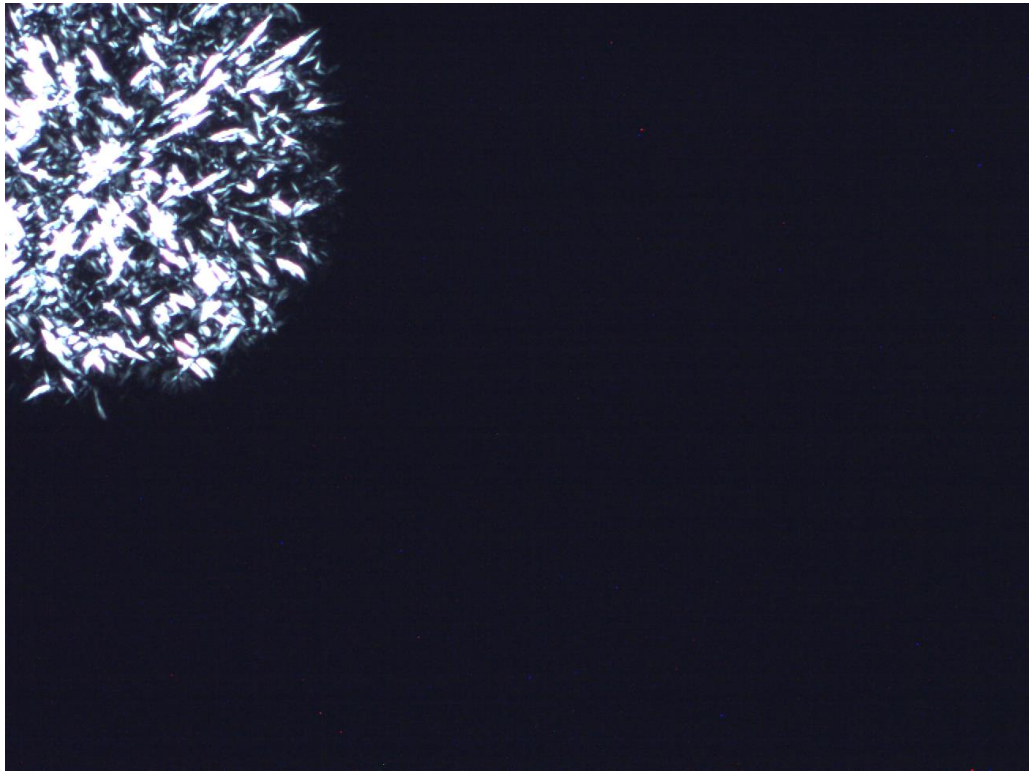

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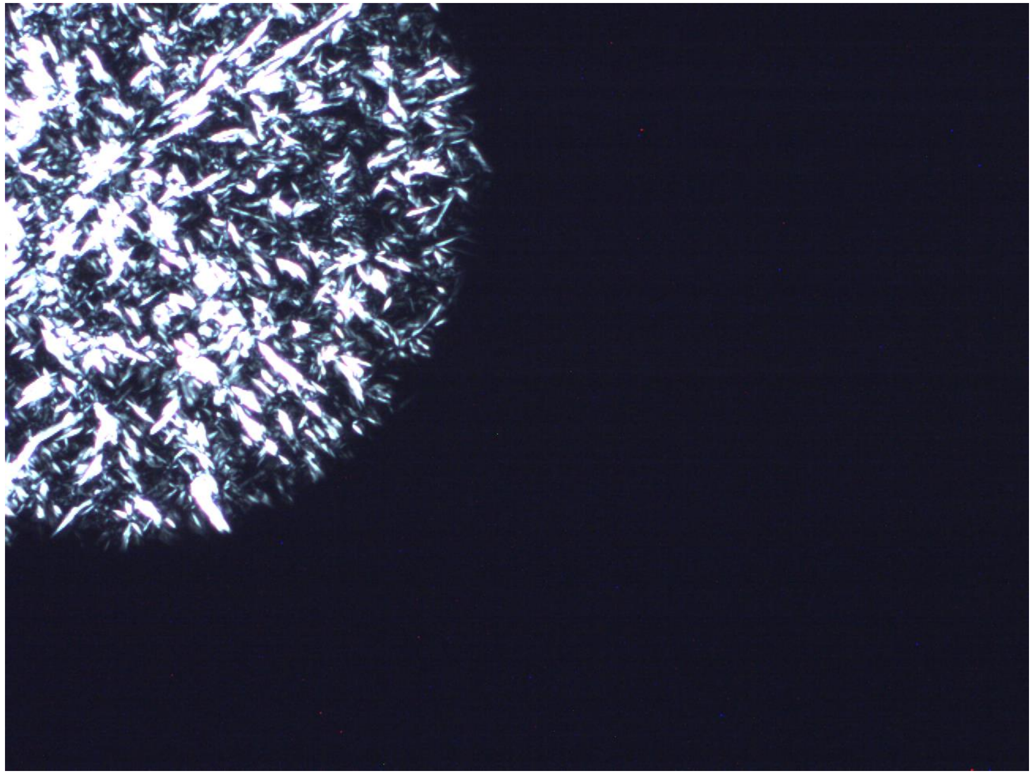

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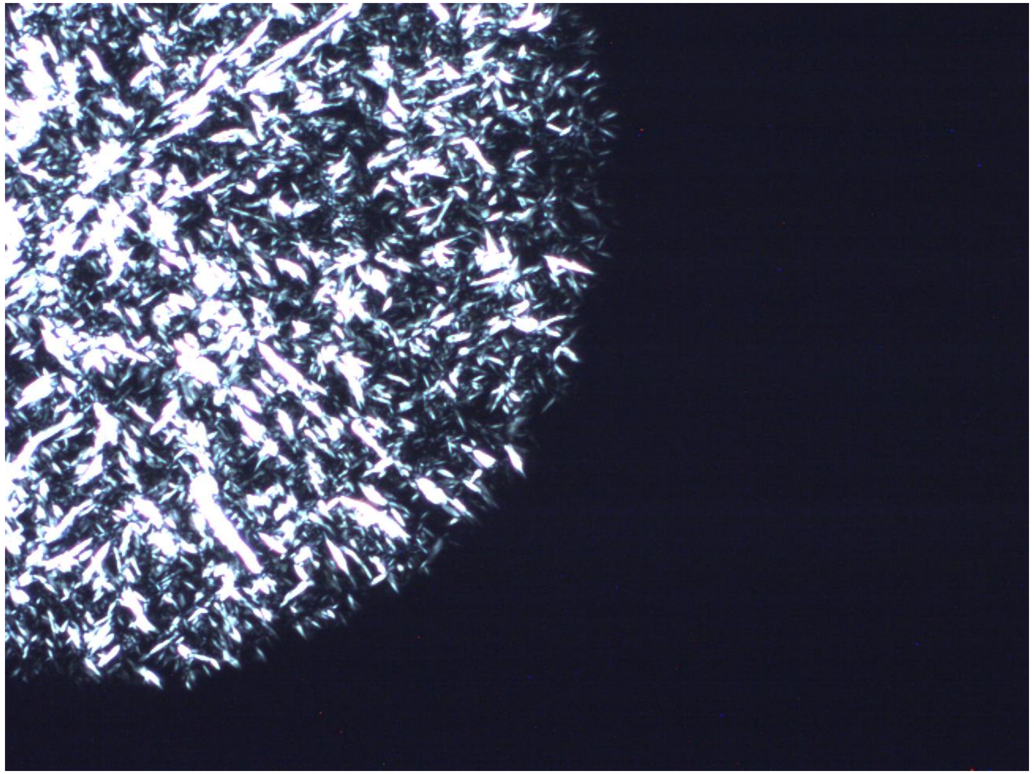

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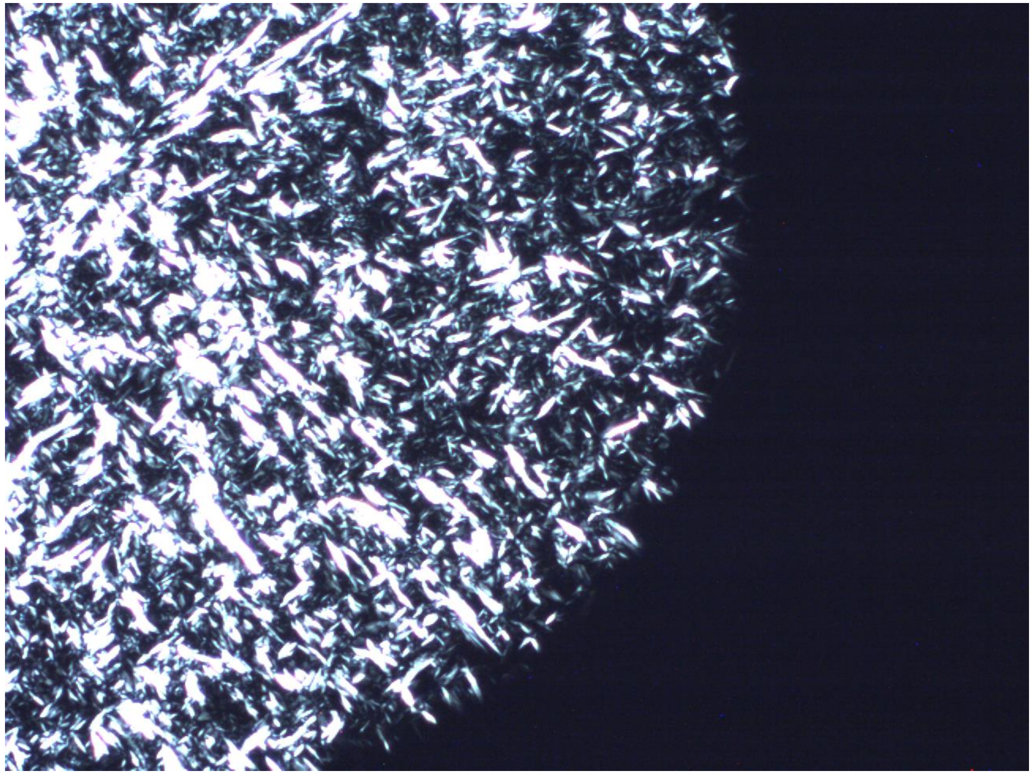

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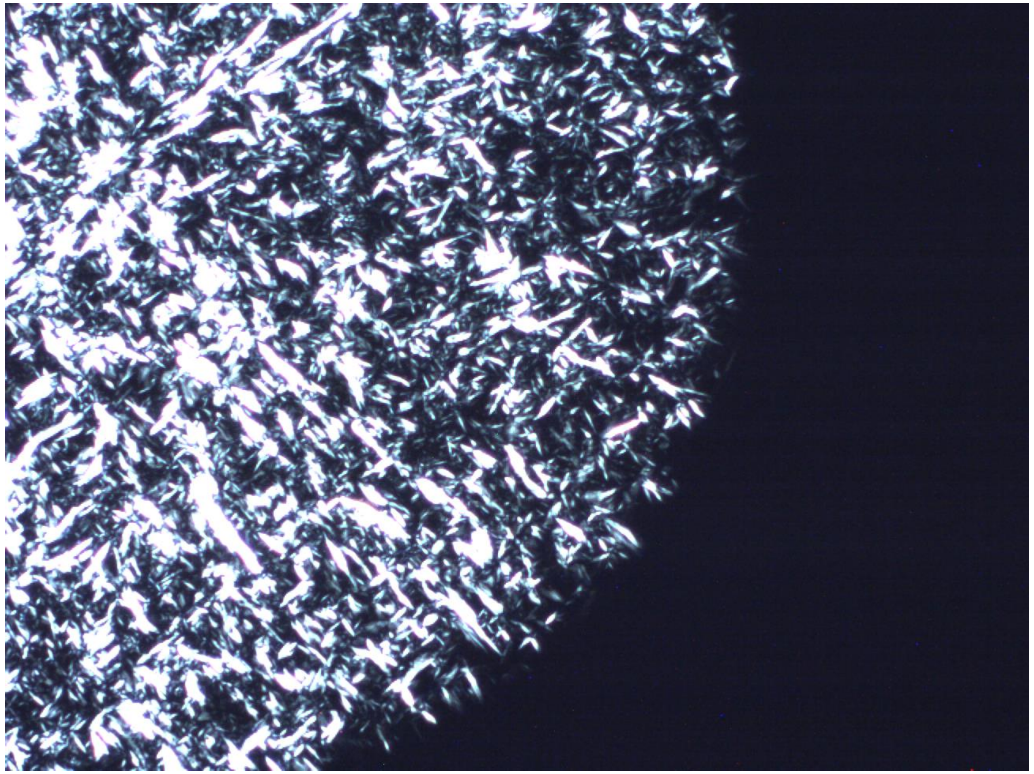
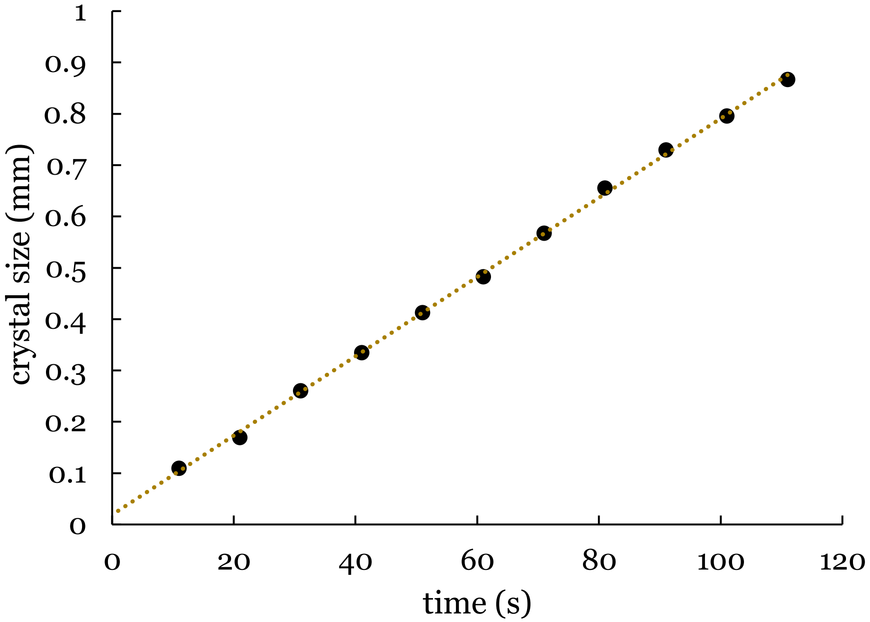
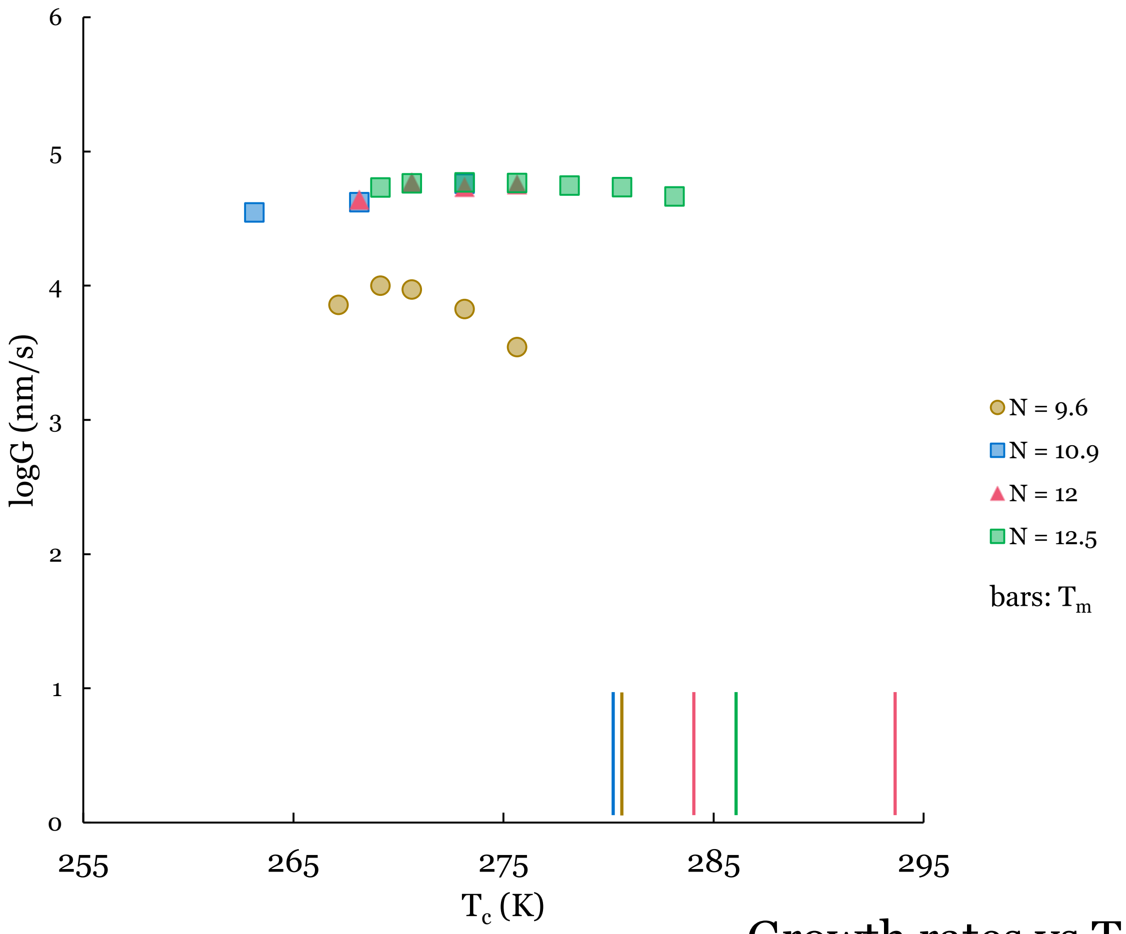
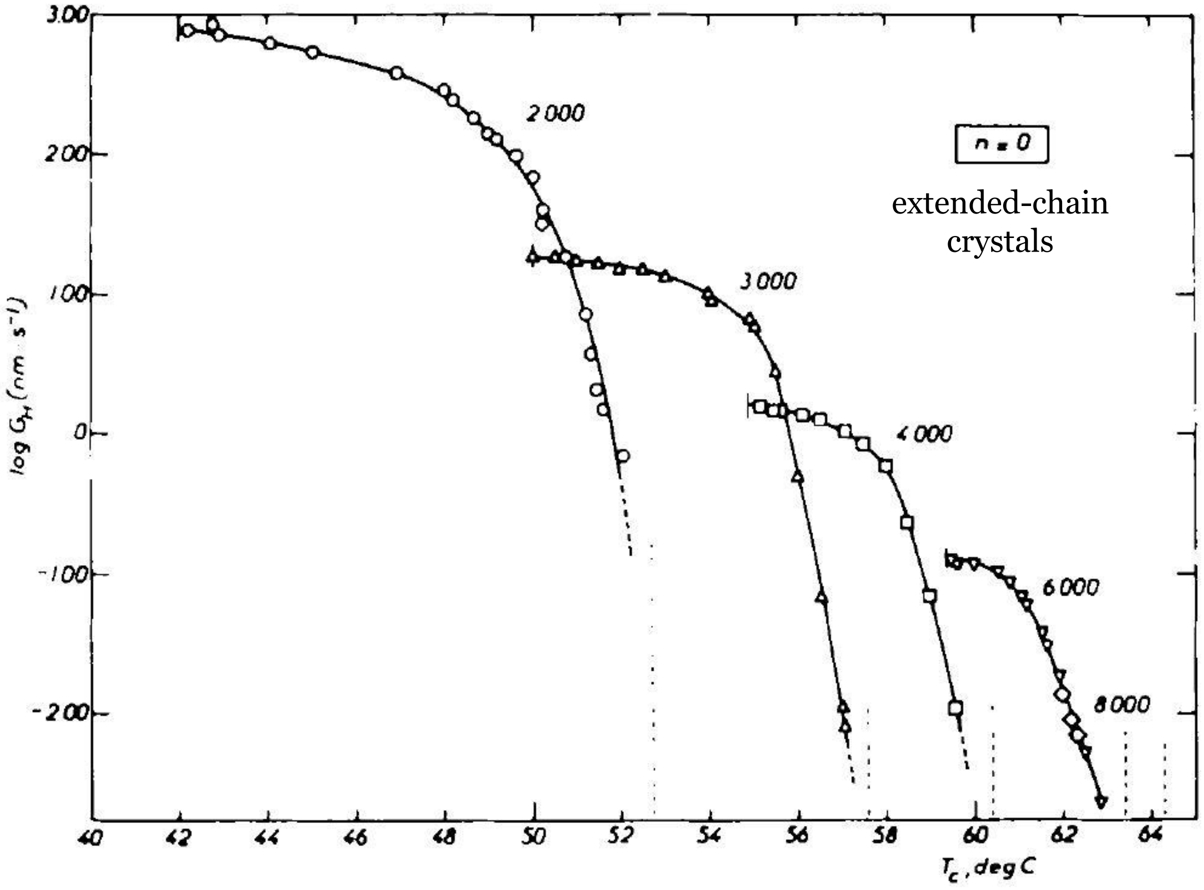




Crystal Growth

Journal of Polymer Science: Polymer Symposia (Vol. 59, No. 1, pp. 31-54).





Growth rates vs T_c (vertical lines: T_m)

Conclusions

- Work done:

1. Evaporative purification achieved PDI ~6 times better
2. DSC measurements (T_m difference between mono- and poly-disperse)
3. Crystal growth rate measurements

- Future work

1. Even lower PDI (larger scale, shorter collection intervals)
2. Crystal growth rate measurements (near T_m)
3. X-ray measurements (lamella information)

References

- Yeates, S. G., Teo, H. H., Mobbs, R. H., & Booth, C. (1984). Ethylene glycol oligomers. *Macromolecular Chemistry and Physics*, *185*(8), 1559-1563.
- Kovacs, A. J., Gonthier, A., & Straupe, C. (1975, January). Isothermal growth, thickening, and melting of poly (ethylene oxide) single crystals in the bulk. In *Journal of Polymer Science: Polymer Symposia* (Vol. 50, No. 1, pp. 283-325). Wiley Subscription Services, Inc., A Wiley Company.
- Buckley, C. P., & Kovacs, A. J. (1976). Melting behaviour of low molecular weight poly (ethylene-oxide) fractions. *Colloid and Polymer Science*, *254*(8), 695-715.
- Blaine, R. L. (2002). Thermal applications note polymer heats of fusion. *Texas Instruments, New Castle Google Scholar*.
- Spěváček, J., & Baldrian, J. (2008). Solid-state 13C NMR and SAXS characterization of the amorphous phase in low-molecular weight poly (ethylene oxide) s. *European Polymer Journal*, *44*(12), 4146-4150.
- Kovacs, A. J., Straupe, C., & Gonthier, A. (1977, January). Isothermal growth, thickening, and melting of polyethylene oxide) single crystals in the bulk. II. In *Journal of Polymer Science: Polymer Symposia* (Vol. 59, No. 1, pp. 31-54). Wiley Subscription Services, Inc., A Wiley Company.

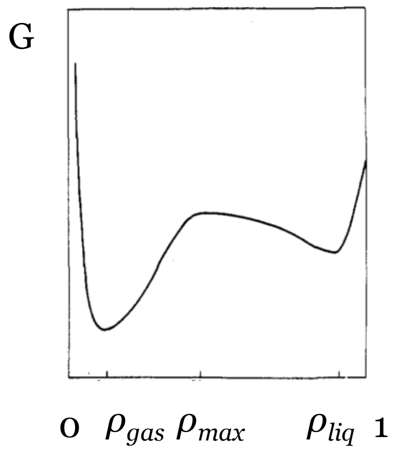
THANK YOU!

Vapor Pressure Calculation

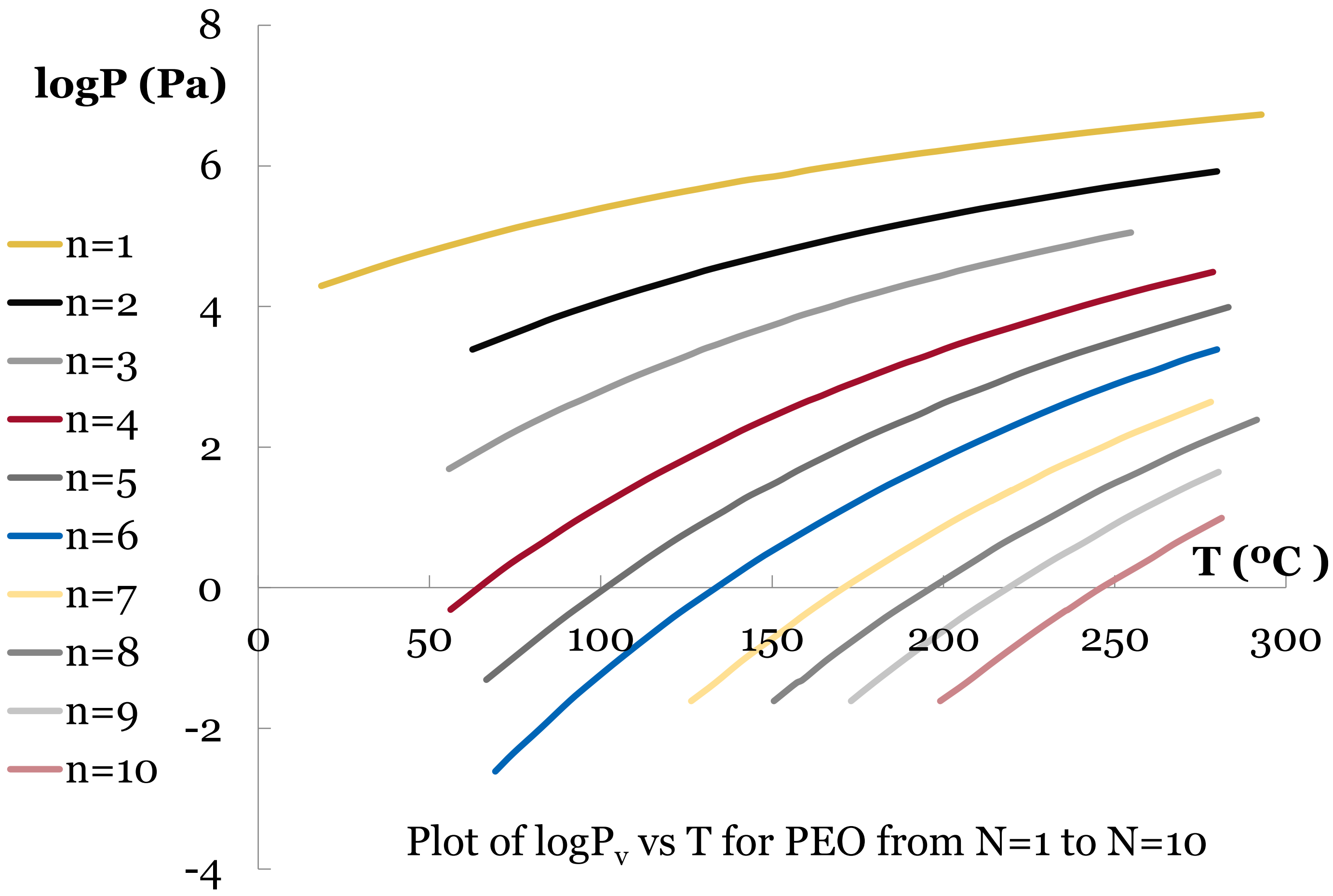
J. Phys. Chem. 80(21), 2352-2362

Sanchez-Lacombe Lattice-Fluid Model

$$G = -\rho + Pv + T\left[(v-1)ln(1-\rho) + \frac{1}{r}ln(\rho/\omega)\right]$$



Plot of free energy vs mass density



Plot of $logP_v$ vs T for PEO from N=1 to N=10

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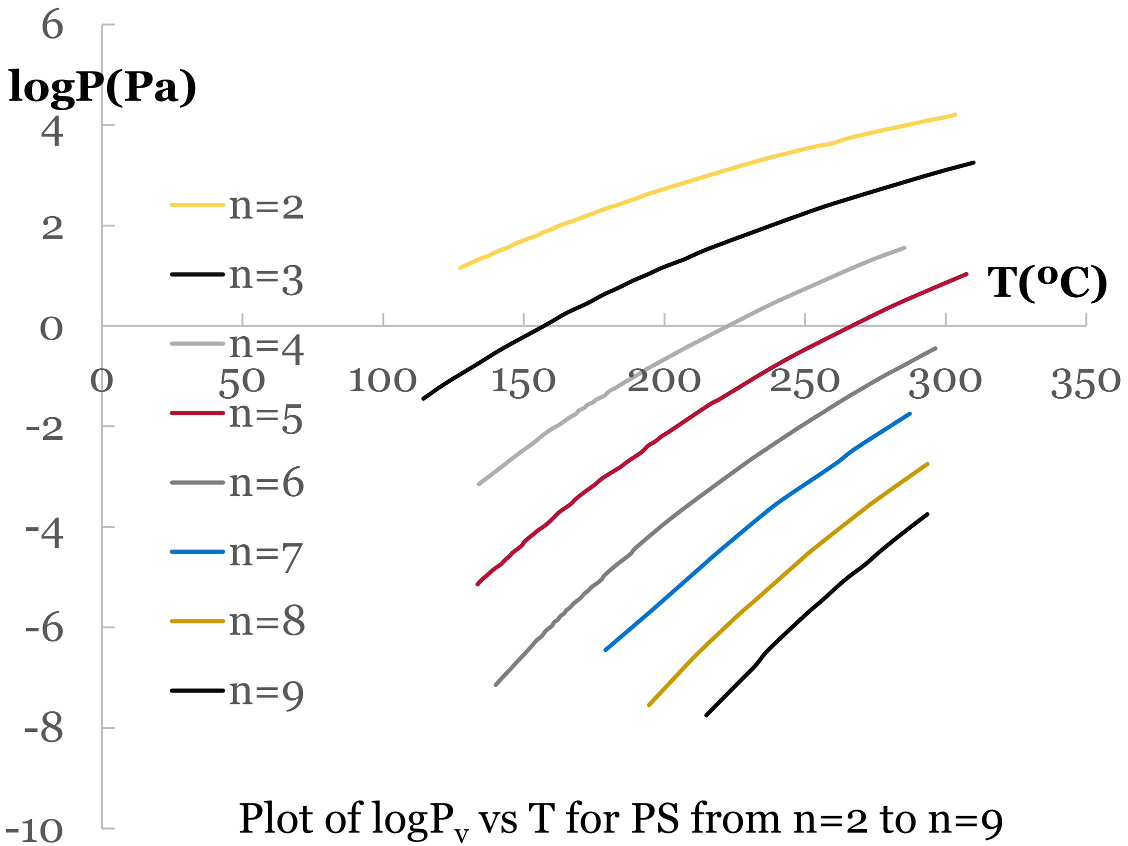
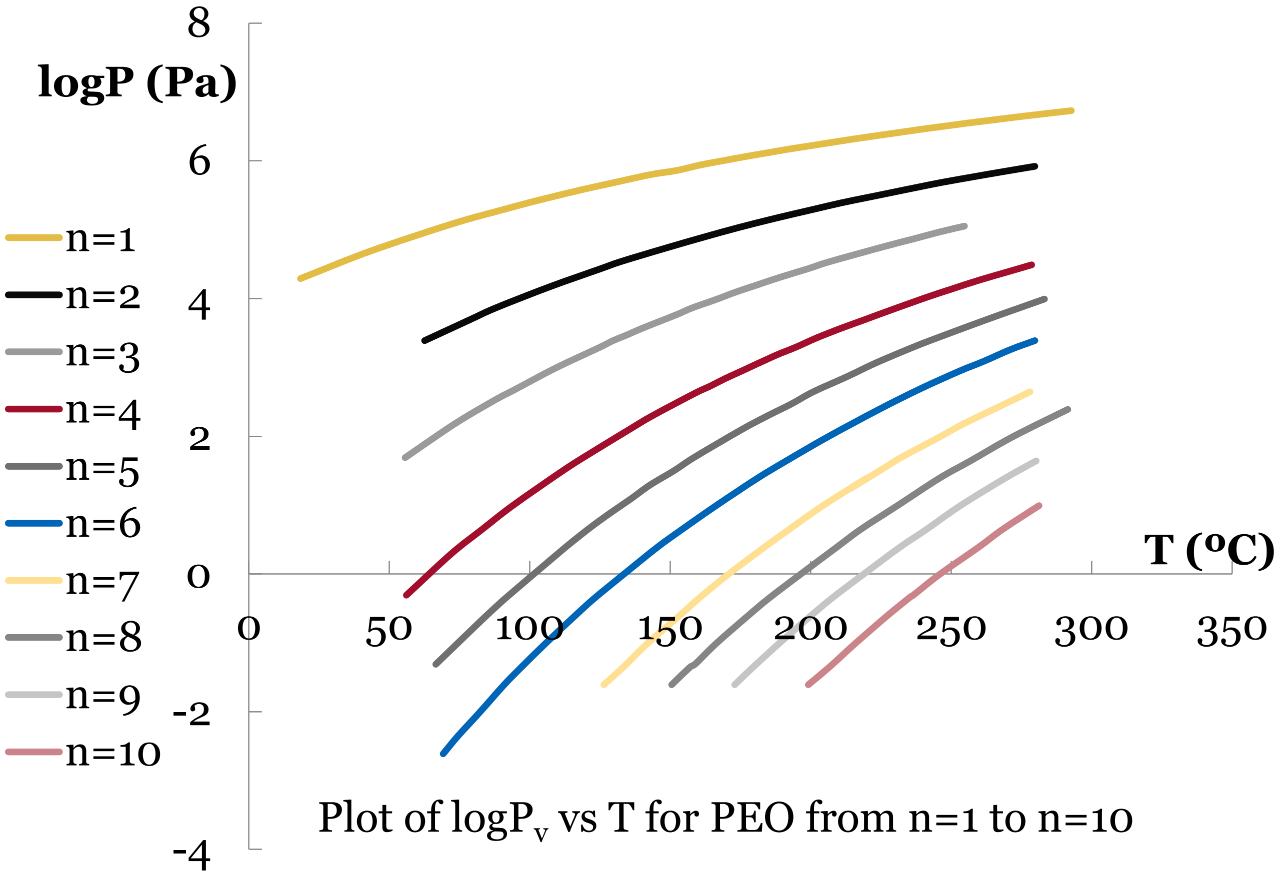
Vapor Pressure Calculation

PHYSICAL REVIEW MATERIALS **1**, 025605 (2017)



Plot of $\log P_v$ vs T for PS from n=2 to n=9



Plot of $\log P_v$ vs T for PEO from n=1 to n=10

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