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A New Way to Measure Low Molecular Weight Polymer

John H Jennings

Jennings Research & Editing 2530 Hillegass Ave. #307 Berkeley CA 94704, USA

Corresponding Author: **John H Jennings**

Abstract

Grubisic, *et al* (1967) [1] used the Einstein viscosity law (1906) [2] as a theoretical basis in calibrating a column for size exclusion chromatography (SEC) and it works well for polymer molecular weight (MW) from 10,000 to 11 million daltons. There are problems measuring polymer MW between 500 and 5000 daltons with SEC. For instance, Chance, *et al* (1995) [3] say that SEC for very low molecular weight suffers from intrinsic viscosities becoming negative for certain polymers due to packing effects. Also, how are the pores going to distinguish small polymers? Modern light scattering detectors, Podzimek (2014) [4], can effectively characterize polymers down to a several hundred daltons. Jennings (2012) [5] published an equation for bubble nucleation in polymer solutions that fairly well agrees with Jennings/Middleman data (1985) [6] and is a new way to measure polymer MW from polystyrene (PS) dimer up to about 5000 daltons. Jennings/Middleman used cyclohexane as the solvent and in this paper, it is easy to show how their equation can estimate low molecular weight polymers and details of the derivation will be shared.

Introduction

Here, the author is discussing his way of measuring low molecular weight polymer. SEC is a way to measure high polymer but fails when applied to low molecular weight polymer. One good way to characterize low MW polymer is light scattering and this is described in Podzimek. Jennings (2012) published his theory for measuring the limit of superheat of polymer solutions and this is outlined in the Results section.

Results

$$\partial T / \partial w_2 = (MW_1/MW_2)(3kT_l^2 / \sigma_1 a) \qquad (18)$$

Eq. (18) is from my June 4, 2012 paper in International Journal of Thermodynamics (ISTANBUL, Turkey). Look at Fig 2 from the Macromolecules paper at the end to see the slopes for 2000 and 4000 MW. The slopes are $\partial T / \partial w_2$, so you solve it this way. I can propose that this equation is a fairly accurate way of measuring molecular weight from 500 to 5000 daltons. Water (H2O) is 18 daltons.

$$MW_2 = (MW_1)(3kT_l^2 / \sigma_1 a) / (\partial T / \partial w_2) \qquad (18) \text{ solved for } MW_2$$

MW2   desired quantity = molecular weight of polmer
MW1   molecular weight of solvent
K   Boltzmann constant
T   temperature of polymer solution
Tl   limit of superheat of solvent
σ1   surface tension of solvent at Tl
a   surface area of solvent molecule at Tl
w2   weight fraction polymer
r   degree of polymerization

In my experiment, cyclohexane was the solvent and the polymer was polystyrene. Second to the end, is the image of the apparatus used to measure the limit of superheat. Jennings/Middleman did not use Argon and the spacing of the Nichrome wire was closer and closer toward the top of the column to allow for a gradient in temperature: Holden/Katz (1978) [7] is the source for the apparatus image.

Discussion
In the original theory article by Jennings (2012) [5], he was thorough in taking dlnA/dK in both the w direction and T direction, which are orthogonal. In the w direction, it was simple, but for the T direction there obtained a lengthy expression that gave the same result, about – 0.2%. Here from International Journal of Thermodynamics are the two results.

$$\lim w2 \to 0 \; (\partial \ln A / \partial w2)/(\partial K / \partial w2) = 1/(6K) = -0.24\% \quad \text{(A)}$$

$$\lim T \to Tl \; (\partial \ln A / \partial T)/(\partial K / \partial T) = \text{complicated expression} = -0.19\% \quad \text{(B)}$$

The reason (A) and (B) do not agree exactly has got to be in the estimate for the surface tension.

For the nucleation rate in polymer solutions, the surface tension has the most influence. The details of the calculation for Eq. (18) above are all laid out in Jennings (2012) [5].

Eq. (18) had its beginning in 2012 and it wasn't until Jennings (2023) [8] that it was proved for dimer (r = 2) up to high polymer (r = infinity). Here we announce that using the rising drop method, it should be possible to measure low molecular weight polymer inexpensively. Notice that the limit of superheat rise for 2000 MW and 4000 MW is of the order of 10 to 15 degrees Centigrade allowing for a rather exact estimate of MW2. The data for bubble nucleation in polymer solutions first appeared in Jennings/Middleman and they have the definitive solution to the problem.

Conclusions
Theoretical work by Blander/Katz (1975) [9] and Siow/Patterson (1973) [10] were combined in Jennings (2012) [5] to produce Eq. (18) above. In this paper, the author reveals the rationale for using Eq. (18) to measure low molecular wight polymer and it is a general equation.

Acknowedgments

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9. Blander M, Katz JL. Bubble Nucleation in Liquids AIChE J. 1975; 21:833-848.
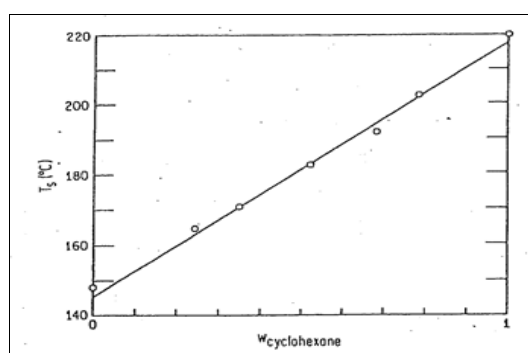10. Siow KS, Patterson D. Surface Thermodynamics of Polymer Solutions J. Phys. Chem. 1973; 77:356-365.

Fig 1: Data on limiting superheat for binary solution of cyclohexane and pentane. Composition is mass fraction
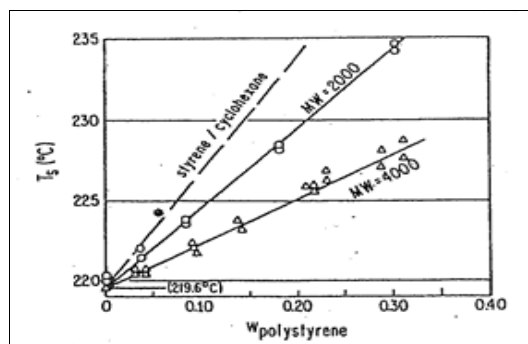

Fig 2: Data on limiting superheat for low molecular weight polystyrene in cyclohexane. T_s for pure cyclohexane is taken as 219.6 ^{0}C
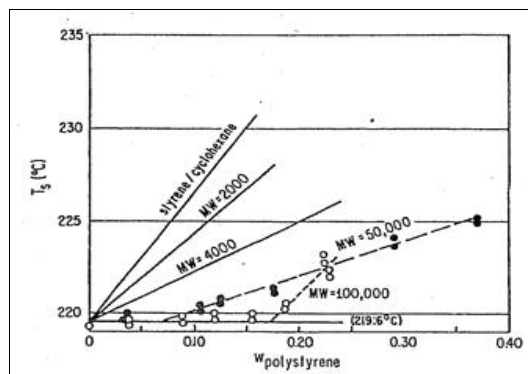

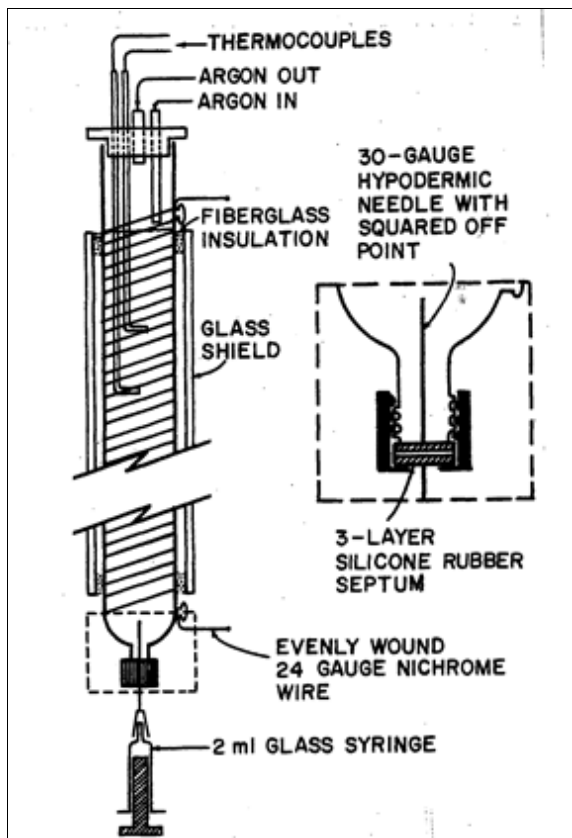**Fig 3:** Data on limiting superheat for high molecular weight polystyrene in cyclohexane

Fig 4: Low gradient rising droplet column and detail