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Establishment of the Flory-Fox Equation and Corroboration of the Fox Equation for Poly(2-vinylpyridine) (P2VP) Using Differential Scanning Calorimetry (DSC)

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Abstract Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the electrical power needed to maintain an equivalent temperature between the sample and reference is recorded as a function of temperature. One particular use of DSC is to measure glass transition temperatures (Tg), or the temperature at which an amorphous polymer changes from a hard, glassy state to a soft, rubbery one. As the molecular weight (MW) of an amorphous polymer increases, its glass transition temperature also increases, but ultimately levels off at a maximum value labeled Tg_∞. Poly (2-vinyl pyridine) (P2VP) is a versatile polymer, often copolymerized with styrene and butadiene to provide adhesion between the fabric and rubber of vehicle tires. DSC was used to evaluate the Tg of several samples of P2VP spanning a wide range of MW. These Tg were plotted as a function of reciprocal number average molecular weight (Mn), producing a Flory-Fox equation of $Tg = 112°C – 1.5e+5°C·g·mol^{-1}Mn^{-1}$ ($r^2 > 0.99$). The Tg resulting from prepared binary mixtures of different molecular weight P2VP were also studied in this experiment. Predicted values of the resulting glass transition temperatures were calculated utilizing the Fox equation: $Tg^{-1} = w_1Tg_1^{-1} + w_2Tg_2^{-1}$ where w represents the weight percent of each molecular weight P2VP component. Resulting Tg were fitted with exponential trendlines ($r^2 > 0.97$) and aligned closely to the Tg predicted by the Fox equation.

Keywords: *Poly(2-vinylpyridine) (P2VP), Flory-Fox equation, Fox equation, glass transition temperature (Tg), differential scanning calorimetry (DSC), polydispersity index (PDI)*

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1. Introduction

Poly (vinyl pyridine) (PVP) polymers are a family of amorphous polymers employed in a wide range of applications due to their adhesive, anti-corrosive, catalytic, remediating, and even antibacterial properties [1,2,3,4,5] [6,7,8,9,10]. Fréchet and de Meftahi attribute this large number of specialty applications to the significant polarity and ligating ability of PVP polymers, brought about by the nitrogen atom of the pendant pyridyl rings [11]. The positioning of this nitrogen atom dictates the magnitude and direction of the dipole moment, as well as strength of the ligating ability for the PVP polymer [11,12,13]. For instance, in poly(4-vinylpyridine) (P4VP) the nitrogen atom is situated *para-* to the polymer backbone, readily accessible for ligating metal ions, hosting organic guest molecules, hydrogen bonding, and protonation [13,14]. However, in isomer poly(2-vinylpyridine) (P2VP), the polymer of interest within this study, the nitrogen atom is situated in the *ortho-* position, hindering coordination to metal ions and binding of organic guest molecules due to steric repulsion with the polymer backbone, but still allowing for specific hydrogen bonding and facile protonation [13]. It is for this reason that P4VP is commonly preferred over its sterically hindered isomer P2VP in the majority of applications listed above. It is speculated that the *meta-* isomer poly (3-vinyl pyridine) (P3VP) is not as prevalent due to a high monomer cost [13].

While P2VP is the most sterically hindered PVP isomer, it remains a versatile polymer with significant applications in the textile and automotive industries [15]. Most notably, P2VP monomer 2-vinylpyrdine (2-VP) is copolymerized with styrene and butadiene to form vinylpyridine latex, a terpolymer which provides the adhesion between the fabric and rubber of vehicle tires, belts, hoses, and conveyor systems [15]. Glass transition temperature (T_g) is perhaps the most important thermophysical parameter for polymers and amorphous materials [16], with the Flory-Fox equation relating T_g to the number-average molecular weight (M_n) of the amorphous polymer [17,18,19]. The equation involves empirical values $T_{g\infty}$, or the theoretical glass transition temperature at infinite molecular weight, and constant K, which are characteristic to the amorphous polymer [17,18,19]. Given the prevalence of PVP polymer P4VP over its more sterically hindered isomer P2VP and the importance of T_g, this study sought to report on Flory-Fox parameters $T_{g\infty}$ and K for P2VP as established by thermoanalytical technique differential scanning calorimetry (DSC). Additionally, as well prepare homogeneous blends to corroborate the Fox equation. Figure 1 displays the structure of P2VP, where *n* denotes the number of repeat units.

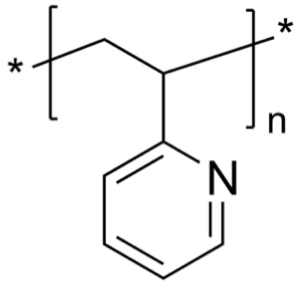

Figure 1. Structure of poly(2-vinylpyridine) (P2VP) repeat unit

1.1. Flory-Fox Equation Background

As previously stated, the Flory-Fox equation describes the relationship between the molecular weight and the glass transition temperature *Tg* of an amorphous polymer, where *Tg* is the temperature at which an amorphous polymer changes from a hard, glassy state to a soft, rubbery one [17,18,19]. As the M_n of an amorphous polymer increases, its glass transition temperature also increases, but ultimately levels off at a maximum value labeled Tg_∞. All *Tg* are characterized by thermal expansion and a sudden change in heat capacity Cp, the latter of which can be measured by differential scanning calorimetry (DSC) [20]. With this being said, this experiment sought to evaluate the *Tg* for several samples of P2VP spanning a wide range of M_n, to establish the Flory-Fox equation and associated Flory-Fox parameters Tg_∞ and *K*. For linear polymers, the Tg value is an increasing function of the M_n, such that Tg varies linearly with the reciprocal number average molecular weight M_n. This dependence is a result of the contribution of chain-end segments in molecular motion. As the number of chain-ends increases the free volume increases due to increasing molecular motion, and therefore the Tg decreases. This relationship is expressed in the following Flory-Fox empirical equation (1):

$$Tg = Tg_\infty - \frac{K}{M_n} \tag{1}$$

$T_{g\infty}$ is the glass transition temperature of an infinite molecular weight

Mn is the number-average molecular weight as g/mol

K is a constant given by eq. (2), with units of ^{o}C mol/g

$$K = 2V_c \rho N_A \frac{1}{\alpha} \tag{2}$$

Where

V_c = the free volume contributed by chain ends in cm^3

ρ = polymer density in g/cm^3

N_A = Avogadro number 6.023 x 10^{23} molecules/mole

α = thermal expansion coefficient per ^{o}C

We have previously studied and established the Flory-Fox equations for polystyrene (PS) and poly(methyl methacrylate) (PMMA) [21,22].

The Fox equation can be used to predict the Tg for miscible blends of polymers. This is shown by equation (3) where *w* represents the weight percent of each of the components. The Fox equation leads to a lower value than would be given by a simple linear rule of mixtures and reflects the effective higher free volume or randomness due to the presence of two components within a mixture. Systems which obey the Fox equation are considered to display intimate and uniform mixing while those that deviate from it, especially those that display two Tg are considered to be poorly mixed. However, when dealing with a binary system, the Fox equation reduces to equation (4).

$$\frac{1}{Tg} = \sum_{i=1}^{n} \frac{w_i}{Tg_i} \tag{3}$$

$$\frac{1}{Tg} = \frac{w_1}{Tg_1} + \frac{w_2}{Tg_2} \tag{4}$$

P2VP has been previously studied extensively with respect to glass transition temperatures and physical and chemical properties [23,24,25,26,27,28]. P2VP is a solid white thermoplastic substance (material) existing as an atactic non-crystalline linear homopolymer that is in a glass-like state at room temperature. The glass formation is due to the lack of structural regularity in the P2VP. Below its glass transition temperature, P2VP exhibits as a hard and stiff, yet brittle state and has frozen glass-like properties at room temperature. It has moderate to high dipole-dipole intermolecular forces and is a vitreous low mechanical strength material.

For linear polymers, the T_g value is an increasing function of the molar mass, such that T_g varies linearly with the reciprocal of the number average molecular weight (Mn). This dependance is a result of the contribution of chain-end segments in molecular motion. As the number of chain-ends increases, the T_g decreases due to the increase of free volume.

2. Materials and Methods

2.1. Experimental Materials

The eleven P2VP samples used to establish the Flory-Fox equation were obtained from Scientific Polymer Products and used without further purification. The weight average molecular weight M_w, number average molecular weight M_n, and polydispersity indices (PDI) for the samples are displayed in Table 1 below. All P2VP samples possessed low PDI indicating narrow molecular weight distributions, which are critical for physical polymer characterization [29]. The combinations of P2VP utilized to prepare the blends were selected from those listed in Table 1, and the methanol used to dissolve the P2VP was reagent grade methanol purchased from VWR.

Table 1. Molecular Weight Distribution Data for P2VP

Mw (g/mol)	*Mn* (g/mol)	PDI (*Mw/Mn*)
2,140	2,070	1.03
3,030	2,970	1.02
4,050	4,010	1.01
9,100	8,700	1.05
38,600	38,500	1.00
219,000	197,000	1.11
404,000	369,000	1.09
514,000	475,000	1.08
650,000	600,000	1.08
944,000	866,000	1.09
1,220,000	1,110,000	1.10

2.2. Experimental Methods

2.2.1. Individual P2VP Sample Preparation

The samples used to establish the Flory-Fox equation were prepared by packing approximately fifteen milligrams of select molecular weight P2VP into a DSC standard aluminum pan. The lids to the standard pans were placed on top of the sample and left unpressed.

2.2.2. P2VP Blend Sample Preparation

In order to prepare the P2VP blends, a solvent blend technique was developed and adopted. Combinations of different molecular weight P2VP with sufficiently large differences in glass transition temperatures were first identified. Each molecular weight P2VP sample was weighed on a Mettler Toledo single pan balance having a precision of four significant figures after the decimal place, in proportions defined in Table 3, Table 4, and Table 5. The samples were added to 3 mL glass vials and 200 µL of methanol was added for dissolution. After complete dissolution, the vials containing the polymer solutions were vortexed to ensure homogeneity. A Pasteur pipet was used to aliquot the dissolved P2VP blends directly into a DSC standard aluminum pan atop a hot plate maintained at 160-180°C. The hot plate acted to drive off the methanol which if ignored, would have acted as a plasticizer, producing inaccurate, decreased Tg values. This step was repeated until a desirable amount of P2VP blend (15-20 mg) had accumulated within the DSC standard pan. Additionally, it is important to note that this step was performed under a fume hood as methanol and its vapors are highly toxic and flammable. As with the individual P2VP samples, the lids to the standard pans were placed on top of the sample and left unpressed.

2.2.3. Differential Scanning Calorimetry (DSC)

A power compensated Perkin Elmer Pyris 1 Differential Scanning Calorimeter was used to record glass transition temperature data for both the individual and blend P2VP samples. The DSC was used in its high temperature mode for the blend P2VP samples and individual P2VP samples of molecular weights greater than 5,000 g mol^{-1}. However, for P2VP samples with molecular weight less than 5,000 g mol^{-1} the DSC was used in conjunction with its Intracooler 1P DSC accessory. All P2VP samples were analyzed under dry nitrogen gas flowing at 20 cm^3 min^{-1} to prevent absorption of moisture or oxidative degradation of the sample. Prior to P2VP sample analysis, an indium standard was used to calibrate the temperature and enthalpy measurements of the DSC. The indium standard underwent two heating and two cooling cycles at a constant rate of 10°C min^{-1} in order to erase any thermal history in the standard. The onset melting temperature and enthalpy measurements for the second heating cycle were used to calibrate the DSC. Once calibrated, the P2VP samples were analyzed under the same specified conditions: two heating and two cooling cycles under dry nitrogen gas flowing at 20 cm^3 min^{-1} and a scanning rate of 10°C min^{-1}. The DSC was programmed to analyze each P2VP sample from 30 to 130°C, a temperature range containing the Tg of the lowest and highest molecular weight samples. The “Tg” option of the Perkin-Elmer *Pyris* thermal analysis software was used to determine the onset, half-Cp, and end Tg values for the second heating cycle of each of the P2VP samples.

2.3. Hazards

According to its safety data sheet, P2VP causes skin irritation, serious eye irritation, and may cause respiratory irritation. It is imperative to avoid breathing P2VP dust or vapors, including those released when handling the sample in powdered or granular form. Safety glasses, gloves, and a fume hood are necessary when handling P2VP in order to avoid exposure to the skin and eyes, as well as inhalation.

Methanol is highly flammable in its liquid and vapor forms and poses severe toxicity if swallowed, inhaled, or if in contact with skin. It also bears specific target organ toxicity following single exposure, category 1. With this being said, methanol must be handled with safety glasses, gloves, and within the confines of an operating fume hood.

3. Results and Discussion

3.1. Establishment of the Flory-Fox Equation

The Flory-Fox equation for P2VP was established by measuring onset Tg of eleven P2VP samples spanning a wide range of Mn. Figure 2 overlays glass transitions in the DSC thermograms of six selected P2VP samples: 3,030; 4,050; 9,100; 38,600; 404,000; and 944,000 g mol^{-1}. It is important to note that the heat flow (y-axis) for each of the thermograms do not represent those as measured by DSC. Each thermogram was translated arbitrarily along the y-axis to produce a figure where several thermograms could be displayed within a single frame. However, the thermograms were deliberately *not* translated along the x-axis in order to keep glass transition data consistent with that of Table 2. Figure 2 clearly demonstrates how Tg originally increases with Molecular weight, but ultimately levels off at a maximum value labeled Tg_∞. This phenomenon is most visible across Mw of 3,030; 404,000; and 944,000 g mol^{-1}, where when Mw is increased by approximately 400,000 g mol^{-1} between 3,030 and 404,000 g mol^{-1}, *Tg* increases significantly, but when *Mw* increased by over 500,000 g mol^{-1} between 404,000 and 944,000 g mol^{-1}, *Tg* is observed not to increase at all.

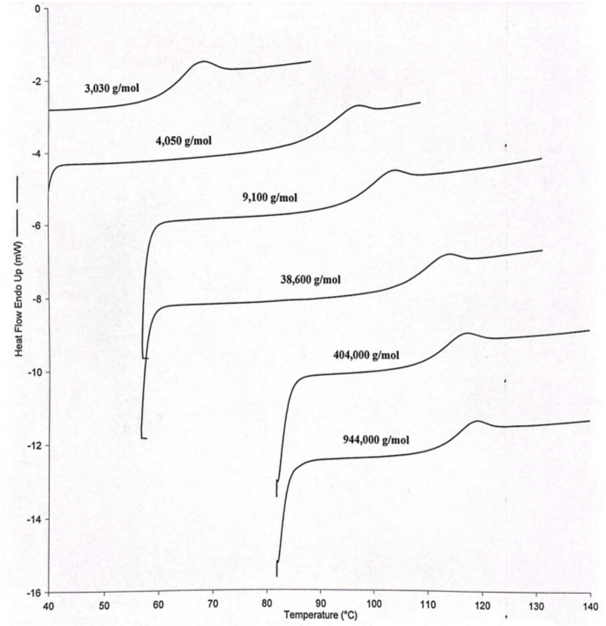

Figure 2. DSC Thermograms for Selected Molecular Weight P2VP

Table 2 summarizes the onset, half-Cp, and end *Tg* data for the eleven *Mw* samples P2VP samples listed in Table 1.

Table 2. *Tg* for P2VP Samples of Various Molecular Weights

Mw (g/mol)	Onset *Tg* (°C)	Half-Cp *Tg* (°C)	End *Tg* (°C)
2,140	42.95	45.93	49.71
3,030	61.22	62.84	65.09
4,050	73.11	76.94	80.11
9,100	96.14	97.96	100.25
38,600	105.52	107.99	110.72
219,000	110.86	112.79	115.02
404,000	110.21	111.86	114.06
514,000	111.79	113.83	116.45
650,000	112.37	113.87	115.94
944,000	112.41	114.27	116.63
1,220,000	113.31	115.26	117.57

Figure 3 is the graphical representation of the onset *Tg* data plotted against *Mw* and set to a logarithmic scale. It represents the typical Flory-Fox plot in which *Tg* first increases linearly with *Mw*, but eventually levels off at a maximum value labeled Tg_∞ regardless of *Mw*. With this being said, the *Tg* of Figure 3 are consistent with those ascertained from the DSC thermograms of Figure 2.

The Flory-Fox equation given by equation (1) can be rearranged so that the Flory-Fox parameters Tg_∞ and *K* can be determined graphically. This rearrangement is shown below where equation (3) resembles the equation of straight line. With this being said, the slope of a plot examining onset *Tg* versus reciprocal molecular weight Mw^{-1}, represents *K* for the particular polymer, while the y-intercept of the same plot denotes Tg_∞.

Figure 4 presents onset *Tg* as a function of reciprocal molecular weight Mw^{-1} ($r^2 > 0.99$).

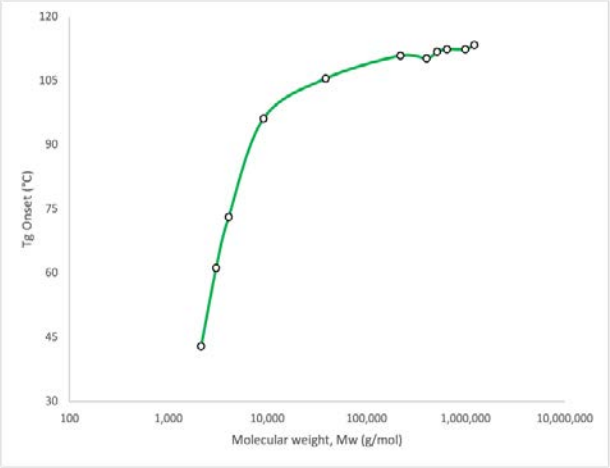

Figure 3. Flory-Fox Plot of Onset *Tg* vs. Molecular Weight *Mw*

$$Tg = Tg_\infty - \frac{K}{Mw} \tag{5}$$

$$Tg = -\frac{K}{Mw} + Tg_\infty$$

$$Tg = -K\frac{1}{Mw} + Tg_\infty \tag{6}$$

$$y = mx + b$$

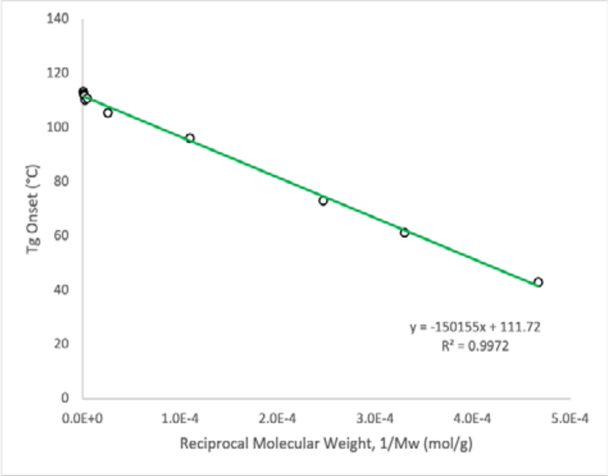

Figure 4. Linear Plot of Tg vs. Reciprocal Molecular Weight, Mw^{-1}

According to Figure 4 the value of K for P2VP was experimentally determined to be 1.5 x 10^5 °C g mol^{-1}, while the value of Tg_∞ was extrapolated at 111.72°C. The literature value for the Tg for P2VP is 104°C [30]. Although experimentally determined K values for P2VP have not been found to the best of our efforts. However, a Flory-Fox plot for P2VP has been shown in reference [31].

3.2. Corroboration of the Fox Equation

Tables 3 through 5 contain the onset *Tg* data for three sets of P2VP blends: 4,050 and 38,600 g mol^{-1}; 3,030 and 219,000 g mol^{-1}; and 3,030 and 9,100 g mol^{-1}. Each of the tables also display onset glass transition temperatures as calculated by the Fox Equation.

Resulting Tg were fitted with exponential trendlines ($r^2 > 0.97$) and aligned closely to the Tg predicted by the Fox equation. Figure 5, Figure 6, and Figure 7 display the measured onset glass transition temperatures and Fox equation predicted Tg values for each of the P2VP blends.

Table 3. Onset *Tg* for 4,050 & 38,600 g mol^{-1} P2VP Blends

Weight Percent Composition		Onset *Tg* (°C)	
4,050 g mol^{-1}	38,600 g mol^{-1}	Measured	Calculated
0	100	102.92	—
20.29	79.71	99.47	98.23
39.68	60.32	95.08	94.14
60.49	39.51	89.82	90.11
79.69	20.31	86.19	86.68
100	0	83.33	—

Table 4. Onset *Tg* for 3,030 & 219,000 g mol^{-1} P2VP Blends

Weight Percent Composition		Onset *Tg* (°C)	
3,030 g mol^{-1}	219,000 g mol^{-1}	Measured	Calculated
0	100	109.41	—
19.88	80.12	101.30	99.81
40.00	60.00	95.74	91.66
59.82	40.18	86.28	84.84
79.76	20.24	78.63	78.93
100	0	73.72	—

Table 5. Onset *Tg* for 3,030 & 9,100 g mol^{-1} P2VP Blends

Weight Percent Composition		Onset *Tg* (°C)	
3,030 g mol^{-1}	9,100 g mol^{-1}	Measured	Calculated
0	100	90.81	—
20.11	79.89	86.57	86.77
40.32	59.68	84.49	83.05
59.82	40.18	79.73	79.75
79.80	20.20	76.66	76.64
100	0	73.72	—

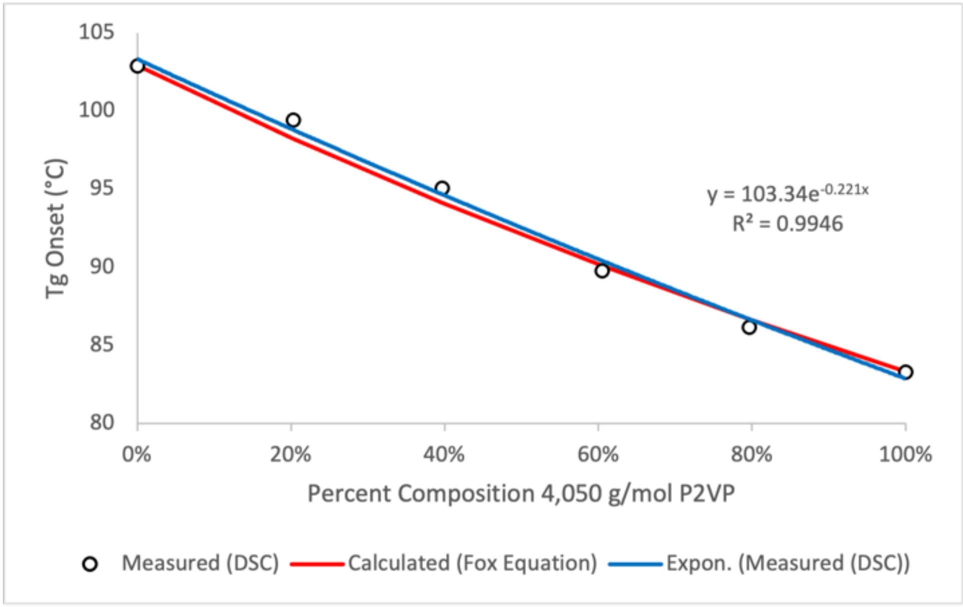

Figure 5. Onset *Tg* for 4,050 & 38,600 g mol^{-1} P2VP Blends

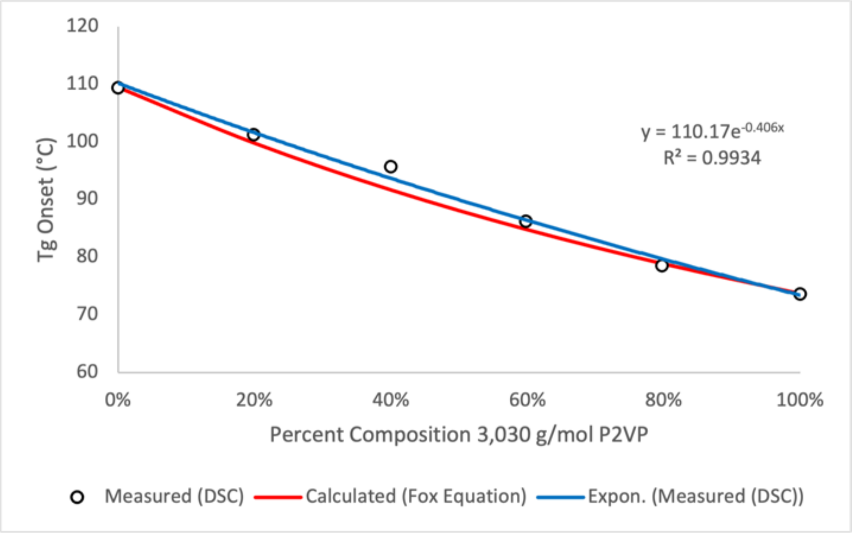

Figure 6. Onset *Tg* for 3,030 & 219,000 g mol^{-1} P2VP Blends

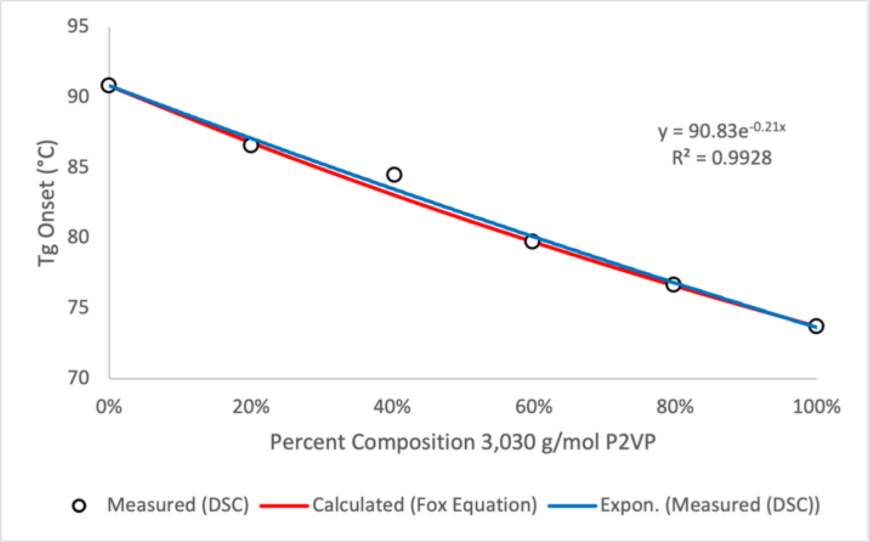

Figure 7. Onset *Tg* for 3,030 & 9,100 g mol^{-1} P2VP Blends

The agreement between onset T_g as measured by DSC and as calculated by the Fox equation demonstrates that the Fox equation can be applied to binary blends of P2VP. The agreement also supports the effectiveness of the solvent blend technique to create perfectly homogeneous blends.

4. Conclusions

The experiment corroborates the Flory-Fox equation for P2VP which relates molecular weight to glass transition temperature. As molecular weight increased, glass transition temperature increased until a certain molecular weight after which the glass transition temperature leveled off. There is a strong, linear correlation between the gravimetric compositions and the glass transition temperatures found using DSC. The experiment serves as an excellent tool for the undergraduate polymer chemistry laboratory as the methodology can be readily adopted for similar experiments with different polymers

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Statement of Competing Interest

The authors declare no competing interests.

List of Abbreviations and Symbols

DSC = differential scanning calorimetry
Mn = number average molecular weight
Mw = weight average molecular weight
P2VP = poly(2-vinylpyridine)
P3VP = poly(3-vinylpyridine)
P4VP = poly(4-vinylpyridine)
PDI = polydispersity index
PVP = poly(vinyl pyridine)
Tg = glass transition temperature

Tg_{∞} = glass transition temperature at infinite molecular weight
$Wt_{1\ 0r\ 2}$ = weight fraction
K -Flory-Fox Constant (^{o}Cg/mol)
V_f - Free Volume
ρ = density
N_a = Avogadro's number
α = coefficient of thermal expansion
mW = milliWatts

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