Journal of Polymer and Biopolymer Physics Chemistry, 2023, Vol. 11, No. 1, 1-10
Available online at http://pubs.sciepub.com/jpbpc/11/1/1
Published by Science and Education Publishing
DOI:10.12691/jpbpc-11-1-1

Establishment of the Flory-Fox Equation for Polymethyl Methacrylate (PMMA) Using Differential Scanning Calorimetry (DSC) and Determination of Tacticity Using Quantitative Proton Nuclear Magnetic Resonance Spectroscopy (qHNMR)

Ronald P. D’Amelia*, Evan H. Kreth

Chemistry Department, Hofstra University, Hempstead, NY, USA
*Corresponding author: Ronald P. D’Amelia, *ronald.p.damelia@hofstra.edu*

Received May 30, 2023; Revised June 30, 2023; Accepted July 11, 2023

Abstract Glass transition temperature (Tg), termed the “melting point of amorphous materials” is the temperature at which an amorphous material changes from a hard, glassy state to a soft, rubbery one. As the number average molecular weight (Mn) of the amorphous material increases, its glass transition temperature also increases, but ultimately levels off at a maximum value labeled Tg_{∞}. Differential scanning calorimetry (DSC) was utilized to evaluate Tg for seventeen samples of polymethyl methacrylate (PMMA) whose Mn values ranged from three thousand to one and a half million. These values were then plotted against reciprocal Mn, producing a Flory-Fox equation of Tg = 135°C – 1.4 x 10^5 °C□g□mol^{-1}/Mn, with a correlation coefficient of 0.98. The Tg of binary mixtures of PMMA of different Mn values were also examined in this experiment. Tg values were calculated using the Fox equation: $1/Tg = w_1/Tg_1 + w_2/Tg_2$ where w represents the weight percent of each PMMA sample. Correlation coefficients of 0.96 and 0.97 were achieved for the graphs plotting Tg against weight percent of the lower Mn value PMMA. Lastly, quantitative proton nuclear magnetic resonance spectroscopy (qHNMR) was utilized to determine the relative tacticity of binary mixtures of isotactic and syndiotactic PMMA. It was determined that the peak integrations for the methylene or methyl hydrogens, at their respective chemical shifts for each PMMA, could be used to determine relative tacticity. These experiments demonstrate the quantitative applications of DSC and NMR, as well as their suitability within the undergraduate chemistry laboratory.

Keywords: *Polymethyl Methacrylate (PMMA), Flory-Fox equation, glass transition temperature (Tg), differential scanning calorimetry (DSC), tacticity, quantitative proton nuclear magnetic resonance spectroscopy (qHNMR)*

Cite This Article: Ronald P. D’Amelia and Evan H. Kreth, “Establishment of the Flory-Fox Equation for Polymethyl Methacrylate (PMMA) Using Differential Scanning Calorimetry (DSC) and Determination of Tacticity Using Quantitative Proton Nuclear Magnetic Resonance Spectroscopy (qHNMR).” *Journal of Polymer and Biopolymer Physics Chemistry*, vol. 11, no. 1(2023): 1-10. doi: 10.12691/jpbpc-11-1-1.

1. Introduction

Polymethyl methacrylate (PMMA), best recognized by its trade names of Lucite, Plexiglass or Perspex, is a synthetic thermoplastic polymer with transparent, rigid, lightweight, and shatterproof properties and belongs to a class of materials called as an engineering plastic [1]. These properties are responsible for the numerous commercial and medical uses of PMMA, ranging from aquarium and hockey rink walls to bone cement and artificial teeth [2,3]. During World War II PMMA was used for many military applications such as submarine periscopes, aircraft windows, bubble canopies for gun turrets and is currently used as rear and front lights and instrument cluster for vehicles, appliances, and lenses for eyeglasses [4]. PMMA can be synthesized by emulsion, solution, or bulk polymerization from methyl methacrylate monomer. Generally, radical initiation is used including living polymerization methods however anionic polymerization can also be performed [5,6]. The structure of PMMA contains methyl and ester functional groups off alternating repeat units. Figure 1 displays an individual PMMA monomer, where *n* represents the number of monomers, or repeating units, in the polymer [7].

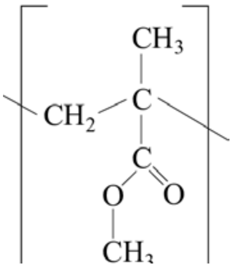

Figure 1. Structure of PMMA Monomer

Glass transition temperature (*Tg*), termed the "melting point of amorphous materials" is the temperature at which an amorphous polymer changes from a hard, glassy state to a soft, rubbery one. As the number-average molecular weight (*Mn*) of the amorphous polymer increases, its Tg also increases but ultimately levels off at a maximum value labeled Tg_{∞}. The Flory-Fox equation relates these parameters for linear amorphous polymers and is given by the equation below.

$$T_g = T_{g\infty} - \frac{K}{M_n} \quad (1)$$

Differential Scanning Calorimetry (DSC) can be used to evaluate when glass transition temperatures occur by measuring changes in heat capacity and thermal expansion [8-10].

2. Background – Glass Transition (Tg) Perspective [11-16]

A solid polymer can be differentiated into the amorphous and semi-crystalline categories. Amorphous solid polymers are either in the glassy state, or in the soft and rubbery or fluid state. The glassy state of a polymer can be described as a state in which cooperative chain motion of the macromolecules are frozen, such that only limited local motion can take place, such as side-group rotational/vibrational motion. These motions exist due to bond angle deformation and bond stretching within the molecules. The typical model of a macromolecule in the amorphous state is the "random coil", however, the amorphous state is better depicted by an irregularly folded chain molecule rather than a completely idealized random coil.

2.1. Glass Transition and Glass Transition Temperature

One of the most important properties of both amorphous and semi-crystalline polymers is their thermal behavior. Understanding this behavior is not only critical for the selection of proper processing and manufacturing conditions, but also for the full understanding of the polymeric physical and mechanical properties.

The most prevalent transition in amorphous polymers, is usually labelled the glass or vitreous transition, in which the linear or volume coefficient of thermal expansion increases. In contrast, in semi-crystalline polymers, the glass transition usually occurs below the melting temperature. The exact description of the molecular motion responsible for the glass transition is undefined, however, it is generally thought to involve macromolecular random chain bond movement, such as groups or segments of the polymer macromolecular relaxing, vibrating or reptating (crawling). Above the T_g, the chain segments can undergo cooperative rotational, vibrational, translational, and diffusional motion. The importance of the glass transition in polymer science was stated by Eisenberg: "The glass transition is perhaps the most important single parameter that determines the application of many non-crystalline polymers now available" [17].

The temperature-dependent properties of amorphous polymers undergo major changes at the glass transition temperature (Tg). The simplest of many definitions of the glass transition temperature (Tg) is the temperature below which the amorphous polymer is glassy, and above which is soft and rubbery. The molecular interpretation of Tg is the temperature of the onset of large-scale motion of molecular chain segments. Below the Tg, the polymer chains' atoms undergo little rotational-vibrational motions or are in a frozen bulk solid state.

The glass transition temperature can be measured in a variety of ways, not all of which yield the same value. The results from the kinetic and thermodynamic nature of the glass transition differ, and the Tg is dependent upon the thermal history of the polymer and the heating/cooling rate of the experiment.

2.2. Theories for Glass Transition (Glassy -to-Rubbery [18]

Many theories regarding the glass transition have been previously developed. They include: the iso-free volume theory by Flory-Fox [19-21], a modified mechanical-free volume phenomenological theory that was explored by the Williams-Landel-Ferry (WLF) equation [22], a modified Free volume Relaxation-Kinetic theory that includes Lattice-Hole/Voids developed by Hirai-Eyring [23], and finally, the Gibbs-DiMarzio thermodynamic theory [24,25] which suggests that the transition is a true second order thermodynamic transition representing an equilibrium between the glass and rubbery state in which the conformational/configurational entropy at equilibrium is zero.

2.3. Free Volume Theory of Glass Transition

The Flory-Fox iso-free volume theory postulates that the glass transition occurs when the free or unoccupied volume in the macromolecule reaches a constant value and does not decrease further as the polymer is cooled below or at the Tg. The fractional value of the total volume is often taken as 0.025, which is so small that segmental jumps become impossible below the Tg [19-21].

The free volume (V_f) of the liquid is defined by $V_f = V_T - V_o$, where V_T is the total volume of the liquid at temperature T and V_o is the theoretical molar volume or occupied volume. The total volume is the sum of the free volume (V_f) and of the occupied volume (V_o). The occupied volume (V_o) includes the van der Waals radii plus the fluctuation volume which is related to the thermal vibrational and rotational motion of the molecule. Thus, the Tg can be viewed as accessing by segmental jumps of the macromolecular chain segments into vacant spaces not occupied by the polymer. The higher the free volume the more easily the jumps can occur and the lower the viscosity or more increase of fluidity.

The glass transition temperature Tg, as explained by the free volume theory, is the temperature at which the free volume V_f reaches a constant value [19-21].

For linear amorphous polymers, the Tg value is an increasing function of the molar mass, such that Tg varies linearly with the reciprocal of the number average molecular weight (M_n). This dependance 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 temperature decreases. This relationship is expressed in the following Flory-Fox empirical equation [19-21]:

$$T_g = T_{g\infty} - \frac{K}{M_n} \qquad (2)$$

where

Tg_∞ = Tg for a given polymer at infinite molecular weight

Mn = number-average molecular weight with units of g/mol

K = a constant with units of °Cg/mol

$$K = 2V_c \rho N_A \alpha^{-1} \qquad (3)$$

where

V_c = the free volume contributed by chain ends, expressed in units of cm^3

ρ = the density of the polymer in g/cm^3

N_A = Avogadro's number (6.023×10^{23} molecules/mole)

α = coefficient of thermal expansion, with units of $°C^{-1}$

2.4. Summary of the Chemical Factors affecting Tg

Molecular weight for linear homopolymers: an increase in molar mass (molecular weight) leads to a decrease in chain end concentrations resulting in a decrease of free volume at the end group region and thus an increase in the glass transition temperature, but ultimately levels off at a maximum value, Tg_∞. Addition of diluents or plasticizers increase free volume thus decrease Tg.

Molecular structure: an insertion of bulky or rigid inflexible side groups, such as a phenyl group, will increase the glass transition temperature T_g due to the decrease in mobility/flexibility. Whereas introducing flexible side chains like acetate groups decrease Tg.

Chemical cross-linking: an increase in cross linking density decreases mobility, leading to a decrease in free volume and thus an increase in the glass transition temperature T_g. Increasing branching increase free volume thus decrease Tg.

Cohesive Energy Density: as a measure of polarity, the presence of polar groups increases the dipole-dipole intermolecular forces which increase interchain attraction and cohesion, making it more difficult for molecular permeation, thus leading to a decrease in free volume resulting in an increase in Tg.

Tacticity: an increase in isotacticity decreases Tg, whereas an increase in syndiotacticity increase Tg. Generally, syndiotactic polymers have greater Tg values than isotactic polymers of the same polymer type. Atactic polymers have Tg somewhere in the middle range.

2.5. The Determination of Tg

Experimental methods of measuring the glass transition (T_g) are based on the physical properties of the polymers converted from the glassy state to the soft rubbery state. Three overall methods have been used:

1. Experiments defined by equilibrium thermodynamics or the Steady-State method, in which the physical properties are measured under static isothermal equilibrium conditions over a temperature range including T_g. Examples include dilatometry, penetrometry, refractometry, calorimetry-specific heat such as DSC or thermal analysis.

2. Experiments defined by dynamic or transport properties or the Dynamic Method, in which the physical polymer properties are measured during the heating of the polymer above T_g, in these methods T_g is measured by extrapolation to obtain isothermal conditions. Examples include: Infrared spectroscopy, NMR, stress birefringence, dielectric loss, stress relaxation, dynamic mechanical properties.

3. Tests related to end-use properties examples include: impact resistance, softening point, and hardness measurement.

2.6. Glass Transition of Polymethyl Methacrylate

One polymer that has been previously studied extensively with respect to glass transition temperatures and physical and chemical properties is polymethyl methacrylate [26-33]. PMMA is a solid white thermoplastic substance (material) existing as a 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 PMMA molecules. Below its glass transition temperature, PMMA exists 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.

3. Background Perspective: Polymer Tacticity [34-44]

For many polymers, including PMMA, can be synthesized so that linear macromolecules have configurational order or stereoregularity [35]. This configurational order in the polymeric backbone of the macromolecule is referred to as tacticity. The definition of polymer tacticity is properly given in a review article by Jenkins which reads as "The orderliness of the succession of configurational repeating monomer units in the main chain of a regular linear homopolymer macromolecule" [36,37]. Tacticity should not be confused with conformational states of the polymer chains in space [38]. Example of different conformations include planar zig-zag. helical, random coils etc. By contrast. tactic configuration of molecular chains refers to the regular organization of groups/substituents along the polymer backbone. There are three types of tacticity in polymers: atactic/heterotactic, isotactic, and syndiotactic. In isotactic macromolecules all the substituents are located on the same side of the macromolecular backbone, whereas in syndiotactic macromolecules the substituents have alternate positions along the chain. Atactic polymers the substituents are placed randomly along the macromolecular chain. Examples of both stereospecific forms for PMMA are shown in Figures 2 and 3.

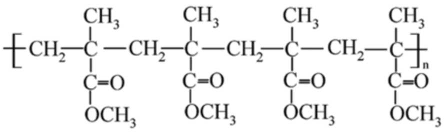

Figure 2. Structure of isotactic PMMA

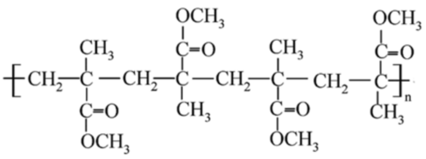

Figure 3. Structure of syndiotactic PMMA

Isotactic and syndiotactic polymers are both stereoregular and thus can be crystalized. Atactic or heterotactic polymers are typically completely amorphous.

3.1. Techniques for Measuring Tacticity

Tacticity can be measured directly using proton or carbon-13 NMR. This technique enables quantification of the tacticity distribution by comparison of peak areas or integral ranges corresponding to known two or three structural units in the polymer molecule depending on the spectral resolution. Changes in the chemical shifts and multiplicity of the different molecular constituents of the polymer, caused by the differences in the stereochemical environment of the polymer chain, can be used to evaluate the polymer tacticity [38].

Other techniques can also be used to measure tacticity in polymers such as x-ray powder diffraction, vibrational FTIR spectroscopy or by indirect means by measuring another physical property such as glass transition or melting temperature, when the relationship between tacticity and that property is well established [38].

3.2. Tacticity and Glass Transition

Tacticity in polymer structures have a significant influence on the glass transition and melting points [39,40]. Syndiotactic polymers usually have a higher T_g than isotactic forms of the same polymer. For example isotactic PMMA (Mw = 300,000 g/mol) has a Tg = 55^{o} C, but syndiotactic (Mw = 50,000 g/mol) has a much higher Tg = 130^{o}C. Isotactic polymer chains are more flexible and therefore have a lower Tg when the pendant groups are all on the same side. Atactic PMMA have a Tg in between the two other tactic forms Tg = 110-120°C.

3.3. PMMA Tacticity and qHNMR

PMMA has been previously studied extensively with respect to tacticity using quantitative proton NMR [42-44]. These studies have shown that in isotactic PMMA one methylene hydrogen is repeatedly exposed to the substituent ester group while the other methylene hydrogen is not in the same environment. This causes two peaks in the proton NMR. In syndiotactic PMMA, the methylene hydrogens both experience the same alternatively substituent group, therefore both methylene hydrogens are in the same electronic environment causing only one peak. Atactic PMMA contains some syndiotactic regions and some isotactic regions, therefore all three peaks are observed.

4. Materials and Methods

4.1. Experimental Materials

4.1.1. Polymethyl Methacrylate (PMMA)

The seventeen samples of various peak molecular weight PMMA used to establish the Flory-Fox equation were obtained from Agilent technologies. The molecular weight distribution data and polydispersity indices (PDI) for these seventeen samples are shown in Table 1 below.

Table 1. Molecular Weight Distribution Data for PMMA

Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mv (g/mol)	PDI (Mw/Mn)
3,040	2,710	2,940	2,900	1.08
4,600	4,000	4,460	4,400	1.11
6,940	6,050	6,650	6,570	1.10
9,590	9,130	9,500	9,450	1.04
13,630	12,870	13,390	13,320	1.04
20,520	19,370	20,200	20,080	1.04
32,340	31,090	31,950	31,830	1.03
46,900	44,760	45,740	45,600	1.02
72,800	69,400	70,900	70,700	1.02
98,550	94,000	96,050	95,750	1.02
156,200	153,600	156,200	155,800	1.02
210,000	204,100	207,900	207,400	1.02
260,900	252,200	257,000	256,200	1.02
538,500	517,000	529,500	528,000	1.02
766,000	725,000	748,500	745,000	1.03
1,020,000	969,000	1,011,000	1,005,000	1.04
1,591,000	1,439,000	1,531,000	1,519,000	1.06

The PMMA samples utilized to prepare the binary mixtures were obtained from Scientific Polymer Products (Sp^{2}). Approximate molecular weights were reported by the supplier and determined by gel permeation chromatography (GPC). All three samples were not reported to contain any high degree of tacticity.

Table 2. Molecular Weights of Scientific Polymer Products PMMA

Molecular Weight (g/mol) GPC	Inherent Viscosity, η_{inh}
15,000	0.11
35,000	0.18
75,000	0.40

Lastly, highly tactic PMMA samples were utilized in the qHNMR portion of this study. The molecular weights and reported tacticity of these samples are shown below in Table 3. These samples were also obtained from Sp^2 and had approximate molecular weights determined by gel permeation chromatography (GPC).

Table 3. Molecular Weight and Tacticity of PMMA used in qHNMR

Molecular Weight (g/mol)	Tacticity
50,000	85% syndiotactic
300,000	95% isotactic

4.2. Experimental Procedure

4.2.1. Differential Scanning Calorimetry (DSC)

The Tg results were obtained using a Perkin-Elmer power compensated Differential Scanning Calorimeter (DSC) model Pyris 1. The DSC was used in its high temperature mode. Calibration of the thermal outputs of the DSC were obtained using an empty reference aluminum pan. Prior to beginning the experiment, the DSC was calibrated for Temperature, heat flow and baseline linearity. This was done by first running empty cells in both the sample and reference compartments to produce a thermal baseline. Highly pure standards of tin, lead and indium were run through four thermal cycles/ramps of two heating and two cooling at a constant rate of 10.0^0C/min. The onset melting and recrystallization temperatures for the standards were used for temperature calibration. The onset melting /recrystallization temperatures are defined as the temperature at the initial endothermic/exothermic change from the thermal baseline. The change in enthalpy (ΔH) was used to calibrate heat flow. The ΔH is found by the peak area under the curve. The endothermic and exothermic transition temperatures as well as the enthalpies of fusion and crystallization were recorded by the Pyris 1 for Windows software. All PMMA samples underwent two heating cycles and one cooling cycle between 40.0 – 160.0□ at a rate of 10□ /min for heating and cooling. The glass transition temperatures and enthalpies of transition were determined using the Perkin-Elmer thermal analysis software *Pyris for Windows*. The 2nd heating thermogram was used to determine the onset, mid-point-1/2 Cp and endpoint temperatures of T_g, as well as endothermic enthalpies of transition. The first heating cycle was used to erase the thermal history of the polymethyl methacrylate samples. All experiments were run under dry nitrogen flowing at 20 cm^3/min. The flowing nitrogen was used to prevent any moisture pickup or oxidative degradation. The experimental analysis is not limited to this specific DSC hardware of software.

PMMA sample was packed into a standard aluminum pan and the lid was left laying on top of the sample, unpressed. Each thermogram was obtained at a rate of 10°C per minute and each glass transition temperature was calculated using the "Tg" option found in the Pyris DSC software package. Selected thermograms for various PMMA samples are shown in Figure 4.

4.2.2. Hot Melt Blend Technique

In order to achieve uniform binary mixtures, or blends, a hot melt blend technique was adopted. This technique involved utilizing a hot plate to heat both PMMA samples until they were fluid, and mechanically mixing them until a homogeneous blend was obtained. The PMMA blends were then cooled rapidly and placed into a standard aluminum pan for Tg evaluation, where a single Tg was observed, confirming the validity of the technique.

4.2.3. Preparation of Isotactic and Syndiotactic PMMA Binary Mixtures

Binary mixtures were prepared by combining isotactic and syndiotactic PMMA in weight ratios of 1:9, 2:8, 3:7, etc. This was performed by weighing an empty three milliliter glass vial, adding isotactic PMMA, syndiotactic PMMA, and then weighing by difference to calculate the precise weights. A Mettler Toledo analytical balance at a precision of 0.1 mg was used to record all weights.

Two milliliters of deuterated chloroform ($CDCl_3$) were then added to each of the PMMA-containing glass vials, and the samples were left to dissolve. An aliquot of this solution was transferred to a Wilmad Pyrex glass 5 mm x 7" thin wall NMR tube for HNMR analysis.

4.2.4. Quantitative Proton Nuclear Magnetic Resonance Spectroscopy (qHNMR)

The HNMR spectra were obtained using a 400 MHz JEOL model ECS-400 NMR spectrometer. Each sample was run as a single pulse, 1D HNMR with a 0.25 Hz resolution and a relaxation time ranging from 8 to 10 seconds. The JEOL Delta NMR software version 6.0.0 (Windows) was used to analyze the individual spectra.

4.3. Hazards

PMMA (CAS# 9011-14-7) is regularly used as a versatile engineering plastic in automobiles, appliances, and many other commercial applications. Because of its biocompatibility and low toxicity, the FDA has approved its uses in many different medical specialties. PMMA has been used for (a) bone cements; (b) contact and intraocular lens; (c) screw fixation in bone; (d) filler for bone cavities and (e) vertebrae stabilization in osteoporotic patients. The FDA has approved PMMA for use in contact with food, as it does not pose any significant health risks unless consumed at high levels. Goggles and gloves are nevertheless required to avoid exposure to the eyes and skin. Waste solutions should be disposed of according to EPA and local guidelines.

5. Results and Discussion

5.1. Establishment of the Flory-Fox Equation

The DSC thermograms for PMMA samples of selected peak molecular weights are shown in Figure 4 below.

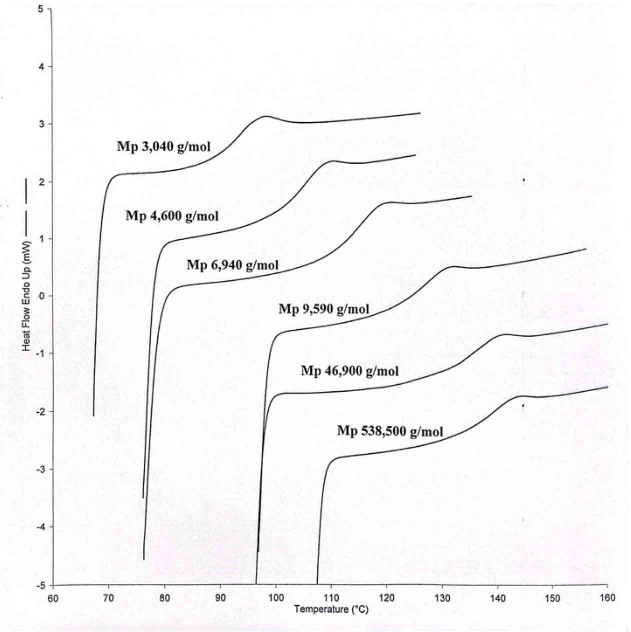

Figure 4. DSC Thermograms for PMMA Samples of Selected Mp

Table 4 summarizes the onset, half-Cp, and end Tg data for the seventeen individual PMMA samples.

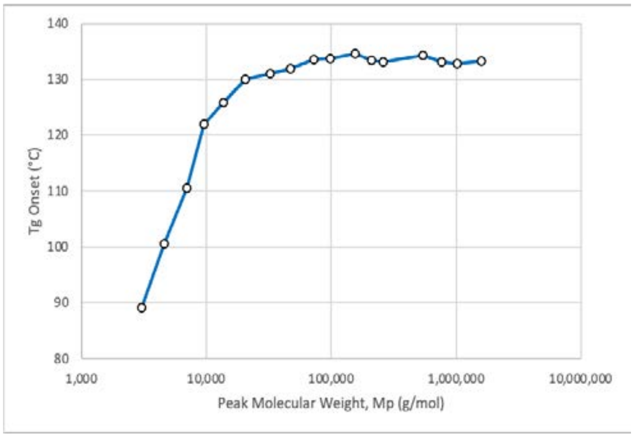

Figure 5. Flory-Fox Plot of Tg vs. Peak Molecular Weight, Mp

Figure 6 illustrates glass transition temperature as a function of reciprocal peak molecular weight. Given the general Flory-Fox equation of $Tg = Tg_{\infty} - K/Mn$, it is established that the value of the slope of the graph of onset *Tg* versus reciprocal molecular weight, represents *K* for the amorphous polymer, while the y-intercept of the same plot denotes Tg_{∞}. Therefore, the value of *K* was experimentally evaluated to be 1.4 x 10^5 °C·g·mol^{-1} for the predominantly syndiotactic PMMA used, while the value of Tg_{∞} was determined to be 134.59 °C. Reported values for Tg_{∞} and K for PMMA are 387K and 2.1 x 10^{-5}°C·g·mol^{-1} respectively [45].

Table 4. Tg for PMMA Samples of Various Peak Molecular Weights

Mp (g/mol)	Onset Tg (°C)	Half-Cp Tg (°C)	End Tg (°C)
3,040	89.034	91.658	94.478
4,600	100.569	103.342	106.450
6,940	110.486	113.773	117.060
9,590	121.961	125.275	128.812
13,630	125.854	129.289	132.712
20,520	129.956	132.771	135.802
32,340	130.973	134.439	137.774
46,900	131.879	135.039	138.490
72,800	133.571	136.478	139.669
98,550	133.651	135.721	138.791
156,200	134.656	137.792	141.160
210,000	133.450	137.330	141.409
260,900	133.049	138.816	142.763
538,500	134.266	137.668	141.099
766,000	133.171	134.889	137.614
1,020,000	132.788	134.209	136.922
1,591,000	133.288	136.532	140.068

Figure 5 is the graphical representation for the onset glass transition temperature data plotted against peak molecular weight, and set to a logarithmic scale. It represents the typical Flory-Fox plot in which *Tg* steadily increases, but ultimately levels off at a maximum value labeled Tg_{∞}.

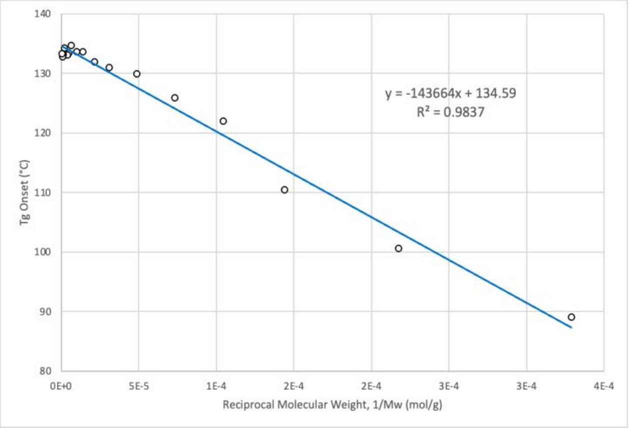

Figure 6. Linear Plot of Tg vs. Reciprocal Peak Molecular Weight, Mp^{-1}

5.2. Corroboration of the Fox Equation

Tables 5 and 6 contain the glass transition temperature data for both sets of polymethyl methacrylate binary mixtures: 15,000 g/mol combined with each 35,000 g/mol and 75,000 g/mol respectively. Both tables also display onset glass transition temperatures for each of the binary mixtures, as calculated by the Fox equation.

Table 5. Onset *Tg* for 15,000 & 35,000 g/mol PMMA Blends

Percent Composition		Onset Tg (°C)	
15,000 g/mol	35,000 g/mol	Measured	Calculated
100	0	82.625	
79.89	20.11	87.866	86.001
60.41	39.59	93.368	89.549
40.30	59.70	94.248	93.528
19.86	80.14	98.647	97.955
0	100	102.675	

Table 6. Onset *Tg* for 15,000 & 75,000 g/mol PMMA Blends

Percent Composition		Onset Tg (°C)	
15,000 g/mol	75,000 g/mol	Measured	Calculated
100	0	83.063	
79.51	20.49	86.662	85.039
59.76	40.24	88.639	87.034
39.51	60.49	89.708	89.179
20.25	79.75	93.085	91.321
0	100	93.686	

Figures 7 and 8 display the measured onset glass transition temperatures, as well as the Fox equation-calculated values for each set of binary mixtures. In both plots, the measured onset glass transition temperatures closely match that of the calculated, indicating experimental accuracy. The correlation coefficients of the trendlines for each plot are greater than 0.96, confirming that both sets of blends follow the Fox equation.

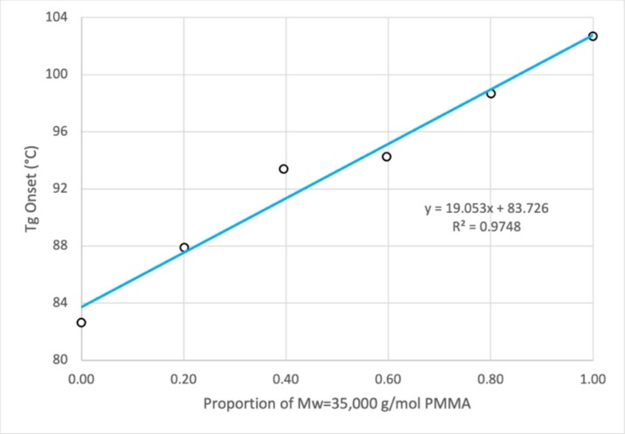

Figure 7. Tg for Binary Mixtures of 15,000 & 35,000 g/mol PMMA

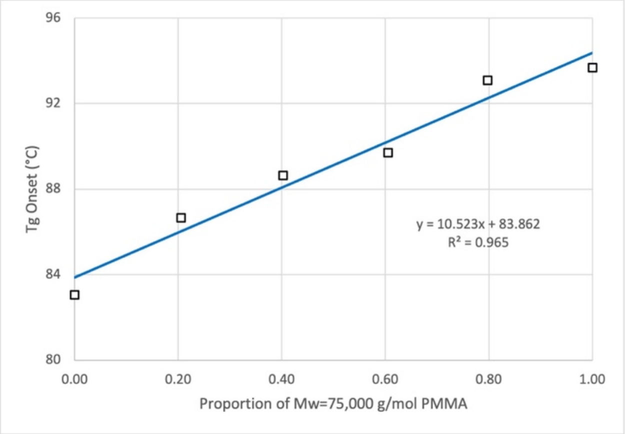

Figure 8. Tg for Binary Mixtures of 15,000 & 75,000 g/mol PMMA

The first portion of this study focused on the effect of number-average molecular weight on Tg of PMMA. However, as mentioned before, tacticity is also a major factor in determining the Tg of an amorphous polymer, such as PMMA. With this being said, this study also aimed to develop a method in which the relative tacticity of PMMA could be measured, so as to better understand its Tg. Further studies to measure the effect of tacticity of the Tg of PMMA will be pursued.

5.3. Determination of Relative Tacticity

Figure 9 is the ^{1}HNMR spectrum with integrated peak areas and labeled chemical shifts for a sample of 95% isotactic PMMA, whereas Figure 10 is the same for an 85% syndiotactic PMMA sample.

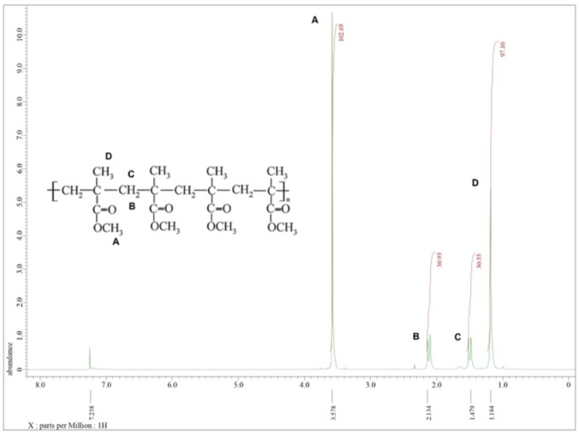

Figure 9. qHNMR Spectrum of 95% Isotactic PMMA

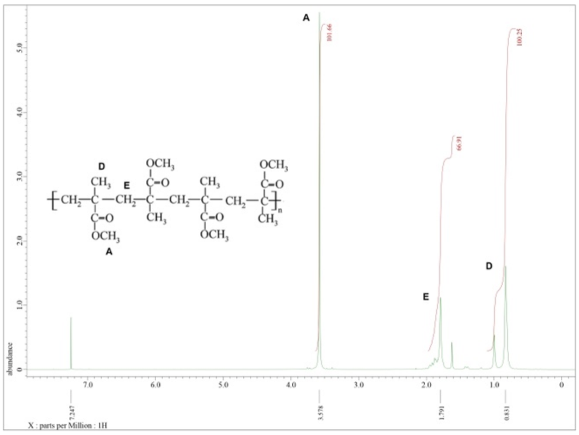

Figure 10. qHNMR Spectrum of 85% Syndiotactic PMMA

The ^{1}HNMR spectrum of isotactic PMMA features four distinct peaks, corresponding to hydrogen atoms in four unique chemical environments, while the ^{1}HNMR of syndiotactic PMMA features only three such peaks. This difference in spectra can be explained by tacticity and the positioning of the repeating pendant ester group in both isotactic and syndiotactic PMMA.

Figure 3 displays the structure of syndiotactic PMMA where it contains alternating pendant (ester) groups. Alternating pendant groups create identical chemical environments for both methylene hydrogens, in which they are each exposed to a pendant (ester) group, as well as an alkyl (methyl) group. Identical chemical environments translate to identical chemical shifts, and therefore the existence of only one methylene hydrogen peak labeled “E” on the ^{1}HNMR spectrum of syndiotactic PMMA (Figure 10).

As seen in Figure 2, the structure of isotactic PMMA contains all pendant groups on the same side of the polymer. This arrangement creates a difference in the chemical environments of each of the methylene hydrogens, as one is exposed to pendant ester groups on both sides while the other is exposed to alkyl methyl groups on both sides. The pendant ester groups contain two highly electronegative, oxygen atoms which deshield the methylene hydrogen and cause a downfield shift in its corresponding ^{1}HNMR peak. On the other hand, the remaining methylene hydrogen is no longer exposed to any highly electronegative pendant ester groups, but instead two electron-donating alkyl methyl groups on either side. This chemical environment contributes the shielding of the remaining methylene hydrogen, and therefore upfield shift in its corresponding ^{1}HNMR peak. The peaks correlating to the less shielded and more shielded methylene hydrogens are labeled “B” and “C” respectively on the ^{1}HNMR spectrum of isotactic PMMA (Figure 9).

Figure 11 is the ^{1}HNMR spectrum for a 50:50 binary mixture of isotactic and syndiotactic PMMA. It is important to acknowledge that in this spectrum, three peaks corresponding to the methylene hydrogens exist. One peak corresponds to each methylene hydrogen in isotactic PMMA, while the third, centermost peak corresponds to both methylene hydrogens in syndiotactic PMMA.

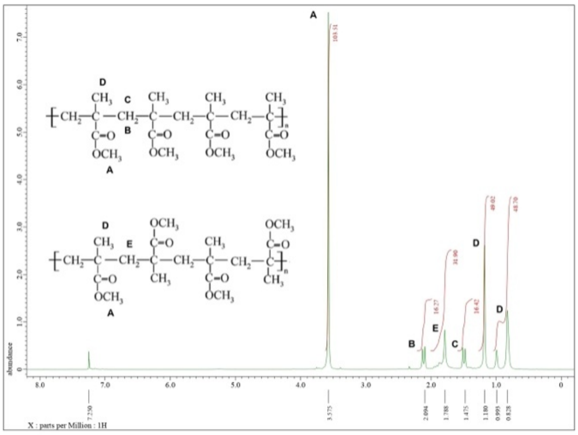

Figure 11. qHNMR spectrum of 50:50 binary mixture of isotactic to syndiotactic PMMA

Tables 7 and 8 summarize the chemical shift and normalized integration values for the 50:50 isotactic to syndiotactic PMMA binary mixture.

Table 7. Chemical Shift and Normalized Integration Values for Isotactic PMMA

Label	Hydrogen(s)	Chemical Shift, δ (ppm)	Integration
A	ester	3.575	6.36
B	less-shielded methylene	2.094	1.00
C	more-shielded methylene	1.475	1.01
D_I	methyl	1.180	3.01

Table 8. Chemical Shift and Normalized Integration Values for Syndiotactic PMMA

Label	Hydrogen(s)	Chemical Shift, δ (ppm)	Integration
A	ester	3.575	6.36
D_S	methyl	0.828	2.99
E	methylene	1.788	1.96

As summarized in the tables above, and confirmed by the ^{1}HNMR spectra of isotactic and syndiotactic PMMA, tacticity does not affect the chemical shift or integration values of the pendant ester group hydrogens. On the other hand, this cannot be said for any other type of hydrogen in PMMA. For instance, as mentioned before, isotacticity creates two unique chemical environments for the two methylene hydrogens of PMMA. This is confirmed by the appearance of two peaks, chemical shifts of 2.094 and 1.475 ppm for the less-shielded and more-shielded methylene hydrogens respectively, and normalized integration values of 1.00 and 1.01. Additionally, it was observed that the peak corresponding to the methyl hydrogens appeared at different chemical shifts for isotactic and syndiotactic PMMA, 1.180 and 0.828 ppm respectively.

Figures 12 and 13 plot the percentage of isotactic PMMA achieved by qHNMR against that measured by gravimetric analysis. In order to calculate the percentage of isotactic PMMA achieved by qHNMR in Figure 12, the peak integrations of the methylene hydrogens in isotactic PMMA (B and C) and syndiotactic PMMA (E) were utilized according to the formula below.

$$\%\, Isotactic\ PMMA = \frac{B+C}{B+E+C} \cdot 100 \tag{4}$$

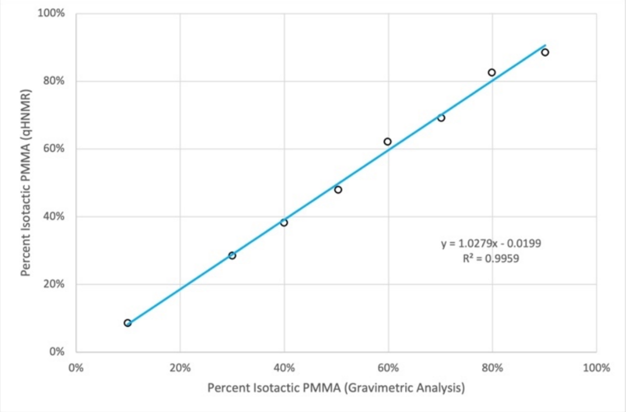

Figure 12. Percent isotactic PMMA in binary mixtures by gravimetric analysis and qHNMR of methylene hydrogens

However, in order to calculate the percentage of isotactic PMMA in Figures 13, the peak integrations of the methyl hydrogens in isotactic PMMA (D_I) and syndiotactic PMMA (D_S) were used according to the formula below.

$$\%\, Isotactic\ PMMA = \frac{D_I}{D_I+D_S} \cdot 100 \tag{5}$$

Strong correlation coefficients greater than 0.99 for Figures 12 and 13 indicate that the percentage of isotactic PMMA measured by qHNMR closely matches that achieved by gravimetric analysis. With this being said, qHNMR of the methylene or methyl hydrogens can be used to not only differentiate between primarily isotactic and syndiotactic samples of PMMA, but also to determine relative tacticity in any given PMMA sample.

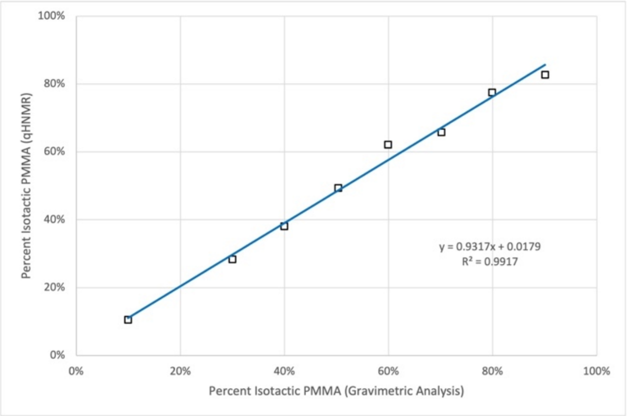

Figure 13. Percent isotactic PMMA binary mixtures by gravimetric analysis and qHNMR of methyl hydrogens

6. Conclusions

The experiment corroborates the Flory-Fox equation 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. $T_{g\infty}$ of 135 ^{o}C and the constant K of 1.4 x 10^{5} ^{o} C g mol^{-1} were determined for syndiotactic PMMA. There is a strong, linear correlation between the gravimetric compositions of binary mixtures of PMMA and the glass transition temperatures found using DSC. HNMR can be used to differentiate between primarily isotactic or syndiotactic PMMA samples. Where the peak integration of the methylene or methyl hydrogens in the qHNMR spectra of PMMA can be used to determine relative isotacticity or syndiotacticity in PMMA samples. 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.

Acknowledgements

We acknowledge the support from a Hofstra University HCLAS Research and Development Grant.

List of Abbreviations and Symbols

DSC = differential scanning calorimetry
NMR = nuclear magnetic resonance spectroscopy
HNMR = proton nuclear magnetic resonance spectroscopy
qHNMR = quantitative proton nuclear magnetic resonance spectroscopy
Tg = glass transition temperature
PMMA = poly (methyl methacrylate)
PDI = polydispersity index
$w_{1\text{ or }2}$ = weight fraction
Tg_{∞} = Tg at infinite molecular weight
K = Flory-Fox constant (°Cg/mol)
Mn = number average molecular weight
Mw = weight average molecular weight
Mv = viscosity average molecular weight
η_{inh} = inherent viscosity
V_f = free volume
ρ = density
N_a = Avogadro's number
α = coefficient of thermal expansion
mW = milliwatts

References

[1] Wikipedia, “Polymethyl Methacrylate,” June 20, 2023. [Online]. https://en.wikipedia.org/wiki/Poly(methyl_methacrylate) [Accessed June 26, 2023].

[2] Team Xometry, “Everything You Need To Know About Acrylic (PMMA)” May 4, 2022. [Online]. https://www.xometry.com/resources/materials/acrylic-pmma/ [Accessed June 26, 2023].

[3] Shawn Wasserman. “What is PMMA and How is It Used in the Medical World?” September 25, 2019. [Online]. https://www.ansys.com/blog/what-is-pmma-how-it-is-used-healthcare [Accessed June 26, 2023].

[4] The Editors of Encyclopedia Britannica, “*Polymethyl methacrylate*” May 25, 2023 [Online]. https://www.britannica.com/science/polymethyl-methacrylate [Accessed June 26, 2023].

[5] Ali, U., Juhanni Bt., K., Karim, A., Buang, N.A. “A Review of the Properties and Applications of Poly (Methyl Methacrylates) (PMMA)” Polymer Review, 55:4, 678 – 705 (2015).

[6] Forte, M.A., Silva, R.M., Tavares, C. J., Silva, R.F. “Is Poly (Methyl Methacrylate) (PMMA) a Suitable Substrate for ADL?: A Review” Polymers, 13, 1346 – 1374, (2021).

[7] Duval-Terrie, C., Lebrun, L. “Polymerization and Characterization of PMMA” J. Chemical Ed. 83, #3, 443-446 (2006).

[8] Wikipedia, “Differential scanning calorimetry,” May 19, 2023. [Online]. https://en.wikipedia.org/wiki/Differential_scanning_calorimetry [Accessed June 26, 2023].

[9] Blanchard, L.P. Hesse, J. Malhotra, S.L. “Effect of Molecular Weight on Glass Transition by Differential Scanning Calorimetry” *Can. J. Chem*, 52, 3170-3175 (1974).

[10] D’Amelia, R. P., Khanyan, B., “An Experimental Review: Evaluation of the Flory-Fox Equation for the Relationship of Glass Transition Temperature (Tg) vs Molar Mass of Polystyrene Using Differential Scanning Calorimetry (DSC),” *Journal of Polymer and Biopolymer Physics Chemistry*, 10(1), 10-17, August 2022.

[11] Collins, E.A., Bares, J., Billmeyer, F.W., *Experiments in Polymer Science*, Wiley-Interscience, New York 1973.

[12] Sperling, L. H., *Introduction to Physical polymer Science*, 4th edition Wiley-Interscience, Hoboken, New Jersey, 2006.

[13] Alger, M., S. M. *Polymer Science Dictionary*, Elsevier Applied Science, New York, New York, 1989

[14] Rabek, J. F., Experimental Methods in Polymer Chemistry – Principles and Applications, Wiley-Interscience, New York, New York, 1980.

[15] Elias, H-G., Macromolecules Vol 1, Structure and Properties, Volume 2, _ Synthesis and Materials, Plenum, New York, New York, 1977.

[16] Flory, P.J. *Principles of Polymer Chemistry*” Cornell Press Ithaca, New York, 1953

[17] Mark, J. E., Eisenberg, A., Graessley,W.W , Mandelkern, L., Samulski, E.T., Koenig, J.L. and Wignall, G.D., *Physical Properties of Polymers, 2nd* ed. American Chemical Society, Washington, DC, 1993.

[18] Abiad, M.G., Carvajal, M.T., Campanella, O.H. “A Review on Methods & Theories to Describe the Glass Transition Phenomenon: Applications in Food & Pharmaceutical Products,” Food Eng. Res. 1, 105-132, (2009)

[19] Fox, T.G., & Flory, P.J.” Second Order Transition Temperatures and Related Properties of Polystyrene I Influence of Molecular Weight” *J. Applied Phys*. 21 (6), 581-591 (1950).

[20] Fox, T.G., & Flory, P.J. “The Glass Temperature and Related Properties of Polystyrenes Influence of Molecular Weight” *J. Polymer Sci*, 14, 315-319, (1954).

[21] Fox, T.G. & Loshaek, S. “Influence of Molecular Weight and Degree of Crosslinking on the Specific Volume and Glass Temperature of Polymers” J. Polym. Sci., 15, 371- 390 (1955)

[22] Williams, M.L., Landel, R.F., & Ferry, J.D.: “The Temperature Dependence of Relaxation Mechanism in Amorphous Polymers and Other Glass Forming Liquids”, *J. Am. Chem. Soc.* 77, 3701-3707 (1955).

[23] Hirai, N. Eyring, H. “Bulk Viscosity of Polymer Systems” *J. Polymer Sci*. 37, 51-70, (1959).

[24] Gibbs, J.H. & DiMarzio, E.A. “Nature of the Glass Transition and The Glass State” *J. Chem Phys*, 28, 373-383 (1958).

[25] Gibbs, J.H.” Nature of the Glass Transition in Polymers” *J. Chem. Phys.* 25, 185-185 (1956).

[26] Beevers, R. B. White, E.F.T., “Dependence of the Glass Transition Temperature of PMMA on Molecular Weight” Trans. Faraday Soc., 56, 744-752 (1960)

[27] Dudek, T. J.; Lohr, J. J. “Glass Transition Temperature of PMMA Plasticized with Low Concentrations of Monomer and Diethyl Phthalate” J. of Applied Polymer Sci. 9, 12, 3795-3818, (1965)

[28] Kabomo, M.T.; Blum, F.D. “Glass Transition Behavior of PMMA Thin Films” Polymer Preprints, American Chemical Society, (Jan 2001).

[29] Kabomo, M. T.; “Glass Transition Behavior of Thin Poly (methyl methacrylate) Films on Silica”, Masters Theses 2151 (2002).

[30] Roth, C.B.; Pound, A.; Kamp, S.W.; Murray, C.A.; Dutcher, J.R. “Molecular-Weight Dependence of the Glass Transition of Freely-Standing PMMA Films”, Eur. Phys J.E. 20, 441-448 (2006).

[31] Mohammadi, M.; Fazli, H., Karevan, M.m Davoodi, J, “The Glass Transition Temperature of PMMA: A Molecular Dynamics Study and Comparison of Various Determination Methods” European Polymer Journal, 91, 121-133, (2017).

[32] Zhang, L, Torkelson, J.M. “Emhanced Glass Transition Temperature of Low Molecular Weight PMMA by Initiator Fragments Located at Chain ends” Polymer 122 194-199 (2017)

[33] Startsev, O.V., Lebedev, M.P. “Glass Transition Temperature and Characteristic Temperatures of α Transition in Amorphous Polymers Using the Example of PMMA” Polymer Science, Series A 60, 911-923 (2018).

[34] Wikipedia, “Tacticity,” June 26, 2023. [Online]. https://en.wikipedia.org/wiki/Tacticity [Accessed June 26, 2023].

[35] Bovey, F.A. “Configurational Sequence Studies by NMR and the Mechanism of Vinyl Polymerization” Pure and Applied Chem. 15 (3-4), 349 – 368 (1967)

[36] Jenkins, A.D., Kratochvil, P., Stepto, R.F.T., Suter, U.W. “Glossary of Basic Terms in Polymer Science (IUPAC Recommendations)”, Pure Appl. Chem., 68, Issue 12, 2287 – 2311 (1996)

[37] Jenkins, A.D. “Stereochemical Definitions & Notations Relating to Polymers”, Pure Appl. Chem. 53, 733, (1981)

[38] Woo, E.M.; Chang, L. “Tacticity in Vinyl Polymers” Encyclopedia of Polymer Science and Technology (2011)

[39] Thompson, E.V. “Dependence of the Glass Transition Temperature of PMMA on Tacticity and Molecular Weight” J. Polymer Science – Part A-2, 4, 199 – 208 (1966)

[40] Chang, L.,; Woo, E.M. “ Tacticity Effects on Glass Transition and Phase Behavior in Binary Blends of PMMA of Three Different Configuration” Polymer Chem. 1, 198-202 (2010)

[41] Chat, K., Tu, W,; Unni, A.B.; Adrjanowicz, K. “ Influence of Tacticity of the Glass Transition Dynamic of PMMA under Elevated Pressure and Geometrical Nanoconfirement” Macromolecules 54, 18, 8526 – 8537 (2021)

[42] Schilling, F.C.; Bovey, F.A.; Bruch, M.D.; Kozlowski, S. “Observations of the Stereochemical Configuration of PMMA by Proton Two-Dimensional J- Correlated and NOE-Correlated NMR Spectroscopy” Macromolecules 18, 7, 1418 (1985)

[43] Ober, C.K. “Polymer Tacticity in Simulated NMR Spectra” J. Chemical Ed. 66, #8, 645-647. (1989)

[44] Goni, I.; Gurruchaga, M.; Valero, M.; Guzman, G.M. “Determination of the Tacticity of PMMA Obtained from Graft Copolymers” Polymer, 33, #14, 3089 – 3094, (1992).

[45] Fried, J.R., *Polymer Science & Technology*, Prentice Hall PTR, Upper Saddle River, 2003, 180.