SHEN, JIALONG. The Structural Bases for Polymer Glass Transition Temperatures. (Under the direction of Dr. Alan E. Tonelli.)

The glass transition temperatures ($T_g$s) observed for chemically distinct polymers range over several hundred K, and the molecular bases for this wide variability are largely unknown. Different structural factors are generally interdependent, making it difficult to predict or even rationalize the $T_g$s of polymers.

In this dissertation work, we have synthesized structurally analogous polyesters and polyamides that are wholly amorphous and have compared their $T_g$s in a well-controlled manner with the aid from their rotational isomeric states (RIS) model. In addition, three tactic PMMAs were selected as model polymers for the search of a possible conformational origin for their vastly different $T_g$s and dynamic fragility indices. The arrangement of the work is described as follows:

In the first chapter, fundamentals of the polymer glass transition temperature and the glass transition problem in general are reviewed. In the second chapter, a series of wholly amorphous linear aliphatic co- and tetra- polyesters are synthesized via bulk melt step-growth polymerization, and their glass transition temperatures were compared as a function of ester group contents. In the third chapter, glass transition temperatures were determined using DSC for melt blended, melt polymerized, interfacial polymerized, and solution polymerized amorphous or low crystallinity aliphatic polyamides. Many of these polyamides are structurally analogous to the polyesters described in the second chapter, with only one varying structural factor; i.e., intermolecular interactions, and their $T_g$s were
compared. In the fourth chapter, dynamic fragility indices for PMMAs with different tacticities were measured using DSC. Rotational Isomeric State (RIS) conformational model results were used to explain the conformational origin of their large differences in Tgs and fragilities.
The Structural Bases for Polymer Glass-Transition Temperatures

by

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APPROVED BY:

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DEDICATION

To my wife, my parents, and my daughter and son.
BIOGRAPHY

Jialong Shen was born in the beautiful city of Hangzhou, China. After receiving his B.E. in Textile Engineering at Donghua University (Shanghai, China), he started his graduate study at NCSU in 2010. He joined the research group of Dr. Alan E. Tonelli where he completed his M.S. in Textile Engineering with researches focused on the formation of inclusion compound between urea and polymers. He enrolled in the Ph.D. program in Fiber and Polymer Science in 2012 and continued to work with Dr. Tonelli on a project aiming at a fundamental understanding of the structural bases of polymer glass transition.
ACKNOWLEDGEMENTS

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Chapter 1  Background

1.1  Definition of glass transition

1.1.1  Viscosity Consequence: Relaxation time reaches experimental time scale

Cooling of liquids, polymer melts or small molecule liquids, decreases their specific volume and increases their viscosity. As it is cooled below its nominal melting or crystallization temperature (if present) in a manner that the underlying crystallization is avoided, a further decrease in temperature causes specific volume and other thermodynamic variables to follow the extrapolation of the equilibrium line from above the melting temperature for a limited temperature range. Depending on the cooling rate, at some lower temperature it becomes too viscous so that molecules move too slowly and do not have enough time to reorient to the equilibrium state at that temperature, i.e., they deviate from the equilibrium line. A slower cooling rate permits longer relaxation times and therefore the deviation occurs at lower temperatures, which is the case for glass 2 compared to glass 1 in Figure 1.1. The temperature at which the extrapolation of the equilibrium liquid line intersects with the extrapolation of the glass line is called the glass transition temperature ($T_g$). Lowering temperature even further below this point, causes the specific volume to continue to decrease, but only with a smaller thermal expansion coefficient similar to that of the crystal. As a result, it takes even longer for molecules to equilibrate towards the equilibrium state and to be observed in a single experiment or even in a scientist’s life time; i.e., they are effectively ‘frozen’. The non-equilibrium material called a glass is thus obtained. It is worth noting that, when the temperature is not too far below its $T_g$ or when we have access to extraordinarily long observational time scales, a glass is always working
itself towards the equilibrium supercooled liquid state or stable crystal, and this process is called physical aging.\textsuperscript{3}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Specific volume vs. temperature plot for liquid that has underlying crystalline phase and is able to produce glasses with different densities depending on cooling rate.\textsuperscript{2}}
\end{figure}

A recent research\textsuperscript{4} demonstrated the behavior of an amber sample that has been geologically aged for two million years, a time scale that is not otherwise accessible by us. As is shown in Figure 1.2, the volume or enthalpy of the aged amber decreased towards the equilibrium value and the subsequent heating exhibits a fictive temperature ($T_f$), which was introduced by Tool\textsuperscript{5,6} to indicate the ‘state’ of the glass and was defined as the temperature where the new glass line intersects with the equilibrium liquid line. The structure of the glass is characterized by the equilibrium liquid structure at $T_f$.\textsuperscript{7} The physical aging phenomenon substantiates the argument that whether the glass is fluid or solid depends on the relative time scale of the observation.
1.1.2 Ehrenfest Transition Order: Thermodynamic manifestation\(^{1,5}\)

Although not accurate, the glass transition was formally thought of as a second-order phase transition for its resemblance with the classical second order transition. According to Enrenfest\(^8\), a first order phase transition, e.g., melting and vaporization, has a continuous free energy function and discontinuities in its respective first partial derivative of the free energy. Therefore, entropy \(S\), volume \(V\), and enthalpy \(H\) are discontinuous at first-order transition:\(^{1,5}\)

\[
\left[ \frac{\partial G}{\partial T} \right]_p = -S
\]

\[
\left[ \frac{\partial G}{\partial P} \right]_T = V
\]
\[
\begin{bmatrix}
\frac{\partial (G_T)}{\partial (1/T)} \\
\frac{\partial (1)}{\partial (T)}
\end{bmatrix}_p = H
\]

Examples include the volume step decrease during the crystallization as is shown in Figure 1.1, and the release of a “latent heat”.

A second order transition manifests continuities in both the free energy function and its first partial derivatives and discontinuities in its second partial derivatives. Hence, at second-order transition heat capacity \( C_p \), compressibility \( k \), and thermal expansion coefficient \( \alpha \) exhibit a sudden change:\(^1_5\)

\[
-\left[ \frac{\partial^2 G}{\partial T^2} \right]_p = \left[ \frac{\partial S}{\partial T} \right]_p = \frac{C_p}{T}
\]

\[
\left[ \frac{\partial^2 G}{\partial P^2} \right]_T = \left[ \frac{\partial V}{\partial P} \right]_T = -kV
\]

\[
\left[ \frac{\partial}{\partial T} \left[ \frac{\partial (G_T)}{\partial (1/T)} \right]_p, \right] = \left[ \frac{\partial H}{\partial T} \right]_p = C_p
\]

\[
\left[ \frac{\partial}{\partial T} \left[ \frac{\partial G}{\partial P} \right]_T, \right] = \left[ \frac{\partial V}{\partial T} \right]_p = \alpha V
\]

The major difference between classical second order transition and glass transition is the non-equilibrium nature of the latter. If we assume the lowest free energy state as the equilibrium state and it can be followed at any temperature, glass transition would be absent and equilibrium liquids will result from both above and below the supposed transition temperature. For this reason, glass transition exists under the premise of its free energy being larger than the equilibrium liquid, \emph{i.e.}, non-equilibrium. (See Figure 1.3) This feature gives
rise to the proposition of a kinetic transition albeit there is still much to debate about. Never-
theless, it is widely acknowledged that the measured glass transition is influenced by
kinetics and is path dependent.⁹

1.1.3 Kinetics: An example of cooling rate dependence

In A.J. Kovacs’s 1958 work¹⁰, the cooling rate dependence of polymer glass transition temperature was demonstrated using poly(vinyl acetate) (PVAc) cooled at two different rates differing by over 3 orders of magnitude. The resultant glass transition temperatures differ by about 10 K. (See Figure 1.4.) It is empirically true that, for many polymers, for every order of magnitude change in cooling rate $T_g$ decreases about 3-5 K.¹¹ In order to obtain a more accurate estimate of cooling rate dependence of $T_g$ for a specific polymer,
information about the temperature dependence of relaxation times in the temperature range including $T_g$ is needed.\textsuperscript{2}

Figure 1.4. Specific Volume vs. Temperature plot of Poly(vinyl acetate) (PVAc). The change in slope is a result of liquid to glass transition. The thermal expansion coefficient is shown for the fast-cooling curve (0.02 hr).\textsuperscript{10}

1.1.4 The Kauzmann Paradox: Entropy Catastrophe

In his 1948 seminal paper\textsuperscript{12}, Kauzmann plotted entropy difference between liquid and stable crystal versus temperature scaled by melting entropy and melting temperature
respectively. (See Figure 1.5) The extrapolation to lower temperatures of available experimental data for a variety of glass formers would result in the vanishing of the entropy difference between the liquid and crystal at a finite temperature, which was later termed conventionally as the Kauzmann temperature, $T_k$. In other words, the entropy of the liquid becomes lower than the entropy of the corresponding crystals at temperatures below $T_k$ and therefore constitute the entropy crisis or Kauzmann’s paradox. This entropy difference, sometimes called excess entropy, is roughly equal to the configurational entropy when we assume vibrational entropy of the liquid is similar to that of the crystal. Basically, Kauzmann found that if we were to trust the extrapolations, the configurational entropy disappears at some temperature below dynamic glass transition temperatures. Because configurational entropy cannot be negative and only the vibrational entropy is allowed to decrease further, the total entropy must have a kink at $T_k$. This fact leads to the question of whether $T_k$ sets a lower temperature limit for the liquid to stay liquid. Whether there is a pure thermodynamic transition at $T_k$ is still being debated. Objections involve the non-coincidence of $T_k$s with different observables and the non-convergence of the free energy of the two phases at $T_k$. Kauzmann personally did not believe in a pure thermodynamic transition and resolved this problem by arguing that the kinetic spinodal always intervene before temperature is lowered to $T_k$. 
1.1.5 Types of glass formers

Although man-made silicate glass has been known for more than nine thousand years, it was not until the 1930s when people started to study its structure and attempted to summarize the requirements for certain materials to be glass formers."Among those studies, Zachariasen’s 1932 study\textsuperscript{15} is the most cited which allegedly\textsuperscript{16} due in part to his famous and frequently reproduced two-dimensional representation of the proposed three-dimensional \( \text{A}_2\text{O}_3 \) random network. (See Figure 1.6.) At the time, oxides were the only known glass formers and thus rules proposed in his study were only applicable to oxide glasses.
Nevertheless, the idea of a covalently bonded continuous random network is still widely used and accepted as the basis for understanding the structure of glasses despite the fact that direct experimental detection of the three-dimensional atomic arrangements is still technologically not achievable. However, recent scanning transmission electron microscopy (STEM) study\textsuperscript{17} of bilayer vitreous silica on graphene substrate directly imaged the 2-D atomic structure which resembles Zachariasen’s 2-D diagram. (See Figure 1.7.)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{glassy_A2O3.png}
\caption{Two-dimensional schematic diagram of glassy $\text{A}_2\text{O}_3$.\textsuperscript{16}}
\end{figure}
Nowadays, many different types of materials have been prepared into a glassy state. The renewed question should be “what do we need to do to produce materials in their glassy state?” instead of “what kind of material can form a glass?”, because essentially all materials can be rendered amorphous.\textsuperscript{18}

Generally, glass-forming materials are categorized by the group and properties of their constituent elements, \textit{e.g.}, organic, inorganic, metallic, ionic, chalcogenide etc., and by their sizes or topologies, \textit{e.g.}, small molecule, polymer, and networks. Making the categorization more confusing, combinations of the foregoing categories prevail in the literature. A unique categorization, based on the decreasing degree of importance of covalent bonds to glass formation, has been used.\textsuperscript{19} A network glass like silica glass (SiO\textsubscript{2}), for instance, needs the interchanging of its covalent bonds to manifest its glass transition, while

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Atomic-resolution annular dark-field scanning TEM (ADF-STEM) image of 2D silica glass supported on graphene with its colored carton representation on the left. (Red represents oxygen atoms and yellow represents silicon atoms)\textsuperscript{17}}
\end{figure}
polymer glasses have their backbone bonds intact, but with the diffusional motion of chain segments taking on the pivotal role. Due to the wide range of materials involved, a perfect categorization does not exist. Nevertheless, the foregoing method summarized in Table 1.1 is only intended to offer a general sense of the groups of materials often recognized as glass formers.

Table 1.1. Types of glass formers.\textsuperscript{19–21}

<table>
<thead>
<tr>
<th>Category</th>
<th>Relevant interactions*</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Network glasses</td>
<td>Interchange of primary bonds; i.e., covalent bonds</td>
<td>Silica (SiO\textsubscript{2}), Boric oxide (B\textsubscript{2}O\textsubscript{3}), Phosphoric oxide (P\textsubscript{2}O\textsubscript{5})</td>
</tr>
<tr>
<td>Modified networks</td>
<td>Interchange of primary bonds or diffusional motion of broken chain segments</td>
<td>SiO\textsubscript{2}+Na\textsubscript{2}O, P\textsubscript{2}O\textsubscript{5}+K\textsubscript{2}O</td>
</tr>
<tr>
<td>Linear or Branched polymer</td>
<td>Diffusional motion of chain segments</td>
<td>All organic polymers and some inorganic polymers; i.e., Sulfur, Selenium, Phosphate</td>
</tr>
<tr>
<td>Hydrogen bonded glasses</td>
<td>Interchange of hydrogen bonds</td>
<td>Ethanol, n-Propanol, Propylene glycol, 1,2-Propanediol, Glycerol</td>
</tr>
<tr>
<td>Small molecule glass formers</td>
<td>Motion of the whole molecule and van der Waals’ interaction</td>
<td>Orthoterphenyl, Toluene, 2-Methyl pentane, 2-Methyltetrahydrofuran, Dibutyl phthalate</td>
</tr>
<tr>
<td>Salt and salt mixtures</td>
<td>Interchange of Ionic bonds</td>
<td>ZnCl\textsubscript{2}, BeF\textsubscript{2}, K\textsubscript{2}CO\textsubscript{3}:MgCO\textsubscript{3}, KNO\textsubscript{3}:Ca(NO\textsubscript{3})\textsubscript{2}</td>
</tr>
<tr>
<td>Solution of Electrolytes</td>
<td>Collective effects of all possible intermolecular interactions; ionic, H-bonding, van der Waals.</td>
<td>H\textsubscript{2}O-HCl, H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O, and even pure H\textsubscript{2}O</td>
</tr>
<tr>
<td>Metallic glass</td>
<td>Metallic, ionic, covalent bonds</td>
<td>Fe\textsubscript{83}B\textsubscript{17}, Fe\textsubscript{80}P\textsubscript{13}C\textsubscript{7}, Pd\textsubscript{82}Si\textsubscript{18}</td>
</tr>
</tbody>
</table>

* The nature of bonding in some cases are not clear and therefore exceptions exist.

Besides the atomic or molecular glasses (formed at atomic or molecular level) mentioned above, analogies with different length and time scales are available in other systems. Colloids particles with micrometer size scale can be studied by microscopy and exhibit
similar growth of viscosity and relaxation time, dynamical heterogeneity, aging behavior, and variation in fragilities as regular atomic glasses do, when replacing temperature with volume fraction as the variable to control liquid to glassy behaviors. As shown in Figure 1.8(a), a certain volume fraction of the colloidal spheres exhibit glassy properties. Biological systems with larger length scales in their highly dense states are illustrated in Figure 1.8(b) and (c) as being analogous to glassy behaviors.

![Figure 1.8](image)

**Figure 1.8.** (a) Micrometer-sized colloidal spheres (b) Dense viscous droplet of living cells squeezed between two plates (c) Slow dynamics of a dense swarm of ants.

### 1.1.6 Working definitions with respect to specific T\textsubscript{g} observing instruments

It is not uncommon that the value of the reported T\textsubscript{g} for the same polymer varied by more than 20 °C when different deterministic methods were used; e.g., dynamic loss tangent peak vs. dilatometry operated at 1°C/min. We recall the empirical relationship between temperature and a molecule’s dynamics; 20 degree higher in temperature corresponds to roughly six orders of magnitude increase in the dynamics. Clearly, these two reported T\textsubscript{g}s must not mean the same thing for the polymer, and using the wrong T\textsubscript{g} without any reference to the method of determination is useless and even dangerous when critical
application is concerned. For this reason, it is beneficial to summarize some common measurement techniques so that the physical meaning of the reported $T_g$ in each measurement is clear and an informed selection can be made.

1.1.6.1 Differential Scanning Calorimetry (DSC)

DSC measurements detects $T_g$ by locating a step increase in heat capacity $C_p$, which occurs over a relatively wide temperature range. A typical DSC thermogram plots heat flow against temperature, the shape of which resembles the heat capacity vs. temperature curve. The difference is that heat flow is defined as heat divided by time and therefore depends on the heating rate. The higher the heating rate, the more heat is needed per unit amount of time to increase the temperature by the same amount and finishes earlier. Thus, it is often suggested to increase the heating rate in order to increase the absolute magnitude of the jump in the heat flow for detecting weak $T_g$ signals. Obviously there is a trade-off between DSC’s sensitivity and temperature lag, a balance of the two is usually selected to carry out the measurement. Nevertheless, heat flow vs. temperature curve can be viewed intuitively as the heat capacity change over temperature. The midpoint temperature is usually selected to represent $T_g$ and is defined as the temperature at half-height of the heat capacity change between the extrapolated onset and extrapolated end temperatures. The two extrapolated temperatures are the points of intersection of the tangent line drawn at the point of greatest slope with the baselines before and after the transition and is illustrated in Figure 1.9. It is also shown that the enthalpy curve (broken line) of the system can be calculated as the integral of the heat capacity curve (solid line), and the fictive temperature can be obtained as the temperature at the point of intersection of the extrapolated
glass and liquid lines. It is also worth mentioning that DSC is conventionally used to measure T_g on heating due to the difficulties in the calibration of the cooling rate. Nowadays, new instrument and new calibration material, such as some liquid crystalline material which do not supercool, are available to facilitate an accurate T_g determination on cooling. Nevertheless, most of the T_g's reported in the literature were measured during heating.

![Figure 1.9. Specific heat capacity C_p and enthalpy H versus temperature for an uncured acrylate adhesive, where T_b is the beginning of the transition, T_e is the end of the transition, T_i is the extrapolated onset, T_2 is the extrapolated end.](image)

1.1.6.2 Dilatometry

Though it is laborious, dilatometry is the most important classical method for the determination of T_g based on the detection of the change in the coefficient of thermal expansion, i.e., the rate of change of specific volume with temperature, when going through T_g. Most common types of dilatometer use the fluid confinement method to measure
volume change or a push-rod method$^{33}$ to measure length change. They both have the advantage of highly accurate continuous measurements of volume or length as a functions of time, temperature, and pressure.$^9$ The classical set-up used in Kovac’s PVAc study is shown in Figure 1.10. Modern set-ups usually are equipped with a linear variable differential transformer (LVDT) for automated measurements and a detachable sample container for eliminating the tedious glass sealing process.$^{29}$

![Figure 1.10. Assembling steps of Bekkedahl’s volume dilatometer]$^{31}$
1.1.6.3 Thermomechanical Analysis (TMA)

Features of Thermomechanical Analysis (TMA) are the use of a non-oscillatory mechanical probe and the measurement of its displacement as a function of time or temperature.\textsuperscript{34} The main variations of TMA instruments are that of the design and working mode of the probe.\textsuperscript{35,36} Figure 1.11 shows examples of TMA instrument geometries and their operating modes. It is common to refer to TMA operated under expansion mode with no load using a flat probe as linear thermodilatometry owing to its ability to measure linear thermal expansion coefficients. It has the advantage of employing smaller samples than required for dilatometry.\textsuperscript{33} Compared to DSC, it has the disadvantage of limited heating rate due to the heat transfer problem.\textsuperscript{37}

![Figure 1.11. TMA probe geometries and operating modes\textsuperscript{34}](image)

There are some differences between expansion mode and penetration mode. Expansion mode detects positive abrupt changes in the slope of thermal expansion, while the penetration mode identifies the abrupt negative changes in the slope as the signal of a transition. The intersections of the two tangent lines of the curve below and above the transition in each mode are termed $T_g$ and $T_s$ (softening temperature) respectively. $T_s$ depends on the
applied force as well as the contact area, and thus has different physical meaning than $T_g$.\textsuperscript{35}

Figure 1.12 demonstrates the effect of load on the TMA curve using the penetration probe. The thermal curve without added load manifests expansion behavior similar to that of the true expansion mode. Three extrapolated transition temperatures, though different, are in close proximity to each other, and therefore it is not uncommon to see reported $T_g$s which are actually $T_s$ values.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{tma_penetration_effect_of_loading.png}
\caption{Effect of loading on TMA curve under penetration mode.\textsuperscript{34}}
\end{figure}

1.1.6.4 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) commonly\textsuperscript{38} applies a known sinusoidal strain to the sample and measures the resulting stress. The ratio of stress to strain is the dynamic mechanical modulus, which contains in-phase ($E'$ or $G'$) and out-of-phase ($E''$ or
G") components. The in-phase components, termed storage moduli, measure the mechanical energy stored per cycle and the out-of-phase components, termed loss moduli, show the energy dissipated. The ratio of loss modulus to storage modulus is referred to as loss tangent or tangent delta. There are three common criteria for determining $T_g$ from DMA. The intersection of two tangent lines, one originating from the glassy state and the other from the point of greatest slope during the storage modulus drop, is defined as $T_g$, which is suggested by ASTM E1640-13. In addition, peaks of loss modulus and tangent delta are also reported as $T_g$ by others. As can be seen from Figure 1.13, $T_g$ determined from storage modulus is generally lower than that from the peak of loss modulus, which is in turn lower than that of the tangent delta. There are also many variations of measurement geometries and modes used in DMA and the data obtained from any of these are in principle equivalent.

$T_g$ values determined from DMA depend not only on the criterion chosen, but also on the frequency of the applied stimulus. Figure 1.14 shows that increasing frequencies cause the increase in $T_g$s (defined as the highest temperature peak of loss modulus, also known as the $\alpha$ relaxation peak). It is also apparent that, at very high frequency, the $\alpha$ and $\beta$ relaxation peaks overlap with each other. For the sake of reproducibility, a frequency of 1 Hz which gives the $T_g$ value very close to DSC’s is often used. DMA has particular advantage over DSC in measuring $T_g$ of highly crystalline, cross-linked, or multicomponent materials, where DSC’s signal of change in the $C_p$ is very weak.
Figure 1.13. Isochronal plot of viscoelastic functions from DMA.\textsuperscript{38}

Figure 1.14. Frequency dependence of loss maxima position on the temperature scale for $\alpha$ and $\beta$ relaxations in poly(methylacrylate).\textsuperscript{38}
1.1.6.5 Dielectric Relaxation Spectroscopy (DRS)

Dielectric spectroscopy’s working principle is analogous to DMA’s in the sense that sinusoidal voltage is used as the external stimulus in place of mechanical deformation. Similarly, the complex permittivity has both real and imaginary components. The real component indicates the capacitive characteristic or energy storage ability, while the imaginary component is associated with the conductive property or energy loss.\textsuperscript{41,42} Isothermal frequency scans are usually used in temperature increments of 0.2K.\textsuperscript{43–45} Loss spectra of the $\alpha$ relaxation at each temperature are usually fitted with an empirical Havriliak–Negami (HN) equation and its fitting parameters can be used to calculate the frequency (relaxation time) of the maximum loss. Temperature dependence of the relaxation time is then fitted with the Vogel–Fulcher–Tamman (VFT) equation, which describes non-Arrhenius temperature dependence near $T_g$. From the fit, the interpolated temperature at which the relaxation time equals 100s is customarily defined as $T_g$.

1.1.6.6 Ellipsometry

An ellipsometer equipped with temperature control accessories is able to measure film thickness as a function of temperature and therefore $T_g$ can be readily determined as the intersection of the extrapolations from glassy and rubbery lines.\textsuperscript{46} (See Figure 1.15) It is also possible to obtain $T_g$ from the thermal expansivity as a step going through the glass transition and is analogous to $C_p$ and other second derivative properties as described in Section 1.1.2.
1.1.6.7 Fluorescence spectroscopy

Fluorescence spectroscopy utilizes the temperature dependence of the fluorescence of dye molecules, especially their solvatochromic property, which is believed to be sensitive to local stiffness and modulus.\textsuperscript{47,48} 1-pyrenylmethyl methacrylate (MPy) is often used as a dye labeled monomer, which can be copolymerized into the polymer of interest in a trace amount $\sim 0.7$-$1.2$ mol\%.\textsuperscript{47,48} $T_g$ can be determined from the temperature dependence of the intensity ratio of the third to first vibrionic band peaks ($I_3/I_1$) of the dye. (See Figure 1.16)
Figure 1.16. a) Example of normalized extrinsic fluorescence spectra of blend of MPy-labeled PMMA in PEO at 150 °C (bottom), 100 °C (middle), and 50 °C (top) b) Intensity ratios ($I_3/I_1$) are plotted against temperature, solid lines are linear regressions from rubbery and glassy results separately. 47
1.2 Classical Theories of Glass Transition

1.2.1 Gibbs-DiMarzio-Adam Theory

In his 1956 paper, Flory\textsuperscript{49} developed a lattice model of polymer solutions to specifically account for the conformational contribution of converting polymer chains in perfectly ordered states to randomly disordered states which effect was previously omitted. The concept of a temperature dependent equilibrium flexibility, $f$, was introduced and was defined as the fraction of bonds bending out of the co-linear lowest energy states. Flexibility decreases as temperature is lowered. When $f$ is sufficiently small and chain length is sufficiently long, there exists a situation when the disordered state become less stable than the perfectly ordered state. An apparent paradox arises for even smaller $f$s, in which case the expression for total number of arrangements drops below unity, which is unphysical and can be avoided by prior invocation of crystallization.\textsuperscript{49,50}

This resolution for the paradox was not satisfying Gibbs, who later in the same year wrote a short letter questing its implication to the noncrystallizing polymers and its possibility of being interpreted as glass transition.\textsuperscript{50} Two years later, Gibbs and DiMarzio (GD)\textsuperscript{51-53} proposed a second-order transition at temperature $T_2$, at which the configurational entropy vanishes. In the view of GD theory, $T_g$ is the experimental manifestation of the underlying thermodynamic second-order transition which sets the lower limit at infinite time scale. The variations of $T_2$ with molecular weight\textsuperscript{51}, percentage and flexibility of plasticizer\textsuperscript{54}, and composition of copolymers\textsuperscript{52} mirror perfectly the variation of $T_g$s with these respective variables. However, it does not explain why the decrease of configurational entropy results in the slowing down in the dynamics.
In 1965, Adam and Gibbs (AG) published their study “On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids”, which effectively connected dynamics with thermodynamic. It relates the size of the cooperative rearranging region (CRR), which is defined as the smallest region that can change configurations independently from its neighbors, to the configurational entropy of the macroscopic sample as an inverse function. When the energy barrier for the rearrangement is assumed to be directly proportional to the size of the CRR, one can derive an Arrhenius expression for the relaxation time:\[^{13}\]

\[
\tau_R = \tau_0 e^{\frac{B}{T S_c(T)}}
\]

where \( B \) is constant, and \( S_c(T) \) is the configurational entropy of the sample. Further assumption can be made of the nearly temperature independence of \( \Delta C_p \) between the specific heat of the equilibrium liquid and glass at \( T_g \). Both Williams-Landel-Ferry (WLF) and Vogel-Fulcher-Tammann (VFT) types of empirical relationships can then be derived.\[^{13,55}\]

Nowadays, AG Theory is still influencing new theories, e.g., Freed’s Generalized Entropy Theory, which was built on Lattice Cluster Theory (LCT), invokes AG’s relationship between structural relaxation time and configurational entropy. Modern theory like random first-order transition theory (RFOT) weaved together independent lines of research into the same framework; AG theory is one of them and the other two being mode-coupling theory (MCT) and spin glass theory.\[^{58}\]

1.2.2 Free Volume Theory

Despite its variations in possible definition, free volume concept has been pervasive in the literature for explanation of polymers’ various behaviors associated with the
glass transition. A common way of introducing free volume concept into different studies\textsuperscript{20,60,61} is through the invoking of Doolittle’s equation,\textsuperscript{62} which relates the viscosity to fractional free volume:

\[
\eta = Ae^{B_{V_o}^{V_f}}
\]

where \(\eta\) is viscosity, A and B are constants, \(V_o\) is the occupied volume taken as the extrapolated absolute zero volume, and \(V_f\) is the free volume (total volume minus occupied volume). It is basically replacing the temperature term with relative free volume ratio \((V_f/V_o)\) in a simple Arrhenius type expression of a so-called Andrade equation.\textsuperscript{62} Volumes are then related to temperature through the aid of coefficients of thermal expansion.

At this point, it is necessary to clarify some of the differences that exist in defining the free volume. Free volumes are often obtained in a same way as the difference between the total volume and the occupied volume but have different meanings due to the different definitions of the occupied volume. In Doolittle’s definition the occupied volume is a temperature independent hard-core volume, while in Fox and Flory’s papers\textsuperscript{63,64} the occupied volume is a temperature dependent volume taking into account the vibrational contribution. Therefore, Doolittle’s free volume basically follows the rate of change of the total volume whereas Fox and Flory’s free volume’s rate of change excluded the contribution from the solid. (Volumes of glass and crystal respond similarly to temperature\textsuperscript{2})

It is now obvious that a common way\textsuperscript{20,60} of defining the coefficient of thermal expansion for free volume, \(\alpha_f\), as the difference between that of the liquid and glass is actually referring to Fox and Flory’s definition. It is natural to follow that this value goes to zero when temperature is lowered below glass transition temperature; free volume is
effectively “frozen in” and remains constant. However, in Doolittle’s definition $\alpha_f$ is non-zero both above and below glass transition temperature; free volume decreases continuously when temperature is lowered with the rate of shrinkage greater and smaller, above and below $T_g$, respectively. White and Lipson\(^6\) in their perspective paper suggested to use “total free volume” for referring to free volume of the Doolittle type and use “excess free volume” to address the free volume of Fox and Flory’s. See Figure 1.17 for illustration of different types of free volumes.

**Figure 1.17 Differences between definitions of free volumes existed in the literature.**\(^6\)

Williams-Landel-Ferry (WLF)\(^6\) employed “fractional free volume”, $f$, defined as excess free volume divided by total volume instead of using the total free volume to hard-core volume ratio or so-called “relative free volume”:

$$\eta = Ae^{B/T}$$
Constant B was assumed to be of the order of unity and was taken as 1. Take nature logarithms on both sides gives: 
\[ \ln \eta = \ln A + 1/f. \]
Two equations can be written for temperature \( T \) higher than \( T_g \) and for reference temperature \( T_g \). Subtract the later from the former gives logarithm of viscosity ratio in base \( e \):

\[
\ln \frac{\eta_T}{\eta_{T_g}} = \frac{1}{f_T} - \frac{1}{f_{T_g}}
\]

Substituting fractional free volume as a function of temperature into the Doolittle’s equation followed by simple algebraic rearrangements and changing of base from \( e \) to 10, WLF form results:

\[
\log a_T = -\frac{1}{2.303 f_{T_g}} \left[ \frac{T - T_g}{\left( \frac{f_{T_g}}{\alpha_f} \right) + T - T_g} \right]
\]

where \( \alpha_f \) is the coefficient of thermal expansion of the free volume, \( f_{T_g} \), is the fractional free volume at \( T_g \). By comparing to the universal constants, \( f_{T_g} \) was found to be 0.025 and \( \alpha_f \) to be 4.8×10\(^{-4}\) per degree. Fox and Flory, however, considered these constants to vary among different materials. Nevertheless, they did hold the view of glass being an iso-free-volume state.\(^{60,64}\)

The main objection to the free volume theory and other theories based on density fluctuation is that new experimental results\(^ {61,65,66}\) indicated volume or density is not the cause of the slow dynamics near \( T_g \); it manifests similar slow down with a constant volume or fixed density experiment just as it would in a constant pressure study.
1.3 Chemical Structures and Polymer Glass Transition Temperatures

1.3.1 Motivations

Among the most important parameters characterizing the behaviors of polymers is their glass-transition temperature, $T_g$, which is essentially the temperature where the chains in a bulk amorphous polymer solid begin to change conformations and move, resulting in dramatic alterations in their macroscopic behaviors. Below $T_g$ amorphous bulk polymers are generally glassy, with high moduli and low reversible extensibilities. Above $T_g$, they become easily deformable and are eventually able to evidence viscous flow. While semi-crystalline polymers cannot flow above $T_g$, the chains in their non-crystalline regions do gain limited conformational mobility, and generally confer an overall substantial increase in sample toughness, because their crystallites are now embedded in and held together by a much softer amorphous matrix. Due to the dramatic changes occurring in the behavior of polymer materials as they are warmed above their glass-transitions, including their time-dependent responses, their processing and use temperatures must necessarily be higher and lower than their $T_g$s for an amorphous thermoplastic application.

Though it is not trivial to determine the $T_g$s of some highly crystalline polymers,$^{67}$ all polymers should have physically meaningful $T_g$s due to the nature of the chain folding crystallization mechanism, which precludes them from being 100% crystalline. Moreover, polymers are not the only category of material that forms a glass. Any liquid, without being interrupted by crystallization, is bound to acquire amorphous rigidity upon cooling and therefore becomes a glass.$^{11,68}$ Hence the prerequisite of forming a glass is simply the existence of some barriers to crystallization resulting from the asymmetry in the chemical structure of the material and/or from the insufficiency of the thermal energy to reorganize.
molecules into crystals.\textsuperscript{19} 2-Methylpentane is such a molecule that possesses sufficient asymmetry in chemical structure to prevent itself from crystallization. For window glass, on the other hand, rapid cooling from above the liquidus temperature to below the optimal crystallization temperature is required. The viscosity increases from $10^2$ poises in the melt to about $10^{13}$ poises in the glass where it becomes so viscous that the system drops out of equilibrium; this departure from the equilibrium density constitutes another definition of glass transition temperature.\textsuperscript{69} Despite its appearance in a wide variety of materials, from covalently bonded inorganic networks; long-chain polymers; hydrogen bonding species; and ionic salt mixtures; to metallic system, the nature of this slowing-down into a glassy state is still not understood.\textsuperscript{68,70–73} Furthermore, the glass-transition temperatures ($T_g$s) observed for chemically distinct polymers range over several hundred K whereas the molecular bases for this wide variability are still largely unknown.

Because of the absence of a satisfactory theoretical foundation, sometimes the best we can do in terms of predicting unmeasured $T_g$s of new polymers is through the use of a pragmatic, empirical, additive method\textsuperscript{74}, although it has the apparent drawback of possibly being inapplicable to the prediction of the $T_g$s of new polymers not included in the empirical dataset.\textsuperscript{75}

\subsection{1.3.2 The complexity of the task}

One of the reasons that glass physics is a somewhat contentious subject seems to result from its non-equilibrium nature.\textsuperscript{73} There are many experimental variables that affect the glass transition temperature of a polymer, e.g., the pressure, the rate of cooling, the
physical aging, the number average molecular weight, the degree of crystallinity, the morphology, etc. In addition, three factors pertinent to the molecular bases for their $T_g$s are commonly suggested as being pivotal: 1. The inherent conformational flexibilities of their individual chain backbones; 2. The sizes or steric bulk of their side-chains; and 3. The interactions (steric, dipolar, hydrogen-bonding, van der Waals, etc.) between polymer chains.\textsuperscript{11,76} For example, the $T_g$s of the polymer pairs Poly(ε-caprolactone) (PCL) and Poly(ε-caprolactam) (nylon-6) and Polyethylene and atactic-Polypropylene differ in both cases by \~100 °C. While the first pair have the same conformational behavior and no side-chains, but distinct ester and amide group interactions (factor 3.), the second pair have similar and comparatively weaker van der Waals interchain interactions, but distinct conformational behaviors (factor 1.) and w/ or w/o methyl side-chains (factor 2.). From these two comparisons, which ignore the effects of crystallinity on the $T_g$s of their amorphous domains, it is clear all three structural factors can be important in determining the glass-transition temperatures of polymers.

Because these three factors are usually structurally interdependent, it can be difficult to predict or even rationalize the $T_g$s of polymers with different chemical structures. When the $T_g$s of two polymers with different molecular structures, or microstructures, are compared, we have to be aware that more than one of the above factors, and likely all three, will be distinct. This difficulty is clearly illustrated in three very recent experimental and theoretical examinations of the molecular bases for polymer glass-transition temperatures.

Two recent papers, one experimental and the other theoretical, serve to re-emphasize the complex connectivity between various structural factors and their influence on the
glass-transition temperatures, $T_g$s, of polymers. Sokolov et al. attempted to analyze experimentally the effect of polar interactions on polymer dynamics characterized by $T_g$s and fragility indices $m$, where $m = \partial \log(\tau)/\partial (T_g/T)|_{T=T_g}$ is a measure of the slowing down of the motional relaxation time ($\tau$) near $T_g$. They examined polymers that had side-chains of similar sizes, but with different dipole moments either directly attached to or separated by an identical spacer unit from the backbone. Their investigation served as an impetus for Xu and Freed to extend their generalized entropy theory (GET) of glass formation to account for specific van der Waals interactions between and among the molecular components of polymers, their backbones and side-chains. Individually or taken together, these papers illustrate the complex nature of the molecular/structural bases of polymer $T_g$s.

The experimental investigation by Sokolov et al. compared the $T_g$s and fragilities, $m$, of three different classes of polymers: 1. Polypropylene (PP), poly(vinyl chloride) (PVC), and poly(vinyl alcohol) (PVOH), 2. Polystyrene (PS), poly(2-, 3-, and 4- methystyrene) (P2,3,4MS), and poly(2-, 3-, and 4-chlorostyrene) (P2,3,4ClS), and 3. Polyisoprene (PIP) and polychloroprene (PClP). These were selected to provide comparisons between polymers with nonpolar and polar groups attached directly to (PP, PVC, PVOH) or that were separated by similar spacers from the backbone (PS, P2,3,4MS, P2,3,4ClS) and between polymers with directly attached non-polar or polar groups, with distinct backbone flexibilities (PP, PVC, PIP, PClP).

However, their selection of polymers for comparison to learn about the effect of polar interactions on polymer dynamics characterized by $T_g$s and $m$s, were in most instances less than optimal. PP, PVC, and PVOH and PIP and PClP not only have non-polar groups or different directly attached polar groups, but their conformational flexibilities are
distinct as well. Comparison of their chain dynamics cannot therefore be attributed solely or even principally to different polar interactions. Similar differences in conformational flexibilities also apply to the comparison of chain dynamics in PS, P2MS, P3MS, P2ClS, and P3ClS. Only in the case of PS, P4MS, and P4ClS is the comparison between T_g's and m's likely uncomplicated by distinct conformational flexibilities. This is because the distant para-substituents -CH_3 and -Cl are not expected to alter the conformational flexibilities of P4MS and P4ClS from that of PS.^{78,79} However, PS, P4MS, and P4ClS have para-phenyl ring substituents that differ in sizes, as well as charges, which still complicates the comparison of their T_g's.

Interestingly, Sokolov et al.'s experimental study^{77} inspired an even more recent theoretical paper “Generalized Entropy Theory of Glass formation in polymer Melts with specific Interactions” by Xu and Freed.^{56,57} They extended Freed’s generalized entropy theory (GET)^{80,81} to include specific interactions that reflect the molecular structures of polymer repeat units. Prior applications of the GET were limited to the simplest polymers, with all united atom groups within their repeat units, which interacted with a common averaged van der Waals energy. Figure 1.18 describes the extension of GET used by Xu and Freed that includes 3 distinct van der Waals energies for interactions between backbone and non-terminal side chain units (\(\epsilon_{11}\)), between backbone and terminal side-chain units (\(\epsilon_{12}\)), and between the terminal side-chain units (\(\epsilon_{22}\)). In addition to these specific van der Walls interactions, the lattice cluster theory (LCT),^{57} which is employed in the GET also includes a measure of chain stiffness represented by bending energies for both the polymer backbones (\(E_b\)) and their side-chains (\(E_s\)).
Consequently, Xu and Freed’s extension of the GET of glass formation to include specific interchain interactions has two van der Waals energy parameters ($\epsilon_{11}$ and $\epsilon_{22}$, since $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$) and two chain stiffness energy parameters ($E_b$ and $E_s$), which may not, as assumed by them, be independent of each other. This makes it difficult to attribute the resulting chain dynamics ($T_g$s and $m$s) to single specific structural sources, such as solely van der Waals interactions or chain stiffnesses.

Though in direct opposition to their stated goals, both papers\textsuperscript{56,77} rather demonstrate the complex connectivity between various structural factors and their influence on the glass-transition temperatures of polymers. More importantly they demonstrate the critical need for isolating the effects of single structural features when comparing polymer $T_g$s, such as is only partially achieved by Sokolov \textit{et al.}\textsuperscript{77} in the case of PS, P4MS, and P4ClS.

The critical nature of isolating the effects of single structural features when comparing polymer $T_g$s received further emphasis from Müller, whose recent review paper\textsuperscript{82} describes the $T_g$s of semiconducting polymers and their impact on the stabilities of polymer solar cells. He points out that “knowledge of the glass transition temperature is critical for (1) optimization of post-deposition processing protocols, (2) the thermal stability of the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{lattice_model.png}
\caption{Lattice model of Xu and Freed for polymer chains in melts with specific interactions.\textsuperscript{56}}
\end{figure}
semiconductor nanostructure, (3) dewetting and delamination of thin films, and (4) the mechanical properties of polymer semiconductors, which must be considered if flexible optoelectronic applications are to be targeted.”

Using the following structural features, Müller attempts to interpret the \( T_g \)s of two classes of semi-conducting polymers, polyfluorenes (PFs) and poly(p-phenylenevinylene)s (PPVs):

1. Constitution of the whole polymer chain: influence of molecular weight
2. Constitution of chain segments: influence of chain rigidity
3. Constitution of a single repeat unit: influence of the length and bulkiness of pendant groups.
4. Influence of \( \pi-\pi \) interactions between polymer chain segments.

Their \( T_g \)s are presented in Table 1.2 and Table 1.3. Though originally derived for flexible vinyl polymers like polystyrene and poly(methyl methacrylate), the effect of molecular weight on the \( T_g \)s of semi-conducting polymers can also be described by the Flory-Fox equation\(^{25}\).

Beginning with the PF polymers shown in Table 1.2, careful examination of their repeat unit structures makes clear that more than one of the four structural factors suggested by Müller as affecting their \( T_g \)s are distinct for each potential pair-wise comparison. The same conclusion also applies to the four PPVs in Table 1.3. For example, choosing to use persistence length \( (l_p) \) as a measure of chain rigidity (structural factor 2), the 3 semi-conducting polymers MEH, PF2/6, and PF8, with \( l_p = \sim 6, \sim 7, \) and \( \sim 8.5 \) nm, respectively, are expected to have \( T_g \)s that increase in the same order. Instead, their corresponding \( T_g \)s are
65-66, 56-80, and 65-72 °C, with ranges reflecting the effect of molecular weight, suggesting that $l_p$s and $T_g$s are not correlated. In further support of this observation are the $l_p$ ~0.9 nm and $T_g$ ~ -3 to 9 °C of regioirregular poly (3-hexyl thiophene) (P3HT) and the $l_p$ ~0.85 nm and $T_g$ ~ 65 to 72 °C of PF8, and the comparison of $l_p$s ~ 0.9 nm, 2.9 nm and $T_g$s ~ (-3 to 9), (12 – 14) °C for regioirregular, regioregular P3HT.

**Table 1.2 Glass Transition Temperature $T_g$s of Fluorene-Based Polymers**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>$M_n$ (kg mol$^{-1}$)</th>
<th>PDI</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F6</td>
<td><img src="image" alt="Structure" /></td>
<td>17</td>
<td>4.1</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Structure" /></td>
<td>16</td>
<td>2.8</td>
<td>103</td>
</tr>
<tr>
<td>F8</td>
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<tr>
<td></td>
<td><img src="image" alt="Structure" /></td>
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<td>2.1</td>
<td>140</td>
</tr>
<tr>
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<td>123</td>
</tr>
<tr>
<td>APFO-18</td>
<td><img src="image" alt="Structure" /></td>
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<tr>
<td>APFO-Green9</td>
<td><img src="image" alt="Structure" /></td>
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</tr>
<tr>
<td></td>
<td><img src="image" alt="Structure" /></td>
<td>10</td>
<td>1.9</td>
<td>192</td>
</tr>
</tbody>
</table>
Regarding structural factor 3 (Influence of the Length and Bulkiness of Pendant Groups), we see in Table 1.3 that PPVs with side-chains have substantially lower T\textsubscript{g}s than unsubstituted PPV. The reduction from the T\textsubscript{g} of PPV is seen to depend on the chemical type of branch, as well as its bulkiness. However, the four PPVs in Table 1.3 are different in structural factors 2 and 4 (Influence of π–π Interactions between Polymer Chain Segments), as well. Based on the first four PF entries in Table 1.2, Müller concludes that the longer the alkyl side chains the lower their T\textsubscript{g}s. Once again, however, this T\textsubscript{g} comparison is rendered suspect because the T\textsubscript{g}s of these PFs may also differ due to structural factors 2 and 4.

Table 1.3 Glass Transition Temperature T\textsubscript{g} of PPV Derivatives\textsuperscript{82}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>(M_n) (kg mol(^{-1}))</th>
<th>PDI</th>
<th>(T\textsubscript{g}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPV</td>
<td><img src="image" alt="PPV Structure" /></td>
<td>-</td>
<td>-</td>
<td>220</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td><img src="image" alt="MDMO-PPV Structure" /></td>
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<td>16.7</td>
<td>18</td>
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<td></td>
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<tr>
<td>MEH-PPV</td>
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<td>1.6</td>
<td>65</td>
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<tr>
<td></td>
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<td>45</td>
<td>3.2</td>
<td>66</td>
</tr>
<tr>
<td>MPE-PPV</td>
<td><img src="image" alt="MPE-PPV Structure" /></td>
<td>53</td>
<td>2.3</td>
<td>111</td>
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<tr>
<td></td>
<td></td>
<td>65</td>
<td>3.9</td>
<td>111</td>
</tr>
</tbody>
</table>
1.3.3 Justifications

Though many experimental studies have been undertaken to establish the connections between the chemical structures and the glass transition temperatures of polymers, we could find none performed on polymers whose microstructures were controlled in a manner that permitted a systematic assessment of the individual contributions made to their $T_g$s by 1. their conformational flexibilities, 2. the steric bulk of their side-chains, and 3. inter-chain interactions.

Consider atactic Poly(Styrene/p-BrStyrene) copolymers obtained by bromination of atactic Polystyrene (PS) as an example, because of the large distances between p-Br in the side-chain and the atoms in the backbone, the conformations of all copolymers are closely similar, independent of composition and sequence of S and p-BrS units. This can be confirmed by their invariant backbone carbon $^{13}$C NMR chemical shifts and by their very similar zero-shear viscosities.$^{83}$ Hence their $T_g$s should not be affected by 1. inherent chain flexibilities, but only by 2. side-chain size and 3. inter-chain interactions. The combination of these two factors cause their $T_g$s to range linearly with composition from 97.2 °C for PS to 140.1 °C for Poly(p-BrS)$^{84}$, and are independent of comonomer sequences.$^{83,84}$

Through the above discussion, the importance of comparing the glass-transition temperatures of polymers that differ in only a single structural feature is emphasized. In such comparisons we must also use polymers with sufficiently high molecular weights and that are or can be quenched into totally amorphous samples.
We attempt to achieve these relevant comparisons of polymer $T_g$s using high molecular weight, amorphous, linear, aliphatic co-polyesters and co-polyamides. This selection was prompted by the facts that the inherent conformational flexibilities of structurally analogous linear aliphatic polyesters and polyamides are virtually identical\textsuperscript{85,86}, they have no side-chains, and the interactions between ester and amide groups are markedly different. Comparison of the $T_g$s of several samples with different quantities and locations of either ester or amide groups enabled us to get a measure of the importance of the relative strengths of the interactions between ester or amide groups and the inherent flexibilities of the compared amorphous, linear, aliphatic co-polyesters and co-polyamides.

1.3.4 Approach

Our approach to this problem is the syntheses and comparison of $T_g$s of structurally analogous copolymer pairs which vary in only one structural factor at a time. With the irregularity introduced by the inherent expected randomness from step-growth copolymerization, the crystallinities of copolymers can be significantly reduced to near or wholly amorphous, leaving the $T_g$s of the polymer samples unaffected by crystallinity. In addition, their molecular weights should be high enough to no longer affect their $T_g$s. Their similar, yet variable and controllable, chemical structures, should provide a means to isolate, and in turn assess, each of the structural factors currently believed to be important in determining their $T_g$s.

An example of such analogous polymer pairs is that of polyesters and polyamides. Ester and amide bonds are both rigidly held together by partial double bonds and therefore result in similar planar structures and largely a $trans$ conformation.\textsuperscript{85} The calculated overall
conformational preferences of their constituent backbones are closely similar\textsuperscript{86}, thereby eliminating factor 1. Limiting our choice to amorphous linear aliphatic copolymer pairs, factor 2 can also be eliminated due to the absence of side chains and the effect of Factor 3 alone can be assessed. (See Figure 1.19)

![Figure 1.19 Evaluation of Factor 3 (relative effect of inter-chain interactions).](image)

Glass transition temperatures of structurally analogous n-nylons and n-polyesters would otherwise make perfect analogous pairs if they were able to be quenched into wholly amorphous samples and their T\textsubscript{g}s measured by uniform procedures. (See Figure 1.20) This example clearly shows that the relative effect of hydrogen-bonding vs. dipole-dipole inter-chain interactions alter the glass transition temperature by over 100K. In addition, the glass transition temperatures of both series generally increase with the increase in the number of functional groups per methylene group, though those of polyesters with lower ester group densities show higher experimental values than we expected, probably due to the increasing difficulty of quenching them into the amorphous state due to increasing crystallizabilities. In fact, the intercept with y-axis of the extrapolated line using values from polyesters with higher ester group densities falls in close proximity to what is considered to be the true glass transition temperature\textsuperscript{74} of “amorphous” Polyethylene (PE).
Figure 1.20 Polymer glass transition temperature vs. their functional group density (number of functional groups divided by number of methylenes in the repeating unit).87,88

The profound effect of crystallinity on polymer glass transition temperatures calls for the need to synthesize wholly amorphous samples for the purpose of studying their glass transition temperatures. There are many reports of the syntheses and behaviors of copolyesters and copolyamides, but in almost all instances wholly amorphous samples were not obtained. In the few instances where they were amorphous, their divergent chemical structures prevented the separate assessment of the potential structural factors suggested to influence their glass transition temperatures.

For example, a series of amorphous copolyesters of Poly(ε-caprolactone) (PCL) and Poly(D,L-lactic acid) (PDLLA) were described.89 Unfortunately for our purposes, one of their repeat units is un-branched (PCL), while the other has a methyl side-chain with two different modes of stereo-attachment (PDLLA). Olson et al.90 described a series of amorphous copoly(ester/ether) pre-polymers of low molecular weight that were used for
subsequent cross-linking to form amorphous elastomers. However, one of the repeat units contained a double bond for cross-linking, while the other was fully saturated. Brown and Sheares\textsuperscript{91} also succeeded in synthesizing amorphous polyesters, using ring-opening polymerization of a variety of cyclic diacids and anhydrides. All were unsaturated, but, again unfortunately, contained a variety of ring structures in their backbones. An example of a commercialized amorphous copolyester was made using terephthalic acid and two aliphatic diols, one linear and the other cyclic.\textsuperscript{92} Attempts of synthesizing linear aliphatic amorphous polyamides and polyesters will be discussed separately in the subsequent chapters.

Selection of analogous pairs can be extended to include high molecular weight linear and singly-branched polyester and polyamide samples that are wholly amorphous to further draw $T_g$ comparisons between analogous aliphatic polyester and polyamide samples, like those in Figure 1.21 and Figure 1.22, that differ in only a single structural factor. Hopefully this will enable us to determine the relative magnitudes of factor 1. (Inherent chain conformational flexibility) and factor 2. (Sizes and steric bulk of side-chains) and how they rank in importance to factor 3. (Inter-chain interactions)

\textbf{Figure 1.21 Evaluation of Factor 1 (conformational flexibilities of individual chain backbones)}
Figure 1.22 Evaluation of Factor 2 (steric interactions of side-chains)
Chapter 2  The Glass Transition Temperatures of Amorphous Linear Aliphatic Polyesters

2.1  Abstract

A series of wholly amorphous linear aliphatic co- and tetra- polyesters were synthesized via bulk melt step-growth polymerization, and their glass transition temperatures were determined using DSC and were essentially unaffected by crystallinity. The glass transition temperatures of the polyesters increase linearly with the ratio of ester groups per methylene group. Extrapolations of the ratio to zero ester group content gave a reliable value for the \( T_g \) amorphous polyethylene (PE). The experimental \( T_g \)s manifest a steeper slope on the \( T_g \) vs. ester group content plot compared to those calculated using Van Krevelen’s group contribution method. The intramolecular equilibrium flexibilities were evaluated through the calculation of conformational entropies of individual polymer chains approximated by considering solely the short-range interactions between neighboring groups, as embodied in their RIS conformational models. Their calculated conformational entropies decrease linearly with increasing ester group content.

2.2  Introduction

Despite the long history of recognizing the profound effects of chemical structure on the glass transition of polymers, modern theories have yet to develop direct connections between model compounds and a myriad of real polymers of practical importance, exceptions being only the simplest monomeric structures. The reason for this lag of theoretical understanding, is two-fold:
Firstly, factors pertinent to the molecular bases of polymer glass formation are usually structurally interdependent; it can be difficult to isolate a single effect when comparing different chemical structures. *e.g.*, the following factors are commonly suggested as being pivotal: 1. The inherent conformational flexibilities of individual polymer chain backbones; 2. The sizes, steric bulk, and the relative flexibility of their side-chains; and 3. The interactions (steric, dipolar, hydrogen-bonding, van der Waals, etc.) between polymer chains.\textsuperscript{11,76}

We have to be aware that more than one of the above factors, and likely all three, will be distinct by changing the monomeric structure. This difficulty is clearly recognized in very recent experimental and theoretical examinations of the molecular bases for polymer glass formation.\textsuperscript{56,77,93,94}

Secondly, experimental studies performed on polymers whose microstructures were controlled in a manner that permit systematic assessments of the individual structural contribution to polymer glass formation are scarce, so the relative importance of each factor on the glass formation of real polymers is largely unknown. Undoubtedly, the lack of this experimental information deprives theoreticians of the ability to test a theory’s predictive power against the glass-transition behaviors of real polymers.

In order to select model polymers that differ in only a single structural feature, sufficient theoretical or experimental evidence indicating the similarities of all other factors except the one being compared need to be established. Consider atactic poly(styrene/p-Br-styrene) copolymers obtained by bromination of atactic polystyrene (PS) as an example. Because of the large distances between p-Br in the side-chain and the atoms in the backbone, the conformations of all copolymers are closely similar, independent of composition and sequence of S and p-BrS units. This can be confirmed by their invariant backbone
carbon $^{13}$C NMR chemical shifts and by their very similar zero-shear viscosities.\textsuperscript{83} Hence their $T_g$s should not be affected by 1. inherent chain flexibilities, but only by 2. side-chain size and 3. inter-chain interactions. The combination of these two factors cause their $T_g$s to range linearly with composition from 97.2° C for PS to 140.1° C for Poly(p-BrS)\textsuperscript{84}, and are independent of comonomer sequences.\textsuperscript{83,84}

In another study, the $T_g$s of partially Sulfonated Polystyrene have been found to increase linearly with the percent of sulfonation.\textsuperscript{95} The linearity of copolymers’ $T_g$ dependence on composition irrespective of their comonomer distribution and the chemical nature of the substituents confirmed that conformational characteristics were unaffected and that the sizes and interactions contributed in the same manner, though with presumably a different magnitude, to the increase of the $T_g$s of the copolymers. A recent experimental study\textsuperscript{77} confirmed this point. Comparisons among polystyrene (PS), poly(4-methystyrene) (P4MS), and poly(4-chlorostyrene) (P4ClS) are uncomplicated by distinct conformational flexibilities, while $T_g$ comparisons between other polymers have non-trivial dependences. \textit{e.g.}, the substitutions in ortho- and meta- position augment the effect of substituent sizes on the intrinsic backbone flexibilities, which outweigh the effect of polar interactions on the increased $T_g$s.

To sum up, one has to have adequate information regarding the effects of different structural factors on the polymer backbone flexibility before any conclusion can be drawn about the relative importance of the particular structural factor on glass formation.

At this point, it is necessary to examine with “due diligence” how the backbone flexibility was evaluated in prior studies. When Flory\textsuperscript{49} pointed out the important role of chain inflexibility or stiffness plays in the crystallization of polymers, a flexibility factor,
was defined as the fraction of bonds bent out of their low energy co-linear position. \( f \) is simply the probability of the bond adopting an energetically un-favored conformation with an energy penalty \( \varepsilon \) weighted through a Boltzmann factor. Gibbs\textsuperscript{50} and DiMarzio\textsuperscript{51} (GD) later replaced solvents with holes in adapting Flory’s lattice formulation and interpreted \( T_g \) as an ideal thermodynamic transition of the vanishing number of arrangements when the flexibility factor reaches a lower limit, below which the system become unphysical. GD theory met with success in replicating qualitatively many aspects of the glass transition. Clearly, this decrease in \( f \) while temperature is lowered promotes the rapid decrease in the number of arrangement available for packing a rigid chain.

Similarly, Freed and co-workers\textsuperscript{57,80,96,97} incorporate semi-flexibility into the lattice cluster theory (LCT) using a bending energy, \( E_b \), as the energy difference between trans and gauche conformations. However, difficulties\textsuperscript{57,97} arose in prescribing bending energy to structured monomers; e.g., presence of side chains. In their most recent study\textsuperscript{56}, two separate bending energies, \( E_b \) and \( E_s \), were assigned to backbones and side chains, though these two parameters may not be independent as assumed in their treatment.

Another lattice-based model, \textit{i.e.}, White and Lipson’s\textsuperscript{61,98} locally correlated lattice (LCL) model, does not include explicit terms for polymer flexibilities. A close examination reveals that their three molecular parameters, which are used as adjustable fitting parameters of experimental PVT data, must include the effect of chain flexibility through the variation in \( r \), the number of effective segments per chain molecule, and \( v \), the volume per lattice site or similarly the temperature-independent hard-core volume of the segment.

Schweizer and coworkers’ elastically collective nonlinear Langevin equation (ECNLE) theory\textsuperscript{94,99} utilized the Kuhn length, \( l_k \), and the number of interaction sites in a
Kuhn segment, \( N \), to account for the molecular information of model polymers. In addition to Kuhn length, the characteristic ratio, \( C_\infty \), has been widely used as a parameter for characterizing chain flexibility in the literature\textsuperscript{100–102} of polymer glass transitions. In the phenomenological application of mode coupling theory (MCT) using molecular dynamics (MD) simulation\textsuperscript{102}, \( \lambda \)-exponents found for polymers increase monotonically with increasing intramolecular barriers starting from fully flexible bead-spring chains, whose value is close to the values typical for small molecules. Characteristic ratios were calculated directly from mean squared end-to-end distances obtainable through simulations and are shown to have positive correlation with the calculated \( \lambda \)-exponents.

From the above survey, we conclude that methods developed in the literature to account for the flexibility of polymer chains in the study of their glass transitions were either far from representing real chemical structures or were embedded implicitly in unified parameters. A successful statistical mechanical computational method, the Rotational Isomeric State (RIS) Model, developed by Flory\textsuperscript{85} offers a realistic account of the effect of chemical structure on the intra-chain conformational characteristics of polymers. All RIS conformational models start from knowledge of bond angles, bond lengths, torsional angles and applicable interaction potentials of short chain analogs.

We wish to begin by setting an example for selecting polymers that are structurally well controlled, so that their conformational flexibilities are fixed or can be easily evaluated and tracked using RIS models. The inherent conformational flexibilities or RIS models of structurally analogous linear aliphatic polyesters and polyamides are virtually identical\textsuperscript{85,86} due to the fact that ester and amide bonds are both rigidly contain partial double
bond character and therefore result in similar planar structures and largely a *trans* conformation. For example, poly(ε-caprolactone) (PCL) and poly(ε-caprolactam) (nylon-6) have similar calculated overall conformational preferences and do not possess side chains. Therefore, aside from possible dissimilar effects of crystallinity, their ~100°C difference in *T*\(_g\)s can be attributed to the relative effect of hydrogen-bonding *vs.* dipole-dipole interchain interactions. Glass transition temperatures of structurally analogous n-nylons and n-polyesters are available and meet the foregoing criteria. When the structure approaches polyethylene (PE), however, crystallinity often complicates the comparisons, as evidenced by the increase in polyesters *T*\(_g\)s with decreasing ester group content.

The profound effect of crystallinity on polymer glass transition temperatures calls for the need to synthesize wholly amorphous samples for the purpose of studying their glass transition. However, in almost all instances amorphous samples were only obtained using divergent chemical structures, including different stereosequences or tacticities\(^8^9\), double bonds\(^9^0\), and ring structures\(^9^1,9^2\), which prevented the separate assessment of the potential structural factors suggested to influence their glass transition temperatures. We attempted to synthesize high molecular weight, amorphous, linear, aliphatic co-polyesters or co-polyamides using monomers that have mismatched numbers of methylene groups to prevent their crystallization. Our trials using monomers with medium to long succession of methylene groups, which are widely used in commercial semi-crystalline applications, fail to produce wholly amorphous samples without the aid of rapid quenching.

Recently, completely amorphous linear aliphatic copolyesters were reported.\(^1^0^3\) When ethylene glycol and 1,3-propanediol in the ratios of 40:60 to 20:80 were reacted with succinic acid *via* direct polycondensation reaction with titanium tetraisopropoxide as the
catalyst, the resulting 2,4/3,4 copolyesters produced were totally amorphous with $T_g$s of ~ -30°C. As far as we have been able to determine, this is the only reported synthesis of wholly amorphous linear aliphatic copolyesters. They found their semi-crystalline samples were amorphous when melt quenched in liquid nitrogen, while the 40:60 and 20:80 samples remain the in liquid state until cooled below their $T_g$s.

The behaviors of the 2,4/3,4 copolyesters were subsequently confirmed by us after reproducing their copolymerizations. Due to their distinct room temperature states, i.e., viscous fluids, procedures (dissolution, precipitation, and filtration) normally used to clean up the semi-crystalline polymers were not applicable and the quenching in liquid nitrogen was not necessary for these completely amorphous samples. These two reasons may well explain the existence of a dip in the otherwise linear line for these copolyesters. (See Figure 2.1) For our purpose, the two wholly amorphous 2,4/3,4 copolyesters are the only ideal samples, although they only show a very limited range in the ratio of ester group to methylene group from 0.417-0.435.

In the current study, we have extended the ester group vs. methylene group range by incorporating a longer diol, i.e., 1,6-hexanediol, and the resulting poly(trimethylene succinate-co-hexamethylene succinate) (polyester 3,4/6,4) using 50% each of 1,3-propanediol and 1,6-hexanediol showed a glass transition temperature of -45.2 °C. This clear viscous liquid turned opaque after standing in the laboratory for two months, which indicates its limited crystallizability at room temperature. Further decrease in the ester vs. methylene ratio by replacing succinic acid with adipic acid yielded both 50%:50% and 70%:30% semicrystalline polyester 3,6/6,6. After recognizing that units with six carbons are much faster
crystallizers, we altered the syntheses of the polyester 3,4/6,6 series by using two diols and two diacids. (Subsequently see Table 2.1)

![Graph showing glass transition temperatures.](image)

**Figure 2.1** Glass transition temperatures of poly(ethylene succinate) (PES), poly(trimethylene succinate) (PTS) and their copolyesters with various compositions plotted against the ratio of the number of ester group to methylene group.

2.3 Experimental

2.3.1 Materials

Ethylene glycol (Sigma-Aldrich, anhydrous 99.8%), 1,3-propanediol (Aldrich, 98%), 1,6-hexanediol (Aldrich, 99%), succinic acid (Alfa Aesar, 99+%), and adipic acid (Sigma, 99%) were used without further purification. Chloroform-d, (Aldrich, 99.8 atom % D) was used for $^1$H NMR analysis.

2.3.2 Synthesis of Polyesters

The linear aliphatic co-/tetra- polyesters were synthesized by melt step-growth polymerization. The reactions were carried out in a test tube equipped with a side-arm from which nitrogen and water vapor vent and through a trap filled with water. Monomers were
loaded to the bottom of the test tube along with a magnetic stirrer. Nitrogen was supplied for 10 minutes via a needle piercing the rubber septum test tube stopper to replace the air in the test tube, which was then fitted into an aluminum heating block that was set at 180°C and magnetic stirring was then turned on. Nitrogen was bubbled into the reaction mixture for added agitation once monomers melted and the reaction started. Reactions continued for 24 hours and vacuum was applied from the side arm for an additional 30 min. Finally, the viscous amorphous polyesters were poured into vials for storage.

2.3.3 Calculation of the Ratio of Ester Bonds/CH₂ groups for co-/tetra-polyesters

Following the copolyester nomenclature, our 3,4/6,6 series of polyesters can be named Poly(trimethylene succinate-co-hexamethylene adipate). Despite the fact that there are four distinct repeating units in this polyester series and therefore they should be named tetra-polyesters, varying monomer feed ratios in pairs is much easier to do and has significant advantage when comparing them to polyamides made from nylon salts, which must be prepared in pairs by nature.

The number of ester groups in a repeating unit is 2 for all combinations, while the number of methylene groups varies. For example, poly(trimethylene succinate) (3,4) has 3+2=5 methylene groups and 2 ester groups, which leads to the ratio of 2/5=0.4. Poly(hexamethylene adipate) has 2 esters divided by 10 methylenes and yields the ratio of 0.2. For co-/tetra-polyesters, the average number of methylenes was calculated for each composition. The first way of calculating it is from the point of view of co-polymerization, where we consider only 3,4 and 6,6 units. Take Polyester 80/20 as an example, the average number of methylenes equals the number in homo 3,4 times its composition of 80% plus the number in homo 6,6 times its composition of 20%; 5×80%+10×20%=6. Another way of
calculating it considers all four possible repeating units. Now polyester 80/20 can be viewed as a tetra-polyester composed of the compositions calculated in Table 2.2. Homo polyesters 3,4/6,6/3,6/6,4 have 5,10,7, and 8 methylene groups respectively. The average number of methylene groups in a 80/20 sample is: 5×64%+10×4%+7×16%+8×16%=6. It is not surprising that the results are the same, because we started with the same amount of monomers no matter how we view our product. The ratio is determined as follows; 2÷6=0.333. Hence, the ratio for all samples can be calculated and are used and shown later in Figure 2.6.

2.3.4 ¹H NMR analysis

¹H nuclear magnetic resonance (NMR) was used to estimate copolymer compositions and with spectra recorded at ambient temperature on ~1wt% co-polyester solution in CDCl₃ using a Varian Inova 400 NMR spectrometer, operating at 400 MHz.

2.3.5 FTIR analysis

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed in the range of 700-4000 cm⁻¹ on a Nicolet Nexus 470 Spectrometer equipped with a Nicolet OMNI Germanium Crystal ATR sampling head. 64 scans with a resolution of 4 cm⁻¹ were collected.

2.3.6 DSC thermal analysis

Differential scanning calorimetric (DSC) thermal scans were performed with a Perkin Elmer DSC-7 instrument, which was calibrated using the three-point method with undecane, indium, and zinc. Nitrogen was used as the purge gas. DSC data were analyzed with Pyris software. Glass transition temperatures of the Polyester 3,4/6,6 series were calculated on the second heating (rate of heating = 10 °C/min) following cooling at -40 °C/min
from above the melting temperature of polyester 6,6 using the half $\Delta C_p$ method. Note that liquid nitrogen quenching was not used. The effect of cooling rate is minimal and can be ignored. Those samples with a measurable $T_g$ are either totally amorphous or have very low crystallinity at the beginning of the second heating. (See Figure 2.5)

### 2.3.7 Conformational Entropy Calculation

A Rotational Isomeric State (RIS) model was used to estimate the unperturbed isolated single chain conformational entropy of homo- and co-polyesters at 298.15K. The parametrization of the statistical weights were adopted from Flory and Williams’s study on polyamides and polyesters$^{85,86,104}$, and from Tonelli’s study on polymer melting$^{105,106}$. The conformational partition function, $Z$, was readily obtained through matrix multiplication of preassigned statistical weight matrices. Entropy can be calculated from the partition function $Z$ using the usual statistical thermodynamics relation:

$$S_{conf} = R \left[ \ln Z + T \left( \frac{d \ln Z}{dT} \right) \right]$$

### 2.4 Results and Discussions

FTIR was used to confirm the formation of Polyesters. In Figure 2.2, amorphous linear aliphatic poly(40% ethylene -co-60% trimethylene succinate) (P2434 40-60) is compared with commercial poly(ε-caprolactone) (PCL). The dominant carbonyl group peaks located at the same wavenumber for both P2434 40-60 and PCL, indicating the formation of ester bonds. The absence of a small peak corresponding to the carbonyl group in the carboxylic acid chain ends confirmed the relatively high percent of reaction and resultant molecular weight. The difference in the peak intensities in the range between 2800 and 3000 cm$^{-1}$ is due to the fact that P2434 40-60 contains significantly less methylene groups
per ester group. The difference in the number of peaks in the lower wavenumber region (below 1500 cm\(^{-1}\)) is caused by the stark contrast in their physical states, \(i.e.,\) semi-crystalline solid \(v.s.\) amorphous liquid. The interactions in the amorphous liquid phase are more disordered and dispersed and therefore absorb energy over a broad frequency range with fewer well defined levels.

**Figure 2.2.** FTIR spectra comparing synthesized amorphous linear aliphatic poly(40% ethylene -co-60% trimethylene succinate) (P2434 40-60) with commercial poly(\(\varepsilon\)-caprolactone) (PCL)
\(^1\)H NMR was used to determine the composition of the co-/tetra-polyesters. In Figure 2.3, all hydrogen resonances are identified on their monomer structures. Since the \(^1\)H chemical shifts of diol/diacid are not sensitive to the type of diacid/diol connected to the next diol/diacid, a maximum of 8 peaks can be identified using the data in the literature\(^{103,107}\). An example of a \(^1\)H NMR spectrum of a 50/50 polyester 34,66 sample is shown in Figure 2.4. Each peak was assigned a specific position according to the numbering system used in Figure 2.3. 7 peaks were distinguishable in the recorded spectrum, with a corresponding composition of A:C:B:D = 22.42%:24.10%: 26.23%:27.24% using the resonance integrals obtained from the spectrum. This composition was largely preserved from the equal molar feed ratio with a variation of about 2%, and therefore it will be more convenient to simply use feed ratio in our subsequent discussion of the effect of ester content on the glass transition temperature of the polyesters.

Figure 2.3. Chemical structures of monomer moieties exist in co-/tetra-polyesters with numbers indicating different positions of hydrogen atoms. (A) 1,3-propanediol, (B) 1,6-hexanediol, (C) Succinic Acid and (D) Adipic Acid

With the irregularity introduced by the inherent expected randomness from step-growth copolymerization, the crystallinities of copolymers can be significantly reduced to near or wholly amorphous, leaving the \(T_g\)s of the polymer samples largely unaffected by
crystallinity. DSC thermal analysis showed that samples with 80/20, 70/30, and 60/40 of 3,4/6,6 had no sign of melting peaks, and therefore were not able to crystallize during the relatively slow rate of cooling (−40 °C/min). However, the 50/50, 40/60, and 30/70 samples show a noticeable exothermic cold crystallization peak before their respective melting peak upon heating at 10 °C/min. By comparing the heat of cold crystallization and the heat of melting, we can conclude that 50/50 was wholly amorphous and sample 40/60 contained very low degree of crystallinity at the beginning of the heating. Samples 30/70, 20/80, and 66 are semi-crystalline with increasing degrees of crystallinity as the 66 diad population increases. (See Table 2.2) In fact, starting from sample 40/60, the highly crystallizable 66 diad populations dominate, with thermal properties approaching that of neat polyester 6,6.

Figure 2.4. ¹H NMR Spectrum of a 50/50 polyester 34,66 sample in CDCl₃ at ambient temperature.
In addition to acquiring wholly amorphous samples, their molecular weights should be high enough to no longer affect their $T_g$s. This is especially important considering the fact that we’ve decided to use catalyst free polymerizations due to the difficulties involved in sample purification processes; i.e., the usual precipitation method does not work for a liquid sample. We evaluated the effect of molecular weight by measuring the $T_g$ of our reproduced P2434 40-60 and then compared it with the value reported in the cited study in which catalyst was used and GPC read very high molecular weight using polystyrene (PS) as standard. Notwithstanding the validity of using a chemically distinct standard for determining molecular weight, the small difference ~2 K in $T_g$ between the two assures that our procedure generated polymers with molecular weight high enough to no longer greatly affect their $T_g$s.

![Figure 2.5 DSC Thermograms of Polyester 3,4/6,6 Series on second heating.](image)

57
Table 2.1 Second Heating in DSC for Polyester 3,4/6,6 Series

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Feed ratio (mol%)</th>
<th>T_m (°C)</th>
<th>ΔH_m (J/g)</th>
<th>T_c (°C)</th>
<th>ΔH_c (J/g)</th>
<th>T_g (°C)</th>
<th>ΔC_p (J/g°C)</th>
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<tr>
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<td>50</td>
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<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>40</td>
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<td>50</td>
<td>-</td>
<td>50</td>
<td>54.1</td>
<td>98.1</td>
<td>-</td>
</tr>
</tbody>
</table>

| 34          | 100   | -     | -     | -     |          |          |              |              |
| 80/20       | 64    | 4     | 16    | 16    |          |          |              |              |
| 70/30       | 49    | 9     | 21    | 21    |          |          |              |              |
| 60/40       | 36    | 16    | 24    | 24    |          |          |              |              |
| 50/50       | 25    | 25    | 25    | 25    |          |          |              |              |
| 40/60       | 16    | 36    | 24    | 24    |          |          |              |              |
| 30/70       | 9     | 49    | 21    | 21    |          |          |              |              |
| 20/80       | 4     | 64    | 16    | 16    |          |          |              |              |
| 66          | -     | 100   | -     | -     |          |          |              |              |

a PD=1,3-Propanediol  HD=1,6-Hexanediol  SA=Succinic Acid  AA=Adipic Acid
b Melting upon second heating
c Crystallization upon second heating
d From reference 108

Table 2.2. Calculated Diad Probabilities (%) for Polyester 3,4/6,6 Series

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Diad Probabilities (%)</th>
</tr>
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<td>4</td>
</tr>
<tr>
<td>66</td>
<td>100</td>
</tr>
</tbody>
</table>

a Calculated from feed ratios assuming equal reactivity. Sample calculation: for 80/20, the 34 diad probability is derived from the probability of finding 1,3-propanediol (in competition with finding 1,6-hexanediol) times the probability of finding Succinic Acid (in competition with finding Adipic Acid) i.e., 80%×80% = 64%.
The obtained $T_g$s vary linearly with the ratio of the number of ester groups to the number of methylene units, and the fitted linear line can be used to predict the glass transition temperature of neat polyester 6,6, which was not observable by DSC due to its high degree of crystallinity. (See Figure 2.6) When the ester/CH$_2$ ratio of 0.2 for the neat 66 sample is plugged into the fitted equation it yielded 207 K, which agrees closely with the $T_g$ of 200 K reported in the literature considering the fact that this $T_g$ was determined by a penetration test in a thermomechanical analyzer (TMA)$^{109}$. Extrapolation of the ratio to zero ester group content gives a $T_g$ of 177K for amorphous polyethylene (PE), which agrees with the value of 188±10 K obtained by extrapolation of DSC observations performed on amorphous poly ethylene-vinyl chloride (E-V) copolymers.$^{110}$

![Figure 2.6. Glass transition temperatures of linear aliphatic 3,4/6,6 polyesters synthesized by us plotted against the ratio of the number of ester groups per methylene group.](image)
The first reason for choosing the functional group ratio as the comparison variable is its convenience for compiling values of polymers with different monomers. For instance, P2434 40-60 can be plotted on the same graph with the benefit of broadening the data range for a better fit. In fact, even without the input from P2434 40-60, the linear fit from Polyester 3,4/6,6 series alone falls in close proximity to the experimental value. Another advantage is the ability to extrapolate towards two extremes (0 and 1), as has been demonstrated in the case of polyethylene (PE). Plotting against weight and molar fractions were also attempted, but showed inferior linear fittings compared to the one using the functional group ratios. Because of the big disparities in monomer sizes, molar fractions resulted in fittings inferior to weight fraction, which was in turn surpassed by using the functional group ratios. Furthermore, one might recall that the widely used Fox equation assumes direct proportionality between the inverse of $T_g$s. When $T_g$s themselves are plotted against weight fractions, a convex function results. However, in the situation where the difference in $T_g$s of the pure components are not too large, a linear relationship should suffice.

Due to the absence of a satisfactory theoretical foundation, sometimes the best we can do in terms of predicting unmeasured $T_g$s of new experimental polymers is through the use of a pragmatic, empirical, additive method, although it has the apparent drawback of possibly being inapplicable to the prediction of the $T_g$s of new polymers not included in the empirical dataset. The idea is simple; the properties of the polymer containing both components should fall between the properties of the two neat polymers. We hereby adopted Van Krevelen’s group contribution method, not as a theoretical foundation but rather as a guide for general trends observed in the literature, subject to the author’s careful selection of valid data. The calculated $T_g$s of this polyester series using Van Krevelen’s
group contribution method manifest similar linearity with the ester group content and are 3 to 17K higher than the measured $T_g$s. (See Figure 2.7)

![Graph showing experimental vs. Van Krevelen’s group contribution method](image)

**Figure 2.7. Experimental vs. Van Krevelen’s group contribution method**

The intramolecular equilibrium flexibilities were evaluated through the calculation of conformational entropies of individual polymer chains approximated by considering solely the short range interactions between neighboring groups, as embodied in their RIS conformational models\textsuperscript{85,86}. Their calculated conformational entropies decrease with increasing ester group content. The trend is more like a convex function, though within a limited range the linearity is significant. (See Figure 2.8 ) This is due to the fact that rigid and essentially all trans ester bonds effectively separate the conformational interdependence of rotational angles on both sides. $T_g$ can be equally well plotted against conformational entropy. (See Figure 2.9) A possible ester-ester coupling effect for shorter aliphatic
monomers was not observed or reflected by producing non-monotonic variation of $T_g$s. The overall linear variation of $T_g$s suggests both the effect of inherent conformational flexibility and the effect of intermolecular interactions on the $T_g$s of linear aliphatic polyesters contribute additively to the whole; because there is no reason to expect opposite variations of the same magnitude would exist and cancel each other.

![Graph showing conformational entropy vs ester to CH$_2$ ratio](image)

**Figure 2.8. Conformational Entropy per mole of Backbone Bonds vs. Ester Bond to CH$_2$ group ratio.**

The reason for studying the variation in entropy (S) for the purpose of understanding glass transition is because of the concomitance of $T_g$ and an abrupt change in the rate of entropy change as a function of temperature. If no change in the slope were to occur, the entropy of the system would drop below that of the crystalline state and therefore pose an entropy crisis. The resolution is the existence of a kink or a change in the slope of the entropy vs temperature curve to avoid the unphysical negative entropy. We emphasize
that the conformational entropy calculated in our study using RIS model only makes up a fraction of the configurational entropy, which should include the inter-chain interactions and packing effect. In turn, configurational entropy is believed\textsuperscript{80,112} to contribute only a fraction to the total entropy to which the other major contributor is the vibrational entropy\textsuperscript{113}. Despite its small value compared to the configurational entropy, whose variation was theorized to be responsible for the extent of cooperativity of polymer transport or relaxation properties\textsuperscript{55}, its non-monotonic variation as a function of composition and sequence distribution was shown to account for the large deviations from the simple Fox equation for copolymer T\textsubscript{g}s.\textsuperscript{83,114–116} There are sufficient reasons to believe that in the case of polymers intra-chain flexibility assumes a major role in promoting the onset of glass transition in comparison to the effect of intermolecular interactions and packing which are largely responsible for small molecule glass formation\textsuperscript{49–51,53,102}. Thanks to the smooth approximately linear variation of conformational entropy with ester to methylene ratios, the observed T\textsubscript{g}s also have a linear dependence on the ratios.

It is interesting to note that the $\Delta C_p$ increases with increasing ester content accompanied by increase in T\textsubscript{g}. This heat capacity jump at T\textsubscript{g} was previously used as an indication of material dynamical fragility, which is the steepness of the temperature dependence of the change in viscosity or in the case of polymer the structural relaxation time.\textsuperscript{112} The higher the heat capacity jump, the more fragile the material is. As the ester content increase the chain stiffens and therefore become more fragile. This is in accordance with the general perception of the molecular basis of polymer fragility.\textsuperscript{43,80,117} However, the empirical relationship between heat capacity jump and fragility was reported to fail for polymers.\textsuperscript{118} The amorphous polyester series we have synthesized thus provide an ideal system for future
study of the fragility dependence on chain flexibility and intermolecular interactions and for testing theoretical predictions\textsuperscript{96}.

![Figure 2.9. $T_g$ vs. Conformational Entropy per mole of Backbone Bonds](image)

2.5 Conclusions

In this study, a series of wholly amorphous linear aliphatic co- and tetra- polyesters were synthesized \textit{via} bulk melt step-growth polymerization, and their glass transition temperatures were determined using Differential Scanning Calorimetry (DSC). The crystallinities of these copolyesters were significantly reduced to near or wholly amorphous states, leaving the $T_g$s of the polymer samples essentially unaffected by crystallinity. The molecular weight of the copolyesters were concluded to be high enough to no long affect their...
T₉s by comparing the measured T₉s to that of claimed high molecular weight samples reported in the literature.

The glass transition temperatures of the polyesters increase linearly with the ratio of ester groups per methylene group. Extrapolation of the ratio to zero ester group content gives a T₉ of 177K for amorphous polyethylene (PE). The calculated T₉s of this polyester series using Van Krevelen’s group contribution method manifest similar linearity with the ester group content and are 3 to 17K higher than the measured T₉s. The intramolecular equilibrium flexibilities were evaluated through the calculation of conformational entropies of individual polymer chains approximated by considering solely the short range interactions between neighboring groups, as embodied in their RIS conformational models. Their calculated conformational entropies decrease approximately linearly with increasing ester group content. The potential ester-ester coupling effect for shorter aliphatic monomers was not observed or reflected by non-monotonic variation of T₉s. The overall linear variation of T₉s suggests both the effect of intramolecular conformational flexibility and the effect of intermolecular interactions contribute linearly to polymer T₉s.

Finally, further work using this model polyester series for assisting experimental verification of theoretical predictions were suggested.
Chapter 3  Synthesis of Amorphous Linear Aliphatic Polyamides and their glass
transition temperatures

3.1  Abstract

Glass transition temperatures were determined for melt blended, melt polymerized,
interfacial polymerized, and solution polymerized amorphous or low crystallinity aliphatic
polyamides. $T_g$ values of our synthesized polyamides cover the entire compositional vari-
ation range and qualitatively show a steeper dependence on amide content dependence than
both the trend for the n-Nylons and group contribution predictions. A complication arises
for the possible blocky nature of our synthesized polyamides, whose phase separated $T_g$s
could vary by as much as 100° C. Thus amide content influences $T_g$ in a more complex
way than ester content influenced the $T_g$ of the analogous polyesters.

3.2  Introduction

Originating from the prediction of closely similar conformational characteristics of
analogous linear aliphatic polyamides and polyesters by Rotational Isomeric State (RIS)
model\textsuperscript{85,86}, our efforts to synthesize and compare $T_g$s of amorphous model polymers, whose
structures are controlled in a manner that permits isolation and evaluation of their relative
effect on glass formation have been successful for linear aliphatic polyesters. The current
study is mainly concerned with the synthesis of analogous linear aliphatic polyamides that
are also wholly amorphous, so that the heat capacity step changes are easily identifiable in
DSC thermograms and their $T_g$s can be reliably determined and compared to each other
and their corresponding aliphatic polyesters.
A survey of the literature including patents revealed that most reported amorphous nylons were either non-linear or non-aliphatic. In the case of linear aliphatic nylons, it was found that at least three different repeating units are required to produce terpolymides that are largely amorphous under normal quenching rates. This confirmed our initial failed attempts to produce amorphous samples when only two sets of monomers were copolymerized. Consequently, we explored various combinations of ter- and tetra-polyamides having repeating units of some of the most common nylon types.

The most common route for polyamide synthesis is the direct melt polymerization; reacting diamine with dicarboxylic acid or amino acid with itself. In the former case, which is often called AA-BB type of monomers, perfect stoichiometry is required in order to obtain high molecular weight. This is often facilitated by the formation of nylon salts whose water solution pH values can be readily checked to ensure precise balance.

Melt blending is another convenient way of making ter or tetra-polyamides owing to the relatively fast transamidation reactions observed above their melting points. Commercially available nylons can thus be melt blended regardless of their own respective synthesis methods; e.g., melt polymerized nylon 66 with ring-opening polymerized nylon 6.

A critical requirement for melt polymerization and melt blending is that the materials have to stay in the molten state so that the randomization via transamidation can be utilized to reduce crystallinity. It is well known that the melting point of polyamides increase nearly linearly with increasing amide content. On the other hand, linking groups like the amide group are more susceptible to degradation than the hydrocarbon parts of the chain. Melt processes described above become impractical when we incorporate
shorter diamines and dicarboxylic acids, which are thermally unstable, albeit with extremely high melting points for their polyamides.

It is therefore advantageous to utilize low temperature polymerization methods, i.e., interfacial and solution polymerization, for the synthesis of polyamides containing ethylenediamine and 1,3-diaminopropane. Interfacial polymerization involves the reaction of diacid chlorides dissolved in an organic phase with diamines dissolved in an aqueous phase at the interface between the two immiscible phases. This reaction, also known as the Schotten-Bauman reaction, has equilibrium constants that are about two orders of magnitude higher than those of diamines with diacids. Inorganic acid acceptors, such as sodium hydroxide and sodium carbonate can be added to the aqueous phase to neutralize the HCl byproduct. An organic acid acceptor, such as trimethylamine, is often used in the solution polymerization, although in some studies the solvent N-methyl-2-pyrrolidone (NMP) also acts as acid acceptor for hydrochloric acid.

3.3 Experimental

3.3.1 Materials

Ethylenediamine (Alfa Aesar, 99%), 1,3-diaminopropane (Alfa Aesar, 98%), 1,6-diaminohexane (Alfa Aesar, 98+%), succinic acid (Alfa Aesar, 99+%), adipic acid (Sigma, 99%) succinyl chloride (Alfa Aesar, 96%), adipoyl chloride (Alfa Aesar, 98%), triethylamine (Sigma-Aldrich, ≥99%), N-methyl-2-pyrrolidone (BDH, ACS, 99.0+%), N,N-Dimethylformamide (Sigma-Aldrich, anhydrous, 99.8%), chloroform (Alfa Aesar, ACS, 99.8+%), 2-butanone (Sigma-Aldrich, ACS reagent, ≥99.0%), and N,N-Dimethylacetamide (Sigma-Aldrich, anhydrous, 99.8%) were used without further purification.
3.3.2 Melt Blending of Polyamides

Polyamides pellets were first ground into powders, weighed, and mixed by hand according to the prescribed composition of the blend. The mixed powder was then passed through an Atlas mini extruder operated at 280° C. The extruded material was then cut into pellets and served as the starting material for prolonged transamidation reaction done at 280° C in a reaction tube continuously purged with nitrogen.

3.3.3 Melt Polymerization of Polyamides

The experimental set-up used for melt polymerization of polyesters is also applicable to polyamides. The difference is that polyamide synthesis starts with making the salts of different combinations of diamines and diacids. The detailed recipe for preparing nylon salts can be found in a classic polymerization method text and can be summarized as follows. Equal molar amounts of diamine and diacid were dissolved in ethanol separately in two Erlenmeyer flask and then the two solutions were mixed with stirring. A white precipitate of the salt formed immediately accompanied by warming from its exothermic nature. In the case of diamines in the liquid state at room temperature, they were directly measured by Eppendorf pipette and dropped into the ethanol solution of diacid with stirring. The mixture was allowed to cool to room temperature, filtered, washed with ethanol and air dried overnight. All nylon salts were further dried in a vacuum oven at 60° C. Co-/tetra-polyamides were made using varying amount of different salts. A mixture of salts is loaded into the reaction tube, which is equipped with a side arm for the release of by-product water and purging nitrogen, and then heated above its melting temperature and the reaction started. Temperature is gradually increased in the case of very crystallizable samples in order to keep it in the molten state. Simultaneously the temperature is increased and the
pressure is decreased at the last reaction stage to help increase the molecular weight of the sample. The resultant amorphous polyamides, while still hot, needed to be poured into a petri dish for solidification, because the viscosity increases dramatically at lower temperatures. Another way of retrieving the polyamide is by breaking the reaction tube after solidification, as is suggested for semi-crystalline polyamides.

3.3.4 Interfacial Polymerization

Interfacial Polymerizations w/ and w/o blending were attempted. The unblended type was done with an unperturbed interface between water and organic solvent phases. The film formation at the interface was not obvious compared to that of the higher carbon number aliphatic monomers. Reasons could be the greater hydrophilicity of both monomers; i.e., short diamines and diacid chlorides. Hence, the migration of diamines to the organic phase was impeded and the greater rate of migration of diacid chlorides to the aqueous phase causes them to be more susceptible to hydrolysis. The blending type of reactions were carried out both in a household blender and a large beaker in which a mechanical stirrer or magnetic stir bar could be inserted. Chloroform, toluene, carbon tetra-chloride, and other common chlorinated hydrocarbons were used to contain the diacid chlorides. A dripping funnel was used to add the organic phase containing diacid chlorides dropwise into the vigorously stirred aqueous phase containing diamines and acid absorber; e.g., NaOH. The resultant powder is then filtered and washed three times alternatingly with water and organic solvent. The water soluble sample was purified by dialysis against water to remove water soluble byproduct and unreacted monomers. The water solution of the product was then evaporated to retrieve the solid sample.
3.3.5 Solution Polymerization

Solution polycondensation reactions eliminate the aqueous phase and presumably give a better chance for the reaction between diamines and diacid chlorides. Triethylamine (TEA) was added as an acid absorber together with diamines into the solvent of choice, e.g., N-Methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), chloroform, and dimethylacetamide (DMAc), which were precooled to 0°C. Diacid chlorides react with NMP at room temperature, so care must be taken to precool the NMP to lower temperatures before mixing the two. The reaction was carried out in an Erlenmeyer flask in an ice bath through the dropwise addition of one solution into the other accompanied by vigorous magnetic stirring. Copolymerization was accomplished by premixing the same monomers in the same solution for a better chance of random reaction upon addition to another premixed monomer solution.

For the 2,4/3,4 copolyamide series, the resultant material includes polyamide and TEA-HCl salt, except in the case of chloroform as solvent, and can be filtered. For the highly crystalline samples, water can be used to dissolve TEA-HCl away from the product mixture. For amorphous or low crystallinity samples, chloroform was found to be a good solvent for TEA-HCl, but not a solvent for polyamides, and therefore can be used to wash TEA-HCl away. In the case of 3,4/6,6 tetra-polyamide series, solids collected from filtration transition from a mixture of polyamide and TEA-HCl to only TEA-HCl and back to a polyamide and TEA-HCl mixture when compositions are varied. (See Figure 3.18 for proof of the absence of polyamide from the solid obtained with the first filtration of the reaction mixture). For NMP soluble polyamides, the clear filtrate was precipitated using a 2 fold quantity of 2-butanone. The solid resulting from precipitation was then filtered and air
dried. All powder samples were kept in vacuum oven for at least 1 day at 60° C before characterization.

3.3.6 FTIR analysis

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed in the range of 700-4000 cm\(^{-1}\) on a Nicolet Nexus 470 Spectrometer equipped with a Nicolet OMNI Germanium Crystal ATR sampling head. 64 scans with a resolution of 4 cm\(^{-1}\) were collected. FTIR was used to confirm the formation of amide groups, and to detect any impurities.

3.3.7 DSC thermal analysis

Differential scanning calorimetric (DSC) thermal scans were performed with a Perkin Elmer Diamond DSC-7 instrument, which was calibrated using a three-point method with undecane, indium, and zinc. Nitrogen was used as the purge gas. DSC data were analyzed with Pyris software. Glass transition temperatures of the nylons were determined upon heating at a rate of 10, 20, or 30° C/min using the half $\Delta C_p$ method.

3.3.8 TGA

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer Thermogravimetric analyzer. Nitrogen gas was used to purge the furnace. Samples were heated from 25 to 600° C at a rate of 20° C per minute and Pyris software was used to analyze the data. TGA was used to estimate the water content in amorphous polyamides and to determine the thermal degradation temperatures.
3.3.9 XRD

Wide-angle X-ray diffraction was done using a Philips XLF, ATPS X-ray diffractometer with an OMNI Instruments customized auto-mount and copper tube. The tube produces X-rays with a wavelength of 1.54Å. The diffraction intensities were measured every 0.1° over a 2θ range of 5-40°. The data was analyzed using TXRD 5.1 software. XRD was used to evaluate the crystallinity of the polyamides and was also used to identify impurities.

3.3.10 POM

Polarized optical microscopy (POM) was performed on a Nikon Eclipse 50i POL Optical Microscope equipped with a CCID-IRIS/RGB color video camera made by Sony Corp. Photographs were taken by using crossed polarizers and a ¼ λ plate. POM was used to compare the difference in crystallizabilities of different solution polymerized polyamides and to confirm the essentially isotropic nature of amorphous sample.

3.3.11 Dilute solution viscometry

A Cannon-Ubbelohde #2 E433 viscometer was used to measure the intrinsic viscosities of polyamides for the determination of their molecular weights. A starting concentration of 0.4g/dL of nylon in m-cresol was prepared, and was diluted by repeatedly adding pure m-cresol into the viscometer. The flow time at each concentration was measured three times, and the difference between each reading was less than 1 second. The intrinsic viscosities were obtained as the intercept on the y axis of the extrapolated $\frac{\eta_{sp}}{c}$ vs. c linear fit to zero concentration. Molecular weights was calculated using the intrinsic viscosities determined in this experiment and the Mark-Houwink Equation specific to the polymer, solvent, and specified temperature.
3.4 Results and Discussions

3.4.1 Melt blending of Polyamides

Four different polyamides were employed in the melt blending study. They are nylon 6,10 synthesized by ourselves, commercial samples of nylon 6,6, nylon 6, and nylon 11. According to their intrinsic viscosities determined in m-cresol at room temperature, suitable Mark-Houwink Equations were used to calculate the molecular weights of the different nylons. Nylon 6,10 synthesized by melt polymerization from salt has an intrinsic viscosity of 1.28 dL/g and a calculated molecular weight of 14,000. Nylon 6,6 purchased from Sigma Aldrich has an intrinsic viscosity of 1.02 dL/g and a calculated molecular weight of 23,000. Nylon 11 also purchase from Sigma Aldrich has an intrinsic 0.99 dL/g and a calculated molecular weight of 25,000. Nylon 6 purchased from BASF with a labeled molecular weight of 60,000 has an intrinsic viscosity of 2.05 dL/g and a calculated molecular weight of 70,000. Based on these MWs, the potential effect of molecular weight on $T_g$ is alleviated for the melt blended samples.

In all of our attempts, fully amorphous samples were not obtained. However, the heat capacity changes become more apparent with an increasing degree of mixing and decreasing crystallinity. $T_g$s measured for short time melt blended samples of various composition range from 38 to 43 °C, which is not a very big range and is consistent with literature reported values. In the case of the melt blend of equal weights of four different nylons, for 11 hours at 280° C produced a sample with a single melting point at 178 ° C and a heat of fusion of 31J/g. The glass transition temperature of this sample determined on the second heating was 23° C. This is quite a low $T_g$ compared to the normal 38-43° C range. Similarly, a largely amorphous terpolymer of nylon-6, nylon-6/6, and nylon-12 was reported to have
a glass transition temperature of 20° C\textsuperscript{126}. After 24 hours of vacuum baking at 200° C, the 
\( T_g \) of this terpolymer was raised to 30° C. The author concluded that \( \varepsilon \)-caprolactam, lauro-
lactam, and water contained in the as-received sample collectively plasticized it and re-
duced its \( T_g \).

However, we would like to point out that comparing \( T_g \)s of the wholly amorphous
polyamides to those determined in the semi-crystalline state is not fair. First, intercon-
nected crystalline phases inevitably constrain the motions of the amorphous phases and 
therefore increase the \( T_g \) of the semi-crystalline polyamide. Second, the effect of crystal-
linity is commonly eliminated by rapid quenching, which can induce cooling effects on the 
measured \( T_g \) in the subsequent heating scan. \textit{e.g.}, Nylon 66 melt quenched in liquid nitro-
gen from 270 to -196°a C. If the sample is small enough so that the whole process can be 
done in a little less than a second, the cooling rate is roughly 500 degree per second, which 
equals to 30,000 degree per minute. Almost 3000 times faster than the common scan rate 
of 10 degree per minute used in DSC. Empirically, \( T_g \) shifts 3 degree higher for every order 
of magnitude increase in the cooling rate\textsuperscript{2}. That is about a 10-degree rise in \( T_g \) for the 
quenched sample. Third, unreacted monomers and water absorption are equally likely to 
pose an effect for those semi-crystalline samples that are used without further purification.
Vacuum baking as done by Davis\textsuperscript{126} will most likely increase the \( T_g \) of the semi-crystalline 
sample further. The impression that amorphous polyamide is more susceptible to water is 
caused by the rate not the ability of absorbing moisture. Crystals act as obstacles for the 
transportation of water molecules into the binding sites and thus delay the equilibration 
process. In addition, functional groups inside the crystal lattices are usually not accessible 
by water molecules. Thus total water absorption is less compared to amorphous samples.
This does not imply that the amorphous phase of the semi-crystalline polyamide, which is responsible for the glass transition signal, is any less likely to absorb moisture.

Hence, it is not necessary to attribute the low \( T_g \) completely to the plasticizing effect. Instead, based on this study and our observations we are convinced that this relatively low \( T_g \) is in fact the true \( T_g \) of the amorphous state.

### 3.4.2 Melt Polycondensation Polyamides

Melt polymerization of polyamide usually requires the preparation of different nylon salts. As can be seen in Figure 3.1, most nylon salts melt between 170 and 210° C. It is interesting to note that, regardless of differences in their monomer size and the location of the melting point of the salt, there appears an endothermic peak over a much narrower range, between 210-230° C, accompanied by a step up in the baseline for all salt samples. This thermal event somewhat resembles that of the glass transition with an enthalpy relaxation peak. However, it is considered not possible due to its higher temperature compared with the melting point of the crystal and also to the much larger heat capacity change compared to regular values observed at the glass transition. It seemed to us that this heat capacity jump might be caused by the further disruption of local order through the dissociation or randomization of part of the hydrogen bondings that existed in the melt not far above the melting point of the crystal. Because of their occurrence in a similar temperature range, they must have the same origin. However, we do not know how this thermal event will evolve during the continuous polymerization or in the repeated heating and cooling experiment. Thus, future work to study the nature of this thermal event is justified.
Figure 3.1 DSC thermograms of nylon salts

The compositions of the co- or tetra- polyamides were chosen based on the knowledge of their analogous linear aliphatic co- or tetra- polyesters; i.e., compositions that suppress crystallization. Tsai et al. \(^{103}\) reported wholly amorphous copolyesters using different ratios of ethylene glycol and 1,3-propanediol copolymerized with succinic acid. Our experiences indicate polyesters with long methylene spacing crystallize rapidly. It is therefore natural to postulate that shorter methylene spacing aids in preventing crystallization. We replaced diols in Tsai’s study with analogous diamines, i.e., ethylene diamine and 1,3-diaminoproane, to synthesize their analogous polyamides.

Synthesis of polyamide 24 has been reported using solution-liquid polycondensation and interfacial polymerization\(^{139}\), while the synthesis of polyamide 34 was only re-
ported using interfacial polymerization in the context of membrane fabrication. Co-polymerization of poly(ethylene-co-trimethylene succinamide)s have, however, not been studied in the past.

We have used direct melt polymerization, and two-step solution-liquid high-pressure polymerization described by Wang et al. for the synthesis of polyamide 34. In the direct melt method the nylon salt is melted in a reaction tube fitted in an aluminum heating block. The two-step technique requires as the first step dissolution of salt in water (60%) and heating of this solution in an autoclave with temperature gradually increasing over 5 hours from 150 to 250°C. In the second step, the cooled product was retrieved from the autoclave and loaded into a reaction tube purged with nitrogen. The temperature was raised from 90 to 250°C gradually over 4 hours. Conventionally, the term two-step also refers to a closed system in the first step and reduced pressure in the second step and this practice was considered standard and used in both syntheses. Samples obtained were dark pinkish and brownish solid respectively, and were dissolved in 25 ml dichloroacetic acid and precipitated into 200 ml of methanol. Solids were collected by filtration and were vacuum dried before characterization.

Figure 3.2 shows DSC thermograms of polyamide 34 (N34) obtained from two different methods. Both N34 have endothermic peaks higher than 250°C with the one from the two-step method at ~ 350°C. Such a high melting point (concomitantly degradation, see TGA) caused difficulty in maintaining the reactants in the melt, and severe thermal degradation renders melt polycondensation impractical.
One way of getting around this issue is by mixing in more stable longer aliphatic diamines and diacids. We demonstrate the effectiveness of the short aliphatic diamines and diacids in preventing crystallization through the syntheses of the polyamide 3,4/6,6 series.

![Figure 3.2 DSC thermograms of N34 obtained by regular melt polymerization and a two-step high pressure polymerization.](image)

For the polyamide 3,4/6,6 series, 80/20, 70/30, 60/40, and 50/50 mole percentages of 34 and 66 salts were chosen because of the amorphous nature of their analogous polyesters. These samples turned out to be amorphous except for sample 80/20, which crystallized during the reaction and could not be melted without degradation. The glass transition temperature of the amorphous samples were determined to be in the range of 23-28°C,
which is much lower than what we expected from both estimation methods. From the trend plotted using n-nylon literature reported values, the T_g's for these polyamides were expected to range from 75 to 81°C. From Van Krevelen’s group contribution method, the expected range is from 52 to 55°C. (See Figure 3.3) Despite their differences in absolute values, T_g's of polyamide 3,4/6,6 series with compositions that produce wholly amorphous samples have similar insensitivity to the variation of amide content compared to the trend for n-nylons and T_g values from Van Krevelen’s group contribution method.

![Figure 3.3 T_g's of Polyesters and Polyamides Estimated using Van Krevelen’s Group Contribution Method in the range of the current study.](image)

Possible explanations for the low T_g's are at least twofold. First, due to the thermally unstable 1,3-diaminopropane, the reaction cannot be maintained for long at a relatively high temperature of ~ 200°C. A two-step process was attempted to avoid the high temperature. Nylon salts were first melted at around 190°C, reaction started rapidly, and after 5
minutes the temperature was lowered to 160° C for further reaction. Although we were able to maintain the reaction for a much longer time, the reaction rate was obviously not fast enough at this lower temperature to make any significant improvement to our amorphous samples. The intrinsic viscosity in m-cresol for polyamide 3,4/6,6 50/50 sample was determined in a Cannon-Ubbelohde Viscometer to be 0.12 dL/g at room temperature. (Result would be somewhat higher than what is reported here if we factor in the 5% water content determined later by TGA)

In addition to their possibly low molecular weight, moisture content may also drastically affect the glass transition temperatures. Gaymans et al.\textsuperscript{142} reported $T_g$s for dried Nylon 4,2, for sample conditioned at 50%RH, and for wet sample to be 120, 70, and -15° C, respectively. The variations of $T_g$ and its broadening with water content in polypeptides and proteins is widely studied.\textsuperscript{143–148} It is reasonable to expect that with the increasing amide content, the properties of our amorphous polyamides become more relevant to those found in polypeptides and proteins. Our observation that amorphous samples with higher amide content are hygroscopic is thus reasonable. Similar to what has been described in Davis’s\textsuperscript{126} study of amorphous polyamides, crystallinity was developed over time at room temperature, because their glass transition temperatures are close to room temperature as evidenced by the increase of opacity of the surface layer. Materials on the surface of the bulk samples became hydrated easily and gain sufficient amount of mobility for crystallization.

Because either of the two factors discussed above alone could possibly account for the difference in the absolute values compared to the predictions, it becomes important to estimate the relative influence of each factor on the reduction of $T_g$. Thermogravimetric
analysis (TGA) was performed to estimate the water content in the as-synthesized sample and sample that has been dried in a vacuum oven at 60 °C for 40 hours. In Figure 3.4, initial weight losses of about 5% and 1.8%, respectively, at 170 °C for melt polymerized nylon (MPN) 3466 7030 as-synthesized and Vacuum dried, respectively. Longer desiccation time was used in the literature and should be used if we wish to decrease the water content further. The difference of about 3% weight loss is unambiguously caused by water that can be removed after 40 hours of vacuum drying at 170° C.

The effect of this 3% water content on $T_g$ is evaluated using DSC and is shown for MPN 3466 7030 as-synthesized (See Figure 3.5) and Vacuum dried (See Figure 3.6). As can be seen in Figure 3.5, the as-synthesized the sample shows a prominent thermal effect at the glass transition; the heat capacity change is easily identified by DSC which is usually not very sensitive for determining the $T_g$ of semi-crystalline polyamides. After being cooled in the DSC pan at different cooling rates, the prominent thermal signature was retained with only a slight lower $T_g$ value for the slower cooling rate.
Figure 3.4 TGA of Vacuum oven dried SPN3434 4060 and MPN3455 7030, and as-synthesized MPN3466 7030.

Figure 3.5 DSC thermograms for as-synthesized melt polymerized nylon (MPN) 3466 7030 after different thermal histories.
In Figure 3.6, the vacuum dried sample displays a 4° C higher T_g value and a reduced thermal effect (heat capacity increase) on the first heating compared to the as-synthesized sample. However, the same T_g signal was not identifiable on the 2nd heating up to 80° C. An incipient heat capacity rise was seen at the end of the 2nd heating scan so a 3rd heating scan was done up to 180° C in order to detect any thermal event that was missed in the first two heating scans due to the limited temperature scan range. A T_g was detected on the 3rd heating at 83.5° C, with a heat capacity change of 0.133 J/g°C, which is similar to that of the T_g identified on the first heating. Until 180° C, no detectable T_g-like thermal event was seen. A pair of mutually off-setting small exothermic and endothermic peaks appeared around 160° C, and the same thermal event was also seen for the as-synthesized sample. On the 4th heating scan, a T_g with a much more prominent thermal effect (0.516 J/g°C) manifested itself at 14.5° C. We are surprised by the 70° C variation of the glass transition temperature on subsequent heating scans of the same sample within the same
DSC experiment, because we did not expect a block copolymer to be formed in the melt polymerization due to the randomization from rapid transamidation. Therefore, it will be helpful to study this phenomenon using a sample synthesized using a different method, which will be discussed later in more relevant sections.

To estimate the effect of amide content on $T_g$, a wider range of functional group to methylene group CH$_2$ ratio, both higher and lower amide contents, than that provided by the amorphous polyamide 3,4/6,6 series would be helpful. Generally, it is easier to synthesize polyamides with longer methylene group runs using melt polymerization, because of their low melting temperature and consequently lower required polymerization temperature and less thermal degradation. Longer polymerization times make it possible to increase their molecular weight. Another advantage is their higher hydrophobicity and lower sensitivity of their $T_g$ values to environment humidity.

The DSC thermogram of a terpolyamide formed from equal molar amounts of Nylon 66 and 610 salts, and $\alpha,\omega$-aminoundecanoic acid is shown in Figure 3.7. Crystallinity was greatly suppressed and a cold crystallization exothermic peak was observed on the second heating after being cooled from the melt at a moderate DSC cooling rate of 40° C/min. The melting point is much lower than that of their parent homopolyamides, and the $T_g$ at 10.3° C is also lower than those reported for the semi-crystalline homopolyamides. This sample indicates that a low $T_g$ can be obtained for a relatively high molecular weight sample that is less hydrophilic. It therefore lends support to the suggestion that the $T_g$ of a truly amorphous aliphatic polyamide may be lower the widely recognized values for semi-crystalline polyamides.
In summary, despite the possibility that low molecular weight and hydrophilicity could dramatically reduce the glass transition temperatures of polyamide samples, they are nevertheless ~80°C higher than their analogous polyesters. It is also worth noting that both from estimation and experiment, $T_g$s of the polyamides seem to be relatively insensitive to the amide group content, which might be the result of saturation of the hydrogen bonding interactions. A full range comparison of $T_g$s of polyesters and polyamides were calculated using the group contribution methods and is plotted in Figure 3.8. It is used as an indication of the general trend reported in the literature with the careful selection of reasonable values by the author and a large number of data points for the fit to be reliable. Thus, it can serve as a guide to the author for showing what values others are reporting.
Figure 3.8 Full range comparison of Tgs of Polyesters and Polyamides

The variation of the functional group to methylene group ratio provided by amorphous the polyamide 3,4/6,6 series is very limited, so experimental values for both lower and higher amide contents are needed to have a better estimation of the entire range. A lower amide content data point was provided by the terpolymer of nylon 6,6, nylon6,10, and nylon11. A Tg lower than traditionally reported for semi-crystalline polyamides was obtained for this low crystallinity sample. Polyamides with higher amide content require the use of shorter and thus less thermally stable monomers and are difficult to synthesize in the melt without substantial degradation. For this reason, they were synthesized at low temperature and will be discussed in the low temperature method section.
On the other hand, the 70° C difference in $T_g$ for the same sample on consecutive DSC scans was rather confounding. The possibility that our melt polymerized sample possesses multiple $T_g$s corresponding to different blocks is neither substantiated nor refuted due to the limited temperature range scanned. Since a range of 70° C already covers the whole $T_g$ variation range with amide content estimated by the group contribution method, it is premature to draw any conclusion about the effect of amide content on $T_g$ at this point.

3.4.3 Low Temperature Synthesis of High Amide Content Amorphous Polyamides

3.4.3.1 Interfacial polymerization of the N 2,4/3,4 series

Formation of polyamides were confirmed first by FTIR in all instances. (See Figure 3.9, Figure 3.10, and Figure 3.11) The most prominent indication of amide formation is the appearance of N-H stretching near 3300 cm$^{-1}$, which is absent in their corresponding monomer pairs. (See Figure 3.9, because a nylon salt is basically a physical mixture of the monomers) Another characteristic region is between 1500 and 1700 cm$^{-1}$ where amide I and amide II bands appear. Amide I is caused by carbonyl stretching and amide II is caused by N-H bending.

An example comparison between our sample and commercial nylon is shown in Figure 3.10. The only difference is the relative intensities of C-H stretching peaks; due to a lower percentage of CH$_2$ in the chains of our samples, which show smaller C-H peaks. The same can be said about all other interfacial polymerized polyamide 2,4/3,4 series. (See Figure 3.11)
Figure 3.9 FTIR spectra of N34, N24, and their corresponding salts

XRD was used to compare the crystal structures of different Nylon 2,4/3,4 polyamides with varying compositions. It is clear from Figure 3.12 that their crystal structures change from that of one homopolyamide to that of the other with varying compositions, and that near the equal percentage range of monomers the crystal structures are less well defined and manifest broad halos.
Figure 3.10 FTIR spectra of our Nylon 2,4 and Commercial Nylon 6

Figure 3.11 FTIR Spectra of interfacial polymerized Nylon 2,4/3,4 series
However, the closer it gets to the composition showing amorphous halos the lower the yield; in Figure 3.12 good intensity could not be obtained for the 40%:60% sample due to the limited amount of sample available to us at that time. It is now clear that the water solubility of the amorphous samples is the cause of low yield from the interfacial method.

![Figure 3.12 XRD Diffractograms of interfacial polymerized Nylon 2,4/3,4 series](image)

**Figure 3.12 XRD Diffractograms of interfacial polymerized Nylon 2,4/3,4 series**

DSC thermograms for homopolyamides 24 and 34 synthesized by interfacial polymerization are shown in Figure 3.13. The large exothermic peak over 300° C for N 24 is consistent with the literature. The large exothermic peak for interfacial polymerized
N34 is located at similar temperature as that of the N34 synthesized by regular melt polymerization. (Compare Figure 3.2 with Figure 3.13) We have also included N34 samples retrieved from the aqueous and organic phases of the reaction media. Although not shown here, both have polyamide FTIR signatures.

![DSC thermograms of interfacial polymerized N24, N34 of different states. Compare the endothermic peak and heat capacity step up.](image)

Figure 3.13 DSC thermograms of interfacial polymerized N24, N34 of different states. Compare the endothermic peak and heat capacity step up.

Though the majority of product collected was solid, part of the product is water soluble and the other part is organic solvent soluble, both of which are not usually collected. A striking feature was observed for all four samples; a heat capacity jump at around 210°C. The question of whether this is a $T_g$ surfaced. It is obvious to us that the heat capacity increase was too large for normal polymeric materials. It also seems reminiscent of the heat
capacity change in the melting of nylon salt. (See Figure 3.1) The universality of this feature in so many different samples demands an answer and is left for future investigation. Nonetheless, we should for now preclude this from being reported as a glass transition phenomenon for the reasons stated above. Because of the close to amorphous state observed from XRD, the $T_g$s of interfacial polymerized N2434 30-70 and 40-60 were determined to vary from 116 to 143° C, which is higher than $T_g$s of our other polyamides, and is also slightly higher than the trend seen in the n-Nylons.

3.4.3.2 Solution polymerization of N2434 40%60% and Nylon 3,4/6,6 series

The low yield of the amorphous sample with a 40%60% 24:34 composition obtained from interfacial polymerization was found to be caused by the solubility of the sample in water. Therefore, this and other samples with low crystallinity compositions were attempted using solution polymerization.

For homopolymer N24 and N34, water can be used to remove byproduct TEA-HCl. For water soluble samples, chloroform can be used to dissolve the TEA-HCl salt, thereby avoiding contact of amorphous samples with water. After one wash, only very small amounts of TEA-HCl remained in the sample as evidenced by FTIR (See Figure 3.14) and XRD (See Figure 3.15). After two washes with Chloroform, neither FTIR nor XRD was able to detect any impurities.
Figure 3.14 Purification process of SP N2434 4060 tracked by FTIR.

Polarized optical microscopy (POM) was used to compare the crystal structure of the homopolyamides and to confirm the amorphous nature of the N2434 4060 sample. In Figure 3.16 and Figure 3.17, it is clearly shown that N24 has many small spherulites, while N34 has fewer larger ones. This means N24 has a higher crystallizability than N34, and N34 is the unit that suppress crystallization. In Figure 3.17, the 40%:60% sample shows only a pink background, while the 60%:40% shows some degree of crystallinity.
After the sample was purified and confirmed it was then tested on TGA to estimate water content. (See Figure 3.4) About 1% weight loss can be attributed to water content remaining after vacuum drying. The $T_g$ determined from DSC was 47.2° C, and was within the regular range but a little lower than what was expected from its high amide content.

The nylon 3,4/6,6 series was synthesized in a similar way, except the purification process. As can be seen from Figure 3.18, the first filtration from the N3466 60-40 reaction solution was only TEA-HCl. Polyamide was thus dissolved in the NMP and can be precipitated out using two-fold of 2-butanone. Figure 3.19 shows the FTIR spectra of the whole Nylon 3,4/6,6 series, and it clearly shows the increase of C-H stretching with the increase
amount of 6,6 units. XRD (See Figure 3.20) clearly indicated that the sample with a 70-30 composition has the least crystallinity.
T$_g$s of SP 3466 70-30 and 60-40 were determined using DSC. In Figure 3.21, SP3466 70-30 manifest a prominent glass transition event at 51$^\circ$ C with a large endothermic enthalpy relaxation peak. This value is very close to the group contribution prediction. However, the T$_g$ dropped to 21$^\circ$ C on the second heating scan. Despite the difference in synthesis method, both vacuum dried melt polymerized MPN3466 70-30 and solution polymerized SPN3466 7030 manifested large T$_g$ drops on a subsequent heating scan. Yet, only one T$_g$ was detected in each case during a single heating scan.
Figure 3.19 FTIR spectra of SP N3,4/6,6 series
Figure 3.20 XRD of SP N3,4/6,6 series
Figure 3.21 DSC thermograms of SP3466 70-30 1st heating scan (upper panel) and 2nd heating scan (lower panel)

Solvent-cast and as-synthesized powder SPN3466 6040 (See Figure 3.22) show similar changes in $T_g$, but are more consistent with a blockiness speculation. Instead of having just one changed $T_g$ value, the solvent cast sample showed a single $T_g$ changed into two separate $T_g$s, one higher and one lower. The as-synthesized sample was shown to have three distinct glass transition thermal events on the first heating, and the middle $T_g$ disappeared on the second heating scan. If this is also the case for the two different N3466 70-
30 samples, then we should set the temperature scan range outside of what has been used in order to find possibly an additional missing $T_g$. However, why does the as-synthesized MPN3466 70-30 not exhibit this phenomenon? Can a 3% or so difference in water content somehow prevent phase separation? We do not have explicit answers to these questions at the moment. Careful studies of the monomer sequences in these samples are required to make definite conclusions.

About a 100°C difference of the two separated $T_g$ is however a really significant observation, because it exceed the range of n-Nylon $T_g$ trend, and is much wider than what is predicted from group contribution method. Therefore, the amide content dependence of $T_g$s is rather sensitive for polyamides and probably is more complex than the dependence of ester group content on the $T_g$s of its analogous polyesters.

### 3.5 Conclusions

The $T_g$s were determined for melt blended, melt polymerized, interfacial polymerized, and solution polymerized samples of largely amorphous aliphatic polyamides. $T_g$s obtained from Van Krevelen’s group contribution method and those measured for the n-Nylon series were used as guidelines for establishing reasonable $T_g$ values. $T_g$s determined on first heating are compiled in Figure 3.23 in a $T_g$ vs. amide to methylene ratio plot. $T_g$ values of our synthesized polyamides cover the entire variation range and qualitatively have steeper amide content dependences than both guidelines. Severe amide group coupling seemed possible for repeating units with short methylene sequences. For longer monomers, Flory’s conformational analysis was proven accurate by a recent quantum mechanical calculation. A complication arises for the possible blocky nature of our synthesized
polyamides whose phase separated $T_g$s could vary by as much as $100^\circ$ C. Amide content influence on $T_g$ in the polyamides is more complex than the ester content influence on the $T_s$ of analogous polyesters.

Figure 3.22 DSC thermograms of SP3466 60-40 1st and 2nd heating scans of solvent casted (upper two) and powder sample (lower two).
Figure 3.23 Compilation of $T_g$ data according to amide to methylene ratio.

3.6 Future work

A direct continuation of this study would involve the solution blending of N34 and other nyons and study the miscible $T_g$s and phase separation or de-wetting upon annealing.
Chapter 4  Glass Transition Temperatures and Dynamic Fragilities of Isotactic-, Syndiotactic-, and Atactic Poly (methyl methacrylate)s (PMMA)s and Relationships with Their Single Chain Conformational Characteristics

4.1 Abstract

Three PMMAs with different tacticities offer the possibility to evaluate any conformational contributions to their glass transition temperatures, \( T_g \), and dynamic fragilities. Common qualitative comparisons of the structures and \( T_g \)s of polymers do not include PMMAs due to their identical monomeric structure. However, it is well known that different tactic forms of PMMA have different \( T_g \)s; isotactic (i) PMMA’s \( T_g \) is the most peculiar at 60-70K lower than that of the chemically identical syndiotactic (s) and atactic (a) PMMAs. A similar trend was reported for their fragilities in a recent study, (Ngai, K. L.; Gopalakrishnan, T. R.; Beiner, M. Polymer 2006, 47, 7222–7230), where data acquired from several different studies was analyzed on the same Angell’s plot and found fragility indices, \( m \), of 181 for s-PMMA and 147 for i-PMMA. On the other hand, \( m \) values ranging from 90 to 145 have been reported for a-PMMA in the literature. Because of the wide range of the reported values, most likely to the differences in materials and instrumentation employed, new dynamic fragility measurements were conducted. We used DSC in order to provide reliable comparisons of the dynamic fragilities of two stereoregular PMMAs and three a-PMMAs with different molecular weights. The \( m \)s determined for a-PMMAs showed a prominent molecular weight dependence and the comparison of s- and i-PMMAs was consistent with previous studies. Rotational Isomeric State (RIS) conformational Model results were used to explain the conformational origin of the low and high \( T_g \) and fragility of i-PMMA and s-PMMA, respectively.
4.2 Introduction

The nature of the glass transition is widely accepted as one of the most complex and interesting unsolved problems in condensed matter physics\textsuperscript{13,14,23,68,70,71,73,151–153}, and has broad implications in diverse fields of study, ranging from the physics of liquids\textsuperscript{12,154–156} to that of colloids,\textsuperscript{22} and even to the dynamics of biological systems.\textsuperscript{23} In polymer science and engineering, the glass transition temperature (T\textsubscript{g}) is essentially the temperature where the chains in a bulk amorphous polymer solid begin to change conformations and move irreversibly, resulting in dramatic alterations in their macroscopic behaviors. Therefore, T\textsubscript{g} is one of the most important parameters determining the processing and uses of polymer materials.

When a liquid is cooled close to T\textsubscript{g} from above, provided that crystallization is avoided, its viscosity and relaxation time increase dramatically. In this temperature range the dynamics of polymers deviate from Arrhenius temperature dependencies and are generally described by Williams-Landel-Ferry\textsuperscript{60} (WLF), or equivalently Vogel-Fulcher-Tamman\textsuperscript{157} (VFT) type empirical equations. A T\textsubscript{g}-scaled Arrhenius plot\textsuperscript{158} is widely used to compare the rapidity of the change of the dynamic properties of polymers having different T\textsubscript{g}s when their respective T\textsubscript{g}s are approached. The slope of the logarithm of the property parameter at T\textsubscript{g}, which is defined as the temperature at which an arbitrary relaxation time or viscosity is reached, with respect to a dimensionless temperature scale\textsuperscript{159} is known as the dynamic fragility:

\[
m = \frac{d \log x}{d \left( \frac{T_g}{T} \right)} \bigg|_{T = T_g}
\]
where \( x \) is a dynamic property such as viscosity, relaxation time, etc.. The validity of using dynamic fragility to compare polymer dynamics lies in the fact that it is effectively a \( T_g \)-normalized activation energy:\(^{21}\)

\[
m = \frac{E_g}{\ln 10 \ R \ T_g}
\]

where \( E_g \) is the apparent activation energy\(^{160}\) at \( T_g \), and \( R \) is the gas constant. Liquids exhibiting nearly Arrhenius temperature dependence of dynamics have very small \( m \)s, and are categorized as strong liquids; e.g., silica glass (SiO\(_2\)) has a temperature-independent activation energy that can be reasonably attributed to the energy requirement of breaking Si-O bonds. Conversely, fragile liquids show non-Arrhenius temperature dependence, and are characterized by large \( m \)s; their activation energies grow enormously at temperatures approaching their \( T_g \), and therefore fail to be described by a simple activated dynamics\(^{66}\).

\( T_g \) and fragility are not only of scientific interests, but also have technological significance. Relationships between chemical structures (building blocks) and their resultant \( T_g \)s and fragilities (product properties), and the correlation between the two parameters have attracted much effort in the past and remains a topic of open discussion.\(^{19,43,46,56,57,74,77,117,161-167}\) Roland et al.\(^{43}\) experimentally measured the dielectric relaxation of several groups of structurally closely related polymers and found that polymer backbone and/or side group rigidities contribute qualitatively to the increase in their fragilities. This viewpoint is commonly accepted\(^{21,118,164}\). However, the means to define or to quantify a polymer’s rigidity, or equivalently its flexibility, remain elusive. The most common qualitative way is to compare the rotational barriers of the backbone bond rotations and side groups separately.\(^{117}\) However, this can be futile when one compares polymers with the same monomeric unit, but that are connected differently to the backbone; \( i.e. \), different
stereo- and/or regiosequences. Thus, consideration of the flexibility of several consecutive monomeric units is needed to describe the local chemical environment that is believed to be responsible for segmental relaxation behaviors in polymers.

Freed et al.\textsuperscript{56,57} recently extended their generalized entropy theory (GET) to include three specific interaction parameters and separate bending energies $E_b$ for chain backbone and $E_s$ for side chains in the lattice cluster theory (LCT) formulation. Adam-Gibbs (AG) Theory is used to relate structural relaxation time to the configurational entropy, and from there the isobaric fragility can be readily calculated. Although it seems promising in providing implications about the influence of changes in molecular details on real polymer glass formation behavior, the current capability of tailoring realistic structural details is still limited. However, the development of LCT and GET demonstrated the enormous complexity of the task.

The requirement of combined consideration of flexibility of several consecutive monomeric units and specifically taking into account the side chain interactions and steric hindrance is met by adopting the Rotational Isomeric State (RIS) conformational model developed by Flory\textsuperscript{85} to understand a variety of polymer behaviors. After several decades of development, RIS descriptions of almost all common polymers are now available\textsuperscript{168}. In order to test the RIS model’s ability to offer useful information in understanding the glass transition problem, and specifically to identify the conformational differences among polymers possessing the same monomeric units but different connectivities, poly(methyl methacrylate) (PMMA) becomes a natural candidate. This is because it is well-known that three tactic PMMAs show different values of $T_g$, of which isotactic (i) PMMA’s is the most peculiar at 60-70 K lower than that of its chemically identical siblings, syndiotactic (s) and
atactic (a) PMMAs.\textsuperscript{169,170} A similar trend for PMMA fragilities was reported in a recent study,\textsuperscript{167} where data acquired using several different means were analyzed on the same Angell’s plot and found fragility indices $m$ of 181 for s-PMMA and 147 for i-PMMA. On the other hand, a-PMMA has reported $ms$ ranging from 90 to 145 in the literature. Therefore, PMMAs with three different tacticities offer the possibility to evaluate possible conformational contributions to polymer glass transition temperatures and dynamic fragilities.

There have been several RIS models\textsuperscript{171–174} developed for PMMAs, and it was noted\textsuperscript{175} that one of the earlier RIS models\textsuperscript{173} failed to reproduce solution $^{13}$C-NMR chemical shifts of a-PMMA using the $\gamma$-gauche conformational effect. Thus, the newest RIS model\textsuperscript{174} must be revisited to verify the applicability of its use in prediction of $^{13}$C-NMR chemical shifts. The first PMMA RIS model was also used to calculate the difference in entropy between PMMA stereoisomers and yielded a difference of 0.34 eu/mol at 400K compared to the calorimetrically measured difference of 3 eu/mol.\textsuperscript{170} The large discrepancy between the RIS calculated and measured difference does not necessarily suggest a conformational entropy contribution that is small nor does it reject the validity of RIS models as effective tools to analyze polymer conformations. The reason for this entropy discrepancy might be the isomeric state treatment; \textit{i.e.}, replacing the continuous bond rotation potential with a finite number of discrete states of narrow rotational potential minima separated by very high potential energy barriers. It is this feature which makes it possible to adopt matrix multiplication methods to calculate the conformational partition function $Z$.\textsuperscript{85} It is worth noting that most of the conformational information depends on the derivative of
In $\ln Z$, which is less sensitive to the absolute value of $Z$ than the entropy is.\textsuperscript{168} Because entropy directly depends on $\ln Z$, experimental values of $S$ cannot be evaluated unambiguously from the RIS model.

In the current study, new dynamic fragility measurements were performed using differential scanning calorimetry (DSC) in order to provide reliable comparisons of the dynamic fragilities of the different tactic PMMAs. The possible conformational origin responsible for the dependence dynamic fragilities on local polymer structures will be discussed.

4.3 Experimental

4.3.1 Materials

95% isotactic, 85% syndiotactic poly(methyl methacrylate)s (PMMA)s and two atactic PMMAs with average molecular weights of 15,000 and 75,000 g/mol were purchased from Scientific Polymers Inc.. Atactic poly(methyl methacrylate) with a molecular weight of 996,000 g/mol was purchased from Sigma-Aldrich. All PMMAs were used without further purification. Chloroform-d (99.8 atom% deuterium) was purchased from Cambridge Isotope Laboratories, Inc.

4.3.2 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed in the range of 700–4000 cm\textsuperscript{-1} on a Nicolet Nexus 470 Spectrometer equipped with a Nicolet OMNI Germanium Crystal ATR sampling head. 64 scans with a resolution of 4 cm\textsuperscript{-1} were collected.
4.3.3 NMR Spectroscopy

Proton Nuclear Magnetic Resonance (¹H NMR) spectra were recorded on 1wt% PMMA solutions in CDCl₃ using a Varian Inova 500 NMR spectrometer operated at 500 MHz at ambient temperature. The ¹H NMR spectra were used to calculate stereo diad and triad contents.

4.3.4 DSC

Differential scanning calorimetric (DSC) thermal scans were performed with a Perkin Elmer DSC-7 instrument, which was calibrated using the three-point method using undecane, indium, and zinc. Nitrogen was used as the purge gas. A baseline with no sample was collected before each continuous DSC experiment, and was subtracted from the subsequent data collected to remove any baseline curvature caused by the instrument. PMMA samples were first heated to 170 °C to remove any thermal history and then were cooled at different cooling rates, namely 100, 50, 20, 5, 1, and 0.1 °C / min, each of which was followed by a standard heating scan at 20 °C/min. The specific temperature range of the measurement varied with the T₉ of each PMMA and was set to cover an overall temperature range of 90 °C with T₉ centered in the middle. The cooling rates employed in this study extend over three orders of magnitude which was suggested in a recent study to be critical for the accurate determination of dynamic fragility from DSC¹⁷⁶.

Due to the difficulty in finding a suitable material for the calibration of DSC cooling scans, because most materials tend to undercool, glass transition signals observed during cooling are usually weak and inaccurate. (Some liquid crystal standards¹⁷⁷ do not show undercooling, but they are not routine calibration materials used on most DSC instruments) Therefore, it is customary to determine T₉ on a heating scan. However, depending on the
previous thermal history and the heating rate adopted, DSC heat flow curves can manifest overshoot or undershoot to the detriment of the accuracy of the measurement of \( T_g \). Coming to the rescue is the limiting fictive temperature determined on a heating scan which is recognized to be almost equivalent\(^{178}\) to the \( T_g \) value that might otherwise be determined on the previous cooling scan. Hence, it is convenient to replace \( T_g \), which is most naturally defined in cooling from above, with a limiting fictive temperature determined on the next heating scan. In the literature, fictive temperature\(^{179}\) is sometimes used instead of the more accurate limiting fictive temperature\(^{178,180}\) to mean the limiting value of fictive temperature when the material is cooled through the transition region. We do not make a distinction between the two in our latter discussion.

The empirical exponential relation links measured \( T_g \) with the cooling rate using an activation energy, a gas constant and a pre-exponential constant. Dynamic fragility was also defined as a \( T_g \)-scaled activation energy. Combining these two relations results in a formula for dynamic fragility \( m \);\(^{179}\)

\[
\log \frac{q}{q_{ref}} = m - m \frac{T_f^{ref}}{T_f}
\]

It is clearly shown in the above equation that, dynamic fragility can be determined either from the slope or from the intercept of the plot between logarithm of reduced cooling rate and inverse of the reduced fictive temperature.

The main utility of the DSC experiment in this study is thus to measure fictive temperatures of PMMAs on heating at a standard rate, 20 °C/min, after being cooled at different rates. Moynihan’s method\(^{180}\) was used to determine the fictive temperature of PMMAs. It is an area matching procedure that was later put into a precise mathematical expression:
\[ \int_{T_f}^{T \gg T_g} (C_{pl} - C_{pg}) dT = \int_{T \ll T_g}^{T \gg T_g} (C_p - C_{pg}) dT \]

in which, \( T_f \) is the fictive temperature to be determined, \( C_{pl} \) is the liquid state heat capacity, \( C_{pg} \) is the glass state heat capacity, and \( C_p \) is the apparent heat capacity from the measurement. In the graphic representation, (See Figure 4.1) the shaded area corresponds to the integral on the right hand side and the area included in the trapezoid formed by red dashes represent the integral on the left hand side. The location of the thick red vertical dash is adjusted in the area matching process and is equal to the numerical solution of the foregoing equation. The principle of enthalpy or the area equivalence resides in the original definition\(^6\) of the fictive temperature where the glass property vs. temperature line intersects with equilibrium melt property vs. temperature line. This property can be enthalpy, volume, refractive index etc.\(^{180}\)

Shown in Figure 4.2 is the example of an integrated isotactic PMMA heating scan. Enthalpy is continuous through the transition region, but manifests a retardation of the change in the slope from glass to equilibrium. At the end of the process, the total enthalpy returns to the equilibrium value as if the process was done through a sudden change of slope or a kink at the intersection of two enthalpy lines. The kink corresponds to a discontinuous jump in its derivative, heat capacity, and is represented by the vertical dash line in Figure 4.1.

Wang et al.\(^{179}\) developed a simple method of obtaining fictive temperatures from an enthalpy differencing procedure, except for the reference fictive temperature at standard heating rate after a standard cooling rate, for which Moynihan’s method\(^{180}\) was used. The idea is to compare the enthalpy differences between the reference scan and scans that were previously cooled at different cooling rates:
\[ \Delta H(q) = \int_{T_1}^{T_2} (C_{p\text{standard}} - C_{p\text{non-standard}})dT \]

A positive enthalpy difference increases the estimated fictive temperature of the nonstandard scan from that of the standard through an approximate relation:

\[ T_f = T_{f\text{standard}} + \frac{\Delta H(q)}{\Delta C_p} \]

where \( \Delta C_p \), is the heat capacity difference between liquid and glass in a standard scan at standard fictive temperature.

Figure 4.1 Graphic definition of fictive temperature using isotactic-PMMA heating scan at 20\(^\circ\)C/min after a 0.1/min cooling scan.
Figure 4.2 Definition of fictive temperature on an enthalpy vs. temperature plot using example of isotactic-PMMA heating scan at 20°C/min after a 0.1/min cooling scan.

Once \( T_f \) as a function of cooling rate is obtained, a plot of \( \log(q/q_{ref}) \) vs. \( T_f^{ref}/T_f \) can be constructed. The negative of the slope or the intercept of the linear fit is the dynamic fragility index value, \( m \), we are trying to measure in this study. An example is shown in Figure 4.3 for our syndiotactic PMMA that has been cooled at 6 different cooling rates extending over three orders of magnitude.
4.4 Results and Discussions

4.4.1 FTIR

Fourier transform infrared (FTIR) spectroscopy was performed on all five PMMAs, and expanded regions between 750 and 2000 cm\(^{-1}\) are presented in Figure 4.4. The vibrational peaks from 1100 to 1300 cm\(^{-1}\) were assigned to the coupled contribution of \(\nu_a(C-C-O)\) and \(\nu(C-O)\) modes\(^{181}\) that are widely acknowledged to be highly sensitive to conformational changes\(^{182,183}\). It is clearly shown that isotactic PMMA has conformation-induced peaks that are very distinct from the other four PMMAs, which are closely similar. The most prominent are the absence of a peak at 1061 cm\(^{-1}\) and the merging of a doublet between 1240 and 1271 cm\(^{-1}\). (It is not surprising to see the nearly identical absorption peaks
of syndiotactic and atactic PMMAs considering the fact that both have high racemic diad contents.)

Figure 4.4 FTIR spectra of all five tactic PMMAs in the range of 700 to 2000 cm$^{-1}$. 
4.4.2 NMR

Proton NMR was used to determine the stereo-triad contents of the PMMAs. In Figure 4.5, three different types of proton resonances are identified as methyl ester, β-methylene, and α-methyl. The latter two have shown sensitivities to local microstructures with multiple splittings; β-methylene protons are sensitive to tetrad or even longer sequences, which unfortunately are not separately integratable. α-methyl protons have three well separated resonances resulting from three stereo-triads; i.e., mm, mr, and rr. The percent contents of each of these three triads were calculated using the integrated resonance peak areas and are summarized in Table 4.1. Diad contents were estimated by assuming half of the mr content contribute to mm and the other half to rr. It has confirmed that 95% isotactic PMMA indeed contains 94.7% meso diads and 85% syndiotactic PMMA has 84.2% racemic diads. It is also apparent from the Table 1 that the two atactic PMMAs have similar triad contents and almost the same diad contents. The difference between the two must therefore be a result of other factors; e.g., molecular weights.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Manufacturer provided information</th>
<th>NMR Triad Content</th>
<th>NMR Diad Content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n$ (Da)</td>
<td>$T_g$ (°C)</td>
<td>Cat#</td>
</tr>
<tr>
<td>15K a-PMMA</td>
<td>15,000</td>
<td>88</td>
<td>424</td>
</tr>
<tr>
<td>75K a-PMMA</td>
<td>75,000</td>
<td>115</td>
<td>037B</td>
</tr>
<tr>
<td>Isotactic PMMA</td>
<td>300,000</td>
<td>38</td>
<td>689</td>
</tr>
<tr>
<td>Syndiotactic PMMA</td>
<td>50,000</td>
<td>105</td>
<td>908</td>
</tr>
</tbody>
</table>
Figure 4.5 Proton NMR spectra of four tactic PMMAs and their peak assignments.

4.4.3 DSC

A total of 6 heating scans were collected for each PMMA sample at our selected reference heating rate of 20 °C / min. In Figure 4.6, DSC heating scans of isotactic-PMMA at 20 °C / min after being cooled at different rates are shown. As the heating rates decreases, the enthalpy relaxation peak becomes more prominent. This is caused by the sample’s attempts to restore its total enthalpy to its equilibrium value on the reheating. The slower the previous cooling rate, the longer the time was provided for the sample to acquire its equilibrium value during the process of being cooled through the glass transition. This is equivalent to the effect of a longer isothermal annealing time at a temperature not far below the glass transition temperature. Thus the total enthalpy value of the sample before reheating
is smaller for the annealed (or aged) and slow-cooled samples. As a result, the sample requires more heat (enthalpy) to offset the amount lost in the cooling or annealing and finally reaches its equilibrium melt value far above the glass transition region.

![Diagram of DSC heating scans at 20 °C/min after being cooling at different rates, example shown is isotactic-PMMA.](image)

**Figure 4.6** DSC heating scans at 20 °C/min after being cooling at different rates, example shown is isotactic-PMMA.

After using Moynihan’s method to obtain $T_f$ from the standard cooling and heating scan, the convenient enthalpy differencing method was used to estimate $T_f$s from the non-standard cooling rates. Figure 4.7 shows an example of the heat flow difference plot of isotactic PMMA. Here, the heat flow or heat capacity of the standard heating scan was subtracted by that of the other heating scan. The zero heat capacity line corresponds to the standard scan itself and by definition has zero enthalpy difference. Other non-standard heating scans have peaks above and/or below the zero line. These curves were integrated
with the areas below zero line taken as negative. $T_f$s were then obtained using the empirical relationship relating $T_f$ and enthalpy difference. Fragility value can then be calculated.

Figure 4.7 Enthalpy differencing method used to estimate $T_f$ from non-standard cooling rates, example shown is isotactic PMMA.

$T_f$s of non-standard were also obtained individually using Moynihan’s method without using the convenient enthalpy differencing procedure in order to estimate its reliability. Figure 4.8 compares the fragility plots of isotactic PMMA with and without using the enthalpy differencing method. Large discrepancies were found for this and other PMMAs and the fragility values obtained using the enthalpy difference method tend to be on the low side and do not effectively show differences among the different PMMAs. In light of this observation, results from the enthalpy differencing method were rejected. The possible cause of its failure could be the thermorheological complexity of the polymer
compared to thermorheologically simple small molecules for which this method was originally developed. It seems to us that the empirical relation provided in the original study does not apply well to polymers.

![Figure 4.8 Comparison of fictive temperatures and their fragilities obtained from Wang et al.’s enthalpy differencing method and Moynihan’s method.](image)

The resulting dynamic fragilities obtained in this study using DSC are presented in Table 4.2 along with the $m$ values reported in the literature. $m$ values for atactic PMMAs showed an apparent positive variation with molecular weight, and its significance will be discussed in the next section. Our values of $m$ for isotactic and syndiotactic PMMAs confirm the literature reported comparisons using dielectric spectroscopy.
Table 4.2 Comparison of fragilities measured in the current study to literature values

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$m$, Current study by DSC</th>
<th>$m$, Literature$^{21,44,118,167,186}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15K a-PMMA</td>
<td>76</td>
<td>90,103,115,120,145</td>
</tr>
<tr>
<td>75K a-PMMA</td>
<td>121</td>
<td></td>
</tr>
<tr>
<td>996K a-PMMA</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>Isotactic PMMA</td>
<td>120</td>
<td>147</td>
</tr>
<tr>
<td>Syndiotactic PMMA</td>
<td>173</td>
<td>181</td>
</tr>
</tbody>
</table>

4.4.4 Molecular weight dependence of fragility

In the inset of Figure 4.9, a positive correlation between the fragility of a-PMMAs and their molecular weights is evident. This is consistent with the observation of Andreozzi et al.$^{60}$ in their study of the enthalpy relaxation of monodispersed atactic PMMAs with a PDI of less than 1.1 and an average molecular weight range of 1,450-55,900 g/mol. There, fragilities increased from ~ 90 for the lowest molecular weight sample and increased to ~120 for the two highest molecular weight a-PMMAs. Questions regarding the saturation of molecular weight were posed but no answers were possible, because unfortunately the highest molecular weight in their study was 55,900 g/mol. This molecular weight is closest to our s-PMMA and 75K a-PMMA and should prove to be relevant to the importance of other factors; i.e., tacticities etc. Despite the fact that different fitting procedures were used to calculate $m$, results are strikingly similar for our 75K a-PMMA and their 55,900 g/mol sample. This also lends support to the argument that the high fragility of syndiotactic PMMA is not due to its molecular weight. The saturation was not reached according to the even higher fragility of our high molecular weight a-PMMA. The only discrepancy is the
low value of $m$ for our 15K a-PMMA, for which their sample reached an $m$ of ~115. Ours lies in the range commonly observed for low molecular weight polymers and molecular liquids.\textsuperscript{118}

Figure 4.9 Relationship between dynamic Fragility and heat capacity change at glass transition temperature for all PMMA samples. Heat capacity change at $T_g$ was measured using Pyris software accompanies Perkin Elmer DSC-7 on -0.1/+20 °C/min.

While their fragility value starts to approach a plateau of ~120 at a low molecular weight of 4,900 g/mol, our 15K a-PMMA manifests a fragility well below the value for moderately high molecular weight samples; theirs is lower than and ours higher than the entanglement molecular weight range of 5,800-10,100 g/mol for PMMAs of different stereoregularities, respectively. Therefore, the entanglement molecular weight does not seem to be responsible for the molecular weight dependence of fragility of PMMAs. In addition,
the Kuhn segment length was reported\textsuperscript{187} to be non-critical for the molecular weight dependence of polymer fragility either. While the fragilities of polystyrene (PS)\textsuperscript{159} have a strong molecular weight dependence, poly(dimethylsiloxane) (PDMS) has virtually no molecular weight dependence even for 8-mers.\textsuperscript{188} Another peculiar example is polyisobutylene (PIB), which is one of the strongest polymers and shows a slightly negative correlation with molecular weight.\textsuperscript{187}

Sokolov and co-workers\textsuperscript{187} raised the interesting proposition that the conformational states of different polymers could be responsible for the different molecular weight dependences of fragility for polymers that have distinct structures; \textit{i.e.}, symmetric or not. It was speculated that asymmetric monomeric units impart a large number of conformational states related to their stereo-regularity. The combinatorial conformational states thus increase rapidly with increasing molecular weight. They continued to use the argument, from the energy landscape theory, that a wider distribution of energy minima is responsible for the increase in fragility. The proposition provided a promising line of thinking notwithstanding its flaws with respect to details of the application of rotational isomeric states model, which was admittedly beyond the scope of that study.

It is worth noting that although increasing molecular weight increases the total number of conformational states of a single chain, but this increase barely compensates the loss in the number of possible arrangement in packing a longer chain into a space filled with other long chains. Therefore, the total configurational entropy, including both the intra-chain conformational contribution and inter-chain packing contribution, drops as a result of an increase in molecular weight. The total number of minima in the energy landscape actually decreases, which is in contradiction to the author’s argument. In addition,
the increase in the combinatorial numbers of states is universal for all polymers regardless of their symmetry and it does not explain which condition causes the saturation of properties to take place.

A closer look at the chemical structures of the polymer is usually required in order to draw any conclusion on the structural factor dependencies of their different properties. In the case of PDMS, the fact that it bears two very different valence angles at oxygen and silicon atoms (143 and 110°), respectively, was often neglected. Unlike carbon-carbon backbones, the planar trans conformations of PDMS are not rectilinear and form a loop within about 11 units. This is not to say that PDMS tends to form cyclic structures by itself, but rather a reminder that details such as these could be easily overlooked but might be relevant. Considering the experimental result that even at 8 repeat units level the molecular weight is irrelevant to the fragility of PDMS, it seems reasonable to assume that the factor that determines fragility of PDMS develops and stabilizes in chains as short as 8 units and is thus very local.

A recent molecular dynamic simulation study of the variation of fragility of network-forming inorganic glasses with composition, under the realm of constraint theory of glass formation, reached a conclusion that non-directional bonding, and consequently a heterogeneous distribution of interactions result in high fragility. Because of the partial resemblance of PDMS to network forming silica in terms of bond types, it is natural to explore their connections. Silica has very low fragility, which does not depend on molecular weight, because a piece of glass is essentially a gigantic single molecule. These similarities seem to favor our speculation that local structures, i.e., valence bond angles etc., are relevant to the fragility of PDMS.
Furthermore, PDMS is one of the most flexible polymers due in part to its relatively longer Si-O bonds which alleviate steric hindrances resulting from congested pairwise gauche+ gauche- conformations. The experimental results of Roland, Ngai, and co-workers showed that poly(methylphenylsiloxane) (PMPS) and poly(methyltolylsiloxane) (PMTS) have very similar fragilities and relaxation behavior at ambient pressure compared to that of the PDMS, despite their pendent groups being bulkier compared to methyls. However, it was shown that all properties of PMTS are more sensitive to pressure than PMPS. It seems clear that, the backbone structures, not the functionalities or size of the side groups, of the siloxanes are ultimately responsible for their similar fragilities. The similar properties at atmospheric pressure and yet different tendencies for deviation at elevated pressure supports our speculation that backbone conformations were unaltered at ambient pressure regardless of the substitution.

A very recent study by Sokolov and co-workers found a surprising result that might provide new insight into the explanation of the molecular weight dependence of fragility and glass transition temperatures. They suggest chain relaxation of polymers measured by viscosity does not differ compared to the structural relaxation of small molecules. Consequently, it is polymer segmental relaxations which are responsible for different polymer glass transition temperatures. They proposed that two important time and length scales might be important in discerning between rigid and flexible polymers with respect to their different molecular weight dependences of fragility and $T_g$. A length scale of 1-2 nm corresponding to the cooperative rearrangement region estimated from Adam-Gibbs (AG) theory is related to the time scale of segmental relaxation. Another length scale is the molecular dimension evaluated by the radius of gyration and is related to the time scale...
of chain relaxation. When a rigid polymer has a radius of gyration far beyond the length scale of segmental relaxation, the chains remains un-ergodic in the time domain of segmental dynamics and a portion of the conformational states are not accessible. Increasing molecular weights result in an increase of the inaccessible part of the configurational space and therefore a stronger temperature dependence or fragility. However, this type of reasoning is still in its early form and does not constitute a definite answer to the mechanism behind the molecular weight dependences of \( T_g \) and fragility.

It seems natural to ask whether the chain rigidity is truly responsible for the molecular weight dependence of PMMA \( T_g \)'s. If so, the two stereo-regular samples should show two extremes in their molecular weight dependences. Unfortunately, our current experimental results do not include molecular weight variation for stereo-regular PMMAs. It thus remains interesting to test this assumption using different molecular weight samples of stereo-regular PMMAs in the future.

In summary, the mechanism of the differences in molecular weight dependence of fragility is still unclear. In most cases, simpler explanations, such as the original free volume theory, are more favorable. Therefore, for more flexible polymers, the decrease in the end group content with molecular weight does not have much of an effect on \( T_g \) as it does for more rigid polymers.\(^{186}\)

4.4.5 Heat Capacity change at \( T_g \) vs. dynamic fragility

It is now generally acknowledged that the heat capacity change accompanying the glass transition as a thermodynamic representation of fragility has positive correlation only with inorganic glasses and shows a negative correlation in the case of polymers.\(^{118,186,191}\) As was seen in Figure 4.9, our results follow this expected trend. In the case of atactic PMMAs
of different molecular weight, there is also a parallel negative correlation between molecular weight and heat capacity change at $T_g$. It is unclear whether molecular weight is the cause for both the increase in fragility and decrease in heat capacity change. It is also possible that the heat capacity change reflects something more fundamental than what governs the fragility. In short, the system becomes more complicated with the increase in molecular weight and correlations that fit small molecules fail in the case of polymers. We are convinced that thermorheological simplicity breaks down with increased molecular weight.

### 4.4.6 Stereo-regularity dependence of fragility

We begin this discussion by assuming that stereo-regularity affects fragility through its influence on the chain flexibility. Chain flexibility, in turn, plays a critical role in affecting polymer fragility. However, there is no consensus on how to quantify flexibilities of polymer chains. Examples of the quantities used in the past include the flexibility factor, bending energy, Kuhn length, and characteristic ratio.

In Figure 4.10, fragilities of PMMAs are plotted as a function of meso (m) diad content and a negative correlation between the two was observed. This trend is consistent with literature where coupling parameters were found to be 0.51 for syndiotactic PMMA and 0.44 for isotactic-PMMA in addition to the fragilities of 181 and 147, for the former and latter, respectively. In the coupling model, a higher coupling parameter indicated higher intermolecular coupling and cooperativity. This type of parameter, however, is a manifestation of this particular relaxation experiment instead being a quasi- *a priori* parameter determined by independent studies. Hence, we were not able to obtain molecular basis information from the coupling parameter.
Characteristic ratios ($C_\infty$), on the other hand, were determined for almost all polymers from many independent researches and can be easily located in many polymer handbooks. Therefore, we chose this parameter as a possible relevant quantity for the characterization of polymer chain flexibility. Another reason for this selection is that, rotational isomeric state (RIS) models usually reproduce this quantity quite well after careful parametrization, through which molecular level insights can be obtained.

On the right y-axis of Figure 4.10, two limits of $C_\infty$ were set as 7.3 for s-PMMA and 10.3 for i-PMMA and the curvature of the dash line was drawn qualitatively to the shape of Figure 6 of ref. 45\textsuperscript{173}, but on a negative scale for the purpose of guiding the eye to see the negative correlation. As the meso diad content increases, characteristic ratio of PMMA increases and fragility decreases. We have the empirical knowledge\textsuperscript{43,117} that rigid polymer chain tends to experience frustration in packing and therefore manifest higher fragility. It is thus natural to expect s-PMMA to be more rigid than i-PMMA, both from its high $T_g$ and high fragility. However, the $C_\infty$ of s-PMMA is smaller than i-PMMA. By the usual definition, smaller $C_\infty$ corresponds to higher flexibility. Using $C_\infty$ as a measure of flexibility therefore gives us such a contradicting conclusion, because s-PMMA is both flexible and fragile. Correction of $C_\infty$s to their respective $T_g$s using estimated temperature coefficients reduces the difference by about 1.5, which is not significant enough to reverse the trend. So we conclude that $C_\infty$ is not a suitable quantity for correlating the flexibility of stereo-regular PMMAs with their glass transition phenomena. $C_\infty$ may be an irrelevant parameter, because $T_g$ and fragility are probably determined on a smaller scale of polymer chains; \textit{i.e.}, a more local environment.
Figure 4.10 Relationship between dynamic fragility and meso diad content for all PMMA samples. Right y-axis was set to scale with characteristic ratio as a function of meso diad content as estimated by Vacatello and Flory\textsuperscript{173} using rotational isomeric states (RIS) model. Dash curve was dawn qualitatively as concave function to guide the eye.

The conformational analysis results obtained by Vacatello and Flory\textsuperscript{173} made it clear that the low $C_\infty$ value of s-PMMA is caused by its tendency to circle back on itself due to the persisting continuation of the lowest energy $t,t,t,t$ conformation. The fact that s-PMMA was only able to crystallize with the aid of solvent\textsuperscript{173} indicates its frustration in packing into a crystal lattice and implies its high tendency to form a glass, which is in fact a working definition of fragility. A comparison of the number of local conformational energy minima at a four-bond level revealed another aspect of local flexibilities; 76 possible conformations were identified for i-PMMA, which is in stark contrast to s-PMMA’s 30. More conformational choices undoubtedly imparts i-PMMA with larger conformational
freedom to respond to any outside stimuli, be it thermal or dielectric. In this sense, i-PMMA is more flexible than s-PMMA.

It is therefore reasonable to conclude that despite its larger chain dimensions, as evidenced by the larger characteristic ratio, i-PMMA is conformationally more flexible at a length scale most relevant to glass transition. This local conformational freedom reduces segmental relaxation time and alleviates any constraint put upon it during cooling process, and therefore is a plausible origin of the low $T_g$ and fragility of i-PMMA.

4.5 Conclusions

In summary, dynamic fragilities of two stereo-regular PMMAs and three varying molecular weight a-PMMAs were measured using DSC in order to provide reliable comparisons of their dynamic fragilities. The $m$s determined for a-PMMAs showed a prominent molecular weight dependence and that of the s-PMMA and i-PMMA were consistent with previous study. Heat capacity changes at $T_g$ correlate negatively with the fragilities of polymers probably due to the breakdown of their thermorheological simplicity. Rotational Isomeric State (RIS) conformational model results were used to explain the conformational origin of the low and high $T_g$s and fragilities of i-PMMA and s-PMMA, respectively.
Chapter 5  Conclusions and Future Work

5.1 Conclusions

A series of wholly amorphous linear aliphatic co- and tetra- polyesters were successfully synthesized via bulk melt step-growth polymerization. The glass transition temperatures of the polyesters increase linearly with the ratio of ester groups per methylene group. Their calculated conformational entropies decrease approximately linearly with increasing ester group content. The potential ester-ester coupling effect for shorter aliphatic monomers was not observed or reflected by a non-monotonic variation of $T_g$s. The overall linear variation of $T_g$s suggests both the effect of intramolecular conformational flexibility and the effect of intermolecular interactions contribute linearly to polymer $T_g$s.

The analogous linear aliphatic amorphous polyamides were synthesized using melt, interfacial, and solution polymerization. Their $T_g$s were determined along with a few other low crystallinity polyamides obtained through melt blending, and melt polymerization. $T_g$s obtained from Van Krevelen’s group contribution method and from the literature value reported for the n-Nylon series were used as guidelines for establishing reasonable $T_g$ values. $T_g$ values of our synthesized polyamides cover the entire variation range and qualitatively have steeper amide content dependencies than both guidelines. A complication arises for the possible blocky nature of our synthesized polyamides, whose phase separated $T_g$s can vary by as much as 100K. Amide group content influence on $T_g$ in the polyamides is more complex than the ester content influence on the $T_g$s of analogous polyesters. Comparison of the $T_g$s of analogous polyesters and polyamides yielded differences of the order of 100K, which suggests the profound effects of hydrogen bonding vs. dipole-dipole interactions.
In addition to $T_g$ values, the steepness of the change in relaxation time near $T_g$ is another important quantity for studying the glass transition problem. This quantity, dynamic fragility $m$, was measured using DSC for each of the two stereo-regular PMMAs and three a-PMMAs with varying molecular weight. The $m$s determined for a-PMMAs showed a prominent molecular weight dependence, while those of the s- and i-PMMA were consistent with previous studies. Heat capacity changes at $T_g$ correlated negatively with the fragilities of PMMAs. The characteristic ratio of PMMA chain dimensions manifest an opposite variation with fragility, which suggests its irrelevancy to the glass transition phenomenon, probably due to differences in the length scale dependence. The number of local conformational energy minima, or related conformational entropies, obtained from RIS model results was proposed to be responsible for the apparent flexibility differences observed from their distinct $T_g$s and fragilities.

5.2 Future work

The heat capacity jump at $T_g$ was previously used as an indication of material dynamic fragility. For the inorganic glasses, which this concept was originally proposed for, the higher the heat capacity jump, the more fragile the material. However, this empirical relationship failed for many polymers including our own PMMAs. It is interesting to note that the $\Delta C_p$ increases with increasing ester content accompanied by increases in $T_g$. As the ester content increases so does the chain stiffens and therefore is believed to become more fragile. This is in accordance with the general perception of the molecular basis of polymer fragility and is also consistent with the foregoing empirical relationship. It is thus interesting to measure the fragilities of these amorphous polyesters to test theoretical predictions.
For amorphous polyamides synthesized by solution polymerization, a direct continuation of the study is the solution blending of N34 and other nyons to study the miscible $T_g$s and phase separation or de-wetting behaviors observed upon annealing. Those experiments will help elucidate the cause of the separate $T_g$s different by 100K that were observed.

For the PMMA fragility study, variation in the molecular weight of the stereo-regular samples will provide more insights into the origin of the different extent of molecular weight dependences of fragilities observed for different polymers.
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