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An abstract of
A thesis submitted to the Faculty of Emory College of Arts and Sciences
of Emory University in partial fulfillment
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Abstract

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The study of the glass transition in miscible blends is an important area of polymer research because this transition is crucial to understanding miscible blend behavior. There are two main theoretical ideas, self-concentration and thermal concentration fluctuations, that define blend component behavior during the glass transition and the relevant length scale of blend interactions. This project has two parts that use a relatively new fluorescence technique to measure the glass transition temperature (T_g) of individual components within polymer blends with the aim of providing insight into miscible blend T_g behavior. In part one, the T_g of polystyrene (PS) was measured in bulk PS/poly(vinyl methyl ether) (PVME) blends for a range of compositions, and in part two, the T_g deviation with varying distance from a PS/PVME interface in a four-layer PS/PVME system was investigated. Unfortunately, there were experimental issues in both parts of the project that will require some re-measuring of the data presented.

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Introduction

The Glass Transition and Miscible Blends

The polymer glass transition is an intense topic of discussion in the research community because polymer behavior and properties differ greatly above and below the glass transition temperature (T_g). The glass transition temperature is the temperature where, upon cooling, a polymer or blend changes from a liquid or rubbery state to a glass. As the polymer is cooled, the density or free volume decreases in a relatively linear fashion. At the glass transition, the rate changes and slows down. After the transition, the decrease in free volume becomes approximately linear again. High T_g polymers are stiff and rigid, while low T_g polymers are elastic and flexible. To create a custom made polymer with certain physical properties, one must either create a brand new polymer or blend two or more known polymers together. It is much more difficult to create a new polymer with certain desired qualities, and so a lot of focus has been turned to blending polymers.

Miscible blends are composed of two or more polymers that will not phase separate when mixed together. Because most polymers phase separate when mixed together, miscible blends are rare. The Flory-Huggins theory[1] predicts the free energy of mixing as a function of the entropy and enthalpy of mixing. While entropy always favors mixing by lowering the free energy of mixing, the entropy of mixing for polymers approaches zero as the polymer chain length increases. Therefore, enthalpy determines polymer miscibility. Enthalpy, which decreases miscibility as it increases, is described in terms of the interaction parameter χ, which is the energy (relative to thermal energy k_bT) needed to remove two molecules from their neat solutions and put them into the opposite solution.[1] Typical values of χ usually disfavor mixing. Miscible blends are commonly defined as exhibiting only one T_g.[2] In these experiments, we focused on polystyrene (PS)/poly(vinyl methyl ether) (PVME) blends, due to the vast amount of literature available. The T_g of PS is 100 °C and PVME has a T_g of -49 °C, and their chemical structures are shown below in Figure 1.

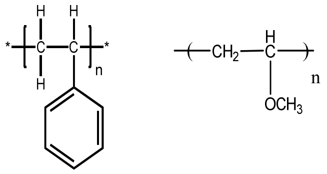

Figure 1. PS and PVME monomers.

<u>T_g Measurement Techniques</u>

Differential scanning calorimetry (DSC) is the standard method of measuring neat polymer and blend T_g. DSC measures the overall blend glass transition by plotting the change in heat flow as the temperature is increased. Figure 2a shows DSC curves for a series of PS/PVME blends. Up arrows indicate the start of the glass transition, crosses indicate the transition midpoint, and down arrows mark the endpoint. These symbols correspond with the bottom, middle, and top curves respectively in Figure 2b, which is compared to the fluorescence measurements later in this thesis. Figure 2a shows how the blend transition DSC curves broaden and cover a larger range of temperatures compared to the neat single component transitions. The extent of the broadening is more obvious in Figure 2b, especially with PS concentrations of 40-70%. The significance of this broadening will be discussed later. It is important to note that the T_g of a PS/PVME blend measured with DSC varies significantly with molecular weight (MW). Figure 2c shows the variation of the glass transition temperatures of PS/PVME blends when made using PS at slightly different MWs (weight average molecular weight, M_w, of 57 000 and 95 000 g/mol).

Dielectric relaxation spectroscopy (DRS) is a method that has been used to measure the behavior of dielectrically active polymers. DRS is capable of measuring the T_g of just one component, but only if one polymer is dielectrically active and the other blend component is inactive. Because PS is not dielectrically active, it cannot be measured using this technique, but DRS can measure the PVME component T_g in PS/PVME blends.

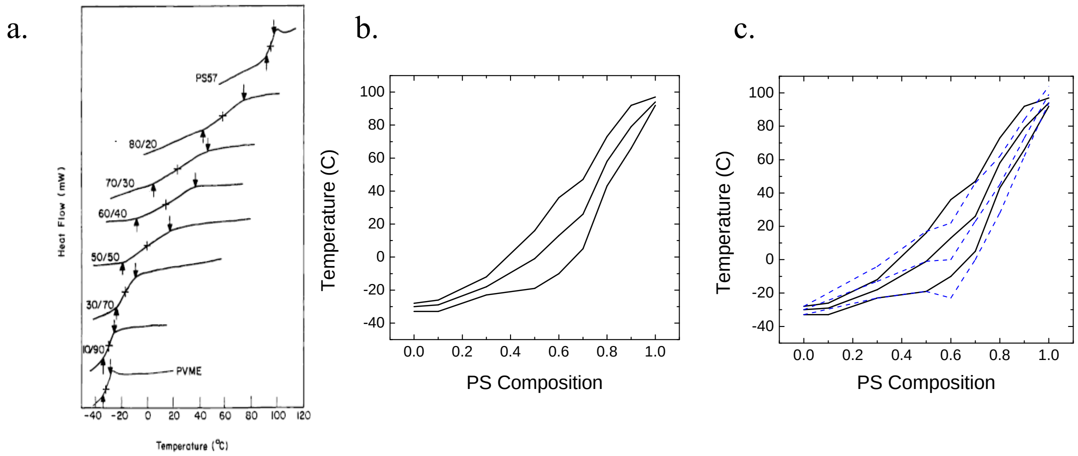

Figure 2. a. DSC curves for PS/PVME of M_w = 57 000 and 99 000 g/mol respectively. Figure reproduced from reference 2 with permission. **b.** Plot of DSC start (bottom line), middle (middle line), and endpoint (top line) temperatures from Figure 2a versus PS composition. The range of glass transition temperatures broadens considerably with PS concentrations of around 40 to 70 percent. **c.** Temperature variation of DSC glass transitions of PS/PVME blends using PS polymers with similar molecular weights. Solid black line is from Figure 2b and represents the low M_w PS (at 57 000 g/mol) and the dashed blue line is the high M_w PS (at 95 000 g/mol).

Figure 3 plots the inferred T_g of PVME in various PS/PVME blends using DRS. The bold line is the blend T_g obtained via DSC. The PVME data points, obtained using DRS, suggest that PVME in PS/PVME blends experience a separate relaxation or glass transition from the overall T_g and possible PS transition. The dashed and dotted lines are the estimated T_gs of PVME and PS using the Lodge-McLeish model that will be discussed later.

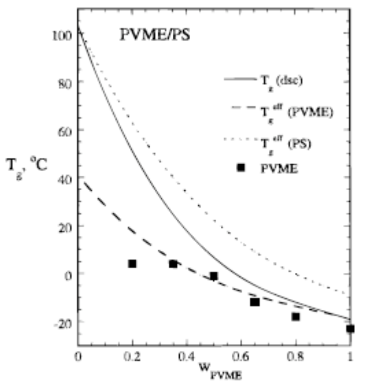

Figure 3. The dielectric PVME (squares) and blend DSC (solid line) data for PVME/PS blends. The PS and PVME dotted lines are T_gs estimated using the Lodge-McLeish model. Figure reproduced from reference 3 with permission.

Ellison and Torkelson have recently developed a fluorescence method that can be used to measure neat PS T_g. Unlike the previously mentioned techniques, fluorescence allows direct measurement of just the PS blend component behavior. Figure 4a shows how the fluorescence spectrum intensity of a pyrene methacrylate monomer, the fluorophore monomer used in these experiments, increases with decreasing temperature. Fluorescence intensity is temperature dependent, increasing with decreasing temperature, because fluorophores are more likely to emit excess energy via fluorescence at lower temperatures rather than lose energy via non-radiative decay or internal conversion.[4] In polymers, as the temperature is decreased the polymer free volume decreases, which constricts fluorophore movement and leads to increased photon emission. At the glass transition, the rate the intensity increases experiences a break or change in slope because the rate at which the free volume decreases slows down.[4] Figure 4b shows how the rate that intensity increases with decreasing temperature breaks at the PS T_g. The sharpness of the transition or break in intensity versus temperature slope also depends on film thickness. In thin films that do not display bulk T_g, the contrast in slope change at the transition becomes weaker with decreasing film thickness.[4]

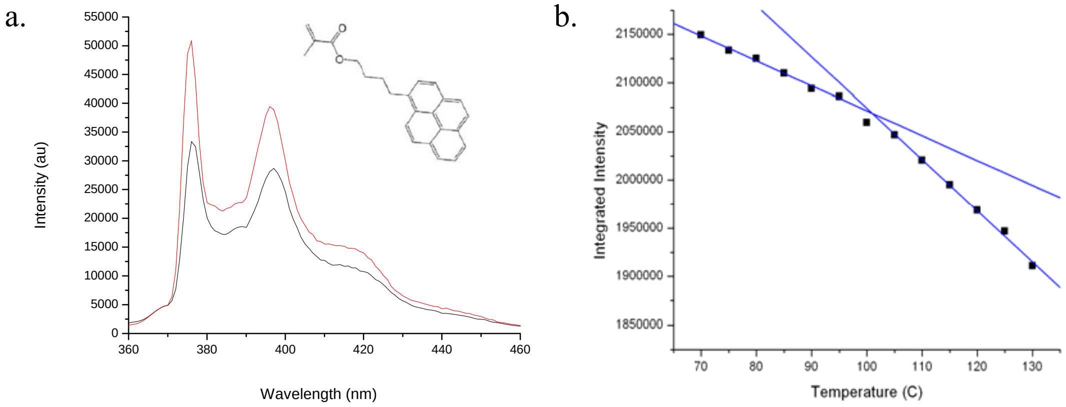

Figure 4. a. Intensity spectra of pyrene-labeled PS films (2 – 2.5 μm thick) taken at two different temperatures. The top red line was taken at 65 °C and the lower intensity line was from a measurement at 115 °C. The intensity units are arbitrary. Inset molecule is the pyrene monomer used. **b.** Intensity versus temperature plot of a neat bulk PS film. The slope change, T_g, is determined by linearly fitting the data and finding the intersection of the lines.

Miscible Blend Behavior

It is important to study the behavior of individual miscible blend components, especially near the glass transition temperature, because they have different dynamics from the overall blend. Although macroscopically a miscible blend looks uniform, the local microscopic level exhibits different concentrations and dynamics from the blend, known as local or dynamic heterogeneity.[5] The local concentration is the effective concentration experienced in some relevant volume, while the global concentration is the average effective concentration experienced by the entire blend.[6]

Miscible blends have two characteristic behaviors that occur during the glass transition that are believed to arise from local heterogeneity.[6] The first is that each component experiences a separate glass transition. When cooling a PS/PVME blend, it is believed that the high T_g component PS will undergo the glass transition first and become essentially locked into place. The low T_g component, PVME, will still be able to wiggle around the vitrified high T_g component. PVME will finally turn into a glass near the end of the global transition. The second characteristic is that the blend glass transition occurs over a broader range of temperatures than either pure component.[6] This transition broadening can be clearly seen in the DSC curves in Figure 2a. By labeling PS with pyrene, we intend to measure the PS behavior near T_g to possibly gain further insight on blend properties and behavior.

To understand local dynamics, two things need to be known: how much do local dynamics influence global behavior and what relevant volume accurately predicts the behavior of the dynamic heterogeneity influencing the overall miscible blend dynamics.[5] There are two main predictive theories that describe the glass transition and miscible blend behavior using a relevant volume or length scale in predicting local influences on global behavior.[5]

Self-Concentration and Thermal Concentration Fluctuations

The first theory covered will be self-concentration.[3] Self-concentration states that on a polymer chain A, a monomer A will be inherently rich in concentration of itself because it is connected directly to two other A monomers. Because each component experiences a different environment, each will have a distinct relaxation, as can be seen in the DRS data in Figure 3. The Lodge-McLeish (LM) model[3] uses the Kuhn length, which is the chain length needed to fold onto itself (~1 nm),[7] as the relevant length for estimating the self-concentration within a local region, or the “relevant volume”, surrounding a monomer A, illustrated in Figure 5.

The Kuhn length is a measure of polymer flexibility. High T_g polymers like PS have longer Kuhn lengths because they are less flexible. Because high T_g components have larger relevant volumes, they have lower self-concentrations.[3] A lower self-concentration means that the polymer has a concentration closer to the overall blend concentration, and thus will exhibit a T_g similar to the blend. Low T_g components have smaller relevant volumes, higher self-concentrations, and are expected to have dynamics closer to their pure dynamics.[3]

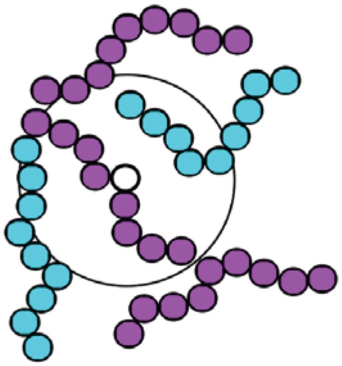

Figure 5. Illustration of the relevant volume around a monomer of interest defined by the Kuhn length in the Lodge-McLeish model.

The second major predictive theory is thermal concentration fluctuations (TCF).[6] TCF are transient local regions that have higher or lower than expected blend component concentrations, and are thought to be the cause of transition broadening.[6] At higher temperatures, TCF occur too quickly to make a significant impact on blend dynamics.[5] Near T_g, the regions fluctuate in and out of existence slowly; and because they last longer, they have a stronger influence on blend dynamics. The relevant length is temperature dependent, growing larger as the temperature decreases. Near T_g, the relevant length can reach ~ 10 nm.[3] Unlike with self-concentration, higher molecular weight (MW) polymers experience greater TCF, because bigger chains move slower and thus allow TCF to last longer.[3]

Both of these models attempt to describe miscible blend behavior and the relevant volume to predict blend dynamics, but both have significant issues. Although the LM model is assumed to be temperature independent,[3] decreasing the temperature towards T_g causes the high T_g component to begin to experience temperature dependent behavior.[8] The low T_g component, however, still follows the LM model.[7] PVME in PS/PVME blends shows a good fit to the LM model when 20-60% PVME, but deviates at low concentrations (10%, 6%, and 4%).[5] The self-concentration of PVME also exhibits a significant variation with molecular weight without a clear trend, which disagrees with the LM model's assumed independence from polymer chain size.[5]

The main unresolved issues of local dynamics in miscible blends are defining the relevant length (or volume) and the extent local concentration determines global dynamics.[8] At high temperatures, the LM model is a good fit for both blend components, and TCF occur too rapidly to make a significant contribution to blend behavior. At low temperatures near T_g, the high T_g component begins to show temperature dependence and deviates from the LM model, while the low T_g polymer is still in agreement.[7] Here, TCF become an important contributor to blend dynamics. Recently, Kumar, Colby, and coworkers have proposed a model that combines the ideas of self-concentration, found in the LM model, with TCF, which appears to work reasonably well with a relevant volume of ~ 1 nm.[7]

Interfaces and Multilayer Systems

In a recently submitted study by Kim *et al.*[9] it was found that for an immiscible binary polymer system, the layer beneath the top layer has a strong influence on the dynamics of the layer above it, and that these effects can be seen tens of nanometers from the blend interface. The direction (±) and amount of deviation from T_g depends on the layer below it. Figure 6a shows a plot of the T_g of the PS top layer on top of a 500 nm thick variable polymer underlayer versus the top layer PS thickness, as illustrated in Figure 6b. Three different polymers are used as underlayers, one with a T_g much higher than PS, the second with a T_g much lower than PS, and a third with a T_g almost the same as the T_g of PS. As the PS top layer is made thinner, the PS exhibits an increasingly similar T_g to the underlayer T_g. As seen in Figure 6a, the high T_g bottom layer poly(4-vinylpyridine) (P4VP) increases the top layer PS T_g, while the low T_g underlayer poly(n-butyl methacrylate) (PnBMA) causes a T_g reduction of the top PS layer. As the PS layer's thickness increases, the interface's influence on PS T_g decreases. An interface can be thought of as essentially a region between two layers with a 50/50 blend composition. In layered systems, TCF and self-concentration models would predict that interfacial effects would be confined to the immediate region of 50/50 blend composition. However, since these effects are not confined to such a short distance, these models are not sufficient to explain the interfacial effects on global behavior.

Although self-concentration and TCF can be used to predict overall blend behavior using a small local volume, such ideas do not explain how interfaces can influence a layer's T_g tens of nanometers away. If the relevant volumes of the LM model and TCF are correct, only the immediate interfacial area would be expected to have a T_g different from the neat polymer layers. To investigate how far away interfacial effects penetrate from a polymer-polymer interface, i.e. a local region of 50/50 blend composition, a unique four-layer system of PS and PVME was devised, as illustrated in Figure 7. Three PS layers act as the top layer and a single PVME layer as the bottom layer. Changing the thickness of a variable PS layer between the 15 nm thick pyrene-labeled PS layer to be measured and the PVME layer will provide data on the variation of T_g with distance from the interface.

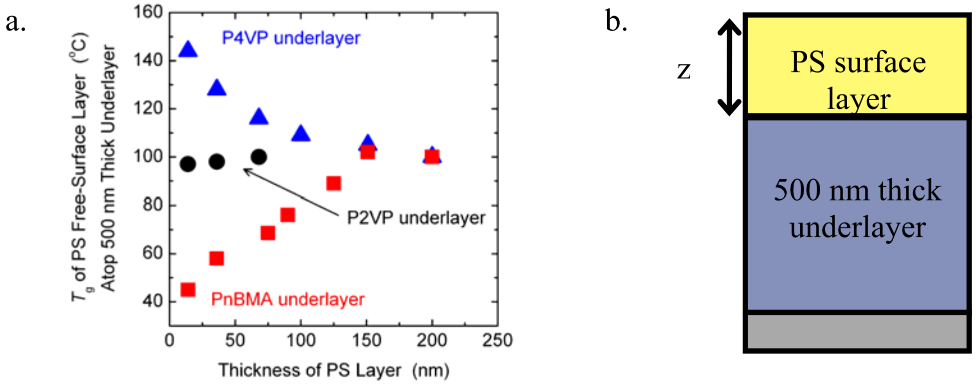

Figure 6. a. T_g of PS top layer as a function of thickness on top of a 500 nm thick underlayer of PnBMA, poly(2-vinylpyridine) (P2VP), and P4VP. T_g bulk: 299 K (PnBMA), 374 K (P2VP), and 413 K (P4VP). Data taken from reference 9. **b.** Schematic of variable thickness, z, PS top layer and set 500 nm thick variable polymer underlayer.

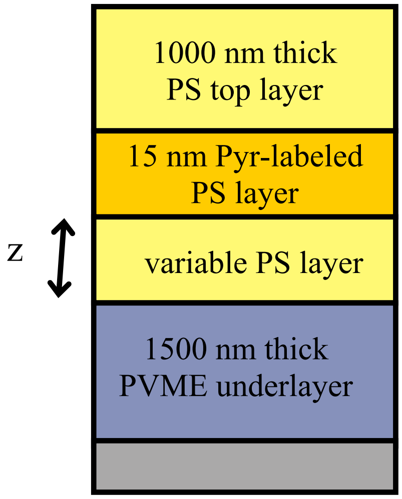

Figure 7. Schematic of the four-layer PS/PVME system. Variable layer thickness, z, is planned to range from 0 to 300 nm thick.

Purpose

The purpose of these experiments is to explore the use of fluorescence to analyze PS blend component dynamics, which is not possible with common analysis techniques, as well as PVME interfacial effects on PS. Part I of the experiments measures the behavior of PS over a range of PS/PVME compositions. It also acts as a control experiment to validate the fluorescence technique. Part II investigates the variation of T_g in a PS layer with distance from a PS/PVME interface.

Experimental

Pyrene Monomer Synthesis

For the fluorescence measurements 1-pyrenyl butyl methacrylate was synthesized in a procedure outlined by Jungki Kim, Connie Roth, and Rodney Priestley (June 2007). Pyrene has a high quantum yield, and is thus an excellent choice for a fluorophore. Because free pyrene evaporates from doped films, pyrene-labeled PS was used instead to ensure that the PS component was being measured.[4] Methacroyl chloride was added to 1-pyrene butanol in an esterification reaction to yield the pyrene-labeled methacrylate monomer. The reaction progress was checked about every 24 hours using thin layer chromatography (TLC), and a previously made pyrene-labeled monomer was used as the standard. After the reaction mixture reacted for approximately 65 hours, the product was separated from side products using liquid-liquid extraction. The product was then purified by recrystallization multiple times. Product purity was verified using NMR.

Polymer Synthesis

Only two polymers were not made in the lab. PVME used in both parts of the experiment was purchased from Scientific Polymer Products, Inc with M_w = 90 000 g/mol and polydispersity index (PDI) of 2.5. The PDI is the weight average molecular weight, M_w, divided by the number-average molecular weight, M_n. High molecular weight PS that was not pyrene-labeled used in part II had M_w = 2 000 000 g/mol and PDI = 1.30 purchased from Pressure Chemical Co. All other PS used in parts I and II for these experiments was synthesized via free-radical polymerization in a heated oil bath.

Part I:

Low MW PS was used to promote polymer mixing and to prevent phase separation when films were heated to high temperatures above T_g. The PS was polymerized at 60 °C for six hours to yield M_w = 74 500 g/mol, PDI = 1.65, pyrene-labeled PS was made to have ~ 1 pyrene dye monomer per chain. M_w was determined using a Gel Permeation Chromatography device at Georgia Tech.

Part II:

The PS was polymerized at 50 °C for 24 hours to give an estimated M_w of 700 000 g/mol and PDI of 1.6. Higher MW PS was used in order to keep the interfaces between miscible layers narrow, otherwise the miscible polymers would have diffused across the interface and caused it to widen.[10] Diffusion of the pyrene-label would be problematic in layered films because the effective distance from the PS/PVME layer to the fluorescent layer would not be the original film thickness.

Sample Preparation

Part I:

Solutions of 20-weight percent (wt%) total polymer were dissolved in toluene. A 50/50 labeled/unlabeled PS mixture with the same 74 500 g/mol M_w was used to dilute the pyrene intensity signal. Even one pyrene methacrylate monomer per chain gave off too much signal. Only blend compositions of neat PS, 95/5, 90/10, 85/15, 80/20, 75/25, and 70/30 PS/PVME were measured. Blends less than 70 percent PS could not be measured because the Watlow Series 96 heater we used is not capable of cooling below room temperature. The measurements would also require a temperature range below 0 °C, which would have caused ice to form on the sample and disrupted the fluorescence measurements. Films were spin-coated at 1500 rpm onto green quartz slides to produce 2-2.5 micron thick films, which is thick enough to be considered as bulk and avoid thin film T_g reductions. Film thickness was verified by spin-coating solutions onto silicon pieces and measuring the thickness using a J. A. Woollam Co., Inc. ellipsometer. The films were then annealed at least twelve hours under vacuum at 20-30 °C above the anticipated T_g, but well below the phase separation temperature, to remove residual solvent.

Part II:

PS used for the variable and bulk layers were purchased from Pressure Chemical Co., while the pyrene-labeled PS was synthesized in the lab. Bulk layer PS solutions of 4.5-wt% were spin-coated directly onto green quartz slides. All solutions were dissolved in toluene. This film was vacuum annealed for at least twelve hours at ~125 °C. In addition, 17-wt% PVME solutions were spin-coated directly onto clear quartz slides and annealed under vacuum at room temperature for at least twelve hours. The only variable PS layer made so far was 300 nm thick and was spin-coated at speeds around 2300 rpm from a 2.5-wt% PS solution. The film was spun onto mica and then incorrectly floated onto the 1500 nm thick PVME layer. The pyrene-labeled PS layer was made as thin as possible, while still producing enough fluorescence signal. The 15 nm thick films were made from 0.5-wt% pyrene-labeled PS spin-coated onto mica at speeds around 2500 rpm. After annealing for at least twelve hours under vacuum at ~ 125 °C, the films were then floated onto the bulk 1000 nm thick PS layer on the green quartz. After drying the floated layers, the two bilayers were sandwiched together and placed into a vice that was allowed to equilibrate to 130 - 135 °C in an oven for at least two hours before hand. The four-layer system was then annealed for 30 minutes in the vice under pressure. The correct preparation would have been to float the variable layer onto the floated 15 nm thick layer, then sandwich and anneal the tri-layer and the PVME layer together, because PVME is water soluble.

All film thicknesses were verified using ellipsometry. The solutions were spun onto a piece of silicon at the start, every 5 - 6 films, and at the end to ensure the right thickness was achieved and remained consistent.

Fluorimeter Procedure

The fluorescence measurements were taken using a PTI QuantaMaster fluorimeter. Initial spectra were taken at room temperature to ensure that the intensity was not too high (~ 70 000 counts). The sample was then heated to the maximum temperature, which was 20-30 °C above the blend's anticipated T_g. The sample was allowed to equilibrate to within ± 0.1 °C before holding an additional 15 minutes to take a measurement. A few subsequent measurements were made to check for photobleaching. Next, the temperature was dropped 5 °C, allowed to equilibrate to within ± 0.1 °C, and then measured after holding an additional five minutes. The lowering five degrees, equilibrating, and holding five minutes before measuring process was repeated until the temperature was approximately 30 °C below T_g. To check for photobleaching, the temperature was raised back up to the initial maximum temperature, equilibrated to within ± 0.1 °C of the maximum temperature, and then held for 15 minutes before taking the final spectrum.

The same fluorimeter procedure was used for both experimental parts. The excitation wavelength was set to 324 nm and emission wavelength spectra were taken from 360 – 460 nm. Excitation slit widths in part I corresponded to 5 nm bandpass for PS blends above 80/20 and 1 nm bandpass for the rest. Emission slit widths corresponded to 2.5 nm and 2 nm bandpasses for compositions above and below 80/20. The angle of incidence in part I was set at 24° and 12° above and below the 80/20 blend. In part II, emission and excitation widths were set at 5 nm and 3 nm bandpasses. The angle of incidence was set to 20°. The total integrated intensity at each temperature was determined by integrating the area beneath the pyrene fluorescence spectrum. The glass transition temperature was identified by the change in slope of the intensity versus temperature graph as seen in Figure 4b. As the temperature decreases, intensity increases. At the glass transition, the rate at which the intensity increases slows down is due to the decreased rate of free volume shrinkage.

Results and Discussion

Part I:

The intensity versus temperature graphs shown in Figure 8 are from an 85/15 PS/PVME blend and neat PS. Both show increasing intensity with decreasing temperature with a break in the slope occurring at T_g. As the PS component becomes more dilute, the sharpness of the slope change decreases and becomes less obvious, which could suggest that the transition occurred over a greater temperature range and experienced broadening. This is interesting because the TCF and self-concentration models predict a broadening of the blend transition, but not necessarily a broadening of individual component T_gs.

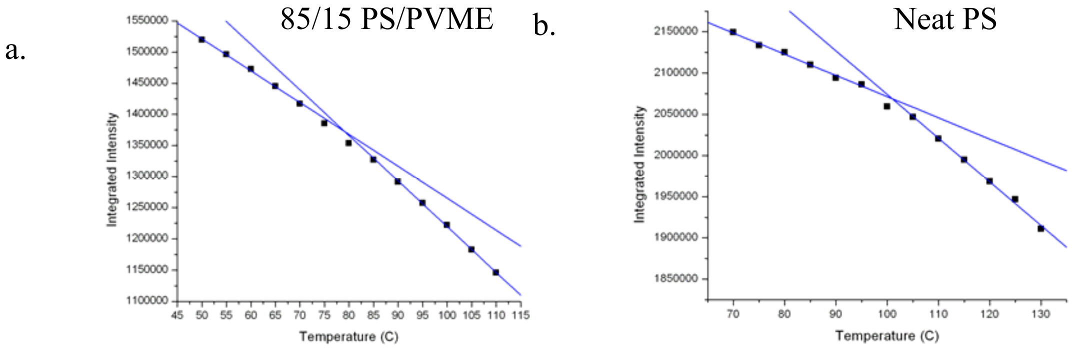

Figure 8. Intensity versus temperature plots for bulk (2 – 2.5 µm thick PS films) of **a.** 85/15 PS/PVME (T_g = 79 ± 2 °C) and **b.** neat PS (T_g = 101 ± 2 °C). Note that the transition becomes more subtle and appears to cover a larger temperature range in the 85/15 blend.

In these experiments, the T_gs of blends ranging from neat PS down to 70/30 PS/PVME, done in incremental PS compositional decreases of five percent, were measured. The T_gs were identified as breaks in the intensity versus temperature slopes. These results were compiled into the blue circles shown in Figure 9, where each data point corresponds to two to three measurements. These data in Figure 9b and are compared to DSC data from the literature, and to intrinsic fluorescence data obtained by Andy Pahner. Intrinsic fluorescence is fluorescence that is emitted directly by the molecule of interest, in this case the phenyl rings of PS. Using the pyrene monomer is considered extrinsic fluorescence because pyrene, not the PS phenyl group, acts as the fluorophore. For the intrinsic measurements, the excitation wavelength was 260 nm and the emission spectra were taken from 265-415 nm wavelengths. The excitation and emission bandpasses were 5 nm and 2.5 nm, and with an angle of incidence of 30°.

In Figure 9b, extrinsic and intrinsic fluorescence T_g data are compared to the published DSC data from Wagler *et al*. for PS/PVME blends that have polymers with similar molecular weights. The black lines indicating the DSC curve data from Wagler *et al*, see Figure 2b, were obtained by heating up the sample rather than with the cooling process used for these experiments. The polymers used in the Wagler *et al*. paper are PS with M_w = 57 000 g/mol, PDI = 1.09 and PVME with M_w = 99 000 g/mol, PDI = 2.13.[2] The top line is the endpoint of the glass transition (down arrows in Figure 2a), the middle line is the midpoint of the blend T_g, and the bottom line is the beginning of the transition (up arrows in Figure 2a), as measured on heating.

The blue circles in Figure 9a and 9b are the extrinsic fluorescent data from this study. The blue data points correspond with the top DSC line up to the 80/20 blend. After the 80/20 blend, the points move away from the top DSC line and rise towards higher temperatures. Andy Pahner did a complementary intrinsic fluorescence study of the same PS/PVME blends with the same molecular weight PS and PVME and used the same procedures outlined in part I of the experimental section. He used the intrinsic fluorescence of the PS phenyl rings for his measurements. The intrinsic data are the red triangle data points shown in Figure 9b and the values are listed in Table 1. Andy Pahner's data up to 85/15 corresponds with the blend T_g found by DSC, and then begins to follow the DSC curve transition endpoint line.

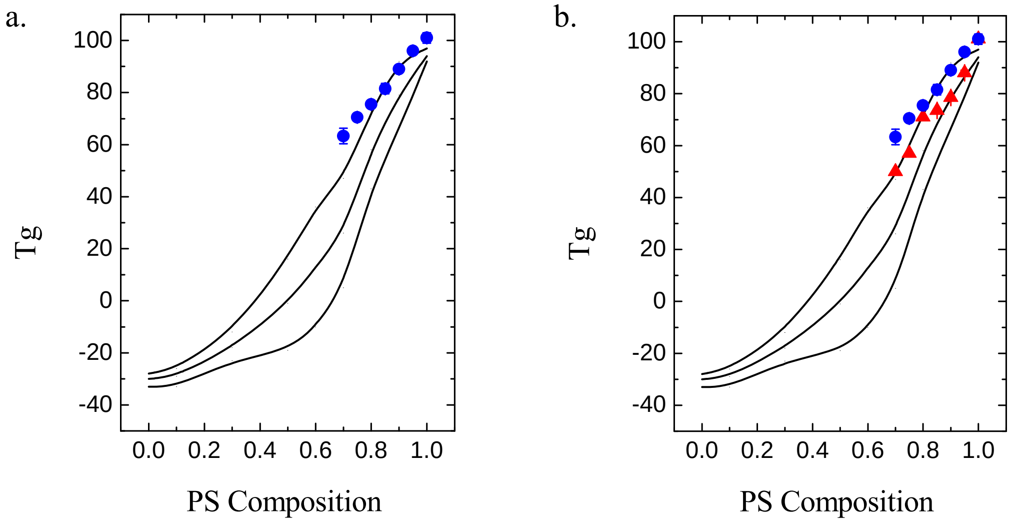

Figure 9a. Extrinsic fluorescence T_g versus blend composition plotted with DSC data obtained from reference 2 (see Figure 2b). **b.** Extrinsic and Andy Pahner's intrinsic fluorescence data plotted with DSC data obtained from reference 2.

Compositions (PS/PVME)	Extrinsic Fluorescence T_g +/- Error (°C)	Intrinsic Fluorescence T_g +/- Error (°C)	DSC Transition Endpoint (°C)	DSC Overall Blend T_g (°C)
1	101 ± 2	101 ± 1	97	94
95/5	96 ± 1	88 ± 1		
90/10	89 ± 1	78.5 ± 1	92	79
85/15	81.5 ± 2	73.5 ± 1		
80/20	75.5 ± 1	71 ± 1	73	58
75/25	70.5 ± 2	57 ± 2		
70/30	63.3 ± 3	50 ± 2	47	26

Table 1. Extrinsic and intrinsic fluorescence and DSC endpoint and blend T_g data with corresponding PS/PVME compositions. DSC data taken from reference 2.

Most of the differences between extrinsic and intrinsic fluorescence T_g values in Table 1 and Figure 9b are probably due to the fact that in mid- to late February it was discovered that the particular heater used for the extrinsic fluorescence measurements was not using the proper calibration curve, and was thus displaying incorrect temperature values. Because the temperature offsets were not consistent, the data cannot be simply adjusted. The extrinsic measurements began in early July and ended in early December, but it is unknown how long the heater had been malfunctioning and whether or not any data can be salvaged.

Let us consider if the chemical differences between the pyrene-label and the PS phenyl ring could have caused the difference between the intrinsic and extrinsic fluorescence data. Hydrogen bonding between the aromatic PS ring's hydrogens and the oxygen in the PVME side group allows the two polymers to mix.[11] If pyrene were to have a different hydrogen bond strength than the PS phenyl group, the pyrene dye would tend to prefer a different environment than the PS phenyl group and thus measure a different T_g. The charge separation between the aromatic carbon and hydrogen, when the aromatic hydrogen is hydrogen bonding to the oxygen in PVME, resembles heterolytic cleavage. If the aromatic carbon–hydrogen bond was heterolytically cleaved, it would yield a carbanion and a proton. The aromatic compound that can best stabilize the negative charge on the carbanion will be more acidic, and therefore more likely to hydrogen bond with the oxygen on PVME. Pyrene has a larger π system, i.e., it has more conjugated double bonds, than the PS phenyl group and so will be able to delocalize and stabilize the negative charge better. If pyrene does have an increased tendency to hydrogen bond with PVME, it would measure a lower Tg than expected because it will be more associated with the low Tg component. However, pyrene (MW = 202 g/mol) is almost 2.5 times larger than the PS phenyl group (MW of benzene is 78 g/mol), which might suggest that pyrene has a reduced solubility in PVME. In order to avoid issues caused by any chemical differences between the pyrene-label and the PS phenyl rings, very dilute concentrations of pyrene fluorophores were used. Therefore, the pyrene monomer is taken to have little effect on PS behavior; and so, it is predicted that our data and the intrinsic fluorescence data would give the same PS component T_g for each PS/PVME blend. In neat PS systems, it has been previously demonstrated that the T_gs obtained from pyrene and intrinsic fluorescence both match each other and with DSC data.[12] Thus, it is expected that both intrinsic and extrinsic fluorescence T_g data would give similar T_g values for the same PS/PVME blends.

There are potential issues with comparing the Wagler *et al*. DSC data to fluorescence data. DSC measures the overall blend glass transition by heating the sample up from a glass to a liquid. The beginning and endpoints of these DSC transitions also tend to appear unclear. With other DSC data presented in the Wagler *et al*. article, there was considerable T_g value variation with MW, as seen in Table 2 and Figure 2c, for PS/PVME blends. Andy Pahner's data tends to agree with the blend T_g in Figure 9b. This is unusual because the fluorescence data should be higher than the blend T_g, because the fluorescence should be measuring the PS component T_g. Since the M_w used for the fluorescence studies and DSC were not exactly the same, then the different M_w could account for the seemingly unusual intrinsic data trend. Because the M_w used for the

Composition	Midpoint T_g (°C)		Endpoint T_g (°C)	
PS/PVME	M_w = 57 000 g/mol	M_w = 95 000 g/mol	M_w = 57 000 g/mol	M_w = 95 000 g/mol
Neat PS	94	99	97	104
90/10	79	73	92	84
80/20	58	45	73	62
70/30	26	23*	47	46

Table 2. DSC T_g variation with PS M_w data from reference 2. *In the paper the original value is 93, but the figure with the DSC curves showed a T_g near 20 °C.

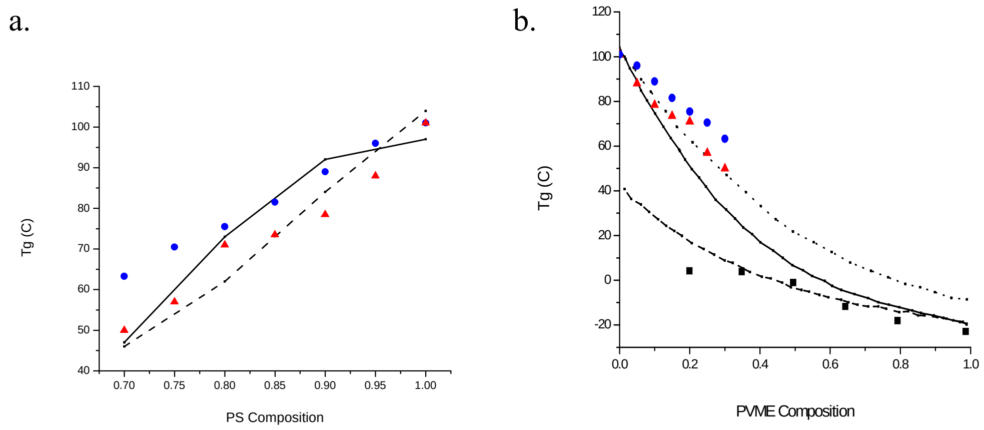

Figure 10. a. DSC endpoint T_g of M_w = 57 000 g/mol (solid line) and M_w= 95 000 g/mol (dashed line) PS obtained from reference 2 (see Figure 2), plotted with intrinsic (red triangles) and extrinsic (blue circles) fluorescence T_g obtained with M_w = 74 500 g/mol. **b.** Digitized form of Figure 3 plotted with intrinsic (red triangles) and extrinsic (blue circles) fluorescence T_g. Good agreement is found between the intrinsic fluorescence data of the PS component with the LM model prediction.

intrinsic fluorescence T_g data is between the M_ws shown in Table 2, the intrinsic data should follow a trend somewhere between the two endpoint data sets. In Figure 10b, the intrinsic data follow the higher MW PS, except for the 80/20 blend. The T_g variation between the two MW PS reaches about 10 °C. Figure 10b is almost the same as Figure 3, where the DRS inferred PVME T_g was plotted in comparison to the PS/PVME blend T_gs obtained from DSC and the LM model predicted T_gs of PS and PVME. In Figure 10b the intrinsic and extrinsic fluorescent T_g data have been plotted on a digitalized version of Figure 3. Intrinsic fluorescence shows good agreement with the PS component T_g predicted by the LM model.

Part II:

Single layer PS film T_gs were determined using the same change in slope described in part I in order to verify that the synthesized polymer would measure T_g correctly. The thin films were tested for a certain amount of T_g reduction expected in published data for similar film thicknesses. In Figure 11a is shown a plot of film T_g minus T_g bulk versus film thickness, the red upside-down triangles are extrinsic fluorescence data obtained from 300 and 15 nm thick pyrene-labeled PS single layer films. The black squares are data points obtained from published data.[13] The film T_g reaches the bulk value at around 70 nm film thickness. The T_g values listed in Table 3 that were obtained from the 15 nm pyrene-labeled PS seems to be within an acceptable range, and the 300 nm pyrene-labeled PS is in agreement with bulk T_g.

Part II Film Thickness (nm)	Part II Film T_g Deviation ($T - T_g$) (± 5°C)	Ellison and Torkelson Film Thickness (nm)	Ellison and Torkelson T_g Deviation ($T - T_g$) (± ~ 2°C)
15	-20	14	-38
15	-20	13	-36
		17	-25
		17	-25
		19	-24
		22	-20
		20	-18
		36	-7
300	0	68	2
300	0	427	1
		557	-1

Table 3. 300 and 15 nm pyrene-labeled PS film T_g deviation compared to similar film thicknesses also measured with the pyrenyl methacrylate monomer. Ellison and Torkelson data obtained from reference 13.

The graph of intensity versus temperature for a 15 nm thick single layer PS film, shown in Figures 11b, has a weaker break or change in slope than that for neat bulk (2 – 2.5 μm thick) PS film in Figure 8b. This is expected because Ellison and Torkelson found that the change in the intensity versus temperature slopes become weaker and less noticeable in thin films.[13] Figure 11c has a slightly more noticeable break for a 300 nm thick PS film, but the change in slope is still very weak.

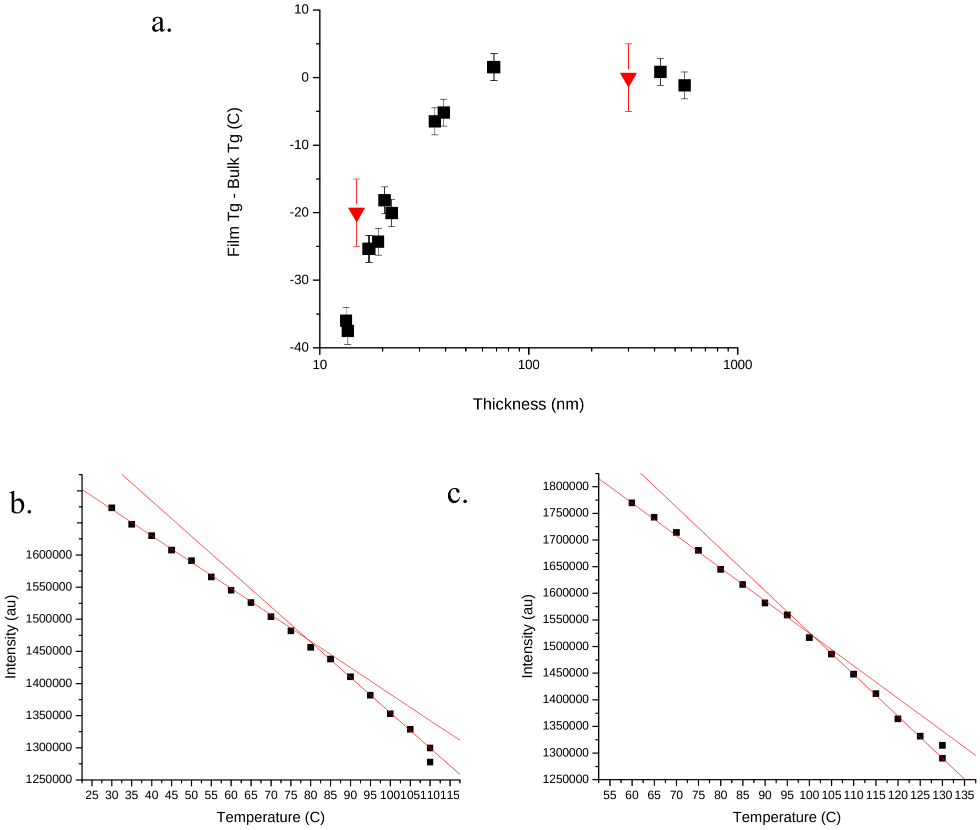

Figure 11. a. PS film T_g minus T_g bulk as a function of film thickness. Black squares are taken from reference 13, while the triangles are from this study. **b.** The intensity versus temperature graph of a 15 nm thick PS film (T_g = 80 ± 5° C). **c.** The intensity versus temperature graph of a 300 nm thick PS film (T_g = 100 ± 5° C).

Next a four-layer system was tested that had a bulk 300 nm thick variable layer. This was measured to verify that the fluorescence measurements would yield the expected bulk T_g, but the four-layer system was unfortunately prepared incorrectly so that the PVME layer was partially dissolved. This could have created an uneven interface between the 15 nm thick pyrene-labeled PS and the 300 nm thick variable PS layer. If part of the 15 nm thick pyrene-labeled PS layer was exposed to air, it would have exhibited the reduced T_g from bulk seen in Figure 11a instead of the expected bulk T_g. If this was the case, then because of the uneven interface, the 15 nm thick pyrene-labeled PS layer could have experienced a range of T_gs, some parts exhibiting a T_g reduced from the bulk and some parts exhibiting a mean bulk T_g. A range of T_gs could explain the very faint slope change in Figure 12.

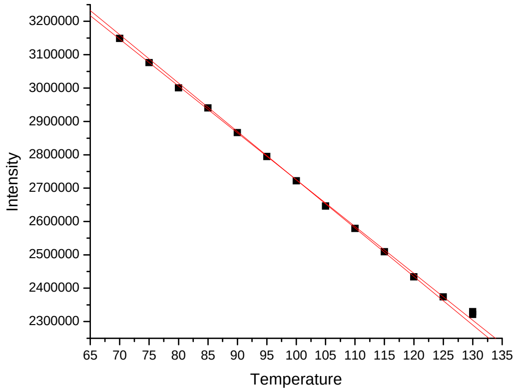

Figure 12. Intensity versus temperature of a four-layer system with a 300 nm thick variable layer T_g = 98 °C.

<u>Conclusions</u>

<u>Part I:</u>

Pyrene methacrylate monomer was successfully synthesized and then polymerized with styrene. The experiments in Part I used a 50/50 composition of pyrene-labeled to unlabeled low MW PS to measure the T_g of PS in PS/PVME blends with variable compositions. Even with the heater malfunction, extrinsic PS T_g data decreased with increasing PVME concentration. The PS component transition appeared to broaden or at least weaken when mixed with PVME, compared to the intensity versus temperature slope change of neat PS. The differences between the complementary intrinsic and extrinsic fluorescence data are attributed to the heater malfunction. DSC and these particular fluorescence measurements are two different techniques that measure glass transition by heating and cooling respectively. DSC just measures the overall blend transition, which have somewhat ambiguous start and end points. These measurements also used polymers with slightly different MW than that of Wagler *et al.*'s.[2] Within that publication there are several DSC curves of different MW PS/PVME blends, which show significant variation of blend T_g with MW. The next step for this part of the project will be to redo the fluorescence measurements using the exact same polymer for both intrinsic and extrinsic fluorescence in order to avoid possible MW variations, as well as to pursue complementary DSC data measurements with our particular polymers.

Part II:

Thin 15 nm and bulk 300 nm thick films with high MW pyrene-labeled PS were tested to make sure that the right T_g was being exhibited. The expected weakening of the break in intensity versus temperature plot for the 15 nm films were observed in the thin films, which was expected.[13] It is unusual that the 300 nm thick bulk films exhibited a similar weak break in the slope. The 15 nm thick films experienced a T_g reduction that was barely within an acceptable range, but we wanted to move forward with the multilayers because we were running out of time. Thus, a more careful control will be pursued in the future.

Several four-layer PS/PVME systems with 300 nm thick variable layers were made and measured, but were inappropriately prepared. The 300 nm thick variable layer should have been floated onto the 15 nm thick pyrene-labeled layer instead of the PVME layer, which dissolved in the water used to float the films onto the PVME. Figure 12 shows a very weak slope change, but it does exhibit a T_g close to the expected bulk PS value. Nevertheless, the 300 nm thick variable layer four-layer system will be redone. Other variable layer thicknesses to be tested will be 150, 60, and 30 nm. Another set-up that may be attempted would be to switch the locations of the green and clear quartz slides in the four-layer assembly so that the PVME layer rests on the green quartz and the bulk PS layer is on the clear quartz slide. This would reduce the amount of polymer the fluorescence would have to travel through by at least 500 nm.

References

1. Hiemenz, P. C. and Lodge, T. P. (2007). *Polymer Chemistry*. Boca Raton, FL: CRC Press.

2. Wagler, T., Rinaldi, P. L., Hae, C. D. and Chun, H. *Phase Behavior and Segmental Mobility in Binary Blends of Polystyrene and Poly(vinyl methyl ether)*. Macromolecules, 2000. **33**: p. 1778 – 1789.

3. Lodge, T. P. and McLeish, T. C. B. *Self-Concentrations and Effective Glass Transition Temperatures in Polymer Blends*. Macromolecules, 2000. **33**: p. 5278 – 5284.

4. Ellison, C. J. and Torkelson, J. M. *Sensing the Glass Transition in Thin and Ultrathin Polymer Films via Fluorescence Probes and Labels*. Journal of Polymer Science Part B: Polymer Physics, 2002. **40**: p. 2745 – 2758.

5. He, Y., Lutz, T. R., and Ediger, M. D. *Segmental and terminal dynamics in miscible polymer mixtures: Tests of the Lodge-McLeish model*. Journal of Chemical Physics, 2003. **119**(18): p. 9956 – 9965.

6. Colmenero, J. and Arbe, A. *Segmental dynamics in miscible polymer blends: recent results and open questions*. Soft Matter, 2007. **3**: p. 1474 – 1485.

7. Kumar, S. K., Shenogin, S., and Colby, R. H. *Dynamics of Miscible Polymer Blends: Role of Concentration Fluctuations of Characteristic Segmental Relaxation Times*. Macromolecules, 2007. **40**: p. 5759 – 5766.

8. Kant, R., Kumar, S. K., and Colby, R. H. *What Length Scales Control the Dynamics of Miscible Polymer Blends?* Macromolecules, 2003. **36**: p. 10087 – 10094.

9. Kim, S., Roth, C. B., Priestley, R. D., Sandoval, R. W., Mok, M. M., Broadbelt, L. J., and Torkelson, J. M. *Tuning the Glass Transition Temperature by 100 K in Nanostructured Heterogeneous Polymers*. Submitted March 2010.

10. Jones, R. A. L. and Richards, R. W. (1999). *Polymers at Surfaces and Interfaces*. Cambridge, UK: Cambridge University Press.

11. Robeson, L. M. (2007). *Polymer blends: a comprehensive review*. Munich, Germany: Hanser Verlag.

12. Mundra, M. K., Ellison, C. J., Rittigstein, P., and Torkelson, J. M. *Fluorescence studies of confinement in polymer films and nanocomposites: Glass transition temperature, plasticizer effects, and sensitivity to stress relaxation and local polarity*. European Physical Journal Special Topics, 2007. **141**: p. 143 – 151.

13. Ellison, C. J. and Torkelson, J. M. *The distribution of glass-transition temperatures in nanoscopically confined glass formers*. Nature Materials, 2003. **2**: p. 695 – 700.