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Sung S. Park April 15, 2012

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By

Sung S. Park

Dr. Connie Roth
Adviser

Department of Physics

Dr. Fereydoon Family

Committee Member

Dr. Khalid Salaita

Committee Member

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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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We investigate the miscibility and the phase separation temperature T_s of a miscible polymer blend polystyrene (PS) /poly(vinyl methyl ether) (PVME). We have developed a fluorescence technique to measure T_s with the ultimate goal of finding the effect of electric fields on the miscibility of polymer blends. In developing this fluorescence method, we discuss the effects of different fluorophores, the sensitivity of the blend to moisture, and the correlation between reproducibility and the fluorescently labeled PS content. Based on these findings, we find a substantial difference in T_s between samples cast on clear quartz slides and on ITO-coated slides. Even though T_s under the presence of electric fields was not attained within the time limit, this study has laid the groundwork for continuing florescence studies on the effect of electric fields on the miscibility of PS/PVME blends.

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Acknowledgements

I would like to thank Dr. Connie Roth for giving me an opportunity to work in the lab and experience science beyond the undergraduate level. I would also like to thank Annika Kriisa for all her help from beginning to end. Dr. Roth and Annika have been incredibly helpful in answering questions and guiding me through the research over the past two years. Many thanks to Dr. Fereydoon Family and Dr. Khalid Salaita for being on my committee.

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Introduction

In the last decades, the miscibility of polymer blends has been one of the most important subjects in the polymer science. A miscible polymer blend is two or more existing polymers homogeneously mixed together at a molecular level such that there is only one phase present. Polymers may be blended together for various reasons. One important reason is that a new material that has a combination of the properties of each individual polymer can be obtained. Several factors have been known to affect the miscibility of polymer blends such as blend composition, film thickness, cast solvent, or temperature. One interesting factor is the presence of an electric field on polymer blends. This study will focus on how an applied electric field can tune and control the miscibility of polymer blends.

Miscibility of Polymers and Flory-Huggins Theory

Unlike small molecules, different kinds of polymers usually segregate into different regions when they are mixed together, and it is rare to find a pair of polymers that form a miscible polymer blend. This phenomenon can be explained by the Flory-Huggins theory, a mathematical equation which describes the Gibbs free energy of polymer solutions and blends:[1]

$$\frac{\Delta G_{mix}}{kT} = \frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \chi\phi_A\phi_B$$

Here, k is the Boltzmann constant, T is the absolute temperature, ϕ_A and ϕ_B are the volume fractions of the two polymer components, N_A and N_B are the degrees of polymerization of the two polymer components, and χ is the interaction parameter between the two polymers. The necessary condition for the two polymers A and B to mix is that the Gibbs free energy of mixing, ΔG_{mix}, must be negative. The first two terms, which represent the entropy change of mixing, become very small since most polymers can easily have degrees of polymerization of 1000 or more ($N_A \geq 1000\ and\ N_B \geq 1000$) while small molecules or solutions have degrees of polymerization of 1 ($N_A = 1\ and\ N_B = 1$). This makes the last term, which represent the enthalpy change of mixing, play a dominant role in determining the miscibility of two polymers. That is, unless the last term $\chi\phi_A\phi_B$, in particular the Flory parameter χ, is negative, the mixing of two polymers is unlikely to occur.

The chi parameter χ is called the interaction parameter which measures how two polymers are likely to interact with each other and usually follows the form:

$$\chi(T) = A + \frac{B}{T}$$

In practice, A and B are treated as parameters that can be either positive or negative.[1] If there is some specific kind of attractive interaction between the two polymers, B becomes negative. A is harder to interpret but is believed to be related to molecular packing of the system. For the miscible blend pair studied in this thesis, A is positive and B is negative, forming a lower critical solution temperature (LCST) type phase diagram. In summary, for a miscible polymer blend pair, we can conclude that there must exist some attractive interaction between the two individual polymers.

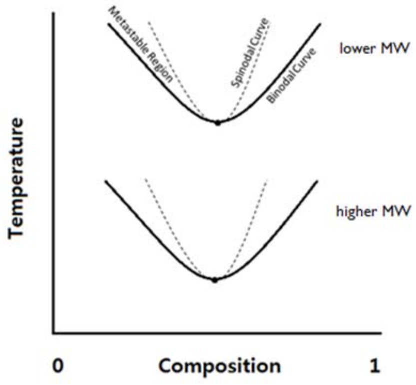

Figure 1. Schematic of polymer blends showing a lower critical solution temperature (LCST) behavior. Higher molecular weight polymer blends have less miscibility and thus lower LCST than lower molecular weight polymer blends.

PS/PVME: A Prototypical Miscible Blend

Of the various pairs of miscible blends, polystyrene (PS) and poly(vinylmethylether) (PVME) stand as one of the most prototypical miscible blends. They show a lower critical solution temperature (LCST) behavior on a phase diagram, meaning there exists a critical temperature below which PS/PVME remain miscible and above which PS/PVME phase separate. This critical temperature depends on various factors such as the composition or the molecular weight of individual polymers.

Interestingly, the LCST of PS/PVME system was observed to rise by about 40°C when all of the hydrogens on PS were deuterated.[2] The study of this isotope effect was further examined with selectively deuterated PS to investigate which part of PS, backbone or phenyl ring, was responsible for the interaction with PVME.[3] When backbone-deuterated PS (PS-d3) / PVME blends were compared with the aromatic deuterated PS (PS-d5) / PVME blends, the PS-d5/PVME system exhibited higher LCST over the entire composition, while the PS (PS-d3) / PVME system was found to be unchanged. This indicates that it is the phenyl rings of PS that are involved in the interaction with PVME.

Given that the mixing of polymers induces a negligible change in entropy, it is clear that this particular interaction between the phenyl rings of PS and PVME is the source of the compatibility of this blend. Green *et al.* indeed showed that this interaction involves a weak C-H to O hydrogen bond between the aromatic hydrogens on the PS and the oxygen of the PVME.[4] Specifically, the para and meta hydrogens and to a lesser extent, due to steric issues, the ortho hydrogen form a weak C-H to O hydrogen bond with the oxygen of the methoxyl group of PVME. The solvent dependence of the PS/PVME blend also adds support to this claim as the blend is not miscible when cast from solvents that are known to form C-H to O hydrogen bonds.[5,6] Although these C-H to O bonds are considerably weaker than regular hydrogen bonds, they must play large enough roles to make the blend miscible due to the amplification properties of polymers. Large macromolecules can have many such weak bonds.

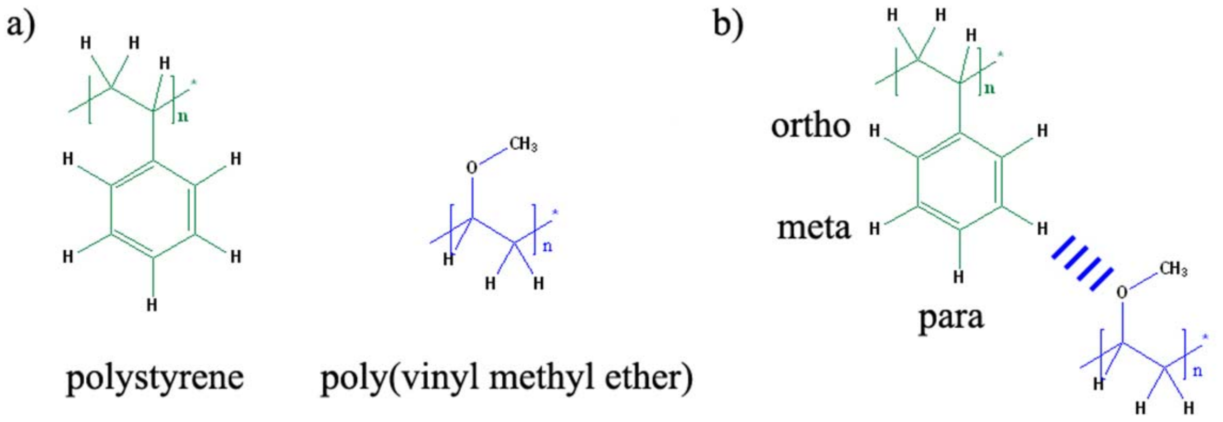

Figure 2. a) Chemical structures of polystyrene and poly(vinylmethylether) b) schematic of PS/PVME system in a miscible phase. A weak hydrogen bond is drawn (blue dashed lines) between an aromatic hydrogen of PS and an oxygen of PVME.

Previous Fluorescence Method to Measure Phase Separation

As it was stated earlier, the PS/PVME blend has a critical temperature at which the polymers begin to phase separate. While there are various methods of detecting this phase separation temperature, a fluorescence method provides an ideal tool for the accurate determination of the early stages of phase separation. Halary *et al*. were the first to demonstrate the use of fluorescence in detecting the phase separation temperature of PS/PVME blends.[7] They observed a sharp increase in fluorescence intensity of an anthracene dye embedded in the backbone of PS as the blend phase separated. This increase in intensity resulted from the fluorescent dye moving away from the fluorescence quencher groups, which were the oxygens of the PVME in this case. Static quenchers such as oxygens limit the fluorescence intensity of nearby fluorophores.[8] When the fluorescent intensity at a single wavelength was measured as a function of increasing temperature, a sudden increase in intensity was observed, and the separation temperature was defined where this sharp increase occurred. This temperature was lower than that determined from light scattering, but equivalent to that measured by small angle neutron scattering (SANS) experiments, indicating that fluorescence is as sensitive as SANS in detecting the phase separation temperature.[9]

The effects of the molecular weight on the LCST phase diagram of the PS/PVME system was also investigated using the same fluorescence method.[10] As the molecular weight of PS increased while that of PVME was kept constant, the phase separation temperature was observed to decrease. The Flory-Huggins theory explains that since higher molecular weight polymers have higher degree of polymerization than lower molecular weight polymers, they are expected to have less contribution from the entropy of mixing and thus less miscibility.

Effects of Electric Field on Mixing

The application of electric fields as a means of modifying materials has become popular in polymer studies. Electric fields have been known to induce and change the structure of polymers between different morphologies. Xu *et al.* observed induced sphere-to-cylinder transition in thin films of asymmetric polystyrene-b-poly(methyl methacrylate) diblock copolymers,[11] and Schaffer *et al.* osbserved electrically induced structure formation in thin liquid films.[12] Electric fields can also affect phase transitions, as Schoberth *et al.* found that electric fields favored mixing and reduced the order-disorder transition temperature in a block copolymer.[13]

The effect of electric fields on mixing was first investigated by Debye and Kleboth.[14] For a mixture of 2,2,4-trimethylpentane and nitrobenzene small molecules, the presence of an electric field of $4.5 \times 10^6 \frac{\mathrm{V}}{\mathrm{m}}$ enhanced the mixing of two liquids by 0.015K. Wirtz *et al*. also studied the effect of electric fields on the miscibility of a polystyrene/cyclohexane polymer-solvent system, and it was demonstrated that electric fields enhanced the mixing as large as 0.05K.[15] Even though both results showed that the electric fields increased the miscibility for these upper critical solution temperature (UCST) type mixtures, their effects were very small and the change in the critical temperature was only a tiny shift in both cases.

In contrast to the studies on small molecules and polymer systems, Reich and Gordon observed huge shifts in the phase separation temperature of a PS/PVME blend when electric fields were applied.[16] The phase separation temperature decreased under an electric field, and this change in temperature was found to be directly proportional to the square of the electric field applied. For the single composition studied of 33/67 PS/PVME blend composition by weight, a decrease of 53.5K was measured for an electric field strength of $2.72 \times 10^7 \frac{\mathrm{V}}{\mathrm{m}}$.

Lee *et al*. also demonstrated similar results with a poly(vinylidene fluoride) (PVDF) / poly(1,4-butylene adipate) LCST-type polymer mixture.[17] When the critical temperature was measured under an electric field of $9.6 \times 10^6 \frac{\mathrm{V}}{\mathrm{m}}$, a decrease of 19K was observed. This particular study, however, may not clearly articulate the role of electric fields on the miscibility as PVDF is known to be piezoelectric. Piezoelectric polymers undergo a change in shape under the influence of electric fields, so it is unclear whether the observed decrease in miscibility was due to the nature of the electric field or the piezoelectricity of PVDF.

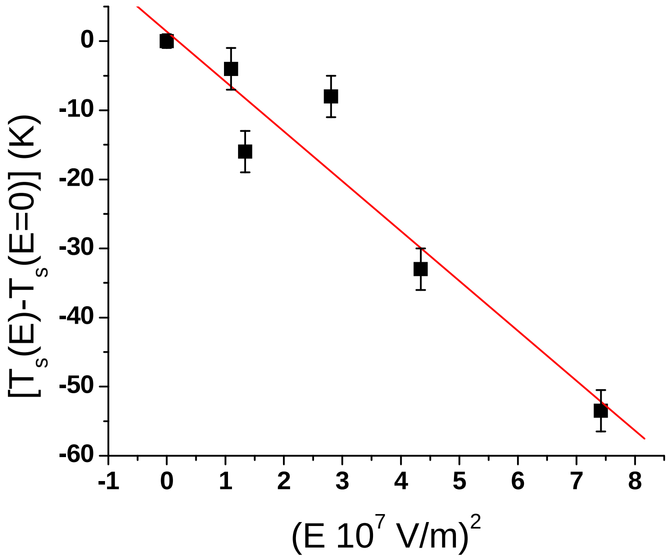

Figure 3. Change in phase separation temperature as a function of electric field squared. [Data taken from Reich and Gordon[16]]

Purpose: Modified Flory-Huggins Theory under Electric Fields

It is believed that the free energy of mixing under the presence of an applied electric field (E) can be described by adding an additional free energy term to the general Flory-Huggins equation:

$$\frac{\Delta G_{mix}}{kT} = \left(\frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \chi\phi_A\phi_B\right) - \frac{1}{2}\varepsilon_0\varepsilon(\phi)E^2$$

The electric field term $-\frac{1}{2}\varepsilon_0\varepsilon(\phi)E^2$, where ε_0 denotes the dielectric permittivity of free space and $\varepsilon(\phi)$ denotes the dielectric constant of the blend, is the most accepted model that accounts for the free energy due to the electric field. However, reliable experimental data have been lacking to test this model.

The objective of these experiments is to explore the effect of the electric fields on the miscibility of PS/PVME polymer blends using a fluorescence method. This thesis has two parts.

Part I deals with developing the fluorescence technique to reliably detect the phase separation temperature of the polymer blend. Part II maps out the phase diagram of PS/PVME blends when no electric field is applied and investigates how it changes under the presence of an electric field.

Experimental

Polymer Synthesis

PVME used in both Part I and II was purchased commercially from Scientific Polymer Products and measured[18] to have M_w = 65.5 kg/mol, M_w/M_n = 3.95. PS for Part I was synthesized in the lab via free radical polymerization to yield a neat (no fluorescent label) PS with M_w = 75.0 kg/mol, M_w/M_n = 1.79. A higher MW, neat PS purchased from Polymer Laboratories with M_p = 1,460 kg/mol, M_w/M_n = 1.04, was also used in Part I. PS for Part II was purchased from Pressure Chemical and measured to have M_w = 25.0 kg/mol, M_w/M_n = 1.06.

Fluorescently labeled PS (PS*) was synthesized in the lab via free radical polymerization with trace levels of 1-pyrenylmethyl methacrylate fluorophores to yield 1-pyrenylmethyl methacrylate labeled PS (short-Py-PS*) with M_w = 76.7 kg/mol, M_w/M_n = 1.70, and 1-pyrenylbutyl methacrylate labeled PS (long-Py-PS*) with M_w = 77.5 kg/mol, M_w/M_n = 1.67.

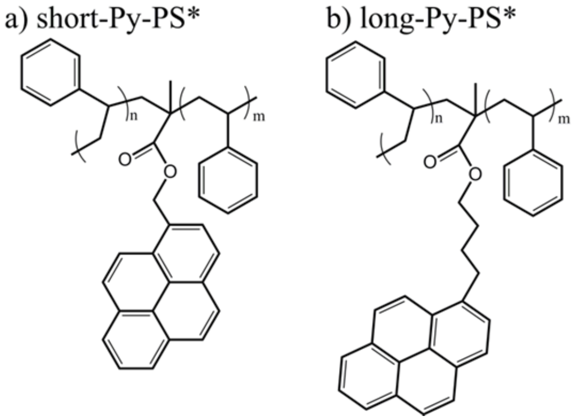

Figure 4. Chemical structures of fluorophore labeled PS: a) 1-pyrenylmethyl methacrylate labeled PS (short-Py-PS*) and b) 1-pyrenylbutyl methacrylate labeled PS (long-Py-PS*).

Sample Preparation

Part I:

Solutions of 20 wt% (PS/PS*)/PVME polymers were dissolved in toluene. Samples were prepared by spin coating solutions onto clear quartz slides at 1500 rpm to produce 2-2.5 μm thick films. Film thickness was determined by spin coating another film onto a silicon piece and measuring the thickness using a J.A. Woollam Co., Inc. ellipsometer. After spin coating, the films were annealed under vacuum at 80 ℃ for 24 hours to remove toluene. These films were then stored in the open air until a procedural change was made to store them under vacuum at room temperature.

Part II:

Solutions of 22 wt% (PS/PS*)/PVME polymers were dissolved in toluene. Samples were spin coated onto ITO-coated quartz slides at 5000 rpm to produce 1.8-2.2 μm thick films. ITO (indium tin oxide) is a conducting oxide ideal for this study because of its electrical conductivity and optical transparency. Wires were glued onto the corner of the slides by silver paste. The films were then annealed at least 60 hours under vacuum at 80 ℃ to remove residual solvent. Two samples were pressed against each other, with polymer sides facing each other, in a vice at 80 ℃ for an hour. All edges of the sandwiched samples were covered by polydimethylsiloxane (PDMS) to eliminate air gaps between the conducting plates during electric field experiments and stored under vacuum at room temperature until needed.

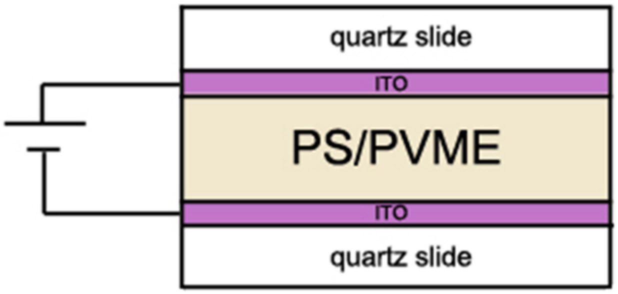

Figure 5. Schematic of sample preparation for E-field measurement. An electric field is produced by applying a voltage across the polymer blend. The magnitude of the electric field is directly proportional to the magnitude of the voltage applied and inversely proportional to the thickness of the blend (E = V/D).

Measurement Procedure

Part I:

The fluorescence measurements were taken using a Photon Technology International QuantaMaster fluorimeter. The polymer blend cast on a quart slide was covered by another clean quart slide to ensure minimum exposure to the air during the measurement. Prior to the measurement, the samples were annealed at 80 °C for at least 10 min to ensure thermal equilibrium. Excitation and emission slits were set to 5.0 nm (ex) and 4.5 nm (em) bandpass, and the excitation wavelength was 324 nm. The angle of incidence was set to 24°.

For emission spectrum scans, the sample was measured for an emission spectrum at a constant temperature, then heated up 2.5 °C, allowed 5 min to equilibrate, and measured for another emission scan, until at least 150 °C was reached. For the time-based scans, the temperature was increased to 160 °C at a rate of 1 °C/min, while simultaneously measuring the fluorescence intensity during a 3 s time window every 15 s at a wavelength of 376 nm.

Part II:

The same fluorimeter procedure was used in Part II except for small changes. The sample was annealed at 120 ℃ for at least 10 min prior to the measurement. Excitation and emission slits were set to 4.5 nm (ex) and 4.0 nm (em) bandpass for normal slides and 5.0 nm (ex) and 5.5 nm (em) bandpass for ITO-coated slides. The angle of incidence was set to 30° for ITO-coated slides.

Results and Discussion

Part I:

The first step in this study was to develop a fluorescence technique in our lab and compare if our data agreed with the existing literature value. For this, Annika Kriisa (a graduate student I worked with) focused on anthracene labeled PS, including the same fluorophore Halary's group used,[18] and I studied alternative fluorescence dyes, pyrene with long (C-4) and short (C-1) tethers. The pyrene fluorophore has a couple of advantages over anthracene in that it has a better quantum yield and can be easily synthesized in our lab.

Figure 6a and 6b show the emission spectra I collected for a (45/5)/50 PS/long-Py-PS*/PVME blend collected at different temperatures. The emission intensity over the entire wavelength range decreased from 80 ℃ to 120 ℃ (Fig. 6a) but started to increase after 120 ℃ (Fig. b), indicating the onset of phase separation. The integrated intensity of these spectra is plotted in Figure 6c as black dots. A sharp increase in intensity was observed at $T_s = 117.5$ ℃, and this was consistent with the data Annika Kriisa collected for a (45/5)/50 PS/short-Py-PS*/PVME blend ($T_s = 120.0$ ℃), shown as blue dots in Figure 6c. The T_s value for this particular composition and molecular weight blend (PS M_w = 75.0 kg/mol) seemed to agree with the data from Halary *et. al* ($T_s \cong 131$ °C),[7] although they used a lower MW (PS $M_\mathrm{w} = 67.0$ kg/mol) and thus a higher T_s than ours was expected. The integrated intensity of a second sample of the same composition, although its emission spectra are not shown here, is plotted as red dots in Figure 6c. This sample was stored in the open atmosphere for one extra day before being measured and showed a slightly lower T_s value ($T_s = 115.0$ °C) than the previous samples.

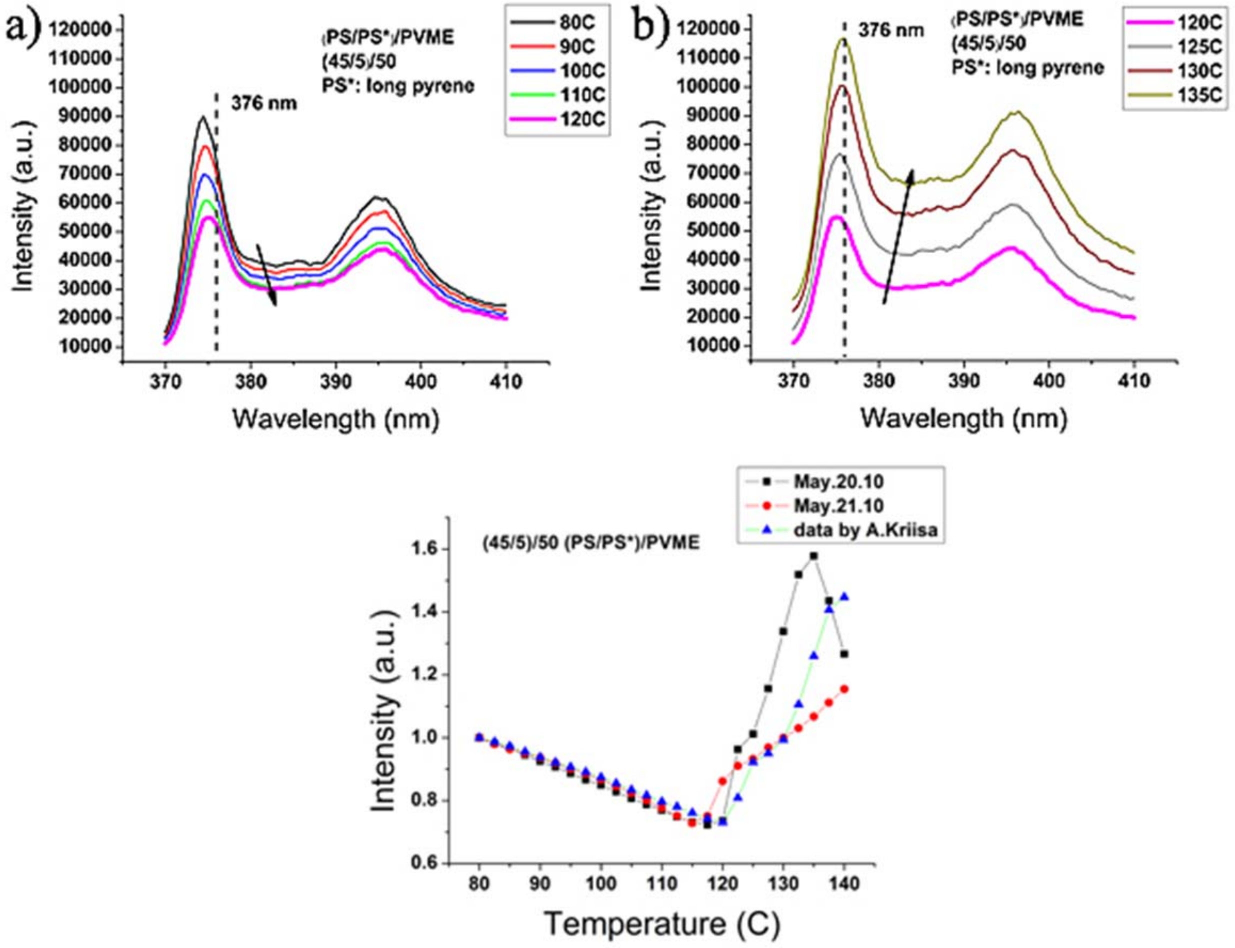

Figure 6. Fluorescence emission spectra for a (45/5)/50 PS/long-Py-PS*/PVME blend: a) the intensity steadily decreases as temperature increases until phase separation b) the intensity quickly increases as temperature increases after phase separation. The y-axis for a) and b) has the same scale and the spectrum for 120 ℃ (magenta) is marked bold for direct comparison. c) the integrated intensity of the spectra agrees with the data by Annika.

However, when I measured two additional samples, prepared previously by Annika, for a (45/5)/50 PS/short-Py-PS*/PVME blend, unexpected results were encountered, as shown by the red and blue lines in Figure 7. Instead of showing the pattern of steadily decreasing intensity followed by a sudden increase, they showed the opposite, and the T_s values could not be determined from these samples. Noticing that the samples were all stored not under vacuum but exposed to the open air, I tried putting the third sample under vacuum for 62 hours before measuring it. The result showed that even though it yielded a lower separation temperature ($T_s = 100.0$ °C) than the expected value of $T_s = 120.0$ °C (black dots in Fig. 7), at least the desired pattern was retained (dark cyan lines in Fig. 7). Thus, we concluded that the interaction of the PS/PVME blends with the open atmosphere, most likely with the water moisture since PVME is polar and likely to interact with other polar molecules, disturbs the miscibility of the polymer blends and that it is best to always store the samples under vacuum. Annika later supported this moisture hypothesis by storing the samples under the N_2 atmosphere and observing no such unexpected behaviors.

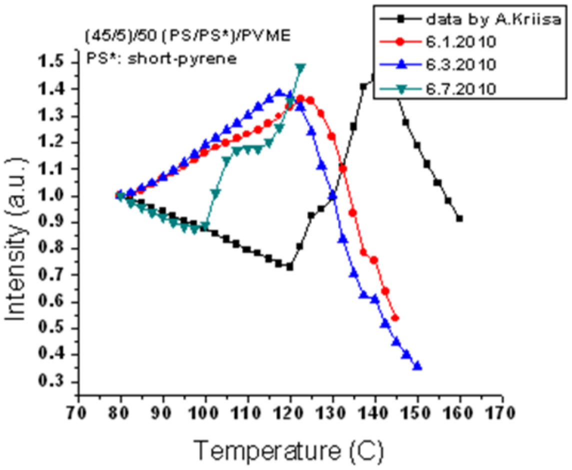

Figure 7. Integrated fluorescence intensity for a (45/5)/50 PS/short-Py-PS*/PVME blend. The samples stored in the open air show unexpected behavior (blue and red). The sample previously stored in the open air but later annealed under vacuum show improved shape of the intensity (dark cyan). Data taken by A.Kriisa for sample stored under vacuum.

To test which fluorophore, the short-pyrene or the long-pyrene, was more prone to the “moisture effect”, I deliberately stored both samples in the open atmosphere, recording the time spent exposed to the moisture, and observed which one showed the decrease in T_s earlier. Figure 8 shows the time-based emission scans at 376 nm as a function of temperature at a ramping rate of 1 $℃/\mathrm{min}$ for (45/5)/50 PS/PS*/PVME blends. The phase separation temperature can be quantified by making linear fits to the data before and after the sharp increase in intensity and defining the intersection of the two linear fits as the phase separation temperature. All the time-based scans for a (45/5)/50 PS/short-Py-PS*/PVME blend stored under vacuum showed consistent T_s values with an average of $T_s = 123.5$ ℃ (Fig. 8a). However, when the samples of the same composition were stored in the open environment, a decrease in the phase separation temperature was observed (Fig. 8b). Figure 8b shows that as the time spent exposed to the open atmosphere increased from $t = 23$ hr, $t = 120$ hr, to $t = 330$ hr, the phase separation temperature decreased from $T_s = 123.5$ ℃, $T_s = 120.0$ ℃, to $T_s = 104.0$ ℃, respectively. Note that even though one sample was exposed to the air for 23 hours, no change in T_s value was detected, showing some resistance of PS/short-Py-PS*/PVME blend to the moisture. Compared to the short-pyrene labeled blends, (45/5)/50 PS/long-Py-PS*/PVME blends stored under vacuum produced less reproducible data (Fig. 8c). Moreover, Fig. 8d shows that the decrease in T_s when exposed to the air occurred earlier for the long-pyrene labeled blend ($t = 26$ hr) than the short-pyrene labeled blend ($t = 120$ hr). These results indicated that the long-pyrene fluorophore is more vulnerable to moisture than the short-pyrene fluorophroe and that using the short-pyrene as the main fluorescent dye would yield more consistent and reproducible data for this study.

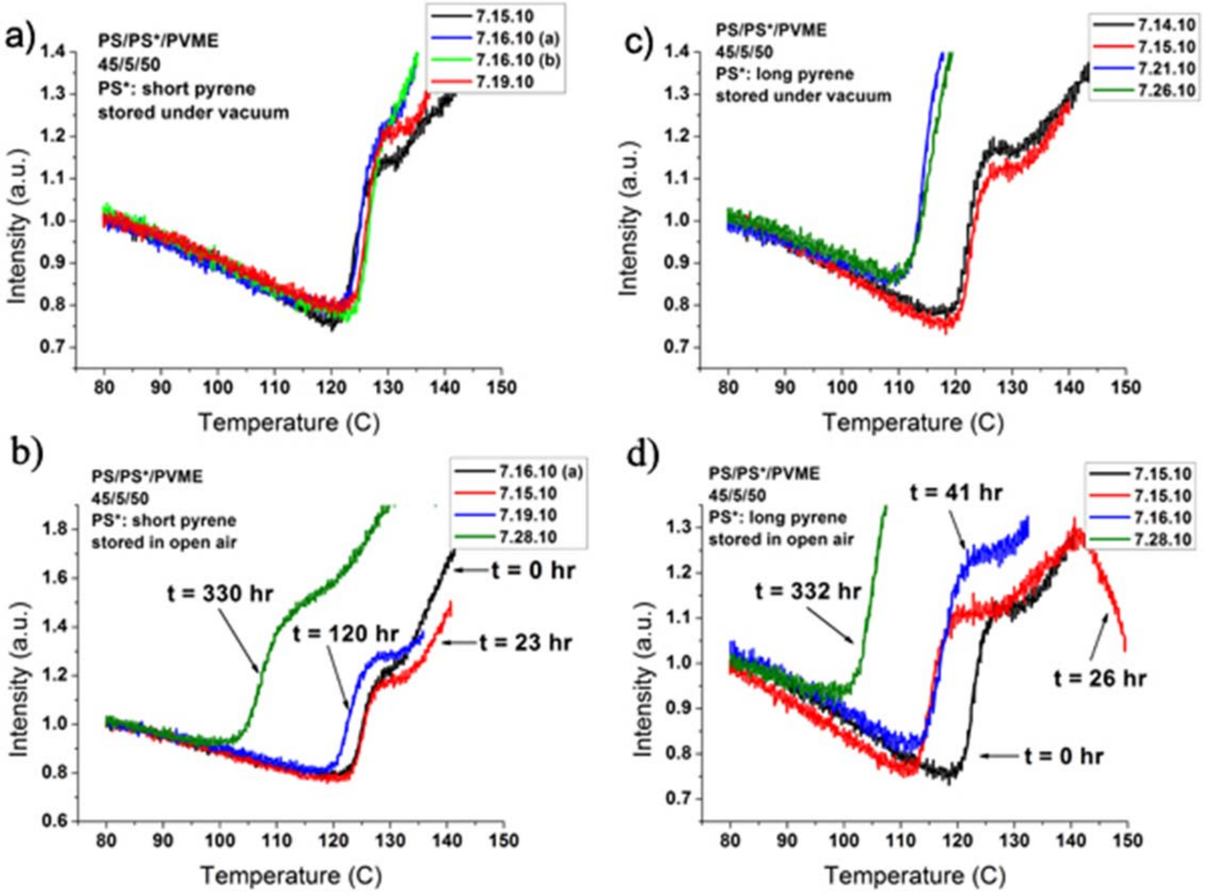

Figure 8. Time-based fluorescence emission scans at 376 nm at a heating rate of 1 ℃/min for long-pyrene and short-pyrene labeled blends stored in different conditions: a) short-Py-PS* blend stored under vacuum produces consistent T_s values with an average of $T_s = 123.5$ ℃. b) short-Py-PS* blend shows lower T_s values when stored in the open air for $\mathrm{t} > 120\ hr$ c) long-Py-PS* blend stored under vacuum shows reproducibility issues d) long-Py-PS* blend shows lower T_s values when stored in the open air for $\mathrm{t} > 26\ hr$

The heating rate for all the time-based scans in this paper was kept constant at 1 ℃/min because the heating rate relative to the phase separation process has been known to affect the phase separation temperature.[7,10] Figure 9 shows data obtained by Annika Kriisa on the effects of different ramping rates on T_s values.[18] In general, the phase separation temperature is higher for faster heating rates than it is for slower rates.

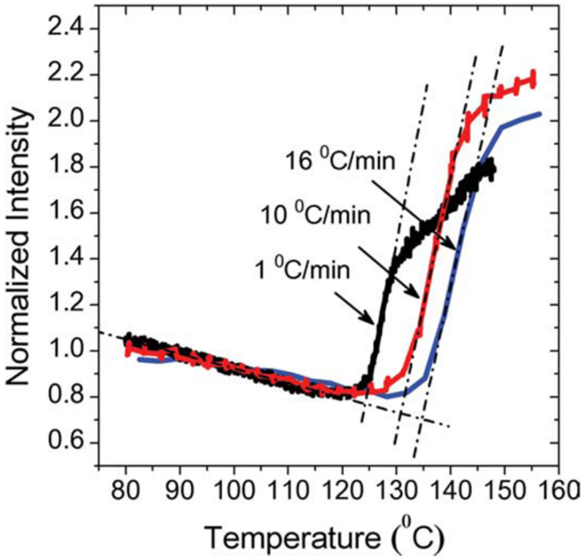

Figure 9. Fluorescence intensity at 382 nm for a (45/5)/50 (PS/short-Py-PS*)/PVME blend as a function of temperature collected at different ramping rates.[18]

In an attempt to measure the effects of different MWs by varying only the MW of neat PS, we needed to minimize the content of the PS* so that blend properties are dominated by the neat PS. I measured and compared four different PS* content compositions (1%, 2%, 3%, and 5%), as shown by Figure 10a-d. The blends of PS* content below 5% were found to have issues with reproducibility, and even the 5% PS* composition, although it yielded the most reproducible data, was not completely free from the same problem. Seeing that the reproducibility seemed to improve as the PS* content increased, I tried measuring a (40/10)/50 PS/short-Py-PS*/PVME composition to see if the pattern was indeed the case. Figure 10e shows the result of this measurement, whose reproducibility proved the most ideal for the study and suggested that the fluorescent dye to PS ratio is important to reproducibility of the data. However, the (40/10)/50 PS/PS*/PVME composition defeated the purpose of reducing the PS* content, and this called for a way to reduce the PS* content while maintaining the fluorescent dye to PS ratio the same. This led me to polymerize a new set of short-pyrene labeled PS, multiplying the content of the fluorophore short-pyrene by five, such that the new short-Py-PS* would have five times more fluorescent dyes than the old PS* per chain on average. This meant that a (48/2)/50 PS/new-PS*/PVME blend would have the same amount of fluorescence dyes as the (40/10)/50 PS/old-PS*/PVME and thus theoretically the same reproducibility as well. Figure 10f shows the data for the (48/2)/50 PS/new-PS*/PVME blend, and they indeed demonstrated the same ideal reproducibility as Figure 10e.

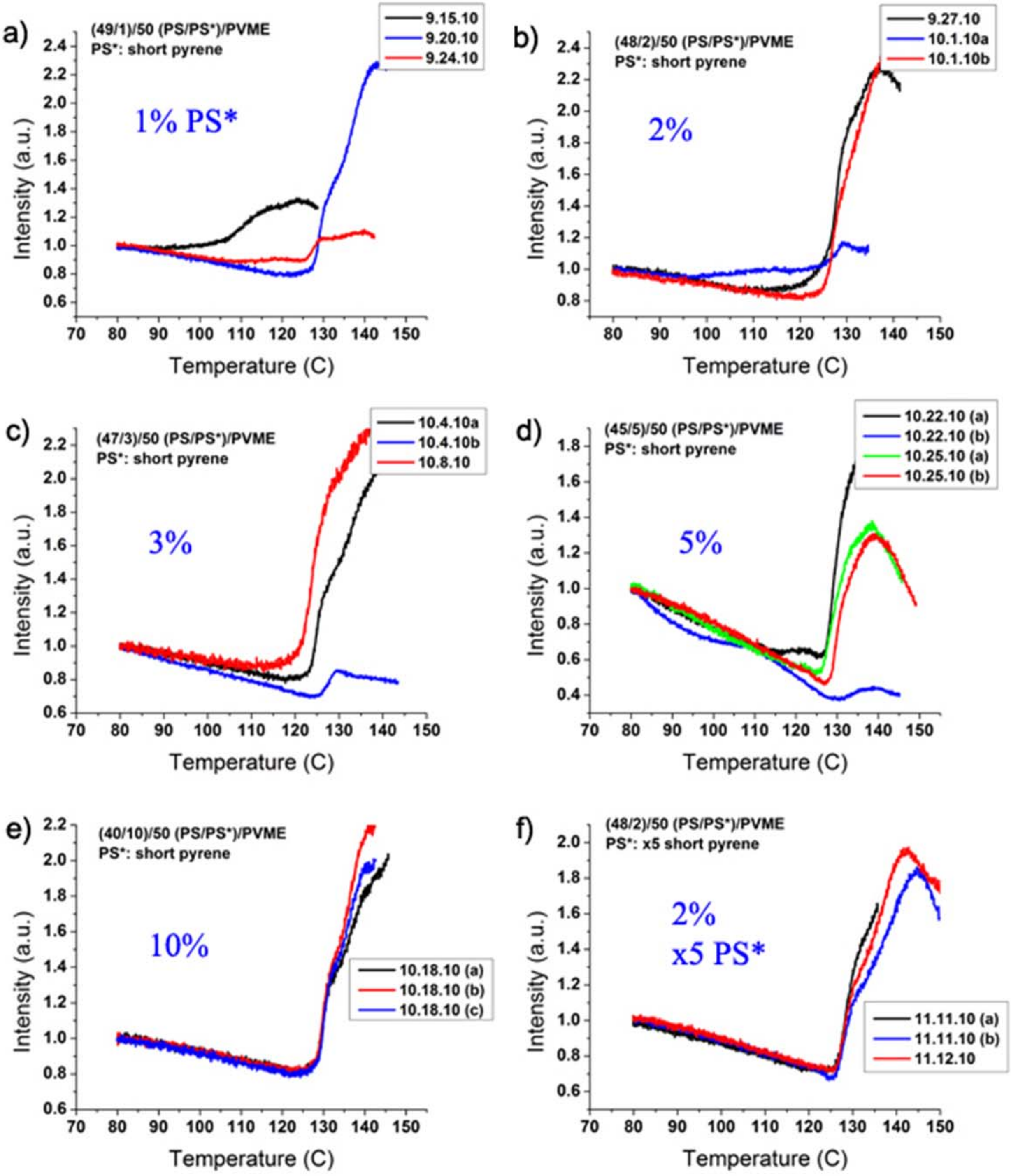

Figure 10. Reproducibility of fluorescence emission scans for different PS* contents: a) 1% PS*, b) 2% PS*, c) 3% PS*, d) 5% PS*, e) 10% PS*, and f) 2% new short-Py-PS* that has five times more fluorophores.

Using the new PS* as the fluorescent label, I investigated the molecular weight dependence of polymer blends on the phase separation temperature. Figure 11 shows the time-based scans for a high PS MW weight (M_p = 1,460 kg/mol) of (48/2)/50 PS/PS*/PVME blend. All three measurements yielded the phase separation temperature of $T_s = 111.5$ °C with reliable reproducibility. This value was also comparable to the data published by Halary *et al*, who had $T_s \cong 117.0$ °C for PS M_w = 1,660 kg/mol.[10] As it was discussed in the Introduction, the higher MW polymer blends showing LCST behavior are less miscible than lower MW blends and have a lower T_s as a result. My data agrees with this MW effect, validating our fluorescence method to detect T_s: as the MW of matrix PS was varied from M_w = 75.0 kg/mol to M_p = 1,460 kg/mol, the phase separation temperature decreased from $T_s = 125.5$ °C to $T_s = 112.0$ °C (Fig. 10f and Fig. 11).

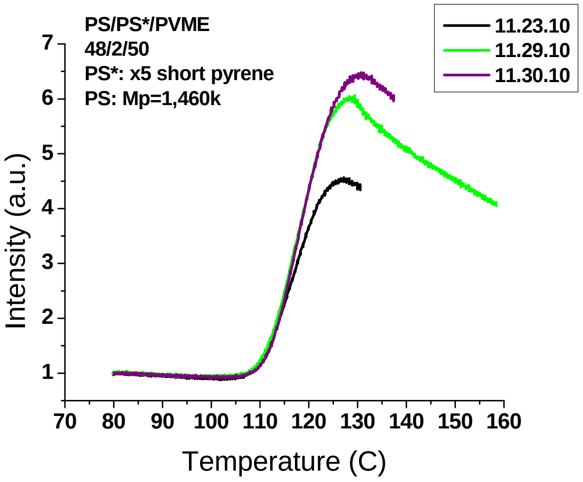

Figure 11. Time-based scans for high MW PS/PS*/PVME blends. The phase separation temperature for this blend was determined to be $T_s = 111.5$ °C.

We had now built upon the fluorescence technique first introduced by Halary *et al.*[7] and developed our own procedures by figuring out the storing condition of samples, which fluorophore to use, and how to improve reproducibility with increasing PS* content. This method allowed us to publish a paper[18] that discusses the effects of four different fluorophores on T_s (Fig. 12). The data I collected for long and short pyrenes contributed to the discussion in the paper, while Annika focused on the other two fluorophores, which were anthracene-ctr-PS* (same as that used by Halary *et al.*) and anthracene-sgr-PS* (Fig. 13). Our paper demonstrates that the different fluorescent dyes are equally sensitive to detecting the phase separation in PS/PVME blends, although the proximity of the fluorophores to the PS backbone has been found to influence the measured T_s value. Both fluorescent dyes, pyrene and anthracene, consistently indicated phase separation a few degrees earlier when located closer to the PS backbone. With the procedures all set up and published in the paper, we were now prepared to move onto the next phase of the experiment which involves electric fields.

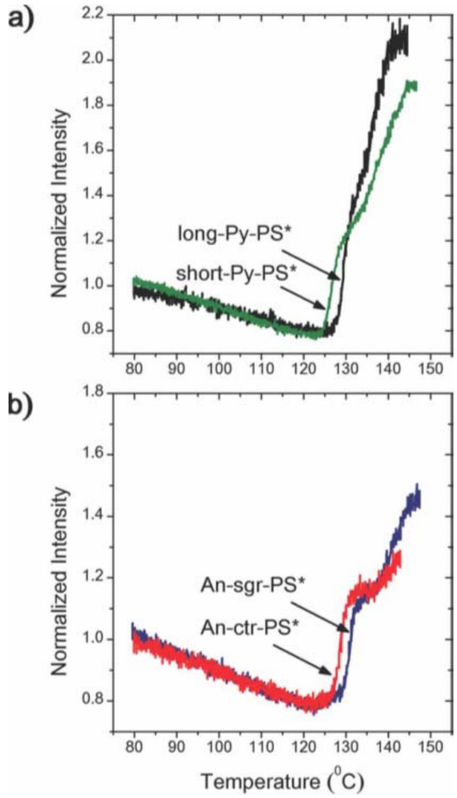

Figure 12. Fluorescence intensity for (45/5)/50 (PS/PS*)/PVME blends as a function of temperature at a heating rate of 1℃/min. Both short-Py-PS* and An-ctr-PS*, which are bonded closer to the backbone PS than long-Py-PS* or An-sgr-PS*, indicate the phase separation earlier.[18]

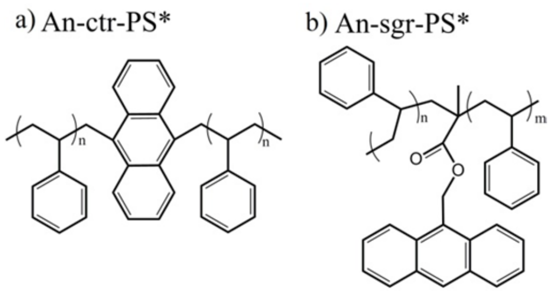

Figure 13. Chemical structures of fluorophore labeled PS studied by Annika in our paper:[18] a) anthracene center-labeled PS (An-ctr-PS*) and b) 9-anthracenylmethyl methacrylate labeled PS (An-sgr-PS*).

Part II:

To investigate the effect of electric fields on the miscibility of PS/PVME blends, two procedural changes to Part I were necessary. First, instead of using clear quartz slides, we needed to use ITO-coated conducting quartz slides so we could apply a voltage across two sandwiched samples and generate an electric field between them. Second, instead of using one sample for only one measurement, we needed to devise a procedure that could reuse the same sample for multiple measurements. Halary *et al*. argued that this procedure was more likely for low MW blends as high MW blends, once phase separated, would take a much longer time to remix below T_s.[7] This procedure was desired because, as we were interested in finding $\Delta T_s = T_s(E) - T_s(E = 0)$, using the same sample for each $T_s(E)$ and $T_s(E = 0)$ value would define ΔT_s much better than using different samples for $T_s(E)$ and $T_s(E = 0)$. It could also reduce the cost and time in preparing samples.

In transitioning from using clear to ITO-coated quartz slides, we needed to see if there were any differences in T_s values between samples cast on clear slides and those cast on ITO-coated slides. First, I measured T_s values for five different compositions of PS/PVME blends cast on clear slides. The results were plotted and a polynomial function was fitted to the data to produce a phase diagram (Fig. 14). Since PS used in Part II had lower molecular weight (M_w =

25.0 kg/mol) than PS used in Part I (M_w = 75.0 kg/mol), the increase in T_s values was expected over the entire composition range. For comparison, one T_s value for a (45/5)/50 (PS/short-Py-PS*)/PVME blend from Part I (Fig. 10f) is plotted in Figure 14, which shows $\Delta T_s \approx 22$ ℃ between molecular weights for the same composition.

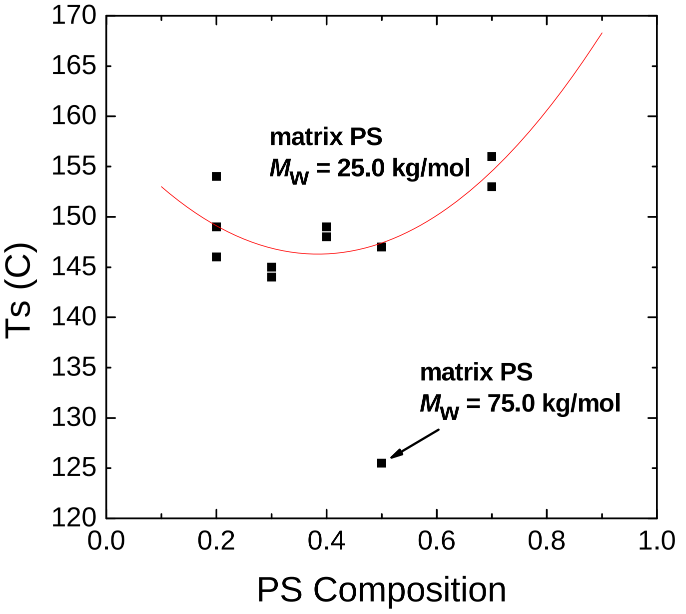

Figure 14. Phase diagram of PS/PVME blend on clear quartz slides with PS matrix M_w = 25 kg/mol. A polynomial function (red line) is fitted to the data and the T_s value from Part I is reproduced for comparison.

Next, in an attempt to map out a new phase diagram for blends cast on ITO-coated slides to be compared to Figure 14, I measured the time-based scans at 379 nm for (40/10)/50 (PS/PS*)/PVME blends on ITO-coated slides. However, as Figure 15 indicates, the results had serious reproducibility issues and no sharp increases in intensity were observed. We could not reliably detect from these data the phase separation temperatures for PS/PVME blends when no electric field is applied, $T_s(E = 0)$, so we needed to figure out what was causing the problem.

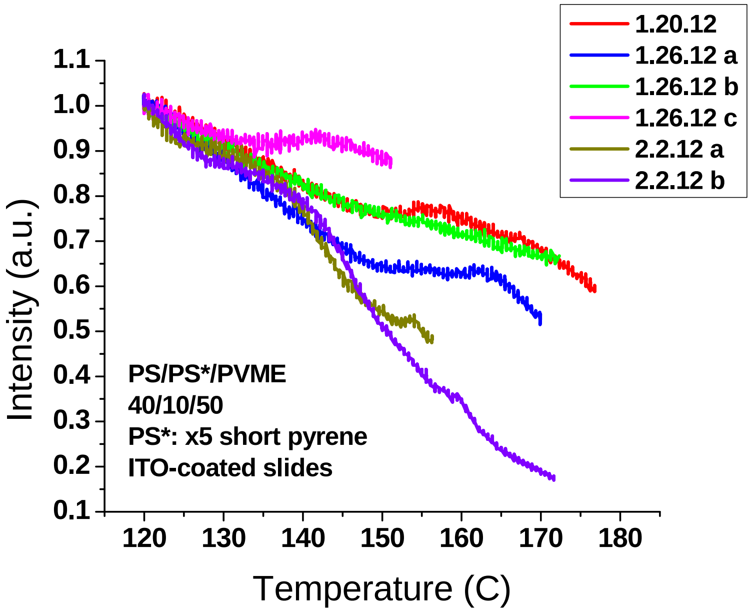

Figure 15. Fluorescence intensity as a function of temperature at 379 nm for PS/PVME blends on ITO-coated slides, showing reproducibility issues.

Annika and I came up with four possible solutions to resolve this issue. First was to give the samples a longer heat treatment (120.0 °C for 2 hours) than before (120.0 °C for 30 minutes) prior to measuring them to ensure as complete mixing and thermal equilibrium as possible. By this time, Annika had succeeded in reusing the same sample on clear quartz slides for multiple measurements and getting the same results at each attempt only if she annealed the sample at 120.0 °C for 2 hours just prior to each measurement. Figure 16 shows the time-based scan data collected by Annika at a heating rate of 1 °C/min. The top most emission scan (brown line) represents her very first measurement on a sample, and each emission scan below denotes her successive measurement made on the same sample, all the way down to the 8th measurement (black line). For the first measurement, she annealed the sample at 120.0 °C for 30 minutes and obtained a phase separation temperature $T_s = 139.6$ °C. For the next 2nd, 3rd, 4th, and 5th measurements, she cooled the sample down to 120.0 °C, gave the heat treatment for 2 hours, and repeated the emission scan until she reached 151.0 °C. The T_S values were determined to be 143.1 °C, 143.5 °C, 143.6 °C, and 143.0 °C, respectively. For the last 6th, 7th, and 8th measurements, she varied the annealing time to 1 hour, 30 minutes, and 30 minutes and observed a decrease in T_S as the annealing times decreased.

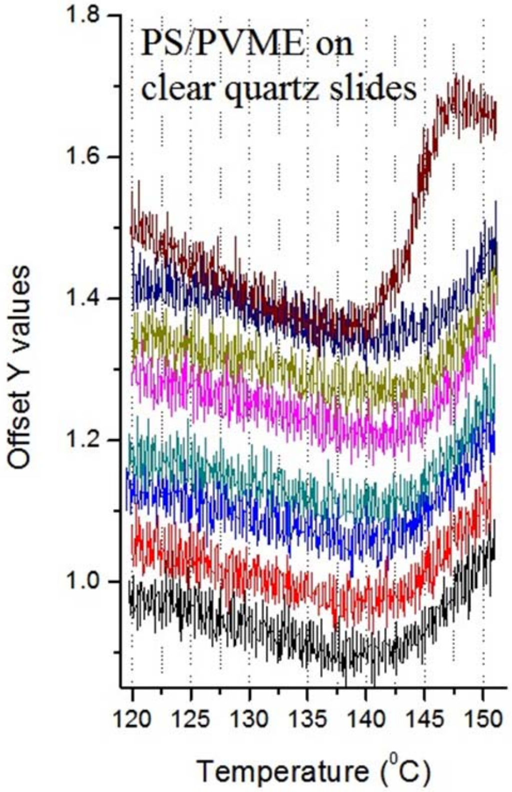

Figure 16. Multiple fluorescence measurements for a single PS/PVME sample cast on clear quartz slide. When the sample is annealed at 120 °C for 2 hours, complete remixing seems to take place which reproduces the same T_S at each measurement. [Data taken by A. Kriisa]

When I repeated the above procedure on samples cast on ITO-coated slides, however, the same reproducibility behavior in Annika's data was not observed. Figure 17 shows my two attempts at remixing the samples by annealing them at 120.0 °C for 2 hours, both of which failed to detect the phase separation temperature $T_S(E = 0)$. This suggested that thermal equilibrium was not what prevented the samples on ITO slides from showing an increase in intensity.

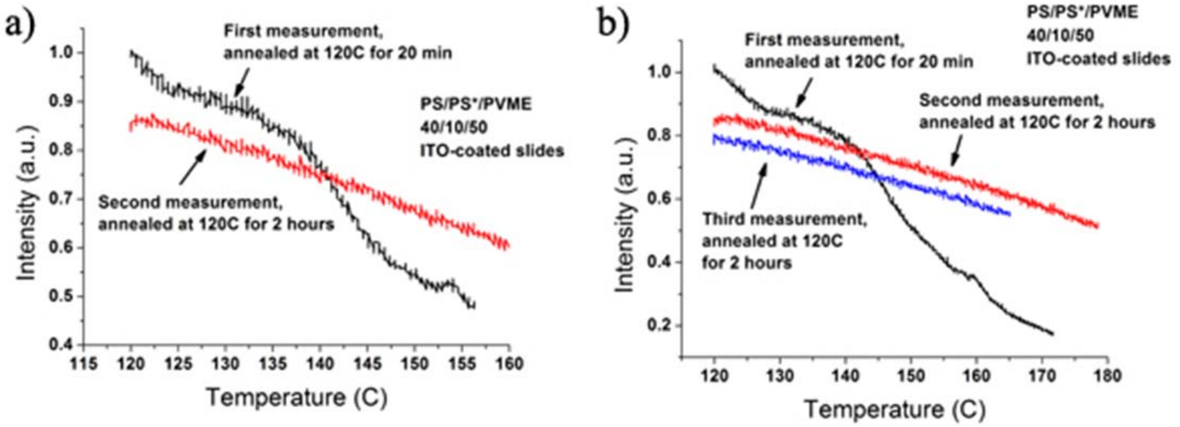

Figure 17. Time-based scans for a (40/10)/50 (PS/PS*)/PVME blend before and after annealing at 120 ℃ for 2 hours. Even after annealing, no indication of phase separation was detected in both samples.

The second solution was to increase the PS* content because ITO transparency is not 100%, which lowers signal intensity, and we had solved a reproducibility issue before by increasing the PS* content (Fig. 10). When I increased the PS* content from 10% to 13%, cast the (37/13)/50 (PS/PS*)/PVME blends both on clear and ITO slides, and compared their time-based scans, the results still showed no improvements for the samples on ITO slides on either the reproducibility or detecting T_s (Fig. 18).

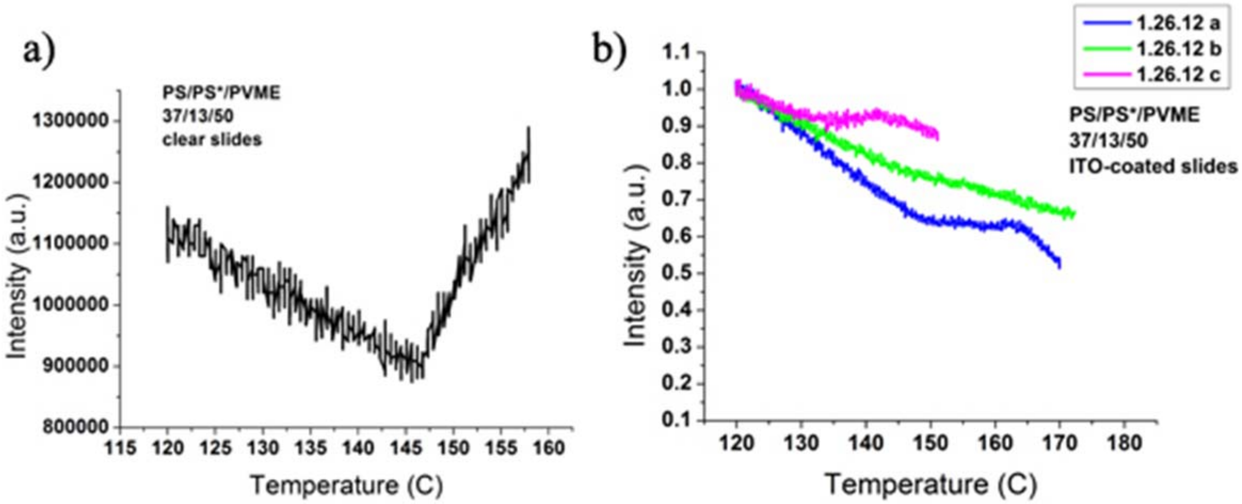

Figure 18. Comparison of a (37/13)/50 (PS/PS*)/PVME blend: a) samples cast on clear quartz slides and b) samples cast on ITO-coated slides. The samples on ITO-coated slides do not show improvements on either the reproducibility or detecting T_s even when the PS* content is increased.

The third solution I tried was to collect and inspect the whole emission spectrum for the samples on ITO-coated slides. It was possible that, due to the presence of ITO and for this lower molecular weight PS, the spectrum for PS/PVME blends might have changed and I was measuring at a wavelength ($\lambda = 379$ nm) that did not ideally reflect the change in emission intensity. The result showed that even though there was a change in the shape of the spectrum from what we observed for the higher molecular weight (45/5)/50 PS/long-Py-PS*/PVME blend cast on clear slides (Fig. 6), the fluorescence intensity in any region between 375 nm and 440 nm would have reflected the change in intensity well enough and detected phase separation had it occurred.

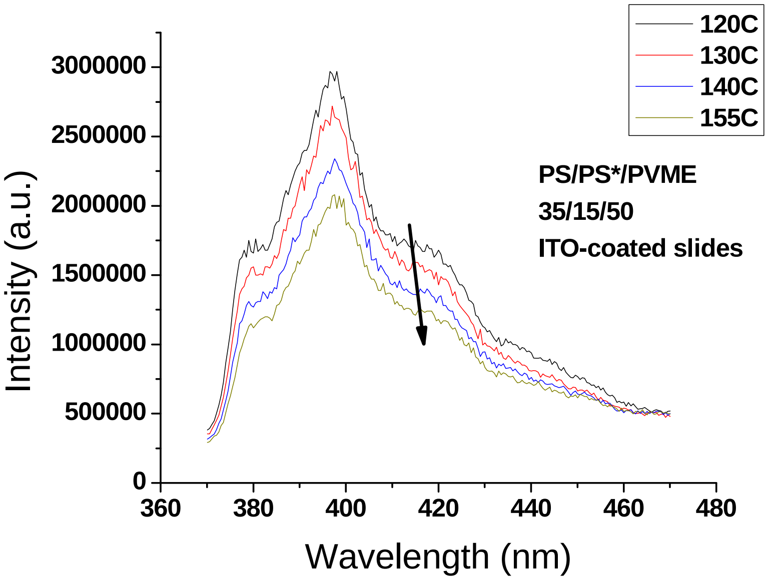

Figure 19. Fluorescence emission spectra for a (35/15)/50 PS/PS*/PVME blend on ITO-coated slide collected at different temperatures. No phase separation is detected from $120\ ^\circ\mathrm{C}$ to $155\ ^\circ\mathrm{C}$.

The one last possibility I could think of was that the phase separation temperature for samples cast on ITO-coated slides was different. I noticed that the random behavior in fluorescence intensity shown by samples on ITO slides resembled much the random behavior shown by samples on normal clear slides after phase separation. This led me to think that the PS/PVME blends on ITO slides could be phase separating at a much lower temperature, and was already phase separated when I annealed them at 120 ℃. To verify this hypothesis, I took a time-based scan starting from 80 ℃. As Figure 20 indicates, the PS/PVME blend cast on an ITO-coated slide was indeed observed to phase separate at $T_s = 106.8\ ^\circ\mathrm{C}$, which was about 40 ℃ lower than what was observed for the same blend on clear quartz slides (Fig. 14). Our current explanation for this result is that there exists either an unidentified interaction between the polymer blend and ITO, or that heat transfer to the blend is significantly higher due to the conducting ITO positioned between the heater and the polymer blend. However, these are only hypotheses at this moment and further discussions on the influence of ITO on PS/PVME blends should be dealt with care until future studies give more insight into this subject.

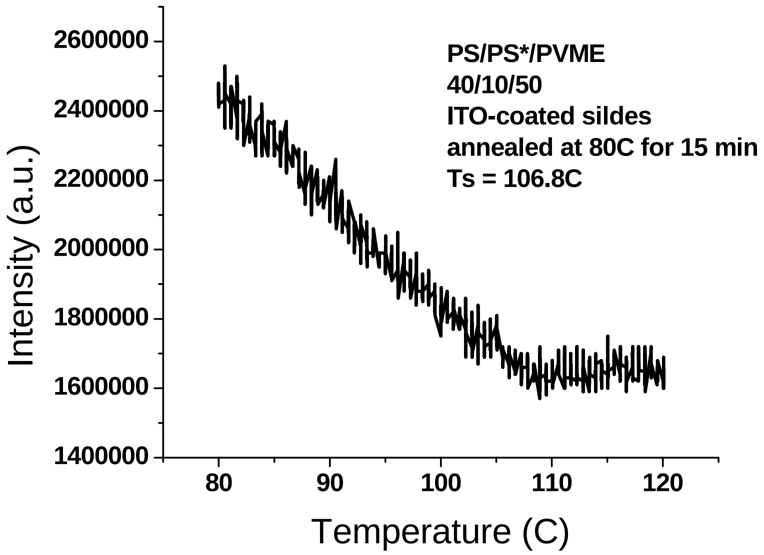

Figure 20. Time-based scan for a PS/PVME blend cast on ITO-coated slide. The phase separation for this sample occurred at $T_s = 106.8$ ℃.

Even though the samples on ITO slides were found to have substantially lower T_s values than expected, we could still apply electric fields and find their effects on the miscibility of PS/PVME polymer blends as we are only looking for the change in T_s, that is, $\Delta T_s = T_s(E) - T_s(E=0)$, of which $T_s(E=0)$ was found to be 106.8 ℃ in Figure 20. However, when I applied a voltage across the two sandwiched samples, even with special care, a current was found to flow between them, which would introduce dielectric breakdown in the system and thus void the measurement. No further attempts at applying the voltage could be made due to the time limit, but in this study I have found samples on ITO-coated slides have much lower T_s than those on clear quartz slides, and this will contribute to detecting $T_s(E=0)$ and making procedural changes to annealing conditions for future continuing studies.

Conclusions

This study was carried out with an aim to investigate the effect of electric fields on the miscibility of PS/PVME polymer blends, represented by the phase separation temperature T_s. A fluorescence method was developed to reliably detect the phase separation temperature. The T_s value could be determined by observing the fluorescence intensity at a single wavelength as a function of increasing temperature and locating the point where a sudden increase in intensity occurred. The sharp increase in fluorescence intensity is attributed to the removal of the static quenchers in PVME from the fluorescent dyes covalently bonded to the backbone of PS.

In developing this fluorescence method, we encountered a moisture problem, which I resolved by making procedural changes to the storing conditions of samples. I also found that short-Py-PS* labeled blends are more resistant to moisture than long-Py-PS* labeled blends. In addition, I have observed improved reproducibility as the PS* content increases and polymerized a new set of short-Pyrene labeled PS* that was used as the main fluorophore in this study. These works contributed to publishing our paper on characterization of PS/PVME blends using fluorescence.[18]

To examine the effect of electric fields on the phase diagram of PS/PVME blends, I mapped out a phase diagram for PS/PVME blends cast on clear quartz slides when no electric field was applied. However, a substantial difference in the phase separation temperature between the samples on clear slides and the sample on an ITO-coated slide was observed, possibly signifying an unknown interaction between PS/PVME blends and ITO, or higher heat transfer than expected to the polymer blend on conductive ITO-coated slides. With $T_s(E = 0)$ defined as 106.8 °C, I tried to measure a T_s under the presence of an electric field. But I failed to prevent current flow across the samples, and $T_s(E)$ could not be obtained within the time limit. However, this study has laid the groundwork for continuing florescence studies on the miscibility of the PS/PVME blends under the presence of electric fields, and future studies can be built upon the materials presented here.

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