

INTERDIFFUSION IN THIN POLYMER FILMS

Summer School on Neutron Small Angle Scattering and Reflectometry

NIST Center for Neutron Research

June 18-23, 2012

Bulent Akgun, Michael Dimitriou, Sushil K. Satija

Abstract

The evolution of a segment density profile as a function of time across an interface between a thin polystyrene film and a thin deuterated polystyrene film will be investigated using the NG7 horizontal neutron reflectometer. The aim of this measurement is to provide hands on experience in data collection, reduction, and analysis for neutron reflectivity measurements of thin polymer films.

T, time

1. Objectives of the experiment

The objectives of this experiment are:

- a) To determine the time evolution of segmental density profile between PS and dPS thin films above their glass transition temperature, T_g .
- b) To check the validity of the reptation theory at short times and to extract diffusion coefficients.
- c) To determine the effect of thickness (confinement) on interdiffusion.
- d) To learn how to properly perform reflectivity measurements of polymer thin films and have fun.

2. Introduction

Thin polymer films have gained enormous interest in recent years due to their applications in emerging technologies such as solar cells, fuel cells, etc. and their scientific importance in understanding the behavior of polymer chains at or near interfaces. Their structure and dynamics under confinement have been extensively studied. For example, glass transition temperature, T_g , for various polymers on various substrates using different thicknesses and molecular weights have been investigated by many scientists. Even though some generally accepted results have been established there are still debates and contradictory results for identical systems measured under similar conditions using the same technique.

There are multiple methods used to measure T_g of thin polymer films such as measuring the thermal expansion coefficients in the glassy and rubbery state, or measuring the mobility of chains by using gold markers etc. For each technique there are

advantages and disadvantages. Since above T_g , polymer chains are in a rubbery state and are able to move, measuring the mobility or diffusion of polymer chains can yield valuable information on T_g . The diffusion coefficients of polymer chains in thin films can easily be obtained by performing interdiffusion experiments. The interdiffusion problem is also important for understanding the crack healing after mechanical failure, phase separation of polymeric blends, and adhesion between polymer films.

Interdiffusion between melts of high molecular weight polymer thin films has received both theoretical and experimental interest. Earlier studies have focused on diffusion distances much larger than the unperturbed chain radius of gyration, R_g , using infrared microdensitometry,¹ forward recoil spectrometry² and secondary ion mass spectrometry (SIMS).³ These studies proved that the reptation model of de Gennes⁴ and Doi and Edwards⁵ with the extension of Graessly⁶ are in very good agreement with experiments for times longer than the reptation time, τ_d , however, differences between the theories are visible at shorter times, i. e. length scales shorter than R_g . It is challenging to obtain information at these short length scales with high resolution when the interfaces of interest are buried. Dynamic SIMS (DSIMS) and neutron reflectivity (NR) both probe the buried interfaces and yield information for short length scale motion. NR becomes the major technique for interdiffusion experiments since DSIMS is a destructive technique and the depth resolution is not as good as NR. NR has a sub-nanometer depth resolution and it is a non-destructive technique. Selective deuteration of one component provides the necessary neutron contrast for the measurement.

According to the reptation model of de Gennes, the polymer chain reptates along its own contour within a fictitious “tube” formed by the entanglements of the neighboring

polymer chains that constrain movement of polymer chains perpendicular to the contour of the tube. Reptation theory predicts that there are four different regions in which different parts of the polymer chain moves at different length scales. For times shorter than the entanglement Rouse time, τ_e , chain segments display Rouse-like motion within the tube and the mean square displacement of monomers, $\langle r^2 \rangle$, scales with $t^{1/2}$. At times longer than τ_e and shorter than the Rouse relaxation time, τ_r , the time at which the motion of the each segment becomes coordinated over the entire length of the chain, the movement of segments perpendicular to the tube is restricted but segments have a free movement along the tube. In this second regime $\langle r^2 \rangle$ scales with $t^{1/4}$ and it is considered as the signature of reptation. The reptation time, τ_d , is the time required for a polymer chain to disengage from its initial “tube”. Between τ_r and τ_d , reptation is the dominant motion and $\langle r^2 \rangle$ scales with $t^{1/2}$. For longer times than τ_d segmental displacement is simply a center of mass diffusion and $\langle r^2 \rangle$ scales with t . In our experiment we will not reach reptation time where chain moves a distance equal to its R_g but we will probe interdiffusion at shorter times.

De Gennes,⁷ Tirrell⁸ and Wool⁹ have studied the time evolution of the segmental density profile across the interface and predicted a discontinuity in the segmental density profile for times shorter than τ_d and beyond τ_d where the error function profile is recovered. This prediction is not very realistic since Rouse motion should instantly smear out the concentration profile. Interdiffusion experiments done on polystyrene/deuterated polystyrene (PS/dPS)¹⁰⁻¹² and poly(methyl methacrylate)/deuterated poly(methyl methacrylate) (PMMA/dPMMA)¹³⁻¹⁴ thin films using NR showed that in fact there is a very fast broadening of the interface for times shorter than τ_e .

Karim et al.⁹ studied the interdiffusion for PS/dPS thin films using NR and he found that the diffusion rate slows down for $t > \tau_e$ with time till the bulk diffusion rate is reached. Later, Stamm and coworkers¹⁰ investigated the same system using NR and found different time regimes. They analyzed their data using an error function between the polymer films. At the beginning there was a very fast intermixing of polymer segments over a distance of approximately 3 nm. After fast intermixing, for intermediate times there was almost no further intermixing. In the last regime, polymer segments were moving across the interface but with a smaller exponent than predicted by theories. Lin et al.¹³ elucidated the effect of film thickness on the interdiffusion of PMMA/dPMMA system using NR. They demonstrated that the rate of interdiffusion strongly depends on the thickness of the bottom film. Polymer films that have a thickness less than R_g have effective diffusion constants 2 orders of magnitude smaller than the bulk diffusion constant. The dynamic slowdown of polymer chains in the bottom layer was attributed to conformational changes the polymer chains experience when they are confined.

3. Experimental

3.1. Materials

Polystyrene (PS) and deuterated polystyrene (dPS) with number averaged molecular weights of 525 kg/mol are purchased from Polymer Source Inc. and used without further purification. The polydispersity index of these polymers is smaller than 1.17. Toluene (J. T. Baker 99.9%) is used as received. Silicon wafers 76 mm in diameter and 5 mm thickness are purchased from El-Cat Inc. Silicon wafers 100 mm in diameter and 0.6 mm thickness are purchased from Semiconductor Processing Company.

3.2. Procedure

Bilayer samples will be prepared on 5 mm thick polished silicon wafers. Wafers will be cleaned by a treatment with freshly prepared “piranha” solution (70/30 v/v H₂SO₄ (50%)/ H₂O₂ (30%)) at 90-100 C for 45 minutes and will then be rinsed with copious amount of distilled water and dried with a stream of technical grade nitrogen. Oxide layer will be removed from the cleaned wafer by etching in a 5% HF solution. Approximately 20 nm, 40 nm and 80 nm thick dPS layer will be spun cast using various concentrations of dPS solutions in toluene. Thickness of the spun-cast film depends on the molecular weight, concentration of the solution, and spinning speed. The dPS layer will be annealed at 150 C for 12 h to remove any residual solvent and relax the stresses built during the spin coating process. An approximately 20 nm thick PS film will be prepared on a piranha cleaned 0.6 mm thick polished silicon wafer by spin coating. The sides of the film will be scored with a razor and film will be floated off onto a pool of deionized water. The floated film will then be picked up with the dPS film covered thick silicon substrate to form the bilayer sample. The bilayer film will be dried at 60 C under vacuum overnight to remove residual solvent and water trapped between the layers. In this experiment we will change the thickness of the dPS layer to understand how confinement affects the diffusion of polymer chains in the perpendicular direction. Therefore we are going to prepare three samples in which the top layer thickness will be identical and kept close to the R_g of the polymer chains and bottom layer thickness will be varied from $1R_g$ to $4R_g$ (Figure 1).

X-ray reflectivity (XR) will be measured prior to neutron reflectivity measurements. NR measurement will be performed first for the as-prepared sample and

then the bilayer sample will be annealed at 135 C for various times and NR measurements will be taken after each annealing step to follow the evolution of concentration profile between the layers. Reflectivity data will be analyzed using a step profile with an error function to represent the roughness between the layers.

Figure 1. Schematic of the bilayer samples that will be measured in summer school. Each sample will be measured by a different group.

3.3. NG7 Horizontal Neutron Reflectometer

Reflectivity measurements will be performed on the NG7 horizontal reflectometer. NG7 is originally designed for measuring liquid-air interfaces which can only be achieved using a horizontal geometry. NG7 uses a fixed wavelength of 4.75 Å. The schematic of NG7 is shown in Figure 2. A tilting pyrolytic graphite monochromator is located at the bottom 1 cm of guide NG7. The resulting beam profile is approximately 50 mm in width with a maximum height of 10 mm. The reflectometer is designed for incident wavelengths $\lambda=2.35, 4.1, 4.75, 5.5$ Å. The beam is filtered against thermal neutrons after the monochromator with either a graphite filter for $\lambda =2.35$ Å or a liquid nitrogen cooled beryllium filter for $\lambda > 4$ Å. The neutron flight tubes have $2\theta c$ super mirrors mounted on their vertical surfaces to reduce losses due to horizontal beam divergence. All flight tubes have single crystal sapphire windows and are evacuated to

reduce losses from air scattering. The pre- and post-sample flight paths are 2 m in length and each has a pair of independently controlled LiF slits for collimation of the incident or scattered beam. Horizontal collimation is also available before and after the sample position. A beam monitor detector located after the second collimating slit samples a portion of the beam incident on the sample and allows the primary detector data to be scaled to absolute reflectivities. The instrument has two available detectors: (1) a 2.5 cm diameter cylindrical ^3He proportional counter or (2) an ORDELA linear position sensitive ^3He proportional counter with a 10 cm position-sensitive length and a 4 cm width. The detector is used without the final set of collimation slits.

Figure 2. Schematic of NG7 horizontal neutron reflectometer.



4. Results

The critical steps of sample preparation, alignment procedures, and data collection for XR and NR and data analysis using REFLPAK¹⁵ will be demonstrated during the real hands on experiments. To give an example, after the reflectivity data is collected, it is plotted as a function of momentum transfer vector in the perpendicular direction, q_z . Figure 3 demonstrates representative XR and NR data for an as-deposited bilayer sample of dPS/PS which has a 36 nm thick dPS layer next to substrate and 48 nm thick PS layer next to air surface. XR measurement gives complementary information to NR. The overall thickness and the roughness at the substrate interface and at air interface can be extracted from the XR prior to NR. These values are usually used in NR data analysis to minimize the number of fit parameters.

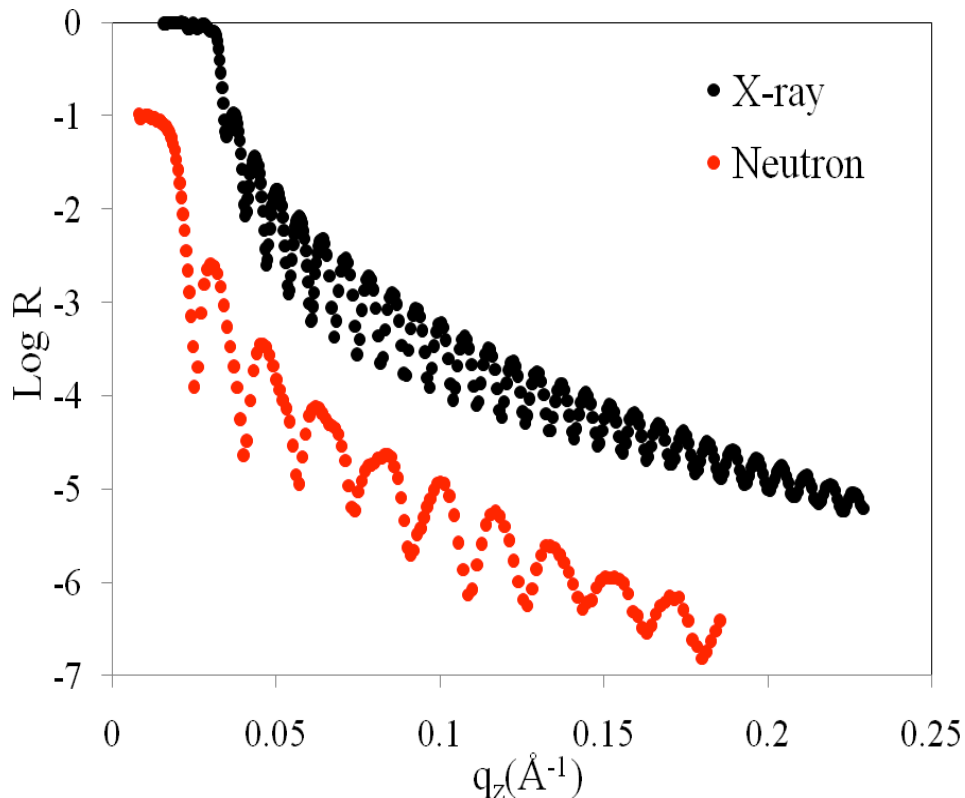


Figure 3. X-ray reflectivity (XR) and neutron reflectivity (NR) curves as a function of perpendicular wave vector, q_z , for an as-cast dPS/PS bilayer film which has 38 nm thick

bottom dPS layer and 46 nm thick top PS layer. NR data has been shifted an order of magnitude for clarity.

Question: From raw reflectivity data, the thickness of the film can be obtained at large q values using the following equation:

$$d = 2\pi / \Delta q$$

where d is the thickness of the film and Δq is the spacing between two successive minima or maxima. These two curves belong to the same sample. Why is the spacing between the successive minima is different?

After the data analysis for the as-cast films, the sample will be annealed at 135 C in a vacuum oven for a period of time and NR will be measured. This process will be repeated 3 or 4 times to collect NR data as a function of annealing time. The change in the NR curve as a function of annealing time is demonstrated in Figure 4 for the same dPS/PS bilayer sample. It is clear that the reflectivity curve changes dramatically after annealing the sample for 30 minutes but then the additional annealing causes only minor changes. During the annealing, polymer chains are mobile and they move across the interface which increases the interfacial width between the polymer films.

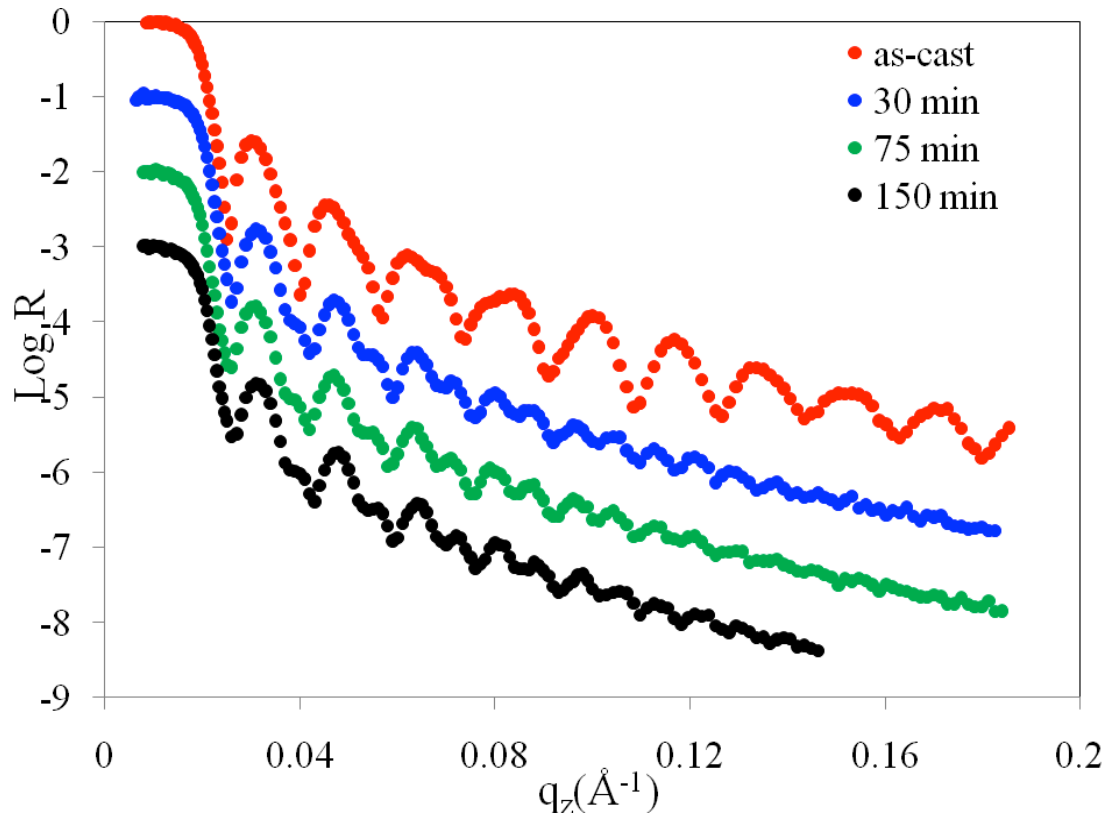


Figure 4. NR as a function of q_z for the same bilayer sample in Figure 3 for as-cast, after 30, 75, and 150 min annealing at 120 C.

Interfacial width is the main parameter we are trying to obtain in these experiments. We will be following the change in interfacial width as a function of time to be able to obtain the diffusion coefficients and verify the time scaling factors.

References

1. Klein, J.; Briscoe, B. J. *Proc. R. Soc. London* **1979**, *A365*, 53.
2. Kramer, E. J.; Green, P. F.; Palmstrom, C. J. *Polymer* **1984**, *25*, 473.
3. Whitlow, S. J.; Wool, R. P. *Macromolecules* **1989**, *22*, 2648.
4. de Gennes, P.-G. *J. Chem. Phys.* **1980**, *72*, 4756.

5. Edwards, S. F. ; Doi, M. *The Theory of Polymer Dynamics* ; Oxford University Press : Oxford, 1988.
6. Graessly, W. W. *Adv. Polym. Sci.* **1974**, *1*, 16.
7. de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
8. Prager, S. ; Tirrell, M. V. *J. Chem. Phys.* **1981**, *75*, 5194.
9. Kim, Y. H. ; Wool, R. P. *Macromolecules* **1983**, *16*, 1115.
10. Karim, A. ; Mansour, A. ; Felcher, G. P. ; Russell, T. P. *Phys. Rev. B* **1990**, *42*, 6846.
11. Stamm, M. ; Huttenbach, S. ; Reiter, G. ; Springer, T. *Europhys. Lett.* **1991**, *14*, 451.
12. Karim, A. ; Felcher, G. P. ; Russell, T. P. *Macromolecules* **1994**, *27*, 6973.
13. Kunz, K. ; Stamm, M. *Macromolecules* **1996**, *29*, 2548.
14. Lin, E. K. ; Wu, W. ; Satija, S. K. *Macromolecules* **1997**, *30*, 7224.
15. Kienzle, P. A.; O'Donovan, K. V.; Ankner, J. F.; Berk, N. F.; Majkrzak, C. F.;
<http://www.ncnr.nist.gov/reflpak>. 2000-2006