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Effects of Film Thickness and Molecular Weight on the Interfacial Dynamics of Atactic Poly(methyl methacrylate)[†]

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We have investigated the surface vibrational dynamics at the polymer–vacuum interface of atactic poly(methyl methacrylate) thin films supported on SiO_x/Si(100) as a function of film thickness and molecular weight. The highly surface-sensitive and nondestructive technique of inelastic helium atom scattering probes the vibrational dynamics at the true polymer–vacuum interface due to the lack of helium atom penetration into the film. For higher molecular weight samples (350 kg/mol), scattering spectra differ between films of thicknesses of fractions of the bulk radius of gyration compared with thicker films due to substrate interactions. A difference in the line shape of the scattering spectra is also present for lower molecular weight samples (60 kg/mol) compared with the thick, higher molecular weight samples. The differences in scattering spectra indicate a reduction of interfacial surface vibrational motion for both the thin, high molecular weight, and low molecular weight films as compared to thick, high molecular weight films. Our experiments demonstrate that dynamics at the interface of polymer thin films are unchanging until the films are thin enough for substrate interactions to influence vibrations at the true interface.

Introduction

Polymer thin films are used in a wide and increasing variety of industrial and technological applications from packaging to microelectronics. The confinement of a polymer in a thin film changes the properties of the polymer. This effect was first noticed in dewetting studies by Reiter, in which films of thicknesses less than the polymer end-to-end distance were found to be less dense and dewet at temperatures less than the bulk value.¹ Because dewetting requires the higher polymer mobilities present above the glass transition temperature, this result indicated a reduction in the glass transition temperature (T_g) of thin polymer films.¹ Ellipsometry measurements were subsequently carried out by Keddie et al. to determine the overall glass transition temperature of supported polystyrene (PS) and poly(methyl methacrylate) (PMMA) films as a function of film thickness and molecular weight.^{2,3} A reduction in the glass transition temperature compared to bulk values was observed for PS films on treated Si(111) and PMMA on evaporated Au. A slight increase in the overall T_g was observed for PMMA films on SiO_x/Si(111) with decreasing film thickness. Little dependence on molecular weight was observed for either system.^{2,3} In the time since these initial papers were published, the properties of thin films have been widely examined, though many questions remain unanswered.

From early investigations of the glass transition temperature in polymer thin films, it was thought that the reductions in the observed glass transition temperature were due to enhanced mobility in the free surface layer of the polymer. A number of experiments have therefore investigated the enhanced mobility of the free surface layer of thin films. Specific properties that

have been examined include diffusion, relaxation, and mean-square displacement of the interfacial layer. Embedding of nanoparticles in films,^{4,5} tracer or probe diffusion,^{6–8} and numerous other methods have been used to investigate diffusion in polymer films. Relaxation and surface layer density have been explored through fluorescence quenching of labeled and inherently fluorescent supported polymer thin films.^{9,10} The rate of change of the fluorescence intensity has a discontinuity as the films are cooled past T_g . The location of the transition depends on the position of the fluorescent layer in the film. The highest temperature transitions occur at the substrate layer, the lowest at the free surface layer, with a smooth gradient of transition temperatures at locations in between. These results suggest that mobility, as measured by relaxation, is greatest at the free surface layer.⁹ Relaxation of defects created by ion scattering and nanoparticle embedding has also been explored.^{11,12} Neutron scattering studies have measured the mean-square displacement of polymer films.¹³ In these studies, researchers find that the mean-square displacement increases linearly with temperature until approximately 1.2 T_g (bulk), at which point the dependence on temperature becomes nonlinear. In thin films, the mean-square displacement is suppressed compared to the bulk for all temperatures, and becomes increasingly suppressed as the film thickness decreases.¹³ Scanning probe microscopy (SPM) has been used to determine local elastic properties of polymer thin films.^{14–16}

Multiple types of polymer motion that are relevant to understanding thin film dynamics have been accessed through these techniques. Bulk motion of polymer chains is explored in dewetting studies. Exploration of segmental motion has been of great interest and is the most widely studied area in the literature due to the direct correlation between segmental motion and the glass transition.¹⁷ In contrast, neutron scattering has been used to probe local motion in the overall polymer film as well as diffusion between interfaces, etc.^{13,18}

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One important aspect of mobility that has not yet been explored is the local motion of the polymer at the topmost molecular layer of the polymer–vacuum interface. Studies of the interface should provide additional information on the origin of the observed increased mobility of polymer thin films. The technique used in this study, low energy helium atom scattering (HAS), is a highly surface-sensitive and nondestructive probe of the surface vibrational dynamics of the topmost molecular layer of polymer thin films. Molecular beams have been used widely in the past to study the effects of confinement in the simplest molecular systems, such as the transition from monolayer to bulk behavior of rare gas atoms adsorbed on single crystal substrates.^{19,20}

In comparison to previous techniques used to investigate polymer thin films, helium atom scattering is most similar to neutron scattering.^{21–23} Similar types of information can be obtained from the two techniques, though HAS is more surface-sensitive because helium atoms scatter from the electron density approximately 3 Å from the film surface. The two techniques couple to vibrational modes with different cross sections. With a helium atom beam (10–60 meV), we probe low energy, sagittally polarized surface vibrations of molecular groups that are present at the topmost surface layer with microsecond resolution. HAS has traditionally been used to study the structure and dynamics of single crystals and simple adsorbates on single crystals. Recent experiments have expanded the range of helium atom scattering to include more complex organic mono- and multilayers such as self-assembled monolayers,^{24–28} alkanes,^{29–31} carboxylic acids,³² liquids,³³ and fatty acids.³⁴ Polymer thin films are significantly more complicated than simple adsorbate–substrate systems and SAMs, but we have reported previously that we are able to obtain information about these systems from analysis of inelastic scattering spectra.^{35,36} The broad inelastic scattering spectra obtained for polymer thin films are more similar, in some respects, to heavier rare gas scattering (Ar, Kr, Xe) from complex materials in which broad direct inelastic and thermal desorption peaks are analyzed rather than single and few phonon processes.^{33,37}

In this paper, we have compared the low energy, neutral helium atom scattering spectra from PMMA thin films on SiO_x/Si as a function of film thickness and molecular weight. We are interested in identifying the threshold thickness at which substrate interactions begin to influence interfacial dynamics. We have also probed the vibrational dynamics as a function of molecular weight. Our results provide a different but complementary picture of dynamics at the polymer interface, which should aid in the understanding of the origins of enhanced mobility at the polymer interface.

Experimental Section

Experiments were conducted in a high angle- and energy-resolution helium atom scattering apparatus, which has been described in detail elsewhere.^{38,39} Briefly, it consists of a cryogenically cooled supersonic helium beam source, an ultra-high vacuum (UHV) scattering chamber equipped with surface characterization tools, a precollision chopper (chopper to sample distance of 0.547 m), and a rotating, long flight path quadrupole mass spectrometer detector (sample to ionizer distance of 1.004 m). The rotating detector and independent crystal angular drive allow for the incident and final angles to be independently varied. The angular collimation yields a resolution of 0.22°, and the $\Delta v/v$ for most beam energies used is less than 1%. This design allows for precise measurements of scattering angles and energy exchange with the surface by acquisition of the time-

TABLE 1: Parameters Used for Polymer Experiments^a

| M_w (kg/mol) | h (nm) | h (R_g) |
|----------------|----------|---------------|
| 350 | 88 | 5.9 |
| 350 | 85 | 5.7 |
| 350 | 9.7 | 0.64 |
| 350 | 5.6 | 0.37 |
| 350 | 5.2 | 0.35 |
| 60.0 | 58 | 9.3 |
| 60.0 | 6.0 | 0.97 |
| 60.0 | 5.0 | 0.81 |
| 60.0 | 2.0 | 0.33 |

^a M_w is the molecular weight, h is the film thickness, and R_g is the bulk radius of gyration. Thicknesses are given in both units of nanometers and the bulk radius of gyration.

of-flight (TOF) of scattered helium atoms. A cross-correlation time-of-flight technique with a pseudorandom chopping sequence is used to maximize the signal-to-noise ratio.^{40,41} Cross-correlation chopping allows for a duty cycle (percent the wheel is open versus closed) of up to 50%.⁴⁰ In contrast, regular TOF single-slot chopping has a 1% duty cycle. The raw signal is deconvoluted using the matrix method discussed in ref 42. Due to the fact that signal is collected in multiple channels, cross-correlation can be used advantageously to study certain types of spectra, such as the broad features noted in this work.⁴³

High (350 kg/mol, $M_w/M_n = 1.15$, $R_g(\text{bulk}) = 15$ nm) and low (60 kg/mol, $M_w/M_n = 1.10$, $R_g(\text{bulk}) = 6.2$ nm) molecular weight atactic PMMA samples (PolySciences) were spin coated on the native oxide layer of Si(100) to make samples of several thicknesses. Parameters for each of the samples can be found in Table 1. Please note that we have provided the relative thicknesses in terms of the bulk radius of gyration, $R_g(\text{bulk})$. This scaling is common and is generally useful for comparing polymers of different molecular weights. The scaling cannot, however, be exactly correlated with actual film thickness because the chain conformation of polymers, and hence their radius of gyration, changes in a thin film relative to the bulk. The SiO_x/Si(100) substrates were cleaned by sequential sonication in toluene, acetone, and methanol. The thin films were annealed under argon for 120 min at 413 K. The sample thickness was measured *ex situ* by ellipsometry before and after the scattering experiment to quantify any changes in the thickness of the films over the course of the experiment. Optical microscopy and atomic force microscopy were used *ex situ* to further assess the smoothness of the film. PMMA samples were inserted in the scattering chamber (base pressure of 10^{-9} – 10^{-10} torr) and annealed at the beginning of each experimental run at 440 K for 30 min. The samples were subsequently cooled at 5 K/min to the lowest temperature used and spectra taken for the various temperatures. Changes to the cooling rate from 2 K/min to approximately 35 K/min did not affect the results. Because of the low scattering signal from the polymers, highly ordered pyrolytic graphite (HOPG) was used for precise beam energy and position calibration. From thermogravimetric analysis, the PMMA sample began to degrade at temperatures above approximately 550 K in a nitrogen atmosphere, which agrees well with the literature value of 543 K.⁴⁴ Scattering experiments were therefore not performed at temperatures above 490 K. Slow relaxation of the polymer films occurs over time, and as a result, care is taken to minimize the time samples are kept in the vacuum environment. Because of the large beam spot size on the sample and the fact that data are taken in the multiphonon regime (as discussed below), slight changes to the polymer morphology should not affect our results. We have seen that multiple spectra collected for a single sample are identical within

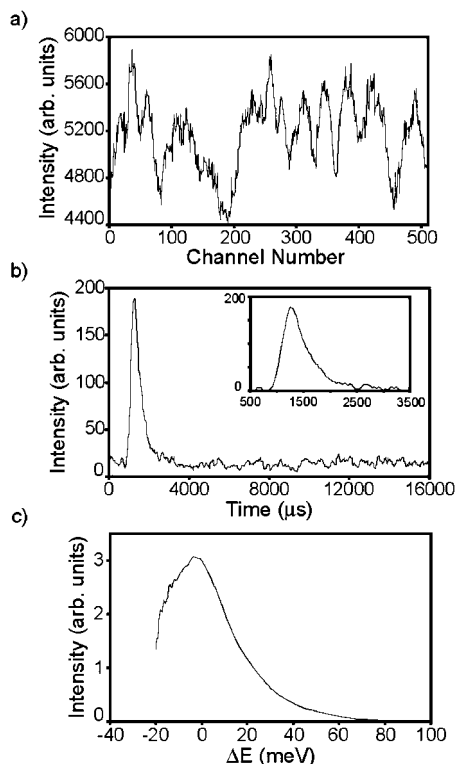


Figure 1. (a) Raw data collected using a cross-correlation time-of-flight technique. (b) The deconvoluted spectrum plotted in the time domain. The inset shows the inelastic scattering feature in the time domain with a linear background subtracted. (c) The same spectrum converted to the energy transfer domain. The PMMA sample used for these figures has a molecular weight of 350 kg/mol, a film thickness of 88 nm, and sample temperature of 200 K. The scattering geometry is $\theta_i = \theta_f = 24.68^\circ$.

the noise of the experiment over the time scale that samples are in the vacuum environment.

Results

We have compared the scattering from PMMA samples of different thicknesses and molecular weights in the specular geometry with incident and final angles of 24.68 and 37.68° and beam energies of 29 and 41 meV (7.46 \AA^{-1} with $\Delta K = 2.65 \text{ \AA}^{-1}$ to 8.86 \AA^{-1} with $\Delta K = 3.16 \text{ \AA}^{-1}$). All angles are defined with respect to the surface normal. From experiments performed using nonspecular scattering geometries, we find that the scattering has a subspecular intensity maximum.

Raw signal from the cross-correlation chopping technique and the corresponding deconvolution and conversion to energy are shown in Figure 1 for a high molecular weight sample of 350 kg/mol with a thickness of 88 nm and a beam energy of approximately 30 meV. In Figure 1a, the raw data are shown. Due to cross-correlation chopping, the signal from a single feature is collected in multiple bins. This signal is deconvoluted to give Figure 1b, shown in the time domain. The inset shows the width of the inelastic feature more clearly. A nonlinear transformation is then performed to convert from the time domain to the energy transfer domain (Figure 1c). The broad inelastic feature in energy transfer spans approximately from $\Delta E = E_f - E_i = -20 \text{ meV}$ to $\Delta E = 80 \text{ meV}$. The energy-loss portion of the curve ($\Delta E < 0$) arises from the creation of vibrational excitations in the film due to He collisions, and the energy-gain side ($\Delta E > 0$) arises due to the annihilation of surface vibrations in the film during He collisions. When higher

beam energies are used, the energy-loss side is broadened, but the energy-gain side remains relatively constant.

Scattering spectra from samples of different thicknesses were taken at surface temperatures between 200 and 490 K. The range of surface temperatures was chosen to best compare with neutron scattering studies.¹³ In particular, we wanted to obtain spectra at sufficiently low temperatures and at high enough temperatures to observe the behavior of the films above $1.2 T_g(\text{bulk})$. The maximum intensity of every spectrum taken at a surface temperature of 200 K is set to 1.0, and this scaling factor is then used to scale all spectra taken in that temperature progression. In this way, the difference in intensity decay as well as full-width at half-maximum can be systematically investigated.

I. Thickness Dependence for Scattering from PMMA of Molecular Weight 350 kg/mol. To determine the threshold thickness at which differences in the energy transfer spectra arise for the 350 kg/mol samples, spectra were taken for a variety of different sample thicknesses. As we have reported previously, in the more glancing geometry ($\theta_i = \theta_f = 37.68^\circ$), the spectra are essentially superimposable.³⁵ In the more normal scattering geometry ($\theta_i = \theta_f = 24.68^\circ$), the intensity decay of the peak maximum with surface temperature is the same, while the full-width at half-maximum changes with film thickness (Figure 2). In Figure 2, we have plotted mean scattering spectra obtained by averaging several spectra of different film thicknesses that were essentially superimposable. For the mean spectrum labeled “thick”, we have averaged spectra from samples with thicknesses of 9.7, 85, and 88 nm. The mean spectrum labeled “thin” was calculated using the average of scattering spectra from samples with thicknesses of 5.2 and 5.6 nm. In Figure 2, the change in full-width at half-maximum (fwhm) between the thinnest films compared with the thicker films becomes more pronounced at higher temperatures. We have also plotted the raw data for these five thicknesses and the average and standard deviation at a surface temperature of 490 K (Figure 3). It is clear from this figure that the 9.7 nm spectra have the same line shape as the 85 and 88 nm films, whereas the spectra from the 5.2 and 5.6 nm samples have a smaller fwhm. The average spectra and standard deviation for these thicknesses are also shown in order to emphasize that the difference between the spectra is outside the standard deviation (Figure 3b). In fact, the difference observed between the fwhm of the thin and thick samples lies outside the standard deviation of the averaged curves for all surface temperatures. We additionally compared the spectra in the time domain to verify that the difference observed in the spectra of thin and thick samples is not an artifact of the conversion to the energy transfer domain. That the thickness at which the line shape of the spectra changes is 5.6 nm indicates that the difference in spectra observed arises at fractions of the bulk radius of gyration. As noted in the Experimental Section, the bulk radius of gyration provides a rough means of comparing the thickness of different polymer samples rather than an absolute scaling. For even slightly thicker samples, such as the 9.7 nm film, the spectra are superimposable on spectra of samples several times thicker. (In our first paper on polymer thin films, we noted that the difference in scattering spectra arose at thicknesses of 10.5 nm.³⁵ A wider sampling of sample thicknesses with improved methods and statistics has shown that the actual threshold is lower).

II. Comparison of Scattering from PMMA with Molecular Weights of 350 and 60 kg/mol. For the low molecular weight (60 kg/mol) PMMA films, samples of thicknesses of 2.0, 5.0, 6.0, and 58 nm were used. Overlays of the different

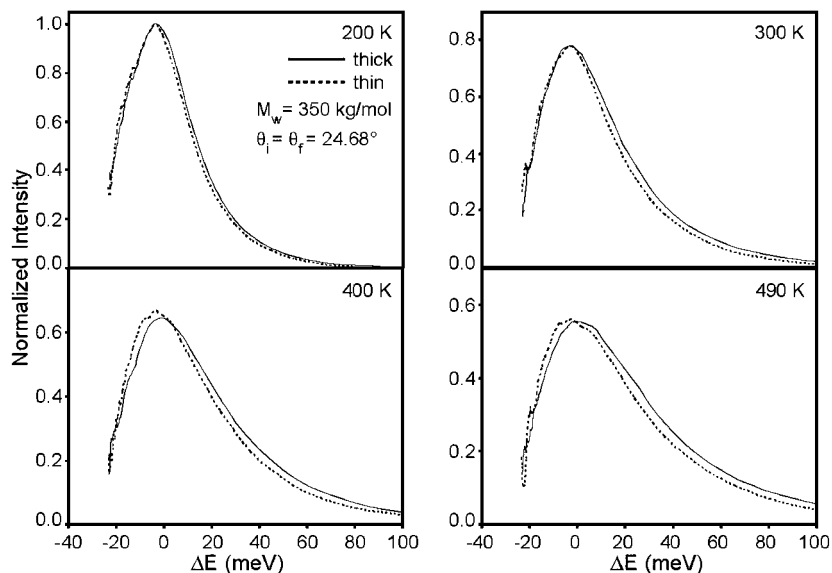


Figure 2. Overlay of averaged scattering spectra for PMMA samples of different thicknesses with a molecular weight of 350 kg/mol, a beam energy of 30 meV, and initial and final angles of 24.68°. The solid line is the average of spectra for sample thicknesses of 9.7, 85, and 88 nm, and the dashed line indicates the average of spectra for thicknesses of 5.2 and 5.6 nm. The intensity of the peak maximum is normalized to 1.0 for the 200 K spectra, and this scaling factor is used to scale the rest of the spectra. Surface temperatures are listed on the plots.

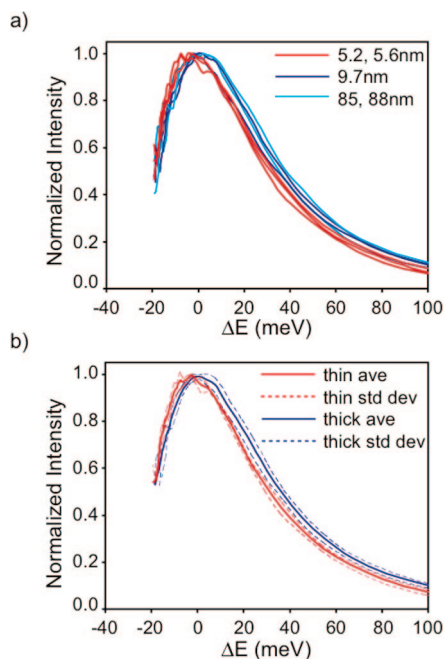


Figure 3. (a) Overlay of scattering spectra from 350 kg/mol PMMA thin films with a surface temperature of 490 K and thicknesses of 5.2 nm (red), 5.6 nm (red), 9.7 nm (blue), 85 nm (light blue), and 88 nm (light blue). The maximum peak intensity is normalized to 1.0. A beam energy of 30 meV and a scattering geometry of $\theta_i = \theta_f = 24.68^\circ$ are used. (b) A plot of the average (—) and standard deviation (---) for samples of thicknesses of 5.2 and 5.6 nm spectra (red) compared to 9.7, 85, and 88 nm (blue). The sample parameters are the same as those used in part a.

sample thicknesses for scattering geometries of $\theta_i = \theta_f = 37.68^\circ$ and $\theta_i = \theta_f = 24.68^\circ$ show that, while some scatter is observed in the spectra, all of the spectra can be superimposed, even the thinnest sample. The 2.0 nm samples are the thinnest samples we can consistently spin coat, but we expect that a difference between the spectra of thick and thin films would arise for even thinner samples in agreement with our result for higher molecular weight films. This will be explored at the end of the Discussion section.

A comparison of the spectra of low molecular weight and thick, high molecular weight samples at $\theta_i = \theta_f = 24.68^\circ$ is shown in Figure 4. In this figure, averaged scattering spectra are shown for the more normal angles as a function of energy transfer. Helium atom collisions with the lower molecular weight samples have a smaller probability of annihilating vibrational excitations and a higher probability of creation events. The shift in the position of the peak maxima between the two samples is not as pronounced as seen for the thin and thick samples of higher molecular weight. The difference observed between the lineshapes of low molecular weight films and thick, high molecular weight films lies outside the standard deviation for all surface temperatures.

Discussion

We observe differences in the scattering spectra between thin and thick high molecular weight (350 kg/mol) PMMA films. We also see a difference between the spectra of low (60 kg/mol) molecular weight films of any thickness compared to thick, high molecular weight samples. The difference observed in each case is exhibited by a lower intensity of the scattering spectra on the energy-gain side ($\Delta E > 0$) and a slightly higher intensity on the energy-loss side ($\Delta E < 0$) for the thin, high molecular weight or low molecular weight films in comparison with thick, high molecular weight films (Figures 2 and 4). The lower intensity on the energy-gain side of the spectrum indicates that there is a lower probability of helium atoms annihilating surface vibrational modes for the thin, high molecular weight and low molecular weight films. The higher intensity on the energy-loss side indicates that there is a higher probability of collisional excitation of vibrational modes for the thin, high molecular weight and low molecular weight films. The difference in probabilities for vibrational excitation stems from a difference in the density of states and from the propensity for excitation in each system. Theory relates the density of states to the intensity and line shape of the multiphonon spectra.⁴⁵ The multiphonon spectra are therefore a direct probe of the surface vibrational dynamics of the topmost interface. As we will argue below, the difference between the line shape of the spectra between the thin and thick high

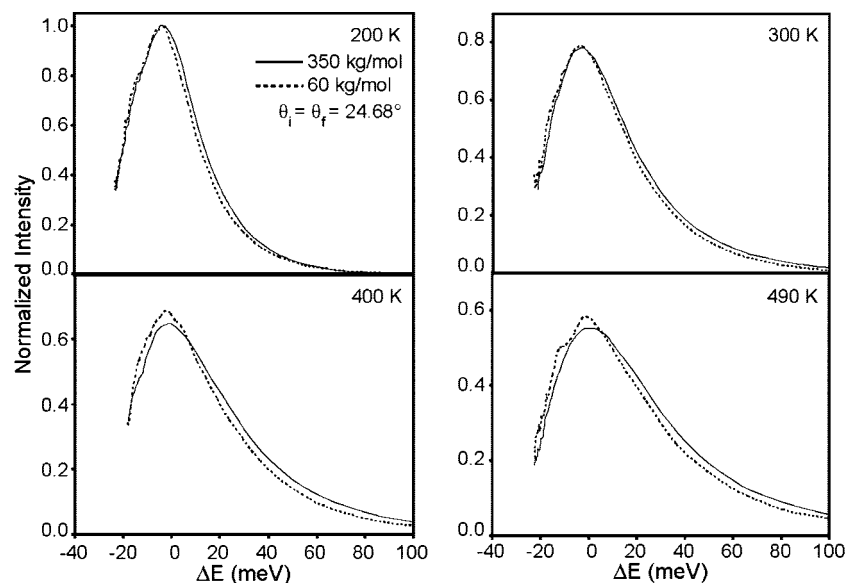


Figure 4. (a) Comparison of averaged scattering spectra for samples of different molecular weights. The solid line is the average of spectra for thicknesses of 9.7–88 nm with a molecular weight of 350 kg/mol, and the dashed line is the average of spectra for thicknesses of 2.0–58 nm with a molecular weight of 60 kg/mol. The parameters used were a beam energy of 30 meV and initial and final angles of 24.68°. Surface temperatures are listed on the plots.

molecular weight films is due to substrate interactions. Our results regarding differences in mobility as a function of molecular weight will be compared to multiple examples from the literature.

Our results for energy transfer to the surface are similar to a previous helium atom scattering study of a fatty acid monolayer.³⁴ Comparison is made to this study because it is one of the few HAS studies of a complex organic film in which scattering is reported only in the multiphonon regime. The maximum amount of energy transferred to the surface and the shape of the energy-loss side of the spectra are approximately the same. Comparison with the approximate thermal energy of $2kT$ on the energy-gain side of the spectrum shows that the fatty acid molecules are able to transfer slightly more energy from the surface to the He atoms than for the polymer thin films.³⁴ This change in elasticity is attributed to differences in the vibrational density of states and the propensity of each surface to transfer energy to the He atoms. In particular, helium atoms may couple more strongly to the topmost molecular groups of an ordered fatty acid monolayer than to the disordered polymer, and the structure of these systems may additionally impact the density of states. Semiclassical scattering theories that relate the density of states to the intensity and line shape of the multiphonon spectra have been used to analyze scattering from a fatty acid monolayer⁴⁶ and we have previously used this theory to model scattering from a variety of polymer thin films.³⁶

The differences we observe in the scattering spectra arise at more normal scattering geometries. As the incident scattering angle approaches the surface normal, the total energy of the incident beam remains constant while the ratio of the perpendicular momentum to the parallel momentum increases. The increase in perpendicular momentum tends to increase overall energy transfer to the system and the likelihood of multiple scattering events. As a result, as the scattering angle approaches a more normal geometry, subtle differences in the density of states and the propensity for surface vibrational excitation are more likely to be observed. That we do not observe changes in the scattering spectra at more glancing scattering angles indicates that a threshold in the perpendicular momentum is needed for changes in the scattering spectra to be observable. Further

discussion and results that show the difference in scattering spectra for a range of scattering geometries have been included in a previous article.³⁵

We have seen a difference in the surface vibrational dynamics of high molecular weight films as a function of film thickness. When polymer thin films are near an attractive surface, multiple points of interaction are created between the polymer and the surface. These interactions serve to inhibit the mobility and segmental motion of the polymer thin films.¹⁷ If the film is sufficiently thin, this decreased mobility should also affect the interfacial dynamics, which is consistent with our results, in that dynamics of the topmost interfacial layer are suppressed in comparison to thicker samples at fractions of $R_g(\text{bulk})$.

Neutron scattering studies also show changes in the overall film dynamics for the thinnest samples of PMMA (1730 kg/mol).¹³ For the bulk polymer, the mean-square displacement increases linearly with temperature until $1.2 T_g(\text{bulk})$ at which point the increase becomes nonlinear with temperature. As the film thickness decreases, the mean-square displacement is suppressed but has the same features as the bulk. At a thickness of 8.0 nm ($0.3 R_g(\text{bulk})$), however, the mean-square displacement increases linearly for all temperatures, though this thickness may not be the threshold value for this behavior. It is intriguing that the change we observe in the scattering spectra also arises at $0.37 R_g(\text{bulk})$.

Our results on the dynamics of the interface help to further inform studies of the glass transition temperature. In particular, we observe a relatively sharp transition in the vibrational dynamics at very small distances from the substrate. The change in the line shape of the scattering spectra arises at $0.37 R_g(\text{bulk})$; by $0.64 R_g(\text{bulk})$, the interfacial vibrational dynamics are the same as that for films several $R_g(\text{bulk})$ thick. In comparison, studies of the overall glass transition temperature of thin films on noninteracting substrates show a decrease in the glass transition temperature starting when the films are several $R_g(\text{bulk})$ thick. The overall glass transition gradually decreases as the film thickness decreases. Studies of the glass transition temperature in the free surface layer also show reductions of T_g starting at thicknesses of several times $R_g(\text{bulk})$. We observe that substrate interactions affect the interface on length scales

much shorter than the effect on overall and free surface layer T_g . Our results suggest that the gradual changes observed in the glass transition temperature and segmental dynamics of the free surface layer and the overall films starting at several times the bulk radius of gyration of the film are a consequence of the interface comprising a greater percentage of the total film thickness rather than a change to the interfacial dynamics. These results may also support early hypotheses of a liquidlike layer at the polymer–vacuum interface^{3–5,47} because until the films are sufficiently thin, the interfacial molecular dynamics are similar. The hypothesis of a liquidlike layer was used to suggest why thin films had enhanced surface mobility that would result in a reduced thin film T_g compared with the bulk.^{3–5,47}

Another aspect of polymer thin films that we explored was the dependence of the scattering spectra on molecular weight. Our results indicate that the propensity for annihilation events at the topmost interfacial layer of the lower molecular weight films are reduced compared to the higher molecular weight films. The difference between the inelastic scattering curves of high and low molecular weight films is less pronounced than the effect we have observed between thin and thick films at the higher molecular weight.

Precedent for differences arising as a function of molecular weight exists in studies of the glass transition of supported and unsupported polymer thin films. For supported PS thin films studied by fluorescence, only a small dependence of the difference in thin film versus bulk glass transitions ($T_g - T_g(\text{bulk})$) on the molecular weight (5.0–3000 kg/mol) is observed when measurements are taken as the sample is cooled.⁴⁸ Upon heating the sample, however, a dependence on the molecular weight was observed using both ellipsometry (31.6–1571 kg/mol) and X-ray reflectivity (303 and 2890 kg/mol).^{49,50} Extensive studies on the molecular weight dependence of the glass transition temperature in unsupported PMMA and polystyrene (PS) thin films have been performed.^{51–53} Two different regimes are found, a low molecular weight regime in which the reduction in the glass transition is not dependent on molecular weight and a high molecular weight regime (approximately 500–1300 kg/mol) in which a dependence is observed. Results for unsupported PMMA films are the same as for the unsupported PS films except that the magnitude of the reduction is a factor of 3 less than that for unsupported PS films due to stronger inter- and intramolecular interactions in PMMA caused by the polar methyl ester side group.⁵² In summary, the current literature shows that the dependence of segmental motion on molecular weight is a function of substrate effects, thermal history, and the exact range of molecular weights tested. The literature shows that precedence exists for a dependence of segmental motion on molecular weight. Our results that are sensitive to local motion also exhibit a molecular weight dependence.

For the low molecular weight samples, we did not observe a difference in the interfacial dynamics between films of various thicknesses down to $0.33 R_g(\text{bulk})$. This is the thinnest film we could coat consistently. We expect that, in the thin film limit, differences should arise in the scattering spectra. Our results are consistent with the literature, which suggests that the bulk radius of gyration cannot be used to normalize the critical thickness observed for a film of a given molecular weight to determine the critical thickness for a sample of a different molecular weight. In a study of the overall glass transition of free-standing PS thin films as a function of molecular weight, the square root of the molecular weight is plotted versus threshold film thickness, below which the observed glass

transition is less than the bulk glass transition.⁵³ The resultant plot is nonlinear, indicating that the threshold thickness is not linearly dependent on the bulk radius of gyration.⁵³ It is therefore not unexpected that a dependence of the scattering on thickness for lower molecular weight samples is not observed over the range of thicknesses used.

Conclusions

In summary, we have investigated the surface vibrational dynamics at the interface of PMMA thin films on $\text{SiO}_2/\text{Si}(100)$ as a function of film thickness and molecular weight using inelastic helium atom scattering. Due to the lack of neutral helium atom penetration into the film, the measurement performed herein is highly and unusually surface-sensitive, in contrast with glancing X-ray and neutron scattering techniques, and provides detailed information about dynamics at the polymer–vacuum interface. Differences in the scattering spectra are directly correlated to changes in interfacial vibrational dynamics of the polymer thin films. For high molecular weight (350 kg/mol) films, we have found no difference in the scattering spectra as a function of film thickness down to thicknesses of $0.37 R_g(\text{bulk})$. At this point, a difference arises in the full-width at half-maximum of the spectra of the thin films compared to the thick films, indicating changes in the surface vibrational dynamics due to substrate interactions. We have additionally observed a difference between the scattering spectra of high and low (60 kg/mol) molecular weight films, where the propensity for annihilation events of the surface vibrational dynamics of the low molecular weight films are reduced compared to higher molecular weight films.

Our results have significant consequences for studies of mobility in confined polymer films. We have found that the vibrational dynamics at the interface are constant until the films become thin enough for substrate effects to inhibit the interfacial mobility. This result provides new insight into previous studies in the literature in which gradual changes are observed in the mobility of the free surface layer or overall film as a function of film thickness. Our results suggest that the gradual changes observed in the mobility of the free surface layer and the overall films starting at several times the bulk radius of gyration of the film are a consequence of the interface comprising a greater percentage of the total film thickness rather than any change to the interfacial dynamics. Differences in the dynamics of the topmost interface occur only when the films become thin enough for substrate interactions to influence interfacial mobility.

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