Brillouin Light Scattering Studies of the Mechanical Properties of Polystyrene/Polyisoprene Multilayered Thin Films

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SYNOPSIS

We have used Brillouin light scattering (BLS) to investigate the mechanical properties of thin polystyrene (PS) and polyisoprene (PI) films incorporated in a multilayer geometry consisting of alternating layers of the two polymers. All samples had a total thickness h $\sim$ 1600 Å, and consisted of between 2 and 10 individual polymer films; individual layer thicknesses were as small as 160 Å. Ellipsometry was used to determine the thickness of the PS and PI layers. The velocities of several high-frequency film-guided mechanical waves were measured using BLS and the results are compared with values calculated using an effective medium approach. The effective elastic constants of the multilayered films were obtained from those determined for thick films of PS and PI. Remarkable agreement was obtained between the measured and calculated velocities even for samples in which the individual layer thicknesses were much less than the unperturbed size of the polymer molecules. These results suggest that the mechanical properties of polymers change very little even when the molecules are forced into highly confined geometries. © 1996 John Wiley & Sons, Inc.

Keywords: polymer multilayered films • mechanical properties

INTRODUCTION

Thin polymer films are very important in technological applications ranging from adhesion to optical coatings. For many applications it is important to know the mechanical properties of these thin films. As films are made thinner such samples may exhibit qualitatively different behavior than bulk polymers. An important length scale for polymers is the end-to-end distance of the polymer molecule $R_{EE} \sim 2R_g$, where R_g is the radius of gyration of the molecule. While polymer films with thicknesses $h > R_{EE}$ are expected to have properties very similar to bulk polymers, chain confinement may affect the physical properties of films with $h < R_{EE}$. Reiter[1] has used X-ray reflectivity measurements to infer that such films have a lower density than the bulk value. Low-frequency viscoelastic properties of confined polymer melts[2] studied using a surface forces apparatus have shown a longitudinal modulus ratio which was larger than the bulk value for films with thicknesses as large as $5R_g$.

Recent measurements of the glass transition temperature, T_g, in thin polymer films have shown deviations of T_g from the bulk value.[3-7] Keddie et al.[3] showed that polymer molecules with R_{EE} values that differed by a factor of 5 exhibited quantitatively similar T_g reductions with decreasing film thickness, suggesting that chain confinement is not the primary cause for the reductions in T_g. Rather, for very thin films, the properties of the interfaces dominate the measured material properties. A striking example of the effect of the substrate was observed in T_g measurements of thin films of poly(methyl methacrylate) (PMMA). With decreasing film thickness, T_g was observed to increase for PMMA on Si(111) with the native oxide layer and to decrease for PMMA films on Au.[4] Qualitatively different behavior has

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been observed for PS films on Si substrates with different surface preparations.[3,5] The effect of the free surface has been isolated and studied in Brillouin light scattering (BLS) studies of freely standing PS films.[6] Competition between the effects of the free surface and that of the substrate are responsible for the variation in the reported behavior of the glass transition temperature for thin supported polymer films.

Another clear example of the effect of the substrate is observed in BLS measurements of supported films, for which the long-wavelength sound velocities for the film–substrate combination are determined primarily by the mechanical properties of the substrate for film thicknesses much less than the penetration depth of the acoustic waves $\delta \sim 3000$ Å.[8] Since supported films have two different film interfaces, film–air and film–substrate, each of which could have opposite effects on the measured properties, very thin supported films are not ideal systems for studying the effects of molecular confinement on polymer properties.

An alternate method for measuring the properties of very thin films is to stack many thin films to form a multilayer structure. An important distinction between multilayer samples with very thin individual layers and very thin single films is that in the multilayer samples the total film thickness can be made large enough so that substrate and/or free surface effects do not dominate the mechanical or thermal behavior. An additional advantage of this sample configuration is that, for a film consisting of many layers, most of the individual layers have only one type of interface.

In this article we describe BLS measurements of film-guided acoustic waves in multilayered films consisting of alternating layers of polystyrene (PS) and polyisoprene (PI). By using multilayer samples consisting of a large number of very thin polymer layers we are able to infer the mechanical properties of individual polymer layers with thicknesses as small as $h \simeq 160$ Å. Such layers are much thinner than the R_{EE} value of the polymer molecules studied. By varying the individual layer thicknesses in different multilayered films, we are able to compare the mechanical properties of highly confined polymer molecules to those of thick ($h > R_{EE}$) films.

EXPERIMENT

For multilayered films consisting of alternating layers of two polymers, the mechanical properties of the individual layers can be determined reliably only if there is sufficient contrast between the mechanical properties of the two polymers. In general this can be accomplished by using one polymer which is a glass and another polymer which is a rubber at the measurement temperature. The polymer samples[9] used in these studies were polystyrene (PS: $\bar{M}_w = 767,000$, $\bar{M}_w/\bar{M}_n = 1.11$) and polyisoprene (PI: $\bar{M}_w = 414,000$, $\bar{M}_w/\bar{M}_n = 1.06$). At room temperature PS is glassy ($T_g \simeq 100°C$), and PI is rubbery ($T_g \simeq -70°C$). The $\bar{M}_w$ values correspond to R_{EE} values of 610 and 500 Å, respectively, for the PS and PI molecules. Solutions of PS in toluene, and PI in heptane, were prepared with polymer concentrations ranging from 0.45% to 1.7%. Polymer films were made using a spincoating technique. A few drops of PS solution were first spun onto a cleaned glass slide to make a PS film. A PI film was then spincoated directly on top of the existing PS film. Since heptane is not a solvent for PS, it was not expected to affect the PS film. Ellipsometry measurements of the PS film thickness before and after rinsing with heptane showed small differences that were similar to those observed in comparisons of different areas of the same sample. The above procedure resulted in the formation of a PS/PI bilayer film which was then cut, and floated onto the surface of deionized water. A piece of the bilayer film was transferred to a Si(001) wafer and then allowed to dry. During this drying process some small cracks were observed to form, but most of the film surface remained visually free of defects. This water transfer procedure was iterated to create the desired multilayered Si/(PS/PI)^N film, which consisted of the Si(001) substrate covered by N (PS/PI) bilayers. For samples with the alternate structure, Si/(PI/PS)^N, a slightly different procedure was required. In this case a PI layer was spun directly onto a Si(001) wafer. PS/PI bilayers were then successively floated onto the sample as desired, followed by water transfer of a single PS layer to complete the multilayer sample. To ensure that all individual layers of each polymer had the same thickness within a particular multilayer sample, each multilayer was prepared using pieces from a single bilayer film. In addition, only the portion of the film near the center of the glass slide was used to make multilayer samples. This was done to avoid the regions near the edge of the glass slide which have large variations in film thickness.

For the present study a series of films with equal amounts of PS and PI were prepared. The total thickness of each of these films, consisting of between 1 to 5 bilayers or 2 to 10 individual polymer layers, was $h \simeq 1600$ Å. The individual layer thicknesses ranged from 800 Å for the two layer films

down to 160 Å for the 10 layer films. Once prepared, the multilayer samples were placed in a room-temperature evacuated chamber for several hours and then stored in an inert atmosphere shielded from light.

Ellipsometric studies of the multilayer samples were performed using an Exacta 2000 Faraday modulated fast-nulling ellipsometer from Waterloo Digital Electronics. The angle of incidence, θ_i, was 60°, and the wavelength of light was λ = 6328 Å. The area of the light spot on the sample was $\sim$ 3 mm^2, and it was possible to find regions of this size that did not contain cracks or other visible defects on all of the multilayer samples. The ellipsometric angles P (polarizer) and A (analyzer) were measured directly to within ±0.003°. To use ellipsometry results to calculate the individual layer thicknesses in multilayered films the refractive indices, n_{PS} and n_{PI}, of the constituent polymers must be known for λ = 6328 Å. To measure n_{PS} and n_{PI} a series of PS and PI films with 250 Å $< h <$ 2000 Å was prepared. The ellipsometric angles P and A were measured for each film thickness, and the results were compared with values calculated using input values of the refractive indices. The values n_{PS} and n_{PI} were then varied until good agreement was obtained for the P and A values for all film thicknesses. The refractive index values which gave the best fit to the ellipsometry data were n_{PS} = 1.59 ± 0.01 and n_{PI} = 1.516 ± 0.005.

Brillouin light scattering (BLS) is a powerful, nondestructive technique for the study of the high-frequency elastic properties of thin films. For supported films the mechanical boundary conditions at the free and supported surfaces give rise to a series of film-guided acoustic phonons called Rayleigh and Sezawa modes.[8] These modes are of mixed polarization, i.e., they have both longitudinal and transverse components. The film-guided modes are dispersive with a phonon velocity that varies with the product of the phonon wavevector and the film thickness $Q_{\parallel}h$. For isotropic media only two elastic constants, c_{11} and c_{44}, are needed to describe the set of velocity dispersion curves that can be compared with experimental data. For materials with hexagonal symmetry (such as films with properties that vary in the direction normal to the film) four independent elastic constants (c_{11}, c_{13}, c_{33}, and c_{44}) are required.

BLS studies were carried out using a 3 × (1 + 1), high-contrast, tandem Fabry–Perot interferometer. Laser light of wavelength λ = 5145 Å was focused onto the sample using angle of incidence θ_i values of 40°, 50°, and 60°. The 180° backscattered light was collected using the same focusing lens so that the phonon wavevector parallel to the film surface is given by $Q_{\parallel} = \dfrac{4\pi}{\lambda} \sin \theta_i$. The measured frequency shift f in the BLS experiment determines the phonon velocity v through the relation $v = 2\pi f / Q_{\parallel}$. The Si(001) substrate absorbs some of the incident laser radiation, which results in sample heating ($\simeq$ 16°C/100 mW).[10] Preliminary experiments showed that $\sim$ 100 mW of laser power incident on a thin film containing PI could damage the sample. To avoid this problem a neutral density filter (attenuation by a factor of 10) was used to limit the laser power incident on the sample to be <10 mW. The area of the focused light spot on the sample in the BLS experiments was $\sim$ 30 μm^2. This spot was always placed within the larger sample area that was measured using ellipsometry. For all of the BLS studies the free spectral range of the interferometer was 16 GHz. Frequencies of the film guided modes were determined to within ±0.1 GHz.

RESULTS AND DISCUSSION

For a proper analysis of the BLS data it is first necessary to determine the thicknesses of the individual polymer layers in each of the multilayer samples. Since each sample is constructed by stacking pieces of a single bilayer film, there are only two unknown parameters to be determined: h_{PS}, the thickness of the PS layers and h_{PI}, the thickness of the PI layers. The total film thickness is $h_{total} = N(h_{PS} + h_{PI})$, where N is the number of bilayers in the multilayered film. The actual values of h_{PS} and h_{PI} were determined by detailed comparison of the ellipsometry data to results calculated for the multilayer geometry using the matrix method of Hayfield and White.[11] The individual layer thicknesses were determined to within ±3 Å, which results in a maximum uncertainty (for the maximum number of individual layers of 10) in h_{total} of ±30 Å. This produces a maximum uncertainty in the $Q_{\parallel}h$ values of about 2%. Table I gives the individual layer thicknesses h_{PS} and h_{PI} as determined using ellipsometry for the 10 samples used in this study. The data in Table I show that for the Si/(PI/PS) sample, as well as the 6- and 10-layer samples, the thicknesses of the PS and PI constituent layers are equal to within a few angstroms. These films have identical compositions but different layer thicknesses and numbers. Comparisons between such samples allow us to isolate and study the effects of chain confinement on the mechanical properties of the polymers.

To compare the mode velocities measured for the multilayer samples to calculated values, the elastic constants of the two constituent materials must be known. The elastic constants of PS have been determined for annealed bulk samples by BLS measurements of the longitudinal and transverse phonons:[12] c_{11} = 5.36 GPa and c_{44} = 1.30 GPa. We have determined the elastic constants for thick, unannealed PS films ($h \gg R_{EE}$) by fitting the measured velocities of film-guided modes to calculated results.[13] The data were described very well by a set of two elastic constants, c_{11} = 5.7 GPa and c_{44} = 1.39 GPa, differing only slightly ($\sim$ 10%) from those obtained from the bulk measurements of Lindsay et al.[12] It is surprising that a very good fit was obtained to the data for the spincoated, unannealed PS films using only two elastic constants which corresponds to isotropic symmetry. We investigated this result further by measuring additional films with thicknesses as small as 580 Å. By including this additional data we obtain a larger range of $Q_{\parallel}h$ that enabled us to fit all of the data to a model which allows for anisotropy along the film normal direction (hexagonal symmetry with the c-axis along the film normal). In this model the mechanical properties of the films are described by four elastic constants instead of two. In the fit of the enlarged data set we obtain c_{11} = 5.49 GPa, c_{13} = 2.82 GPa, c_{33} = 5.64 GPa, and c_{44} = 1.38 GPa. These values obtained for hexagonal symmetry satisfy very closely the criteria for isotropic symmetry: $c_{11} = c_{33}$ and $c_{12} = c_{13} = c_{11} - 2c_{44}$. Fitting the enlarged data set to a model with isotropic symmetry we obtain: c_{11} = 5.54 GPa and c_{44} = 1.38 GPa. The velocity dispersion data for the PS films are shown in Figure 1, together with curves calculated using the best-fit isotropic elastic con-
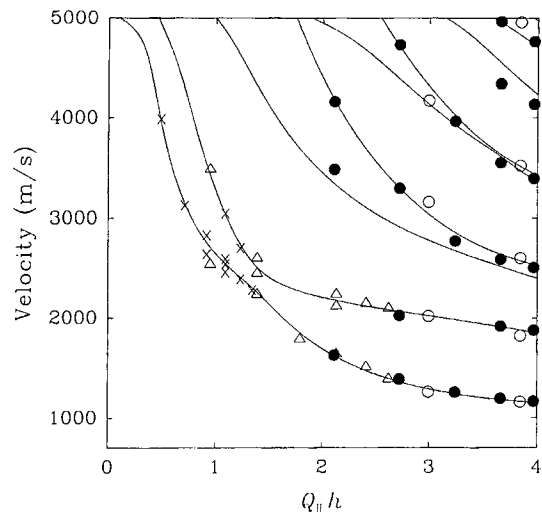

Figure 1. Velocity dispersion curves for PS. The symbols represent velocities of film-guided modes measured using BLS for four different film thicknesses: ($\times$) h = 580 Å; ($\triangle$) h = 1140 Å; ($\bullet$) h = 1730 Å;[13] ($\bigcirc$) h = 2450 Å.[13] The solid curves were calculated using the best fit elastic constants listed in Table II.

stants. Based on the fitted results, we estimate that the anisotropy in the mechanical properties along the film normal direction is small, corresponding to differences of less than 10% in the in-plane and out-of-plane elastic constant values.

We performed BLS measurements of the bulk longitudinal phonon in PI to obtain a value for the longitudinal sound velocity v_l = 2088 m/s. This value, from which the elastic constant c_{11} can be calculated, agrees well with previously reported values.[14] Similar measurements involving the transverse phonon in PI have not yet been reported. In

Table I. Individual PI and PS Layer Thicknesses for Each of the Multilayer Samples as Determined by the Comparison of Ellipsometry Measurements to Calculated Values

Sample Configuration	Thickness of PI Layer, h_{PI} (Å)	Thickness of PS Layer, h_{PS} (Å)	Total Film Thickness (Å)
Si/(PS/PI)	795	733	1528
Si/(PI/PS)	767	768	1535
Si/(PS/PI)^2	428	367	1590
Si/(PI/PS)^2	363	410	1546
Si/(PS/PI)^3	304	295	1797
Si/(PI/PS)^3	290	290	1740
Si/(PS/PI)^4	200	185	1540
Si/(PI/PS)^4	244	188	1728
Si/(PS/PI)^5	157	157	1570
Si/(PI/PS)^5	160	160	1600

Individual layer thicknesses are accurate to within $\sim$ ±3 Å.

addition, there are no reported BLS measurements of film-guided phonons in PI. To determine the high-frequency elastic constant c_{44} for PI we used BLS to measure the velocities of a number of film-guided modes for a single PI film. For the PI film $h = 1570$ Å $\gg R_{EE}$. By performing BLS measurements on this film at angles of incidence θ_i of 10°, 15°, 20°, 25°, 30°, and 45°, we were able to observe film-guided modes in the range $0.7 < Q_{\parallel}h < 2.8$. Because of the limited amount of data, the fit to the data is only well behaved for isotropic symmetry. Because the unannealed PS films, which are in the glassy state, have isotropic mechanical properties, it is reasonable to assume that the PI film which is well above its glass transition temperature ($T_g \simeq -70°C$) is also isotropic. Using the value of c_{11} determined from the measurements of the bulk longitudinal phonon in PI we varied c_{44} to obtain reasonable agreement between the measured and calculated film-guided mode velocities. The best-fit elastic constant values for PI are given in Table II. To the best of our knowledge this is the first time BLS has been used to determine c_{11} and c_{44} for PI.

In Figure 2 we show the calculated velocity dispersion curves for PI (solid line) using the elastic constants determined for thick ($h \gg R_{EE}$) films, which are listed in Table II. The symbols correspond to the measured velocities of film-guided modes for the 1570 Å thick PI film and the solid curve is a fit to these data points. The lowest velocity (Rayleigh) mode, which is primarily transverse, was not observed. The transverse components of the observed modes, however, allow us to determine c_{44}. From the data in Table II it is evident that, although PI is rubbery and PS is glassy at room temperature, the value of the high-frequency elastic constants are of the same order $[(c_{11,PS} - c_{11,PI})/\frac{1}{2}(c_{11,PS} + c_{11,PI}) = 35\%$ and $(c_{44,PS} - c_{44,PI})/\frac{1}{2}(c_{44,PS} + c_{44,PI}) = 54\%]$. The elastic constants of PS and PI are sufficiently different, however, that the film-guided modes of
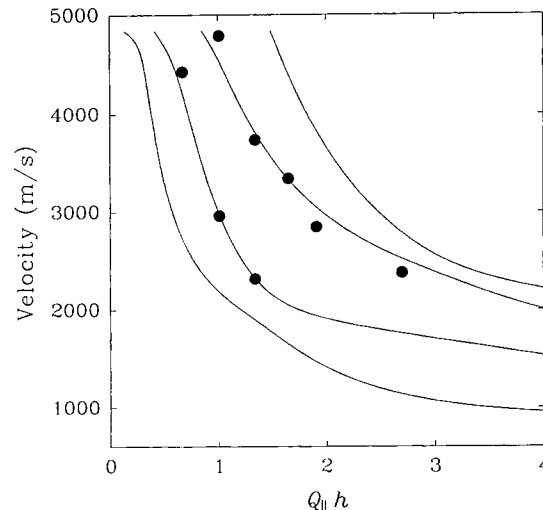

Figure 2. Velocity dispersion curves for PI. The symbols represent velocities of film-guided modes measured using BLS for a thick ($h = 1570$ Å) PI film. The solid curves were calculated using the best fit elastic constants listed in Table II.

PS and PI are easily distinguishable, as can be seen by comparing the curves in Figures 1 and 2. Also evident from Figures 1 and 2 are the relatively large differences between the phonon velocities of PS and PI for values of $Q_{\parallel}h$ between 2 and 4. It is for this range of $Q_{\parallel}h$ that BLS data for the multilayer samples were acquired.

In Figure 3 we show a BLS spectrum obtained for the 10-layer film with the structure Si/(PS/PI)^5. The prominent feature nearest to the central peak is the Rayleigh mode, and there are a number of Sezawa modes which are observed at higher frequencies. The Rayleigh mode is the most intense feature in all of the BLS spectra for the multilayer samples. The linewidth of the Rayleigh mode was measured to be 0.7 GHz, which is only slightly larger than the 0.5 GHz instrumental width. This narrow

Table II. Elastic Constants for PS and PI Determined for Bulk and Thick Film Samples Using BLS

Mechanical Property	PS Films	PS Bulk[a]	PI Films	PS/PI Superlattice $h_{PS} = h_{PI}$
ρ (g/cm^3)	1.06	1.06	0.92	0.99
c_{11} (GPa)	5.54	5.36	4.0	4.8
c_{13} (GPa)	2.78	3.10	2.4	2.6
c_{33} (GPa)	5.54	5.36	4.0	4.6
c_{44} (GPa)	1.38	1.30	0.80	1.0

Also shown are effective elastic constants calculated using the method of Akcakaya and Farnell[18] with the condition $h_{PS} = h_{PI}$ using the PS and PI elastic constants listed in columns 1 and 3.
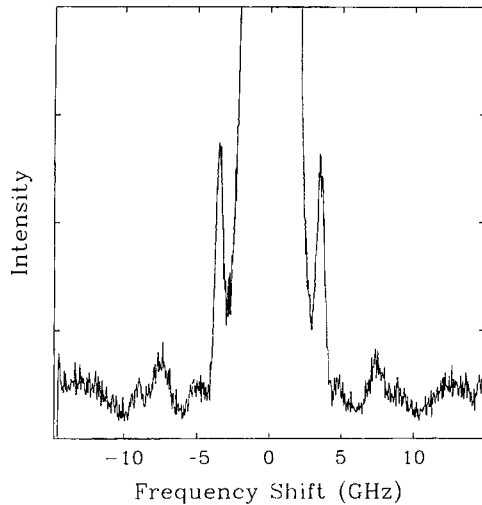[a] From Lindsay et al.[12]

Figure 3. BLS spectrum obtained for the multilayer sample Si/(PS/PI)[5].

linewidth and the large intensity of the Rayleigh mode make it an ideal feature for use in comparisons between different multilayer samples. Since the sample quality, and hence the signal-to-noise ratio in the BLS spectra, varied between different multilayer samples, not all of the modes seen in Figure 3 can be observed in all BLS spectra. Of the five modes observed in Figure 3, at least three, one of which was the Rayleigh mode, were resolved in all spectra.

The elastic constants of the constituent materials can be used to calculate the properties of the multilayer samples in one of two ways. The exact solution to the problem requires separate dispersion curves to be calculated for each multilayer sample. Such a technique has been applied to samples which contain only a few layers such as $Si/SiO_2/Si$ (ref. 15) as well as polymer bilayers.[16] An alternative approach is to consider an infinite PS/PI superlattice, and generate effective elastic constants for this bulk medium.[17] For isotropic constituent layers the resulting effective elastic constants will be those of a medium with hexagonal symmetry. Although this approach is not exact when applied to a multilayered film consisting of a finite number of layers it allows a single set of elastic constants to be used for all of the multilayer samples. The method described by Akcakaya and Farnell[18] for calculating these effective elastic constants was used. This effective medium approach exactly describes the boundary conditions between the PS and PI layers, but only approximates those at the free surface and the substrate. Effective elastic constants can be expected to describe accurately the mechanical properties of

a sample with a large number of layers because most of the mechanical boundary conditions are satisfied exactly. It is not obvious, however, that the technique will adequately describe bilayer samples in which boundary conditions are described accurately by the effective medium approach at only one of the three boundaries. The elastic constants calculated using the effective medium approach with $h_{PS} = h_{PI}$ are also given in Table II. Figure 4 shows a portion of the dispersion curves calculated using the effective elastic constants as well as the data for the two bilayer samples Si/(PS/PI) and Si/(PI/PS). For the Si/(PI/PS) sample, which satisfies the condition $h_{PS} \simeq h_{PI}$, one can see from Figure 4 that the measured velocities of the film-guided modes are very close to the calculated curves. The agreement is especially good for the Rayleigh mode. This somewhat surprising result occurs because the elastic constants of the two constituent materials are of the same order and the boundary conditions at the substrate and free surface are approximately satisfied. The success of the effective medium approach for the bilayer samples indicates that any deviations from calculated values for other multilayer samples containing larger numbers of PS/PI bilayers is a result of changes in the mechanical properties of the constituent polymer layers.

In Figure 5, the calculated velocity dispersion curves are shown with the measured values of the film-guided phonon velocities for the multilayer samples Si/(PI/PS), Si/(PI/PS)[3], Si/(PS/PI)[3],
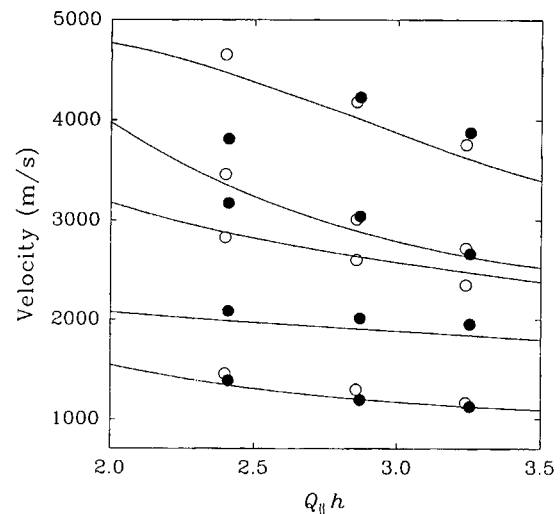

Figure 4. Calculated velocity dispersion curves using effective elastic constants from Table II. The symbols represent the measured velocities of film-guided modes for the Si/(PS/PI) (O), and Si/(PI/PS) (●) bilayer samples.
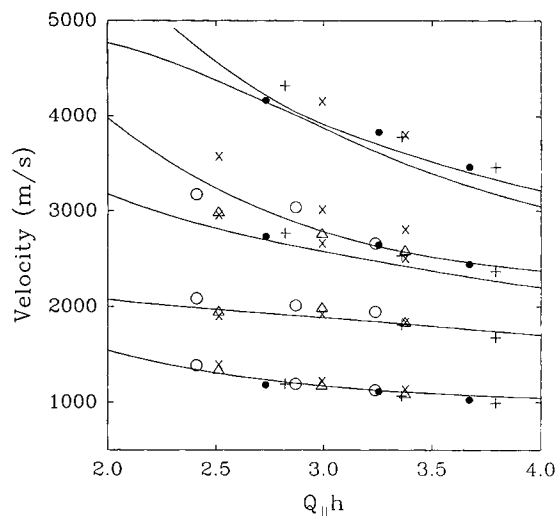
Figure 5. Calculated velocity dispersion curves using the effective elastic constants from Table II. Symbols are the measured velocities of film-guided modes for all samples with $h_{PS} \simeq h_{PI}$. The symbols are (O) Si/(PI/PS); (●) Si/(PI/PS)^3; (+) Si/(PS/PI)^3; (△) Si/(PI/PS)^5; and (×) Si/(PS/PI)^5.

Si/(PS/PI)^5, and SI/(PI/PS)^5. It can be seen from this figure that the velocities of the observed modes for all of the samples show remarkable agreement with the calculated curves. The effective medium elastic constants used to calculate the dispersion curves for the multilayer samples are determined directly from the elastic constants determined for thick PS films and a thick PI film as discussed previously. The agreement between the measured and calculated Rayleigh mode velocities (primarily determined by the effective shear elastic constant c_{55}) is particularly good. This is especially surprising in light of the fact that no parameters have been adjusted to obtain the calculated curves. The measured velocities of the higher order Sezawa modes are all slightly larger than the velocity values calculated using the effective medium elastic constants. A small change (+20%) of the c_{11} value for either PS or PI removes the discrepancies between the measured and calculated velocity values for all of the modes. The implications of the agreement between the data and the curves calculated using the effective medium elastic constants are striking. All of the measured velocities are consistent with elastic constants of the individual layers that have the same values (to within 20%) as those for thick $(h \gg R_{EE})$ films. Most notably, for the 10-layer films, Si/(PS/ PI)^5 and Si/(PI/PS)^5, very good agreement is obtained with the calculated values. The elastic constants of the PS and PI layers are the same as those

of thick films even though the thickness of the constituent polymer layers is only 160 Å. For these films the individual layer thickness is less than one third of the unperturbed size of the PS or PI molecules.

The fact that the high-frequency mechanical properties of the multilayer samples are not noticably changed as the layers are made much thinner than R_{EE} is interesting when compared to the variations in T_g observed for single supported films. An important distinction between single films and multilayered films is the nature of the film interfaces: the single films have a single polymer/air interface and a single polymer/substrate interface, whereas most of the interfaces within the multilayered films occur between two different polymers. The different interfaces will likely have different effects on the film properties. The only study of T_g effects on samples with interfaces similar to those in the multilayered films is that of bulk block copolymers[19] in which it was found that the T_g value of a polymer microphase was reduced if it was dispersed in a polymer with a lower T_g value. For microphase dimensions comparable to the film thicknesses studied in ref. 3–6, the T_g reductions for the microphases were much smaller than for the single films. For both the block copolymer work and the present work, the polymers are symmetrically confined and as a result do not have free surfaces. Since it has been shown[6] that the presence of free surfaces produces very large reductions in T_g, it is perhaps not surprising that elastic properties similar to bulk values are obtained for the layers within the multilayered films in the present work.

It is worth noting that the elastic constants for the unannealed, spincoated PS films discussed above are not substantially different from the bulk, although the molecules may be quenched into nonequilibrium shapes. In the present work we have shown that in multilayered films with individual layer thicknesses of less than one third of R_{EE}, corresponding to polymer molecules that are necessarily highly oblate, changes in the elastic constants are small.

The advantage of using multilayered films to determine the elastic properties of very thin films is clearly displayed in Figures 1 and 2. For $Q_{\|}h$ between 2 and 4, there are large differences between the velocities of film-guided modes in PS and PI films. By constructing multilayered films we were able to study films with individual layer thicknesses of only 160 Å, but with a total film thickness of 1600 Å corresponding to $Q_{\|}h$ values between 2 and 4. If single supported films of $h = 160$ Å were studied instead, the range of $Q_{\|}h$ probed in the BLS experiment

would be within the range $0.2 < Q_\parallel h < 0.4$. Referring again to Figures 1 and 2, one can see that for $0.2 < Q_\parallel h < 0.4$, the PS and PI phonon velocities, especially those of the Rayleigh mode, are very similar. The similarity of the Rayleigh velocities is necessary since the Rayleigh mode velocity of any supported film, regardless of the film material, must approach that of the substrate material as the thickness of the film approaches zero. The sensitivity of the BLS technique to small changes in the elastic properties of thin films depends strongly on the range of $Q_\parallel h$ that is used for the BLS measurements. We estimate that for the $Q_\parallel h$ range probed in the present work 20% changes in the elastic constants of the individual layers can be resolved by observation of film-guided acoustic phonons in the multilayer samples.

SUMMARY AND CONCLUSIONS

Measuring the mechanical properties of very thin polymer films supported by substrates is complicated by the fact that the measured properties are very strongly influenced by those of the substrate. A sample geometry which avoids this difficulty is the stacking of very thin layers within multilayered films. The mechanical properties of the multilayer sample are determined by those of the constituent polymer layers. We have used PS/PI multilayered films as a means of investigating the properties of polymer layers, which have thicknesses that are much less than the unperturbed size of the polymer molecule, i.e., h_{PS}, $h_{PI} \gg R_{EE}$. An effective medium theory was used to calculate the elastic constants of a PS/PI superlattice. The same set of effective elastic constants could be used to describe multilayered films for the entire range of layer thicknesses considered, including films with individual layers with $h \simeq 160$ Å $\gg R_{EE}$. From this we can infer that the mechanical properties of these very thin polymer layers are very similar to those of the bulk polymer. Further studies involving the mechanical properties of very thin, freely standing films, which are also not dominated by substrate properties, are currently in progress.

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