Direct Spincasting of Polystyrene Thin Films onto Poly(methyl methacrylate)

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ABSTRACT: The low vapor pressure solvent 1-chloropentane was used to directly spincast polystyrene (PS) films onto poly(methyl methacrylate) (PMMA) with smooth surfaces and sharp interfaces. Interface roughness after removal of the PS layer with cyclohexane was determined with scanning force microscopy to be <1 nm. Dynamic secondary mass spectroscopy revealed an interfacial width below the resolution limit of ~10 nm. Large area bilayers with smooth surfaces could be created. In addition, direct spincasting with 1-chloropentane allows the production of thin PS films (<15 nm) and films of low molecular weight (<5 kDa) PS, all of which would be impossible to produce for this important model system by the traditional water-transfer method. 1-Chloropentane was confirmed to be a sufficiently selective solvent for PS by measuring the Flory–Huggins \( \chi \) parameters of 1-chloropentane with PS and PMMA, respectively, with inverse gas chromatography. In the search for a suitable selective solvent, the authors have also examined the role of vapor pressure in spincasting smooth films over a wider molecular weight (4.3–190 kDa) and thickness range (~5–500 nm) than previously reported. Only solvents with low vapor pressure produced high quality PS films. Methylcyclohexene can also be used to produce excellent, directly cast PS/PMMA bilayers, but with a smaller molecular weight and thickness window compared with 1-chloropentane. ©2006 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 44: 3234–3244, 2006

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INTRODUCTION

The production of thin polymer films and model bilayer or multilayer systems is important for a number of technological applications and fundamental studies that range from dewetting and stability characterization to surface enrichment and interfacial property determination (e.g., refs. 1 and 2). Important experimental techniques such as X-ray reflectivity,3,4 neutron reflectivity,3 forward recoil spectrometry,5 and secondary ion mass spectrometry (SIMS)6 require the use of thin planar films to investigate interfacial and surface properties and composition gradients. Planar films are furthermore ideal from a theoretical standpoint for many continuum models7–9 and numerical simulations10–12 because of the correspondence of physical boundaries to computationally cheap numerical boundaries.13 To reach the full potential of above-mentioned experimental tools and to provide quantifiable data for comparison with various theories, the ability to produce uniform films and bilayers is essential.

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Spin casting a polymer from solution onto a spinning substrate is a simple, well-established means of creating thin films (~10–1000 nm). Although spin casting is a well-established experimental technique, thin film formation and the quality of the film produced is the result of a complex dynamic process still under active investigation. Many theoretical and experimental studies aim to determine which parameters (vapor pressure, solubility, viscosity/glass transition, concentration gradients etc.) are the most important ones in general and which parameters dominate as a function of solution concentration and film thickness (e.g., refs. 17–19). Interestingly, not all good solvents produce high quality, smooth films. Dependences on vapor pressure, glass transition temperature of the polymer, and polymer/solution concentration have been noted or implicated in particular as important parameters that control the spin casting dynamics and quality of the films produced.

Increasingly, layered thin film polymer systems are used as model systems for a number of studies, including model studies of reactive compatibilization of blends. Finding selective solvents to accomplish direct casting of bilayers is relatively easy for polymers that differ greatly with respect to dispersive interactions and dipole moments. For example, binary systems such as polystyrene (PS) spun onto poly(2-vinylpyridine) (P2VP) can be spun with an accepted selective solvent such as toluene, as P2VP is much more polar than PS and not soluble in toluene. For polymer pairs more similar in their solubility properties, the conventional general method for production of polymer bilayers is to spin cast one layer onto the desired substrate, spin the other polymer onto a hydrophilic substrate such as glass or mica, float this polymer thin film onto water, and then pick the floating thin film up on top of the bottom layer still supported by the substrate (e.g., refs. 27). This method is tedious and is somewhat of an art form. It often results in cracked, folded, or overlapping layers, and can be damaging for water-sensitive polymers and functional groups. Furthermore, the molecular weight of the polymer to be floated has to be above a critical molecular weight and/or the film has to be thicker than a critical thickness for the transfer to be successful at all. Spin casting of one layer directly onto another is thus preferable as it eliminates most of the problems associated with floating. Solvents used for direct casting of the top layer have to fulfill two conditions: (i) the bottom layer should have minimal solubility in the solvent used to cast the top layer and (ii) the solvent/polymer solution used for the top film needs to produce smooth and even thin films. Preferably, the solvent should also pose few health risks and not involve safety issues.

The present study will focus on the ubiquitous poly(methyl methacrylate) (PMMA) and PS system. PMMA and PS is a widely used model system for investigations that include interfacial width measurements, block copolymer morphology, antireflection coatings, physical blending, dewetting dynamics, isotope driven segregation, and reactive compatibilization. Our own immediate interest and need for direct casting is driven by the use of water-sensitive functional groups in PS/PMMA model systems in studies of interfacial reactions. With glass transition temperatures relatively close to each other that are easily accessible with moderate annealing temperatures, coupled to the wealth of information known about thin film and bulk properties, PS/PMMA will continue to be an important and useful model system. To date, despite this relative importance, PS and PMMA bilayer system could only be created with the floating method. This is due in large part to the fact that even though this polymer pair is highly immiscible for systems where both polymers have number average molecular weights (Mn) higher than ~15 kDa, they share many common solvents. PMMA has a fixed dipole moment due to the carbonyl groups. In contrast, PS is relatively unpolar intrinsically, but the aromatic side group is easily polarized, resulting in an induced dipole moment. Therefore, many common organic solvents such as toluene, tetrahydrofuran (THF), and chloroform are good solvents for both. This tendency to have cosolvency is also reflected in the similarity in their respective solubility parameters (δ). The popularity of PS and PMMA as a model system might be in part due to the fact that these polymers can be readily processed in or spun from a common solvent (e.g., refs. 30–34). Direct spinning of PS on top of PMMA, or PMMA on top of PS, having to fulfill the difficult constraints of finding a selective solvent that also produces good films, is therefore not a straightforward task. Yet, being able to directly produce PS/PMMA bilayers would be very expedient and useful because of the prevalence of the use of PS and PMMA as model systems. Despite this focus...
on PS/PMMA systems, the methods used to select appropriate solvents should be also helpful in the selections of successful solvents for direct casting of smooth films for other polymer systems.

A set of candidate solvents have to be evaluated systematically for their ability to directly spin bilayers of PS onto PMMA. Cyclohexane is an obvious candidate solvent for direct casting because it is the solvent of choice to differentially dissolve PS layers or PS domains in PS/PMMA samples. However, cyclohexane is unsuitable for direct casting of PS/PMMA bilayers. Because of dynamic effects related to its high vapor pressure, cyclohexane will not spin cast PS into uniform thin films. Although the vapor pressure of the solvent and evaporation rate has been shown to have a dramatic effect on the quality of the spun thin films, most studies were conducted with relatively high molecular weight polymers. Because of an incomplete understanding and the lack of “scaling” rules for molecular weight (i.e., viscosity) and thickness, we investigated a number of solvents for PS for their ability to spin smooth PS films over a wider range of molecular weights and thickness than previously reported to provide a guide on which differential solvents will also produce smooth films, the second boundary constraint of spinning high quality PS/PMMA bilayers.

The polymer–solvent $\chi$ values in the fourth ($\chi_{PS}$) and sixth ($\chi_{PMMA}$) column of Table 1 are calculated from the solubility parameters tabulated by Mark using

$$\chi = 0.34 + \frac{V_r}{RT} (\delta_p - \delta_s)^2$$

where $V_r$ is the reference volume, $R$ is the universal gas constant, $T$ is the absolute temperature of the solution ($T = 273$ K), and $\delta_p$ and $\delta_s$ refer to the solubility parameter of the polymer and solvent, respectively. The two other columns showing polymer–solvent $\chi$ values (fifth and seventh column) were taken from Brandrup et al. for the highest concentration and lowest temperature recorded. The final two columns directly answer if the solvent dissolves PS or PMMA (yes indicates a solution is formed at room temperature).

### Table 1. Solvent Properties

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$P_{sat}$ $^a$ (kPa)</th>
<th>$d^a$ (MPa$^{1/2}$)</th>
<th>$\chi_{PS}^b$</th>
<th>$\chi_{PS}^a$</th>
<th>$\chi_{PMMA}^b$</th>
<th>$\chi_{PMMA}^a$</th>
<th>PS</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>3.8</td>
<td>18.3</td>
<td>0.35</td>
<td>0.31</td>
<td>0.34</td>
<td>0.45</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>1-Chloropentane</td>
<td>4.4</td>
<td>17.1</td>
<td>0.46</td>
<td>*</td>
<td>0.45</td>
<td>*</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Methylcyclohexene</td>
<td>4.9</td>
<td>16.1</td>
<td>0.71</td>
<td>0.67</td>
<td>0.69</td>
<td>*</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>10.0</td>
<td>17.4</td>
<td>0.41</td>
<td>*</td>
<td>0.40</td>
<td>*</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>12.6</td>
<td>18.9</td>
<td>0.34</td>
<td>0.69</td>
<td>0.34</td>
<td>*</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>13.0</td>
<td>16.7</td>
<td>0.51</td>
<td>0.79</td>
<td>0.50</td>
<td>*</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>15.2</td>
<td>17.6</td>
<td>0.39</td>
<td>0.29</td>
<td>0.38</td>
<td>*</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>21.6</td>
<td>19.0</td>
<td>0.34</td>
<td>*</td>
<td>0.35</td>
<td>*</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Chloroform</td>
<td>26.2</td>
<td>18.9</td>
<td>0.34</td>
<td>0.17</td>
<td>0.34</td>
<td>*</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

$^a$ $\chi$ values not recorded for the system.

$^b$ Values taken from Brandrup for the lowest concentration and temperature.

$^c$ Values calculated from solubility parameters.
Two selective solvents for PS with respect to PMMA, 1-chloropentane and methylcyclohexane, were found to create uniform PS/PMMA bilayers with sharp interfaces. PMMA was found to be completely immiscible in 1-chloropentane and methylcyclohexane. In contrast, 1-chloropentane has been determined to dissolve and spin PS with $M_n$ ranging from $4-190$ kDa (range of polymers used in this study) and thicknesses of $5-500$ nm with completely uniform films on inorganic substrates and PMMA layers. Methylcyclohexane has a much narrower range of thicknesses ($10-50$ nm) and $M_n$s ($3-15$ kDa) for production of uniform PS films.42 Because of the more limited application range of methylcyclohexane, we focus here primarily on bilayers created with 1-chloropentane. These bilayers were characterized with dynamic SIMS, scanning force microscopy (SFM), and visible light microscopy (VLM). We observe uniform PS and PMMA films and sharp interfaces between these polymers after direct spin casting from either selective solvent.

**EXPERIMENTAL**

**Solvents/Polymers**

All solvents were purchased from Fisher Scientific or Sigma-Aldrich and used as received. PS and PMMA were purchased from Polymer Source and Scientific Polymer Products and used as received. The solubility parameters $\delta$ of the polymers used along with their polycdispersity index and weight average molecular weight ($M_w$) are listed in Table 2. PS was dissolved in the solvents listed in Table 1 at $\sim3\%$ by polymer mass. PMMA was dissolved in toluene at $3\%$ by polymer mass. Solutions were prepared by the sonication of the polymers in the solvent for 10 min, stored for a minimum of 12 h, and filtered with a $0.45 \mu m$ (pore size) Teflon filter before spincasting. Sonication is known to be able to cause some changes in molecular weight distribution,43 particularly for high molecular weight polymers, but the expected changes44 are not significant enough for the work presented here, which does not depend critically on the use of monodisperse polymers.

**Spin Casting**

Silicon (100) wafers were purchased from Wafer World and typically broken into $\sim1$ cm by $\sim1$ cm square substrates. Substrates were cleaned in a solution of 1:1:3 H$_2$SO$_4$:H$_2$O$_2$:H$_2$O, heated to $50 \degree C$ for 20 min, and then thoroughly rinsed in deionized water. Finally, the substrates were soaked in a solution of 1:10 HF:H$_2$O for 1 min and rinsed in deionized water to create an hydrogen-passivated (Si-H) substrate.

All solutions were spun cast with a Headway spin coater on the substrates at 2200 rpm for 15 s. For multilayer films the lower PMMA-33 layer was annealed at $140 \degree C (T_g \sim103 \degree C)$ for several minutes to allow the solvent to fully evaporate before the upper layer was spun. Single layer films, used to assess the ability of spinning smooth films, and the upper layers of the multilayer systems were not annealed to prevent any potential smoothing of the layers before characterization. As the solution concentrations were always $\sim3\%$, the thicknesses of the PS-59 layers produced depended on the solvent used. The thickness is primarily controlled by the viscosity of the solution and the propensity for the solvent to evaporate. The layer thickness was characterized with a Rudolph Research AutoEL-III single wavelength ellipsometer.

**Table 2. Polymer Properties**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$ (kDa)</th>
<th>PDI</th>
<th>$\delta$ (MPa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-4.3$^a$</td>
<td>4,300</td>
<td>1.06</td>
<td>18.7</td>
</tr>
<tr>
<td>PS-12$^a$</td>
<td>12,200</td>
<td>1.27</td>
<td>18.7</td>
</tr>
<tr>
<td>PS-19$^b$</td>
<td>19,300</td>
<td>1.07</td>
<td>18.7</td>
</tr>
<tr>
<td>PS-59$^a$</td>
<td>59,000</td>
<td>1.06</td>
<td>18.7</td>
</tr>
<tr>
<td>PS-116$^b$</td>
<td>115,700</td>
<td>1.08</td>
<td>18.7</td>
</tr>
<tr>
<td>PS-190$^b$</td>
<td>190,000</td>
<td>-</td>
<td>18.7</td>
</tr>
<tr>
<td>PMMA-33$^b$</td>
<td>33,300</td>
<td>1.05</td>
<td>18.6</td>
</tr>
</tbody>
</table>

$^a$ Polymer Source.

$^b$ Scientific Polymer Products.

**Surface Characterization**

Single layers of PS-59 were spun cast from solution with the listed solvents and immediately viewed under a Nikon Labophot II visual light microscope to characterize the smoothness of the films. VLM data were recorded with an attached Spot RT CCD camera. SFM (Autoprobe CPR scanning force microscope from Thermomicroscopes) was used in contact mode to determine the topography and root-mean-square (RMS) roughness of the PS-59 films. Multiple SFM
scans of \(40 \times 40 \, \mu m^2\) were acquired and averaged to determine the RMS roughness for each film. SFM images were corrected line by line to account for the SFM scanner motion on an arch. Any obvious artifacts were excluded before the RMS roughness was determined.

For the PS-59/PMMA-33 bilayer systems, SFM topography scans of \(40 \times 40 \, \mu m^2\) were performed on the upper and lower layers of both bilayer systems to measure the RMS roughness. The lower layers were scanned prior to spin casting the upper layers. The upper layers were scanned immediately after spinning.

Single layers of PS, spanning PS-4.3 to PS-190 and thicknesses from 5 to 400 nm, were also qualitatively characterized with VLM and SFM.

**Interface Characterization**

SFM and DSIMS have been used to provide a relatively comprehensive picture of the interfaces produced. SFM topographic scans of the PS-59/PMMA-33 systems were performed on the lower layer of the bilayer system over a \(40 \times 40 \, \mu m^2\) sample area to measure the RMS roughness prior to spin casting the upper layers. The upper PS-59 layer was spun directly onto the PMMA-33 or P2VP and the PS-59 smoothness of the top surface was again characterized with SFM. Subsequently, the top PS-59 layer was removed with cyclohexane, which dissolves PS-59 but not PMMA-33. The now exposed bottom PMMA-33 layer was characterized with SFM to determine its RMS roughness to assess if direct spinning affects the smoothness and flatness of the polymer–polymer interface. The thickness of the PMMA layers were determined using ellipsometry before the top PS-59 layer was spun and again after the top layer was removed with cyclohexane.

A SIMS deuterium depth profile was recorded at the Analytical Instrumentation Facility at North Carolina State University with a CAMECA IMS-6F magnetic sector spectrometer with a depth resolution of \(\sim 10\,\text{nm}\). The profile was used as a preliminary characterization tool to determine if the PS/PMMA interfacial width exceeds the depth resolution of the SIMS, or if not, to establish an upper limit on the interfacial width of the PS and PMMA bilayer. Cs\(^+\) primary beam impact energy of 14.5 keV was used. Use of Cs at 14.5 keV showed no significant charging. The Cs profiles were obtained with 20 nA into a \(200 \times 200 \, \mu m^2\) raster area with detection of 60 \(\mu m\) diameter circle at the center.

**1-Chloropentane/Polymer Phase Behavior**

Inverse gas chromatography (IGC) was used to comparatively characterize the phase behavior of 1-chloropentane with PMMA and PS within the concentration limit of pure polymer at temperatures of 423, 433, and 443 K. Experiments were conducted with a commercially available GC using capillary columns coated with PMMA (\(M_w \sim 996\,\text{kDa}\)) \((1193.7 \, \text{cm} \times 3.0 \, \mu m \times 0.053 \, \text{cm ID})\) and with PS (\(M_w \sim 200\,\text{kDa}\)) \((844.5 \, \text{cm} \times 5.0 \, \text{mm} \times 0.053 \, \text{cm ID})\). 1-chloropentane was injected as a sharp spike into the columns. The resulting elution profiles were fitted and regressed for the partition coefficient (\(K\)) using the CCCIGC model.\(^{46}\) The Flory–Huggins interaction parameter \(\chi\) was then calculated based on \(K\).

The most important mass transfer resistances occurring in the column are axial diffusion in the gas phase, diffusion in the polymeric stationary phase, and dispersion in the gas phase. The IGC analysis was performed at The Center for the Study of Polymer–Solvent Systems at The Pennsylvania State University.

**RESULTS AND DISCUSSION**

At first, the ability to spin smooth and uniform PS layers and the role of vapor pressure was assessed. Single layer PS-59 films cast from all solvents on inorganic substrates were characterized with VLM at a magnification of 200. Typical morphologies as observed in the VLM are displayed in Figure 1 as examples. Smooth films could be produced with low vapor pressure solvents such as 1-chloropentane [Fig. 1(a)], whereas high vapor pressure solvents resulted in poor film quality even if the solvent was an excellent solvent for PS-59, for example, THF and chloroform [see Fig. 1(b,c)]. The films were characterized further with SFM to quantitatively determine the surface roughness (see example in Fig. 2). We found that the roughness of the film is essentially the same over the entire film surface. Therefore, we choose as scan sites for roughness determination only sample area without visible particulates (i.e., silicon dust produced by etching or particulates from the air). The RMS roughness reported here was determined by averaging the RMS roughness from
three $40 \times 40$ $\mu m^2$ scans on different areas of the substrate surface. The surface roughening from high vapor pressure solvents resulted in relatively isotropic features near the center of the sample and more elongated radial structures near the edges (see Figs. 1 and 2). This indicates that the radial flow of the solution during spinning orients the roughening features. Since the RMS and peak–peak measures for roughening did not depend on location, that is, center versus edge, the radial solvent flow is not directly involved in causing the instability of the film that leads to the roughening. This observation is consistent with prior experiments on higher molecular weight PS films (~200 and 1000 kDa), in which the roughness features were attributed to Marangoni instabilities. For rough films, thicknesses were not recorded with ellipsometry because the surface roughness causes errors in the determined value. The two solvents that produced smooth films as judged by VLM also produced the smallest RMS roughness as measured with SFM (0.56 nm for toluene and 0.48 nm for 1-chloropentane). Films with noticeably rough morphologies in VLM had RMS roughnesses as measured with SFM much greater than films produced from toluene and 1-chloropentane. Films cast from chloroform had the greatest RMS roughness of ~16 nm. The surface modulation, and hence RMS roughness, is dominated by low spatial frequencies for most rough samples (see Figs. 1 and 2). The measured RMS roughnesses for the roughest films are as follows: 16 nm for chloroform, 10 nm for THF, 9 nm for carbon tetrachloride, and 8.8 nm for cyclohexane. The measured RMS values are plotted against solvent vapor pressure in Figure 3. The figure reveals a strong correlation between RMS roughness and solvent vapor pressure. The linear fit for the data is used to show the correlation relation and is only empirical and not related to any model or theory. The calculated

Figure 1. Optical micrographs of PS-59 thin films (60–90 nm, 100×). (a) film spun with 1-chloropentane (low $P_{\text{sat}}$); (b) film spun with tetrahydrofuran (high $P_{\text{sat}}$); (c) film spun with chloroform (highest $P_{\text{sat}}$).

Figure 2. SFM image of PS-59 thin film spun cast from tetrahydrofuran.
correlation coefficient is 0.96, which shows a very strong relation. Prior observation with higher molecular weight PS shows a qualitatively similar behavior in that high vapor pressure solvents create rough surfaces.\textsuperscript{19,20} However, the correlation to vapor pressure was not as high and linear for the higher molecular weights polymers as the one observed in the present study.

In contrast to the correlation observed for solvent vapor pressure and roughness, plotting RMS roughness against the Flory–Huggins parameter as seen in Figure 4 reveals essentially a complete lack of correlation to the RMS roughness. We were only able to produce smooth films with relatively low vapor pressures ($<5$ MPa) solvents, irrespective of the $\chi$ parameters.

Since there is little available information on the phase behavior of 1-chloropentane/PS and 1-chloropentane/PMMA, yet 1-chloropentane had the potential of be a differential solvent that spins single layer PS well, IGC was used to solve for the Flory–Huggins $\chi$ parameter for both systems at temperatures of 423, 423, and 443 K to infer preferential solvent characteristics more quantitatively. Measuring the $\chi$ parameter for PS/1-chloropentane also allowed the inclusion of the 1-chloropentane thin film roughness measurements in Figure 4, comparing roughness with $\chi$ parameters. Using IGC, $K$, the partition coefficient, and $D$, the diffusion coefficient, were determined for each system from the best fit between the experimental and model elution curves. The $\chi$ value was then calculated for each temperature and system using $K$. The results are displayed in Figure 5 for PS and PMMA for the three temperatures. Also, included in the figure are $\chi$ values determined by IGC for PS/cyclohexane at similar temperatures.\textsuperscript{45} The determined $\chi$ value of PS/1-chloropentane is near $\chi_{\text{critical}}$ and roughly the same as $\chi$ for PS/cyclohexane at these temperatures (NB Cyclohexane is an accepted selective solvent for washing PS from PMMA). The PMMA/1-chloropentane $\chi$ values are much higher than the values for PS/1-chloropentane. The lower solubility of PMMA, that is, higher $\chi$ for PMMA, is supported by the fact that PMMA with a molecular weight greater than ~20 kDa does not dissolve in an excess amount of 1-chloropentane at room

**Figure 3.** Relation between vapor pressure and PS-59 film roughness.

**Figure 4.** Relation between the Flory–Huggins interaction parameter ($\chi$) of various PS-59/solvent systems and film roughness.

**Figure 5.** Calculated $\chi$ values for PS and PMMA in 1-chloropentane at temperatures ranging from 423 to 443 K. PS in cyclohexene (an accepted selective solvent for PS and PMMA) has similar $\chi$ values to PS in 1-chloropentane. (Vertical line = 160 °C).
temperature. The selectivity was qualitatively confirmed by removing the PS-190 domains in an annealed PS-190/PMMA-75 thin film blend. Identical results to washing with cyclohexane have been observed as can be seen from the images displayed in Figure 6 for a 50/50 PS-190/PMMA-75 mixture. Since 1-chloropentane also produced high quality spun cast thin films, 1-chloropentane was an excellent candidate to directly cast PS on top of PMMA with a high quality interface and was further investigated for its ability to produce bilayers of excellent quality.

The PS-59/PMMA-33 bilayers spun cast using 1-chloropentane as the solvent for PS were characterized with SFM and ellipsometry. SFM topographs of the upper PS-59 layer yield RMS roughnesses of the PS-59 surface that are comparable with the low values obtained for monolayer PS-59 films spun from toluene of ~0.6 nm. The interfacial roughness of the PMMA-33 was determined with SFM to be ~0.4 nm by characterizing the PMMA-33 surface after the PS-59 film was spun, annealed, and subsequently removed through preferential dissolution in cyclohexane. The observed value is very small and comparable with the PMMA-33 surface roughness determined before the upper PS-59 film was spun. This suggests that 1-chloropentane does not swell the PMMA-33 layer enough to allow the PS-59 to interpenetrate the PMMA-33 at the polymer–polymer interface or for the PMMA-33 layer to be distorted and roughened by the highly shearing flow of the PS-59 solution as it is spun on top of the PMMA-33. Ellipsometry measurements on the PMMA-33 film before spinning the upper layer and after the upper layer was spun and subsequently removed by a cyclohexane wash reveal essentially identical thicknesses of 69.4 and 69.8 nm, respectively. No PMMA-33 is lost during the spinning of the top PS-59 layer, nor through the washing with cyclohexane. The PMMA-layers, and by implication the PS/PMMA interface, is very stable throughout the processing for the bilayers. These results show that 1-chloropentane produces a smooth PS top layer and, most importantly, it does not reduce or roughen the bottom PMMA layer when spin casting the top PS layer.

As a complement to the SFM measurements, DSIMS was used to directly characterize the interface between layers without washing off the PS film. For SIMS analysis, a bilayer of a ~200 nm thick 15/85 w/w dPS-58/PS-59 mixture and ~100 nm PMMA-33 was used. The dPS-58 was added to PS-59 to distinguish easily between PMMA and PS. Figure 7 displays a plot of the dPS volume fraction as a function of sample depth. The SIMS data reveals a sharp PS/PMMA interface within the depth resolution of the SIMS of about 10 nm. This indicates that the interface did not roughen significantly and is in agreement with the SFM characterization of the washed bilayers. Improved characterization of the interfacial width with higher depth resolution and a direct comparison with floated films is presently underway using X-ray reflectivity. Initial results show that the interface is indeed very sharp.47

PS/PMMA bilayers were also directly spun cast on larger area substrates with extremely small PS-59 film thicknesses and with low $M_w$ PS-4.3 to demonstrate some of the extended
The capabilities of the direct spinning method. PS-59 films spun on 4-in.-diameter silicon wafer covered with a 100-nm PMMA-33 film produce smooth films across the entire surface. The thickness of the film was characterized at 10 locations along a straight line across the entire sample. The average deviation of the thickness was less than 1 nm from the average PS thickness of 50 nm. A solution of 59 kDa PS with a low concentration of 1 mg/mL spun onto a Si-H substrate produced a thickness of 7 nm as measured by ellipsometry. The same solution spun on top of a 60-nm PMMA-33 film produced a smooth, uniform upper PS layer, as characterized with VLM. A solution of low molecular weight PS (5 kDa) spun on top of a 60-nm thick PMMA-33 film also produced a uniform film. All three types of bilayers would be impossible to produce without use of the direct spin casting method.

Qualitative characterization with VLM and SCF of single layer PS cast from 1-chloropentane solution to 5-400 nm in thickness revealed that these films are of comparable quality to films cast from toluene solutions for molecular weights ranging from PS-4.3 to PS-190.

Solutions of PS in methylecyclohexane also produced high quality PS films, although within a narrower range of molecular weights and film thicknesses. PS-4.3, PS-12, and PS-19 dissolved in methylecyclohexane. As expected, PS-59 and PS-190 did not dissolve in methylecyclohexane. Uniform films would be expected based on methylecyclohexane’s relatively low vapor pressure. Indeed, PS with molecular weight <19 kDa dissolved in methylecyclohexane resulted in smooth films at low concentrations, which resulted in small film thicknesses. However, thicker films spun with concentrations greater than 12 mg/mL produced an array of morphologies, presumably on account of the relatively poor solubility of PS-12 in methylecyclohexane: 12 mg/mL solutions produced cracks, and 18 mg/mL solutions produced a wavy, rough morphology typical of high vapor pressure solvents. The complexity of spincasting in general, that is, the dependence on molecular weight and thickness, and thus direct spincasting is exemplified by methylecyclohexane. Because of its small PS molecular weight window, methylecyclohexane can be referred to as a limited selective solvent. In general, methylecyclohexane is expected to be selective over a different set of polymers than 1-chloropentane, but this set does include PS/PMMA, the focus of this study. Indeed, PS/PMMA bilayers of good quality could be produced with methylecyclohexane within the PS molecular weight and thickness limitations observed. Overall, the only advantage of methylecyclohexane over 1-chloropentane for the purpose of casting PS bilayers is related to the solubility of the bottom PMMA layer. PMMA with a molecular weight less than ~3 kg/mol will dissolve in 1-chloropentane, but will not dissolve in methylecyclohexane. Thus, PS can be spun onto lower molecular weight PMMA from methylecyclohexane than from 1-chloropentane. We note that both selective solvents also produce good PS films when the PS is spun directly onto P2VP films. It is important to note that methylecyclohexane is a selective solvent for a set of different polymer pairs than 1-chloropentane. Here, we are primarily concerned with the PS and PMMA system, but methylecyclohexane might be the selective solvent of choice for other polymer combinations.

CONCLUSIONS

1-chloropentane produces spun cast PS films with a comparable RMS roughness as those spun from toluene. Smooth, sharp interfaces between bilayers can be produced from spin casting of PS from 1-chloropentane directly onto PMMA, as observed by SFM and DSIIMS. The interface between PS/P2VP bilayers is also sharp as observed with SFM. There is no significant reduction in thickness or roughening after spin casting.
casting the upper PS layer and subsequent removal with a known selective solvent. 1-chloropentane thus preserves a bottom layer consisting of either P2VP or PMMA.

In addition to extending the fabrication ability to very thin and very low molecular weight PS films, direct casting of PS/PMMA bilayers is particularly important for the study of planar model systems that involve watersensitive reactive functional groups. Some of us are in the process of exploiting this advantage of the direct casting method in studies of the reaction kinetics of endfunctionalized PS and PMMA that includes the water-sensitive acyl chloride moiety.34

Candidate solvents for directly casting bilayer systems other than PS/PMMA have to satisfy the constraints of not only being a selective solvent but also to produce smooth films. Our results show that to satisfy the latter constraint, the solvent will most likely have to have a low vapor pressure. Our results are thus not limited to the capricious PS/PMMA system, but should provide guidance about the suitability of selective solvent for directly casting layers structures in general.

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REFERENCES AND NOTES

16. This process is also often referred to as spin coating. However, we are interested in the polymer film itself and in investigating the system variables that produce a high quality polymer thin film. This corresponds to a vantage point that emphasizes polymer solution aspects, rather than a substrate vantage point that emphasizes substrate property modifications (e.g. protective coating, friction reduction, etc.).
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