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ORIGINAL CONTRIBUTION

S. Affrossman
M. Stamm

The effect of molecular weight on the topography of thin films of blends of poly(4-bromostyrene) and polystyrene

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S. Affrossman (✉)
Department of Pure
and Applied Chemistry
University of Strathclyde
Cathedral Street
Glasgow G1 1XL, UK
e-mail: s.affrossman@strath.ac.uk
Tel.: +44-141-5482299
Fax: +44-141-5484822

M. Stamm
Institut für Polymerforschung
Dresden e.V., Hohe Strasse 6
Postfach 12 04 11 01005 Dresden
Germany

Abstract Blends of polystyrene and poly(4-bromostyrene) phase-separate during spin-casting onto silicon wafers to give a thin film with islands of poly(4-bromostyrene) in a sea of polystyrene. Variation of the molecular weights of the blend components shows that the poly(4-bromostyrene) and polystyrene influence the film structure in different ways. For poly(4-bromostyrene) of a given molecular weight, the ratio of the observed feature height to the overall film thickness remained constant as the film thickness increased. Moreover, the mean height of the topographical features was independent of the polystyrene but decreased with the molecular weight of the brominated polymer. It is concluded that the substrate–poly(4-bromostyrene) interaction dominates the formation of topography and consequently, though the islands are poly(4-bromostyrene), the mean height of the topographical features is greater the lower the molecular weight of the brominated polymer. The polystyrene has a secondary role, altering the thermodynamics or viscosity of the blend, thereby controlling the number of islands formed: the higher the molecular weight of the polystyrene the greater the number of islands.

Key words Polymer blends · Thin films · Topography · Polystyrene · Molecular weight

Introduction

The surface of thin films of partially compatible polymer blends may exhibit roughness because of phase separation during casting and the resulting topography has been studied for films of several binary polymer mixtures [1–7]. The film structure depends on the various physical forces in the system during casting, i.e. polymer–polymer, polymer–solvent and polymer–surface interactions, combined with the effects of restricted polymer diffusion as the solvent evaporates. Systematic variation of the blend component compatibility has shown that the extent of preferential segregation of one component to the polymer–air interface and the appearance of topography are related to the strength of the polymer–polymer interaction [6]. Solvent–polymer interactions also influence the structure and it has been reported that changing the solvent from good to poor for one component leads to an inversion of the topography [4]. With all the systems the topography varies with blend composition and it is apparent from the studies that the changes in topography frequently follow a trend, i.e. at low concentrations of one component, islands of that component are observed. At high concentrations the islands coalesce to form a sheet with holes, whilst at the composition where the islands start to coalesce a ribbonlike structure is observed.

The solvent is not essential for the development of topography. Ermi et al. [5] have shown that the topography can be observed in films which have been freed of solvent by heat treatment. Further, the film can be cycled between smooth and rough structures by changing the temperature. The same sequence of island–ribbon–sheet topography with change in blend composition, observed for the solvent-cast films, was obtained with the solvent-free system. Ermi et al. [5] also showed that the topography obtained with thin films of solvent-free polystyrene–poly(vinyl methyl ether) blends correlated with the bulk polymer phase behaviour, with the critical concentration on the bulk phase diagram corresponding to the composition of the thin film giving the most pronounced ribbonlike structure .

The shapes of the bulk phase binodal/spinodal curves depend on the molecular weights of the components [8], therefore, for thin blend films the molecular weight provides a tool for the variation of the polymer–polymer interactions. Even if the substrate surface and any solvent are unchanged, the polymer–substrate interactions will also depend on the polymer weight. Consequently, the molecular weight is an important parameter in determining the structure of thin blend films and this work examines the effect of the variation of the relative molecular weight on the topography of thin solvent-cast films of an incompatible blend, polystyrene–*b*–poly(4-bromostyrene), in the region of island formation.

The polystyrene–*b*–poly(4-bromo$_x$styrene) system, $0 \le x \le 1$, has been extensively studied. Early work by Bruder and Brenn [9] showed the sensitivity of thin films of the blend to the substrate surface chemistry, a property which was later exploited by Krausch et al. [10] to plate one component preferentially on preformed areas of a substrate. The glass-transition temperatures, T_g, of polystyrene and poly(4-bromostyrene) are about 103 and 142 °C, respectively [11]. Annealing the initial metastable cast films above the T_g of poly(4-bromostyrene) does not remove the features but causes polymer segregation and changes in the feature profiles [6, 12]. The film structure of the as-cast unannealed polystyrene–*b*–poly(4-bromo$_{1.0}$styrene) consists of adjacent blocks of the mainly pure components with little surface segregation [2]; therefore, it is postulated that the influence of the substrate chemistry is most apparent in the virgin film. Thus, the present study investigates the effect of molecular weight on the structure of unannealed films of polystyrene–*b*–poly(4-bromo$_{1.0}$styrene).

Experimental

Methods

The silicon wafer substrates were cleaned with a sulphuric acid–peroxide mixture, which leaves an oxide surface. Toluene solutions of blends were made containing 40% w/w poly(4-bromostyrene) and with polymers of various molecular weights. Films were cast by dropping 50 μl 5% w/w polymer blend solution onto a spinning wafer in one aliquot. The rate of rotation was selected between 1000 and 4000 rpm. The film thickness was determined using atomic force microscopy (AFM) by profiling over a scratched groove.

AFM imaging was carried out using a Digital Instruments Nanoscope III SPM controller with a Multimode AFM head (Digital Instruments, Santa Barbara, Calif., USA) and a type J scanner (lateral scan range of 125 μm, 5 μm z range). Images were recorded in contact mode using "v" shaped silicon nitride cantilevers with 200-μm arms and a nominal force constant of about 0.12 N m^{-1}. Typical scan rates were between 0.2 and 2.0 Hz. Throughout the study, the tip–sample force used was the minimum compatible with satisfactory imaging of the surface. No image smoothing or noise removal was carried out, but the 5 × 5-μm^2 images were planarised. The 10 × 0.625 or 20 × 1.25-μm^2 images of the scratched films were analysed without image processing.

Materials

The parameters of the low polydispersity polystyrenes used are listed in Table 1. Molecular weights were obtained by gel permeation chromatography utilising a polystyrene standard. Poly(4-bromostyrene) samples were obtained by bromination of polystyrene with standard procedures [2]. With the exception of the polystyrene (M_w 196 kg mol^{-1}) obtained from Polymer Laboratories, UK, the polymers were synthesised at the Max Planck Institute fur Polymerforschung, Mainz. Polystyrenes were used in the hydrogen or deuterated form. Blends are designated as BrS*X*–PS*Y*, where *X* and *Y* are the kilogram molecular weights of the poly(4-bromostyrene) and polystyrene, respectively.

Results and discussion

Estimation of typical film dimensions

A 3D topograph of a typical blend film with the island features varying in height and width is shown in Fig. 1a. The spectrum of heights (Fig. 1b) shows two peaks corresponding to the range of valley and island heights, respectively. The difference in the peak maxima positions was taken as the mean feature height. The area fraction covered by the islands was obtained from the integral of the peak corresponding to the islands relative to the integral of the total height spectrum. For consistency, the spectrum was partitioned into an island peak and a valley peak midway between the peak maxima.

In order to estimate the film thickness, the film was scratched and a topograph taken over the edge of the scratch. The previously described procedure for

Table 1 Parameters of the low polydispersity polymers used

Polymer	Origin	M_w (kg mol^{-1})	M_w/M_n
Poly(4-bromostyrene)	Max Planck Institute, Mainz	106	1.05
Poly(4-bromostyrene)	Max Planck Institute, Mainz	255	1.04
Poly(h_8-styrene)	Polymer Laboratories Ltd., UK	196	1.02
Poly(d_8-styrene)	Max Planck Institute, Mainz	720	1.10
Poly(h_8-styrene)	Max Planck Institute, Mainz	1251	1.11

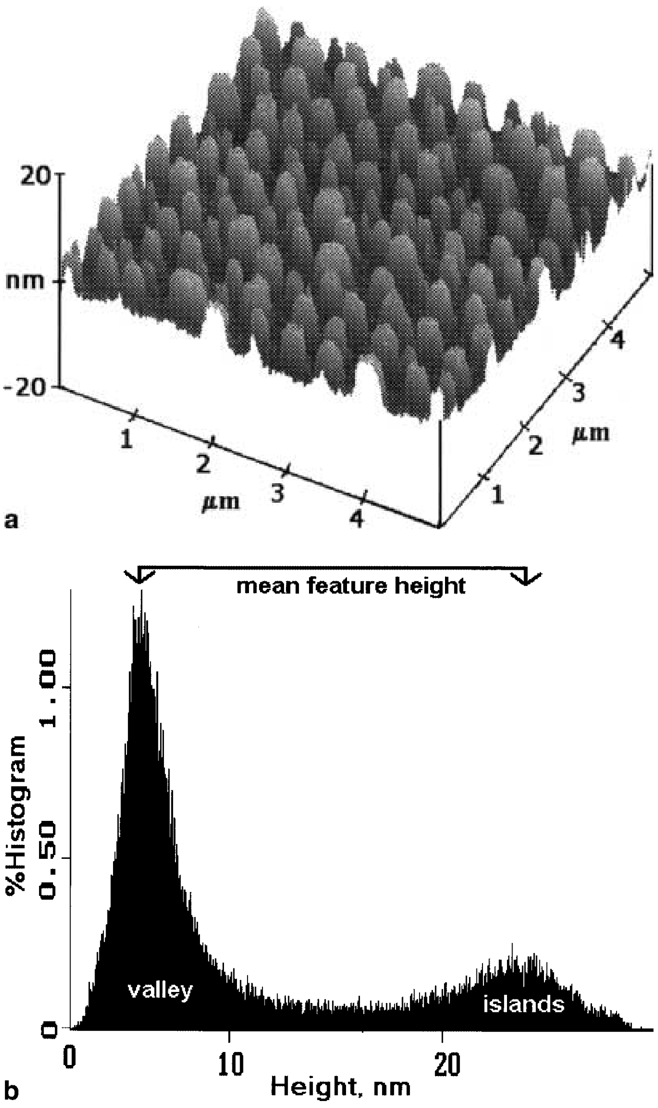

Fig. 1 Atomic force microscopy (*AFM*) data for a typical blend: **a** 3D topograph; **b** feature height spectrum

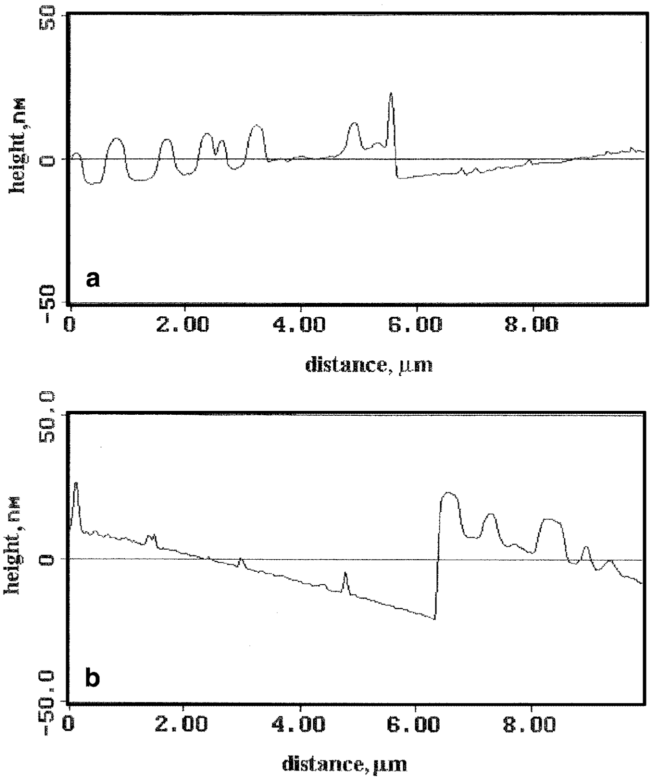

Fig. 2 AFM sections over edge of scratched film: **a** low-molecular-weight blend, BrS106–PS196; **b** high-molecular-weight blend, BrS255–PS1251

estimating the mean difference in the height of the valley and the island features was found to be impractical for determining the mean difference in the height of the substrate surface and the top of the film. The difficulties were attributed to the greater height differential, the increased scan length and, especially, any wall of polymer created at the sides of the trench during scratching, which aggravated the nonplanarity of the sample. Typical cross sections across a scratched surface of low-molecular-weight and high-molecular-weight blends are given in Fig. 2. The profiles show a relatively smooth substrate surface then a sharp rise to the polymer surface. The latter appears corrugated as the profile goes through island features. Taking cross sections of the scan, it was possible to allocate a line corresponding to the bottom of the lowest valleys, and the difference in height between this and the substrate surface, allowing for any tilt, was taken as the thickness of the base film, i.e. less the topographical features. The total film thickness was obtained by adding the mean feature height to the base thickness. Even though the latter measurement was obtained at several points along the scratch, the error was greater than for the mean feature height, which was obtained by averaging data over many islands in a 5×5-μm^2 area. The accuracy of the total thickness was estimated to be about ±10%.

Relationship between spin rate and film thickness

Figure 3 shows the effect on the total film thickness of increasing the spin rate for the two blends BrS106–PS196 and BrS255–PS1251, which cover the extremes of molecular weight used. The data show that the total film thickness decreases with spin speed, as expected. Within the error of measurement, both blends fit the same curve, indicating that the spin speed is a more important factor than the molecular weight of the components at the solution concentration used.

Relationship between feature height and film thickness

The mean feature height is plotted against the total film thickness for the blends BrS106–PS196, BrS106–PS720, BrS255–PS196 and BrS255–PS1251 in Fig. 4. There is an apparently linear relationship between the mean feature height and the total film thickness, i.e. the mean feature height is a constant fraction of the total thickness for a given blend but, unlike the thickness, it depends on the molecular weight. The data for PBrS106–PS196 and PBrS106–PS720 coincide, whilst blends PBrS255–PS196 and PBrS255–PS1251 coincide on a line displaced to lower mean feature heights. The conclusion is that the mean feature height is determined only by the molecular weight of the brominated polymer, even if the polystyrene component relative weight is increased sixfold.

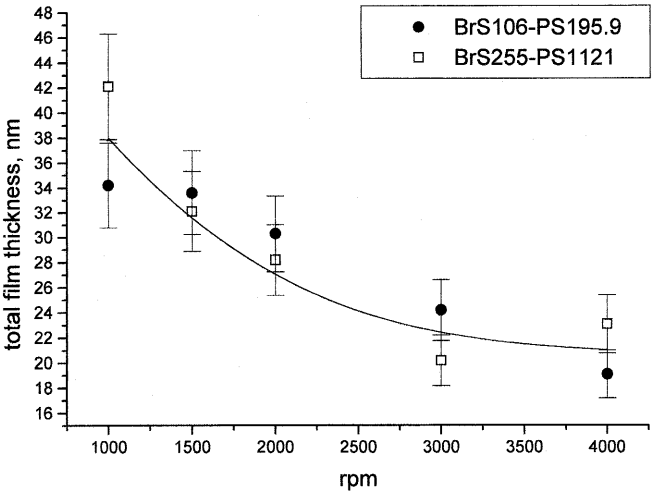

Fig. 3 Total film thickness versus casting speed for blends BrS106–PS196 and BrS255–PS1251

The structure of thin films of blends of polystyrene and poly(4-bromostyrene) can be described as adjacent blocks of the almost pure polymer components [2]. It follows that the relative volume occupied by the components may be obtained from the heights and the area occupied by the features. If the mean height of the features is a constant fraction of the film thickness for a given blend, then the area fraction occupied by the poly(4-bromostyrene) should also be constant, assuming that the shape of the blocks does not change. The area fractions of poly(4-bromostyrene) are shown in Fig. 5 plotted against film thickness for the blends BrS106–PS196 and BrS255–PS1251. The poly(4-bromostyrene) area fractions are approximately constant over the range of film thickness, but the value depends on the molecular weight of the brominated polymer.

Inspection of a section of a typical feature of the BrS255–PS1251 blend (Fig. 6a) shows that the blocks have steep sides and that the tops are relatively flat. The volume fraction of the poly(4-bromostyrene) calculated from measurement of the area fraction occupied by the islands and the mean step height is 0.36. The relative densities of poly(4-bromostyrene) and polystyrene are 1.34:1; thus, the volume fraction of poly(4-bromostyrene) in a bulk 40% w/w mixture is 0.33, which compares well with the AFM value of 0.36, considering the errors in the latter measurements.

A similar calculation for the BrS106–PS196 blend gave a poly(4-bromostyrene) relative volume of 0.39. Part of the discrepancy between this value and the bulk volume fraction may be the result of a slight change in the shape of the features of the lower-weight blend

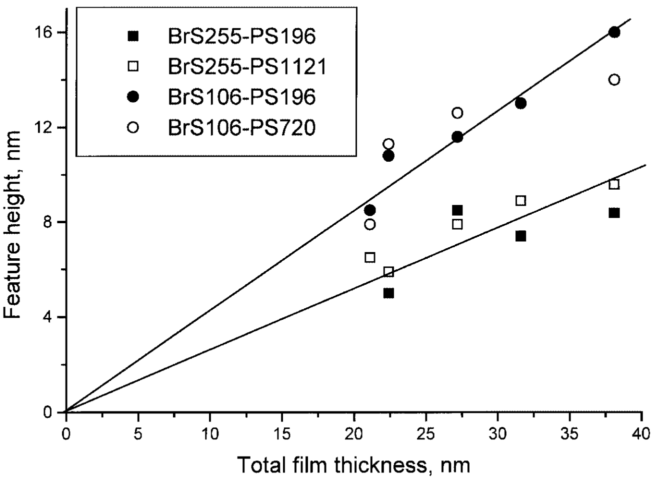

Fig. 4 Mean height of islands versus total film thickness for blends BrS106–PS196, BrS106–PS720, BrS255–PS196 and BrS255–PS1251

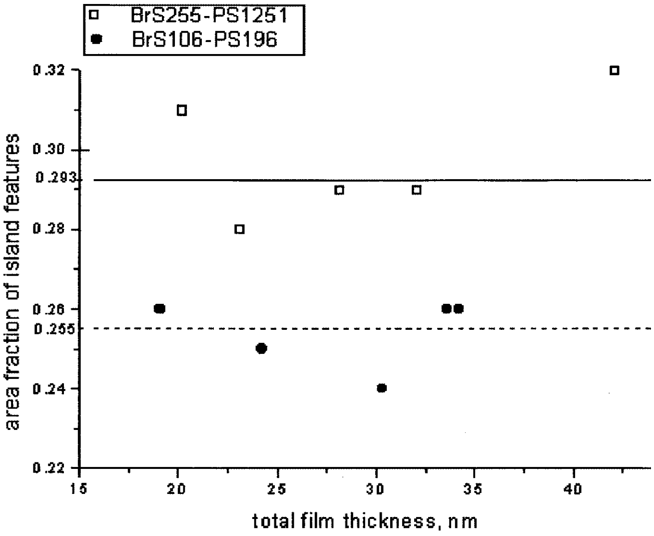

Fig. 5 Area fraction occupied by poly(4-bromostyrene) versus total thickness for blends BrS106–PS196 and BrS255–PS1251

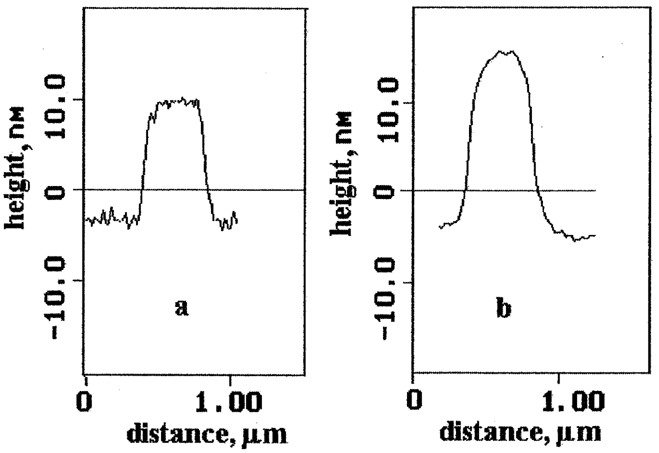

Fig. 6 Profiles of typical islands of blends **a** BrS255–PS1251 and **b** BrS106–PS196

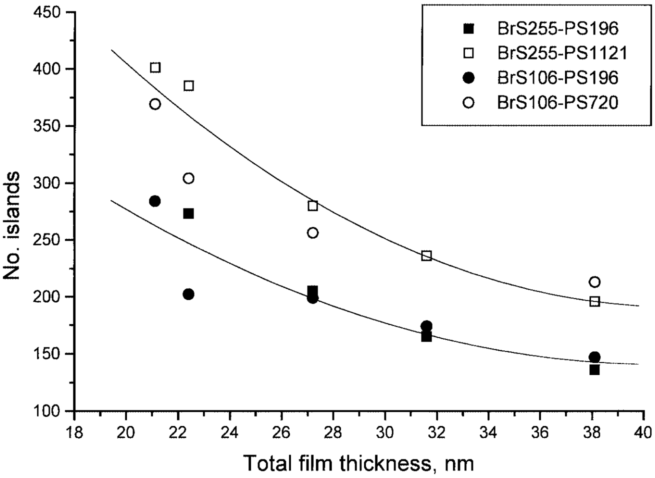

Fig. 7 Number of islands in 5-μm^2 area versus total thickness for blends BrS106–PS196, BrS106–PS720, BrS255–PS196 and BrS255–PS1251

(Fig. 6b): the blocks are more rounded than the square model assumed. The blocks may also be less than 100% single component. The lower-molecular-weight poly(4-bromostyrene) will be more mobile than higher-weight polymers and it is pertinent that annealing such films produces rounded features [6].

Poly(4-bromostyrene) of a given molecular weight occupies a fixed fraction of the surface irrespective of the molecular weight of the polystyrene blend component. Increasing the thickness of the film gives a corresponding increase in the height of the blocks, but does not alter the area occupied. These data lead to the conclusion that the mechanics of film formation is dominated by the adsorption of the brominated polymer. The relative feature height is determined only by the area left for the fixed amount of polystyrene. Increasing the molecular weight of the poly(4-bromostyrene) increases the fraction of the area occupied, consistent with the greater affinity of high-weight molecules for adsorption from solution compared to low-molecular-weight homologues, and thus decreases the relative height of the block.

Though the poly(4-bromostyrene) controls the area fraction occupied and consequently the feature height, the polystyrene does influence the film structure. The number of islands for various blends is plotted against the film thickness in Fig. 7. The data show that the number of islands depends on the film thickness, but there is also a molecular-weight effect. The data divide into two groups: blends BrS106–PS196 and BrS255–PS196 lie close to one line and blends BrS106–PS720 and BrS255–PS1251 lie near another line displaced to a higher numbers of islands. The number of islands does not depend on the poly(4-bromostyrene) but does depend on the polystyrene molecular weight, in contrast to the relative area results. An increase in the molecular weight of the polystyrene results in an increase in the number of islands formed, but does not result in a change in their aspect ratio.

There are two factors which could influence the number of islands formed. Firstly, the shape/position of the binodal/spinodal curves may change with molecular weight, thereby changing the extent of the displacement of the fixed blend composition from the equilibrium curve. Unfortunately, little information is available for the bulk phase behaviour of the poly(4-bromostyrene)–*b*–polystyrene system, other than a phase diagram for a polystyrene–poly(styrene-*co*-4-bromostyrene) blend which exhibits upper critical solubility temperature behaviour [13]. Secondly, the film is formed by the diffusion of the polymers into their separate blocks at the stage when the solvent is being rapidly removed. There will be local diffusion giving nuclei of poly(4-bromostyrene), which can grow by diffusion from the less immediate surroundings and by coalescence. Increasing the molecular weight of the polystyrene will hinder the diffusion of the poly(4-bromostyrene) and, therefore, increase the number of islands at the stage when the film freezes.

Generally, the structures generated during spin-coating of polymer blends of mainly incompatible components are controlled by processes which partially compete against each other. Initially, segregation of components to substrate or air surfaces may take place, depending on the concentrations in the remaining solution. This process may be expected to be in competition with polymer phase separation, which occurs during complicated nonlinear flow processes when a thin solution film forms and solvent further evaporates. Structure formation is then determined by a complicated path through the ternary phase diagram, where concentration changes with solvent evaporation and lateral phase separation. The differing solubilities and diffusion coefficients of the components also have to be considered. In particular, in the later stages the processes are far from equilibrium and the system becomes frozen, because the rapid evaporation of solvent reduces chain movement. A theoretical treatment is very difficult [14]. Nevertheless, it has been shown that with a careful choice of system it is possible to recognise trends arising from a process which dominates film formation.

Conclusions

The structure of thin cast films of polystyrene–*b*–poly(4-bromostyrene), on silicon wafers retaining the oxide, is determined primarily by the interaction of the brominated polymer with the substrate. Consequently, though the islands are poly(4-bromostyrene), the mean height of the observed topographical features is greater the lower the molecular weight of the poly(4-bromostyrene).

The polystyrene has a secondary role, altering the thermodynamics, or viscosity, of the blend, thereby controlling the number of islands formed.

These results provide some insight into the complicated processes which take place during spin-coating of incompatible blends.

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