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Solvent swelling of roll-cast triblock copolymer films

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Polystyrene–polybutadiene–polystyrene triblock copolymers were roll-cast from toluene solutions to form globally oriented films. As-processed films, containing process-related residual stresses, were exposed to solvent vapours. Three solvents were used in this study: toluene, which is a non-preferential solvent for polystyrene and polybutadiene; methyl-ethyl-ketone, which is a preferential solvent for the polystyrene blocks; and hexane, which is a preferential solvent for the polybutadiene block. Microstructural changes accompanying the solvent swelling of films with cylindrical and lamellar morphology were monitored using two-dimensional small angle X-ray scattering. Solvent swelling significantly improved the symmetry of the hexagonal packing of the cylindrical domains, which was initially distorted due to the roll-casting flow field. Solvent swelling was also found to improve the long range order in roll-cast film with lamellar morphology. Various phenomena were found to accompany the swelling and deswelling of films with both cylindrical and lamellar morphology with the three different solvents used. Especially intriguing results were observed for the case of swelling both morphologies in hexane. For films with a lamellar morphology, after 1 h of swelling and 2 h of subsequent deswelling the d-spacing decreased by 18%. For films with cylindrical morphology, a similar decrease of 9% was observed. Molecular models are presented to explain these microstructural changes, that are closely linked to the mobility of the glassy polystyrene blocks, the relaxation of process-related stress and the ability of the polybutadiene–polystyrene junctions at the interfaces to reposition and accommodate volume changes. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: block copolymers; roll-casting; swelling)

INTRODUCTION

The study of systems containing a block copolymer swollen with a low molecular weight solvent is well documented in the literature, and is briefly reviewed here. Most of the previous work in this area has addressed diblock copolymers swollen most often in a solvent preferential for one of the blocks and less frequently in a non-preferential solvent. Very little is reported in the literature on the swelling of triblock copolymers. All of the studies, with the exception of two, have addressed unoriented polydomain copolymers.

In most cases, the microstructural changes that accompany solvent swelling of a block copolymer are related to the interfacial area per junction, σ_{AB}, which is shown schematically in *Figure 1* for a triblock copolymer with lamellar morphology. The top of the figure depicts a molecule in a bridge configuration. Two molecules in loop configurations are shown at the bottom of the figure. It has been shown that the ratio of loops to bridges in lamellar forming triblock copolymers is 60:40[1].

For the simple case of a lamellar morphology, the volumes, v_A and v_B, occupied by each block in the unswollen polymer are given by:

$$v_A = v_{A1} + v_{A2} = \sigma_{AB} l_A$$

$$v_B = \sigma_{AB} l_B \qquad (1)$$

in which l_A and l_B are the thicknesses of the two phases, and v_{A1} and v_{A2} are the contributions of each of the two end blocks to the total 'A' volume of each molecule.

If, for example, a solvent which is ideally preferential for the B block is added to the system, its volume, v_s, is added only to that of the B block resulting in:

$$v_A = \sigma'_{AB} l'_A$$

$$v_B + v_s = \sigma'_{AB} l'_B \qquad (2)$$

in which the primed terms represent the swollen state.

In order to compensate for the additional volume, v_s, either σ'_{AB}, l'_B or both must be larger than σ_{AB} and l_B respectively. When the A and B blocks are above their respective glass transition temperatures both the area per junction and the thickness of the B layer may change. When σ'_{AB} is larger than σ_{AB}, l_A must decrease to maintain a constant value of v_A. However, in a case where the A block is below its glass transition temperature, the locations of the junctions between the blocks remain fixed as do the values of σ_{AB} and l_A. In such a case the additional volume due to the preferential solvent can only result in an increase in l_B.

If instead, a non-preferential solvent is added to the system, both the A and B phases gain additional volume, (v_{sA} and v_{sB}, respectively):

$$v_A + v_{sA} = \sigma'_{AB} l'_A$$

$$v_B + v_{sB} = \sigma'_{AB} l'_B \qquad (3)$$

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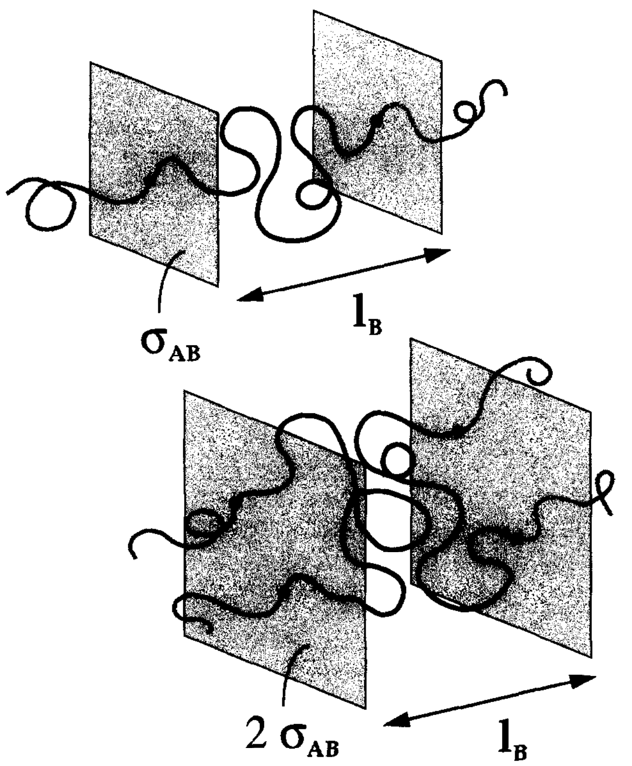

Figure 1 A schematic representation of the interfacial area per junction, σ_{AB}, for a triblock copolymer with lamellar morphology. The top of the figure depicts a molecule in a bridge configuration. Two molecules in loop configurations are shown at the bottom of the figure

In this case eventually after sufficient non-preferential solvent is added, we expect $\sigma'_{AB} > \sigma_{AB}$, $l'_A > l_A$ and $l'_B > l_B$. However, in the case of a stressed structure (e.g. from processing), initially only σ_{AB} might increase, whereas l_A and l_B decrease due to chain relaxation.

For reasons of simplicity, the examples presented above have referred to a lamellar morphology. Similar, yet somewhat more complicated expressions may be developed for a triblock copolymer with cylindrical morphology.

We note that morphological changes that occur upon swelling may be due not only to volume changes. Since preferential and non-preferential solvents may change the effective value of the interaction parameter χ_{AB}, the morphology may change due to variations in the segregation power between the two blocks.

One of the earliest studies in the field that we are aware of is by Douy *et al.*[2] who used small angle X-ray scattering to study the structure of several diblock copolymers in preferential solvents. For a solution of a polystyrene–polyisoprene diblock copolymer in isoprene monomer, they reported a spherical morphology for which the cubic lattice parameter increased, and the diameter of the spheres decreased, upon increasing the solvent concentration from 10 to 40 wt%. They also studied solutions of polyisoprene-poly-2-vinylpyridine diblock copolymer in ethyl acetate, which is a preferential solvent for the polyisoprene block, and found that the poly-2-vinylpyridine formed cylindrical domains for solvent concentrations ranging from up to 38 wt%. The concentration was varied by slow solvent evaporation. Higher solvent concentrations resulted in a decrease in the distance between the cylinders and a decrease in the cylinder diameter. Polystyrene–polyisoprene and polystyrene–polybutadiene diblock copolymers with lamellar morphology were studied in toluene solutions, which Douy *et al.*[1] refer to as a preferential solvent for polystyrene. These solutions were studied in the range of 2–42 wt% solvent. As the solvent concentration increased, an increase in the thickness of the more soluble polystyrene layers was observed, which was offset by a smaller decrease in the thickness of the polyisoprene layers, resulting in a net increase in the inter-lamellar d-spacing. The authors offered no explanation to accompany their findings.

Additional work in this area was presented in a paper in English by Skoulios[3], who co-authored the first account of the work which was published earlier in French[4]. The swelling of a lamellar polystyrene-poly-2-vinylpyridine diblock copolymer was studied using toluene as a preferential solvent for the polystyrene block. The inter-lamellar d-spacing was measured by small angle X-ray scattering, and the thickness of each layer was calculated from geometrical considerations using the weight fraction of the solvent and its partition coefficient for the two blocks. The inter-lamellar d-spacing was observed to increase only slightly upon swelling to a content of 35 wt% solvent, whereas the thickness of the polystyrene layers greatly increased (by about 50%) due to polystyrene's affinity for toluene, whereas the thickness of the poly-2-vinylpyridine layers greatly decreased (by about 40%). It was proposed that the thickness of the poly-2-vinylpyridine layers decreased to compensate for the increase of σ_{AB}. Swelling a polystyrene-poly-2-vinylpyridine diblock copolymer with cylindrical polystyrene domains in octanol (a preferential solvent for the poly-2-vinylpyridine block) also resulted in a decrease in cylinder diameter as a result of the lateral spreading of the junctions at the cylinder surface.

Hashimoto and co-workers[5–10] conducted a series of studies in which small angle X-ray scattering was used to probe the microstructure of several systems consisting of a diblock copolymer in a preferential or a non-preferential solvent. In the first paper in that series[5], a polystyrene–polybutadiene diblock copolymer in tetradecane (preferential for the diene block) was studied as a function of temperature and polymer concentration. For polymer concentrations in the range 8–60 wt%, the morphology of the system was reported to be polystyrene spheres in a polybutadiene matrix. Increasing the polymer concentration in that range resulted in a decrease in the distance between neighbouring spheres an in a slight increase in sphere diameter. At a polymer concentration of 60 wt%, a transition to a cylindrical morphology was observed.

Toluene was chosen as a non-preferential solvent in a study of solutions of a polystyrene–polyisoprene diblock copolymer with equal block molecular weights[7]. Samples for SAXS were taken at various time intervals from a Petri dish, initially containing a relatively dilute solution of 9.5 wt% polymer, from which the solvent was allowed to evaporate over a period of 50 h. Additional samples were taken to determine the polymer concentration. A lamellar morphology was observed to develop at concentrations above 20 wt% polymer. For polymer concentrations below 70 wt%, the lamellar d-spacing was found to increase with increasing polymer concentration (in spite of the deswelling), and it was proposed that this was due to increasing segregation power between the two blocks as the polymer concentration increased in presence of a neutral solvent. That is, as more solvent leaves the system, the junction points at the interfaces move closer to each other in order to decrease the interfacial area, resulting in an increase of domain size normal to the interface, i.e. an increase in d-spacing. For polymer concentrations above 70 wt% polymer, the authors claimed to observe a decrease in d-spacing with increasing polymer concentration, which they base upon only two data points (at 70 and 100 wt% polymer). However, in view of the proximity of the d-spacings measured at these concentrations and of the size of the error bars in *Figure 6* in Ref.[7], one might well argue that the d-spacing maintains a constant value in this range. The authors write that the 'decrease' in the d-spacing in this range is due to the locations of the junctions at the interface being frozen in, which results in a shrinkage in domain size perpendicular to the interface upon further solvent removal.

The study of solutions of polystyrene–polyisoprene diblock copolymers with lamellar morphology in a neutral solvent was extended to lower polymer concentrations using dioctyl phthalate[8]. The dependence of the inter-lamellar d-spacing on polymer concentration was similar to that observed in the study using toluene[7].

In a more recent study[10], the same research group studied toluene solutions of polystyrene–polyisoprene diblock copolymers with morphologies ranging from spheres to lamellae. They found that the d-spacings for each morphology increased with increasing polymer concentrations below the vitrification concentration, and levelled out or decreased for polymer concentrations above the vitrification concentration. The vitrification concentration is the concentration at which the glass transition temperature of the polystyrene microdomains reaches room temperature, and was measured by differential scanning calorimetry (DSC) to be around 70–75% polymer by volume for toluene solutions.

There are several very significant differences between the studies by Hashimoto and co-workers and the present study: the starting point for the Hashimoto group studies is a solution of an unoriented diblock copolymer, the structure of which is monitored by SAXS as the polymer concentration increases due to solvent evaporation. Those studies were conducted for relatively low polymer concentrations from about 20 wt% up to about 70 wt%. In contrast, in the present study we start with a well oriented triblock copolymer containing no solvent, and we monitor both the uptake and discharge of solvent. Our study is conducted for relatively high polymer concentrations of about 70 wt% and higher.

The swelling of oriented polystyrene–polybutadiene–polystyrene triblock copolymers with lamellar[11] and cylindrical morphologies[12] has been studied previously by Keller and co-workers. Oriented samples were produced by melt extrusion and were subsequently annealed at 150°C.

In the first part of the study[11], oriented samples with lamellar morphology were allowed to swell in vapours of hydrocarbons from the series hexane–dodecane, preferential for the polybutadiene middle block. Dimensional changes were monitored using an optical microscope, and were found to be highly anisotropic. Two regions of swelling were reported. For short swelling times (e.g. up to 2 h when swelling with decane), a reversible process was observed in which the sample dimensions perpendicular to the lamellae increased while no change was observed parallel to the lamellae. Upon deswelling, the sample dimensions returned to their original values. Beyond this reversible region, the changes in the dimensions of the samples were not reversible upon swelling and subsequent deswelling. In this irreversible region, some increase in the dimensions parallel to the lamellae was noted accompanied by a smaller increase in the dimensions perpendicular to the lamellae.

Similar experiments were conducted on oriented samples with cylindrical morphology[12] using hexane, octane and decane. For all three solvents, a dimensional increase in the direction perpendicular to the cylinders preceded a dimensional increase in the direction parallel to the cylinders. The swelling process is initially reversible. However, as in the case of swelling lamellae[11], for long swelling times, the changes in the dimensions of the samples with cylindrical morphology were not reversible upon swelling and subsequent deswelling.

In addition to measuring the changes in sample dimensions, the swelling of the samples with cylindrical morphology was also measured by small angle X-ray scattering. The authors hypothesised that the evolution of the scattering pattern during swelling might indicate cylinder break-up into columns of spheres. Transmission electron microscopy was also used to probe the structures formed upon swelling. Sections for transmission electron microscopy were prepared from samples that had been swollen and then dried out for 2 days since X-ray scattering indicated that the structure of these samples remained unchanged from that of the swollen samples. Micrographs viewing parallel to the extrusion direction showed long-range hexagonal packing of cylindrical polystyrene microdomains. Viewing normal to the extrusion direction showed an arrangement of dots, which were mostly arranged with local hexagonal order. More complex structures were also seen when viewing normal to the extrusion direction. Samples swollen for longer periods of time showed evidence of a square lattice in both parallel and perpendicular directions. The authors were not able to determine the final structure, but conclude that in the reversible region of swelling the polystyrene cylinders remain intact, whereas in the irreversible region of swelling the cylinders undergo either a transformation to spheres or to a more complex network of cylindrical morphology.

A much more recent study[13] has also addressed solvent swelling of oriented block copolymers. In this study, the penetration of pure and mixed solvents into thin films of two polystyrene–polymethyl methacrylate diblock copolymers was investigated by neutron reflectivity. Thin films were spin-coated onto silicon substrates from toluene solutions and were subsequently annealed at 170°C to allow the formation of a multilayered lamellar structure parallel to the substrate. The films were then placed in a solvent saturated environment for 4 h prior to measurement. In one set of experiments, cyclohexane (a preferential solvent for the polystyrene block) was used and in a second set of experiments, a mixture of 75/25 methanol/toluene (which swells both blocks) was used. In the case of cyclohexane, only the top most polystyrene layer of the film was swollen, with no penetration into the underlying layers. The 75/25 methanol/toluene mixture was found to penetrate the layers to different extents as a function of depth. The authors pointed out that nearly all of the swelling occurs in the direction normal to the lamellae due the lateral confinement of the thin films by the substrate.

In summarising the results of previous studies, we find that for a diblock with lamellar morphology, increasing the content of a *preferential* solvent up to 30–40 wt% results in an increase in the inter-lamellar d-spacing[2–4,7]. Higher solvent contents are reported to lead to a decrease in the interlamellar d-spacing[7,8]. Similar results are also observed when swelling a lamellar morphology with a *non-preferential* solvent[10]. Swelling a cylindrical morphology with a *preferential* solvent up to about 35 wt% solvent results in a decrease in cylinder diameter[2–4] and in the distance between cylinders[2]. Swelling a cylindrical morphology with a *non-preferential* solvent results in an increase in the distance between cylinders up to about 30 wt% solvent and results in a decrease in the distance between cylinders for solvent concentrations greater than 30 wt%[10].

This brief review of the literature has focused on swelling block copolymers with low molecular weight non-polymeric solvents, and has not addressed the subject of swelling a block copolymer with a homopolymer. Additional information on the latter may be found, for example, in references[14,15].

The present paper focuses on the solvent swelling of oriented triblock copolymer films that were prepared by roll-casting. It complements our previous study[16] that dealt with the thermal annealing of roll-cast films. During the roll-casting process, a block copolymer solution is processed between rotating cylinders, while at the same time the solvent is evaporated at a controlled rate. As the solvent evaporates, the polymer concentration increases, and the block copolymer microphase-separates into globally oriented structures. For detailed information on roll-casting we refer the reader to some of our other studies[17–19].

Depending on the composition of the block copolymers used, the roll-cast films in this study consisted of uniaxial cylindrical polystyrene microdomains assembled on a hexagonal lattice in a polybutadiene matrix, or of unidirectional lamellar domains of polystyrene and polybutadiene.

EXPERIMENTAL

Films of polystyrene–polybutadiene–polystyrene triblock copolymers were cast from toluene solutions containing 40 wt% polymer, using the roll-casting technique. Films were prepared from two commercial block copolymers manufactured by Dexco Polymers (12012 Wickchester, Houston, TX 77079). The first material used was Vector grade 8550-D, in which the molecular weight of each of the polystyrene end blocks was 10 700, and that of the polybutadiene middle block was 52 000[20]. Vector 8550-D contains 28 wt% polystyrene so that upon microphase separation from a neutral solvent, polystyrene cylinders form in a polybutadiene matrix. The other material employed was Vector grade 4461-D, in which the molecular weight of each of the polystyrene end blocks was 18 500, and that of the polybutadiene middle block was 45 000[21]. Vector 4461-D contains 45 wt% polystyrene and microphase separates to form alternating lamellae of polystyrene and polybutadiene.

Roll-cast films were dried in a vacuum oven at 50°C for 48 h in order to remove all traces of the solvent. These films were not annealed above the glass-transition temperature of the polystyrene segments of the block copolymer, as is common practice in many studies, and are referred to as 'unannealed'.

The effects of solvent swelling on the roll-cast films were studied at room temperature using small angle X-ray scattering at the National Synchrotron Light Source (Brookhaven National Laboratory). Experiments were performed at a wavelength of $\lambda = 1.54$ Å on the Time-Resolved Diffraction Facility (station X12B) using a custom-built two-dimensional gas delay-line detector (10 × 10 cm, 512 × 512 pixels), interfaced to a real-time histogramming memory system[22].

In situ sample swelling was conducted by exposing unannealed roll-cast films to solvent vapours using a sealed sample chamber containing a solvent reservoir. The reservoir was separated from the main chamber by means of a seal which was opened at the beginning of each experiment (t = 0). Three solvents were used in this study: toluene, which is a non-preferential solvent for polystyrene and polybutadiene; methyl-ethyl-ketone (MEK), which is a preferential solvent for the polystyrene blocks; and hexane, which is a preferential solvent for the polybutadiene block. As the films were swollen, 2-D SAXS patterns were recorded periodically. Swelling lasted between 30 min and 1 h, after which the solvent reservoir was resealed and drained. A 'deswelling' experiment was then conducted, in which the solvent was allowed to evaporate from the swollen sample for up to 2 h during which 2-D SAXS patterns were again periodically recorded. The exposure time for all SAXS patterns was 1 min.

Additional experiments were conducted in order to quantify the increase in the weight of the films during exposure to solvent vapours and the subsequent weight decrease during deswelling. These measurements were accomplished using a Mettler AE 240 balance interfaced to a Thinkmate® personal computer. In each experiment a roll-cast film was placed on the weighing tray, which was within a sealed enclosure inside the balance, and its initial weight was recorded. Solvent was then introduced in to the sealed enclosure, and the weight of the film was recorded as a function of time. Swelling was conducted for a predetermined time, after which the solvent source was removed and a deswelling phase began. Weight measurements were automatically recorded every 10 sec for swelling and deswelling times smaller than 15 min, every minute for times between 15 min and 1 h, and every 5 min for times greater than 1 h.

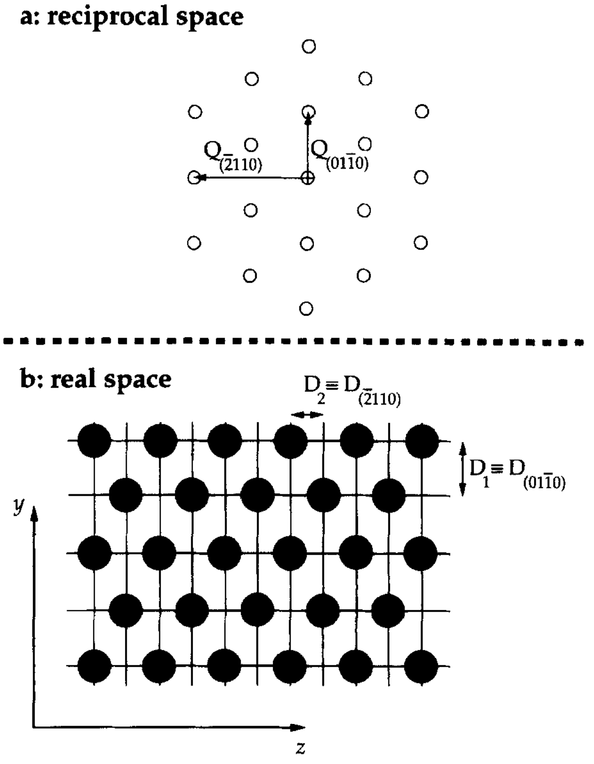

Figure 2 A schematic representation of the first few reflections in reciprocal space (a) of the small angle X-ray scattering pattern of an ideal two-dimensional hexagonal lattice (b). The two scattering vectors, $Q_{(01\bar{1}0)}$ and $Q_{(\bar{2}110)}$, indicated in (a) correspond to the real space d-spacings $D_{(01\bar{1}0)}$ and $D_{(\bar{2}110)}$, shown in (b). These d-spacings are referred to as D_1 and D_2, respectively

RESULTS AND DISCUSSION

Cylindrical morphology

For the analysis of our results we employ the same methodology used in our previous study on the thermal annealing of roll-cast films[16]. *Figure 2a* shows a schematic representation of the first few reflections in reciprocal space of the small angle X-ray scattering pattern of an ideal array of cylinders on a hexagonal lattice, which is schematically pictured in *Figure 2b*. The two scattering vectors, $Q_{(01\bar{1}0)}$ and $Q_{(\bar{2}110)}$, indicated in *Figure 2a* correspond to the real space d-spacings $D_{(01\bar{1}0)}$ and $D_{(\bar{2}110)}$, shown in *Figure 2b*. For the purpose of the analysis of the hexagonal structures of roll-cast films of cylindrical morphology, these d-spacings are referred to as D1 and D2, respectively. For an ideal hexagonal lattice $D1/D2 = \sqrt{3}$.

In all the SAXS experiments conducted, the path of the X-ray beam was oriented parallel to the direction of the flow field created during roll-casting (i.e. tangential to the rolls). We refer here to a coordinate system which is consistent with our previous publications on roll-casting[16–19] in which this direction is termed *x*, the direction normal to the film surface is termed *y*, and the third (neutral) direction is termed *z*.

Figure 3a shows a two-dimensional small angle X-ray scattering pattern of an unannealed roll-cast film of cylindrical morphology before exposure to solvent vapours, which indicates that the $(01\bar{1}0)$ planes of the hexagonal lattice are parallel to the surface of the film (i.e. the *xz* plane).

As we have previously shown[16], small angle X-ray scattering with the beam incident along the [0001] direction of an unannealed roll-cast film indicates distortion of the hexagonal lattice. This can be seen in *Figure 3a* by the fact that the $(01\bar{1}0)$ and the $(0\bar{1}10)$ reflections are further away from the origin than the other four first order reflections. This distortion corresponds in real space to a ratio of D_1/D_2 smaller than $\sqrt{3}$ (i.e. the horizontal $01\bar{1}0$ planes are closer to each other than they appear in *Figure 2b*). This distortion has also been observed by transmission electron microscopy of the unannealed roll-cast films of cylindrical morphology at zero tilt (i.e. electron beam along the [0001] direction)[16].

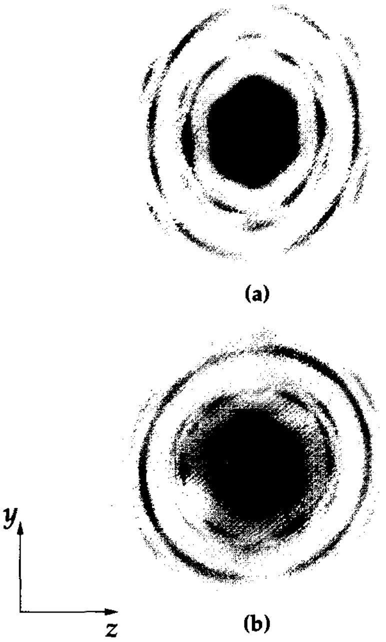

Figure 3 (a) A two-dimensional small angle X-ray scattering pattern of an unannealed roll-cast film of cylindrical morphology before exposure to solvent vapors, with the X-ray beam normal to the *yz* plane (i.e. along *x*) of the film. The pattern represents a distorted hexagonal lattice. This can be seen, for example, by the fact that the $01\bar{1}0$ and the $0\bar{1}10$ reflections are further away from the origin than the other four first order reflections. (b) A two-dimensional small angle X-ray scattering pattern of the same film recorded after exposure to toluene vapours and subsequent deswelling, exhibiting improved symmetry

Swelling experiments conducted with unannealed roll-cast films of cylindrical morphology lasted 45 min with each of the three solvents used, and were followed by 105 min of deswelling. The microstructural changes in the films resulting from the swelling and deswelling processes were monitored by periodically recording 2-D SAXS patterns and by plotting the d-spacings D_1 and D_2 (*Figure 4a*) and their ratio D_1/D_2 (*Figure 4b*) as a function of time. The changes in the weight of the films due to swelling and deswelling are shown in *Figure 4c*.

The as-cast films have d-spacings of $D_1 = 230$ Å and $D_2 = 150$ Å before exposure to solvent vapours so that the ratio D_1/D_2 has an initial value of 1.51. As the films are exposed to solvent vapours, an increase in both d-spacings is initially observed with increased swelling time. For all three solvents the increase in the value of D_1 is larger than the increase in the value of D_2, leading to a trend in the value of the ratio D_1/D_2 toward the value of $\sqrt{3}$ (*Figure 4b*), corresponding to perfect hexagonal packing. A similar trend was observed as a function of thermal annealing time in our previous study[16].

The changes in the d-spacings are due to two factors. The first is the addition of the solvent volume to that of the polymer, and the second is stress relaxation via molecular reconfiguration. The latter becomes possible due to the additional mobility of the polystyrene end blocks gained by the decrease in their effective Tg following solvent penetration in to the polystyrene domains.

In the case of swelling in toluene vapours, there is initially an increase in the values of both D_1 and D_2, however, the value of D_2 is observed to level out after about 15 min of exposure to toluene. During these initial 15 min, the d-spacings change mainly due to the simple addition of the volume of the toluene vapours to that of the polymer. After 15 min of exposure to toluene, enough solvent has entered the polystyrene domains to lower their effective Tg and to allow stress relaxation (Mori *et al.*[10] have shown this decrease in the Tg of polystyrene to occur with about 30% toluene present). From this point until the end of the 45 min swelling phase, the value of D_2 remains constant and the additional solvent that enters the polymer serves to decrease the distortion of the hexagonal lattice by increasing the value of D_1 in order to reach the favourable stress-free ratio of $D_1/D_2 = \sqrt{3}$.

Larger changes in D_1 and D_2 are measured for swelling in hexane than for swelling in toluene. Hexane is a preferential solvent for polybutadiene and initially swells only the polybutadiene matrix. During the initial swelling period, the polystyrene domains remain below their Tg and the locations of the polybutadiene–polystyrene junctions at the cylinder surfaces remained fixed. Hence, the increase in the volume of the polybutadiene phase may be accommodated only in the *xy* plane of the films, since dimensional changes along the cylinder axis (the *z* direction) are not possible. These constraints result in the relatively large changes that are recorded in the values of D_1 and D_2. After some 30 min of exposure to hexane vapours enough solvent[23] has penetrated the polystyrene domains to allow

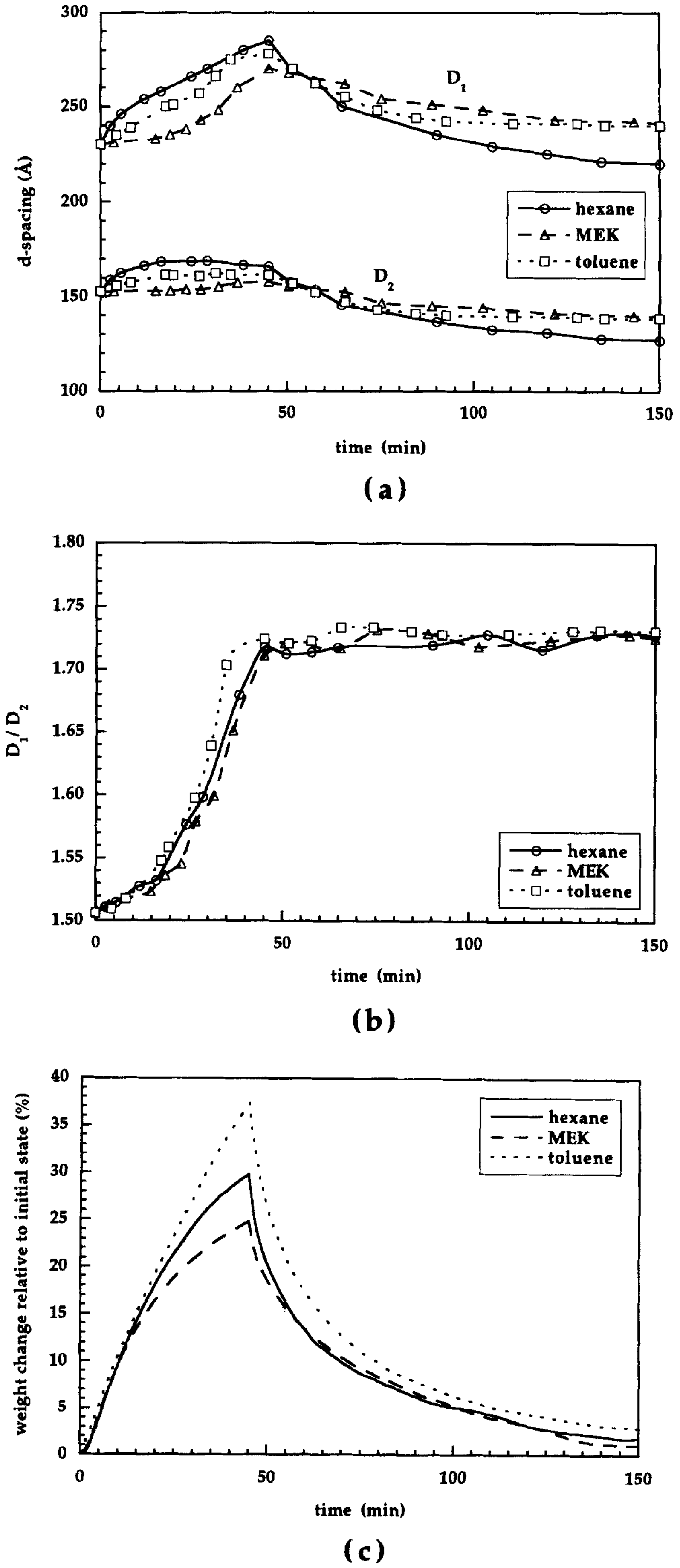

Figure 4 (a) A plot of the d-spacings D_1 and D_2 as a function of time during solvent swelling and subsequent deswelling of roll-cast films with cylindrical morphology. Swelling lasted for 45 min followed by 105 min of deswelling. (b) A plot of the ratio D_1/D_2 as a function of time. As the film is exposed to solvent, the ratio D_1/D_2 increases and levels out at about $\sqrt{3}$, which corresponds to a perfect hexagonal lattice. During the deswelling phase the ratio D_1/D_2 maintains its value of approximately $\sqrt{3}$. (c) Changes in the weight of roll-cast films with cylindrical morphology as a function of swelling and subsequent deswelling

molecular reconfiguration and stress relaxation, and a slight decrease in the value of D_2 is observed.

Swelling in MEK vapours causes a continuous increase in both D_1 and D_2 throughout the 45 min of exposure to solvent. However, the changes recorded in the values of D_1 and D_2 are smaller than those recorded for swelling in both toluene and hexane vapours, since most of the MEK penetrates only the polystyrene cylinders which initially make up only 25% (by volume) of the polymer.

The changes in D_1/D_2 following exposure to toluene vapours occur somewhat more rapidly than those observed with exposure to hexane and MEK (*Figure 4b*). Since both components are soluble in toluene, it diffuses more readily throughout the film and reaches the polystyrene domains faster. The slower swelling response with hexane and with MEK vapours stems in each case from different reasons: hexane is a preferential solvent for the polybutadiene matrix which initially makes up 75% (by volume) of the polymer and offers an unobstructed path for penetration throughout the film. However, due to its preference for the matrix, hexane is slower in penetrating the polystyrene domains and lowering their effective Tg. In the case of MEK, the delay in the system's response is due to the fact that there is no direct contact between the polystyrene domains and the MEK vapours. In the x direction, the solvent must first diffuse through the polybutadiene outer layer of the roll-cast film (formed because of polybutadiene's lower surface tension) before reaching the cross-section of the cylinders[24,25]. In the transverse directions, the solvent must also diffuse through the polybutadiene matrix in order to reach the polystyrene domains.

Exposing the films of cylindrical morphology to solvent vapours was qualitatively found to have a similar effect on the microstructure to that of thermal annealing[16], causing the 2-D SAXS patterns to became less distorted with increased exposure. This effect can be seen in *Figure 3b*, which presents the 2-D SAXS pattern recorded after exposure to toluene vapours and subsequent deswelling (compare to *Figure 3a*).

With all three solvents, the ratio D_1/D_2 maintained a constant value of essentially $\sqrt{3}$ throughout the deswelling process, that was started after 45 min of exposure to solvent. Films swollen in toluene and MEK exhibited similar d-spacings at the end of the 105-min deswelling process ($D_1 = 240$ Å and $D_2 = 140$ Å) whereas the values for films deswollen from hexane were smaller ($D_1 = 220$ Å and $D_2 = 127$ Å). As the hexane leaves the polymer, the polystyrene domains quickly go below their Tg and the locations of the polybutadiene–polystyrene junctions at the cylinder surfaces become fixed. At this point volume changes are again limited to the xy plane and result in the decrease to smaller d-spacings.

D-spacings similar to those measured after 105 min of deswelling were measured for control samples that were exposed to solvent for 45 min and subsequently left to deswell at ambient conditions for 1 week followed by 24 h in a vacuum oven at 50°C (below the Tg of the polystyrene blocks) so that essentially complete deswelling occurred in 105 min. Annealing the deswollen control samples resulted in $D_1 = 260$ Å and $D_2 = 150$ Å and $D_1/D_2 = 1.73$ for all three solvents.

Lamellar morphology

Figure 5a shows a two-dimensional small angle X-ray scattering pattern of an unannealed roll-cast film of lamellar morphology before exposure to solvent vapours. The reflections in *Figure 5a* indicate that the lamellae lie in the xy plane (also known as the 'perpendicular orientation'[26–28]). The azimuthal broadening of the reflections is due to the presence of many small grains with numerous helicoid surface twist boundaries, which have been observed in unannealed roll-cast films of lamellar morphology[16].

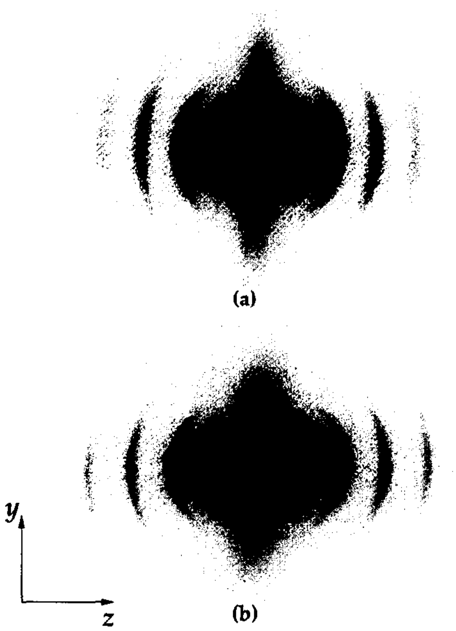

Figure 5 (a) A two-dimensional small angle X-ray scattering pattern of an unannealed roll-cast film of lamellar morphology before exposure to solvent vapors, with the X-ray beam normal to the yz plane (i.e. along x) of the film. The broadening of the reflections is due to the presence of numerous grains which are slightly misaligned. (b) A two-dimensional small angle X-ray scattering pattern of the same film recorded after exposure to toluene vapours and subsequent deswelling, exhibiting sharper reflections which indicate improved order

Swelling experiments similar to those described in the previous section were also conducted on samples with lamellar morphology. Swelling times were 30 min for toluene, and 60 min for both hexane and MEK followed by 2 h of deswelling with all solvents. The exposure time for toluene was chosen to eliminate the possibility of complete dissolution of the films, which was observed at longer exposure times. Swelling and deswelling the films was found to slightly improve the long range order of the lamellae, as can be seen by comparing *Figure 5a* and *5b*.

The d-spacing for the lamellar microstructure is plotted as a function of swelling/deswelling time in *Figure 6a*, along with the corresponding weight changes shown in *Figure 6b*. The differences between the three curves in *Figure 6a* are evidence of the different phenomena that accompany the swelling and subsequent deswelling with the three solvents used.

As we showed in the previous section for cylindrical morphology, the changes in the d-spacing of the lamellar morphology are also due to both the addition of the solvent volume to that of the polymer, and to stress relaxation via molecular reconfiguration.

The most complex behaviour is observed for hexane. A sharp increase in d-spacing from 250 to 305 Å is observed during the first 16 min of exposure to the solvent. The d-spacing maintains this value for about 10 min and then starts to decrease, reaching 280 Å after 1 h of swelling. This decrease in d-spacing occurs while the film is still exposed to hexane vapours, which as seen in *Figure 6b*, continue to

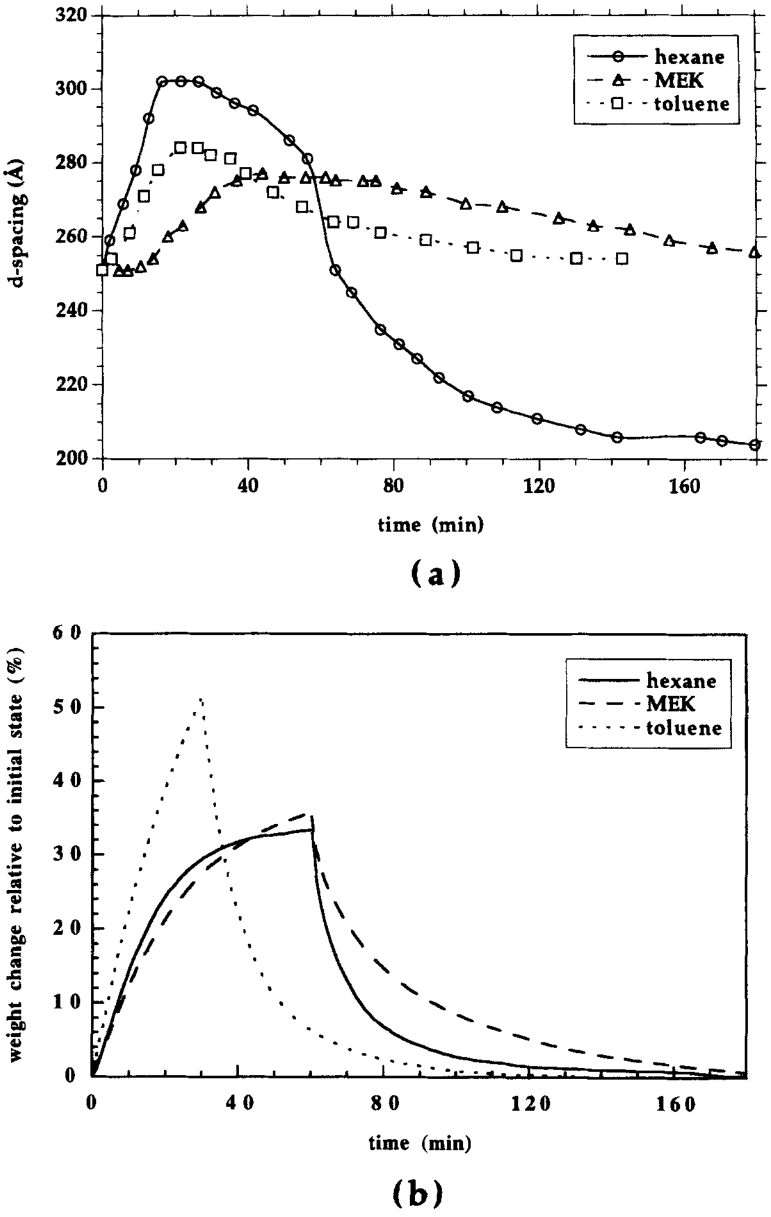

Figure 6 (a) A plot of the inter-lamellar d-spacing as a function of time during solvent swelling and subsequent deswelling of roll-cast films with lamellar morphology. Swelling lasted for 30 min in toluene and for 1 h in toluene and MEK, and was followed by 2 h of deswelling. (b) Changes in the weight of roll-cast films with lamellar morphology as a function of swelling and subsequent deswelling

penetrate the film and add to its weight. When the deswelling phase begins, there is a sharp and substantial decrease in the d-spacing which levels out at 205 Å (significantly less than that of the unswollen film) after 2 h of deswelling. We note that previously[16] we found that thermal annealing of unswollen films of the same composition resulted in an equilibrium d-spacing of 270 Å.

When comparing *Figure 6a* and *6b*, we observe that although the film takes on a larger amount of toluene than hexane during the respective swelling experiments, a larger change in d-spacing is measured for swelling in hexane than for swelling in toluene. Since hexane is a preferential solvent for polybutadiene, it initially penetrates only the rubber layers which results in an increase in the volume of these layers. However, since the neighbouring polystyrene domains are below their glass transition temperature, the locations of the polybutadiene–polystyrene junctions at the interfaces are fixed and can not reposition themselves to accommodate the changes in the volume of the polybutadiene layer. Hence, at this stage of the process the increase in the volume of the polybutadiene layers is translated mainly to an increase in their thickness resulting in a 'one-dimensional' swelling process (*Figure 7b*).

In the second phase of the swelling process, a plateau is reached (16–26 min), which may indicate the largest extension of the bridge (and entangled loop) tie-molecules between the polystyrene layers. Another possible explanation for the plateau is an offset to the continued swelling of the polybutadiene layers created by a decrease in the thickness of the polystyrene layers. This decrease results from sufficient hexane entering the polystyrene domains to cause the Tg of polystyrene to drop below room temperature and to therefore allow repositioning and an increase in the lateral spacing of the polybutadiene–polystyrene junctions[23]. The increase in the distance between the junctions results in a decrease in the thickness of the polystyrene layers, in which the molecules now have to reconfigure closer to the interface to compensate for the movement of the junctions (*Figure 7c*). This process is clearly indicated from 26 min onward, in which a net decrease in d-spacing is

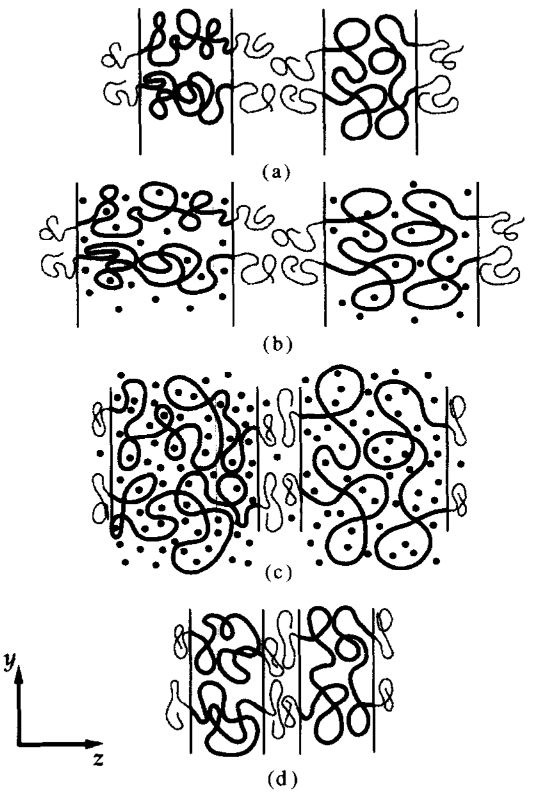

Figure 7 A schematic representation of the molecular reconfigurations that accompany the swelling of roll-cast films with lamellar morphology in hexane vapours and the subsequent deswelling. The thick black lines represent the polybutadiene blocks, the thinner gray lines represent the polystyrene blocks and the circles represent the hexane molecules. Molecules in both bridge and loop configurations are shown. (a) The molecular configuration prior to swelling. (b) The locations of the polybutadiene–polystyrene junctions at the interfaces are fixed and can not reposition themselves to accommodate the changes in the volume of the polybutadiene due to the selective penetration of hexane to the rubber domains in the early stages of swelling. At this stage of the process, the increase in the volume of the polybutadiene layers is translated mainly to an increase in their thickness. (c) When enough hexane enters the polystyrene domains to allow repositioning of the polybutadiene–polystyrene junctions, they drift further apart. An increase in the distance between the junctions results in a decrease in the thickness of the polystyrene layers, in which the molecules now have to reconfigure closer to the interface to compensate for the lateral movement of the junctions. (d) When the deswelling process starts, the hexane leaves the polymer very quickly, causing a rapid increase in the Tg of the polystyrene and freezing in the new locations of the polybutadiene–polystyrene junctions. The polybutadiene chains rearrange themselves according to the frozen-in position of the junctions, which results in a 'one-dimensional' deswelling process accompanied by a significant decrease in the thickness of the polybutadiene layers

observed (*Figure 6a*) while the film is still exposed to hexane vapours which continue to enter the film as indicated by continuous increase in the weight of the film (*Figure 6b*).

When the solvent penetrates the polystyrene domains, the molecules which were stretched out in the direction of flow during the roll-casting process may rearrange themselves in less stressed configurations. As the molecules become less stretched in the x direction, their dimensions increase in the y and z directions. The increase in the z direction leads to an increase in d-spacing, which offsets the decrease in d-spacing due to the lateral spreading of the junctions. The swelling and shrinking of the domains due to solvent penetration, and the molecular rearrangement due to stress relaxation occur simultaneously. Hence, the changes in the d-spacings that are measured by SAXS reflect the *net* outcome of these processes.

When the deswelling process starts after 1 h of swelling, the hexane leaves the polymer very rapidly due to its high vapour pressure (20.2 kPa at 25°C)[29]. The hexane leaves the polystyrene layers (for which it is a poorer solvent), causing a rapid increase in the Tg of the polystyrene[23,30] and freezing in the new molecular arrangement in the polystyrene layers and hence the new locations of the polybutadiene–polystyrene junctions. Although the Tg of the polystyrene layers quickly increases as the hexane leaves the film, the polybutadiene chains (which are always well above their Tg) can rearrange themselves according to the frozen-in position of the junctions, which results in a 'one-dimensional' deswelling process accompanied by a significant decrease in the thickness of the polybutadiene layers (*Figure 7d*).

To summarise, the preference of the hexane for the rubber block leads to different degrees of molecular mobility in the two phases at different stages of the swelling and deswelling processes. Molecular mobility in the polystyrene domains allows stress relaxation to take place. This mobility also results in an increase in the lateral spacing of the junctions at the interfaces, which is frozen in upon deswelling and which results in the overall net decrease in d-spacing observed.

A d-spacing of 205 Å was measured for the control samples that were exposed to hexane for 1 h and left to deswell at ambient conditions for 1 week followed by 24 h in a vacuum oven at 50°C. This indicates that the microstructural reconfiguration was essentially completed after 2 h of deswelling. The d-spacing recorded for a control sample which was subsequently annealed at 120°C was 270 Å, which coincides with the d-spacing measured for annealed roll-cast films that did not undergo swelling/deswelling[16].

A much simpler mechanism accompanies swelling with toluene. In the first phase, the d-spacing increases from its initial value of 250 Å before swelling, to about 285 Å after 22 min of swelling. Toluene is a non-preferential solvent for the system studied and is a good solvent for both the polystyrene and the polybutadiene phases. As a result, the weight increase due to the uptake of toluene is greater than the weight increase that accompanies swelling in hexane (*Figure 6b*). The toluene easily penetrates both phases and drops the Tg of the polystyrene blocks below room temperature, so that the locations of the polybutadiene–polystyrene junctions are not fixed and the lamellae are free to swell in all three dimensions while simultaneously relieving process-related stress. This explains why a smaller increase in d-spacing was measured for swelling in toluene than for swelling in hexane, where most of the volume was added by expansion only in one dimension.

A d-spacing of 285 Å is maintained until the end of the 30-min swelling phase, and is followed by a gradual decrease to a d-spacing of 255 Å during the 2 h of deswelling. A d-spacing of 250 Å was measured for the control samples that were completely deswollen from toluene. The d-spacing recorded for a control sample, which was subsequently annealed at 120°C, was again 270 Å.

When swelling with MEK, an increase in d-spacing from 250 to 275 Å is observed during the first 37 min, after which the d-spacing levels out for the remainder of the 1 h swelling phase. The d-spacing very gradually decreases to 255 Å during the 2 h of deswelling. A d-spacing of 255 Å was measured for the control samples that were completely deswollen from MEK. As in the other cases, the d-spacing recorded for a control sample, which was subsequently annealed at 120°C, was 270 Å.

MEK is a selective solvent for the polystyrene phase. As the solvent enters this phase, it lowers its Tg and increases the mobility of the polystyrene blocks. Since the polybutadiene blocks are always above their Tg, the junctions at the interface are not confined to fixed positions, as was the case with the initial phase of swelling in hexane vapours. The junctions have the freedom to reposition themselves as additional MEK enters the polymer, allowing some three-dimensional changes in volume. Smaller increases in d-spacing are observed when swelling in MEK than when swelling in toluene, because less solvent enters the polymer (*Figure 6b*) due to only one phase (polystyrene) being soluble in MEK.

SUMMARY

Swelling roll-cast films with cylindrical and lamellar morphology was found to have a similar effect to thermal annealing, and resulted in an improvement in the symmetry of the packing of the microdomains. This phenomenon was observed for both the preferential and non-preferential solvents used and is due to stress relaxation on the molecular level. Swelling roll-cast films with both cylindrical and lamellar morphology and subsequent deswelling were found to progress differently for the three solvents used. The microstructural changes that accompanied the swelling of the structures were closely linked to the mobility of the glassy polystyrene blocks, the relaxation of process-related stress and the ability of the polybutadiene–polystyrene junctions at the interfaces to reposition and accommodate volume changes.

Our results suggest that a thorough understanding of swelling and deswelling kinetics could be utilised to tailor a specific dimensional response of a block copolymer to solvent exposure.

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