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Morphology and Micromechanical Behaviour of SBS Block Copolymer Systems

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Summary: By means of transmission electron microscopy (TEM) and uniaxial tensile testing, the connection between the morphology and the micromechanical properties of selected styrene-rich styrene/butadiene block copolymers was studied with respect to their molecular architecture. In particular, the structure-property correlation of a lamellae forming asymmetric linear SBS triblock copolymer was examined by systematically varying the sample preparation techniques and testing temperature. The molecular architecture was found to influence directly the morphology formation of the block copolymers. Different mechanisms such as drawing of the lamellae, shearing in the rubbery phase and rotation of the lamellar axis were observed. From room temperature down to the temperature close to glass transition temperature of the soft phase, a homogeneous plastic drawing of glassy lamellae was perceptible.

Keywords: blends; electron microscopy; mechanical properties; micromechanisms; morphology; SBS block copolymers

Introduction

Block copolymers lie at focus of intensive research activities in the contemporary macromolecular science and technology. This is attributable to a wide range of fascinating fundamental issues associated with the understanding of self-assembly processes, their potential application possibilities in nanotechnology etc. The concerns regarding the past successes and future perspectives as well as the challenges in the field of these nanostructured heteropolymers have been addressed recently by Lodge [1].

At sufficiently high molecular weight and low polydispersity, the block copolymer molecules are known to self-assemble into a variety of ordered structures in the melt and solid state by a process called microphase separation transition. The latter is a consequence of the intramolecular phase separation between homopolymer chains linked together by means of a covalent bond [2].

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Mechanical properties, especially the balance of strength, stiffness and toughness, are important for many everyday applications of polymeric materials. The styrene/butadiene block copolymers, which assure the transparency of the products due to the presence of inherent nano-scale heterogeneity, offer the possibility of tailoring application relevant mechanical properties by suitably choosing the molecular and processing parameters. An inevitable aspect in the structure-properties correlations of the block copolymers is the understanding of micromechanical processes of deformation, which firmly bridges the mechanical properties with polymer morphology.

Styrene/diene block copolymers (dienes: butadiene or isoprene) are seldom used as pure materials [3,4]. Instead, they are alloyed with other polymers such as polystyrene homopolymer. The objective of mixing these copolymers into standard polystyrene is to toughen the latter while preserving the transparency. Due to higher production costs of block copolymers, it is desired to enhance the toughening ability of block copolymers, i.e., to develop the copolymers which are better compatible with polystyrene so that less amounts of block copolymer is needed to achieve a good level of stiffness/toughness ratio. In addition, one is interested to keep the diene content as low as possible to suppress the ease of thermal degradation of the products without making any compromise in the toughness level. To meet these demands, in recent years, new types of styrene/butadiene block copolymers have been developed [4-6] and even introduced as commercial products in the market. Special emphases have been put on designing copolymers having variable molecular architectures, e.g., asymmetric conformation, modified interfacial profile etc.

The aim of this paper is to discuss how the molecular architecture and the resulting morphology of selected polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) triblock copolymers are connected with their mechanical and micromechanical behaviour. A brief review of the structure-property correlation in styrene/diene block copolymers is given and the results on styrene-rich block copolymers (total styrene content, $\Phi_{PS} \sim 70\%$) are presented in detail.

Structure-Property Correlation in Block Copolymers

Generally, nanostructures that are formed in the solid state in block copolymers are of practical interest. In the classical sense, these structures are adjusted by changing the relative composition of the chemically linked chains. Figure 1 shows schematically the morphologies observed in classical two-component block copolymers (e.g., both styrene/butadiene di- and triblocks). These morphologies in styrene/diene block copolymers are responsible for different kinds of micromechanical mechanisms and mechanical behaviour. This fact illustrates the significance of morphology control in block copolymers from practical point of view. It should be stressed that, for good mechanical properties of styrene/butadiene block copolymers, the rubbery polybutadiene (PB) block should be anchored on both the ends by polystyrene (PS) blocks that are glassy at room temperature.

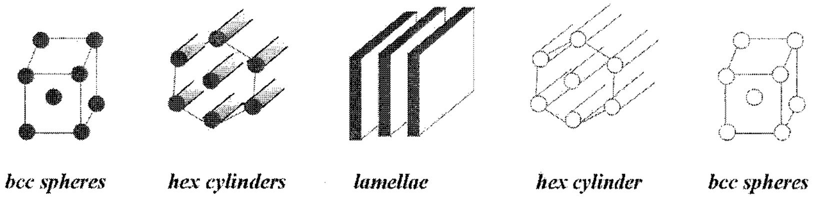

Figure 1. Scheme showing the classical block copolymer morphologies with decreasing □ volume content, where □ and ■ represent different constituents.

In diblock copolymers, the nature and the dimension of the microphase separated structures are adjusted by changing composition and molecular weight of the constituents. In the strong segregation limit, with increasing polystyrene (PS) content, body centred cubic spheres, hexagonal arranged cylinders and three dimensional 'gyroid' network of polystyrene (PS) domains dispersed in the matrix of polyisoprene were observed in polystyrene-b-polyisoprene (SI) diblock copolymers [9]. With further increase in the PS content, the alternating layers of PS and PB lamellae, and then the structures mentioned above in the reversed order were found.

Further possibilities for the fine-tuning of block copolymer nanostructures are provided by blending and processing [3-7]. Three-component block copolymers and their derivatives form an additional variety of microphases, which may allow novel routes to developing materials having new property profile [7-9]. It has been known for some time that the modification of molecular architecture may significantly alter their phase behaviour and opens up new horizon of morphology control in these copolymers [6,10-12]. Due to architectural modifications of block copolymers, limitations because of composition (e.g., in an AB diblock) can be overcome to achieve a particular morphology and, hence, improved mechanical properties. These new morphologies and new routes to control block copolymer nanostructures have posed new challenges for polymer scientists to clarify their complex structure-property correlations.

Experimental

Materials

The important characteristics of the block copolymers studied are collected in Table 1. The details of the morphology of respective copolymers may be found in the references mentioned in the parentheses. The samples provided by the BASF Aktiengesellschaft, Ludwigshafen were synthesised by butyl-lithium initiated living anionic polymerisation. Asymmetric star block copolymers (ST1-S74 and ST3-S74) were prepared by joining the living S_1BS_2 or $S_1(S/B)S_2$ chains (where S/B stands for a polystyrene-co-polybutadiene random copolymer; the polystyrene blocks S_1 and S_2 are of different lengths) using oligofunctional coupling agent. Except LN1-S74, which is a linear symmetric SBS triblock copolymer, the remaining block copolymers possess non-classical molecular structure (asymmetric structure, tapered transition, etc., see table 1). Note that the net composition of the copolymers studied is nearly constant (ca. 70 vol.-% styrene).

One of the copolymers chosen to prepare blends with homopolystyrene hPS (PS015, PS033 and PS190) by solution casting was an asymmetric star block copolymer (ST3-S74, volume fraction of PS, Φ_{ST} = 0.74; see Table 1). Each star block copolymer has 4 asymmetric SBS arms in average, one of which is much longer than the others. The longest arm is styrene-rich while the shorter ones are butadiene-rich [6]. Three different types of hPS samples were used: PS015 (M_w =

15 000 g/mol and M_w/M_n = 1.29), PS033 (M_w = 33 000 g/mol and M_w/M_n = 1.81) and PS190 (M_w = 190 000 g/mol and M_w/M_n =2.3). The first two have molecular weights much smaller than that of the longest PS outer block of the star block copolymer while the third one has an M_w higher than that of all the PS blocks.

Sample Preparation

Table 1. The characteristics of the block copolymers studied; LN and ST stand for linear and star architectures, respectively.

Samples	§M_w (g/mol)	§M_W/M_n	*Φ_{PS}	Remarks
LN1-S74	87 700	1.07	0.74	symmetric SBS triblock, sharp transition with the pure PB mid-block, linear architecture [12]
LN2-S74	105 100	1.13	0.74	asymmetric S_1BS_2 triblock copolymer, ($S_1 \neq S_2$), tapered transition [12,13]
LN4-S65	139 200	1.20	0.65	random PS-co-PB copolymer as rubbery mid-block, symmetric outer PS blocks, linear architecture [5,13]
ST1-S74	9 800	1.99	0.74	highly asymmetric star architecture, each arm with S_1BS_2 structure ($S_1 \neq S_2$), sharp transition
ST3-S74	100 000	1.91	0.74	Structure similar to ST1, each arm with $S_1(S/B)S_2$ structure ($S_1 \neq S_2$), S/B is a random copolymer of PS and PB [6]

§ number average (M_n) and weight average (M_w) molecular weight determined by gel permeation chromatography using PS calibration

- total styrene volume content determined by Wijs double bond titration procedure

The samples were prepared by three different methods: solution casting (using toluene as solvent), compression moulding (melt casting at 190°C and 200 bar pressure) and injection moulding (mass temperature 250°C and mould temperature 45°C). Solution cast films were prepared form 3% (weight/volume) solution of each polymer in toluene allowing the solvent to evaporate over a period of about a week followed by vacuum drying at 23°C for several days and finally annealing for 48 hours in a vacuum oven at 120°C.

Tensile Testing

Macroscopic tensile tests using injection and compression moulded bars and solution cast films were carried out using universal tensile machine (Zwick 1425 or Instron 1407) at a cross head speed of 50 mm/min at different temperatures. At least 6 specimens of each sample were tested.

Transmission Electron Microscopy (TEM)

Morphological details of the samples were investigated by means of a transmission electron microscope (TEM, Joel 200 kV) using ultramicrotomed thin sections (~70 nm thick). Prior to the TEM inspection, butadiene phase was selectively stained by osmium tetroxide (OsO_4).

Results and Discussion

Effect of Chain Architecture on Block Copolymer Morphology

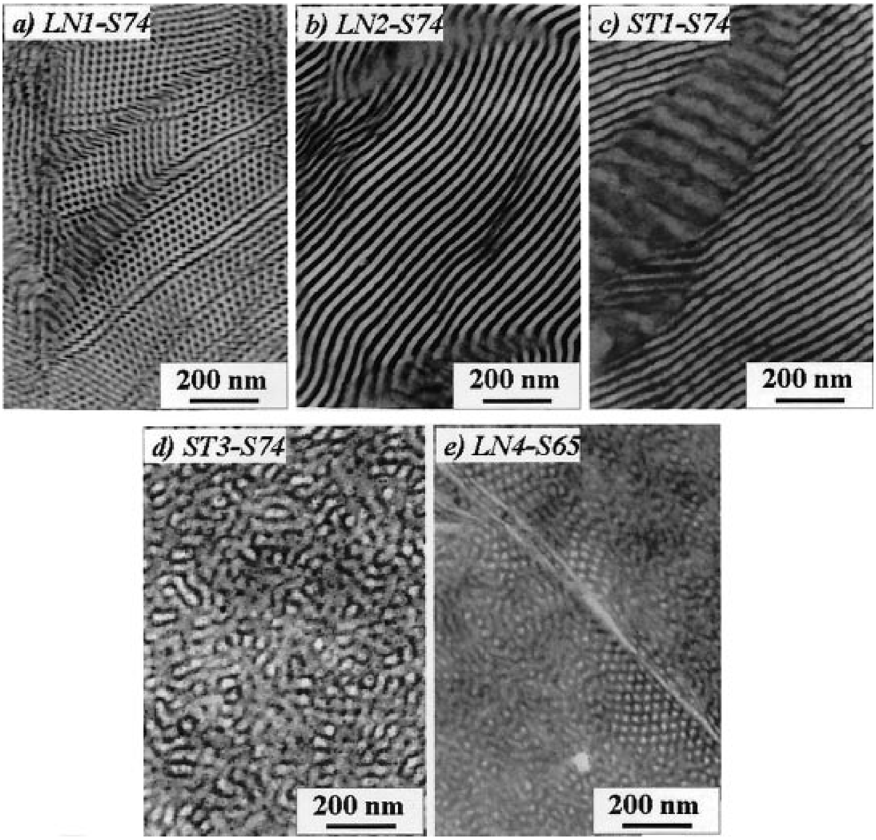

Figure 2. Representative TEM micrographs of the block copolymers studied; sample notations are given; note that the samples have nearly identical net chemical composition ($\Phi_{PS}\sim$ 0.70).

The equilibrium morphology of the linear block copolymers presented in table 1 have been the object of our previous studies [12,13]. Hence, only a brief account of them will be given, and the star block copolymers are discussed in more detail. Fig 2 illustrates the equilibrium morphology of the block copolymers prepared by solution casting. The micrographs of different samples in Fig 2 (a-e) are arranged in such a way that the variation of morphologies as a result of modified architecture follow in the order: PS matrix (LN1) → Lamellae (LN2, ST1) → bicontinuous-like morphology (ST3) → PS domains (LN4).

It is known from literature that an SB diblock copolymer with about 70 vol.-% PS forms hexagonal polybutadiene (PB) cylinders dispersed in PS matrix [9], and the same will be observed in a symmetric SBS triblock copolymer as shown by TEM image of LN1-S74 in Fig 2a. The change in molecular architecture may completely change the classical picture of morphology formation in block copolymers by overcoming the precondition of altering composition to adjust the morphology.

As demonstrated by our studies, one may notice a wide range of microphase separated structures produced by the variation of block copolymer architectures at constant styrene/butadiene composition (Fig 2). In spite of the net chemical composition equivalent to that of LN1-S74 (Fig 1a) the asymmetric linear block copolymer having a tapered composition profile (LN2-S74 in Fig 2b) and an asymmetric star block copolymer having neat transition (ST1-S74 in Fig 2c) show lamellae. Obviously, the block copolymers having asymmetric architecture exhibit the significant deviation in the composition in which a particular morphology will be formed. The star block copolymer (ST3-S74 in Fig 2d), with 74 vol-% PS and lacking a pure PB as the rubbery phase shows a larger deviation from the classical block copolymer phase diagram. In this star block copolymer, the deviation is substantiated by the presence of a PS-co-PB random copolymer as rubbery block, which contains a considerable part of total polystyrene and hence increases the effective rubber volume fraction. The latter would favour the formation of morphology corresponding to the structure of a diblock copolymer having lower PS content. As a result, a bicontinuous-like morphology is formed. A closer inspection of Fig 2d reveals that the PS struts (grey domains) seem to form an interpenetrating network dispersed in the PS-co-PB matrix. This morphology looks very similar to the ‘gyroid’ phase observed in block copolymer systems. Finally, at a slightly lower total PS content (65 vol.-% polystyrene) than the rest of the block copolymers, the linear copolymer LN4-S65, which has about 32% by volume of PS as outer pure glassy blocks, forms the glassy domains dispersed in the rubbery matrix [12]. This morphology resembles the structure of classical SBS thermoplastic elastomers, which contain about 30% polystyrene, the composition nearly reverse of LN4-S65.

Table 2. Differential scanning calorimetry (DSC) data of the block copolymers showing the glass transition temperature (T_g) of the soft and the hard phases, heating rate 10°C/min.

Polymer:	**$T_{g\text{-}PB}$ (soft phase)/°C**	**$T_{g\text{-}PS}$ (hard phase)/°C**
LN1-S74	-98	101
LN2-S74	-53	101
LN4-S65	-34	70
ST1-S74	-81	103
ST3-S74	-60	104

It is interesting to note that the change in molecular architecture and hence the morphology formed in the solid state is associated with a shift in the glass transition temperature of the polybutadiene phase ($T_{g\text{-}PB}$), see table 2. With the exception of LN4, where there is a decrease in glass transition temperature of PS phase ($T_{g\text{-}PS}$), the value of $T_{g\text{-}PS}$ in other samples remains nearly constant. The rise in $T_{g\text{-}PB}$ is a sign of intermixing of polystyrene chains with the polybutadiene phase. The latter depresses the mobility of the PB phase by introducing segments having bulky pendant groups [12]. The elevation of $T_{g\text{-}PB}$ in ST3 and LN4 is obvious because of the presence of PS-co-PB random copolymer as rubbery block. The substantial increase of $T_{g\text{-}PB}$ even in block copolymers having pure butadiene rubbery blocks (e.g., ST1-S74) suggests that a part of shorter PS chains might have been incorporated into the former. This possible intervention of PS chains, which is augmented by asymmetric conformation, is in line with the recent postulation by Matsen

[14], which allows the increase of soft phase volume fraction in the block copolymers having modified architectures. However, in fact, besides the volume fraction of the phases, the thermodynamics at the interface is the key factor that plays a decisive role in determining the interfacial curvature, i.e., via the interaction parameter of the two species in contact [9]. Thus, a change in chemical nature of the blocks at the interfacial region (neat versus tapered or random) should affect the thermodynamic equilibrium and the resulting morphology.

Effect of Processing Methods on Morphology

The equilibrium morphologies of the block copolymers outlined above are stable ones. These were observed independent of preparation conditions. The processing history may significantly alter the orientation and order of the microdomains [15]. Here, we discuss the influence of sample processing condition taking the lamellar block copolymer LN2-S74 as an example.

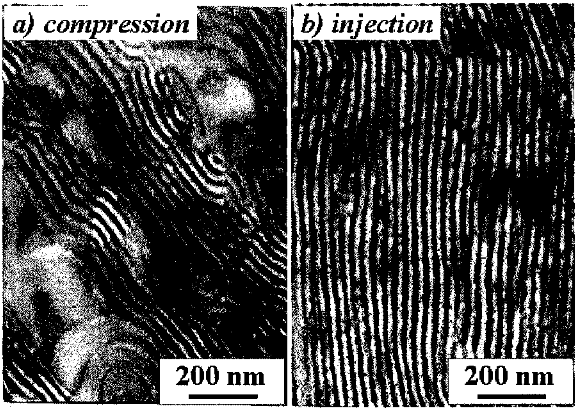

Figure 3. Representative TEM micrographs showing microphase separated morphology of the lamellar block copolymer LN2-S74 in compression mould (left) and injection mould in the middle of the moulded bar (right: injection direction vertical); the equilibrium structure is shown in Fig 2b.

The structures of the block copolymer in compression and injection moulds are qualitatively similar to that found in the solution cast film. The compression-moulded sample shows the well developed lamellar morphology with different orientation of the grains. In Fig 3a, one can notice both edge-on and flat-on views of the lamellar microdomains. The lamellae in the injection mould (Fig 3b) are highly oriented in the flow direction. It should be kept in mind that the morphology of an injection mould can change from one end of the bar to the other and even across its width. In the copolymer studied, especially the continuity of the lamellae was found to be highly affected by the shear force. The orientation of the microstructures along the flow direction is known to cause a pronounced anisotropy in mechanical deformation behaviour [16].

The results discussed so far provide an excellent experimental evidence of possibility of modifying the block copolymer phase diagram via a change in molecular architecture. Thus, the architectural modification of block copolymers may open an interesting way of controlling their morphology and mechanical properties.

Morphology Formation in Block Copolymer/PS Blends

As introduced earlier, the styrene/butadiene block copolymers are often used in combination with polystyrene homopolymer (hPS). It is well known that the length of the homopolymer chains (here hPS chains) relative to that of the corresponding block (here PS block) of the block copolymer plays a vital role in the phase behaviour of the block copolymer/homopolymer blends [9,17].

The low molar mass homopolymer, which is easily assimilated by the corresponding block domains can be used to change the dimension of a given morphology and even to produce new morphologies corresponding to another net composition. Hence, the method of blending with homopolymers can be helpful to locate the position of a 'new' morphology in the phase diagram.

Fig 4 shows the morphology of the star block copolymer ST3-S74 and three different blends with hPS having different molecular weights. In the blends, the hPS weight content is 20% each. The TEM image of ST3 is also included in order to compare the morphology with that of the blends. Three kinds of morphologies can be observed: microphase separated 'bicontinuous' structure (Fig 4a), microphase separated lamellar structures (Fig 4b,c) and macrophase separated morphology containing hPS particles embedded in ST3-S74 matrix.

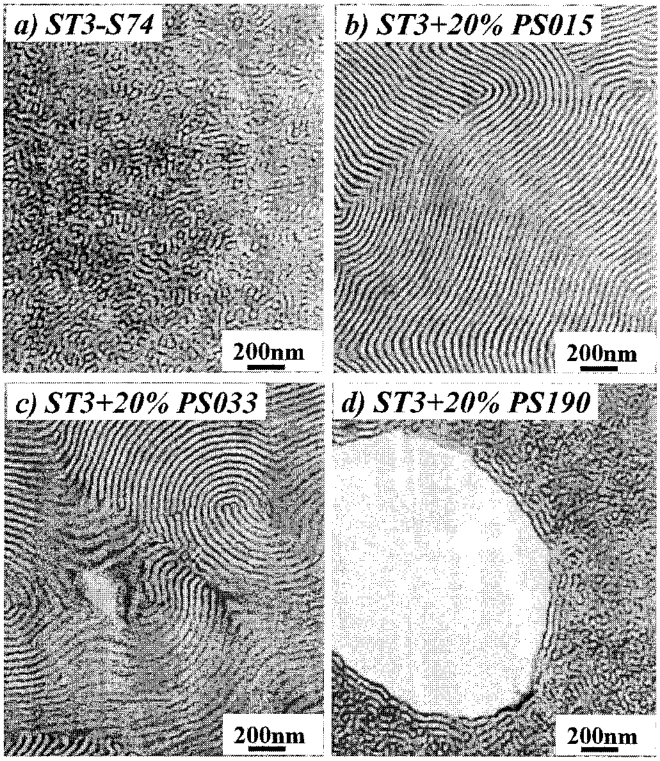

Figure 4. Representative TEM images of pure star block copolymer ST3-S74 (a), and blends containing 20 wt.-% of homopolystyrene having different molecular weights (b-d).

The polystyrene samples differ in their molecular weights. PS015, PS033 and PS190 have the weight average molecular weight (M_w) of 15 000 g/mol, 33 000 g/mol and 190 000 g/mol, respectively. On the other hand, the molecular weight of the longest polystyrene block in the star block copolymer is in the range of 50 000-70 000 g/mole. Obviously, PS015 and PS033 have shorter chains that can be easily accommodated by the PS blocks of the star molecules. Hence, an addition of 20 wt.-% of PS015 and PS033 leads to the formation of morphology corresponding to higher polystyrene content (lamellar morphology in Fig 4b,c). Since the resulting morphology is a lamellar one (and the type of morphology to be expected for a block copolymer having lower PS content than for the lamellae is 'gyroid' phase), the microphase separated structures observed in the pure ST3-S74 can be considered as being, at least, very close to the 'gyroid' morphology.

Increasing the molecular weight of the added polystyrene (hPS) decreases the entropy of these chains and the hPS chains cannot diffuse into the PS block of the block copolymer. These hPS chains tend to segregate towards the middle of the domains and finally, if the molecular weight is too high, these are even expelled out of the PS domains leading to the formation of macrophase separated hPS particles dispersed in the matrix block copolymer. The molecular weight of the PS190 is obviously much higher than the corresponding block in the block copolymer. Hence the added polystyrene predominantly forms the hPS particles leaving the morphology of the surrounding matrix unchanged (Fig 4d).

The discussion outlined above in case of solution cast samples may not be valid for the mixtures produced by extrusion or injection moulding. The processing may dramatically influence the morphology of the binary block copolymer/hPS blends. Particularly, in ST3-S74/hPS blends, a typical net-work-like structure was formed [23].

Mechanical and Micromechanical Properties

a. Influence of molecular architecture and morphology

Provided that the rubbery PB block is chemically bound to glassy PS blocks, the mechanical behaviour of the phase separated styrene/butadiene block copolymer systems is generally governed by their morphologies. Due to the formation of a wide range of morphologies in a narrow composition range, a great variety of mechanical behaviour was observed in the investigated block copolymers. Fig 5 exemplifies this diversity in linear block copolymers.

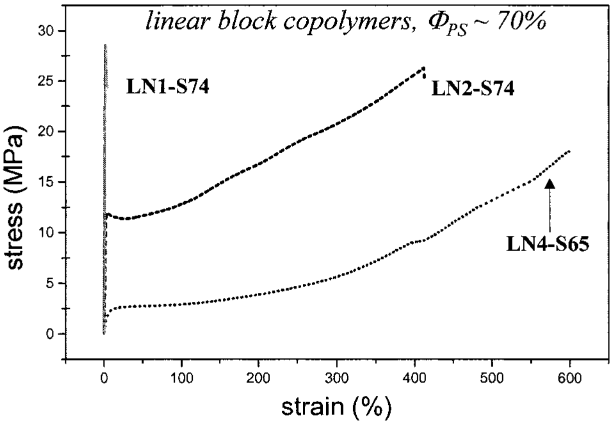

Figure 5. Stress-strain curves of the linear block copolymers using compression-moulded samples according to IS0 527; tensile testing at 23°C and 50 mm/min.

The mechanical behaviour ranges from that of classical SBS thermoplastic elastomer (TPE) to tough thermoplastics and to that of a hard and semi-brittle polymer. This behaviour can be directly correlated to the type of morphologies observed. The TPE character of the sample LN4-S65 is attributed to the morphology comprising dispersed PS domains in the rubbery matrix. Likewise, the highly ductile behaviour of the sample LN2-S74 is a consequence of lamellar morphology. On the other hand, the semi-brittle behaviour of LN1-S74 is correlated with the existence of PS matrix (see Fig 2 for the basic morphologies). The diversity in the mechanical properties are, indeed, the expression of different micromechanical processes, which are discussed in our recent publications [12,18,19]. In the following, we concentrate on the deformation behaviour of a lamellar block copolymer sample (viz., LN2-S74) prepared by different methods and loaded at different temperatures. The micromechanical behaviour of the block copolymers as a function of morphology is summarised in Table 3.

Table 3. Summary of micromechanical mechanisms observed in different block copolymers as a function of morphology (summarised from ref. [12,18,19]).

PS matrix **(e.g., LN1-S74)**	**Alternating lamellae** **(e.g., LN2-S74)**	**PS cylinders** **(e.g., LN4-S65**
Crazing with possible void formation in the PS matrix, deformation structures less affected by orientation of PB domains	Yielding of lamellae and fish-bone formation as dominating mechanisms for deformation parallel and normal to the lamellar orientation, respectively	Fragmentation of glassy cylinders, healing up of deformed structures on removing load (a reason for excellent reversibility)

b. Influence of sample processing method

As already indicated earlier, processing might have a dramatic impact on the morphology and mechanical behaviour of block copolymers. Fig 6 plots the stress-strain curves of lamellar block copolymer LN2-S74 processed by three different methods: solution casting, compression moulding and injection moulding. The compression moulded and injected samples met the requirements of standard test (ISO 527) while miniaturised tensile bars (50 mm long, 0.5 mm thick) were prepared from solution cast films. Therefore, the comparison of properties is rather qualitative.

What one can immediately notice in Fig 6 is the significantly high yield stress (ca. 29 MPa) of injection mould. The yield points of solution cast films and compression moulded lie nearly at the same low level (12 MPa). Another noticeable difference is in the tensile strength (maximum stress at break). The tensile strength decreases in the following order: solution cast film → compression mould → injection mould. It is well known that the tensile strength in styrene/diene block copolymers is a direct function of extent of phase separation [3]. Thus, decreasing tendency of tensile strength in the sequence noted above can be correlated to the decreasing degree of phase separation. The structures in solution cast films are closest to the equilibrium ones, which ensure the largest tensile stress while the injection mould has the smallest chance of forming the well phase-separated morphology owing to the rapid cooling of highly sheared melt. On the other hand, the highest yield stress of the injection mould can be attributed to the orientation of lamellae along the flow direction. Note that the injection-moulded bars were loaded parallel to the injection direction, i.e., parallel to the lamellae orientation direction.

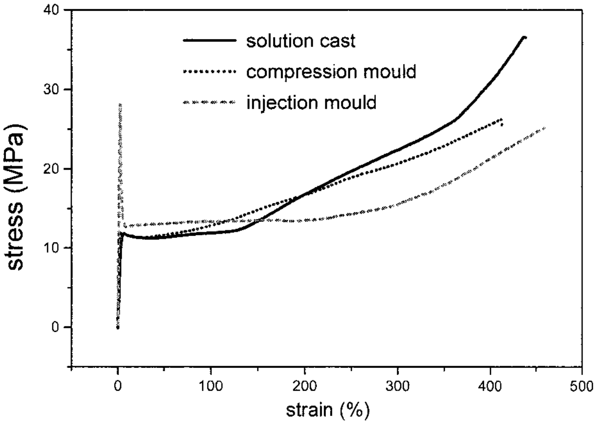

Figure 6. Stress-strain curves of the lamellar block copolymer (LN2-S74) samples prepared by different methods; injection mould was strained parallel to the injection direction.

The strong influence of processing on the mechanical properties observed indicates that the microdeformation of these samples is governed by different mechanisms. The stress-strain curves (and hence the underlying deformation mechanisms) plotted in Fig 6 can be divided into two categories: a) solution cast and compression mould, and b) injection mould.

In Fig 7, the details of deformation structures observed in solution cast film of the lamellar block copolymer LN2-S74 are presented. The thin section for TEM studies of deformation structures were prepared from tensile bar deformed in the tensile test (sectioning close to the fracture surface). For the purpose of comparison, morphology of this copolymer without deformation is included in Fig 7a.

The TEM micrographs show regions of different structures –lamellae with different forms, thicknesses and long periods. A few of them have been marked as c, d and e (Fig 7b), whose larger magnifications are presented in bottom of Fig 7. The copolymer has originally a long period of 33 nm and a thickness of PS lamellae of 18 nm.

The magnifications in Figs 7a, 7c, 7d and 7e are directly comparable. One can notice that, after deformation to different degrees, the lamellar thicknesses and spacings have been reduced by more than 50% in regions c and d, an indication of a large plastic deformation which arises obviously from the effect of so-called *thin layer yielding* [18].

Due to similarity between the thickness of PS lamellae and that of craze fibrils in bulk homopolystyrene (both in the range of 10-20 nm), the drawing of the PS lamellae can be envisioned as being analogous to the drawing of the craze fibrils, where the PB lamellae in its liquid-like state act comparable to the microvoids and don't hinder the flow-process of the adjacent PS layers. The plastic yielding of glassy PS lamellae, which occurs if the thickness of these layers is below a critical value, is the idea of above mentioned mechanism of *thin layer yielding* [18].

The plastic deformation of glassy lamellae observed in the asymmetric lamellar block copolymer corresponds to the earlier studies of Kawai et al. on unoriented films who showed using TEM and SAXS that during plastic deformation shearing and kinking processes occurs prior to the disruption of glassy lamellae [20,21]. At higher strains, formation of 'fish-bone structure' ('chevron' morphology [16]) characterised by a four point SAXS pattern was observed. Recently Cohen and co-workers reported that during deformation parallel and perpendicular to the lamellar orientation, destruction of lamellar structure and formation of 'chevron' morphology, respectively occur [16].

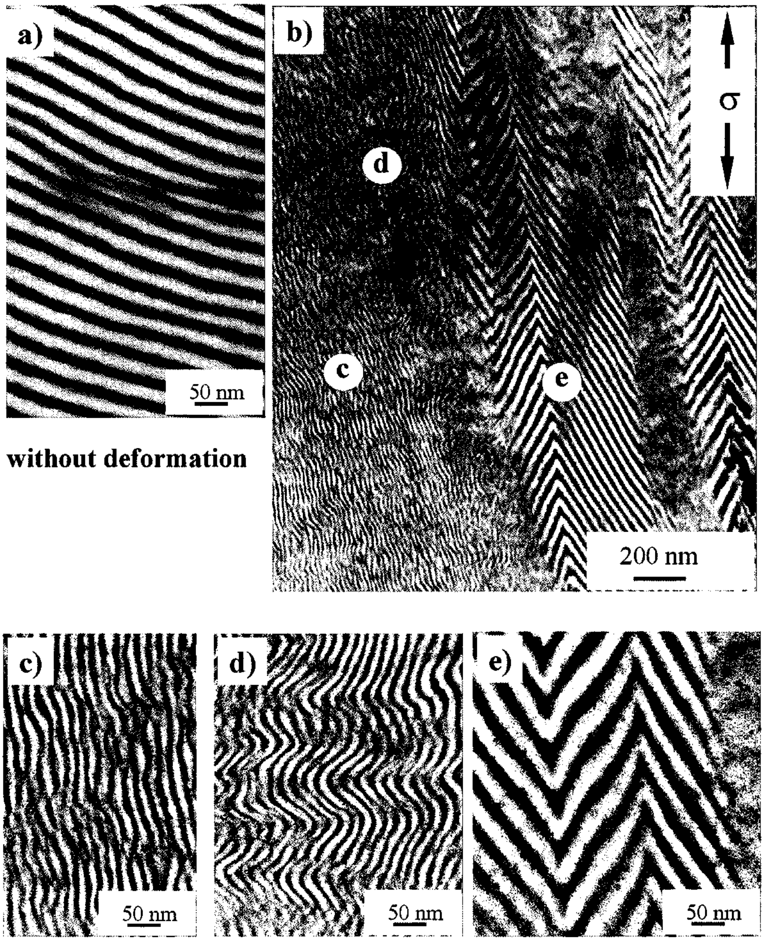

Figure 7. TEM micrographs showing the morphology of solution cast LN2-S74 without (a) and after (b-e) deformation; the picture in (a) is for comparison with that in (c,d,e), which represent the higher magnifications of regions indicated in Fig 7b; strain direction vertical.

It is interesting to note that undulations with waves are formed in highly drawn lamellae in Fig 7d. These waves appear to evolve by snapping back of the deformed lamellae by release of elastically stored energy after breaking of the tensile specimen. Due to 'polygranular' nature of the solution cast sample, the regions with lamellae perpendicular to the deformation direction lead to the formation of 'chevron'-like morphology. Note that the lamellae in Fig 7e have larger spacing than in the original sample. In consistence with the results of Cohen et al. [16], the lamellar spacing is markedly higher in the 'hinge' of the chevron morphology due to higher dilation of the rubbery PB layers. The increase in the PS lamella thickness further suggests the rotation of lamellar axis during tensile loading.

The strain induced structural changes developed in compression and injection moulded samples provide additional insight into deformation mechanism of the lamellar block copolymer (Fig 8). In the compression mould, there are manifold deformation structures. There are regions, where thickness and periodicity of lamellae changed to different extent after deformation, which represent the different states of plastic deformation of lamellae. In some regions, the lamellae appear to be similar to that of undeformed sample. These might have been formed by rotation of lamellae, which were originally not aligned along the deformation direction, and were not necessarily subjected to drawing. There are even regions, where the PB lamellae are much wider than the PS ones. This can be attributed to the separation of lamellae from each other if these lie perpendicular to the strain direction. On account of the lower Young's modulus and very low glass transition temperature, the polybutadiene lamellae are strongly stretched (dilated) forming isolated regions where PB lamellae (dark) are much thicker than in the undeformed sample (compare Fig 8a with Fig 3a).

By loading injection moulded samples along the flow direction (Fig 8b; compare with Fig 3b), more uniform deformation structures were observed at large deformation. The ordered lamellae structures of the block copolymer has been completely destroyed by plastic deformation. One can estimate the local draw ratio of the PS lamellae of more than 4, suggesting that the local strain of several hundred percent can be achieved by the drawing of glassy phase alone. The yielding of glassy layers as a cause of increased ductility has been discussed in detail in [18]. In the oriented injection moulded sample, the dominant deformation mechanism is, hence, the homogeneous plastic yielding of the layers causing a destruction of an original well-ordered lamellar morphology. On the other hand, in 'polygranular' solution cast films or compression moulds, the principal deformation mechanism at large strains comprise the rotation of the lamellae and lamellar grains towards the strain axis, the shearing in the rubbery layers and the plastic drawing of the glassy lamellae. The shearing in the PB lamellae leading to the higher orientation of polybutadiene chains was confirmed recently by means of FTIR spectroscopy [21].

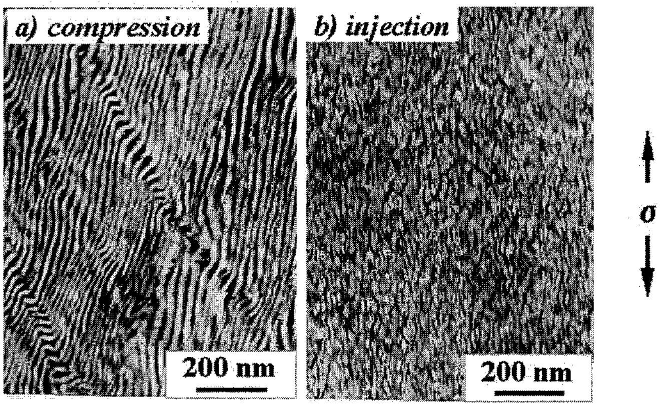

Figure 8: Representative TEM micrographs showing strain induced structural changes in the lamellar block copolymer LN2-S74 in compression mould (left) and injection mould (right); for morphology before deformation see Fig 3; deformation direction is shown by arrow.

c. Influence of temperature

It has been demonstrated that the macroscopic mechanical properties and underlying micromechanical mechanisms in the block copolymer are mainly governed by the nature and alignment of microphase separated structures. So far we have addressed the influence of modified molecular architecture on the morphology formation of block copolymers. We have noted that these modifications are generally associated with a strong $T_{g\text{-}PB}$ rise (Table 2), which restrict the lower service temperature of the polymer. Let us examine the deformation behaviour of the lamellar block copolymer LN2-S74 from room temperature down to the temperature close to the glass transition temperature of the soft phase, $T_{g\text{-}PB}$ (details will be available in a future publication [22]).

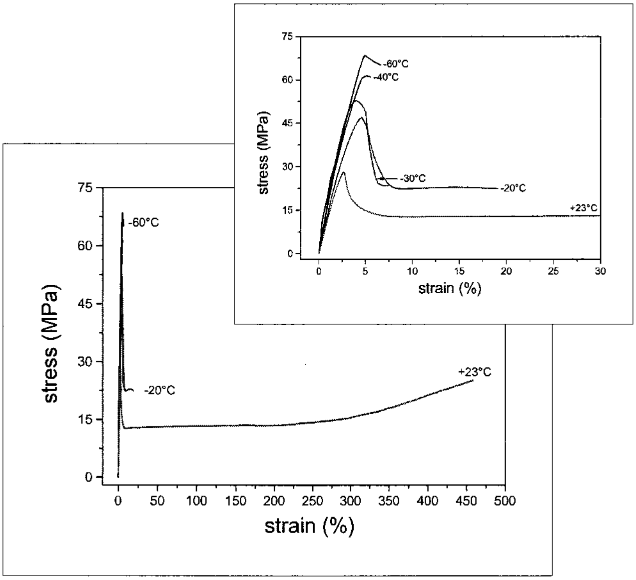

Figure 9. Stress-strain curves of the injection moulded lamellar block copolymer LN2-S74, loaded at different temperatures as indicated at a rate of 50 mm/min; initial part of the curves are magnified in the inset.

Representative stress-strain curves of LN2-S74 measured at different temperatures are plotted in Fig 9. With decreasing temperature, as expected, the strain at break decreases while the yield stress (a measure of strength) and Young's modulus (a measure of stiffness) increases. At a temperature ≤ –40 °C the block copolymer shows a brittle behaviour. Above –40°C, a ductile failure accompanied by a necking of the tensile specimens occurred. In spite of the neck formation and ductile nature of deformation, the strain at break was drastically reduced on lowering the test temperature: e.g., from about 450% (at +23°C) to about 20% (at –30°C). In contrast, the stiffness and strength increase almost linearly with decreasing temperature. The steep decrease in ductility of the lamellar block copolymer at lower temperatures, which is caused by the inability of the neck to extend over the large volume of tensile bar, is indeed an undesirable property.

As indicated previously, a massive increase in the $T_{g\text{-}PB}$, which is an indicator of the occurrence of polystyrene chains in the polybutadiene phase, should have a correlation with a drastically decreased strain at break. The PS chains that reside inside the PB phase seem to stiffen the rubbery layer to such an extent that the PB lamellae can hardly undergo shearing at lower temperatures. Thus, at the vicinity (~-50°C) and below of $T_{g\text{-}PB}$, the sample breaks in a brittle manner.

The ductile nature of deformation at lower temperatures is also manifested in the TEM micrographs of the lamellar block copolymer LN2-S74 deformed at –30°C. The thin sections for the TEM were prepared from a location very near to the fracture surface. The results are presented in Fig 10. The lamellae at –30°C have been plastically drawn homogeneously over a large specimen area. The deformation structures at –30°C and +23°C are qualitatively equivalent to each other. In the necked region, no craze-like zones were observed either.

In spite of the similarity of deformation mechanism at room temperature and at –30°C, the samples showed drastic reduction in the macroscopic strain at break. Due to a localisation of deformation in a limited area of the neck. The sample underwent fracture before the neck could extend macroscopically over the whole tensile specimen. Possible reason for the inability of the neck extension could be found in the fact that the test temperature approaches the glass transition of the soft phase. Therefore, a gliding of the PS lamellae between the soft parts is limited and local dangerous stress concentration can appear. However, it is remarkable that a a homogeneous drawing of the glassy layers (PS) even at the temperature 130°C below its glass transition temperature is possible.

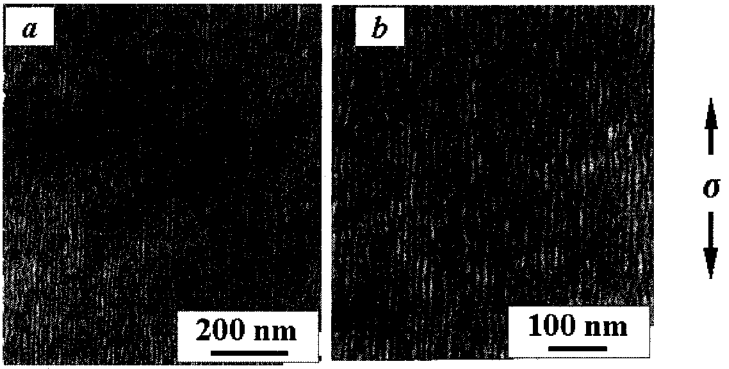

Figure 10. Lower (left) and higher (right) magnifications of TEM micrographs showing strain induced structural changes in injection moulded lamellar block copolymer LN2-S74 at –30°C; deformation direction is shown by arrow.

Summary and Outlook

We have studied the correlation between morphology and micromechanical properties of selected styrene-rich styrene/butadiene block copolymers with respect to their molecular architecture by transmission electron microscopy and uniaxial tensile testing. In particular, the structure-property correlation of an asymmetric linear SBS triblock copolymer was explored by the variation of sample processing methods as well as loading temperature. The micromechanical behaviour was found to be dependent on the alignment of microphases studied. Even at a temperature slightly above the soft phase T_g and far below the hard phase T_g, the glassy polystyrene lamellae showed a ductile behaviour attributable to the nano-scale morphology of the block copolymer systems. In future, systematic studies should concentrate to precisely elucidate how the block copolymer architecture affects the phase behaviour and micromechanical properties of their blends with homopolymers.

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