Asymmetric PS-block-(PS-co-PB)-block-PS block copolymers: morphology formation and deformation behaviour

Rameshwar Adhikari\(^1\), Trinh An Huy\(^2\), Matthias Buschnakowski\(^1\), Goerg H Michler\(^1\) and Konrad Knoll\(^3\)

\(^1\) Department of Engineering, Martin Luther University Halle-Wittenberg, D-06099 Halle/Saale, Germany
\(^2\) Department of Mechanics, Hanoi University of Technology, 01 Dai Co Viet Hanoi, Vietnam
\(^3\) BASF Aktiengesellschaft, Polymer Research, GKT/I-B1, D-67056 Ludwigshafen, Germany

E-mail: rameshwar.adhikari@iw.uni-halle.de

New Journal of Physics 6 (2004) 28
Received 20 October 2003
Published 2 March 2004
Online at http://www.njp.org/ (DOI: 10.1088/1367-2630/6/1/028)

Abstract. Morphology formation and deformation behaviour of asymmetric styrene/butadiene triblock copolymers (total polystyrene (PS) content \(\sim 70\%\)) consisting of PS outer blocks held apart by a styrene-co-butadiene random copolymer block (PS-co-PB) were investigated. The techniques used were differential scanning calorimetry, transmission electron microscopy, uniaxial tensile testing and Fourier-transform infrared spectroscopy. A significant shift of the phase behaviour relative to that of a neat symmetric triblock copolymer was observed, which can be attributed to the asymmetric architecture and the presence of PS-co-PB as a soft block. The mechanical properties and the microdeformation phenomena were mainly controlled by the nature of their solid-state morphology. Independent of morphology type, the soft phase was found to deform to a significantly higher degree of orientation when compared with the hard phase.
1. Introduction

One way of combining the useful properties of different homopolymers is to covalently join the respective polymer chains into a single macromolecule forming a block copolymer. Owing to their ability to self-assemble in a variety of ordered array of nanostructures, which have potential technological applications, these copolymers lie at the focus of contemporary macromolecular research [1]. The physical properties of these copolymers depend principally on their morphology (i.e. nature, size and alignment of the nanostructures). Thus, the control of block copolymer morphology is an issue of fundamental practical importance.

Phase behaviour of block copolymer systems prepared by anionic polymerization has been the object of several studies [2]–[4]. The synthetic techniques have been extended to prepare ABC-type triblock copolymers [5]–[8] as well as miktoarm block copolymers [9]–[12]. In particular, the monodisperse diblock copolymer systems and their blends have been intensively investigated (discussed by Hamley [13]). Recently, the application of controlled radical polymerization technique has been shown to be a reliable route towards the development of block-copolymer-based nanotechnology [14].

Phase behaviour of semicrystalline polymers have been found to be altered significantly by physical confinement of the surrounding. In this regard, diblock or triblock copolymers containing at least one crystallizable component provide model systems for the study of polymer crystallization under confined environment as discussed in several recent papers [8, 15, 16].

Styrene/diene block copolymers such as polystyrene-block-polybutadiene-block-polystyrene (SBS) and polystyrene-block-polyisoprene-block-polystyrene (SIS) triblock copolymers are often used as thermoplastic elastomers (TPEs). From the practical point of view, these materials represent an excellent class of heterogeneous polymers allowing the adjustment of mechanical behaviour via a change in composition and in various molecular parameters [13, 17]. In particular, the fine-tuning of mechanical and micromechanical behaviour of the block copolymers has been the subject of several recent studies. It has been demonstrated that
the asymmetry of the outer blocks in ABA-type block copolymers, the presence of a tapered sequence at the interfacial region, and various molecular topologies may have a pronounced influence on the phase behaviour of these nanostructured materials [18]–[20].

The block copolymers having different topologies (diblock, triblock, star block, graft block, etc) have been studied previously [9]–[12], [22]–[25]. The investigation of the effect of various molecular parameters on rheological and mechanical behaviour of block copolymers, especially of styrenic TPEs, was the object of such studies [23]–[25].

For mechanical properties of polymeric materials, the micromechanical processes of deformation and fracture play an important role as these processes determine the ultimate properties of the materials. It has been found that the tensile properties of styrene/butadiene block copolymers are directly associated with the nature of nanostructures formed [21, 26]. Up to now, structure–property correlation in classical block copolymer architectures as a function of their nanostructured morphology has been analysed.

In designing the articles made of styrene/diene block copolymers one has to take into account several aspects like mechanical stability (strength), toughness, stiffness, optical properties and also the resistance against degradation by environmental factors. The concern of adjusting the rheological properties is important to make the polymers easily processable. From the view of stability against thermal and photodgradation, it is desirable to keep the fraction of the diene component as low as possible and to produce morphologies capable of undergoing high degree of plastic deformation (energy-absorbing processes). In the styrene/butadiene triblock copolymers, this can be achieved by using a random copolymer of styrene and butadiene as the rubbery mid-block. However, this causes a limitation in the range of application temperatures by increasing the glass transition temperature of the soft phase to some extent. As a result, the effective volume fraction of the components and the extent of incompatibility may be altered significantly, which has a great influence on the phase behaviour of the resulting block copolymers. Hence, the correlation between molecular structure, morphology evolution, and deformation behaviour of these block copolymers needs a critical analysis.

A number of recent studies, experimental [11, 12], [18]–[25] as well as theoretical [27]–[29] ones, have demonstrated that a modification in the molecular architecture of block copolymers may open a new possibility of controlling their morphology in the melt and in the solid state. In addition to the influence of molecular architecture on the phase behaviour, several recent studies deal with the impact on fracture behaviour [30], micellization phenomena [31], chain dynamics [32], etc. The intention of our previous studies has been to elucidate the interrelation between these modifications and deformation mechanisms in technically interesting block copolymer systems [18]–[20]. In this paper, we attempt to explore further the impact of block copolymer architecture, and report the morphology formation and deformation mechanisms of styrene/butadiene block copolymers possessing, instead of a pure polybutadiene (PB) mid-block, a random copolymer of styrene and butadiene (PS-co-PB).

Generally, macroscopic tests such as tensile testing, creep, relaxation or hysteresis tests provide the bulk properties of materials. Microscopic morphologies and structures of heterogeneous polymers are generally studied by electron microscopy and scattering techniques. On the other hand, the morphological information on the molecular scale can be obtained by spectroscopic methods such as Fourier-transform infrared (FTIR) spectroscopy. A combination of two or more of these techniques enables more precise understanding of complex structure–property correlation in polymeric materials. Hence, the goal of this study is to collect complementary information on structure and properties of individual phases of nanostructured
Table 1. Characteristics of the block copolymers investigated.

| Samples | $M_n$ (g mol$^{-1}$)$^a$ | $M_w/M_n$$^a$ | $\Phi_{ST}$$^b$ | Molecular architecture                  |
|---------|-----------------------|--------------|----------------|----------------------------------------|
| ST3     | 85 700                | 2.10         | 0.74           | Highly asymmetric star, small PS core  |
| LN3     | 127 300               | 1.10         | 0.74           | Highly asymmetric linear copolymer     |
| LN4     | 116 000               | 2.30         | 0.65           | Linear symmetric copolymer             |

$^a$ Number-average ($M_n$) and weight-average ($M_w$) molecular weight determined by gel permeation chromatography (GPC) using PS calibration.

$^b$ Total styrene volume fraction determined by Wijs titration and procedures.

Figure 1. Schemes showing the molecular architecture of the investigated block copolymers; white and dark colours stand for PS and PB phases, respectively.

block copolymers by using different techniques, which provide information on different length scales.

2. Experimental

2.1. Materials and sample preparation

The characteristics of the block copolymers investigated in this study are given in table 1 and the molecular structures are schematically illustrated in figure 1. The details concerning the synthesis and characterization of these block copolymers may be found in [24], [33]–[35]. All the samples were synthesized by butyl-lithium initiated living anionic polymerization. The block copolymers ST3, LN3 and LN4 have total styrene volume fraction of 0.74, 0.74 and 0.65, respectively. Therefore, each polymer is compositionally asymmetric. It should be noted that, owing to the equal length of outer PS blocks, LN4 is a linear symmetric block copolymer with respect to its architecture. All the polymers have one feature in common: the presence of PS-co-PB as a rubbery block. With respect to architecture, ST3 and LN3 are highly asymmetric, i.e. the molar ratio of longer to shorter outer PS blocks is much higher than unity. The asymmetric star-shaped
copolymers were synthesized by twofold addition of an initiator and a final coupling step [24], and the resulting polymer molecules have four arms on average.

The samples were prepared by solution casting. For this purpose, films about 0.5 mm thick were prepared from 3% (w/v) solution of the samples in toluene by evaporating the solvent in about 2 weeks followed by subsequent vacuum drying. Finally, the films were annealed under reduced pressure for 48 h at 120 °C.

2.2. Techniques used

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC 820 in the temperature range −120 to 150 °C with a rate of 10 K min⁻¹ using the cycle heating–cooling–heating to determine the glass transition temperature of the constituent components. The heat flow and the second derivative of the heating scans were used for the analysis of the glass transition temperature. The weight of each sample was approximately 10 mg.

Uniaxial tensile testing was used to characterize the mechanical deformation behaviour of the block copolymers. Tensile bars of total length 50 mm and width 4 mm were cut from the solution cast films, which were strained at 23 °C at a cross-head speed of 50 mm min⁻¹ using a Zwick universal tensile machine. At least six samples were tested.

The microphase-separated morphologies of the samples were imaged by means of transmission electron microscopy (TEM) using osmium tetroxide (OsO₄) as a selective staining agent for the butadiene phase. The ultrathin sections (about 70 nm) of the samples were cut using a Leica ultramicrotome, which were investigated with a TEM (200 kV TEM, JEOL, JEM 2010).

Rheo-optical FTIR spectroscopy was employed using the Perkin–Elmer FTIR spectrometer S2000 equipped with a special stretching device to monitor the strain-induced molecular orientation in individual phases. Infrared spectra were recorded with a resolution of 2 cm⁻¹ in the wavenumber range 700–3500 cm⁻¹. The rheo-optical measurements were carried out during stretching specimens in different strain steps with a polarizer adjusted alternately parallel and perpendicular to the stretching direction. For FTIR spectroscopic measurements, thin films about 40 μm thick were prepared by compression moulding of copolymer pellets at 180 °C.

By FTIR investigations, using the ratio of the absorbances of beams polarized parallel (\(A_{||}\)) and perpendicular (\(A_{\perp}\)) to the deformation direction, the dichroic ratio \(R = A_{||}/A_{\perp}\) and the degree of orientation \(f\) can be calculated:

\[
f = \frac{R - 1}{R + 2} \frac{R_0 + 2}{R_0 - 1},
\]

where \(R_0 = 2 \cot^2 \psi\) is the dichroic ratio for perfectly aligned chains oriented parallel to the deformation direction and \(\psi\) the angle between the direction of the vibrational transition moment and the polymer chain axis. Thus, if the transition moment angle is known the degree of orientation may be easily quantified.

For the quantitative characterization of chain alignment in individual phases during uniaxial deformation, bands around 1028 and 966 cm⁻¹ were selected for the PS and the PB phases, respectively. The band at 1028 cm⁻¹ was assigned to bending vibration of aromatic C–H bonds [36]; its transition moment angle was observed to be perpendicular to the chain axis [37].
Table 2. Glass transition temperature of different phases in the investigated block copolymers and their morphologies.

| Samples | \( T_{g(PS)} \) (°C)\(^a\) | \( T_{g(soft)} \) (°C)\(^a\) | PS wt% in PS-co-PB\(^b\) | PS wt% as hard phase\(^c\) | Expected morphology | Observed morphology |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| ST3     | 100             | −60             | 0.35            | 60              | Lamellae        | Co-continuous   |
| LN3     | 102             | −50             | 0.42            | 55              | Lamellae        | Lamellae        |
| LN4     | 70              | −34             | 0.52            | 28              | PS cylinders    | PS domains      |

\(^a\) Glass transition temperature of hard PS phase \( (T_{g(PS)}) \) and that of soft PS-co-PB random copolymer phase \( (T_{g(soft)}) \).
\(^b\) Calculated using Fox’s equation assuming volume fraction–weight fraction.
\(^c\) Difference between total PS content and PS present in the PS-co-PB phase.

band at 966 cm\(^{-1}\) was assigned to an out-of-plane C–H bending mode in \textit{trans}-1,4-butadiene [38]; its transition moment angle was also observed to be approximately perpendicular to the chain axis [39, 40].

3. Results and discussion

3.1. Estimation of hard/soft volume ratio using DSC data

One principal advantage of styrene/butadiene block copolymers from practical point of view is that the constituent homopolymer chains have widely separated glass transition temperatures \( (T_g) \). At sufficiently high molecular weight, \textit{trans}-1,4-polybutadiene (PB) and general-purpose polystyrene (PS) homopolymers have \( T_g \) of about −100 and +100 °C, respectively. Being incompatible systems, the \( T_g \) of PS and PB blocks in a styrene/butadiene block copolymer generally should correspond to that of corresponding homopolymers. However, in the present case, in contrast with the conventional styrenic TPEs, the rubbery block is made up of a random copolymer of styrene and butadiene (PS-co-PB). Hence, it may be expected that \( T_g \) of the soft phase is increased relative to that of the pure PB \( (T_{g(PB)}) \). Generally, the extent of the \( T_g \) shift depends on the interaction between components, i.e. the amount of styrene content present in the rubbery block. Thus, larger the amount of styrene content in the rubbery block farther will be the shift in \( T_g \). In this way, the extent of increase in \( T_{g(PB)} \) may be used to roughly estimate the amount of PS chain segments present in the random copolymer block. Since the glass transition temperature at lower temperatures for each copolymer corresponds to that of soft PS-co-PB phase, it will be denoted by \( T_{g(soft)} \) in the subsequent discussions. The \( T_g \) of the different phases of the investigated block copolymers determined by DSC are listed in table 2.

In fact, relative to that of pure PB the \( T_{g(soft)} \) of the samples is shifted towards higher temperature (table 2) and follows the order LN4 (−34 °C) → LN3 (−50 °C) → ST3 (−60 °C). It means that the amount of PS chain segments contained by PS-co-PB block is highest for LN4 and the least for ST3.

Numerous attempts have been made to relate the glass transition temperature of a miscible mixture to the compositions [41]. Assuming that butadiene and styrene sequences are fully mixed in the soft phase of the SBS block copolymers investigated, the \( T_g \) of a random copolymer may be successfully estimated by the Fox equation. Given the weight fractions of the components,
one can calculate the $T_g$ of a random copolymer of styrene and butadiene:

$$\frac{1}{T_{g(\text{soft})}} = \frac{w_{\text{PS}}}{T_{g(\text{PS})}} + \frac{w_{\text{PB}}}{T_{g(\text{PB})}},$$

(2)

where $w_x$ and $T_{g(x)}$ are the weight fraction and the glass transition temperature of the component $x$, respectively, and $T_{g(\text{soft})}$ the glass transition temperature of the soft phase (i.e. PS-co-PB). Conversely, one can estimate the amount of PS weight fraction present in the copolymer knowing the $T_g$ of the random copolymer.

Using $T_{g(\text{PS})}$ and $T_{g(\text{PB})}$ as +100 and $-100 \degree C$, respectively, and from the experimentally determined $T_g$ of the soft phase given in table 2, one can estimate the weight fraction of styrene present in the random copolymer blocks of each block copolymer by equation (2). The calculated styrene weight fraction of 0.52 in LN4 is in good agreement with the value adjusted during the polymerization process (styrene/butadiene ratio = 1:1, [24]). The weight fractions of the styrene chain segments present in the random blocks of ST3 and LN3 calculated in a similar way are approximately 0.35 and 0.42, respectively (see table 2).

It should be noted that all the block copolymers studied are asymmetric with respect to their composition: ST3, LN3 and LN4 contain 74, 74 and 65% by volume of total PS. Since a part of PS is accommodated in the PS-co-PB blocks, the total volume fraction of the PS as hard phase is significantly reduced. The estimated volume fractions of PS as hard phase in ST3, LN3 and LN4 are 60, 55 and 28%, respectively (see table 2).

### 3.2. Microphase-separated morphology of block copolymers

In a styrene/butadiene diblock copolymer having 74 and 65% of PS, hexagonal PB cylinders (equivalent to figure 2(a)) and bicontinuous ‘gyroid’ morphology, respectively, are formed [14]. However, due to modified architecture and resulting new effective phase volume ratio, a significant shift in the morphology formation occurs. On the basis of a classical phase diagram (even by considering only the effective volume fraction of the components (table 2)), one may assign lamellar morphology for ST3 and LN3, and PS cylinders for LN4. However, it should be noted that the influence of molecular architecture and that of the modified interfacial structure on the microphase separation behaviour cannot be disregarded. These parameters are decisive in the microphase separation phenomena of the block copolymers [27, 42] (see below).

The representative TEM images of the block copolymers studied are given in figure 2, which illustrate their equilibrium morphologies. For comparison, the morphology of a linear symmetric SBS triblock copolymer (LN1, $\Phi_{\text{PS}} \sim 0.74$ [20]) is also presented. In these micrographs, brighter and darker areas correspond to glassy (PS) and rubbery (PB or PS-co-PB) phases, respectively. The images of different samples are arranged in such a way that the variation of morphologies follows the order: PS matrix with PB cylinders as expected (LN1) $\rightarrow$ lamellae (LN3) $\rightarrow$ bicontinuous-like (ST3) $\rightarrow$ PS domains (LN4). All the samples show phase segregation on the nanometre scale. The long period of the microphase-separated structures is about 30–50 nm, whereas the thickness of the PS domains or lamellae lies in the range 15–30 nm (see table 3).

As mentioned earlier, the decrease in the actual volume fraction of PS as hard phase owing to the presence of a PS-co-PB as rubbery block favours the formation of morphologies corresponding to lower overall PS content. The soft/hard volume ratio in the linear symmetric
block copolymer LN4 is approximately 72 : 28 (table 2). Thus, as expected, domains of PS dispersed in the matrix of PS-co-PB are formed (see figure 2(d)). Besides the influence of modified interfacial tension, there is no direct impact of molecular architecture in its morphology. Indeed, this morphology resembles the structure of classical SBS TPEs, which contain about 28% PS (see e.g. [21]), the overall composition nearly the reverse of LN4. However, the domains have a diffuse boundary with the matrix, and a well-defined hexagonal lattice of the ordered structure is missing. Additionally, the order–disorder transition temperature ($T_{\text{ODT}}$) was found to depress highly in this block copolymer [24]. With these characteristics, this block copolymer represents a weakly segregated system.

In ST3 and LN3, besides the impact of modified phase volume ratio, there is an influence of the asymmetric architecture in agreement with earlier experimental [12] and theoretical [27]–[29] works on asymmetric block copolymers. At high asymmetries (e.g. if the molecular

---

**Figure 2.** Representative TEM micrographs of the solution cast block copolymers studied compared with a linear symmetric block copolymer having 74% PS; (a) LN1, (b) LN3, (c) ST3 and (d) LN4.
Table 3. Mean inter-domain spacing ($L$) and PS domain thickness ($D_{PS}$) for the block copolymer system measured using TEM micrographs.

| Samples     | $L$ (nm) | $D_{PS}$ (nm) |
|-------------|----------|---------------|
| ST3         | 32       | 18            |
| ST3 + 20% PS015 | 40     | 21            |
| LN3         | 32       | 17            |
| LN3 + 20% PS015 | 38     | 20            |
| LN4         | 33       | 17            |
| LN4 + 35% PS015 | 46     | 27            |

weight ratio of the outer A blocks is too high), a stable lamellar phase was predicted in an asymmetric ABA triblock copolymer even at compositions where the volume fraction of A was higher than 0.70 [27]. It was proposed that even a part of shorter outer A blocks can be pulled into the middle B block domains at high asymmetries. A similar situation of high asymmetry is present in sample LN3. In fact, we had reported the formation of lamellar morphology in highly asymmetric ABA triblock copolymers in our previous works [19, 20]. Thus, there is also a contribution of the asymmetric architecture for the development of lamellar structure in LN3 (figure 2(b)). It should be noted that, due to the presence of random PS-co-PB as a rubbery block, the volume fraction of PS as hard phase is already reduced to about 0.55 (see table 2), which alone would satisfy the condition for lamellar morphology even ignoring the impact of asymmetric architecture.

Interestingly, the largest deviation was observed in ST3 whose overall composition and mid-block constitution is identical with that of LN3. Neither the morphology corresponding to effective phase volume ratio (60% PS as hard phase; table 2) nor the one predicted by the theory of asymmetric block copolymer [27] can be assigned to ST3 owing to the star-shaped architecture and large polydispersity. However, one may anticipate that a large part of short PS chains (especially those from the PS core and short outer blocks; see figure 1) can be mixed with the rubbery PS-co-PB blocks. The concept of partial mixing of PS chains with the rubbery phase in asymmetric block copolymers was supported by the dynamic mechanical analyses of several block copolymers [43]. The TEM micrograph of ST3 (figure 2(c)) reveals that the PS struts (grey domains) form an interpenetrating network embedded in the PS-co-PB matrix. This morphology closely resembles the ‘gyroid’ phase observed in block copolymer systems.

The morphologies presented in figure 2 were obtained by changing the block copolymer architecture at approximately 70% PS content. Particularly, all the basic morphologies of the block copolymer were produced. Thus, our experimental results demonstrate that the modification of molecular structure of the block copolymers allows an independent control of microphase morphology and composition.

Complementary information on the phase behaviour and morphology of block copolymers can be obtained by the addition of a low-molar-mass polystyrene homopolymer (hPS) to the block copolymer. Figure 3 illustrates the representative TEM images of blends of the investigated block copolymers with PS015 (an hPS having weight-average molecular weight $M_w = 15$ 100 g mol$^{-1}$) at lower hPS concentrations. Since the molecular weight of the added hPS is lower than that of the corresponding block of the block copolymers, the former chains should be accommodated in the PS block domains of the latter. The molecular weight of the longest PS block in asymmetric
block copolymers ST3 and LN3 lies in the range 60 000–90 000 g mol$^{-1}$. The outer PS block in LN4 has a molecular weight of about 18 000 g mol$^{-1}$.

The addition of 20 wt% PS015 to ST3 turns the co-continuous morphology to a lamellar one (see table 3) suggesting that the morphology of pure ST3 is one corresponding to lower PS content than that required for lamellar structure. Since the stable morphology observed in the styrene/diene systems at lower PS content than required for lamellae is a ‘gyroid’ phase, the equilibrium structure of ST3 is close to the bicontinuous ‘gyroid’ morphology. The addition of the same amount of PS015 to LN3 leads, however, to an increase of long periods and widening of PS lamellae (see table 3). It suggests, at least, that the lamellar morphology of LN3 does not lie at the border line between the lamellar and cylindrical structures and, hence, confirms the architecture-induced lamellar structure of this sample.

The addition of 35 wt% of PS015 to LN4 transforms the morphology from dispersed PS domains to one comprising layers and co-continuous domains. This confirms the validity of assignment of morphology of PS domains (disordered PS cylinders or spheres; figure 2(d)) dispersed in rubbery PS-co-PB matrix for LN4. A well-defined morphology corresponding to one of the stable block copolymer phases was not observed in this blend.

Finally, it should be stressed that, in fact, besides the volume fraction of the phases in block copolymers, 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 [13]. Thus, a change in the chemical nature of the blocks at the interfacial region (neat versus tapered or random) should affect the thermodynamic equilibrium and the resulting morphology.

3.3. Deformation behaviour of block copolymers

Tensile stress–strain curves of the block copolymers measured at room temperature ($23{^\circ}C$) are plotted in figure 4.
The asymmetric block copolymers ST3 and LN3 exhibit yielding at a strain of about 4% strain, which represents the onset of plastic deformation of the polymers. The yield stress is about 10 MPa. After the yield point, the deformation is accompanied by a so-called ‘cold drawing’ process until about 100% and then the stress level rises monotonically in both block copolymers. Both copolymers (with lamellar or co-continuous morphology) show a ductile behaviour characterized by a large degree of plastic deformation.

The sample LN4 shows, as expected from its phase morphology, a tensile behaviour similar to that of an SBS TPE [21] at room temperature. This represents predominantly an entropy-elastic behaviour. A shoulder (corresponding to a yield point where the plastic deformation of glassy domains begins) at a strain of about 10% was observed. The sample showed an elongation at break of several hundred per cent and a large degree of strain recovery.

A closer inspection of the initial part of stress–strain diagram of sample ST3 reveals that there are two different yield points located at a strain of about 4 and 20%. Independent of sample preparation methods and thickness of tensile bars, the phenomenon of ‘double yielding’ was always observed in ST3. The presence of these well-separated yield points makes its mechanical deformation behaviour resemble that of different polyethylene (PE) samples discussed in the literature [44, 45]. The presence of two different yield points in PE has been discussed in terms of different micromechanical processes at the initial stage of plastic deformation. According to a widely accepted model, the yielding in semicrystalline polymers is governed by two structurally well-defined processes [44, 45]: the slip of the crystal mosaic blocks in the crystalline lamellae corresponding to the first yield point, and the shear yielding of the crystal blocks resulting in the second yield points (see [46] for details on the yielding processes in ST3).

In the previous section, we have shown that the modified architecture of block copolymers leads to the formation of different kinds of morphologies at constant composition, which determine the ultimate mechanical properties of the materials. A symmetric SBS triblock
A copolymer with equivalent composition as ST3 and LN3 would form a PS matrix (see figure 2(a)) and undergo a brittle fracture [20]. Owing to the lamellar (e.g. LN3) and co-continuous (e.g. ST3) morphologies, that result from their special molecular architecture, LN3 and ST3 show a ductile behaviour instead. Hence, it can be concluded that tensile properties studied are affected directly by the nature of microphase-separated morphology; the molecular architecture of the block copolymers plays an indirect role.

In the following, we discuss the strain-induced structural changes found in the block copolymers. Actually, the macroscopic mechanical properties measured during a uniaxial tensile testing are the expressions of how the structural details on different length scales of the materials react towards the applied stress. Hence, the micromechanical properties form a bridge between the morphology of the polymers and their macroscopic mechanical behaviour. Figures 5 and 6

Figure 5. Representative TEM micrographs of solution cast ST3 film after tensile deformation; strain direction is indicated by an arrow.
Figure 6. TEM images showing the morphology of solution cast LN3 film after tensile deformation; strain direction is indicated by an arrow.

represent the morphology of the samples ST3 and LN3, respectively, after deformation. The sections for the TEM studies were taken from the specimens broken in tensile tests from the locations close to a fracture surface.

By means of small-angle x-ray scattering, Dair et al [47, 48] recently studied the deformation behaviour of block copolymers revealing ‘gyroid’ morphology using both unoriented and oriented samples. It was suggested that the glassy PS struts undergo irrecoverable permanent plastic deformation on tensile loading. The deformation structures given in figure 5 provide direct evidence of the plastic deformation of glassy phase in a block copolymer revealing co-continuous ‘gyroid’-like morphology (ST3). Unlike the microphase-separated structures of the undeformed specimen, after deformation, the structures have a preferential orientation along the strain direction. The mean inter-domain spacing has decreased from \( \sim 32 \) to \( \sim 18 \) nm. The most important message of these deformation structures is that the co-continuous morphology
deforms via the plastic drawing and preferential orientation of microphases towards the strain direction. Finally, at higher deformations, a parallel array of highly drawn fibrils persist (see figure 5).

The deformation structures of the lamellar block copolymer LN3 are presented in figure 6. In accordance with earlier results on lamellae forming block copolymers, the deformation structures comprise highly drawn lamellae. The intensive plastic deformation causes a significant decrease in the lamellar long period. In contrast with the polygranular structure of the undeformed sample, where the lamellae were found to align in all possible directions, tensile deformation has caused the microphase-separated morphologies to orient preferentially along the strain direction. This suggests further the rotation of the whole grain structure towards the strain axis. Fish-bone-like structures are evolved by the lamellae, situated initially normal to the strain axis [49].

The deformation of LN4 was studied in our previous paper [50]. It was concluded that the cylinder-like PS domains undergo fragmentation at higher deformation, which regenerate again after removal of load. No plastic drawing of glassy PS domains was observed at room temperature.

The homogeneous plastic deformation of glassy PS lamellae without formation of localized deformation zones such as crazes was explained by the mechanism of ‘thin-layer yielding’ [18]. According to this mechanism, the yield stress of the layers decreases on decreasing the dimension of glassy layers from the macroscopic to the nanoscopic scale. Finally, when the thickness of these layers is in the range of 20 nm, these are able to undergo a large homogeneous plastic flow. Actually, the layers with the thickness in the range of 10 nm are shown to possess higher chain mobility (decreased glass transition temperature) [51, 52], which substantiates the idea of yielding of PS layers below a critical thickness.

3.4. Strain induced molecular orientation behaviour

3.4.1. Influence of block copolymer phase behaviour and morphology. Figure 7 presents the orientation behaviour of individual phases (i.e. PS and PB) of the block copolymers caused by uniaxial stretching. The curves represent average orientation of the individual chains located in a macroscopic volume. The degrees of orientation, determined by using equation (1) as discussed in the experimental section, are plotted in a common x-axis, which enables a direct comparison of extent of orientation in individual phases at different stages of deformation.

At first glance, it can be noticed that the PB chains shows stronger orientation when compared with the PS chains independent of the nature of morphology in agreement with our earlier results [53]. Both PB and PS phases orient almost linearly with strain in ST3 (figure 7(a)). The linear and monotonic increase in the degree of orientation with strain in ST3 implies that the co-continuous morphology is progressively destroyed with strain. Close to fracture, the original morphology is completely transformed into the highly drawn filaments all aligned towards deformation direction (see figure 5). The collapse of double ‘gyroid’ morphology in an SBS block copolymer at higher deformation was proposed recently based on the small-angle scattering experiments by Sakurai et al [54], which correlates well with the evolution of morphology comprising highly drawn filaments observed in this study.

In LN3 (figure 7(b)) and LN4 (figure 7(c)), the PB phase orients more steeply than PS at lower strains (up to about 50% strain). It suggests that the initial stage of deformation is dominated by gliding movement (slip of hard domains past each other) of the glassy domains or lamellae. The latter causes a strong increase in soft-phase orientation allowing a negligible alignment of the
chains in the hard phase itself. In the lamellar block copolymers (LN3), additionally, formation of fish-bone-like morphology (chevron-patterns) takes place at higher strains (see figure 6) where the soft phase is strongly dilated. The latter may contribute instantaneously to increase the chain orientation in the soft phase. In contrast, no pronounced chevron morphology appears in ST3 (see figure 5). As a consequence, LN3 allows a stronger orientation in PB phase when compared with ST3.

Figure 7. Degree of orientation of individual phases in different samples measured by FTIR spectroscopy plotted as a function of applied strain: (a) ST3, (b) LN3 and (c) LN4.
As the soft phase forms matrix in LN4, the applied stress is received earliest by the rubbery phase at all the deformation stages. This explains satisfactorily a stronger molecular orientation of the butadiene phase in this block copolymer than in both LN3 and ST3.

The orientation in the styrene phase can be correlated well with molecular structure and morphology of the block copolymers studied. There are two different kinds of contributions for the orientation of PS phase: orientation of PS from PS-co-PB (soft phase) and PS outer blocks (hard phase). However, it is impossible to independently evaluate these two contributions.

Although the degree of orientation increases with strain, the extent of orientation in the PS phase of LN4 is very weak. Since the molecular weight of PS outer blocks in LN4 is about 18,000 g mol$^{-1}$, it is sufficient to create good physical cross-links but not for the formation of stable entanglements with each other. Thus, PS domains undergo brittle fracture before an intensive drawing process can begin. This fragmentation process, which takes place at the stage of plastic-to-rubber transition [55]–[57], can contribute only insignificantly to the measured degree of orientation. Thus, the weak molecular orientation of the PS phase observed in LN4 results almost solely from the orientation of PS chain segments present in the PS-co-PB copolymer.

In LN3 and ST3, the large plastic deformation (necking and drawing) of the PS lamellae or the PS struts embedded in the PS-co-PB phase takes place, which is indicated by a drastic reduction in the inter-domain spacing and domain thickness after deformation as discussed in the previous section. The plastic deformation processes such as shearing, kinking and drawing of the glassy phase [56, 57] is accompanied by the chain orientation along the stretching direction. Hence, this leads to a higher degree of orientation of the PS phase. Additionally, the DSC of the copolymers showed that sample LN3 contains much larger amount of PS chain segments than ST3 in the rubbery PS-co-PB block (see table 2). Thus, the contribution from these segments to the degree of orientation in LN3 is much higher. As a result, the overall degree of PS phase orientation in LN3 is higher when compared with that in ST3.

3.4.2. Molecular orientation during loading/unloading cycle. A deeper insight into the deformation behaviour of the copolymers, both on microscopic and molecular scales, can be obtained by subjecting the materials to deform in a loading–unloading cycle. These tests are particularly useful in characterizing the reversibility and extent of plastic deformation in elastomeric polymers. In one such test, a specimen can be deformed in a tensile test to a given strain and unloaded again up to zero stress. Figure 8(a) shows typical stress–strain curves of LN3 and LN4 (initially loaded to a strain of 200%) after a consecutive loading–unloading cycle. Figure 8(b) plots the residual strain recorded after such tests on loading the samples to different degrees of tensile deformation. One can clearly see that the residual strain of the sample LN4 is much smaller when compared with that of LN3. Thus, the former has far better reversibility than the latter. In other words, the extent of irrecoverable plastic deformation is considerably high in LN3, which makes it resemble a thermoplastic polymer (such as polypropylene (PP) or polyethylene). The non-recoverable plastic deformation is correlated with the intensive plastic drawing of lamellae (see figure 6). In contrast, low value of residual strain for LN4 explains that its initial morphology is almost completely regenerated after the removal of load [50].

It is interesting to study whether these macroscopic phenomena occurring during loading and unloading stages of deformation have correlations with the molecular orientation behaviour of these polymers. Figure 9 compares the orientation–strain curves of LN3 and LN4 compared with that of a dynamic vulcanizate (DV; PP/EOC weight ratio 30 : 70) based on PP and
Figure 8. Mechanical properties of LN3 and LN4 determined by tensile testing compared: (a) strain–strain curves for loading/unloading cycle (ultimate strain 200%) and (b) residual strain plotted against applied strain.

ethylene/1-octene copolymer (EOC). Details on the orientation behaviour of the DV can be found elsewhere [50].

On loading the sample, the DV shows a high degree of orientation in the rubbery EOC phase. After unloading, the orientation in the EOC phase decreases strongly, indicating a reversible orientation behaviour of molecular chains. The orientation in the hard phase (crystalline PP) increases in the loading stage which, in contrast, remains practically unchanged during unloading. The plastically deformed PP phase remains fixed in its position and hinders the recovery of the orientation in the soft phase [50]. The behaviour of the nanophase-separated block copolymer is completely different from the DV, in which the dimension of phase separation lies in the range of a few hundred nanometres.

On loading the block copolymers, the orientation in both the phases increases with strain, which after unloading is recovered almost complete reversibly. Even in the lamellar block copolymer (LN3), where the strain recovery is too small, the degree of orientation drops to a
very low level (close to that of undeformed sample). The pronounced recovery of the orientation (i.e. a reversible orientation) in both the phases of the block copolymers is attributable to a strong interaction between the component chain, which is enhanced not only by a chemical junction between the incompatible blocks but also by the presence of PS-co-PB copolymer as the soft phase. A similar effect of relaxation of chains on annealing of the SBS block copolymers drawn to high deformation was reported by Zhao [58]. In the present study, a slightly different picture may be expected if the change in the degree of orientation during unloading is measured for a sample stretched close to fracture because the deformation to this extent results in a highly anisotropic morphology and a much higher degree of final orientation. Nevertheless, the asymmetric architecture of the lamellar block copolymer might have played a key role to cause a reversible molecular orientation of the constituent phases. This aspect should be explored further in future.

4. Conclusions

This study demonstrates that the combination of microscopic and spectroscopic techniques enables a more precise understanding of complex structure–property correlation of nanostructured block copolymer systems. The results can be concluded as follows.

1. A large variety of microphase-separated structures is obtained by changing the molecular structure of the copolymers at nearly constant composition. The mechanical properties
and the microdeformation phenomena are mainly dependent on the microphase-separated morphology of the block copolymers. The molecular architecture of the copolymers exercises only a secondary influence.

2. A large degree of plastic deformation of the glassy phase is responsible for the observed ductile behaviour of the block copolymers possessing lamellar and co-continuous morphology. In particular, the bicontinuous morphology of the block copolymer is transformed to a fibrillar structure at large deformation leading to a strong decrease in inter-domain spacing.

3. On the molecular scale, the strain-induced orientation behaviour is dependent on the nature of microphase-separated structure. Independent of morphology type, the soft phase deforms to a significantly higher degree of orientation when compared with the hard phase. After unloading, the orientation in both component phases is found to rapidly relax in spite of an irreversibly deformed microscopic morphology.

Acknowledgments

We are grateful to the German Science Foundation (DFG) and Government of Sachsen-Anhalt for financially supporting a part of this work. We are indebted to Mrs S Ilisch and Mrs S Goerlitz for performing tensile testing and TEM studies, respectively. We also thank Professor H-J Radusch for providing the facilities for FTIR and DSC characterization of the block copolymer samples.

References

[1] Lodge T P 2003 Macromol. Chem. Phys. 204 265
[2] Hasegawa H and Hashimoto T 1996 Comprehensive Polymer Science Suppl. 2 (Oxford: Pergamon) p 497
[3] Hashimoto T, Koizumi S and Hasegawa H 1994 Macromolecules 27 1562
[4] Zhu Y, Gido S P, Iatrou H, Hadjichristidis N and Mays J W 2003 Macromolecules 36 148
[5] Abetz V and Goldacker G H 1999 AIP Phys. Today 2 32
[6] Bates F S and Fredrickson G H 1999 Macromolecules 32 1226
[7] Balsamo V and Stadler R 1999 Macromolecules 32 3994
[8] Pispas S, Floudas G and Hadjichristidis N 1999 Macromolecules 32 9074
[9] Yang L, Hong S, Gido S P, Velis G and Hadjichristidis N 2001 Macromolecules 34 9069
[10] Hadjichristidis N, Pispas S, Pitsikalis M, Iatrou H and Vlahos C 1999 Adv. Polym. Sci. 142 71
[11] Lee C, Gido S P, Poulos Y, Hadjichristidis N, Tan N B, Trevino S F and Mays J W 1997 J. Chem. Phys. 107 6460
[12] Hamley I W 1998 The Physics of Block Copolymers (Oxford: Oxford Science Publications)
[13] Greszta D, Mardare D and Matyjaszewski K 1994 Macromolecules 27 638
[14] Kajiwar A, Maeda K, Kubo N and Kamachi M 2003 Macromolecules 36 526
[15] Loo Y-L, Register R A, Ryan A J and Dee G T 2001 Macromolecules 34 8968
[16] Bates F S and Fredrickson G H 1998 Thermoplastic Elastomers 2nd edn (Munich: Hanser) p 336
[17] Michler G H, Adhikari R, Lebek W, Goerlitz S, Weidisch R and Knoll K 2002 J. Appl. Polym. Sci. 85 683
[18] Adhikari R, Godehardt R, Lebek W, Weidisch R, Michler G H and Knoll K 2001 J. Macromol. Sci.–Phys. 40 833
[19] Adhikari R, Michler G H, Huy T A, Ivankova E, Godehardt R, Lebek W and Knoll K 2003 Macromol. Chem. Phys. 204 488
[20] Holden G 2000 Understanding Thermoplastic Elastomers (Munich: Hanser)
[21] Weidisch R, Laatsch J, Michler G H, Arnold M, Schade B and Fischer H 2002 Macromolecules 35 6585

New Journal of Physics 6 (2004) 28 (http://www.njp.org/)
[23] Shim J S and Kennedy J P 1999 J. Polym. Sci.–Polym. Chem. 37 815
[24] Knoll K and Nießner N 1998 Macromol. Symp. 132 231
[25] Shim J S and Kennedy J P 2000 J. Polym. Sci.–Polym. Chem. 38 279
[26] Honeker C C and Thomas E L 1996 Chem. Mater. 8 1702
[27] Matsen M W 2000 J. Chem. Phys. 113 5539
[28] de la Cruz M O and Sanchez I C 1986 Macromolecules 9 2501
[29] Milner S T 1994 Macromolecules 27 2333
[30] Ryu C Y, Ruokolainen J, Fredrickson G H and Kramer E J 2002 Macromolecules 35 2157
[31] Minatti E, Borsali R, Schappacher M, Deffieux A, Soldi V, Narayanan T and Putaux J-L 2002 Macromol. Rapid Commun. 23 978
[32] Mijović J, Sun M, Pejanović S and Mays J W 2003 Macromolecules 36 7640
[33] Knoll K, Niessner N, Wunsch J and Gauspohol H 2002 US Patent Specification 6369160
[34] Knoll K and Nießner N 1998 ACS Symp. Ser. 696 112
[35] Geiger K, Knoll K and Langela M 2002 Rheologica Acta 41 345
[36] Liang C Y and Krimm S 1958 J. Polym. Sci. 27 241
[37] Painter P C and Koenig S L 1977 J. Polym. Sci. Polym. Phys. Edn 15 1885
[38] Dechant J 1972 Ultrarotspektroskopische Untersuchungen an Polymeren (Berlin: Akademie Verlag)
[39] Sakurai S, Sakamoto J, Shibayama M and Nomura S 1993 Macromolecules 26 3351
[40] Sakamoto J, Sakurai S, Doi K and Nomura S 1993 Polymer 34 4837
[41] Hale A and Bair H E 1997 Thermal Characterization of Polymeric Materials 2nd edn (San Diego: Academic) p 747
[42] Hodrokoukes P, Floudas G, Pipas S and Hajdichristidis N 2001 Macromolecules 34 650
[43] Huy T A, Hai L H, Adhikari R, Weidisch R, Michler G H and Knoll K 2003 Polymer 44 237
[44] Brooks N W, Unwin A P, Ducket R A and Ward I M 1995 J. Macromol. Sci.–Phys. 34 29
[45] Balsamo V and Müller A J 1993 J. Mater. Sci. 12 1457
[46] Adhikari R, Buschnakowski M, Henning S, Goerlitz S, Huy T A, Lebek W, Godehardt R, Michler G H, Lach R, Geiger K and Knoll K 2004 Macromol. Rapid Commun. 25 653
[47] Dair B J, Honecker C C, Alward D B, Avgeropoulos A, Hadjichristidis N, Fetters L J, Capel M S and Thomas E L 1999 Macromolecules 32 8145
[48] Dair B J, Avgeropoulos A, Hadjichristidis N and Thomas E L 2000 J. Mater. Sci. 35 5207
[49] Cohen Y, Albalak R J, Dair B J, Capel M S and Thomas E L 2000 Macromolecules 33 6502
[50] Huy T A, Adhikari R, Michler G H and Radusch H-J 2002 Macromol. Symp. 184 153
[51] Wang X and Zhou W 2002 Macromolecules 35 6747
[52] Hartmann L, Gorbatschow W, Houvere J and Kramer F 2002 Eur. Phys. J. E 8 145
[53] Huy T A, Adhikari R and Michler G H 2003 Polymer 44 1247
[54] Sakurai S, Isobe D, Okamoto S, Yao T and Nomura S 2001 Phys. Rev. E 63 061803
[55] Sakurai S, Sakamoto J, Shibayama M and Nomura S 1993 Macromolecules 26 3351
[56] Fujimora M, Hashimoto T and Kawai H 1978 Rubber Chem. Technol. 51 215
[57] Hashimoto T, Fujimora M, Saito K, Kawai H, Diamant J and Shen M 1979 Advances in Chemistry Series-Multiphase Polymers ACS p 257
[58] Zhao Y 1992 Macromolecules 25 4705