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Deformation behavior of styrene-*block*-butadiene-*block*-styrene triblock copolymers having different morphologies

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Abstract

Deformation behavior of styrene-*block*-butadiene-*block*-styrene (SBS) triblock copolymers having different morphologies was investigated. Due to the combination of different methods which provide information on different deformation levels (macroscopic, microscopic and molecular) complex deformation mechanisms for each type of SBS block copolymer (including glassy-rubber alternating lamellae, rubber cylinders in glassy matrix and hard domains in soft matrix morphology) could be revealed. In combination with tensile tests, Fourier transform infrared (FTIR) spectroscopy was successfully applied to study the change of orientation in individual phases using the absorption bands at 1493 and 966 cm^{-1} for polystyrene (PS) and polybutadiene (PB) phases, respectively. For all the block copolymers investigated the PB phase always oriented stronger than the PS phase because of its lower Young's modulus. However, differences in orientation in both phases were influenced by an appropriate stress distribution within the specimens during deformation, which, in fact, depends on the morphology of the polymers. Additionally, atomic force microscopy revealed local morphological changes during uniaxial stretching, which, in fact, depend on the arrangement of the structural units.

Keywords: SBS block copolymer; Deformation behavior; FTIR spectroscopy

1. Introduction

The increased interest for a better understanding of the structure–property relationships and the deformation mechanisms of polymers require new experimental methods which allow the characterization of transient structural changes during mechanical processes. In this respect, rheo-optical measurements have emerged as very informative and have been applied to obtain data on orientation, conformation and crystallization during mechanical treatment of a wide variety of polymers [1,2]. Generally, a rheo-optical method includes a mechanical test under static conditions (tensile test, stress relaxation, cycle test, etc.) carried out simultaneously with an optical measurement. Among optical methods such as X-ray diffraction, NMR spectroscopy, polarized fluorescence or birefringence, the Fourier transform infrared (FTIR) spectroscopy has become one of the most frequently applied tools in rheo-optics [3–5]. For example, optical birefringence can be used efficiently for the characterization of the average orientation of polymers but without discrimination between the amorphous and crystalline phases or between different phases in heterogeneous polymers. In different, X-ray diffraction can be used for crystalline polymers only, but it is restricted to amorphous samples. The advantage of the infrared spectroscopy is its sensitivity, rapidity and the ability to investigate the changes not only in separate structural units but also in various phases of multiphase systems.

As the FTIR spectroscopy only indicates an average value, detailed information of the morphology and the micromechanical processes must be revealed using other methods, such as microscopy. The direct imaging technique of atomic force microscopy (AFM) allows very direct determination of the micromechanical processes dependent on the local morphology with a resolution in nanometers [6, 7]. The main advantage of AFM is the imaging of structural details without any chemical treatment (staining or etching) of the specimens and its variety in localized regions of the materials. In combination with special deformation devices, AFM also allows a direct study of micromechanical mechanisms of polymers during in situ tests [7].

The deformation behavior of block copolymers was intensively studied based mainly on electron microscopy (e.g. TEM) and scattering technique (SAXS) [8–11]. Styrene-*block*-butadiene-*block*-styrene (SBS) block copolymers having different morphologies such as rubbery domains in glassy matrix [12,13], alternating soft-hard

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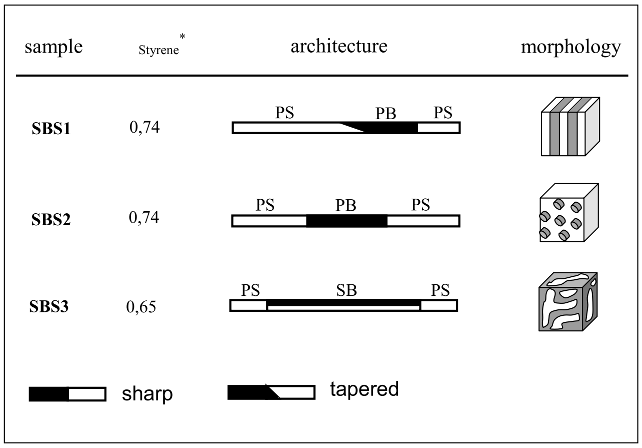
lamellae [14,15] and glassy cylinders in rubbery matrix [16–18] were frequently used to investigate the deformation mechanisms. Recently, some specific applications of electron microscopic and atomic force microscopic techniques in the study of micromechanical behavior of such types of SBS block copolymers were presented by Michler and co-workers [19,20]. On the other hand, structural changes of these materials correlated to macroscopic changes have been successfully studied by means of FTIR spectroscopy through analysis of individual orientation behavior using appropriate absorption bands [21,22]. The molecular orientation behavior of the SBS block copolymers, particularly with respect to their molecular architecture should be, however, still explored. In this paper, the molecular deformation behavior of various types of SBS block copolymer with different morphologies will be presented. Deformation models gained from rheo-optical FTIR spectroscopy measurements were supported by morphological investigations using the AFM technique. It was shown that the combination of the methods mentioned above yields an excellent tool to characterize the deformation behavior in heterogeneous polymers [23].

2. Experimental part

2.1. Materials

The SBS block copolymers studied in this work were commercial products containing a similar chemical composition (about 70 vol% of styrene) but they revealed different morphologies as shown schematically in Fig. 1. Since the length of the component blocks and the existence of the chemical linkages between immiscible blocks limit the phase separation in block copolymers, a microdomain structure with a finer dispersion of the various phases can be obtained. The morphology development of this type of block copolymer was already discussed in details in other publications [24,25]. Hence, some characteristics of the investigated block copolymers are listed in Fig. 1. The samples differ from each other mainly by their molecular architecture and interfaces between the soft and hard blocks. As SBS1 has an asymmetrical architecture and a tapered interface between the longer PS outer block and the PB block a lamellar morphology exists. SBS2, having a linear symmetrical architecture with a sharp interface, reveals PB cylinders embedded in the PS matrix. In SBS3, instead of a PB middle block a styrene–butadiene random copolymer (SB) was used and the polymer shows a morphology with cylindrical-like hard domains within the soft SB matrix.



* total styrene volume fraction

Fig. 1. Characteristics of the block copolymers studied.

2.2. Sample preparation

All the samples investigated were prepared by solution casting. Films about 50 μm thick were dissolved from 3% solution of the sample in toluene by slowly evaporating at room temperature. Finally, the films were dried and annealed in vacuum for 48 h at a temperature of 120 °C (nearby the glass transition temperature of PS) under reduced pressure to enhance the perfection of ordered equilibrium morphologies. These could be used directly for the AFM investigations without further preparation. For the FTIR experiments, the films were cut into strips having 20 mm length and 10 mm width.

2.3. Measurements

An atomic force microscope of the type Multimode (Digital Instruments, California) was used for studying the morphology and deformation structures of the sample. The microscope was operated in tapping mode at room temperature using a silicon cantilever with a resonant frequency of 300–400 kHz and a spring constant of 15 N/m. Stretching of the samples above their yield strains was performed outside of the microscope, and then the films were fixed onto the sample holder in deformed stage. The images presented in this article are the tapping mode phase images taken under moderate tapping (set point ratio ~0.7).

FTIR measurements were carried out at room temperature using the spectrometer S2000 of Perkin Elmer. A miniaturized stretching device, which fits into the sample compartment of the spectrometer, was used for uniaxial extension of both ends of the film; thus the same part of the film remained in the beam during elongation. The FTIR spectra were recorded from a total of 16 scans at a resolution of 2 cm^{-1} using radiation polarized alternatively parallel and then perpendicular to the draw direction during the mechanical treatment (tensile test in stepwise modus). Polarization of the infrared beams was performed with a polarizer placed between the stretching device and the MCT detector. The spectrum examined covers the range between 700 and 3500 cm^{-1}.

Mechanical behaviors of the SBS block copolymers were characterized by uniaxial tensile testing using a universal testing machine (Zwick 1425). The test conditions were comparable to the stretching procedure in the FTIR experiments; the specimen dimensions in both types of measurement were the same.

2.4. Theory of infrared dichroism

FTIR spectroscopy allows determination of the second moment of the orientation function related to any chemical unit. The theory of infrared dichroism for determining the molecular orientation of polymers goes back to the work of Fraser [26] and Krimm [27] 50 years ago. Using polarized infrared irradiation, for any absorption band, the anisotropy in the stretched films is expressed by the dichroic ratio R defined as

$$R = \frac{A_{\parallel}}{A_{\perp}} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the measured absorbances with the infrared beam polarized parallel and perpendicular, respectively, to the stretching direction. Thus, the average of the second order orientation function f is calculated by

$$\langle P_2(\cos\theta)\rangle = f = \frac{R-1}{R+2}\cdot\frac{R_0+2}{R_0-1} \tag{2}$$

where $R_0 = 2\cot^2\psi$ is the dichroic ratio of perfectly aligned chains oriented parallel to the draw direction and ψ is the angle between the direction of the vibrational transition moment and the polymer chain axis; θ is the angle between the chain axis and the stretching direction. The transition moment angle can be found theoretically from the group theory [1]. However, it can also be calculated if the corresponding degree of orientation is determined from an independent experimental method such as X-ray diffraction or from another absorption band with well-defined transition moment attributed to the same chemical units. Thus, if angle ψ is known and assuming that its values do not change during the deformation, the degree of orientation is easy to quantify. Another important assumption in this connection is that angle ψ remains unchanged in different materials, that is, it is specific for particular vibrations only.

In a uniaxial extension f varies between 0 for an isotropic material and 1 for a perfectly oriented sample in the stretching direction; for a perfectly oriented sample perpendicular to the stretching direction, however, $f = -0{,}5$.

Furthermore, in the case of a small absorption anisotropy in the sample during deformation instead of the dichroic ratio the dichroic difference ΔA can be used to calculate the orientation function (i.e. the degree of orientation) [28].

In our case, owing to the high PS content in the SBS block copolymers (approximately 70 wt%), only the band at 966 cm^{-1} was suitable for quantitative investigation of chains in the PB phase. Other bands were either overlapped by PS bands or they had insufficient intensities. However, some absorption bands could be taken to investigate the orientation in the PS phase. Fig. 2 shows the orientation of the PS phase in SBS 1 associated with different absorption bands at 1069, 2848 and 1493 cm^{-1}. As the transition moment angle for every vibration is not precisely known the dichroic functions are shown instead of the degree of orientation. The dichroic function DF is defined as

$$\text{DF} = \frac{R-1}{R+2} \tag{3}$$

which differs from the degree of orientation f by a constant factor only. Since the transition moment direction for these bands are roughly perpendicular to the chain axis, which can be estimated from the group theory [1], the negative DF values indicate a parallel orientation of the PS chains to the draw direction. As seen in Fig. 2, the dichroic effect of the PS phase in the SBS block copolymers investigated could be detected most suitably by the analysis of the band at 1493 cm^{-1}. Thus, the bands at 1493 and 966 cm^{-1} were selected for the PS phase and the PB phase, respectively, for the quantitative characterization of chain alignment during the deformation process. The band at 1493 cm^{-1} was assigned to an in-plane phenyl ring deformation mode $\nu_{19\text{A}}$ [29], its transition moment angle was recognized to be perpendicular to the chain axis [30]. The band at 966 cm^{-1} was assigned to an out-of-plane CH bending mode in *trans*-1,4-butadiene [31], its transition moment angle was also observed to be roughly perpendicular to the chain axis [22].

In the quantitative analysis the absorbance A was determined at the peak maximum applying an appropriate base line. The choice of basic line influences the absolute values of absorbance and dichroic ratio a little, but it does not reserve the trend with strain. The degree of orientations were evaluated by using Eq. (2). During stretching both absorption bands mentioned above did not change their vibrational wavenumbers.

In Fig. 3 the change of the absorption peaks at 966 cm^{-1} is shown in detail depending on the nominal strains. At the undeformed stage ($\varepsilon = 0\%$), the parallel and perpendicular absorbances exhibit no difference indicating a randomly oriented sample. At high deformation ($\varepsilon = 300\%$), however,

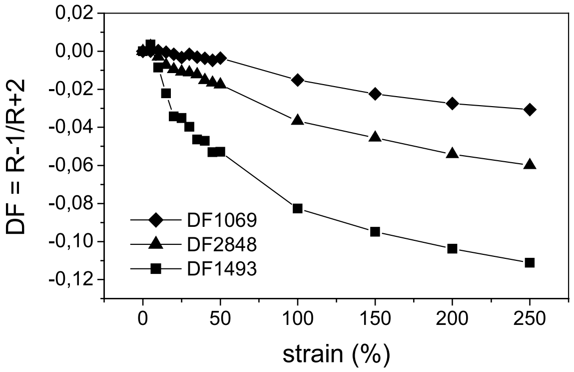


Fig. 2. Strain dependence of the dichroic functions DF for the PS phase of SBS3 determined at different absorption frequencies. The values shown in the graph indicate the frequencies used for the quantitative investigations.

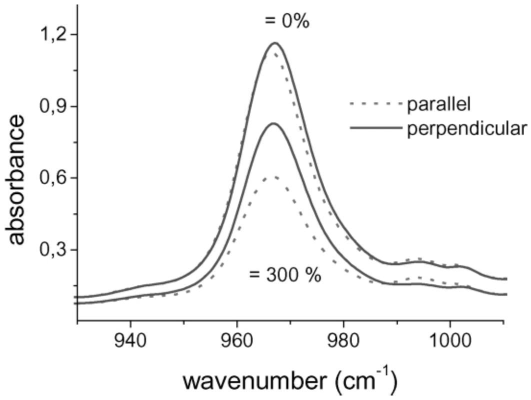


Fig. 3. The 966 cm^{-1} band of SBS1 depending on the polarization direction and strain.

significant differences of the absorbances parallel and perpendicular to the stretching direction arise. During deformation, this band indicates a σ-dichroismus resulting in a higher perpendicular absorbance compared to that of the parallel one (i.e. $R < 1$). In general, the intensity of the absorbances decreases by stretching because of the film thickness reduction.

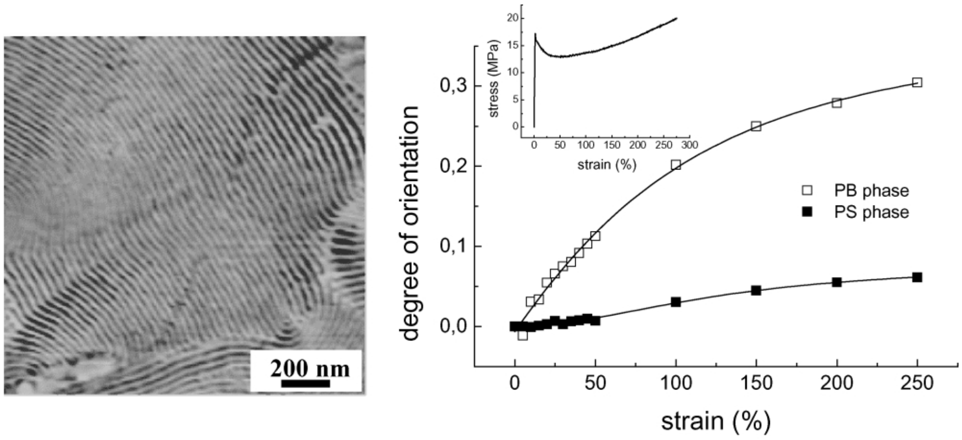
3. Results and discussion

Fig. 4 shows the morphology (a) and the mechanical behavior (b) of SBS1. In our AFM phase images the dark phase always shows the soft phase and the bright phase shows the hard phase. It is obvious that SBS1 possesses a morphology containing alternating PB and PS lamellae with a lamellar thickness of approximately 20 nm, which, in fact, does not fit into the classical phase diagram of styrene–butadiene diblock copolymers [24]. The mechanical behavior is demonstrated by a stress–strain diagram as well as an orientation-strain diagram, which allows a characterization of average molecular deformation in both the PS and PB phases. Due to the presence of a necking zone in the specimens during stretching, the strain values denoted in this figure are nominal values only and are not the local strain at the point of measurement. Therefore, in this figure an exact correlation between the stress–strain and orientation-strain curves cannot be expected. Nevertheless, it is obvious that at every deformation stage the PB phase shows a clearly larger orientation compared to the PS phase.

During deformation the lamellar morphology should give an equivalent stress distribution in both the soft and hard phases. Owing to the lower Young's modulus the applied stress localizes first in the soft phase and therefore the butadiene chains can orient earlier and stronger than the styrene chains. The orientation in the PS phase at this initial deformation stage is rather weakly. Hence, above the yield point, the applied stress should be strong enough to deform the rigid lamellae and the styrene chains orient significantly with increasing strain. This phenomena was interpreted in literature as the so-called strain-induced plastic-to-rubber transition [22,32], which related to the increase of stress with the strain above the yield point. In contrast to the PS phase, in this deformation stage the orientation of PB chains shows a slight change with strain because the applied stress is transferred more and more into the hard phase.

In Fig. 5 the morphology (a) and the mechanical behavior of SBS2 (b) are shown. Unlike SBS1, SBS2 possesses a morphology having hexagonal ordered PB cylinders in the PS matrix which, in principal, is expected for the given chemical composition. Nevertheless, similar to SBS1 the soft phase here orients stronger than the hard phase, particularly at high deformations. As the matrix consists of a brittle material (PS) the block copolymer shows a typical brittle mechanical behavior with a high strength and a low strain at break with only a very small plastically deformation (see the insert in this figure). Accordingly, an intrinsic increase in the orientation behavior in both the soft and the hard phase can be observed in the same way.

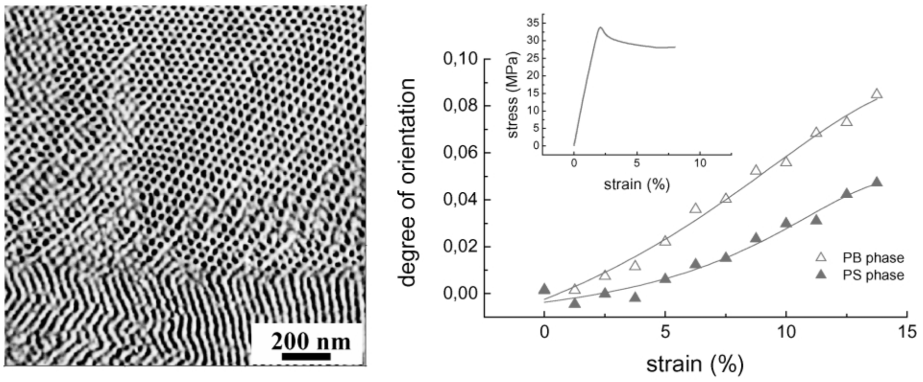
The fact of a higher orientation in the PB phase compared



a)

b)

Fig. 4. AFM phase image showing the microphase separated morphology (a) and the deformation behavior in macroscopic (inset) and molecular level (b) of SBS1.



a) b)

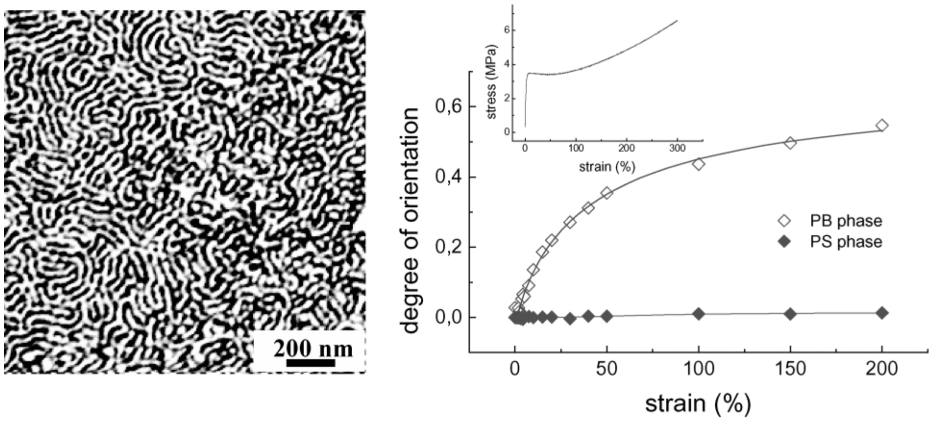
Fig. 5. AFM phase image showing the microphase separated morphology (a) and the deformation behavior in macroscopic (inset) and molecular level (b) of SBS2.

to that of the PS phase can be more clearly seen in the case of SBS3 as shown in Fig. 6. In this polymer the SB soft phase forms the matrix, in which PS hard domains are irregularly dispersed. In contrast to SBS2 this block copolymer shows a larger elongation at break without necking of the specimen during the uniaxial deformation. Furthermore, the very high orientation in the soft phase here can be indisputably interpreted as the result of two effects: the lower Young's modulus and the matrix role of this phase.

Hong et al. [33] investigated the deformation behavior of Kraton, a commercial SBS block copolymer with a morphology similar to SBS3. The authors found a high orientation of the PB chains, but no orientation of the PS chains. Furthermore, it was found that the degree of orientation in the PB phase determined by using different absorption bands was different. The reasons for these observations are: on the one hand, the transition moment angle for different absorption bands is different; and on the other hand, it has been shown both theoretically [34] and experimentally [35] that the orientation of chain segments in the amorphous regions are conformation dependent. Therefore, the chain segments of different conformations in the same parent chain can have different orientations.

Sakamoto et al. [36] used the absorption bands at 1493 and 966 cm^{-1} to investigate the molecular orientation of SBS triblock copolymers with cylindrical microdomains of polystyrene. Their results indicated that PB chains are oriented parallel to the stretching direction as also shown in our results, but that no orientation in the glassy PS could be detected by stretching because of the bad signal-to-noise ratio of the PS band used to evaluate the degree of orientation. In our case, the very low orientation of the PS phase in SBS3 as well as its comparatively high orientation in SBS1 and SBS2 demonstrates that the orientation stage of the PS phase actually depends on the internal strain in this phase which, in fact, depends on the morphology of the block polymers. Therefore, in some SBS block polymers we could observe the orientation of PS chains while no orientation could be detected in others.

In Fig. 7 the orientation behavior of both the PS and PB phase in SBS block copolymers investigated are compared



a) b)

Fig. 6. AFM phase image showing the microphase separated morphology (a) and the deformation behavior in macroscopic (inset) and molecular level (b) of SBS3.

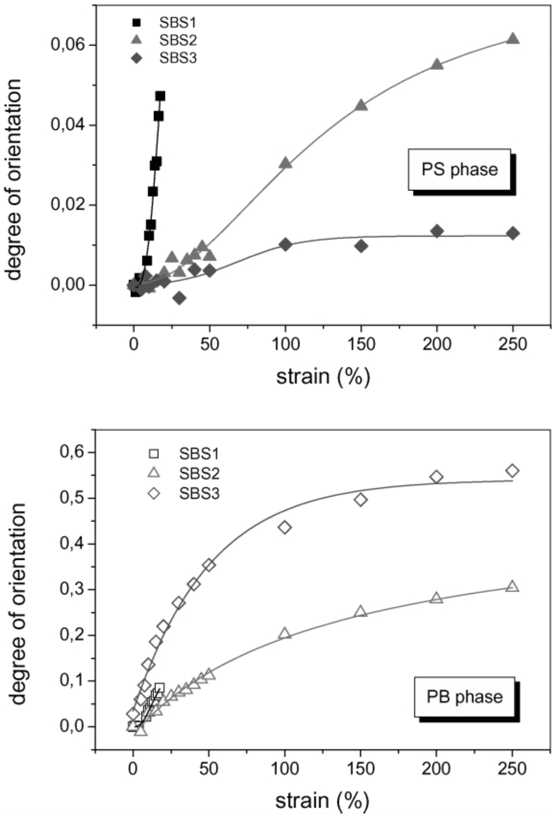


Fig. 7. Orientation behavior of individual phases in SBS block copolymers having different morphologies.

directly to each other. It is obvious that depending on the morphology and as a consequence of stress distribution within the specimen during deformation, the orientation in the individual phases is very different. Note that the onset of the orientation of the PS phase of SBS3 so well as the stronger increasing of the degree of orientation of the PS phase of SBS1, respectively, seems to correlate with the onset of increasing stress above their yield points. Furthermore, the orientation of the PB phase is always stronger than that of the PS phase regardless of the morphology of the materials. Hence, the orientation behavior in the SBS block copolymers investigated is typical of non-crystalline block copolymers, in which the molecular chains in hard and soft segments orient in the stretching direction at all elongations leading always to positive values of degree of orientation. In contrast, if the hard domains are partially crystalline, the non-crystalline segments still present a orientational behavior as before, while the crystalline regions pointed out a transverse (negative) chain orientation at low elongation [37], which can be explained by the 'continuum mechanics' [38].

Moreover, by an exact observation of the orientation-strain curves, the strain dependence of the degree of orientation for all the materials can be divided into three steps. The orientation changes only a little at small strains and then increases steeply; finally it increases gradually at higher strains. According to Rodriquez-Cabello et al. [39] using the frequency shift in the Raman spectrum to investigate the structural change of stretched bulk polymer, the first stage of deformation corresponds to the elastic region, the second stage to the transient region from elastic to plastic deformation, and the third stage to the plastic deformation region. However, different stages in the real orientation curve can be detected depending on the internal strain in the individual phases, which, in turn, depends on the morphology of materials as well as the alignment of their structural units relative to the stretching direction.

4. Deformation models in SBS block copolymers

Generally, the mode of deformation induced in the SBS block copolymer depends strongly on the morphology and the microdomain orientation [40,41]. For example, crazing was the main fracture mechanism of styrene–butadiene diblock copolymers of spherical or cylindrical PB domain morphology in PS matrix, while crazing and shear yielding were observed for the lamellae morphology [42]. Moreover, the deformation behavior upon stretching is different for regions having different arrangement and orientation of structural units (PS or PB domains) with respect to the stretching direction. The macroscopic mechanical response as well as the average molecular orientation is a result of the combination of contributions from all regions. For all our solution cast samples it is assumed that in undeformed stage, the characteristic regions, in which lamellae or cylinders are spatially ordered, are randomly oriented. However, in our models presented here, only regions which provide a major contribution to understanding the deformation mechanisms of the materials, are considered.

4.1. Block copolymers having alternating lamellae structure

Usually, the solution cast films do not give any anisotropy of the sample morphology. During stretching, however, the alignment of lamellae related to the draw direction play an important role in deformation of lamellae and therefore in the orientation of chains within the lamellae as well as in the average orientation of the individual phases. For example, shear yielding (i.e. lamellar drawing) should be dominant in the lamellae which are randomly oriented or oriented perpendicular to the stretching direction, while crazing should occur in the lamellae oriented parallel to the stretching direction [42,43]. Moreover, the thickness of lamellae seems to strongly influence the deformation of lamellae. Recently, Michler and co-workers presented a new deformation mechanism for triblock copolymers having lamellae structure called 'thin layer yielding mechanism' [19,24] which provides an explanation for the ductile fracture behavior of the material. At high deformation a chevron-fold morphology dominates the deformed structure of this type of SBS block copolymers [15,40], particularly by the lamellae situated perpendicular to the draw direction. Thus, at low deformations we can distinguish between two borderline cases: lamellae aligning parallel or perpendicular to the draw direction. In Figs. 8 and 9 the morphologies of SBS1 at deformation stages and the tapping mode AFM phase images including the corresponding deformation mechanisms at the molecular level are shown schematically. In these figures the number 1 denotes the undeformed stage, while the numbers 2 and 3 are thought as the in-line morphology during the stretching procedures. Note that because of the anisotropy of deformation the AFM data are only supplementary to the orientation results. Thus, the local strain can be roughly estimated by comparing the thickness of the lamellae before and after stretching.

In the case of the lamellae aligned parallel to the draw direction, assuming the same thickness for PS and PB lamellae in the undeformed stage, their distinct difference in the deformed stage can be seen in Fig. 8. This can be explained by a new deformation mechanism called 'hard layer slipping'. With reference to the distinct difference in the Young's modulus, in lamellar SBS block copolymers the PS phase forms the hard layer and the PB phase the soft layer, respectively. The layers are combined together chemically, so that alternated layers of different nature cannot be laterally disconnected toward each other along the lamellar boundaries during parallel stretching. On the other hand, because of the chemical junctions and the molecular architecture with two PS outside blocks, the phase interface is very stabile towards a mechanical loading. Thus, in the initial stage of deformation the PS lamellae can slightly slip towards each other without significant microscopic distortion at the expense of the high extensibility of the PB interlayer, resulting in a higher orientation of the PB chains compared to that of the PS chains (position 2 in the model in Fig. 8). Owing to the higher Poisson's ratio of the soft phase compared to that of the hard phase, the PB layers appear clearly thinner than the PS ones. Moreover, at higher deformation the PS lamellae containing a lot of chain ends may be fragmented into smaller domains, and the consequent gradual phase inversion finally results in separate PS domains dispersed in the PB lamellae (position 3 in the model in Fig. 8). The fragmentation of PS lamellae can be developed after the yielding point [15,43] and it provides an explanation for the extensive stress softening of the block copolymer. After sufficient yielding development, final structure might have resulted from the growth of microcavities to local microcracks and further macrocrack propagation [40].

If the sample was deformed perpendicular to the lamellar alignment direction the dilation of the PB layers can be

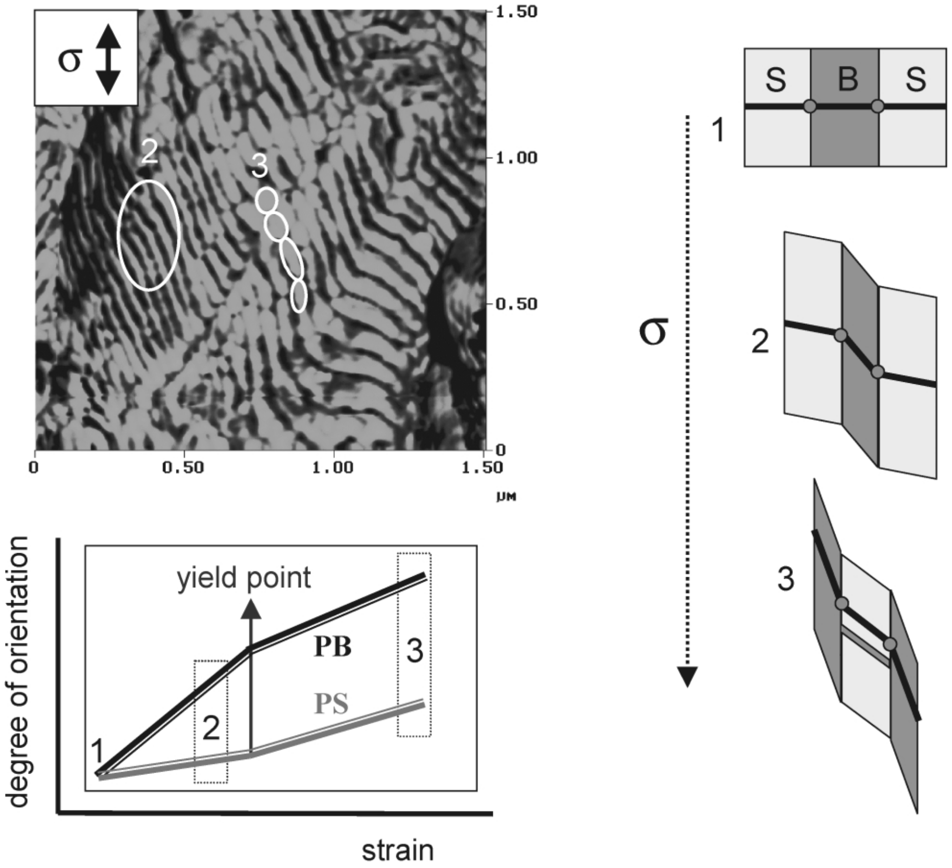


Fig. 8. Deformation mechanism of SBS block copolymers with lamellar morphology during uniaxial strain: stress in parallel direction to the orientation of the lamellae, the micrograph is an AFM phase image.

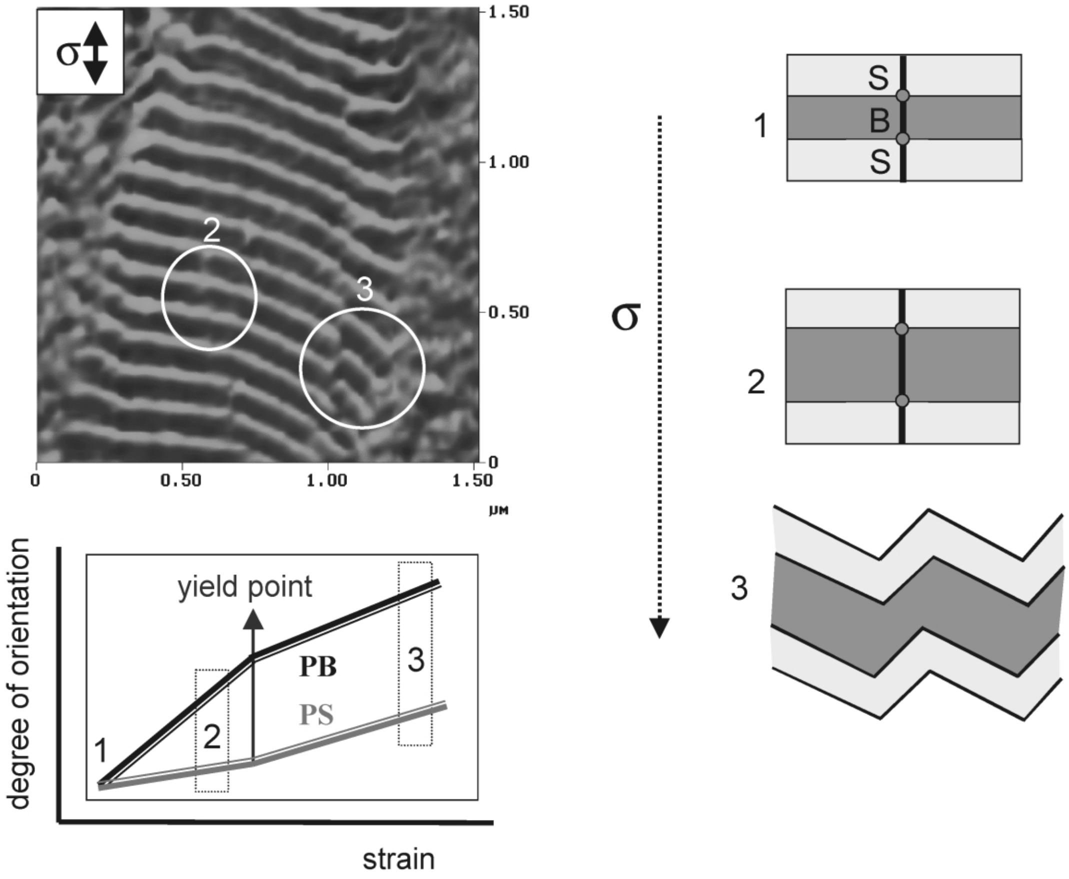


Fig. 9. Deformation mechanism of SBS block copolymers with lamellar morphology during uniaxial strain: stress in perpendicular direction to the orientation of the lamellae, the micrograph is an AFM phase image.

clearly observed as shown in the AFM image in Fig. 9. This situation provides a favorable stress field for the orientation of the chains occurring across the lamellae, i.e. parallel to the draw direction. In this position, the PB chains reveal very extensive elongation as a result of their high extensibility between a network of rigid PS junctions. At higher deformation these lamellae are deformed regularly in zigzags (chevron morphology) by predominant shear yielding. Note that, due to the heterogeneous stress distribution within the specimen during deformation a uniformly continuous change of the morphology should be developed in small regions only. However, a general transition from an oriented lamellar into the chevron morphology was convincingly established using 2D SAXS [15]. Generally, two mechanisms for the transformation of the layered structure to the 'chevron' structure are suggested: (1) the undulation instability of lamellae, which associates with the yield point of the stress–strain curve [44] and (2) the tilting of the layers in regions surrounding defects, which nucleates and propagates local kink bands parallel to the stretching direction into adjacent regions with increasing strain [15].

Thus, the morphological transitions discussed here are interpreted in the literature in term of shearing, kinking and break up of lamellae [32,43]. However, at very high deformation, the morphology in all cases, i.e. by parallel, perpendicular or diagonal deformation related to the lamellar axis, is similar—a highly stretched rubber matrix with anisotropic fragmented glassy domains [15].

4.2. Block copolymer having soft domains in the hard matrix

The typical micromechanical mechanism of this type of SBS block copolymer is dominated by craze initiating and growth by cavitation in the glassy matrix [13,20]. These crazes, however, are considerably different than the typical crazes in styrene–butadiene diblock copolymer as well as in styrene homopolymer [13]. For example, as a consequence of the anisotropic cell arrangement of the PB cylinders the crazes in SBS block copolymer are not planar. Furthermore, close examination reveals that the fibrils contain PB domains. Cavitation of the glassy matrix rather than the rubber cylinders, in contrast to styrene–butadiene diblock copolymers [41], was attributed to the high concentration of chain ends in the PS phase [13], which substantially decreases the critical cavitational stress [45].

Our results reveal that the plastic deformation of the matrix at a high yield stress is the reason for a strong orientation especially in the PS phase at low nominal strain, which is not observed in other types of the SBS block copolymers investigated. In this SBS block copolymer the necking does not instantaneously proceed over the specimen because of the presence of PB cylinders and hence the necking can be localized. Thus, the orientation behavior may be related to the craze development. Craze growth in diblock copolymer depends on the alignment of PB cylinders and it takes place preferentially through regions in which the cylinder axes are transversely oriented to the stretching direction [41]. In our case, the PB cylinders are expected randomly aligned to the stretching direction. This is schematically shown as a small dark rectangle within a big light PS rectangle in Fig. 10. By the existence of a glassy matrix, during deformation the applied stress is firstly localized in the PS phase. Foremost, if this stress is strong enough to extend the rigid matrix, the stress can be effectively transformed into the soft cylinders leading to a considerable increase in the degree of orientation in both the PS and PB phases. Since above the yield point both craze length and density can approach constant values [13], elongation must occur by craze widening into micronecks in which the material is highly oriented. Hence, at this deformation stage the PB phase can be deformed properly due to its lower Young's modulus indicating a stronger orientation compared to that of the PS phase (position 3 in Fig. 10) and in good agreement with the fibril role of rubber domains within crazes as mentioned above. Finally, the crazes and micronecking grow macroscopically and the specimen breaks brittle.

4.3. Block copolymer having hard domains in the soft matrix

According to Seguela and Prud'homme [17] using SAXS to investigate deformation mechanisms of SBS block copolymers having a soft matrix, during elongation spherical PS domains were deformed to ellipsoids along the stretching direction and PS cylinders could be aligned along the stretching direction. Furthermore, investigations of Pakula et al. [16] indicated that at low deformation the morphology of the deformed block copolymer is controlled by the initial alignment of PS cylinders, but at high deformation chevron-like morphology dominated the deformed structure. In addition, Odell and Keller [46] using TEM proposed the break down of glassy cylinders into smaller fragments, particularly when the sample was deformed parallel to the cylinder axis.

In such type of morphology the applied stress always concentrates in the matrix, also in the soft phase. In addition to the lower Young's modulus effect discussed above, it leads to a very high deformation of this phase compared to that of the hard domains. Thus, the consequence is a clearly higher orientation of the soft phase, even at low deformation stage as shown schematically in Fig. 11. At the initial stage of deformation PS cylinders could be turned in the stretching direction (it cannot be seen in Fig. 11) indicating no change in overall orientation degree of this phase because of the random alignment of cylinders at the undeformed stage. This situation promotes the breaking down of cylinders similar to the lamellar morphology at the next stage of deformation. The following yielding process involves breakdown or fragmentation of long PS cylinders,

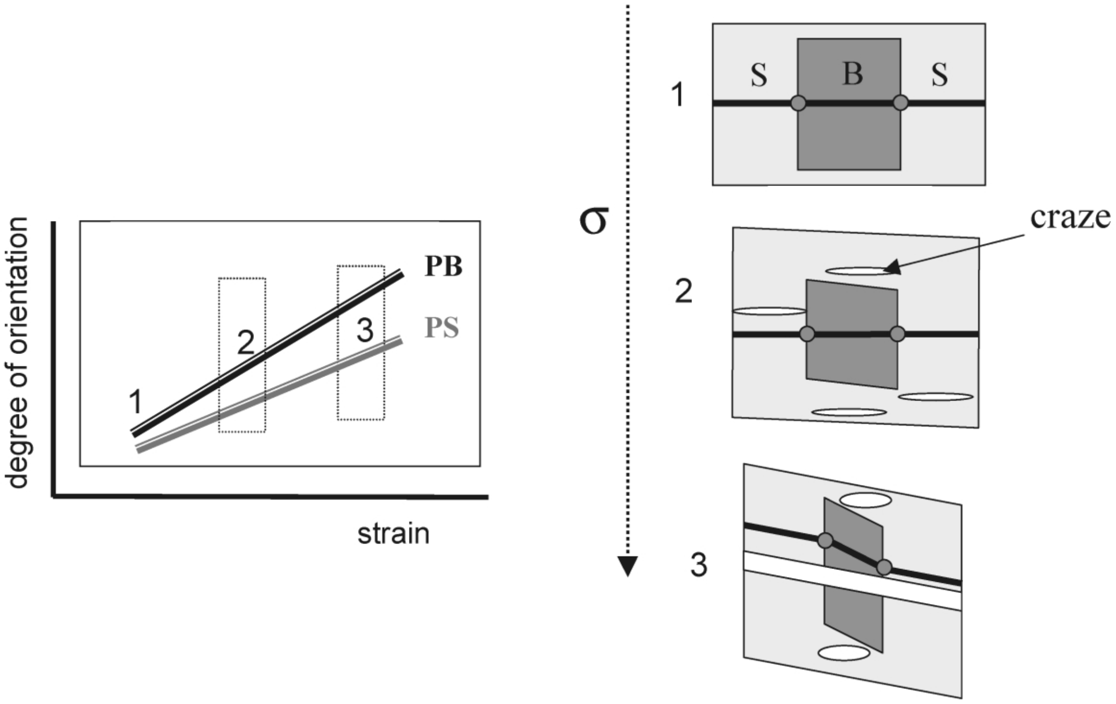


Fig. 10. Deformation mechanism of block copolymers with PB cylinders in PS matrix during uniaxial strain.

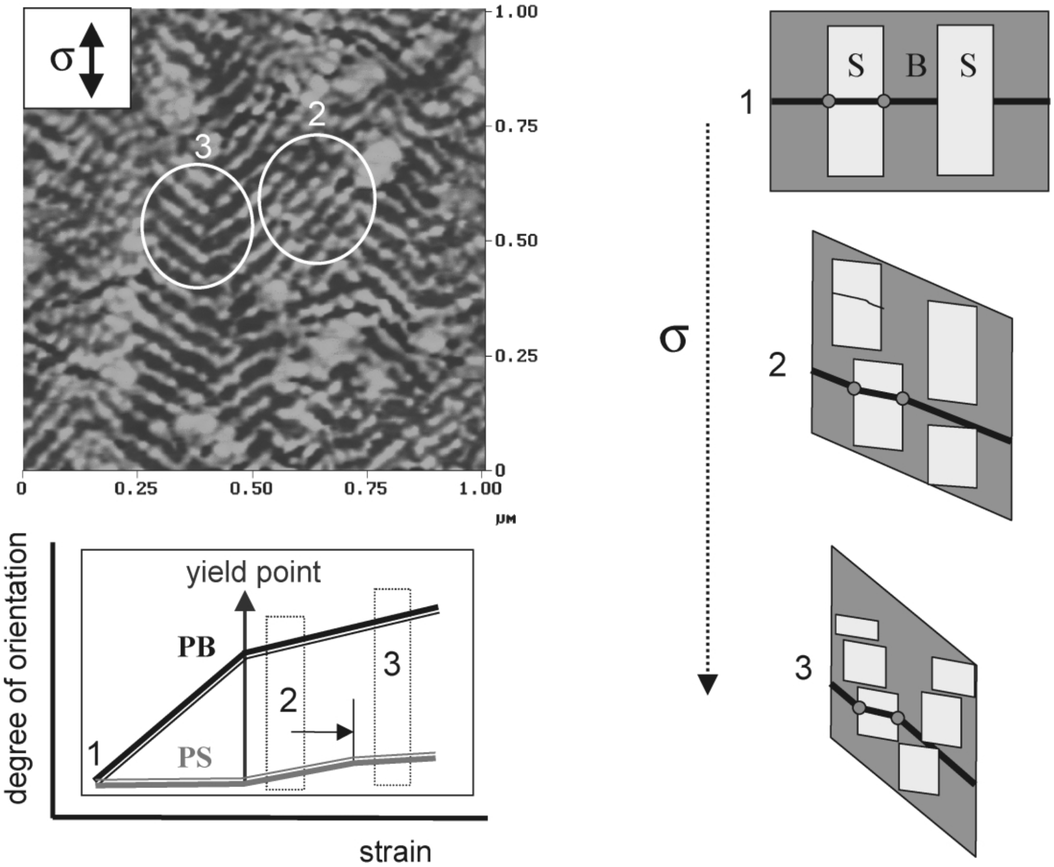


Fig. 11. Deformation mechanism of block copolymers with PS domains in PB matrix during uniaxial strain, the micrograph is an AFM phase image.

giving rise to short glassy domains (position 2 in Fig. 11), which are accompanied by a slight increase in the orientation of the PS phase because of its unsatisfactory extensibility. Unlike lamellae, the fragmentation of PS domains does not lead to a strain softening of the polymer because of their discontinuous role. Finally, the formation of chevron-fold like morphology takes place (position 3 in Fig. 11), which, however, leads to a constancy of orientation with strain of already plastically deformed PS domains. After the fragmentation of glassy cylinders, PS domains acting as physical crosslinks or reinforcing fillers may restrict the extensibility of the rubber chains in a denser network and as a consequence the PB chains show a weaker increase of orientation at high deformation.

5. Conclusions

Using the FTIR spectroscopy the deformation mechanisms at molecular level were investigated separately for different types of SBS block copolymers. The absorption bands at 1493 and 966 cm^{-1} were used to characterize effectively the orientation of the PS and PB phases, respectively. Molecular orientation behavior in uniaxial stretching depends substantially on the initial morphology and is related well to the stress–strain behavior. The yield point seemed to be responsible for intrinsic orientational changes in both the PB and PS phases. Furthermore, the average orientation in the individual phase was influenced by the stress distribution depending on the alignment of structural units of specimens. In all the SBS block copolymers investigated, an orientation of chains in the stretching direction during deformation was established. It was found that the PB chains always oriented stronger than the PS chains. This is caused primarily by the lower Young's modulus of the soft phase compared to that of the hard phase. In SBS1 having alternating lamellar structure, the alignment of lamellae relative to the stretching direction influenced strongly the appearance of the deformed morphology. Lamellae aligned parallel to the stretching direction deformed by a new deformation mechanism called hard layer slipping, following the breaking down at higher deformation. For the lamellae aligned perpendicular to the stretching direction, after the widening of PB layers a chevron-fold morphology appeared by shear yielding. In SBS2 having PB cylinders in PS matrix, the degree of orientation in both phases goes in the same way. Here, the brittle behavior in the macroscopic level can be explained by a craze development in the microscopic level and the very high degree of orientation of the PS phase in the molecular level occurred already at small applied strains. For SBS3 having glassy domains in the soft (SB) matrix, the difference in the orientation behavior between the PS and the PB phase was found most clearly because of two effects: the lower Young' modulus of the soft phase, and its matrix role which permits a concentration of the applied stress in this phase resulting in a very high local elongation and therefore a very high orientation of PB chains even at low deformation. The fragmentation of long glassy cylinders, which was caused by their plastic deformation at small local strains was the reason for the low degree of orientation in the PS phase at all deformation stages.

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