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Polymer 44 (2003) 1237–1245

polymer

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Influence of interfacial structure on morphology and deformation behavior of SBS block copolymers

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Abstract

Linear styrene-*block*-butadiene-*block*-styrene (SBS) triblock copolymers having different interfacial structures were investigated. In spite of the nearly equivalent chemical composition (about 70 vol% of styrene), these copolymers show significantly different morphologies. It was shown that the origin of the modified morphology in asymmetric block copolymers is the intermixing of short polystyrene (PS) chains or chain segments into the polybutadiene (PB) phase. It has a consequence of an increase in the glass transition temperature of the soft phase (PB phase here) and a significant decrease of the whole relaxation time of the materials. The larger the interfacial volume, the more PS molecules can mix into the PB phase. Moreover, it seems that the extent of the stress transfer in heterogeneous polymeric systems is crucially influenced by the interface. The tapered interface in an SBS block copolymer, for example, permits a more effective stress transfer compared to the sharp interface resulting in a higher degree of orientation in the individual phases of the materials.

Keywords: Styrene-*block*-butadiene-*block*-styrene block copolymers; Morphology; Interfacial structure

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1. Introduction

Block copolymers allow the construction of new complex morphologies on account of balance of the relative incompatibility and molecular architectures with unique qualities, which the classical polymer blends cannot show [1]. In contrast to poly(styrene-*block*-butadiene) SB diblock copolymers, poly(styrene-*block*-butadiene-*block*-styrene) SBS triblock copolymers have significantly greater variety of accessible morphological structures due to their versatile architectural possibilities [2,3].

As shown in Fig. 1, the morphology formation in block copolymers is influenced by different factors. In addition to the parameters such as monomer types or chemical composition, the processing history plays a significant role. It is even crucial whether the block copolymer samples are prepared from melt or solution. During the melt processing, the morphology can be influenced by varying conditions such as temperature, pressure, shear rate or processing time. On the other hand, the choice of solvent is important for structure formation from evaporating solutions. Block copolymers with identical chemical composition can exhibit different morphologies by the application of different solvents [4,5]. Moreover, by use of specific solvents, block copolymers with different compositions can result in the same morphology [6]. Annealing of the samples further changes the degree of phase segregation and morphological order [4,7]. Furthermore, through the variation of the polymerization conditions such as polymerization temperature, type and concentration of the initiator, molecular features (e.g. molecular weight, polydispersity, molecular architecture or phase transition) can be adjusted in a purposeful manner [8,9].

Block copolymers with two different types of incompatible monomers can be organized in a variety of molecular architectures like diblock, triblock, multi-block, star block or graft block, which result in different morphologies and mechanical properties. Due to the covalent junctions, constituent segments do not segregate on a macroscopic level, but at sufficiently small polydispersity they rather arrange into periodic microscopic domains [1–3,9,10,11]. Depending on the effective volume fraction of the component A (i.e. the portion of the substances that is actually available for morphology formation of the system), the highly ordered morphology of the AB diblock copolymers in the strong segregation limit can go more or less continuously through a phase inversion as shown schematically in Fig. 2 [2,12]. Due to the repulsive

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PII: S0032-3861(02)00630-4

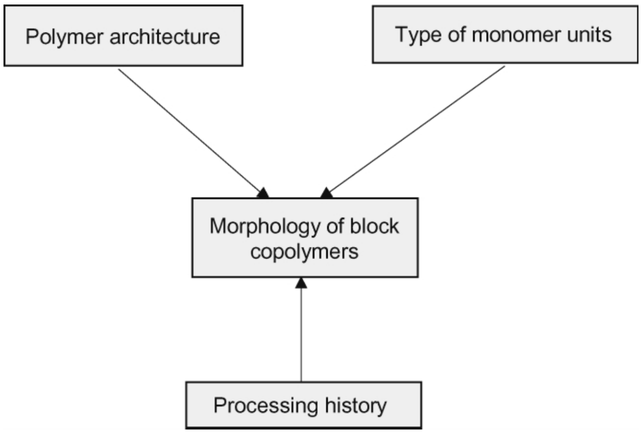


Fig. 1. Important factors influencing the morphology of a block copolymer.

interactions between chains A and B, they are stretched normal to the interface. The mixing of the incompatible segments A and B within the strong segregation limit occurs only in the narrow interfacial region with a characteristic interface thickness $t \cong 2$ nm such as for styrene/butadiene systems [10,13].

The interface in a heterogeneous system is a region of gradient composition and constitutes a volume, whose quantity depends on the driving force of the phase separation. It is of great practical interest because, it is believed to determine many of the bulk mechanical properties such as tensile and impact strength or fracture toughness [14]. In contrast to ordinary polymer blends, where chain ends are mainly located at the surface boundary [15], the junction points are strongly localized at the interface in block copolymers [10]. In this region, the chains are stretched [16], thus the thermodynamic properties of an interface are not governed by the same thermodynamic constraints as those imposed on bulk phases. Hence, the molecular mobility and therefore the morphology formation of block copolymers are influenced strongly by the structure of the interfaces. In the literature, several techniques are reported to study the polymer–polymer interfaces [17] including small angle X-ray scattering [18], small angle neutron scattering [19], solid state high resolution nuclear magnetic resonance spectroscopy [20] or transmission electron microscopy [21], etc. Recently, Schuster and co-workers [22] proposed a new method of determining the volume fraction and the thickness of the interfacial layer in elastomer blends using dynamic mechanical analysis (DMA).

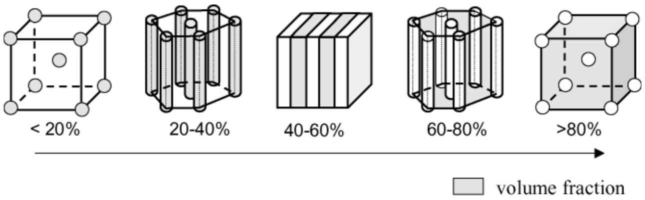


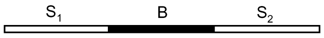
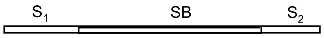
Fig. 2. Highly segregated morphology observed in diblock copolymer (schematic).

Block copolymers which are synthesized by living anionic co-polymerization usually yielded well-defined block lengths and a narrow polydispersity [23]. In such procedures, the molecular architecture and the interface profile can be varied without changing the homogeneity and integrity of the constituent phases [8,24]. The purpose of present work is to discuss the influence of interfacial structures of some SBS block copolymers on their morphology and mechanical deformation behavior.

2. Experimental section

2.1. Materials

Linear SBS block copolymers with different interface structures and architectures are investigated. Characteristics of block copolymers used in this study including molecular architecture, number average molecular weight M_n and polydispersity M_w/M_n are shown in Fig. 3. One can distinguish between sharp and tapered block transitions, which are characterized by different composition profiles in the phase boundaries. While in block copolymers having sharp transition, the average composition profile varies suddenly along the chain, in the tapered ones it changes continuously from unity to zero. LN1-S74 is an SBS triblock copolymer having symmetric PS end blocks and sharp block transitions. In contrast, LN2-S74 has highly asymmetric PS outer blocks and contains a tapered transition between the PB and the longer PS block. The ratio of longer to the shorter PS blocks is more than four. The tapered interface may cause an increase of toughness, but simultaneously decreases the stiffness and the heat distortion temperature [25]. In LN4-S65, a styrene/butadiene random copolymer (S/B) is present instead of a pure polybutadiene center block. However, in this material the outer PS blocks only amount to about 32% volume fraction. The introduction of the random S/B middle block in this block copolymer has the advantage that it possesses

Sample	Molecular architecture	Φ_{PS}	M_n (kg/mol)	M_w/M_n
LN1-S74	 S_1 B S_2	0,74	82	1,07
LN2-S74	 S_1 B S_2	0,74	93	1,13
LN4-S65	 S_1 SB S_2	0,65	116	1,20

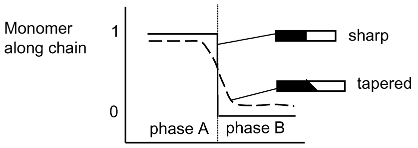


Fig. 3. The characteristics of the block copolymers used in this study, the total styrene volume fraction Φ_{PS} was determined by Wij's method; the number average (M_n) and weight average (M_w) molecular weights were determined by gel permeation chromatography (GPC).

improved processing and thermal properties without altering the viscosity even at significantly higher molecular weight [8].

2.2. Scanning force microscopy (SFM)

Generally, scattering techniques and electron microscopy are employed in order to study the morphology of polymers. In recent years, SFM has been successfully used to resolve morphologies of heterogeneous polymers including block copolymers. In this work, morphological investigations were carried out by a SFM (multi-mode atomic force microscope, Digital Instruments, Inc.). The SFM was operated in tapping mode using silicon cantilevers with a resonant frequency of about 300 kHz and spring constant of about 15 N/m. The height and the phase data were simultaneously collected. Only the phase images are presented in this work. Thin films of the samples were prepared using the procedure discussed in Ref. [27]. The films and the bulk samples were prepared by solution casting from 3% solution in toluene by slowly evaporating the solvent in about 2 weeks followed by subsequent annealing for 48 h at a temperature of 120 °C under reduced pressure. In this way, a well-defined morphology close to the equilibrium was expected.

2.3. Differential scanning calorimetry (DSC)

DSC measurements were performed with a Mettler DSC 820 in the temperature range from − 120 to 150 °C applying a heating rate of 10 °C/min using the cycle heating–cooling–heating. The heat flow and the second derivative of the heating scans were used for the analysis of the glass transition temperature. The weight of samples was approximately 10 mg, which is small enough to avoid problems with temperature gradients.

2.4. Dynamic mechanical analysis

DMA was carried out using the DTA Torsion Rheometer System (Rheometric Scientific) in torsion and temperature-sweep mode. The measurements were performed with a frequency of 1 Hz, at a temperature range from − 120 to 120 °C and at a heating rate of 2 °C/min. Test specimens of the dimension of 30 mm × 10 mm × 4 mm were prepared from injection molded samples.

On the other hand, stress relaxation experiments were performed, using a dynamic mechanical analyzer DMTA 3e (Rheometric Scientific) in tensile mode. The instrument is equipped with a temperature chamber, which enables a constancy of the temperature of less than 0.1 K. DMA was carried out in the frequency temperature sweep mode at temperatures from − 30 to 80 °C and frequency from − 0.01 to 50 Hz at a heating rate of 1 °C min^{-1}. The master curve can be created by horizontal shifting of the experimental curves measured at different temperatures along the frequency axis to the reference temperature of 30 °C.

2.5. Tensile testing

The tensile specimens were prepared by injection molding (mass temperature 245 °C and mould temperature 45 °C). The tensile specimens were tested according to ISO 527 at room temperature (23 °C) and at a cross head speed of 50 mm/min using a universal tensile machine (Zwick 1425). At least 10 samples were tested in order to get a good statistics of measured values.

2.6. Fourier-transform infrared (FT-IR) spectroscopy

FT-IR investigations were carried out using a Perkin–Elmer FT-IR spectrometer S2000 equipped with a MCT detector. The spectrum examined covers the range between 500 and 3500 cm^{-1}. First, thin films were prepared by means of a special pressing device. From the molded sheets, specimens of dimension 20 mm × 10 mm × 0.05 mm were cut. A special stretching machine, developed in our group, which allows applying a uniaxial stretching of the thin films, was placed in the sample compartment of the spectrometer. The measurements were performed with the polarizer adjusted alternatively parallel and perpendicular to the stretching direction. The incident radiation area had a diameter of 5 mm. Twenty-five scans were averaged at 2 cm^{-1} resolution.

Using the ratio of the absorbance from beams polarized parallel ($A_{\|}$) and perpendicular ($A_{\perp}$) to the deformation direction, the dichroic ratio was calculated using:

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

To characterize the selective orientation in individual phase of the SBS block copolymers studied in this work, the dichroic function DF was employed, which was given by:

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

The magnitude of DF is directly proportional to the degree of orientation.

3. Results and discussion

The morphology of SBS block copolymers are shown in Fig. 4. The components tend to phase separate because of the thermodynamic incompatibility (solubility parameter $\delta_{\text{PS}} = 9.1$ and $\delta_{\text{PB}} = 8.4$ $(\text{cal/cm}^3)^{1/2}$) [26]. Details about the contrast mechanism in the SFM images and the morphology formation in the block copolymers covered in this study are already described in another publication [27]. In general, the contrast in the phase SFM image depends not only on the sample properties but also on the chosen

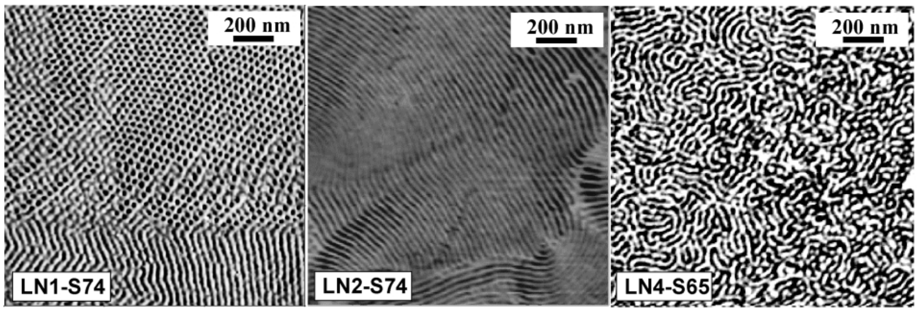


Fig. 4. Representative SFM phase images illustrating the microphase separated morphology of the SBS triblock copolymers having different interfacial structure.

experimental conditions [28]. In SFM images presented here, PB and PS domains appear dark and bright, respectively. In spite of the similar chemical composition (approximately 70% styrene volume fraction), one can observe a significantly different morphology. These morphologies are found not only in solution cast samples but also in injection or compression moulds [29]. This suggests that these are stable morphologies of the samples.

While in the case of LN1-S74 with sharp phase transitions PB cylinders are clearly arranged in a hexagonal lattice in the PS matrix, LN2-S74 with tapered interface shows an unambiguous lamellar structure. In different, LN4-S65 shows a complex morphology with disordered polystyrene domains dispersed in the dark rubbery matrix. Thus, the morphology of LN1-S74 corresponds to the classical phase diagram of diblock copolymers without any modification of interfacial structure (see Fig. 2). In contrast, LN2-S74 possesses an asymmetric structure with two PS outer blocks having different lengths and a different interfacial structure (tapered interface) (see Fig. 3). Hence, the mobility of the outer PS blocks is very different which should play an important role in morphology formation of this material.

The molecular mobility can be well characterized by the position of the glass transition temperature (T_g) of the components. Fig. 5 shows the DSC curves for the investigated block copolymers. It is obvious that the glass transition temperature T_g of the PS phase in LN1-S74 and LN2-S74 remains unchanged, while it appears very broad in LN4-S65. The T_g of the polystyrene phase can be more clearly observed in the corresponding DMA curve (Fig. 6). A significant shift of the T_g of the PB phase towards higher temperature occurs in the sequence LN1-S74 → LN2-S74 → LN4-S65. Generally, the main factors affecting the T_g values are thermal histories of the sample, system pressure, diluent types and concentration, molecular weight and distribution, and polymer structure [30]. Because the block copolymers were prepared at identical conditions, only the latter two factors appear to be important.

The classical model for the effect of molecular weight on T_g is [31,32]

$$T_g = T_g^{\infty} - \frac{C}{\bar{M}_n} \tag{3}$$

where T_g^{∞} is the glass temperature of samples of infinite molecular weight and C is a material constant. This model suggests that the transition temperature reaches a limiting value if the number average molecular weight $\bar{M}_n$ is above a critical value. In our case, the molecular weight of the PB blocks does not differ much from each other, and is far above 10,000 g/mol, i.e. in the range, where the molecular weight has only a negligible influence on the position of glass temperature. Therefore, the clarification of the shifting

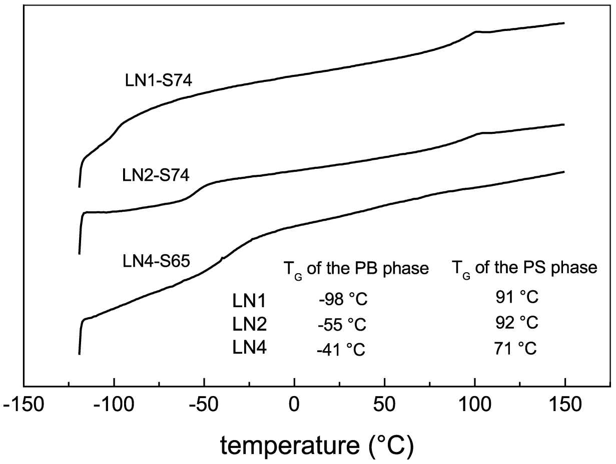


Fig. 5. DSC curves of the SBS triblock copolymers investigated.

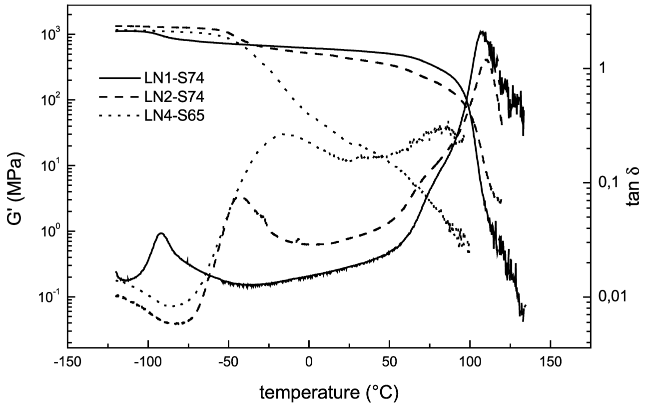


Fig. 6. DMA curves of the SBS triblock copolymers investigated; storage modulus (G') and loss angle (tan δ) are plotted against temperature.

in T_g of the PB phase should be found in the difference of interfacial structures. As a result of the irregular structures at the interface, a part of the soft segments is seriously restricted in mobility and hence behave as flexible components only at elevated temperatures. For example, in thermoplastic polyurethanes (TPU), the shift of the glass transition of the soft phase was explained by an increased amount of hard segments that are 'dissolved' in the soft matrix [33].

Referring to the position of glass transition temperature of PB phase, the DMA results presented in Fig. 6 reveal some interesting phenomena. The plateau region of the storage modulus curve (G' vs. temperature) above the transition of PB phase is widest and flattest in LN1-S74 followed by LN2-S74; and it does not even exist in LN4-S65. These phenomena are the result of the much stronger phase separation in the sample LN1-S74. In contrast, only a weak phase separation is present in LN4-S65. On the other hand, since material in the interfacial regions will have transitions between those for pure PS and pure PB phase, the level of losses in the rubbery plateau region will be increased by their volume in the interface [34]. This means that the interfacial volume increases in the sequence LN1-S74 → LN2-S74 → LN4-S65. By the increase of the interfacial volume, phase interaction is enhanced, so the mobility of chains in individual phases is more dependent on each other. In principle, short PS chains of LN2-S74 with high mobility may be mixed into the PB phase. This assumption is supported by the analysis of the area under tan δ curves. This area refers to the number of the molecular chains, which participates in the thermal transition process at the glass transition temperature. The broad transition of LN4-S65, followed by LN2-S74, is the result of a broad distribution of relaxation time in the PB phase [35]. This can only be explained by the intermixing of PS segments into the PB domains resulting in an increase in the effective fraction of the PB phase without changing the total chemical composition.

To conclude the DMA results, LN2-S74 with higher effective soft phase volume fraction (PB) compared to LN1-S74 possess a lamellar morphology. A quantitative determination of the portion of PS segments in the PB phase is not possible because, their miscibility is not known. Recently, Schuster and co-workers [22] presented how one obtains the quantitative information about the interfacial volume (and the amount of each component) in reinforced rubbers by analyzing the loss modulus curves with a specific fitting procedure. However, these calculations showed that two obvious separate loss modulus maxima for two well-defined phases have to be present. In our case, at about 100 °C, the specimens flowed strongly. Hence, no clear peak of T_g for the PS phase could be found.

Furthermore, a closer look at the DMA curve of LN2-S74 in Fig. 6 reveals an additional peak at about 74 °C. This peak may be attributed to the presence of a separate phase. However, the presence of PS segments in PB phase of LN2-S74 is not resolved by microscopic methods such as the TEM or the SFM. It may also be due to the compatibility of the short PS chains with the PB chains. Moreover, according to their rheological properties, two different polymer chains can be miscible, partial miscible or non-miscible. In the non-miscible case, PS domains may be clearly observed inside PB lamellae as shown Fig. 7 in an SBS star block copolymer having the similar chemical composition as the block copolymers investigated. This specific morphology has been termed as 'two-component three-phase' morphology [29].

Due to the presence of about 32 vol% of polystyrene as hard component, PS domains dispersed in S/B rubbery matrix are observed at LN4-S65. The obviously broad glass transition of LN4-S65 proves the existence of a mixed phase (i.e. the random S/B center block) with varying composition in this material [36]. The weak segregation of LN4-S65 related to its large interface volume permits a good phase interaction, but also causes a high compatibility between the components. Therefore, in context of its quite high polydispersity, a highly ordered structure for this block copolymer is not expected.

In addition, to estimate the interaction between the PS and the PB phase in SBS block copolymers, relaxation experiments were carried out. The variation of Young's modulus curves gives information about the mobility of macromolecular chains. The isothermal frequency scan measurements of the Young's modulus (E-modulus) carried out at different temperatures are shifted on the frequency axis according to the time–temperature superposition principle to get a master curve. The relaxation master curves of the SBS block copolymers investigated at a reference temperature of 30 °C are presented in Fig. 8. It is marked only by a horizontal shifting of measured curve as in so-called 'rheological simple' materials. That means that only one relaxation process of the materials can be observed. The relaxation curves shift to lower modulus of elasticity in the sequence LN1-S74 → LN2-S74 → LN4-S65. The different shape of the relaxation curves indicates

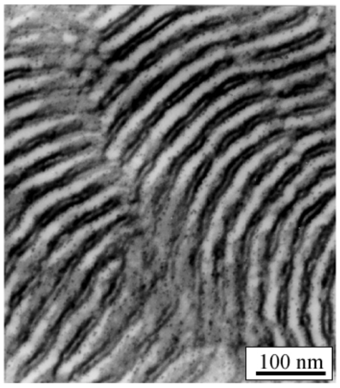


Fig. 7. TEM micrograph showing the morphology of a lamellar SBS star block copolymer having the same chemical composition as LN2-S74 (i.e. 74% volume fraction of PS) with PS domains in PB lamellae, OsO_4 staining.

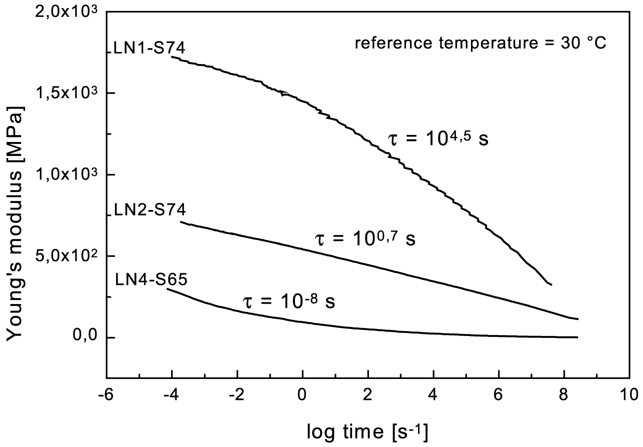


Fig. 8. Time-dependence of the Young's modulus of SBS triblock copolymers.

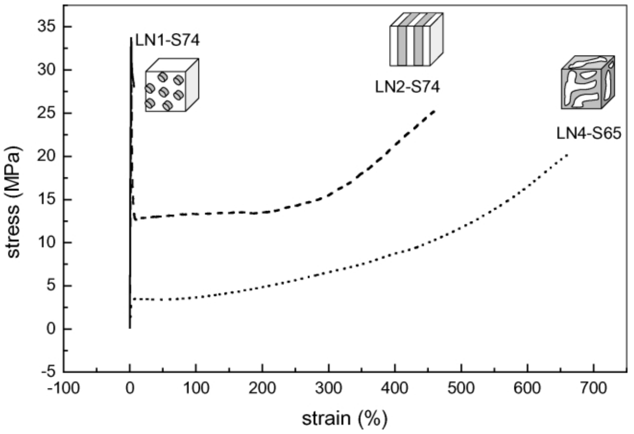


Fig. 9. Stress–strain diagrams of the investigated SBS triblock copolymers, injection molded samples tested at 23 °C at 50 mm/min.

different stages in the true relaxation spectrum of each specimen at the given measuring windows. Normally, at the reference temperature of 30 °C, the PB chains are in the entropy elastic state and can move very well, whereas the PS chains should remain inflexible, because they remain still in the glassy state. With increasing interfacial volume, the PS chains can penetrate more strongly into the PB phase. In this way, PS molecules in PB phase show an increased mobility. As a consequence, the relaxation time of material, which is the average value of the mobility of the whole chains in different phases, decreases. The relaxation times τ are determined according to the fit procedure of Wortmann [37]. Recently, Pechhold and co-workers [38] investigated the influence of morphology on the dynamics of the PB glass process in SBS block copolymers. They concluded that the difference in morphology did not influence the glass transition temperature and the relaxation time as long as the geometrical confinement applied on the PB phase is the same in different polymers. In our case, by the intermixing of short PS chains or PS chain segments into the PB phase, the nature of this phase was changed leading to the change of the dynamics of the PB phase. Thus, larger the interfacial volume, the more PS molecules can mix into the PB phase.

According to their morphology and phase behavior, the block copolymers investigated show different mechanical behavior. Fig. 9 shows the stress–strain diagrams of the injection molded block copolymer samples. Similar behavior is observed in samples prepared by solution casting [27]. The mechanical properties profile changes from brittle to elastomeric behavior. While LN1-S74 with PS matrix shows the behavior typical of a brittle material with high strength and low extensibility, LN2-S74 possesses a pronounced necking zone and possesses a good plastic ductility. After the yield, a drastic decrease in stress is followed by a slow strain hardening. The stress–strain curve of LN4-S65 resembles that of styrenic thermoplastic elastomers.

In general, the mechanical properties of heterogeneous polymer systems are governed by compatibility of the constituents and therefore by composition, morphology and interfacial structure [2]. In this context, three main factors at three different length scales play a dominant role [39]:

1. The details of the stress field applied at the interface and in particular the ratio between the shear and the tensile component of the stress field in the plane of the interface [40] (macroscopic scale).
2. The plastic deformation processes of the polymers on both sides of the interface, in particular those of the softer constituent (microscopic scale).
3. The molecular structure at the interface which is responsible for the transfer of stress between the phases (molecular scale).

In this study, the last one is of interest. The question is: whether the interfacial structure has an influence on the mechanical behavior of SBS block copolymers at a given chemical composition and morphology. In order to answer this question, a specific investigation method should be used which allows a direct determination of structural changes in individual phases induced by deformation. Rheo-optical Fourier transformed infrared (FT-IR) spectroscopy represents a valuable tool in this respect. In this study, FT-IR investigations have to be carried out simultaneously with in situ tensile tests. The principle of the FT-IR spectroscopy is the measurement of the anisotropy of absorption in oriented specimens [41–43].

For quantitative evaluation, the absorption bands at 967 and 1069 cm^{-1} are selected for butadiene and styrene phases, respectively. The band at 967 cm^{-1} is assigned to the out-of-plane wagging vibration of trans CH=CH double bonds [44]. The band at 1069 cm^{-1} characterizes partly the skeletal vibration of (C–C) single bonds and partly the in plane ν(C–C) stretching vibration of the aromatic ring [45]. According to the group theory [43], the transition moment angle of the respective bands is assumed to be about 90°. This means, a decrease of DF corresponds to an increase in orientation and vice versa.

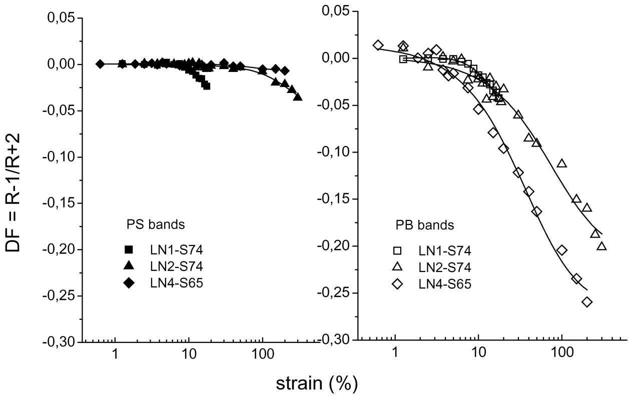


Fig. 10. Orientation behavior of SBS triblock copolymers expressed in terms of dichroic function DF.

The selective orientation behavior of the SBS block copolymers investigated is presented in Fig. 10. It is shown that regardless of the morphology of polymers, the PB phase is always oriented stronger than the PS phase. This is attributed to the lower Young's modulus of the PB phase compared to that of the PS phase. In both the block copolymers LN1-S74 and LN2-S74, the PS phase is deformed strongly resulting in a high orientation in this phase. In contrast, the PS phase in LN4-S65 does not deform plastically and only a very low orientation of PS chains results. In LN1-S74 the earlier increase in orientation of PS chains during deformation is the reason for its brittle behavior. Detailed discussion on the structural changes in molecular level of the triblock copolymers investigated in this study can be found in another publication [46].

Within the framework of this contribution, it is important to clarify whether the interfacial structure influences the selective deformation behavior. For this purpose, orientation behavior of two SBS block copolymers with similar chemical composition (PS volume fraction = 74%) and morphology but different interfacial structure and molecular architecture were comparatively investigated. These copolymers were LN2-S74 and ST1-S74 (the morphology of sample ST1-S74 is discussed in detail in Refs. [29,47]). In Fig. 11, the selective orientation behavior for LN2-S74 (possessing a tapered interface in a linear architecture) and ST1-S74 (with sharp interface in a star architecture) is compared. For LN2-S74 and ST1-S74, the lamellar long periods were 28 and 37 nm, respectively.

The orientation curves of the samples show a discontinuous process corresponding to their macroscopic behavior with obvious yielding in stress–strain diagram. Yielding is accompanied by transfer of a significant fraction of the stress from the hard phase to the soft phase. On account of the presence of similar morphology (i.e. alternating PS and PB lamellae), the extent of stress distribution should be nearly the same in both the block copolymers. However, different orientation behavior was clearly observed. LN2-S74 shows higher orientation both in the soft and the hard phases. In heterogeneous polymeric systems, where the components have different elastic moduli, a stress gradient occurs. The quality of stress transfer is influenced significantly by the interface. It seems that by an interface containing tapered block transitions, the stress can be transformed more effectively between the difference phases. Therefore, both the PS and PB phase could be stretched in a similar manner at a lower deformation speed. It leads to the better elongation in the local fields and hence the higher orientation of the individual phases.

4. Conclusions

Generally, the phase behavior of the block copolymers is determined by three experimentally controllable factors: the overall degree of polymerization N, architectural constrains characterized by n (n is functionality of the coupling agent) and the composition f (overall volume fraction of the A component) and the A–B segment–segment (Flory–Huggins) interaction parameter χ [48]. Hence, as shown schematically in Fig. 12(a), the phase diagram of SBS block

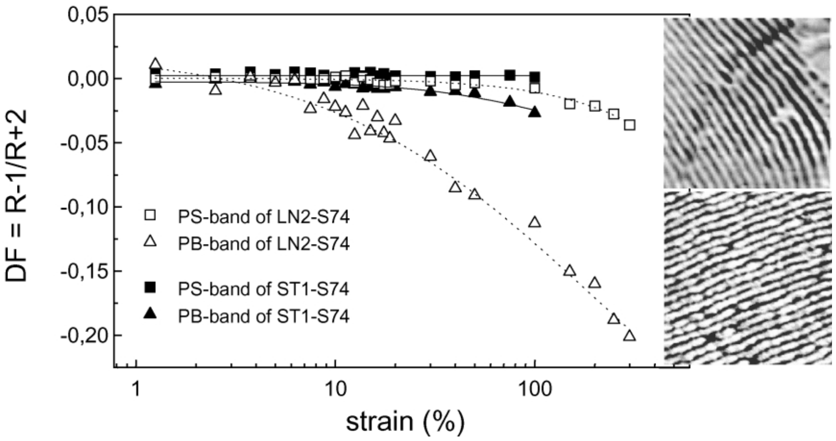


Fig. 11. Orientation behavior of the SBS block copolymers having similar (lamellar) morphology but differing in interfacial structure: LN2-S74 and ST1-S74 have tapered and 'neat' interfaces, respectively; a small part of SFM phase images of the samples are shown in inset.

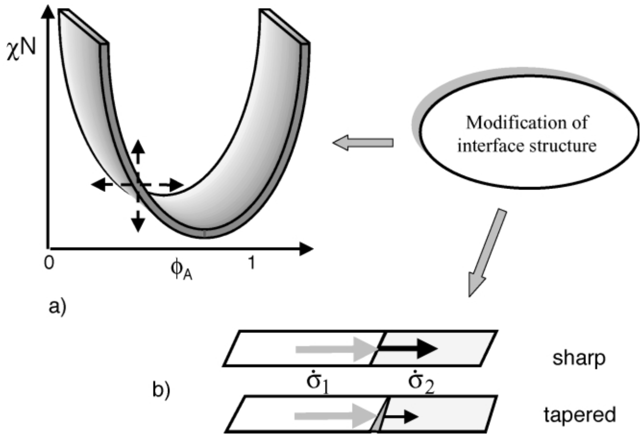


Fig. 12. Scheme showing the influence of interfacial structure on the phase diagram (a) and the stress transfer (b) in SBS block copolymers.

copolymers can be significantly influenced by the modification of the interfacial structure. Thus, only the morphology of LN1-S74 (hexagonally arranged PB cylinders in the PS matrix for PS volume fraction of 74%) with sharp interface fits into the classical diblock copolymer phase diagram. Depending on their interfacial structure, the remaining block copolymers LN2-S74 and LN4-S65 show the alternating lamellar morphology and the complex morphology with hard PS domains dispersed in the soft matrix, respectively. The effective portion of the mixed components is displaced for the benefit of the PB phase. Thus, the intermixing of short PS chains or PS chain segments into the PB phase leads to an increase of the glass transition temperature of the PB phase as well as to a significant decrease of the whole relaxation time of the materials. Also, the hard/soft volume ratio in SBS triblock copolymers can be adjusted via interfacial modification, which results in different morphologies.

Moreover, the extent of the stress transfer is influenced by the nature of the interfacial structure, which controls the deformation behavior of the individual phases. The tapered interface with a gradual composition profile can act as a stress absorber and permits a more uniform distribution of the applied stress. Hence, both the PS and the PB phases can be more elongated leading to a higher orientation. As shown schematically in Fig. 12(b), by transformation of the applied stress from one phase to the other, the deformation speed can be significantly decreased by a tapered interface ($\dot{\sigma}_1 > \dot{\sigma}_2$ for sharp interfaces, $\dot{\sigma}_1 \gg \dot{\sigma}_2$ for tapered interfaces) permitting a more uniform stress distribution and hence a more effective elongation in both the phases.

Acknowledgements

We would like to thank the Bundesministerium für Bildung und Forschung (BMBF, the MaTech Program), the Kultusministerium des Landes Sachsen-Anhalt, the Deutsche Forschung Geminschaft (DFG) and the Max-Buchner-Forschungsstiftung for financially supporting of this research and Dr Th. Lüpke (University Halle-Wittenberg) for useful discussions.

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