Morphology and Micromechanical Deformation Behavior of SB-Block Copolymers. II. Influence of Molecular Architecture of Asymmetric Star Block Copolymers

R. ADHIKARI,[1] G. H. MICHLER,[1] W. LEBEK,[1] S. GOERLITZ,[1] R. WEIDISCH,[2] K. KNOLL[3]

[1] Institute of Materials Science, Martin Luther University Halle-Wittenberg, 06099 Halle, Germany

[2] Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

[3] BASF Aktiengesellschaft, Polymers Laboratory ZKT/I-B1, D-67056, Ludwigshafen, Germany

ABSTRACT: The influence of molecular architecture on morphology, mechanical properties, and micromechanical deformation behavior of asymmetric styrene/butadiene star block copolymers is investigated by transmission electron microscopy (TEM) and uniaxial tensile testing. In contrast to diblock copolymers, star block copolymers having 74% polystyrene (PS) show a lamellar morphology. Furthermore, tapered asymmetric star block copolymers having a PS core reveal additional PS domains inside the PB lamellae not observed in untapered star block copolymers. The introduction of tapered sequences in star block copolymers results in a significant improvement of tensile properties due to the increased interfacial width between the phases as well as differences in morphology. The investigated star block copolymers show a homogeneous plastic deformation of PS lamellae. This mechanism is called thin-layer yielding of PS lamellae. The lamellae are locally deformed via inhomogeneous necking and drawing. Lamellae which are not oriented parallel to the load direction are twisted to the deformation direction. Neat star block copolymers (without tapered chains) exhibit a premature failure of PS lamellae arising from the decreased interfacial width, which results in a decrease of their ultimate strain. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 701–713, 2002

Key words: SB star block copolymer; tapered block copolymer; mechanical properties; homogeneous deformation; micromechanisms; electron microscopy

INTRODUCTION

Block copolymers represent an interesting class of nanometer-structured materials that enable us to create polymer materials with tailored mechanical properties for specific applications because of the large variety of available structures and molecular architectures.

In poly(styrene-*b*-isoprene) (PS-*b*-PI) diblock copolymers, body centered cubic (BCC) spheres, hexagonal packed cylinders, ordered bicontinuous double diamond (OBDD), and lamellar structures[1] were found. In the weak segregation limit, perforated layers and cubic bicontinuous structure (gyroid) were observed in addition.[1] Recently, attention was paid to block copolymers with complex architectures. Examples for such block copolymers are ABC triblock copolymers and star block copolymers, which require the control of complex anionic polymerization tech-

Table I   Characteristic Parameters of the Investigated Samples

Sample	M_n (g/mol)[a]	M_w/M_n[a]	Φ_{PS}[b]	Arm No.	Remarks
ST1-S74	91,800	1.99	74	ca. 4	PB core, sharp transition
ST2-S74	109,200	1.69	74	ca. 4	PS core, tapered block transition
LN1-S74	82,000	1.07	74	Linear	Symmetric PS outer blocks

[a] Determined by GPC using PS calibration.
[b] Total styrene volume fraction determined by ^{1}H-NMR spectroscopy. The materials were provided by BASF.

niques. These polymeric materials provide a much larger variety of morphologies than diblock copolymers. They show in several cases highly fascinating morphologies such as investigated by Stadler and coworkers (summarized in ref. [1]). It was shown that the molecular architecture has a pronounced influence on morphology and phase diagrams [e.g., by Gido and coworkers (see ref. [1] chapter 2), who have recognized that an increasing molecular asymmetry in graft copolymers results in a shift of the morphological phase diagram].

Furthermore, the use of two incompatible polymer blocks allows the combination of advantages of both materials.[1] An example is the variation of the ratio of hard and soft sequences in thermoplastic elastomers (TPE). In such TPEs, representing a class of triblock copolymers of PS and polybutadiene (PB), the mechanical performance of vulcanized rubber is combined with the straightforward processing of thermoplastics due to the physical network of flexible chains.[1,2]

Tapered block copolymers (TBC) allowing the production of materials with tailored properties are of special interest with respect to our investigations. In such copolymers, the composition along the chain backbone shows a continuous variation rather than a sharp interfacial composition profile. As a result of this tapered transition between immiscible blocks, the interface is significantly broadened. The incorporation of sufficiently long tapered sequences in a poly(styrene-b-butadiene) (PS-b-PB) diblock copolymer can drive the copolymer close to its order–disorder transition (ODT), and the blocks are not strongly segregated, but show a weak segregation in spite of using block copolymers with rather high molecular weights.[3–5] Recently, star block copolymers were investigated by many authors[5–9] and special attention was paid to their enhanced rheological as well as mechanical properties compared to that of their linear analogues.[8,10] The influence of arm number, arm molecular weight, and chemical composition on morphology and physical properties[8,11,12] are of particular interest.

The asymmetric star block copolymers used in this work are especially important for commercial applications because the mechanical properties can be easily adjusted by designing end blocks of suitable lengths without changing the type of monomers. One possibility for an asymmetric architecture in star block copolymers is the use of only one longer PS arm and a different number of short PS arms. The long PS arm, having a high molecular weight, reveals mainly two advantages.

First, it provides a necessary physical crosslinking important especially for the strength of the TPE. Second, longer PS arms enable the miscibility with an additional PS homopolymer with a significantly higher molecular weight, as compared to the case of diblock copolymers. The advantage of blending a star block copolymer with a homopolymer is the reduction of material price while still maintaining transparency and strength. The shorter low molecular weight end PS blocks, on the other hand, endow the system with good processibility and deformability.

Whereas in Part I of this study the deformation behavior of asymmetric star block copolymers was investigated with respect to different morphologies (with and without PS particle), in the present study, two asymmetric star block copolymers with different molecular architecture are compared. The aim of this article is to discuss the correlation between molecular architecture, morphology, mechanical properties, and micromechanical deformation behavior of asymmetric styrene/butadiene star block copolymers.

EXPERIMENTAL

Materials

Characteristic data of block copolymers (ST1-S74 and ST2-S74) used in this study are shown in Table I. Both types of star block copolymers consist of about four asymmetric PS arms. Synthesis and characterization of these star block copoly-
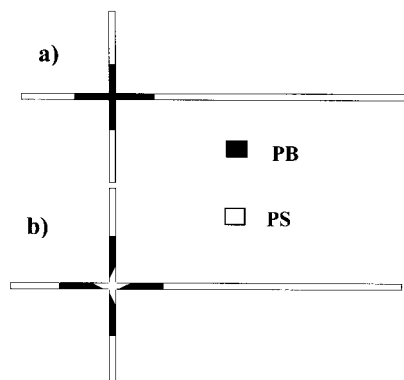
Figure 1 Molecular structure of star block copolymers: (a) ST1-S74 (asymmetric four-arm block copolymer containing a sharp transition); (b) ST2-S74 (asymmetric four-arm star block copolymer having a tapered block transition).

mers is described by Knoll and Nieβner.[3,5] Sample ST2 consists of a PS core with tapered transition to PB. In contrast to sample ST2, sample ST1 has a PB core without tapered transition. However, both types of star block copolymers possess PS as outer arms. In addition, both samples are asymmetric with respect to the length of the PS arms (i.e., one of the PS arms shows a higher molecular weight). The molecular structure of both star block copolymers are schematically outlined in Figure 1.

Injection-molded (mass temperature, 220°C; mold temperature, 45°C) as well as compression-molded (240°C) samples were used. Solvent-cast films were also investigated to compare these samples with their equilibrium morphology. For this purpose, about 0.5-mm-thick films were cast from a 3% solution in toluene followed by an evaporation process of about 2 weeks and subsequent annealing at a temperature of 120°C in a vacuum oven.

Tensile Testing

The tensile tests were carried out at a crosshead speed of 50 mm/min by using a universal tensile machine according to the standard ISO 527. At least 10 samples were tested to get good statistics of the measured values. Because tensile specimens with a smaller size were used for investigation of solution cast films, these results are not directly comparable with other samples.

Transmission Electron Microscopy (TEM)

A small block of each sample cut from the bulk specimen was dipped in aqueous OsO_4 solution

for several days at room temperature to selectively stain the butadiene phase. Thin sections, about 50 nm in thickness, were cut from unstrained and strained specimens by using a Reichert ultramicrotome, Ultracut E, operated at room temperature for investigation of morphology and deformation structures, respectively. For investigation of deformation structure, thin sections were cut from the strained tensile specimens close to the fracture surface. These sections were examined by using a JEOL 200-kV transmission electron microscope.

RESULTS AND DISCUSSION

To get the equilibrium morphologies, solution cast films (toluene, neutral solvent) are investigated. The influence of processing conditions on mechanical properties are studied by using compression-molded and injection-molded star block copolymer ST2-S74. The discussion starts with a detailed explanation of morphology followed by mechanical properties and micromechanical deformation mechanisms.

Morphology of Star Block Copolymers

Figure 2(a,b) shows TEM micrographs of solution-cast samples of the star block copolymers ST1-S74 (sharp transition) and ST2-S74 (tapered transition). Because the samples were cast from toluene, a solvent neutral for both the constituents, the structures are assumed to be close to equilibrium.

Both samples contain 74% of the volume fraction of PS and possess a lamellar morphology consisting of alternating PS and PB lamellae. According to Leibler's theory, a hexagonal morphology (PB cylinders in PS matrix) would be expected in a diblock copolymer with similar chemical composition.[13] This means that the morphology of these star block copolymers does not fit into the common morphology scheme of diblock copolymers because of their asymmetric architecture. Characteristics of morphology are shown in Table II.

Considerable morphological differences are observed between samples ST1-S74 and ST2-S74 because of the change of the molecular architecture:

First, the morphology of sample ST1 [Fig. 2(a)] shows a higher long-range order than sample ST2-S74 [Fig. 2(b)]. The smaller long-range order observed in ST2-S74 can be attributed to the pres-
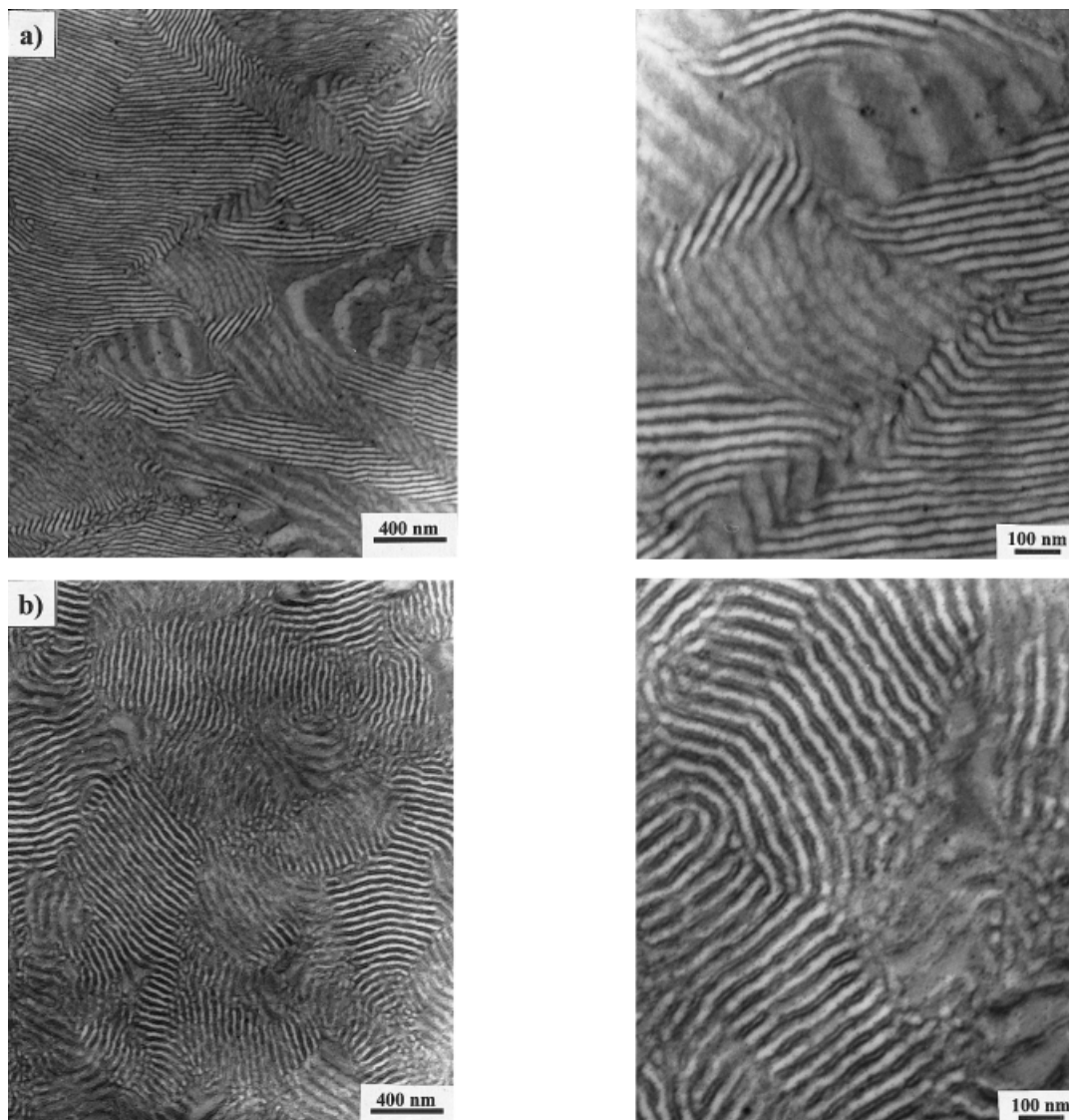
Figure 2 Lower (left) and higher (right) magnifications of TEM images of solution-cast films of sample ST1-S74 (a, top) and ST2-S74 (b, bottom). The sections were cut perpendicular to the film surface.

ence of a tapered sequence in its block architecture. The tapered sequence leads to the formation of a broadened interface arising from increased miscibility of both blocks. This broadened interface drives the system toward weak segregation compared to strongly segregated phases in the absence of a tapered sequence.[4,14] It is well known from theoretical and experimental work[1] that within the weak segregation limit the density profile is considered to vary sinusoidally in space and the components are highly interpenetrated. This is associated with a decrease of long-range order, confirming our discussion for tapered-star block copolymers.

Second, higher magnification TEM images of ST2-S74 [Fig. 2(b)] reveal a row of small PS spheres or cylinders ($\sim$ 6 nm diameter) inside the PB lamellae. This kind of domain is not found in ST1-S74, reflecting the influence of the molecular architecture on morphology of star copolymers.

As already mentioned in the experimental section (Fig. 1), molecules of ST2-S74 have a small PS core, whereas ST1-S74 molecules have a PB core. The result indicates that the PS core, chemically coupled to the PB chains in the star block copolymer ST2-S74, is responsible for the formation of scattered PS domains inside the PB lamellae. Furthermore, the shorter PS arms might be

Table II   Long Period and Thickness of PS Lamellae in Unstrained and Strained Block Copolymer Samples Determined by Analyzing TEM Micrographs

Sample	Preparation	Long Period, L (nm)		D_{PS} (nm)		ΔL (%)[a]
		Unstrained	Strained	Unstrained	Strained	
ST1-S74	Injection molding	37	22	24	15	32
ST1-S74	Solution casting	34	—	22	—	—
ST2-S74	Compression molding	39	22	20	13	41
ST2-S74	Injection molding	42	28	20	14	50
ST2-S74	Solution casting	46	—	24	—	—

[a] Decrease in lamellar long period due to deformation.

mixed together with the PS core inside the PB lamellae, as discussed by Knoll and Nießner,[3] who proposed that these domains might have been formed by the PS core and PS blocks of butadiene-rich short arm stars that are partly demixed from the styrene-rich stars. In the case of sample ST2-S74, the chains of the PS core must be placed within the PB lamellae for geometrical reasons. These domains, which practically belong to the butadiene phase, contribute to strengthen the volume fraction of the rubbery component, which further favors the formation of lamellae structure instead of PB cylinders.

For practical applications, morphologies developed via processing conditions (e.g., injection molding, extrusion, compression molding, etc.) and their influence on mechanical properties are quite important. Figure 3(a,b) shows TEM micrographs of injection-molded samples ST1-S74 and ST2-S74, respectively. As shown, the morphology observed in injection-molded samples is mainly of lamellar type, as already observed in solvent-cast films.

Figure 3(a) shows structural details of the injection-molded sample ST1-S74, which is principally the same as observed for the solution-cast sample [Fig. 2(a)]. The sample exhibits a lamellar morphology which is in agreement with the observations by Hashimoto et al.[7] and Yamaoka,[15] who have also reported the existence of lamellar morphology in a styrene/butadiene star block copolymer with approximately the same composition. The TEM micrographs in Figure 3(b) show a lamellar arrangement of PS and PB in sample ST2-S74. As already observed for the solution-cast sample [Fig. 2(b)], it also contains a row of small PS domains inside the PB lamellae. The long period and thickness of PS lamellae of both injection-molded samples are given in Table II.

The noteworthy difference between solution-cast samples and injection-molded samples is the orientation of the lamellar structure. In the injection-molded sample, the lamellae are preferentially oriented in the injection direction, which is the result of shear stress in the melt, an effect well known from the processing of other polymers. In both injection-molded samples (ST1 and ST2), the lamellae aligned parallel to the direction of the shear field have an extended long-range order. Many research groups have studied shear orientation in block copolymer systems[16–18] and demonstrated that phase behavior of block copolymers may be significantly altered by a shear field. The knowledge of the orientation process in block copolymers is particularly interesting because it provides the possibility of understanding and predicting anisotropic material properties and failure mechanism.

To study the influence of processing conditions on morphology and mechanical properties, compression-molded samples are studied as well. Figure 4 shows the morphology of compression-molded sample ST2-S74. The structural details observed in compression-molded samples are principally the same as found in solution-cast as well as in injection-molded specimens. However, the lamellae do not show a pronounced long-range preferential orientation, as expected for compression molds.

Our results show that star block copolymers discussed in the present study have a lamellar morphology with arrangement and orientation of the lamellae, depending on sample preparation. The morphology of the investigated star block copolymers is not found to match the common morphology scheme of diblock copolymers. Furthermore, rows of PS domains embedded in the PB lamellae in sample ST2-S74 are also not observed in common diblock copolymers. In particular, the morphology of ST2-S74 resembles the three-phase morphology reported by Shibayama
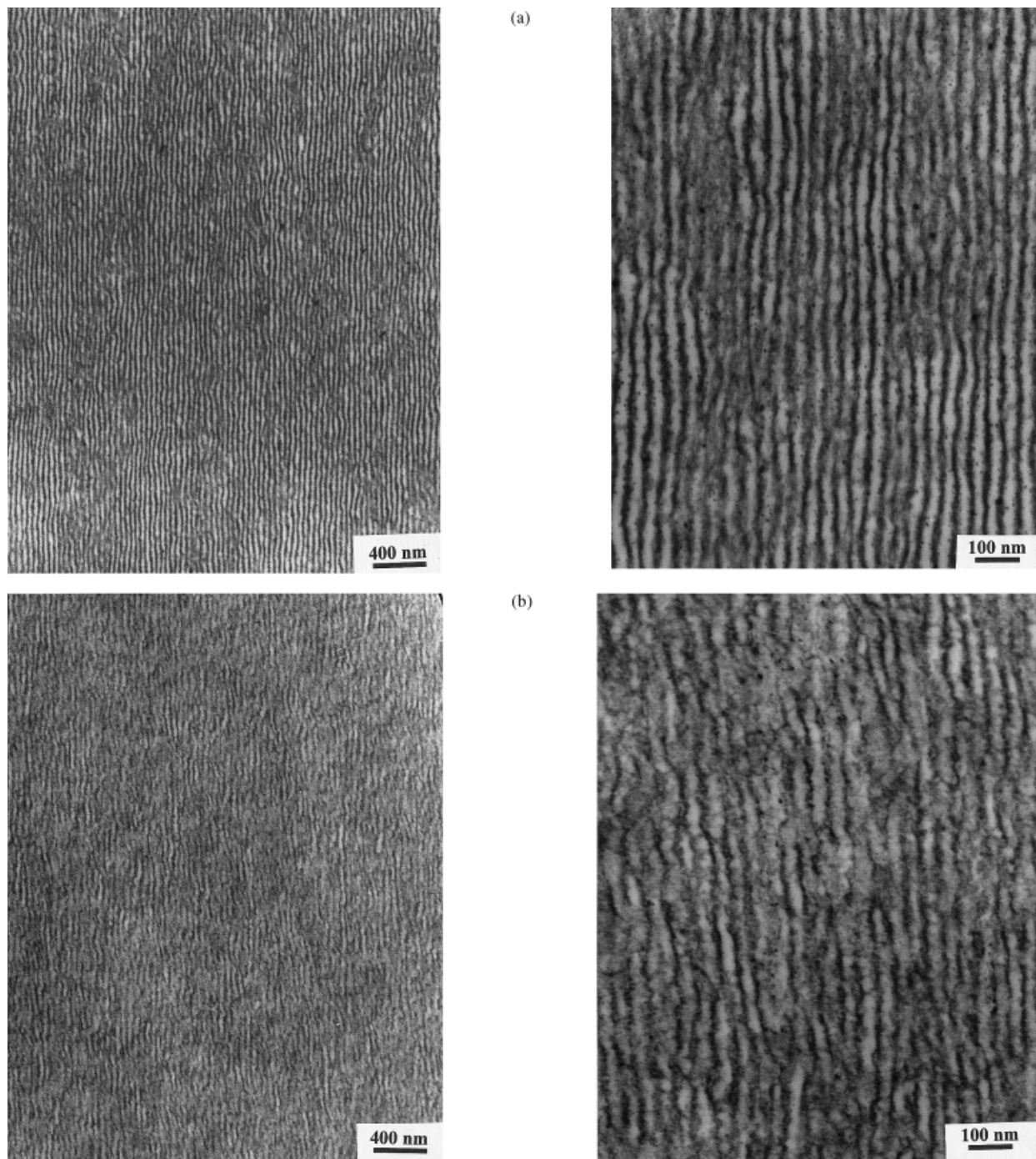
Figure 3   Lower (left) and higher (right) magnifications of TEM images of injection-molded star block copolymers: (a) ST1-S74 and (b) ST2-S74; injection direction, vertical.

et al. in ABC triblock copolymer.[19] Because three distinct phases (PS lamellae, PB lamellae, and PS domains in PB lamellae) emerge from the two-component (PS and PB) system upon microphase separation, the peculiar morphology observed in ST2-S74 may be termed as two-component three-phase morphology.[20]

Mechanical Properties

For industrial applications, properties of compression-molded and especially injection-molded samples are more important than solution-cast samples. Hence, we focus our discussion on the tensile properties of injection- and compression-molded
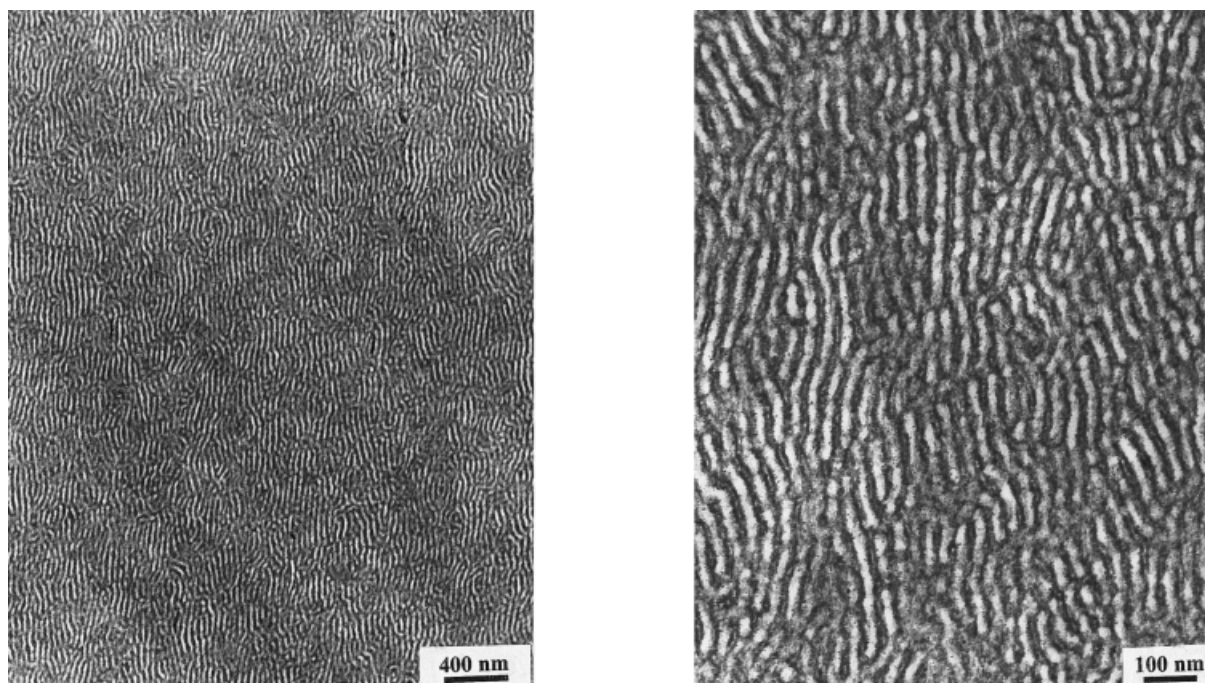
Figure 4 Lower (left) and higher (right) magnifications of TEM micrographs of compression-molded ST2-S74; compression direction, horizontal.

samples. Another reason is that solution-cast tensile specimens have a smaller size, which makes it difficult to compare their mechanical properties.

Mechanical properties of the investigated star block copolymers determined by tensile tests are presented in Table III. To compare the mechanical properties of star block copolymers with linear triblock copolymers, the properties of a symmetric poly(styrene-*b*-butadiene-*b*-styrene) (SBS) triblock copolymer (designated as LN1-S74) with equivalent chemical composition as ST1-S74 and ST2-S74 and Figure 5(a). Significant differences in mechanical properties between samples ST1-S74, ST2-S74, and LN1-S74 are observed, demonstrating the influence of block architecture on mechanical properties.

Tensile properties of the block copolymers used in this study are characterized by a well-defined yield point. The degree of plastic deformation is, however, quite different. Both star block copolymers show a much larger plastic deformation than the SBS triblock copolymer. Furthermore, the absorbed energy is much larger for the star block copolymers reflected by the large area under the corresponding stress–strain curves. The deformation of both star blocks is accompanied by a formation and subsequent elongation of a neck, whereas the SBS triblock copolymer undergoes a brittle fracture before a stable neck is formed.

The star block copolymers ST1-S74 and ST2-S74 show a surprisingly large strain at break of about 110 and 257%, respectively. LN1-S74, hav-

Table III   Comparison of Tensile Properties of the Block Copolymers Measured at a Strain Rate of 50 mm/min

Materials	Preparation	Young's Modulus (MPa)	Yield Stress (MPa)	Strain at Break (%)	Tensile Strength (MPa)
ST1-S74	Injection molding	1570	27	110	16
ST2-S74	Compression molding	1015	17	390	28
ST2-S74	Injection molding	1205	24	257	20
ST2-S74	Solution casting[a]	—	22	320	26

[a] About 0.5-mm-thick samples having total length of 50mm.
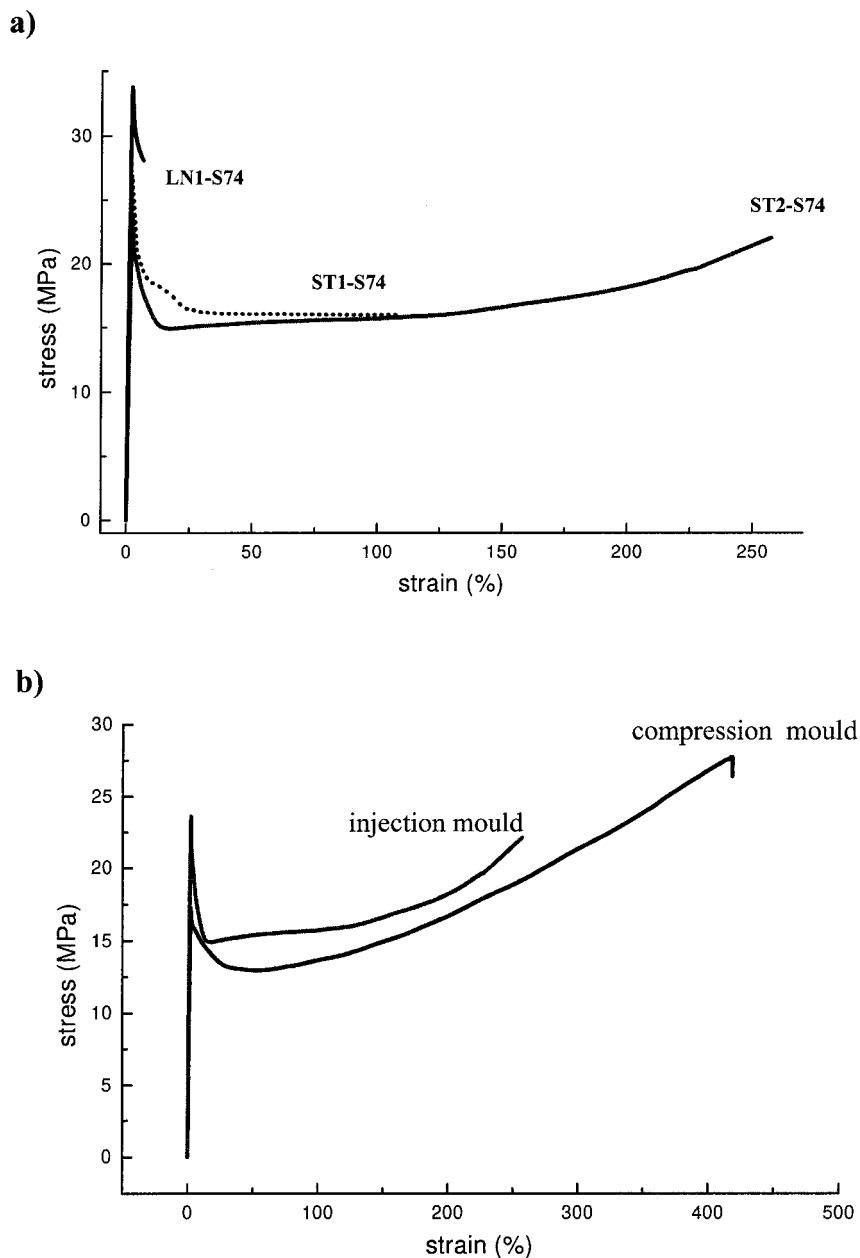
a)

b)

Figure 5 (a) Stress–strain curves of the star block copolymers in comparison with that of a symmetric SBS triblock copolymer; tensile testing of injection molds; (b) stress–strain curves of injection and compression-molded ST2.

ing equivalent chemical composition, on the other hand, shows a strain at break of only about 10%. It should be mentioned that LN1-S74 has a hexagonal structure that provides additional reasons for their different tensile properties. SBS triblock copolymers with lamellar structure usually have lower PS content, and therefore, cannot be directly compared with our star block copolymers. Quirk and Morton[10] have compared the tensile and rheological properties of star-shaped het-

eroarm styrene/butadiene thermoplastic elastomers with SBS thermoplastic elastomers. It has been shown that star block copolymers exhibit improved tensile properties than their linear analogues. Recently, Shim and Kennedy[8] have investigated various thermoplastic elastomers on the basis of PS and polyisobutylene and proven the superiority of star block copolymers over their linear counterparts with respect to tensile as well as rheological properties.

The improved mechanical properties of star block copolymers presented in this article may be discussed by considering the following two aspects: (a) asymmetric molecular architecture and morphology; and (b) role of tapered block transition.

Star block copolymers provide more physical crosslinks than triblock copolymers because of the larger number of PS arms. The asymmetric nature of architecture is associated with the advantage that the longer PS arm improves the strength of the material, whereas the shorter PS arms are simultaneously responsible for enhanced deformation of the material.[21] Both of these effects are present in the star block copolymers ST1-S74 and ST2-S74, which are reasons for their improved tensile properties.

Asymmetric molecular architecture can have a pronounced influence on the morphology formation of block copolymers, as demonstrated by the investigations of Lee et el. in graft copolymers.[22] In a recent publication, they have shown that asymmetric block structure in graft copolymer leads to a strong shift in phase diagram. Clearly, the formation of lamellae-like morphology in our star block copolymers indicates the influence of molecular architecture. Formation of lamellar morphology in ST2-S74 is further favored by the tapered block transition, as will be discussed later.

Both star block copolymers consist of about four arms; on average, one of these has a much longer PS outer block. The difference between them is the existence of a tapered transition in sample ST2-S74 resulting in additional PS domains inside the PB lamellae. Because these PS domains are chemically coupled to the PB chains, they can act as additional energy sinks[23] associated with enhanced dissipation of energy, which prevents a premature failure of the samples. In addition, these PS domains that act similar to a filler in particle-filled rubbers clearly enhance the effective strength of the PB lamellae, because an effective stress transfer can occur between PS domains and PB lamellae.

It was demonstrated that phase behavior of tapered block copolymers differ considerably from that of common triblock copolymers,[4,24–26] which indicate a strong shift in mechanical behavior. Recently, Asai[24] showed that an SB diblock copolymer, containing a tapered transition between the PS and PB chains, reveals a strong improvement of tensile properties. It was assumed that the energy dissipation in tapered block copolymers is much larger than in block copolymers

without tapered transition. Incorporation of tapered chains in a block copolymer results in a decrease of interfacial energy due to enhanced miscibility of the phases.[4,14,27,28] This enhanced miscibility is connected with an increasing interfacial width, and then the phase behavior is close to a weakly segregated system. In weakly segregated block copolymers, it was shown[29–31] that an increasing interfacial width is responsible for a significant improvement of tensile properties of block copolymers. By using neutron reflectometry (NR) and small-angle neutron scattering (SANS), it was demonstrated that tensile properties in those block copolymers (small interaction parameter and interfacial width of about 8 nm) are significantly improved compared to corresponding homopolymers. By using these results, it is possible to understand higher ductility of sample ST2-S74 (tapered star block) compared to sample ST1-S74.

To describe the influence of sample preparation on mechanical properties, compression-molded ST2-S74 was also investigated. Figure 5(b) compares stress–strain curves of injection-molded and compression-molded specimens of sample ST2-S74. It is visible that injection-molded specimens have a yield strength at 24 MPa compared to 17 MPa in the case of compression-molded samples. In contrast, injection-molded samples have lower strain at break (ϵ_B = 257%) than compression-molded samples (ϵ_B = 390%). These differences in mechanical properties between the injection-molded and compression-molded samples may be attributed to different orientations of the morphology and polymer chains.

Micromechanical Deformation Behavior

Cavitation was accepted as dominating deformation mechanism in diblock copolymers. In addition, mechanisms such as craze termination, craze coalescence, and craze diversion were observed in poly(styrene-*b*-butyl methacrylate) (PS-*b*-PBMA) diblock copolymers.[30] Star block copolymers investigated in this study, however, show a new homogeneous plastic deformation of PS lamellae.

It was already discussed in Part I of this study that asymmetric lamellae forming star block copolymers show a deformation mechanism called thin-layer yielding. The characteristic of this deformation mechanism is the large homogeneous deformation of the PS lamellae together with the PB lamellae, if the thickness of PS lamellae remains below a critical value of about 20 nm. Here,
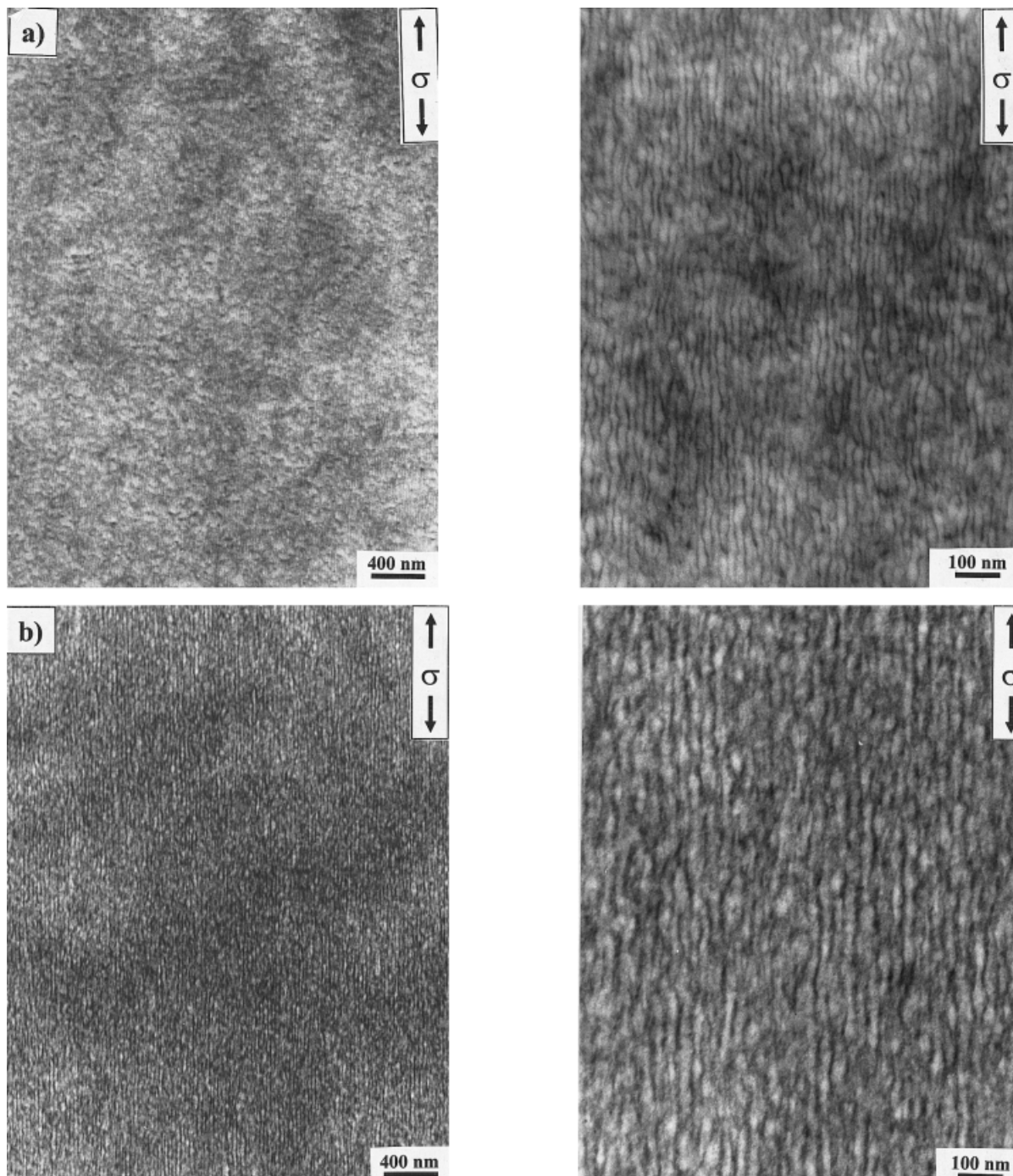
Figure 6   Lower (left) and higher (right) magnifications of TEM images showing the structural changes after deformation in injection-molded star block copolymers: (a) ST1-S74 and (b) ST2-S74.

we intend to discuss the influence of the molecular architecture on the deformation mechanism of the block copolymers.

Figure 6 shows the deformation structure observed in injection-molded star block copolymers. In injection-molded ST1, the PS lamellae are highly deformed in strain direction, forming alternating thinner and thicker regions. This indicates that the PS lamellae show locally an inhomogeneous deformation. It is obvious from Figure 6 that PS lamellae in sample ST1-S74 undergo a necking process resulting in a premature failure
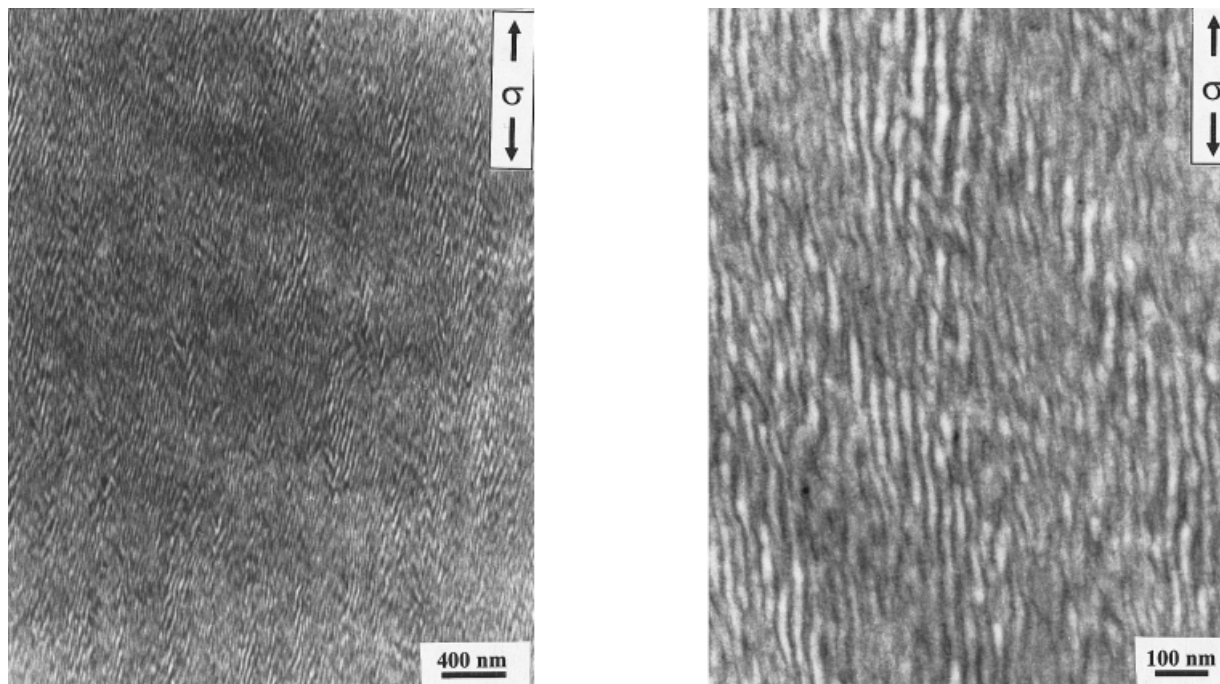
Figure 7 Lower (left) and higher (right) magnifications of TEM images revealing the structural changes after deformation compression-molded ST2-S74.

of PS lamellae. The smaller interfacial width of sample ST1-S74 compared to sample ST2-S74 is associated with a premature failure of PS lamellae before a stable neck may be formed. Here, the stress transfer between both phases is less effective than in sample ST2-S74 with broadened interface. This pronounced tendency of necking of PS lamellae may be regarded as a reason for the decreased strain at break of sample ST1-S74 compared to ST2-S74.

The injection-molded ST2 displays a large deformation of PS as well as PB lamellae toward the strain direction. Large plastic deformation of the PS lamellae is obvious from the reduction in long period and thickness (Table II). Local deformation zones are not observed during tensile deformation. Therefore, the deformation mechanism may be described as homogeneous plastic flow of both PS and PB lamellae. A closer inspection of the micrographs in Figure 6 reveals, however, that the deformation of the lamellae themselves is not completely homogeneous. It seems that a local microscopic necking and drawing of the PS lamellae occurs. Average thickness of PS lamellae is reduced to about half during deformation. However, locally the PS lamellae show a larger plastic deformation ($\lambda_{PS} > 4$). This indicates that an inhomogeneous plastic flow of PS lamellae occurs via micronecking and drawing and a subsequent

rupture of necked PS lamellae into small fragments finally leads to the ultimate fracture of specimens. The necking process of the PS lamellae is accompanied by chain orientation and strain hardening.

The principal deformation mechanism observed in compression-molded ST2 (Fig. 7) is the same as in injection-molded specimens, but the deformation seems to be more inhomogeneous in compression-molded samples because of a lack of a preferential orientation. Lamellae are only partially oriented parallel to the external strain direction (see Fig. 4) and only those lamellae are deformed in strain direction as in the case of the injection-molded samples. However, the lamellae with other orientations are twisted to the deformation direction followed by drawing in strain direction. This two-step mechanism (rotation and stretching of lamellae) yields the observed larger elongation at break and enhanced absorbed energy of compression-molded samples.

The asymmetric molecular architecture and broadened interfacial width (due to the presence of a tapered block sequences) of sample ST2-S74 give rise to an enhanced stress distribution between both phases, resulting in a larger strain at break and tensile strength. The deformation processes as observed in the TEM investigations can be summarized in a scheme shown in Figure 8.
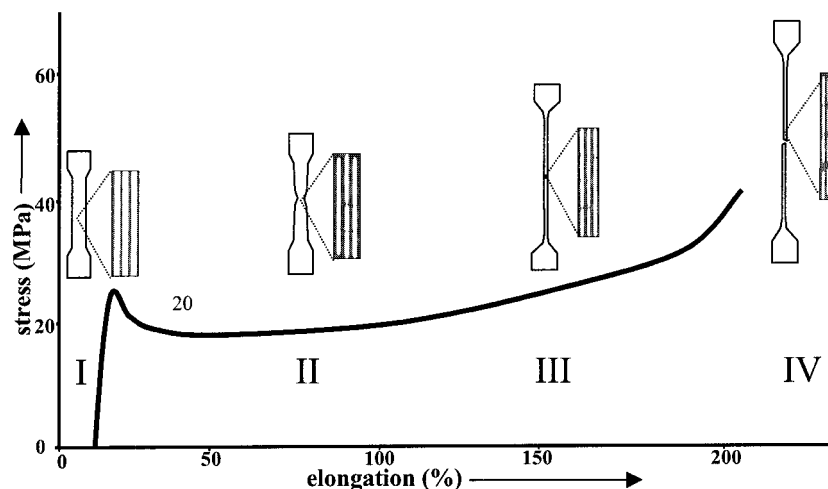
Figure 8 Schematic drawing revealing the deformation mechanism in star block copolymers during uniaxial tensile deformation; regions I–IV stand for different states of deformation of the tensile bar and lamellae.

Deformation processes involved in different stages, as shown in Figure 8, are as follows:

I. Elastic deformation before yield point
II. Necking and drawing of PS lamellae accompanied by shearing in the PB phase
III. Strain hardening as a result of chain-orientation
IV. Rupture of PS lamellae and elongation of PS fragments upon their ultimate failure.

CONCLUSION

In the present study, the influence of molecular architecture of star block copolymers on morphology, mechanical properties, and deformation behavior are investigated. For the first time, star block copolymers with quite complex asymmetric architectures are examined, which are also important for commercial applications. It is clearly shown that the tensile properties of tapered asymmetric star block copolymers are improved compared to star block copolymers without tapered block sequences. This is correlated to differences in morphology and deformation behavior, which can be summarized as follows.

The star block copolymers studied in this work possess basically a lamellar morphology arising from their asymmetric molecular architecture. The tapered star block copolymer shows additional PS domains inside the PB lamellae. In contrast, block copolymers with the same composition of 74% PS reveal a hexagonal structure. The

preferential orientation of lamellae in injection-molded samples is due to shear stress acting during the process of injection molding.

Star block copolymers possess improved mechanical properties compared to symmetric triblock copolymers. Improved mechanical properties observed for the tapered star block copolymer are related to its broadened interface arising from the enhanced miscibility and the presence of the PS domains inside the PB lamellae.

As already reported in Part I of this study, the PS lamellae in star block copolymers are deformed via a thin-layer yielding mechanism, a large homogeneous plastic deformation of PS lamellae, if their thickness remains below a critical value (about 20 nm). Improved energy dissipation of tapered star block copolymers arises from the decrease of critical stresses at the interface and a more effective stress transfer between PS and PB phases. This results in a large plastic deformation of PS lamellae responsible for the large degree of strain hardening observed in these samples. Moreover, the presence of PS domains within the PB lamellae act as filler in the PB lamellae, which increases both strength and effective volume fraction of the rubbery phase.

It is interesting that the combination of both asymmetric architecture and introduction of tapered block sequences in star block copolymers result in a significant improvement of mechanical properties.

REFERENCES

1. Hamley, I. The Physics of Block Copolymers; Oxford Science Publications: Oxford, 1998.
2. Holden, G. in Thermoplastic Elastomers, 2nd ed.; Holden, G., Legge, N. R., Quirk, R. P., Schroeder, H. E., Eds.; Hanser Publishers: Munich, 1998; Chapter 4.
3. Knoll, K.; Nieβner, N. Macromol Symp 1998, 132, 231.
4. Laurer, J.; Smith, S. D.; Sameth, J.; Mortensen, K.; Spontak, R. J. Macromolecules 1998, 31, 4975.
5. Knoll, K.; Niessner, N. in Quirk, R. P., Ed.; ACS Symposium Series: Applications of Anionic Polymerisation Research; 1998; Vol. 696, p 112.
6. Ishizu, K.; Kitano, H.; Ono, T.; Uchida, S. Polymer 1999, 40, 3229.
7. Hashimoto, T.; Satoshi, K.; Hasegawa, H.; Izumitani, T.; Hyde, S. T. Macromolecules 1992, 25, 1433.
8. Shim, J. S.; Kennedy, J. P. J Polym Sci, Part A: Polym Chem 1998, 37, 815.
9. Uchida, S.; Ichimura, A.; Ishizu, K. Polymer 1999, 40, 1019.
10. Quirk, R. P.; Morton, M. in Thermoplastic Elastomers, 2nd ed.; Holden, G., Legge, N. R., Quirk, R. P., Schroeder, H. E., Eds.; Hanser Publishers: Munich, 1998; Chapter 4.
11. Turner, C. M.; Sheller, N. B.; Foster, M. D.; Lee, B.; Corona-Galvan, S.; Quirk, R. P.; Annis, B.; Lin, J.-S. Macromolecules 1998, 31, 4372.
12. Hadjichristidis, N.; Pispas, S.; Pitsikalis, M.; Iatrou, H.; Vlahos, C. in Advances in Polymer Science; Springer-Verlag: Berlin, 1999; Vol. 142.
13. Leibler, L. Macromolecules 1980, 13, 1602.
14. Hodrokoukes, P.; Floudas, G.; Pipas, S.; Hajdichristidis, N. Macromolecules 2001, 34, 650.
15. Yamakoma, I. Polymer 1998, 39, 1765.
16. Wiesner, U. Macromol Chem Phys 1997, 198, 4679.
17. Pople, J.; Hamley, I.; Fairclough, J.; Ryan, A. J.; Hill, G.; Price, C. Polymer 1999, 40, 5709.
18. Polis, D.; Smith, S. D.; Terril, N. D.; Ryan, A. J.; Morse, D. C.; Winey, J. K. I. Macromolecules 1999, 32, 4668.
19. Shibayama, M.; Hasegawa, H.; Hashimoto, T.; Kawai, H. Macromolecules 1982, 15, 274.
20. Adhikari, R.; Michler, G. H.; Huy, T. A.; Ivankova, E.; Godehardt, R.; Knoll, K. manuscript in preparation.
21. Ma, J.-J.; Nestegard, M. K.; Majumdar, B. D.; Sheridan, M. M. in ACS Symposium Series: Applications of Anionic Polymerization Research; 1998; Vol. 696, p 159.
22. Lee, C.; Gido, S. P.; Poulos, Y.; Hadjichristidis, N.; Tan, N. B.; Trevino, S. F.; Mays, J. W. Polymer 1998, 39, 4631.
23. The term energy sinks was used by Quirk and Morton in ref. 10 to explain the role of physically crosslinked PS domains in PS-polydiene-PS TPE; this might be used in our case too, because the presence of small PS domains inside the PB phase may act similar to a physical network.
24. Asai, S. Polym Prepr 1996, 37, 706.
25. Moctezuma, S. A.; Martinetz, E. N.; in ACS Symposium Series: Applications of Anionic Polymerisation Research; 1998; Vol. 696, p 129.
26. Sameth, J.; Spontak, R. J.; Smith, S. D.; Ashraf, A.; Mortensen, K. J Phys 1996, 3, 59.
27. Hashimoto, T.; Tsukuhara, Y.; Tachi, K.; Kawai, H. Macromolecules 1983, 16, 648.
28. Zielinski, J. M.; Spontak, R. J. Macromolecules 1992, 25, 5957.
29. Weidisch, R.; Stamm, M.; Schubert, D. W.; Arnold, M.; Budde, H.; Höring, S. Macromolecules 1999, 32, 3405.
30. Weidisch, R.; Ensslen, M.; Michler, G. H.; Fischer, H. Macromolecules 1999, 32, 5375.
31. Weidisch, R.; Michler, G. H.; Fischer, H.; Arnold, M.; Hofmann, S.; Stamm, M. Polymer 1999, 40, 1191.