

# Morphology and Micromechanical Deformation Behavior of Styrene–Butadiene Block Copolymers. IV. Structure–Property Correlation in Binary Block Copolymer Blends

R. Adhikari,<sup>1</sup> G. H. Michler,<sup>1</sup> S. Henning,<sup>1</sup> R. Godehardt,<sup>1</sup> T. A. Huy,<sup>1</sup> S. Goerlitz,<sup>1</sup> K. Knoll<sup>2</sup>

<sup>1</sup>*Institute of Materials Science, Martin-Luther Universität Halle-Wittenberg, D-06099 Halle/Saale, Germany*

<sup>2</sup>*BASF–Aktiengesellschaft, Polymer Research, GKT/I-B1, D-67056 Ludwigshafen, Germany*

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**ABSTRACT:** The structure–property correlation in blends consisting of styrene/butadiene block copolymers forming alternating polystyrene (PS) and polybutadiene (PB) lamellae, and PS domains in rubbery matrix was investigated by different microscopic techniques (transmission electron microscopy, scanning force microscopy, and scanning electron microscopy), uniaxial tensile testing, and dynamic mechanical analysis. Unlike the pure lamellar block copolymer, the blends showed predominantly disordered wormlike morphology formed by the intermolecular mixing. These structures allowed a precise control of stiffness/toughness ratio of the blends over a wide range. The blends showed a

gradual transition from predominantly viscoplastic to elastomeric behavior with increasing triblock copolymer content. The results demonstrated that the binary block copolymer blends provide the unique possibility of tailoring mechanical properties on the basis of nanostructured polymeric materials. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1219–1230, 2004

**Key words:** block copolymers; blends; morphology; micro-mechanical mechanism; mechanical properties; electron microscopy

## INTRODUCTION

An ideal polymer blend is one that combines the useful properties of constituent partners. One would be interested to produce the polymer mixtures or compounds or copolymers whose properties are even superior to those of either component. Interesting examples in this respect are the block copolymers based on polystyrene (PS) and poly(*n*-butyl methacrylate) (PnBA), in which the tensile strength was found to exceed that of both components in a certain composition window.<sup>1</sup>

For practical applications, polymer mixtures are preferred that allow a balance of important mechanical properties such as stiffness, strength, and ductility.<sup>2</sup> In practice, however, polymer pairs seldom show linear dependency of mechanical properties with composition. At a given composition, the properties of one of the components often dominate. For example, a sudden change in elongation at break was observed in the binary mixture of a star block copolymer and

polystyrene homopolymer (hPS) at 20 wt % hPS content.<sup>3</sup> Despite an option of price reduction, the decreased ductility (compared to that of the pure star block copolymer) was, indeed, a disadvantage of these blends.

Compared with an intensive investigation on the thermodynamics and phase behavior of block copolymers, only limited information is available on their blends. In an earlier study on binary blends of polystyrene-*block*-polybutadiene (SB) diblocks, Hoffman et al.<sup>4</sup> reported a microscopic demixing of blend partners, with two maxima in the domain size distribution. Jiang et al.,<sup>5</sup> Hadziioannou and Skoulios,<sup>6</sup> and Hashimoto et al.<sup>7–9</sup> investigated binary blends consisting of diblocks and triblocks. In these studies, the blends were microphase separated; and depending on the blend composition and molecular weight of the copolymers, morphology transitions were also observed.

Studies of Hadziioannou and Skoulios<sup>6</sup> and Hashimoto et al.<sup>7–9</sup> on a series of blends of lamellar diblocks and triblocks consisting of polystyrene (PS) and polyisoprene (PI) demonstrated that the phase behavior of the binary block copolymer mixtures is mainly governed by copolymer composition, blend composition, and molecular weight ratio of the copolymers (i.e.,  $M_1/M_2$ , where  $M_i$  stands for the molecular weight of the *i*th block copolymer).<sup>6,8,9</sup> If  $M_1/M_2 < 5$ , complete miscibility of the block copolymers was observed in

Correspondence to: R. Adhikari (rameshwar.adhikari@iw.uni-halle.de).

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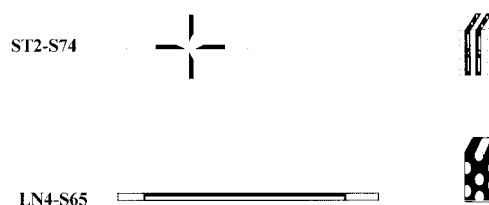
which the domain periodicity ( $L$ ) followed the power law:  $L \sim M_n^{2/3}$ , where  $M_n$  is the sum of mole fraction of each block copolymer multiplied by corresponding number-average molecular weight. When  $M_1/M_2 > 10$ , only a partial miscibility of two lamellar block copolymers resulted in macrophase separation of lamellae having two distinct periodicities.<sup>10</sup> A morphology entirely different from that of the parent block copolymers was reported in blends of styrene/butadiene star block copolymers with nearly identical chemical composition ( $\Phi_{PS} = 0.7$ ) by Jiang et al.<sup>5</sup> In particular, coexistence of cylindrical and wormlike structures was observed. The molecular weight of one of the star block copolymers was about 7 times higher than that of the other. The blends showed macrophase-separated composite structures containing microphase-separated domains inside. Learning from the earlier studies<sup>4,5,11,12</sup> and based on our own results,<sup>4,5,11–14</sup> we can conclude that the phase behavior of binary mixtures of two-component block copolymers seems to be strongly influenced by the chain architecture of the components as well.

Recent investigations of Spontak et al.<sup>15</sup> on the blends of symmetric ( $\Phi_{PS} = 0.5$ ) and asymmetric block copolymers ( $\Phi_{PS} = 0.85$ ) showed that the blends show the same microstructure as that of the pure diblock having equivalent overall composition.

It was shown that blending of a lamellar-forming diblock with  $\Phi_{PS} = 0.32$  and one with  $\Phi_{PS} = 0.60$  can induce the formation of bicontinuous cubic structure in certain ranges of composition. In contrast, blending of a diblock forming a lamellar phase with  $\Phi_{PS} = 0.44$  with a diblock forming a bicontinuous cubic structure with  $\Phi_{PS} = 0.66$  resulted in the formation of a lamellar phase even when the overall composition was  $\Phi_{PS} = 0.62$  (composition in which a bicontinuous structure is expected in a diblock).<sup>7</sup> It means that a single phase approximation cannot be used while considering the phase behavior of blends of block copolymers having different molecular weights; that is, the blend morphology does not necessarily reflect the morphology of a pure copolymer with an equivalent composition. Hasegawa and Hashimoto<sup>7</sup> showed that the interfacial curvature and packing density should be considered as important parameters while discussing the phase behavior of binary block copolymer blends.

A brief survey of the literature discussed above reveals that research interests are growing in the study of phase behavior of binary blends of block copolymers, although these materials have found no considerable industrial interest because of higher manufacturing costs of both the blend components. As a consequence, less (or almost no) attention has been paid to the deformation behavior and mechanical properties of these blends.

Binary block copolymer blends, both blend partners being microphase-separated, may offer the possibility



**Figure 1** Architecture and morphology (schematic) of the copolymers used to prepare binary blends. The black and white colors represent polybutadiene and polystyrene phases, respectively.

of tailoring mechanical properties by reorganizing the macromolecular segments. In particular, the blends showing a partial miscibility at the molecular level may open a new horizon of adjusting mechanical properties of the polymer blends. Hence, this study aims at the structure–property correlation in binary blends consisting of an asymmetric star block copolymer and a symmetric triblock copolymer, both based on styrene and butadiene.

## EXPERIMENTAL

### Materials

The samples used in this study were styrene/butadiene block copolymers of star and triblock architectures prepared by sequential anionic polymerization (see Fig. 1). The synthesis and characterization of these block copolymers have been described elsewhere by Knoll and Nießner.<sup>11,12</sup> The star-shaped and linear block copolymers were designated as ST2-S74 (styrene volume fraction 74%) and LN4-S65 (total styrene volume content 65%), respectively.

Detailed analyses have shown that the star molecules in ST2-S74 have approximately four asymmetric arms (on average) and one of them is much longer than the others.<sup>12</sup> Each arm has an SBS triblock structure, and the middle PB block has a tapered interface toward the inner polystyrene block that forms the molecule core. The longest PS block in the star molecule has a molecular weight in the range of 70,000–90,000 g/mol, and the ratio of molecular weight of the longest block to that of the shorter ones is more than 6.

The linear block copolymer LN4-S65 has symmetric outer polystyrene blocks held together by a random copolymer of polystyrene and polybutadiene (PS-*co*-PB). The total styrene volume fraction in this copolymer is 65%, whereas PS outer blocks amount to about 32%.<sup>12</sup>

### Sample preparation

The samples were cast from solution using a neutral solvent (toluene) and also prepared by injection mold-

ing. The solvent was allowed to evaporate in a period of about 2 weeks to allow the formation of well-ordered morphology. The films were dried at room temperature for a few days and annealed for 48 h at a temperature of 120°C (above the glass-transition temperature of polystyrene) in a vacuum oven.

After mixing the blend components in an extruder, tensile bars were prepared by injection molding according to ISO 527 (mass temperature 225°C; mold temperature 45°C). The blends consisted of 20, 40, 60, and 80% by weight of LN4-S65.

### Tensile testing

Tensile bars of total length 50 mm and width 4 mm were cut from about 0.5 mm thick solution-cast films. Both injection-molded and solution-cast samples were strained at a crosshead speed of 50 mm/min using a universal tensile machine at room temperature (23°C). At least 10 samples were tested to obtain a good set of statistics for the measured values.

### Electron microscopy

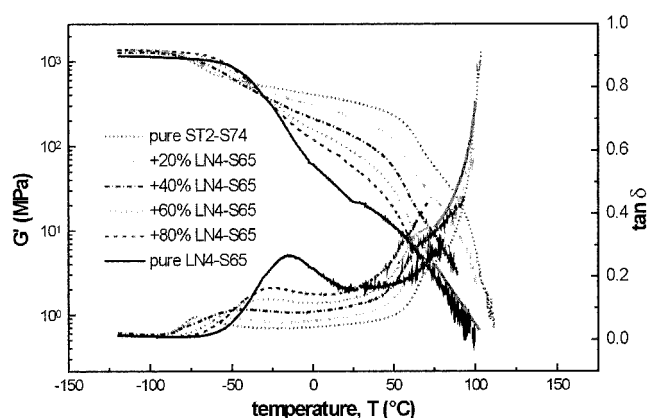
The morphology of the samples was investigated by a transmission electron microscope (200 kV TEM, JEM 2010, JEOL, Tokyo, Japan). Ultrathin sections of the samples ( $\sim 70$  nm) were microtomed from a bulk specimen that was immersed in an aqueous solution of osmium tetroxide for several days to selectively stain the butadiene phase. To investigate the strain-induced structural changes, the specimen was taken from the deformed tensile bars close to the fracture surface. Fracture surfaces of specimens broken in the tensile tests were analyzed by scanning electron microscope (JSM 6300, JEOL).

### Scanning force microscopy

For the investigation of the bulk morphology of the samples by scanning force microscopy (SFM), a pyramidal specimen cut from each solvent cast film was microtomed using a Leica ultramicrotome (Leica, Wetzlar, Germany) at cryo-temperature, and the microtomed face was investigated with an SFM (multi-mode atomic force microscope; Digital Instruments, Santa Barbara, CA). The SFM was operated in tapping mode using super sharp silicon cantilevers with a resonant frequency of about 300 kHz (spring constant  $\sim 15$  N/m; Nanosensors, Neuchatel, Switzerland). Height and phase data were simultaneously collected. The SFM images presented in this article are unfiltered phase images recorded under moderate tapping force.

### Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was carried out by the DMTA Mark 3E (Rheometric Scientific, Piscataway,



**Figure 2** DMA spectra of ST2-S74/LN4-S65 blends: note that the  $T_{g-PB}$  shows a gradual increase with increasing LN4 content (see also Table I), measured at a frequency of 1 Hz.

NJ) in torsion and temperature-sweep mode. The measurements were performed at a frequency of 1 Hz within a temperature range from  $-120$  to  $120$ °C and at a heating rate of  $1$ °C/min. The test specimens (dimensions  $30 \times 10 \times 2$  mm) were prepared from injection molds.

## RESULTS AND DISCUSSION

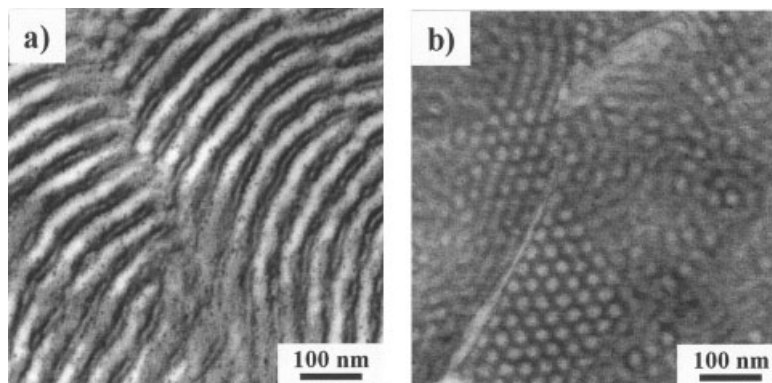
### Phase behavior and equilibrium morphologies

The styrene/butadiene block copolymers used in this study were ST2-S74 and LN4-S65 (Fig. 1): one having thermoplastic properties (ST2-S74) and another one having thermoplastic elastomeric properties (LN4-S65) (discussed later).

DMA spectra of the blends given in Figure 2 make it obvious that the glass-transition temperature of the butadiene phase ( $T_{g-PB}$ ) increases almost linearly with increasing LN4 content, which is an indication of incorporation of bulky styrene segments in the flexible butadiene phase.

The intensity of loss peaks ( $\tan \delta$ ) and the area under these peaks, as well as the inclination of plateau region in the  $G'$  versus  $T$  curves, have been discussed in the literature as indicators for phase miscibility.<sup>16,17</sup> With increasing LN4 content, the intensity of the loss peak for the soft phase and the area under these peaks enlarges, suggesting that the volume of materials taking part in the interaction at this region increased with LN4 content (i.e., intensification of mixed phase). A continuous inclination of the plateau region in  $G'$  versus  $T$  curves further implies the gradual increase in mixed phase, which is softer and leads to a decrease in storage modulus. It should be noted that the copolymer LN4 possesses a midblock (random PS-co-PB), which already contains a considerable amount of styrene segments bound to the rubbery phase. Hence, the addition of LN4 to ST2 has a consequence of contin-





**Figure 3** TEM micrographs showing the morphology of solution-cast block copolymer samples: (a) ST2-S74 and (b) LN4-S65. OsO<sub>4</sub> staining causes the butadiene phase to appear dark.

uously increasing the mixed-phase volume fraction in the blends.

Meanwhile, the glass-transition temperature of the styrene phase ( $T_{g-PS}$ ) remains almost unchanged, suggesting the presence of pure polystyrene phase. However, at higher LN4 content, it was difficult to detect a  $T_{g-PS}$ . By means of differential scanning calorimetry (DSC), the glass-transition temperature of the polystyrene phase in the pure block copolymer LN4 was found to be about 87°C, clearly below the glass-transition temperature of PS homopolymer. The lower  $T_{g-PS}$  observed was, of course, also a consequence of lower molecular weight of the polystyrene outer blocks (~ 18,000 g/mol) in sample LN4. However, a more significant contribution to the  $T_{g-PS}$  depression may be caused by the partial mixing of the polystyrene end blocks with the random styrene-*co*-butadiene (PS-*co*-PB)<sub>n</sub> middle block. This essentially suggests that a pure polystyrene phase is absent in sample LN4.

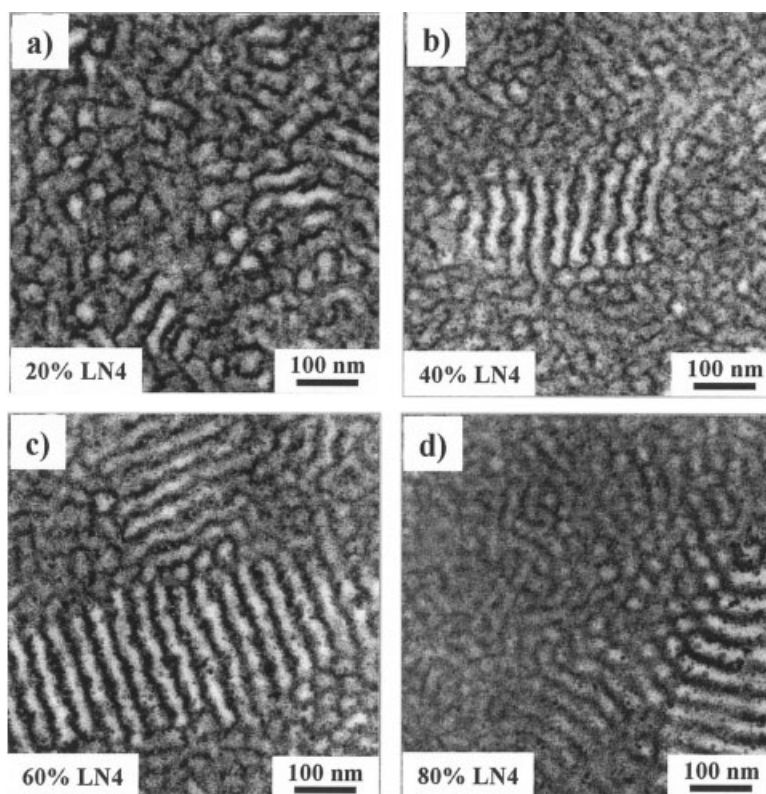
The detailed morphology of the star block copolymer and the triblock copolymer are discussed elsewhere.<sup>18,19</sup> The star block copolymer possesses a unique “two-component three-phase” morphology consisting of alternating layers of polystyrene and polybutadiene, the latter containing scattered polystyrene domains embedded in the polybutadiene phase [see Fig. 3(a)]. The lamellar morphology of the star block copolymer endows this polymer with a ductile thermoplastic property (discussed later). The triblock copolymer consists of polystyrene domains dispersed in the matrix of PS-*co*-PB random copolymer. It may be easily noticed in Figure 3(b) that the boundary between the polystyrene domains and the rubbery matrix is diffuse, indicating a phase mixing at the interface that would lead the system toward the weak segregation. The absence of pronounced long-range order is also an evidence of the weak segregation behavior of this block copolymer. Nevertheless, a hexagonal ordering of the PS domains may be observed at a few locations [as illustrated by Fig. 3(b)]. Because of

the existence of dispersed glassy domains in the rubbery matrix, this block copolymer possesses the properties typical of an SBS thermoplastic elastomer (discussed later).

Equilibrium morphology of binary ST2/LN4 blends is given in Figures 4 and 5. An addition of 20 wt % LN4 to the star block copolymer ST2 leads to a transition from an ordered lamellar structure to a worm-like morphology with highly reduced long-range order [compare Fig. 4 with Fig. 3(a)]. With the destruction of lamellar structure, the small PS domains initially embedded in PB lamellae of ST2 become less pronounced in the blends. With increasing LN4 content, the disordered domain structure persists, but the bright stripes of lamellae, with the spacing smaller than that of pure ST2, are always phase separated. The size of PS domains in the blends have nearly the same thickness distribution as that of the pure star block copolymer (~ 20 nm), which at higher LN4 content (80 wt %) drops to a level of pure LN4 (~ 15 nm).

In binary blends of monodisperse block copolymers with well-defined morphologies, the phase behavior may be predicted by the knowledge of the total phase volume ratio of the components. Because the phase volume ratio and morphologies of both the block copolymers ST2 and LN4 deviate substantially from the classical picture, it is impossible to assign the binary block copolymer blends a particular classical morphology. The blend morphologies are unconventional, and hence rather complex, and difficult to interpret. However, three points are quite obvious (see Fig. 4):

1. The addition of 20 wt % LN4 (a thermoplastic elastomeric component) to the star block copolymer ST2 turns the lamellar morphology of the latter to one consisting predominantly of hard domains (bright regions in Fig. 4) dispersed in the matrix of the soft (dark regions in Fig. 4) component.



**Figure 4** TEM images showing morphology of solution-cast ST2/LN4 blends: the blend composition is shown; OsO<sub>4</sub> staining causes the butadiene phase to appear dark.

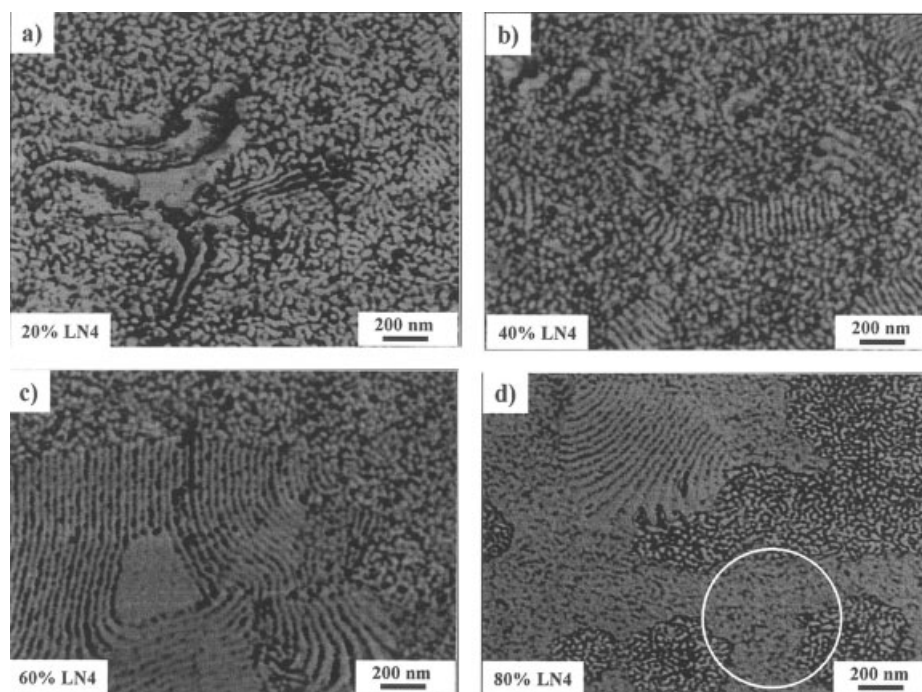
2. The blends show a considerable compatibility, which is supported by DMA results as well. The morphologies mentioned in the first point might have been caused by the intermolecular mixing of the different copolymer blocks. Thus the blends investigated represent a partially miscible system.
3. Lamellae-forming molecules seem to be segregated from the rest of the molecules in the blends. The star block copolymer was produced by coupling asymmetric SBS molecules.<sup>12</sup> Because the coupling is a random process it may result in the mixture of stars having different molecular weights. The star might also have a variable number of longer and shorter arms. The polystyrene blocks in the copolymer molecules are practically polydisperse. In other words, there are both styrene-rich and butadiene-rich stars. Stars having at least one longest PS outer block is styrene-rich and those having only short PS blocks are butadiene-rich. The larger styrene-rich molecules might phase separate and contribute mainly to form lamellar macrodomains<sup>14</sup> (see below). Note that the “two-component three-phase” morphology typical of ST2 is not found in these macrodomains.

In the TEM images of the blends (Fig. 4), two kinds of hard domains are apparent: (1) “white” domains

almost sharply separated from the “dark” rubbery phase and (2) “gray” domains having diffuse boundary with the rubbery phase. The “white” domains qualitatively resemble the PS lamellae of pure ST2, whereas the “gray” ones resemble the PS domains of LN4. The majority of the hard PS domains in pure LN4 are poorly segregated and not well ordered [see Fig. 3(b)]. Because the “dark” regions in the TEM image result from the preferential staining of the double bond containing the butadiene phase, the presence of an increasing volume of “gray” regions suggests the formation mixed phase in the blend.

To summarize the results from the TEM, the binary blends show both microphase- and macrophase-separated structures. The macrodomains have microphase-separated morphology that resembles the structure of neither of the blend partners. In fact, the evolution of microphase morphology in the blends appears to be provoked by the reorganization of copolymer molecules. Additional information concerning the partial miscibility of the block copolymers studied may be obtained by scanning force microscopic studies of the cryo-ultramicrotomed surfaces of the binary blends.

Because the phase signals in SFM are sensitive to a material's heterogeneity,<sup>20–23</sup> the contrast in the phase images can be used to extract more qualitative information on the phase behavior of the binary blends. In concurrence with the results from the TEM, the notion



**Figure 5** SFM phase images showing morphology of solution-cast ST2/LN4 blends (note the existence of three distinguishable “phases” at higher LN4 see text); at lower LN4 content these phases become indistinguishable; the blend composition is shown.

of the segregation of a fraction of star molecules to form the lamellar macrophase is further supported by SFM phase images presented in Figure 5, in which the regions of alternating layers are more pronounced [see, e.g., Fig. 5(d)]. Additionally, the morphology appear to be formed by three different areas (or microphases), especially at higher LN4 content: bright PS domains embedded in the dark rubbery matrix characteristic of LN4, alternating layer structures (lamellar macrophase), and close packed wormlike domains forming an apparently cocontinuous structure [indicated by a white circle in Fig. 5(d)]. The latter might have originated by union of butadiene-rich stars and LN4 molecules and may represent the mixed phase. Star molecules having a higher amount of styrene may phase-separate and contribute to form lamellar structures.

Because a fraction of stars is butadiene-rich and contains the PS arms having molecular weight in the same range as that of LN4 molecules, the former are compatible with the LN4 molecules and may form a common domain structure. This compatibilization is further favored by the presence of random copolymer middle block of rather high molecular weight in LN4. Nonetheless, molecules of the block copolymers ST2 and LN4 are partly phase-segregated, giving rise to domains of different sizes and forms.

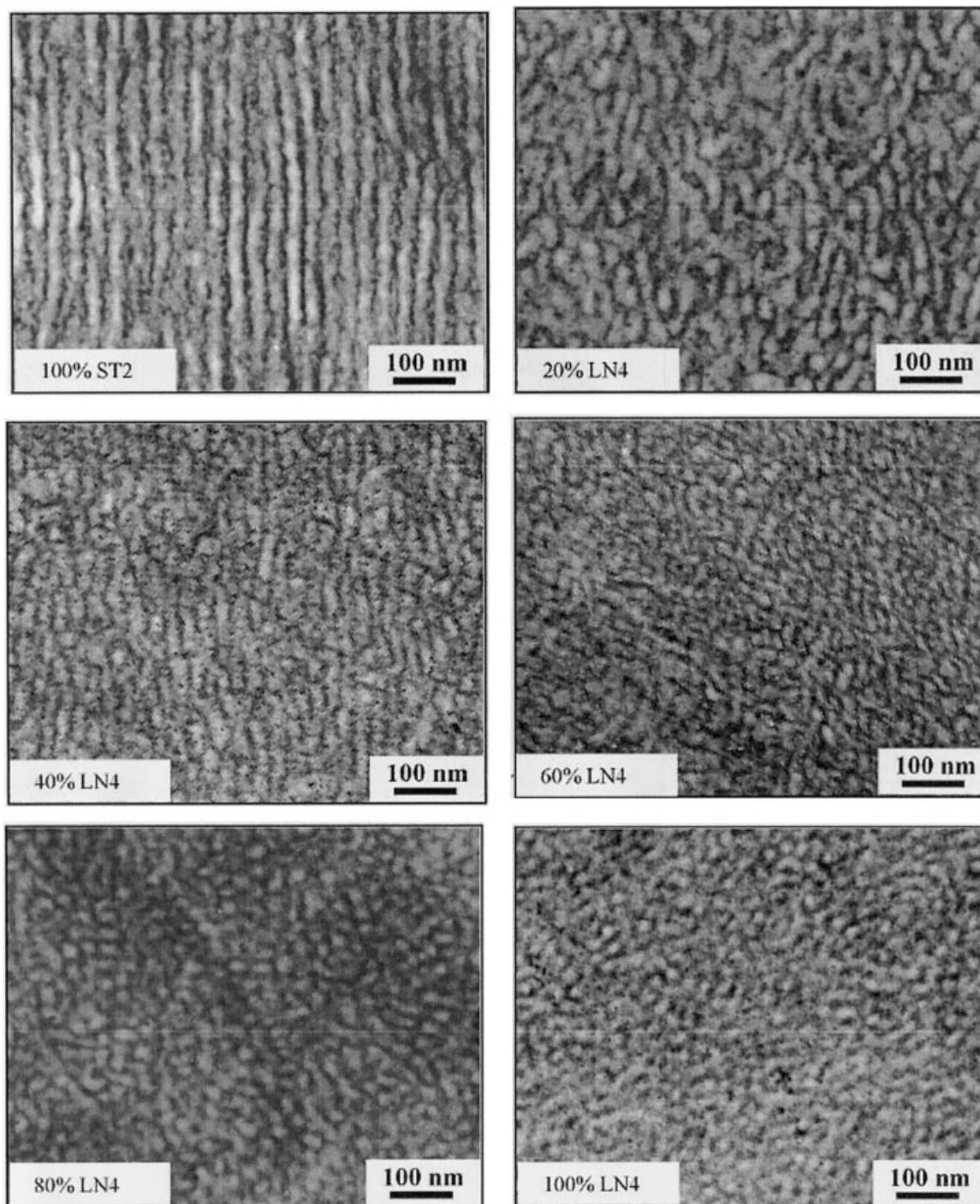
Macrophase separation of block copolymer molecules resulting in the coexistence of different microphase-separated structures was reported by several

authors in different systems.<sup>4,5,10</sup> Although Hashimoto et al.<sup>10</sup> found the coexistence of lamellae with different periodicity in a blend of copolymers having a large molecular weight difference, Jiang et al.<sup>5</sup> reported the strange structures evolving from the incompatibility between the copolymer molecules of different molecular weights. The formation of macrophase-separated domains in the binary blends investigated, in spite of nearly equivalent molecular weights, should be assigned to different molecular architecture of the block copolymers.<sup>14</sup>

### Morphology of injection-molded samples

The investigation of block copolymers at thermodynamic equilibrium is the foundation of physical characterization of these materials (e.g., through phase diagram). In the technical applications of block copolymers, however, this situation is never attained especially because of the technological constraints like limited processing time and associated economic concerns. Therefore, analysis of correlation between the nonequilibrium structures (i.e., the influence of processing conditions) and mechanical properties should find a more intensive consideration. Hence, the morphology of binary blends was analyzed using injection-molded blends (Fig. 6). Injection-molded blends were further used to correlate the mechanical behavior (e.g., tensile testing) with their micromechanical deformation behavior.

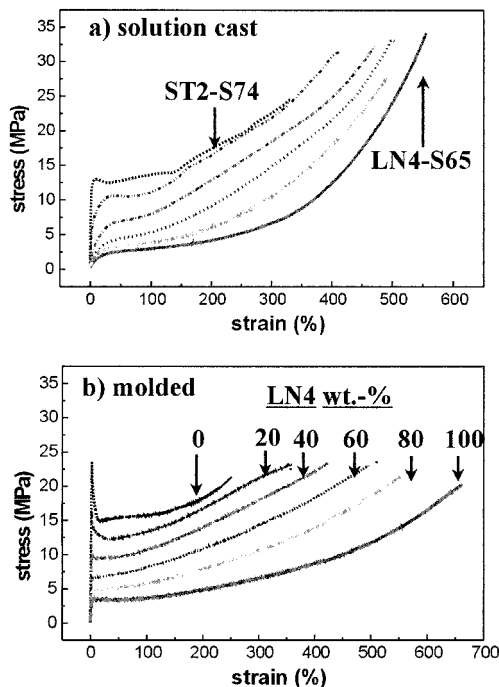




**Figure 6** TEM images showing morphology of injection-molded ST2/LN4 blends; injection direction vertical; the blend composition is shown;  $\text{OsO}_4$  staining causes the butadiene phase to appear dark.

It has been already discussed that the blends show partial miscibility at the molecular level. In injection-molded samples, macrophase separation of the component block copolymers is suppressed by the shear stress and rapid cooling of the melt. Hence, the melt does not have enough time to form well-separated nanostructures during this process. The phase-separated lamellar domains observed clearly in the solu-

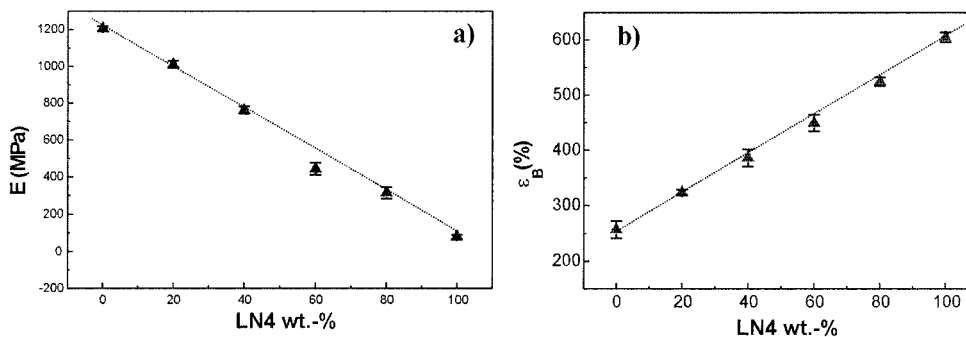
tion-cast samples are not distinct in Figure 6. Similar to the solution-cast films, a transition in morphological behavior (i.e., formation of disordered morphology) is observed at an LN4 content of 20 wt %. Basically, two types of morphologies are apparent: at lower LN4 content (0–20 wt %), lamellar morphology prevails, which qualitatively resembles the structure of pure ST2. At higher LN4 content (40–80 wt %), the struc-



**Figure 7** Stress-strain behavior of the binary ST2/LN4 blends at room temperature: (a) solution-cast samples and (b) injection-molded samples. Crosshead speed 50mm/min.

tures are qualitatively comparable to that of pure LN4. The structural reorganization (“disorder”) appearing with increasing LN4 content has been shown to have a strong influence on the achieved toughness level and underlying crack propagation mechanisms.<sup>13</sup>

In contrast to the conventional polymer blends, where an amorphous soft phase (e.g., rubber) is dispersed in the matrix of hard thermoplastic phase, no percolation of soft phase (i.e., no phase inversion) may be observed in the blends of ST2 and LN4. This results from the absence of macrophase separation of corresponding block copolymer microdomains, which is partly attributed to high shear stress of injection molding and partly to the partial miscibility of the similar block domains of the constituent copolymers.



**Figure 8** (a) Young's modulus and (b) elongation at break plotted as a function of blend composition in ST2/LN4 blends (injection-molded samples tested at a rate of 50 mm/min at room temperature).

### Tensile properties and micromechanical behavior

Stress-strain curves of binary block copolymer blends are given in Figure 7. The mechanical behavior shifts gradually from a thermoplastic to an elastomer with increasing LN4 content.

The gradual disappearance of an alternating layer structure (characteristic of the sample ST2) associated with the appearance of spherulike domains dispersed in rubbery matrix (characteristic of LN4) with increasing LN4 content is the reason for the observed continuous shift in mechanical behavior.

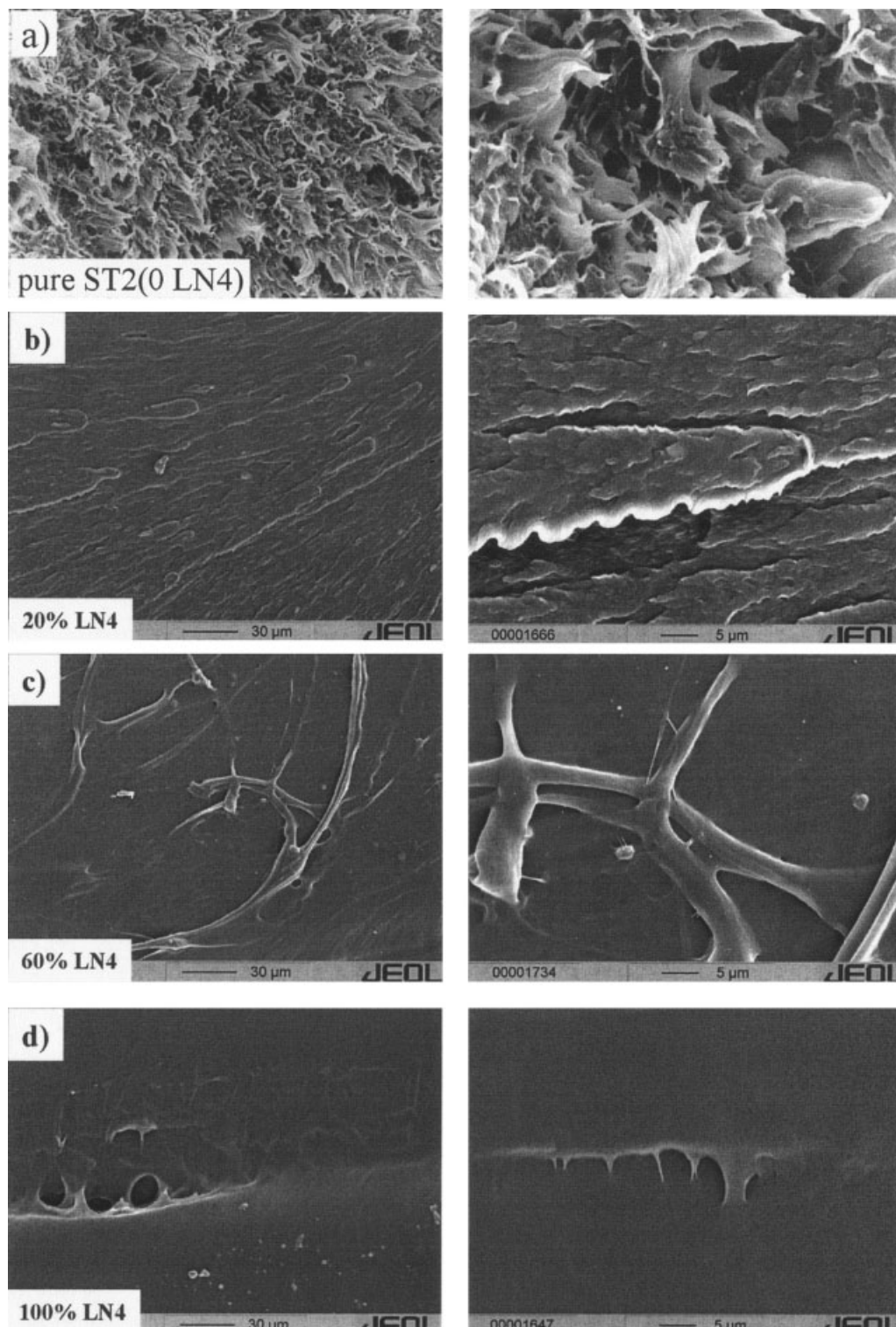
In solution-cast samples, where the domains are randomly oriented, the yield stress is lower than that of injection-molded blends [Fig. 7(a)]. The yield point, which does not appear pronouncedly in solution-cast ST2, becomes indistinct with increasing LN4 concentration. In contrast, the yield point in the injection-molded samples [Fig. 7(b)] is visible until an LN4 content of 60 wt %. Because the injection-molded samples were loaded parallel to the injection direction, the appearance of the more pronounced yield point in these samples is attributable to the orientation of microdomains by shear field.

A linear dependency of Young's modulus ( $E$ ) and elongation at break ( $\epsilon_B$ ) with composition, as demonstrated in Figure 8, manifests the possibility of fine-tuning stiffness and ductility of the investigated binary block copolymer blends over a wide range.

The values of  $\epsilon_B$  increase with LN4 concentration, whereas the stress at break remains more or less constant. The higher level of maximum stress achieved in solution-cast samples than that in injected-molded samples is attributable to better phase separation in the former. In solution-cast styrenic block copolymers, the morphologies are close to equilibrium and the chains are better phase-separated, thus ensuring the higher tensile strength.<sup>24</sup>

With increasing LN4 content, the amount of elastic deformation in the blends progressively increases, making it more difficult to analyze the strain-induced structural changes at a microscopic scale. Important

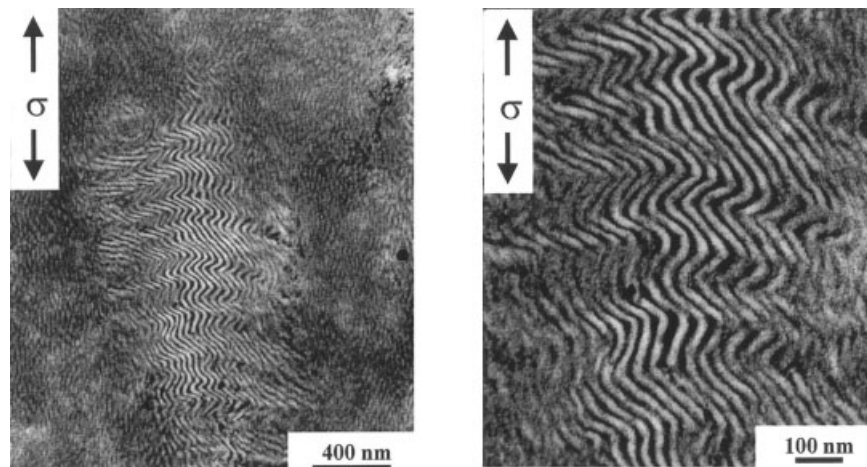




**Figure 9** Lower (left) and higher (right) magnification of SEM micrographs showing fracture surface morphology of injection-molded bars broken in the tensile tests: (a) pure star block copolymer ST2, (b) blend with 20 wt % LN4, (c) 60 wt % LN4, and (d) pure linear block copolymer LN4

inferences on micromechanical processes of deformation may be obtained by analyzing the fracture surfaces of the specimens broken in tensile tests. Representative fracture surface morphology of some binary blends is presented in Figure 9.

The fracture surface of pure star block copolymer shows the ductile deformation accompanied by a large plastic stretching and fibrillation [Fig. 9(a)]. In contrast, the LN4 reveals a flat, nearly structureless fracture surface [Fig. 9(d)]. An extremely flat fracture sur-



**Figure 10** TEM micrographs of different magnifications showing strain-induced structural changes in solution-cast ST2/60 wt % LN4 blend with a deformed lamellar region. The sample was taken from the specimen broken in a tensile test after relaxation; deformation direction is shown by arrows; OsO<sub>4</sub> staining causes the butadiene phase to appear dark.

face may also be formed by the deformation of a brittle material attributed to unconstrained propagation of rapidly advancing crack. In a thermoplastic elastomeric polymer such as LN4, the fracture occurs by a process called “tearing” and the material, strongly drawn during the tensile deformation, is pulled back to its original position. In fact, a perfectly flat surface should be formed in a perfect elastomeric polymer. The residual strain, a measure of deviation from elastomeric behavior, might indicate the presence of inhomogeneities, which show a considerable local (visco)plasticity. Consequently, the fracture surface morphology does not have a perfectly flat appearance. Hence, a smooth fracture surface of the polymer LN4 [Fig. 9(d)] correlates well with excellent reversibility of this thermoplastic elastomer.<sup>25</sup> Only a few areas composed of highly stretched fibrils, indicative of local plastic deformation, may be observed.

The fracture surface morphology changes rather unexpectedly at an LN4 content of 20 wt % [Fig. 9(b)]. The fracture surface shows the structures, which are more characteristic of LN4. The leaflike structures with wavy boarder are visible that are formed by the snap-back of highly stretched material fibrils and signify the viscoelastic deformation of this blend. In a previous study using the styrene/butadiene block copolymer blends, we showed that a transition from highly ordered lamellar morphology to one consisting of dispersed PS domains results in a change in crack propagation mechanism from microvoid coalescence to shear flow.<sup>13</sup> Furthermore, a transition in the micromechanical behavior associated with a change in phase morphology was revealed by microhardness measurements of the binary block copolymer blends.<sup>26</sup>

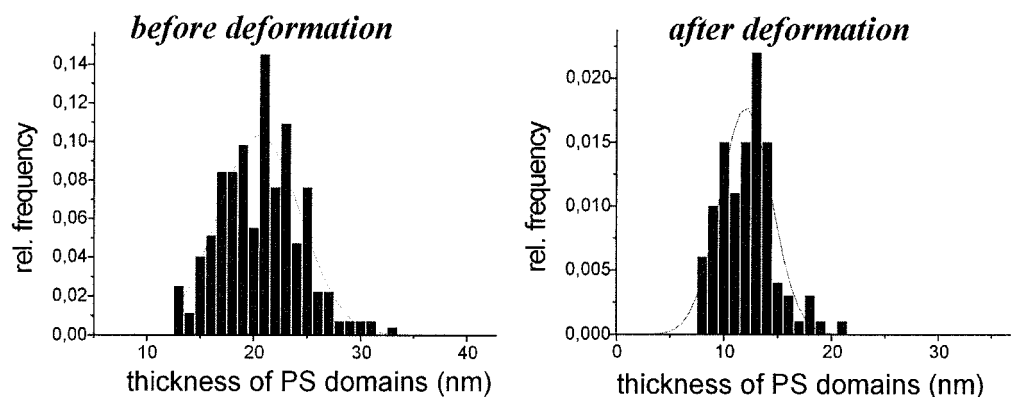
With increasing LN4 content, the fracture surface becomes increasingly smoother, suggesting the increasing tendency of elastomeric deformation. The

extent of plastic deformation decreases, and the fracture surface shows isolated regions of plastically drawn materials [e.g., note the highly drawn filaments in Fig. 9(c)]. At higher LN4 content (e.g.,  $\geq 60$  wt %), the fracture surface largely resembles that of pure LN4.

Micromechanical behavior of the pure block copolymers ST2 and LN4 was previously discussed in Michler et al.<sup>27</sup> and Huy et al.<sup>28</sup> It was mentioned that ST1 shows a large homogeneous plastic deformation of lamellae (thin layer yielding mechanism<sup>27</sup>), whereas LN4 exhibits principally an elastic behavior. The deformation mechanisms is coupled with the orientation of microstructures as well.

As discussed earlier, the morphology of the binary blends becomes more complex with increasing LN4 content, and the rubberlike deformation becomes increasingly dominating as the elastomeric phase practically forms the matrix. These factors introduce difficulty in the determination (especially in the quantification) of strain-induced microstructural changes in the samples. Therefore, deformation structures in a solution-cast blend containing 60 wt % LN4 (where the macrophase separation predominates) were investigated by TEM. The representative TEM micrographs are given in Figure 10.

At first glance, it may be noticed that lamellar grains are turned into chevronlike patterns (or “fishbone” structures) similar to those observed in oriented cylindrical and lamellar block copolymers subjected to tensile deformation perpendicular to the domain orientation direction.<sup>29,30</sup> Almost all the “bone axes” in these “fish bones,” however, are perpendicular to the strain direction in contrast to the deformation structures in lamellar block copolymer.<sup>29</sup> A low-magnification TEM image reveals that the deformed ellipsoidal wormlike PS domains in the rubbery “matrix” are aligned in the



**Figure 11** Distribution of polystyrene domains in a blend consisting of 40 wt % ST2 and 60 wt % LN4, before and after tensile deformation, measured in corresponding TEM micrographs.

strain direction. This is an indication of plastic deformation of the matrix domains. Furthermore, after deformation, the average thickness of PS lamellae was reduced from about 22 to about 15 nm in this sample, a clear indication of irrecoverable plastic deformation (i.e., drawing) of the glassy PS domains (see Fig. 11).

The plastic deformation of the PS domains (both having lamellae-like structure and dispersed domains) tells us further that the hard dispersed domains formed in the blends (other than the lamellae) before deformation were not the pure styrene domains of LN4 because alone, the PS end blocks in LN4 molecules are not capable of undergoing intensive plastic drawing (PS molecular weight of  $\sim 18,000$  g/mol is much smaller than  $2 \times M_e$ , where  $M_e$  is the molecular weight between the entanglements).

Because the “bone axes” (such axes are named as “kink boundaries” in the literature<sup>29</sup>) produced by deformation are almost always perpendicular to the strain axis, the dispersed lamellar grains must have been rotated toward the macroscopic deformation direction. Obviously, the “fishbone” structures were formed by the snap-back of the plastically deformed lamellae when the elastic energy absorbed by the matrix was released. Hence, the deformation of this sample is mainly controlled by the predominantly entropic-elastic stretching of the matrix.

## CONCLUSIONS

Morphology, mechanical properties, and deformation behavior of binary blends consisting of styrene/butadiene block copolymers possessing different microphase-separated morphologies were investigated by different microscopic techniques and tensile testing. The results may be summarized as follows:

1. In contrast to a well-ordered lamellae-like morphology of the pure star block copolymer, the

blends showed a predominantly disordered morphology. The mixtures represented a partially compatible system in which both microphase and macrophase separation of the blend components (which were themselves microphase separated) were observed. On the other hand, the macrophase separation was suppressed in the injection-molded samples.

2. The mixtures exhibited a gradual change from predominantly plastic deformation behavior to the predominantly rubberlike deformation behavior with the increasing linear block copolymer (thermoplastic elastomer) content. This gradual shift in mechanical behavior is characterized by a linear variation of Young's modulus, yield strength, and soft phase glass-transition temperature with composition. The studied binary blends allow a balance of stiffness/toughness ratio over a wide range. Hence, the binary block copolymer blends provide the unique possibility of tailoring mechanical properties on the basis of nanostructured polymeric materials.

The experimental results obtained so far are not sufficient to precisely understand the phase behavior of binary block copolymer blends in which at least one of the components has an asymmetric architecture. Thus future works should concentrate on the detailed analyses of the morphology formation and micromechanical deformation mechanisms of such blends, especially by considering the influence of molecular weight ratio of the similar blocks contained in the same molecule as well as in different molecules.

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