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Transition from Crazing to Shear Deformation in Star Block Copolymers

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ABSTRACT: Polystyrene-*b*-*n*-butyl methacrylate, PS-*b*-PBMA, star block copolymers having different strengths of segregation are investigated with respect to their deformation behavior. Disordered block copolymers are deformed by craze mechanism corresponding to the glassy homopolymer comprising the block copolymer. At the order−disorder transition (ODT), a transition from crazing to shear deformation is observed. Closer investigations reveal the shear yielding of lamellar grains with different orientations. This observation is clearly in contrast to deformation behavior of diblock copolymers that show a cavitation mechanism. Shear deformation in microphase-separated star block copolymers demonstrates the influence of molecular architecture on deformation behavior. Tensile properties of star block copolymers are compared with di- and triblock copolymers. It is found that star block architecture results in an increase of strain at break compared to di- and triblock copolymers. The yield stress is lower compared to triblock copolymers, indicating the influence of architecture and entanglements.

Indroduction

Much effort has been made to optimize polymer properties to design materials for a specific use. The enhancement of toughness in rubber-modified materials or polymer blends depends on their morphology. It is well-known that the impact properties of homopolymers can be improved by the incorporation of a dispersed elastomeric phase which is due to multiple crazing or multiple cavitation with shear yielding, macroscopically shown by the phenomenon of stress-whitening.[1,2] However, most polymer blends are incompatible and usually form macrophase-separated morphologies causing low interfacial strength and toughness. Special efforts have to be done to receive morphologies with small, uniformly distributed particles.

In contrast to polymer blends, block copolymers form various ordered morphologies, for example gyroid or perforated lamellae, via self-assembly on the size scale of typically 10−100 nm. Block copolymers show usually a macroscopic grain structure in the size scale of 1−10 μm.[3−6] Recently, Stadler et al.[7−9] have reported new morphologies in ABC triblock copolymers consisting of three different components (e.g., PS-*b*-PB-*b*-PMMA), which demonstrates the complexity of structural formation of block copolymers in comparison with other polymeric systems. Furthermore, morphology and phase behavior star block copolymers and multigraft copolymers have been intensively studied.[10−12] Thermoplastic elastomers (TPE's) are an example of nanometer structured polymeric materials where the mechanical properties can be tailored by optimizing processing conditions to achieve the desired morphology. To provide particular mechanical properties, the use of block copolymers opens a wide field of possibilities due to different microphase-separated morphologies available.

Many studies were attributed to the correlation between deformation behavior and morphology of PS-*b*-PB diblock copolymers.[13−16] Schwier et al.[13] have proposed a model for craze growth in PS-*b*-PB diblock copolymers based on void formation in the PB domains under the concentrated stresses of the craze tip. This is followed by drawing and fibril formation in the PS phase. It was shown that block copolymers do not show a crazing mechanism because the microphase-separated morphologies on the nanometer-scale are too small to initiate crazes.[15] Block copolymers deform by the two-step cavitation mechanism, much different from PS, where the craze growth occurs via crazing mechanism. In PS, a local stress field builds up followed by the formation of crazes consisting of thin craze fibrils. The undeformed PS material is transformed into craze fibril material (highly deformed PS) by a drawing mechanism. In contrast to crazing in PS, in block copolymers the first step of deformation is always[15] the deformation of the rubber phase up to a critical stress followed by the formation of voids. The second step is the deformation of the glassy matrix and growth of crazes typically called a cavitation mechanism. The growth of crazes occurs by different mechanisms in PS (crazing) and diblock copolymers (cavitation).

Polis and Winey observed kink band formation in poly(styrene-*b*-ethylene propylene) diblock copolymers by applying steady shear strain.[16] Recently, Thomas and co-workers[17−19] reported the deformation of gyroid phase in block copolymers and deformation behavior of hexagonal morphology in triblock copolymers via SAXS and TEM. In our previous study, deformation mechanisms in block copolymers were discussed depending on morphology and phase behavior.[20−22] Recently, we have proposed a unified correlation between phase behavior and deformation behavior of block copolymers. While deformation behavior of disordered block copolymers

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Table 1. Characterization Data of Used Di-, Tri-, and Star Block Copolymers Comprising of PS and PBMA[a]

sample	$M_{n,AB}$[a] [g/mol] (D)	% PS[b] {NMR}	$M_{n,block}$ [g/mol] (D)	% AB* {GPC}	no. of arms	χN
PS-*b*-PBMA		70	315 000			39
PBMA-*b*-PS-*b*-PBMA		52	201 100			21.4
PS−PBMA star block copolymers						
ST31	25 100 (1, 19)	54	116 500 (1, 12)	15	4.6	13.1
ST 32	36 600 (1, 17)	55	180 100 (1, 14)	15	4.9	19.8
ST 33	52 600 (1, 14)	53	262 000 (1, 15)	20	5.0	28.9
ST 34	68 600 (1, 16)	52	351 000 (1, 19)	23	5.1	40.8
ST 35	81 200 (1, 17)	52	456 000 (1, 16)	24	5.6	50.3

[a] Molecular weight (M_n), volume fraction (Φ_{PS}), arm molecular weight, AB fraction in the star block copolymers, number of arms, polydispersity (M_w/M_n), and χN values at 120 °C. Block copolymers used in this study. [b] Total molecular weights and polydispersity determined by size exclusion chromatography (SEC); values are based on the PS standards. [c] Volume fraction of PS determined by ^{1}H NMR.

corresponds to the glassy homopolymer comprising the block copolymer, in the ordered state the craze growth via cavitation and mechanisms of craze stopping and craze diversion have been found.[23] But this correlation does not reflect the influence of molecular architecture of block copolymers on deformation behavior. Recently, deformation behavior of block copolymer/homopolymer blends have been reported by Yamaoka,[24] and Drolet, Fredrickson,[25] and Ryu et al.[30] have reported about the influence of molecular architecture on deformation behavior of block copolymers. Drolet and Fredrickson[25] have calculated enhanced average chain bridging fractions of internal blocks for pentablock copolymers compared to triblock copolymers causing enhanced toughness as confirmed by Ryu et al.[30]

In the present study a transition from crazing to shear deformation will be reported initiated by a change from diblock to star block architecture using materials comprising of PS and PBMA.

Experimental Section

The synthesis of PS-*b*-PBMA diblock copolymers was previously described by Arnold et al. and star block copolymers by Arnold.[26] Measurements with size exclusion chromatography (SEC) were carried out using a Knauer-SEC with a RI/Visco-detector and a PS standard linear column. The volume fraction of the diblock copolymers was estimated by ^{1}H NMR. The molecular weights, compositions, and morphologies of diblock copolymers used in this study are summarized in Table 1.

The investigated block copolymers were dissolved in toluene, and the solvent was allowed to evaporate slowly over a period of 5−7 days at room temperature. Then the films were dried to constant weight in a vacuum oven at 120 °C for 3 days, thus allowing equilibrium structures to form. To investigate the micromechanical deformation behavior, sections with a thickness of about 0.5 μm were strained in a 1000 kV high-voltage electron microscope (HVEM, JEOL 1000) with an in-situ tensile device, which gives the possibility to study the craze growth and propagation. The advantage of HVEM investigations is the use of thicker sections for closer comparison to bulk materials. Furthermore, externally strained samples were investigated in the HVEM, which allowed us to examine possible decomposition of PBMA in the electron beam.

All investigations were performed at room temperature; however, a small increase of temperature during in-situ testing occurs arising from the electron beam. This effect can be partially avoided by using externally strained samples. The strain rate, as well as total strain, may be controlled qualitatively during in-situ testing. However, the externally strained samples provide more exact data concerning strain rate and total strain. Experiments were done in a light microscope. The strain rate of all investigated samples is about 0.1 mm/min, and this may vary for different regions of the sample. All externally strained samples were deformed up to a strain near the yield point of approximately 2%, while the onset of crazing has been noted at strains below the yield point. Afterward, the external strained samples were investigated in the HVEM. To obtain the craze growth more precisely, a small notch was introduced in all samples.

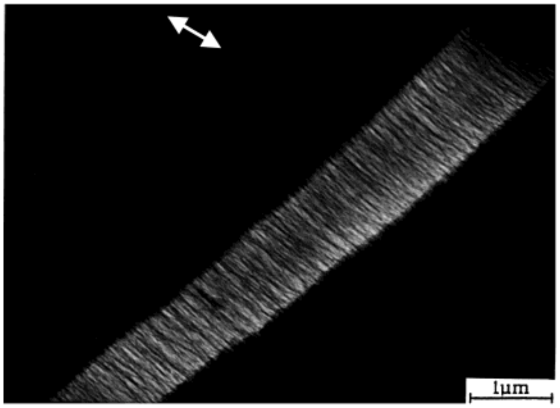

Figure 1. HVEM micrograph of craze structure in PS with M_n = 313 kg/mol.

Tensile tests were performed using an universal testing machine (Zwick 1425). For each sample at least 10 samples were measured in order to avoid preparation effects. The tensile specimens (dog bones) had a thickness of 0.5 mm and a total length of 50 mm. The toughness of the diblock copolymers can be estimated as absorbed energy from stress−strain curves.

Results and Discussion

To investigate the influence of molecular architecture on deformation behavior, block copolymers with different architectures comprising of polystyrene and poly(butyl methacrylate) were studied by in-situ HVEM. For the star block copolymers samples with different strengths of segregation, χN, are used. χN can be varied by changing temperature (this results in a change of χ) or molecular weight (expressed by polymerization degree N). To vary χN, we have used samples with different molecular weights. The small interaction parameter between PS and PBMA[37] allows to study disordered and weakly segregated star block copolymers (by using samples with different N) while arm molecular weight remains above the PS entangle-ment molecular

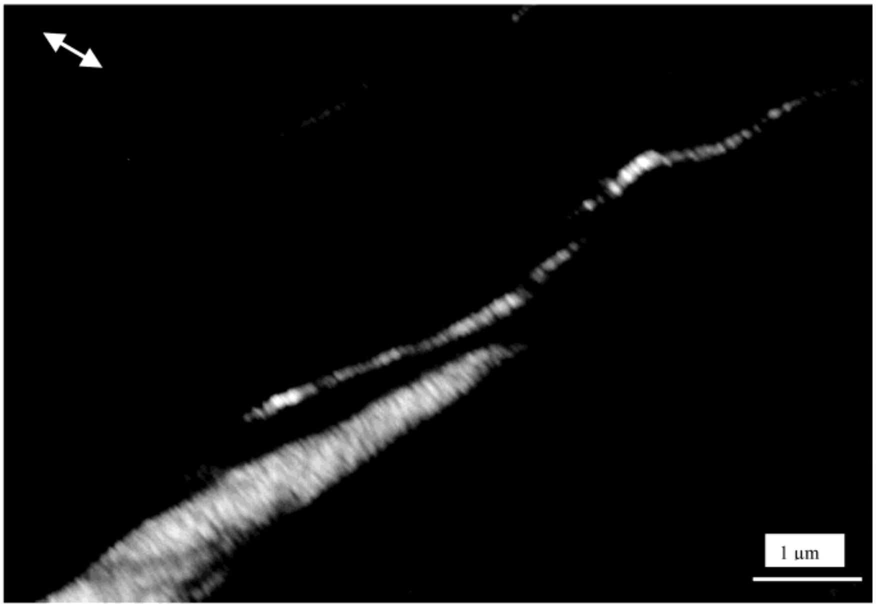

Figure 2. HVEM micrograph of craze structure of the disordered PS−PBMA star block copolymer ST32 at $\chi N = 19.8$ ($\Phi_{PS} = 0.55$, $M_n = 180.1$ kg/mol,) which is deformed via crazing. Strain direction is parallel to craze fibril direction (stained with RuO_4).

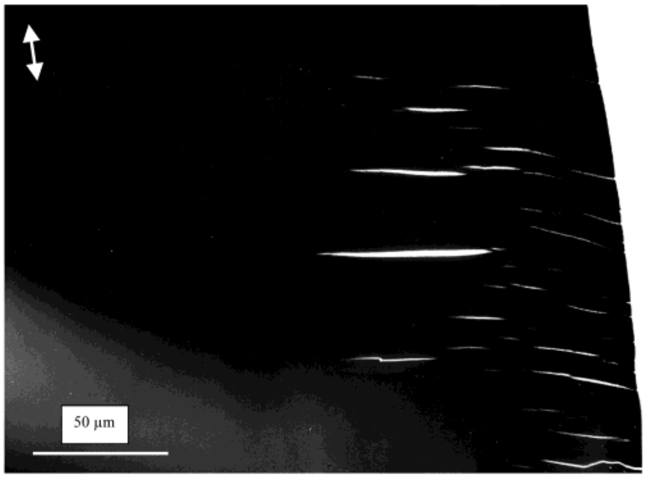

Figure 3. Lower magnification of craze structure of the disordered PS−PBMA star block copolymer ST32 at $\chi N = 19.8$ ($\Phi_{PS} = 0.55$, $M_n = 180.1$ kg/mol,) which is deformed via crazing. Strain direction is parallel to craze fibril direction (stained with OsO_4).

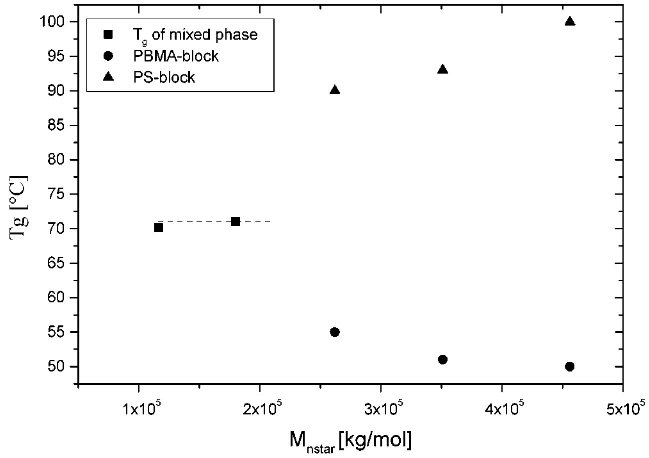

Figure 4. Dependence of glass transition temperature of star block copolymers ST31−ST35 on total molecular weight.

weight (arm molecular weight $M_n > 35\,000$ g/mol except sample ST31; see Table 1).

Crazes are narrow deformation zones formed under large external stresses usually observed in PS. A typical craze structure found in PS is shown in Figure 1. The material within the crazes is deformed into craze fibrils coexisting with voids through large stresses. The diameter of the craze and distances between the craze fibrils are 5−15 nm and 10−50 nm, respectively, close to that observed by other authors.[27] Figure 2 shows a typical deformation structure of the disordered star block copolymer ST32. The observed deformation structure is very similar to polystyrene (Figure 1), which indicates that disordered block copolymers deform by crazing. The low-magnification TEM image in Figure 3 shows local deformation zones propagating perpendicular to the external strain direction and can clearly be recognized as crazes. The pattern of deformation structure does not change during in-situ tests starting from the initial undeformed state which proves that the mixed phase in sample ST32 is not deformed by the two-step mechanism of cavitation but shows a crazing mechanism. The absence of a microphase-separated morphology avoids the deformation of the PBMA phase (soft phase) as a first step of the cavitation mechanism. Therefore, the mixed phase deforms by craze mechanism. This confirms our previous discussed results that disordered block copolymers are deformed by the mechanism of the corresponding homopolymer (PS) independent of their molecular architecture.[23] In contrast to sample ST32, sample ST31 appears to be very brittle due to low arm molecular weight (25.100 g/mol) below the entanglement molecular weight of PS. Thus, crazes have not been observed due to unstable crack propagation.

Figure 4 shows the dependence of glass transition temperature of the star block copolymers on arm molecular weight. Sample ST32 ($M_n = 180$ kg/mol) shows only one glass transition temperature, confirming its disordered state as confirmed by TEM. χN dictates the degree of segregation of A and B blocks, where N is the polymerization degree and χ the Flory−Huggins interaction parameter. For a symmetrical diblock copolymer, the order−disorder transition (ODT) is predicted by Leibler[28] using a mean field model by $(\chi N)_{ODT} = 10.5$. However, for star block copolymers the $(\chi N)_{ODT}$ shifts

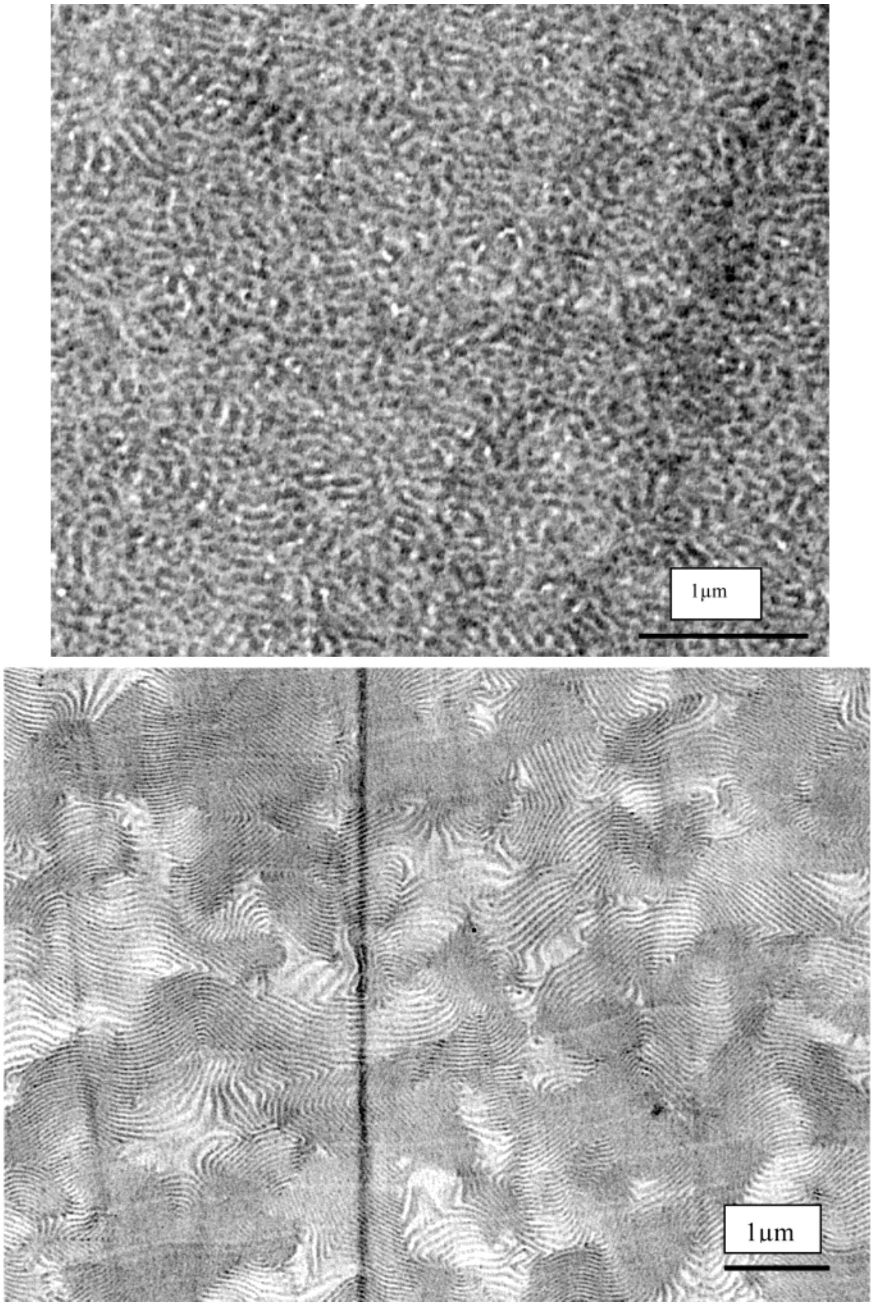

Figure 5. Morphology of weakly segregated PS−PBMA star block copolymers (a, top) ST33 ($\chi N = 28.9$) and (b, bottom) ST35 ($\chi N = 50.3$); stained with RuO_4.

toward higher values,[38] explaining the disordered state of sample ST32.

As the strength of segregation, χN, increases, the block copolymers undergo a order−disorder transition (ODT) and an ordered structure is formed. In contrast to strongly segregated block copolymers between 10.5 < χN < 12.5, the phases are weakly segregated, and the morphology is only less ordered with small grain sizes. Within the weak segregation limit (WSL) the microscopic density profile of the components is considered to vary sinusoidal in space, and the chains of the components interpenetrate to a high degree.

The morphology of sample ST33, shown in Figure 5a, is lamellae, and microphase separation is confirmed by the observation of two T_g's by DSC (Figure 4). Morphology is less ordered compared to strongly segregated block copolymers due the weakly segregated phases.

Investigation of deformation behavior of sample ST33 reveals the coexistence of crazes and shear zones. Shear deformation is not observed throughout the entire sample; thus, crazing is still the dominant deformation mechanism in this sample, and it appears to be brittle. With further increase of molecular weight, χN increases, and the sample becomes more incompatible. It is shown in Figure 5b that the lamellar morphology of sample ST35 has a higher long-range order and larger grain sizes than sample ST33 as a consequence of higher incompatibility.

From the previous proposed scheme,[23] a cavitation mechanism and mechanisms of craze stopping and diversion of crazes are expected for microphase-separated diblock copolymers. This is shown in Figure 6a for a PS-*b*-PBMA diblock copolymer to illustrate the large difference in deformation behavior between diblock and star block copolymers. Details of deformation behavior of microphase-separated diblock copolymers are discussed in previous studies.[21−23]

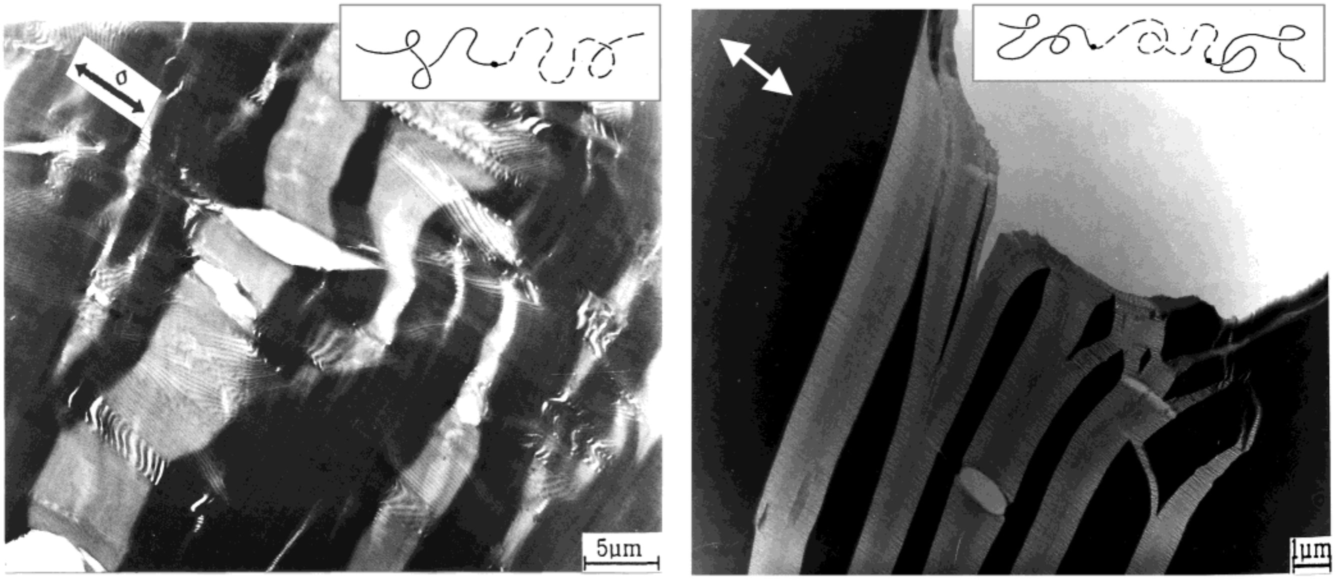

Figure 6. (a, left) HVEM micrograph of deformation zones of an intermediately segregated PS-*b*-PBMA diblock copolymer at $\chi N = 39$ already discussed in detail in our previous study[21] ($\Phi_{PS} = 0.70$, $M_n = 315$ kg/mol, lamellae). The craze propagation is influenced by morphology and does not occur perpendicular to the external stress direction in all cases and (b, right) HVEM micrograph of craze structure of a weakly segregated PBMA-*b*-PS-*b*-PBMA diblock copolymer at $\chi N = 21.4$ ($\Phi_{PS} = 0.52$, $M_n = 201$ kg/mol, lamellae) which deforms by cavitation (micrographs are reproduced from R. Weidisch et al.[23]).

Interestingly, samples ST34 and ST35 show a transition to shear deformation as shown in Figure 7a. In contrast to samples with smaller χN, shear deformation is the dominant deformation mechanism in the material. While di- and triblock copolymers deform by crazing (Figure 6a,b), with star block copolymers shear deformation is observed arising from the influence of molecular architecture on deformation behavior.

In contrast to diblock copolymers, showing a transition from crazing to cavitation at the order−disorder-transition, ODT, star block copolymers reveal a *transition from crazing to shear deformation,* suggesting that disordered star block copolymers are still deformed by crazing and ordered star block copolymers show the formation shear deformation zones.

Shear deformation is well-known from homopolymers and several rubber-modified polymers. For example, polycarbonate is deformed by shear yielding and was also observed in rubber-modified PC, rubber-modified PMMA, and modified epoxy.[29] Shear deformation zones usually propagate about 45° toward the direction of external stress. In rubber-modified polymers, multiple shearing is initiated in the matrix (for example, PC) due to the effective distance of rubber particles, causing an enhanced toughness of the material. In star block copolymers, a high volume fraction of the material is deformed and is turned into highly deformed material by shear yielding, causing a multiple shear deformation as shown in Figure 7a. Figure 7b shows a higher magnification of shear zones where grains with different orientations are deformed of about 45° toward the external stress field by shear yielding. Shear yielding of lamellar grains occurs more homogeneously, in contrast to the highly local nature of craze formation in di- and triblock copolymers. The shear zones comprise of lamellar grains deformed via shear yielding as shown in Figure 7b. To understand the importance of grain structure, shear deformation of lamellar morphology has to be investigated in detail.

While in homopolymer the network density and in polymer blends the effective distance of rubbery particles cause a shear yielding, in star block copolymers the molecular architecture and grain morphology are associated with a transition to shear deformation. Recently, Kramer and co-workers[30] have reported shear deformation in pentablock copolymers, in contrast to their tri- and diblock analogues. Drolet and Fredrickson[26] have calculated enhanced average bridging fractions of internal blocks for pentablock copolymers compared to triblock copolymers, initiating a transition to shear deformation. For star block copolymers, increased fraction of entanglements is present compared to the case of triblock copolymers, thus causing a transition to shear deformation. In addition, reduction of yield stress occurs due to low molecular weight of PS arms compared to that of triblock copolymers. Smith et al.[31−33] have shown that enhanced local mobility of polymer segments and reduced yield stress may result in strain hardening and can eliminate strain softening of the material, resulting in enhanced toughness. In star block copolymers, the reduced yield stress and enhanced mobility of polymer chains in thin PS lamellae (thickness about 10 nm) may result in a transition to shear deformation. Recently, we have observed homogeneous "thin layer yielding" in asymmetric PS−PB star block copolymers associated with strain hardening and increase in toughness.[34−35] By mixing PS to the star block copolymer, thickness of the PS lamellae is possible to vary between 10 and 30 nm. A transition from homogeneous deformation to crazing is observed at a PS content of 20%, corresponding to a thickness of PS lamellae of about 20 nm, indicating the existence of a critical lamellae thickness as already reported by van der Sanden et al.[36] They have recognized a brittle-to-tough transition in PS/PE blends at a critical PS layer thickness of about 50 nm. Concluding from these studies, two reasons could be discussed for the transition to shear deformation in star block copolymers:

1. Molecular architecture: This is associated with increased fraction of entangled PS chains (compared to di- and triblocks), enhanced stress distribution due to star block architecture, and reduced yield stress arising from the low molecular weight of glassy arms (compared

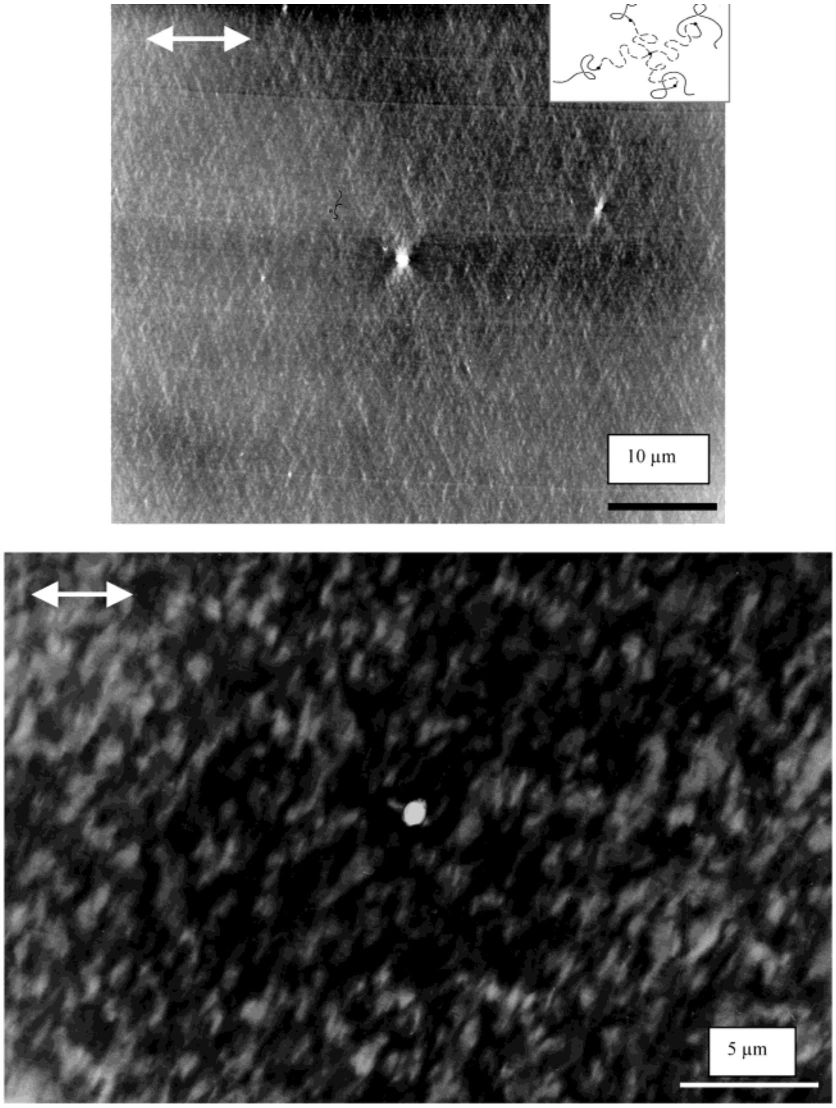

Figure 7. (a, top) HVEM micrograph of shear zones of the weakly segregated PS−PBMA star block copolymer ST35 at $\chi N = 50.3$ ($\Phi_{PS} = 0.52$, $M_n = 456$ kg/mol, lamellae) which deforms by shear deformation. Strain direction is about 45° to propagation direction of shear bands. (b, bottom) Higher magnification of shear zones of the weakly segregated PS−PBMA star block copolymer ST35 ($\Phi_{PS} = 0.52$, $M_n = 456$ kg/mol, lamellae) which deforms by shear deformation. Strain direction is about 45° to propagation direction of shear bands (stained with RuO_4).

to diblock copolymers with the same total molecular weight).

2. Thickness of glassy lamellae: It is much smaller compared to diblock copolymers with the same overall molecular weight. For PS−PBMA star block copolymers, the thickness of PS lamellae is about 10−15 nm, far below the critical thickness found in our recent studies[34,35] and by van der Sanden et al.[36]

It is well-known that a transition to multiple shear deformation can markedly increase the toughness of rubber-modified polymer blends, therefore also expected for block copoylmers. Figure 8 compares tensile properties of diblock, triblock, and star block copolymers comprising of PS and PBMA. While diblock copolymer shows a strain at break of about 40%, it decreases sharply to about 5% for the triblock copolymer.[22] The decrease in strain at break for the triblock copolymer have been attributed to the loss of long-range order of lamellar morphology due to higher miscibility, thus resulting in the absence of energy-absorbing mechanisms such as craze stopping and craze diversion as discussed in our previous paper.[23] The star block

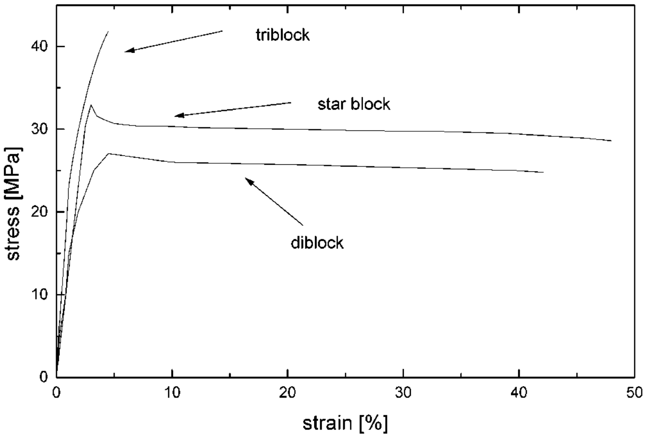

Figure 8. Tensile properties of block copolymers depending on molecular architecture: stress−strain diagrams of different a intermediately segregated PS−PBMA diblock copolymer, a weakly segregated triblock copolymer, and the weakly segregated star block copolymer ST35 (see Table 1) measured at strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4}\ s^{-1}$.

copolymer shows a strain at break of about 50%, the largest of the materials compared. The long-range order in the star block copolymer is about the same of the triblock copolymer due its high miscibility. Thus, tensile properties of the star block copolymer should rather be compared with the triblock copolymer than with the diblock copolymer. (Intermediately segregated diblock copolymers show a high long-range order and therefore show craze stopping and diversion of crazes, resulting in an enhanced absorbed energy.) The yield stress of the star block copolymer is much lower than that of the triblock copolymer, confirming that a large number of low molecular weight PS arms reduces the yield stress. Furthermore, a brittle to tough transition occurs due to the change of architecture from triblock to starblock. The star block architecture is initiating a transition to shear deformation explaining the strong increase in absorbed energy. Even if one compares the star block copolymer with the diblock copolymer, the star block still has a higher strain at break, demonstrating new ways of toughening of polymers by using star block copolymers.

Conclusions

The present study reports on the deformation behavior of PS−PBMA star block copolymers. Star block copolymers with different molecular weights are studied using samples with different χN (disordered state to weakly segregated limit). Disordered star block copolymers deform by crazing, confirming the previously suggested scheme of deformation behavior in block copolymers.[23] It confirms that disordered block copolymers are deformed by the same mechanism as the corresponding glassy homopolymer comprising the block copolymer independent of molecular architecture. At the ODT, a transition from crazing to cavitation is expected from previous results for diblock copolymers. However, a transition from crazing to shear deformation is found, reflecting the influence of molecular architecture on deformation behavior. Two reasons are found for this transition: First, the molecular architecture is associated with increased fraction entangled PS chains and reduced yield stress due to low molecular weight of glassy arms (compared to diblock copolymers). Second, the thickness of glassy lamellae is below the critical thickness found in our recent study[34,35] and by van der Sanden et al.[36] While the recently proposed scheme of deformation behavior has been focused on the influence of phase behavior on deformation in diblock copolymers, the present study reports on the influence of molecular architecture on deformation behavior. Furthermore, grain structure of morphology is found to be important for deformation behavior (shear yielding of lamellar grains).

The change of deformation mechanism from crazing to multiple shear deformation at the ODT provides reasons for the large increase in strain at break of the star block copolymer. A brittle to tough transition is initiated by the change in molecular architecture from triblock to star block, confirming recent results reported by Kramer and co-workers[30] on pentablock copolymers and by Drolet and Fredrickson[25] on enhanced bridging fractions of chains in pentablock copolymers. Our results ones again demonstrate the nonclassical property profile of block copolymers, using new ways for toughening of polymers.

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References and Notes

(1) Bucknall, C. B. *Toughned Plastics*; Appl. Sci. Publ. Ltd.: London, 1977.
(2) Michler, G. H. *Kunststoffmikromechanik*; Carl Hanser Verlag: München, 1992.
(3) Hashimoto, T.; Yamasaki, K.; Koizumi, S.; Hasegawa, H. *Macromolecules* **1994**, *26*, 1562.
(4) Thomas, E. L.; Alward, D. B.; Kinning, D. J.; Martin, D. C.; Handlin, D. L.; Fetters, L. J. *Macromolecules* **1987**, *20*, 1651.
(5) Winey, K. I.; Gobran, D. A.; Xu, Z.; Fetters, L. J.; Thomas, E. L. *Macromolecules* **1994**, *27*, 2392.
(6) Spontak, R. J.; Smith, S. D.; Ashraf, A. *Macromolecules* **1993**, *34*, 2233.
(7) Beckmann, J.; Auschra, C.; Stadler, R. *Macromol. Rapid Commun.* **1994**, *15*, 67.
(8) Krappe, U.; Stadler, R.; Voigt-Martin, I. *Macromolecules* **1995**, *28*, 4558.
(9) Stadler, R.; Auschra, C.; Beckmann, J.; Krappe, U.; Voigt-Martin, I.; Leibler, L. *Macromolecules* **1995**, *28*, 3080.
(10) Hadjichristidis, N.; Tselikas, Y.; Iatrou, H.; Efstratiadis, V.; Averopoulos, A. *J. Macromol. Sci., Pure Appl. Chem. A* **1996**, *33*, 1447.
(11) Gido, S. P.; Lee, C.; Pochan, D.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1996**, *29*, 7022.
(12) Pochan, D.; Gido, S. P.; Pispas, S.; Mays, J. W. *Macromolecules* **1996**, *29*, 5099.
(13) Schwier, C. E.; Argon, A. S.; Cohen, R. E. *Polymer* **1985**, *26*, 1985.
(14) Argon, A. S.; Cohen, R. E. In Kausch, H. H., Ed.; *Crazing in Polymers*; Springer Verlag: Berlin, 1983; Vol. 1.
(15) Argon, A. S.; Cohen, R. E. In Kausch, H. H., Ed.; *Crazing in Polymers*; Springer Verlag: Berlin, 1990; Vol. 2.
(16) Polis, D. L.; Winey, K. *Macromolecules* **1998**, *31*, 3617.
(17) Dair, B. J.; Thomas, E. L. *J. Mater. Sci.* **2000**, *35*, 5207.
(18) Honeker, C. C.; Thomas, E. L.; Albalak, R. J.; Hadjuk, D. A.; Gruner, S. M.; Capel, M. C. *Macromolecules* **2000**, *33*, 9395.
(19) Honeker, C. C.; Thomas, E. L.; Albalak, R. J.; Hadjuk, D. A.; Gruner, S. M.; Capel, M. C. *Macromolecules* **2000**, *33*, 9407.
(20) Weidisch, R.; Ensslen, M.; Michler, G. H.; Fischer, H. *Macromolecules* **1999**, *32*, 5375.
(21) Weidisch, R.; Schreyeck, G.; Ensslen, M.; Michler, G. H.; Stamm, M.; Schubert, D. W.; Arnold, M.; Budde, H.; Höring, S.; Jerome, R. *Macromolecules* **2000**, *33*, 5495.
(22) Weidisch, R.; Michler, G. H.; Arnold, M.; Fischer, H. *J. Mater. Sci.* **2000**, *35* 1257.
(23) Weidisch, R.; Esslen, M.; Michler, G. H.; Arnold, M.; Budde, H.; Höring, S. *Macromolecules* **2001**, *34*, 2528.
(24) Yamaoka, I. *Polymer* **1998**, *39*, 1765.
(25) Drolet, F.; Fredrickson, G. H. *Macromolecules* **2001**, *34*, 5317.
(26) Arnold, M.; Hofmann, S.; Weidisch, R.; Michler, G. H.; Neubauer, A.; Poser, S. *Macromol. Chem. Phys.* **1998**, *199*, 31.
(27) Donald, A. M.; Chan, T.; Kramer, E. J. *J. Mater. Sci.* **1981**, *16*, 669.
(28) Leibler, L. *Macromolecules* **1980**, *13*, 1302.
(29) Haward, R. N. *The Physics of Glassy Polymers*; Applied Publishers Ltd.: London, 1997.
(30) Ryu, C. Y.; Ruokolainen, J.; Fredrickson, G. L.; Kramer, E. J.; Hahn, S. F. *Macromolecules* **2002**, *35*, 2157.
(31) Smith, R. J. M.; Brekelmans, W. A. M.; Meijer, H. E. H. *J. Mater. Sci.* **2000**, *35* 2869.
(32) Smith, R. J. M.; Brekelmans, W. A. M.; Meijer, H. E. H. *J. Mater. Sci.* **2000**, *35* 2855.
(33) Smith, R. J. M.; Brekelmans, W. A. M.; Meijer, H. E. H. *J. Mater. Sci.* **2000**, *35* 288.
(34) Adhikari, R.; Lebek, W.; Goerlitz, S.; Michler, G. H.; Weidisch, R.; Knoll, K. *J. Appl. Polym. Sci.*, in press.
(35) Adhikari, R.; Goerlitz, S.; Weidisch, R.; Michler, G. H.; Knoll, K. *J. Appl. Polym. Sci.*, in press.
(36) van der Sanden, M. C. M.; Meijer, H. E. H.; Lemstra, P. J. *Polymer* **1993**, *34*, 2148.
(37) Weidisch, R.; Stamm, M.; Schubert, D. W.; Arnold, M.; Budde, H.; Höring, S. *Macromolecules* **1999**, *32*, 3405.
(38) Floudas, G.; Hadjichristidis, N.; Iatrou, H.; Pakula, T.; Fischer, E. W. *Macromolecules* **1994**, *27*, 7737.

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