A Novel Scheme for Prediction of Deformation Mechanisms of Block Copolymers Based on Phase Behavior

R. Weidisch,*,† M. Ensslen,‡ G. H. Michler,‡ M. Arnold,§ H. Budde,§ S. Höring,§ and H. Fischer⊥

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003; Martin-Luther-Universität Halle-Wittenberg, Institut für Werkstoffwissenschaft, 06099 Halle, Germany; Martin-Luther-Universität Halle-Wittenberg, Institut für Technische und Makromolekulare Chemie, 06099 Halle/Saale, Germany; and TNO Institute of Applied Physics, P.O.Box 595, Eindhoven, The Netherlands

Received July 20, 2000; Revised Manuscript Received December 19, 2000

ABSTRACT: Block copolymers having different strengths of segregation are investigated with respect to their deformation behavior. Disordered block copolymers are deformed by the mechanism which corresponds to a glassy homopolymer. A crazing mechanism is observed for block copolymers with polystyrene as matrix. At the order−disorder transition (ODT), a change from crazing to cavitation mechanism is observed, confirming the change of deformation mechanism at the ODT. For intermediately and strongly segregated block copolymers, observed mechanisms of termination and diversion of crazes are caused by both the increased long-range order and larger grain size with increasing incompatibility. A novel scheme is proposed which summarizes the deformation behavior of block copolymers depending on strength of segregation, χN. It is now possible to predict the deformation mechanism of a diblock copolymer system only from strength of segregation. Since the mechanical properties are also influenced by strength of segregation, it is possible to create materials with tailored properties utilizing temperature or pressure. The property profiles of different block copolymer systems are summarized to demonstrate the exceptional combination of high strength and toughness of intermediately segregated block copolymers. The presented scheme only represents a qualitative picture of deformation behavior of block copolymers and is only a first step to a future predictive modeling.

Introduction

Block copolymers are a new class of self-assembled nanostructured materials, where the structure and size of their morphology can be controlled via molecular architecture. Self-assembled materials provide a versatile means to create desired nanostructures in bulk materials or at interfaces, which have potential applications in biomaterials, optics, and microelectronics.[1,2] Mechanical properties, which are of large importance for technical applications, are also relevant for other material properties (e.g., optical, electrical, thermical). Furthermore, physical properties of block copolymers can be systematically controlled by choosing compositions, relative lengths of the blocks, and architecture.[3−5] Block copolymers form various ordered morphologies via self-assembly on the size scale of 10−100 nm and usually display a macroscopic grain structure in the size scale of 1−10 μm. In diblock copolymers different morphologies have been reported including perforated lamellae and gyroid structure.[6−8] Recently, Stadler et al.[9−11] 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.

Thermoplastic elastomers (TPE's) such as poly(styrene-*b*-butadiene-*b*-styrene) represent an important class of materials class based on block copolymers. These materials are widely used for different technical applications and combine the mechanical performance of vulcanized rubbers with the straightforward processing of thermoplastics due to the physical network of flexible chains.[12] Many efforts have been done to optimize polymer properties for a specific use through material design. 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.[15] 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.[16] The deformation in block copolymers occurs via a two-step cavitation mechanism.

Despite many studies on block copolymers, there are no models available to predict the deformation behavior of block copolymers on the basis of phase behavior. Since it is well-known that phase behavior of block copolymers has an influence on morphology, a pronounced influence on deformation behavior and mechanical properties can also be expected. For weakly segregated block copolymers a significant improvement of tensile strength and Young's modulus was observed, mainly due to the broadened interfacial width between the blocks.[17] Furthermore, the deformation behavior of weakly segre-

---

† University of Massachusetts.

‡ Institut für Werkstoffwissenschaft.

§ Institut für Technische und Makromolekulare Chemie.

⊥ TNO Institute of Applied Physics.

* Corresponding author. Present address: Martin-Luther-Universität Halle-Wittenberg, Institut für Werkstoffwissenschaft, 06099 Halle, Germany. E-mail: roland_weidisch@yahoo.com.

10.1021/ma001272p CCC: $20.00

gated diblock copolymers was reported depending on morphology and phase behavior.[23] In these studies, however, only PS-*b*-PBMA diblock copolymers were investigated. To establish a unified correlation between deformation mechanisms and phase behavior of block copolymers, different block copolymers are investigated. Hence, we present a novel scheme for the prediction of deformation behavior of block copolymers based on phase behavior.

First, the deformation mechanism of different block copolymer systems depending on strength of segregation, χN, will be discussed. In addition, a scheme of deformation mechanisms of block copolymers based on phase behavior will be proposed. Second, the correlation between phase behavior and mechanical properties of block copolymers will be discussed.

Experimental Section

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 on the order of 0.5 μm were strained in a 1000 kV high-voltage electron microscope (HVEM, JEOL 1000) with 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 a 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. The 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 more precise craze growth, a small notch was introduced in all samples.

Tensile tests were performed using a 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 was estimated as absorbed energy from stress−strain curves.

The craze initiation stresses, σ_c (Figure 7), are obtained from stress−strain curves where the curves deviate from their linear slope. It is possible to obtain the craze initiation stress from the dependence of craze density on elongation.[24] The value of σ_c is obtained from the extrapolation of this curve to zero craze density. However, some problems arise from the exact determination of elongation during the in-situ experiments in HVEM. Furthermore, exact values of the onset of the crazing process depends on the local value of elongation in the sample which could also lead to errors. Therefore, we compared σ_c determined from stress−strain curves as well as from craze densities at different strains. In both cases the onset of crazing correlates with the onset of plastic deformation in the stress−strain diagram. Therefore, we used this criterion in addition for all samples in Figure 7. The dependence of σ_c on composition reflects the correlation between deformation microstructure and tensile properties.

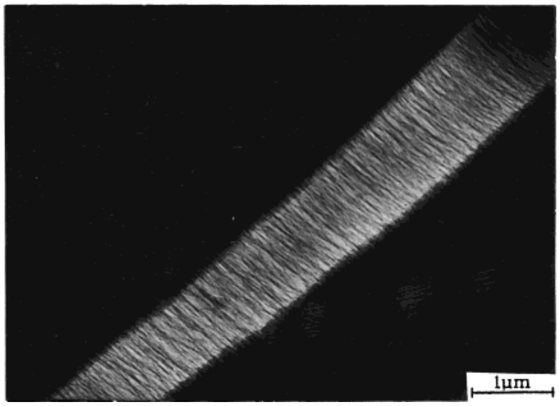

Figure 1. HVEM micrograph of craze structure in PS with $M_n = 313$ kg/mol.

Results and Discussion

A Scheme for Prediction of Deformation Mechanisms of Block Copolymers Depending on Strength of Segregation. The scheme proposed in this paper represents the deformation behavior of disordered, weakly, intermediately, and strongly segregated diblock copolymers. The order−disorder transition (ODT) of block copolymers has been intensively studied by many authors.[18] 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[19] using a mean-field model by $(\chi N)_{ODT} = 10.5$. At the ODT a lamellar morphology is formed in the case of symmetrical composition. 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. Between the WSL and strong segregation limit (SSL), an intermediate segregation regime (ISR) at $12.5 < \chi N < 95$ has been identified where the chains are more stretched than in the strong segregated regime due to coarsening of the density profile as χN is increased from the WSL.[20] The interface is then broadened, and the junction points are not completely localized in the interfacial region. In the strong segregation limit (SSL) at $\chi N > 100$, the interface is sharp and the phases are completely separated. The interfacial width of strongly segregated block copolymers is about 1−2 nm.[21]

To establish a unified correlation between phase behavior and deformation mechanisms of block copolymers, samples with different strength of segregation are used. χN can be varied by changing temperature (this results in a change of χ due to temperature) or molecular weight (expressed by polymerization degree N). We used both ways to confirm the discussed correlation. To demonstrate the validity of our scheme, different block copolymer systems were used.

Crazes are narrow deformation zones formed under large external stresses which are 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 fibrils is 5−15 nm, and the distance between the fibrils is 10−50 nm. These values are close to that observed by other authors.[22] A typical deformation structure of a disordered block copolymer is shown in Figure 2. The observed deformation structure is very similar to that of polystyrene

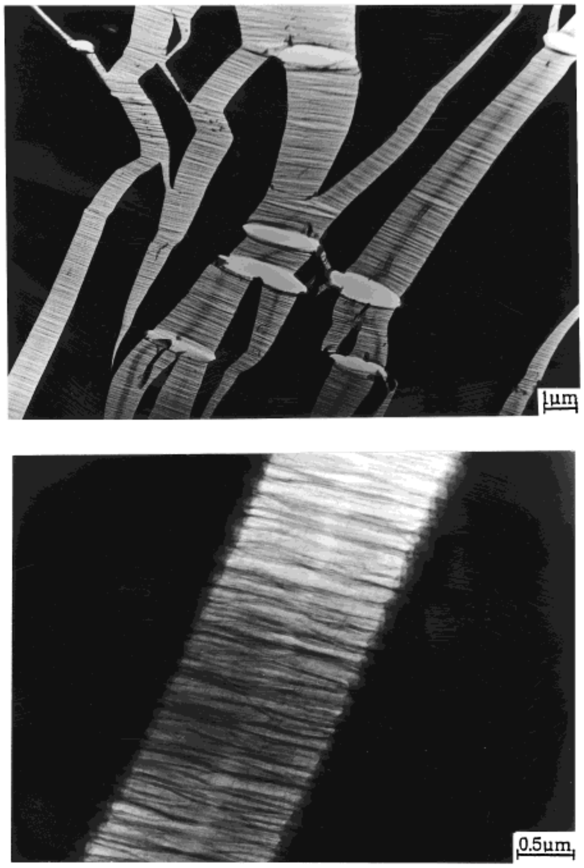

Figure 2. HVEM micrograph of craze structure (lower and higher magnification) of a disordered PBMA-*b*-PS-*b*-PBMA triblock copolymer at $\chi N = 9.80$ ($\Phi_{PS} = 0.48$, $M_n = 93.3$ kg/mol), which is deformed via crazing. Strain direction is parallel to craze fibril direction.

(Figure 1), which indicates that deformation in disordered block copolymers occurs via crazing. The poly(butyl methacrylate-*b*-styrene-*b*-butyl methacrylate) triblock copolymer, PBMA-*b*-PS-*b*-PBMA, shown in Figure 2 exhibits a strength of segregation $\chi N = 9.80$. This confirms that this sample is disordered according to theory of Leibler.[19]

As the strength of segregation, χN, increases, block copolymers undergo a order−disorder transition (ODT) and an ordered structure is formed. Between $10.5 < \chi N < 12.5$ the phases are weakly segregated, and the morphology is only less ordered with small grain sizes compared to strongly segregated block copolymers. Figure 3 shows a deformation structure in a weakly segregated PBMA-*b*-PS-*b*-PBMA triblock copolymer with lamellar morphology (52% PS). The deformation structure is different from that shown in Figures 1 and 2. In contrast, the light PBMA phase in Figure 3 is locally highly deformed under elevated stresses. The PBMA lamellae are deformed up to a critical cavitation stress, and then the PBMA forms voids. This is followed by a large plastic deformation of PS lamellae finally resulting in the craze structure shown in Figure 3. The observed deformation mechanism is the two-step cavitation mechanism as already observed by Schwier et al.[14] in PS-*b*-PB diblock copolymers.

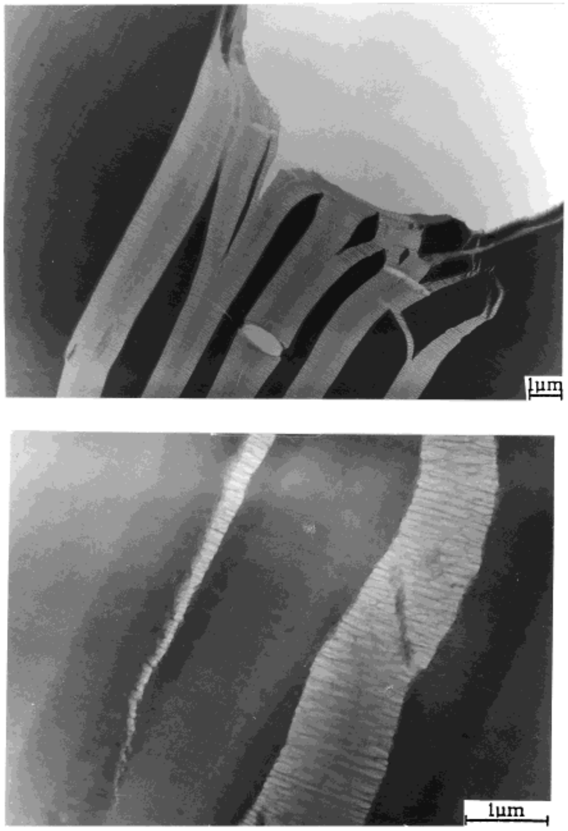

Figure 3. HVEM micrograph of craze structure (lower and higher magnification) of a weakly segregated PBMA-*b*-PS-*b*-PBMA diblock copolymer at $\chi N = 21.50$. ($\Phi_{PS} = 0.52$, $M_n = 201$ kg/mol, lamellae) which is deformed via cavitation. Strain direction is parallel to craze fibril direction.

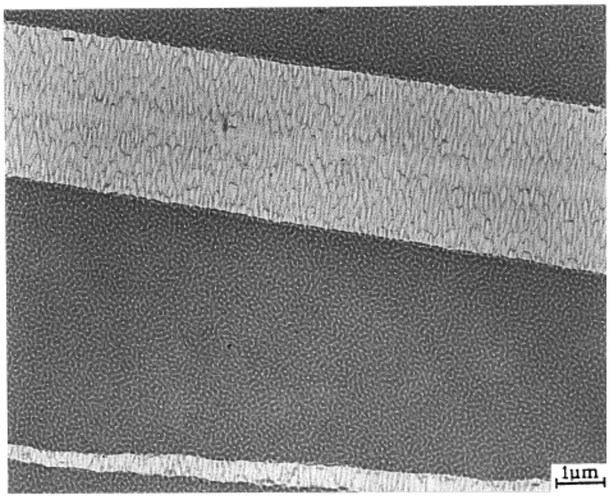

Figure 4. TEM micrograph of the initial state of cavitation mechanism in a lamellar PS-*b*-PBMA diblock copolymer observed in a thin film ($\Phi_{PS} = 0.67$, $M_n = 450$ kg/mol).

To confirm that craze growth in ordered diblock copolymers occurs via cavitation, the initial state of cavitation in a thin PS-*b*-PBMA film is shown in Figure 4. The sample in Figure 4 clearly shows a nonequilibrium morphology which differs from that of the bulk equilibrium morphology due to the 50 nm thickness of the film used. However, a comparable small long-range order is also observed in weakly segregated block copolymers. In contrast to the crazing mechanism in PS, in block copolymers the first step of deformation is always[14] the void formation of the rubbery or soft phase. The second step is the deformation of the glassy matrix under elevated stress concentration and growth of crazes which is typically called a cavitation mechanism. The growth of crazes occurs by different mechanisms in PS (crazing) and diblock copolymers (cavitation). In

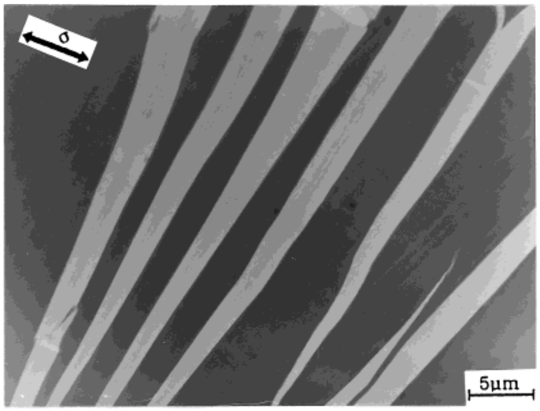

Figure 5. Craze propagation in a weakly segregated PBMA-*b*-PS-*b*-PBMA triblock copolymer (same sample as in Figure 3). The crazes mainly propagate perpendicular to the direction external stress.

Figure 6. 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[23] ($\Phi_{PS} = 0.70$, $M_n = 315$ kg/mol, lamellae). The craze propagation is influenced by morphology and does not occur perpendicular to the external stress direction in all cases.

PS, a local stress field builds up which is followed by the formation of crazes consisting of thin craze fibrils. The undeformed PS material is transformed into craze fibril material (highly deformed PS) via the drawing mechanism. It is visible in Figure 4 that both components show a large degree of plastic deformation arising from the deformation of the lamellar structure, which is clearly consistent with results of Schwier et al.[14] The light PBMA phase cavitates which is followed by the plastic deformation of the dark PS phase, resulting in a cellular craze structure formed via cavitation mechanism. In contrast, the absence of a microphase separated morphology in disordered block copolymers makes a cavitation as the first step of a cavitation mechanism impossible. In this case, the deformation occurs via crazing. We can conclude that block copolymers in the disordered state show the same deformation mechanism as the corresponding glassy homopolymers. It was already shown[23] that disordered PS-*b*-PBMA diblock copolymers are also deformed via crazing.

As the incompatibility increases, the phases enter the intermediate segregation region (ISR). Within the ISR, the long-range order of morphology increases. The cavitation mechanism is also the basic deformation mechanism for intermediately and strongly segregated diblock copolymers. Deformation structures in strongly segregated block copolymers were already reported by Argon and co-workers[14−16] and are not presented in this study. The increasing grain size within ISR and SSL is associated with additional mechanisms of termination and diversion of crazes. While crazes in hompolymers and weakly segregated block copolymers mainly propagate perpendicular to the direction of stress applied, for intermediately and strongly segregated diblock copolymers propagation of crazes is strongly influenced by the orientation of grains. This is shown in Figures 5 and 6 where the craze propagation in a weakly segregated PBMA-*b*-PS-*b*-PBMA triblock copolymer is compared with an intermediately segregated PS-*b*-PBMA diblock copolymer. For the intermediately segregated PS-*b*-PBMA diblock copolymer with $\chi N = 39$, large deformation zones can be observed (Figure 6). This was already discussed in our previous study for a sample with $\chi N = 55.3$.[24] Crazes with a thickness up to 5−6 μm arise from a coalescence of thin deformation zones not observed in weakly segregated block copolymers. Furthermore, mechanisms of termination and diversion of crazes are observed in intermediately segregated block copolymers as discussed in detail in our previous study.[24] It is obvious in Figure 6 that crazes do not propagate perpendicular to external stress field in all cases, and the difference arises from the influence of morphology on craze propagation. It was shown in one of our previous papers[25] that the long-range order significantly increases as χN increases from 16.1 (WSL) to 33.45 (ISR). The grain size increases with increasing incompatibility from about 500 nm up to 3−5 μm. Mechanisms such as diversion and termination of crazes are only effective in a large volume element if the grain size is larger than about 2 μm. If the grain size is comparable to the thickness of single crazes (about 500 nm to 1 μm in contrast to thick crazes arising from coalescence), the influence of morphology on craze propagation is less pronounced. In weakly segregated block copolymers the craze propagation mainly occurs perpendicular to direction of external stress field, whereas in intermediately and strongly segregated block copolymers it occurs perpendicular to the direction of the lamellae in the respective grains. Thus, craze propagation may be stopped or diverted at domain boundaries which should decrease the craze propagation velocity.

In contrast to intermediately segregated block copolymers, strongly segregated block copolymers have a much smaller interfacial width. For a strongly segregated block copolymer, the same deformation mechanism has been observed as for intermediately segregated block copolymers. Recently, it was shown that the craze initiation stress, σ_c, of PS-*b*-PBMA shows a maximum at about 70−80% PS exceeding that of PS.[24] Figure 7 compares the craze initiation stresses of PS-*b*-PBMA and poly(styrene-*b*-hexyl methacrylate), PS-*b*-PHMA, diblock copolymers. PS-*b*-PHMA are strongly segregated at molecular weights used in our study (see Table 1) according to χ between PS and PHMA given by Ruzette et al.[26] It is shown in Figure 7 that a maximum in σ_c does not exist for the system PS-*b*-PHMA. Since a decreasing interfacial width is observed with increasing χ, it is responsible for the absence of a maximum in σ_c for PS-*b*-PHMA. This means that an increasing interfacial width is associated with increasing craze initiation stresses. A broadened interface decreases critical stresses at the interface which avoids a premature failure and finally results in an enhanced toughness of the material. Using this information, it is reasonable that termination

Table 1. Characterization Data of Samples: Molecular Weight (M_n), Volume Fraction (Φ_{PS}), Morphology, and χN Values at 120 °C (Using Refs 25, 28, and 31)

sample[c]	used in Figure	$10^{-3}M_n$[a]	Φ_{PS}-block[b]	morphology (TEM)	χN
PBMA-*b*-PS-*b*-PBMA	2	93.3	0.48	disordered	9.80
PBMA-*b*-PS-*b*-PBMA	3, 5	201.5	0.52	lamellae	27.50
PS-*b*-PBMA	6	315.0	0.70	lamellae	39.0
PBMA-*b*-PMMA	9	214.0	0.75	PBMA-cylinder	122.80
PBMA-*b*-PMMA	9	125.3	0.77	PBMA-cylinder	71.70
PS-*b*-PBMA	7	426.0	0.72	lamellae/cylinder	48.10
PS-*b*-PenMA	11	216.5	0.73	PenMA-cylinder	59.60
PS-*b*-PHMA	11	238.0	0.74	PenMA-cylinder	93.03
PS-*b*-PBMA	10	278.0	0.51	lamellae	29.50
PS-*b*-PenMA	10	184.3	0.52	lamellae	46.90
PS-*b*-PHMA	10	225.0	0.50	lamellae	78.10
PS-*b*-PBMA	7, 4	450.0	0.67	lamellae	50.10

[a] Total molecular weight and polydispersity determined by size exclusion chromatography (SEC), values are based on the PS standards. [b] Volume fraction of PS determined by ^{1}H NMR. [c] Abbreviations: PS-*b*-PBMA = poly(styrene-*b*-butyl methacrylate); PBMA-*b*-PMMA = poly(butyl methacrylate-*b*-methyl methacrylate); PS-*b*-PenMA = poly(styrene-*b*-pentyl methacrylate); PS-*b*-PHMA = poly(styrene-*b*-hexyl methacrylate).

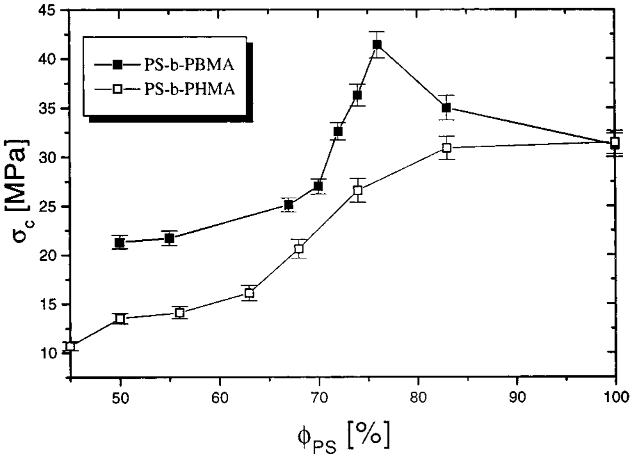

Figure 7. Dependence of craze initiation stress σ_c on volume fraction of PS for PS-*b*-PBMA (already discussed in ref 24) and PS-*b*-PHMA diblock copolymers (M_n > 200 kg/mol).

and diversion of crazes are more effective for intermediately segregated block copolymers because of enhanced stress transfer across the interface and decreased critical stresses at the interface (energy adsorption).

Figure 8 represents a unified scheme of deformation mechanisms for disordered, weakly segregated, intermediately segregated, and strongly segregated diblock copolymers. It shows a schematical representation of deformation mechanisms of diblock copolymers depending on strength of segregation, χN and reveals the correlation between micromechanical deformation mechanisms and phase behavior. While for disordered block copolymers the deformation occurs via crazing (Figure 8a), the ODT is associated with a transition from crazing to cavitation mechanism (Figure 8b). Within the ISR also a cavitation mechanism can be observed as already found for weakly segregated block copolymers. However, for intermediately segregated block copolymers mechanisms of diversion and termination of crazes can be found in addition (Figure 8c). For ordered block copolymers craze propagation mainly depends on local orientation of grains. Within the SSL, principally the same deformation mechanisms can be observed as in the ISR (Figure 8d). This also includes mechanisms of lamellae rotation[24] and kink band formation reported by Winey et al.[27] The most striking difference between SSL and ISR is the enhanced craze initiation stress in the ISR as shown in Figure 7.

While the ODT can be considered as reason for the transition from crazing to cavitation mechanism in weakly segregated block copolymers, the increasing grain size with increasing χN is associated with observation of additional deformation mechanisms of termination and diversion of crazes.

It is important to discuss the conditions for the proposed scheme:

1. In the case of diblock copolymers the molecular weight of the glassy block must be much larger than the entanglement molecular weight: $M_n \gg 2M_e$ (M_e = entanglement molecular weight).

2. The ratio of shear modulus of matrix, G_m, and soft/rubbery, G_r, phase must fulfill the following condition: $G_r/G_m < 0.1$. If this ratio is larger than 0.1, the rubbery/soft phase cannot cavitate before the craze initiation stress of the matrix is reached. The reason is the high bulk modulus of the rubbery/soft phase, for example polybutadiene. The bulk modulus is given by $K = E/3(1 - 2\nu)$, where E is Young's modulus and ν is Poisson's ratio. The bulk modulus of PS is 3.30 GPa compared to 1.77 GPa for PB (293 K). The intrinsic cavitation strength of a PB domain is 60 MPa.[15,16] According to Bucknall and co-workers,[28] the critical cavitation stress increases with increasing ratio G_r/G_m and decreasing particle size (which is small for block copolymers compared to rubber modified polymers) until it becomes too large to observe a cavitation mechanism.

However, using more complex block copolymer architectures (for example, star block copolymers) might be connected with other conditions which, however, cannot be considered in the present study.

Correlation between Phase Behavior and Mechanical Properties. It is known from our previous studies[29,30] that mechanical properties of block copolymers are strongly influenced by deformation behavior. Thus, we can assume that a unified correlation between phase behavior and tensile properties might exist as well. For PS-*b*-PBMA diblock copolymers, the mechanical properties achieve an optimum in the ISR where the interface is broadened.[29]

Recently, we reported[30] that the smaller interfacial width of strongly segregated block copolymers is associated with a deterioration of tensile properties. Figure 9 compares the tensile property of an intermediately segregated PMMA-*b*-PBMA diblock copolymers with that of a strongly segregated PMMA-*b*-PBMA diblock copolymer. Surprisingly, the intermediately segregated

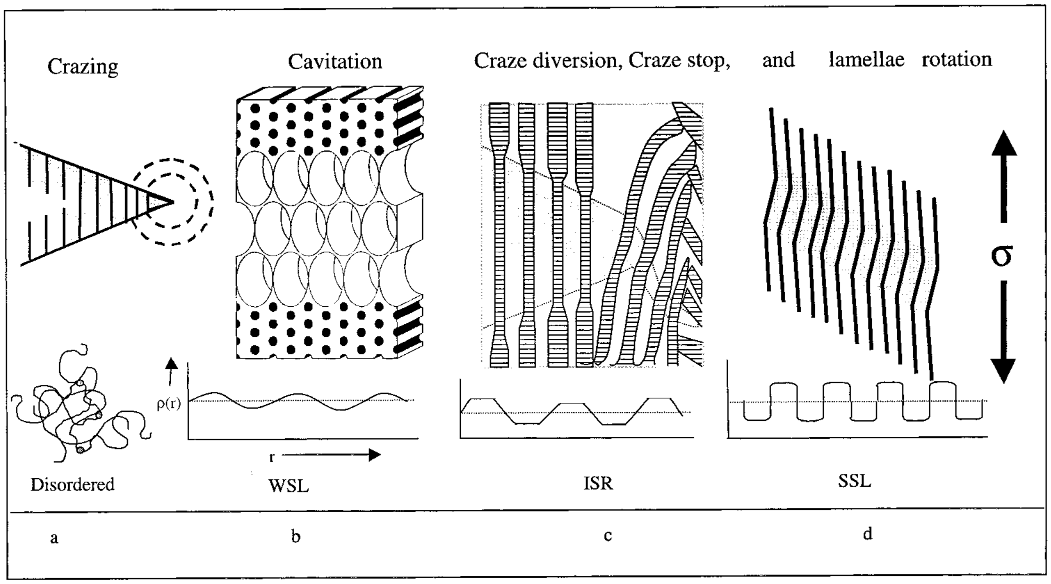

Figure 8. Schematic presentation of deformation mechanisms of diblock copolymers depending on strength of segregation, χN: (a) disordered block copolymers are deformed via crazing independent of their molecular architecture. The deformation mechanism is the same as observed in the corresponding glassy homopolymer. (b) WSL: weakly segregated diblock copolymers are deformed via two-step cavitation mechanism as reported by Schwier et al.[14] Diblock copolymers undergo a transition from crazing to cavitation mechanism at the order–disorder transition. (c) ISR: intermediately segregated diblock copolymers also show basically a cavitation mechanism. However, termination and diversion of crazes can be observed in addition as a result of the influence of morphology on craze propagation. Other deformation mechanisms are also possible depending on morphology and type of tilt grain boundary (rotation of lamellae and kink bands). (d) SSL: strongly segregated diblock copolymers show same mechanisms as observed for intermediately diblock copolymers including lamellae rotation. Strongly segregated block copolymers reveal a much lower craze initiation stress as shown in Figure 7 and discussed in the text.

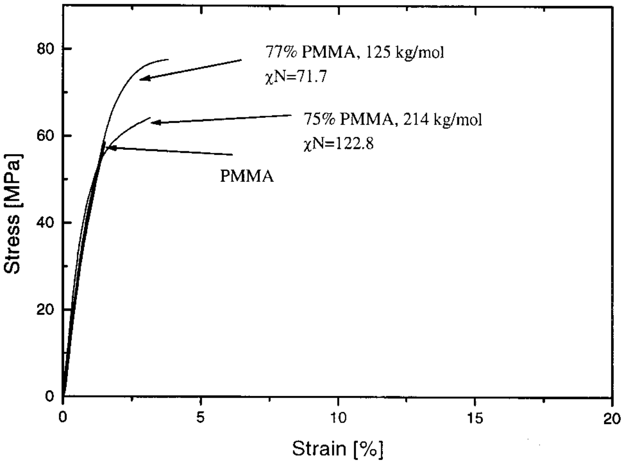

Figure 9. Stress–strain curves for PBMA-*b*-PMMA diblock copolymers with different molecular weights and PMMA (M_w = 205 kg/mol) at a strain rate of $\epsilon = 1.6 \times 10^{-4}$ s^{-1}. The sample with lower molecular weight is intermediately segregated and shows a better property profile than the material with higher molecular weight (strongly segregated).

block copolymer shows a superior property profile despite its lower molecular weight when compared to the strongly segregated material. The tensile strength of the intermediately segregated diblock copolymer exceeds that of PMMA.

Self-assembly in block copolymers gives the possibility to create "smart materials" where deformation mechanisms as well as mechanical properties are controlled by phase behavior and morphology. This may lead to new designs of polymeric materials based on microphase separated block copolymers. Prediction of deformation mechanisms of a diblock copolymer system is possible from strength of segregation, χN, by using the scheme in Figure 8. A change of χN by temperature or molecular weight is associated with a change of deformation mechanism and tensile properties. This also yields the possibility to create a material that changes its deformation mechanism and tensile property via changes in temperature or pressure. It should be noted that the interaction parameter is influenced by pressure in addition.

To establish a correlation between interaction parameter (interfacial width) and mechanical properties of block copolymers, systems with different χ parameters are compared. For this purpose, a series of diblock copolymers with different alkyl methacrylate blocks (Table 1) are investigated with respect to their tensile properties. The glass transition temperature depends of the length of alkyl methacrylate block, but it was found to have only a small impact on our results (this holds true for different compositions). The χ parameters for the different block copolymers are given in recent studies.[26,30,31] Figure 10 shows the dependence of tensile strength and strain at break on χ for a series of poly(styrene-*b*-alkyl methacrylate) diblock copolymers. It is obvious that both tensile strength and strain at break decrease with increasing incompatibility. While the tensile strength for PS-*b*-PBMA diblock copolymers is comparable with PS, significant lower values are found in the case of poly(styrene-*b*-pentyl methacrylate), PS-*b*-PenMA, and PS-*b*-PHMA block copolymers. Figure 11 represents a correlation between tensile properties and χN. While PS-*b*-PHMA samples are strongly segregated, PS-*b*-PenMA and PS-*b*-PBMA diblock copolymers are intermediately segregated. For weakly segregated PBMA-*b*-PS-*b*-PBMA triblock copolymers a steep increase of tensile strength is observed. In contrast, the adsorbed energy shows a maximum in the ISR. For weakly segregated triblock copolymers the tensile strength increases at the expense of toughness. It was already

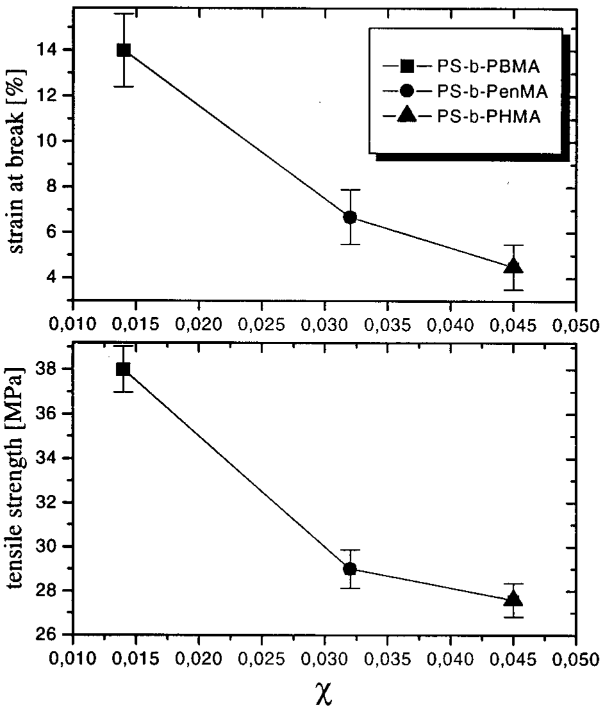

Figure 10. Dependence of the tensile strength and strain at break on Flory–Huggins interaction parameter χ for poly(styrene-*b*-alkyl methacrylate) diblock copolymers with about 70% PS (see Table 1) at a strain rate of $\epsilon = 1.6 \times 10^{-4}$ s^{-1}.

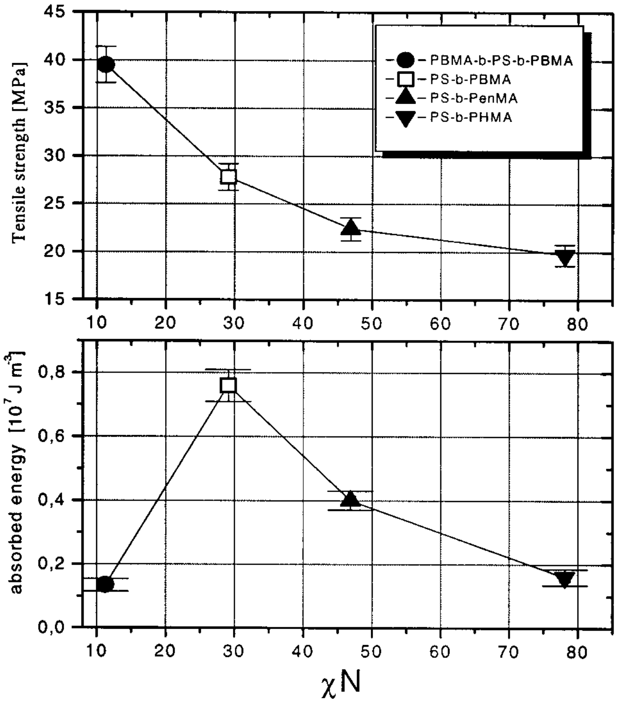

Figure 11. Dependence of the tensile strength and adsorbed energy on χN for different poly(styrene-*b*-alkyl methacrylate) diblock copolymers and PBMA-*b*-PS-*b*-PBMA triblock copolymers with about 50% PS (see Table 1) measured at strain rate of $\epsilon = 1.6 \times 10^{-4}$ s^{-1}.

reported that the ODT is associated with a brittle-to-tough transition.[25]

Figure 12 summarizes the property profile of different block copolymers with respect to different strengths of segregation compared to commercial polymer materials. It is shown that classical materials show either a high toughness or a high stiffness and strength. For example, rubber toughened polymers show a steep decrease in stiffness and tensile strength with increasing rubber content. It is usually difficult to obtain materials with a high toughness and a high stiffness and strength. This can only be realized with high-performance polymeric materials which are quite expensive. It is therefore an aim of materials science to achieve the property profile of high-performance polymers by using more common monomers like styrene, butadiene, and poly(alkyl methacrylate)s. It has been demonstrated in Figure 11 that strength of segregation influences the property profile of diblock copolymers. While the property profile for disordered and strongly segregated diblock copolymers is similar to classical materials or corresponding homopolymers, nonclassical property profiles are observed with intermediately and weakly segregated block copolymers. Some differences between ISR and WSL are observed for mechanical properties. For intermediately segregated block copolymers a combination between high toughness, high stiffness, and strength is shown in Figure 11 as discussed in detail in our previous paper.[29] However, for weakly segregated block copolymers, a very high stiffness and strength are observed at the expense of toughness (Figure 11). This is due to the small long-range order of weakly segregated block copolymers which makes deformation mechanisms such as termination and diversion of crazes less effective in a larger volume element. For block copolymers, a minimum grain size (about 2 μm) is necessary to achieve a larger toughness.[32] Of course, there are other combinations of molecular architecture and morphology that may be used to obtain tailored property profiles. However, it is necessary to vary all of these parameters to obtain a more detailed correlation between phase behavior, deformation behavior, and mechanical properties.

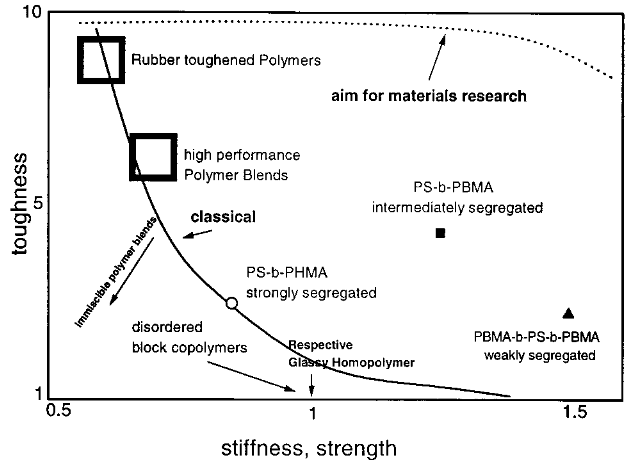

Figure 12. Qualitative presentation of dependence of toughness on tensile strength and stiffness for different polymeric systems which demonstrate the influence of strength of segregation on property profile. Disordered block copolymers show the same property profile as the corresponding homopolymers. Nonclassical property profiles exist for intermediately and weakly segregated block copolymers.

Conclusions

The present study summarizes the deformation behavior of diblock copolymers depending on phase behavior. A new scheme is proposed for deformation mechanisms of diblock copolymers depending on strength of segregation. The proposed scheme is proved by using a variety of block copolymers, which demonstrates the existence of a unified correlation between the phase behavior and deformation mechanism. Using this scheme, it is possible to predict the deformation behavior of diblock copolymers only from the knowledge of strength of segregation. While a crazing mechanism may be found for disordered block copolymers, the deformation occurs via cavitation in the WSL. Within the ISR, both diversion and termination of crazes are observed in addition to a pure cavitation mechanism. This correlation allows an understanding of the change in mechanical properties as the strength of segregation increases. Using data from this paper and previous publications, it is possible to provide a unified picture of deformation behavior and mechanical properties of weakly segregated block copolymers.[23,24,32]

Change of deformation mechanism from crazing to cavitation at the ODT provides reasons for the large change observed in mechanical properties (brittle−tough transition[25]) and in diameter of craze fibrils.[23] Furthermore, the importance of microphase separated morphologies of block copolymers for deformation behavior and mechanical properties becomes apparent. Also, for mechanical properties it is demonstrated how the interaction parameter influences tensile strength as well as strain at break.

From the knowledge of correlation presented in Figures 8 and 12, it is possible to predict the deformation mechanisms and the qualitative property profile of a block copolymer system. Prediction of property profile of complex materials is an important issue of materials science. It is, however, not possible to describe the influence of complex architectures, yet the crazing mechanism observed in disordered block copolymers is independent of their architecture. Our results also give the possibility to understand the nonclassical property profile of weakly segregated block copolymers, which reveal an exceptional combination of high tensile strength and stiffness. This was recently reported in our previous study on PS-*b*-PBMA and PBMA-*b*-PS-*b*-PBMA block copolymers.[32] The presented scheme in Figure 8 is only a qualitative presentation of the correlation between deformation behavior and phase behavior of block copolymers and is only a first step to a future predictive modeling.

Acknowledgment. R. Weidisch acknowledges financial support from Deutsche Forschungsgemeinschaft (DFG). R.W. also acknowledges help from R. Adhikari (Halle) and K. Laverdune (Amherst) and many useful discussion with Prof. S. P. Gido (Amherst) about grain boundaries and grain size. This work was supported in part by the Landesprojekt Sachsen-Anhalt “Neue Funktionswerkstoffe auf der Grundlage schwach entmischter Blockcopolymere”.

References and Notes

(1) Tirell, D. A. *Nature* **1997**, *390*, 336.
(2) Chen, Z. R.; Kornfield, J. *Polymer* **1998**, *39*, 4679.
(3) Haward, R. N.; Young, R. J. *The Physics of Glassy Polymers*; Chapman & Hall: London, 1997.
(4) Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: New York, 1998.
(5) *Thermoplastic Elastomers*; Legge, N. R., Holden, G., Schroeder, H. E., Quirk, R. P., Eds.; Hanser: Muinch, 1996.
(6) Hamley, I. W.; Koppi, K. A.; Rosedale, J. H.; Bates, F. S.; Almdal, K.; Mortensen, K. *Macromolecules* **1993**, *26*, 5959.
(7) Hadjuk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Kim, G.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1994**, *27*, 4063.
(8) Förster, S.; Khandpur, A. K.; Zhao, J.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W. *Macromolecules* **1994**, *27*, 6922.
(9) Beckmann, J.; Auschra, C.; Stadler, R. *Macromol. Rapid Commun*. **1994**, *15*, 67.
(10) Krappe, U.; Stadler, R.; Voigt-Martin, I. *Macromolecules* **1995**, *28*, 4558.
(11) Stadler, R.; Auschra, C.; Beckmann, J.; Krappe, U.; Voigt-Martin, I.; Leibler, L. *Macromolecules* **1995**, *28*, 3080.
(12) Morton, M. In *Encyclopedia of Polymer Science and Technology*; Bikales, M., Ed.; Wiley-Interscience: New York, 1971; Vol. 15, pp 508−530.
(13) Yamaoka, I. *Polymer* **1998**, *39*, 1765.
(14) Schwier, C. E.; Argon, A. S.; Cohen, R. E. *Polymer* **1985,** *26*, 1985.
(15) Argon, A. S.; Cohen, R. E. In Kausch, H. H., Ed.; *Crazing in Polymers*; Springer-Verlag: Berlin, 1983; Vol. 1.
(16) Argon, A. S.; Cohen, R. E. In Kausch, H. H., Ed.; *Crazing in Polymers*; Springer-Verlag: Berlin, 1990; Vol. 2.
(17) Weidisch, R.; Michler, G. H.; Fischer, H.; Hofmann, S.; Arnold, M.; Stamm, M. *Polymer* **1999**, *40*, 1191.
(18) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem*. **1990**, *41*, 525.
(19) Leibler, L. *Macromolecules* **1980,** *13*, 1302.
(20) Matsen, M. W.; Bates, F. *Macromolecules* **1996**, *29*, 1091.
(21) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *J. Chem. Phys*. **1990**, *92*, 5677.
(22) Michler, G. H. *Ultramicroscopy* **1984**, *15*, 81.
(23) 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.
(24) Weidisch, R.; Ensslen, M.; Michler, G. H.; Fischer, H. *Macromolecules* **1999**, *32*, 5375.
(25) Weidisch, R.; Michler, G. H.; Arnold, M. *Polymer* **2000**, *41*, 2231.
(26) Ruzette, A.; Banerjee, P.; Mayes, A. M.; Pollard, M.; Russell, T. P.; Jerome, R.; Slawecki, T.; Hjelm, R.; Thiyagarajan, P. *Macromolecules* **1998**, *31*, 8509.
(27) Polis, D. L.; Winey, K. *Macromolecules* **1998**, *31*, 3617.
(28) Bucknall, C. B. In Haward, R. N., Young, R. J., Eds.; *The Physics of Glassy Polymers*; Chapman & Hall: London, 1997.
(29) Weidisch, R.; Stamm, M.; Michler, G. H.; Fischer, H.; Jerome, R. *Macromolecules* **1999**, *32*, 742.
(30) Weidisch, R.; Stamm, M.; Schubert, D. W.; Arnold, M.; Budde, H.; Höring, S. *Macromolecules* **1999**, *32*, 3405.
(31) Scherble, J.; Stark, B.; Stühn, B.; Kressler, J.; Schubert, D. W.; Budde, H.; Höring, S.; Simon, P.; Stamm, M. *Macromolecules* **1999**, *32*, 1859.
(32) Weidisch, R.; Michler, G. H.; Arnold, M.; Fischer, H. *J. Mater. Sci*. **2000**, *35*, 1257.

MA001272P