

The Influence of Molecular Weight on the Large Deformation Behavior of SBS Triblock Copolymer Elastomers

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Synopsis

Engineering stress-strain properties were determined for two polystyrene-polybutadiene-polystyrene (SBS) triblock copolymer elastomers, one consisting of blocks of molecular weight 7000/43000/7000 and the other, 16000/85000/17000. In addition, various blends of these two materials were prepared in order to vary the number-average molecular weight of the blocks in a systematic way while maintaining polystyrene content in the range of 25-28 wt %. Samples were solvent cast from benzene or benzene/heptane mixtures and annealed before testing. Ring specimens were extended to rupture at varying strain rates on an Instron tensile tester. Results indicate that number-average molecular weight has a marked influence on stress-strain behavior over the range of molecular weights and testing conditions employed. The observed behavior is consistent with a systematic increase in the proportion of a mixed interfacial region between the pure polystyrene and polybutadiene domains as molecular weight decreases. The interfacial region contributes to mechanical hysteresis, rate sensitivity, and toughness in the SBS materials. Scanning electron photomicrographs of fracture surfaces also showed systematic changes with molecular weight.

INTRODUCTION

The advantageous combination of thermoplastic processing characteristics and elastomeric properties is a well-known feature of various types of triblock copolymers.¹⁻⁵ Processing of these materials is known to proceed more easily as the molecular weights of the constituent blocks decrease. However, the influence of molecular weight on physical properties is less well established, particularly in relation to the large deformation mechanical properties. Early studies of styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) triblocks focused on the pronounced effect of compositional changes in these materials, although it was also concluded that molecular weight changes at constant composition should have little or no effect on the stress-strain behavior^{1,6,7} as long as the overall molecular weight was above a critical value required for domain formation.⁸ Molecular weight distribution was also felt to be of minimal importance.⁶ Other studies indicated that such parameters as temperature and strain rate,⁹⁻¹² plasticization or swelling,^{10,11,13} and solvent casting procedure^{14,15} all influence the large deformation behavior of triblock copolymer elastomers, although it was not clear if the demonstrated effects were dependent upon the overall molecular weight of the material.

In view of recent theories of domain formation¹⁶⁻¹⁹ in block copolymers, total insensitivity of the engineering properties of triblock copolymers to changes in molecular weight would be surprising. These theories account for the fact that a significant proportion of the triblock copolymer material may be contained in a mixed interfacial region lying between domains of relatively pure block components. According to the theory of Meier,¹⁸ the volume fraction of this interfacial region is expected to increase as block molecular weights decrease at constant overall triblock composition. Although the interfacial region has at times escaped direct observation via either x-ray diffraction²⁰ or electron microscopy,²⁻⁵ recent SAXS measurements of the interfacial thickness of SI diblocks have been performed successfully.²¹ Also numerous studies^{2-5,14,22,23,25-27} of large and small deformation viscoelastic behavior of triblock copolymers have repeatedly indicated the presence of an interfacial layer. In several of these studies,^{22,23,25} quantitative models were proposed to account for the influence of the interfacial region's mechanical properties which were taken to be intermediate between those of the constituent block homopolymers.

In the present study, we have examined the influence of changing block molecular weight on the stress-strain behavior of two SBS triblock copolymers. In addition various blends of these two triblocks were prepared in order to investigate the influence of varying the number-average molecular weight of the constituent blocks in the SBS material. Through variations in the strain rate and by changing the method of specimen preparation, a clear and systematic dependence of the mechanical behavior on molecular weight has been observed. The nature of this molecular weight dependence is consistent with an increase in the volume fraction of interfacial region as molecular weight decreases.

EXPERIMENTAL

Two research-grade SBS triblock copolymer elastomers were generously provided by the Shell Chemical Company. These two samples, designated 16/85/17 (high molecular weight) and 7/43/7 (low molecular weight) were blended in various proportions to provide the series of samples indicated in Table I. Films of about 2.5-mm thickness were prepared by solvent casting, either from benzene or from a 60/40 volumetric mixture of benzene and heptane, according to procedures employed in an earlier study.²⁸ The films were annealed under vacuum at 100°C for 8 hr, and dimensional changes were observed as reported previously;²⁸ however, this phenomenon was less noticeable for the films cast from the mixed solvent, particularly for those samples rich in the 16/85/17 triblock.

The morphologies of these samples were not observed directly by transmission electron microscopy. An earlier study of similar benzene-cast SBS triblocks containing about 29% styrene has shown²⁵ that annealed samples exhibit a domain morphology which may be interpreted as hexagonally packed spheres or cylinders of polystyrene within a continuous polybutadiene matrix. In this investigation we obtained scanning electron micrographs of Au/Pd-coated surfaces of samples 16/85/17, 7/43/7, and the 50:50 blend fractured in liquid nitrogen.²⁹ Stress-strain experiments were conducted on an Instron tensile tester at strain rates from 85%/sec (50 in./min) to 0.34%/sec (0.2 in./min). Ring specimens (typically 2.2 cm I.D., 2.6 cm O.D.) were employed in all tests; rings were

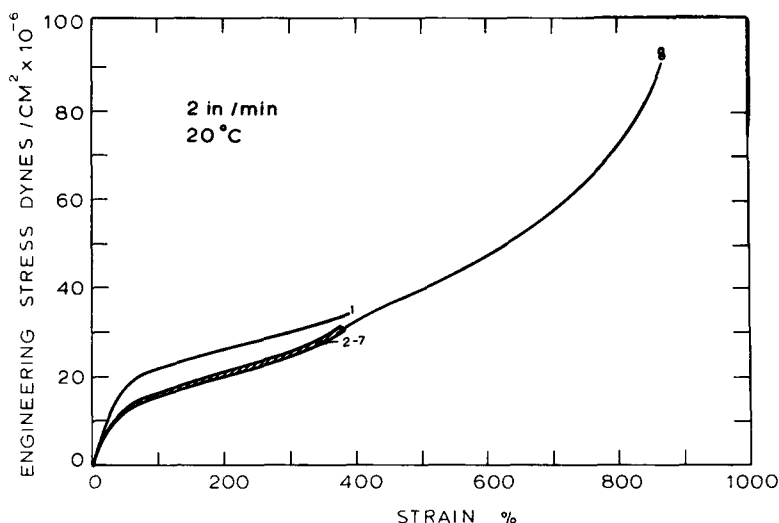


Fig. 1. Mullins effect for a benzene-cast 16/85/17 specimen. A rest period of at least 4 hr was allowed between runs. Initial length corrected for the small permanent set in runs 2-8.

cut from the annealed sheets using a specially designed fly-cutter mounted in a drill press. Each set of stress-strain data reported here represents an average over two or more runs on a given sample using a new specimen each time. The shapes of the stress-strain curves were entirely reproducible for various annealed specimens of the same sample. There was considerable scatter in the failure points owing to unavoidable surface flaws introduced during cutting of the ring specimens.

For all samples, there was a marked stress-softening or Mullins effect^{23,24} depicted in Figure 1 for benzene-cast 16/85/17. As seen in Figure 1, the stress-softening effect can be removed only up to the point at which the prestretch is stopped, data beyond that point essentially exhibiting behavior of a virgin specimen. Thus, all subsequent results reported in this paper were obtained on virgin specimens pulled first time to the point of rupture. We may note on the basis of numerous preliminary experiments not reported here that the stress-softening hysteresis seen in Figure 1 became more noticeable as the content of 7/43/7 increased in the blended samples.

RESULTS

The stress-strain behavior of three benzene cast samples is shown in Figure 2. The curves for the other two samples listed in Table I (i.e., 75:25 and 25:75) fell between the appropriate curves in Figure 2. In general, the behavior of samples 16/85/17 and 7/43/7 bracketed the response of the three triblock blends which always varied in a systematic and ordered way between these limits. Thus, although the entire set of samples in Table I was tested, a presentation of the results on the two pure triblock samples and the 50:50 blend will be sufficient for further analysis.

Figures 3-5 show the rate dependence of the stress-strain behavior of the benzene-cast samples. In addition to preserving the order established in Figure

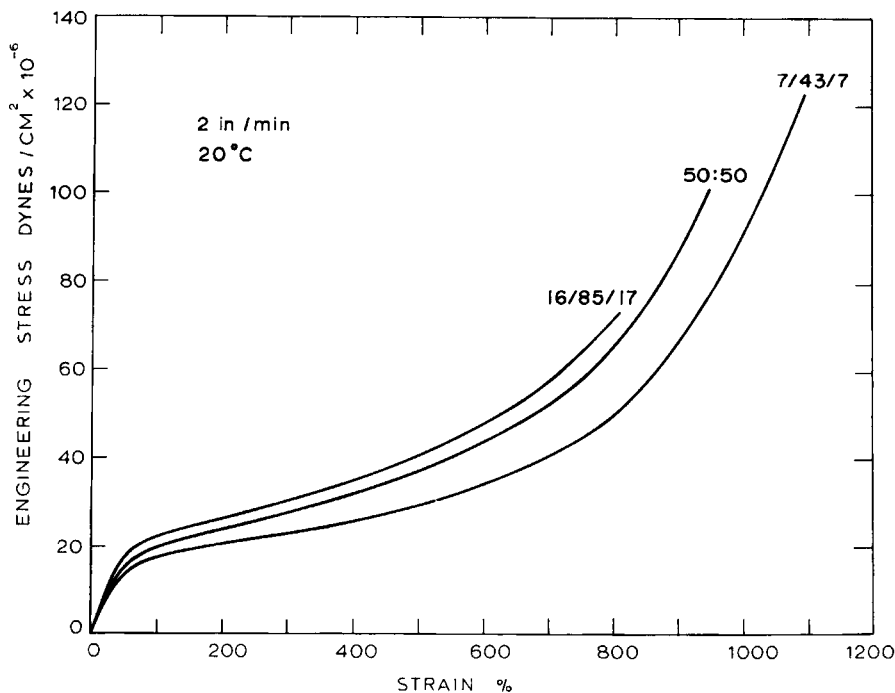


Fig. 2. Characteristic ordering of the stress-strain response for the benzene-cast samples.

2 (i.e., under the same test conditions, 16/85/17 exhibits the lowest strains at a given stress and 7/43/7 the highest strains) there is a very significant ordering of the rate sensitivities in the three materials, with sample 7/43/7 showing the largest rate dependence. The failure points crudely describe the expected failure envelope, ranging from low breaking strains at low extension rates through a region of high strain at break for intermediate rates and back to low strains at the highest rates. This failure envelope is most clearly seen in the data for the

TABLE I
Triblock Samples

Sample code	Number-ave. MW ^a S/B/S	Equilibrium swelling ratio ^b	Permanent set, ^c %	Polystyrene, wt %
2443	16/85/17	3.5	2.4; ~0; 6.0	28
75:25	12/68/13	—	—	27
50:50	10/57/10	4.1	—	26
25:75	8/49/8	—	—	25
2445	7/43/7	4.1	6.9; 2.5; —	25

^a In thousands.

^b In isoctane at 20°C on specimens cast from benzene solution; swelling ratio V/V_0 is calculated on a polystyrene-free basis; some "swelling creep" observed for 2445.

^c Stretched to rupture at 2 in./min or more slowly; results represent average over at least three determinations; first entry—benzene-cast samples; second entry—benzene/heptane-cast samples; third entry—benzene-cast samples swollen to equilibrium in isoctane.

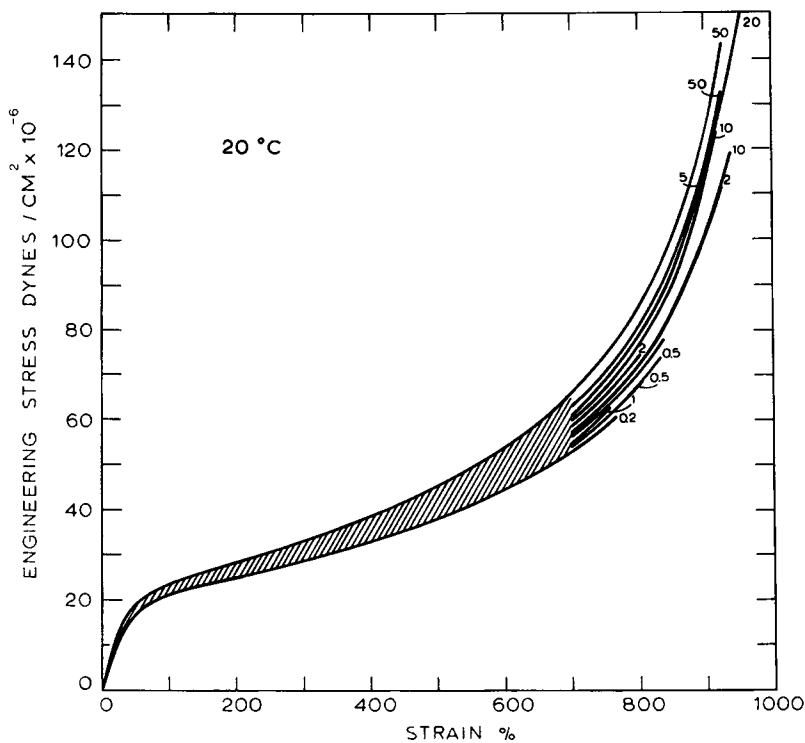


Fig. 3. Dependence of the stress-strain behavior on strain rate for benzene-cast 16/85/17. Cross-head speeds, in inches per minute, are indicated near the appropriate curves.

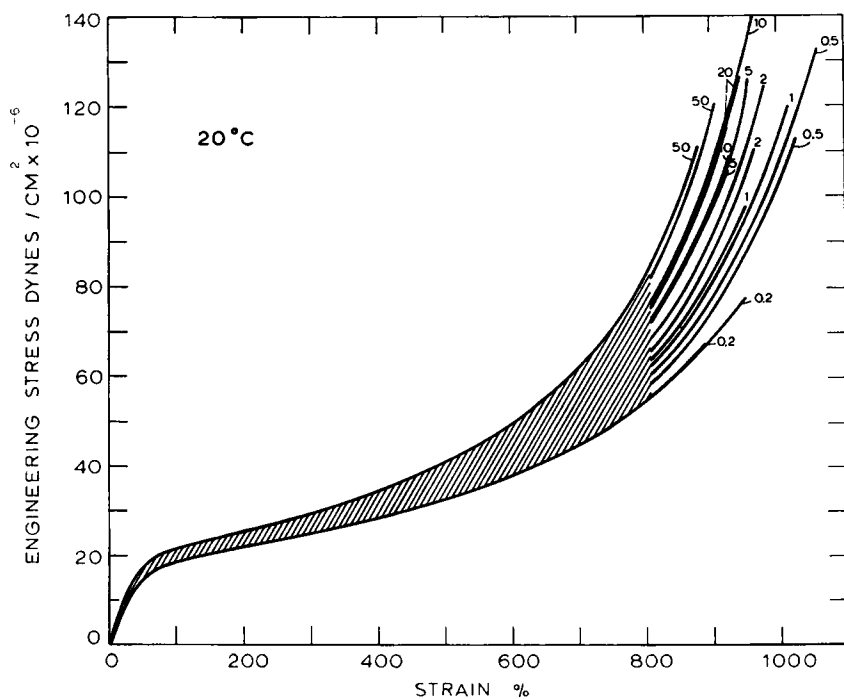


Fig. 4. Rate dependence of benzene-cast 50:50.

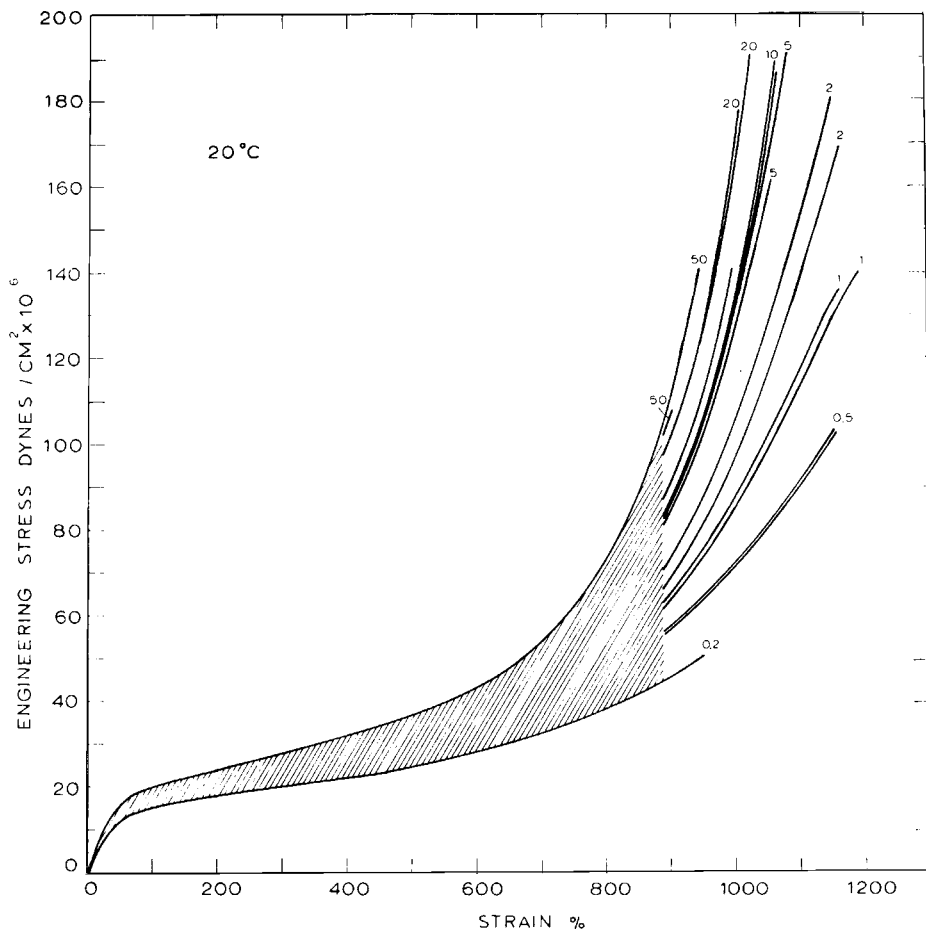


Fig. 5. Rate dependence of benzene-cast 7/43/7.

low molecular weight triblock. In all curves of Figures 3–5, there is evidence of the characteristic upturn at high strains often attributed to finite extensibility³⁰ of the network chains and/or reinforcing effects of the filler particles.^{7,10} It is evident that the sharpness of the upturn is diminished at lower extension rates and its location is shifted to higher strains.

Similar tests of the rate sensitivity were conducted on the three materials cast from solution in a 60/40 benzene/heptane mixture. These results, shown in Figures 6–8, are strikingly different from the previous results. The 16/85/17 sample exhibits little rate dependence except at the very highest strains, whereas the spread of the curves for the other two samples remains relatively unchanged.

A final set of stress–strain data was obtained on a series of benzene-cast specimens of 16/85/17. Tests were conducted on the unswollen (bulk) polymer and at various stages of swelling (4 hr, 10 hr, 120 hr) in isooctane. The results, shown in Figure 9 along with the swelling curve insert, indicate the expected change in stress levels as well as significant changes in the shapes of the stress–

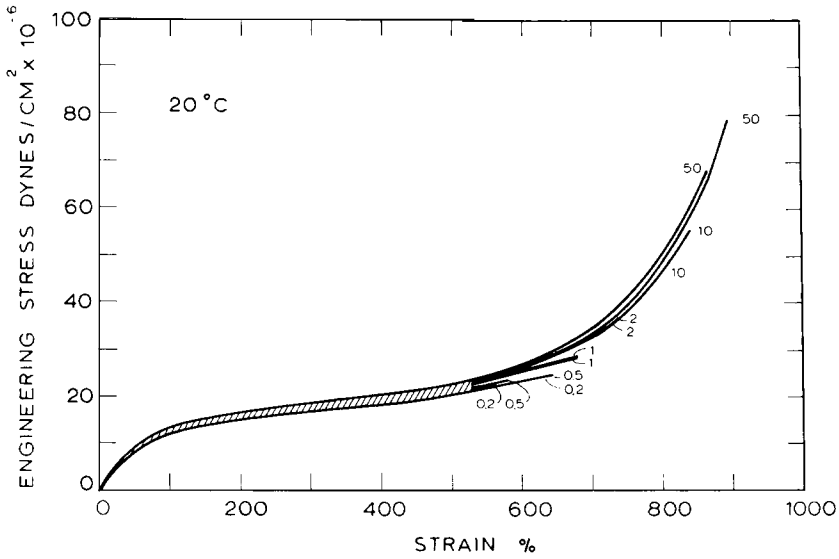


Fig. 6. Dependence of the stress-strain behavior on strain rate for 16/85/17 specimens cast from a 60/40 benzene/heptane solvent mixture.

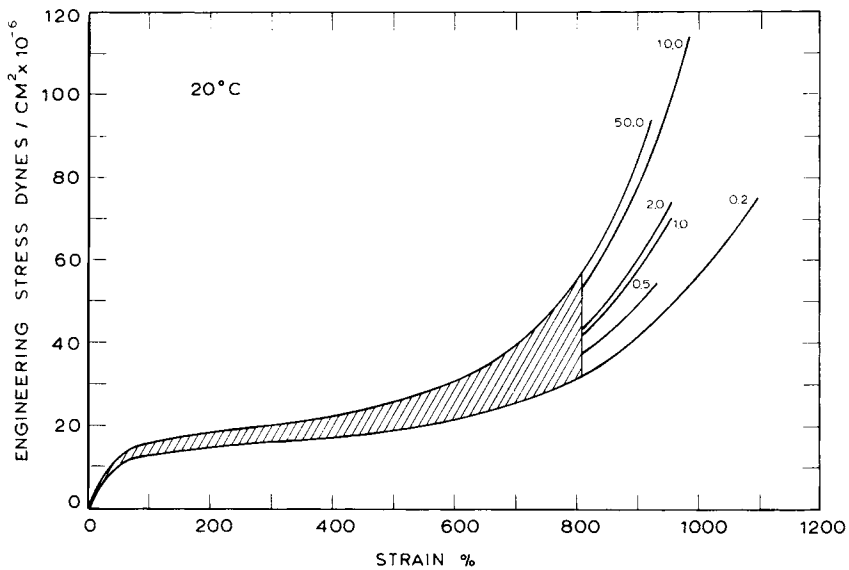


Fig. 7. Rate dependence of benzene/heptane-cast 50:50.

strain curves. At higher degrees of swelling, the upturn in the stress-strain curve (roughly marked by the arrows in the two upper curves) is not observed up to the point of rupture. Attempts to conduct similar tests on 7/43/7 failed owing to its tendency to flow under very low stresses when swollen significantly in isooctane.

Finally, we have attempted to determine whether the low-temperature failure mechanism, as evidenced by fracture surfaces produced in liquid nitrogen, is

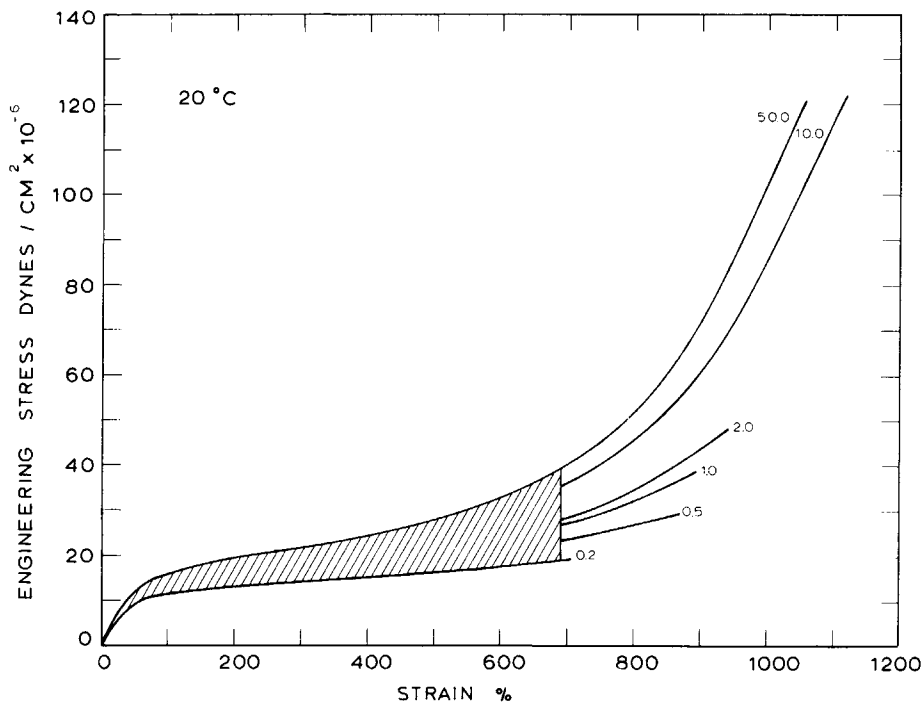


Fig. 8. Rate dependence of benzene/heptane-cast 7/43/7.

influenced by changes in molecular weight of the block copolymer segments. Figure 10 shows several of these scanning electron photomicrographs of benzene-cast samples of the two triblocks. It is evident that the fracture surface of the lower molecular weight 7/43/7 sample exhibits larger physical features. The photographs of the 50:50 mixture (not shown) revealed fracture surface features which were of intermediate size.

DISCUSSION

From the data presented above, it is evident that molecular weight changes at constant composition exert a strong influence on the large deformation behavior of these SBS triblock copolymer elastomers. This is particularly clear in terms of the marked difference in the rate sensitivity of the stress-strain curves of Figures 3-5. This rate dependence may be examined in more detail by considering the amount of stress relaxation¹⁰ occurring at a given stretch ratio ($\lambda = L/L_0$) over the period of time ($t = \lambda/\dot{\lambda}$) covered by the experiments. Figure 11 shows the true stress, $\lambda\sigma$, plotted against log time for benzene-cast samples of 16/85/17 and 7/43/7. At the lowest strains, the rate of stress relaxation is essentially equal in the two materials, but this relaxation rate increases very rapidly with strain for the low molecular weight triblock.

There are several possible explanations for the marked difference in rate sensitivity seen here. The viscoelastic response of the polybutadiene phase may vary with molecular weight owing to possible differences in the entanglement

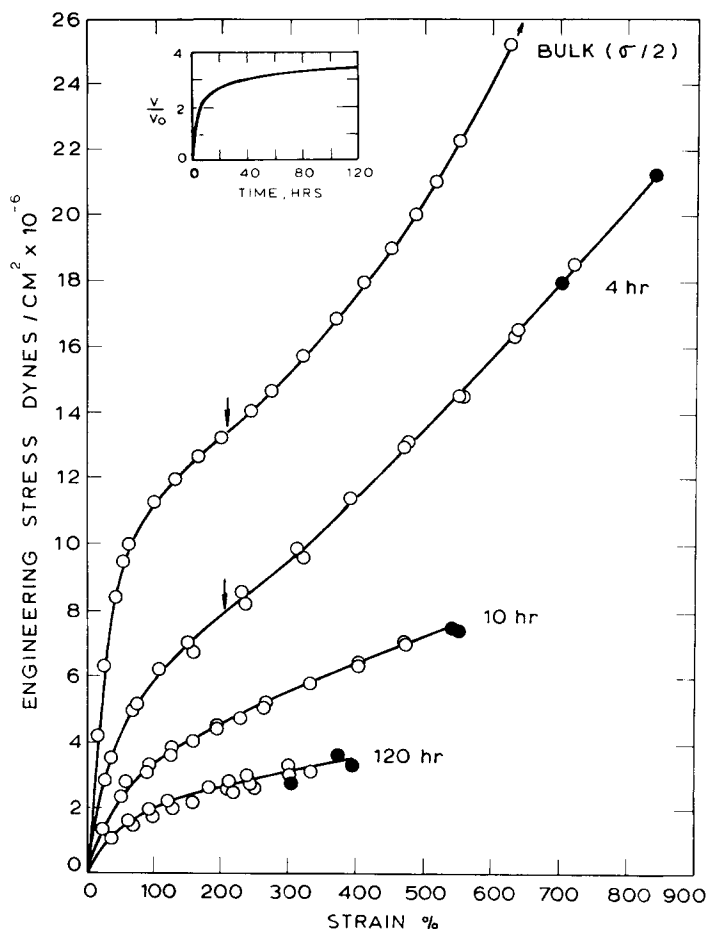


Fig. 9. Stress-strain behavior (2 in./min) of benzene-cast specimens of 16/85/17 swollen to different extents in isoctane at 20°C. The swelling curve is shown as an insert. Black dots indicated the failure point in repeated experiments. The stresses for the unswollen specimen have been halved for convenience in plotting; stress for the swollen specimens are based on the swollen cross section.

structures obtained during phase separation. Alternatively, the deformability of the pure polystyrene domains may increase as molecular weight decreases. Finally, a contribution to the stress-strain behavior by a mixed interfacial region, having properties intermediate between that of polystyrene and polybutadiene, may become more significant as molecular weight decreases.

The first possibility listed above seems unlikely in view of the fact that polybutadiene mechanical response, even taking entanglement slippage into account, is expected²⁵ to be relatively rate insensitive at 20°C over the range of test speeds employed here. The second explanation, large-scale plastic flow of *pure* polystyrene domains has been proposed previously,^{10,13,14} and this would be expected to be a very rate-sensitive phenomenon. Polystyrene deformation would not be expected to be a highly recoverable phenomenon at 20°C, however. Thus, considering the rather small permanent set values listed in Table I, pure poly-

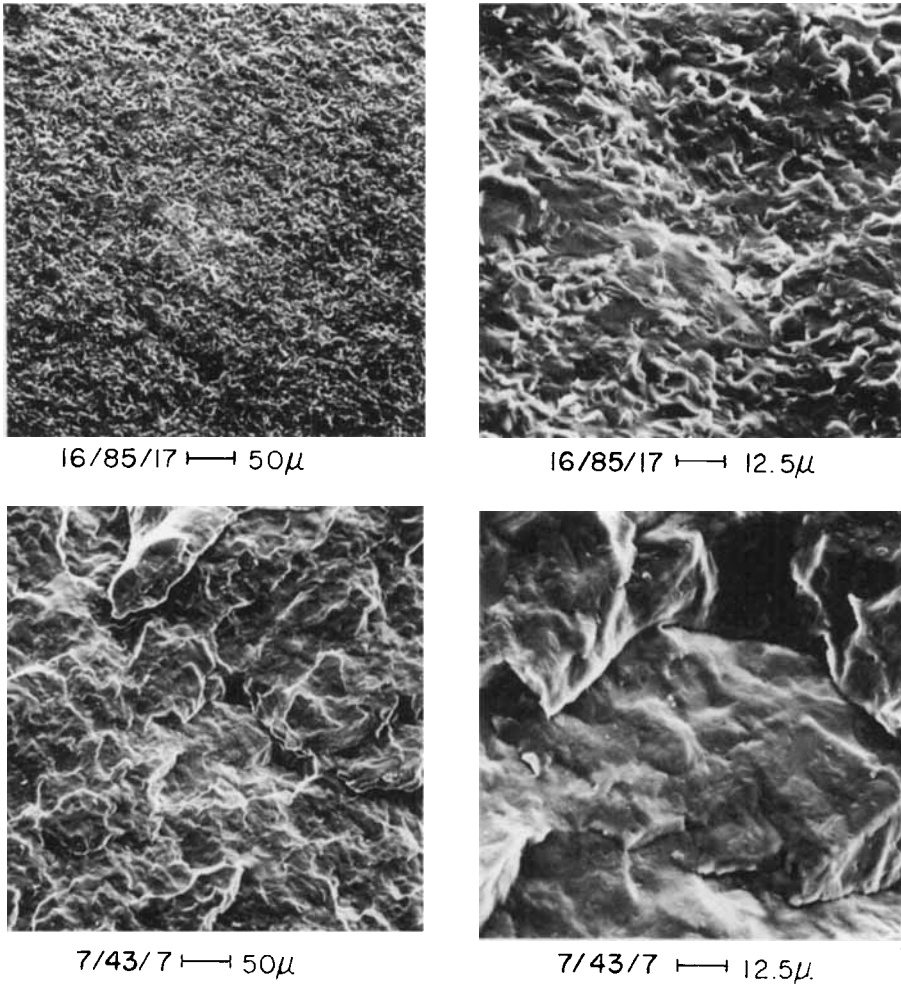


Fig. 10. Scanning electron micrographs of LN₂ fracture surfaces of benzene-cast (16/85/17) and (7/43/7)

styrene deformation does not appear to be entirely responsible for the observed behavior, although at the very highest stresses and strains near rupture some contribution from this source may be expected. Thus, much of the overall rate dependence seen in Figures 3–5 is attributed to an interfacial region which exhibits far more rate sensitivity than a pure polybutadiene network and which is more recoverable from large deformation than expected for pure polystyrene at these temperatures. If the properties of the interfacial material vary in a smooth fashion through the interfacial region, as postulated in earlier experimental studies,^{22,25} and in some recent theoretical work,¹⁹ it is not unexpected that the rate sensitivity begins to appear at the low levels of stress and strain seen in Figures 3–5, well below the point at which pure polystyrene deformation is anticipated. Furthermore, the systematic increase in rate sensitivity observed in passing from Figure 3 to Figure 5 can be explained by a systematic increase

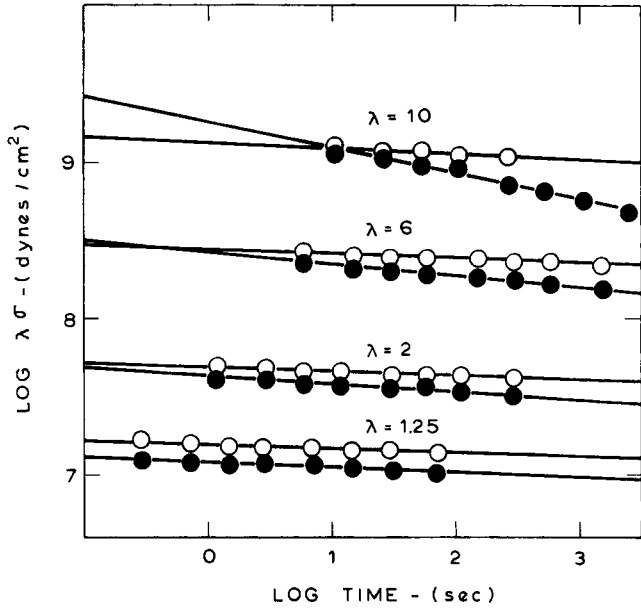


Fig. 11. Stress relaxation data obtained at various levels of strain: (●) 7/43/7-BZ; (○) 16/85/17-BZ.

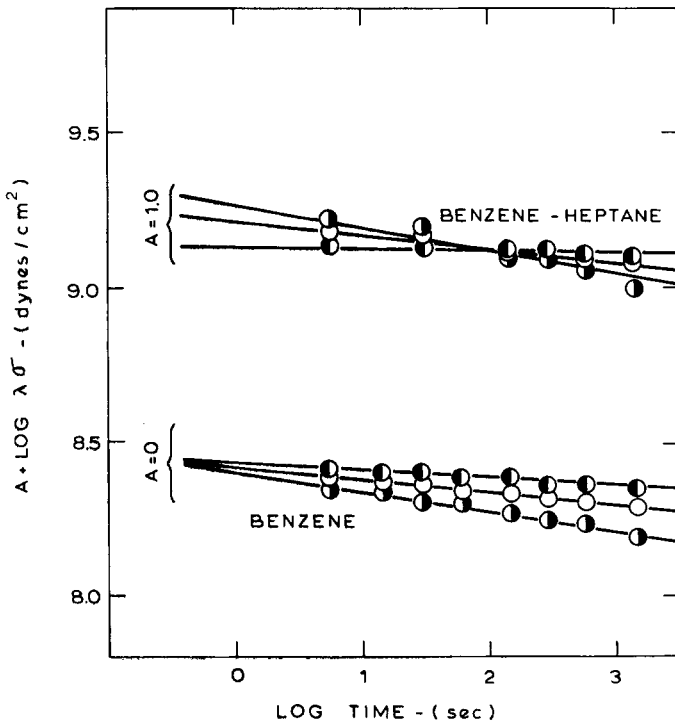


Fig. 12. Comparison of the stress relaxation in benzene-cast and benzene/heptane-cast samples at a stretch ratio $\lambda = 6$: (●) 7/43/7; (○) 50:50, (●) 16/85/17.

in the proportion of the interfacial material as molecular weight decreases, a hypothesis which is supported by theory.¹⁸

The results of the experiments on benzene/heptane-cast samples add further support for the deformation mechanisms described above, i.e., that a mixed interfacial region is primarily responsible for the observed rate dependence and that the influence of this mixed region, along with its volume or weight fraction, increases with decreasing molecular weight. The benzene/heptane mixture was chosen on the basis of its known ability¹⁵ to preferentially precipitate polystyrene during the solvent casting process, thereby reducing domain expansion and phase mixing at the polystyrene-polybutadiene interface. The 60/40 benzene/heptane ratio was the critical mixture which would just dissolve the high molecular weight 16/85/17 sample. It was observed, however, that the 7/43/7 triblock dissolved rather easily in this solvent mixture. Thus, the results shown in Figure 6 indicate that the amount of interfacial material is greatly diminished in the 16/85/17 material. The stress-strain behavior of this sample is essentially that of a polybutadiene network, i.e., very little rate dependence and almost no permanent set. If there is any deformation in the pure polystyrene domains in this sample, it must occur only at the highest stresses and strains in agreement with the discussion above. The other two samples cast from the mixed solvent retain a significant proportion of their interfacial material owing to the presence of the low molecular weight styrene blocks contributed by the 7/43/7 triblock; as seen in Figures 7 and 8, the rate sensitivity of these samples remains relatively unchanged. Thus, a distribution of end-block molecular weights can in some instances exert a marked influence on mechanical properties as a result of the tendency of lower molecular weight fractions to contribute to an interfacial layer. This polydispersity effect may be less pronounced, however, if a very good solvent for the highest molecular weight is used in the casting procedure or if samples are injection or compression molded.

Figure 12 compares the stress relaxation behavior at $\lambda = 6$ for samples obtained via the two different solvent casting procedures. As expected, the 16/85/17 line is essentially horizontal for the benzene/heptane-cast sample, while the 7/43/7 and 50:50 data show similar amounts of stress relaxation for both casting procedures. In addition, the level of stress was affected by the solvent casting procedure so that for the benzene/heptane cast samples the stress relaxation data intersect over the time range indicated. The reduction in stress level is greatest for 16/85/17 and least for 7/43/7. This is consistent with a greater decrease in the effective filler volume for the high molecular weight sample. Since the effective filler volume will consist of the pure polystyrene domains plus some proportion²⁵ of the mixed interfacial region, the observed changes in stress levels are consistent with a large decrease in interfacial volume for benzene/heptane-cast^{16/85/17} and relatively less reduction of this layer in the other two samples.

Other evidence is contained in the data to support the concept of increased interfacial contribution at lower molecular weights. The ordering of the stress-strain curves observed in Figure 2 is contrary to expectation if only polybutadiene chains are taking part in the deformation. Qualitatively, it would be anticipated that the 16/85/17 triblock with longer polybutadiene chains between domains, would exhibit a more pronounced plateau of relatively easy extensibility in its stress strain curve than the 7/43/7 sample, which has shorter chains between domains. The fact that the opposite is observed in Figure 2 again points to an increased amount of extensible interfacial material in the 50:50 and

7/43/7 samples. Also, the systematic increase in hysteresis of the type shown in Figure 1 which was observed as the testing program moved down through the various samples of Table I is consistent with earlier experimental and theoretical work which attributes this behavior to the interfacial morphology of triblock copolymers.²³

The evidence provided by the scanning electron micrographs is more difficult to interpret. It is clear, however, that even at cryogenic temperatures the mechanical response is influenced by changes in molecular weight. The larger surface features seen for the 7/43/7 material may reflect a more highly interconnected interfacial morphology, consistent with the discussion above. We recognize that our inability to provide transmission electron micrograph data on the domain morphology leaves some questions regarding the interpretation of our mechanical properties data. In particular, it has been pointed out³¹ that around 25 wt % styrene, SB diblock copolymer morphology changes from polystyrene spheres to polystyrene cylinders in a continuous polybutadiene matrix. However, our own earlier work on an SBS triblock containing 29% styrene indicated that annealed benzene-cast samples were isotropic in their dynamic mechanical properties; this indicates that if cylindrical domains were present, they were neither highly interconnected nor highly aligned. We similarly expect that in the range of styrene contents covered in the present study (25–28%), any tendency to transfer from spherical to cylindrical morphology throughout the series of samples will have only minor influence on the large deformation mechanical behavior and that other effects such as the interfacial layer discussed above will dominate. We also have assumed that in the various blended samples, the endblocks mix without prejudice.^{6,7,28} If a bimodal domain size distribution were formed, however, a somewhat revised interpretation of the blend data might be required.

Finally, we note from Figure 9 the possibility that deformation of the interfacial region contributes to the overall toughness and to the desirable engineering properties of these materials. As swelling progresses, the stress-strain curves of Figure 9 lose the characteristic upturn or strain-hardening capacity at high strains. In carbon black-filled elastomers, this increased toughness at high strains has been attributed to slippage of polymer chains along the carbon black surface³² so that the load-bearing capacity of neighboring chains is equalized and the stress is distributed among a larger number of chains. Deformation and density rearrangements³³ within the interfacial layer can play a similar role in block copolymers so that the stress distribution in the relatively weak polybutadiene phase becomes more uniform. When the swelling solvent penetrates and disrupts the interfacial region to a significant extent, the probability of morphological rearrangement to transfer stress onto less highly oriented chains is diminished. Thus, the networks fail at lower strains without exhibiting the characteristic strain-hardening upturn in their mechanical response. It should also be noted that swelling moves the overall mechanical response closer to equilibrium rubbery behavior, and this also tends to suppress the upswing in the stress-strain curve.

SUMMARY

Regardless of the interpretation proposed, the data presented above show conclusively that molecular weight changes at essentially constant composition

can exert a profound influence on the large deformation mechanical response of SBS triblock copolymer elastomers. The influence of molecular weight is observed even at the extreme conditions of fracture at cryogenic temperatures. Changes in molecular weight distribution may also be important, depending upon the procedure employed in sample preparation.

All the evidence presented supports the conclusion that a mixed interfacial region contributes to the large deformation behavior of SBS triblocks. It is concluded that, at constant copolymer composition, the proportion of the overall material contained in this interfacial region increases as molecular weight decreases, in qualitative agreement with theory. The interfacial region contributes to the Mullins-effect hysteresis of these triblock materials and to the rate dependence of the stress-strain behavior. This latter effect can be suppressed to a large extent by proper choice of the casting solvent so as to minimize the amount of interfacial material. The interfacial material also contributes to the desirable toughness or strain-hardening characteristics observed at high elongations in these filled elastomers.

While the results presented here were all obtained at essentially constant polystyrene content (25–28%), it is anticipated that the observed molecular weight effects would be preserved as long as the polybutadiene phase remains continuous. At molecular weights above that of the high molecular weight 16/85/17 sample employed here, the effect of molecular weight is expected¹⁸ to become less significant. In SIS triblocks, a similar influence of molecular weight is expected although the effect may be less pronounced owing to the fact that polystyrene is less compatible with polyisoprene than with polybutadiene. Thus, the interfacial region will be less pronounced in SIS triblocks.

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