# Synthesis and Properties of Block Copolymers. 4. Poly(*p*-*tert*-butylstyrene–diene–*p*-*tert*-butylstyrene) and Poly(*p*-*tert*-butylstyrene–isoprene–styrene)

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ABSTRACT: Linear triblock copolymers have been synthesized containing end segments of poly(*p*-*tert*-butylstyrene) and polydiene center blocks. Stress–strain measurements indicated that at certain compositions and segment molecular weights extensive phase blending between the two components occurred. However, at high end segment content (50 wt % and greater) and moderately high end segment molecular weight, sufficient phase separation existed so that the block copolymers exhibited mechanical properties reminiscent of conventional thermoplastic elastomers. The existence of some phase blending was confirmed by an examination of the block copolymer morphology via x-ray scattering and electron microscopy. Triblock copolymers containing end segments of poly(*p*-*tert*-butylstyrene) and polystyrene showed moderately good mechanical properties and only limited phase blending when the end segment possessed nearly equal degrees of polymerization. Considerable phase blending was observed when the dissimilar end segments had nearly the same number-average molecular weight.

Anionic, termination-free polymerization systems are recognized as being capable of leading to the preparation of linear[1] and star shaped[2–5] triblock copolymers of controlled molecular weights and composition. Interest has been generated particularly in those triblock copolymers wherein the end blocks are thermoplastic materials and the center block is elastomeric. At ambient temperatures, these triblock copolymers exhibit mechanical behavior similar to that of rubber vulcanizates. This unique behavior, adumbrated by Alfrey,[6] occurs without benefit of chemical cross-links or the addition of reinforcing agents.

Under suitable conditions, the thermoplastic component of these triblock materials microphase separate into spherical, cylindrical, or lamellar shaped domains. These domains can function as both multifunctional cross-link points and reinforcing filler. It has been suggested[7,8] that the strength of these triblock copolymers is related, at least in part, to the ability of these domains to deform under stress. It has been reported[9] that when poly($\alpha$-methylstyrene), whose glass transition temperature is substantially higher than that of polystyrene, replaced polystyrene as the end segments, a significant increase in both the engineering and true stress was observed. This can be rationalized on the basis that the yield stress of poly($\alpha$-methylstyrene) domains is probably larger than those of polystyrene at identical temperatures.

In order to gain further insight into the influence of the end-block glass transition temperature, a study was undertaken involving the replacement of polystyrene with poly(*p*-*tert*-butylstyrene) in linear ABA block copolymers. The poly(*p*-*tert*-butylstyrene) was of further interest in that the solubility parameters[10–12] for this end block and the prospective polydiene center segment indicate possible compatibility between the prospective blocks. The calculated solubility parameter (following Small)[10] for poly(*p*-*tert*-butylstyrene) is 8.12 (cal/cm$^3$)$^{1/2}$. The reported literature values[13] for the polybutadiene and polyisoprene fall within the range of 8.1–8.6 and 7.9–8.35 (cal/cm$^3$)$^{1/2}$, respectively. This suggests the probable compatibility of poly(*p*-*tert*-butylstyrene) with either or both polydienes. Calculated values, though,[10–12] suggest that poly(*p*-*tert*-butylstyrene) should be more compatible with polyisoprene than with polybutadiene. The extent of compatibility would affect the degree of microphase separation and hence the integrity of the domains. Thus, it was deemed appropriate to study the effect of block compatibility upon the mechanical behavior of these copolymers, especially in view of the favorable glass transition temperature of poly(*p*-*tert*-butylstyrene).

## Experimental Section

The anionic polymerizations involved the rigorous purification of monomers, solvents, and reactors. These procedures were those described elsewhere.[14] The initiator was distilled *sec*-butyllithium with benzene as the polymerization solvent. Polymerizations were carried out at 25 °C. Termination was accomplished with degassed methanol. This was done to prevent the chain coupling reaction[15] which can occur when termination is accomplished by exposure of the active chain ends to the atmosphere.

The *p*-*tert*-butylstyrene monomer was obtained from the Dow Chemical Co. The monomer was reported to contain 95% of the para isomer. Analysis of the monomer by gas and mass chromatography verified that the para isomer was present in the amount claimed.

The Waters Ana-Prep instrument was used with seven 4-ft. Styragel columns having porosities ranging from $2 \times 10^3$ to $5 \times 10^6$ Å. The characteristics of this column set have been reported elsewhere.[16] This column arrangement has been shown by McCrackin[17] to yield molecular weights for polystyrene samples nearly identical to the absolute values without the need for column broadening corrections.

Tetrahydrofuran, at 35 °C, was the carrier solvent and the detector was the Waters differential refractometer. Solution concentrations were 0.25% (w/v). A 1 mL min$^{-1}$ flow rate was used and full loop (2 mL) injections were made. The instrument was equipped with a 5-mL syphon. All of the triblock copolymers listed in this work contained less than 1 wt % (based on total block copolymer weight) of poly(*p*-*tert*-butylstyrene) homopolymer. Furthermore, none of the chromatograms indicated the presence of diblock material.

The values of $\overline{M}_n$ and the second virial coefficients ($A_2$) were determined in toluene solutions at 37 °C. The Hewlett-Packard osmometers (Models 502 and 503) were used with gel cellophane 450 or S and S-08 membranes. For each sample four concentrations were used. The values of $\overline{M}_n$ were determined by the usual $(\pi/c)^{0.5}$ vs. $c$ plots. Prior to measurements on the triblocks, the osmometers were checked with solutions of the National Bureau of Standards 705 polystyrene. The standard deviation in the molecular weights of the NBS polystyrene was about 4%.

The polydiene microstructure and poly(*p*-*tert*-butylstyrene) content of the triblock copolymers were determined from *o*-dichlorobenzene solutions by use of the HR 300 Varian Associates NMR spectrometer. The polyisoprene microstructure was determined using Chen's[18] method while the technique of Santee et al.[19] was used for polybutadiene. The polyisoprene segments contained 70% cis-1,4, 24% trans-1,4, and 6% 3,4 units while the polybutadiene contained 35% cis-1,4, 57% trans-1,4, and 8% 1,2 units.

The morphological examination was carried out by the combined techniques of small-angle x-ray scattering and electron microscopy. The equipment and techniques used have been previously described.[4,20,21]

The films of the triblock copolymers were cast from solutions containing 10% (w/v) polymer in a 9:1 mixture of benzene and *n*-heptane. The films were formed over stretched cellophane. The solvent mixture was allowed to evaporate slowly at room temperature for a period of about 5 days. The cast films were then dried under vacuum for about 1 week at room temperature. The samples examined

Table I
Molecular Characteristics of Linear Triblock Copolymers Containing Poly(*p*-*tert*-butylstyrene)

| Sample[a] | $\overline{M}_s \times 10^{-4}$,[b] g mol$^{-1}$ | $\overline{M}_n \times 10^{-4}$,[c] g mol$^{-1}$ | $A_2 \times 10^3$, mol cm$^3$ g$^{-2}$ | Wt % poly(*p*-*tert*-butylstyrene) |
|---|---|---|---|---|
| bSIbS-1 | 11.0 | 10.9 (±3%)[d] | $0.8_3$ | 30 |
| -2 | 11.2 | 10.7 (±3%) | $1.2_3$ | 40 |
| -3 | 14.4 | 14.3 (±4%) | $0.7_6$ | 51 |
| -4 | 14.6 | 13.6 (±4%) | $0.7_7$ | 62 |
| -5 | 14.8 | 14.5 (±4%) | $1.1_9$ | 42 |
| bSBbS-4 | 13.5 | 14.2 (±9%) | $1.2_8$ | 44 |
| -5 | 15.2 | 16.3 (±4%) | $1.3_2$ | 33 |
| -6 | 15.5 | 15.4 (±5%) | $1.1_3$ | 20 |
| -8 | 12.3 | 12.4 (±4%) | $0.8_1$ | 50 |
| -12 | 10.8 | 11.0 (±5%) | $0.8_2$ | 30 |
| -13 | 7.1 | 6.8 (±3%) | $1.5_0$ | 40 |
| -15 | 6.0 | 6.2 (±3%) | $1.3_5$ | 50 |
| -16 | 14.6 | 14.7 (±3%) | $1.0_9$ | 63 |
| -17 | 9.6 | 9.4 (±3%) | $1.3_4$ | 60 |
| -18 | 9.4 | 9.2 (±2%) | $1.1_2$ | 50 |
| -19 | 6.8 | 6.8 (±6%) | $1.1_4$ | 60 |
| -20 | 6.7 | 6.6 (±2%) | $1.3_9$ | 50 |
| -22 | 16.4 | 16.3 (±2%) | $0.8_1$ | 50 |
| -23 | 14.5 | 14.8 (±3%) | $0.8_3$ | 74 |
| -24 | 10.0 | 10.3 (±4%) | $1.3_3$ | 40 |
| bSBS-1 | 14.0 | 14.3 (±5%) | $1.4_9$ | 20[e] |
| -2 | 14.0 | 14.8 (±4%) | $1.3_5$ | 20[e] |

[a] bS = poly(*p*-*tert*-butylstyrene), S = polystyrene, I = polyisoprene, B = polybutadiene. [b] $\overline{M}_s$ = stoichiometric molecular weight; g of monomer/mol of initiator. [c] Toluene solutions at 37 °C. [d] Estimated limits. [e] Total poly(*p*-*tert*-butylstyrene) and polystyrene composition.

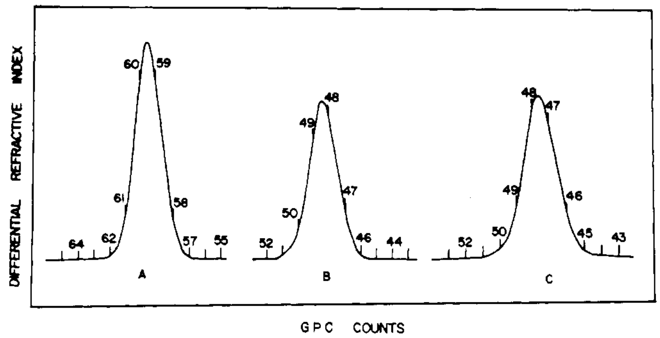

**Figure 1.** Gel permeation chromatograms of poly(*p*-*tert*-butylstyrene) (A), poly(*p*-*tert*-butylstyrene–isoprene–*p*-*tert*-butylstyrene)-3 (B), and poly(*p*-*tert*-butylstyrene–butadiene–styrene)-1 (C).

by electron microscopy were microtomed at liquid nitrogen temperature and stained with osmium tetroxide.[22] For the small-angle x-ray measurements, the intensity readings were observed at angular intervals of 20 s. Exposure times were of about 200 s duration.

The stress–strain measurements were run on the solvent-cast films. The specimens were in the form of a microdumbbell and were about 0.2 to 0.3 mm thick. An Instron tensile tester with a cross-head speed of 5 cm/min was used at room temperature. Six to eight specimens were measured for each sample. The data obtained were then averaged using the results from all of the samples examined.

For the low and high temperature studies, the microdumbbells were analyzed in an Instron environmental chamber. The temperature range was from 23 to 95 °C.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used in an attempt to determine the glass transition temperatures of the triblock copolymers. The instrument was calibrated using lead and indium.

## Results and Discussion

**Block Copolymer Synthesis.** The anionic polymerization of *p*-*tert*-butylstyrene was found to proceed without complications in both the preparation of the homopolymer and the triblock copolymers. Under the polymerization conditions used in this work, the hydrogens of the *tert*-butyl group of the monomer and polymer proved unreactive with regard to the hydrogen–metal exchange reaction involving the active chain ends as has been observed for toluene.[23-28] Polymerization of the *p*-*tert*-butylstyrene in benzene and benzene–tetrahydrofuran (~1 vol % ether) yielded poly(*p*-*tert*-butylstyrene) in quantitative yields and with near-monodisperse molecular weight distributions. This latter feature is indicated by the chromatogram in Figure 1 of a low molecular weight poly(*p*-*tert*-butylstyrene). The number-average molecular weight of this sample was 7.8 × 10$^3$ g mol$^{-1}$ and the ratio of $\overline{M}_w/\overline{M}_n$, from gel permeation chromatography, was found to be $1.0_4$. A poly(*p*-*tert*-butylstyrene) with a number-average molecular weight of 2 × 10$^5$ g mol$^{-1}$ was found to have a similar molecular weight distribution.

In regard to triblock formation, *p*-*tert*-butylstyrene was found to behave in a fashion similar to styrene. The crossover from the poly(*p*-*tert*-butylstyryl) anion to isoprene or 1,3-butadiene appeared to occur rapidly as observed by the disappearance of the red coloration of the anion. Following the formation of the diene center block a small amount (≃1 mL) of either tetrahydrofuran or triethylamine was added to accelerate the reaction between the polydienyllithium and the *p*-*tert*-butylstyrene. The polar "promoter" was added in view of the apparently slow crossover reaction observed between dienyllithium chain ends and styrene in hydrocarbon solvents.[29-31] Figure 1 contains representative chromatograms of these linear triblock copolymers containing polydiene center blocks. As can be seen, the molecular weight distributions can be classified as near-monodisperse. Table I contains the characterization data of the linear block copolymers synthesized in this work. Parenthetically, it should be noted that the values listed for the second virial coefficient are similar to those reported[32] for linear di- and triblocks containing polystyrene and polybutadiene.

**Stress–Strain Properties.** The ultimate strength of triblock copolymers is apparently, in part, associated[7,8] with the ability of the plastic domains to resist deformation, a deformation which when it takes place can occur[33] in a reversible fashion. In view of the favorable glass transition tempera-

Table II
Tensile Properties of bSIbS Triblock Copolymers

| Sample | Poly(*p*-*tert*-butylstyrene), wt % | End segment $\overline{M}_n$ × $10^4$, g $mol^{-1}$ | % set | $\sigma_b$, kg $cm^2$ | $\lambda_b$ |
|---|---|---|---|---|---|
| 1 | 30 | 1.6 | | | |
| 2 | 40 | 2.1 | | | |
| 5 | 42 | 3.0 | | ~1 | ~19 |
| 3 | 51 | 3.6 | 67 | 82 ± 5 | ~17 |
| 4 | 62 | 4.2 | 49 | 169 ± 15 | 10.1 |

Table III
Tensile Properties of bSBbS Triblock Copolymers

| Sample | Wt % (bS) | End segment $\overline{M}_n$ × $10^{-4}$, g $mol^{-1}$ | % set | $\sigma$, kg $cm^{-2}$ | $\lambda_b$ |
|---|---|---|---|---|---|
| 13 | 40 | 1.4 | | 0.2 ± 0.01 | 9.2 ± 0.2 |
| 15 | 50 | 1.6 | | 2.8 ± 0.3 | ~24 |
| 20 | 50 | 1.7 | 350 | 31 ± 9 | ~19 |
| 19 | 60 | 2.1 | 60 | 312 ± 21 | 8.1 ± 0.2 |
| 12 | 30 | 1.6 | | 1.5 ± 0.1 | ~27 |
| 24 | 40 | 2.1 | | 60 ± 11 | 17.2 ± 0.8 |
| 18 | 50 | 2.3 | 54 | 251 ± 19 | 9.8 ± 0.1 |
| 17 | 60 | 2.8 | 96 | 342 ± 17 | 8.1 ± 0.2 |
| 6 | 20 | 1.5 | | 1.2 ± 0.1 | 5.1 ± 0.1 |
| 5 | 33 | 2.7 | | 221 ± 23 | 8.4 ± 0.1 |
| 4 | 44 | 3.1 | | 339 ± 31 | 8.6 ± 0.1 |
| 22 | 50 | 4.1 | 105 | 466 ± 37 | 7.6 ± 0.1 |
| 16 | 63 | 4.6 | 200 | 362 ± 31 | 7.4 ± 0.2 |
| 23 | 74 | 5.5 | | 342 ± 17 | 8.1 ± 0.2 |
| 8 | 50 | 3.1 | | 391 ± 18 | 7.6 ± 0.03 |

ture[34,35] (131–134 °C) of poly(*p*-*tert*-butylstyrene) it was initially surmised in this work that the replacement of polystyrene by this polymer in linear triblocks might lead to an enhancement of the engineering and true stress of these materials as was observed[9] for samples containing poly($\alpha$-methylstyrene).

Although poly(*p*-*tert*-butylstyrene) exhibits a glass transition temperature intermediate between polystyrene and poly($\alpha$-methylstyrene), another factor must be considered, to wit, that microphase separation can occur to a degree that yields discrete domains containing the end blocks.

The calculations[10–12,36] of the solubility parameters for poly(*p*-*tert*-butylstyrene) and the two polydienes suggest that the end segments in these triblock systems should be more compatible with polyisoprene than with polybutadiene. However, since reported[13] literature values for polybutadiene and polyisoprene fall within a range of values, the compatibility of poly(*p*-*tert*-butylstyrene) with either or both of these polydienes is possible.

The indication that poly(*p*-*tert*-butylstyrene) and polyisoprene are, to a certain extent, compatible is fortified by the mechanical properties of the bSIbS block copolymers. The three lowest molecular weight triblocks of this series appeared not to differ appreciably from uncross-linked polyisoprene of equivalent molecular weight. Essentially, these materials were tacky and were found to flow with time at ambient temperature. Table II lists the triblocks of the polyisoprene series together with tensile data, where applicable.

Virtually no tensile strength was obtained for those triblocks having molecular weights as high as $10^5$ g $mol^{-1}$. Only two members of the polyisoprene series exhibited significant tensile strengths. In order to achieve measurable values for the engineering stress, microphase separation is essential. Therefore, the tensile properties of these triblock copolymers demonstrate that poly(*p*-*tert*-butylstyrene) and polyisoprene are to a large extent mutually compatible. This behavior is somewhat reminiscent of the situation observed for diblock copolymers containing polystyrene and poly($\alpha$-methylstyrene).[37–41]

Parenthetically, we have noted that hydrogenation of the polyisoprene block yields triblock materials which exhibit tensile strengths comparable to the conventional SBS and SIS materials. This, of course, indicates that effective microphase separation occurs in the hydrogenated bSIbS materials. Calculations of the respective solubility parameters also indicate that this is the case.

In contrast, when polybutadiene was used to replace polyisoprene, a series of triblocks exhibiting significant tensile strengths was obtained. However, relative to the reported tensile strengths for SBS copolymers, bSBbS triblock materials having both larger overall molecular weights and/or end segments were required in order to obtain comparable values for the engineering stress. Table III lists the polybutadiene containing triblock copolymers and their corresponding tensile strengths. These values are reported as the arithmetic means together with their corresponding 95% confidence values.

From Table III and Figure 2, it can be seen that those bSBbS block copolymers having end-block molecular weights between 1.4 and 1.7 × $10^4$ g $mol^{-1}$ exhibit low tensile strengths. When the overall molecular weight ranges from 7 × $10^4$ to 1.5 × $10^5$ g $mol^{-1}$ and the end segment molecular weight is about 1.6 × $10^4$ g $mol^{-1}$ the copolymers possess low strength. However, an apparent increase in the end segment molecular weight of about $10^3$ g $mol^{-1}$ is accompanied by an apparent tenfold increase in engineering stress.

If some degree of compatibility exists between poly(*p*-*tert*-butylstyrene) and polybutadiene, one would not expect a single unique value for the critical molecular weight needed for microphase separation. In other words, the critical size may be dependent upon the relative molecular weights of the blocks and the composition. In contrast, Meier[42] has predicted a critical molecular weight for polystyrene domain formation to be about $10^4$ g $mol^{-1}$ for block polymers containing a polydiene and polystyrene.

Figure 3 shows the stress–strain behavior of the triblocks having 20 to 40 wt % of end block. It can be readily seen that, in the 6.0 × $10^4$ to 7.0 × $10^4$ g $mol^{-1}$ molecular weight range,

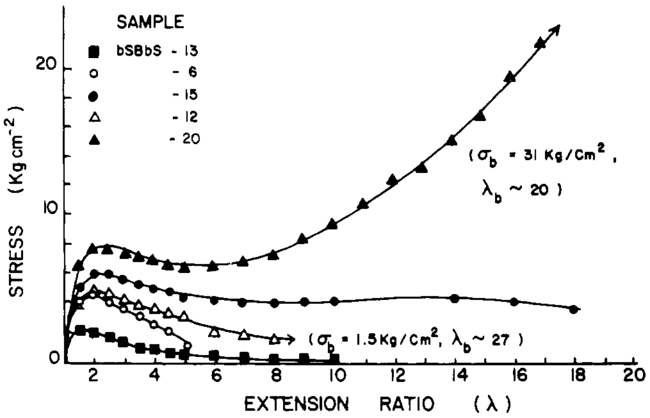

**Figure 2.** Stress-strain behavior of low strength bSBbS triblock copolymers.

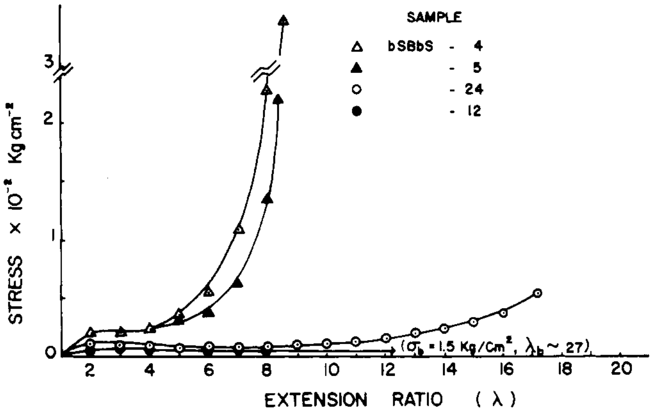

**Figure 3.** Stress-strain behavior of bSBbS triblock copolymers.

not even the sample containing 40 wt % poly(*p-tert*-butylstyrene) showed any appreciable strength. The limited range of triblock molecular weights corresponding to significant tensile strengths is not surprising if one considers that the minimum critical molecular weight of poly(*p-tert*-butylstyrene) for apparent domain formation is about $1.5 \times 10^4$ g mol$^{-1}$. Hence for a poly(*p-tert*-butylstyrene) charge of 20, 30, and 40 wt %, the minimum triblock molecular weights would have to be $1.5 \times 10^5$, $1 \times 10^5$, and $7.5 \times 10^4$ g mol$^{-1}$, respectively. In contrast, with the poly(styrene–butadiene–styrene) copolymers, these same end-block compositions at much lower block molecular weights showed correspondingly much higher tensile strengths. For example, a tensile strength of 112 kg cm$^{-2}$ for an SBS triblock having a molecular weight of about $8.0 \times 10^4$ g mol$^{-1}$ and only a 20 wt % styrene charge has been reported.[43]

The stress-strain behavior of triblocks at 50 wt % poly(*p-tert*-butylstyrene) is shown in Figure 4. It was only at this poly(*p-tert*-butyl styrene) composition that a wide range of tensile strengths could be obtained. The tensile strength increased from a low of 2.8 kg cm$^{-2}$ for a triblock with an $\overline{M}_n$ of $6.2 \times 10^4$ g mol$^{-1}$ to a high of 466 kg cm$^{-2}$ for a triblock having an $\overline{M}_n$ of $1.6 \times 10^5$ g mol$^{-1}$. As the overall molecular weight of the bSbS block copolymers increased, a yield phenomenon became apparent. Most likely at the higher molecular weights the plastic phase is semicontinuous.

Holden, Bishop, and Legge[44] have reported the stress-strain behavior for an SBS triblock having a molecular weight of 7.3 $\times 10^4$ g mol$^{-1}$ and a polystyrene content of 65 wt %. Its behavior was characterized by a high-yield stress followed by a short draw and then rupture. The elongation at break was 85%. In contrast, triblocks synthesized with 60 to 70 wt % poly(*p-tert*-butylstyrene) have stress-strain behaviors (Figure 5) not characterized by short elongations at break. Furthermore, drawing did not lead to immediate rupture; instead elastic extension is evident. The drop in stress after the yield point is the result of relaxation processes in the samples oc-

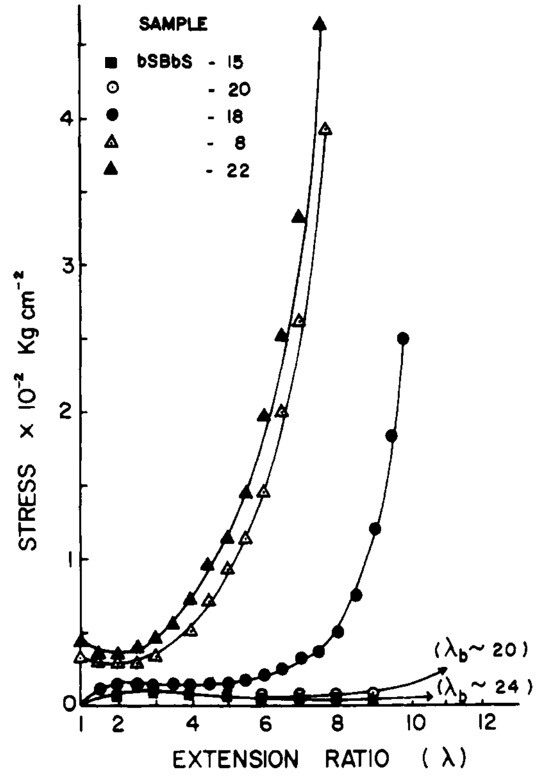

**Figure 4.** Stress-strain behavior of bSBbS triblock copolymers containing 50 wt % poly(*p-tert*-butylstyrene).

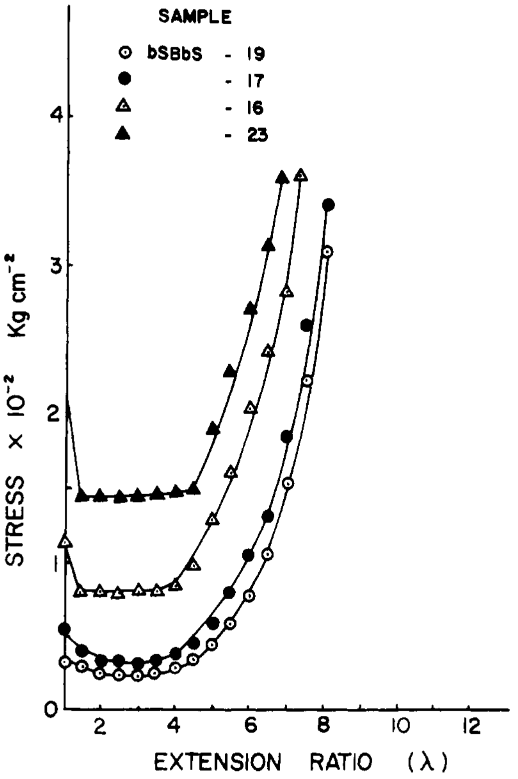

**Figure 5.** Stress-strain behavior of bSBbS triblocks containing 60 and 70 wt % poly(*p-tert*-butylstyrene).

Table IV
Tensile Properties of SBS and bSBS Triblock Copolymers

| Sample[a] | $\overline{M}_n \times 10^{-4}$, g mol$^{-1}$ | $\overline{DP}_n$[b] poly(*p-tert*-butylstyrene) segment | $\overline{DP}$[b] polystyrene segment | Tensile strength $\sigma_b$, kg/cm$^2$ | Extension at break ($\lambda_b$) |
|---|---|---|---|---|---|
| bSBS-1 | 14.3 ± 5% | 89 | 136 | 34 ± 2 | ~19 |
| bSBS-2 | 14.8 ± 4% | 111 | 114 | 139 ± 21 | 13.0 ± 0.4 |
| bSBbS-6 | 15.4 | 96 | | 1.2 ± 0.2 | 5.1 ± 0.4 |
| SBS-20[c] | 13.6 | | 132 | 127 ± 27 | 8.1 |

[a] All samples had an end segment content of 20 wt %. [b] These $\overline{DP}_n$ values have the same error limits as the measured overall $\overline{M}_n$ values. [c] From C. R. Strauss (ref 45).

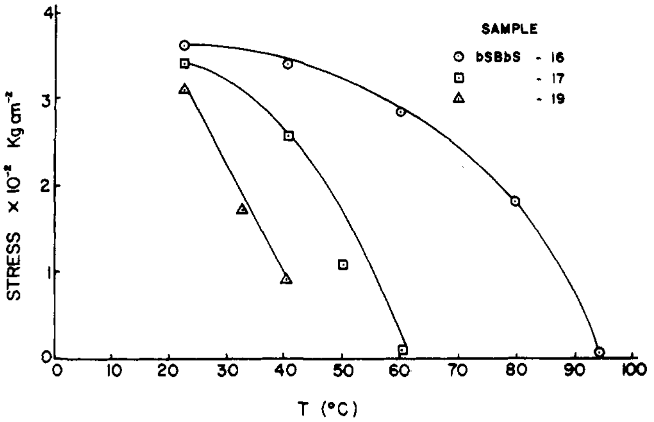

**Figure 6.** Tensile strength–temperature variations of bSBbS block copolymers.

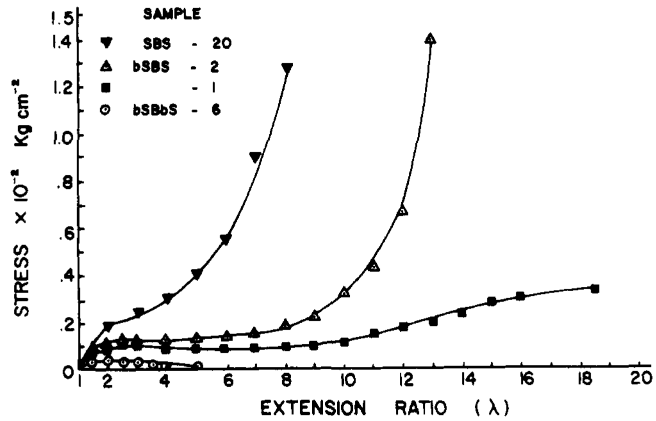

**Figure 7.** Stress–strain behavior of SBS, bSBS, and bSBbS block copolymers.

curring more rapidly than the strain rate. Characteristic of this group of triblocks is that neither the tensile strengths nor the elongations at break varied greatly. However, differences did occur in the initial stress–strain behaviors. An increase in the end-block molecular weight was accompanied by a significant increase in the yield stress.

When one considers those triblocks having up to and including 50 wt % end block, then the data of Table III indicate that, with increasing end-block length, essentially a corresponding increase in tensile strength is obtained. Yet, for the triblocks having 60 and 70 wt % of poly(*p-tert*-butylstyrene) the same trend was not followed. This difference is not unexpected, since at these high end block compositions the morphology is most likely that of a continuous plastic phase with dispersed rubbery domains, whereas, below 50 wt % composition the plastic domains are dispersed within the rubbery matrix. The fact that, above what is believed to be minimal molecular weight range (1.5–2.0 × $10^4$ g mol$^{-1}$) for the end block, the tensile strength varies according to the length of the end block strongly suggests that a degree of phase blending is occurring between polybutadiene and poly(*p-tert*-butylstyrene). It has been reported in the literature that, once above a minimum end-block size for SIS triblock, increasing the polystyrene content did not affect the tensile strength.[43] Yet, with SBS triblock, the tensile strength increased with increasing end-block length. This difference had been attributed to the fact that polystyrene is more compatible with polybutadiene than with polyisoprene.

Figure 6 shows the effect of temperature upon the tensile strength for those triblocks containing 60 wt % poly(*p-tert*-butylstyrene). It can readily be seen that only with the highest molecular weight does the strength remain high over an extended temperature range. For the lowest molecular weight triblock the tensile strength falls rapidly with increasing temperature. Strauss[45] has reported a limiting temperature of 65 °C for an SBS triblock of comparable molecular weight but having only a 40 wt % polystyrene charge.

In summation, although poly(*p-tert*-butylstyrene) has a favorable glass-transition temperature, the higher degree of compatibility of the blocks affects the mechanical properties. Thus, in order to achieve significant tensile strength, it was necessary to synthesize triblocks of either higher overall molecular weight or higher weight percent poly(*p-tert*-butylstyrene), as compared to triblocks having polystyrene end segments.

**bSBS Triblock Copolymers.** Morton[43] has reported the enhancement of tensile strength for SBS triblocks when the copolymers were solution blended with poly($\alpha$-methylstyrene) homopolymer. It was found that reinforcement of strength was optimized when the blended homopolymer and the end block both possessed the same molecular weights.

These results suggested the possibility of using polystyrene as a reinforcement agent for the weaker members of the poly(*p-tert*-butylstyrene) triblock series. However, instead of mechanically blending polystyrene with the triblocks, ABC triblocks were synthesized. They possessed poly(*p-tert*-butylstyrene) as one end block (A) and polystyrene as the other end block (C). Two ABC triblocks having similar overall molecular weights and the same weight percent of total thermoplastic content were synthesized. However, these triblocks differed in that one possessed end blocks of similar molecular weights while the other had end blocks of similar degree of polymerization.

Table IV lists the triblocks synthesized and their tensile strengths, while Figure 7 shows their stress–strain behavior. For comparison purposes the data also include a triblock having only poly(*p-tert*-butylstyrene) as end blocks and one having polystyrene end blocks. It is of interest to note that the bSBS triblock having end blocks of the same degree of polymerization exhibits a tensile strength which is comparable to that of the SBS triblock material.

It appears that reinforcement occurs when the degrees of polymerization are similar. However, implicit in this conclusion is that poly(*p-tert*-butylstyrene) and polystyrene are

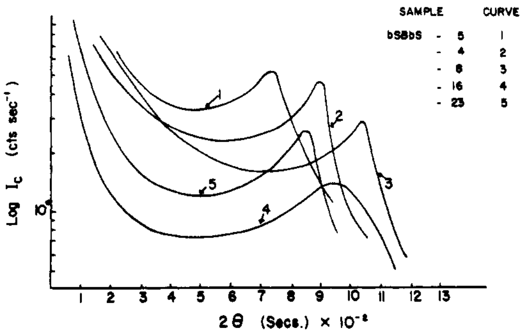

**Figure 8.** Small-angle x-ray scattering of bSBbS copolymers of varying composition.

mutually compatible. Theoretical considerations of microphase separation in block copolymers have been presented by Krause.[46-48] Parameters considered included block molecular weights, number of blocks per chain, and the interaction parameters between the homopolymers. The results show that covalent bonding in a block copolymer has a significant effect in solubilizing its segments.

Another factor which should be considered is that the molecular weights of the poly(*p-tert*-butylstyrene) end blocks are within range of an apparent critical molecular weight with regard to domain formation. Hence, it is quite possible that the bSBS triblock possessing the greatest strength does not represent a reinforcement phenomenon but rather a three-phase system consisting of separate domains of poly(*p-tert*-butylstyrene) and polystyrene dispersed within a rubbery matrix. In other words, for this triblock, the poly(*p-tert*-butylstyrene) is possibly of sufficient molecular weight to ensure formation of poly(*p-tert*-butylstyrene) domains capable of absorbing stress.

**Glass Transition Temperature Measurements.** As has been indicated above, stress–strain measurements suggest a degree of compatibility between poly(*p-tert*-butylstyrene) and polybutadiene. Hence, it was of interest to determine the number of glass-transition temperatures that might be detected in those triblocks having significant strengths. If multiple transitions could be discerned, this would help to substantiate the conclusion drawn from the stress–strain measurements, as well as to offer some insight into the morphology of the triblocks.

On the basis of the results obtained with the Perkin-Elmer differential scanning calorimeter, multiple transitions could neither be verified nor ruled out. It was difficult to determine where exactly the slope of the recorded heat capacity curve was changing. Furthermore, reproducibility left much to be desired. Increasing instrument sensitivity only resulted in more erratic responses. It appears that some other means should be used if meaningful transitions are to be observed.

In contrast to our results, Toporowski and Roovers[49] were successful in detecting glass transitions ranging from −7.1 to 98.5 °C for a series of *low* molecular weight ($<2.3 \times 10^4$ g mol$^{-1}$) SI and SIS block copolymers. Their results indicated the existence of a single phase in some of their samples.

**Small-Angle X-Ray Scattering.** A study of the small-angle x-ray scattering behavior of the higher molecular weight triblocks of poly(*p-tert*-butylstyrene–butadiene–*p-tert*-butylstyrene) was carried out. The triblocks were in the form of films cast from benzene–heptane (9:1, v/v) solutions. The vacuum dried films were used without any further treatment, such as annealing.

For heterophase polymers such as these, the intensity of the x-ray scattering peaks is dependent upon the electron density difference between the different microphases. Hence it is obvious that the degree of phase separation will affect the scattering intensity. One very apparent feature of the scattering behavior was found to be the relatively low intensity of x-ray scattering. A maximum intensity of only five counts per second was obtained for the triblock containing 30 wt % poly(*p-tert*-butylstyrene). The other triblock scattering intensities were found to be lower.

**Table V**
**X-Ray Data for bSBbS Block Copolymers**

| Sample | Copolymer segment $M_n \times 10^{-4}$, g mol$^{-1}$ | Wt % (end block) | Bragg spacing, Å |
|---|---|---|---|
| bSBbS-5 | 2.7–10.9–2.7 | 33 | 441 |
| bSBbS-4 | 3.1–8.0–3.1 | 44 | 349 |
| bSBbS-8 | 3.1–6.2–3.1 | 50 | 302 |
| bSBbS-22 | 4.1–8.2–4.1 | 50 | 402 |
| bSBbS-16 | 4.6–5.5–4.6 | 63 | 331 |
| bSBbS-23 | 5.5–3.8–5.5 | 74 | 374 |

These low intensities were most likely caused by phase blending. This effect would tend to diffuse any electron density difference between poly(*p-tert*-butylstyrene) and polybutadiene. On the other hand, poly(*p-tert*-butylstyrene) having a large aliphatic butyl group per polymer repeat unit may not have an electron density sufficiently different from that of polybutadiene to give higher intensities, such as have been encountered in the x-ray scattering of triblocks of polystyrene and polybutadiene.[20,21,50,51] The electron densities expressed as mole of electron per cubic centimeter[52] were calculated for polystyrene, polybutadiene, and poly(*p-tert*-butylstyrene) and were found to be 0.565, 0.496, and 0.523, respectively. These values are at best approximations, since in their calculation it was necessary to use reported polymer densities, which can vary. Nevertheless, the closeness in value for the electron densities of poly(*p-tert*-butylstyrene) and polybutadiene suggests a probable cause for the relatively low intensity of scattering for these triblocks, especially since the intensity of x-ray scattering at a particular angle is proportional to the square of the difference between the electron densities of the separate phases.

Figure 8 shows the respective scattering curves for the triblocks studied. These were obtained by smoothing out the original point scattered curves. The experimental points which were obtained at relatively short exposure time (about 3 min for each point) were found to be scattered to such an extent that only one major peak could be discerned for each triblock studied. Therefore, lesser peaks associated with probable lattice dimensions or domain sizes could not be determined with any degree of certainty. Thus, having only one peak for each scattering pattern, only the main Bragg spacing (i.e., the distance between centers of nearest neighboring domains) could be obtained.

Table V lists those triblocks whose x-ray scatterings have been determined together with their respective Bragg spacings. The Bragg distances were computed from the familiar Bragg equation[53] which for low angles reduces to:

$$D = \lambda/2\theta$$

where $D$ is the spacing, $\lambda$ is the wavelength of radiation used (1.54 Å), and $2\theta$ is the angle expressed in radians at which the major peak appears.

With increasing composition of poly(*p-tert*-butylstyrene) one would expect morphological changes to occur. This reasoning is based upon an analogy to the reported morphological changes that occur with increasing polystyrene content for block copolymers of polystyrene and polybutadiene.[50,53-55] Hence, at 30 and 40 wt % of poly(*p-tert*-butylstyrene), there most likely are plastic domains within a rubbery matrix, while at the 60 and 70% levels rubbery domains are dispersed within

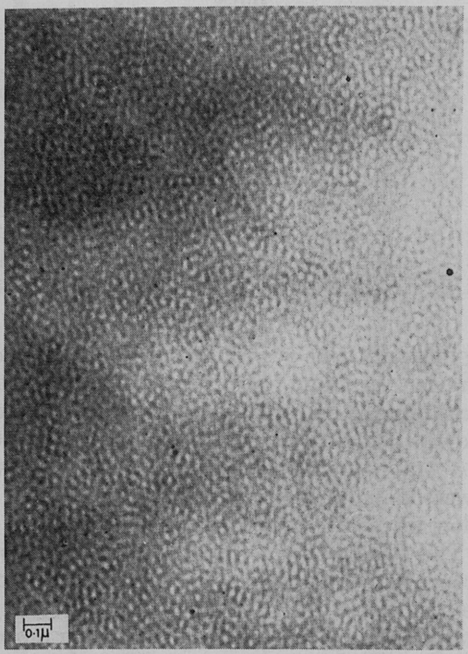

**Figure 9.** Electron micrograph of bSBS-1 block copolymer.

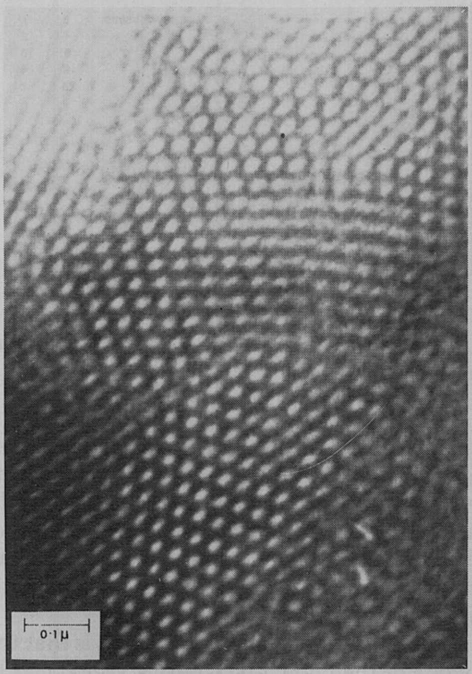

**Figure 10.** Electron micrograph of bSBS-2 block copolymer. Domain diameter equal to 235 (±15) Å. The nearest interdomain distance is 435 Å and the next nearest interdomain distance is 745 Å.

a continuous plastic matrix. The Bragg spacings for the 74 and 63 poly(*p-tert*-butylstyrene) wt % levels approach in value those of the 33 and 44 wt % samples, respectively. This suggests that the morphologies of the 44 and 63 wt % material are similar, as are those of the 33 and 74 wt % samples, except insofar as has been mentioned above; there would be an inversion in the composition of the microphases.

When the composition remains constant as for the bSBbS-8 and bSBbS-22 triblocks, it would be expected that an increase in overall molecular weight would lead to an increase in interdomain distances. It was found that the peak for the higher molecular weight sample, bSBbS-22, shifted to a lower angle and that the Bragg spacing increased by 100 Å. Unlike the other triblock copolymers where the Bragg spacings showed a less than $M^{1/2}$ dependency, the two samples where composition was nearly constant apparently show Bragg spacings which are directly proportional to overall molecular weight.

In conclusion, the x-ray scattering data indicate some phase separation in these samples, but the lack of detail in the scattering curves seemingly shows that phase blending is also present in these bSBbS samples.

**Electron Microscopy.** The morphology of some of the block copolymers synthesized in this work was examined by transmission electron microscopy. Without exception, the bSBbS block copolymers failed to reveal the presence of discrete, i.e., spherical, cylindrical, or lamellar-like, domains of either component. The lack of well-defined phase-separated domains in the bSBbS block copolymers serves to fortify the previous conclusions pertaining to morphology drawn from the stress–strain properties and small-angle x-ray scattering behavior of these materials. This lack of domain definition was observed in all of the microtomed samples cut at three different angles to the plane of the cast films of the bSBbS block copolymers.

The two ABC block copolymers containing end segments of poly(*p-tert*-butylstyrene) and polystyrene were also examined by electron microscopy. Figure 9 is a micrograph of sample bSBS-1. This micrograph can be interpreted as indicating extensive phase blending of the dissimilar end segments with the polybutadiene center segment. By contrast, for example, an SBS material containing 30 wt % polystyrene with relatively low terminal segment molecular weights ($\overline{M}_n = 7.5 \times 10^3$ g mol$^{-1}$) was found[21,56] to show more pronounced phase separation than does the bSBbS-1 sample. The relatively low tensile strength of this sample can also be taken as evidence for the lack of reasonably well-segregated phases.

However, an examination of the bSBS-2 block copolymer revealed the existence of reasonably discrete, well-defined spherical domains (Figure 10), domains which apparently were a blend of the two end segments. The dramatic change in the morphology in the bBSB materials in going from a copolymer (bSBS-1) with end segments of nearly equal molecular weight to one (bSBS-2) where the end segments possess equivalent degrees of polymerization is unexpected and, to our knowledge, has not been predicted theoretically. This finding is even all the more surprising when one considers that the weight percent of poly(*p-tert*-butylstyrene) is higher in the bSBS-2 sample than it is in the bSBS-1 material. Nonetheless, this latter triblock exhibits reasonably well-defined end segment domain formation, a feature which the tensile strength tends to suggest.

An analysis of the domain diameters and inter-domain distances indicates the presence of spherical polystyrene–poly(*p-tert*-butylstyrene) blended domains arranged in a cubic lattice, an arrangement reminiscent of the domain arrangements observed in other linear[57] and star-shaped[4] block copolymers. The scatter in the values for the domain diameter precludes an accurate determination of the type of cubic lattice present in this sample.

It should be noted that other ABC block copolymers have been synthesized and examined.[58–60] In two cases the dissimilar end segments, polystyrene–poly(α-methylstyrene)[58] and polystyrene–poly(2-vinylpyridine),[60] were found to coexist in the domains formed. The apparent compatibility between the poly(*p-tert*-butylstyrene) and polystyrene is reminiscent of that observed[37–41] in polystyrene–poly(α-methylstyrene) block copolymers. We have noted (via DSC measurements) that 50/50 wt % blends of poly(*p-tert*-butylstyrene) and polystyrene homopolymers exhibit, at least to a certain extent, two-phase behavior, a situation similar to that reported[37,38] for blends of polystyrene and poly($\alpha$-methylstyrene). Thus the bSBS-2 sample seems to be an example of a three-component system wherein incipient compatibility between two components, poly(*p-tert*-butylstyrene) and polybutadiene, has been minimized by enhanced compatibility between the two end segments. This was not anticipated based on the solubility parameters and apparently shows the importance of specific interactions. However, a comparison between samples shows that the formation of the relatively well-defined end block domains found in sample bSBS-2 is apparently dependent upon the respective chain lengths of the end segments. Thus it may be that the higher molecular weight of the poly(*p-tert*-butylstyrene) segment of the bSBS-2 sample is sufficient to lead to enhanced incompatibility between this end segment and polybutadiene. Nonetheless, it is somewhat surprising that equalization of the end segment degrees of polymerization should bring about such a profound alteration in the sample morphology.

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