Synthesis and Properties of Block Copolymers. 3. Polystyrene–Polydiene Star Block Copolymers

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ABSTRACT: Polystyrene–polydiene star block copolymers containing up to 29 arms have been synthesized by anionic polymerization using divinylbenzene as the linking agent. It was found that the tensile strength of these star block copolymers was superior to linear, three- and four-armed block copolymers of equivalent composition and segment molecular weights. An examination of the rheology of these star block copolymers in the melt state revealed that viscosity is *independent* of the degree of branching and depends only on the molecular weight of the diblock copolymer arm. Identical results were obtained for the intrinsic viscosities in the good solvent tetrahydrofuran. It was also observed that gel permeation chromatography can detect differences in the degree of branching (up to at least 15 arms) for a series of star block copolymers where arm molecular weight and composition were held nearly constant.

Elastomeric SDS block copolymers, where S is a polystyrene block and D is a polydiene block, are materials which exhibit high elasticity, excellent tensile strengths, and thermoplastic behavior. Perhaps the most striking characteristic of these copolymers is their unusually high tensile strength. Tensile strengths of 300 kg cm^{-2} at elongations of more than 1000% are exhibited at ambient temperature. The properties cited are attributed to the fact that a two-phase system is formed, due to the incompatibility of the A and B blocks. The aggregation of the minority component, polystyrene, results in the formation of small domains which can be spherical, cylindrical, or lamellar in shape.

The termination-free system of homogeneous anionic polymerization is known to lead to the preparation of well-defined linear block copolymers.[2–4] This polymerization system also lends itself to the preparation of star-shaped homopolymers.[5–32] Thus far, two proven methods have been used: (1) the reaction of a polyfunctional electrophile species with monocarbanionic chains,[5–24] and (2) the application of an anionic polymerization of styrene followed by the addition of divinylbenzene.[25–32] The polymerization of this difunctional monomer yields a microgel nodule which then serves as the nucleus of the polystyrene star.

A third reported method involves the use of either *n*-butyllithium[33] or short-chain polystyryllithium[34] and divinylbenzene to form polystyrene stars. However, the validity and usefulness of this method for the preparation of star polymers containing a well-defined number of uniform arms of known molecular weight remains to be demonstrated. Buchard and co-workers[33,34] reported only weight-average molecular weights for their polystyrene stars. It was shown,[5] though, some time ago that the appropriate molecular weight for the determination of the number of arms in a star polymer is via the ratio of the number-average molecular weight of the star to that of the arm. Also, Buchard and co-workers[33,34] did not report any information regarding the polydispersity of their polystyrene stars.

Parenthetically, we have observed that neither the reaction of *n*-butyllithium or *sec*-butyllithium with *m*-divinylbenzene leads to the formation of a soluble, multifunctional initiator. Furthermore, the species formed by reacting short-chain polystyryllithium and *m*-divinylbenzene was found to yield polydisperse polybutadiene and polystyrene. It was apparent that only part of the available carbon–lithium species at the center of this multifunctional initiator was capable of initiating these monomers. This slow, and incomplete, initiation step is probably due to steric hinderance in the polydivinylbenzene nodule.

The aim of this work was to prepare star block copolymers and to examine their mechanical properties, rheology, and morphology. The linking agent of choice for the preparation of star block copolymers having more than four arms was divinylbenzene while silicon tetrachloride was used for the preparation of the three- and four-armed materials. Both types of linking agents led to the preparation of star block copolymers virtually free of diblock impurities and possessing a well-defined number of branches.

Experimental Section

The anionic polymerizations involved the rigorous purification of monomers, solvents, linking agents, and reactors. All monomer, solvent, and linking agent purifications were conducted under high vacuum (10^{-6} Torr) using procedures described elsewhere.[35] The initiator was sublimed *sec*-butyllithium.

Divinylbenzene Purification. The divinylbenzene (Chemical Samples and Monomer Polymer Laboratories) was purified in a manner similar to styrene.[35] The neat divinylbenzene was stirred, on the vacuum line, over finely ground calcium hydride for at least 24 h with periodic degassing. Following this treatment, the divinylbenzene was distilled into a flask containing the hydrocarbon soluble[36] *n*-butyl- and *sec*-butylmagnesium. The use of this organometallic as a purifying agent for styrene has facilitated the preparation[37,38] of near-monodisperse polystyrenes with molecular weights as high as 4.5×10^7 g mol^{-1}.

The divinylbenzene was exposed to the dialkylmagnesium compound until a bright yellow color developed. The onset of this color with styrene is indicative of the completeness of the purging step. The divinylbenzene was then collected via distillation, diluted to a 10% (v/v) solution in benzene or *n*-hexane, and stored at approximately −10 °C until use. In this fashion, the purified divinylbenzene could be kept at least 3 months without polymerization occurring.

Silicon tetrachloride was distilled on the vacuum line and diluted with benzene to yield approximately a 10% solution. The concentration was determined by titration with standardized NaOH solution.

Two types of divinylbenzene were used in this work. Initially, *m*-divinylbenzene was used as the linking agent. Gas chromatography analysis revealed that this material was 95% divinylbenzene and that 92–93% of the divinylbenzene was the meta isomer. Later, divinylbenzene consisting of a mixture of the meta and para isomers was used. This divinylbenzene was shown to be 93% pure and the meta/para isomer ratio was nearly 2/1. Both types of divinylbenzene were found to be equally effective in the linking of the diblock chains. The major "impurity" in both types of divinylbenzene was ethylvinylbenzene.

Star Block Copolymer Synthesis. The synthesis of the linear triblock copolymers and the linear arms of the star block copolymers followed procedures outlined elsewhere.[35] Following the completion of the two-stage sequential polymerization of styrene and the diene for the diblock copolymers, a small amount of the benzene solution was removed from the reactor. The polymer was isolated, after termination with degassed methanol, and used for molecular weight characterization.

The linking agent was then added to the remaining diblock copolymer solution. Initially, the linking reaction was carried out at 25 °C for 24 h. Later, though, the temperature of this step was increased

to 50 °C. At this temperature the linking reaction is complete in 30 min when divinylbenzene was used. Final star block copolymer concentrations ranged from 20 to 40%.

It should be noted that the diene polymerization should be carried out to at least 95% conversion when divinylbenzene is the linking agent. The presence of too much residual diene will lead to the formation of gelled or very high viscosity products. It has recently been claimed[39] that soluble, branched triblock copolymers containing polystyrene and a polydiene can be synthesized by adding divinylbenzene concurrently with the diene in this anionic polymerization. However, our experience with this procedure has shown that gelation occurs when the DVB/RLi ratio is 3 or greater. This, of course, is the result of the fact that divinylbenzene can copolymerize with the diene.

Following the completion of the linking reaction, the polymerization was terminated, antioxidant added, and the polymer isolated by freeze drying for at least 48 h.

Gel Permeation Chromatography. The Waters Ana-Prep instrument was used with seven 4-ft. Styragel columns having porosities ranging from 2×10^3 to 5×10^6 Å. The experimental characteristics of this seven-column set have been reported elsewhere.[21] Tetrahydrofuran was the carrier solvent and the detector was the Waters differential refractometer. Solution concentrations were ¼% (w/v) and less. A 1 ml min^{-1} flow rate was used. Full loop (2 ml) injections were made. The instrument was equipped with a 5-ml syphon. The relative amounts of star block copolymer and diblock copolymer in the sample were determined by measurement of the relative areas of each species in the respective gel permeation chromatograph. The polystyrene homopolymer content in these block copolymers was less than 1 wt %.

The calibration of the seven-column Styragel set was accomplished using 19 polystyrene standards. These samples included those from Pressure Chemicals, Waters Associates, the National Bureau of Standards, and from this laboratory. The plot of log $[[\eta]\overline{M}_w]$ vs. elution count was generated by running each polystyrene standard at three concentrations, ¼, ⅛, and 1/16% (w/v), and then determining the peak elution count by extrapolating to zero concentration. The peak elution count of each linear and branched block copolymer was determined in the same fashion. This was done since it was noted that the slopes of the peak elution count vs. concentration plots for some star block copolymers were different even though the "zero concentration" elution counts were similar.

Number-Average Molecular Weights. The values of $\overline{M}_n$ were determined in toluene solutions at 37 °C. The Hewlett-Packard osmometers (Models 502 and 503) were used with S and S-08 membranes. For each sample, four concentrations of 10, 7.5, 5, and 2.5 g/l. were prepared. The number-average molecular weights were determined by the usual $(\pi/c)^{0.5}$ vs. c plots. Prior to any measurements, the osmometers were checked with solutions of the National Bureau of Standards 705 polystyrene. The standard deviation in the molecular weights of the NBS 705 was slightly less than 3%.

It should be noted that six of the M_n values reported in this paper are greater than 5×10^5 g/mol. The relative insensitivity of membrane osmometry to samples with molecular weights this high is well recognized. However, this was partially compensated for by the fact that the star block copolymers exhibit surprisingly low viscosities. Hence, toluene solutions of 10 g/l. could be used with no difficulty in these high-speed osmometers.

Dilute-Solution Viscosity Measurements. Intrinsic viscosity measurements were run in tetrahydrofuran at 25 °C. A commercial low shear capillary viscometer was used. The shear dependence of $[\eta]$ was checked for the star block copolymers and found to be negligible. The temperature dependence of $[\eta]$ was checked in toluene for four polystyrene–polyisoprene star block copolymers. The values of $[\eta]$ were found to be independent of temperature over the range of 25 to 55 °C.

Glass Transition Temperature Measurements. A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used to determine the glass transition temperature of the polydiene component in the star block copolymers. The instrument was calibrated on the melting temperatures of indium (156 °C) and lead (327 °C) for the high-temperature range while n-dodecane (−9.6 °C) and n-octane (−56.5 °C) were used for the low-temperature range. The glass transition temperature for the polyisoprene was −64 ± 2 °C while that of the polybutadiene was −93 ± 3 °C.

Microstructure and Polystyrene Composition Determinations. These parameters were determined from carbon tetrachloride solutions by use of the HR 300 Varian Associates NMR spectrometer. The polyisoprene microstructure was determined using Chen's[40] method while that of the polybutadiene utilized the technique of Santee et al.[41] The polyisoprene segments contained 70% cis 1,4, 24% trans 1,4, and 6% 3,4 addition while the polybutadiene contained 35% cis 1,4, 57% trans 1,4, and 8% 1,2 addition.

Dynamic Viscosity Measurements. The storage and loss moduli of both linear and star block copolymers were determined by the use of the Rheometrics Mechanical Spectrometer.[42] The temperature range covered was from 80 to 150 °C. The parameters of G' and G'' were determined using the eccentric rotating disks.

Electron Microscopy. The electron microscopy was performed on stained, ~400 Å thick microtomed films with the aid of a JEOL 120U transmission electron microscope. Microtoming was done with a diamond knife at liquid nitrogen temperature. Following microtoming, the films were exposed to OsO_4 vapor at room temperature.

Solvent Casting. The films of the linear and star block copolymers were prepared from solutions containing 10% (w/v) polymer in either 9:1 mixtures of benzene and heptane or tetrahydrofuran and methyl ethyl ketone. The films were formed over stretched cellophane. The solvent was allowed to evaporate slowly at room temperature for a period of 5 to 7 days. The cast films were then dried under vacuum for 1 week at room temperature.

Molded Films. The molding conditions used were to "premold" the polymer for 10 min at 140 °C at about 4000 psi platen pressure between sheets of uncoated cellophane. The samples were then remolded at the same temperature at a pressure of 20 000 psi. Cooling was accomplished under pressure at a rate of about 1 °C/min.

Stress–Strain Measurements. The star block copolymer films were 0.02 to 0.03 cm thick and were used in the form of a microdumbbell for the stress–strain measurements. An Instron-type tensile tester with a crosshead speed of 5 cm/min was used at room temperature. Five specimens were measured for each sample. The data obtained were then averaged using the results from the five specimens.

For the low and high temperature studies, the microdumbbells were stretched in an Instron environmental chamber. The temperature range used was −40 to 85 °C.

Results and Discussion

Star Block Copolymer Synthesis. Homogeneous anionic polymerization was used to prepare the polystyrene–polydienyllithium diblock copolymers which were subsequently used in the linking reactions to form the star block copolymers. Purified[43–45] *sec*-butyllithium was used as the initiator since it is recognized[45,46] that this organolithium reacts rapidly with styrene in hydrocarbon solvents. Following the completion of the diblock synthesis, the linking agent was added.

The formation of the three- and four-armed block copolymers containing either polybutadiene or polyisoprene was accomplished with silicon tetrachloride. This linking agent has been observed[21] to result in incomplete linking when a stoichiometric amount is reacted with polyisoprenyllithium. In the main, only unlinked diblock and three-armed branched polymer are obtained under these conditions. However, the butadienyllithium chain end will react in a virtually complete fashion with silicon tetrachloride.[9,14,21] Hence, the synthesis of a four-armed star block copolymer was facilitated by adding several butadiene units to the isoprenyllithium chain end prior to the addition of the silicon tetrachloride. The use of this procedure has been reported elsewhere.[47,48] The effectiveness of this procedure is shown in Figure 1 which is a gel permeation chromatogram of a four-armed star block copolymer.

Unlike the use of a polyfunctional halogenated linking agent which can only lead to star molecules with a number of branches equal to the functionality of the linking agent, the use of divinylbenzene resulted in the formation of star block copolymers possessing up to 29 branches. The polymerization of the divinylbenzene led to the formation of small polydivinylbenzene nuclei in the star block copolymers. In the case of the linking of poly(styryl)lithium with divinylbenzene, the average degree of branching was found[27] to be dependent on the ratio of divinylbenzene to active chain ends and on the molecular weight of the linear precursor. Similar findings were made in this work involving the dienyllithium chain ends.

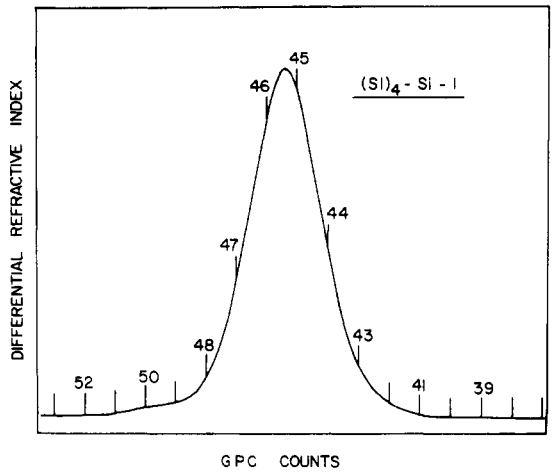

Figure 1. Gel permeation chromatogram of $(SI)_4$-Si-1 block copolymer.

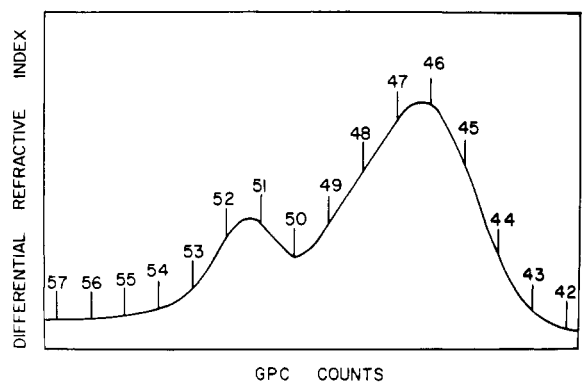

Figure 2. Gel permeation chromatogram of $(SI)_x$-DVB-2 block copolymer.

Initially, it was thought that a polar cosolvent, e.g., tetrahydrofuran, would have to be utilized in order to promote the reaction between the dienyllithium chain end and divinylbenzene. This conclusion was based on the fact that a dienyllithium species and styrene are known[49-51] to react slowly relative to the homopropagation rate of styrene. Hence it was assumed, by analogy, that lacking a polar promoter divinylbenzene might fail to react with all of the available dienyllithium chain ends. This could then result in diblock present at the end of the linking reaction.

Figure 2 is a representative gel permeation chromatogram of a star block copolymer synthesized by the use of tetrahydrofuran as the polar cosolvent. It is apparent that this material contained a substantial amount of unlinked diblock copolymer. This result is similar to what was reported[26,27] for the linking of poly(styryl)lithium via *m*-divinylbenzene in tetrahydrofuran. Later work[52] in these laboratories revealed that nearly quantitative linking can be achieved with the divinylbenzene–tetrahydrofuran system if the divinylbenzene solution is slowly added with *rapid* mixing.

The linking of the diblock chains by divinylbenzene was found to proceed to virtual completion in benzene in the absence of a polar cosolvent. Figure 3 is a chromatogram of a star block copolymer possessing an average number of arms of 15. Additional chromatograms of these star block copolymers are presented elsewhere.[53,54] It has been observed in this work that divinylbenzene reacts rapidly with dienyllithium chain ends in benzene within the temperature range of 25–60 °C. This behavior was not expected based on the reported[49-51] reactivity of styrene with dienyllithium species. Rempp, though,

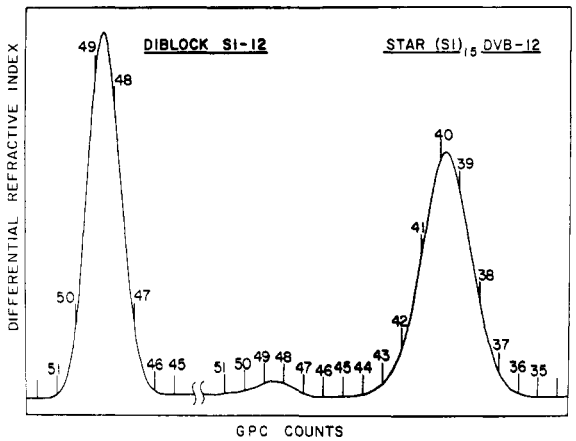

Figure 3. Gel permeation chromatogram of $(SI)_{15}$-DVB-12 block copolymer.

has reported[55,56] that *m*-divinylbenzene will react with the active chain end of 2-vinylpyridine. Since styrene does not react in a similar fashion, this indicates that the electron affinity of divinylbenzene is greater than that of styrene.

Table I contains the characterization data of the linear and star block copolymers synthesized in this work. The weight-average molecular weights have been determined by the use of the GPC universal calibration approach.[57,58] As can be seen, the $\overline{M}_n$ and $\overline{M}_w$ values are virtually the same for the linear and star block copolymers containing three or four arms. The divinylbenzene linked stars however possess, in the main, $\overline{M}_w$ values larger than their number-average molecular weights. This, of course, is to be expected given the random nature of the linking reaction used.

However, it can be seen that anomalous $\overline{M}_w$ values were obtained for the $(SI)_9$-DVB-15, $(SB)_{15}$-DVB-5, $(SB)_{29}$-DVB-4, and $(SIS)_{22}$-DVB-1 star block copolymers. These results can be tentatively explained by the fact that the universal calibration approach cannot be applied[59-61] for "highly" branched polymers. It should also be noted that these star block copolymers exhibit unsuspected intrinsic viscosity results; i.e., at constant arm molecular weight and composition, the intrinsic viscosity is apparently *independent* of the degree of branching. This feature will be discussed later in this paper. Thus, in view of these anomalies, the $\overline{M}_w$ values recorded in Table I for the more extensively branched materials should be viewed with some skepticism.

However, the data recorded in Table I does show that the divinylbenzene linked block copolymers can be prepared with a varying number of arms ranging between at least 5 to 29 branches per star. Furthermore, the linking reaction is sufficiently effective so as to lead to virtually complete linking.

Stress-Strain Properties of Star Block Copolymers. A prominent feature of the elastic behavior of the elastomeric block copolymers is their high tensile strength. Two plausible theories have advanced mechanisms to account for the enhancement of the tensile strength of elastomer networks, and either or both may apply to elastomeric block copolymers. One theory[62] explains the enhancement of the tensile strength of reinforced elastomers in terms of the redistribution of stresses by the filter particle after one or more elastomer chains have broken. The main role of a filler particle is thus to inhibit individual chain breakages from initiating catastrophic rupture. This explanation requires filler particles to be firmly attached to the elastomer network. The polystyrene domains can then act as stress absorbers,[63,64] whereby stresses upon the elastomeric segments are transmitted to the plastic domains which have the capacity to yield and distort, thus absorbing energy and delaying rupture.

Table I
Molecular Characterization of Linear and Star Block Copolymers

Sample[a]	Wt % polystyrene	$\overline{M}_n$ (arm),[b] 10^{-3} g mol^{-1}	$\overline{M}_n$,[b] 10^{-3} g mol^{-1}	$\overline{M}_w$,[c] 10^{-3} g mol^{-1}	DVB/RLi	Wt % unlinked diblock copolymer
SIS-1	32		127	130		
SIS-2	31		104	104		
SIS-13	29		92	95		
$(SI)_3$-Si-12-1	29	73	230	240		0
$(SI)_3$-Si-15-1	29	77	222	225		0
$(SI)_3$-Si-17	37	51	146	150		0
$(SI)_4$-Si-1	29	62	240	250		
$(SI)_5$-DVB-11	34	70	360	770	3.0	2
$(SI)_6$-DVB-6	31	51	305	650	3.2	2
$(SI)_6$-DVB-8	26	78	485	1000	4.4	2
$(SI)_7$-DVB-17	27	54	366	677	4.5	0
$(SI)_7$-DVB-5-1	32	72	500	1200	12.6	9[d]
$(SI)_7$-DVB-3	32	66	450	643	3.3	3
$(SI)_9$-DVB-4	27	70	630	895	6.1	3
$(SI)_9$-DVB-15	21	127	1100	1000	6.0	2
$(SI)_{15}$-DVB-12	30	71	1100	1500	8.0	2
SBS-1	30		80	82		
$(SB)_4$-Si-1	43	48	190	200		3
$(SB)_6$-DVB-1	30	30	180	280	4.0	1
$(SB)_{29}$-DVB-4	26	30	870	465	11.0	2
$(SB)_{15}$-DVB-5	24	20	300	275	7.0	1
$(SB)_6$-DVB-6	43	21	120	240	4.0	1
$(SB)_9$-DVB-7	32	14	130	190	5.0	1
$(SIS)_{22}$-DVB-1	33	80	1800	1700	13.0	0

[a] S = polystyrene; I = polyisoprene; B = polybutadiene. The number-average number of arms is given by the subscript. The number listed for each sample refers to the order in which the respective samples were made. [b] The standard deviation of the $\overline{M}_n$ values was not greater than ±5%. [c] Via the universal calibration procedure. All peak elution counts were obtained by extrapolation to zero concentration for the determination of $\overline{M}_w$ via the universal calibration procedure. [d] This star block copolymer initially contained about 23% unlinked diblock copolymer. This was probably due to an impurity in the divinylbenzene solution. Fractionation reduced the amount of diblock copolymer to the amount listed in the last column. The $\overline{M}_n$ reported for this star block copolymer is a corrected one which takes into account the diblock component.

Table II
Stress–Strain Data for Linear and Star Block Copolymers Containing Polystyrene and Polyisoprene

	Solvent cast films			Molded films		
Sample	σ_b, kg/cm^2	λ_b	True stress, (kg/cm^2) × 10^{-3}	σ_b, kg/cm^2	λ_b	True stress, (kg/cm^2) × 10^{-3}
SIS-1	340 ± 7	11.3	3.8			
SIS-2	332 ± 9	11.1	3.7	261 ± 40	11	2.9
SIS-3	345 ± 11	11.1	3.8	250 ± 30	10.9	2.7
$(SI)_3$-Si-12-1	369 ± 15	12.7	4.7	296 ± 14	11.1	3.3
$(SI)_3$-Si-15-1	384 ± 6	12.1	4.6			
$(SI)_3$-Si-17	375 ± 10	10.7	4.0			
$(SI)_4$-Si-1	380 ± 20	11.1	4.2	308 ± 15	11.2	3.5
$(SI)_6$-DVB-6	390 ± 9	10.4	4.1	372 ± 7	10.0	3.7
$(SI)_7$-DVB-8	410 ± 17	11.7	4.8	390 ± 30	11.0	4.3
$(SI)_7$-DVB-17	400 ± 15	10.4	4.2	390 ± 15	10.1	3.9
$(SI)_7$-DVB-5-1	390 ± 10	12.5	4.9			
$(SI)_7$-DVB-3	400 ± 5	10.3	4.1	390 ± 10	9.2	3.7
$(SI)_9$-DVB-4	430 ± 7	11.5	4.9	420 ± 20	10.7	4.5
$(SI)_9$-DVB-15	395 ± 10	11.3	4.5			
$(SI)_{15}$-DVB-12	376 ± 13	11.2	4.2	369 ± 3	9.0	3.3
$(SIS)_{22}$-DVB-1	405 ± 10	11.0	4.5			

[a] Cast from benzene/heptane: 9/1 (v/v). It was noted that films cast from tetrahydrofuran–methyl ethyl ketone, 9/1 (v/v), exhibited stress–strain characteristics virtually identical with those films cast from the benzene/heptane system.

The second theory[65] postulates enhanced strength if the chains in the network possess substantially the same length and are equally stressed. This can be achieved in the linear elastomeric block copolymers if the entanglement cross-links in the elastomer phase are able to redistribute uneven stresses.

The stress–strain results for a series of linear and star block copolymers containing polystyrene and polyisoprene are shown in Table II. It is apparent that the tensile strengths for both molded and solvent cast films of the star block copolymers are greater than that observed for the linear materials. This is especially pronounced for the compression molded

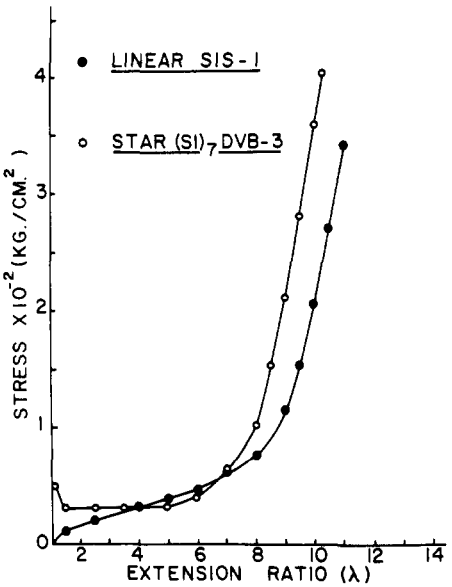

Figure 4. Stress–strain behavior of SIS-1 and $(SI)_7$-DVB-3 block copolymers.

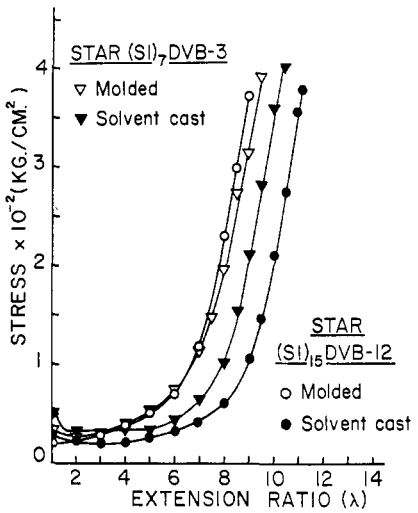

Figure 5. Stress–strain behavior of molded and solvent cast films of star block copolymers.

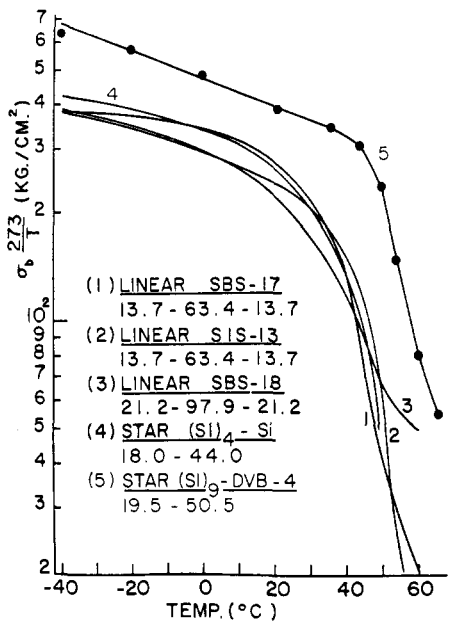

Figure 6. Effect of temperature on tensile strength of linear and star block copolymers.

films. It should be pointed out that these comparisons are drawn, for the most part, for samples of nearly equivalent composition and segment molecular weights.

An example of this comparison is shown in Figure 4 for solvent cast films. Upon elongation the linear triblock, SIS-1, of 32% polystyrene content, shows no yielding whereas the star block copolymer, $(SI)_7$-DVB-3, does. Generally, the existence of a yield point is attributed to a quasicontinuous polystyrene phase. However, an examination[66] of the morphology of annealed films of the $(SI)_7$-DVB-3 sample by electron microscopy revealed that this star block copolymer exhibited discrete, spherical polystyrene domains apparently arranged in a body centered cubic latice. This arrangement of the polystyrene domains thus appears to be similar to that observed[54] for the linear SIS-1 block copolymer. Hence, the yield point observed at low strain for the $(SI)_7$-DVB-3 sample does not appear to be due to the existence of interconnected polystyrene domains.

The data of Table II illustrate the effect of branching on both the nominal (engineering) and true stress of the linear and star block copolymers. Since the stress–strain properties of these materials are, at least in part, influenced by the extent of branching, the stress–strain behavior of these star block copolymers was examined with regard to the conditions of film formation. For the case of the linear triblock copolymers, it was found[67] that films prepared by compression molding possess noticeably lower tensile strengths than films formed by solvent casting. These differences have been taken as illustrating the difficulties involved in achieving good phase separation of the two components under molding conditions for these linear triblock copolymers.

The tensile strengths of molded and solvent cast films were thus compared. These results are recorded in Table II. It is apparent that solvent cast films of linear, three-armed and four-armed block copolymers exhibit higher tensile strengths than do their compression molded counterparts. However, the differences in tensile strengths virtually disappear for the multiarmed (six arms or more) star block copolymers. This seemingly demonstrates that moderately extensive branching can facilitate, from a kinetic standpoint, effective phase separation which can then result in the attendant formation of a more uniform and coherent polystyrene domain arrangement. Preliminary studies[66] of the morphologies of compression molded films of these star block copolymers seemingly substantiate this premise. An additional interesting feature was the observation that those star block copolymers with six or more arms could be molded into clear, strong films at temperatures as low as 120 °C whereas the linear, three- and four-armed materials required a minimum temperature of 140 °C. These combined observations can be taken as a qualitative demonstration that the melt viscosities of these multiarmed star block copolymers are surprisingly low, even though some of these star block copolymers apparently have $\overline{M}_w$ values in excess of 5×10^5 g mol^{-1}. Dynamic viscosity data for some of these star block copolymers will be presented later in this paper.

Another distinguishing feature of the multiarmed star block copolymers is the low amount of permanent set (10 to 20%) exhibited by these materials after break. This may be contrasted with values of 50 to 100% observed for the linear block copolymers.

Without exception, it has been our observation that the stress–strain behavior of the molded multiarmed block copolymers can be characterized by tensile strengths nearly

equal to those obtained from solvent cast films. However, the molded films generally break at lower elongations (λ_b) than do their solvent cast counterparts. This behavior can be seen in Figure 5. This demonstrates that the molded films of the multiarmed star block copolymers retain some "memory" of their conditions of fabrication. Nonetheless, the conditions of fabrication apparently influence the mechanical properties of these multiarmed star block copolymers to a lesser extent than is seen for the more conventional linear, three- and four-armed materials.

The temperature dependence of the tensile strength of star block copolymer $(SI)_9$-DVB-4 was compared, Figure 6, with three linear triblock copolymers and the four-armed star, $(SI)_4$-Si-1. As can be seen, the tensile strength of this nine-armed material was markedly greater than the other four block copolymers over the entire temperature range. In addition, the network of the nine-armed star was less prone to disintegrate at temperatures approaching the glass transition temperature of the polystyrene. Furthermore, the flexural modulus of the nine-armed star was found to be less than that exhibited by the other four materials when the measurement temperature approached the glass transition temperature (−64 °C) of the polyisoprene. This latter feature may presumably be due to the high segment density of polyisoprene near the center of the nine-armed star block copolymer.

The higher tensile strengths of these multiarmed star block copolymers can be ascribed to several features: to wit, a permanent cross-link site at the center of the polyisoprene chain, a more ordered and uniform arrangement of smaller polystyrene domains than is observed for the conventional triblock copolymers,[54,55,66] and the formation of polystyrene domains involving less of a two-phase interfacial region between the polystyrene domains and the polyisoprene matrix. This latter comment is based on small-angle x-ray studies[69] of these multiarmed star block copolymers.

The permanent cross-link at the center of these star block copolymers can serve to distribute the applied stress in an equitable fashion to the polystyrene domains. This effect is probably enhanced, as proposed by Case,[65] by the fact that all of the polyisoprene segments possess a near-monodisperse distribution of chain lengths.

With regard to the polystyrene domains it has been our observation[53,54] that these multiarmed star block copolymers apparently form *smaller* domains than observed for linear materials, e.g., domain diameters of 323, 203, and 280 Å have been determined for annealed films of samples SIS-1, $(SI)_6$-DVB-8, and $(SI)_9$-DVB-4. Thus, these multiarmed star block copolymers apparently possess a greater number of polystyrene domains per unit volume than comparable linear materials. This highly dispersed polystyrene component could be expected[62] to lead to an enhancement of tensile strengths. An additional point along this line is the role of the polydivinylbenzene "microgel" nucleus of the multiarmed star. For the multiarmed star block copolymers these microgel nuclei possess number-average molecular weights ranging from 2.5×10^3 g mol^{-1} for $(SI)_6$-DVB-6 to 1.6×10^4 g mol^{-1} for $(SI)_{15}$-DVB-12. Hence, the polydivinylbenzene *may* serve as a "secondary" filler particle with number-average functionalities ranging from six to fifteen. However, the contribution, if any, of the polydivinylbenzene component to the mechanical properties of these star block copolymers remains to be elucidated.

A further point which distinguishes these multiarmed star block copolymers from their linear counterparts is the observation[70] that the star block copolymers undergo, on elongation, less dewetting than the linear materials. This can be attributed to the branched architecture of the star block copolymers which allows an equitable distribution of stress throughout the network.

In addition to the foregoing rationalizations, the demonstrated "high" temperature performance of these star block copolymers may be partially dependent on the number of arms in the star block copolymer. In order that a given star molecule become "lost" to the network all polystyrene segments but one must be removed from their respective domains. Hence, a multiplicity of arms may be a prominent contributing factor as to the ability of the nine-armed star in maintaining an elastically effective network in a temperature region (ca. 65 to 85 °C) where the networks of the linear and four-armed block copolymers have disintegrated.

Morphology studies[53,54,66] carried out on some of the polyisoprene containing linear and star block copolymers of Table I have shown that the polystyrene domains in these materials are spherical and that they are apparently arranged in a body centered cubic array. It has been reported elsewhere[71–76] that unannealed solvent-cast thin films of linear and four-armed block copolymers with compositions similar to the polystyrene–polyisoprene materials in Table I contain nonspherical polystyrene domains, i.e., cylindrical or lamellar in shape. Our findings[53,54,66] on both annealed and unannealed microtomed specimens from solvent-cast films have shown that polystyrene domains in our samples are spherical. Annealing brought about a change in sample dimensions similar to those reported by Cohen and Tschoegl.[77] This change in sample dimensions was reflected by a decrease in the interdomain distances. However, annealing exerted no significant change in the size or shape of the polystyrene domains. It should be noted that the conclusions regarding polystyrene domain shape presented elsewhere[71–76] were based on electron micrographs limited to one projection of the domain arrangement. Our findings[53,54,66] are based on microtomed specimens cut in three planes from the block copolymer films. The conclusions we have reached regarding polystyrene domain shape are similar to the results of other authors[78–88] for linear block copolymers in the composition range of the linear and star block copolymers prepared in this work.

It should be recalled that the morphology of a solvent-cast film is not a true thermodynamic equilibrium morphology but that the film morphology is established at some time during the evaporation process and thus represents some solution morphology. Nonetheless, it has been our observation that the favored morphology of the polystyrene–polyisoprene block copolymers in Table I is apparently that of a body centered cubic arrangement of spherical polystyrene domains and that this morphology is achieved from a variety of solvents and solvent mixtures used to cast the films. These results are in contrast to the apparent findings[75,76] that the morphology of a linear SBS block copolymer (Kraton 1101) was markedly dependent upon the solvent system used to cast the films.

It has been recognized for some time[67,89–91] that for linear triblock copolymers, the minimum polystyrene molecular weight needed to form "coherent" domains is about 10^4 g mole^{-1}. If the molecular weights of the end segments drop below this value, a pronounced decrease in tensile strength is observed. This has been ascribed to inefficient phase separation resulting from the relatively low molecular weight of the polystyrene segments, a conclusion which has received both theoretical[89,90] and experimental verification.[67,91]

In view of this recognized lower molecular weight limit which exists for linear SDS block copolymers it was deemed of interest to examine the multiarmed block copolymers with reference to the relationship between polystyrene segment molecular weight and tensile strength. These results are presented in Table III.

An inspection of the data in Table III readily reveals that branching enables these polystyrene–polybutadiene materials with polystyrene segments with number-average molecular weights of 8000 to 9000 to exhibit surprisingly high tensile

Table III
Stress–Strain Data for Linear and Star Block Copolymers Containing Polystyrene and Polybutadiene

Sample	Polystyrene $\overline{M}_n$, 10^{-3} g mol^{-1}	Wt % polydivinyl-benzene	λ_b	σ_b,[a] kg cm^{-2}
SBS-1[b]	12		11.5	300 ± 15
SBS-PCJ-4[b]	9		10.5	140 ± 10
$(SB)_6$-DVB-1	9	6	8.3	420 ± 15
$(SB)_{29}$-DVB-4	7.8	5	8.2	300 ± 10
$(SB)_{15}$-DVB-5	5	5.5	8	30 ± 5
$(SB)_6$-DVB-6	9	4	6.7	350 ± 20
$(SB)_9$-DVB-7	4.4	8	8	35 ± 7

[a] Solvent cast films. [b] Linear block copolymers: SBS-PCJ-4 had segment molecular weights of (9.0-42-9.0) × 10^3 g mol^{-1}. This sample was synthesized by Juliano.[92]

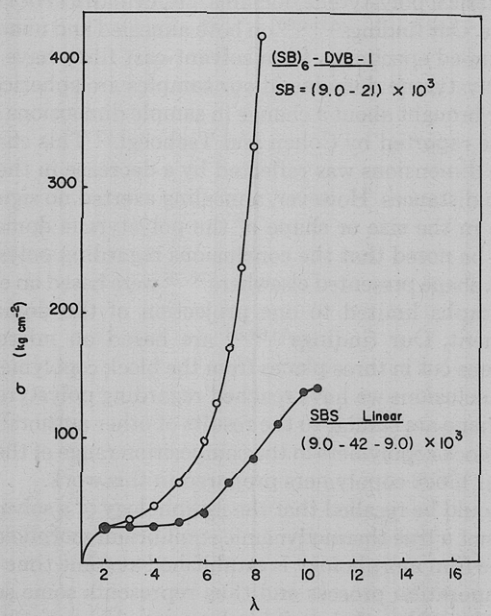

Figure 7. Stress–strain behavior of linear and star block copolymers.

strengths whereas the linear equivalent (SBS-PCJ-4) shows a relatively low value (Figure 7). Even those multiarmed block copolymers with very low molecular weight polystyrene segments show measurable tensile strengths whereas the linear equivalents exhibit virtually zero tensile strength.[67] These results pose then the question as to the mechanism by which branching enables the end polystyrene segments to form domains capable of resisting an applied stress whereas identical end segments in a linear triblock form relatively ineffective domains. Lacking detailed insight into the morphology of these "short armed" stars it is presently impossible to comment on the role of domain size and shape with regard to their mechanical properties.

However, some information can be gained from an inspection of an electron micrograph (Figure 8) of the unannealed $(SB)_6$-DVB-1 block copolymer. This micrograph apparently shows a lamellar array for the two components. It should be noted that the *overall* composition of the polydivinylbenzene and polystyrene is 36 wt %. This composition is in the region where the lamellar array is anticipated.[89] However, the stress–strain behavior of this material fails to show any stress softening, a characteristic found previously for linear triblock copolymers exhibiting a lamellae-like morphology. This ob-

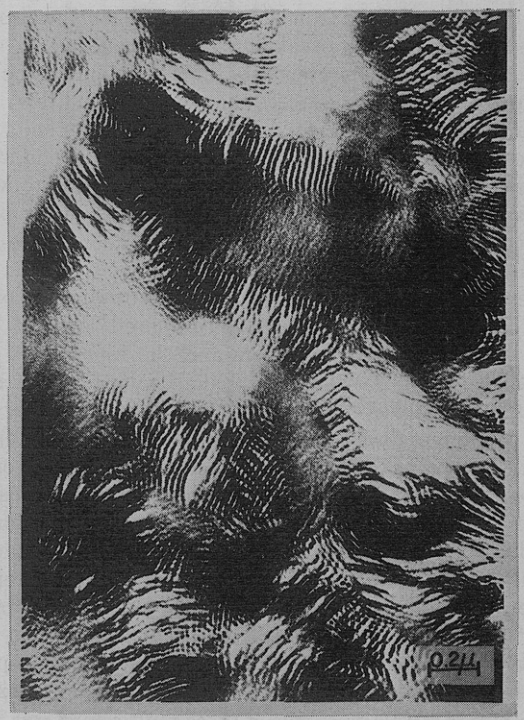

Figure 8. Electron micrograph of an unannealed film of the $(SB)_6$-DVB-1 star block copolymer. Film cast from a 9/1 tetrahydrofuran–methyl ethyl ketone mixture. The large white areas are the result of delamination during microtoming.

servation can be tentatively explained by an inspection of Figure 8. There it can be seen that the polystyrene lamellae lack the continuous arrangement which has been observed previously[87] for the linear block copolymers. The "fragmented", random array of these lamellar polystyrene domains may thus be the reason why these short-armed stars with polystyrene–polydivinylbenzene compositions of 36% or more fail to exhibit stress softening at low strain. This behavior was observed irrespective of the type of solvent or mixture of solvents used to cast the films. The solvent-cast films and molded specimens were also found to exhibit virtually identical stress–strain behavior in the region of low strain.

Hence, it can be seen that branching in block copolymers brings about features unanticipated from the numerous observations made in the past on the linear materials. One feature which remains to be clarified with regard to these short armed star block copolymers is the contribution of the polydivinylbenzene component to the morphology of these systems. It should be noted that these materials contain a significantly larger amount (on a weight percent basis) of polydivinylbenzene than do the polystyrene-polyisoprene multiarmed star block copolymers. This is, of course, a consequence, in part, of the fact that the molecular weight of the arms of these star block copolymers is one-half to one-third that of the polystyrene-polyisoprene materials discussed earlier in this paper.

Rheological Behavior of the Star Block Copolymers. It has long been recognized that the linear block copolymers exhibit, in the melt, abnormally high viscosities and that these viscosities are shear dependent. The fact that the melt viscosities are high has been attributed to the fact that even in the melt a two-phase domain structure exists.[93–95] Hence, since the polystyrene domains can be considered to represent cross-link sites, the effect of branching in block copolymers might be anticipated to lead to even higher melt viscosities than exhibited by linear materials. An additional potential complicating feature for star block copolymers is that it has been observed that the steady-flow Newtonian melt or con-

Table IV
Dynamic Viscosities of Linear and Star Block Copolymers

Sample	$\bar{M}_n$(arm), 10^{-3} g mol^{-1}	$\bar{M}_n$, 10^{-3} g mol^{-1}	Temp, K	$\lvert\eta^*\rvert$, P[a] $\omega = 1$	$\omega = 10$	$\omega = 100$
SIS-2		104	403	2.2×10^6	3.5×10^5	4×10^4
			423	1.4×10^6	2.3×10^5	3×10^4
$(SI)_7$-DVB-17	54	366	403	1.7×10^6	2.3×10^5	3×10^4
			423	1.4×10^6	1.8×10^5	2×10^4
SIS-1		127	403	2.7×10^6	3.5×10^5	4×10^4
			423	1.8×10^6	2.4×10^5	3×10^4
$(SI)_4$-Si-1	62	240	403	2.3×10^6	3.3×10^5	4×10^4
			423	1.7×10^6	2.3×10^5	3×10^4
$(SI)_9$-DVB-4	70	630	403	2.5×10^6	3.1×10^5	4×10^4
			423	1.8×10^6	2.3×10^5	3×10^4
$(SI)_{15}$-DVB-12	71	1,100	403	2.9×10^6	3.5×10^5	4×10^4
			423	2.3×10^6	2.9×10^5	3.5×10^4
SBS-1		80	403	2.5×10^6	4.2×10^5	5.6×10^4
			423	1.2×10^6	2.5×10^5	4.4×10^4
$(SB)_{29}$-DVB-4	30	870	403	3.2×10^5	1×10^5	2.5×10^4
			423	1.5×10^5	4×10^4	1.7×10^4
$(SB)_{15}$-DVB-5	20	300	403	2.1×10^3	2.1×10^3	
			423	6×10^2	7×10^2	

[a] $\lvert\eta^*\rvert = (G'^2 + G''^2)^{1/2}/\omega$.

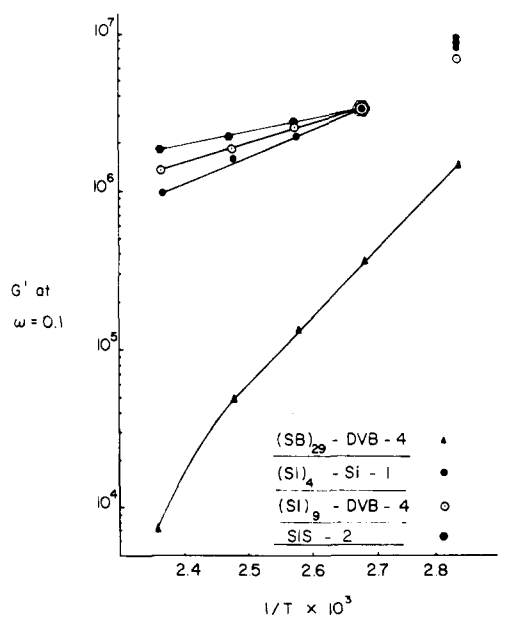

Figure 9. Storage modulus vs. temperature for one linear and three star block copolymers at constant frequency (ω = 0.1 rad/s).

centrated solution viscosities of branched polydienes can be *larger* above a certain molecular weight than linear material of the same molecular weight.[14,96-98] Below this critical molecular weight these star-shaped polydienes exhibit viscosities lower than their linear analogues, behavior which is in accord with theory.[99]

The dynamic viscosities of linear, three- and four-armed block copolymers have been reported elsewhere.[100] For linear and branched material with equivalent segment molecular weights and compositions, branching brought about very little change in either the steady flow or dynamic viscosities at temperatures of 403 and 433 K. We have measured the dynamic viscosities of some linear and star block copolymers over a wide shear range and some of these results are shown in Table IV.

For the case of the polystyrene–polyisoprene materials it is apparent that branching brings about virtually no change in the dynamic viscosities of these materials as one goes from the linear to branched configuration. The data in Table IV show that the dynamic viscosities are dependent upon arm molecular weight but not upon the overall degree of branching. In fact, the viscosities of linear materials are equal (or nearly so) to viscosities exhibited by species of up to 15 arms, even though the branched materials possess a permanent cross-link site at the center of the polydiene chain. This independence of viscosity on molecular weight, i.e., extent of branching, is, of course, not the behavior observed for homopolymer stars in the melt[14,96-98] or in dilute or concentrated solutions.[5,6,18,19,24,96]

The dynamic viscosities presented in Table IV cannot be taken as being equal to the steady flow viscosity. It has been previously shown[100] that $\lvert\eta^*\rvert$ is about 1.5 to 3 times larger than η when compared at equivalent frequencies and shear rates. This difference has been attributed,[100] in part, to the probability that the domain network can be partially disrupted under steady flow but not under the conditions of small amplitude oscillations.

Some additional insight into the independence of the rheological parameters on the extent of branching at constant arm molecular weight and composition can be seen in Figure 9 where the dynamic storage modulus (at constant frequency) is recorded against the reciprocal of temperature for three polystyrene–polyisoprene materials. It is apparent that nearly identical behavior is observed for these materials even though there is a better than 13-fold difference in the apparent weight-average molecular weights between the SIS-2 and $(SI)_9$-DVB-4 block copolymers. Also, the crucial nature of arm molecular weight in influencing the viscoelastic parameters of these multiarmed star species is demonstrated by the marked difference in the values of the storage moduli observed between the polystyrene–polyisoprene block copolymers and the 29-armed polystyrene–polybutadiene star. It should be kept in mind that this latter block copolymer has a higher number-average molecular weight than any of the three polyisoprene materials.

The storage and loss moduli for this 29-armed material are shown in Figures 10 and 11. Two points are to be noted. At 423 K the star block copolymer begins to exhibit Newtonian behavior at low frequencies. This characteristic is generally not observed for conventional linear block copolymers nor have

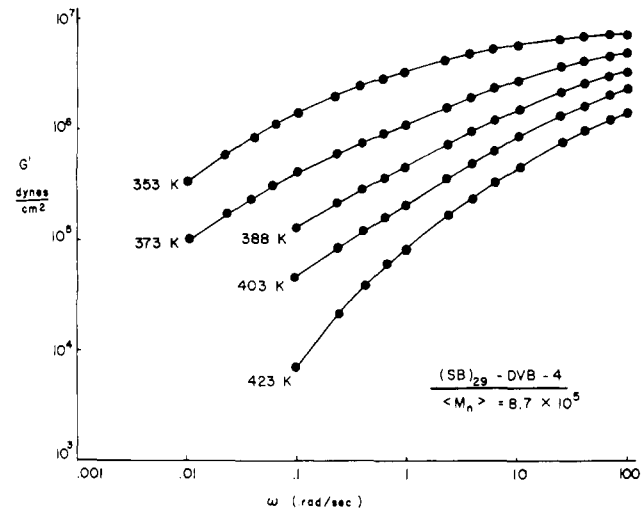

Figure 10. Storage modulus vs. frequency for the $(SB)_{29}$-DVB-4 star block copolymer.

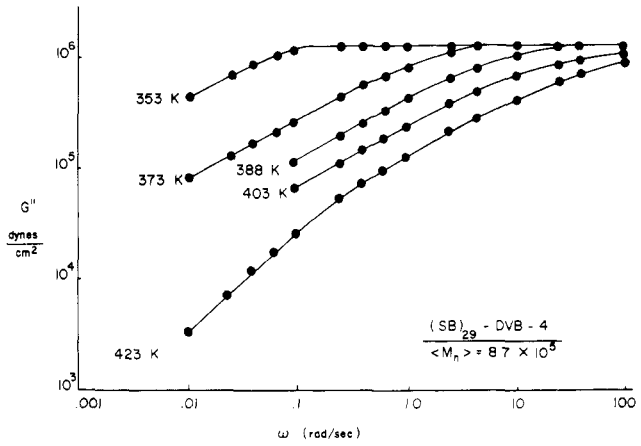

Figure 11. Loss modulus vs. frequency for the $(SB)_{29}$-DVB-4 star block copolymer.

we observed this behavior for the star block copolymers with arms having molecular weights greater than 5×10^4 g mol^{-1}.

Also, both the loss and storage moduli are markedly temperature dependent at a constant frequency for the $(SB)_{29}$-DVB-4 block copolymer. This is reflected in the values of the loss tangent, the dissipation factor tan δ, which are recorded in Table V.

As can be seen from Table V, when above the glass transition temperature of polystyrene the loss tangent at a given frequency increases as the temperature is increased while at constant temperature, tan δ decreases with an increase in frequency. This general trend has been reported previously[100] for linear, three- and four-armed block copolymers. The values for tan δ shown in Table V demonstrate that G' is relatively small compared to G''. This apparently indicates that little in the way of a domain network exists in this 29-armed material at these higher temperatures and that this network deteriorates rather rapidly as temperature is increased. As a point of comparison, previously reported[100] values of tan δ for linear and star block copolymers are noticeably smaller at equivalent temperatures and frequencies than the corresponding values in Table V.

Intrinsic Viscosity and GPC Behavior of Star Block Copolymers. The dynamic viscosities of the star block copolymers revealed an independence of viscosity on the number of branches when the arm molecular weight and composition

Table V
Loss Tangent Values for the $(SB)_{29}$-DVB-4 Star Block Copolymer

Freq, rad/s	Tan δ at temp= 353 K	373 K	388 K	403 K	423 K
0.01	1.30	0.85			
0.1	0.93	0.78	1.04	1.52	4.04
1.0	0.38	0.77	1.0	1.15	1.65
10	0.24	0.46	0.73	0.86	0.98
100	0.18	0.19	0.37	0.48	0.71

were held nearly constant. This behavior has also been observed in intrinsic viscosity measurements on these star block copolymers. These data are presented in Table VI. It can readily be seen that when one compares stars where both arm molecular weight and composition are kept virtually constant, no significant change can be seen in the intrinsic viscosities of these materials, even up to 29 arms. This behavior is substantiated in part, when the value of $[\eta]$ obtained for the $(SIS)_{22}$-DVB-1 star block copolymer is compared with those values obtained for stars $(SI)_3$-12, $(SI)_5$-DVB-11, $(SI)_6$-DVB-8, $(SI)_7$-DVB-5, $(SI)_9$-DVB-4, and $(SI)_{15}$-DVB-12. As was the case for the dynamic viscosities, the molecular weight of the arm controls the intrinsic viscosity; e.g., this can be seen in a comparison of the star block copolymers $(SI)_4$-SL-1, $(SI)_6$-DVB-6, $(SI)_7$-DVB-3, and $(SI)_9$-DVB-15 with the stars listed above. Finally, a comparison of the triblock SIS-1 with the $(SI)_7$-DVB-3 seemingly demonstrates that there exists very little difference in the intrinsic viscosity between a linear and star material when the composition and segment molecular weights are held nearly constant.

This behavior is not predicted by theory[101-103] nor has it been observed for star materials containing homopolymer arms. This behavior is apparently related to the fact that the arms of these block copolymer stars contain incompatible segments. One model that may reflect the conformation of these star block copolymers in dilute solution is that these species may be spherical in shape, i.e., a vesicle of polydiene surrounded by a shell of polystyrene. This model is qualitatively suggested by the observed independence of the intrinsic viscosity on the extent of branching for a series of star block copolymers where the arm molecular weight and composition remain nearly constant. Detailed experimental verification of this model though remains to be obtained.

It is important to note that even though intrinsic viscosity is a parameter insensitive to the degree of branching, gel permeation chromatography can readily separate star block copolymers having various degrees of branching but possessing arms of nearly equivalent compositions and molecular weights. This can be seen in the last column of Table VI which lists the peak elution counts for both linear and star block copolymers. An additional point to be made is that gel permeation chromatography, like dilute solution viscometry, is sensitive to arm size, i.e., the higher the molecular weight of an arm, the shorter the residence time of the star block copolymer in the Styragel columns. An example of this can be seen in a comparison of the elution counts of the $(SI)_6$-DVB-8 and $(SI)_9$-DVB-4 star block copolymers. This comparison reveals that the star block copolymer with the larger arm, the $(SI)_6$-DVB-8 sample, has a lower peak elution count than the $(SI)_9$-DVB-4 block copolymer. This difference in elution count is evident even though the $(SI)_9$-DVB-4 sample has the higher degree of branching.

These combined results suggest that gel permeation chromatography can, within certain limits, detect differences in the degree of branching in these star block copolymers.

Table VI
Intrinsic Viscosities of Linear and Star Block Copolymers

Polymer	$\overline{M}_n \times 10^{-3}$, g/mol	Diblock $\overline{M}_n$ $\times 10^{-3}$, g/mol	Wt % polystyrene	$[\eta]_{THF}^{25°C}$, dl/g	Elution count
SIS-1	127		32	1.12	46.0
SIS-2	104		31	0.90	47.4
SIS-13	92		29	0.78	48.0
$(SI)_3$-Si-12-1	230	73	29	1.33	44.0
$(SI)_3$-Si-15-1	222	77	29	1.26	44.3
$(SI)_3$-Si-17	146	51	37	0.87	46.4
$(SI)_4$-Si-1	240	62	29	1.20	44.2
$(SI)_5$-DVB-11	360	70	34	1.30	40.9
$(SI)_6$-DVB-6	305	51	31	0.92	42.3
$(SI)_6$-DVB-8	485	78	26	1.38	40.0
$(SI)_7$-DVB-17	366	54	27	1.04	41.8
(SI)(DVB-17)		54	27	0.55	50.4
$(SI)_7$-DVB-3	450	66	32	1.12	41.8
$(SI)_7$-DVB-5-1	500	72	32	1.34	39.6
$(SI)_9$-DVB-4	630	70	27	1.34	40.4
$(SI)_9$-DVB-15	1100	127	21	1.56	39.7
$(SI)_{15}$-DVB-12	1100	71	30	1.36	39.0
(SI)(DVB-12)		71	30	0.69	49.0
$(SIS)_{22}$-DVB-1	1800	80[a]	33	1.25	39.0
(SIS)(DVB-1)	80		33	0.69	48.8
SBS-1	80		30	0.98	47.7
$(SB)_4$-Si-1	190	48	43	1.21	44.8
$(SBS)_6$-DVB-1	180	30	30	0.82	44.9
(SB)(DVB-1)		30	30	0.41	52.9
$(SB)_{29}$-DVB-4	870	30	26	0.78	42.3
(SB)(DVB-4)		30	26	0.39	53.0
$(SB)_{15}$-DVB-5	300	20	24	0.73	45.3
(SB)(DVB-5)		20	24	0.31	54.7
$(SB)_6$-DVB-6	120	21	43	0.58	46.3
(SB)(DVB-6)		21	43	0.30	54.6
$(SB)_9$-DVB-7	130	14	32	0.47	47.6
(SB)(DVB-7)		14	32	0.23	56.5

[a] Linear triblock arm.

However, the arm length of a star block copolymer is of at least equal importance in controlling the elution behavior of these branched block copolymers. The effect of arm size on the peak elution count can be seen in a comparison of the elution behavior of the $(SI)_6$-DVB-8 and $(SI)_3$-Si-15-1 star block copolymers. Here, the three-armed sample elutes 4.3 counts (20.2 ml elution volume) after the six-armed star. Other comparisons can also be made. Suffice it to say that the data in Table VI seemingly demonstrate that the elution performance of these star block copolymers is controlled by both arm size and the degree of branching. Furthermore, when arm molecular weight and composition are held nearly constant, these results show that gel permeation chromatography can separate materials that differ only in the average number of arms per star block copolymer. It should be mentioned, though, that with the current lack of absolute values for the weight-average molecular weights of these multiarmed star block copolymers, it is impossible to determine the relative contributions of the degree of branching and the arm length on the elution characteristics of a star block copolymer.

These findings, coupled with the unanticipated intrinsic viscosity results, are probably responsible for the fact that several of the $\overline{M}_w$ values recorded in Table I are less than the measured values for the number-average molecular weights. Hence, it must again be stressed that the weight-average molecular weights recorded in Table I for the multiarmed star block copolymers should be viewed with caution.

Concluding Discussion. It is apparent that the multiarmed star block copolymers exhibit a series of unanticipated properties in both bulk and dilute solution, properties which have not been reported for other branched copolymers, i.e., graft copolymers. Perhaps the most intriguing feature of these materials has been the virtual independence of viscosity with regard to the extent of branching when arm molecular weight and composition is held nearly constant. This observation seemingly suggests that the polystyrene and polydiene segments are segregated with the polydiene core surrounded by a thin shell of polystyrene. One consequence of this model is that polydiene entanglements in the melt state may occur, in the main, in an intramolecular fashion. As mentioned previously, though, definitive experimental evidence for this model is currently lacking.

The tensile strengths obtained for the star block copolymers conclusively demonstrate the influence of a cross-link site at the center of the polydiene component, an influence evident in the values of both the nominal and true stresses. The tensile strengths of these star block copolymers are dependent on the morphological parameters (domain size and shape) and as was previously mentioned branching apparently leads to the formation of polystyrene domains somewhat smaller in size than are encountered in the linear block copolymers of equivalent segment molecular weights and compositions.

There remain many features of these multiarmed star block copolymers which have yet to be elucidated in a quantitative fashion. Paramount among these is the mechanism by which the "short armed" star block copolymers exhibit their surprisingly high tensile strengths. These materials thus combine useful mechanical properties and high molecular weights with low viscosities in the melt state. We are aware that this latter feature of low melt viscosity is of considerable importance and value in the processing characteristics of any block copolymer material.

It would thus seem that these multiarmed star block copolymers represent a new, and perhaps important, type of block copolymer. The resolution of many of the intriguing properties exhibited by these materials, however, must await further work in this area.

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