

Flow-Induced Structure and Rheology of a Triblock Copolymer

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Synopsis

Linear viscoelastic properties are found to be a sensitive measure of flow-induced structural changes in a block copolymer. Styrene-butadiene-styrene block copolymer (SBS) with 26% polystyrene (PS) forms a macrostructure in the quiescent state with grains of the order of 1–10 μm . Within each grain, phase separation gives rise to a regular two-phase microstructure with cylindrical PS domains with radius of the order of 200 Å. Large-amplitude oscillatory shear ($\gamma = 4.5$) at temperatures between 139 and 181°C was applied to alter the grain structure with the objectives of removing the discontinuities at the grain boundaries and of aligning the domains into a continuous ultrastructure. The SBS behaved like a solid ($\tan \delta < 1$ at low ω) before and like a liquid ($\tan \delta > 1$) after shear modification. This change expressed itself in the removal of the long relaxation times from the linear viscoelastic spectrum; the intermediate and low relaxation times were not affected by the shear modification. The viscoelastic spectrum slowly recovered during annealing with recovery times of the order of the longest relaxation time of the quiescent structure. Birefringence studies showed that the SBS did not recover into its original grain structure but into a highly oriented domain structure. The discontinuities at the grain boundaries could not be removed completely.

INTRODUCTION

Styrene-butadiene-styrene (SBS) block copolymers have the ability to form a regular two-phase structure, which is present both in the solid state¹ and in the melt.^{2,3} For most materials the minor component forms discontinuous domains in the continuous major component. Depending on the volume ratio of the two components, the discontinuous phase is present as spheres, cylinders, or lamellae of uniform dimension. Their dimension is prescribed by the molecular weight of the blocks and their compatibility.⁴ Copolymers with cylinders and lamellae have the potential for forming a stable bicontinuous structure; the initially discontinuous phase becomes continuous by arrangement into parallel cylinders or parallel lamellae, which then connect across the entire sample.⁵⁻⁷ A bicontinuous two-phase structure in a polymer would be advantageous for many technical applications.

This study is solely concerned with the rheology of SBS in which the styrene forms cylindrical domains. The natural structure of SBS with volume fraction of polystyrene (PS) between approximately 0.20 and 0.30 is of cylindrical domains aligned in grains⁸; the direction of the orientation of the grains varies randomly. Systematic processing methods are needed to eliminate the grain structure by making the domain orientation uniform and then healing the short domains into longer domains. The domains originally have an aspect ratio (L/D) of about 50, which would increase to infinity for sample

spanning domains. Methods of generating long-range domain order by flow have been suggested and demonstrated by Folkes et al.,⁵ and Hadziioannou,⁷ and Terrisse.⁹ Little is known, however, about the dynamics of flow-induced structuring. To design and implement a processing flow that produces a desired structure, we must first completely understand the mechanisms of structural change.

Rheological measurements have been used effectively for monitoring physical changes in the copolymer. Rheological properties of SBS react very sensitively to small changes in chemical or physical structure; chemical changes can be excluded in our experiments by sample stabilization and by careful experimentation. Shear modification above the glass transition temperature T_g of PS has a large effect on the linear viscoelastic behavior of SBS as demonstrated by the change in the relaxation time spectrum. Mechanisms of deformation and recovery are proposed to interpret rheological evidence of a transition of the SBS from a quiescent state to a strained state. Whole-field birefringence confirms this interpretation.

BACKGROUND

Rheology

The steady-shear viscosity of SBS as a function of shear rate is similar to that of conventional homopolymers, except at the limit of low shear rate where no zero-shear viscosity is found.³ Dynamic measurements¹⁰ confirm the shape of the steady-state curve, although the slope of the low-frequency region in complex viscosity is greater than the low-shear-rate region of the steady-state viscosity curve.

The experimental flow curves are typical of yield-stress fluids,¹¹ although adding a yield stress to a shear thinning constitutive equation does not completely describe the thixotropic behavior observed at low rates. An alternative is suggested by the existence of two levels of structure in the material, which contribute differently depending on the time scale of the deformation. This is the dual-structure model proposed recently,¹² and this is borne out by the kinds of material effects seen in this study.

For low-molecular-weight SBS, a region of zero-shear viscosity is seen above the microphase separation temperature T_{MS} .^{13,14} At T_{MS} , the melt undergoes a transition from two separate phases into a single compatible phase. T_{MS} increases very rapidly with molecular weight.¹⁵ For the high-molecular-weight copolymer used in this study, oxidative degradation was observed before T_{MS} could be reached; we are thus restricted to the two-phase melt region of our material.

Structuring

Folkes et al.⁵ structured SBS by extruding it under vacuum at 120°C through a contraction into a glass tube. The plug produced was examined through a variety of methods, including low-angle x-ray diffraction,¹⁶ swelling,^{17,18} transmission electron microscopy (TEM),¹⁹ birefringence,²⁰ and mechanical testing.^{21,22} They attributed the appearance of long-range domain

order to the combined effects of shear flow and solidification of the melt on the cooler walls of the glass tube.

Terrisse⁹ investigated the mechanism for flow structuring on styrene-isoprene-styrene (SIS) block copolymers in oscillatory shear. At frequencies above 0.01 s^{-1} , the domain structure of SIS was found to be destroyed, and no global domain orientation could be produced. Shearing below a critical frequency, however, generated substantial orientation, as evidenced by TEM and small angle x-ray scattering (SAXS). Problems of reproducibility arise owing to an ill-defined strain history introduced into the sample during loading and unloading processes in the Couette-type apparatus. Folkes and Keller¹⁷ attempted to repeat Terrisse's procedure with no success.

Hadziioannou et al.^{6,7} used a sandwich-shear apparatus in oscillatory flow to structure SIS block copolymers. They operated at a low frequency of 0.01 s^{-1} and shear amplitude of up to 10.0. As a result of the flow, the cylindrical styrene domains were organized in a hexagonal lattice throughout the material (measured by SAXS and TEM). Their sample exhibited a monocrystalline domain structure, and this structure was improved by annealing above the glass transition temperature of PS.

Lee²³ sheared SIS in a cone-and-plate rheometer (Rheometrics RMS 7200) at a low frequency of $\omega = 0.01 \text{ s}^{-1}$. He discovered that oriented samples had a region of constant viscosity at low frequencies. The effect of strain seen was small owing to the low maximum strain ($\gamma_{\text{max}} = 0.95$). Lee did not succeed in applying time-temperature equivalence to his data in order to obtain master curves, nor did he investigate the influence of shearing temperature on the flow-induced structuring.

EXPERIMENTAL

Sample Preparation and Shear Modification

The material used in this study is a commercial styrene-butadiene-styrene block copolymer, Kraton D-1102, from Shell Corporation. The number-average molecular weight is 81,300, $M_w/M_n = 1.34$, and polystyrene composes 26% by weight.²⁴ The copolymer was cleaned by twice precipitating a 10% toluene solution into isopropanol. The clean copolymer was then cast from toluene solution with 0.5 wt% Irganox 1010 (Ciba-Geigy) as an antioxidant; the drying time was 24 h in all cases. The films were then annealed at 150°C for 24 h.

The cast SBS samples were shear modified in a Rheometrics RDS 7700 cone-and-plate rheometer in large-amplitude ($\gamma = 4.5$) oscillatory shear. Each sample underwent a small number of cycles (two to four, depending on the temperature), at a low rate (0.01 rad/s), and at temperatures ranging from 139 to 181°C .

Linear Viscoelastic Characterization

As an indication of structural changes in the sample, the viscoelastic behavior of the sample was measured before and after shear modification in small-strain oscillatory shear ($\gamma = 0.03$) at temperatures from 115 to 190°C . Below 115°C , the sample slipped from the surface of the plate, and at temperatures above 190°C , visible oxidation occurred.

Samples cut from the cast and annealed films were placed on the bottom plate of the rheometer and heated to the experimental temperature and the cone was lowered into the sample. The sample thus experienced some squeezing flow in the loading process. The whole-field birefringence of the sample, after loading and quenching, indicated some orientation due to the flow. The level of birefringence, however, was far below that achieved by shearing. As a check of the influence of loading, the moduli measured with cone-and-plate (squeeze flow during loading) and parallel disks (no flow during loading) were compared and were found to be identical; therefore, the squeezing history was assumed to be negligible for all subsequent analyses.

RESULTS AND DISCUSSION

Time-Temperature Superposition

It has been shown for SBS^{25,26} and other copolymers²⁷ that solid-state mechanical data obtained at different temperatures between the two T_g 's can be superposed. Moreover, master curves have been determined in the melt at temperatures above the glass transition temperature of PS.^{10,13,14} We have similarly superposed the rheological data measured above T_g of PS by using the classic time-temperature equivalence.²⁸

The linear viscoelastic behavior of the SBS cast films was determined in a temperature range above the glass transition temperature of polystyrene (Figs 1 and 2). The shift factors a_T as a function of $1/T$ are plotted in Figure 3. For many polymers, in a temperature range far above a glass transition, the

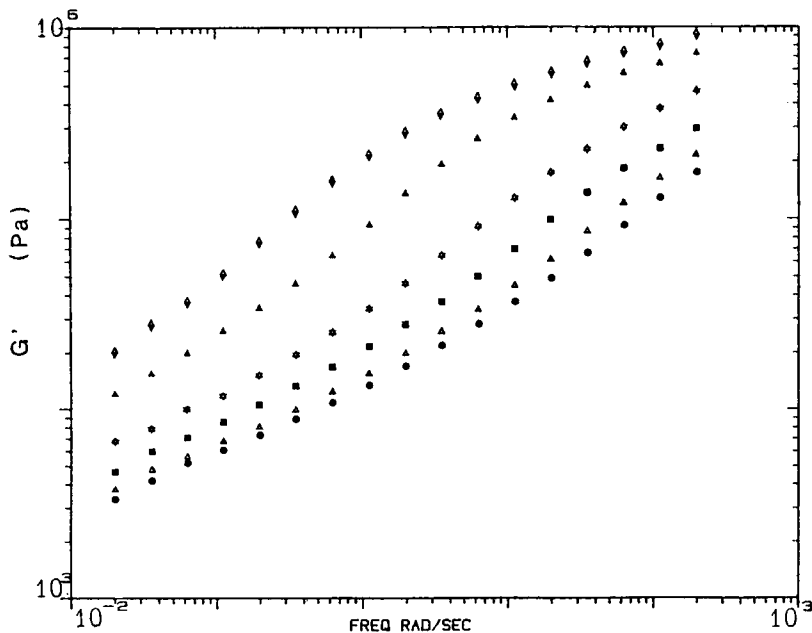


Fig. 1. Evolution of storage modulus with frequency at various temperatures: 107°C (◆); 118°C (▲); 139°C (☆); 160°C (■); 181°C (△); 196°C (●).

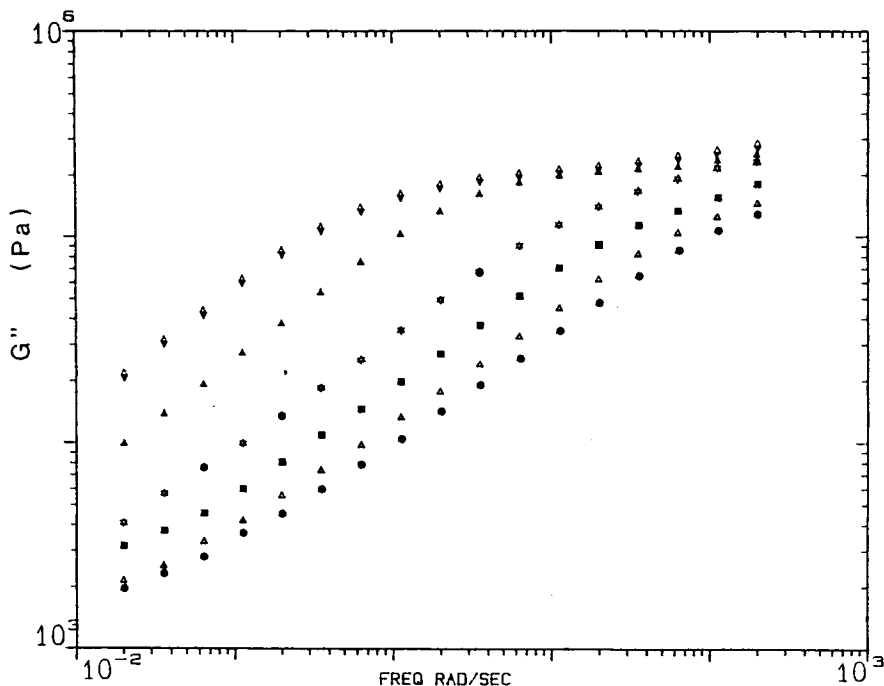


Fig. 2. Evolution of loss modulus with frequency at various temperatures: 107°C (◊); 118°C (▲); 139°C (☆); 160°C (■); 181°C (△); 196°C (●).

evolution with temperature of a_T is described by an Arrhenius relation:²⁸

$$\log a_T = -\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

Between T_g and $T_g + 100$ K, a_T varies with temperature according to a WLF equation²⁸:

$$\log a_T = \frac{-c_1(T - T_0)}{c_2 + (T - T_0)}$$

As SBS is a two-phase material, two glass transitions exist; one is about -90°C for PB, and the other is near 100°C for PS. The temperature range investigated here is far above T_g of PB but below $T_g + 100$ K of PS; the temperature dependence of PB is thus given by an Arrhenius relation and of PS by the WLF equation. To determine which of these relations describes the evolution of a_T with temperature, $\log a_T$ has been plotted versus $1/T$ in Figure 3. One can see that the variation of $\log a_T$ with $1/T$ is not a straight line and is therefore not of Arrhenius type.

To fit the WLF equation, we plotted $T - T_0$ versus $(T - T_0)/\log a_T$, and a straight line was obtained with a correlation coefficient $r = 0.996$; the slope and the intercept give values of $c_1 = 3.39$ and $c_2 = 74.16$ K. The agreement between the WLF equation and the measured shifts is excellent, as shown in

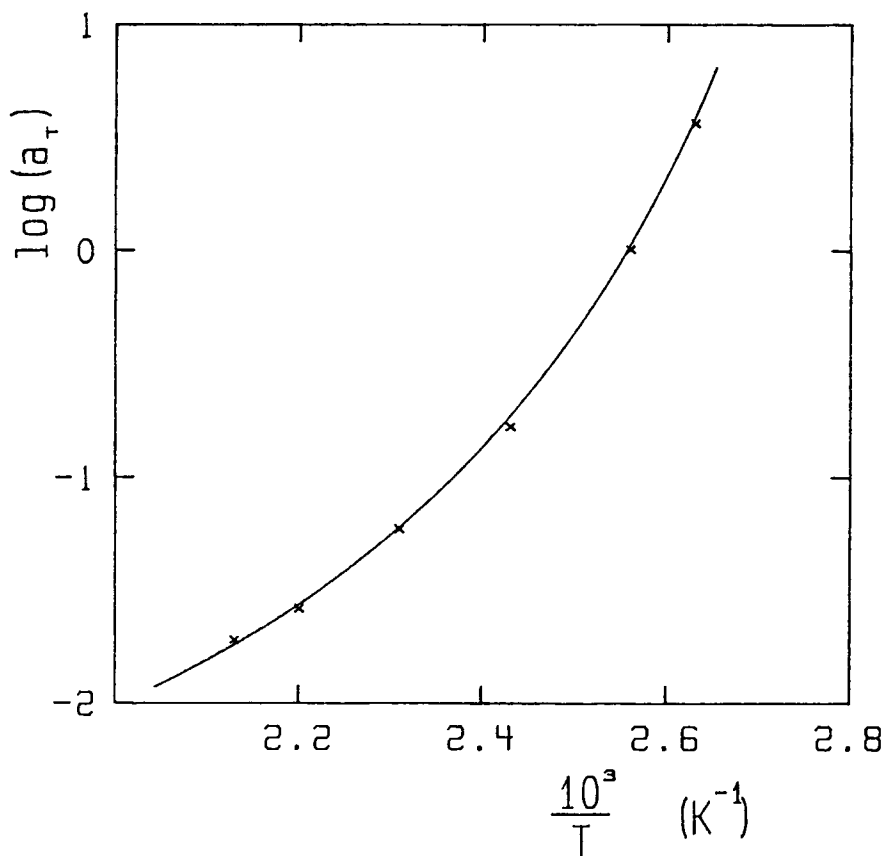


Fig. 3. Arrhenius plot of experimental shift factors (\times) and fitted WLF equation ($-$) at $T = 118^\circ\text{C}$.

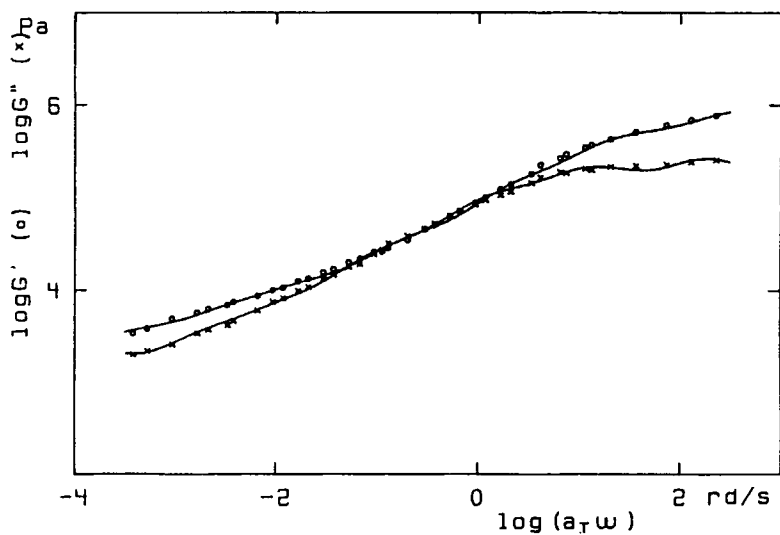


Fig. 4. Master curves of storage (\circ) and loss moduli (\times) and fitted master curves (solid lines) at $T = 118^\circ\text{C}$ for isotropic SBS. The parameters of the fitted discrete spectrum are given in Table I.

Figure 3. It is not possible to use the universal coefficients for a WLF equation as the reference temperature of $T_{\text{ref}} = T_g + 50 \text{ K}$ has no meaning because of the existence of two T_g in SBS. That a WLF curve was found to fit the data implies that the rheological response is due not only to the relaxation of the majority PB but also to the minority PS.

Relaxation Behavior

Three typical regions corresponding to different types of viscoelastic behavior can be distinguished in master curves of storage modulus and loss modulus (Figure 4).

At high frequencies (above 10 rad/s), the material is at the end of the rubbery plateau. In that range of frequencies, PS is in the glassy state and the domains of PS act as the junctions of a rubbery network.

The intermediate frequencies, between 0.1 and 10 rad/s, correspond to the glass transition region of PS; this is shown by the evolution of $\tan \delta$ which goes through a maximum (Fig. 5). In that region, the motion of PS chains in their domains allows relaxation of the whole SBS chain, implying the large decreases in both G' and G'' .

In the range of low frequencies (below 0.1 rad/s), one can see a second plateau. This behavior cannot be attributed to the entanglements of PS chains because the molecular weight of PS is lower than the critical molecular weight between entanglements. For a homopolymer, a flow zone should be observed with G' decreasing as ω^2 , and G'' as ω , implying that G'' takes higher values than G' . SBS block copolymer does not present the usual behavior of a homopolymer. The storage modulus is larger than the loss modulus, which is characteristic of a solid, not of a liquid. Furthermore, the slopes of G' and G'' are much smaller than 2 and 1.

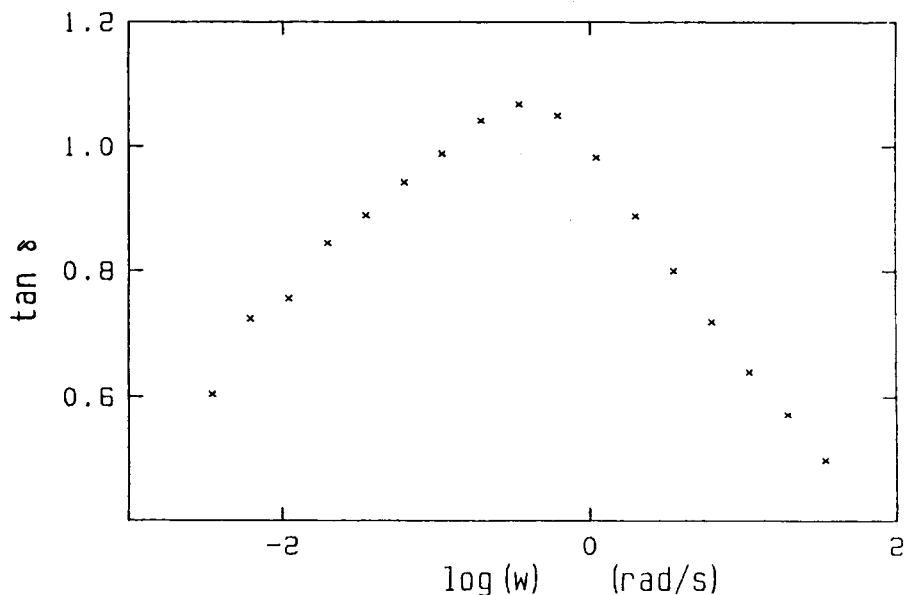


Fig. 5. Evolution of loss tangent with frequency at $T = 118^\circ\text{C}$.

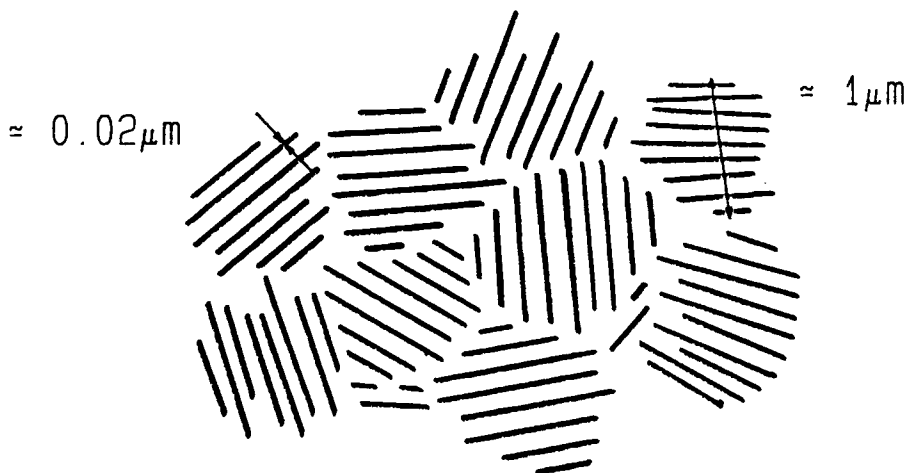


Fig. 6. Morphology of SBS cast film.

This specific behavior at low frequency can be attributed to the morphology of SBS cast films (Fig. 6). Cylindrical domains of PS align upon phase separation. The region of alignment, denoted "grain," has been estimated from TEM to be of the order of a micrometer.²⁴ The direction of the orientation varies randomly from grain to grain, so that the material is isotropic on a macroscopic scale. The existence of two levels of structure, domains and grains, implies that we can expect different behavior from macromolecules within a grain than from those between grains. Because of

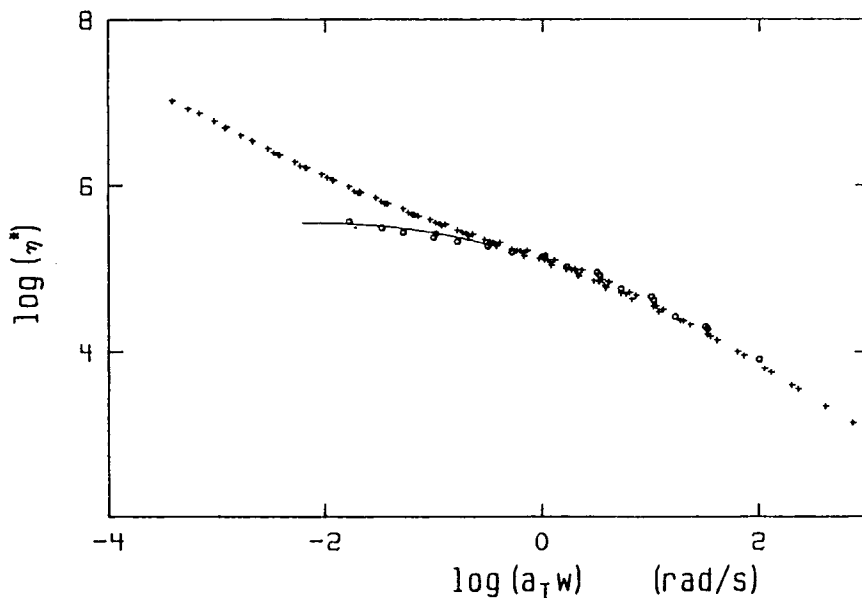


Fig. 7. Master curve of complex viscosity at $T = 118^\circ\text{C}$ for isotropic SBS (+) and SBS sheared at 139°C (o).

greater topological constraints, the relaxation of the chains that link the grains occurs on a longer time scale.

The hypothesis of two contributions to the relaxation mechanism is also supported by the evolution of complex viscosity with frequency (Fig. 7). In the frequency range above 0.1 rad/s, SBS has the usual shear-thinning behavior of homopolymers. However, at lower frequencies, no steady-state value is observed, and η^* increases when ω decreases. This apparent yield behavior is attributed to tie molecules between the grains that prevent the grains from deforming as individual units because of their long relaxation times.

Linear Viscoelasticity of Shear-Modified Samples

In order to obtain a global orientation of PS domains, the samples were subjected to high-strain, low-frequency, oscillatory shear experiments. Before and after shear modification, the linear viscoelastic properties were determined in small-strain, oscillatory shear.

We found, as Lee²³ did on SIS, that both moduli G' and G'' take on lower values, especially at low frequencies. Moreover, after a few cycles at high deformation, G' and G'' reach limited lower values. The saturation level of G' and G'' was used as the criterion to determine the best conditions for shearing. As a higher strain reduces the number of cycles needed to reach saturation, the value of 4.5 was chosen for strain amplitude. To avoid any disruption of PS domains, the shearing was performed at 0.01 rad/s. The master curves of storage and loss moduli for SBS sheared at 139°C are compared with the unsheared state in Figures 8 and 9.

Notice that, at high frequencies, the curves of G' and G'' for the strained and unstrained states are the same. On the other hand, at low frequencies in

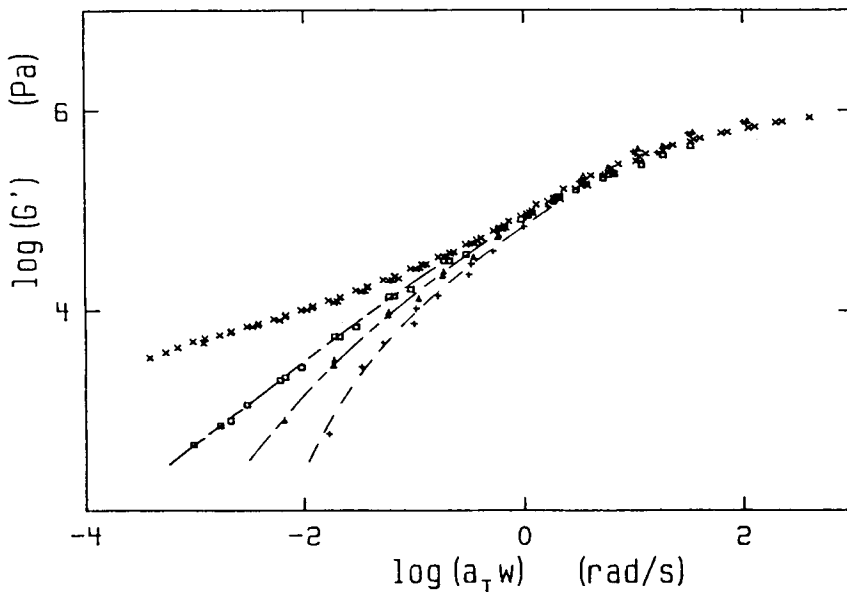


Fig. 8. Master curves of storage modulus at $T = 118^\circ\text{C}$ for isotropic SBS (\times), SBS sheared at 181°C (\square), sheared at 160°C (Δ) and sheared at 139°C ($+$).

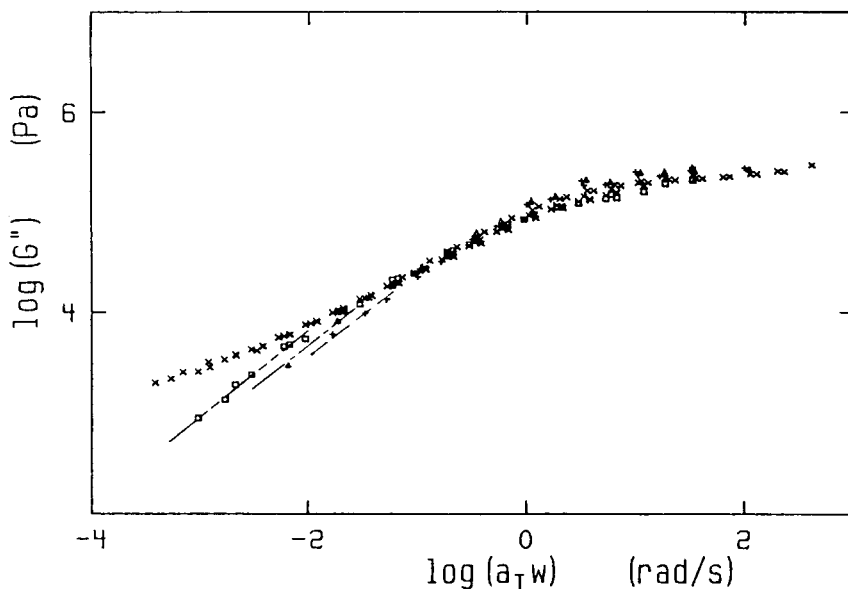


Fig. 9. Master curves of loss modulus at $T = 118^\circ\text{C}$ for isotropic SBS (\times), SBS sheared at 181°C (\square), sheared at 160°C (Δ), and sheared at 139°C ($+$).

the strained samples, the second plateau disappears and G' takes on lower values than G'' . Moreover, G' reaches a slope of 1, G'' a slope of 2, and η^* reaches a plateau characteristic of liquids (Fig. 7). It should be noted that this leveling off of η^* is not due to thermodynamic miscibility ($T > T_{\text{MS}}$), as in the cases reported by Chung and Gale¹⁴ and Gouinlock and Porter¹³; rather, at $T < T_{\text{MS}}$, a liquid state of the material has been reached by shear modification.

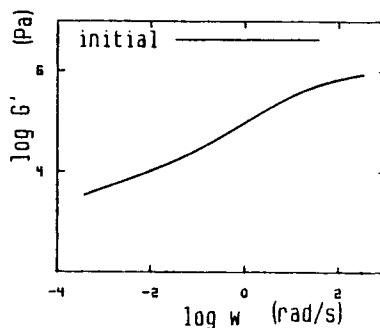
We can hypothesize that the changes seen in the viscoelastic properties of SBS are due to the disruption of grain boundaries as first proposed by Weill and Pixa.²⁹ Grains consist of close-packed, aligned domains, which make the grain act a single unit. Upon shearing at low rates, this cohesiveness will cause the grain to rotate rather than to break up (Fig 10). In order for a grain to rotate, however, any molecules or entanglements that span the grain boundary must be disengaged; also, domains that cross a grain boundary must be destroyed. Thus, just after shearing, PS domains are aligned preferentially in the direction of shearing. To check this, the samples were viewed through crossed polaroids. A circumferentially oriented sample would cause extinction of the source of $0, 90, 180,$ and 270° , producing a Maltese cross image. The structured samples of SBS produced a distinct Maltese cross. Also, there was detectible anisotropy in the samples when they were stressed in the direction of the flow versus the direction perpendicular to this.

In this interpretation, since the links between the grains have disappeared, only relaxation of the chains within the grains can be observed. This explains the unchanged behavior of the moduli at high frequencies and the flow behavior at low frequencies.

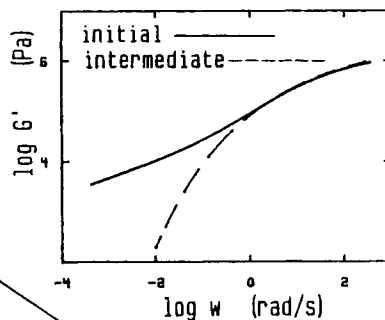
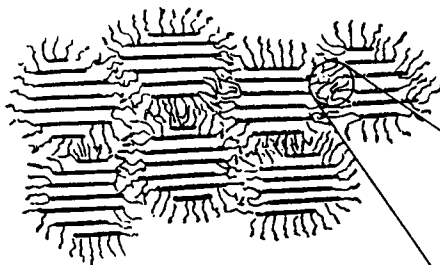
The influence of shearing temperature on the curves will be interpreted in terms of recovery.

PROPOSED MECHANISM

(A) Initial State



(B) Intermediate State



Figs. 10(A, B). Mechanism of deformation when shearing at low rate.

Relaxation Time Spectra

In the general theory of linear viscoelasticity, the relaxation modulus of a material can be written as a discrete spectrum

$$G(t) = \sum_{i=1}^N g_i e^{-(t)/\lambda_i}$$

where g_i and λ_i are the relaxation moduli and relaxation times. Storage and

TABLE I
Relaxation Time Spectrum for Isotropic SBS

λ_i (s)	g_i (Pa)
5.532×10^{-5}	1.334×10^6
5.158×10^{-3}	4.560×10^5
7.857×10^{-2}	3.396×10^5
6.620×10^{-1}	1.355×10^5
8.205	2.999×10^4
8.811×10^1	6.026×10^3
4.618×10^2	3.707×10^3
8.896×10^3	3.540×10^3

loss moduli are then given by

$$G'(\omega) = \sum_{i=1}^N g_i \frac{(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2}$$

$$G''(\omega) = \sum_{i=1}^N g_i \frac{\omega\lambda_i}{1 + (\omega\lambda_i)^2}$$

Parameters were determined from our data using a finite difference Levenberg-Marquardt routine.³⁰ Values of λ_i and g_i for the unsheared state are listed in Table I; the fit to the master curve is shown in Figure 4.

Based on our proposed mechanism, the calculated spectrum should be divided into two spectra relative to each kind of chain. A set of long relaxation times is associated with the chains between the grains and a set of short relaxation times with the chains within a grain. Although we are unable to separate accurately the sets of relaxation times because of the interaction of the different kinds of chains, the shortest are representative of chains between domains and the longest representative of chains that span the grain boundaries.

The discrete values of λ_i and g_i calculated for SBS sheared at 139°C are listed in Table II; the fit to the data is shown in Figure 11. This spectrum can be compared to the spectrum associated with the unstrained state (Fig. 12).

TABLE II
Relaxation Time Spectrum for SBS sheared at 139°C

λ_i (s)	g_i (Pa)
5.460×10^{-5}	1.317×10^6
1.310×10^{-3}	5.596×10^5
1.880×10^{-2}	3.772×10^5
1.054×10^{-1}	2.279×10^5
3.660×10^{-1}	1.408×10^5
1.365	7.288×10^4
1.515×10^1	1.040×10^4

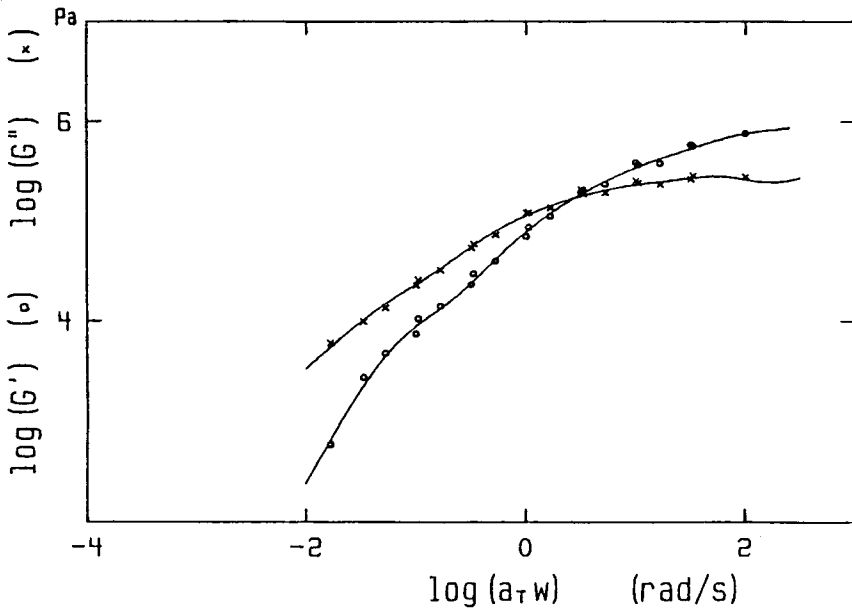


Fig. 11. Master curves of storage (○) and loss moduli (×) and fitted master curves (solid lines) at $T = 118^{\circ}\text{C}$ for SBS sheared at 139°C .

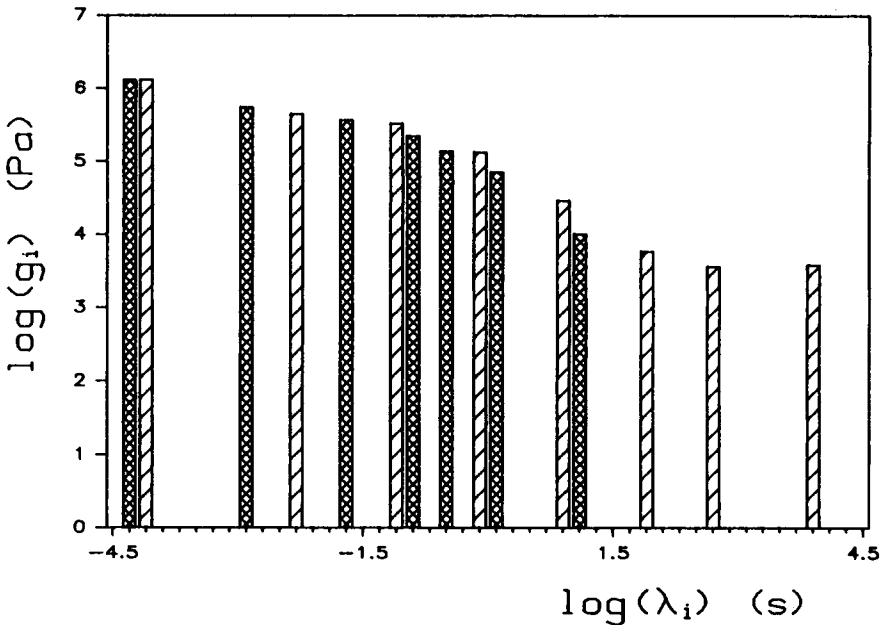


Fig. 12. Relaxation time spectra for isotropic SBS (///) and SBS sheared at 139°C (×××).

Notice that the longest relaxation times, those related to the chains that link the grains together, disappear after shearing, but the short relaxation times of the spectrum remain relatively unchanged. This supports the interpretation that it is the grain boundaries that are disrupted without any modification of the PS domains.

Temperature Effects

To determine the effect of temperature on the shearing process, two additional shearing temperatures were investigated, 160 and 181°C (Figs. 8 and 9). The number of cycles used in these experiments was greater than at 139°C since the increased mobility of the molecules made the shearing process less efficient. From the curves we see that the effect of shearing becomes less pronounced with increasing shearing temperature.

To determine the effect of molecular relaxation on the shearing process, annealing of sheared samples was performed. During annealing, both moduli were measured at a frequency of 0.05 rad/s every 3 min up to a total time of 45 min. The results are reported in Figure 13 and show that G' and G'' increase during the annealing. Notice also that the higher the annealing temperature, the faster is the increase of both moduli.

The effect of temperature on sheared samples can be explained in terms of the results from annealing. At high temperatures of shearing, the molecular chains are highly mobile; this allows relaxation and recovery during the large-deformation, low-rate experiment. Recovery of stress is assumed to be associated with the healing of the structure (PS domains and PB phase) across the grain boundaries, as sketched in Figure 14. This implies that the values of storage and loss moduli will be greater for samples that are shear modified at high temperatures than at low temperatures. Also, at all but the lowest shearing temperatures, the results will not represent the true effects of the shearing but will reflect the superposition of shearing and recovery.

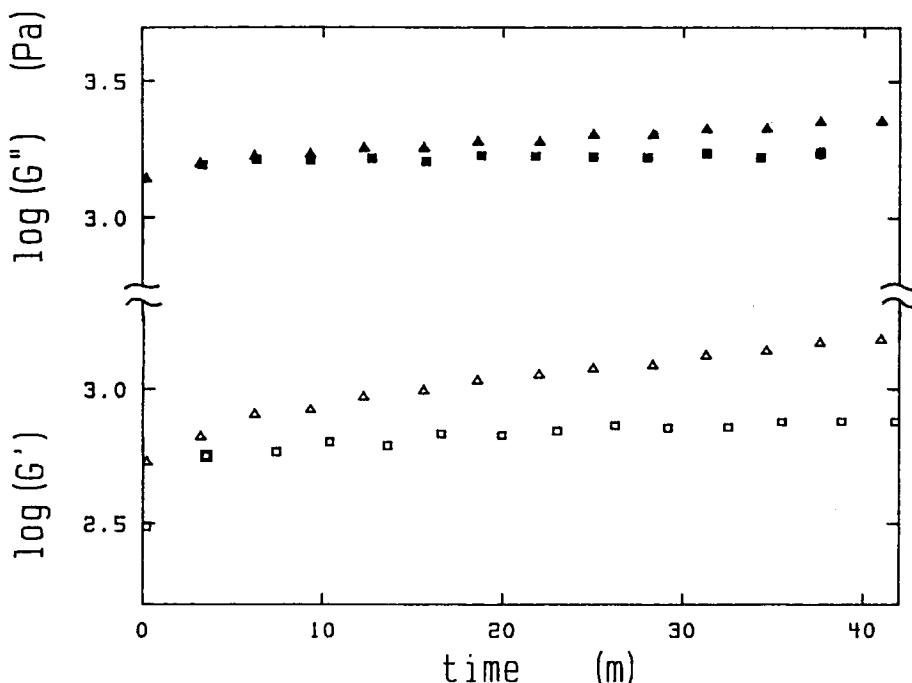


Fig. 13. Evolution of storage and loss moduli at a frequency of 0.05 rad/s during annealing of sheared SBS at various temperatures: $T = 160^{\circ}\text{C}$, G' (□), G'' (■); $T = 181^{\circ}\text{C}$, G' (△), G'' (▲).

Final State (after recovery)

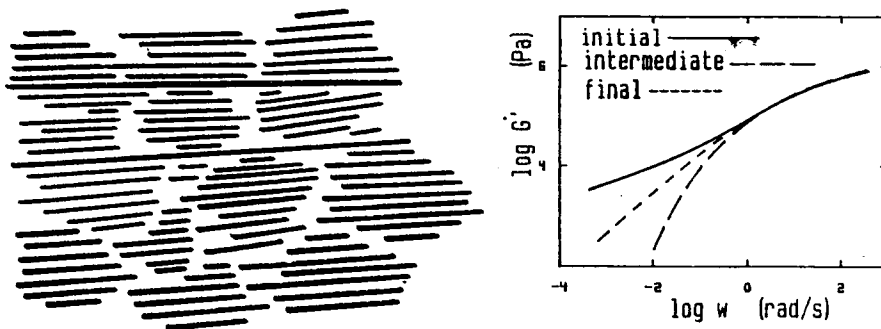


Fig. 14. Healing of grain boundaries during annealing.

The increase of G' and G'' with annealing time is postulated to be due to the healing of grain boundaries to form a new structure with many PS domains aligned in the shear direction. Because of the incompatibility of PS and PB, PS blocks of the former links between grains will diffuse through the PB matrix in order to reach their own phase. Thus, the destroyed grain boundaries re-form, and G' and G'' increase. This interpretation is in agreement with the results of SAXS obtained by Hadziioannou⁷ on SIS, which showed that during annealing the organization of aligned domains is not destroyed but is improved by the disappearance of defects.

CONCLUSIONS

Linear viscoelastic data (G' and G'') indicate that molten SBS behaves like a solid before and like a liquid after shear modification. Shear modification removes the longest relaxation times from the spectrum. Otherwise, the spectrum is essentially the same for the unsheared and the shear-modified samples. Shear modification is assumed to disrupt the grain boundaries; however, it does not alter the PS domains within the grains. Whole-field birefringence of the samples suggests that the grains rotate as a result of shear modification yielding long-range domain alignment.

Linear viscoelastic data of both states, unsheared and shear modified, can be presented in master curves with a temperature shift factor a_T that follows a WLF equation. The shift factor is not affected by shear modification.

The samples recover after shear modification which is reflected in the increase of modulus with time. The mechanism associated with annealing of shear-modified samples is the healing of the grain boundaries to form a new macrostructure with a majority of PS domains aligned in the shear direction. This model is supported by birefringence, which is maintained even after long times of annealing. We therefore conclude that the samples do not really recover to their presheared state but to a new state of large-scale order (and long relaxation time). The recovery time was found to be of the same order as the longest relaxation time of the sample before shear modification.

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