

Rheology of Copolymer Solutions V. A Solution of an SB Block Copolymer in 1-Chlorohexadecane

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Received March 3, 1978

The nonlinear viscoelasticity was studied for a 20% solution of a styrene-butadiene diblock copolymer in 1-chlorohexadecane, which was a non-solvent for the polystyrene block at low temperatures in the range 15–70°C of rheological measurements. At temperatures higher than 50°C, the rheological properties were similar to those of homopolymer solutions. At 40°C, the viscosity at low rates of shear was affected by the flow history. The viscosity measurement at this temperature was subjected to a large error of unknown origin. At temperatures lower than 30°C, the solution exhibited marked nonlinear rheological behavior even at the lowest strain and rate of shear studied; *e.g.*, 0.14 and 0.0005 s⁻¹, respectively. The rate dependence of the viscosity at relatively low rates of shear could be interpreted in terms of the Casson theory based on the concepts of the thread-like sequence structures of hard polystyrene domains and their destruction due to the stress in the flow. At low temperatures, the shear stress increased in double steps at the start of shear flow of a sufficiently high rate of shear and the strain dependence of the relaxation modulus was very large in the range of shear lower than 1 shear unit. The strain-dependent constitutive equation of Bernstein, Kearsley, and Zapas could describe consistently the qualitative features of the rate dependence of the viscosity, the stress growth at the start of steady flow, and the strain dependence of the relaxation modulus.

INTRODUCTION

Rheological Properties of melts and solutions of block copolymers are quite different from those of homopolymers. A marked thixotropy is often observed, that is, the viscosity becomes smaller when the sample has been exposed to a high shear, the temperature-rate of shear reduction rule is not applicable, and so on.¹⁻¹¹⁾ These features have some similarity to those of dispersed systems of solid particles in polymeric liquids.¹²⁾ The similarity may be comprehended if the copolymer system is assumed to have a domain structure due to microphase separation, where the domain of one component is much harder than the other.

In preceding papers^{8,9,11)} we have studied nonlinear rheological properties of block copolymer solutions in time-dependent flow to understand the rheological properties in terms of constitutive equations. The polymer was a 4-armed star-branched styrene-butadiene block copolymer, in which polystyrene blocks were attached to the ends of a star-branched polybutadiene. In a liquid paraffin solvent, a precipitant for polystyrene at any temperature studied, the "solution" was a gel of a high-elastic property. In 1-chlorohexadecane solvent, which became a solvent

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for polystyrene block just in the middle of the temperature range of measurements, the solution did not exhibit thixotropic nor plastic behavior but typical viscoelastic behavior. The viscoelastic properties were describable with the strain-dependent constitutive equation which had a wide applicability to homopolymer solutions. The rheological properties of the solutions in 1-chlorohexadecane were characterized by a relaxation mode of a very long relaxation time. The relaxation strength of the mode decreased very rapidly with increasing shear, increasing temperature, and decreasing concentration. Thus the solutions in 1-chlorohexadecane showed no similarity to dispersed systems but rather to homopolymer solutions in view of the constitutive equations. The precipitated polystyrene blocks did not behave like dispersed solid particles but like cross-linking points connecting a few molecules to give a strain- and temperature-sensitive aggregate structure. This type of behavior is probably related to the small size of the precipitated polystyrene domains and is not specially difficult to describe with the phenomenological method developed for homopolymer systems.

In the present paper we report on the rheological behavior in time-dependent flow of a solution of a styrene-butadiene diblock copolymer in 1-chlorohexadecane. As compared with the previous systems, the present solution is expected to involve larger domains of precipitated polystyrene blocks due to the different geometry of the polymer and the higher molecular weight of the polystyrene block. Thus we can expect to find time-dependent rheological functions for the sample which exhibits typical behavior of dispersed systems in steady shear flow as exemplified at the beginning of this paper. Studies of the similar idea are apparently in progress elsewhere.¹⁰⁾

MATERIAL AND METHOD

The sample polymer studied here was a styrene-butadiene diblock copolymer Solprene 486 supplied from Phillips Petroleum Company. The polymer will be called SB for short in this paper. The number average molecular weight M_n was evaluated from the osmotic pressure as 1.44×10^5 and the content of styrene was 28.8%.¹³⁾ The molecular weight of the polystyrene block was calculated as 4.14×10^4 from the figures given above. It may be noted that the molecular weight and the content of styrene of Solprene 486 are not much different from the values, 1.85×10^5 and 31.0%, respectively, of Solprene 411 studied in previous papers.^{8,9,11)} The latter was a styrene-butadiene block copolymer of a 4-armed star-branched structure.¹¹⁾ Due to the different geometries, the length of a styrene block of Solprene 486 is approximately 3 times larger than that of Solprene 411.

The solvent was 1-chlorohexadecane (Tokyo Chemical Industry Co. Ltd.), which will be abbreviated as CC for cetyl chloride in the following. In this solvent, a polystyrene of molecular weight 1.98×10^4 (Standard polystyrene batch 2a from Pressure Chemical Co.) started to precipitate from the solution at 25°C when the temperature was lowered and a polystyrene of molecular weight 5.1×10^4 (batch 7a) at 50°C. Thus CC will not be a solvent for a polystyrene of the size of the styrene block at low temperatures in the range of rheological measurements, 15–70°C. The results for a 20% solution are described in this paper. The results for 10 and 15%

solutions are qualitatively the same as that for the 20% solution.

Shear stresses were measured for simple shear flow of flow histories as illustrated in Fig. 1. The viscosity growth function $\bar{\eta}(t, \dot{\gamma})$ and the viscosity decay function $\tilde{\eta}(t, \dot{\gamma})$ are respectively the ratios of shear stresses to the rate of shear $\dot{\gamma}$ at the start (Fig. 1A) and on the cessation (Fig. 1B) of steady shear flow. Obviously the limiting values

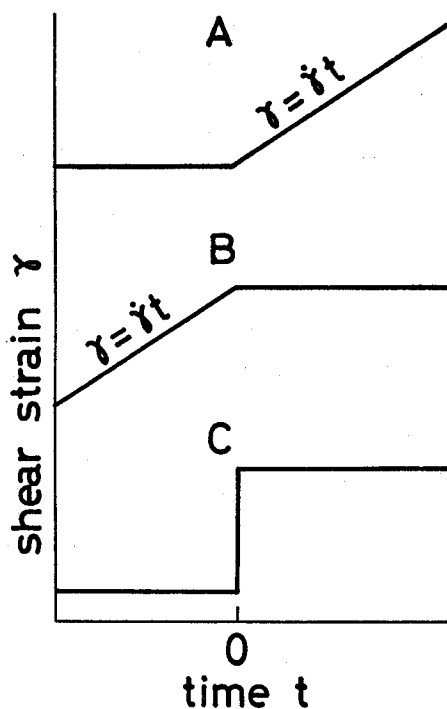


Fig. 1. Flow histories studied. A, sudden start of shear flow of constant rate of shear $\dot{\gamma}$; B, sudden cessation of steady shear flow; C, step-like simple shear. Shear stress was measured for $t > 0$ in each case.

$$\lim_{t \rightarrow \infty} \bar{\eta}(t, \dot{\gamma}) = \lim_{t \rightarrow 0} \tilde{\eta}(t, \dot{\gamma})$$

are equal to the steady shear viscosity $\eta(\dot{\gamma})$. The strain-dependent relaxation modulus $G(t, \gamma)$ is the ratio of the shear stress to the magnitude of shear γ on the application of a constant shear strain (Fig. 1C).

The quantities $\bar{\eta}(t, \dot{\gamma})$, $\tilde{\eta}(t, \dot{\gamma})$, and $\eta(\dot{\gamma})$ were measured with a rheometer of a cone-and-plate type (Multipurpose Rheometer, Iwamoto Seisakusho Co., Ltd.).¹⁴⁾ The relaxation modulus $G(t, \gamma)$ was measured with a relaxometer of a cone-and-plate type, whose details have been reported previously.¹⁵⁾

RESULTS

Observation on Plasticity and Thixotropy

On playing with the 20% solution of SB in CC it was readily noticed that the

surface roughness caused by stirring or otherwise persisted as long as a few days. Also it took a few days for perceptible flow to occur in the sample attached to a vertical wall of a vessel. On the other hand, the sample could be easily kneaded as could a homopolymer solution of comparable molecular weight and concentration and the stresses relaxed to within the limit of detection (1 Pa) in an hour in the measurements of $\tilde{\eta}(t, \dot{\gamma})$ or $G(t, \dot{\gamma})$. These features imply that the SB solution in CC is probably a viscoelastic liquid of marked nonlinearity and that the retardation time at small stresses is extremely long. If the time-scale of observation is less than a day, as is the case for studies of ordinary homopolymer solutions, and if the apparatus has a very high sensitivity, the SB solution may be classified as a pseudo-plastic material, which will not flow until the stress exceeds a small but finite critical value.

In the measurements of the steady shear viscosity, a symptom of thixotropy was observed at 40°C. At this temperature, the viscosity at low rates of shear measured after a rest of more than 10 hours was much higher than that after shearing at $\dot{\gamma} \approx 1 \text{ s}^{-1}$ for a while. Once sheared at this rate of shear, the sample did not show any systematic hysteresis as far as the measurements were performed intermittently with no interception of more than several hours. However, at 40°C the viscosity measurements at low rates of shear were subjected to an error of $\pm 20\%$, which was larger than that for ordinary performance of the apparatus, even after shearing. At other temperatures studied the phenomenon of thixotropy was not detected and the viscosity measurements did not involve any unusual error.

Steady Shear Viscosity

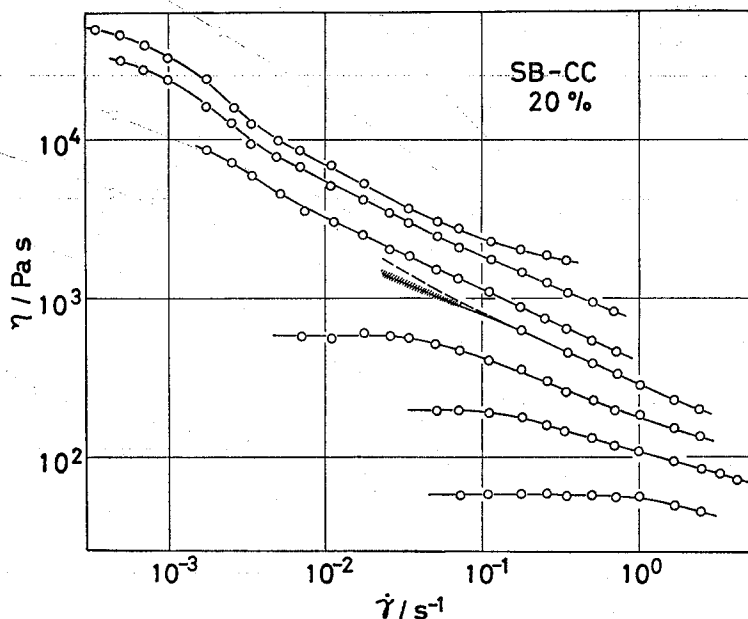


Fig. 2. Steady shear viscosity η plotted against rate of shear $\dot{\gamma}$. Temperatures of measurements are 15.8, 20, 30, 40, 50, 60, and 70°C from top to bottom. Dashed line for 40°C represents values obtained after more than 10 hours rest at room temperature. Hatched line represents average values of many runs obtained after shearing at $\dot{\gamma} \approx 1 \text{ s}^{-1}$ for a while.

Figure 2 shows the steady shear viscosity $\eta(\dot{\gamma})$ for the 20% SB solution in CC. The dashed line for 40°C represents the data obtained after more than 10 hours rest at the room temperature. The hatched line represents the average of scattered data obtained after shearing at $\dot{\gamma} \approx 1 \text{ s}^{-1}$ for a while.

At temperatures higher than 50°C, the viscosity varied with the rate of shear $\dot{\gamma}$ in a way qualitatively similar to that of homopolymer solutions. In other words, it remained independent of $\dot{\gamma}$ at low rates of shear and decreased with increasing $\dot{\gamma}$ at high rates of shear. At lower temperatures, the viscosity did not level off with decreasing rate of shear in the range of measurement. At the two lowest temperatures, at which the range of measurements was extended to quite a low rate of shear, a very fast decrease of $\eta(\dot{\gamma})$ was observed in the range of $1 \times 10^{-3} \text{ s}^{-1} < \dot{\gamma} < 4 \times 10^{-3} \text{ s}^{-1}$. Thus the curve may be divided into two portions, a convex portion at low rates of shear and an approximately linear portion at high rates of shear (except for the three points at the highest rates of shear for 15.8°C). The rate of decrease of η with $\dot{\gamma}$ at high rates of shear was relatively low and was not affected by temperature very much.

Figure 3 gives the Casson plot¹⁶⁾ for the data given in Fig. 2. The square root of the shear stress $(\dot{\gamma}\eta)^{1/2}$ is plotted against the square root of the rate of shear. At the lowest three temperatures, the data points for low rates of shear lay approximately on straight lines as indicated with dashed lines, so that they satisfied the Casson equation

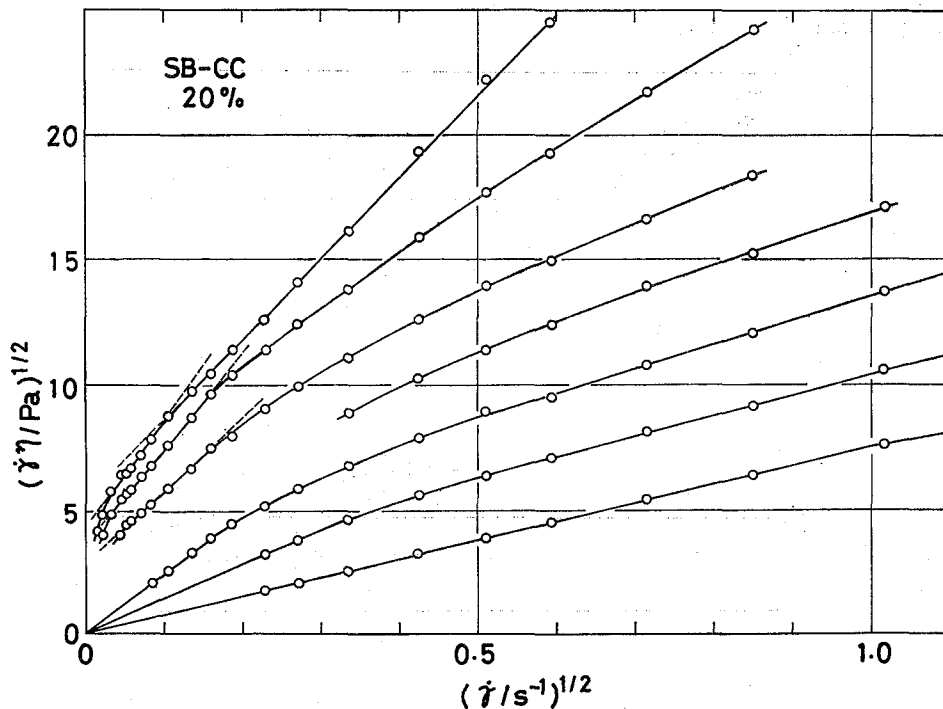


Fig. 3. Casson plot for data of Fig. 2. Square root of shear stress $(\dot{\gamma}\eta)^{1/2}$ is plotted against square root of rate of shear $\dot{\gamma}^{1/2}$. Dashed lines are drawn to show that data points over certain ranges of $\dot{\gamma}^{1/2}$ lie on straight lines at low temperatures.

$$(\dot{\gamma}\eta)^{1/2} = \sigma_y^{1/2} + a\dot{\gamma}^{1/2} \quad (1)$$

where σ_y and a are constants. The "yield value" σ_y evaluated from the intercept of the straight line on the ordinate was of the order of 10 Pa. At 15.8°C, the points for higher rates of shear could be approximated by another straight line with a lower slope and a higher yield value. At other temperatures, the Casson plot gave convex curves at high rates of shear. The shape of whole curves at 20 and 30°C was similar to that observed for the dispersion of solid particles in polymer solutions.¹⁷⁾

The straight portion of the Casson plot may be associated with the existence of thread-like sequence structures of solid particles and their destruction due to stress in accord with the Casson theory. If this is the case, the yield stress should be related to the tensile force to break the threads into smaller fractions.¹⁶⁾ The elongated structures of polystyrene domains have actually been observed with the electron microscope in cast films of styrene-butadiene block copolymers.¹⁸⁾ The existence of two straight portions in the Casson plot for 15.8°C may indicate the existence of two types of breakable points in the thread-like structure; the straight portion at the lower rates of shear corresponds to the destruction at weaker points, which give rise to a lower yield value and which cannot survive in steady flow at high rates of shear.

On the other hand, it is not likely that the SB solution in CC can support a shear stress as large as 10 Pa without flowing in a very long time scale in view of the observation of the preceding section. If measurements were performed at a sufficiently low rate of shear, say 10^{-5} s^{-1} , the point in Fig. 3 would deviate from the straight line and lie close to the origin. The polystyrene domains would change shape through creep under very low stresses in the flow expected to occur in the range of extremely low rates of shear. Thus we can imagine a few types of structural change from the Casson plot depending on the range of rate of shear. However, the study of viscosity alone is apparently insufficient to go further into the structural change of the SB solution in the flow.

The downward deviation of the Casson plot at high rates of shear is probably due to the non-Newtonian behavior of the polybutadiene block solution, in which domains of polystyrene blocks are dispersed. In the case of the dispersion of solid particles in a polymer solution, the similar downward deviation can be fully accounted for if the rate dependence of the viscosity of the polymer solution is taken into consideration.¹⁷⁾ Since polybutadiene chains are attached to polystyrene domains in the case of the SB solution, the viscosity of the matrix solution cannot be evaluated separately.

Viscosity Growth and Decay Functions and Relaxation Modulus

In this section we study the time-dependent functions $\bar{\eta}(t, \dot{\gamma})$, $\tilde{\eta}(t, \dot{\gamma})$, and $G(t, \dot{\gamma})$ of the SB solution in CC at 20°C. The results obtained at 15.8°C were in qualitative agreement with those at 20°C. Measurements were not performed so extensively at higher temperatures.

Figure 4 gives the viscosity growth function $\bar{\eta}(t, \dot{\gamma})$. The function $\bar{\eta}(t, \dot{\gamma})$ increased monotonously with time at the lowest rate of shear studied. At the second lowest rate of shear it increased with time, passed over a maximum, and then leveled off to approach the steady value $\eta(\dot{\gamma})$. The existence of a maximum in $\bar{\eta}(t, \dot{\gamma})$ at

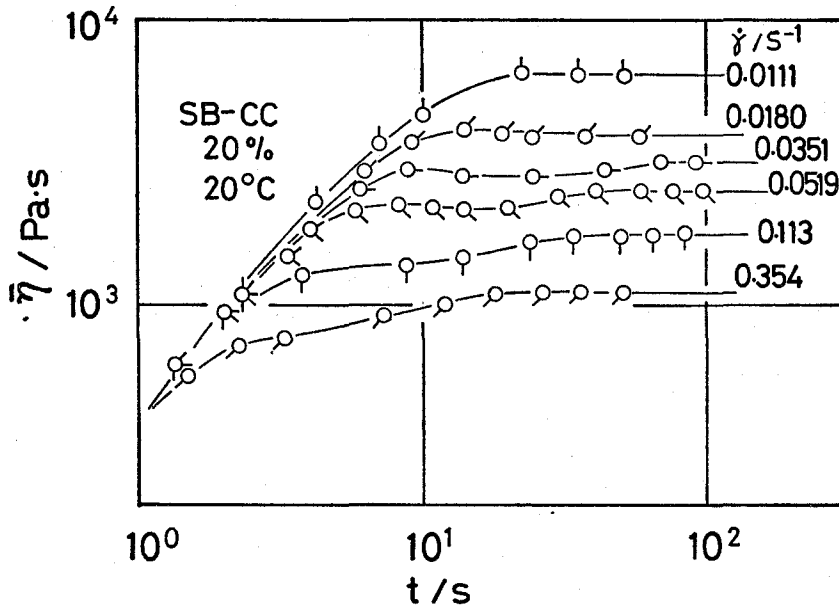


Fig. 4. Viscosity growth function $\bar{\eta}$ plotted against time t for 20% solution of SB in CC at 20°C.

high rates of shear is a well-known phenomenon for ordinary homopolymer solutions and is called the stress overshoot.¹⁹⁾ At higher rates of shear, 0.0351 and 0.0519 s^{-1} , the function $\bar{\eta}(t, \dot{\gamma})$ passed over a maximum and a minimum before leveling off. This type of behavior, *i.e.*, a maximum followed by a minimum in $\bar{\eta}(t, \dot{\gamma})$, has only been reported for a solution of a polystyrene which consists of two components of extremely different molecular weights.²⁰⁾ At still higher rates of shear the maximum became indistinct and the function $\bar{\eta}(t, \dot{\gamma})$ appeared to increase in two steps as a function of time. The amounts of shear strain γ_m applied to the sample before $\bar{\eta}(t, \dot{\gamma})$ attained maxima were 0.26, 0.35, and 0.47 at $\dot{\gamma}=0.0180, 0.0351,$ and $0.0519 s^{-1}$, respectively. These values are smaller by one order than the values, 2.5–3.5, for homopolymer solutions.

The data of Fig. 4 are replotted in Fig. 5, where the shear stress $\dot{\gamma}\bar{\eta}$ at the start of steady shear flow is plotted against the amount of shear γ . The shear stress increased along a straight line of 45° slope with increasing shear until it became to increase more slowly at a certain critical strain determined for each rate of shear. It may be noted that the change from the line of 45° slope to the flatter curve occurred quite sharply in a limited range of strain. This is not the case for homopolymer solutions, for which the change occurs gradually over a wider range of strain. The first increase of stress in proportion to the strain may be due to the elastic deformation of whatever structure existed in the sample at rest and the deviation therefrom to the destruction of the original structure.²¹⁾ The sharp change from the first increase to the flatter portion may indicate that the structural change in the SB solution is more definite and sharp as compared with the change of the temporary entanglement network due to the chain slipping in homopolymer solutions. This conjecture is not in conflict with the concepts of the thread-like structures in the SB solution and their

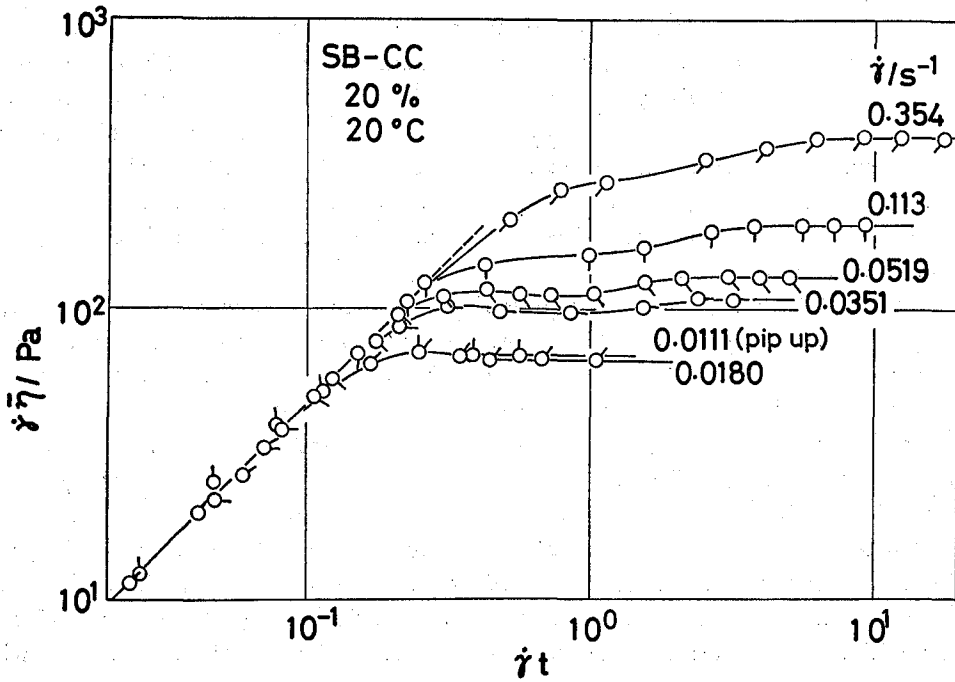


Fig. 5. Replot of data of Fig. 3. Shear stress $\dot{\gamma}\bar{\eta}$ is plotted against magnitude of shear $\dot{\gamma}t$.

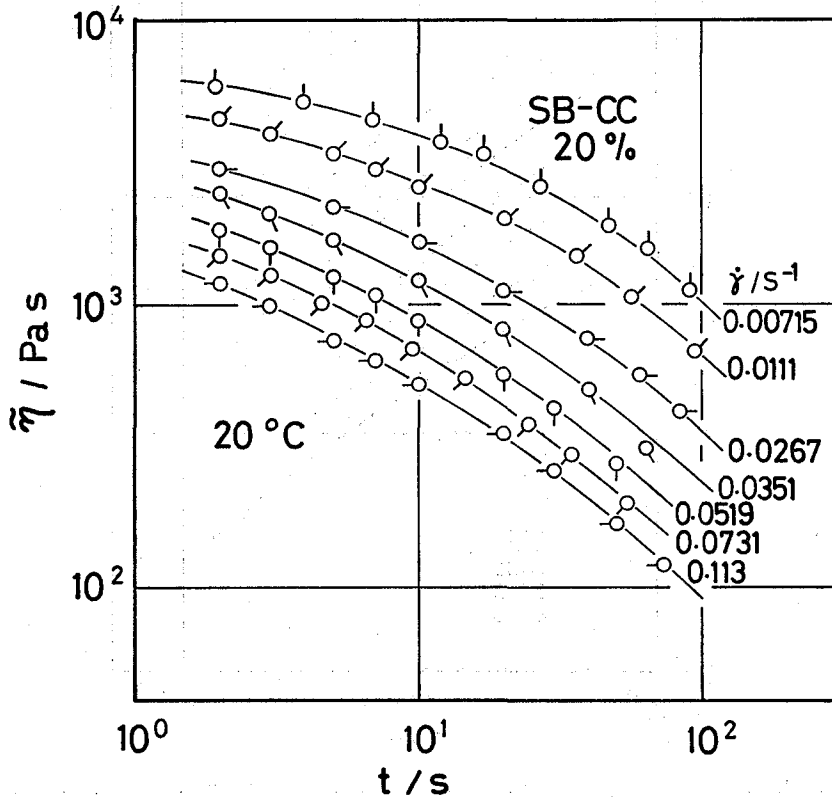


Fig. 6. Viscosity decay function $\bar{\eta}$ plotted against time t for 20% solution of SB in CC at 20°C.

destruction in shear as discussed in relation to the Casson plot.

Figure 6 shows the viscosity decay function. The function $\tilde{\eta}(t, \dot{\gamma})$ decreased rather gradually over all the range of time. It did not decrease very rapidly even at the longest time studied indicating the existence of relaxation modes of very long times beyond the range of measurements. The stress decreased to within the detectable limit of the apparatus in an hour so that the residual stress, if at all, was smaller than 1 Pa at any rate of shear. The effect of rate of shear was slightly larger at longer times than at shorter times.

The relaxation modulus $G(t, \gamma)$ is shown in Fig. 7. The relaxation modulus decreased rather gradually with time, as the function $\tilde{\eta}(t, \dot{\gamma})$ did, over the range of time studied. This result implies the contribution to stress of relaxation modes of very long times beyond the range of measurements. In order to see the effect of shear strain, we replotted $G(t, \gamma)$ against γ in Fig. 8. Apparently the strain dependence of $G(t, \gamma)$ in the range of $\gamma < 1$ was much larger than in the range of larger γ . The relaxation modulus depended on the shear strain even at the lowest strain studied, so that it was not possible to determine if there was any definite limiting value, *i.e.*, the linear relaxation modulus, at the limit of vanishing strain. The effect of varying strain was almost the same at any time. In more details the relaxation modulus at 50 s exhibited a stronger dependence on γ at small and large strains as compared with

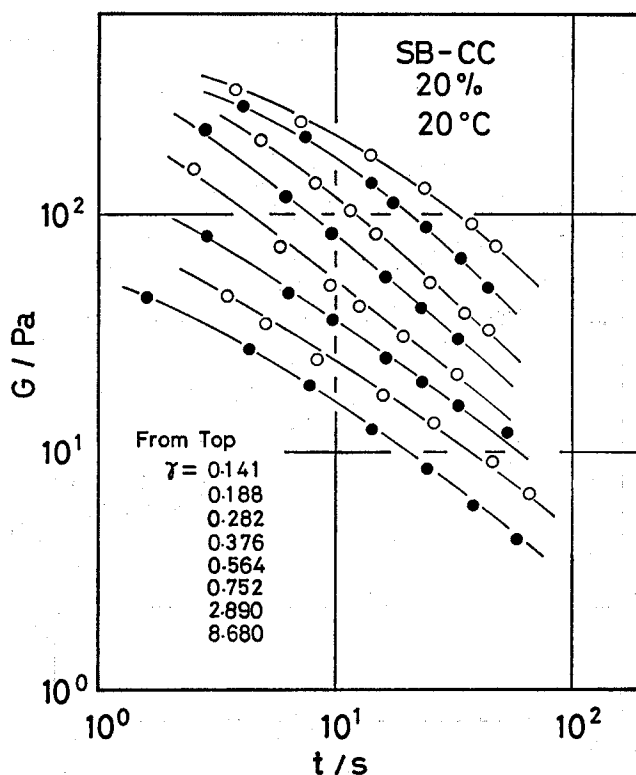


Fig. 7. Strain-dependent relaxation modulus G plotted against time t for 20% solution of SB in CC at 20°C.

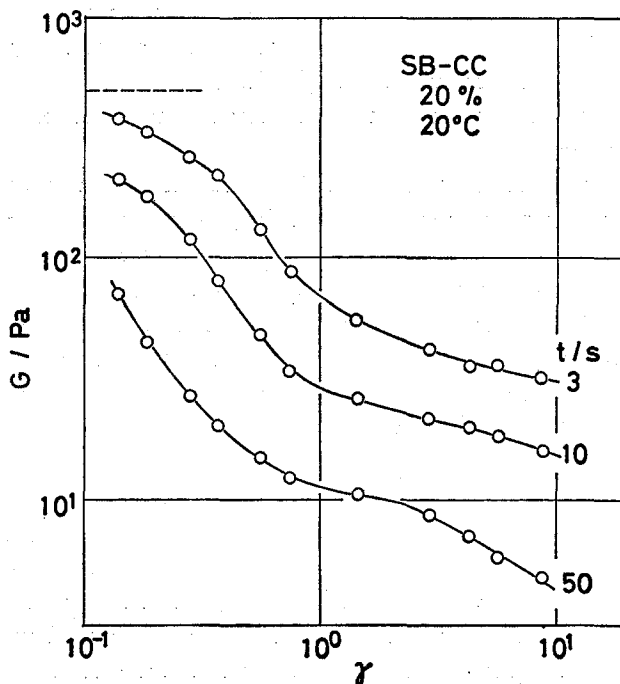


Fig. 8. Dependence of relaxation modulus G on magnitude of shear γ . Data were taken from curves of Fig. 7 at $t=3, 10,$ and 50 s.

those at shorter times. The curves for 3 and 10 s showed a trend to level off at small strains. The dashed line in Fig. 8 represents the modulus calculated from the line of 45° slope in Fig. 5. This modulus may possibly give the upper limit of the relaxation modulus. In order to examine this conjecture, we will have to perform measurements for γ of the order of 10^{-2} .

DISCUSSION

The rheological behavior of the SB solution in CC was largely affected by varying temperature as seen in Fig. 2. At temperatures higher than 50°C , the rate dependence of viscosity was quite similar to that of homopolymer solutions. Thus the domain structure, if at all, of the solution does not contribute to support much extra stress at high temperatures. On the other hand, the rate dependence of viscosity at low rates of shear was very large at low temperatures so that the viscosity increased enormously with decreasing rate of shear. At sufficiently low temperatures, say lower than 20°C , the stress in the steady flow may be mainly supported by the thread-like structures of domains of polystyrene blocks as suggested in relation to the Casson plot of Fig. 3. The variation of the length of threads with varying shear rate, caused by the disruptive force due to the shear stress, may give rise to the strong rate dependence of viscosity in accord with the Casson theory. If this is the case, the stress growth as shown in Fig. 5 should be related to the process of disruption of the structures. At 40°C , which separates the temperature ranges of two typical rheological properties, the flow

behavior of the solution was unstable. An application of optical methods, *e.g.*, the light scattering method, may be employed to study the structural changes associated with the phenomena as discussed in this paragraph. Preliminary studies have revealed that a large turbidity is induced on the application of shear stress to a solution of the SB in liquid paraffin.²²⁾

As suggested earlier, the SB solution in CC is likely to have a very weak relaxation mode of extremely long relaxation time, probably of the order of $10^4 \sim 10^5$ s, at low temperatures. Apart from this relaxation mode, a considerable contribution to stress comes from strain-sensitive relaxation modes of long relaxation times, which lie beyond the range of measurements with the present techniques. The full elucidation of the constitutive equation for the SB solution in CC requires some means for measuring very low stresses at very long times. On the other hand, some of the important features of the present result can be consistently interpreted in terms of the strain-dependent constitutive equation of Bernstein, Kearsley, and Zapas, (BKZ model)²³⁾, which has been applicable to many homopolymer solutions²⁴⁾ and a few block copolymer solutions.^{9,11)}

According to the BKZ model, one can evaluate the shear stress for the simple shear flow of any flow history with the knowledge of the strain-dependent relaxation modulus $G(t, \gamma)$. The relaxation modulus of slight or no strain dependence is associated with the viscosity growth function $\bar{\eta}(t, \dot{\gamma})$ which increases monotonously with time. A fast decrease of $G(t, \gamma)$ with increasing γ is associated with a maximum in $\bar{\eta}(t, \dot{\gamma})$ at high rates of shear and the maximum is predicted to appear at a shorter time as the fast decrease of $G(t, \gamma)$ occurs at a smaller strain γ .²⁵⁾ The relaxation modulus for the SB solution decreased rapidly at small strains and was affected only slightly by γ at large strains. Thus one can predict with the BKZ model the qualitative features of the viscosity growth function with a maximum followed by a minimum. Actually one can obtain a series of curves similar to those of Fig. 4 by using the BKZ model and a suitable function to simulate the strain dependence of $G(t, \gamma)$.

It can also be shown^{23,24)} that if the relaxation modulus is described with a single relaxation time τ , then the variation of $G(t, \gamma)$ with γ should be analogous to the variation of the viscosity $\eta(\dot{\gamma})$ with a reduced rate of shear $\dot{\gamma}\tau$. We can see some analogy between a curve of Fig. 8 and a curve for 20°C of Fig. 2. Each curve decreases rapidly at small values of argument and slowly at large values of argument. It is true that the relaxation modulus cannot be approximated by a single relaxation mode and so it may be dangerous to put too much stress on the correspondence. However, the correspondence stated in this and the preceding paragraph may give a good clue to determine the constitutive equation for such a complicated system as the SB solution. It is encouraging to imagine that the flow properties over certain times can be described with the simple BKZ model for systems which might show pseudo-plastic behavior.

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