

Rheology of Styrene–Butadiene Diblock Copolymers in Selective Solvent: Mechanisms of Thixotropy and Thermally Induced Rheological Transition

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ABSTRACT: Styrene-rich butadiene–styrene (BS) diblock copolymers dispersed in dibutyl phthalate (DBP) formed *micelles* with B cores and S cilia. As the concentration was increased, these micelles arranged themselves on a *macrolattice*, and the system began to show plasticity and also thixotropy. When the temperature was raised, the system underwent a transition from plastic to viscoelastic behavior. This rheological transition was found to be associated with disordering of the macrolattice. The mechanism was interpreted as follows. With increasing temperature, the S and B blocks intermix more extensively in the interphase, making the interphase more diffuse. The mobility of the B–S junctions in the diffuse interphase increases, and hence, the stability of the macrolattice is reduced. This interpretation is supported by the following two findings: no transition occurred when the micelle cores were crosslinked in order to prevent intermixing of the B and S blocks and to anchor the junctions tightly on the cores; no plastic behavior was observed for DBP solutions of tapered block copolymers (tBS) with the characteristics comparable to those of the BS/DBP micellar solutions. In such a tBS solution, micelles with a diffuse BS interphase were formed, and the macrolattice became unstable. Thixotropy of the system having a macrolattice was apparently caused by breakage of the macrolattice but not necessarily that of the micelles. In fact, the macrolattice system of BS micelles with crosslinked B cores exhibited thixotropy, while random suspensions of the micelles were neither plastic nor thixotropic.

KEY WORDS Block Copolymer Solution Rheology / Butadiene–Styrene Diblock Copolymer / Micelle System / Macrolattice / Nonlinear Dynamic Behavior / Plasticity / Viscoelastoplasticity / Disordering of Macrolattice / Plastic-to-Viscoelastic Transition / Thixotropy /

Solutions of diblock copolymers such as styrene–butadiene (SB) systems in a selective solvent, which dissolves one of the blocks but precipitates the other, show anomalous rheology.^{1–3} These solutions often exhibit a yield value^{1–3} as well as thixotropy.¹ The residual stress after cessation of steady flow agrees with the yield value.² Furthermore, these solutions show nonlinear behavior in oscillatory shear and plastic flow in steady shear. We call such behavior *viscoelastoplasticity*.⁴ This behavior is considered to result from the presence of some higher order structure in the system.¹

Recently, we examined the rheology and the internal structures of such SB solutions in detail.^{5–7}

When an SB diblock copolymer (30 wt% S content and the number average molecular weight M_n 5.2×10^4) was dispersed in *n*-tetradecane (C14) which dissolves only B blocks, micelles with precipitated S cores and dissolved B cilia were formed. This system was designated as a *micelle* system. With increased solution concentration, these micelles eventually arranged themselves in a regular three-dimensional array of a simple cubic type, which we termed a *macrolattice*. The micelle system having the macrolattice exhibited plastic flow and nonlinear dynamic behavior.^{5–7} With rise in temperature or dilution, the macrolattice lost its long-range order, but the micelles themselves remained unbroken. The formation and disordering of the

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macrolattice was clarified by SAXS measurements and found to correspond to the rheological transition from plastic to viscoelastic behavior.⁵⁻⁷

In previous papers,^{5,8} we proposed an idea for the force stabilizing the macrolattice against deformation. We considered as follows. In a micelle system above a certain critical concentration, the micelles are arranged on a macrolattice with their cores situated at the lattice points. The cilia assume a conformation having the maximum conformational entropy when the segments of the ciliary chains occupy uniformly the space in the matrix phase. On subjecting the system to shear strain, the micelles are displaced and the concentration profile of the dissolved cilia segments is distorted. This change in concentration profile increases the free energy of the system and gives the macrolattice a restoring force. The thermodynamic force stabilizing the macrolattice is essentially similar to this restoring force which provides a free energy minimum in the undeformed state of the macrolattice.

This idea is supported by the following two experiments. First, the critical concentration for SB/C14 solutions was determined from the micelle size to be that concentration at which the segments of the B cilia began to fill the matrix phase uniformly, *i.e.*, the critical threshold.^{9,10} In these solutions, the precipitated S cores and their radii were essentially independent of the SB concentration. The cores acted as rigid anchors for the dissolved blocks, and the critical concentration could be estimated in a simple way.⁹ Second, the plasticity of the micelle system disappeared when C14 was replaced by low molecular weight homopolybutadiene (hB).^{11,12} The freely mobile hB molecules compensated for the change in local concentration profile of the ciliary B segments induced by shear strain, thereby reducing the stability of the macrolattice. However, some problems still remain (to be solved). One is the mechanism of the transition of rheological behavior accompanying the thermally induced disordering of the macrolattice. Our preliminary experiments⁹ indicated that the critical temperature at which the macrolattice became disordered became higher with increasing molecular weight M_{SB} in SB samples having a fixed composition. For SB having a smaller M_{SB} , the interphase between S cores and B cilia became more diffuse with rising temperature.⁹ This tendency appeared to play a key role in the thermally induced

transition of both rheology and the macrolattice. Another problem is the mechanism of thixotropy often exhibited by micelle systems having a macrolattice. In this study, these two problems are investigated.

EXPERIMENTAL

Materials

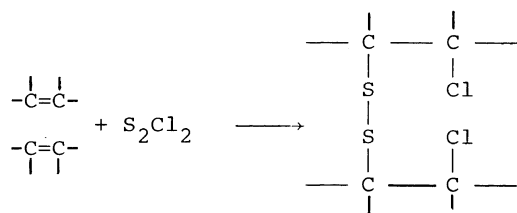
The systems examined in this study were mainly dibutyl phthalate (DBP) solutions of S-rich butadiene-styrene (BS) diblock copolymers. Three BS samples, BS11, BS12, and tBS21, were prepared by anionic polymerization. The samples BS11 and BS12 were pure diblock copolymers synthesized as follows. First, the styrene monomer was allowed to polymerize in benzene with *s*-butyl lithium at room temperature. After 48 h when all styrene monomers were converted to living polymers, a prescribed amount of butadiene monomer was distilled into the reaction vessel and allowed to polymerize at room temperature. After 5 days, all butadiene monomers were consumed and the reaction was terminated with methanol. Butylhydroxytoluene (about 0.1 wt% of the product BS) was added to the benzene solution as an antioxidant. The entire solution was freeze-dried to recover the BS diblock copolymer. The sample tBS21 was prepared using essentially the same method except that styrene and butadiene monomers were introduced simultaneously into the reaction vessel. This procedure gave a tapered structure, confirmed by the degradation reaction described below.

The molecular characteristics of the samples were determined using a gel permeation chromatograph (GPC: Toyo Soda Ltd., Model HLC-801 A) with a triple detector system, consisting of a built-in refractometer, a UV-absorption detector (Toyo Soda Ltd., Model UV-8), and a low-angle laser light scattering photometer (Toyo Soda Ltd., Model LS-8) connected in series. The carrier solvent was chloroform. Commercially available PS samples (Toyo Soda Ltd., TSK PS's) were used for calibration.

The block S content in the sample tBS21 was determined by degrading the B segments¹³ and analyzing the residual block PS. The procedure was as follows: To a 1 wt% tBS21/chlorobenzene solution, 4 ml of 5 wt% OsO₄/benzene and 40 ml of 5 wt% *t*-butyl hydroperoxide/*t*-butyl alcohol solutions were added for one gram of B blocks in the

sample. The solution was refluxed at 90°C for 15 min, cooled, and poured into methanol. White powder (block PS) and a black gel containing partly degraded and partly crosslinked B blocks were precipitated and styrene fragments released from the tapered portion were removed by filtration. The residue was dissolved in chloroform, and the insoluble gel was removed by filtration. The remaining block PS was then analyzed by GPC. Table I shows the sample codes and characteristics of these copolymers. For comparison, our previous data on some SB diblock copolymers^{1,4-6,9} are also shown.

We allowed the B segments of the sample BS11 and BS12 to crosslink in order to compare the rheology of BS/DBP micelle systems having similar characteristics but crosslinked with respect to the B cores in one and not in another. The crosslinking of B cores was carried out in 6 wt% BS11 and 15 wt% BS12 DBP solutions. These solutions exhibited no plasticity and could easily be stirred during the crosslinking reaction. 2.5 mol of sulfur monochloride S₂Cl₂ per mol of C=C bonds of the B segments were added to them. The reaction proceeded as follows¹⁴:



After the reaction mixture had been gently stirred for 15 min at room temperature, the product was precipitated with excess *n*-hexane. Unreacted S₂Cl₂ and DBP were washed out thoroughly with a 15 wt% carbon disulfide/*n*-hexane solution. The precipitated sample was then dispersed in benzene, and the solution was freeze-dried to recover the crosslinked block copolymer sample. The increase in the weight of the BS copolymer due to this reaction was about 8.9% for BS11 and about 5.4% for BS12. Infrared (IR) spectra showed that 54 and 43% of the C=C bonds of the B segments underwent a reaction in the samples BS11 and BS12, respectively. Table I also shows the characteristics of these crosslinked samples. The crosslinked samples were not soluble in C14, a good solvent for PB only, while the original (uncrosslinked) BS11 and BS12 samples were readily dissolved in C14 to form

Table I. Characteristics of polymer samples

1) Raw block copolymer

Code	10 ⁻⁴ M _n	M _w /M _n	PS content/wt%	
			Overall	Block PS
BS11	9.2	1.08	82.5	82.5
BS12	4.0	1.06	87.7	87.7
tBS21	8.7	1.06	82.6	72.5
cSB ^a	5.2	1.5	29.5	18.2
SB1 ^b	6.6	1.06	30.0	30.0

2) Crosslinked block copolymer micelles

Precursor	Code	Fraction of reacted C=C bonds ^c
BS11/DBP (6)	$\frac{S_2Cl_2}{-B(X)S11}$	54%
BS12/DBP (15)	$\frac{S_2Cl_2}{-B(X)S12}$	43%

^a Phillips Solprene 1205 (ref 5).

^b Reference 9.

^c Determined from IR spectra.

micelles with S cores and B cilia. On the other hand, DBP dissolved both the original and crosslinked samples to yield micellar solutions.

Although the structural characteristics of the samples with the crosslinked B cores were not examined by SAXS, some changes such as a small contraction of the cores were probably caused by a crosslinking reaction. A few cores may have been agglomerated by intra and inter-micellar crosslinking to yield a broad distribution of micelle core size. However, it may be, judging from the results of the solubility test described above, that the extent of agglomeration is not very large. Thus, micelles with tightly crosslinked B cores, possibly having rather non-uniform size distribution, were apparently obtained by the reaction mentioned above.

DBP solutions were prepared by mixing prescribed amounts of the copolymer and DBP with excess methylene chloride, and evaporating the methylene chloride.² Our preliminary solubility test showed even a low molecular weight homopolybutadiene with *M*=2000 to be insoluble in DBP. Hence we expected that in DBP solutions of the sample having the shortest B block (*M_n* ≈ 5000 for BS12), B segments were precipitated. Since the volume fraction of the (S+DBP) phase was much

larger than that of the precipitated B phase, micelles with spherical B cores and S cilia were expected to be formed in DBP solutions.¹⁵ The systems examined were designated as solute code/solvent code (wt% of the solute). For example, BS11/DBP(16) and B(X)S11/DBP(17) represent 16 wt% and 17 wt% DBP solutions of the original and cross-linked BS11 samples, respectively.

Rheological measurements

Steady flow and dynamic measurements were carried out with a laboratory rheometer (an Autoviscometer L-III, Iwamoto Seisakusho, Kyoto) mounted with a Couette assembly. The radii R_1 and R_2 of the bob and cup were 12.5 and 15.0 mm, respectively, and the height h of the bob was 70.0 mm.

For some micellar systems examined here, the dynamic stress profile against a sinusoidal strain was not sinusoidal but contained higher-order odd harmonics. This stress profile was analyzed assuming a constitutive equation of the Fourier series type defined by eq 1, and the nonlinear dynamic moduli⁵ G_j' and G_j'' were determined numerically.

$$\gamma = \gamma_0 \sin \omega t, \quad \sigma = \gamma_0 \sum_j [G_j' \sin j\omega t + G_j'' \cos j\omega t] \quad (1)$$

The details are described elsewhere.⁵ Steady flow data were represented as a plot of the apparent shear rate $\dot{\gamma}_{app} = 2R_2^2 \dot{\Omega} / (R_2^2 - R_1^2)$ versus the steady shear stress at the bob wall, where $\dot{\Omega}$ denotes the angular velocity of the cup.

The double-step shearing test was used to examine the thixotropy and rheopexy of the systems. First, a given system was sheared with a high shear rate $\dot{\gamma}_i$ until the steady state was attained. The shear rate was then changed to a lower value $\dot{\gamma}_s$ and the stress recovery was measured as a function of time. About 5 s were required for the rheometer to change the shear rate from $\dot{\gamma}_i$ to $\dot{\gamma}_s$. Whenever necessary to eliminate preshearing effects, the sample was annealed in the rheometer in the following way: the sample was kept at 80°C for 30 min, then slowly cooled to the measuring temperature, usually 25°C, and further annealed for 4 h. In this way, we could always obtain reproducible results representative of the behavior of the original solution free from previous history of deformation.

RESULTS

Transition of Rheological Behavior

Figure 1 shows the steady flow behavior of BS11/DBP solutions with 10, 14, and 16 wt% concentrations at 25°C. A rheological transition from viscoelastic to plastic behavior took place between 14 and 16 wt%, and was similar to that found in cSB/C14 and cSB/DBP systems. In these latter systems, it was confirmed by SAXS that the rheological transition was accompanied by the formation of a macrolattice from a random dispersion of micelles.⁵

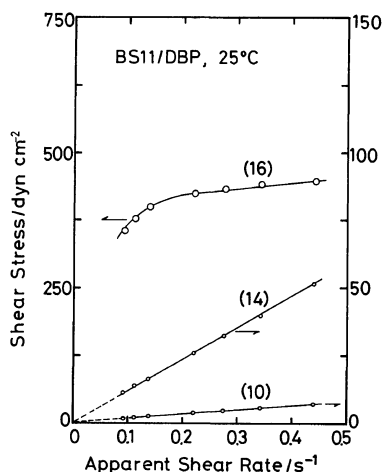


Figure 1. Steady flow behavior of the BS11/DBP system at three concentrations at 25°C.

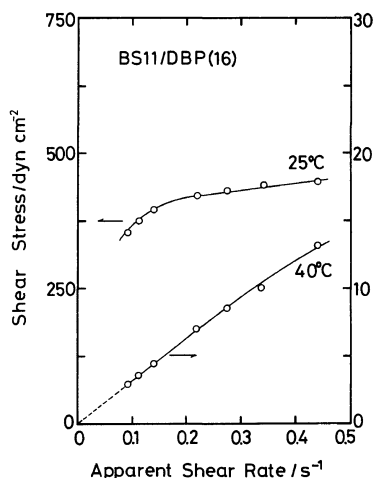


Figure 2. Steady flow behavior of the BS11/DBP(16) system at 25 and 40°C.

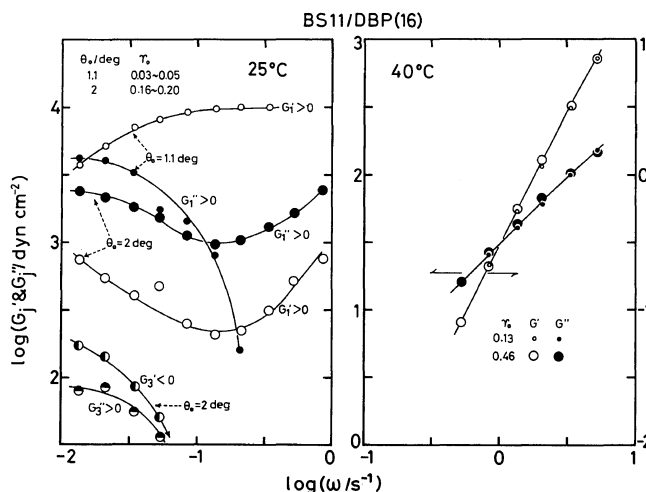


Figure 3. Dynamic behavior of the BS11/DBP(16) system at 25 and 40°C.

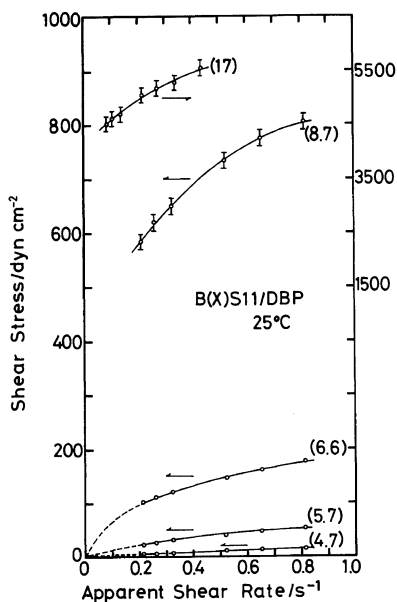


Figure 4. Steady flow behavior of the B(X)S11/DBP system at five concentrations at 25°C.

The temperature dependence of the rheological behavior was examined for the BS11/DBP(16) system. Figures 2 and 3 show the steady flow and dynamic behavior of this system at 25 and 40°C, respectively. It can be seen that a thermally induced transition, essentially similar to that found in the cSB/C14 and cSB/DBP systems, occurs between these temperatures; a disordering of the macrolat-

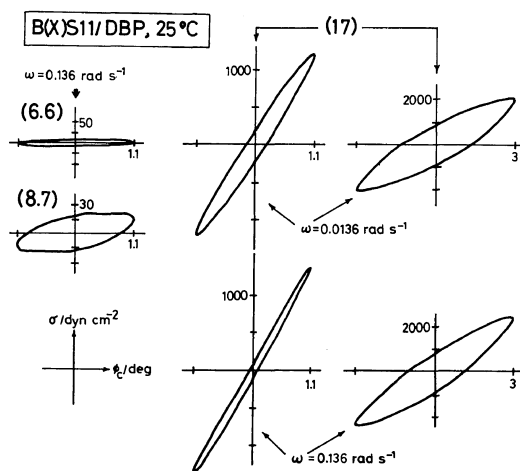


Figure 5. Typical Lissajou's patterns of the B(X)S11/DBP system at various concentrations at 25°C.

tice took place with rising temperature.⁵ In fact, a preliminary SAXS test showed the macrolattice to be disordered at about 30°C in this BS11/DBP(16) solution.¹⁶

The left panel of Figure 3 illustrates nonlinear behavior of the BS11/DBP(16) system at 25°C typical of a micelle system having a macrolattice. For the amplitude of the cup $\theta_0 = 1.1^\circ$ the system exhibited dynamic behavior free from higher order harmonics, but for $\theta_0 = 2^\circ$ the behavior was nonlinear and the system exhibited thixotropy. This thixotropic behavior is discussed in the following section. On the other hand, the system at 40°C did

not show plastic flow but exhibited linear dynamic viscoelasticity as is illustrated in the right panel of Figure 3.

The results from a similar test on B(X)S11/DBP systems are illustrated in Figures 4 and 5, which show the steady flow behavior and some typical Lissajou's patterns at 25°C, respectively. It can be seen that this system undergoes a viscoelastic to plastic transition at a concentration between 6.6 and 8.7 wt%. The transition is again similar to those found in other systems⁵ including the BS11/DBP system.

Figures 6 and 7, respectively, show the steady flow and dynamic behavior of the B(X)S11/

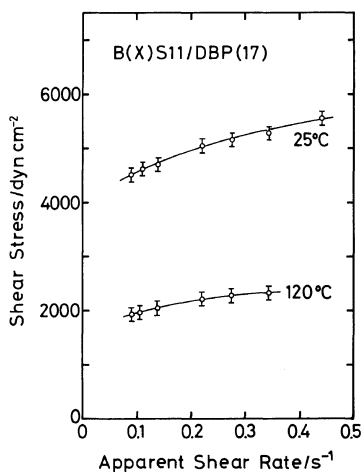


Figure 6. Steady flow behavior of the B(X)S11/DBP(17) system at 25 and 120°C.

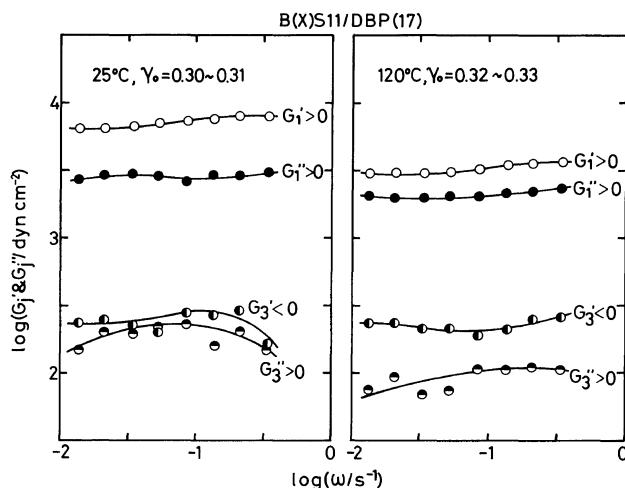


Figure 7. Dynamic behavior of the B(X)S11/DBP(17) system at 25 and 120°C.

DBP(17) system at 25 and 120°C. Even at 120°C, the system still exhibits the features of a micelle system having a macrolattice:⁵ plastic flow and nonlinear dynamic behavior, *i.e.*, the plateau of the fundamental harmonics G_1' and G_1'' and the large contribution of the higher odd harmonics G_3' and G_3'' . At temperatures above 150°C, the system became dark brown probably due to a partial degradation of crosslinked B blocks. However, the rheology of the system was still plastic even at these high temperatures. A preliminary SAXS test showed that in the B(X)S11/DBP(17) system, an ordered array of microdomains was formed and persisted up to a temperature as high as 120°C.¹⁶ The structure may be essentially a macrolattice similar to that found in cSB/C14 systems.¹⁶

The behavior of the tBS21/DBP system was in contrast to that of BS11 and B(X)S11/DBP systems. Figure 8 shows the steady flow behavior at 25°C of this system at several concentrations. This system does not exhibit plasticity even at a concentration as high as 29.7 wt%, although micelles are formed in it.

In our previous rheology and SAXS experiments,^{5,6,9} we demonstrated that solutions of a tapered block copolymer (cSB) have a critical concentration c^* for the rheological and structural transition higher but a critical temperature T^* lower than those of a corresponding pure diblock copolymer (SB1), which has nearly the same S content and molecular weight, but no tapered portion in the chain (*cf.* Table I).

Comparing the behavior of tBS21, BS11, and B(X)S11/DBP and other systems, we may deduce that the rheological transition from plastic to viscoelastic behavior occurs probably as a result of a disordering of the macrolattice. We also notice that in the B(X)S11/DBP system the macrolattice becomes disordered by dilution but not by a rise in temperature (up to 150°C). On the other hand, the tBS21/DBP system apparently forms no macrolattice in the ranges of concentration and temperature examined in this study. We have not yet succeeded in determining the exact structure of the macrolattice and/or size of the micelles in these tBS21, BS11, and B(X)S11 systems because of the lack of de-smear scattering profiles.

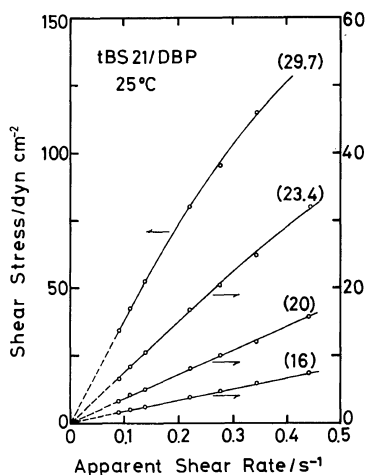


Figure 8. Steady flow behavior of the tBS21/DBP system at various concentrations at 25°C.

Thixotropy and Rheopexy

Figure 9 shows typical Lissajou's patterns obtained for the BS11/DBP(16) system at 25°C. When θ_0 is 1.1 deg, the Lissajou's pattern is almost elliptic at $\omega = 0.0136 \text{ rad s}^{-1}$. At a frequency of 0.136 rad s^{-1} , the pattern becomes almost rectilinear and the system is nearly elastic (*cf.* Figure 9, upper row). From such stress profiles G_1' and G_1'' were evaluated by eq 1, but virtually no contribution of G_3' and G_3'' was found (*cf.*, Figure 3). In contrast to the previously reported cSB/C14(20) system which was nearly elastic for small amplitude oscillation,^{4,5} the BS11/DBP(16) system possesses a certain loss mechanism even for small amplitude oscillation.

When $\theta_0 = 2^\circ$, nonlinear dynamic behavior was found at a low frequency ω of $0.0136 \text{ rad s}^{-1}$. However, at higher frequencies, the system showed anomalous behavior. During the first few cycles of oscillation with $\theta_0 = 2 \text{ deg}$ at $0.0524 \text{ rad s}^{-1}$, the system exhibited a lozenge-shaped Lissajou's pattern. The maximum stress was about 450 dyn cm^{-2} , which is larger than that of the Lissajou's pattern at $0.0136 \text{ rad s}^{-1}$. The Lissajou's pattern at $0.0524 \text{ rad s}^{-1}$ gradually changed its shape to nearly elliptic and the maximum stress also became smaller. Finally after 20 cycles of oscillation, the pattern became a closed ellipsoid with a maximum stress of about 300 dyn cm^{-2} , as seen in Figure 9. Thus, a thixotropic decay of stress took place during the first 20 cycles of oscillation. After the stationary state was reached at $0.0524 \text{ rad s}^{-1}$, ω was switched to $0.0136 \text{ rad s}^{-1}$. Then, after 20 cycles of oscillation the Lissajou's pattern resumed its original lozenge shape. This indicates a rheoplectic stress recovery of the system.

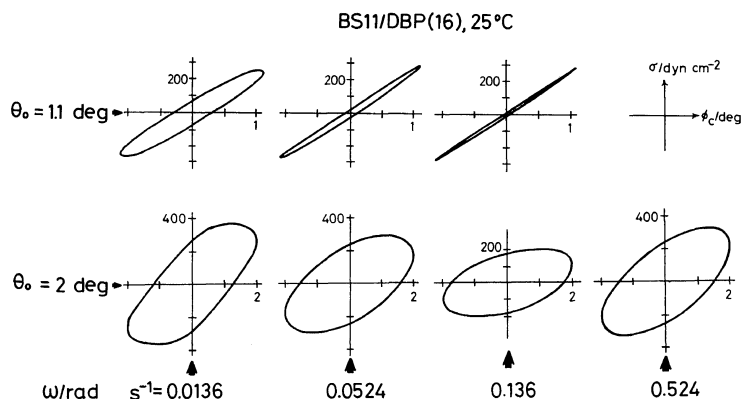


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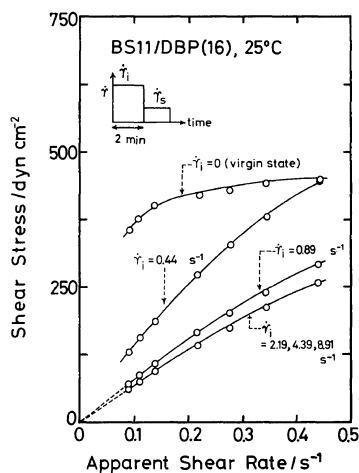


Figure 10. Shear rate dependence of transient and steady shear stresses of the BS11/DBP(16) system at 25°C in the second shearing step. Pre-shearing was made for 2 min, and the transient stress was measured 5 min after shearing at the second rate. The numerical values in the figure indicate pre-shearing rates.

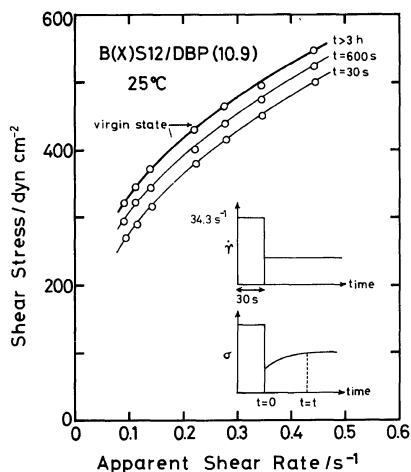


Figure 11. Shear rate dependence of transient and steady shear stresses of the B(X)S12/DBP(10.9) system at 25°C in the second shearing step. Pre-shearing at 34.3 s⁻¹ was made for 30 s, and the transient stress was measured 30 and 600 s after shearing at the second shear rate.

When ω increased to 0.136 rad s⁻¹, the pattern became smaller in size and more nearly elliptic in shape, as seen in the lower row of Figure 9. With an increase in ω to 0.524 rad s⁻¹ and higher, the system showed a completely elliptic Lissajou's pattern in the stationary state after only a few cycles of os-

cillation. In this high frequency region, the maximum stress in the stationary state increased with increasing ω .

To examine the thixotropy and rheopexy of the BS11/DBP(16) system in a steady shear flow at 25°C, we employed the double-step shearing test. The values of $\dot{\gamma}_i$ chosen were 0.44, 0.89, 2.19, 4.39, and 8.91 s⁻¹. The system showed a very slow stress recovery, reaching a steady state (virgin state) after 10 h shearing at $\dot{\gamma}_s$. Therefore, the stress measured 5 min following the change in $\dot{\gamma}_i$ to $\dot{\gamma}_s$ was taken as the transient stress immediately after the change in shear rate.

Figure 10 shows the $\dot{\gamma}_s$ dependence of the transient and steady-state shear stresses of this system in the range of $\dot{\gamma}_s$ below 0.44 s⁻¹. It can be seen that significant thixotropy is caused by shearing at $\dot{\gamma}_i$. Particularly, a significant stress decay is seen in the low shear rate region rather than in the high rate region. The pre-shearing at $\dot{\gamma}_i$ higher than 2.19 s⁻¹ gives almost identical transient (5 min) flow curves passing through the origin. On the other hand, the BS11/DBP(14) system showed no thixotropy (*cf.* Figure 1).

The double-step shearing test was also made on micelle systems having crosslinked B cores. Figure 11 shows the results on the B(X)S12/DBP(10.9) system at 25°C. Because of the weight increase caused by a crosslinking reaction, the amount of the polymer in this system corresponds to that of the 10.2 wt% BS12/DBP solution. In spite of this low polymer concentration, the B(X)S12/DBP(10.9) system exhibited a very high level of shear stress (500 times as large as the corresponding BS12/DBP solution) and exhibited significant plasticity. As seen from Figure 11, the system also shows significant thixotropy after pre-shearing for only 30 s at a high shear rate of $\dot{\gamma}_i = 34.3$ s⁻¹ and a subsequent rheopexic stress recovery, which took 3 h to complete.

All these results suggest that only micelle systems having a macrolattice are plastic and exhibit thixotropy and rheopexy.

DISCUSSION

Mechanism of Thermally Induced Disordering of the Macrolattice

In micelle systems such as those described here and in previous publications,^{4-6,9} it appears that

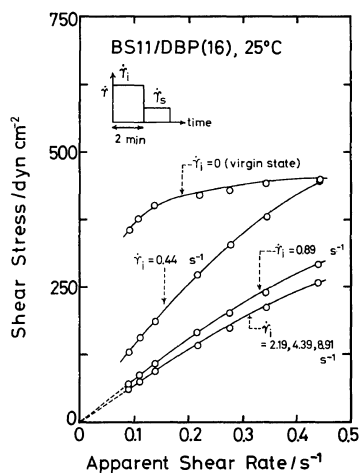


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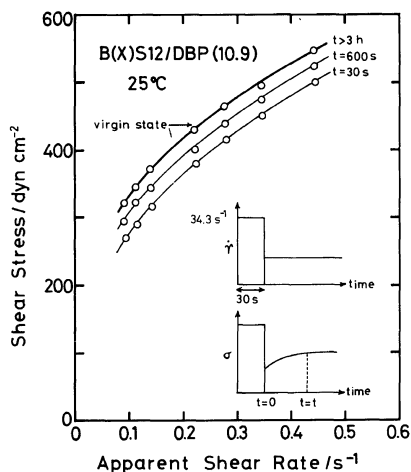


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Mechanism of Thermally Induced Disordering of the Macrolattice

In micelle systems such as those described here and in previous publications,^{4-6,9} it appears that

macrolattices are formed only when the segment concentration of the cilia in the matrix phase exceeds a certain critical value often called the critical threshold.¹⁰ Shear strain imposed on the macrolattice induces a change in the local concentration of the segments of cilia. The force against this change may be related to the osmotic compressibility κ ($= -c\partial c^{-1}/\partial\pi$, where π is the osmotic pressure and c the segment concentration). In the semidilute region, π increases rapidly with c obeying a scaling rule,^{17,18} and κ becomes smaller. As the concentration c increases further, the solution becomes osmotically incompressible ($\kappa \cong 0$) and practically no concentration fluctuation occurs.^{18,19}

This concept may be applied to the present micelle systems having macrolattices. The small κ of the matrix phase of the micelle system strongly prevents the occurrence of changes in local concentration and forces each cilium to take on a conformation which compensates for the concentration changes otherwise induced by the deformation of the macrolattice. In other words, the small osmotic compressibility leads to the demand for a uniformly filling of the matrix phase with the segments of ciliary blocks. On the other hand, each cilium always tends to assume a conformation having the largest possible conformational entropy. Thus, the macrolattice must be formed in such a way that these two contradicting demands are satisfied at the same time. Therefore, when the macrolattice is deformed, the concentration profile in the matrix phase should be distorted, if the cilia do not change their conformation. However, if the concentration gradient is compensated, each cilium should assume either an extended or a collapsed conformation having a less favorable entropy. Both of these effects increase the free energy of the system and drive the micelles to form a macrolattice.

The osmotic driving force is similar to the thermodynamic force operating in bulk block copolymers,^{20,21} where the overall segment density must be uniform. The domain size and morphology in bulk block copolymers correspond to the chain conformation having the largest entropy subject to this constraint.^{20,21} The micellar solution differs from the bulk block copolymer in that the freely mobile solvent molecules exist in the former and not in the latter. The gradient of the block segment density (or more precisely, concentration) profile is unfavorable but not completely inhibited in the

micellar solution, since the overall density of the solution is always kept uniform by the solvent molecules. In such a micellar solution, there still remains a demand that the matrix phase be filled uniformly with the block segments, though it is much weaker than in bulk block copolymers, because the (osmotic) compressibility is not as small as in the bulk. The driving force for macrolattice formation in the micellar solution should therefore disappear or diminish by some factor which reduces this demand. This occurs, for example, when the solution is diluted below its critical threshold.

If we compare the critical concentrations c^* for systems having micelles of roughly similar size, we find that $c^* > 29.7$ wt% for tBS21/DBP, $c^* \cong 14 \sim 16$ wt% for BS11/DBP, and $c^* \cong 6.6 \sim 8.7$ wt% for B(X)S11/DBP, all at 25°C. On the other hand, the critical temperature T^* for these systems at about 16 wt% are as follows: $T^* \leq 25^\circ\text{C}$ for tBS21/DBP(16), $T^* = 25 \sim 40^\circ\text{C}$ for BS11/DBP(16), and $T^* > 150^\circ\text{C}$ for B(X)S11/DBP(17).

Although the sizes of the micelle B core in BS11, B(X)S11, and tBS21/DBP systems may not be exactly the same, the difference may not be sufficient to explain the difference in T^* of these systems. Probably, the most essential factor is whether the B core is crosslinked or not. An increase in temperature enhances the segmental motion of the blocks, and as a result, decreases the segregation power for S and B blocks. However, the B cores of the sample B(X)S11 were densely crosslinked (see Table I), and did not swell in a good solvent to B blocks such as C14 and never in a nonsolvent such as S blocks. In the B(X)S11/DBP system, the crosslinked B blocks and ciliary S blocks hardly intermix with one another at the interphase, whereas in the uncrosslinked BS11/DBP system, intermixing occurs and the interphase becomes more diffuse as the temperature rises. In a tapered block copolymer, the intermixing of the components should take place more easily. In fact, it was reported that the interphase of a tapered block copolymer is more diffuse than that of the corresponding pure block copolymer.²² Thus, the difference in interphase structure and that in the tendency for the interphase to become more diffuse with an increase in temperature appear to be responsible most importantly for the thermally induced transition of these systems.

One may question as to why an intermixed and

diffuse interphase between the core and matrix phases leads to the macrolattice disordering. The driving force for macrolattice formation is essentially the tendency that local concentration fluctuations are suppressed by the change in conformation of the cilia. The point is that the resulting entropy change arises from the condition that one end of each cilium is fixed within a rather narrow interphase surrounding the rigid core. In micelles with crosslinked cores, one end of each cilium is so tightly bound to a core that ease of movement is not permitted at any temperature. In micelles with uncrosslinked cores, the anchored end of each cilium may acquire a large mobility as the temperature rises, because the interphase becomes more diffuse. In micelles of tapered block copolymers, the interphase may be diffuse even at room temperature. In such cases, the cilium can compensate for local concentration change with no appreciable change in its conformation.

Another question is concerned with the extent to which intermixing in the diffuse interphase is required to cause macrolattice disordering. Rheological study alone cannot answer this question, and more quantitative structural research must be carried out.

Mechanism of Thixotropy and Rheopexy

The results presented above indicate that micelle

systems having a macrolattice are plastic and exhibit thixotropy and rheopexy, while random dispersions of micelles are neither plastic nor thixotropic. These features are independent of the viscosity of the system. Thus, thixotropy and rheopexy of micelle systems are due to the disruption and reformation of macrolattices but not necessarily to the breaking up of micelles. In fact, an SAXS test confirmed the presence of micelles in the BS11/DBP(16) system sheared prior to SAXS measurement.¹⁶

If the above consideration is correct, the rate of rheoplectic stress recovery should be faster in the system having a more stable macrolattice. As discussed in the previous section, the driving force for macrolattice formation emerges at the critical concentration c^* and becomes stronger with increasing concentration. Therefore, the stress recovery is slower for solutions slightly above c^* rather than for more concentrated solutions, although the viscosity of the latter is higher than that of the former. This fact was first pointed out by Kotaka and White.¹

In this connection, we should like to mention another type of thixotropy found for micelle systems with *no* macrolattice. An example is cSB blended with a low molecular weight homopolybutadiene (coded as chB, $M_n = 2000$). Since chB is a nonsolvent to S blocks, the cSB molecules form micelles with S cores and B cilia. However, the

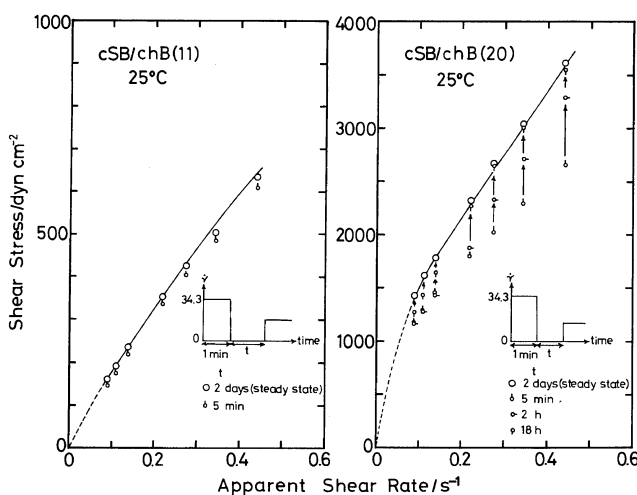


Figure 12. Shear rate dependence of transient and steady shear stresses of 11 (left) and 20 wt% (right) blends of cSB/chB at 25°C in the second shearing step. Pre-shearing at 34.3 s^{-1} was made for 1 min, the blends were then rested for 5 min, 2 h, and 18 h at 25°C, a second step shear was imposed, and the transient stress was measured 1 min after.

systems had no macrolattice and were not plastic but viscoelastic.^{11,23,24} The cSB/chB blend showed the Weissenberg effect during the shearing. The system was then kept at rest for certain periods of time t (5 min, 2 h and 18 h) before being subjected to a second shearing at $\dot{\gamma}_s$. The transient stress was measured 1 min after imposition of the second shear $\dot{\gamma}_s$. The results are shown in Figure 12 for blends of 11 and 20 wt% cSB in chB at 25°C, which were presheared at 34.3 s^{-1} for one min. The blends clearly exhibit thixotropy, especially in the high shear rate region. The 11 wt% blend almost returned to the steady (virgin) state after a 5 min rest at 25°C, while the 20 wt% blend required an 18 h rest or more to reach the steady state. The steady state was also attained by the thermal annealing described in EXPERIMENTAL.

The behavior of these cSB/chB blends is quite different from that of micelle systems having a macrolattice. The thixotropic stress decay occurs at higher shear rates. The stress recovery is slower in more concentrated blends. Usually, thixotropy is attributed to the disruption of *some* structure existing in the system, but these blends have no macrolattice. Thus, their thixotropic behavior may be attributed to the breakage of micelles. For the rigid S core to be broken by shearing, the medium must be viscous enough to generate a large shear stress. In fact, the stress of about 10^5 dyn cm^{-2} or more was generated during the pre-shearing at 34.3 s^{-1} . For stress recovery following the disruption of micelles, the cSB chains must aggregate to reform the micelles, and their mobility should determine the rate of recovery. Therefore, the stress recovery is slower in more concentrated blends.

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