Rheological behaviour of block copolymers in the disordered state: effects of molecular weight and block length ratio

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(Received 13 December 1990; accepted 16 January 1991)

The effects of molecular weight and block length ratio on the rheological behaviour of polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymers in the disordered state were investigated. For the study, SIS triblock copolymers were synthesized via anionic polymerization, and linear dynamic viscoelastic properties (i.e. dynamic storage and loss moduli, G' and G'') of the SIS block copolymers were measured at various temperatures as functions of angular frequency (ω), using a cone-and-plate rheometer. The disordered state of the samples was determined by the threshold temperature at which the plot of log G' *versus* log G'' becomes virtually independent of temperature as the temperature was increased. It has been found that when the block length ratio is kept the same, the melt elasticity of SIS block copolymers in the disordered state becomes independent of molecular weight, while the viscosity increases with molecular weight, and the block length ratio greatly influences both melt viscosity and elasticity.

(Keywords: rheological behaviour; block copolymers; molecular weight; block length ratio)

INTRODUCTION

During the past three decades, block copolymers have enjoyed many commercial successes. Among the many block copolymers, polystyrene-based block copolymers have attracted much attention from polymer scientists. They possess many interesting and unique physical–mechanical properties and consequently their use in many industrial applications has grown considerably in recent years. It is well documented in the literature[1,2] that in polystyrene-based block copolymers, the polystyrene phase separates on a microscopic scale, thereby creating a physically crosslinked network structure at room temperature. What makes matters more complicated is that the morphological state of the microdomains varies with the polystyrene content f in a polystyrene-based block copolymer. According to the literature[3,4], a transition from lamellar to cylindrical microdomain structure occurs at an f of $\sim$0.35 and a transition from cylindrical to spherical microdomain structure occurs at an f of $\sim$0.2. The size of the polystyrene spherical microdomains is believed to be of the order of a few hundred ångstroms at room temperature. But as the temperature is raised, the microdomains in the block copolymer disappear at a certain critical temperature, referred to as the order–disorder transition temperature (T_r) or microphase-separation transition temperature[5].

In the past, several research groups reported measurements of the rheological properties of block copolymers; specifically, some investigators[6–9] reported the steady-state shear flow properties, and others[10–19] reported the oscillatory shear flow properties of microphase-separated block copolymers. As mentioned above, since block copolymers undergo a phase transition at T_r, those with microdomain structures at $T < T_r$ will give rise to different rheological characteristics from those in the disordered state at $T > T_r$. So far there has been no systematic experimental study reported in the literature dealing with the effects of molecular weight and block length ratio on the rheological properties of block copolymers in the disordered state.

Very recently, we synthesized a series of polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymers having different block ratios and molecular weights, and measured their linear dynamic viscoelastic properties. In this paper we shall report rheological behaviour of the SIS block copolymers in the disordered state, with emphasis on the effects of molecular weight and block length ratio.

EXPERIMENTAL

Materials

Three SIS copolymers having different block length ratios and block molecular weights were synthesized via anionic polymerization. *Table 1* gives a summary of the molecular characteristics of the block copolymers synthesized. In the polymerization, sec-butyllithium was used as the initiator to first polymerize styrene monomer anionically and then to copolymerize isoprene monomer with this 'living' polystyrene to form polystyrene-*block*-polyisoprene (SI) copolymer. The latter was then reacted

0032-3861/92/020294-12

Table 1 Summary of the molecular characteristics of the SIS block copolymers investigated

Sample code	Block mol. wt. ($\times 10^{-3}$)	Total mol. wt. ($\times 10^{-3}$)	Polystyrene (wt%)	Morphology of microdomain	T_r (°C)
K1107	10.0S-120.0I-10.0S	140.0	14.3	Spheres	220
SIS-A	7.40S-99.0I-7.40S	113.8	13.0	Spheres	180
SIS-B	5.85S-27.3I-5.85S	39.0	30.0	Cylinders	90
SIS-C	7.30S-13.4I-7.30S	27.7	52.0	Lamellae	105

with the stoichiometric amount of 1,2-dibromoethane to couple the SI diblock copolymers into linear SIS triblock copolymers.

The block molecular weights of the SIS block copolymers synthesized in this study were determined by measurement of the molecular weight of polystyrene precursor using gel permeation chromatography (g.p.c.) and the weight fraction of polystyrene block using nuclear magnetic resonance (n.m.r.) spectroscopy. N.m.r. spectroscopic analysis indicated that the polyisoprene consisted of ~6 wt% 3,4-polyisoprene, ~94 wt% 1,4-polyisoprene, and no detectable amount of 1,2-polyisoprene in the SIS block copolymers.

Also included in the study was a commercial grade of SIS block copolymer (Kraton 1107, Shell Development Company) with molecular characteristics as given in *Table 1*.

Sample preparation

Samples for viscoelastic measurements were prepared by first dissolving a predetermined amount of block copolymer into toluene in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the solvent. The evaporation of toluene was carried out initially in open air at room temperature for 1 week and then in a vacuum oven at 40°C for 3 days. The last trace of toluene was removed by drying the samples in a vacuum oven at an elevated temperature by gradually raising the oven temperature up to 110°C. The drying of the samples was continued, until there was no further change in weight. Finally, the samples were annealed at 130°C for 10 h.

Measurement of dynamic viscoelastic properties

A Model R16 Weissenberg rheogoniometer (Sangamo Control Inc.) in the cone-and-plate mode (25 mm diameter plate and 4° cone angle with a 160 μm gap) was used to measure the dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, as functions of angular frequency (ω) at various temperatures, for each of the block copolymer samples in the ordered and disordered states, respectively. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. The temperature control was accurate to within ± 1°C. In oscillatory shear flow measurements a fixed strain of 0.003, which was well within the linear viscoelastic range of the materials investigated, was used. All experiments were conducted in the presence of nitrogen in order to preclude oxidative degradation of the samples.

Plateau modulus of the SIS block copolymers was determined using a Rheometrics dynamic spectrometer (RDS-7700) in the parallel-plate mode (50 mm plates with a 2 mm gap), by taking temperature scans of $G'(\omega)$ at temperatures from -100 to ~140°C with an angular frequency of 10 Hz, and also by taking frequency scans of $G'(\omega)$ at angular frequencies from 0.1 to ~500 Hz at the T_r of each block copolymer studied. In the dynamic spectrometer experiments, the values of strain from 0.05 to 0.005 were used, depending upon the temperature chosen for each sample. It was determined that these values of strain were well within the linear viscoelastic range of the materials investigated.

RESULTS AND DISCUSSION

Determination of disordered state for the SIS block copolymers employed

There are basically two different experimental methods which allow the determination of the order–disorder transition temperature T_r of block copolymers. They are the electromagnetic radiation method (small-angle X-ray or neutron scattering) and the rheological method. The former has been used extensively by different research groups[20–28]. In the use of the rheological method, some investigators[8–10] advocated use of plots of steady-state shear viscosity (or dynamic viscosity) *versus* shear rate (or angular frequency), and others[17–19] advocated use of logarithmic plots of G' *versus* G''. In a recent paper, Han and co-workers[28] reported that the value T_r for an SIS block copolymer determined from small-angle X-ray scattering agreed very well with that determined from log G' *versus* log G'' plots.

Figure 1 gives plots of log G' *versus* log G'' for K1107 at various temperatures. Similar plots are given in *Figure 2* for SIS-A, in *Figure 3* for SIS-B and in *Figure 4* for SIS-C. It can be seen in *Figures 1–4* that for temperatures below a certain critical value, plots of log G' *versus* log G'' vary with temperature, but they become virtually independent of temperature at and above the critical temperature. According to the criterion suggested by Han and co-workers[17–19], the temperature at which plots of log G' *versus* log G'' cease to vary with temperature may be regarded as the order–disorder transition temperature T_r. The values of T_r determined for the four SIS block copolymers are given in *Table 1*.

Figure 5 gives logarithmic plots of dynamic viscosity $\eta'(\omega)$ *versus* angular frequency ω for K1107 at various temperatures, where $\eta'(\omega)$ was determined using the expression $\eta'(\omega) = G''(\omega)/\omega$. Similar plots are given in *Figure 6* for SIS-A, in *Figure 7* for SIS-B and in *Figure 8* for SIS-C. It can be seen in *Figures 5–8* that at temperatures below a certain critical value, plots of log η' *versus* log ω (open symbols) at low values of ω exhibit *yield* behaviour, commonly observed in concentrated suspensions or in highly filled molten polymers[29]. In 1970, Arnold and Meier[8] reported that plots of log η' *versus* log ω for an SIS block copolymer exhibited *yield*

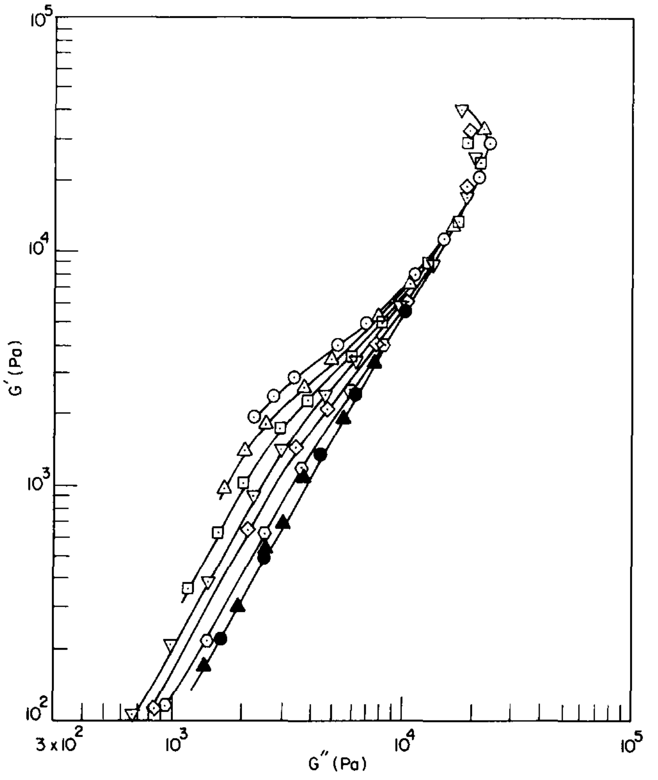

Figure 1 Plots of log G' *versus* log G'' for K1107 at various temperatures (°C): (⊙) 160; (△) 170; (⊡) 180; (▽) 190; (◇) 200; (⊙) 210; (●) 220; (▲) 230

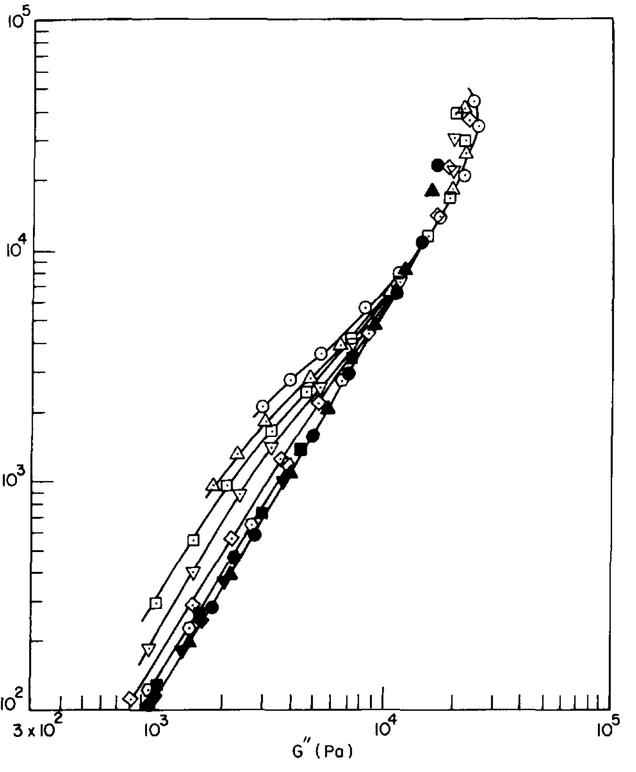

Figure 2 Plots of log G' *versus* log G'' for SIS-A at various temperatures (°C): (⊙) 120; (△) 130; (⊡) 140; (▽) 150; (◇) 160; (⊙) 170; (●) 180; (▲) 190; (■) 200; (▼) 210; (◆) 220; (●) 230

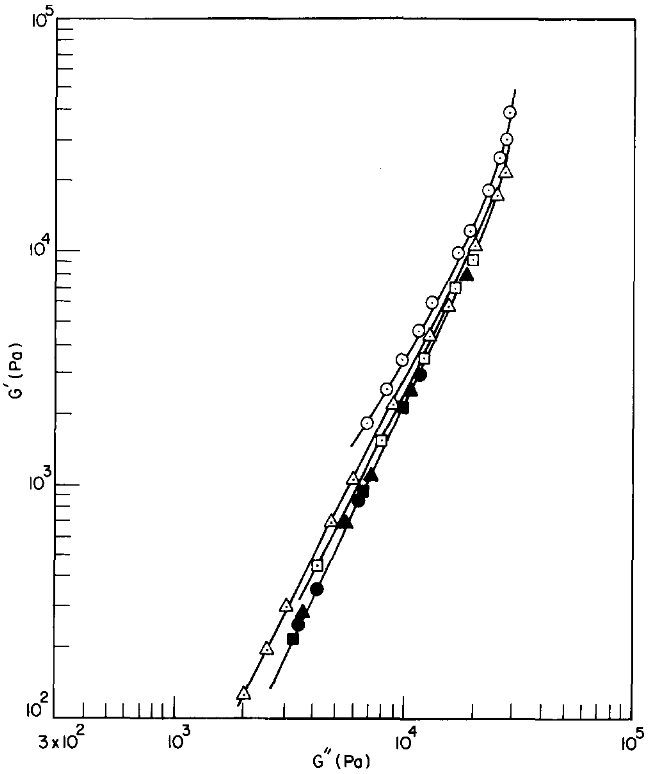

Figure 3 Plots of log G' *versus* log G'' for SIS-B at various temperatures (°C): (⊙) 70; (△) 80; (⊡) 85; (●) 90; (▲) 95; (■) 100

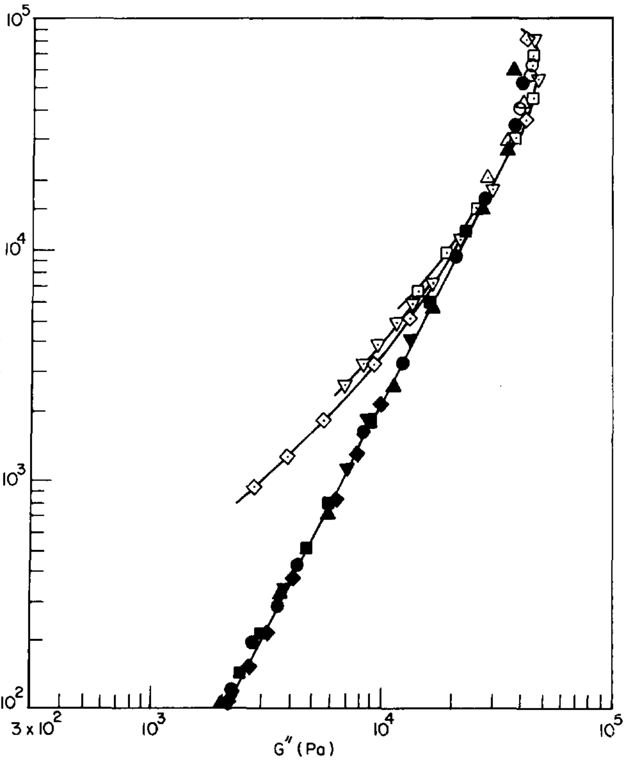

Figure 4 Plots of log G' *versus* log ω for SIS-C at various temperatures (°C): (⊙) 80; (△) 85; (⊡) 90; (▽) 95; (◇) 100; (●) 105; (▲) 110; (■) 115; (▼) 120; (◆) 130

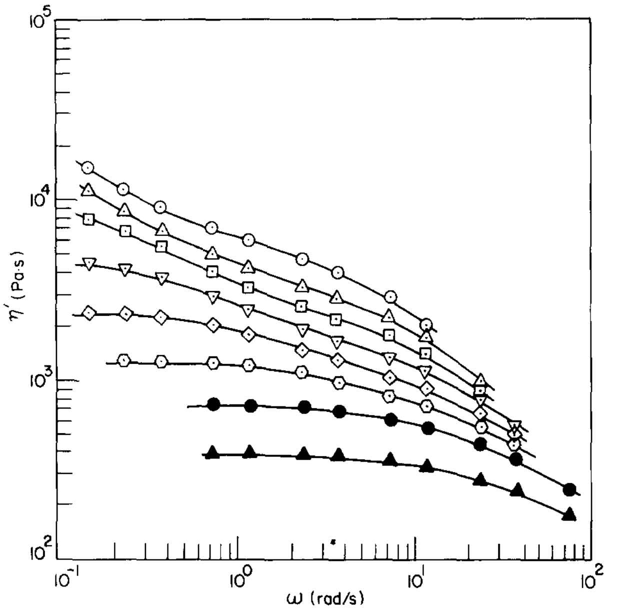

Figure 5 Plots of log η' *versus* log ω for K1107 at various temperatures. Symbols are the same as in *Figure 1*

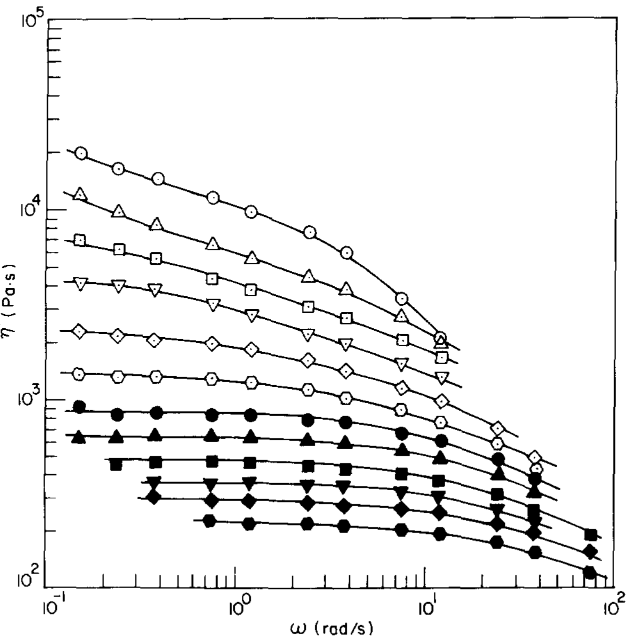

Figure 6 Plots of log η' *versus* log ω for SIS-A at various temperatures. Symbols are the same as in *Figure 2*

behaviour at low values of ω, but Newtonian behaviour as ω was increased above a certain critical value. They interpreted this experimental observation as an indication that the microdomains present in the block copolymer were destroyed under oscillatory shear flow, giving rise to a disordered state. They suggested that such behaviour may be regarded as an indication of phase transition from an ordered state to the disordered state. Several years later, Chung *et al.*[9,10] drew the same conclusion by observing that a transition from non-Newtonian behaviour to Newtonian behaviour occurred in plots of log η' *versus* log ω for a polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) copolymer as the temperature was increased.

Let us now compare the values of T_r as determined from plots of log G' *versus* log G'' with those which might be determined from plots of log η' *versus* log ω. Comparison of *Figure 1* with *Figure 5*, and *Figure 2* with *Figure 6*, leads us to conclude that, for K1107 and SIS-A block copolymers having the spherical microdomain structure, plots of log η' *versus* log ω give a value of T_r about 20°C lower than that determined from plots of log G' *versus* log G''. Similar observation can be made for SIS-B having cylindrical microdomain structure, by comparing *Figure 3* with *Figure 7*. It should be pointed out that earlier the value $T_r = 180°\mathrm{C}$ for SIS-A as determined from plots of log G' *versus* log G'' was corroborated by using small-angle X-ray scattering[28]. It

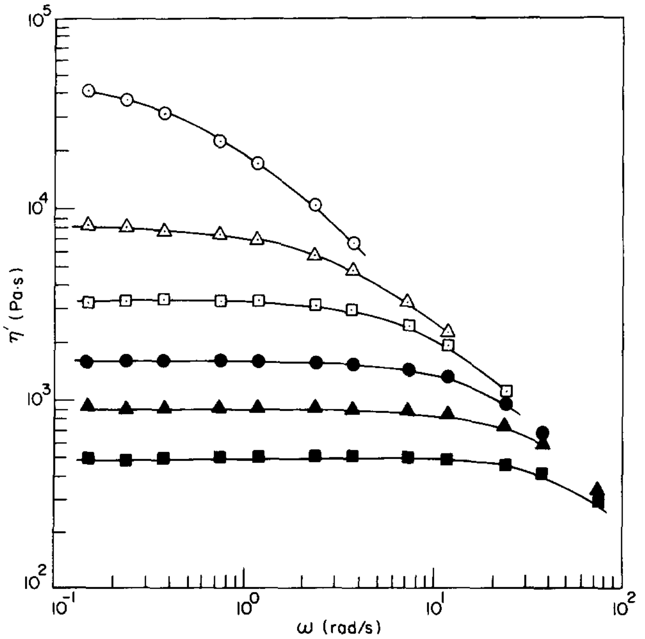

Figure 7 Plots of log η' *versus* log ω for SIS-B at various temperatures. Symbols are the same as in *Figure 3*

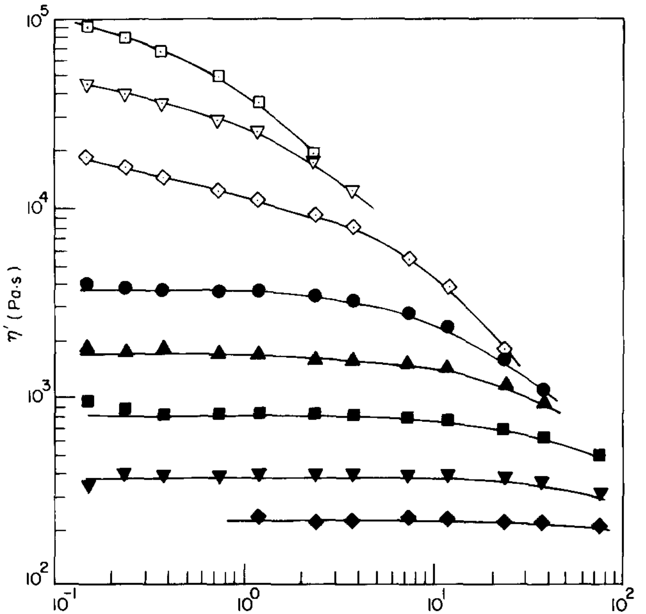

Figure 8 Plots of log η' *versus* log ω for SIS-C at various temperatures. Symbols are the same as in *Figure 4*

is of interest to note that for SIS-C having the lamellar microdomain structure, plots of log η' *versus* log ω give rise to virtually the same value of T_r (105°C) as that determined from plots of log G' *versus* log G''. It can be concluded from the above observations that the viscous response of block copolymers having spherical or cylindrical microdomain structures is not as sensitive to a variation in temperature as the elastic response. It should be recalled that in general the elastic response of polymers is much more sensitive than the viscous response. Moreover, as pointed out by Han[29,30], the use of shear stress is more appropriate than the use of shear rate, and the use of G'' is more appropriate than the use of ω, in correlating rheological properties of multiphase polymeric systems including the microphase-separated block copolymers under discussion here. It should be mentioned that some investigators[9–12,16] used frequency–temperature superposition to obtain master curves for microphase-separated block copolymers. However, as pointed out by Han and Kim[17], the use of frequency–temperature superposition for microphase-separated block copolymers is not justifiable, due to the fact that when plots of log G' *versus* log G'' for a block copolymer show temperature dependency, from the rheological point of view the block copolymer may be regarded as a different material at each temperature.

Linear dynamic viscoelastic properties of SIS block copolymers in the disordered state

Let us now examine rheological behaviour in the disordered state (i.e. at $T > T_r$) of the SIS block copolymers employed. *Figure 9* gives plots for log η'_r *versus* log ωa_T, and *Figure 10* gives plots of log G'_r *versus* log ωa_T, for K1107 and SIS-A, in which a_T is a shift factor, η'_r is the reduced dynamic viscosity defined by $\eta'_r = (\eta'/a_T)(\rho_0/\rho)(T_0/T)$, and G'_r is the reduced storage modulus defined by $G'_r = G'(T_0/T)(\rho_0/\rho)$, where T is the absolute temperature, T_0 is a reference temperature (220°C in the present case), ρ is the density at T, and ρ_0 is the density at T_0. Note that frequency–temperature superposition is applicable to the block copolymers in the *disordered* state. It can be seen in *Figure 9* that the zero-shear viscosity for K1107 is greater than (~2.3 times) that of SIS-A. This can be explained by the difference in molecular weight between the two block copolymers, namely, K1107 has a total molecular weight greater than (~1.22 times) that of SIS-A (*Table 1*). It should be remembered that K1107 and SIS-A have approximately the same block length ratio (i.e. $f = 0.14$ for K1107 and $f = 0.13$ for SIS-A).

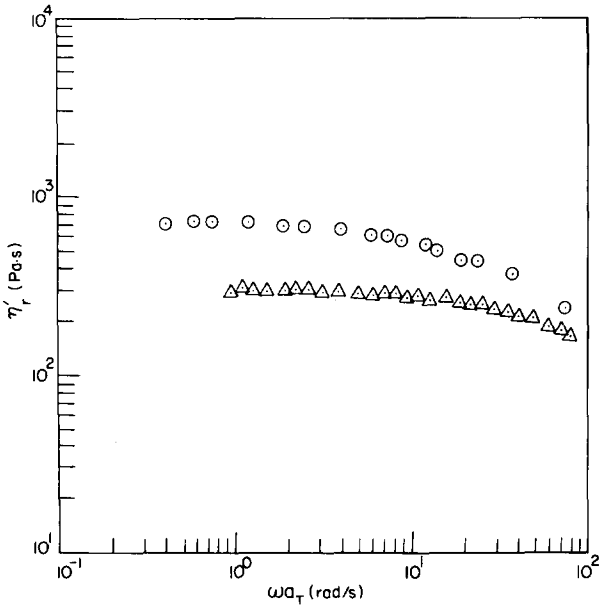

Figure 9 Plots of log η'_r *versus* log ωa_T in the disordered state for: (○) K1107; (△) SIS-A. The reference temperature is 220°C

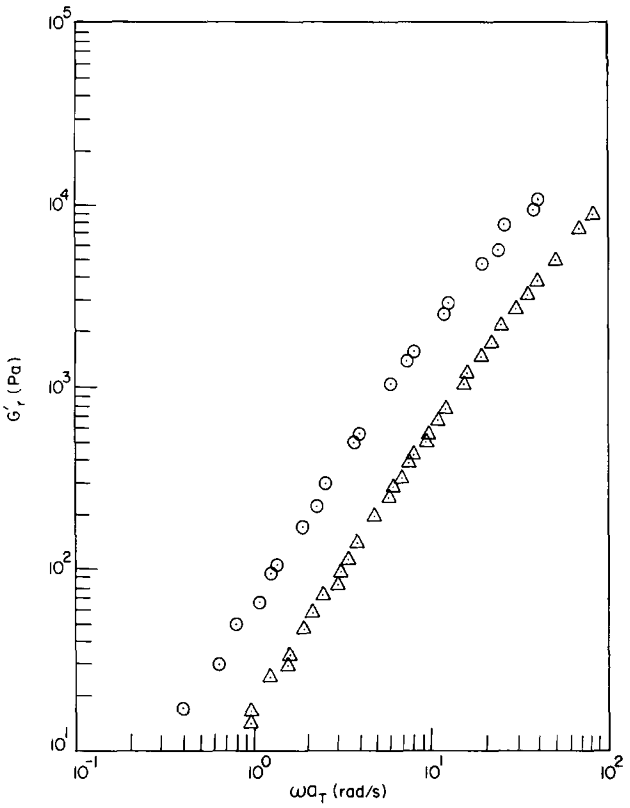

Figure 10 Plots of log G'_r *versus* log ωa_T in the disordered state for: (○) K1107 and (△) SIS-A. The reference temperature is 220°C

It can be seen from *Figure 10* that values of G'_r for K1107 are greater than those for SIS-A. One may then be tempted to conclude that in the disordered state, K1107 is more elastic than SIS-A. However, when values of G' are plotted against values of G'' in logarithmic coordinates, we observe from *Figure 11* that K1107 and SIS-A give a single correlation, suggesting that the elasticity of the two block copolymers in the *disordered* state is the same. This rather interesting observation is consistent with the observations made previously for molten homopolymers[31–34]. Note that although the molecular weights of the polystyrene block in K1107 and SIS-A, respectively, are lower than the entanglement molecular weight (M_e) of polystyrene, which is ~18 000, the molecular weights of the polyisoprene block in the respective block copolymers are much greater than the M_e of polyisoprene, which is ~6000. Thus both K1107 and SIS-A may be regarded as entangled flexible, linear copolymers. According to Han and Jhon[33], plots of log G' *versus* log G'' for entangled, flexible linear homopolymers should be independent of molecular weight and virtually independent of temperature. Although K1107 and SIS-A are not homopolymers, the molecular interpretation of Han and Jhon would equally be applicable to explain the correlation that we observe in *Figure 11*.

Figure 12 gives plots of $\log \eta_r'$ *versus* $\log \omega a_T$, and *Figure 13* gives plots of $\log G_r'$ *versus* $\log \omega a_T$, for SIS-A, SIS-B and SIS-C. It can be seen from *Figure 12* that SIS-A is much more viscous than SIS-B and SIS-C. Since the total molecular weight of SIS-A is much greater than that of SIS-B or SIS-C, we can see why the viscosity of SIS-A is much greater than that of SIS-B and SIS-C. However, it is of interest to observe in *Figure 12* that although the total molecular weight of SIS-C is slightly less than the total molecular weight of SIS-B (*Table 1*), SIS-C is more viscous than SIS-B. This observation seems to suggest to us that in situations where the difference in total molecular weight between block copolymers is rather small, the difference in block length ratio plays an important role in controlling rheological properties of block copolymers in the disordered state. Notice that the weight fraction of the polystyrene block, f, in SIS-C is 0.52, while it is 0.30 in SIS-B.

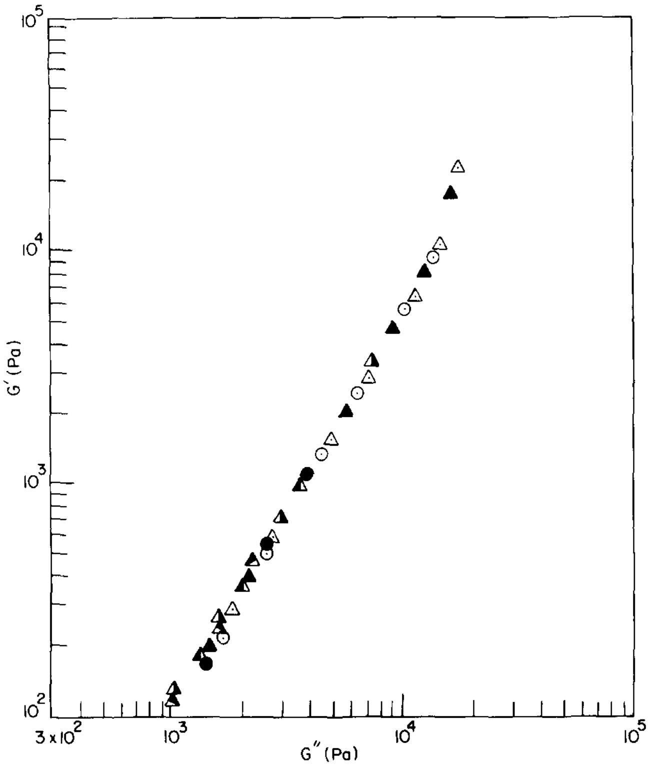

Figure 11 Plots of $\log G'$ *versus* $\log G''$ in the disordered state. K1107 at temperatures (°C): (○) 220; (●) 230. SIS-A at temperatures (°C): (△) 180; (▲) 190; (▲) 200; (▲) 210; (▲) 220; (▲) 230

We observe from *Figure 13* that the differences in G_r' between SIS-A and SIS-C are about four orders of magnitude. However, when using plots of $\log G'$ *versus* $\log G''$, we observe from *Figure 14* that values of G' for SIS-A are only three times the values for SIS-C. This observation seems to point, once again, to the fact that the block length ratio plays a very important role in determining the extent of melt elasticity of block copolymers in the disordered state.

According to Han and Jhon[33], in the linear region the plot of $\log G'$ *versus* $\log G''$ for entangled, monodispersed homopolymers is related to the plateau modulus G_N^0 by:

$$\log G' = 2\log G'' + \log(6/5G_N^0) \qquad (1)$$

If we assume that equation (1) is also applicable to the disordered block copolymers under consideration, we can conclude from *Figure 14* that the plateau modulus of SIS-C must be larger, by a factor of ~3, than that of SIS-A. Further discussion about the plateau modulus of block copolymers will be deferred until we present experimental results below. Notice in *Figure 14* that the slope of $\log G'$ *versus* $\log G''$ plots is slightly less than 2 (~1.8). This is attributed to the fact that the block copolymers, SIS-A and SIS-C, have the polydispersity of ~1.2 owing to the presence of uncoupled diblocks (~20 wt%).

Plateau modulus of SIS block copolymers

As briefly mentioned above, in the disordered state the SIS block copolymers employed in this study are regarded as entangled macromolecules, because the molecular weights of the polyisoprene block in the SIS block copolymers are much larger than the M_e of homopolymer polyisoprene, which is known to be ~6000. The fundamental question that we wished to answer was to what extent does the polyisoprene block in an SIS block copolymer contribute to the M_e of the

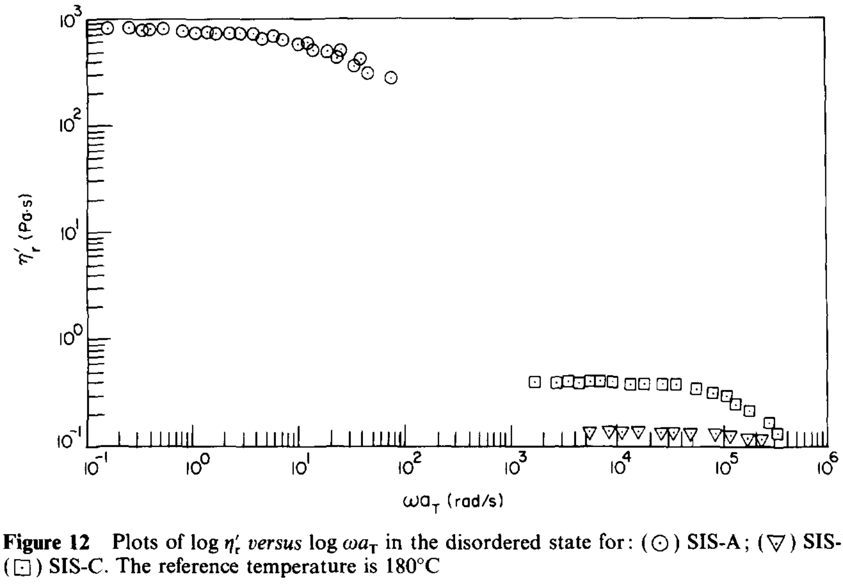

Figure 12 Plots of $\log \eta_r'$ *versus* $\log \omega a_T$ in the disordered state for: (○) SIS-A; (▽) SIS-B; (□) SIS-C. The reference temperature is 180°C

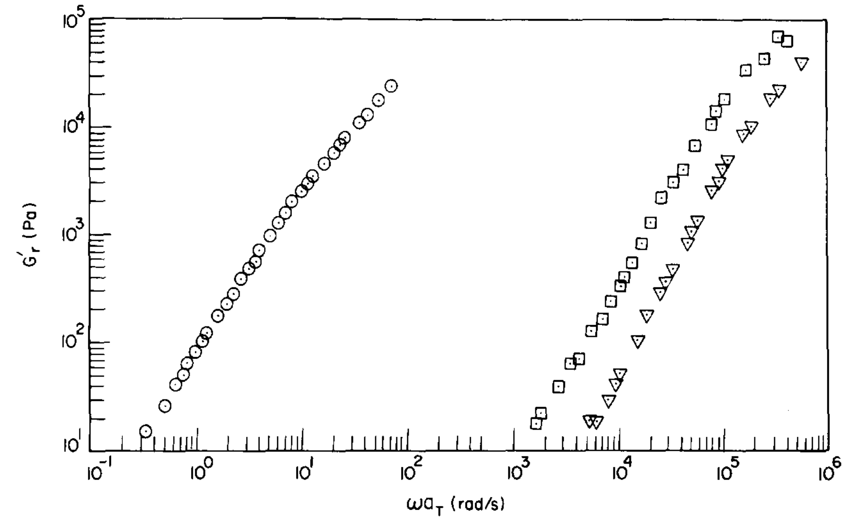

Figure 13 Plots of log G_r' *versus* log ωa_T in the disordered state for: (○) SIS-A; (▽) SIS-B; (□) SIS-C. The reference temperature is 180°C

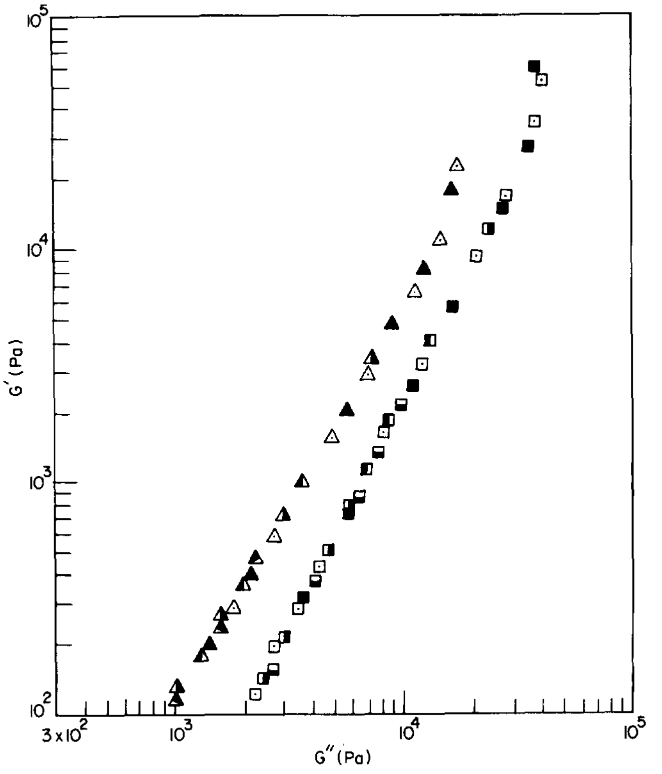

Figure 14 Plots of log G' *versus* log G'' in the disordered state. SIS-A at temperatures (°C): (△) 180; (▲) 190; (▲) 200; (▲) 210; (▲) 220; (▲) 230. SIS-C at temperatures (°C): (□) 105; (■) 110; (◨) 115; (◧) 120; (⬓) 130

block copolymer in the disordered state at temperatures much higher than the glass transition temperature of polyisoprene. In an effort to answer the question, we made an attempt to measure the plateau modulus G_N^0 of SIS block copolymers in the disordered state, so that we could calculate the M_e of the block copolymers using the following expression, which was suggested for flexible, linear homopolymers[35–37]:

$$G_N^0 = \rho RT/M_e \tag{2}$$

where ρ is the density, R is the universal gas constant and T is the absolute temperature.

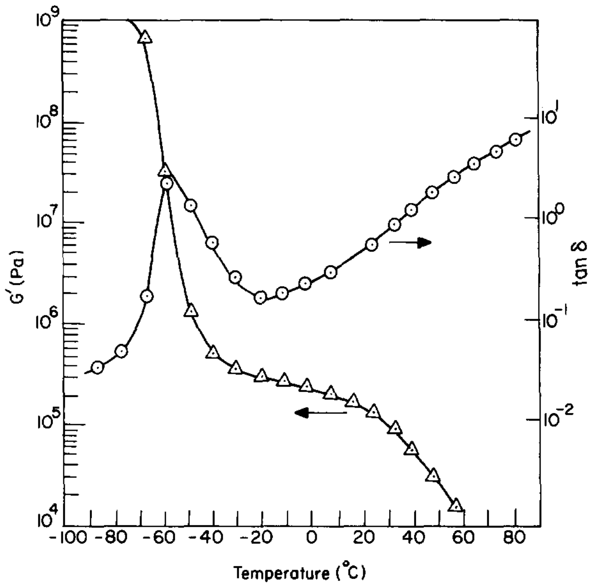

Figure 15 Temperature sweep at $\omega = 10$ rad s^{-1} of storage modulus G' (△) and loss tangent tan δ (○) for homopolymer polyisoprene

There are two ways of measuring the plateau modulus of a polymer using the rheological technique, namely, by performing either a temperature sweep, at a fixed angular frequency, of storage modulus G' and loss tangent tan δ, or a frequency sweep, at a fixed temperature, of storage and loss moduli, G' and G''. When frequency–temperature superposition is applicable, both experiments are expected to yield the same value of plateau modulus.

Figure 15 gives the results for the temperature sweep of G' and tan δ, at an angular frequency ω of 10 rad s^{-1}, for a nearly monodisperse polyisoprene having an M_w of 9×10^4. Notice that no plateau region is observed in *Figure 15* in the temperature range from −80 to 60°C, over which measurements were taken. Under such circumstances, earlier Kraus and Rollmann[38] suggested that G_N^0 be determined from the value of G' at which tan δ goes through a minimum. Using this procedure we have determined the value of $G_N^0 \simeq G'(\tan \delta_{\min})$ to be $\sim 3.24 \times 10^5$ Pa. *Figure 16* gives the results for the

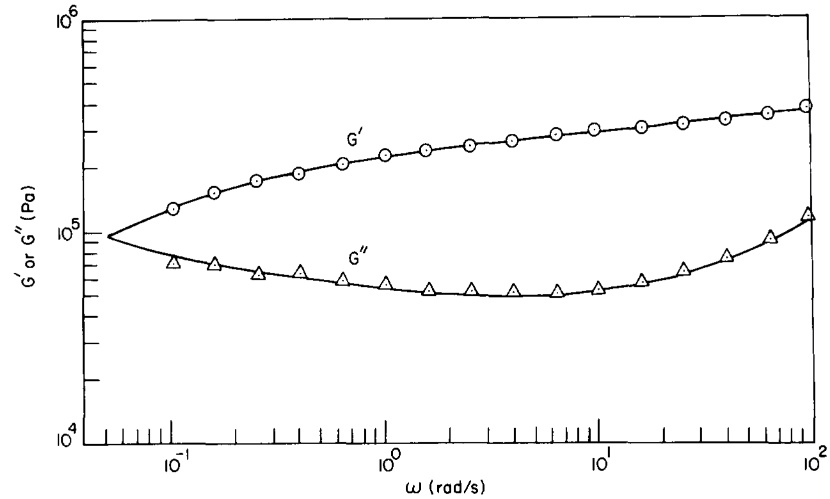

Figure 16 Frequency sweep at −20°C of the storage modulus G' (○) and loss modulus G'' (△) for homopolymer polyisoprene

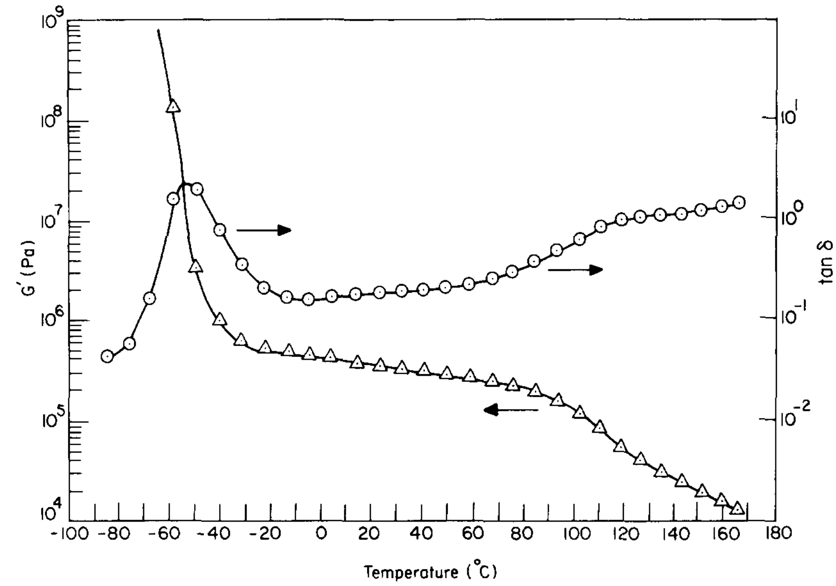

Figure 17 Temperature sweep at $\omega = 10 \text{ rad s}^{-1}$ of the storage modulus G' (△) and loss tangent tan δ (○) for SIS-A

frequency sweep of G' and G'' for polyisoprene at −20°C. Notice that no plateau region in G' is observed in *Figure 16*. But from *Figure 16* we have a crossover modulus G_c of 0.92×10^5 Pa. We have calculated the value of G_N^0 to be 3.24×10^5 Pa when using $G_N^0 = 3.52G_c$. Earlier, a suggestion[39] was made to determine the value of G_N^0 for monodisperse homopolymers by the relationship $G_N^0 = 3.56G''_m$, where G''_m is the maximum value of G'' in log G'' *versus* log ω plots. It should be mentioned that the value of G''_m is about the same as that of G_c for monodisperse homopolymers. Therefore we can conclude that $G_N^0 = 3.24 \times 10^5$ Pa for polyisoprene as determined from $G'(\tan \delta_{\min})$ is reasonable.

Figure 17 gives the results for the temperature sweep of G' and tan δ at $\omega = 10 \text{ rad s}^{-1}$ for SIS-A. From *Figure 17* we hoped to observe a plateau region at a temperature above ∼180°C, i.e. in the disordered state of SIS-A. However, owing to the very low values of G' above 160°C, we could not observe a plateau region above 160°C, and thus were unable to determine G_N^0 of SIS-A using the temperature sweep displayed in *Figure 17*. It should be remembered that the T_r for SIS-A is ∼180°C. *Figure 18* gives the results for the frequency sweep of G'_r and G''_r for SIS-A with reference temperature at 180°C. In the range of frequencies studied, we do not have a plateau region for G'_r, but we have a crossover modulus G_c of 0.65×10^5 Pa. We have found that the G_c for K1107 is 0.7×10^5 Pa, which is very close to that for SIS-A. This seems to suggest that the value of G_c is insensitive to the total molecular weight of block copolymer, as long as the block length ratio is kept the same.

Figure 19 gives the results for the temperature sweep of G' and tan δ at $\omega = 10 \text{ rad s}^{-1}$ for SIS-B. It should be remembered that the T_r for SIS-B is ∼90°C. In the temperature range studied, in *Figure 19* we do not have a plateau region for G' at $T \geqslant 90$°C. *Figure 20* gives the results for the frequency sweep of G'_r and G''_r for SIS-B with reference temperature at 90°C. In the range of frequencies studied, we do not have a plateau region for G'_r, but we have a crossover modulus G_c of 1.3×10^5 Pa, which is about twice the value of G_c for SIS-A (*Figure 18*).

Figure 21 gives the results for the temperature sweep

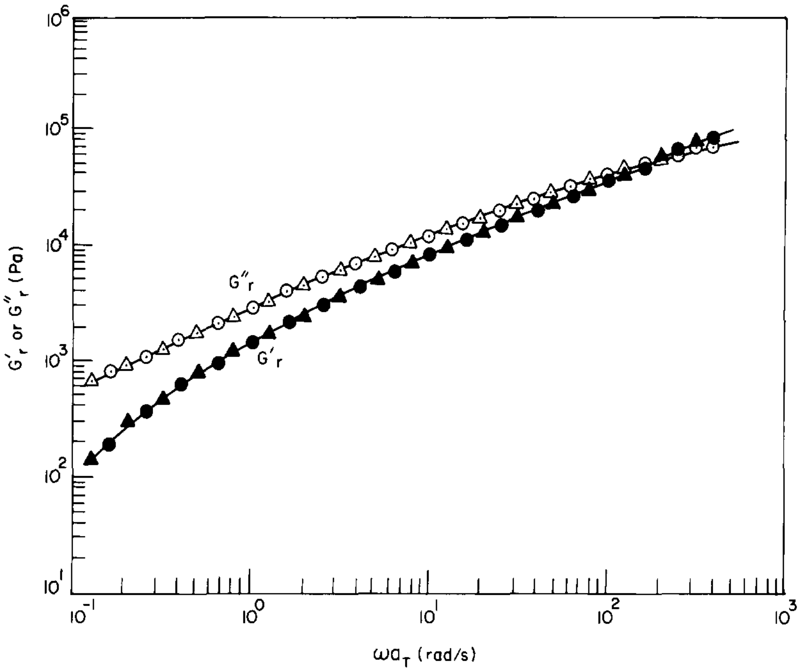

Figure 18 Plots of log G'_r (closed symbols) *versus* log G''_r (open symbols) for SIS-A with reference temperature at: (⊙, ●) 180°C; (△, ▲) 190°C

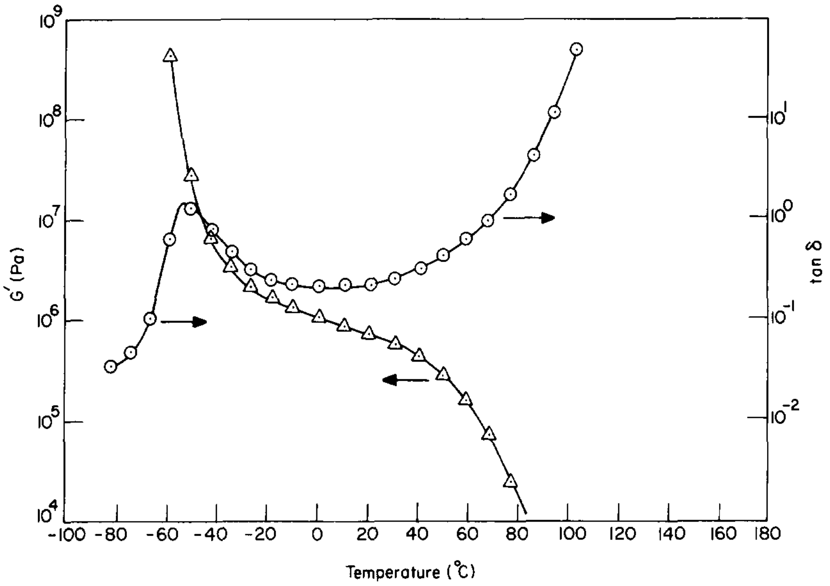

Figure 19 Temperature sweep at $\omega = 10$ rad s^{-1} of the storage modulus G' (△) and loss tangent tan δ (⊙) for SIS-B

of G' and tan δ at $\omega = 10$ rad s^{-1} for SIS-C. It should be remembered that the T_r for SIS-C is ~105°C. In the temperature range studied, in *Figure 21* we cannot observe a plateau region for G' at $T \geqslant 105$°C. *Figure 22* gives the results for the frequency sweep of G'_r and G''_r for SIS-C with reference temperature at 105°C. In the range of frequencies studied, we do not have a plateau region for G'_r, but we have a crossover modulus G_c of 1.7×10^5 Pa, which is ~30% greater than the value of G_c for SIS-B (*Figure 20*) and about three times the value of G_c for SIS-A (*Figure 18*).

At present there is no relationship, empirical or theoretical, established which will enable one to calculate G_N^0 from G_c, for SIS block copolymer in the disordered state. However, it seems reasonable to assume that the larger the value of G_c, the larger the value of G_N^0 will be. If we assume that for block copolymers in the *disordered* state G_N^0 is proportional to G_c (i.e. $G_N^0 = \alpha G_c$, α being a constant), we can conclude from *Figures 18* and *22* that the G_N^0 of SIS-C is about three times larger than the G_N^0 of SIS-A. This observation, together with equation (1), explains why in *Figure 14* the log G' *versus* log G'' plot for SIS-C lies below the log G' *versus* log G'' plot for SIS-A. We can then conclude from the above observations that the plateau modulus of an SIS triblock copolymer strongly depends on block length ratio.

The seemingly complex relationship between plateau modulus and block length ratio in the SIS block copolymers employed in this study can be understood by observing how far the two polystyrene endblocks are

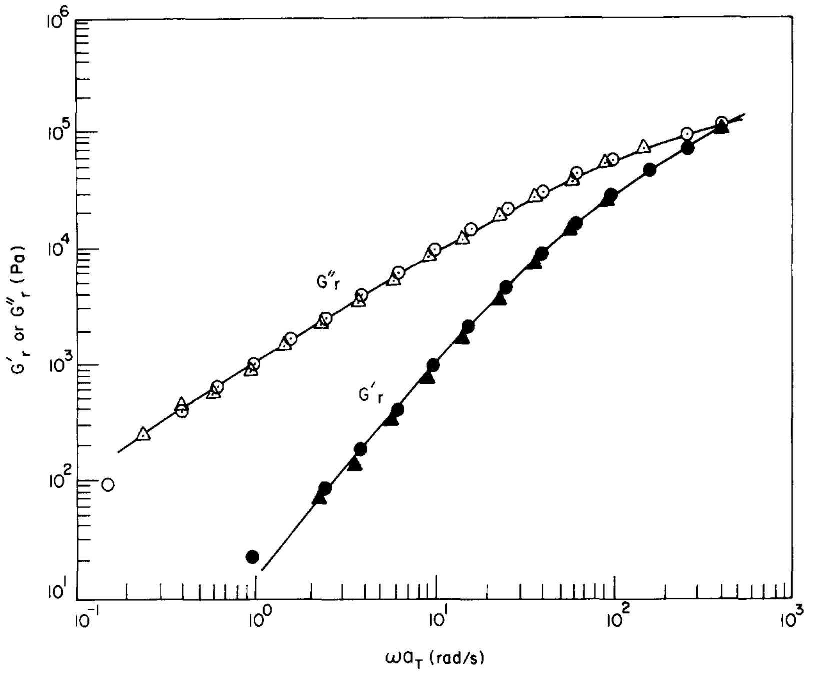

Figure 20 Plots of log G'_r (closed symbols) *versus* log G''_r (open symbols) for SIS-B with reference temperature at: (⊙, ●) 90°C; (△, ▲) 100°C

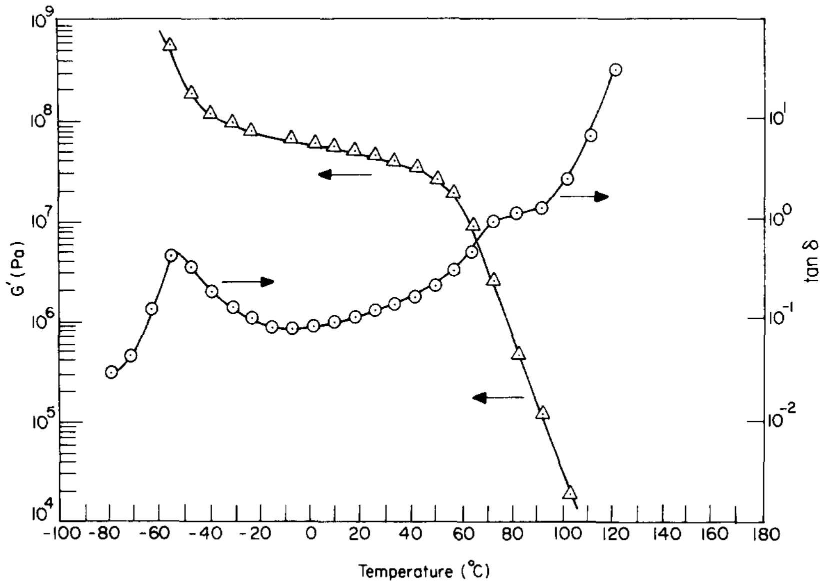

Figure 21 Temperature sweep at $\omega = 10\,\mathrm{rad\,s^{-1}}$ of the storage modulus G' (△) and loss tangent tan δ (⊙) for SIS-C

separated from each other by the polyisoprene midblock (*Table 1* for information on block molecular weights). To be specific, notice that SIS-A and SIS-C have about the same length of polystyrene endblock ($M_w \simeq 7300$), but in SIS-A the two polystyrene endblocks are separated from each other by a very long polyisoprene midblock ($M_w = 99\,000$), whereas in SIS-C the two polystyrene endblocks are separated from each other by a relatively short polyisoprene midblock ($M_w = 13\,400$). Under such circumstances, the two polystyrene endblocks in SIS-C may function cooperatively as if they form a single, long polystyrene chain having an effective molecular weight of 14 600. On the other hand, the two polystyrene endblocks in SIS-A are so far apart, that there would be little cooperative motion between the two and thus the effective length of polystyrene endblock would be just the same as a single polystyrene endblock ($M_w = 7400$). This qualitative picture seems to explain why the value of G_c for SIS-C is much larger than that for SIS-A. Using the same logic, we can now explain why the value of G_c for SIS-B is about twice the value of G_c for SIS-A, because the distance between the two polystyrene endblocks in SIS-B is much shorter than that in SIS-A, although the molecular weight of the polystyrene endblock in SIS-B is even slightly smaller than that in SIS-A.

CONCLUSIONS

In the present study we have presented experimental results, showing that the melt elasticity, as interpreted

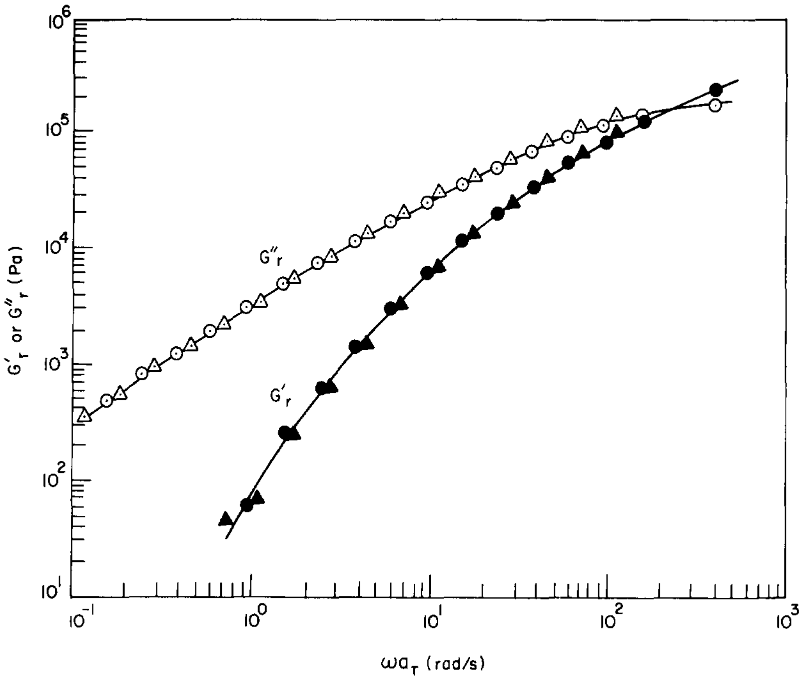

Figure 22 Plots of log G'_r (closed symbols) *versus* log G''_r (open symbols) for SIS-C with reference temperature at: (⊙, ●) 105°C; (△, ▲) 115°C

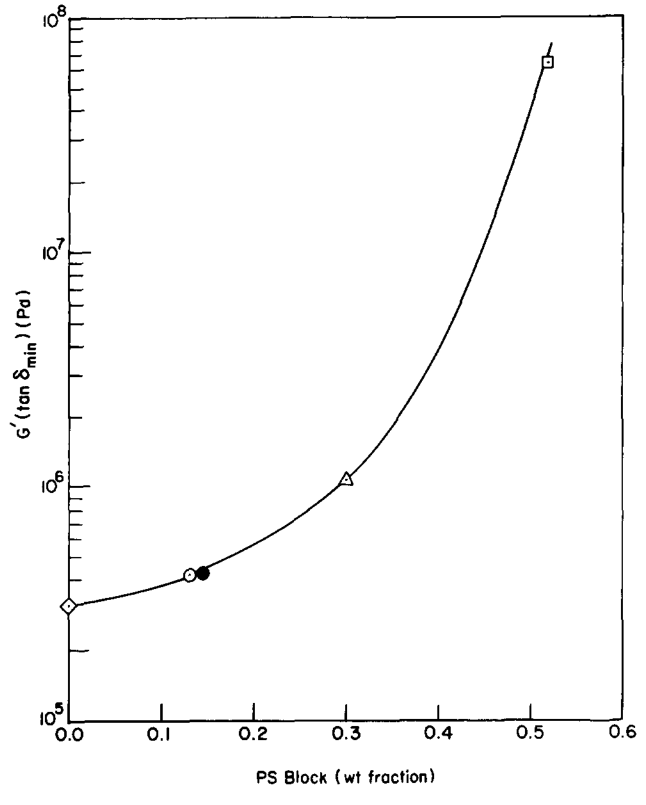

Figure 23 Plots of plateau modulus *versus* weight fraction of the polystyrene block in microphase-separated SIS triblock copolymer: (⊙) SIS-A; (●) K1107; (△) SIS-B; (□) SIS-C. Also given in the plot is the plateau modulus of homopolymer polyisoprene (◇)

by plots of log G' *versus* log G'', for entangled block copolymers in the disordered state is independent of the total molecular weight, as long as the block length ratio is kept constant, and, also, virtually independent of temperature. On the other hand, it was observed that the melt viscosity depends on both the total molecular weight and block length ratio. This study presents further that the block length ratio plays a very important role in determining the plateau modulus of an SIS block copolymer in the disordered state.

It should be pointed out that the rheological behaviour of block copolymers in the *ordered* state would be quite different from that in the *disordered* state. To be specific, the rheological behaviour of SIS block copolymers in the ordered state would depend very much on the morphological state of microdomains: spherical, cylindrical or lamellar microdomain structure. *Figure 23* shows how, for instance, the plateau modulus of SIS triblock copolymers in the *ordered* state increases with the weight fraction of polystyrene endblock (i.e. block length ratio). At present there is no theory available which will enable the prediction of the rheological behaviour of entangled block copolymers in the disordered or ordered state. This is an area which deserves the attention of polymer scientists.

REFERENCES

1 Burke, J. J. and Weiss, V. (Eds) 'Block and Graft Copolymers', Syracuse University Press, Syracuse, 1973
2 Ceresa, R. J. (Ed.) 'Block and Graft Copolymerization', Wiley, New York, 1973
3 Meier, D. J. *J. Polym. Sci. C* 1969, **26**, 81; *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* 1970, **11** (2), 400
4 Ohta, T. and Kawasaki, K. *Macromolecules* 1986, **19**, 2621
5 Leibler, L. *Macromolecules* 1980, **13**, 1602
6 Kraus, G. and Gruver, J. T. *J. Appl. Polym. Sci.* 1967, **11**, 2121
7 Holden, G., Bishop, E. T. and Legge, N. R. *J. Polym. Sci. C* 1969, **26**, 37
8 Arnold, K. R. and Meier, D. J. *J. Appl. Polym. Sci.* 1970, **14**, 427
9 Chung, C. I. and Gale, J. C. *J. Polym. Sci., Polym. Phys. Edn* 1976, **14**, 1149
10 Chung, C. I. and Lin, M. I. *J. Polym. Sci., Polym. Phys. Edn* 1978, **16**, 545
11 Guinlock, E. and Porter, R. S. *Polym. Eng. Sci.* 1977, **17**, 535

12 Widmaier, J. M. and Meyer, G. C. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 2217

13 Vinogradov, G. V., Dreval, V. E., Zabigina, A. Ya., Plotnikova, E. P. and Sabai, O. Yu. *Rheol. Acta* 1978, **17**, 258

14 Pico, E. R. and Williams, M. C. *Polym. Eng. Sci.* 1977, **17**, 573

15 Fesko, D. G. and Tschoegl, N. W. *J. Polym. Sci. C* 1971, **35**, 51; *Int. J. Polym. Mater.* 1974, **3**, 51

16 Bates, F. S. *Macromolecules* 1984, **17**, 2607

17 Han, C. D. and Kim, J. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1741

18 Han, C. D., Kim, J. and Kim, J. K. *Macromolecules* 1989, **22**, 383

19 Han, C. D., Baek, D. M. and Kim, J. K. *Macromolecules* 1990, **23**, 561

20 Hashimoto, T., Tsukahara, Y. and Kawai, H. *J. Polym. Sci., Polym. Lett. Edn* 1980, **18**, 585

21 Hashimoto, T., Shibayama, M., Kawai, H., Watanabe, H. and Kotaka, T. *Macromolecules* 1983, **16**, 361

22 Hashimoto, T., Tsukahara, Y. and Kawai, H. *Polym. J.* 1983, **15**, 699

23 Mori, K., Hasegawa, H. and Hashimoto, T. *Polym. J.* 1985, **17**, 799

24 Hashimoto, T., Kowsaka, K., Shibayama, M. and Kawai, H. *Macromolecules* 1986, **19**, 754

25 Roe, R. J., Fishkis, M. and Chang, J. C. *Macromolecules* 1981, **14**, 1091

26 Zin, W. C. and Roe, R. J. *Macromolecules* 1984, **17**, 183

27 Bates, F. F. and Hartney, M. A. *Macromolecules* 1985, **18**, 2478

28 Han, C. D., Baek, D. M., Sakurai, S. and Hashimoto, T. *Polym. J.* 1989, **21**, 841

29 Han, C. D. 'Multiphase Flow in Polymer Processing', Academic Press, New York, 1981, Ch. 3

30 Han, C. D. 'Rheology in Polymer Processing', Academic Press, New York, 1976, Ch. 7

31 Han, C. D. and Lem, K. W. *Polym. Eng. Rev.* 1983, **2**, 135

32 Han, C. D. and Chuang, K. H. *J. Appl. Polym. Sci.* 1985, **30**, 2431

33 Han, C. D. and Jhon, M. S. *J. Appl. Polym. Sci.* 1986, **32**, 3809

34 Han, C. D. *J. Appl. Polym. Sci.* 1988, **36**, 167

35 Ferry, J. D. 'Viscoelasticity of Polymers', 3rd Edn, Wiley, New York, 1980

36 Graessley, W. W. *Adv. Polym. Sci.* 1974, **16**, 1

37 Doi, M. and Edwards, S. F. 'Theory of Polymer Dynamics', Clarendon, London, 1986

38 Kraus, G. and Rollmann, K. W. *J. Appl. Polym. Sci.* 1977, **21**, 3311

39 Raju, V. R., Menezes, V., Marin, G., Graessley, W. W. and Fetters, L. J. *Macromolecules* 1981, **14**, 1668