BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 25, pp. 4833–4839, 1995
Elsevier Science Ltd
Printed in Great Britain

Rheological behaviour of binary mixtures of polystyrene-*block*-polyisoprene copolymers in the disordered state

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(Received 29 September 1994; revised 2 May 1995)

The rheological behaviour of binary mixtures of polystyrene-*block*-polyisoprene (SI diblock) copolymers in the disordered state was investigated. For this study, two SI diblock copolymers having different molecular weights and block length ratios were synthesized via anionic polymerization, and then binary mixtures were prepared to measure their linear viscoelastic properties (namely, dynamic storage and loss moduli, G' and G'', as functions of angular frequency ω) at various temperatures. The disordered state of the block copolymers and their mixtures was determined by observing a critical temperature, often referred to as the order–disorder transition temperature (T_{ODT}), at and above which logarithmic plots of $\log G'$ *versus* $\log G''$ become independent of temperature and have a slope of 2 in the terminal region. We found that $\log G'$ *versus* $\log G''$ plots for the binary mixtures lie between those of the constituent components, and at a fixed value of G'' the value of G' increases monotonically with increasing blend composition. The composition dependence of the linear viscoelastic properties of the binary mixtures was investigated by preparing reduced plots using two different methods of determining reference temperature T_0: (i) at an equal distance from the glass transition temperature of the polystyrene block ($T_{\mathrm{g,PS}} + 55°\mathrm{C}$) in the respective block copolymer and also (ii) at an equal distance from the T_{ODT} of the respective block copolymer ($T_0 = T_{\mathrm{ODT}} + 10°\mathrm{C}$). We found that the two different methods yielded very different composition dependence of the linear viscoelastic properties of the binary mixtures of SI diblock copolymers.

(Keywords: block copolymer; order–disorder transition; linear viscoelastic properties)

INTRODUCTION

Over the past two decades, numerous research papers[1–19] reported on the rheological behaviour of neat block copolymers, but only a few papers[20,21] reported on the rheological behaviour of binary mixtures consisting of a block copolymer and a homopolymer and fewer still, if any, on the rheological behaviour of binary mixtures of block copolymers. It is clear from the literature that the rheological behaviour of neat block copolymers is much more complicated than that of flexible homopolymers in that, in many situations, block copolymers have microdomains (e.g. spheres, cylinders, lamellae or ordered bicontinuous microdomain structures) at temperatures below a certain critical value, often referred to as the order–disorder transition temperature (T_{ODT}). It is also clear from the literature[22,23] that homogeneous block copolymers can be synthesized (i) by choosing constituent components having very good miscibility (e.g. polystyrene-*block*-poly(α-methylstyrene) copolymers), (ii) by controlling the block length ratio (e.g. a very short block on one side relative to the length of the other block), or (iii) by controlling the molecular weight (e.g. a block copolymer having a molecular weight below a certain critical value).

When a homopolymer is mixed with a microphase-separated block copolymer, the rheological behaviour of such a mixture becomes much more complicated than that of a binary mixture consisting of two flexible homopolymers[20,21], because the mixtures consisting of a block copolymer and a homopolymer can undergo both microphase and macrophase transitions[24–30], depending upon (i) the extent of miscibility between the homopolymer and the block copolymer and (ii) the molecular weight of the homopolymer relative to the molecular weight of the block copolymer. It should be mentioned that when a pair of flexible homopolymers, a pair of flexible random copolymers, or a flexible homopolymer and a flexible random copolymer, are mixed, they form either a homogeneous (single-phase) mixture or a two-phase mixture, depending upon the extent of miscibility between the constituent components. During the past decades, the rheological behaviour of binary mixtures of immiscible homopolymers has been reported too extensively in the literature to cite all publications here. Interested readers are referred to a monograph[31] by Han and references therein. Although numerous papers dealing with the rheology of two-phase polymer blends have been published since the publication of the monograph over 14 years ago, the essential features described therein are still valid.

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To date, there have been very few, if any, experimental studies reported on the rheological behaviour of mixtures consisting of two block copolymers, in either the ordered or disordered state. It can easily be surmised that the rheological behaviour of binary mixtures of block copolymers in the ordered state would be much more complicated than that in the disordered state. It should be mentioned that the majority of the commercially available block copolymers (e.g. styrene-based block copolymers) have relatively high molecular weights and consequently their T_{ODT}s are close to or above thermal degradation temperatures. Thus, using such block copolymers it is very difficult, if not impossible, to investigate the rheological behaviour of binary mixtures of block copolymers in the disordered state. For this reason, we very recently synthesized low-molecular-weight polystyrene-*block*-polyisoprene (SI diblock) copolymers and prepared binary mixtures of SI diblock copolymers to investigate their rheological behaviour in the disordered state. This was made possible because the T_{ODT}s of the SI diblock polymers synthesized were sufficiently low to enable us to measure the rheological properties of the mixtures of SI diblock copolymers in the disordered state. In this paper we report the highlights of our findings.

EXPERIMENTAL

Materials

Two low-molecular-weight SI diblock copolymers having different molecular weight and block length ratio were synthesized via anionic polymerization. The molecular characteristics of the block copolymers synthesized are summarized in *Table 1*. For the polymerization, an inert-gas stirred-tank reactor system was employed. The details of the synthesis procedures, including the steps taken to purify the monomers, are described elsewhere[23].

We prepared binary mixtures of SI-Q and SI-R with various blend compositions. Before taking rheological measurements, we determined the T_{ODT} values of the neat SI block copolymers, SI-Q and SI-R, and their mixtures, which are summarized in *Table 2*. It is of interest to observe in *Table 2* that the T_{ODT}s of the (SI-Q)/(SI-R) mixtures are higher than those of the constituent components. This information was very important in the determination of the temperatures at which the rheological measurements of the binary mixtures were to be taken, because the main objective of this study was to investigate the rheological behaviour of (SI-Q)/(SI-R) mixtures in the disordered state, i.e. at temperatures above T_{ODT}.

Table 1 Molecular characteristics and order–disorder transition temperatures of the SI diblock copolymers synthesized in this study

Sample code	$M_{\mathrm{w,PS}}$	$M_{\mathrm{w,PI}}$	$M_{\mathrm{w}}/M_{\mathrm{n}}$	N_{PS}	N_{PI}	ϕ^a
SI-Q	5900	22 100	1.05	57	324	0.15
SI-R	8200	6 800	1.07	79	100	0.44

[a] ϕ is block length ratio defined by $N_{\mathrm{PS}}/(N_{\mathrm{PS}}+N_{\mathrm{PI}})$, where N_{PS} is the polymerization index of PS block and N_{PI} is the polymerization index of PI block in a given SI block copolymer

Differential scanning calorimetry

Glass transition temperatures of the neat SI diblock copolymers and their binary mixtures were determined by differential scanning calorimetry (d.s.c.) (Du Pont 9900), and are also summarized in *Table 2*. All d.s.c. runs were made under a nitrogen atmosphere with a heating rate of 20°C min^{-1}. It is of interest to observe in *Table 2* that the glass transition temperatures of the PS phase ($T_{\mathrm{g,PS}}$) in the neat SI diblock copolymers and also in their binary mixtures are about 66°C, which is estimated to be about 25°C below the glass transition temperature of homopolymer PS having the same molecular weight as the PS block in an SI diblock copolymer. Indeed, such an observation was noted earlier by other investigators[32,33].

Sample preparation

Samples for rheological measurements were prepared by first dissolving a predetermined amount of a neat SI diblock copolymer (10 wt%) (or a binary mixture of SI diblock copolymers) in toluene in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the solvent. The evaporation of solvent was carried out slowly at room temperature for 1 week and then in a vacuum oven at 40°C for 3 days. The last trace of solvent was removed by drying the samples in a vacuum oven at an elevated temperature by gradually raising the oven temperature up to 10°C above the glass transition temperature ($T_{\mathrm{g,PS}}$) of the PS phase in each block copolymer. The drying of the samples was continued, until there was no further change in weight. Finally, the samples were annealed for 10 h at a temperature, which was about 20°C above $T_{\mathrm{g,PS}}$.

Rheological measurement

A Model R16 Weissenberg rheogonimeter (Sangamo Control Inc.) in the cone-and-plate mode (25 mm diameter plate and 4° cone angle with a 160 μm gap

Table 2 Summary of order–disorder transition temperature for the binary mixtures of the SI diblock copolymers investigated in this study

Sample code	T_{ODT} (°C)^a	$T_{\mathrm{g,PS}}$ (°C)	$T_{\mathrm{ODT}}+10$°C	$T_{\mathrm{g,PS}}+55$°C
SI-Q	95	66	105	121
90/10 (SI-Q)/(SI-R)	115	68	125	123
80/20 (SI-Q)/(SI-R)	120	67	130	122
60/40 (SI-Q)/(SI-R)	115	65	125	120
50/50 (SI-Q)/(SI-R)	110	64	120	119
40/60 (SI-Q)/(SI-R)	110	–	120	–
20/80 (SI-Q)/(SI-R)	105	67	115	122
SI-R	100	65	110	120

[a] The values of the T_{ODT} reported here were determined from $\log G'$ *versus* $\log G''$ plots

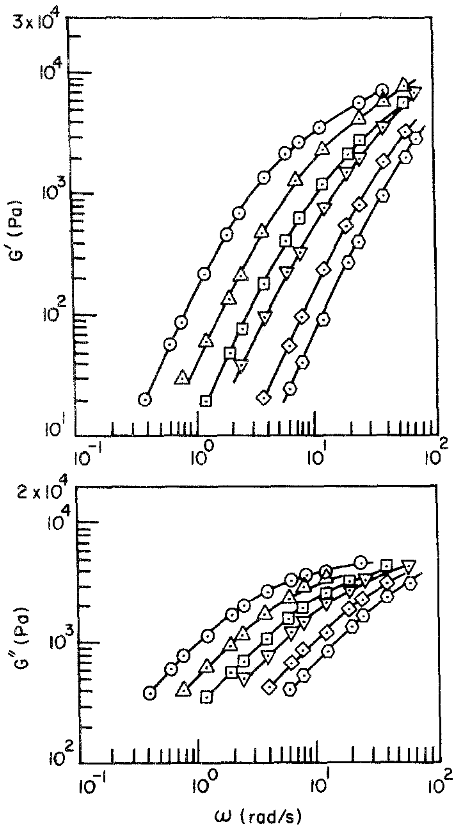

Figure 1 Plots of $\log G'$ *versus* $\log\omega$, and $\log G''$ *versus* $\log\omega$, for the block copolymer SI-Q in the disordered state at various temperatures: ⊙ 95°C, (△) 100°C, (⊡) 105°C, (▽) 110°C, (◇) 115°C, (⊙) 120°C

between the cone tip and the plate) 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 the neat SI block copolymers and also for their binary mixtures. Note that all the rheological measurements were taken at temperatures at or above the T_{ODT} for each material (see *Table 2* for the T_{ODT} values of the neat block copolymers, SI-Q and SI-R, and their binary mixtures). The temperature control was accurate to within ±1°C. In the rheological measurements a fixed strain was used at a given temperature, to ensure that measurements were taken well within the linear viscoelastic range of the materials investigated. All the measurements were conducted under a nitrogen atmosphere in order to avoid oxidative degradation of the samples.

RESULTS AND DISCUSSION

Plots of $\log G'$ *versus* $\log\omega$, and $\log G''$ *versus* $\log\omega$, are given in *Figure 1* for SI-Q at 95, 100, 105, 110, 115 and 120°C, and in *Figure 2* for SI-R at 100, 105 and 110°C. It should be mentioned that similar plots are prepared for each blend composition. However, since the rheological measurements for each blend composition were taken at a different range of temperatures, it is very difficult, if not impossible, to investigate the effect of blend composition on the rheological properties of the (SI-Q)/(SI-R) blends, without the influence of temperatures at which rheological measurements were taken. For such purposes, in dealing with homopolymers one often uses time–temperature superposition to obtain master (or reduced) plots. As will be shown later in this paper, it is not obvious how to assess, using reduced plots, the effect of blend composition on the rheological behaviour of binary mixtures of block copolymers. Therefore, we will first employ an alternative method.

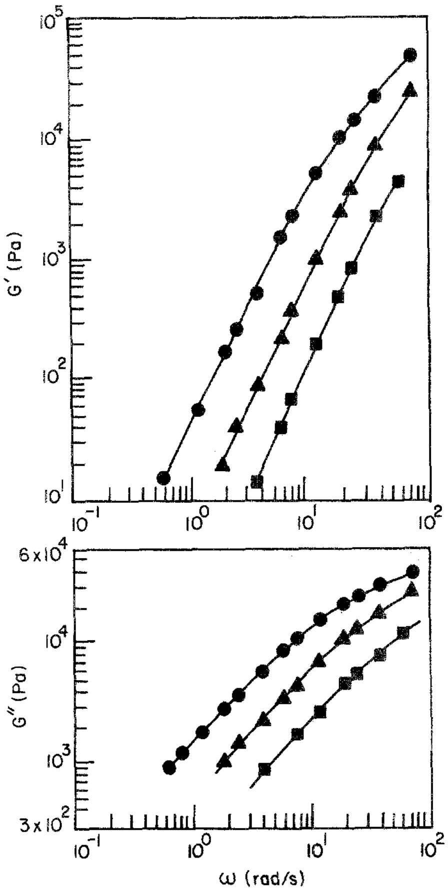

Figure 2 Plots of $\log G'$ *versus* $\log\omega$, and $\log G''$ *versus* $\log\omega$, for the block copolymer SI-R in the disordered state at various temperatures: (●) 100°C, (▲) 105°C, (■) 110°C

Plots of $\log G'$ *versus* $\log G''$ are given in *Figure 3* for SI-Q at 95, 100, 105, 110, 115 and 120°C, and for SI-R at 100, 105 and 110°C. Note that *Figure 3* was obtained without manipulating the data given in *Figures 1* and *2*. The following observations are worth noting in *Figure 3*. (1) The effect of temperature is virtually suppressed, giving rise to a temperature-independent correlation. This has been demonstrated for flexible homopolymers by Han and co-workers[34,35]. (2) In the terminal region, the slope of the plots is virtually 2, which is expected for flexible homopolymers, indicating that indeed the block copolymers SI-Q and SI-R are in the disordered state at temperatures under which the rheological measurements were taken[15–17]. (3) Judging from the values of G' at a fixed value of G'', SI-Q is more elastic than SI-R, because the larger the value of G' the more elastic a polymer is. Note that G' represents the energy stored and G'' represents the energy dissipated while a polymer is subjected to oscillatory shear deformation. This observation is consistent with our expectation in that the molecular weight of SI-Q is higher than that of SI-R, and SI-Q has a much longer polyisoprene (PI) chain than SI-R (see *Table 1*).

Let us examine the plots of $\log G'$ *versus* $\log G''$ for the

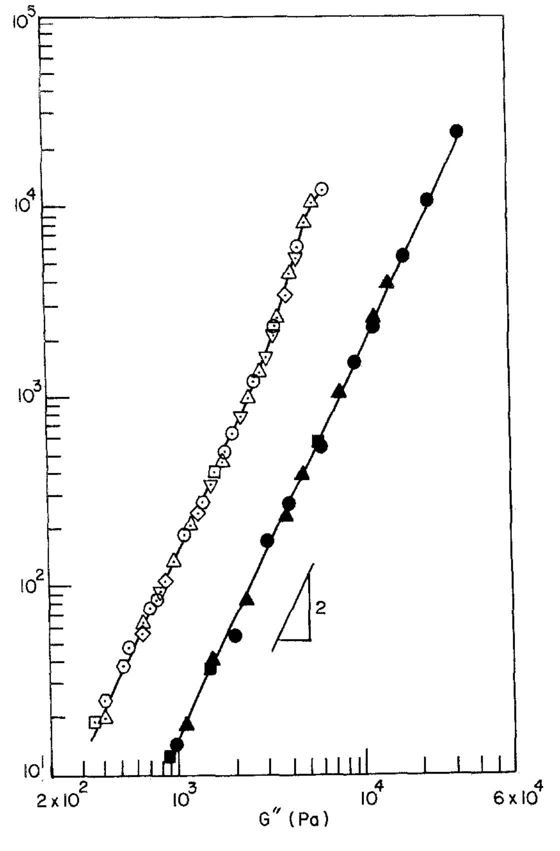

Figure 3 Plots of $\log G'$ *versus* $\log G''$ for: (a) SI-Q at 95°C (⊙), 100°C (△), 105°C (□), 110°C (▽), 115°C (◇), 120°C (⊙); and (b) SI-R at 100°C (●), 105°C (▲), 110°C (■)

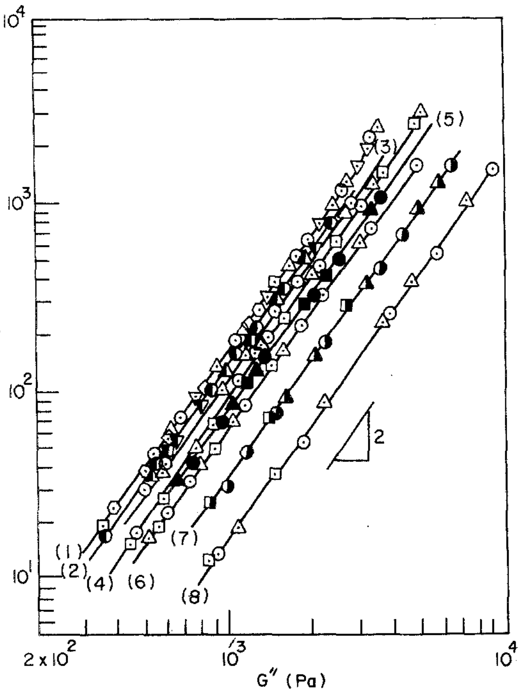

Figure 4 Log G' *versus* $\log G''$ plots for the (SI-Q)/(SI-R) mixtures in the disordered state: (1) neat SI-Q at 95°C (⊙), 100°C (△), 105°C (□), 110°C (▽), 115°C (◇), 120°C (⊙); (2) 90/10 (SI-Q)/(SI-R) mixture at 115°C (◐), 120°C (◭), 125°C (◧), 130°C (▼); (3) 80/20 (SI-Q)/(SI-R) mixture at 120°C (⊙), 125°C (△); (4) 60/40 (SI-Q)/(SI-R) mixture at 115°C (⊙), 120°C (△), 125°C (□); (5) 50/50 (SI-Q)/(SI-R) mixture at 110°C (●), 115°C (▲), 120°C (■); (6) 40/60 (SI-Q)/(SI-R) mixture at 110°C (⊙), 115°C (△), 120°C (□); (7) 20/80 (SI-Q)/(SI-R) mixture at 105°C (◑), 110°C (◭), 115°C (◨); (8) neat SI-R at 100°C (⊙), 105°C (△), 110°C (□)

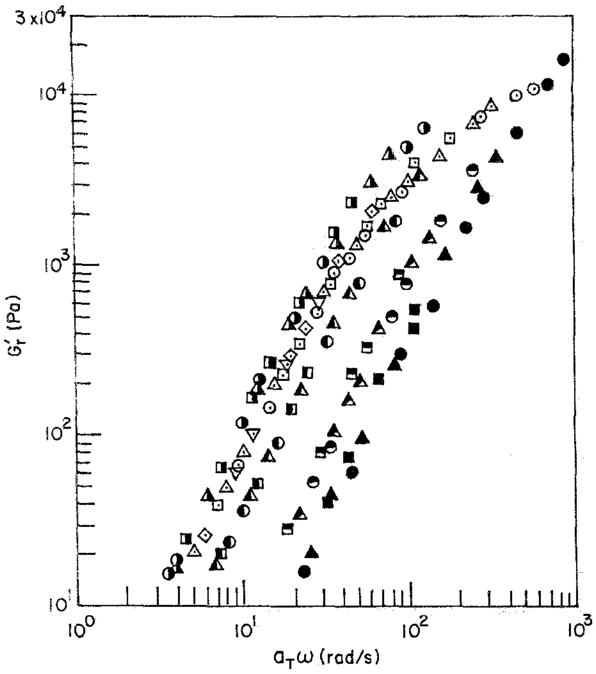

Figure 5 Plots of $\log G'_r$ *versus* $\log a_T\omega$ for the (SI-Q)/(SI-R) mixtures in the disordered state, using the temperature at an equal distance from the glass transition temperature of the polystyrene block ($T_{g,PS}$ + 55°C) in the respective block copolymer as reference temperature: (a) neat SI-Q at 100°C (⊙), 105°C (△), 110°C (□), 115°C (▽), 120°C (◇); (b) neat SI-R at 100°C (●), 105°C (▲), 110°C (■); (c) 60/40 (SI-Q)/(SI-R) mixture at 115°C (◑), 120°C (◭), 125°C (◨); (d) 40/60 (SI-Q)/(SI-R) mixture at 110°C (◐), 115°C (◭), 120°C (◧); (e) 20/80 (SI-Q)/(SI-R) mixture at 105°C (◒), 110°C (◭), 115°C (⬓)

(SI-Q)/(SI-R) mixtures at various temperatures, given in *Figure 4*, which are prepared to investigate the effect of blend composition on their linear viscoelastic properties. It can be seen in *Figure 4* that the $\log G'$ *versus* $\log G''$ plots for each blend composition show temperature independence and have a slope of 2 in the terminal region. It should be remembered that the experimental data for G' and G'' given in *Figure 4* were taken at temperatures above the T_{ODT}s of the respective blends (i.e. in the homogeneous state). It is of great interest to observe in *Figure 4* that $\log G'$ *versus* $\log G''$ plots for the (SI-Q)/(SI-R) binary mixtures lie in a regular fashion between the $\log G'$ *versus* $\log G''$ plots for the constituent components, i.e. at a fixed value of G'' the value of G' (i.e. the melt elasticity) of the binary mixtures increases, approaching the value of G' for the SI-Q, as the amount of the more elastic component, SI-Q, is increased.

Let us now examine reduced plots to investigate the effect of blend composition on the linear viscoelastic properties of the (SI-Q)/(SI-R) binary mixtures. For such purposes, one must first define a reference temperature T_0, to which the data for G' and G'' taken at other temperatures can be shifted. When dealing with amorphous polymers, such as the PS and PI under consideration, it has been suggested that comparison of the rheological properties for different polymers (or different blend compositions) be made at temperatures which are at an equal distance from the glass transition temperatures of the respective polymers (or blends)[36,37]. Such a choice of T_0 is based on the well known concept of iso-free-volume.

Figure 5 gives reduced plots of $\log G'_r$ *versus* $\log a_T\omega$,

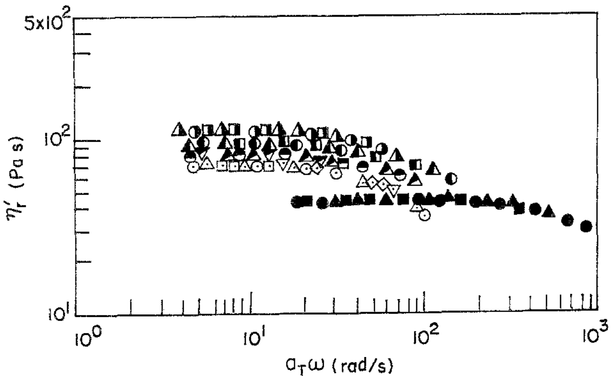

Figure 6 Plots of $\log \eta'_r$ *versus* $\log a_T\omega$ for the (SI-Q)/(SI-R) mixtures in the disordered state, using the temperature at an equal distance from the glass transition temperature of the polystyrene block ($T_{g,PS}$ + 55°C) in the respective block copolymer as reference temperature: (a) neat SI-Q at 100°C (⊙), 105°C (△), 110°C (⊡), 115°C (▽), 120°C (◇); (b) neat SI-R at 100°C (●), 105°C (▲), 110°C (■); (c) 60/40 (SI-Q)/(SI-R) mixture at 115°C (◑), 120°C (▲), 125°C (◨); (d) 50/50 (SI-Q)/(SI-R) mixture at 110°C (◐), 115°C (▲), 120°C (◧); (e) 90/10 (SI-Q)/(SI-R) mixture at 115°C (◓), 120°C (▲), 125°C (⬓), 130°C (▼)

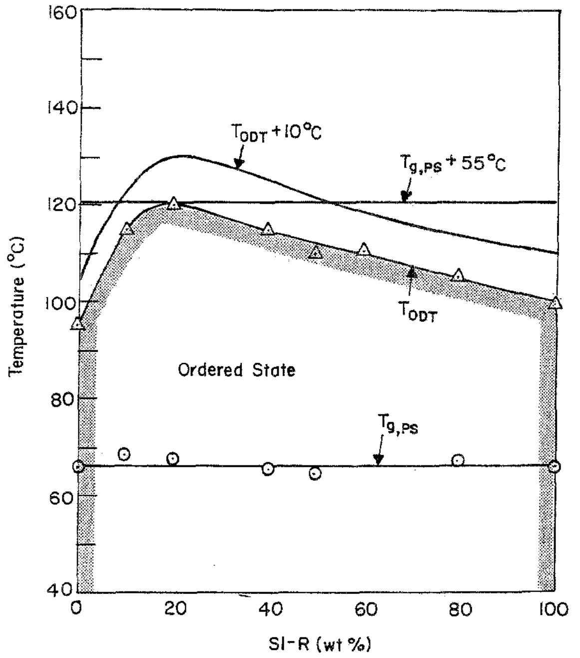

Figure 7 Plots describing the composition dependences of $T_{g,PS}$ and T_{ODT}, and T_0 for the (SI-Q)/(SI-R) mixtures

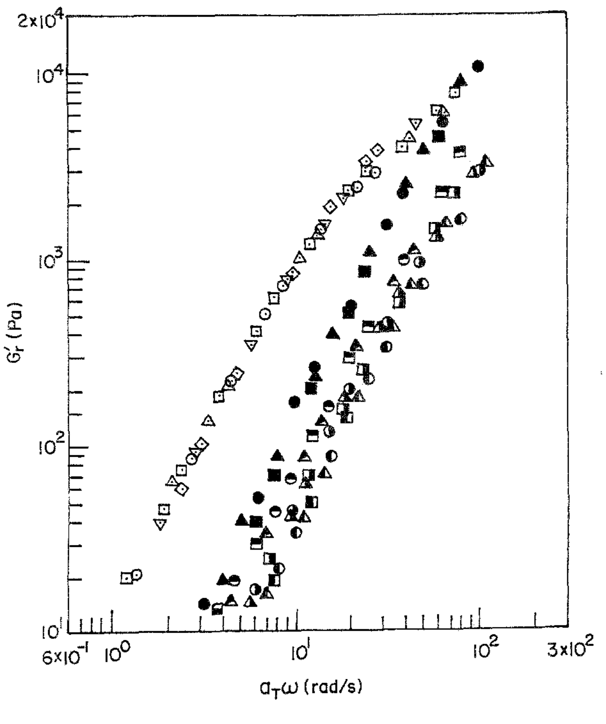

Figure 8 Plots of $\log G'_r$ *versus* $\log a_T\omega$ for the (SI-Q)/(SI-R) mixtures in the disordered state, using the temperature at an equal distance from the T_{ODT} of the respective block copolymer (T_{ODT} + 10°C) as reference temperature: (a) neat SI-Q at 95°C (⊙), 100°C (△), 105°C (⊡), 110°C (▽), 115°C (◇); (b) neat SI-R at 100°C (●), 105°C (▲), 110°C (■); (c) 60/40 (SI-Q)/(SI-R) mixture at 115°C (◑), 120°C (▲), 125°C (◨); (d) 50/50 (SI-Q)/(SI-R) mixture at 110°C (◓), 115°C (▲), 120°C (⬓); (e) 40/60 (SI-Q)/(SI-R) mixture at 110°C (◐), 115°C (▲), 120°C (◧)

and *Figure 6* gives reduced plots of $\log \eta'_r$ *versus* $\log a_T\omega$, for the neat block copolymers SI-Q and SI-R and their binary mixtures, where a_T is an empirical shift factor determined by using $T_0 = T_{g,PS} + 55°C$, G'_r is defined by $G'_r = G'\rho_0 T_0/\rho T$, η'_r is defined by $\eta'_r = \eta'\rho_0 T_0/a_T\rho T$ with $\eta'(\omega)$ being the dynamic viscosity defined by $G''(\omega)/\omega$, and ρ and ρ_0 being the densities at measurement temperature T and reference temperature T_0, respectively. Note that the values of T_0 used in obtaining *Figures 5* and *6* are above the T_{ODT}s of the respective components, i.e. in the homogeneous state (compare the values of $T_{g,PS}$ + 55°C with the values of T_{ODT} in *Table 2*). It should be mentioned that, for clarity, the experimental data for other blend compositions are not included in *Figures 5* and *6*. *Figure 5* shows that the reduced plots of $\log G'_r$ *versus* $\log a_T\omega$ for the 20/80 and 40/60 (SI-Q)/(SI-R) mixtures lie between those of the constituent components SI-Q and SI-R, whereas the reduced plots of $\log G'_r$ *versus* $\log a_T\omega$ for the 60/40 (SI-Q)/(SI-R) mixture lie above those of the constituent components. This is at variance with the observations made in *Figure 4*, i.e. the reduced plots of $\log G'_R$ *versus* $\log a_T\omega$ based on the reference temperature $T_0 = T_{g,PS} + 55°C$ do not exhibit the same composition dependence of dynamic storage modulus as the $\log G'$ *versus* $\log G''$ plots given in *Figure 4*. Further, it is of interest to observe in *Figure 6* that the reduced plots of $\log \eta'_r$ *versus* $\log a_T\omega$ for the entire blend compositions lie above those for the constituent components SI-Q and SI-R.

The choice of $T_0 = T_{g,PS} + 55°C$ as reference temperature, although it lies at or above the T_{ODT} of each blend composition as shown in *Figure 7*, puts us in a dilemma, because the $T_{g,PS}$ lies in the ordered state of the block copolymers investigated. An objection can be raised to this choice of T_0, because the experimental glass transition temperature used to establish the reference temperature is for microphase-separated systems and thus is not appropriate for establishing reference temperatures which permit fair comparison of different homogeneous (disordered) SI diblock copolymers.

Another choice of T_0 would be a temperature which is at an equal distance from T_{ODT}. Therefore in this study we also chose $T_0 = T_{ODT} + 10°C$ as a reference temperature to investigate the effect of blend composition on the linear viscoelastic properties of the (SI-Q)/(SI-R) binary mixtures. *Figure 8* gives reduced plots of $\log G'_r$ *versus* $\log a_T\omega$, and *Figure 9* gives reduced plots of $\log \eta'_r$ *versus*

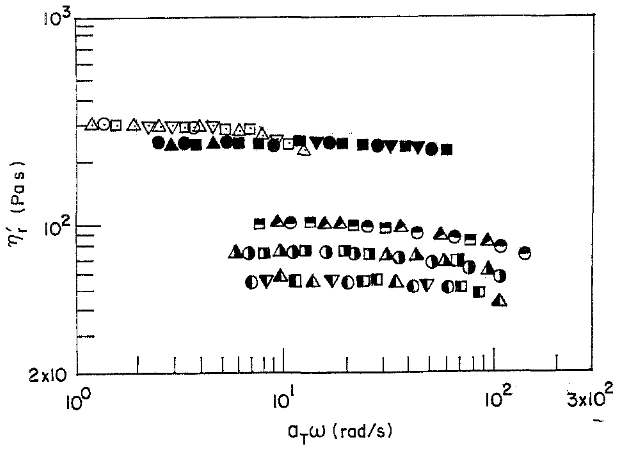

Figure 9 Plots of $\log\eta'_r$ *versus* $\log a_T\omega$ for the (SI-Q)/(SI-R) mixtures in the disordered state, using the temperature at an equal distance from the T_{ODT} of the respective block copolymer (T_{ODT} + 10°C) as reference temperature: (a) neat SI-Q at 100°C (○), 105°C (△), 110°C (□), 120°C (▽); (b) neat SI-R at 100°C (●), 105°C (▲), 110°C (■); (c) 60/40 (SI-Q)/(SI-R) mixture at 115°C (◑), 120°C (◭), 125°C (◨); (d) 20/80 (SI-Q)/(SI-R) mixture at 105°C (◓), 110°C (◭), 115°C (⊟); (e) 90/10 (SI-Q)/(SI-R) mixture at 115°C (◐), 120°C (◭), 125°C (◧), 130°C ▼( )

$\log a_T\omega$, for the neat block copolymers SI-Q and SI-R and their binary mixtures, where a_T was determined by using $T_0 = T_{ODT} + 10°C$, which is in the homogeneous state of the block copolymers, as can be seen in *Figure 7*. It can be seen in *Figures 8* and *9* that over the entire blend compositions investigated, the reduced plots of both $\log G'_r$ *versus* $\log a_T\omega$ and $\log\eta'_r$ *versus* $\log a_T\omega$ lie below those of the constituent components. This observation is at variance with that made in *Figures 5* and *6*, i.e. the choice of $T_0 = T_{ODT} + 10°C$ gives rise to different dependences of G'_r and η'_r on blend compositions from that of $T_0 = T_{g,PS} + 55°C$.

In reference to the curve depicting the reference temperature $T_0 = T_{ODT} + 10°C$ in *Figure 7*, it is clear that the values of T_0 for the (SI-Q)/(SI-R) blends are higher than the values of T_0 for the constituent components SI-Q and SI-R, and thus we expect that the higher the T_0, the lower the rheological properties. In this regard, the dependences of reduced variables G'_r and η'_r on blend composition, displayed in *Figures 8* and *9*, are understandable. Note that the reference temperature $T_0 = T_{ODT} + 10°C$ chosen lies in the disordered state of the block copolymers SI-Q and SI-R and their blends. However, the composition dependence of G'_r given in *Figure 8* is at variance with that given in *Figure 4*. It should be emphasized once again that, as long as a polymer is in the homogeneous state, plots of $\log G'$ *versus* $\log G''$ are independent of temperature, which has its basis in molecular viscoelasticity[35]. Therefore we conclude that plots of $\log G'$ *versus* $\log G''$ are more effective than reduced plots, to investigate the effect of blend composition on the linear viscoelastic properties of binary blends of block copolymers in the homogeneous state.

CONCLUDING REMARKS

In this paper we have shown that plots of $\log G'$ *versus* $\log G''$ are very effective in investigating the effect of blend composition on the linear viscoelastic properties of binary mixtures of SI diblock copolymers in the disordered state. Further, we constructed reduced plots of $\log G'_r$ *versus* $\log a_T\omega$ and $\log\eta'_r$ *versus* $\log a_T\omega$, to investigate the effect of blend composition on the linear viscoelastic properties of binary mixtures of SI diblock copolymers in the disordered state, by choosing a reference temperature T_0 in two different ways: (i) at an equal distance from the $T_{g,PS}$ of the PS block and (ii) at an equal distance from the T_{ODT} of each block copolymer or of each block copolymer composition. We have pointed out that the two different choices of T_0 gave rise to different dependences of reduced variables G'_r and η'_r on blend composition.

It should be pointed out that in $\log G'_r$ *versus* $\log a_T\omega$ plots or $\log\eta'_r$ *versus* $\log a_T\omega$ plots, $a_T\omega$ is an external input variable, representing the intensity of oscillatory deformation imposed on the material, and it has nothing to do with the rheological response of the material. In other words, $\log G'_r$ *versus* $\log a_T\omega$ plots, or $\log\eta'_r$ *versus* $\log a_T\omega$ plots, can be interpreted as being equivalent to the plots of a rheological response (G'_r or η'_r) of a polymer against an input variable ($a_T\omega$). On the other hand, it should be remembered that both G' and G'', which are the quantities derived from the complex modulus G^*, represent the rheological responses of the same material under oscillatory shear deformation. Thus, a $\log G'$ *versus* $\log G''$ plot is tantamount to the plot of one kind of rheological response (the energy stored G') against another kind of rheological response (the energy dissipated G'') while a polymer is subjected to oscillatory shear deformation. It should be noted that the preparation of $\log G'$ *versus* $\log G''$ plots does not require information on reference temperature.

One may be inclined to think that the binary mixtures of SI diblock copolymers in the disordered state, investigated in this study, may be regarded as being analogous to the binary blends of homopolymers having different chain lengths (i.e. different molecular weights). There is, however, an important difference between the two blend systems, in that an SI diblock copolymer consists of two chains of chemically dissimilar structures. Therefore, when two SI diblock copolymers having different block length ratios are mixed, the molecular interactions between the chains in the two separate block copolymers would be much more complicated than those in a binary mixture of homopolymers. At present, however, there exists no theory which enables us to explain, using first principles, the experimental results reported in this paper. This is a subject of future theoretical study.

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