

# Phase separation in entangled polystyrene/poly(vinyl methyl ether) blends

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## Abstract

The entanglement effects on the phase separation of polystyrene/poly(vinyl methyl ether) (PS/PVME) blends were studied by considering the viscoelastic relaxation time and the early stages of dynamic demixing. Particular interest was focused on the blend in which the molecular weight of one component is much higher than that of the other component ( $M_{w, PS} \gg M_{w, PVME}$ ). The viscoelastic relaxation time of high molecular weight PS and PVME in the blends can be clearly separated and the onset of the phase separation process after a temperature jump is delayed to a later time. We suggest that this is due to the formation of a temporary network of the well entangled polymer which needs to relax before phase separation can occur. The results are in good agreement with the theoretical work reported previously by Clarke et al. [Macromolecules 1997;30:4459]. For the blends containing low molecular weight linear and 3-armed star molecules, the viscoelastic effects on the phase separation are not significant since the polymers are not effectively entangled. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Entangled polymer blend; Polystyrene/poly(vinyl methyl ether) blends; Phase separation

## 1. Introduction

Recently a number of experimental studies of the dynamics of phase separation in polymer blends have been analysed using the theoretical approach of Cahn–Hilliard [1–6]. The dynamics of concentration fluctuations have been presented in terms of a thermodynamic driving force and the mobility factors for the component polymers. The effects of entanglements on the mobility and the growth rate expression have been discussed by Pincus and Binder [7,8]. Very recently, Clarke et al. [9] have modified the Cahn–Hilliard theory to treat the system of entangled polymer blends by introducing an elastic term in the free energy to represent the effects of entanglements.

The importance of entanglement effects on the phase separation process in a blend of two linear polymers will be further considered in this work. The effects of the viscoelastic time-scale and the dynamic time-scale on the mobility in the phase separation process were compared by considering rheological measurements together with the kinetic experiments. The experimental work on the early stage dynamics of the phase separation and the viscoelastic relaxation of the entangled polystyrene/poly(vinyl methyl

ether) (PS/PVME) blends will be presented. One component used in this study is a very high molecular weight PS. The delay in the onset of the phase separation of the blend containing this component was noticeable and can be accounted for by the temporary network of entanglements as developed in the theoretical work of Clarke et al. [9]. The phase separation of a blend containing a 3-armed star PS has also been studied in this work and preliminary comments on the effects of the branching on the phase separation of entangled polymer blends will be presented.

## 2. Experimental

### 2.1. Materials and blend preparation

The monodisperse linear and 3-armed star PS samples used in this work are listed in Table 1. The synthesis procedure for the 3-armed star was given elsewhere [10,11]. All PS samples were blended with the same PVME, with molecular weight of  $9.5 \times 10^4$  supplied by Scientific Polymer Products, using toluene as a common solvent. The solution was cast on:

1. cover slips (diameter of 16 mm) to form a thin film of a thickness of 0.15–0.20 mm for the kinetic experiments, and
2. teflon discs (diameter of 25 mm) to form a thin film of a

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Table 1  
PS characteristics

PS sample	$M_w \times 10^{-5}$	Polydispersity	Notation
Linear PS	16.10	1.06	L-PS1610
Linear PS	2.75	1.06	L-PS275
3-armed star PS	2.55	1.09	S-PS255
3-armed star PS	2.22	monodisperse	S-PS222

thickness of 0.25–0.30 mm for the rheology measurements.

The samples were left to dry slowly and kept in a vacuum oven at 40°C. For rheology measurements, two of the samples on teflon discs were removed and carefully placed on top of the third sample to form a sample of a required thickness of 0.8–1.0 mm.

## 2.2. Kinetic and rheology measurements

Cloud point temperatures (extrapolated to zero heating rate) were determined for each blend [12] and the compositions showing the lowest cloud point, as shown in Table 2, were chosen to perform the kinetic and rheology measurements. The critical point is taken as the lowest cloud point temperature as we assume that all systems are monodisperse and the nucleation and growth phenomena can be neglected. The oscillatory dynamic method was used for rheology measurements which were performed on a Rheometrics Dynamics Analyser (RDA II). The objective of the oscillatory measurements is to observe the relaxation time of the PS/PVME blends in the miscible region. Since the molecular weight of each component of the blend is above its entanglement molecular weight, we may expect that although there are a range of relaxation times, it is the longest relaxation time which dominates [13]. The blend samples prepared from solution casting were loaded between the parallel plates. After a preliminary check that the measurements fall in the linear viscoelastic region, dynamic frequency scans from  $10^{-2}$  to  $10^2$  rad/s at fixed temperatures in the one phase region were undertaken under nitrogen atmosphere. It should be emphasised that all the rheological measurements were carried out in the one-phase region of the phase diagram as can be seen from the temperatures given in the figure captions.

Table 2  
PS/PVME blends

PS/PVME	Critical composition	Cloud point temperature
L-PS1610/PVME	10/90	107.5
L-PS275/PVME	20/80	113
S-PS255/PVME <sup>a</sup>	20/80	110
S-PS222/PVME <sup>b</sup>	20/80	110

<sup>a</sup> For kinetic measurements only.

<sup>b</sup> For rheology measurements only.

The kinetics of the phase separation process can be observed by a temperature jump experiment using the light scattering technique. The light scattering apparatus used is a home-made instrument, the details of the instrument being given elsewhere [12]. Homogeneous PS/PVME blends, exhibiting Lower Critical Solution Temperature (LCST) behaviour, initially at room temperature in the one-phase region were transferred quickly into the sample holder which has been heated to a desired final temperature inside two-phase region. The scattered light intensity was collected over a range of scattering angles on a photodiode array, and analysed as discussed in the next section.

## 3. Results and discussion

The plots of the loss modulus,  $G''$ , and the storage modulus,  $G'$ , as a function of frequency,  $\omega$ , for the three blends and for the pure PVME at a fixed temperature of 103.5° in the one-phase region are shown in Figs. 1(a)–4(a). Similar plots at different temperatures are also compared in Figs. 1(b)–4(b). The rheology measurement for pure PS were not carried out because of the high  $T_g$  of the PS ( $\sim 100^\circ\text{C}$ ). All  $G''$  and  $G'$  plots, except for the case of blends with L-PS1610, show that the relaxation processes are in their terminal regions, where  $G''(\omega)$  and  $G'(\omega)$  become linear with slopes of 1 and 2, respectively. The frequency where the crossover of  $G''(\omega)$  and  $G'(\omega)$  occurs (so-called  $\omega_{x\text{-over}}$ ) is inversely proportional to the longest relaxation time. For the L-PS275, S-PS222/PVME blends and the pure PVME (Figs. 2–4), the systems show one  $\omega_{x\text{-over}}$  at high frequency of around 10–100 rad/s, as summarised in Table 3. The relaxation time of pure PVME can be used to compare with those of the blend systems as a standard relaxation of one component. The observation of only one  $\omega_{x\text{-over}}$  would imply that the relaxation processes of PS and PVME components in the low molecular weight linear and 3-armed star blends take place at about the same rate.

The  $G''$  and  $G'$  curves of L-PS1610/PVME blend, shown in Fig. 1, clearly indicate two crossovers of  $G''$  and  $G'$ . Looking at the frequency range of 0–100 rad/s only, one would say that the system is in its terminal region which could be correct considering the contribution of the PVME component. The observed second crossover at a lower frequency is the result of the very slow relaxation of the PS component. This is clear from the observation of a distinct shoulder in the distribution of relaxation times at this point. Such a shoulder or peak is indicative of the terminal relaxation time of a repeating polymer, and would be expected even if there were no cross-over. Since the molecular weight of PS is very high, the relaxation phenomena of PS and PVME components can be observed separately.

From Table 3, the ratio of the two relaxation times of L-PS1610 with L-PS275 in the blends is about 330.

$$\tau(\text{L-PS1610})/\tau(\text{L-PS275}) = 330$$

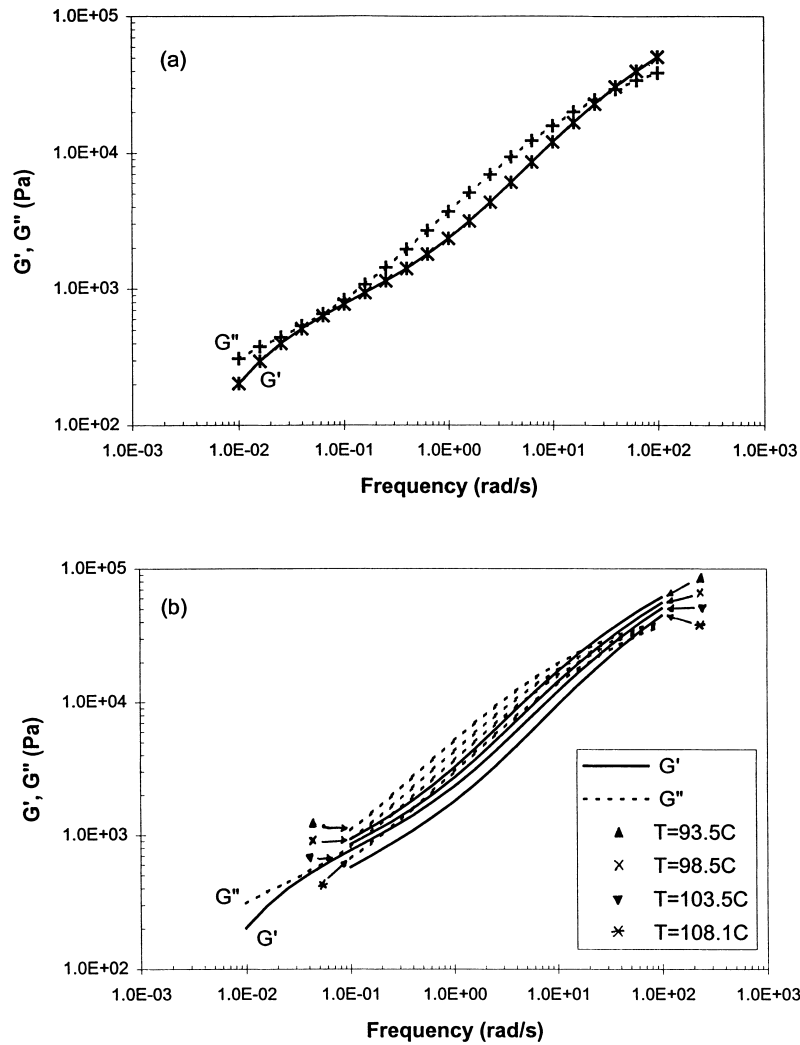


Fig. 1. Plots of  $G''(\omega)$  and  $G'(\omega)$  for L-PS1610/PVME 10/90 blends (Cloud point 107.5°C): (a) at the temperature of 103.5°C; (b) comparison at four different temperatures.

The well-known experimental evidence is that  $\tau \propto M_w^{3.4}$ , so that

$$\tau(\text{L-PS1610})/\tau(\text{L-PS275}) = (1.61 \times 10^6 / 2.75 \times 10^5)^{3.4} = 400$$

Thus, the observed molecular weight effect in the blends is consistent with the known effect of molecular weight. The reptation model of course predicts  $\tau \propto M_w^3$ .

Table 3  
 $\omega_{x\text{-over}}$  and the relaxation time ( $\tau$ ) obtained from rheology results

Blends	$\omega_{x\text{-over}}$ (rad/s)	$\tau = 1/\omega_{x\text{-over}}$ (s)
PVME	$\geq 100$	$< 0.01$
S-PS222/PVME	20	0.050
L-PS275/PVME	15.9	0.063
L-PS1610/PVME	38	0.026
	0.05	20

Considering Fig. 1(b)–4(b) where the effect of varying temperature can be seen, for all systems the whole curves of  $G''(\omega)$  and  $G'(\omega)$  shift to a higher frequency as the temperature is increased inside the miscible region. The relaxation processes speed up at higher temperatures. It should also be noted, for the S-PS222/PVME blend at the phase separation temperature of 113.1°C (Fig. 3(b)), that when the blend is inside the two-phase region, there is a change in shape of both  $G''(\omega)$  and  $G'(\omega)$  curves, indicating an extra contribution to the stress relaxation processes. At high frequencies, the values of  $G''(\omega)$  and  $G'(\omega)$  follow the trend mentioned above but at low frequencies (less than 3 rad/s), i.e. in the terminal region, the relaxation processes seem to be slower than those in the one-phase region. The difference in the effects of shear flow on the viscoelastic properties of PS/PVME blends in the one-phase and two-phase regions have also been reported by Takahashi et al. [14]. They have noted that the shear rate dependence of the viscosity in the two-phase region was different from the

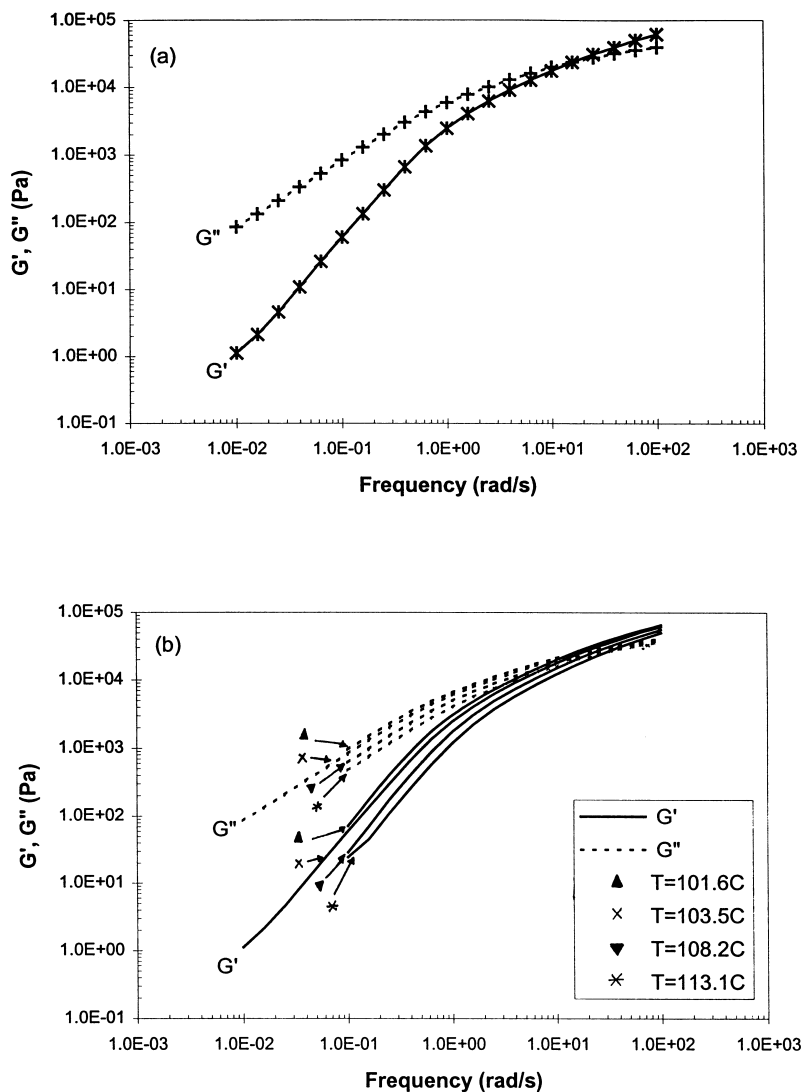


Fig. 2. Plots of  $G''(\omega)$  and  $G'(\omega)$  for L-PS275/PVME 20/80 blends (Cloud point 113°C): (a) at the temperature of 103.5°C; (b) comparison at four different temperatures.

homogeneous region and also varied with composition and temperature.

By reconsidering Figs. 1(b)–3(b) and assuming that the relaxation time scale in the one-phase region is valid inside the two-phase region (near the phase boundary), the relaxation time of the three PS/PVME blends can be estimated to be lower by a factor of 1.31–1.37 for every 5°C increment in temperature. Therefore, at the fixed quench depth of 3°C inside the two-phase region, the relaxation times of PS chains in the blends containing L-PS1610, L-PS275 and S-PS222 are 10.721, 0.019 and 0.021 s, respectively. The difference in the relaxation time of high molecular weight and lower molecular weight linear PS/PVME blends is remarkably large while the relaxation time of lower molecular weight linear PS and star PS/PVME blends is very similar.

The results following the kinetics of phase separation of L-PS1610, L-PS275 and S-PS255/PVME blends at the

quench depth of 3°C inside the two-phase region have been traditionally analysed according to the Cahn–Hilliard theory. During the early stages of spinodal decomposition, the time dependent scattered intensity indicates a difference in the onset of phase separation, as depicted in Fig. 5. The onset of phase separation after the temperature jump for L-PS1610, L-PS275 and S-PS255/PVME blends are in the order of around 300, 20 and 20 s, respectively, as indicated by the arrows in each case. The shorter times are close to the equilibration time after the temperature jump, and are therefore maximum values.

Comparing the relaxation time and the dynamic demixing time for linear PS blends (L-PS1610 and L-PS275), one can see that, at the quench depth of 3°C inside the spinodal, the onset of phase separation of L-PS1610/PVME blend is delayed due to the entanglement effects of L-PS1610. This is in accord with the prediction of viscoelastic effects on the early stages of phase separation recently reported by Clarke

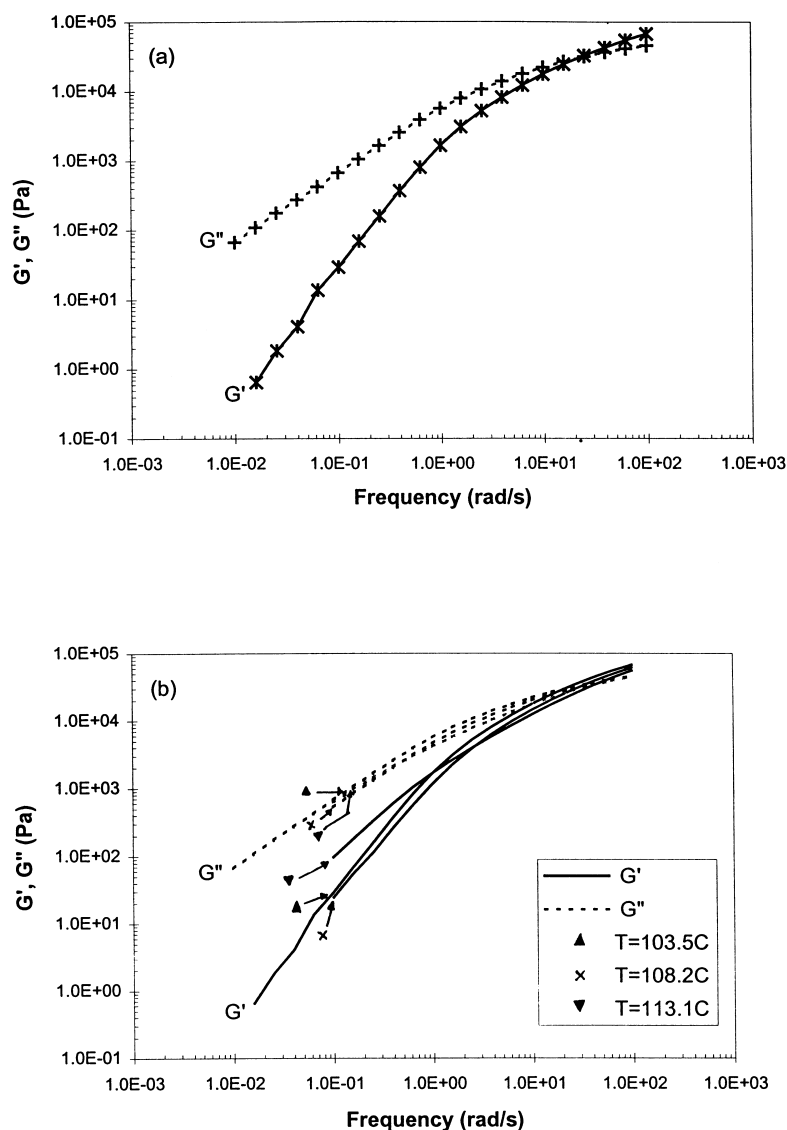


Fig. 3. Plots of  $G''(\omega)$  and  $G'(\omega)$  for S-PS222/PVME 20/80 blends (Cloud point 110°C): (a) at the temperature of 103.5°C; (b) comparison at four different temperatures.

et al. [9]. They treated the polymer blend system in which at least one component is effectively entangled, i.e. when one component has a much larger molecular weight than the other component, so that a temporary network is formed. They have incorporated an elastic term into the free energy and the equation of motion is governed by a double exponential time dependence; the faster mode, representing a relaxation of entanglement, decays, and the slower mode, a modified (slowed) Cahn–Hilliard mode, grows. In general, the prediction shows that when the reptation time of L-PS1610 in a PVME melt is significant compared with the growth rate, there is a delay in the phase separation corresponding to the time needed for the entanglement in the blend to relax before the demixing process can proceed. The details of the theory and a fit to the experimental data can be found in Ref. [9].

Another point we consider is the viscoelastic effects on

the phase separation of the blends with different molecular architecture (L-PS275 and S-PS255/PVME blends). Assuming that the kinetics of the S-PS222 blend are the same as those of the S-PS255 blend, it can be seen that there is no difference either in the rheological relaxation times observed or in the onset of phase separation for linear and star PS at this molecular weight. This is because the linear molecules and the stars are diluted in the PVME melt so that the dominant relaxation process is by constraint release and the effective entanglement molecular weight is quite high ( $M_{e(\text{effective})} = 1/\phi_{\text{PS}} \times M_c$ ) [15]. Therefore, the PS molecules having molecular weight of 255–275 k are not effectively entangled. As a result, the viscoelastic relaxation time would not have noticeable effects on the dynamic demixing time scale. However this effect would be stronger for the case of PS1610 which is well entangled even at  $\phi_{\text{PS}} = 0.1$ . A star PS of this molecular

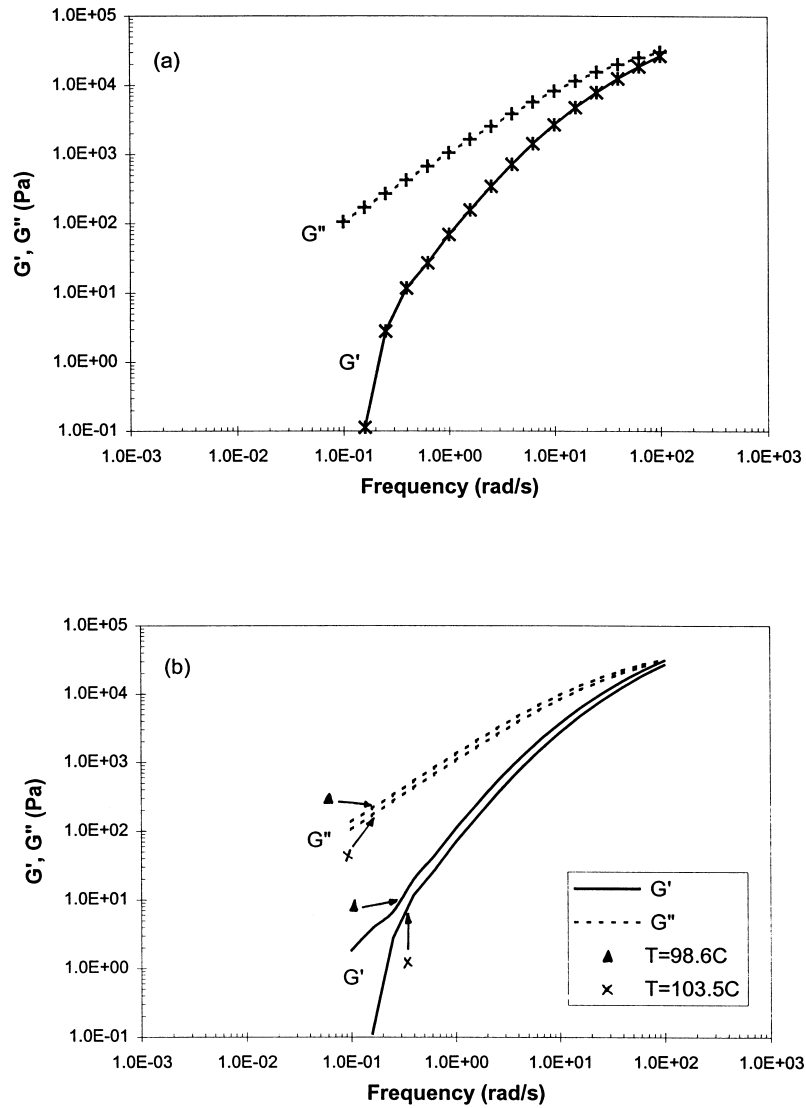


Fig. 4. Plots of  $G''(\omega)$  and  $G'(\omega)$  for pure PVME: (a) at the temperature of 103.5°C, (b) comparison at two different temperatures.

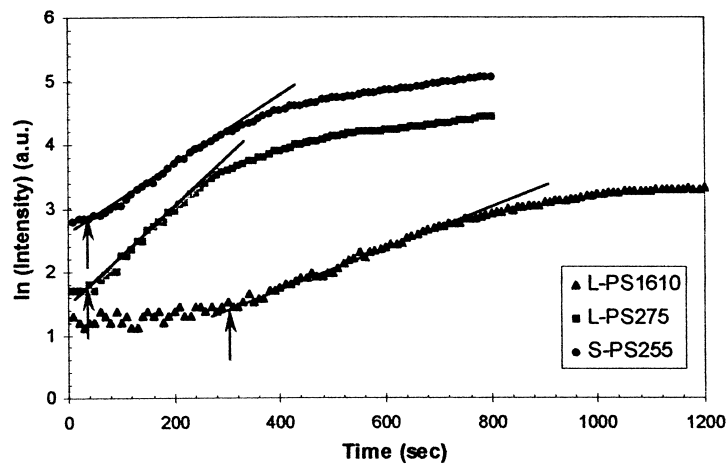


Fig. 5. Comparison of the time dependent scattered intensity for S-PS255, L-PS275 and L-PS1610/PVME blends at the quench depth of 3°C inside the two-phase region.

weight should relax more slowly than the corresponding linear PS.

#### 4. Conclusions

It is shown that the viscoelastic relaxation time of the PS and PVME in their blends can be clearly separated in the rheology measurements when the PS component has a very high molecular weight. The effects of the viscoelastic relaxation process on the early stages of phase separation of the blends are very clear in the case when the PS is well entangled in the PVME matrix, i.e. the molecular weight of PS is much larger than the PVME. The entanglement effects prolong the delay time before the spinodal decomposition process can take place. The results are in good agreement with the theoretical work reported previously [9]. It was predicted that significant effects will occur only when the terminal relaxation time of the slower component is comparable to that of the characteristic time-scale of phase separation. As the rheological data show, this is clearly the case for the high molecular weight PS. In the case of both the lower molecular weight linear PS and the star PS, the terminal relaxation times are many orders of magnitude faster than the phase separation time-scale; hence, no significant effects due to viscoelasticity would be expected.

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#### References

- [1] Hashimoto T, Kumaki J, Kawai H. *Macromolecules* 1983;16:641.
- [2] Yang H, Shibayama M, Stein RS, Shimizu N, Hashimoto T. *Macromolecules* 1986;19:1667.
- [3] Fernandez ML, Higgins JS, Tomlins PE. *Polymer* 1989;30:3.
- [4] Factor BJ, Russell TP, Smith BA, Fetters LJ, Bauer BJ, Han CC. *Macromolecules* 1990;23:4452.
- [5] Guo W, Higgins JS. *Polymer* 1991;32:2115.
- [6] Schwahn D, Janssen S, Springer T. *J Chem Phys* 1992;97(11):8775.
- [7] Pincus P. *J Chem Phys* 1981;75:1996.
- [8] Binder K. *J Chem Phys* 1983;79:6387.
- [9] Clarke N, McLeish TCB, Pavawongsak S, Higgins JS. *Macromolecules* 1997;30:4459.
- [10] Pennisi RW, Fetters LJ. *Macromolecules* 1988;21:1094.
- [11] Khasat N, Pennisi RW, Hadjichristidis N, Fetters LJ. *Macromolecules* 1988;21:1100.
- [12] Pavawongsak S. PhD thesis, Imperial College, London, 1996.
- [13] Doi M, Edwards SF. *The theory of polymer dynamics* ch. 6. Oxford: Clarendon Press, 1986.
- [14] Takahashi Y, Suzuki H, Nakagawa Y, Noda I. *Macromolecules* 1994;27:6476.
- [15] Viovy JL, Rubinstien M, Colby RH. *Macromolecules* 1991;24:3587.