# High-frequency ultrasonic studies of solutions of styrene–butadiene–styrene triblock copolymers

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High frequency ultrasonic measurements are reported on the temperature dependence of sound propagation of dilute solutions of styrene–butadiene–styrene triblock copolymer in toluene. Measurements are also reported on latex systems studied over similar temperature and concentration ranges. The observed increase in attenuation is associated with the effects of phase separation leading to an increase in the viscoelastic processes.

**(Keywords: ultrasonic relaxation; styrene–butadiene–styrene phase separation; latex systems; colloids)**

## INTRODUCTION

It is well known that triblock copolymers undergo phase separation in both the liquid and solid phases. In two previous papers, the ultrasonic relaxation behaviour of dilute[1] and concentrated solutions[2] of styrene–butadiene–styrene (SBS) triblock copolymer have been reported. In dilute solution[1], the ultrasonic relaxation spectrum can be described using a model based on the superposition of relaxation contributions associated with local conformational transitions of the styrene and butadiene segments and normal-mode processes of the whole copolymer chain. Addition of a good solvent, toluene, to the solid triblock copolymer[2] causes an increase in the chain mobility reflected in a decrease in the glass transition temperature. Even in quite dilute solutions, two separate relaxation regions can be identified and it is only when a true solution is generated[1] that a single relaxation process is observed. The observation of two separate local segmental processes may be taken as evidence of phase-separated structure in these swollen gels. In an attempt to study the temperature dependence of the relaxation, the attenuation was investigated over a wide range of temperature[2]. The shift in the relaxation was as anticipated; however, it was observed that the high-frequency limiting values of the attenuation coefficient exhibited a marked temperature dependence. This paper explores further the ultrasonic relaxation properties of these copolymer systems and attempts to determine the origins of the temperature dependence of the high-frequency limiting value of the attenuation coefficient.

Since the initial ultrasonic measurements were performed, extensive small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) have been performed on equivalent systems and have established that phase separation can occur in concentrated solution[3–5]. Studies of stained samples of solids reveal a wide variety of morphology when viewed using electron microscopy, consisting of arrays of spheres, cylinders and lamellae. Theoretical studies of the miscibility of these mixtures[6–9] indicate that a temperature exists where phase separation occurs. Two temperatures will exist depending on whether the corresponding homopolymer's temperature is close to a *LCST* or a *USCT*. In this paper we attempt to connect the variation of the high-frequency ultrasonic behaviour with the process of phase separation in these systems.

## EXPERIMENTAL

### *Materials*

The styrene–butadiene–styrene (SBS) triblock copolymers were obtained from Shell Chemical Co. and were reprecipitated from toluene into methanol, so as to obtain polymer free of antioxidant and plasticizer. The toluene used in the study was dried with calcium hydride before use. The characteristics of the polymers used are

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listed in *Table 1*. The solutions were obtained by first mixing polymer and solvent so as to form a 20% w/v solution and then leaving for three days at 20°C to ensure complete mixing. More concentrated solutions were produced by allowing the gradual evaporation of solvent to obtain concentrations of 30% and higher. The sample of polystyrene latex used was obtained from Dow Chemicals and was a 10% dispersion of 0.714 $\mu$m beads in water, the standard deviation of the bead size being 0.0053 $\mu$m.

### *Acoustic measurements*

Acoustic absorption and velocity measurements were performed over a temperature range from 140 to 430 K and a frequency range from 5 to 1000 MHz. The apparatus and method of measurement have been described in previous publications[1,2]. The precision of temperature control using this apparatus is typically $\pm 1$ K.

### *Viscosity and density measurements*

The viscosities of the solutions were determined using a suspended level viscometer (Poulten and Selfe) operated according to BS188. The densities were measured with a pycnometer at 298 K.

## RESULTS AND DISCUSSION

### *Ultrasonic relaxation in solutions of SBS copolymers*

The relaxation processes associated with the local and normal-mode processes of the polymer chain occur below a frequency of 100 MHz (refs. 1, 2). Cooling of the solutions increases the high-frequency limiting value of the attenuation to a value that is significantly higher than that for the pure solvent (*Figure 1*). Hashimoto *et al.*[3,4] have shown that phase separation in solution can be observed by a SAXS experiment and it may be suggested that this phase-separation process may in some way be responsible for the observed ultrasonic effects. In a previous paper[10] we have explored the effects on the ultrasonic attenuation due to scattering of sound by voids in crystalline polymer and observed that the attenuation coefficient ($\alpha/f^2$) was proportional to $f^2$, $\alpha$ being the absorption attenuation of sound at frequency $f$. If the wavelength of the sound wave is larger than the domain size and multiple scattering can be neglected, then the modified form of the Rayleigh scattering equation due to Okano[11] can be used. If we assume that the scattering centres are the styrene–butadiene domains suspended in toluene, then the equation has the form:

$$\alpha_s = \frac{8\pi^4 f^4 a^3}{v^4}\left[\frac{1}{3}\left(\frac{K_1 - K_0}{K_1}\right)^2 + \left(\frac{\rho_1 - \rho_0}{2\rho_1 + \rho_0}\right)^2\right]\phi \qquad (1)$$

where $a$, $K$, $\rho$, $v$ and $\phi$ denote the radius, bulk modulus, density, velocity of sound and volume fraction, respectively. The subscripts 1 and 0 denote the styrene–butadiene spheres and the continuous medium, respectively. The value of $\alpha_s/f^2$ will have a maximum at a frequency at which the wavelength is comparable with the size of the domain, and this is predicted by a more complete version of the scattering theory[12,13]. The complete analysis of the sound scattering process requires the use of Bessel functions; however, the theory in the long-wavelength limit approximates to the theory of Okano. SAXS studies[3–5] have been carried out since our initial ultrasonic measurements and indicate that the domains size depends on the styrene content of the copolymer and vary in the range 10 to 30 nm. Substitution of these values in equation (1) indicates that the contribution to the attenuation at 750 MHz due to scattering from phase-separated domains is $10^{-25}$ mm$^{-1}$ s$^2$, indicating that the observed increase in ultrasonic attenuation cannot be ascribed to the effects of sound scattering. In order to test the validity of equation (1) for describing the scattering from styrene domains, we have investigated as a model system solutions of polystyrene latices.

**Table 1** Molecular mass and composition of SBS copolymers

| Polymer | Code | $M_w \times 10^{-4}$ | Composition | Comment |
|---|---|---|---|---|
| Triblock copolymers | SBS1 | 17 | 50 wt% styrene | $M_w/M_n = 1.1$ |
| Styrene–butadiene–styrene | SBS2 | 17.1 | 30 wt% styrene | $M_w/M_n = 1.1$ |

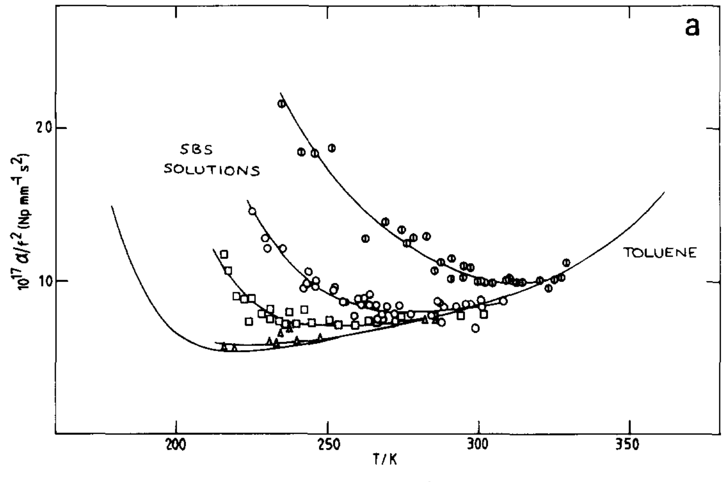

**Figure 1** (a) Temperature dependence of $\alpha/f^2$ at 740 MHz for SBS1 in toluene: (▵) 9.9%; (□) 21.4%; (○)30.1%; (⦶) 43%; the full curve marked 'Toluene' represents the temperature dependence of the attenuation for the solvent toluene and is the average of ditrative data. (b) Temperature dependence of $\alpha/f^2$ at 740 MHz for SBS2 in toluene: (▵) 9.9%; (□) 20.1%

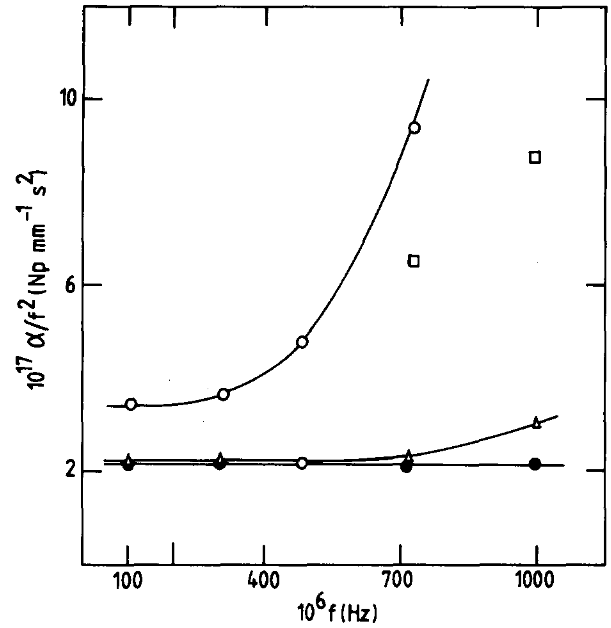

**Figure 2** Frequency dependence of $\alpha/f^2$ for the polystyrene latices: (●) water; (▵) 0.5%; (□) 5%; (○) 10%

*Studies of polystyrene latices*

Measurements were performed over a frequency range from 116 to 1000 MHz at 25°C and over the concentration range from pure water to 10% w/w (*Figure 2*). Unlike the data on SBS in toluene, where there was little or no frequency dependence above 100 MHz, the polystyrene latices exhibit a marked increase in attenuation with increasing frequency. Equation (1) indicates that the attenuation of the sound wave should, in a dilute solution region, vary linearly with the volume fraction of the scattering spheres provided that the velocity does not vary significantly. In practice, the velocity will also be a function of the concentration and will reflect the changes in the compressibility of the solvent and the polymer spheres. This latter term is amplified since it appears, raised to the fourth power, in equation (1). The general shape and concentration–frequency dependence is consistent with that predicted by equation (1) and implies that the changes observed are consistent with a scattering mechanism in these polystyrene latices.

*Origins of the high-frequency attenuation in SBS*

It is clear from a comparison of the data in *Figures 1* and *2* that the origins of the ultrasonic behaviour in these two systems are very different. From our earlier studies[1,2] we can exclude the increase in the attenuation at low temperatures in SBS as being due to relaxation processes, as these occur at frequencies below 100 MHz. Matheson *et al.*[14,15] have observed that in polymer solutions the high-frequency limiting viscosity does not equal the value for the solvent. It was suggested that the high-frequency contribution to the viscosity is associated with the presence of solid impenetrable regions generated by the rigid polymer chains. In the case of the phase-separating SBS in a good solvent the polymer chains will be swollen and hence the 'rigid' polymer chains should be permeable to solvent above the phase-separation temperature. The resultant contribution to viscous losses, as observed by ultrasonic attenuation measurements, will be minimal. Cooling below the phase-separation point will produce spheres of impenetrable styrene regions, which will inhibit solvent flow. The effective high-frequency viscosity will be given by:

$$\eta_{\text{eff}} = \eta_{\text{solvent}}(1 + a\phi + b\phi^2 + \cdots) \tag{2}$$

where $a$ is the Einstein sphere contribution to the viscosity associated with the phase-separated region, $\eta_{\text{solvent}}$ is the viscosity of the solvent and $\phi$ is the concentration of spheres. The above equation is an accurate description of the viscosity behaviour of the system in the low-concentration region. The ultrasonic attenuation for such a system will be described by modification of the Navier–Stokes[16] expression:

$$\frac{\alpha}{f^2} = \frac{2\pi^2}{\rho c^3}\left[\tfrac{4}{3}\eta_s + \eta_v + \frac{(\gamma - 1)}{C_p} Q\right] \tag{3}$$

where $\eta_v$ and $\eta_s$ are respectively the volume and shear viscosities, $\rho$ is the density, $c$ is the velocity of sound, $\gamma$ is the ratio of the specific heat at constant pressure to the value at constant volume and $Q$ is the thermal conductivity. If it is assumed that the thermal part of the solution and the solvent are the same, then substitution of equation (2) into (3) gives:

$$\left(\frac{\alpha}{f^2}\right)_{\text{observed}} = \frac{2\pi^2}{\rho c^3}\left[\frac{4}{3}\eta_{\text{solvent}}(1 + a\phi + b\phi^2 + \cdots) + \frac{(\gamma - 1)}{C_p} Q\right] \tag{4}$$

This can then be rearranged to give:

$$\left(\frac{\alpha}{f^2}\right)_{\text{observed}} = \left(\frac{\alpha}{f^2}\right)_{\text{solvent}} + \frac{2\pi^2}{\rho c^3}\left[\tfrac{4}{3}\eta(a\phi + b\phi^2 + \cdots)\right] \tag{5}$$

The second part of equation (5) is a function of the solvent viscosity and the volume fraction of the phase-separated structures. To a first approximation the volume fraction of the phase-separated structures will not change with temperature and the excess acoustic attenuation will be dominated by the temperature dependence of the viscosity of the solvent. This hypothesis is supported by

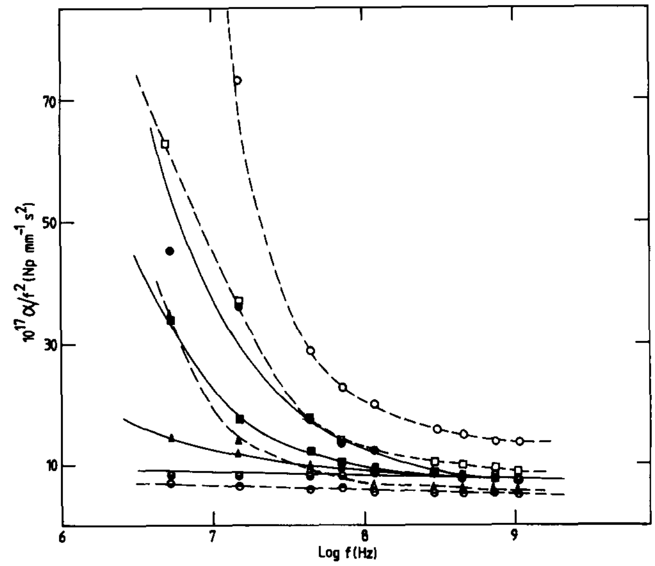

**Figure 3** Frequency dependence of $\alpha/f^2$ for SBS1 solutions: (– – –) 227 K; (⊖) toluene; (▵) 9.9%; (□) 21.4%; (○) 30.1%; (——) 300 K; (⊖) toluene; (▲) 9.9%; (■) 21.4%

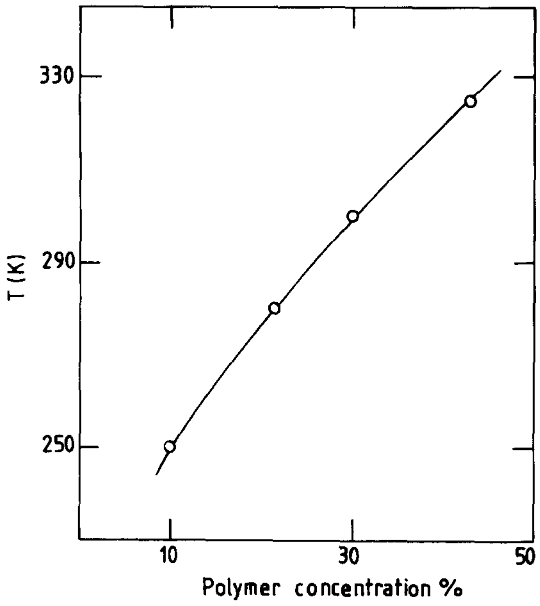

**Figure 4** Concentration dependence of the phase-separation temperature for SBS1 in toluene

a comparison of the shapes of the polymer solution and pure solvent curves as a function of temperature (*Figure 1a*), the temperature dependence of the solution paralleling that of the solvent.

### *Temperature dependence of the relaxation frequency*

A plot of the frequency dependence of the attenuation as a function of temperature for certain concentrations (*Figure 3*) indicates that the relaxation frequency apparently increases with a decrease in temperature. This trend is the direct opposite of what would be expected for a thermally activated relaxation process. However, a careful analysis of the data indicates that this apparent effect is a direct result of the increase in the value of $(\alpha/f^2)$ due to the increased high-frequency limiting attenuation, due to viscous effects, increasing the attenuation coefficient at any particular frequency rather than the anticipated decrease due to the shift of the relaxation to lower frequency with decreasing temperature. This once more confirms the validity of the model represented by equation (5).

### *Identification of phase separation by ultrasonic measurements*

The observed increase in the ultrasonic attenuation of solutions of SBS in toluene at low temperatures is a direct consequence of the effects of the presence of the phase structure on the high-frequency limiting viscosity values and not a consequence of scattering. It is possible from the data in *Figure 1* to identify the temperature at which phase separation occurs and this is shown in *Figure 4*. As expected by theory[10], the temperature at which phase separation occurs increases with concentration and is clearly identified from the ultrasonic measurements.

Comparison of these data with measurements of phase separation using SAXS and SANS indicates that similar values of the concentration–*UCST* plots are obtained[5,17], once more supporting the general conclusions of this paper. Direct comparison of the data is not possible, however, as the equivalent polymers to those used in this study have not as yet been reported.

## CONCLUSIONS

The ultrasonic measurements on SBS in toluene are consistent with phase separation generating impenetrable regions in solution which lead to a marked increase in the high-frequency limiting shear viscosity contribution to the sound attenuation. The data obtained from these measurements are comparable to those obtained from SANS and SAXS measurements in similar systems.

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