Ultrasonic studies of styrene–butadiene–styrene triblock copolymers

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Ultrasonic measurements covering the frequency range 5–1000 MHz are reported on solid styrene–butadiene–styrene triblock copolymers and their solutions in toluene and cyclohexane. In the solid, two distinct relaxation processes were observed, corresponding to the glass transitions of the polystyrene and polybutadiene phases. Two distinct processes were observed also in the swollen solid, the relaxation peaks being shifted to lower temperatures with plasticization of the polymer by the solvent. Comparison of the changes observed with those detected in a similar mixture of the corresponding homopolymers confirms the importance of phase separation in the swollen copolymer. An increase in the high frequency attenuation of semi-dilute solutions can be associated with scattering of the sound wave by micelle structures. The temperature–concentration locus at which this scattering is first observed correlates with other observations of microphase separation in triblock copolymers. At these concentrations, the low frequency relaxation curves deviate from extrapolation from dilute solutions data indicative of significant polymer–polymer entanglement interaction.

Keywords Ultrasonic studies; block copolymers; microphases; concentrated solutions; relaxation; acoustic

INTRODUCTION

The phase separation characteristics of di- and tri-block copolymers are now well established[1–6]. A range of morphologies can be obtained, ranging from spheres to cylinders to lamellae depending on the ratio of styrene to butadiene, and on the conditions used in the sample preparation. The phase-separated solid exhibits two distinct relaxation regions[6–10]. A lower temperature process, occurring at approximately 223K, is associated with the onset of molecular motion in the butadiene phase and a higher temperature transition, located at approximately 393–413K, corresponds to the glass transition of the styrene phase. In contrast intimate blends and random copolymers exhibit only a single broad transition. It has been established by light scattering[11] that phase separation is possible in solutions of these polymers. In our previous studies[12–15] we have shown that ultrasonic attenuation is sensitive to scattering by phase inhomogeneities in solids (at high frequencies) and to losses caused by polymer chain entanglement interactions in solutions (at lower frequencies).

This study was undertaken in order to gain a further understanding of phonon scattering and acoustic absorption phenomena in two-phase fluid systems.

EXPERIMENTAL

Materials

The SBS polymers were obtained from Shell Chemical Company, and were reprecipitated from toluene into methanol so as to obtain polymer free of antioxidant and plasticizer. The solvents, toluene and cyclohexane, were dried with calcium hydride before use. The characteristics of the polymers used are listed in *Table 1*. The sample of polystyrene used in this study was obtained from the Pressure Chemical Company. The *cis* 1,4-polybutadiene was synthesised by polymerization of butadiene in n-pentane at room temperature, n-butyl lithium being used as initiator. Sample solutions of concentration higher than 50% were prepared by gradual evaporation of solvent from *ca.* 30% solution. After the concentration reached an appropriate value, the solution was kept in a sealed vessel for three days at 20°C to ensure complete mixing.

Acoustic measurements

Acoustic absorption and velocity measurements were performed over a temperature range from 140K to 430K, and a frequency range from 5–1000 MHz. The apparatus was the same as that used for high frequency investigations of sound propagation in solid polymers[15]. The precision of temperature control using this apparatus is typically ±1K. The temperature dependence of sound

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velocity and the attenuation constant in the range below room temperature were measured (during cooling) at a cooling rate of *ca.* 0.3K min^{-1}.

Viscosity and density measurements[16]

The viscosities of the solutions were determined using a suspended level viscometer (Poulten and Selfe) operated according to BS 188. The densities were measured with a pycnometer at 293K.

RESULTS AND DISCUSSION

Solid and plasticized films examined at 5 MHz

Films of polymer SBS1 and SBS2 were prepared by solvent casting from toluene. In a previous study of the dielectric properties of the same samples, it was found that SBS-1 and SBS-2 exhibit respectively lamellar and rod-like morphology[17]. The temperature variation of the attenuation at 5 MHz caused by the annealed films and their mixtures with toluene are shown in *Figures 1* and *2*. The polymer SBS1, which contains the higher styrene content, exhibits two relaxations, one at 430K associated with segmental motion in the styrene phase, and the other at 250K denoting the onset of the motion in the butadiene phase. Decreasing the styrene content leads to a reduction in the T_g of the butadiene phase, so that in SBS2 this relaxation occurs at 230K. The temperature dependence of the acoustic attenuation at 5 MHz in pure polybutadiene exhibits a peak at 225K, indicating that the

Table 1 Molecular weights of polymers

Polymer	Code	$M_w \times 10^{-4}$	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
Polystyrene	PS	9.72	M_w/M_n 1.06
Polybutadiene	PB	2	M_w/M_n 1.3

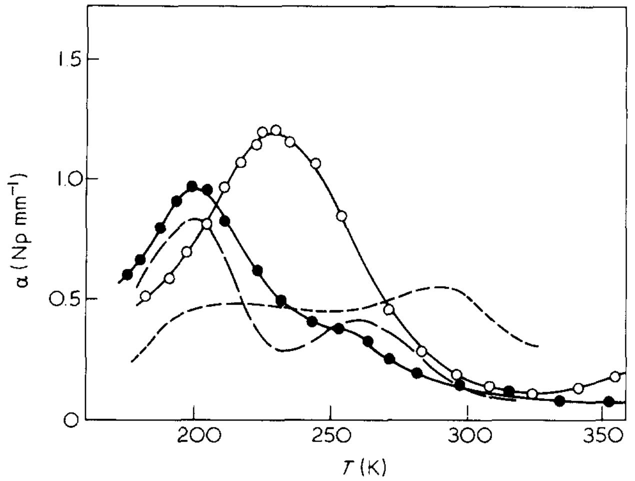

Figure 2 Temperature dependence of the attenuation constant, α(Np mm^{-1}), at 5.5 MHz for SBS2, a mixture with toluene, and a mixture of toluene, polystyrene and polybutadiene. (○) SBS2 solid film; (●) SBS2 73.1%; (— — — —) a mixture of PS, PB and toluene at the ratio of 1 :1 :0.766, (—·—·—) SBS1, 68.5% mixture with toluene for comparison

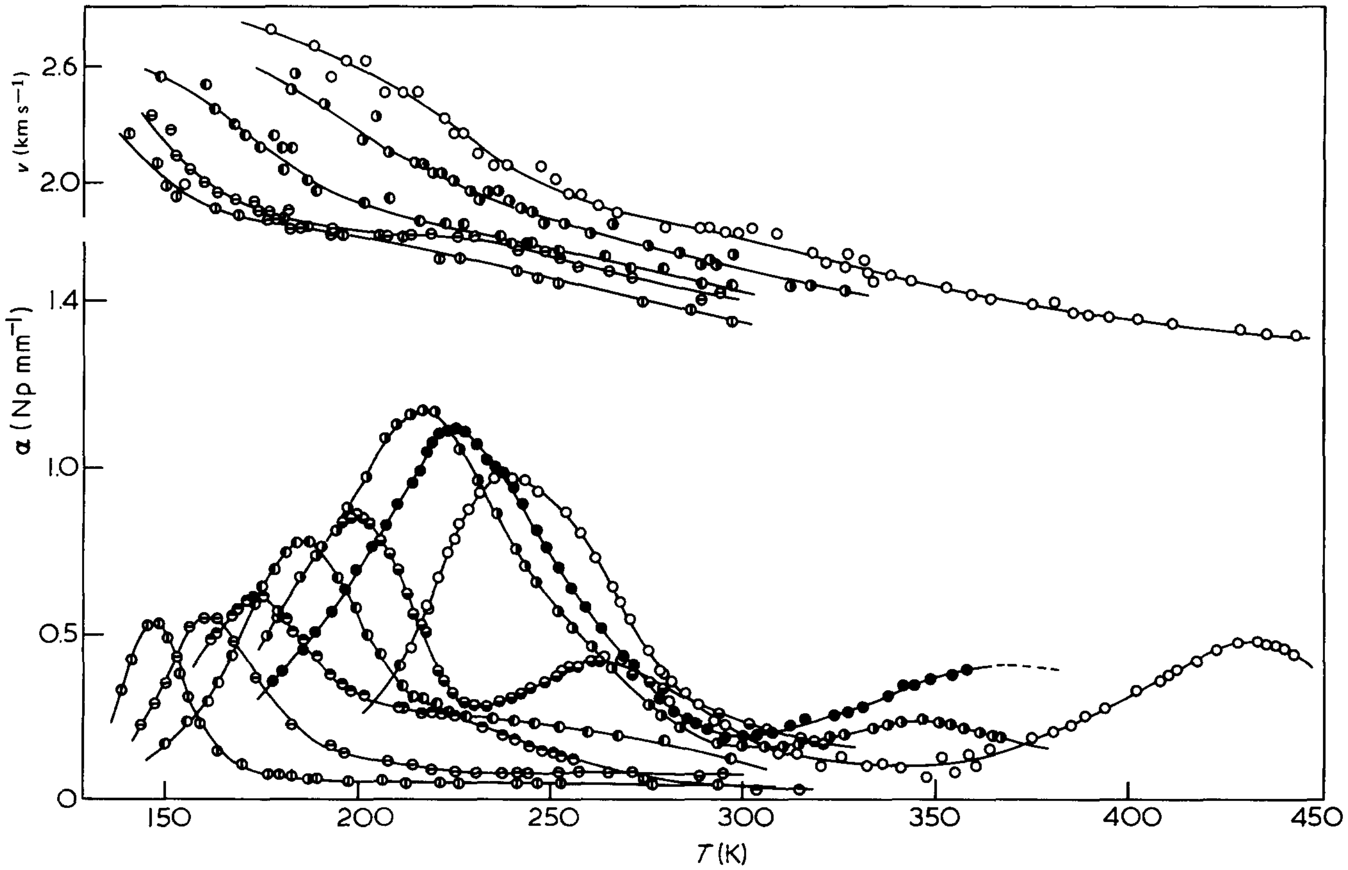

Figure 1 Temperature dependence of the attenuation constant, α(Np mm^{-1}), and sound velocity, v(km s^{-1}), measured at 5.5 MHz for SBS1 and its mixtures with toluene. (○) Solid film; (●) 89.4%; (◑) 83.0%; (◒) 68.5%; (◐) 60.7%; (◓) 50.4%; (⊖) 40.2%; (⦶) 22.3%

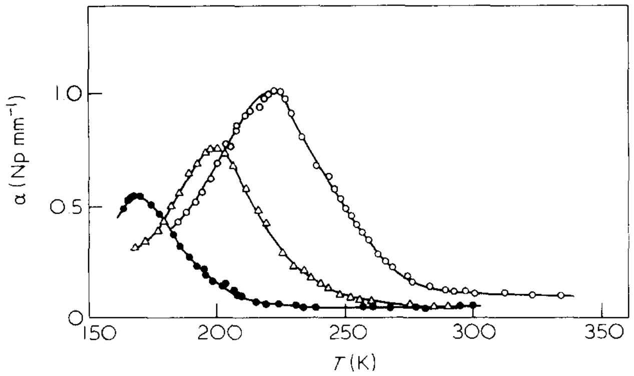

Figure 3 Temperature dependence of attenuation constant, α(Np mm^{-1}), at 5.5 MHz for polybutadiene and its mixtures with toluene. (○) Solid film; (△) 82%; (●) 50%

motion in SBS2 is very similar to that in the pure homopolymer, *Figure 3*. These observations are consistent with other observations of the nature of the phases in these block copolymers[7,10].

Concentrated polymer–solvent systems examined at 5 MHz

Addition of toluene to both SBS and polybutadiene shifts the relaxation of the butadiene segments to lower temperatures, *Figures 1–3*.

The concentration dependence of the relaxation in SBS1 is interesting. In concentrations as low as 60% polymer it is still possible to observe relaxation features associated with the molecular motion in separate blocks. Between 40 and 50% the peaks are asymmetric and a broad tail is seen at the high temperature sides. This indicates that at 40% concentration, the solution is still phase-separated. This is in contrast to a solution of 72% (total weight) of polystyrene and polybutadiene present in a 1:1 ratio (which models the SBS1 polymer), *Figure 3*, for which a broad relaxation feature is observed. This implies that whereas in SBS1 phase separation still occurs to a large extent, in the mixed homopolymers there is a significant amount of interpenetration of chains. At concentrations below 50% the polystyrene relaxation merges with that of the polybutadiene segments, *Figure 4*. Comparison of the 70% solutions of SBS1, *Figure 1*, and SBS2, *Figure 2*, shows an amplitude change in the PS and PB peaks, reflecting the different PS contents. However, the peak temperatures are almost the same, as shown more clearly by the comparisons in *Figures 2* and *4*.

The velocity at 304K changes smoothly with concentration and is represented by an empirical equation given by

$$v(\mathrm{km\,s^{-1}}) = 1.273 + 0.0907w + 0.303\,w^2$$

where w denotes the weight fraction of SBS. However, the amplitude of the polybutadiene maximum loss first rises before showing the expected decrease with dilution, *Figure 1*. This is very similar to the addition of solvent to poly(dimethylsiloxane) of molecular weight above the critical entanglement size[14], and to the addition of toluene to polystyrene[12]. In these two homopolymer systems an explanation was offered[12,14] in terms of entropic fluctuations set up within entangled polymer networks. A similar explanation might well hold in the SBS–solvent systems with chain constraints at the microphase interfaces replacing those of entanglements. However, such an hypothesis cannot be futher tested at this time because it is not yet possible to separate enthalpic and entropic effects at the interfacial region.

Frequency dependence of ultrasound propagation

The ultrasound velocity shows a small dispersion, *Table 2*. This is only just larger than experimental error and does not justify further investigation. The frequency and temperature dependences of the attenuation of SBS1 in toluene are shown in *Figures 5a* to *5c*, and of SBS2 in toluene in *Figures 5d* and *5e*.

At concentrations of polymer below 10% the ultrasonic attenuation curves can be described as the sum of a normal mode relaxation associated with the whole chain (calculated using the theory of Wang and Zimm[18]) and a segmental relaxation which is principally associated with the styrene moiety.

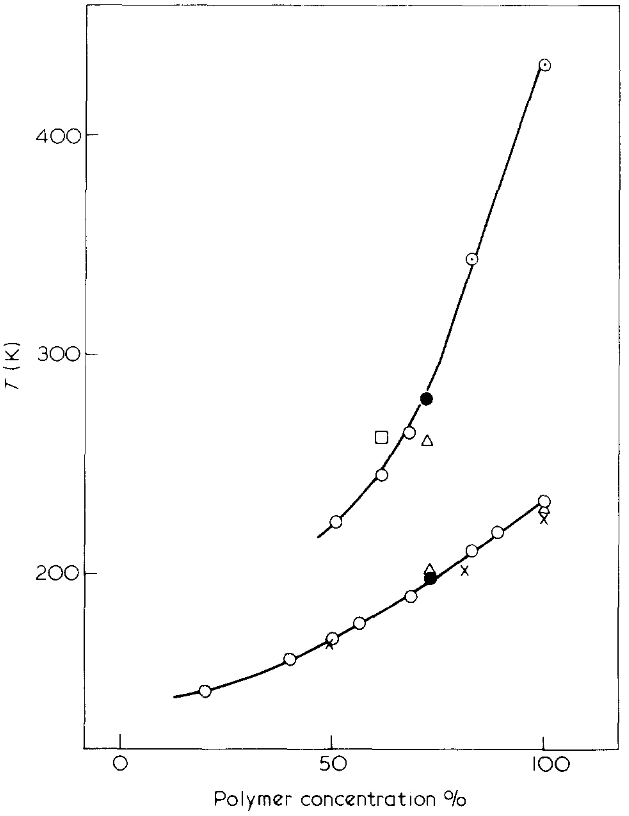

Figure 4 Concentration dependence of the temperature of maximum attenuation at 5.5 MHz. Relaxation of the polystyrene phase (upper curve) and of the polybutadiene phase (lower curve). (○) SBS1; (△) SBS2; (X) polybutadiene; (●) mixture of PS, PB, and toluene (polymer concentration 72%)

Table 2 Variation of velocity 34.8 wt % SBS

Temperature (K)	Frequency (MHz)	Velocity (km s^{-1})
227	72.9	1.68
227	120.7	1.72
241	73.1	1.60
241	120.8	1.60
300	73.4	1.39
300	120.6	1.40

Error in velocity data ±2%

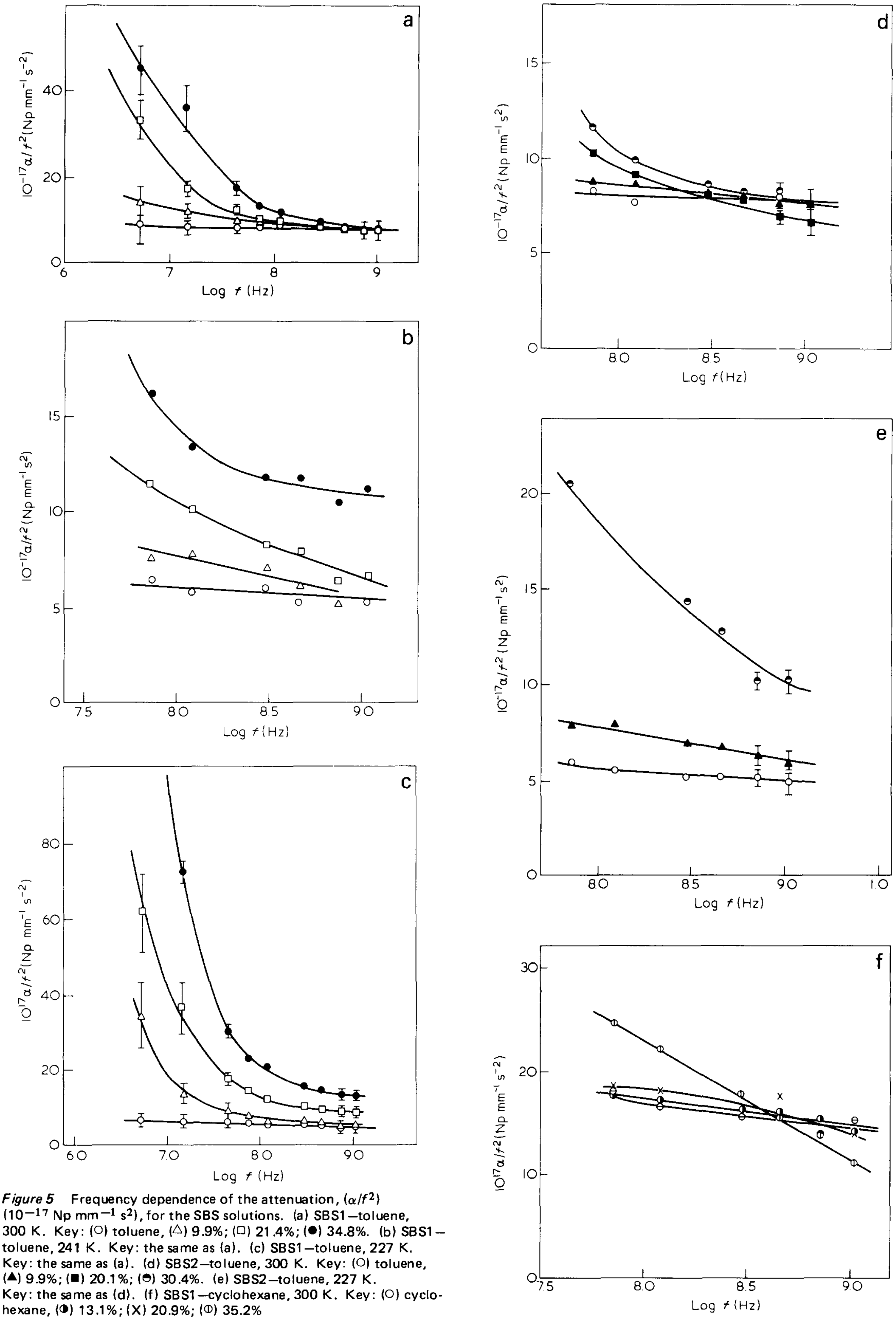

Figure 5 Frequency dependence of the attenuation, (α/f^2) (10^{-17} Np mm^{-1} s^2), for the SBS solutions. (a) SBS1–toluene, 300 K. Key: (○) toluene, (△) 9.9%; (□) 21.4%; (●) 34.8%. (b) SBS1–toluene, 241 K. Key: the same as (a). (c) SBS1–toluene, 227 K. Key: the same as (a). (d) SBS2–toluene, 300 K. Key: (○) toluene, (▲) 9.9%; (■) 20.1%; (◓) 30.4%. (e) SBS2–toluene, 227 K. Key: the same as (d). (f) SBS1–cyclohexane, 300 K. Key: (○) cyclohexane, (◑) 13.1%; (X) 20.9%; (⦶) 35.2%

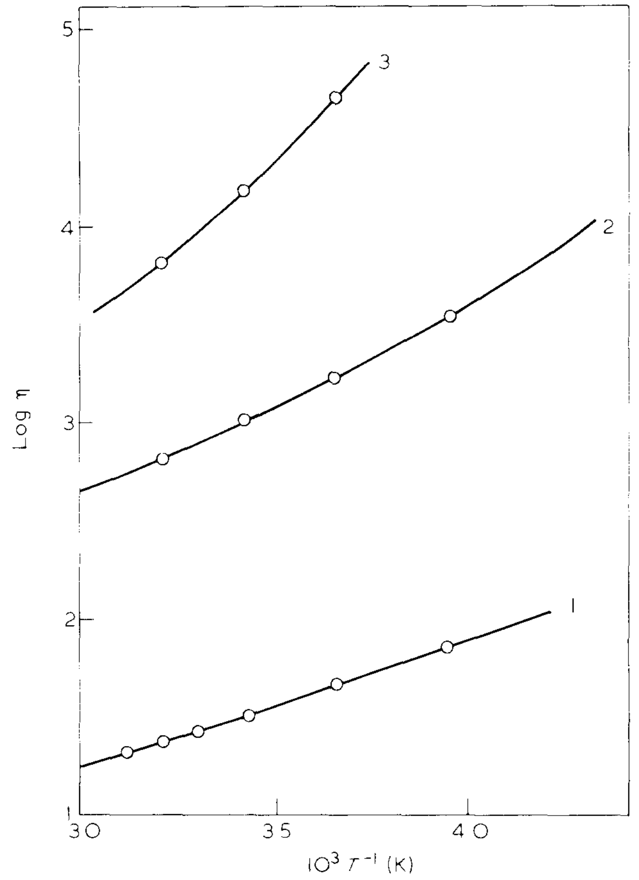

Figure 6 Temperature dependence of viscosity of solutions of SBS1 in toluene. Curve 1, 9.9%; curve 2, 21.2%; curve 3, 34.8%

In more concentrated solutions polymer–polymer entanglement interactions cause non-linearity in the attenuation–concentration relationship (evidenced by non coincidence of the normalized curves) as was observed in polystyrene[12]. These effects are seen, too, as a change in slope of the viscosity temperature plot, *Figure 6*, prior to the microphase separation temperature[19].

The data are particularly interesting in the frequency range above 400 MHz. As is seen in *Figure 5b*, the magnitude of α/f^2 at 241K for solutions of SBS1 concentration 9.9% and 21% is similar to that of the solvent, but that for a 35% solution is surprisingly high. This sudden increase in α/f^2 occurs at a lower concentration at 227K, but is not observed at 300K. This confirms that microphase separation occurs with increasing concentration and decreasing temperature, as indicated theoretically[19].

Microphase separation causes additional attenuation of the sound wave, probably due to phonon scattering and inter-grain heat flow processes[15]. By contrast the attenuation in a cyclohexane solution of SBS1 at 300K is shown in *Figure 5f*, and there is no sign of phase separation.

We have analysed α/f^2 in the range above 400 MHz as follows. The attenuation of toluene[20] is subtracted from the total solution attenuation

$$(\alpha/f^2)_{\text{excess}} = (\alpha/f^2)_{\text{soln}} - (1-w)(\alpha/f^2)_{\text{tol}}$$

where w denotes polymer weight fraction and suffices soln and tol refer to polymer solution and toluene solvent respectively.

Attenuations normalized for concentration ($[\alpha/f^2]_{\text{excess}}w^{-1}$) are shown in *Figure 7*. The curves fall into two groups for homogeneous and phase-separated solutions. Attenuation due to scattering has been observed in crystalline polymers[15], and for Rayleigh scattering α/f^2 should be proportional to f^2 (λ^{-4} scattering law). In this case the difference between the two families of curves increases with frequency, indicating just such a mechanism.

Phase separation constrains conformational motion of chains at the interface, which could be responsible for the high values of $(\alpha/f^2)_{\text{excess}}$ observed in the megahertz region.

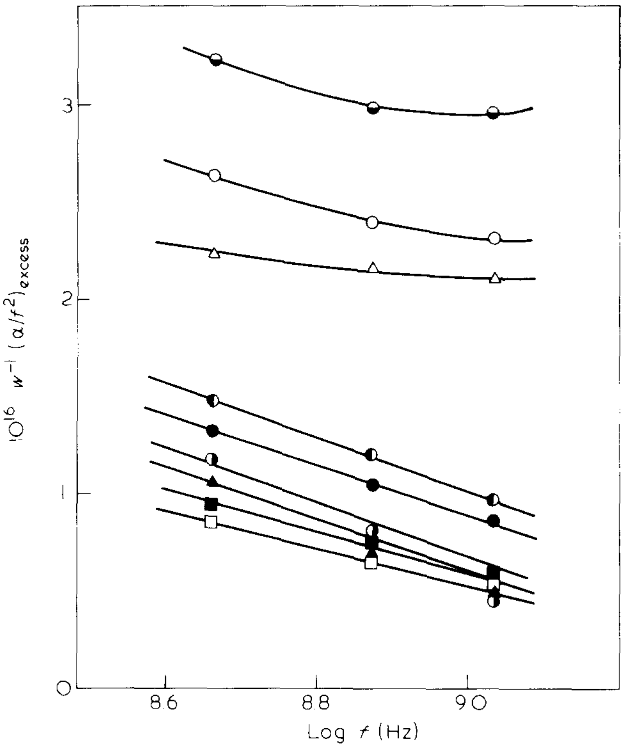

Figure 7 Normalized excess attenuation w^{-1} $(\alpha/f^2)_{\text{excess}}$ (10^{-16} Np mm^{-1} s^2) for SBS1 in toluene. Data at 227 K, (▲) 9.9%; (△) 21.4%; (◒) 34.8%. Data at 241 K, (■) 9.9%; (●) 21.4%; (○) 34.8%. Data at 300 K, (□) 9.9%; (◐) 21.4%; (◑) 34.8%

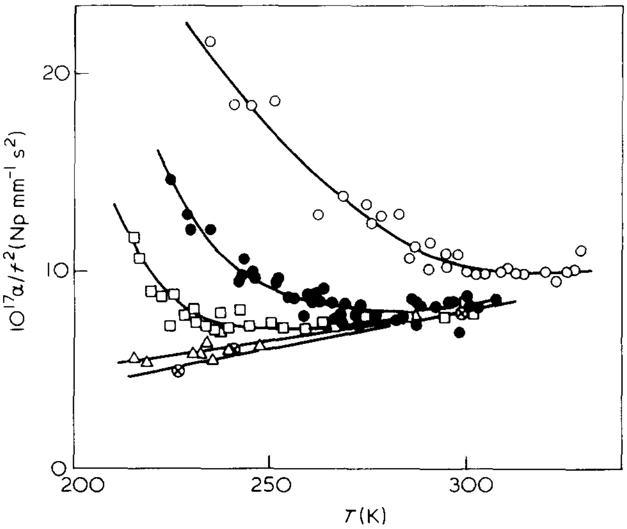

Figure 8 Temperature dependence of attenuation at 740 MHz for SBS1 solutions in toluene. Key: (⊗) toluene; (△) 9.9%; (□) 21.4%; (●) 30.1%; (○) 43%

Temperature dependence of the limiting high frequency absorption

The effects on the high frequency limiting attenuation of cooling homogeneous solutions are summarized in *Figure 8*. The concentration at which this high frequency limiting absorption deviates from that of solvent is again indicative of micelle formation in solution[20–25]. The microphases in solid SBS1 and SBS2 have dimensions of 13 and 20 nm respectively[17]. In solution the domains are swollen and hence the size may increase by a factor of approximately w^{-1}. Thus the microphases could have dimensions of the order of 40 to 60 nm in 30% solutions of these polymers. Thus the λ^{-4} condition will still be valid. Unfortunately it is not possible to use these acoustic scattering measurements in an analysis of exact domain sizes, but the qualitative effects are in agreement with other theories and observations of microphase separation.

CONCLUSIONS

The attenuation of ultrasound, by absorption and scattering, shows the persistence of phase separation from the solid into moderately concentrated solutions. The microphase separation concentration–temperature locus agrees with that predicted theoretically and observed by other techniques.

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