Acoustic studies of heterophase systems: styrene-butadiene-styrene

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(Received 25 April 1977)

Acoustic absorption and velocity measurements are reported over a temperature range from 213 to 293 K on a series of linear and four-arm star styrene–butadiene–styrene triblock copolymers. The loss peak associated with the segmental motion of the butadiene block was studied in detail. Its position, shape and width were found to be sensitive to the composition (styrene–butadiene ratio) and structure of the copolymer. The data is discussed in terms of the effects of morphology and microstructure on the observed dynamics.

INTRODUCTION

Phase separation in styrene–butadiene–styrene (SBS) triblock copolymers has been extensively studied by X-ray diffraction and electron microscopy[1,7]. Solvent cast films are found on annealing to demonstrate a variety of morphologies ranging from spheres to rods to lamellae depending on the ratio of styrene to butadiene and upon the solvent used in casting[3,6]. Well developed morphologies can be obtained either by extrusion[7] or by compression moulding followed by high temperature annealing[9]. The viscoelastic relaxation of such materials has been studied extensively[10–18] dielectric[19,20] and ultrasonic relaxation studies[21] have been relatively few. In general the relaxation spectrum is composed of two principle features; the highest temperature loss occurring at approximately 393–413K depending on frequency of observation and is characteristic of the glass transition process of the polystyrene domains and the lower temperature loss occurring at approximately 223K associated with relaxation in the butadiene domains. Nuclear magnetic relaxation studies[22] have recently been reported on SBS macroscopic single crystals, formed by extrusion. The sample had a unique morphology composed of polystyrene cylinders arranged in a hexagonal array parallel to the extrusion axis within a continuous polybutadiene matrix. The effects of magnetic spin diffusion are very evident in this study and lead to an increase in the magnitude of the butadiene spin–lattice relaxation time (T_1) minima at the expense of the styrene process. Studies of T_1 and the spin–spin relaxation time (T_2) indicate minima at 233 and 373K whilst the rotating frame experiment ($T_{1\rho}$) leads to the observation of a minima at 223K. Consideration of this data in terms of various models indicates the absence of molecular orientation in either of the component phases but does not reveal the effects which morphology may have on the observed relaxation process. In this study the effects of change in the styrene to butadiene composition on the soft block relaxation process are probed.

EXPERIMENTAL

Acoustic absorption and velocity data were obtained using an immersion technique[23] operating at 5 MHz. Methanol was chosen as the immersion fluid for these experiments as it is a non-solvent for the copolymer. No solvent effects were observed during these experiments. Details of the apparatus and the procedure used have been discussed elsewhere[24]. The acoustic attenuation was determined with a precision of better than ± 0.15 dB/cm.

Materials

The polymers used were commercial samples, *Table 1*, reprecipitated to remove antioxidants and plasticizer before use. The samples used in the acoustic measurements were in the form of compression-moulded discs, formed by applying pressure of 20 MN/m^2 at a temperature of approximately 373K. The samples were annealed by holding the disc under pressure for 2 h at approximately 353K. One of the samples was obtained by extrusion of the polymer in the form of a tube. Electron microscopic studies of the morphologies of the samples were in good agreement with those reported in

Table 1 Composition of the triblock copolymers studied

Sample	Type	Styrene (%)	Molecular weight, $M_n \times 10^{-3}$	Source
S1	ABA	23	67	Shell
S2	ABA	29	86	Shell
S3	ABA (extruded star triblock)	23	67	Shell
S4	$(AB)_4$	25	240	Phillips

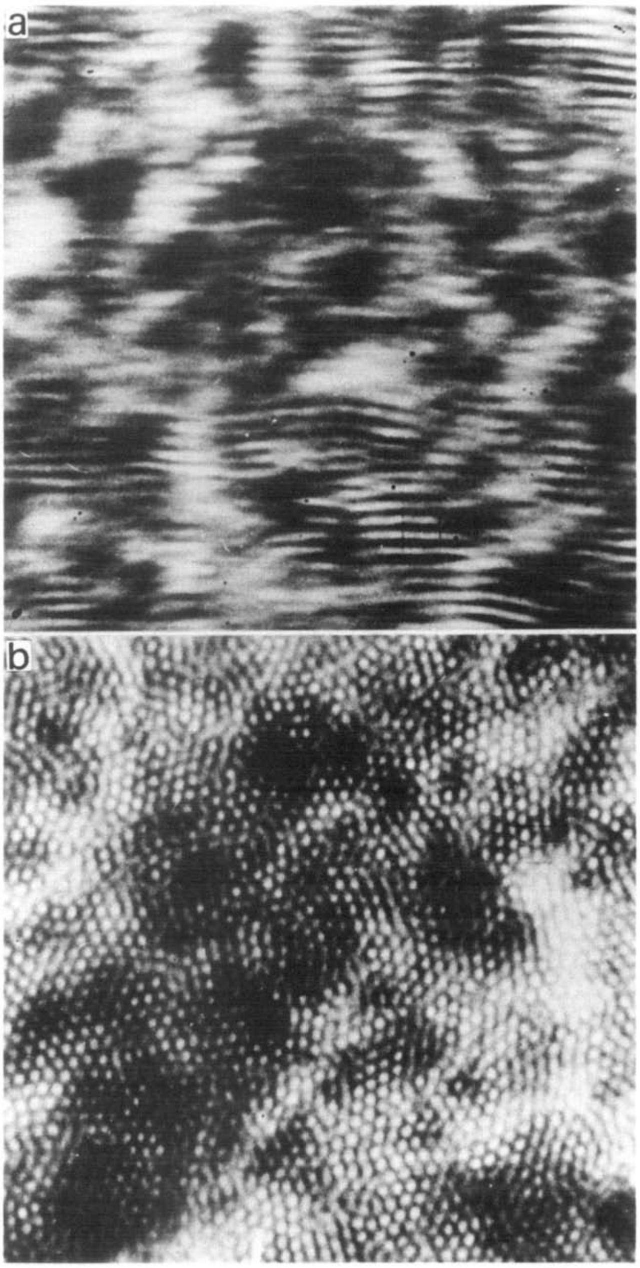

Figure 1 Electron micrographs for sample S3. (a) and (b) are respectively taken parallel and perpendicular to the direction of extrusion

the literature for compression-moulded films[7,9]. The electron micrographs were obtained from OsO_4 stained slice of the samples. In the case of the extruded sample *Figure 1* the electron micrographs across and along the extrusion direction were obtained and clearly indicating the development of cylindrical morphology in this sample. The factors influencing the morhpology in SBS copolymers have been discussed elsewhere[26].

RESULTS AND DISCUSSION

Acoustic attenuation data

Acoustic attenuation data plotted *versus* temperature for the various SBS samples measured at 5 MHz are presented in *Figure 2*. The observed maximum in the loss may be correlated with the minima observed in the n.m.r. studies[22] and can be associated with the segmental motion of the butadiene chains. The activation energy for this process varies slightly with composition of the copolymer and has a value of approximately 107 kJ/mol[26]. The position of the peaks observed, *Figure 2*, are in general agreement with those previously reported from lower frequency observations on a single SBS sample[21].

Although samples S1 and S2 exhibit similar relaxation spectra, the position of the maximum in the loss curve is shifted to higher temperature ~5–8K with increase in the styrene to butadiene ratio. The extruded sample S3 exhibits a loss peak at a higher temperature ~10K than that of the compression-moulded sample S1 with the same styrene to butadiene ratio. The essential difference between these samples is one of morphology. The compression moulded sample is composed of semicontinuous domains of polystyrene, whereas the extruded sample has a much more highly developed cylindrical domain structure orientated parallel to the extrusion direction, *Figure 1*. In the latter sample the polybutadiene chains are significantly more constrained than in the former sample and this is reflected in a shift of the loss peak to higher temperatures.

The 4-arm triblock copolymer S4 exhibits two loss peaks, the lower temperature maximum coincident with that of the non-aligned SBS sample, the higher temperature peak occurring significantly above that of the aligned sample. The lower peak may be associated with the molecular motion of the butadiene chains well away from either the star crosslink or styrene domains. The higher temperature peak corresponds to the motion of the butadiene chains in the neighbourhood of the star and reflects the increased restriction on motion as a consequence of polymer interactions. In all the samples studied the loss peak is asymmetric towards high temperature suggesting restriction of the motion of the butadiene chain by styrene interactions in the region of the styrene–butadiene interface.

Velocity data

The velocity of longitudinal and shear propagation are obtained from a determination of the respective critical

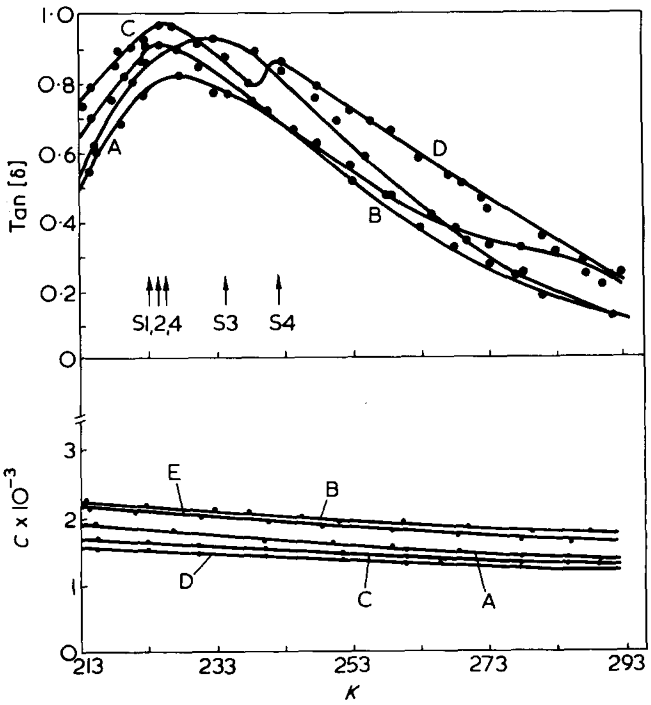

Figure 2 Acoustic data for the styrene–butadiene–styrene copolymers. Composition of copolymers as designated in *Table 1*. (a) A, S1; B, S2; C, S3; D, S4; (b) A, S1; B, S2; C, $S3_{//}$; D, $S3_{\perp}$; E, S4

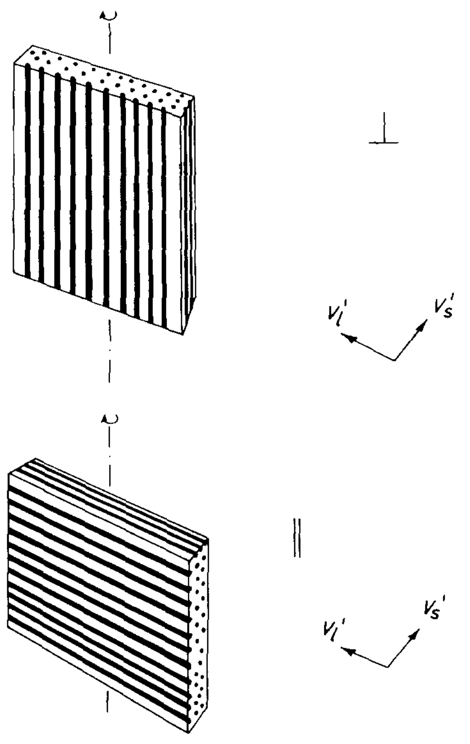

Figure 3 Interaction of a sound wave with an anisotropic system

angles. In the present study the critical angle for shear wave propagation exceeded the available angular aperture and could not be obtained. The variation of the longitudinal velocity with temperature for the three compression-moulded samples were found to be essentially very similar, *Figure 2* and agreed well with previously published values[21]. A slight variation in the absolute magnitude of the velocity with styrene–butadiene ratio was observed, in agreement with sonic velocity measurements (10^2–10^4 Hz) on similar systems[27,28]. In all cases the velocity was independent of the orientation of the sample to the sound beam indicating that the propagation is isotropic. In contrast, the value of the velocity obtained from the extruded sample depended upon the relative directions of the axis of rotation and the extrusion direction, *Figure 3*. The sample is clearly anisotropic and a detailed analysis of the mode of wave propagation becomes complex. When the axis of rotation and the draw direction are coincident propagation occurs perpendicular to the cylindrical axis of the polystyrene domain. Alternatively, when the axis of rotation and draw direction are perpendicular, propagation can now coincide with the cylindrical axis of the polystyrene domains. Since the relative orientation of the cylindrical axis and beam direction are constantly being varied a number of as yet untested assumptions concerned with mode conversion in heterophase systems have to be made before component moduli can be calculated. It is however apparent that the values obtained in the two directions reflect differences in the extent to which the sound wave interacts with the styrene domain.

CONCLUSION

This study has shown that the effect on the chain dynamics of chemical crosslinking (S3) can clearly be observed as the appearance of an additional loss peak. This to the authors knowledge has not previously been observed by ultrasonics. Anisotropy as a result of the development of a high degree of morphological perfection was observed in the velocity study. Further study of the dynamics of this system at higher frequency was precluded because of the high acoustic absorption, however the distinct effects of morphology and crosslinking in the system are vividly demonstrated.

ACKNOWLEDGEMENTS

The authors wish to thank Shell and Phillips Petroleum UK Ltd for supplying samples of the copolymers used in these studies.

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