Ultrasonic studies of solutions of styrene–butadiene copolymers

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Ultrasonic attenuation measurements on solutions of linear and star styrene–butadiene–styrene block copolymers over a frequency range from 10^6 to 10^8 Hz are reported. Activation parameters for the segmental relaxation process in 1,4-dioxane, cyclohexane and toluene were obtained from temperature variation studies. Both the amplitude and the temperature dependence of the relaxation varied with change in solvent.

INTRODUCTION

The effects of molecular weight[1], tacticity[2] and chemical structure[1–4] on the ultrasonic relaxation of dilute polymer solutions have been reported in a series of papers. Attenuation in the frequency range 1–100 MHz has been ascribed to a combination of viscous and enthalpic processes. The viscous loss arises from the high frequency tail of the normal mode relaxation processes. The enthalpic contribution is ascribed to a perturbation of the rotational isomeric structure, localized to a 'segment' involving only a small number of monomer units.

The objectives of this study were: (i) to test the above hypothesis in a system in which the long range relaxation motion may be modified by the block structure of the copolymer; (ii) to identify the effects on the ultrasonic relaxation of a single chemical crosslink; and (iii) to probe the effects of solvent strength on the high frequency relaxation process.

EXPERIMENTAL

Velocity and attenuation measurements

The ultrasonic velocity and attenuation measurements were obtained over a frequency range from 10^6 to 10^8 Hz using a combination of resonant interferometric and pulsed techniques[1]. The mode of operation, description and limitations of these techniques have been reported previously[2]. The estimated error in the observed attenuation was ±2% and in the measured velocity ±0.01%.

Materials

The polymers used in this study were commercial products. The linear styrene–butadiene–styrene copolymers (SBS) were obtained from Shell Chemicals, the star copolymers $(SB)_4$ from Phillips Petroleum, and the polybutadiene from British Industrial Plastics. The polystyrene was a Pressure Chemical standard sample. The molecular weights, molecular weight distributions and trade names of the copolymers are summarized in *Table 1.*

The SBS polymers contained about 0.1% of an antioxidant, 2,6-dibutyl-4-methyl phenol, which was removed by reprecipitation of benzene solutions of the polymer into methanol. The solid polymers were kept in the dark to avoid photodegradation, and freshly prepared solutions were used in all measurements. The compositions of the copolymers were checked using ^{1}H n.m.r. spectroscopy and were found to agree with those quoted by the suppliers. The effects of finite column resolution of the g.p.c. on the molecular weight distribution[5] have not been allowed for in obtaining the values quoted in *Table 1.*

RESULTS

Acoustic attenuation coefficients (α/f^2) were obtained as a function of frequency and temperature for 5% w/v solutions of the copolymers in toluene (*Figure 1*), 1,4-dioxane and cyclohexane. The data were analysed for a distribution of relaxation times using the real part of a Cole–Cole function[1]:

$$\delta(\alpha/f^2)_{\text{polymer}} = \frac{A[1+(f/f_c)^\beta\cos(\pi\beta/2)]}{[1+2(f/f_c)^\beta\cos(\pi\beta/2)+(f/f_c)^{2\beta}]} \qquad (1)$$

where

$$\delta(\alpha/f^2)_{\text{polymer}} = (\alpha/f^2)_{\text{solution}} - (\alpha/f^2)_{\text{solvent}} \times w_{\text{solvent}}$$

where $(\alpha/f^2)_{\text{solution}}$ and $(\alpha/f^2)_{\text{solvent}}$ are, respectively, the attenuation coefficients for the solution and solvent at the frequency of observation, and w_{solvent} is the weight of solvent in unit volume of solution. In all the solutions studied (*Table 2*), the high frequency limiting value of $(\alpha/f^2)_{\text{solution}}$ equalled that of the weight fraction corrected value for the

Table 1 Physical characteristics of styrene–butadiene–styrene copolymers

Polymer	Code	$M_w \times 10^5$	M_w/M_n	Styrene (%)	Source
Linear SBS (30)	TR4113	1.71	1.3	33	Shell
Linear SBS (50)	TR4122	1.70	1.3	50	Shell
Star $(SB)_4$	'Solprene 411'	3.00	1.4	30	Phillips
Polybutadiene	Intene	10.00	2.3	–	British Industrial Plastics

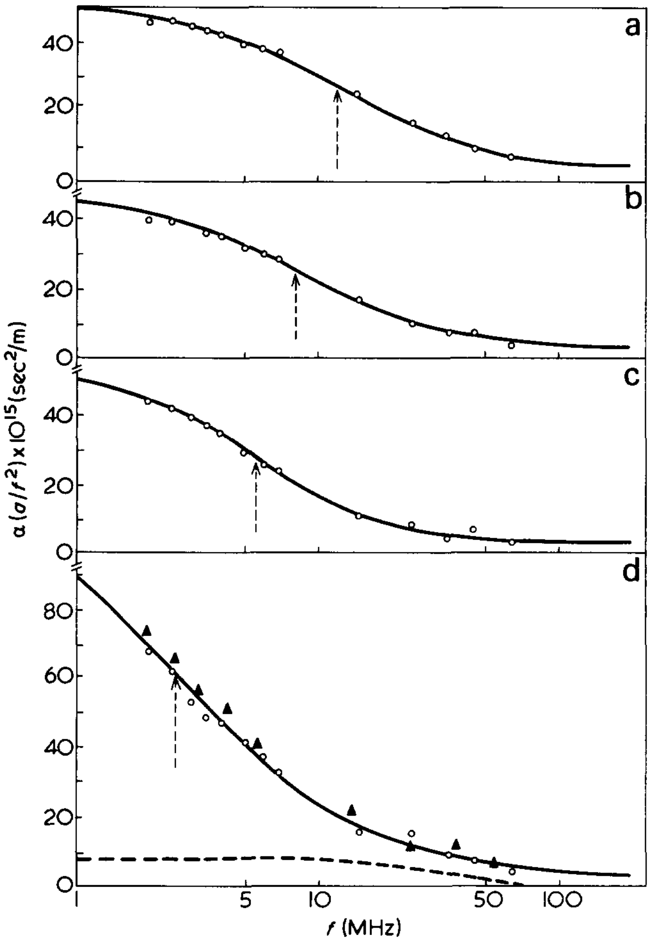

Figure 1 Temperature dependence of the ultrasonic attenuation of a 5% w/v solution of SBS (30) in toluene and a 5.8% w/v solution of $(SB)_4$ at 293K: (a) 323K; (b) 313K; (c) 303K; (d) 293K. $\delta(\alpha/f^2)$ is the contribution to the attenuation from polymer as defined in equation (1). ○, SBS(30); ▲, $(SB)_4$; ———, contribution to the attenuation from polybutadiene

Table 2 Relaxation parameters for 5.0% w/v SBS solutions in three solvents

Polymer	Solvent	Temperature (K)	$A\times10^{15}$ ($\mathrm{sec}^2/\mathrm{m}$)	f_c (MHz)	β
SBS (30)	Toluene	293	120	2.5	0.75
		303	50	5.5	0.92
		313	45	8.0	0.85
		323	48	12	0.85
SBS (50)	Toluene	293	80	5.0	0.80
		303	48	9.5	0.80
		313	44	10	0.90
		323	38	16	0.85
SBS (30)	1,4-Dioxane	293	115	4.0	0.80
		303	97	4.3	0.85
		313	60	5.5	0.95
		323	57	7.0	0.90
SBS (50)	1,4-Dioxane	293	185	3.0	0.77
		303	160	3.6	0.90
		313	100	4.7	0.90
		323	56	8.5	0.90
SBS (30)	Cyclohexane	293	280	1.5	0.82
		303	260	1.6	0.85
		313	210	1.6	0.83
		323	200	2.0	0.82
SBS (50)	Cyclohexane	293	300	1.9	0.82
		303	270	2.1	0.85
		313	170	2.5	0.80
		323	160	2.5	0.82

solvent, indicating the absence of any additional higher frequency relaxation processes in the dissolved polymer. The β parameter in equation (1) equals unity for an ideal Debye relaxation, and when less than unity is referred to as the Cole–Cole distribution parameter; f_c is the mean relaxation frequency and A is the relaxation amplitude corresponding to the sum of contributions from the individual processes responsible for the observed dispersion. The analysis of the data obtained for these copolymers is presented in *Table 2*. The mean activation energies (*Table 3*) for these relaxation processes have been estimated from Arrhenius plots of the characteristic frequency over a 30°C temperature range.

DISCUSSION

Relaxation in linear block copolymers

The activation energies for the observed relaxation are, within experimental error, independent of the size of the block. Variation of the solvent type has a significant effect on this process and the observed values do not correlate with the 'activation' energy for viscous flow[6] (*Table 3*).

The acoustic absorption of polybutadiene in the frequency range is very small (*Figure 1*), so that it is reasonable to assume that the major contribution to the attenuation and dispersion arises from relaxation of the normal mode processes of the whole molecule and/or motion of the styrene moiety. Calculations of the viscoelastic contribution, using the methods discussed previously[2], indicate that this process could have only a minor effect in this region. Therefore it is suggested that the principal cause of the dispersion is relaxation in the polystyrene block.

This hypothesis is supported by the qualitative correlation in the amplitude of the dispersion with the styrene content (*Figure 2*).

The variation of the activation energy with solvent parallels the thermodynamic effectiveness of the solvent, the higher activation energy being observed in the better solvent. This suggests that in cyclohexane the activation energy more closely reflects the intramolecular rotational barrier, the higher values in 1,4-dioxane and toluene arising from different contributions to the ground and 'transition' conformations from stronger solvent–polymer interactions. Unfortunately this cannot be confirmed by static measurements (such as thermal expansion or thermal pressure coefficients) owing to the complex interplay of the various contributory phenomena.

Comparison of the relaxation in linear and star block copolymers

The acoustic absorption curves for the star polymer $(SB)_4$ (*Figure 1*) and an equivalent concentration of SBS in toluene and cyclohexane are indistinguishable

Table 3 Activation parameters for the copolymers and solvents

Polymer	Solvent	Relaxation activation energy (kJ/mol)	Viscous flow activation energy for solvent (kJ/mol)
SBS (30)	Toluene	39	–
SBS (50)	Toluene	34	
SBS (30)	1,4-Dioxane	13	–
SBS (50)	1,4-Dioxane	17	13.5
SBS (30)	Cyclohexane	6	–
SBS (50)	Cyclohexane	9	12.5

Error in acoustic activation energy is typically ±6 kJ/mol.

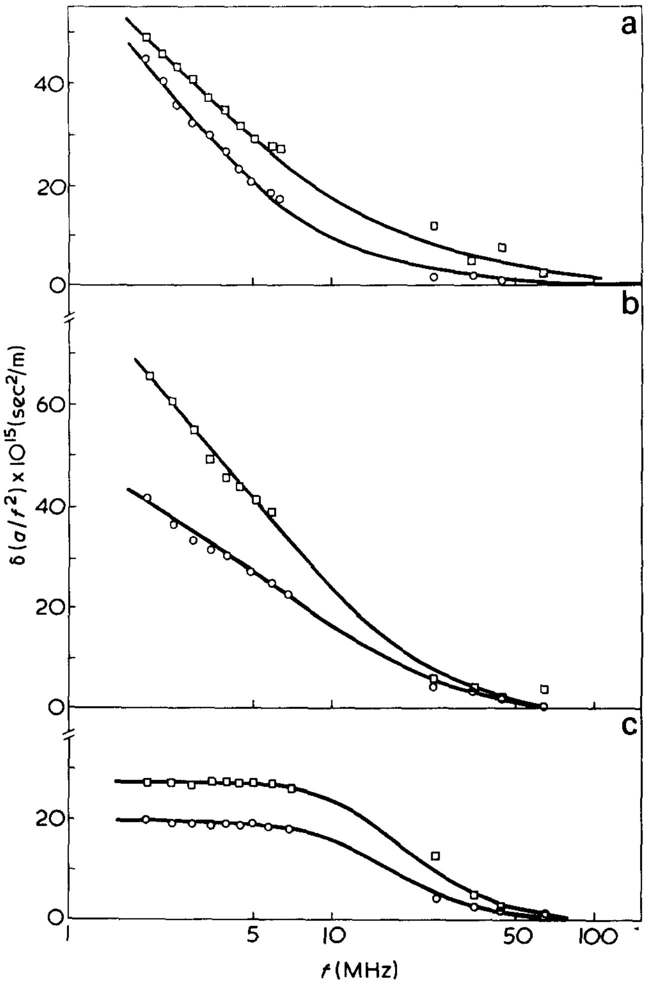

Figure 2 Variation of the ultrasonic attenuation with solvent for 2.5% w/v solutions of linear SBS copolymers at 293K: (a) cyclohexane; (b) 1,4-dioxane: □, SBS(50); ○, SBS(30); (c) toluene δ (α/f^2) is defined as in equation (1)

within experimental error. This observation supports the suggestion that the total mass of styrene in the polymer is the important factor in defining the acoustic relaxation and that normal modes, reflecting the effects of the star structure[7], have a negligible effect on these observations.

Variations of relaxation amplitude with solvent

Two factors can influence the observed amplitude of the acoustic absorption (*Figure 2*): (i) variation of the molecular volume change of relaxation, due to solvent interaction with the polymer; (ii) change of the molecular energy difference between conformational states as a consequence of changes in the relative contributions from inter- and intra-molecular interactions.

Ignorance of the specific conformations involved in the relaxation in the different solvents precludes estimation of dielectric constant effects on the conformational enthalpy difference[8]. As a consequence it is not possible to make allowances for conformational volume changes which could affect the ultrasonic attenuation[9]. However it is clear that solvent does have a very significant influence which could be either enthalpic or volume in effect.

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