Ultrasonic relaxation in dilute polystyrene solutions: 1. Normal mode and conformational processes

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Ultrasonic relaxation data are reported on solutions of polystyrene in toluene, dioxan, *m*-xylene and *p*-xylene over a frequency range of 1–1000 MHz and a temperature range of 293–353K. The data are analysed in terms of two components, a viscoelastic contribution associated with the normal mode relaxations and a more local conformational change of the polymer backbone. The solvent, molecular weight and temperature dependence of the relaxation processes are discussed. An anomalous increase in the amplitude of the acoustic absorption at high temperatures is ascribed to the occurrence of a pseudo helix–coil transition. A picture of the dynamic processes now emerges which rationalizes the apparently disparate earlier studies into a coherent self-consistent description.

INTRODUCTION

A number of workers have reported[1–24] studies of ultrasonic relaxation in solutions of polystyrene (PS). It is now timely to draw together the different aspects and somewhat disparate conclusions of these studies, and to report further measurements which help elucidate the overall picture.

All the observations report the presence of a relaxation in the low megahertz frequency range, although its position, amplitude and interpretation in terms of molecular relaxation processes is still a subject of debate. Although some of the earlier papers[1–8] assumed the relaxation to have an ideal Debye form, later studies[13–17] have established that the relaxation is broader than Debye. The relaxation has been ascribed to conformational changes of the polymer backbone, and the breadth of the relaxation has been explained in terms of a number of specific conformational transitions[8,13,16,18]. An alternative explanation of the breadth of the transition is the presence of a contribution from viscoelastic absorption by normal mode motions of the whole chain[17].

It is relevant to this dichotomy that recent studies[25,26] of poly(dimethyl siloxane)s, (PDMS), with different molecular weights, indicated both a close correspondence between the shear and ultrasonic relaxation spectra in the low megahertz frequency range, and a second relaxation process at high frequencies (above 200 MHz) which correlated well with the behaviour expected for a localized rotational isomeric change. The existence of two separate, well resolved, processes in PDMS supports the concept that ultrasonic relaxation in polystyrene could arise from a combination of segmental and normal mode processes. The lower frequency of the conformational relaxation in PS compared to PDMS would then be consistent with larger steric interactions in the former polymer.

In order to resolve such points, we have extended the frequency and temperature range of measurements, and considered a variety of solvents of different dielectric constant and thermodynamic solvent power.

EXPERIMENTAL

Polymers and solvents

The polystyrene used in this study (Pressure Chemical Company) was of narrow molecular weight distribution with $M_n = 96\,000$. The solvents used were analytical reagent grade when available, or else the best solvent grade. They were redistilled, dried over molecular sieves and filtered with micropore filters prior to use. The solutions were of concentrations less than 50 kg m^{-3}.

Ultrasonic absorption and velocity measurements

Attentuation data were obtained over the frequency range 1–1000 MHz using a combination of three techniques: acoustic resonator (1–10 MHz)[27], low frequency pulse technique (15–150 MHz)[28], and high frequency pulse method (200–1000 MHz)[29]. Velocity measurements were obtained from the peak separation of the acoustic resonator signals and have a nominal frequency of observation of 1.5 MHz. The temperature was controlled using a Lauda thermostat with a precision of approximately ±0.01K.

Data analysis

The observed ultrasonic relaxation curves cannot be analysed as a single ideal relaxation. Following the argument outlined in the Introduction, an analysis based on two different relaxation processes was adopted. A broad low frequency relaxation is assumed to originate in a spectrum of normal mode motions, and a higher frequency relaxation is ascribed to a distribution of segmental rotations.

The contribution from normal mode relaxation can be predicted using a modification of the Wang–Zimm theory[30]

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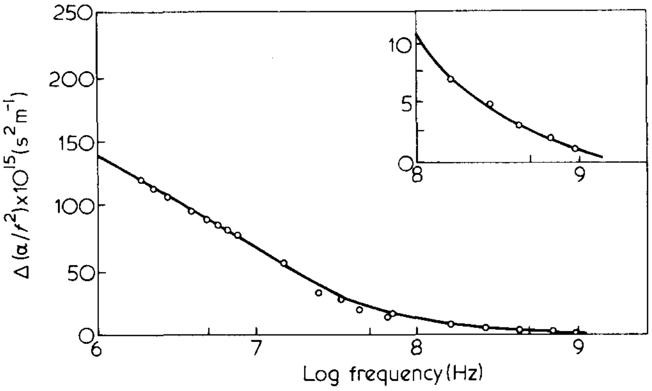

Figure 1 Variation of the ultrasonic absorption as a function of frequency in the range of 1–1000 MHz at 293K. Molecular weight of polystyrene = 89 000 (M_w/M_n = 2.1). ○, polystyrene in toluene (4.2% w/v). Inset shows ultrasonic absorption in the frequency range of 100–1000 MHz

which is applicable up to a concentration of 50 kg m^{-3}. The equations by which the normal modes give rise to a relaxing complex shear modulus, and how the imaginary or loss modulus causes an acoustic absorption are set out in refs. 25 and 26. This viscoelastic absorption is then subtracted from the total absorption over the frequency range of the observations.

The residual relaxation, attributed to segmental relaxation of the polymer backbone, is analysed in terms of a distribution of relaxation processes using the equation:

$$\alpha/f^2 = \frac{A(1 + (f/\bar{f}_c)^{\beta}\cos(\pi\beta/2)}{(1 + 2(f/\bar{f}_c)^{\beta}\cos(\pi\beta/2) + (f/\bar{f}_c)^{2\beta})} \qquad (1)$$

where A is the amplitude of the relaxation, $\bar{f}_c$ is the mean relaxation frequency, and β is the distribution parameter which equals unity for a single ideal relaxation.

The ultrasonic dispersion associated with a rotational isomeric process can be described in terms of the maximum absorption per wavelength per mol and relaxation frequency as follows:

$$\mu_{\max} = \frac{\pi(\gamma - 1)R}{2C_p}\left(1 - \frac{\overline{\Delta V}^0 C_p}{\overline{\Delta H}^0\,\overline{V}^0\theta}\right)\left(\frac{\overline{\Delta H}^0}{RT}\right)^2$$

$$\frac{\exp(-\overline{\Delta G}^0/RT)}{[1 + \exp(-\overline{\Delta G}^0/RT]} \qquad (2)$$

$$\bar{f}_c = \left(\frac{kT}{2\pi h}\right)\frac{\exp(-\overline{\Delta H}^{\ddagger}_{21}/RT)\exp(\overline{\Delta S}^{\ddagger}_{21}/R)}{[1 + \exp(-\overline{\Delta G}^0/RT)]} \qquad (3)$$

where quantities with superscript bar are averages derived from the distribution of relaxation times referred to above; C_p is the specific heat at constant pressure; γ is the ratio of specific heats at constant pressure and volume; θ is the thermal expansion coefficient; ΔG^0, ΔH^0, ΔV^0 are the free energy, enthalpy and molar volume changes associated with the rotational isomerism; and $\overline{\Delta H}^{\ddagger}_{21}$ and $\overline{\Delta S}^{\ddagger}_{21}$ are the mean activation enthalpy and entropy to be overcome in the isomerization from the high energy state to the lower. For dilute solutions it is reasonable to approximate the values of θ, C_p and γ to those of the solvent. The molar concentration of relaxing units need not correspond to the total number of monomer units present in solution. Equation (3) neglects any volume changes, ΔV^0, which may be associated with the rotational isomeric processes, and this assumption will be discussed later in this paper.

RESULTS AND DISCUSSION

Shape of the ultrasonic attenuation curves

The published data in a series of papers[1–10] cover a frequency range from 1–120 MHz, and have led to the suggestion[13] that there may be a further relaxation in the region above 200 MHz. It can be seen now, from data obtained over the frequency range 1–1000 MHz, *Figure 1*, that whilst the relaxation is not ideal there is no evidence of a distinct process above 150 MHz. In retrospect, one can see that the earlier assignment[13] is an artefact of the method used in the analysis. Nevertheless, the question still remains as to whether or not the acoustic absorption due to the segmental conformation change is represented best by a single molecular process with a distribution of relaxation times or by two overlapping ideal processes. A recent analysis of the relaxation behaviour in polystyrene oligomers tend to support the latter view.

Influence of molecular weight

In a previous paper[17] it was shown that the low frequency limiting value of the amplitude of the acoustic attenuation in toluene was a function of molecular weight for polymers with M_n approximately 10 000 or below. However, no detailed conformational analysis could be offered to explain the data. Since then, a series of relevant papers[31–33] on rotational isomerism in 2,4-diphenyl pentane (DPP), 2,4,6-triphenyl heptane (TPH) and 2,4,6,8-tetraphenyl nonane (TPN) have appeared.

In DPP, a single relaxation process was observed at low temperatures and this was assigned to rotational isomerism between the *gauche(g) trans(t)*, or $tg^{\pm}$, state and the all-*trans*, *tt*, conformation of the *meso* isomer, and between *tt* and $g^{\pm}\,g^{\pm}$ conformations of the *racemic* isomer (*Table 1*). The single relaxation observed in the isotactic and syndiotactic isomers of TPH has been ascribed to conformational changes tg^+tg^+ (or g^-tg^-t) to g^-ttg^+ in the *isotactic* isomer, and *tttt* to ttg^+g^+ (or g^-g^-tt) in the *syndiotactic* isomer. Relaxation in the *heterotactic* isomer was fitted by two relaxation functions, each involving one part of the molecule (*Table 1*). Rotational isomerism of the meso diad was g^-ttt (or tg^+tt) to *tttt* while the racemic diad exhibited a relaxation between g^-ttt and $g^-tg^+g^+$ conformations. The relaxation in TPN can be resolved into two processes: a high frequency relaxation ascribed to motions of the preferred syndiotactic diads and described as $\underline{gg}\,tt\,\underline{gg}\,tt\,\underline{gg} \rightarrow \underline{tt}\,tt\,gg\,tt\,\underline{tt}$. This process has an enthalpy difference twice that of the transition in racemic DPP (*Table 1*).

These studies help explain the behaviour of polystyrene in the following ways. First, we note that the relaxation frequencies of the isotactic triads or meso diads always differ from those of the syndiotactic triads or racemic diads. Since atactic polystyrene is predominantly (but not exclusively) syndiotactic, we would expect the relaxation to be non-ideal involving both meso and racemic diad sequences.

The study of TPN indicates the complexity of the motion, even in this relatively short chain. The polymer segmental motion, since it is local, may involve a small number of segments so that the processes identified in the simple model compounds should apply. To illustrate this, we plot the amplitude factors for the segmental relaxation process in a

Table 1 Relaxation processes, amplitude and interstate enthalpy for the various polystyrene oligomers in ethylbenzene (5% w/v) at 293K[31–33]

Model polystyrene	Process	Amplitude $(A) \times 10^{15}$ ($s^2 m^{-1}$)	$\overline{\Delta H^0}$ (kJ mol^{-1})
Meso–DPP	$g^{\pm}t \rightarrow tt$	1.5	5.85
Racemic–DPP	$tt \rightarrow g^{\pm}g^{\pm}$	2.5	5.85
Isotactic–TPH	$tg^{+}tg^{+}g^{-}ttg^{+}$ (or $g^{-}tg^{-}t$) $\rightarrow$	4.2	4.18
Syndiotactic–TPH	$tttt\ ttg^{+}g^{+}$ (or $g^{-}g^{-}tt$)	2.2	6.27
Hetero–TPH			
(i) Meso diad	$g^{-}ttt \rightarrow tttt$ (or $tg^{+}tt$)	3.6	7.94
(ii) Racemic diad	$g^{-}ttt \rightarrow g^{-}tg^{+}g$	1.0	6.69
TPN			
(i) Low frequency	Crank-shaft process favoured	5.0	5.43
(ii) High frequency	$\underline{g}gttggttgg \rightarrow t\underline{t}ggtt\underline{t}t$	1.2	4.60

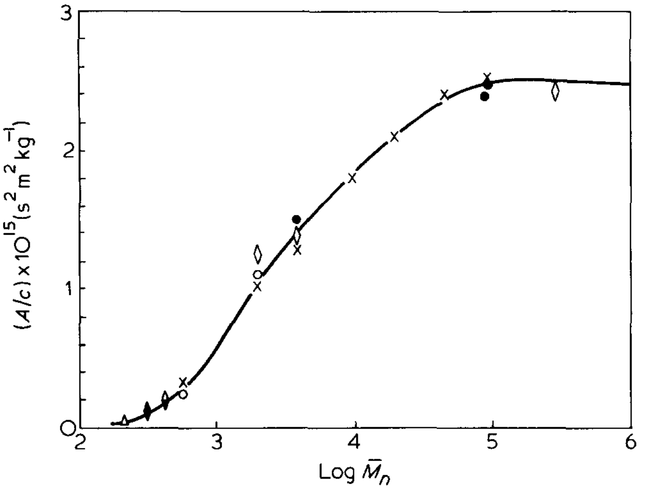

Figure 2 Variation of the relaxation amplitude per unit concentration as a function of molecular weight for polystyrene in toluene at 293K. ○, ref 19; ◇, ref 20; X, ref 21; △, ref 24; ♦, ref 25; ◈, ref 32; ●, this work

range of polystyrenes, the data being obtained after subtraction of the viscoelastic normal mode contributions allowing for appropriate hydrodynamic interactions, as illustrated in *Figure 2*. The mathematical relationships between absorption intensity, normal mode motion and hydrodynamic interaction are set out in detail in refs. 17 and 25.

Relaxation in the higher molecular weight samples is almost ideal, although, for the lower molecular weight samples, a distribution of relaxation times is more appropriate. The amplitudes for the oligomeric materials lie on an extension of the general plot, confirming that the observed relaxation is ascribable to similar rotational isomerism. This is true, too, of the relaxation frequencies and classical non-relaxing absorptions (*Figure 3*). The increase in the latter quantity with molecular weight is consistent with a high frequency limiting viscosity in excess of that of the solvent.

Solvent effects

Previous studies of the ultrasonic relaxation of polystyrene in different solvents have indicated that the relaxation frequency can vary between 1–20 MHz and that the interstate enthalpy may have a value between 0–9 kJ mol^{-1}. Solvent effects observed in infra-red studies of isomerism have been explained on the basis that the dielectric constant of the medium alters the electrostatic contribution to the internal rotational potential. Volume effects may have a significant effect on the magnitude of the observed relaxation process.

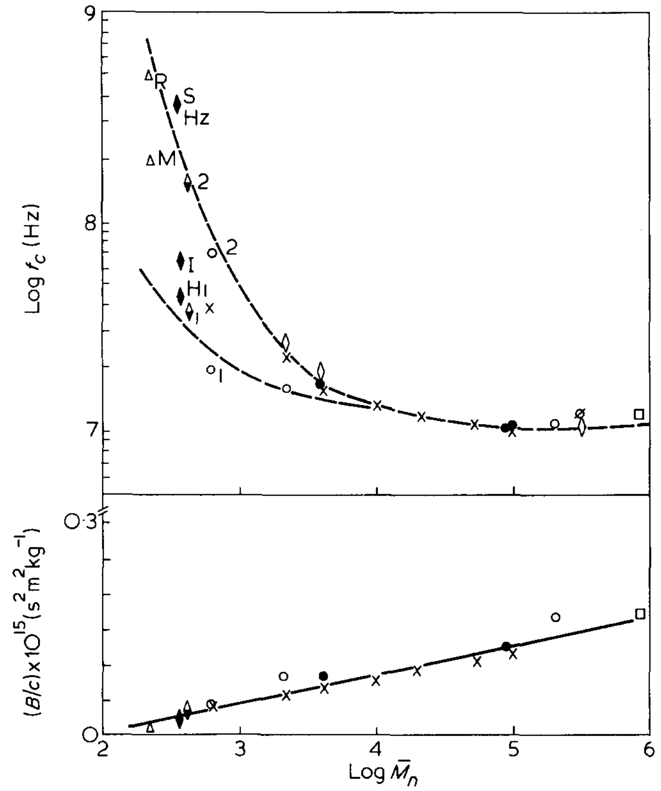

Figure 3 Variation of relaxation frequency and residual absorption per unit concentration as a function of molecular weight for polystyrene in toluene at 293K. □, ref 7; ⊅, ref 9; ○, ref 19; ◇, ref 20; X, ref 21; △, ref 24; ♦, ref 25; ◈, ref 32; ●, this work. *R* = racemic; *S* = syndiotactic; H_1 = heterotactic – fc$_1$; H_2 = heterotactic – fc$_2$; 1 = fc_1, 2 = fc_2; *M* = meso; *I* = isotactic

In an attempt to rationalize the data obtained using a wide range of solvents, we apply a modification of the Onsager Reaction Field. According to this theory the difference between the enthalpy change in the vapour (ΔH_v^0) and that in a particular solvent (ΔH_s^0) can be expressed[44] as:

$$\Delta H_v^0 - \Delta H_s^0 = xh \qquad (4)$$

where x and h are parameters defined for a particular solvent–solute system. x is equal to $(\epsilon - 1)/(2\epsilon + 1)$ and allows for the effect of dielectric constant on the electrostatic polarizability. h equals $(\mu_A^2/r_A^3) - (\mu_B^2/r_B^3)$, where μ_A and μ_B are, respectively, the dipole moments of the states A and B with molecular cavity radii r_A and r_B. Since the dipole moments do change from solvent to solvent only slightly, the variation in the cavity (or molecular) volumes will be the principal

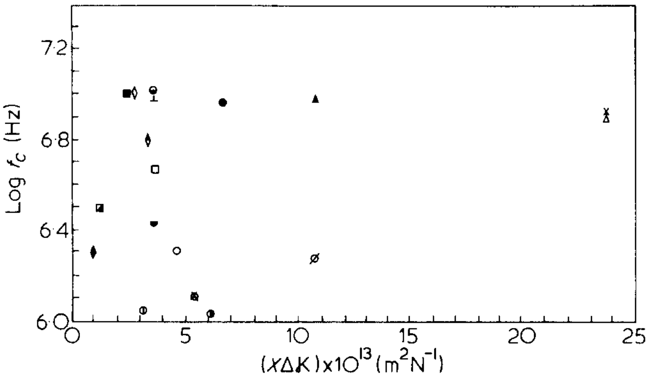

Figure 4 Solvent effect on relaxation frequency of polystyrene at 293K. ▲, methyl ethyl ketone, ref 7; ●, decalin (mixture of *cis* and *trans*), ref 11; X, *N,N*-dimethylformamide, ref 13; □, xylene (mixture of *ortho, para* and *meta*), ref 11; *Φ*, methyl ethyl ketone, ref 16; ⊗, decalin, ref 16; △, *N,N*-dimethylformamide, ref 22; ○, cyclohexane, ref 23; ▾, carbon tetrachloride, ref 23; Φ, benzene, ref 23; ◑, carbon disulphide, ref 23; ◇, benzene, ref 24; ⬘, carbon tetrachloride, ref 24; ◆, cyclohexane, this work; ◪, 1,4-dioxan, this work; ■, toluene, this work; ◒, *p*-xylene, this work; ⊥, *m*-xylene, this work

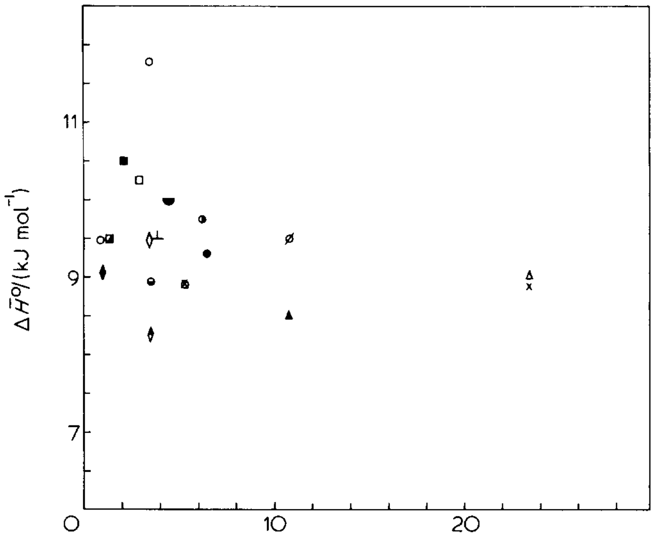

Figure 5 Solvent effect on the interstate enthalpy of polystyrene at 293K. Symbols as in *Figure 4*

source of variation in h. This may come about by different solvation of the two isomers in different solvents, and will be observable as differences in the compressibilities of the solutions.

To examine this, we consider the variation of the relaxation frequency and enthalpy change with $X\Delta\mathscr{K}$ where $\Delta\mathscr{K}$ is the adiabatic compressibility increment due to solute (*Figures 4* and *5*). The lack of any clear correlation implies that, in polystyrene, the isomerization is insensitive to changes in specific solvation or dielectric effects, and $\Delta\bar{V}^0$ is unimportant.

Effect of temperature

The majority of ultrasonic studies of polystyrene in solution have been performed at room temperature or below. However, an abnormal increase in the ultrasonic absorption in the frequency range 6–20 MHz has been reported[11] to occur at 343K. In an attempt to clarify this effect we have measured the ultrasonic relaxation up to a temperature of 353K in toluene, *m*-xylene and *p*-xylene. A striking feature of these results is the marked increase in the region 323–333K (*Figure 6*).

If we assume that, at high temperatures, the whole polymer chain contributes to the observed relaxation, then in the region below 333K there is some restriction of the chain motion. The indications are that the temperature dependence of, and therefore the thermodynamic parameters pertaining to, the relaxations are the same above and below this 'transition' region. Consequently we favour an explanation based upon a change in the number of units free to undergo the rotational conformation change, rather than a change in the *nature* of the isomerization. In strong support of this hypothesis are comparable observations of a pseudo helix–coil or order–disorder transition reported in light scattering, ^{13}C and infra-red studies[15,34–43] of polystyrene solutions in this temperature region. Thus, at the low temperatures, certain sequences in the chain, perhaps associated with isotactic sequences, are ordered or possibly helical and cannot contribute to the conformational absorption spectrum. *Figure 7* shows how, on the assumption of identical conformational energetics for a varying number of rotors, a *linear* plot of $\ln(\mu_m/TV^2)^{1/2}$ (where μ_m is the maximum absorption, determined from the frequency dependence of the attenuation with a precision of ±?%) against T can be obtained, giving the same interstate enthalpy difference, *Table 2*, as that derived from isothermal measurements via the Schottky function and portrayed in *Figure 5*.

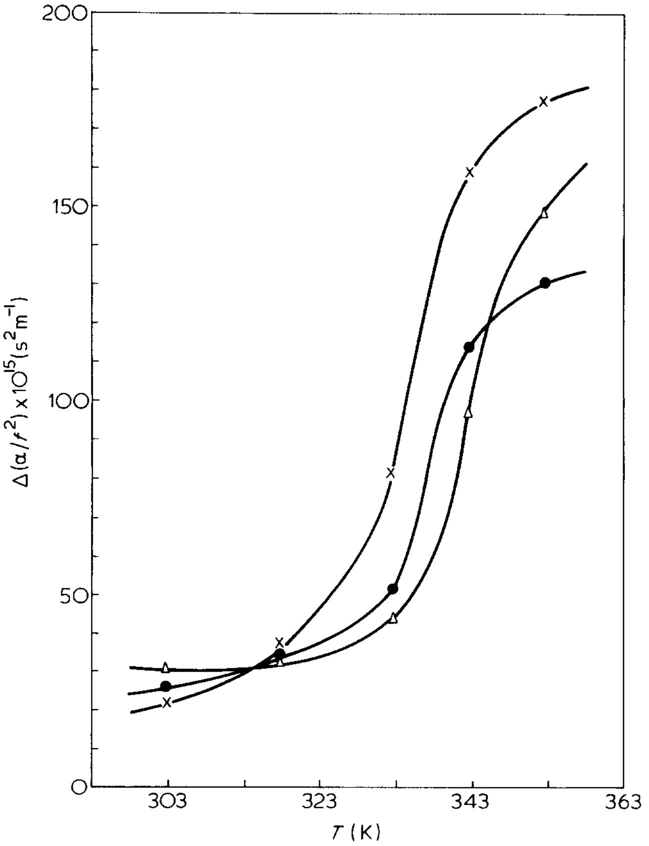

Figure 6 Variation of acoustic absorption as a function of temperature for polystyrene solutions (4% w/v) at 25 MHz. X, polystyrene in toluene; ●, polystyrene in *m*-xylene; △, polystyrene in *p*-xylene

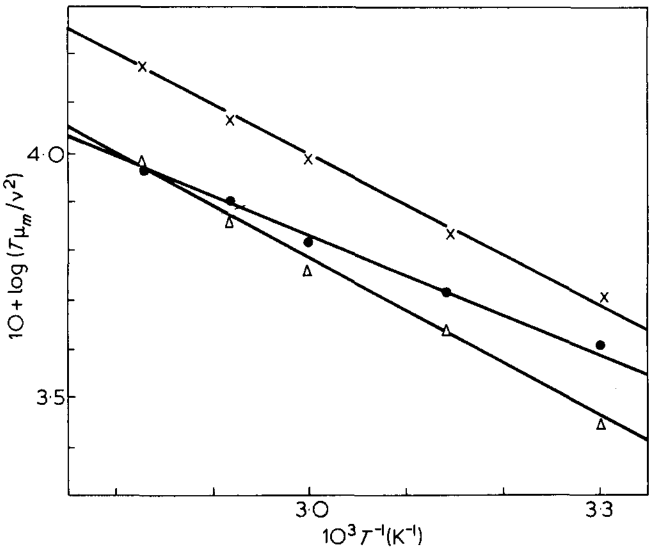

Figure 7 Variation of $\log(T\mu_m/v^2)$ as a function of the inverse of temperature for polystyrene solutions (4% w/v). Molecular weight of polystyrene = 2.1 x 10^5. X, polystyrene–toluene; ●, polystyrene–*m*-xylene; △, polystyrene–*p*-xylene

Table 2 Interstate enthalpy and average number of relaxing units per 'frozen' or helical sequence (*n*) for polystyrene in the various solvents (4% w/v)

Solution	$\overline{\Delta H^0}$/kJ mol^{-1}	*n*
Polystyrene–toluene	8.6	8.6
Polystyrene–*m*-xylene	6.8	6.7
Polystyrene–*p*-xylene	8.8	5.1

CONCLUSION

Ultrasonic relaxation in dissolved polystyrene can be explained in terms of a viscoelastic normal mode contribution (involving a spectrum of such modes) and a conformational relaxation. This latter can now be assigned to specific isomerizations which are relatively insensitive to solvent, are dependent on the chain length in short chain species and which occur only in certain sections of the chain below a transition region 320–330K.

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