Ultrasonic studies of dilute polystyrene solutions: 2. The kilohertz frequency region

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Ultrasonic measurements covering a frequency range 300 KHz–1 MHz at 303K, and made on dilute polystyrene solutions in toluene (2.6% w/v) are reported as a function of molecular weight. For molecular weights below those causing significant interchain interaction, the absorption can be assigned to a segmental conformation change (molecular weight independent), a normal mode viscoelastic loss (molecular weight independent), and a small contribution from a thermal transfer (polymer to solvent) process. For molecular weights above a critical entanglement value, there exists a large very low frequency absorption which is molecular weight dependent and which is ascribed to dynamic changes in chain entanglements. It appears to be more significant in processes stimulated by a compressional perturbation (acoustic) than by an isovolumetric shear perturbation (viscoelastic).

INTRODUCTION

Ultrasonic relaxation in dilute polystyrene solutions in the frequency region above 1 MHz[1–15] is discussed in the previous paper and is attributed to two relaxation processes, the first associated with the high frequency tail of the normal mode relaxation and the second to conformational changes of segments of the polymer backbone[16–19]. An attempt has been made to investigate lower frequencies in dilute solution[20,21]; despite experimental inaccuracies, there was an indication of a further molecular weight dependent acoustic loss, ascribed to heat transfer between the polymer (considered as a sphere containing trapped solvent) and the surrounding equilibrated solvent. Because of the uncertainty attached both to the experimental observations and to the explanation, an attempt is made here to observe more precisely the effect of molecular weight on the very low frequency acoustic loss.

EXPERIMENTAL

Materials

Five narrow molecular weight polystyrene samples (Pressure Chemicals) were used. In addition, one high molecular weight sample prepared by radical polymerization was investigated. The molecular weights of the six samples range from 10^4 to 10^7. Their $\bar{M}_n$ values and molecular weight dispersity were determined by g.p.c. and are listed in *Table 1.* All the polymers were reprecipitated from methanol at 273K and dried in a vacuum oven to constant weight. Redistilled Analar grade toluene, which had been dried over molecular sieves and filtered with micropore filters, was used as a solvent.

Acoustic measurements

An acoustic resonator[22,23] containing 7 cm diameter x-cut quartz crystals and operating with a fundamental frequency of 3 MHz was used in the 300 KHz–1 MHz frequency range. The measurement precision was typically better than 4%. Density and viscosity data were obtained as described previously[24]. In both cases, the precision was better than 0.1%. A Lauda thermostat was used to maintain a constant temperature to ±0.1K.

RESULTS AND DISCUSSION

The frequency and molecular weight dependences of the observed total ultrasonic absorption of 2.6 w/v% polystyrene solutions in toluene at 303K are presented in *Figure 1.* Data obtained by Cochran[24] in the megahertz region are included to indicate how this study extends the data already published. We now discuss separately the various contributions to the observed dispersion.

Table 1 Number average molecular weights, molecular weight distributions and Frisch–Simha criteria ($c[\eta]$) for various polystyrenes used in this study

$M_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$c[\eta]$
1.00	1.06	0.26
2.04	1.03	0.44
5.10	1.01	0.86
9.70	1.06	1.43
26.90	1.05	3.07
1000	1.06	34.00

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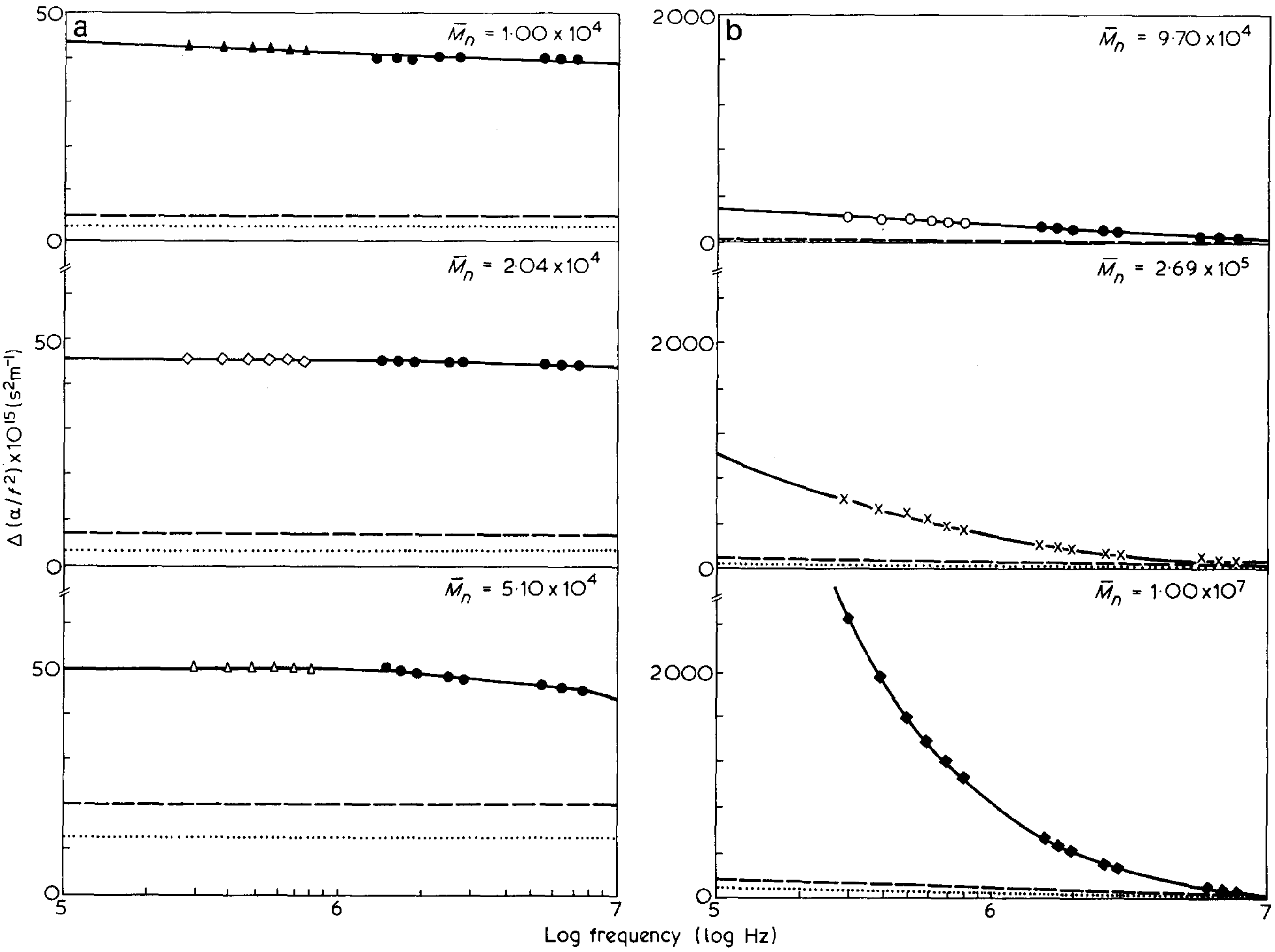

Figure 1 Variation of the ultrasonic absorption as a function of frequency for polystyrene in toluene (2.6% w/v) at 303K. ●, ref 24; ——, total ultrasonic absorption; · · · · ·, calculated viscoelastic contribution; — — · — —, calculated viscoelastic and heat loss contribution. a, $\bar{M}_n$ from 1.0 x 10^4 to 5.1 x 10^4; b, $\bar{M}_n$ from 9.7 x 10^4 to 1.0 x 10^7

Viscoelastic contribution

The contribution from normal mode relaxation was computed using the approximate theory of Wang and Zimm[25] for moderately concentrated polymer solutions. For molecular weights greater than 31 200, i.e. the critical entanglement molecular weight for polystyrene[26], the effects due to interchain interaction must be included in the calculation. A modified mode (k) relaxation time (τ_{km}) is defined by:

$$\tau_{km} = (\eta_0/\eta_c)\,(M_c/M_n)\tau_k \tag{1}$$

where τ_k is the unmodified relaxation time and η_0 and η_c are the solution viscosity and critical viscosity at entanglement, respectively. Since higher normal modes are insensitive to the effects of entanglement, modification is only necessary for the lowest members of the spectrum. In this study the first twelve modes were modified, and the inclusion of higher modes had negligible effect on the calculated viscoelastic losses. The details of the calculation have been described elsewhere[27], and the results are entered on the figures as dotted lines.

Losses due to heat transfer

A model for the prediction of the loss associated with heat transfer between the 'polymer sphere' and the surrounding solvent has been outlined by Ono *et al.*[20]. This may be calculated from:

$$\Delta\left(\frac{\alpha}{f^2}\right) \simeq (2\pi N_A/15\Phi)(\theta_1/C_{p1})^2\,(T\rho v C_{ps}\delta^2 c[\eta])/f_r \tag{2}$$

where C_{p1} and θ_1 are, respectively, the specific heat at constant pressure and the thermal expansion of the solvent, C_{ps} is the specific heat at constant pressure of the solution, N_A is Avogadro's constant, T is temperature, ρ is the density of the solution, v is the velocity of sound in the solution of concentration c and intrinsic viscosity $[\eta]$, f_r is the relaxation frequency, δ is a dimensionless variable such that $|\delta| \ll 1$ and Φ is a 'universal' constant relating $[\eta]$ with molecular weight and polymer volume. The constant, Φ, has been determined by Pyun and Fixman[28] to be 9.40 x 10^{23} mol^{-1}. If we assume that the thermal expansion and specific heat per unit volume are approximately additive, the following relationships are derived:

$$\theta_s = \theta_1(1-\phi) + \theta_2 \tag{3}$$

$$C_{ps} = C_{p1}(1-\phi) + C_{p2}\phi \tag{4}$$

where ϕ is the volume fraction of polymer chain in the polymer sphere and θ_2 and C_{p2} denote the thermal expansion coefficient and specific heat of the pure polymer, respectively. Subscripts 1 and 2 refer to solvent and solute. The value of ϕ can be estimated from:

$$\phi = (V_0\Phi)/(M_0[\eta]) \tag{5}$$

where V_0 and M_0 are the volume and molecular weight of a monomer unit, respectively. The parameter δ may be defined as:

$$(\theta_1/C_{p1}) - (\theta_s/C_{ps}) = (\theta_1/C_{p1})\delta \tag{6}$$

Using equations (2)–(6), the magnitude of the loss due to heat transfer processes can be estimated. This loss due to thermal processes was found to be typically between 3×10^{-15} and 60×10^{-15} s^2 m^{-1} and is only a minor contribution to the total absorption (<6%).

Segmental conformational change

The residual loss after allowance for both viscoelastic and thermal processes (broken lines in *Figure 1*) corresponds to the contribution from segmental processes relaxing at high frequencies (as discussed in the previous paper) and in certain cases a further relaxing component at the lowest frequencies. In the molecular weight range up to approximately 10^5, the loss in the kilohertz region is independent of frequency and may be attributed totally to the sum of the three viscous, thermal and segmental processes.

Chain entanglement

Above a molecular weight of 10^5, a large additional contribution is observed which is frequency dependent in the kilohertz region, and for which a further explanation must be sought.

The extent to which polymer–polymer interactions occur in solution can be estimated by the Frisch–Simha criteria ($c\,[\eta]$), *Table 1*. Using these criteria, we see that the additional relaxation contribution appears at approximately the $c\,[\eta]$ value for polymer–polymer interaction ($c\,[\eta] \sim 1$). Therefore, it appears reasonable to assign the additional loss to energy absorption processes associated with dynamic changes in chain entanglements in solution. The viscoelastic normal mode theory is unable to predict the occurrence of this phenomenon, which appears to be more active in acoustic perturbation than in shear. A similar difference between acoustic and shear observations has been reported[28,30] in poly(dimethylsiloxane), and indicates that chain entanglement causes greater energy losses in dynamic relaxation stimulated by volume or compressional perturbation than by isovolumetric shear perturbation.

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